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# Report of the ICES Advisory Committee on the Marine Environment, 2001

**Helsingør, 5–9 June 2001**

International Council for the Exploration of the Sea
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# ICES ADVISORY COMMITTEE ON THE MARINE ENVIRONMENT

## LIST OF MEMBERS

**5–9 June 2001**

| Participant | Affiliation |
|---|---|
| **Mr S. Carlberg** | Chair |
| **Prof. H.R. Skjoldal** | Chair, Advisory Committee on Ecosystems |
| **Dr A. Calabrese** | Chair, Mariculture Committee |
| **Mr P. Keizer** | Chair, Marine Habitat Committee |
| **Prof. F. Colijn** | Chair, Oceanography Committee |
| **Dr K. Cooreman** | Belgium |
| **Mr R. Alexander** | Canada |
| **Mr S. Mellergaard** | Denmark |
| **Dr E. Ojaveer** | Estonia |
| **Dr J.-M. Leppänen**[1] | Finland |
| **Dr P. Gentien**[1] | France |
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| **Ms J. Doyle** | Ireland |
| **Dr A. Yurkovskis** | Latvia |
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| **Mr. H. Loeng** | Norway |
| **Dr E. Andrulewicz** | Poland |
| **Dr C. Lima** | Portugal |
| **Dr S.A. Patin** | Russia |
| **Dr T. Nunes** | Spain |
| **Dr M. Waldock**[1] | United Kingdom |
| **Dr T. Noji** | United States |
| **Dr J. Pawlak** | ICES Environment Adviser |
| **Dr K. Brander** | ICES GLOBEC Coordinator |
| **Dr J. Nørrevang-Jensen** | ICES Environmental Data Scientist |
| **Dr R. Law** | Chair, MCWG |
| **Dr S. Uhlig** | Chair, WGSAEM |

[1] Unable to attend

All Member Countries were represented at the meeting except Finland, the Netherlands and the United Kingdom.

***Secretariat members participating in the meeting or portions thereof:***

| | |
|---|---|
| Mr D. Griffith | ICES General Secretary |

# EXECUTIVE SUMMARY

The ICES Advisory Committee on the Marine Environment (ACME) met from 5 to 9 June 2001. As part of its work during this period, the ACME prepared responses to the requests made to ICES by the OSPAR Commission and the Helsinki Commission. This report contains these responses. In addition to responses to direct requests, this report summarizes the deliberations of ACME on topics for which advice was not directly requested but for which the ACME felt that there was information that would be of potential interest to the Commissions, ICES Member Countries, and other readers of this report.

As a result of the creation of the Advisory Committee on Ecosystems (ACE), several topics previously handled by ACME have been moved to the remit of ACE and scientific information and advice on these topics can be found in the ACE report for 2001. The topics covered include ecosystem effects of fishing, ecological quality objectives, ecosystem modelling and assessment, marine mammals issues, biodiversity issues, and marine habitat classification and mapping.

## Information in direct response to requests from, or which is relevant to, the work of both the OSPAR Commission and the Helsinki Commission

### Monitoring

In 2001, the ACME continued work on the development of biological effects monitoring programmes. The ACME reviewed the activities of the Sea-going Workshop on Pelagic Biological Effects Methods that is being conducted during 2001 (Section 4.1.1) and considered the implications of the EU Water Framework Directive on biological effects monitoring (Section 4.1.5). The ACME also reviewed the integrated approach to monitoring the effects of the "Erika" oil spill off the coast of France (Section 4.1.3 and Annex 1).

The issue of normalization techniques for contaminant concentrations in sediments was considered in detail, and a Technical Annex on Normalization was adopted (Annex 2), with explanatory comments in Section 4.5.1. Normalization is primarily developed to correct contaminant contents for differences in sediment composition and does not relate to ecotoxicological interpretation, which is a matter that deserves further attention.

The ACME reviewed new information on statistical considerations relative to monitoring programmes (Section 4.6). Methods for the analysis of quarterly and monthly monitoring data are reviewed in Section 4.6.1 (with details in Annex 3), using data sets on contaminants in biota and water. A dynamic sampling strategy that can be used when assessing toxin concentrations in a shellfish population and deciding whether the shellfish are safe to harvest is described in Section 4.6.3, while Section 4.6.4 considers the design of a spatial survey in relation to the detection of hotspots.

### Quality Assurance and Intercomparison Exercises

The ACME reviewed the results of quality assurance-related activities conducted during the past year and provided summaries of this work in Section 5 of this report.

In relation to quality assurance of biological measurements in the Baltic Sea, the ACME reviewed the results of the work on this topic during the past year (Section 5.1). Various activities were reviewed, including experience in the use of the COMBINE Phytobenthos Monitoring Guidelines.

For the OSPAR area, the ACME took note of a final draft of Guidelines for Quality Assurance of Biological Measurements in the OSPAR Area, that have been prepared for final review and completion in early 2002 (Section 5.2). These draft guidelines describe the QA system in relation to survey objectives and design, and contain more detailed QA guidance for every step in sample treatment from sampling to data handling. The detailed guidelines will cover the specific parameters to be monitored, i.e., chlorophyll *a*, phytoplankton, macrozoobenthos, and macrophytobenthos. Other relevant activities include work on the preparation of taxonomic checklists and workshops on the taxonomy of zooplankton species.

A review of the considerable amount of work to develop quality assurance procedures for biological effects techniques, including fish diseases, is contained in Section 5.3. Most of this work is being conducted under the EU-funded project Biological Effects Quality Assurance in Marine Monitoring (BEQUALM).

With regard to chemical measurements, further progress has been made in the development of additional technical annexes for the "Guidelines on Quality Assurance of Chemical Measurements in the Baltic Sea", that were initially prepared in 1997 for the monitoring programmes carried out under the Helsinki Commission (Section 5.4). Technical notes have now been completed on: a) Units and Conversions with Regard to Dissolved Oxygen and Oxygen Saturation; b) the Determination of Organic Carbon in Sea Water; and c) Certified Reference Materials. Initial work was also conducted on the development of quality criteria to be employed in reviewing monitoring data prior to their use in the preparation of data products for environmental assessments (Section 5.5).

A list of certified reference materials (CRMs) for the QA of marine monitoring programmes is included in Section 5.6 and Annex 4 of this report.

**Contaminants in the Marine Environment**

The ACME reviewed new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) (Section 6.1.1) and polybrominated diphenylethers (PBDEs) (Section 6.1.2). The ACME also reviewed information on the application of a hazard assessment procedure to data on volatile organic contaminants in biota in a sector of the southern North Sea (Section 6.1.4 and Annex 6).

The ACME also considered a review on antifouling paint booster biocides and their effects in the marine environment; this review is contained in Annex 5, with a summary in Section 6.1.3.

Noting the concerns about dioxins and dioxin-like chlorobiphenyls in marine fishery products, the ACME conducted a thorough review of current information on this subject, as reported in Section 6.1.5 and Annex 7. In view of the apparent considerable geographical variations in the concentration levels of dioxins and dioxin-like CBs in marine fish and fish products, ICES recommends that analyses of these compounds be included in representative samples in surveys and monitoring programmes.

The topic of endocrine disruption in marine and estuarine species continues to be of high priority and there is a need to develop robust techniques for the detection of endocrine disrupting chemicals and their effects in a variety of organisms. Several national and international studies of endocrine disruption in marine and estuarine areas were reviewed by ACME, as reported in Section 6.2. The ACME encourages the continuation of these studies to establish the causes of the observed effects and whether the problem is increasing or not.

**Report sections responding to requests specific to the OSPAR Commission**

**Using Data with Various Degrees of QA in Temporal Trend Assessments**

An initial response to this question is contained in Section 10.2, with further information and examples contained in Annexes 8, 9, and 10. It is clear that discussion concerning QA screening and the use of QA data needs to take place with the relevant OSPAR subsidiary body to determine the appropriate balance between QA requirements and the use of data of somewhat lower QA standards in temporal trend assessments. Based on the outcome of this discussion, protocols for data acceptability and weighting for use in trend assessments should be developed.

**Eutrophication Status of the Marine Area**

Advice and some standard data products for developing the OSPAR Common Procedure for Identification of the Eutrophication Status of the Maritime Area are presented in Section 11. The data products include plots of trends in concentrations of nitrate and dissolved inorganic phosphorus at salinity 30 for the major estuaries in Northern Europe.

**Data Handling**

The annual review of data handling activities by the ICES Marine Data Centre on contaminants data relevant to the requirements of OSPAR, HELCOM, and AMAP is contained in Section 15.1 of this report. Section 15.2 summarizes the work of the ICES Marine Data Centre in handling nutrients data relevant to the OSPAR programmes. A brief review of the development of the biological community data reporting format and databases for phytoplankton, zooplankton, phytobenthos, and zoobenthos is given in Section 15.3. Finally, initial progress on the development of reporting formats for data obtained using the biological effects techniques adopted by OSPAR is noted in Section 15.4.

## Report sections responding to requests specific to the Helsinki Commission

### Annual Review of Data Quality

The ACME reviewed initial work identifying QA information required for data assessors, however, further work is required for the definition of quality control criteria for assessing the data. This will require further discussion with the relevant HELCOM subsidiary bodies to determine the basis for QA criteria and their application. An initial response to this request is contained in Sections 5.5 and 10.2, with further examples contained in Annexes 8, 9, and 10.

## Information on topics of general interest

### Fish Diseases

An overview of new trends in the occurrence of diseases in wild and farmed fish and shellfish stocks is contained in Section 7.1. Viral Haemorrhagic Septicaemia virus has been isolated from a large number of marine fish species in the North Sea, the Skagerrak, the Kattegat and the Baltic Sea, as well as along the Pacific coast of the USA and Canada. The first outbreaks of this virus in sea-reared rainbow trout in Finland occurred in 2000, with a potential link to the high prevalence of this infection in Baltic herring.

Further work on the statistical analyses of disease prevalence data for dab and flounder was reviewed (Section 7.2). This work concentrated on the development of a new statistical approach to incorporate interpolated values for environmental and fisheries data in the investigation of possible relationships between environmental factors and fish diseases. On the basis of this work, ICES again encourages Member Countries to enhance their efforts to submit historic and current data held in national data banks to the ICES data banks, to facilitate a more comprehensive analysis of the interactions between natural and anthropogenic environmental factors and the health status of marine organisms.

The ACME reviewed information on the potential use of fish parasites as indicators of environmental change (Section 7.3) and noted that, while studies of parasites of marine organisms may be a useful tool in marine monitoring, further targeted research is needed to aid in the identification of cause-effect relationships. Criteria should be carefully defined to select the parasites that can be used as bio-indicators of environmental change and the marine fish species most suitable for this type of monitoring.

### Introductions and Transfers of Marine Organisms

The ACME reviewed information on the status of controlled and accidental introductions and transfers of non-native marine species into the waters of ICES Member Countries (Section 8.1). In terms of controlled introductions, the escape of farmed Atlantic salmon and their occurrence in the wild off the coast of British Columbia, Canada has been noted. In addition, Japanese kelp (*Undaria pinnatifida*), introduced to France for cultivation in 1983, has been found to spread in the wild to the Channel and the coasts of Belgium and the Netherlands.

Problems associated with imports of live seafood, particularly North American lobster, are causing concern in European countries. Lobsters may escape into the wild, and a growing number have been found in coastal areas, particularly near cities with airports. North American lobsters may transfer parasites and diseases to the European lobster, and they may also breed with them, creating hybrids.

An extensive list of databases related to non-indigenous species has been compiled in Section 8.2; most of these databases are accessible via the Internet.

Issues relevant to the transfer of organisms via ships' ballast water and hulls are reviewed in Section 8.3. This material includes an assessment of the types of ship vectors in relation to the introduction of non-native species, and a review of ballast water control and management technologies. A standardized format for collating data on non-native species and the method and fate of their introduction is presented in Section 8.4.

## Marine Biological Communities, Processes, and Responses

Summaries of progress in the North Sea Benthos Project and progress in studies of phytoplankton responses to enhanced nutrient inputs and harmful algal bloom dynamics are reported in Sections 9.1, 9.2, and 9.3, respectively. A review of several widely used statistical methods to analyse biological community data is contained in Section 9.4.

## Environmental Assessments

A brief review of the types and roles of environmental indicators is given in Section 10.4, while a review of recent environmental assessments and the production of Quality Status Reports is contained in Section 10.5.

Contributions to the ICES Environmental Status Report for 2001 have been made concerning oceanographic conditions (Section 10.6.1 and http://www.ices.dk/status/clim0001), harmful algal blooms (Section 10.6.3 and http://www.ices.dk/status/decadal/), and fish and shellfish disease prevalence (Section 10.6.4 and http://www.ices.dk/status/fish_and_shellfish_diseases/index.htm).

## Issues Related to Mariculture

The ACME considered a review of the interactions between seabirds and aquaculture (Section 12). This includes the impact on bird populations of the new feeding opportunities for birds presented by aquaculture, as well as the impacts of birds on mariculture operations in terms of disturbance and loss of product.

## Effects of Extraction of Marine Sand and Gravel on Marine Ecosystems

The ACME reviewed marine extraction activities in ICES Member Countries during 2000 and the results of assessments of the environmental effects of marine extraction activities, as summarized in Section 13.1. Progress on the development of methods to assess localized impacts from aggregate extraction on fisheries was reviewed in Section 13.2, based on a study using GIS mapping procedures.

## Global Programmes

The ACME reviewed recent activities by ICES for the North Atlantic in relation to the Global Ocean Ecosystem Dynamics (GLOBEC) programme (Section 14.1). Progress in the ICES work in relation to the Global Ocean Observing System (GOOS) was also considered, and it was noted that there are several ICES initiatives that are of direct relevance to GOOS (Section 14.2). A review of some of the methodology being employed in the Global International Waters Assessment (GIWA) is contained in Section 14.3.

## Sources of Information Considered by the ACME at its 2001 Meeting

At its 2001 meeting, the ACME considered, *inter alia*, information included in the most recent reports of the following ICES groups:

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|---|---|
| BEWG | Benthos Ecology Working Group |
| MCWG | Marine Chemistry Working Group |
| SGBEAB | Study Group on the Scientific Basis for Ecosystem Advice in the Baltic |
| SGBOSV* | ICES/IOC/IMO Study Group on Ballast and Other Ship Vectors |
| SGEAM | Study Group on Ecosystem Assessment and Monitoring |
| SGGOOS | ICES/IOC Steering Group on GOOS |
| SGNARO | Steering Group for the ICES-GLOBEC North Atlantic Programme and Regional Office |
| SGPHYT | Study Group on an ICES/IOC Microplankton Protist List |
| SGQAB* | ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea |
| SGQAC* | ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea |
| SGQAE* | ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements related to Eutrophication Effects |
| SGSEA* | Steering Group for a Sea-going Workshop on Pelagic Biological Effects Methods |
| WGBEC | Working Group on Biological Effects of Contaminants |
| WGCCC | Working Group on Cod and Climate Change |
| WGEXT | Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem |
| WGHABD | ICES/IOC Working Group on Harmful Algal Bloom Dynamics |
| WGITMO* | Working Group on Introductions and Transfers of Marine Organisms |
| WGMS | Working Group on Marine Sediments in Relation to Pollution |
| WGPDMO | Working Group on Pathology and Diseases of Marine Organisms |
| WGPE | Working Group on Phytoplankton Ecology |
| WGSAEM | Working Group on Statistical Aspects of Environmental Monitoring |
| WGSE | Working Group on Seabird Ecology |
| WGZE | Working Group on Zooplankton Ecology |

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*These groups report directly to ACME.

# 1 INTRODUCTION

The Advisory Committee on the Marine Environment (ACME) is the Council's official body for the provision of scientific advice and information on the status and outlook for the marine environment, including contaminants, as well as a range of other environmental issues, as may be requested by ICES Member Countries, other bodies within ICES, relevant regulatory Commissions, and other organizations.

In handling the requests, the ACME draws on the expertise of its own members and on the work of various expert ICES Working Groups and Study Groups. The ACME considers the reports of these groups and requests them to carry out specific activities or to provide information on specific topics.

The ACME report is structured in terms of the topics covered at the ACME meeting on which it has prepared scientific information and advice.

The topics include both those for which information or advice has been requested by the Commissions or other bodies and those identified by the ACME to enhance the understanding of the marine environment.

Information relevant to the Commissions' requests and specific issues highlighted by the ACME for their attention are summarized in Section 2 for the OSPAR Commission and in Section 3 for the Helsinki Commission, where the individual work items from each Commission are listed and related to relevant sections of the main text.

In 2000, the Council created a new Advisory Committee on Ecosystems (ACE), with the primary responsibility to provide scientific information and advice on the status and outlook for marine ecosystems, and on exploitation of living marine resources in an ecosystem context. Accordingly, some of the issues that ACME has previously considered have been transferred to ACE. Thus, the ACME report will no longer contain sections on issues regarding seabirds or marine mammals, unless the material pertains to contaminants and their effects, nor on marine habitat classification and mapping or ecosystem assessment.

# 2 PROGRESS ON TASKS FOR THE OSPAR COMMISSION, INCLUDING DATA HANDLING

A summary of the progress on the 2001 programme of work requested by the OSPAR Commission is given below, along with reference to the relevant sections and annexes of this report where more detailed information can be found. This summary is provided according to the format of the Work Programme, with the questions on the Work Programme shown in italics and a summary of the ICES advice below in normal print.

## SCIENTIFIC ADVICE

## 1 QUALITY ASSURANCE (QA)

*1.1 To continue to operate the joint ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements Related to Eutrophication Parameters (chlorophyll-a, phytoplankton, macrozoobenthos and macrophytobenthos) in order to co ordinate:*

*a) the development of QA procedures;*

*b) the implementation of QA activities, e.g., the conduct of workshops and intercomparison exercises;*

*c) the preparation of appropriate taxonomic lists of species.*

*This work should cover the biological parameters within the eutrophication monitoring guidelines, namely: chlorophyll-a, phytoplankton, macrozoo benthos and macrophytobenthos. This is a fairly long-term programme (about five years) requiring the participation of scientists and technicians carrying out relevant analyses for this monitoring in laboratories in OSPAR Contracting Parties. Good cooperation should be ensured with the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea.*

A summary of progress in the work of the ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements related to Eutrophication Effects (SGQAE) is provided in Section 5.2 of this report. SGQAE has completed the final draft of Guidelines for Quality Assurance of Biological Measurements in the OSPAR Area. These guidelines describe the various steps in the QA procedure, including critical QA factors and priority QA actions for monitoring chlorophyll *a*, phytoplankton, macrozoobenthos, and phytobenthos. It is intended that relevant OSPAR subsidiary bodies review these guidelines during 2001, with the aim for their adoption in 2002.

## 2 ASSESSMENT TOOLS

### *2.1 Data preparation methods*

*2.1.1 Consider means of including temporal trend data with various degrees of QA (e.g., "fuzzy" data sets (cf SIME 99/3/25)).*

The response to this request is provided in Section 10.2, with further information and examples contained in Annexes 8, 9, and 10. From this response, it is clear that discussion concerning QA screening and the use of QA data needs to take place with the relevant OSPAR subsidiary body to determine the appropriate balance between QA requirements and the use of data of somewhat lower QA standards in temporal trend assessments. In addition, to be useful for the purposes of assessment groups, a workable procedure for QA screening (and weighting of analysis, if incorporated) needs to be simple, transparent, agreed, and compatible with the data available. Further work will be conducted with representative data sets to develop the methodology.

### *2.2 Further development of EcoQOs for sea mammals*

*2.2.1 Provide a synthesis of the status of North Sea populations of sea mammals, including consideration of species that have declined or are threatened from human activities;*

*2.2.2 Provide a synthesis of the health status of sea mammals in the North Sea in relation to the quality of their habitat;*

*2.2.3 Taking into account the outcome of the Oslo Workshop on Ecosystem Approach including the background document prepared for the workshop and the outcome of the Scheveningen Workshop on EcoQOs, provide recommendations for appropriate EcoQO indices for sea mammals based on 2.2.1 and 2.2.2 and suggestions for appropriate EcoQOs for North Sea mammal populations;*

*2.2.4 Prepare provisional estimates for the current levels, reference levels and target levels for the EcoQO indices identified.*

This request will be handled in detail by the new ICES Advisory Committee on Ecosystems.

*2.3 Further development of EcoQOs for seabirds*

*2.3.1 Provide a synthesis of the status of North Sea populations of seabirds, including consideration of species that have declined or are threatened by human activities;*

*2.3.2 Consider the use of seabirds as indicators for environmental quality and short-term and long-term ecosystem effects;*

*2.3.3 Taking into account the outcome of the Oslo Workshop on Ecosystem Approach including the background document prepared for the workshop and the outcome of the Scheveningen Workshop on EcoQOs, provide recommendations for appropriate EcoQO indices for seabirds based on 2.3.1 and 2.3.2 and suggestions for appropriate EcoQOs for North Sea seabird populations;*

*2.3.4 Prepare provisional estimates for the current levels, reference levels and target levels for the EcoQO indices identified.*

This request will be handled in detail by the new ICES Advisory Committee on Ecosystems.

## DATA HANDLING

## 3 DATA HANDLING ACTIVITIES

*To carry out data handling activities relating to:*

*3.1 contaminant concentrations in biota and sediments;*

*3.2 measurements of biological effects;*

*3.3 the implementation of the Nutrient Monitoring Programme.*

*3.4 data on phytobenthos, zoobenthos and phytoplankton species.*

The ICES Marine Data Centre has handled all data submitted in 2000, covering monitoring activities in 1999. However, fewer data submissions occurred this past year in comparison to previous years. For data on nutrients, there have been few data submissions for the past few years. Further information is contained in Sections 15.1 and 15.2 of this report.

Concerning data on phytobenthos, zoobenthos, and phytoplankton species, the Biological Community Data Reporting Format was restructured in the first part of 2001 and is now available for use. The database is open for submission of data beginning in autumn 2001.

## 4 DATABASE DEVELOPMENT

*4.1 Creation of a relational database for data on contaminants in biota, sediments and water*

*4.1.1 Conversion to relational database;*

*4.1.2 Conversion of screening program;*

*4.1.3 Import/export using spreadsheets;*

*4.1.4 Development of programs for data products, including web inventories.*

*Upgrading the contaminants database will begin with a conversion of the existing database to a relational database and continue with conversion of the screening program for data submissions to Visual Basic for Applications. The upgrading will also cater for the inclusion of biological effects data obtained by the methods for which ICES is developing data reporting formats for OSPAR. The upgrade will also permit the import and export of data using spreadsheet files. It will also cover the development of programs for data products from the new database, including the web-based inventories of the data holdings. This upgrading will bring the contaminants database to the same standard as the newly established biological database.*

The upgrading of the ICES database on contaminants in marine media was discussed in detail at the OSPAR/ICES Workshop on Data Submission and Data Exchange with the ICES Environmental Data Centre, held in Copenhagen on 8–9 February 2001. This Workshop developed a number of recommendations for further actions to be taken by ICES in the redevelopment of this database, which will also provide for the inclusion of biological effects measurements in the database. One of the recommendations requested that ICES develop the capability to accept data submissions as comma-separated ASCII files. An exchange format to accommodate this request was prepared in March 2001 and is under test by several OSPAR laboratories during mid-2001 before it is sent out for wider use.

Design of the new relational database structure will begin in late 2001 and the OSPAR Secretariat will serve as the contact point for OSPAR input to and acceptance of the design specifications before any programming begins.

# 3 PROGRESS ON TASKS FOR THE HELSINKI COMMISSION

The present status of work on 2001 requests by the Baltic Marine Environment Protection Commission (Helsinki Commission) is given below, along with reference to the relevant sections and annexes of this report where more detailed information can be found. The requests are shown in italics and a summary of the ICES advice is then given in normal print.

## CONTINUING RESPONSIBILITIES

1) *To coordinate quality assurance activities on biological and chemical measurements in the Baltic marine area and report routinely on planned and ongoing ICES intercomparison exercises, and to provide a full report on the results.*
   *Based on the ICES Council Resolutions in 1994 and the related decision by HELCOM in 1995, joint ICES/HELCOM Steering Groups on Quality Assurance of Chemical Measurements in the Baltic Sea (meaning the Baltic marine area) and on Quality Assurance of Biological Measurements in the Baltic Sea (meaning the Baltic marine area) have been established. ICES is requested to coordinate the work on behalf of HELCOM.*

Progress in the development of quality assurance procedures for biological measurements in the Baltic Sea is summarized in Section 5.1 of this report. In particular, the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB) reviewed experience with the use of the COMBINE Phytobenthos Monitoring Guidelines. The delay in the establishment of a Phytobenthos Project under HELCOM was noted, and continued interest was expressed in this work.

As summarized in Section 5.4 of this report, the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC) has finalized the following material for inclusion in the COMBINE Manual:

- Notes on Certified Reference Material;
- Technical Notes on the Determination of Organic Carbon in Sea Water;
- Technical Notes on Measurement Uncertainty of Analytical Methods;
- Technical Notes on Units and Conversions with regard to Dissolved Oxygen and Oxygen Saturation.

However, as a more detailed treatment of oxygen conversion tables was contained in the 2000 ACME report, the ACME decided that this material should be incorporated in the Technical Note on Units and Conversions with regard to Dissolved Oxygen and Oxygen Saturation instead. These technical notes will be sent to HELCOM for inclusion in the COMBINE manual.

2) *To annually review the quality of data starting 2001 with a test case by SGQAC reviewing contaminants data for thematic assessment. Provided the test case gives an appropriate result, the review should address also other data and also encompass the SGQAB group.*

   *Within HELCOM there is an ongoing discussion on reporting requirements and the increased demand on timely assessments of the state of the Baltic Sea marine environment. Annual review of monitoring data improves the possibilities to provide annual or biennial assessment reports.*

The SGQAC consideration of assessment criteria was reviewed together with relevant work of other ICES Working Groups and an initial response on this request is contained in Sections 5.5 and 10.2, with further examples in Annexes 8, 9, and 10. This work will require further discussion within ICES Working Groups as well as with the relevant HELCOM subsidiary bodies to determine the basis for QA criteria and their application.

# 4 MONITORING TECHNIQUES AND GUIDELINES

## 4.1 Biological Effects Monitoring

### 4.1.1 Sea-going Workshop on the Effects of Contaminants in Pelagic Ecosystems

*Request*

This is part of continuing ICES work to improve the tools available for monitoring the biological effects of contaminants in the marine environment.

*Source of the information presented*

The 2001 reports of the Steering Group for a Sea-going Workshop on Pelagic Biological Effects Methods (SGSEA) and the Working Group on Biological Effects of Contaminants (WGBEC), and ACME deliberations.

*Status/background information*

The ACME reviewed progress made since its 2000 meeting regarding the organization of the ICES/IOC Sea-going Workshop on Biological Effects of Contaminants in Pelagic Ecosystems (BECPELAG). The idea to hold the workshop was originally developed by the Working Group on Biological Effects of Contaminants (WGBEC), when it identified a lack of agreed methods to assess the impact of contaminants in pelagic ecosystems. Earlier workshops arranged under the auspices of ICES and IOC (e.g., the 1990 Bremerhaven Workshop) have successfully stimulated research into the use of biological effects methods to monitor contaminant impacts in benthic ecosystems. Many of the techniques developed have now been incorporated in national and international monitoring programmes. Since benthos constitutes only a part of the marine ecosystem potentially exposed to contaminants, there has been increasing interest to initiate coordinated studies on effects in pelagic ecosystems as a basis for future monitoring programmes.

A Scientific BECPELAG Steering Committee was established for the detailed planning of the workshop. This Steering Committee is chaired by K. Hylland (NIVA, Norway) and consists of experts from ICES Member Countries representing different relevant disciplines (e.g., ecotoxicology, chemistry, hydrography, statistics, monitoring strategies), including representatives of the Norwegian oil industry.

The following main objectives of the BECPELAG workshop were identified:

- to assess the ability of selected methods to detect biological effects of contaminants in pelagic ecosystems;
- based on the results, to recommend methods suitable for future monitoring programmes on biological effects in pelagic ecosystems.

In 2000, a prospectus of the workshop was distributed together with a call to submit proposals for projects to be incorporated in the workshop. More than thirty proposals were submitted and subsequently evaluated by the Scientific Steering Committee. Proposals accepted were presented at the meeting of the Steering Group for a Sea-going Workshop on Pelagic Biological Effects Methods, held at ICES Headquarters in January 2001, and are included in the report of this meeting.

It was decided that the practical work would focus on two North Sea areas with inputs of contaminants into the pelagic ecosystem: a coastal area (German Bight) mostly influenced by riverine inputs and an offshore area with impact from the oil-producing industry (Statfjord oil production area). In both areas, four sampling sites were selected, three within a contamination gradient and a fourth outside the affected area (reference site).

For the provision of samples, seven cruises with the research vessels “Cirolana” and “Scotia” (UK), “Belgica” (Belgium), “Walther Herwig III” (Germany), and “Johan Hjort” and “G.M. Dannevig” (Norway) have been scheduled, covering the period from late February to early September 2001.

At each of the eight sampling sites in the German Bight and the Statfjord area, sampling of water and pelagic organisms (fish embryos/larvae, juvenile/adult herring (*Clupea harengus*), and saithe (*Pollachius virens*) (only at the Statfjord stations, zooplankton, bacteria) took place. In addition, exposure experiments were carried out, for which cages with cod (*Gadus morhua*), three-spined stickleback (*Gasterosteus aculeatus*), and blue mussel (*Mytilus edulis*) were deployed for five to six weeks in the contaminant gradients. The cages were equipped with Semi-permeable Membrane Devices (SPMDs) used to estimate integrated accumulation of hydrophobic contamination from water and with Diffusive Gradients in Thin films (DGTs) used to estimate integrated accumulation of metals from water.

The biological effects methods carried out within the single workshop project can be divided into three categories, as described in Tables 4.1.1.1 to 4.1.1.3.

**Table 4.1.1.1.** Methods applied on field-collected organisms.

| Organisms | Sample | Endpoints |
|---|---|---|
| Bacteria | Whole water sample | Genetic diversity, degradation |
| Phytoplankton | Whole water sample | Photosynthesis |
| Microzooplankton | Whole water sample | Grazing |
| Zooplankton | Whole *Calanus* | Biomarkers, total oxyradical scavenging capacity (TOSC),<br>DNA damage |
| Krill | Haemolymph, whole krill | TOSC, DNA damage, vitellogenin (vg), zona radiata protein (zrp) |
| Fish embryos | Whole | Aberrations |
| Fish embryos and larvae | Whole | EROD, histopathology |
| Fish larvae | Whole | DNA damage |
| Juvenile herring, Adult saithe | Liver | EROD, MT, histopathology |
|  | Plasma, liver | vg, zrp, CYP (protein and mRNA) |

CYP: cytochrome P450; EROD: ethoxyresorufin-*O*-deethylase; MT: metallothionein; TOSC: total oxyradical scavenging capacity; vg: vitellogenin; zrp: zona radiata protein.

**Table 4.1.1.2.** Methods applied on caged organisms.

| Organism | Tissue | Endpoints |
|---|---|---|
| Blue mussel (*Mytilus edulis*) | Gills | MT induction |
|  | Hepatopancreas | MT induction, histochemistry, AChE, BPH, CYP, oxidative damage, antioxidant enzymes, TOSC, DNA damage |

| | | |
|---|---|---|
| | Haemolymph | Immunotoxicity, lysosomal stability (platereader), immunocompetence |
| | Whole mussels, haemolymph | Lysosomal stability, genotoxicity, pathology |
| | Whole mussel | Scope for growth |
| Atlantic cod (*Gadus morhua*) | Liver | MT, EROD, DNA adducts, CYP, (protein, mRNA), GST, histopathology |
| | Bile | PAH metabolites |
| | Plasma | vg, zrp (protein, mRNA) |
| | Muscle | AChE |
| Three-spined stickleback (*Gasterosteus aculeatus*) | Kidney | Spiggin |
| | Liver | EROD, MT |
| | Bile | PAH metabolites |

AChE: acetylcholinesterase; BPH: benzo[*a*]pyrene hydroxylase; CYP: cytochrome P450; EROD: ethoxyresorufin-*O*-deethylase; GST: glutathione-*S*-transferase; MT: metallothionein; TOSC: total oxyradical scavenging capacity; vg: vitellogenin; zrp: zona radiata protein.

**Table 4.1.3.3.** *In vitro* bioassay methods applied on whole water samples, contaminant extracts or concentrates from water.

| **Test system** | **Endpoints** |
|---|---|
| Pure enzyme | AChE inhibition |
| Primary fish hepatocytes | Apoptosis, DNA damage, viability, mitochondrial function, vg, CYP induction |
| Modified cell lines with reporter genes | Dioxin, oestrogen, androgen receptor |
| Bacteria | Microtox, Mutatox |
| Modified yeast with reporter gene | Oestrogen receptor |
| Juvenile salmon (*Salmo salar*) , i.p. injection | Vg, zrp, CYP induction |
| Egg microinjection, salmon | Embryonal development |
| Early life stage, *Danio rerio* | Embryonal development |
| *Corophium volutator* | Toxicity |
| Oyster embryo, *Tisbe* sp., algae | Toxicity |
| *Arbacia punctulata* | Fertilization, embryonal |

| | |
|---|---|
| | development |
| Invertebrate larvae | Toxicity, UV-exposure |
| *Acartia tonsa* | Survival, reproduction |
| *Nitocra spinipes* | Survival, life cycle |

Apart from the logistics required for the workshop, the workshop provides the following central services for all participants:

- Ship time and space on board for participants;
- Chemical analyses in organisms and water extracts;
- A joint database at Bremen University, Germany;
- A statistical analysis of the combined workshop results;
- To a limited extent, equipment, travel expenses, and shipment of samples to participating laboratories.

It is planned that the workshop results will be presented at a wrap-up conference in 2002 and that the results will be published as a set of scientific papers in a special volume of a relevant scientific journal.

A more detailed overview of the objectives and workshop projects is given on the BECPELAG website (http://www.niva.no/pelagic/web).

*Recommendations*

ICES recommends that Member Countries and relevant regulatory Commissions take note of progress made with regard to the ICES/IOC Sea-going Workshop on Biological Effects of Contaminants in Pelagic Ecosystems (BECPELAG).

*Additional comments*

The ACME appreciated the progress made regarding the ICES/IOC BECPELAG Workshop and emphasized that it constitutes a major ICES activity related to the study of biological effects of contaminants in marine ecosystems. There was consensus that the results of the workshop will be of great interest to ICES Member Countries and the regulatory Commissions such as OSPAR and HELCOM.

**Reference**

Hylland, K. 2000. Biological effects of contaminants in pelagic ecosystems – a practical workshop. ICES CM 2000/S:5. 6 pp.

### 4.1.2 Methods for the analysis of PAH metabolites in bile

*Request*

This is part of the continuing ICES work to provide advice on method developments to be used in monitoring biological effects of contaminants in the marine environment.

*Source of the information presented*

The 2001 reports of the Marine Chemistry Working Group (MCWG) and the Working Group on Biological Effects of Contaminants (WGBEC), and ACME deliberations.

*Status/background information*

The measurement of polycyclic aromatic hydrocarbon (PAH) metabolites in fish bile is part of the OSPAR Joint Assessment and Monitoring Programme (JAMP) recommended series of techniques to determine the effect of PAHs on fish health. The technique has become a widely used within the last few years and it is very appropriate that quality assurance is installed early in the process.

At its meeting in 2000, the Marine Chemistry Working Group (MCWG) was informed about a European project then under way with the aim of developing a fish bile reference material certified for PAH metabolites. At that time an intercomparison exercise had been held, and a second was planned. In 2001, MCWG reviewed a summary report which indicated that the intercomparison exercises had met with some success, as preliminary storage trials were under way and the certification process had also begun for two bile materials (one containing oil-derived and the other combustion-derived PAH metabolites). Insufficient data were, however, given to allow an assessment of the robustness of the methodology or the degree of comparability. From the information provided, it appears that the determination of PAH metabolites provides an insight into recent PAH uptake, and neither gas chromatography/mass spectroscopy (GC/MS) nor high-performance liquid chromatography/UV fluorescence (HPLC/UVF) chromatograms appear to be subject to interferences from other compounds (i.e., there are no false positive results). PAH metabolite concentrations depend to some extent on the feeding status, and fish that have fed very recently and have emptied their gall bladders will show lower metabolite levels. This effect will add to the inter-individual spread, and the representativeness of the group average will depend on the group size. However, one positive aspect of using PAH metabolites as a biomarker of exposure is that the measured parameter is linearly dependent on the uptake (or dose) over several orders of magnitude. This means that even if the inter-individual spread may be as large as 50 %, the group average of a low-exposure population will still be easily distinguishable from that of a high-exposure population. Monitoring should, however, be carried out during the same season so as to avoid bias due to temperature differences.

The more abundant PAH metabolites can be measured without great difficulty using either HPLC/UVF or GC/MS. The analytical uncertainty (within-laboratory) will in most cases be lower than the inter-individual spread. However, for comparison of data obtained in different institutes, the between-laboratory comparability must also be assessed.

Regarding the repeatability/reproducibility: Some laboratories have carried out sufficiently large series of determinations to compile long-term control charts, mostly focusing on 1-hydroxypyrene. At the RIKZ laboratory in Middelburg, the Netherlands, an internal reference material was prepared by homogenizing a pool of ten fish bile samples, and storing single-shot quantities of 10 microlitres in separate vials at –70 °C. The Shewhart control chart produced for the period from March 1999 to December 1999 (24 measurements on different days) showed an average of 312 ng $ml^{-1}$, and 2-sigma warning levels at 280 ng $ml^{-1}$ and 344 ng $ml^{-1}$ (sigma = 16 = 5.1 %). Of the 24 data points, 19 are within 1 sigma from the average, three data points are within 2 sigma and two data points are within 3 sigma of the average. During the latest intercomparison held within the EU Standards, Measurement and Testing (EU-SMT) project, repeatabilities of the order of 2–8 % were obtained for standard solutions and for the major components in real samples.

These results appear comparable to those obtained for other chromatographic procedures. Extraction and/or hydrolysis do not seem to be very critical. However, analysts should be aware of the risk of degradation of standard solutions.

Regarding accuracy: since there is no "absolute method", information regarding the accuracy or "trueness" of the results can only be obtained by comparing results from different laboratories or results obtained in the same laboratory using different methods. The current level of interlaboratory comparability can be improved and this is an aim of the current EU-SMT project. During the latest intercomparison, the between-laboratory coefficients of variation (CVs) for 1-hydroxy pyrene were 28 % and 34 % in the oil-exposed and sediment-exposed fish bile samples, respectively (ten laboratories, two measurements each). Between-laboratory CVs were higher for the other compounds, which in some cases could be traced back to co-elution or other technical problems. It is expected that by organizing further intercomparisons, through better contacts between laboratories, and with the availability of (certified) reference materials, most systematic errors will be identified and overcome in the near future.

In reviewing the above MCWG information on PAH metabolites, WGBEC provided two comments:

a) standardization or normalization procedures (e.g., absorbance at 380 nm, protein and especially biliverdin concentration) should be included in the methodology;

b) concerning monitoring, as for most assays on biological material (including other chemical analyses), it is important to standardize to the type of material used, taking into account season, size, age, sex, water temperature, etc. For

PAH metabolites there are no data to indicate that they should be strongly affected by any environmental factor (and not really by enzyme activities either).

The ACME took note of the above information and looked forward to receiving a summary of the conclusions from the final report of this intercomparison study next year.

### 4.1.3 Monitoring the effects of the "Erika" oil spill

*Request*

This is part of the continuing ICES work to keep under review the use of biological techniques to study the effects of contaminants on the marine environment.

*Source of the information presented*

The 2001 report of the Working Group on Biological Effects of Contaminants (WGBEC) and ACME deliberations.

*Status/background information*

The ACME took note of information that had been discussed in the Working Group on Biological Effects of Contaminants (WGBEC) concerning the implications of the "Erika" oil spill for the coastal area of northwestern France.

WGBEC discussed the general impact of the "Erika" oil spill and the preliminary results from the biological and chemical monitoring of the oil spill effects by IFREMER, France. The "Erika", an Italian-owned tanker chartered by Total, a French oil company, sank off the coast of Brittany, France on 12 December 1999. The ship broke into two parts, and the wreck lies about 40 km from shore at a depth of 120 m. The tanker was en route from Dunkirk to Italy, transporting around 30,000 tonnes of oil, part of which gradually leaked into the sea. The first onshore pollution was observed on 23 December. Several successive pollution episodes then occurred, affecting around 400 km of coast between Finistère (South Brittany) and Charente Maritime (mid-Atlantic region), particularly the areas Loire Atlantique and Vendée immediately north and south of the Loire estuary. The oil spill was not limited in scope, but involved a vast dispersion and fragmentation of pollutant products. It was not easy to predict the sectors that would be contaminated or the duration, which was conditioned largely by leakage from the wreck. Operations to pump oil from the ship's tanks were not conducted until the following summer.

A more detailed description of the incident and the monitoring programme is attached as Annex 1. Samples have been taken, but not all biological effect measurements have yet been made. A holistic interpretation must await availability of the full data set, including biological, hydrographical, and chemical data.

*Need for further research or additional data*

The ACME noted that WGBEC intends to discuss the results from the integrated approach on monitoring of the "Erika" oil spill at its 2002 meeting. This activity is expected to form the basis for future work within WGBEC to develop guidelines and protocols for biological and chemical monitoring of oil spills.

The ACME looked forward to receiving further information on this topic.

### 4.1.4 Differences in sensitivities of freshwater and marine organisms to pollution in relation to marine risk assessment

*Request*

This is part of the ongoing work of ICES to improve the tools available for monitoring the biological effects of marine contaminants.

*Source of the information presented*

The 2001 report of the Working Group on Biological Effects of Contaminants (WGBEC) and ACME deliberations.

*Status/background information*

WGBEC discussed draft documents on methodologies to conduct risk assessments of contaminants in the marine environment and in seafood (see also Section 10.1). WGBEC sees the development of a framework for marine risk assessment as an important task. The discussion focused on the key question of differing sensitivities between freshwater and marine organisms as well as the possible contribution of WGBEC members to an ongoing process concerning the development of a marine risk assessment framework.

WGBEC identified some reasons why it is problematic to extrapolate results obtained for freshwater organisms to marine organisms, including some that were also indicated in the draft document. The main problems relate to:

a) the largely unknown potential impact of contaminants on the fifteen phyla and other taxonomic groups that are found in marine environments, but not in fresh water;

b) the complex, and quantitatively little known, processes that govern bioavailability of contaminants in estuarine and marine environments.

An example from the Seine estuary to illustrate problems related to extrapolations of results from assessments in freshwater organisms to marine organisms was reviewed.

A preliminary approach was developed for the evaluation of the ecological risk in the Seine estuary because the French pollution monitoring programme RNO (French mussel watch) revealed very high PCB contamination in coastal waters and more particularly in the Seine estuary and its surroundings. The concentration of CB153 varies between 200–500 ng $g^{-1}$ dry weight in mussels, whereas the median concentration along the French coast is approximately 50 ng $g^{-1}$ (Loizeau *et al.,* 2001). The awareness of such a high chemical contamination led to the establishment of a multidisciplinary research project, the " Programme scientifique SEINE AVAL", conducted by IFREMER and French universities in the period 1996–2000. This applied research project aimed at a better understanding of the functioning of the estuary in order to improve its water quality and its management.

**Eco-epidemiology approach**

An ecotoxicological study was developed according to an eco-epidemiological approach in order to understand the functioning of the estuary and to link (1) sources of toxic effects, (2) early exposure response, and (3) long-term effects and environmental factors.

1) The potential toxicity of chemical aromatic fractions was studied with the Ames test; PCB and PAH concentration levels were analysed in the sediment; the bioaccumulation of PCBs, PAHs, and heavy metals was analysed in the flounder (*Platichthys flesus*) food web and different criteria were estimated in order to characterize the typology of the Seine estuary (e.g., hydrosedimentary dynamics, nature of the bottom estuary).

2) Early exposure response was evaluated with a battery of biomarkers (neurotoxicity, detoxication, genotoxicity, multixenobiotic resistance, lysosomal stability) in two target species, *Platichthys flesus* and zebra mussel (*Dreissena polymorpha*).

3) Mutation effects (*ras* oncogenes and p53), fish diseases (external and internal diseases), and biodiversity of fish populations were determined as long-term effects.

This study illustrates the interest in an integrated model based on an eco-epidemiology approach for the ecological risk assessment in one estuary. Some advanced biomarkers and bioassays can be integrated as useful tools for biological effects determinations. The presentation of the integrated results and the quality of the figures were underlined by WGBEC as a good example for the user groups of policy-makers, industrialists, and management agencies of the environment.

The second phase of this project was started in 2001 and will be conducted over the next four years. Ecotoxicological and chemical approaches have now been targeted on risk assessment of chemical contaminants. The development of biomarkers and bioassays will be conducted for different trophic levels (fish, molluscs, copepods) in order to compare freshwater and saltwater quality. Some classical tools used for risk assessment such as toxic equivalents (TEQ) will be developed according to an ecotoxicological approach with the aim of obtaining a TEQ more adapted for environmental aquatic impact on molluscs (mussels).

The ACME noted the relevance of this topic to the methodologies considered for adoption for the EU Water Framework Directive (see Section 4.1.5, below).

**References**

Loizeau, V., Abarnou, A., Cugier, P., Jaouen-Madoulet, A., Le Guellec, A.M., and Menesguen, A. 2001. A model of PCB bioaccumulation in the sea bass food web from the Seine estuary (Eastern English Channel). Marine Pollution Bulletin, 43(7–12): 242–255.

### 4.1.5 Implications for marine biological (effects) monitoring of the EU Water Framework Directive

*Request*

This is new work to review the implications of the EU Water Framework Directive on monitoring programmes in coastal and marine areas.

*Source of the information presented*

The 2001 report of the Working Group on Biological Effects of Contaminants (WGBEC) and ACME deliberations.

*Status/background information*

The ACME noted that the Water Framework Directive (WFD) was published in the Official Journal of the European Community on 22 December 2000 (European Commission, 2000a). This date marks the start of a timetable whereby EU Member States need to identify and classify the quality of water bodies to ensure that "good ecological status" is achieved. The Directive will have implications for all aspects of marine monitoring and assessment in EU Member States.

Under Article 5 of the Directive, EU Member States are required, for each river basin district, to complete:

- an analysis of its characteristics;
- a review of the impact of human activity on the status of surface waters and on groundwater; and
- an economic analysis of water use.

These analyses are to be completed by December 2004 under the technical specifications set out in Annexes II and III of the Directive and are to be reviewed on a six- year cycle.

Annex II, section 1 deals with the characterization of surface water body types. The initial step is to identify surface water bodies as rivers, lakes, transitional waters or coastal waters or as artificial or heavily modified surface water bodies. Two systems are offered for further defining surface water types:

- Fixed typology – System A;
- Alternative characterization – System B.

The purpose of the typology process is to physically define water body types to ensure that biological comparisons can be made between similar physical types.

It is generally accepted that System A does not give the differentiation required to allow biological reference conditions to be derived. Where System B is used, EU Member States must achieve at least the same degree of differentiation as would be achieved using System A. So surface water bodies within river basin districts shall be differentiated into types using obligatory descriptors in System B and such optional descriptors or combination of descriptors as are required to ensure that type-specific biological reference conditions can be reliably derived. The product defined in the Directive from the typology process is a map or maps showing at least the degree of differentiation required under System A.

Annex V (see Tables 4.1.5.1–4.1.5.3) deals primarily with monitoring and classification. The Edinburgh Conference (European Commission, 2000b) highlighted the lack of estuarine and coastal waters quality classification systems, i.e., a system which takes data from a variety of sources and interprets the data into an overall descriptor such as "Good" or "Poor". The only established schemes encompassing all monitored parameters were in the UK and Norway. Some other countries (e.g., Sweden) have schemes that consider one aspect of environmental quality such as eutrophication.

These schemes go some way towards meeting the needs of the Water Framework Directive but will need to be modified. Key tasks will include:

- defining reference conditions and locating reference condition sites;
- finding indicators for each biological quality element and for each class (high, good, moderate, poor, and bad);
- exploring options for the combination of biological quality elements for overall ecological quality objectives;
- examining the relationship between the ecological quality and chemical standards and, where appropriate, identifying further work that is needed;
- participating in EU-wide intercalibration exercises on reference conditions and the boundaries between the "High" and "Good" status and the "Good" and "Moderate" status.

**Frequency of monitoring**

Different frequencies of monitoring are recommended in the Directive depending on the current ecological quality and the risks to the water body:

- Surveillance monitoring—for all quality elements for at least one year in a six-year cycle or one year in eighteen years, if good status has been achieved and there is no evidence from the review of human impacts that the situation has changed.
- Operational monitoring—for water bodies at risk of failing to meet their environmental objectives and to assess changes in the status of such bodies resulting from the programme of measures. EU Member States will monitor the appropriate biological and hydromorphological quality elements indicative of the pressures to which the body or bodies are subject.

  All priority hazardous substances must be monitored along with other pollutants discharged in significant quantities.
- Investigative monitoring—where the reason for exceedences is not known or where surveillance monitoring indicates that the objectives are not likely to be achieved and operational monitoring has not been established in order to ascertain the causes of a water body failing to achieve its environmental objectives. Investigative monitoring also covers the survey of pollution incidents.

In addition to the outline for monitoring frequencies given above and in Tables 4.1.5.1–4.1.5.3, section 1.3.4 of the Directive contains comments such as:

- "unless greater intervals would be justified on the basis of technical knowledge and expert judgement";
- "frequencies shall be chosen so as to achieve an acceptable level of confidence and precision"; and
- "monitoring frequencies shall be selected which take account of the variability in parameters resulting from both natural and anthropogenic conditions".

It is clear that many of these caveats are particularly applicable to the marine environment where natural variability is high.

**Table 4.1.5.1.** Annex V: Definitions for high, good and moderate ecological status in transitional and coastal waters. (*Where comments for coastal waters differ from those for transitional waters, these are marked in italics.*)

| **Element** | **High Status** | **Good Status** | **Moderate Status** | **Poor Status** | **Bad Status** |
|---|---|---|---|---|---|
| Phytoplankton | The composition and abundance of the phytoplanktonic taxa are consistent with undisturbed conditions.<br>The average phytoplankton biomass is consistent with the type-specific physico-chemical conditions and is not such as to significantly alter the type-specific transparency conditions.<br>Planktonic blooms occur at a frequency and intensity which are consistent with the type-specific physico-chemical conditions. | There are slight changes in the composition and abundance of phytoplankton taxa.<br>Phytoplankton show slight signs of disturbance.<br>There are slight changes in biomass compared to the type-specific conditions. Such changes do not indicate any accelerated growth of algae resulting in undesirable disturbance to the balance of organisms present in the water body or to the physico-chemical quality of the water.<br>A slight increase in the frequency and intensity of type-specific planktonic blooms may occur. | The composition and abundance of phytoplanktonic taxa differ moderately from type-specific conditions.<br>Phytoplankton show signs of moderate disturbance.<br>Biomass is moderately disturbed and may be such as to produce a significant undesirable disturbance in the condition of other biological quality elements.<br>Substantially outside the range…as to impact upon other biological quality elements.<br>A moderate increase in the frequency and intensity of planktonic blooms may occur. Persistent blooms may occur during summer months. | Biological communities deviate substantially from undisturbed conditions. | Large portions of biological communities are absent. |
| Macroalgae<br>**** Combined with angiosperms for coastal waters – see below**** | The composition of macroalgal taxa is consistent with undisturbed conditions.<br>There are no detectable changes in macroalgal cover due to anthropogenic activities. | There are slight changes in the composition and abundance of macroalgal taxa compared to the type-specific communities. Such changes do not indicate any accelerated growth of phytobenthos or higher forms of plant life resulting in undesirable disturbance to the balance of organisms present in the water body or the physico-chemical quality of the water. | The composition of the macroalgal taxa differs moderately from type-specific conditions and is significantly more distorted than good quality.<br>Moderate changes in the average macroalgal abundance are evident and may be such as to result in an undesirable disturbance of organisms present in the water body. | | |
| Angiosperms<br>**** Combined with macroalgae for coastal waters – see above**** | The taxonomic composition corresponds totally or nearly totally to undisturbed conditions.<br>There are no detectable changes in angiosperm abundance due to anthropogenic activities. | There are slight changes in the composition of angiosperm taxa compared to the type-specific communities.<br>Angiosperm abundance shows slight signs of disturbance. | The composition of the angiosperm taxa differs moderately from type-specific communities and is significantly more distorted than at good quality.<br>There are moderate distortions in the abundance of angiosperm taxa. | | |

**Table 4.1.5.1.** Continued.

| **Element** | **High Status** | **Good Status** | **Moderate Status** | **Poor Status** | **Bad Status** |
|---|---|---|---|---|---|
| *Macrophytes and Angiosperms* | *All disturbance-sensitive macroalgal and angiosperm taxa associated with undisturbed conditions are present.*<br>*The levels of macroalgal cover and angiosperm abundance are consistent with undisturbed conditions.* | *Most disturbance-sensitive macroalgal and angiosperm taxa associated with undisturbed conditions are present.*<br>*The level of macroalgal cover and angiosperm abundance show slight signs of disturbance.* | *A moderate number of the disturbance-sensitive macroalgal and angiosperm taxa associated with undisturbed conditions are absent.*<br>*Macroalgal cover and angiosperm abundance are moderately disturbed and may be such as to result in an undesirable disturbance to the balance of organisms present in the water body.* | | |
| Benthic invertebrate fauna | The level of diversity and abundance of invertebrate taxa is within the range normally associated with undisturbed conditions.<br>All the disturbance-sensitive taxa associated with undisturbed conditions are present. | The level of diversity and abundance of invertebrate taxa is slightly outside the range associated with the type-specific conditions.<br>Most of the sensitive taxa of the type-specific communities are present. | The level of diversity and abundance of invertebrate taxa is moderately outside the range associated with the type-specific conditions.<br>Taxa indicative of pollution are present.<br>Many of the sensitive taxa of the type-specific communities are absent. | | |
| Fish fauna<br>(Transitional Waters Only) | Species composition and abundance are consistent with undisturbed conditions. | The abundance of the disturbance-sensitive species shows slight signs of distortion from type-specific conditions attributable to anthropogenic impacts on physico-chemical or hydromorphological quality elements. | A moderate proportion of the type-specific disturbance-sensitive species are absent as a result of anthropogenic impacts on physico-chemical or hydromorphological quality elements. | | |

**Table 4.1.5.2.** Annex V: Hydromorphological (*Morphological*) elements in transitional and coastal waters.

| **Element** | **High Status** | **Good Status** | **Moderate Status** | **Poor Status** | **Bad Status** |
|---|---|---|---|---|---|
| Tidal regime | The freshwater flow regime corresponds totally or nearly totally to undisturbed conditions. | Conditions consistent with the achievement of the values specified above for the biological conditions. | Conditions consistent with the achievement of the values specified above for the biological quality elements. | | |
| Morphological conditions | Depth variations, substrate conditions, and both the structure and condition of the intertidal zones correspond totally or nearly totally to undisturbed conditions. | Conditions consistent with the achievement of the values specified above for the biological conditions. | Conditions consistent with the achievement of the values specified above for the biological quality elements. | | |

**Table 4.1.5.3.** Annex V: Physico-chemical quality elements in transitional and coastal waters.

| **Element** | **High Status** | **Good Status** | **Moderate Status** | **Poor Status** | **Bad Status** |
|---|---|---|---|---|---|
| General conditions | Physico-chemical elements correspond totally or nearly totally to undisturbed conditions.<br>Nutrient concentrations remain within the range normally associated with undisturbed conditions.<br>Temperature, oxygen balance, and transparency do not show signs of anthropogenic disturbance and remain within the range normally associated with undisturbed conditions. | Temperature, oxygen conditions, and transparency do not reach levels outside the ranges established so as to ensure the functioning of the ecosystem and the achievement of the values specified above for the biological quality elements.<br>Nutrient concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of the values specified above for the biological quality elements. | Conditions consistent with the achievement of the values specified above for the biological quality elements. | | |
| Specific synthetic pollutants | Concentrations close to zero and at least below the limits of detection of the most advanced analytical techniques in general use. | Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 without prejudice to Directive 91/414/EC[1] and Directive 98/8/EC[2] (< EQS). | Conditions consistent with the achievement of the values specified above for the biological quality elements. | | |
| Specific non-synthetic pollutants | Concentrations remain within the range normally associated with undisturbed conditions (background levels). | Concentrations not in excess of the standards set in accordance with the procedure detailed in section 1.2.6 without prejudice to Directive 91/414/EC[1] and Directive 98/8/EC[2] (< EQS). | Conditions consistent with the achievement of the values specified above for the biological quality elements. | | |

[1] Council Directive 91/414/EC of July 1991 concerning the placing of plant protection products on the market.

[2] Council Directive 98/8/EC concerning the placing of biocidal products on the market.

## WGBEC discussion of the WFD

The main issues for discussion were:

- the relevance of the WFD for the use of biological effects in environmental assessment;
- the underlying concept of the Directive; and
- modifications or additions to the Directive.

The Directive will base the assessment of environmental quality on ecological parameters (e.g., diversity) and risk assessments of contaminants. In the opinion of WGBEC, this approach disregards much of the knowledge accumulated over the past twenty years.

Shortcomings in the WFD concerning complex contaminant accumulation in aquatic ecosystems, trophic transfers of contaminants in food webs, and links of contaminant effects at the species or individual level with effects on populations or communities were illustrated by two examples. For many contaminants, there is still uncertainty as to the most important pathways for accumulation and, not less important, the ability of different organisms to metabolize and excrete such substances.

The first example concerns a model of PCB accumulation in dab (*Limanda limanda*) and sea bass (*Dicentrarchus labrax*).

The mechanisms leading to the PCB contamination of aquatic biota, especially top predators, have been greatly debated. Earlier studies have emphasized bioconcentration as being the primary mechanism governing contamination in biota.

The term bioconcentration refers to the accumulation of a chemical through uptake from water. Fugacity-based models simulate this process by assuming an equilibrium of chemical substances between the various environmental phases. Such passive exchange processes should cause the distribution of PCBs and other hydrophobic chemical substances to be proportional to the lipid content of organisms, irrespective of their position in food webs. However, several studies have shown that aquatic organisms can exhibit higher PCB concentrations than would be expected if only bioconcentration processes were involved. This would suggest that some other mechanisms, such as biomagnification through trophic transfer, are governing contaminant accumulation in aquatic organisms and especially in top predators. This trophic transfer of contaminants has been taken into account by several authors in their approach to modelling the bioaccumulation in food webs. A model of this type was developed successfully to simulate PCB bioaccumulation in dab (*Limanda limanda*) from the Bay of Seine (Loizeau and Menesguen, 1993). The ability of models to reproduce measured concentrations in biota, and thus their value as predictive tools, depends on the care taken to describe the basic processes leading to bioaccumulation.

A bioaccumulation model was more recently developed by Loizeau *et al.* (2001) to simulate the PCB contamination in the sea bass (*Dicentrarchus labrax*) food web from the Seine estuary. The model relies upon a contaminant mass balance budget for each biological species. Biological processes determine the extent of bioaccumulation processes. In the second version seasonal variation was taken into account, and finally in the third version, the model was coupled with a population dynamics model to describe PCB contamination in each age class.

The second example contains strategies to link contaminant effects at community and individual levels.

Over the past decades there have been some, but not many, events in which contaminants have been linked unequivocally to population or community effects in the marine environment. Some examples are eggshell-thinning in birds of prey, imposex/intersex in gastropods, and reproductive disorders in Baltic seal populations. If experimental studies under controlled conditions give any indication, however, it is probable that many serious ecological impacts are overlooked. There do exist methods to assess effects at an early stage in organisms, but it is difficult to link such effects to changes in populations or communities. The relationship is indicated in Figure 4.1.5.1. For management purposes, there is really a need for methods at the position "?" in the figure. It is also important to be aware that different contaminants will obviously have very different effects and that some contaminants that are now treated as a pool, e.g., PCBs and polybrominated diphenylethers (PBDEs), really constitute compounds with effect profiles ranging from, e.g., carcinogenicity and neurotoxicity to endocrine disruption.

No method is perfect. It is rarely possible to link community-level effects to contaminant inputs; bioassays are generally not very sensitive and biomarker responses may be linked to contaminant inputs, but are poor predictors of ecological effects. There are at least two approaches to improve on current strategies: one is to use knowledge of community structure to identify possibly sensitive species for subsequent biomarker analyses.

A second approach is to combine a suite of selected chemical, biochemical, and physiological responses to obtain a satisfactory estimate for the health of a target organism. Such an estimate may then be used to model risks to the relevant population (and community). The first strategy could be implemented using available techniques, but there may be a lack of sufficient basic knowledge to implement the second strategy.

Discussion of the Directive and its Annexes resulted in a general agreement on some issues:

a) As the Directive is quality-oriented rather than input-oriented, it should be based on the health status of organisms and the ecosystem rather than on a list of chemicals (priority contaminants). The health of an ecosystem should be assessed both at the level of the individual and at higher levels (e.g., population, community).

b) The proposed approach will not take account of the precautionary principle, but will underestimate effects of contaminants.

c) The environmental risk imposed by contaminants does not stop with fish (as indicated in the present version), but should include seabirds and marine mammals. The endpoints appear insufficient, and trophic levels higher than fish are not (yet) mentioned in the WFD.

d) The application of biological effect biomarkers not only offers the advantage over monitoring of a limited number of chemicals of indicating the environmental health status, but also of hinting at threats imposed by novel contaminants or complex mixtures. It is therefore more apt to show early warning signals.

e) There was a general concern about how to define references, and it appears particularly dangerous simply to transfer risk assessment procedures from freshwater to marine systems (see Section 4.1.4, above).

*Need for further research or additional data*

The development of the WFD and the selection of tools within the Directive to monitor the quality of the environment were seen by the ACME as an important area in the years to come. It was noted that members of WGBEC will produce a position paper on this subject intersessionally. Work within the EU-funded project "Biological Effects of Environmental Pollution in Monitoring and Coastal Ecosystems" (BEEP) will hopefully produce some results that can be used to strengthen the monitoring infrastructure of the WFD.

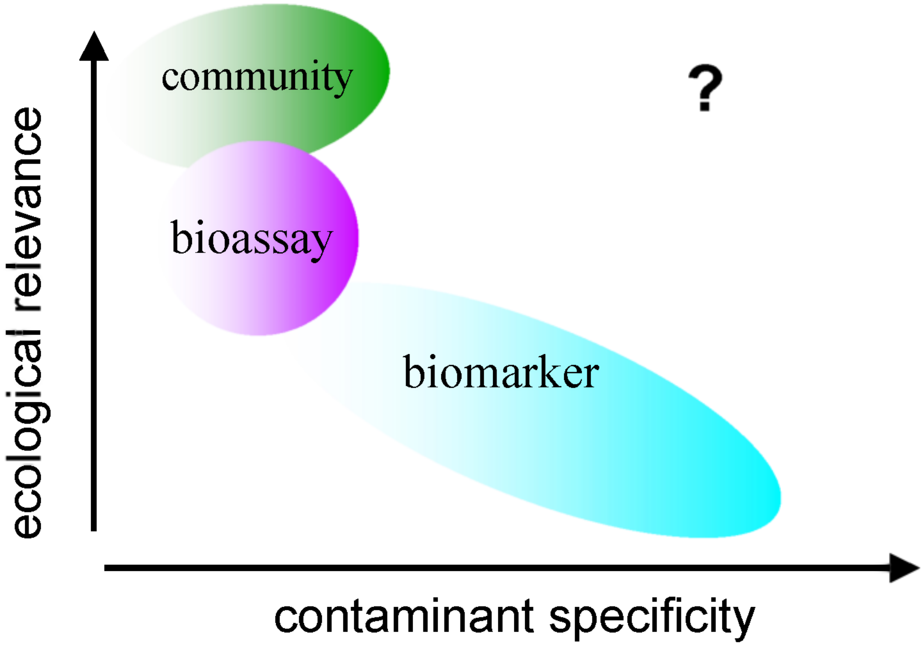


**Figure 4.1.5.1.** Relationship between contaminant specificity and ecological relevance of various biological effects methods.

Annex V of the Directive recommends that, where possible, monitoring should conform with international (ISO/CEN) standards to ensure the provision of data of an equivalent scientific quality and comparability. A number of these standards have still to be developed. It is essential that ICES representatives serve as active participants in the appropriate ISO/CEN groups to ensure that current best practice is promulgated.

ISO/CEN standards provide protocols rather than complete quality assurance. Accordingly, it is essential that the BEQUALM quality assurance system promoted by ICES continues to be developed (see Section 5.3, below).

*Recommendations*

Following deliberations, the ACME expressed its serious concern that the WFD does not include an appropriate biological effects component and therefore may not identify the acute and chronic sub-lethal effects of contaminants on freshwater and marine ecosystems. Monitoring strategies integrating chemical measurements and biological effects measurements at all levels of biological organization have been developed by ICES for the marine area and are being applied as important assessment tools in existing monitoring programmes. Consideration should also be given to their inclusion in the WFD monitoring programmes.

ICES draws the attention of the regulatory Commissions (OSPAR and HELCOM) to the serious concerns regarding the implications of the EU Water Framework Directive on the national monitoring efforts to comply with the existing or recently revised marine monitoring programmes (OSPAR Joint Assessment and Monitoring Programme (JAMP), HELCOM Cooperative Monitoring in the Baltic Marine Environment (COMBINE) Programme).

## References

European Commission. 2000a. Water Framework Directive. Official Journal of the European Communities 22.12.2000 EN L327. Brussels, Belgium.

European Commission. 2000b. Conference Proceedings. Ecological Status of Transitional and Coastal Waters. Towards Classification for the EC Water Framework Directive. 20–22 November 2000, Edinburgh, UK.

Loizeau, V., and Menesguen, A. 1993. A steady-state model of PCB accumulation in dab food web. Oceanologica Acta, 16: 633–639.

Loizeau, V., Abarnou, A., Cugier, P., Jaouen-Madoulet, A., Le Guellec, A.M., and Menesguen, A. 2001. A model of PCB bioaccumulation in the sea bass food web from the Seine estuary (Eastern English Channel) Marine Pollution Bulletin, 43(7–12): 242–255.

## 4.2 Information on Monitoring Techniques and Guidelines relevant to OSPAR

*Request*

This is part of continuing ICES work to improve the tools available for monitoring contaminants and their effects in the marine environment.

*Source of the information presented*

The 2001 report of the Working Group on Biological Effects of Contaminants (WGBEC) and ACME deliberations.

*Status/background information*

In relation to this topic, the ACME referred to information on progress in the ICES/IOC Sea-going Workshop on the Effects of Contaminants in Pelagic Ecosystems, the BEQUALM project, and three other programmes specifically on endocrine disruption in the marine environment (two national programmes: EDMAR (UK), LOES (The Netherlands) and one EU project (COMPREHEND)) which are considered in, respectively, Sections 4.1.1, 5.3, and 6.2.

In addition, the ACME also drew attention to two other programmes (a national programme (the Netherlands) and an EU project) to investigate methodologies for the use of biological effects techniques in ecological risk assessment.

1) A research programme and strategy for effect-based marine monitoring have been established within the Dutch regulatory framework for disposal of dredged material and the marine monitoring programme to assess the quality of the marine environment. This research programme uses biological effects techniques for an integrated chemical and biological effects assessment. In order to be able to effectively manage contaminated harbour sediment in the near future, there is a need to set up systems that would meet both the criteria of integrating effect measurements and an appropriate method to identify chemicals causing the observed effects (e.g., toxicity identification and evaluation (TIE)). In an ongoing research effort concerning the adverse effects of contaminants in the marine and estuarine environment, an instrument is being developed and validated for integrated biological and chemical assessment of ecological hazards using sediment, water, and biota samples. The instrument consists of three main components:

    - *in vivo* bioassays;
    - *in vitro* screening assays;
    - TIE (Toxicity Identification and Evaluation).

    The *in vitro* screening assays concern either broad-spectrum or so-called "toxic-mechanism based" assays as broad-spectrum toxicity, genotoxicity, dioxin-like (Ah-mediated) toxicity, oestrogenic toxicity, and neurotoxicity. The TIE tool under development focuses primarily on the evaluation of the toxicity as observed in *in vitro* screening assays. The tool consists of a range of fractionation techniques combined with a database system, also referred to as the Quality Peak Identification and Database (QPID) system. QPID aims at the identification of organic compounds responsible for effects in screening assays and features a database with gas chromatography/mass spectroscopy (GC/MS) performing characteristics, and physico-chemical and toxicological data for an extended range of environmental chemicals.

2) The new EU project BEEP "Biological Effects of Environmental Pollution in Marine and Coastal Ecosystems" (EVK3–2000–00543 in Sustainable Marine Ecosystems), which started in February 2001, is a pan-European research project and a follow-up activity of the AMAP/EEA/ICES Workshop on Combined Effects in the Marine Environment, held in Copenhagen in November 1998 (ICES, 1999). The goal of the three-year project is to evaluate the use of biological markers determined in marine organisms as a tool for assessing chemical contamination and to investigate the implications of chemical contamination for coastal communities.

    Different types of European coastal environments (Baltic Sea, North Atlantic, Mediterranean Sea) will be investigated by thirty participants (including several members of WGBEC) in order to meet the following objectives:

a) to develop new biological markers ranging over different levels of biological organization;

b) to validate the use of selected biomarkers in specific sites for both routine assessment of chemical contamination and for the improvement of national and international monitoring programmes;

c) to validate a methodology for the biomarker exploration in ecological risk assessment;

d) to prepare information and advice for user groups, policy-makers, and fishery institutions concerning biological effects of chemical contamination on coastal marine resources;

e) to determine the effects of environmental contamination on end-users (fisheries, marine aquaculture);

f) to establish a network of biomarker researchers throughout European countries.

The expected achievements are:

1) to improve and develop knowledge of biological markers in marine organisms exposed to chemical stresses in coastal environments;

2) to determine a standardized battery of biological markers for the implementation of biomarker techniques in national/international monitoring programmes (OSPAR, HELCOM);

3) to investigate a methodology for the use of biomarkers in ecological risk assessment;

4) to improve the quality of environmental data in view of new EU directives for the environment and consumer protection.

More information on BEEP is available on the BEEP website http://www.lptc.u-bordeaux.fr/beep.

The ACME noted these new projects with great interest. Results from the projects will certainly form a basis for future monitoring of biological effects of contaminants in marine systems. The ACME expressed the wish to be kept informed on the progress of these research programmes.

**Reference**

ICES. 1999. Report of the AMAP/EEA/ICES Workshop on Combined Effects in the Marine Environment. ICES CM 1999/E:3.

## 4.3 Information Relevant to the Helsinki Commission Monitoring Programmes

*Request*

This is part of the ongoing work of ICES to keep under review and improve marine monitoring programmes.

*Source of the information presented*

The 2001 reports of the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB), the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), and the Study Group on Ecosystem Assessment and Monitoring (SGEAM), and ACME deliberations.

*Status/background information*

The ACME noted some very positive developments in the HELCOM Cooperative Monitoring in the Baltic Marine Environment (COMBINE) Programme in terms of its ecosystem approach; from the physico-chemical descriptions of the environment in the beginning of the monitoring and assessment programmes towards ecological descriptions of biotopes and the Baltic Sea nature; from description of the status of the open sea, towards environmental assessment of the whole Baltic marine ecosystem under the strong influence of its catchment area. It has also developed in terms of the integrity of the information and cross-disciplinary approaches to environmental problems.

The ACME also noted developments regarding the HELCOM Periodic Assessments. The popular version of the Fourth Periodic Assessment of the Baltic Marine Environment, 1994–1998 (HELCOM, 2001) gives a good impression as a glossy, well-illustrated, clearly structured leaflet.

However, the ACME noted that some important issues are still lacking, such as monitoring of coastal fish and biological effects of harmful substances. In this context, the ACME noted that overviews concerning various biological effects techniques are available in ACME reports, while detailed descriptions are contained in the *ICES Techniques in Marine Environmental Sciences* series.

The ACME also took note of the EU-funded project "Biological Effects of Environmental Pollution in Marine and Coastal Ecosystems" (BEEP) that started in February 2001. The goal of this three-year programme is to evaluate the use of biological markers determined in marine organisms as a tool for assessing chemical contamination and to investigate the implications of chemical contamination for coastal communities. In the regional seas (Baltic Sea, North Sea, Mediterranean Sea), a battery of established and new biological techniques will be applied and evaluated in order to identify those techniques that can be recommended for routine monitoring programmes. The ACME emphasized that the project will be of great interest to HELCOM and will provide useful guidelines for the future monitoring activities in the Baltic Sea.

*Recommendations*

ICES recommends that ICES Member Countries around the Baltic Sea continue efforts on the inclusion of biological effects monitoring programmes in relation to eutrophication and contamination of the Baltic environment.

ICES recommends the continuation of efforts on the development of new techniques that can be useful for marine monitoring programmes, particularly remote and continuous measurements.

ICES also recommends the continuation of efforts on integrated and ecosystem-based assessments of the Baltic marine area.

**References**

HELCOM. 2000a. Guidelines for the Cooperative Monitoring in the Baltic Marine Environment (COMBINE) Programme. http://www.helcom.fi.

HELCOM. 2000b. Outcome of the Workshop on New Assessment Reports and Working Practices of HELCOM MONAS (30–31 October 2000, Gothenburg, Sweden). 29 pp.

HELCOM. 2001. Environment of the Baltic Sea area 1994–1998. Baltic Sea Environment Proceedings, No. 82A. 23 pp.

## 4.4 Arctic Monitoring and Assessment Programme: Developments in Monitoring and Assessment Activities

*Request*

This is ongoing work in cooperation with the Arctic Monitoring and Assessment Programme (AMAP).

*Source of the information presented*

Progress report from the ICES member of the AMAP Assessment Steering Group (Dr H. Loeng) and ACME deliberations.

*Status/background information*

The ACME noted that the main task for AMAP during 2001/2002 is the production of the AMAP assessment reports that will be delivered to the Ministers at their meeting in Inari, Finland in September 2002. To prepare these assessments, AMAP has arranged a number of expert meetings and workshops over the past two years, and additional meetings are arranged for the coming months.

In 2002, AMAP will arrange two major international conferences/symposia as part of its strategy for communicating the results of its 2002 assessments. The Fifth International Conference on Environmental Radioactivity in the Arctic and Antarctic will take place in St. Petersburg, Russia on 16–20 June 2002. This is a joint arrangement between several national and international organizations and agencies, and AMAP. The Second AMAP International Symposium on Environmental Pollution in the Arctic will be arranged by AMAP, together with Finnish institutions, and take place in Rovaniemi, Finland in conjunction with the Ministerial meeting in Inari, Finland in September 2002. This Symposium will be arranged in a similar manner to the First AMAP International Symposium that was held in Tromsø, Norway in 1997 in connection with the Alta (Norway) Ministerial meeting. It is intended that this event will help promote the Inari Ministerial meeting by presenting new and emerging scientific findings.

AMAP is currently mid-way through the work to produce the assessments that will be presented to the Ministerial meeting in Inari, in September 2002. New data and information regarding pollution of the Arctic environment and its implications for the health of human inhabitants of the region are being gathered from national, bilateral, and international programmes being performed in the Arctic and adjacent areas. Part of these data are being compiled at AMAP Thematic Data Centres (TDCs) that are currently being operated for data on contaminants in atmospheric, marine, and terrestrial/freshwater compartments, and for sources and levels of radioactivity. These TDCs are located at the Norwegian Institute for Air Research (NILU), the International Council for the Exploration of the Sea (ICES), the University of Alaska, Fairbanks (UAF), and the Norwegian Radiation Protection Authority (NRPA), respectively. Lack of funding for the core activity of data management, relative to the situation that existed during the equivalent period of AMAP Phase 1, has limited the potential contribution of the AMAP TDCs to the assessments that are currently ongoing.

To facilitate identification of monitoring and research activities in both member countries and other countries that are relevant to the AMAP assessments, an AMAP Project Directory (AMAP PD) has been produced. More than 220 research and monitoring projects are currently registered in the PD. The PD is established as an Internet resource (on-line database) to provide a low-maintenance system that is accessible to the general public. Information compiled in the PD is therefore available to the wider scientific community to improve communication about "who is doing what" in Arctic research and monitoring. Several other organizations (both Arctic Council groups and other national and international organizations) have expressed interest in also entering their information concerning projects and programmes in the AMAP PD. The PD can be found at www.amap.no/amappd.

Four scientific assessments (on 1) persistent organic pollutants, 2) heavy metals, 3) radioactivity, and 4) human health) are being prepared for delivery in 2002. The scientific assessment reports will be produced by AMAP expert groups working under the coordination of the designated Lead Countries. These groups are composed of scientists from the Arctic countries, permanent participants, and some of the observer countries and organizations. Information about the composition of the expert groups and the draft list of contents for the four assessments, together with instructions for the drafting work, have been compiled in a document entitled "Guidelines for the AMAP Phase 2 Assessments". This document is available in electronic form from the AMAP website (www.amap.no).

The AMAP Working Group has decided to employ a scientific journalist from August 2001 to work together with the AMAP Secretariat in drafting the updated "State of the Arctic Environment Report" (SOAER) that will summarize the information contained in the four issue-specific scientific assessment reports.

All countries have expressed their desire to receive copies of the proposed reports and they are currently engaged in finding the necessary funding for their production. Unfortunately, the provision of finances necessary for the production of the reports remains a serious concern. The funding issue is central to the ability of AMAP to deliver its intended assessment reports to the Ministerial meeting in 2002, and the planned contributions for, e.g., the Rio + 10 event.

The Arctic Council is planning to present an Arctic message to the Rio+10 event. It might be expected that material arising from AMAP's 2002 assessments will form a significant part of the documentation supporting this message. One possible requirement might be a need to produce additional copies of the AMAP SOAER for distribution at the Rio+10 meeting. However, a commitment to funding this additional production is required.

In a similar vein, the AMAP 2002 assessments and possible direct AMAP involvement in reports that are planned to be produced by the European Environment Agency (EEA) could contribute to ensuring a high profile for Arctic issues in the European environmental policy debate – the Northern Dimension.

**Relevant literature**

AMAP Report 2000:3. PCB in the Russian Federation: Inventory and proposals for priority remedial actions (Executive Summary).

AMAP Report 2000:4. AMAP Report on Issues of Concern: Updated Information on Human Health, Persistent Organic Pollutants, Radioactivity, and Mercury in the Arctic.

AMAP Report 2000:5. AMAP Report to the Second Ministerial Meeting of the Arctic Council, Barrow, Alaska, U.S.A., October 12–13, 2000.

AMAP Report 2000:6. Report of the Expert Meeting on Sampling and Analysis of Persistent Toxic Substances (PTS), St. Petersburg, May 28 to June 1, 2000.

AMAP Report 2000:7. Minutes from the Fourteenth Meeting of the AMAP Working Group. Trondheim, Norway, September 5–6, 2000.

AMAP Report 2001:1. Guidelines for the AMAP Phase 2 Assessments.

## 4.5 Techniques for Sediment Monitoring

### 4.5.1 Normalization techniques for contaminant concentrations in sediments

*Request*

There is no formal request; this is part of the continuing ICES work on techniques for sediment monitoring and is related to previous requests from the OSPAR Commission.

*Source of the information presented*

The 2001 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS) and ACME deliberations.

*Status/background information*

At the request of ACME in 2000 (ICES, 2000), the Working Group on Marine Sediments in Relation to Pollution (WGMS) prepared a revised “Technical Annex on Normalization of Contaminant Concentrations in Sediments” at its meeting in 2001, based on the 2000 WGMS report. The ACME noted that the comments of ACME presented in its 2000 report (ICES, 2000), as well as earlier ACME advice, have been taken into consideration. In addition, the preliminary outcome of the work package on sieving and normalization of sediments in the EU QUASH (Quality Assurance in Sampling and Sample Handling) intercomparison exercise has been taken into account. The ACME felt that error calculations and examples for demonstrating the application of the normalization approaches presented in the Technical Annex should be appended to the Technical Annex, and noted that these appendices will be produced in due course. The ACME accepted the Technical Annex on Normalization for inclusion in its report as Annex 2, with the comments stated below.

WGMS has stated that the new Technical Annex provides recommendations for a proper application of different approaches of normalization and includes information on their advantages and disadvantages. The preferred approach (recommendation 6 of Annex 2) consists of two possibilities: analysing contaminants in a fine sediment sample or in a sieved fine fraction in order to reduce the analytical uncertainties significantly, followed by normalization with a co-factor that reduces variances due to the natural variability of the geochemical composition of samples.

As pointed out in the 2000 ACME report (ICES, 2000), the widely applied approach of normalizing contaminant concentrations that were analysed in the whole sample, i.e., in the fraction < 2 mm, with a co-factor, suffers from large uncertainties for samples with high proportions of sand and low concentrations of contaminants and normalizers. WGMS 2001 felt that this drawback is overcome with the recommendation to use fine samples or sieved fine fractions for analyses.

WGMS also pointed out that the preliminary results of the QUASH intercomparison exercises clearly demonstrated that variances could be reduced to a large extent by analysing fine samples or sieved fine fractions and that variances could be further reduced by subsequent normalization with co-factors.

As the two-tiered approach based on fines has not yet been applied to large areas, such as the OSPAR area, and its reliability has not yet been proved, the ACME recommended in 2000 that, in the meantime, wide-scale spatial distribution monitoring should avoid normalization through analysis of the fine fraction (ICES, 2000). Although the ACME recognized that the 2000 draft of the Technical Annex was very much improved compared to the earlier version, the ACME repeated its concern that this normalization approach would still not correct for all potential differences in sediment properties. At its 2001 meeting, WGMS addressed this concern and, after discussion, agreed with the ACME comments but ultimately decided that the normalization approach based on fine sediments or sieved fine fractions will improve the statistical power to identify temporal trends and spatial differences in contaminant concentrations compared to the normalization approach based on whole samples. WGMS argued that the normalized data are not intended, nor are they appropriate, for evaluating contaminant loads existing in a certain area. However, in order to avoid any misleading interpretation of data, WGMS followed the ACME recommendation to include the mapping of relevant co-factors in any assessment of spatial data.

The ACME maintained its concerns as to the reliability of partial digestion techniques in trace metals analysis. During the recent QUASH exercise, these partial digestion techniques were tested for only a small number of metal species (Pb, Cd, Zn, Al, Li) and by a very few laboratories. Also, from recent reports on results from QUASIMEME intercomparison exercises, chromium concentrations deriving from partial digestion methods were generally significantly lower than those obtained using a total digestion method; for other metals, the QUASIMEME results, at least for aluminium, seem to confirm the present status of knowledge that the variability between the data obtained by the two digestion methods is dependent on the differences in the mineral composition of the sediment samples. The ACME recommends that sediment partial digestion techniques for metal determinations should not be used on a broad geographical scale due to problems with the determination of the total contaminant contents and the dependence of the efficiency of extraction of metals on the mineralogy of the sediment samples, as well as the absence of reference materials certified for partial digestion methods (ICES, 2000).

After deliberation, the ACME adopted the Technical Annex on Normalization, contained in Annex 2, to replace Technical Annex 2 of the Guidelines for the Use of Sediments in Marine Monitoring (ICES, 1994).

*Need for further research or additional data*

The key feature in the currently accepted approach is that the Technical Annex on Normalization does not consist of methods on the applicability of normalized data for ecotoxicological interpretation. Normalization is primarily developed to correct contaminant contents for differences in sediment composition and does not relate to biological effects. The ACME feels that this matter deserves further investigation.

### References

ICES. 1994. Report of the ICES Advisory Committee on the Marine Environment, 1993. ICES Cooperative Research Report, 198: 45–57.

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 38–40.

### 4.5.2 Methodology for spatial and temporal trend monitoring of sediment quality

*Request*

This is part of continuing ICES work on methods for spatial and temporal monitoring of contaminants in sediments, and the implications for marine environmental programmes in the ICES area.

*Source of the information presented*

The 2001 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS) and ACME deliberations.

*Status/background information*

At its 2001 meeting, the Working Group on Marine Sediments in Relation to Pollution (WGMS) initiated work to recommend a methodology that provides the basis for spatial and temporal monitoring of sediment quality, particularly taking statistical aspects into consideration.

In its 2001 report, WGMS stated that, when discussing the requirements to review the Sediment Monitoring Guidelines and keeping the OSPAR Coordinated Environmental Monitoring Programme (CEMP) in mind, it had given consideration to both temporal trend and spatial surveys. This issue was also considered in the development of the Technical Annex on Normalization (see Section 4.5.1 and Annex 2). WGMS also reviewed a document as a basis for temporal trend monitoring guidelines, but did not produce a separate document on methods for spatial monitoring.

Earlier ICES advice on this issue has been published in several ACME reports. In 1993, the ACME reviewed and approved Guidelines for the Use of Sediments in Monitoring Programmes (ICES, 1994a) based on work by WGMS, at the request of the former Joint Monitoring Group of the Oslo and Paris Commissions, and later adopted by them. These Guidelines comprise an introductory section with generic advice on monitoring, sampling, analysis and data interpretation, followed by four extensive, detailed Technical Annexes. Both in the general and technical parts, advice on methods for spatial and temporal monitoring is included (namely, Technical Annexes 1, 2, and 3 include aspects involved in the different strategies of sampling and analysis, related to the different purposes defined). From 1993 on, Technical Annexes on analytical methods for organic compounds in sediments (CBs, PAHs, and TBT), based mainly on the work of the Marine Chemistry Working Group (MCWG) and WGMS, were reviewed and approved by ACME for inclusion in the ICES sediment monitoring guidelines. Comments on sieving techniques for separation of grain size fractions, and on total organic carbon (TOC) determination were also reviewed by ACME (ICES, 1994b, 1995a).

In addition, more recent reviews have been carried out by ACME of work by the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and MCWG on statistical aspects of spatial and temporal monitoring of sediments based on specific data sets and case studies. Considerations of aspects related to different objectives for, and the design of, spatial and temporal sediment monitoring can be found in the 1995 and 1996 ACME reports (ICES, 1995b, 1996). On the issue of the determination of the number of replicate samples in order to characterize an area, the 2000 ACME report reviewed and advised on work based on case studies: the ACME pointed out that a specific response on this topic would depend on the objectives, e.g., estimating an area mean, mapping of contaminant concentrations, identification of hot spots, or detection of temporal changes. Further, the sampling scheme and the choice of measurements have to be considered, as well as estimates of appropriate components of variability. A continuing need for the further development of sampling allocation strategies was recognized by ACME, as well as the fact that the issue of spatial sampling design should be further developed, and further work based on case studies encouraged (ICES, 2000).

In the ACME discussion of the material prepared by WGMS in 2001, it was noted that the document entitled "Temporal Trend Monitoring" is a brief text, outlining the different approaches which can be taken to temporal monitoring. These may be 1) retrospective studies, i.e., studies of concentrations determined in dated down-core sediments; 2) contemporaneous studies, by repeated surface sediment sampling at the same sites or at different sites within the same area; or 3) the use of sediment traps to collect suspended particulate material regularly at the same sites. Some guidance regarding these approaches is given, as well as brief consideration of the drawbacks and difficulties that may arise in each case.

The ACME noted that this topic will be considered further by WGMS, possibly including discussion with statisticians. Therefore, a more detailed development of the 2001 document describing the different approaches can be expected.

*Need for further research or additional data*

The ACME looks forward to further development of the present work carried out by WGMS, which should include a more fully developed approach to the statistical treatments necessary for identifying and quantifying temporal changes.

**References**

ICES. 1994a. Report of the ICES Advisory Committee on the Marine Environment, 1993. ICES Cooperative Research Report, 198: 20 and 45–57.

ICES. 1994b. Report of the ICES Advisory Committee on the Marine Environment, 1994. ICES Cooperative Research Report, 204: 29–30.

ICES. 1995a. Report of the ICES Advisory Committee on the Marine Environment, 1995. ICES Cooperative Research Report, 212: 33–34.

ICES. 1995b. Report of the ICES Advisory Committee on the Marine Environment, 1995. ICES Cooperative Research Report, 212: 29–33.

ICES. 1996. Report of the ICES Advisory Committee on the Marine Environment, 1996. ICES Cooperative Research Report, 222: 11–14, 39–41.

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 52–53.

## 4.6 Statistical Aspects of Monitoring

### 4.6.1 Methods for the analysis of quarterly and monthly data

*Request*

Item 2 of the 2000 Work Programme from the OSPAR Commission:

2.3 The use of monthly data

2.3.1 Development of provisions for the use of monthly data in these trend detection methods (taking into account that any recommendations should be based on real need and best scientific judgements and should not be driven purely by statistical considerations).

*Source of the information presented*

The 2001 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and ACME deliberations.

*Status/background information*

Following the 1997 ICES/OSPAR Workshop on the Identification of Statistical Methods for Trend Detection, the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) in 1997 and 1998 had discussed several statistical issues concerning the analysis of contaminant inputs data. Further advice concerning specific methodological aspects of trend analysis of input data was requested by OSPAR for 1999. These were addressed at the 1999 WGSAEM meeting and the advice was contained in the 1999 ACME report (ICES, 2000a). For 2000, OSPAR requested further advice on trend assessment tools: To continue the development of trend detection methods in order to:

1) consider further development and assessment of robust smoother methods and the development of appropriate techniques for revealing outlying data values [OSPAR 2000/2.1];

2) consider further development of statistical methods for adjustment of input loads [OSPAR 2000/2.2];

3) develop provisions for the use of monthly data in trend detection methods [OSPAR 2000/2.3].

Items (1) and (2) were fully considered at the 2000 meeting of WGSAEM and the advice was provided in the 2000 ACME report (ICES, 2000b). Due to time limitations, item (3) was only partially addressed. Two approaches were used to de-seasonalize the data: 1) removal of monthly medians; and 2) fitting a sinus function. In both cases, the trend was modelled using a simple linear regression on time. In the first approach, autocorrelation in the residuals is also accounted for by using a first-order auto-regressive model.

As a continuation of the work conducted in 2000 (ICES, 2000b), the 2001 work of WGSAEM addressed new problems related to the erratic behaviour of the season, and pointed out a potential problem with censored data. Both monthly and quarterly data were addressed. Since the trend is not necessarily adequately described by a parametric linear model, non-parametric trend estimation has been applied, while taking seasonal effects into account. Two methods have been considered: 1) a two-stage approach based on a preliminary modelling of the seasonal component by means of a linear model, followed by a LOESS on the residuals, and 2) a single-stage approach, that integrates the seasonality in the LOESS smoother. The details are given in Annex 3.

The following paragraphs summarize the work on the OSPAR request.

**The methods**

In general, the possible presence of a cyclic, or here seasonal, component (i.e., quarterly, monthly, etc.) is accounted for by the following general model (possibly applied locally):

$$Y_i = \mathrm{f}_\mathrm{T}(t_i) + \mathrm{f}_\mathrm{C}(c_i) + \varepsilon_i, \qquad (1)$$

where $Y_i$ is the $i$th measurement, $\mathrm{f}_\mathrm{T}$ represents a parametric or non-parametric trend function that is evaluated at time $t_i$, associated with the $i$th measurement, $\mathrm{f}_\mathrm{C}$ represents a cyclic component that varies with the cycle time $c_i$ (i.e., time during the year) for the $i$th measurement, and $\varepsilon_i$ is a random error term. The variance of $\varepsilon_i$ is not necessarily constant, but may vary inversely proportionally to given weights $w_i$.

Two alternative approaches are considered for the estimation of the trend function and the cyclic component:

In the one-stage approach, least-squares regression (possibly localized) is used to estimate simultaneously the parametric representation of $\mathrm{f}_\mathrm{T}$ and $\mathrm{f}_\mathrm{C}$. When localized, $\mathrm{f}_\mathrm{T}$ is assumed to vary linearly with time $t$ in a local neighborhood of $t_i$ and a weighted regression is used; similarly, $\mathrm{f}_\mathrm{C}$ is assumed to be locally represented by one or two sinusoidal components with unknown phase angles and periods of twelve months for the first component and six months for the second component, if present. In such a one-stage procedure, the neighborhood assumed for both $\mathrm{f}_\mathrm{T}$ and $\mathrm{f}_\mathrm{C}$ is necessarily the same. The procedure is described in detail in Annex 3.

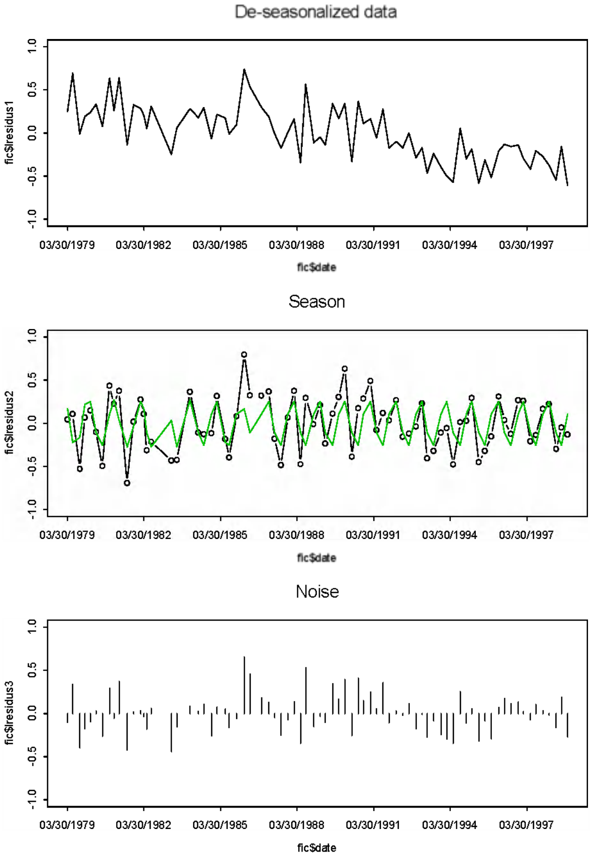
In the two-stage approach, as a first step, least-squares regression is used to estimate the cyclic component (which is again assumed to be adequately represented by one or two sinusoidal components with unknown phase angle and a period of one year). In the applications shown next, the cyclic component is assumed to apply to the entire data set with the same magnitude. In a second step, the trend function is estimated on the basis of the original data corrected from the estimate of the cyclic component.

### Examples

1. Cadmium in oyster (*Crassostrea gigas*) in "Locmariaquer", Brittany.

This application illustrates the two-stage procedure.

Data have been log-transformed in order to stabilize the variance. To visualize the adjustment of the seasonal variations, the Locmariaquer cadmium time series was split into its main components (Figure 4.6.1.1). The top panel shows the de-seasonalized data, i.e., the data after having subtracted the estimated seasonal component. The line with symbols in the middle panel shows the residuals of the original data, having fitted a straight line in time. This curve can be interpreted as an empirical estimate of the seasonality. The gray dotted line in the middle panel shows the fitted seasonal component. This looks irregular owing to the irregular spacing of the data points. The bottom panel shows the difference between the two lines in the middle panel, and can be interpreted as the residuals on the seasonal fit. It can be seen that the parametric model is adequate, except in the early 1980s when the sampling scheme is more irregular, with missing quarters.

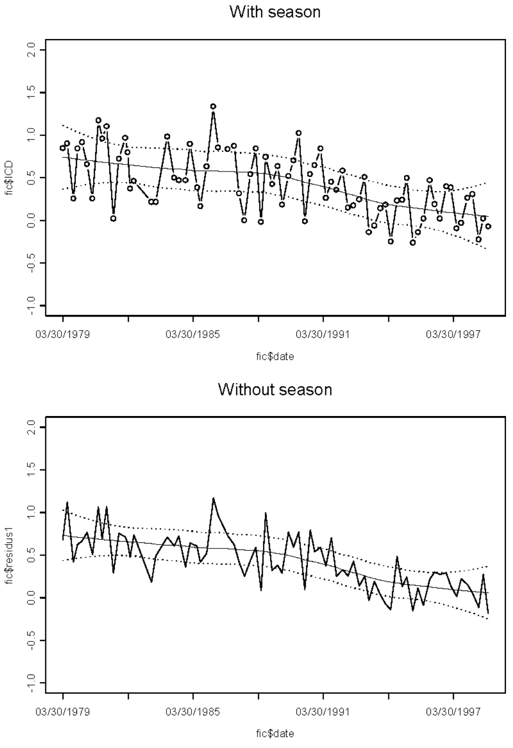


Residus1 = Log concentration minus seasonal component

Residus2 = Empirical and fitted seasonal component

Residus3 = Residuals of season model

**Figure 4.6.1.1.** Variation components of the time series data on cadmium in oysters (*Crassostrea gigas*) at "Locmariaquer".



ICD = Original log concentrations

Residus1 = De-seasonalized log concentrations

**Figure 4.6.1.2.** LOESS applied to the cadmium original series (top) and to the de-seasonalized series (two-stage procedure). Here and in the following examples the LOESS was calculated using a running window (span) of seven years. This is about 1/3 of the whole time series.

The top panel of Figure 4.6.1.2 presents the results of applying a simple LOESS smoother to the original log-transformed data (without taking any account of seasonality at all). The bottom panel shows the fitted trend from the two-stage procedure. Note that the data in the bottom panel are the de-seasonalized data shown in the top panel of Figure 4.6.1.1. The confidence bands from the two-stage procedure (bottom panel) are smaller than when the seasonal effect is not removed (top panel), but the confidence bands from the two-stage approach are likely to be too small, because they neglect uncertainty in the estimation of the seasonal component.

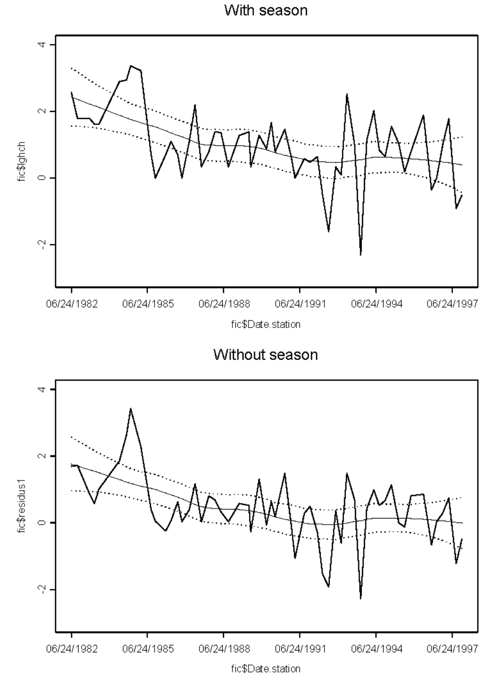
The residual standard error and the confidence bands from the two-stage procedure were compared to those obtained with the single-stage procedure (that estimated both the temporal and seasonal components by LOESS smoothing). The two procedures gave very similar results with a span of ten years: 0.228 and 0.232, respectively, for the residual standard error. Confidence bands were larger in the two-stage approach by a factor of 10 %.

2. Lindane in blue mussel (*Mytilus edulis*) in "Bréville", Normandy

To further compare the two procedures, the methods were applied to the "Bréville" lindane time series, which was more variable, especially for the first five years. The data were also log-transformed.

Figure 4.6.1.3 shows a LOESS smoother applied to both the original log-transformed data (top) and the de-seasonalized data according to the two-stage procedure (bottom). In this case the seasonal component is less important, as can be seen from a comparison of the original and the de-seasonalized data. Only in the last five years does the magnitude of the variations substantially decrease after de-seasonalization.

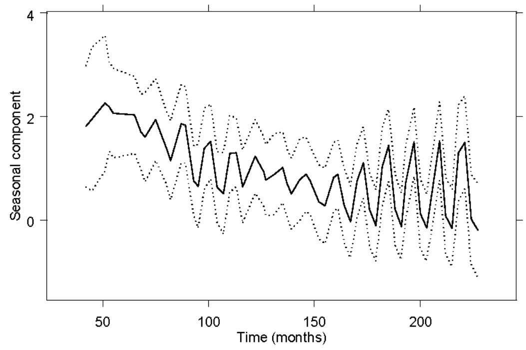
Figure 4.6.1.4 shows the combined fitted trend and seasonal components from the one-stage procedure. Again the one- and two-stage procedures, with a span of seven years, led to very similar results in terms of standard error of the residuals and width of the confidence bands on the estimated temporal trend. Note that in the single-stage procedure, the seasonal pattern is allowed to vary in time. This appears to result in a clear reproduction of the seasonal pattern at the end of the time series, whereas in the early part the seasonal component is estimated to be less important. This example highlights the difference between the two procedures, with a constant season effect modelled by the two-stage procedure opposed to the local view imposed by the single-stage approach. Results of the latter analysis should be carefully interpreted: it is not entirely clear whether the erratic behaviour of the time series is simply due to inaccurate measurements and/or an irregular sampling scheme, or whether this behaviour could be explained through actual seasonal variations in the physiological properties of the bivalves.



Ighch = Original log concentrations

Residus1 = De-seasonalized log concentrations

**Figure 4.6.1.3.** LOESS applied to the lindane original series (top) and to the de-seasonalized series (two-stage procedure) (bottom).

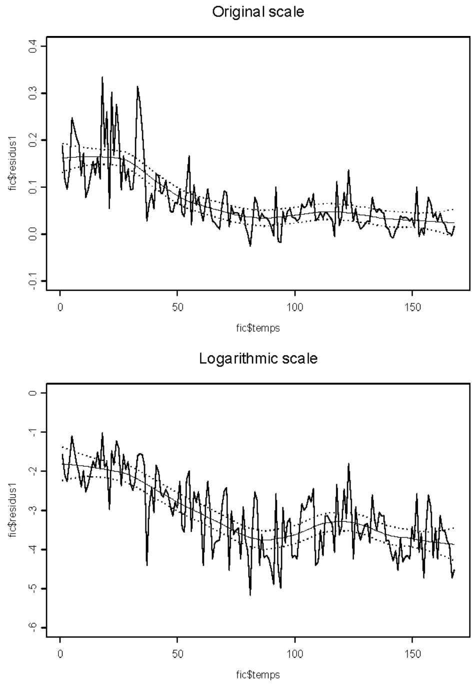


Seasonal component = LOESS smoother accounted for seasonality (single-stage approach)

**Figure 4.6.1.4.** Smoothed estimate of the season with confidence intervals for the single-stage procedure (span = 7 years), applied to the lindane series.

## 3. Herbrum data set on orthophosphate in water runoff

It was interesting here to look at the effect of the log-transformation on the trend estimation using the two-stage procedure. Figure 4.6.1.5 shows the results of the LOESS procedure applied to the data in the original scale (top) and after logarithmic transformation (bottom), in both cases after having subtracted the seasonal component. If the regression results are back-transformed to the original scale, only marginal differences are found. In the middle of the series (bottom), the results are slightly lower presumably due to a large number of “less than” values contained in the data set: while log-transformation stabilizes the variability (including the seasonal component), it may also induce large variation for very small values and thus increase the effect of measurements below the determination limit on the trend.



Residus1 top = De-seasonalized concentrations

Residus1 bottom = De-seasonalized log concentrations

Temps = Time (months)

**Figure 4.6.1.5.** Herbrum orthophosphate time series. Original data (top) and after logarithmic transformation (bottom), after having removed the seasonal effect (two-stage procedure).

**Discussion**

One may conclude that, from a purely theoretical point of view, both approaches, the single-stage and the two-stage procedures, should lead to similar results if a) the trend is slowly varying in time, b) the LOESS smoother is applied over a sufficiently long time span, and c) data are not missing systematically in the ($c$, $t$) plane. The two-stage approach is approximate, whereas the one-stage approach does not use any approximations. The two-stage approach is perhaps more suitable to an exploratory analysis of the data (since it allows to first remove the cyclic component and display the corrected data). Should the data exhibit a cyclic component the size of which itself varies in time, then the two-stage approach could be extended by estimating the cyclic component locally at each time (using a proper time window to determine the weights) and applying in the second step a non-parametric estimation of the trend function (within its own time window) to the residuals. The two-step approach would thus have the advantage of allowing a differentiation between the time spans used for the estimation of a local cyclic component and a local trend. However, it might be preferable to extend the one-stage approach to allow for different smoothing spans for the trend and the seasonal component, but this will require further work. To deal with the erratic season, an iterative approach, called “seasonal LOESS”, developed by Cleveland (1990), might be explored in the future.

*Need for further research or additional data*

Further exploration of the approaches presented is needed, especially with regard to the treatment of seasonality.

**References**

Cleveland, R.B., Cleveland, W.S., McRae, J.E., and Terpening, I. 1990. STL: A Seasonal-Trend Decomposition Procedure Based on Loess. Journal of Official Statistics, 6: 3–73.

ICES. 2000a. Report of the ICES Advisory Committee on the Marine Environment, 1999. ICES Cooperative Research Report, 239: 53–65.

ICES. 2000b. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 42–47, 170–188.

### 4.6.2 Spatial sampling design

*Request*

This is part of the continuing ICES work to provide advice on the development of effective methods for designing monitoring strategies.

*Source of the information presented*

The 2001 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and ACME deliberations.

*Status/background information*

At the 2001 WGSAEM meeting, the basic steps for planning and conducting a spatial study were considered based on experience from satellite data (SeaWifs) on chlorophyll concentrations in the Skagerrak and North Sea. Potential uses for satellite data are:

Planning

- Selecting sampling stations
- Preliminary study of area

Monitoring

- Determining representativity of stations

- Reducing/optimizing sampling stations
- Mapping of eroded material and particle-bounded pollutants and determining critical load to coastal areas
- Mapping of eutrophication and increase in biomass
- Determining the area of influence of pollutants

Dedicated investigations

- Verification and assimilation in models
- Studies of upwelling, frontal zones, and mixing areas
- Studies of possible location for triggering and following the development of algal blooms
- Studying sediments of tidal flats or the marshland vegetation.

Results from the satellite can be integrated into mean levels over months or over a season. Questions that arise in connection with these data include:

1) Optical satellite data will only produce values under cloud-free conditions. This will lead to various uncertainties in different regions and may cause problems in comparing satellite data and *in situ* measurements.

2) A monthly mean or seasonal satellite image will have mean values in different areas based on a different number of observations, and covering different sets of time periods, owing to variable cloud conditions.

3) The satellite chlorophyll *a* will be an integrated signal from the surface with variable depths depending on, e.g., optical quantities. This may cause difficulties in achieving comparable measurements over a wide area.

4) Methods to extract data from satellite information to be evaluated by statistical methods for long-term monitoring still have to be developed.

*Need for further research or additional data*

While traditionally the problem is a lack of data, in this case the main issue is how to reduce vast quantities of data into interpretable summary indicators. Methods and statistical procedures are needed to extract summary measures from the images that can be used, for example, in temporal trend monitoring and studies of spatial variation. One specific method is calculating means and standard deviations over areas of varying size around a station from the satellite images, to determine what area a station represents well.

### 4.6.3 Techniques for dynamic sampling in monitoring programmes

*Request*

This is part of the continuing ICES work to provide advice on the development of effective methods for designing monitoring strategies.

*Source of the information presented*

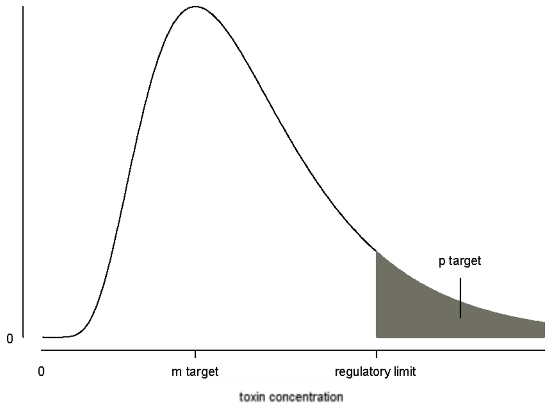
The 2001 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and ACME deliberations.

*Status/background information*

At the 2001 WGSAEM meeting, a dynamic sampling strategy was presented that can be used when assessing toxin concentrations in a shellfish population, and deciding whether the shellfish are safe to harvest. Monitoring is based on taking several pools of shellfish at random from the population, where the number of shellfish in a pool represents a "typical meal". The toxin concentrations in the pools are therefore related to the toxin burdens that a consumer would be exposed to.

Suppose that we can establish a maximum acceptable risk $p_{target}$ that toxin concentrations in a "typical meal" can exceed a pre-specified regulatory limit. Further, suppose that toxin concentrations are log-normally distributed with median $m$ and coefficient of variation $\phi$. Given $p_{target}$ and $\phi$, it is then possible to construct a target level $m_{target}$, such that if $m = m_{target}$, the risk to the consumer is $p_{target}$. This is demonstrated in Figure 4.6.3.1, which shows the distribution of toxin concentrations (in pools of shellfish) about $m_{target}$ and the corresponding proportion of pools $p_{target}$ in which concentrations exceed the regulatory limit.

**Figure 4.6.3.1.** Distribution of toxin concentrations about $m_{target}$ and the corresponding proportion of pools $p_{target}$ in which concentrations exceed the regulatory limit.



It will be "safe" to allow harvesting whenever the median level $m$ is below $m_{target}$, since then the probability of exceeding the regulatory limit will be less than $p_{target}$. To ensure this with reasonable certainty, we allow harvesting only if we can reject the null hypothesis:

$H_0$: $m \geq m_{target}$

in favour of the alternative hypothesis:

$H_1$: $m < m_{target}$,

by, e.g., a one-tailed t-test working on the log-concentration scale. Note that, by allowing harvesting only when we can demonstrate that $m < m_{target}$, we are acting in the interests of the consumer by applying a precautionary health approach.

Clearly, we also have to guard against a sudden increase in toxin concentrations, so harvesting is only allowed for a fixed period (e.g., one week) following sampling. For harvesting to continue further, new samples must be taken, and these must be used to assess whether $m$ is still less than $m_{target}$.

The dynamic aspects of the monitoring programme are:

- The number of pools. The more pools that are sampled, the greater the power of correctly rejecting $H_0$ in favour of $H_1$ when $m < m_{target}$; that is, the more likely we are to allow harvesting when it is safe to do so. It is therefore sensible to take "many" pools when we suspect that $m$ will be "close" to $m_{target}$, and we need good power to discriminate between the two hypotheses. However, when we suspect that $m$ is much less than $m_{target}$, we will need fewer pools to achieve adequate power for rejecting $H_0$ in favour of $H_1$. Conversely, when we suspect that $m$ is much greater than $m_{target}$, there is no point in taking many pools, since we would not expect to harvest anyway.

- The monitoring frequency. When we suspect that $m$ is close to, or well below, $m_{target}$, we wish to monitor every week to ensure maximum possible harvesting opportunities. Conversely, when we suspect that $m$ is much larger than $m_{target}$, there is little point in monitoring every week.

A sensible way of getting a feel for whether $m$ is well below $m_{target}$, close to $m_{target}$, or well above $m_{target}$, is to use the estimate of $m$ from the previous monitoring occasion, $m_{prev}$ say.

A hypothetical example was presented that compared a fixed sampling strategy, in which three pools were taken each week, with the following simple dynamic sampling strategy:

- if $m_{prev} < m_{target}$, sample the next week, and take three pools;
- if $m_{prev} > m_{target}$, sample in two weeks' time, and take only one pool.

In comparison with the fixed sampling strategy, the dynamic sampling strategy resulted in harvesting only a few weeks less each year, but at two-thirds the monitoring cost. It was pointed out that, in practice, the dynamic sampling strategy would be improved by balancing the costs of sampling against the revenue from harvesting, and by taking fewer pools when $m_{prev}$ is much less than $m_{target}$.

### 4.6.4 Spatial design for detecting hotspots

*Request*

This is part of the continuing ICES work to provide advice on the development of effective methods for designing monitoring strategies.

*Source of the information presented*

The 2001 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and ACME deliberations.

*Status/background information*

Spatial surveys are usually aimed at mapping or estimating the mean of some quantity in a survey area. In some contexts, however, the purpose shifts to simply confirming whether or not a particular feature is present. For example, in contaminant monitoring, there may be more concern about the presence of a "hotspot"—a localized region with unduly high levels of some contaminant—rather than with estimating the average concentration of the contaminant over a wider area.

In this context, the problem is simple: how to design or interpret a survey to detect a target in two dimensions. The vertical dimension of the target and its depth below the surface are assumed to be unimportant, and the target is detected if overlaid by one or more sampling points. The following discussion is based on Nicholson (2001), who provides a description of the theory and a review of applications from geology, ecology, archaeology, and pollution monitoring.

For a random survey of $N$ independent sampling points, the problem is reduced to evaluating the probability of no successes for a Binomial distribution with $N$ trials, where the probability of success is given by the relative area of the hotspot, $a$, defined as

$$a = \frac{\text{area of hotspot}}{\text{survey area}} \qquad 0 \leq a \leq 1.$$

As a function of $a$, the probability that the hotspot will be missed by all sampling points is given by

$$\mathrm{Pr}_{\mathrm{ran}}(a) = (1 - a)^{\mathrm{N}}.$$

Since, in general, the probability that the hotspot is missed will decrease with increasing $a$, $\mathrm{Pr}(a^*)$ defines an upper limit for the risk that a target with relative area greater than or equal to $a^*$ is missed, i.e.,

$$\mathrm{Risk(target\ missed} \mid a \geq a^*) \leq (1 - a^*)^{\mathrm{N}}.$$

For a random survey, the formula for the probability that a hotspot is missed applies to any shape of target, even to a fragmented target with total relative area $a$. For systematic surveys, however, the probability is strongly related to the shape of the target. Figure 4.6.4.1a,b shows a realization of a random survey and a fixed survey with a circular hotspot. For the fixed survey, the size of the hotspot is such that it is certain to be detected. In the random survey, however, the hotspot could have slipped between the gaps in the sampling positions.

For a circular target with radius $r$ and total survey area $A$,

$$R = \frac{r}{\sqrt{A/N}}$$

can be defined to be the standardized hotspot radius, a dimensionless measure of target size. Then for a square lattice survey design, the probability that a circular target is missed is given by

$$\Pr_{squ}(R) = \begin{cases} 1-\pi R^2 & 0 < R \le 0.5 \\ 1-R^2\left\{\pi - 4\cos^{-1}\left[(2R)^{-1}\right]\right\} - (4R^2-1)^{0.5} & 0.5 < R \le 0.5^{0.5} \\ 0 & R > 0.5^{0.5} \end{cases}$$

and for a triangular lattice survey design

$$\Pr_{tri}(R) = \begin{cases} 1-\pi R^2 & 0 < R \le 2^{-0.5}3^{-0.25} \\ 1-\pi R^2 + 6R^2 Z - [3(2\sqrt{3}R^2-1)]^{0.5}\ , & 2^{-0.5}3^{-0.25} < R \le 3^{-0.75}2^{0.5} \\ 0 & R > 3^{-0.75}2^{0.5} \end{cases}$$

where $Z = \cos^{-1}(2^{-0.5}3^{-0.25}/R)$.

For a random design, we can write

$$\Pr_{ran}(R) = \left(1 - \frac{\pi R^2 A/N}{A}\right)^N$$

which is approximately given by

$$\Pr_{ran}(R) = \exp(-\pi R^2)$$

for hotspots which are small relative to $A$.

Figure 4.6.4.2 shows the probability of missing a circular hotspot as a function of $R^*$ for these three designs.

The higher efficiency of systematic surveys relative to a random survey applies to circular hotspots. Figure 4.6.4.3 shows an elliptical hotspot of the same area as in Figure 4.6.4.1b, where detection is no longer certain. In fact, as the shape of the hotspot becomes more irregular, so the probability that a hotspot is missed converges to that given by the formula for a random survey for both square- and triangular-lattice designs. In this case, although the logistics of systematic surveys makes them attractive, the formula for a random survey may give a better indication of the risk that a hotspot could be missed.

WGSAEM discussed further sampling schemes that could be adopted. For example, the distance between points, e.g., from east to west, could be modified if there is prior knowledge about the likely orientation and dimensions of an elliptical hotspot, reflecting, e.g., tidal flow.

Adaptive schemes could also be developed where the placing of sampling points could be determined sequentially, depending on whether previous sampling points had indicated a hit or a miss. When a concentration response is also measured at each sampling point, contouring and other spatial mapping tools can be used. The survey may then have more than one objective, for example, to minimize the risk of missing randomly placed hotspots, and to provide a good description of the spatial distribution of contaminant concentrations. One approach to this problem is to allocate the sampling points to minimize the risk that, e.g., a circular hotspot could be missed, and to use a small proportion of data in randomly sited cluster samples to provide information about small-scale spatial variation.

### Reference

Nicholson, M.D. 2001. The Detection of Patches and Trends. Ph.D. Thesis. University of East Anglia, UK.

### 4.6.5 Further analysis of VIC data on the monitoring of temporal trends in contaminants in fish

*Request*

This is an informal request by the OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME) for ICES to review the results of this programme that has been conducted under the framework of OSPAR.

*Source of the information presented*

The 2001 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and ACME deliberations.

*Status/background information*

The Voluntary International Contaminant (VIC) Programme on the monitoring of temporal trends in contaminants in fish was designed to provide information about small-scale temporal and spatial variations, essential for providing estimates of components of variance that may improve the efficiency of the OSPAR monitoring programme. The VIC Programme was conducted within the framework of OSPAR, but review of the outcome by ICES was informally requested in 2000 (ICES, 2000).

In 2001, WGSAEM discussed how to further exploit the information collated in the VIC database.

**Figures 4.6.4.1a, b.** Realizations of random (left) and square-lattice (right) survey designs.

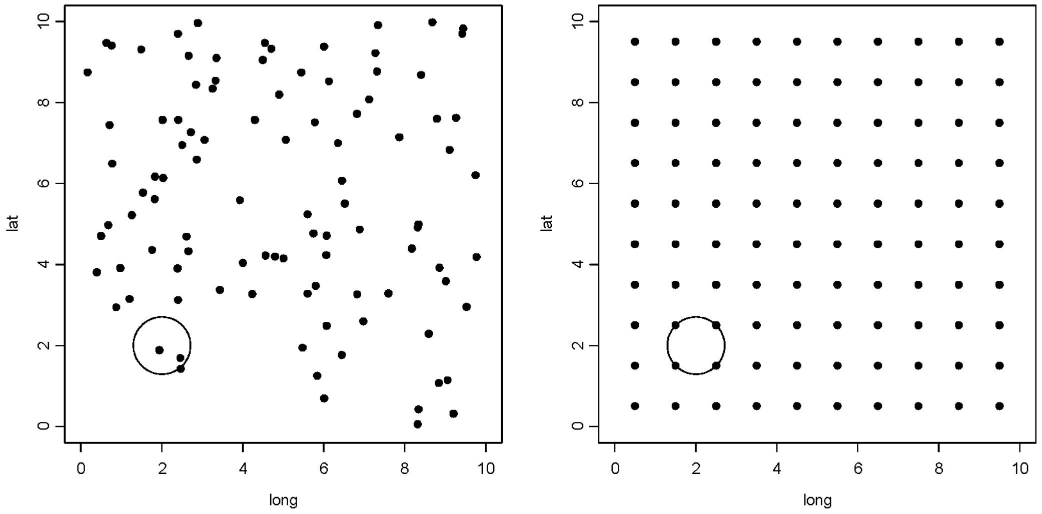


**Figure 4.6.4.2.** Probabilities of missing a circular hotspot for different survey designs.

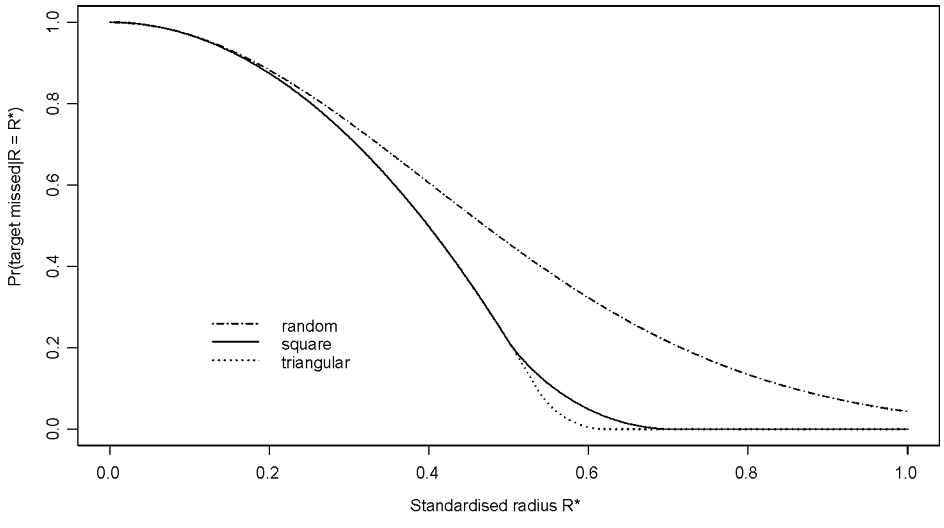
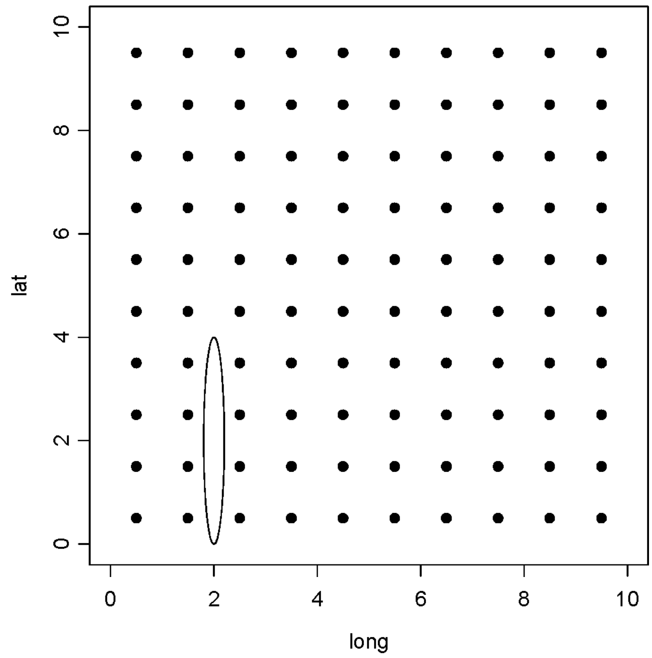


**Figure 4.6.4.3.** Probability calculations are based on the assumption that the hotspots are circular. However, the shape affects the result, and there are situations where a systematic design does not appear to be very effective.



These data have been collected in order to evaluate the implications of the current trend assessment guidelines for samples to be collected at the same time (relative to spawning) and place each year. The general principle is that controlling sampling over a broader spatial/temporal frame may reduce the level of between-year variability in contaminant concentrations.

WGSAEM noted that estimates of spatial and temporal variation in the extended space-time region in the vicinity of monitoring sites can only be derived using the VIC data for a restricted range of sites (Norway, Sweden, and the Netherlands). Hence, it is difficult to draw general conclusions about potential improvements that would arise from possible revisions to the current OSPAR monitoring guidelines, e.g., to collect data in a controlled way over a wider area.

WGSAEM noted that it may be possible to extend the VIC database by using any data in the ICES database that have been collected over a wider spatial/temporal window than strictly allowed by the OSPAR sampling guidelines. Such data could be used in two ways, depending on whether this spatial/temporal variation occurs between or within years.

Spatial/temporal variation in sampling occurring between years might indicate that the guidelines are difficult to follow. For example, if the target for the current guidelines for a length-stratified sample of 25 fish cannot be collected in a short time at the monitoring site, a ship may search within a broader area until a shoal is encountered, at which stage the sample is taken. In subsequent years, fish may be encountered in a different place and at a different time of year. If there is information on this between-year space-time variability, then perhaps the guidelines should be revised from practical considerations, which would allow for sampling across a broader frame in a controlled way.

If spatial/temporal variation in sampling occurs within years, then such data could provide information on the magnitude of spatial and temporal components of variance, which would supplement the information generated by the VIC programme.

In addition to seeking more data on spatial/temporal variation, WGSAEM considered how the VIC data could provide some demonstration of potential benefits of modifying the sampling scheme used for trend assessments. For example, if stratified sampling over a broader temporal/spatial scale could result in reduced variability, different sampling schemes which maintain constant cost (e.g., by off-setting increased sampling costs with reduced analytical costs) but achieve greater power to detect trends in contaminants could be proposed.

The ACME looked forward to review further work on this topic.

## Reference

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 55–57.

# 5 QUALITY ASSURANCE PROCEDURES AND INTERCOMPARISON EXERCISES

## 5.1 Quality Assurance of Biological Measurements in the Baltic Sea

*Request*

Item 1 of the 2001 requests from the Helsinki Commission: to coordinate quality assurance activities on biological and chemical measurements in the Baltic marine area and report routinely on planned and ongoing ICES intercomparison exercises, and to provide a full report on the results.

*Source of the information presented*

The 2001 report of the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB) and ACME deliberations.

*Status/background information*

Development of quality assurance guidelines and procedures for the biological measurements in the HELCOM Cooperative Monitoring in the Baltic Marine Environment (COMBINE) programme has been carried out by the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB) since its establishment in 1992. The following progress has been made since the 2000 meeting of ACME.

SGQAB took note of the draft report from the ICES/HELCOM Workshop and Training Course on Phytoplankton but did not consider the review of the draft report as an adequate action and expressed its concern over not having received the final report.

Experiences in the use of the COMBINE Phytobenthos Monitoring Guidelines were presented to the SGQAB meeting. The COMBINE guidelines are followed by at least two countries (Estonia and Sweden). The establishment of a Phytobenthos Project under the HELCOM framework has been delayed for various reasons, but there was a continuous wish from Finland to lead this activity in the future.

Comments on the ICES Biological Data Reporting Format received by SGQAB were passed on to the ICES Secretariat for consideration. SGQAB decided that further comments on data reporting formats should be submitted to it for review, and not directly to ICES. In reviewing this decision, the ACME agreed that comments regarding the scientific or methodological aspects should be considered by SGQAB, whereas technical comments in relation to the format and its use will need to be handled by the ICES Secretariat. To simplify these submissions, the ACME recommended that all comments be submitted to the ICES Marine Data Centre, which will then forward comments of a scientific nature to SGQAB.

Information on activities within BEQUALM (see Section 5.3, below) was given at the SGQAB meeting as well as information about other activities of relevance for QA procedures. SGQAB strongly emphasized that participation in BEQUALM intercalibrations is needed and relevant also for HELCOM area laboratories.

During the 2000 meeting of SGQAB, a questionnaire concerning experiences associated with the use of new primary production methods in the HELCOM area was produced. However, no replies have been received so far. SGQAB considered the questionnaire once more and decided to request the HELCOM Secretariat to circulate it in parallel with a second distribution to the laboratories.

Members of SGQAB expressed concern regarding the accessibility of the COMBINE manual over the Internet. The location of the links to the COMBINE manual is at present found under several subdivisions and is therefore difficult to reach for individuals working with the actual methods.

A proposal by the ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements related to Eutrophication Effects (SGQAE) to merge SGQAB and SGQAE was discussed. SGQAB decided to postpone any decision on the issue and to continue to hold joint sessions with SGQAE.

*Recommendations*

ICES recommends that comments on the Biological Data Reporting Format should be submitted to the ICES Marine Data Centre, possibly via the discussion forum that has been introduced on the ICES website at http://www.ices.dk/forum/index.htm. The ICES Marine Data Centre should then consider whether the comments submitted are of a scientific nature that needs to be considered by groups such as SGQAB and SGQAE.

### 5.2 Quality Assurance of Biological Measurements in the OSPAR Area

*Request*

Item 1.1 of the 2001 Work Programme from the OSPAR Commission: to continue to operate the joint ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements related to eutrophication parameters (chlorophyll *a*, phytoplankton, macrozoobenthos and macrophytobenthos) in order to coordinate:

- the development of quality assurance procedures;
- the implementation of quality assurance activities, e.g., the conduct of workshops and intercomparison exercises;
- the preparation of appropriate taxonomic lists of species.

*Source of the information presented*

The 2001 report of the ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements Related to Eutrophication Effects (SGQAE) and ACME deliberations.

*Status/background information*

This ongoing request covers a range of activities to coordinate the development of QA procedures, the implementation of QA activities by workshops and intercomparison exercises, and the preparation of appropriate taxonomic lists of species (checklists).

A final draft of Guidelines for Quality Assurance of Biological Measurements in the OSPAR Area has been compiled and is contained in Annex 7 to the 2001 SGQAE report. These draft guidelines describe the different steps in the QA procedures, including data handling. The critical QA factors and priority QA actions for monitoring chlorophyll *a*, phytoplankton, macrozoobenthos from hard and soft sediments, and macrophytobenthos are all treated. Good practice for sampling and analysis of phytoplankton and chlorophyll *a*, soft-bottom macrozoobenthos and hard-bottom macrozoobenthos, and macrophytobenthos complete the compilation. This draft will be circulated this autumn for the comments of experts from different ICES Working Groups including the Benthos Ecology Working Group (BEWG), the Working Group on Phytoplankton Ecology (WGPE), and the Marine Chemistry Working Group (MCWG). These draft guidelines should also be reviewed by the relevant subsidiary bodies in OSPAR so that comments can be returned to SGQAE for preparation of the final guidelines at its 2002 meeting.

The implementation of QA activities also is under way: workshops and intercomparison exercises have been held on several occasions including under the EU-funded BEQUALM project, partly in cooperation with QUASIMEME (for chlorophyll *a*). The BEQUALM project has held two ring tests for chlorophyll *a* measurements and two for identification and counting of phytoplankton cells (see Section 5.3, below).

Activities for the preparation of taxonomic checklists are ongoing in the Study Group on an ICES/IOC Microplankton Protist List (SGPHYT), and there are relevant activities in the Working Group on Zooplankton Ecology (WGZE) and WGPE. A first draft of a checklist for the Baltic Sea will be ready this year. Extension to the remainder of the ICES area is planned, but will take a number of years to complete. The ACME noted that taxonomic checklists are very important for cooperative monitoring programmes and in the handling of biological community data from such programmes.

The ACME recognizes the Workshop held by the WGZE in Germany on the taxonomy of Calanoids as an attempt to steadily improve the quality of identification of zooplankton species. This very much supports the ICES ideas on improved and extended quality assurance of biological data. The incorporation of molecular genetic techniques is highly appreciated, though not excluding the traditional taxonomic characteristics.

Because all of these activities are congruent with those occurring in the Baltic region, coordinated by the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB), joint meetings have been held over the past few years to prevent overlapping work. A proposed merger between SGQAE and SGQAB has been discussed and joint meetings will be held to reach common reporting procedures to both OSPAR and HELCOM.

An extension of the current list of parameters related to eutrophication has been suggested by SGQAE in relation to primary production estimates and zooplankton abundance and species composition. Further consideration of the scientific justifications for these additions will be made.

The ACME reviewed and endorsed a specification for longer-term work activities of SGQAE. The ACME noted that during the 2001 meeting of the OSPAR Environmental Assessment and Monitoring Committee (ASMO) new draft terms of reference for a widened remit were presented and endorsed.

*Recommendations*

ICES stressed the relevance of QA activities on a longer term, including for established monitoring programmes, and therefore recommends that OSPAR continue relevant QA activities after finishing the currently requested activities.

## 5.3 Quality Assurance Procedures for Biological Effects Techniques, including Fish Diseases

*Request*

The ACME keeps under review progress in the development of quality assurance procedures for biological effects monitoring techniques of specific interest to ICES Member Countries and to OSPAR and HELCOM.

*Source of the information presented*

The 2001 reports of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and the Working Group on Biological Effects of Contaminants (WGBEC), and ACME deliberations.

*Status/background information*

Ongoing activities that support quality assurance of methods to measure the biological effects of contaminants include, among other, the publication of *ICES Techniques in Marine Environmental Sciences* (TIMES) leaflets on specific methods, the development of the EU BEQUALM (Biological Effects Quality Assurance in Marine Monitoring) project, and possibly future developments of assessment criteria, e.g., in the EU BEEP project (see Section 4.2, above) and the EU COMPREHEND project (see Section 6.2, below).

Guidelines on quality assurance/quality control (QA/QC) of several ACME-approved biological effects techniques have currently been published or are in the pipeline for publication in the ICES TIMES series. An overview of these publications is given in the reference list at the end of this sub-section.

BEQUALM is an EU-funded project running under the scientific leadership of CEFAS at Burnham-on-Crouch, UK, with the objective of building a European forum that can provide QA/QC for most of the biological effects methods used in major marine monitoring programmes (ICES, 2000). The need for this programme was initially identified by WGBEC and its development was strongly supported by the ACME.

The project has now been running for over two years and has entered its final year. Full details can be found on the BEQUALM website (http://www.cefas.co.uk/bequalm) and a summary and preliminary conclusions are given below.

The Steering Group (see list of partners in Table 5.3.1) for the project reported that all of the scheduled QA exercises within BEQUALM have been carried out broadly on time and the feedback from participants was that this is a much-needed European forum for the development of appropriate quality control systems. For most components, significant progress has been made in the establishment of networks of participants for each work package.

Outputs in the form of CD-ROMs were seen to be a useful training aid and the development of CD-ROMs is being encouraged for each technique.

**Table 5.3.1.** Partners and biological effects techniques in BEQUALM.

| | **Expert Laboratory** | **Work packages** |
|---|---|---|
| Partner 1 | Centre for Environment, Fisheries and Aquaculture Science (CEFAS), (Burnham-on-Crouch, UK)<br>Contact: John Thain | Work package 1 (Central coordination)<br>Work package 2 (Water and sediment bioassays). |
| Partner 2 | Norwegian Institute for Water Research (NIVA) (Oslo, Norway)<br>Contact: Ketil Hylland | Work package 3 (Metallothionein measurement) and Work package 4 (δ-aminolevulinic acid dehydratase (ALA-D) activity). |
| Partner 3 | Institute of Applied Environment Research (ITM) (Stockholm, Sweden)<br>Contact: Lennart Balk | Work package 5 ( DNA adduct measurement). |
| Partner 4 | FRS Marine Laboratory (Aberdeen, UK)<br>Contact: Ian Davies | Work package 6 (P4501A activity)<br>Work package 7 (Imposex/intersex measurement). |
| Partner 5 | NERC Plymouth Marine Laboratory (Plymouth, UK)<br>Contact: David Lowe | Work package 8 (Lysosomal stability *in vitro*). |
| Partner 6 | Centre for Environment, Fisheries and Aquaculture Science (CEFAS), (Weymouth, UK)<br>Contact: Steve Feist | Work package 9 (Liver histopathology, liver nodules and external fish disease measurement). |
| Partner 7 | Institute of Coastal Research, Swedish National Board of Fisheries (SNBF), (Öregrund, Sweden)<br>Contact: Olof Sandström | Work package 10 (Fish reproductive success).<br>[now terminated] |
| Partner 8 | Forschungs- und Technologie Zentrum Westküste, Christian-Albrechts-Universität zu Kiel (CAU) (Büsum, Germany)<br>Contact: Franciscus Colijn | Work package 11 (Chlorophyll *a* and phytoplankton assemblage analysis). |
| Partner 9 | Institut für Meereskunde (IfM) (Kiel, Germany)<br>Contact: Heye Rumohr | Work package 12 (Benthic community analysis). |

The ACME noted that participation levels vary for each exercise depending on the technique, and those directed towards benthos and plankton communities (Work packages 11 and 12) and bioassays (Work package 2) and fish diseases (Work package 9) have more enthusiastic support than some of the biomarker and biochemical approaches. The ACME related the reason for this selectivity to the introduction of the EU Water Framework Directive and the move by OSPAR to an ecosystem approach to environmental management, which dictate that the community-level techniques will become increasingly important and widespread in monitoring programmes.

This brings with it a number of constraints that the Steering Group of BEQUALM has discussed recently. It is quite clear that a centralized QA scheme will have difficulty in meeting the needs for European-wide biological effects technique testing. A simple example is that the species present in the Baltic Sea are very different from those in the Mediterranean Sea and estuarine species are different from those found offshore. A blind testing of species composition is likely to suggest poor competence, when the problem is a lack of familiarity by participants when confronted with samples from foreign waters. Competence for appropriate samples for local conditions should thus be encouraged. The ACME expects that some of the problems relating to the use of the same biological effects techniques in different species will be addressed by the EU-funded BEEP project (see Section 4.2, above).

The way forward for BEQUALM requires consideration. There are a number of possible models that the project could adopt, e.g., a QUASIMEME type of approach or a system akin to the European and National Reference Laboratories that are required by some EC Directives. Cost is an important constraint and the ACME recommends that BEQUALM should not be developed into an overly bureaucratic or costly scheme. There is also a need to address requirements for the most important core of techniques that are needed immediately and those that can be included later. WGBEC identified some methods for which there would be a need for a "new" BEQUALM. They include measurement of proteins (identified during BEQUALM), vitellogenin, acetylcholinesterase inhibition (AChE), measures of DNA integrity, e.g., the COMET assay, scope for growth, cell-based bioassays, antioxidant enzymes (including catalase, glutathione *S*-transferase, glutathione reductase, glutathione peroxidase, superoxide dismutase) and other measures of oxidative stress (e.g., malonedialdehyde (MDA)). There have been some limited intercalibrations for some of the methods in other programmes (e.g., for vitellogenin within the EU-funded project COMPREHEND on endocrine disruption in the marine environment (see Section 6.2), scope for growth, and AChE funded by other sources).

The ACME noted the progress of BEQUALM with satisfaction. The development is seen as very important for the implementation of biological effects methods in marine monitoring programmes.

*Need for further research or additional data*

There is a strong need for a follow-up of BEQUALM. In this respect, the ACME felt that the way forward could best be determined in a joint discussion among international organizations that design, develop, and/or implement biological effects monitoring programmes such as ICES, OSPAR, HELCOM, AMAP, the Monitoring Programme of the Mediterranean Action Plan (MEDPOL), and the EU. In addition, a follow-up might need to be coordinated in combination with other programmes such as the EU BEEP project in which there are also planned intercalibration exercises.

**References and Relevant Literature**

Bocquené, G., and Galgani, F. 1998. Biological effects of contaminants: Cholinesterase inhibition by organophosphate and carbamate compounds. ICES Techniques in Marine Environmental Sciences, 22. 12 pp.

Bucke, D., Vethaak, D., Lang, T., and Mellergaard, S. 1996. Common diseases and parasites of fish in the North Atlantic: Training guide for identification. ICES Techniques in Marine Environmental Sciences, 19. 27 pp.

Galgani, F., and Payne, J.F. 1991. Biological effects of contaminants: Microplate method for measurement of ethoxyresorufin-*O*-deethylase (EROD) in fish. ICES Techniques in Marine Environmental Sciences, 13. 11 pp.

Gibbs, P.E. 1999. Biological effects of contaminants: Use of imposex in the dogwhelk (*Nucella lapillus*) as a bioindicator of tributyltin (TBT) pollution. ICES Techniques in Marine Environmental Sciences, 24. 29 pp.

Hylland, K. 1999. Biological effects of contaminants: Quantification of metallothionein (MT) in fish liver tissue. ICES Techniques in Marine Environmental Sciences, 26. 18 pp.

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 65–69.

Reichert, W.L., French, B.L., and Stein, J.E. 1999. Biological effects of contaminants: Measurement of DNA adducts in fish by $^{32}$P-post-labelling. ICES Techniques in Marine Environmental Sciences, 25. 45 pp.

Roddie, B., and Thain, J. 2001. Biological effects of contaminants: Sediment bioassay with *Corophium volutator*. ICES Techniques in Marine Environmental Sciences, 28.

Rumohr, H. 1999. Soft bottom macrofauna: Collection, treatment, and quality assurance of samples (Revision of No. 8). ICES Techniques in Marine Environmental Sciences, 27. 19 pp.

Scott, A.P., and Hylland, K. 2001. Biological effects of contaminants: Radioimmunoassay (RIA) and enzyme-linked immunosorbent assay (ELISA) techniques for the measurement of marine fish vitellogenins. ICES Techniques in Marine Environmental Sciences, 31.

Thain, J., and Bifield, S. 2001. Biological effects of contaminants: Sediment bioassay with *Arenicola marina.* ICES Techniques in Marine Environmental Sciences, 29.

Smedes, F., and de Boer, J. 1998. Chlorobiphenyls in marine sediments: Guidelines for determination. ICES Techniques in Marine Environmental Sciences, 21. 24 pp

Stagg, R., and McIntosh, A. 1998. Biological effects of contaminants: Determination of CYP1A-dependent mono-oxygenase activity in dab by fluorimetric measurement of EROD activity. ICES Techniques in Marine Environmental Sciences, 23. 16 pp.

Thain, J.E. 1991. Biological effects of contaminants: Oyster (*Crassostrea gigas*) embryo bioassay. ICES Techniques in Marine Environmental Sciences, 11. 12 pp.

## 5.4 Quality Assurance of Chemical Measurements in the Baltic Sea

*Request*

Item 1 of the 2001 requests from the Helsinki Commission: to coordinate quality assurance activities on biological and chemical measurements in the Baltic marine area and report routinely on planned and ongoing ICES intercomparison exercises, and to provide a full report on the results.

*Source of the information presented*

The 2001 reports of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC) and the Marine Chemistry Working Group (MCWG), and ACME deliberations.

*Status/background information*

The ACME reviewed the work of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), noting further progress by SGQAC in the development of Guidelines for the Cooperative Monitoring in the Baltic Marine Environment (COMBINE) Programme. This includes finalization of the following:

- Notes on certified reference materials;
- Technical Notes on Units and Conversions with Regard to Dissolved Oxygen and Oxygen Saturation;
- Technical Notes on the Determination of Organic Carbon in Sea Water;
- Technical Notes on Measurement Uncertainty of Analytical Methods.

Further developments needed include work on the following topics:

1) the development of Quality Criteria to be employed in reviewing monitoring data prior to their use in the preparation of data products for environmental assessments. This will include specifications of the QA information that should be reported with the monitoring data. This work will also include development of a proposal for performance criteria for participating laboratories in the COMBINE programme;
2) review and completion of Quality Assurance guidelines for primary production determinations;
3) review of Quality Assurance guidelines for chlorophyll determination;
4) preparation of updated Technical Notes on Contaminants in Fish. This will include new guidance on the use of procedural blanks and critical steps in the dissection of biota and the homogenization of tissues, based on results of the QUASH project;
5) preparation of updated Technical Notes on Method Validation;
6) preparation of Technical Notes on Persistent Organic Pollutants, covering QA recommendations for the determination of organocholorines and PAHs in water, sediment, and biota;
7) consideration of whether the general part of the QA guidelines is consistent with the new ISO 17025 (substituting ISO 45001).

The ACME expressed its appreciation for the up-to-date development of comprehensive QA Guidelines for the HELCOM COMBINE monitoring programme by SGQAC.

In reviewing the Technical Notes on Units and Conversions with Regard to Dissolved Oxygen and Oxygen Saturation, the ACME noted that the SGQAC document relies on the UNESCO tables which are slightly in error. A note on this topic prepared by the Marine Chemistry Working Group (MCWG) in 2000 takes this error into account and provides the correct formulas to program the calculators so that the correct values of dissolved oxygen are obtained. This MCWG note was published in the 2000 ACME report (ICES, 2000). The ACME agreed that the two notes should be merged, with a minimum degree of editing, and the Chair undertook to do this. The amended Technical Note should then be forwarded to HELCOM.

The ACME noted that the Guidelines on Quality Assurance of Chemical Measurements in the Baltic Sea, including all Technical Notes prepared to date, will be published in the *ICES Techniques in Marine Environmental Sciences* series in early 2002.

*Need for further research or additional data*

The ACME agreed that performance criteria for laboratories participating in the COMBINE Programme should be developed, to be used to give guidance on the level of performance expected of the laboratories. These criteria can also form a vital part of the QA Report.

*Additional comments*

The ACME appreciates SGQAC and SGQAB efforts to cooperate on quality assurance issues in the Baltic Sea with a joint session at their 2001 meetings and the proposal for the next joint session in 2003.

*Recommendations*

ICES recommends that the Notes on Certified Reference Materials, the Technical Notes on the Determination of Organic Carbon in Sea Water, and the Technical Notes on Measurement Uncertainty of Analytical Methods should be transmitted to the Helsinki Commission for inclusion in the COMBINE Manual. The Technical Notes on Units and Conversions with Regard to Dissolved Oxygen and Oxygen Saturation will be merged with the oxygen solubility equations in the 2000 ACME report and also transmitted to HELCOM.

**Reference**

ICES. 2000. Recommended equations for the calculation of solubility of dissolved oxygen in marine waters. *In* Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 199–200.

### 5.5 QA Data to be Submitted to the Database and Potential for a Data Filter

*Request*

Item 2 of the 2001 requests from the Helsinki Commission: to annually review the quality of data starting 2001 with a test case by SGQAC reviewing contaminants data for thematic assessment. Provided that the test case gives an appropriate result, the review should address also other data and also encompass the SGQAB group.

*Source of the information presented*

The 2001 reports of the Marine Chemistry Working Group (MCWG) and the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), and ACME deliberations.

*Status/background information*

The ACME noted that SGQAC had prepared a draft template for QA information at its 2001 meeting. This template will identify the QA information that is required for data assessors and that should be sent together with the monitoring data to the data bank in the regular submissions. SGQAC agreed that there is a need to define quality control criteria for assessing the data.

After reviewing the SGQAC template and much discussion, MCWG prepared a modified draft, which also defined the QA data to be held in the ICES database. This included information on the uncertainty associated with measurements (laboratory precision and bias), limits of detection and determination, blanks and recoveries, and proficiency testing schemes and intercomparison exercises undertaken.

The ACME noted that the revised QA reporting requirements will be complemented with guidelines for how to fill in the QA information and guidelines for users of the data.

The ACME noted that this work is still in progress and will be completed in 2002.

## 5.6 Certified Reference Materials for Use in Marine Monitoring

*Request*

This is part of continuing ICES work on quality assurance related to chemical determinations of contaminants and reporting of the results, and the implications for monitoring programmes of OSPAR and HELCOM.

*Source of the information presented*

The 2001 reports of the Marine Chemistry Working Group (MCWG) and the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), and ACME deliberations.

*Status/background information*

At its 2001 meeting, MCWG considered a very recent scientific publication by J. de Boer and E. McGovern on certified reference materials (CRMs) for organic contaminants for use in monitoring of the aquatic environment, which includes tables of updated lists of those materials (de Boer and McGovern, 2001). MCWG also produced compilations of information on CRMs for the same purpose for trace metals in sea water, marine biota and sediments, and for nutrient compounds in surface sea water and waste water. These compilations are attached as Annex 4.

In its 2001 report, SGQAC also presented an updated table listing currently available CRMs for contaminants and for nutrient compounds, that they intend to update every second year.

This compilation was initiated by MCWG in 1998 for organic contaminants and was first updated in 2000. The results have been reviewed and annexed to ACME reports (ICES 1999, 2000). The ACME has endorsed the views of MCWG on the relevance and usefulness of this compilation, and has recommended that certified reference materials be used in research and monitoring studies on the marine environment, as they are a very important part of the quality control process. The ACME has also proposed that the CRM tables produced by MCWG be regularly updated and widely distributed, making them available and accessible, e.g., on the ICES website (ICES, 2000).

In its 2001 report, MCWG pointed out that the tables provided are for information and do not necessarily infer that the CRMs listed are of an appropriate quality for marine monitoring; it is up to the laboratories to evaluate the CRMs and ensure that they are fit for the purpose, given the individual circumstances and programmes. An updated list of websites, where additional information and details on CRMs can be found, is included in Annex 4.

In addition, MCWG provided information about ongoing projects and current developments regarding CRMs for marine media. Progress in this field associated with research on analytical chemistry has been followed on a regular basis by MCWG, which has discussed the needs and demands for these materials for marine research and monitoring, as part of the quality assurance related to chemical determinations. MCWG reported that the EU Institute of Reference Materials and Measurements, previously the Bureau of Community Reference (BCR), has issued new CRMs, CRM 682 (in mussels) and CRM 718 (in herring), both certified for chlorobiphenyls (CBs), and that CRM 719 for non-*ortho* CBs in chub (a freshwater fish) is in preparation. Also, a new project will provide a two-year feasibility study for new CRMs for polybrominated diphenylethers (PBDEs) in sediments and fish, organochlorine pesticides in fish, and PAHs in mussels. MCWG pointed out that, according to the information available, these materials are intended to be available by 2005, following a full-scale preparatory project to be undertaken if the feasibility studies are successful.

In addition, MCWG considered possible mechanisms for the review and updating of the CRM tables. It was noted that many new certified materials are prepared on a commercial basis each year, and stocks of other previously listed materials may become exhausted so that they are no longer available. The information on these materials is made available by their producers, but there is no specific database identifying CRMs relevant to the marine environment. MCWG considered such a specific database on CRMs for marine environmental monitoring to be very useful for the potential users within marine monitoring and research laboratories. The information needed for the database is presented in Table 5.6.1.

**Table 5.6.1.** Information needed for a CRM database.

| | |
|---|---|
| ***Code*** | |
| *Organization* | |
| *Country of origin* | |
| *Matrix* | |
| *UNITS* | |
| *AS* | |
| [±] *expressed as* | |
| UNITS OF ISSUE | |
| *FORM* | |
| Analytes (concentration)* | |

* indication should be given if the concentration is a certified value or tentative.

It was noted in the MCWG discussion that ICES should consider whether a section of the ICES website could be devoted to information on marine CRMs, with a compilation of direct links to the websites of the producers of these materials for additional information. MCWG also considered that, as a further development and if in accord with ICES policy, a CRM database could be constructed and be continuously updated directly by the producers themselves, thereby providing the most up-to-date information in a more timely manner than can be given following the annual meetings of MCWG.

The ACME reviewed the above information and decided that the CRM tables for trace metals and nutrient compounds prepared at the 2001 meetings of MCWG and SGQAC, together with their footnote comments, as well as the list of websites for additional information and details on CRMs, should be annexed to its report as Annex 4.

The ACME endorsed the proposal of MCWG that a portion of the ICES website should be dedicated to CRMs for use in marine research and monitoring; it was agreed that means should be found within the ICES system so that, as a first step, direct links to the websites of the producers of these materials could be included in the ICES website. In a future stage, this could be developed into a database for marine CRMs, to be regularly updated.

*Additional comments*

The ACME expressed its gratitude and appreciation to E. McGovern (Marine Institute, Dublin, Ireland) and J. de Boer (Netherlands Institute for Fisheries Research, IJmuiden, The Netherlands) for the good quality, exhaustive work carried out on the compilation and update of CRM lists for organic contaminants, and welcomes that the topic of the use of CRMs in the monitoring of the aquatic environment was given wide audience and recognition by publication of their work in the open scientific literature. The ACME expressed the same gratitude and appreciation to P. Woitke (Federal Environmental Agency, Berlin, Germany) and E. Sahlsten (Swedish Meteorological and Hydrological Institute, Oceanographic Services Unit, Göteborg, Sweden) for their new compilation on CRMs for trace metals and nutrient compounds, respectively.

**References**

de Boer, J., and McGovern, E. 2001. Certified Reference Materials for organic contaminants for use in monitoring of the aquatic environment. Trends in Analytical Chemistry, 20(3): 140–159.

ICES. 1999. Report of the ICES Advisory Committee on the Marine Environment, 1998. ICES Cooperative Research Report, 233: 47–56.

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 70–71, 191–198.

## 5.7 Developments within QUASIMEME

*Request*

This item is an ACME initiative to follow the developments in this QA project owing to the long-standing ICES involvement in quality assurance matters.

*Source of the information presented*

The 2001 report of the Marine Chemistry Working Group (MCWG), internal reports from QUASIMEME, and ACME deliberations.

*Status/background information*

The ACME was informed that QUASIMEME has developed a new style and structure of reports that will be submitted to OSPAR and HELCOM, and the initial report was made available in this format for the 2001 meeting of the OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME). This report included a summary of the data from the last full QUASIMEME year (1999/2000), which included rounds 18 and 20 in the scheme.

Information on QUASIMEME can be found on its website: http://www.quasimeme.marlab.ac.uk. This site provides details on Laboratory Performance Studies (LPS), previous newsletters, and information on the project and the test materials used in the LPS. The intercomparison exercise reports are also available on the website.

The overall performance of all laboratories for the last four years, while the subscription scheme has been in operation, was reported at a conference held in Egmond-aan-Zee in the Netherlands in October 1999. Throughout this period and during the initial pilot phase, the data assessments used to obtain the assigned values were based on the robust statistics developed by the Royal Society of Chemistry in the UK.

An alternative approach, using model statistics developed by Cofino *et al.* (2000), has now been applied to the QUASIMEME Laboratory Performance Studies results on a routine basis. QUASIMEME has conducted a series of quality control checks on these methods, comparing them with data obtained from robust statistics. Very good agreement was obtained for analyses under control, but the model statistics were better able to separate the effects due to the application of different analytical methods on the results obtained. The detailed results of these comparisons will be published in due course.

The ACME was informed that the 2002 meeting of MCWG will be provided with overviews of (a) the QUASIMEME Laboratory Performance Studies during the past six years, and (b) the results of the PAH metabolite studies, which will have been completed by then.

**Reference**

Cofino, W.P., van Stokkum, I.H.M., Wells, D.E., Ariese, F., Wegener, J.-W.M., and Peerboom, R.A.L. 2000. A new model for the inference of population characteristics from experimental data using uncertainties in data. Application to interlaboratory studies. Chemometrics and Intelligent Laboratory Systems, 53: 37–55.

# 6 MARINE CONTAMINANTS: DISTRIBUTION, TRANSPORT, AND EFFECTS

## 6.1 Information on Specific Contaminants

*Request*

This is part of the continuing ICES work to keep under review contaminants of interest in a marine environmental context.

*Source of the information presented*

The 2001 reports of the Marine Chemistry Working Group (MCWG) and the Working Group on Biological Effects of Contaminants (WGBEC), and ACME deliberations.

*Status/background information*

The ACME took note of new information on several groups of marine contaminants, as prepared by the Marine Chemistry Working Group (MCWG) and reviewed and commented by the Working Group on Biological Effects of Contaminants (WGBEC).

### 6.1.1 New information on *tris*(4-chlorophenyl) methanol (TCPM) and *tris*(4-chlorophenyl) methane (TCPMe)

Since 1996, the MCWG has kept under review the occurrence of *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in the marine environment. These widespread contaminants are highly bioaccumulative and have been found in fish, birds, invertebrates, and marine mammals from various parts of the world. However, their sources, levels, and distribution in the marine environment are not well studied mainly due to analytical difficulties and interference in analytical methods (ICES, 1996).

Some new data regarding TCPM and TCPMe in marine biota as well as the results of an interlaboratory study (second phase) on the determination of these contaminants in fish samples and a standard solution were presented at the 2001 MCWG meeting. The differences in the analytical procedures used by the participants (six laboratories) were not large. Except for one laboratory that reported technical problems, the results for the analysis of the fish samples were in good agreement with each other, although in many cases the levels were close to the limit of determination. Taking the good agreement for the samples into consideration, the results for the standard solution showed some inexplicably large differences. Overall, the results from these exercises were satisfying and showed that the results for TCPM and TCPMe from these laboratories in North America and Europe are comparable.

Where quantifiable amounts of TCPM and TCPMe were found in fish samples (plaice, sole, herring, and eel), in all cases the samples from Europe showed higher concentrations than those from Canada. Similar differences have been found earlier in marine mammals from both continents (see ICES, 2000). To substantiate these findings more samples, focusing on flatfish (sole, dab, flounder, and halibut), will be analysed during the coming year.

*Need for further research or additional data*

There is a need to obtain more information about the sources, toxicity, and occurrence of TCPM and TCPMe in the marine environment. There is also a need for conducting the MCWG work to investigate the comparability of the analytical methods for the determination of TCPM and TCPMe in marine samples.

*Recommendations*

ICES encourages its Member Countries to gather more information about TCPM and TCPMe in the marine environment by including these contaminants as voluntary determinands in national and international monitoring programmes.

## References

ICES. 1996. Report of the ICES Advisory Committee on the Marine Environment, 1996. ICES Cooperative Research Report, 217: 120–127.

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 74.

### 6.1.2 Polybrominated diphenylethers (PBDEs)

At its 2001 meeting, MCWG discussed both an overview of the results of the first worldwide interlaboratory study on the determination of polybrominated diphenylethers (PBDEs) (de Boer, 2000) and a report on the outcome of a Dutch national study on measurements of PBDEs in different matrices (de Boer *et al.*, 2000). The overview and the report were presented by J. de Boer (The Netherlands).

The first interlaboratory study on PBDE determinations involved eighteen laboratories from nine countries. Samples of biota (eel, mussels, cormorant liver, harbour porpoise liver and blubber oil) and sediments as well as a standard solution were analysed. Determination of the concentrations of the congeners BDE 47, BDE 99, and BDE 209 was set as the main task, with addition of BDE 100, BDE 153, and BDE 154 on a voluntary basis. The measurements of BDE 47 showed good agreement among the laboratories, and the results for BDE 100 were also acceptable. However, the analyses of BDE 99, BDE 153, BDE 154, and particularly BDE 209 require further improvement. This study was a successful first step towards comparable results for the analyses of PBDEs. A next interlaboratory study is currently in preparation.

A Dutch national study on PBDEs included measurements in suspended particulate matter (SPM), sediments, sewage treatment plant (STP) influents and effluents, and biota from the Netherlands. Concentrations and ratios between BDE congeners differed greatly for different matrix types. Thus, the concentration of BDE 47 was highest in fish samples and STP effluent residues, whereas BDE 209 could not be determined in any of the biota samples, but was highest in SPM, sediments, STP influent filtrate, wastewater, and particularly in STP effluent residues. For BDEs in SPM, the highest concentrations were detected in samples from the Western Scheldt area.

In the MCWG discussion, particular concern was expressed about these contaminants as some congeners are accumulated in the brain. It has also been shown that concentrations of tetra- and penta-BDEs are apparently increasing in marine mammals from North America, but not in samples from the Netherlands. Until the mid-1990s, tetra- and penta-BDE concentrations were increasing very rapidly in human milk from Sweden, however, the most recent data from this study indicate that these concentrations have peaked and begun to decline (Guvenius and Norén, 2001). The highest concentrations of PBDEs were found in 1997, while the levels in 2000 were similar to those from 1995. This is related to the EU risk assessment of the penta-mix PBDE formulation and the proposed ban on its production and use within the EU which resulted. In Europe, the bromine industry has reacted by rapidly reducing the use of the penta-mix, and it seems that environmental concentrations have already begun to reflect this change in patterns of use and discharge. In North America, no such restrictions have been proposed and the production and use continue as before, with North America now accounting for over 97 % of the world use of the penta-mix (Hale *et al.,* 2001). In Europe attention should now be paid to the environmental levels of other brominated compounds which are likely to be used as a substitute, such as hexabromocyclododecane.

The ACME was also informed of a temporal trend study undertaken in Sweden which provided parallel information regarding the concentrations of BDE congeners deriving from the penta-mix formulation. In a thirty-year time series of PBDE concentrations in guillemot eggs from the central Baltic Proper, from the end of the 1960s to the end of the 1990s, the concentration of, e.g., BDE 47 increased rapidly, followed by a decrease and a levelling out in recent years (Sellström *et al.*, 1999).

*Need for further research or additional data*

The ACME repeated its statement of 1999 (ICES, 2000) that there is an urgent need for data on the long-term toxicity of PBDEs to marine organisms. The ACME pointed out that research should be conducted on the possible effects of PBDEs on the reproductive, endocrine, and immune systems of marine organisms.

*Recommendations*

ICES recommends that researchers be encouraged to perform experimental studies for implementing the research needs outlined above. ICES also recommends continuing interlaboratory studies on PBDE determinations to achieve further progress in agreement among the laboratory measurements.

*Additional comments*

The ACME expressed its appreciation for the Dutch national study on PBDEs.

**References**

de Boer, J. 2000. First world-wide Interlaboratory Study on Polybrominated Diphenylethers (PBDEs). Organohalogen Compounds, 45: 118–121.

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Guvenius, D.E.M., and Norén, K. 2001. Polybrominated diphenyl ethers in Swedish human milk. The follow-up study. Proceedings of the Second International Workshop on Brominated Flame Retardants (BFR 2001). 14–16 May 2001, Stockholm University, Sweden. pp. 303–305.

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### 6.1.3 Antifouling paint booster biocides

Section 9.1 of the 1999 ACME report includes a general discussion of the identification of "new" contaminants in the marine environment. Subsequent to that report, for 2001 the MCWG was tasked to "review new information concerning new contaminants in the marine environment, report the outcome, and submit results of discussions to WGBEC." Their deliberations this year focused on the chemicals that are being used to replace organotin as an antifoulant.

The MCWG considered a report "The Aquatic Fate and Effects of Antifouling Paint Booster Biocides", that was prepared by K. Thomas, CEFAS, Burnham-on-Crouch, UK. This document provides an excellent summary of the knowledge about the fate and effect of these compounds that have replaced the widespread use of organotin antifouling-paint formulations. The ACME agreed to attach this document as Annex 5 to its report.

The MCWG also considered a report on an ongoing EU programme, Assessment of Antifouling Agents in Coastal Environments (ACE), which includes studies of these new antifoulants (Irgarol 1051, diuron, Sea Nine 211, TCMTB, dichlofluanid, chlorothalonil, TCMS pyridine, and copper/zinc pyrithione). More environmental data will be forthcoming from that programme, and later in 2001 a website and database will also become accessible. Oestrogenic testing of these compounds has also been undertaken within the ACE programme. Some of these compounds also have applications other than their use in antifoulant paints, e.g., diuron, a phenylurea herbicide, has been in use for weed control in non-agricultural applications since the 1950s. New data are available on the biological availability and uptake of the biocides themselves or their degradation products. The fate of these compounds when associated with particulate paint waste is poorly understood. As part of the ACE programme, additional studies are under way to address these issues, to allow the risks posed by each of these compounds to be assessed, and thereby to determine whether they offer a safe alternative to organotin-based antifoulants.

As noted in the 1999 ACME report (ICES, 2000), OSPAR is taking some direct measures to address the general issue of "new" contaminants. OSPAR 2000 adopted the outcome of the first practical application of the dynamic selection and prioritization mechanism for hazardous substances (DYNAMEC), and agreed upon a first revision of the OSPAR List of Chemicals for Priority Action. In the OSPAR revised action plan for 1998–2003, it is noted that the Commission will:

a) further elaborate and refine, by OSPAR 2001, the DYNAMEC mechanism;

b) give priority to the development of programmes and measures for the substances on the OSPAR list of chemicals for priority action. This list will be updated from time to time on the basis of the results of future applications of the DYNAMEC mechanism.

*Need for further research or additional data*

The ACME emphasized that there is a need to continue research on the environmental fate and biological effects of these booster pesticides.

*Recommendations*

ICES encourages researchers in Member Countries to remain vigilant with respect to identifying the introduction of potentially toxic chemicals into the marine environment.

**Reference**

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 1999. ICES Cooperative Research Report, 239: 86–87.

### 6.1.4 Volatile organic contaminants

During the 2000 meeting of MCWG, two presentations had been given concerning the presence of volatile organic compounds (VOCs) in the marine environment. At the time it was already mentioned that VOCs were unlikely to present a significant hazard for organisms and the marine environment as a whole. As a follow-up in 2001, a short presentation and paper were provided that contained the most important findings of a paper recently published by Roose and Brinkman (2001). These authors used a hazard assessment procedure proposed by van Leeuwen *et al.* (1992) that ultimately results in the calculation of a threshold concentration that is unlikely to cause harm to 95 % of the aquatic community. This calculated concentration, HC5, is the hazardous concentration that will affect, at most, 5 % of the species. The concentrations that were found in the environment were generally a factor ten or more below these HC5 values. However, the authors qualified their findings by stating that no information was available concerning possible long-term effects of these contaminants in the marine environment. Even though the conclusions of the paper were based on a large and robust data set, they only relate to a relatively small region (the area off the coast of Belgium) and no information is available for other areas. It is therefore not possible to extrapolate these findings to the marine environment as a whole. During the MCWG discussion, a Norwegian study on the effects of the volatile fraction of oil on fish larvae was mentioned. Benzene is a major constituent of this fraction and the study demonstrated that effects were observed at low concentrations (possibly comparable to those found in the Belgian study).

After discussion of the above information, the ACME decided to attach the summary paper on VOCs as Annex 6 to its report. The ACME noted, however, that only one type of hazard assessment method had been used and that the data employed were only from one region, namely, off the Belgian coast.

*Need for further research or additional data*

There is a need to obtain more information about the occurrence of these compounds in other marine areas and to study their effects, including long-term effects, at low concentrations in the marine environment.

**References**

Roose, P., and Brinkman, U.A.Th. 2001. Volatile organic compounds in various marine organisms from the southern North Sea. Marine Pollution Bulletin (In press).

van Leeuwen, C.J., van der Zandt, P.T.J., Aldenberg, T., Verhaar, H.J.M., and Hermens, J.L.M. 1992. Application of QSARS, extrapolation and equilibrium partitioning in aquatic effects assessment. I. Narcotic industrial pollutants. Environmental Toxicology and Chemistry, 11: 267–282.

### 6.1.5 Dioxins, furans, and dioxin-like CBs in fish

The MCWG discussed a paper entitled "Dioxins and dioxin-like CBs in fish and feed and the current status of legislation in the EU" (Annex 7). This paper includes two appendices with data derived from (1) the SCOOP project (Anon., 2000) which was a European study of literature data on dioxins in food, and (2) a Dutch study on dioxins and PCBs in (mainly) Dutch fishery products. These appendices also include mean dioxin data for samples of Baltic fish. These data were not essentially different from the data in the paper reviewed by MCWG in 2000 entitled "Use of Baltic clupeoids to make fish meal (protein) for the manufacture of fish feed". Therefore, the data cited in that paper (for the maximum levels of dioxins in Danish industrial fish landings) should be considered as correct.

The World Health Organization (WHO) advice for a tolerable daily intake (TDI) for dioxins and dioxin-like chlorobiphenyls (CBs) has been set at 1–4 pg TEQ $kg^{-1}$ body weight (bw). This advice was adopted by the EC Scientific Committee on Food (SCF) and transferred into a temporary tolerable weekly intake (t-TWI) of 7 pg TEQ $kg^{-1}$ bw[a]. The current intake of dioxins by the general European population is above this t-TWI. In the Netherlands, the estimated intake is 1.8 pg TEQ $kg^{-1}$ bw $day^{-1}$, of which 0.25 pg TEQ $kg^{-1}$ bw (14 %) is contributed by fishery products, with the remainder from other dietary items. This demonstrates that simply setting tolerance levels for dioxins and dioxin-like CBs in fish and fishery products will not result in a substantial reduction of the dioxin intake by the population of the Netherlands. Even a total ban on fish consumption would not reduce the dioxin intake to below the t-TWI of 7 pg TEQ $kg^{-1}$ bw. Recently, a tolerance level of 8 pg TEQ $g^{-1}$ wet weight fish flesh for dioxin only was set for eel in the Netherlands. A Dutch tolerance level for fishery products in general, including dioxin-like CBs, is also in preparation. Comparable information on the importance of fish products for the dietary dioxin intake is not available from other countries. Treatment of the fish prior to consumption (baking, frying, smoking, etc.) may also lead to some reduction of the dioxin and CB concentrations in the products as consumed. Annex 7 includes an overview of the available literature on this aspect.

The level of dioxins and dioxin-like CBs in farmed fish can be controlled by selection of the feed. Recent data from the European Scientific Committee on Animal Nutrition (SCAN) show that Pacific fish oil and fishmeal have an approximately eight-fold lower dioxin and dioxin-like CB contamination than that found in European fish oil and fishmeal. This conclusion of the SCAN report has been criticized on account of the distribution of the samples included and the data interpretation. It has been demonstrated that capelin, a North Atlantic pelagic fish caught for meal and oil production, has comparable levels of dioxin as were quoted for the Pacific samples (Auðunsson, 2000).

The sources of dioxins were discussed by MCWG. Forest fires were suggested as a possible (natural) source. However, these cannot be considered as the major source as most of the dioxins in the environment originate from known anthropogenic sources.

In fish, CBs make a larger contribution to the total toxic equivalent (TEQ) values than do the dioxins. Generally, the CB-TEQ is higher than the dioxin-TEQ by a factor of two to three times, but in some cases this ratio has been up to ten times or more. This means that the "dioxin problem" in fish is in reality more of a "PCB problem". MCWG agreed with the approach of including dioxin-like CB-TEQs in the derivation of TDIs and possible tolerance levels. Laboratories conducting dioxin analyses will soon be able to analyse mono-*ortho* CBs in addition to the non-*ortho* CBs, dioxins, and furans. Given the advice of WHO and the SCF, which is based on a total TEQ, and the logical structure of the toxic equivalency factor (TEF) concept, the non-inclusion of dioxin-like CBs would hinder the overall risk assessment of dioxin-like compounds. The inclusion of other compounds which show dioxin-like effects and for which TEF factors can be derived, such as polychlorinated naphthalenes (PCNs), should also be considered in the future.

The limited information available on time trends suggests a decreasing trend of TEQ values in fish, mainly as a result of decreasing levels of PCB contamination. In several countries, dioxin and CB monitoring was terminated at the beginning of the 1990s, partly as a result of financial constraints, and partly because the decreasing values suggested that PCBs were a problem solved. The further development of toxicological knowledge has, however, led to a new situation in which dioxin and CB concentrations in fish are now much closer to the new, lower, levels of concern. MCWG emphasized the risk of an early termination of monitoring programmes in general, which, as in this case, can easily lead to gaps in knowledge and can seriously hinder decision-making processes.

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[a] Based on new scientific information, in May 2001 the SCF amended the t-TWI of 7 pg TEQ $kg^{-1}$ bw to 14 pg TEQ $kg^{-1}$ bw (Anon., 2001).

In the review of the above information by the Working Group on Biological Effects of Contaminants (WGBEC), it was noted by WGBEC that the TEQ values and toxicity evaluations refer to mammalian systems and do not reflect the overall environmental effects of dioxins. Work is under way to develop similar cell-based systems from aquatic species (fish, mussels).

Finally, a recent publication (van der Plas *et al.*, 2000) was discussed. One of the conclusions of this publication was that the majority of the tumour-promoting potential of PCB mixtures resides in the non-dioxin-like fraction, which is not taken into account in the TEQ approach for risk assessment of PCBs and dioxins. This is then likely to result in an underestimation of the tumour-promoting potential of environmental PCB mixtures. MCWG concluded from this information that, given the apparent tumour-promotion potential and other known toxic effects (e.g., neurotoxic effects) of the di-*ortho* CBs, monitoring of these di-*ortho* CBs should be continued in addition to the monitoring of dioxins and non-*ortho* and mono-*ortho* substituted CBs.

*Recommendations*

In view of indications of considerable geographical variations in the concentration levels of dioxins and dioxin-like CBs in marine fish and fish products, ICES recommends that analyses of these compounds be included, in representative samples, in surveys and monitoring programmes.

In the light of knowledge on toxicological levels and tumour-promoting properties of PCB mixtures, ICES recommends that Member Countries maintain CB measurements in their monitoring programmes, preferentially monitoring di-*ortho* CBs in addition to the monitoring of dioxins and non-*ortho* and mono-*ortho* substituted CBs.

**References**

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## 6.2 Progress in Understanding Causes and Effects of Endocrine Disruption in the Marine Environment

*Request*

This is part of the continuing ICES work to keep under review contaminants and their effects of interest in a marine environmental context.

*Source of the information presented*

The 2001 report of the Working Group on Biological Effects of Contaminants (WGBEC) and ACME deliberations.

*Status/background information*

Data or presentations were available to WGBEC on two national programmes (EDMAR and LOES) and an EU project (COMPREHEND). In addition, information was provided on oestrogenic effects in bivalves and some information was given on the development of OECD tests for endocrine disruption and reproductive toxicity in fish (freshwater fish).

**EDMAR**

The following information was taken from the official information on the UK programme on endocrine disruption (EDMAR) and some additional information submitted from the UK. The EDMAR Programme began in June 1998 and continues until the end of 2001. It is investigating whether there is evidence of changes associated with endocrine disruption in marine life and, if so, the possible causes and potential impacts. It follows on from work which demonstrated that flounder (*Platichthys flesus*) in some UK estuaries showed changes consistent with endocrine disruption. Five major UK laboratories are conducting the research: the CEFAS Burnham, Lowestoft and Weymouth laboratories, the Plymouth Environmental Research Centre (PERC), the Centre for Marine and Coastal Studies in Liverpool (CMACS), the FRS Marine Laboratory, Aberdeen (with assistance from the Scottish Environment Protection Agency), and the AstraZeneca Environmental Laboratory, Brixham. The programme has the following objectives:

1) Development of a biomarker of androgen exposure in a suitable marine fish species;

2) Development of biomarkers of oestrogen and androgen exposure in marine crustaceans;

3) Development of simple histochemical methods for measuring vitellogenin/vitellin, oestrogen and androgen biomarkers in small tissue slices of fish and crustaceans;

4) Field surveys using biomarkers for androgen exposure in fish, and for androgen and oestrogen exposure in crustaceans;

5) Isolation/quantification of oestrogenic substances and tracking to sources;

6) Isolation/quantification of androgenic substances and tracking to sources;

7) Field studies to assess the impact of oestrogenic compounds on juvenile and adult salmonids during estuarine migration;

8) Field investigations of endocrine disruptor biomarker responses and reproductive success in a fish species and a crustacean species which breed in estuaries;

9) Laboratory studies of the effects of sewage effluent and other suspect materials on breeding success in sand gobies.

Two biomarkers of androgenic exposure in the three-spined stickleback (*Gasterosteus aculeatus*), induction of the nest-building glue protein, spiggin, and increase of kidney epithelial cell height, have been successfully developed and calibrated. Both showed similar, dose-dependent sensitivity to the model androgen methyltestosterone. Both the spiggin and kidney epithelial height assays are now being used to look for androgenic and anti-androgenic exposure in the field.

The enzyme-linked immunosorbent assay (ELISA) for vitellin induction in male shore crabs (*Carcinus maenas*) and brown shrimp (*Crangon crangon*) from several UK locations provided no evidence of feminization, and laboratory exposures using nonylphenol and diethylstilbestrol were also negative. Work on androgenic disruption utilizing feminized male shore crabs infected with the parasitic barnacle *Sacculina carcini* also did not provide an indication of exposure to masculinizing influences. These results do not necessarily mean that endocrine disruption is not occurring in crustaceans, but indicate that vitellin induction cannot provide evidence of any such disruption in response to oestrogens and androgens. Further studies are focusing on the potential impact in female crabs of exogenous chemicals on ecdysteroid hormones, which are involved in processes such as moulting, reproduction, and locomotor activity. AstraZeneca has produced antisera to purified vitellin from shore crabs, brown shrimp, and marine gammarids in support of the work on crustacean biomarkers. A draft protocol for histological sectioning of copepods has also been developed for future exploration of copepod immunocytochemistry at various life stages.

A protocol has been developed for the immunocytochemical localization of vitellogenin (VTG) and is being tested to determine the range of response in flounder tissue from the Mersey and Welsh Dee. Autoradiography, using radiolabelled oestradiol, has been successfully utilized to locate sites of oestrogen binding for comparison with sites visualized with immunohistochemistry techniques.

Positive staining using immunohistochemical methods has also been achieved in stickleback tissues known to contain the glue protein, spiggin. No significant effects were seen in sand gobies exposed long-term to environmentally realistic concentrations (0.3 % and 0.03 %) of effluent from the Irvine Valley Sewer, Scotland, apart from the development of some nuptial coloration and a reduction in size of a secondary sexual characteristic (urogenital papillae); however, reproductive output was unaffected. By contrast, long-term exposure to 6 ng $l^{-1}$ of the synthetic oestrogenic steroid ethynyloestradiol significantly reduced the reproductive output of gobies; individuals in the treated population were significantly smaller than controls, had smaller seminal vesicles and urogenital papillae, and exhibited inhibition and delay in development of nuptial coloration. Octylphenol induced vitellogenin messenger RNA in gobies at concentrations above 30 µg $l^{-1}$ in a short-term trial and plasma vitellogenin was also produced at the same concentrations; long-term exposure tests are under way.

A culture system for the marine gammarid *Chaetogammarus marinus* has been established, together with a test system for chronic exposures, and an experimental design and operating procedures for culturing and sampling the test organism. However, as vitellin does not appear to be a suitable biomarker of oestrogen exposure in crustaceans, this objective has now been discontinued and unused resources deployed elsewhere in EDMAR.

Efforts to collect significant numbers of three-spined sticklebacks from estuarine populations have so far been unsuccessful, but further attempts with a new method are under way. Sticklebacks from a freshwater source have been acclimated to full salinity sea water and deployed in caged trials in the Tees and Crouch estuaries, with survival after four weeks of 65 % and 90 %, respectively. Further cages have been placed in the Crouch estuary for ten weeks, with good survival rates, as well as in the Tees and Tyne; the spiggin assay has been deployed in conjunction, and has revealed one caged female in the Tees showing spiggin induction. Sexual development of caged males was retarded.

An extensive field sampling programme has provided a comprehensive range of specimens from several species across the UK. There is continued evidence of strong endocrine disruption in flounder and new evidence of endocrine disruption and intersex in the viviparous blenny. Preliminary data also suggest that feminization at a morphological level (e.g., urogenital papillae with a shape intermediate between males and females) is occurring in the sand goby. A substantial body of data is, however, leading to the conclusion that crustaceans (specifically the brown shrimp) are not responding through vitellin induction to mammalian oestrogenic and androgenic endocrine-disrupting substances. This project has recently begun and aims to examine possible effects of sewage-derived oestrogens on salmonid smolt physiology and their adaptation to the marine environment. As salmon are too valuable to use, sea trout smolts are being trapped in the Tees estuary and caged below the Tees barrage and on the Esk estuary. They will be maintained there for as long as possible and their plasma VTG concentrations measured, together with a range of physiological parameters. Toxicity Identification and Evaluation (TIE) procedures identified key oestrogenic compounds from the Tyne and the Tees. Surface water from Howdon sewage treatment works (Tyne) contained the natural female sex hormone 17β-oestradiol, the testosterone degradation product androsterone (paradoxically detected by its simultaneous oestrogenic activity), and an unknown oestrogenic compound. Most of the activity in a water sample from Dabholm Gut (Tees) was also due to 17β-oestradiol, plus the synthetic compounds nonylphenol and *bis*(2-ethylhexyl)phthalate. The only sediment pore waters to demonstrate oestrogenic activity were collected from Dabholm Gut, with the causal substance identified as the natural compound oestra-1,3,5-trien-3-ol. Extracts of sediment particulate material from both estuaries were strongly oestrogenic in comparison with the relatively weak activity in water samples, but only nonylphenol has yet been identified. Work is proceeding to identify the other causes of oestrogenic activity in sediment. An experiment to establish whether feeding on sediment-dwelling invertebrates is the main uptake route for oestrogenic exposure in flounder is now complete and has shown that mussels held in the Tees induce VTG, but not to the extent seen in wild fish. Work is also in progress to identify androgenic substances present in estuarine systems.

## LOES

The Dutch LOES programme is a large-scale baseline study entitled "National Investigation into Oestrogenic Compounds in the Aquatic Environment" (Dutch acronym, LOES) which is being carried out in 1997–2001 (Vethaak *et al.*, 1999). The multidisciplinary LOES project is government-funded and involves various governmental bodies and universities. The Dutch part of the EU-funded programme COMPREHEND (see below) is integrated within LOES. The LOES project aims to:

a) investigate the occurrence and sources of various natural oestrogens and xeno-oestrogens in the Dutch aquatic environment including waste water, rain water, drinking water, and (inland, estuarine, and marine) surface waters;

b) assess oestrogenic/reproductive impacts on sentinel fish species inhabiting this environment.

The first results show that natural hormones, xeno-oestrogens, and oestrogenic activity are present in Dutch waste waters and water systems including estuarine and marine waters (Vethaak *et al.*, 2000). Oestrogenic hormones, bisphenol-A, and phthalates were found in wastewater effluents, and in surface water samples (freshwater and coastal) at concentrations of the order $10^{-9}$ g $l^{-1}$, $10^{-8}$ g $l^{-1}$ and $10^{-5/-7}$g $l^{-1}$, respectively. With the exception of phthalates, these compounds were not found in rain water. Levels of phthalates were much higher in suspended particulate matter (SPM) and sediments, with *bis*(2-ethylhexyl)phthalate (DEHP) concentrations reaching 11 mg kg$^{-1}$ in some estuaries. Alkylphenols and their ethoxylates (APEs), while largely absent from drinking water and fresh water, were found in sediments and SPM in the form of nonylphenol and its ethoxylate (NPE) at concentrations of up to 2.8 µg g$^{-1}$ and 17 µg g$^{-1}$, respectively. Concentrations of NPE in fish tissue reached 500 ng g$^{-1}$. Polybrominated diphenylethers (brominated flame retardants) were commonly found in SPM and sediments (up to 4.6 mg kg$^{-1}$ dry weight decaBDE) and in fish (up to 1.6 mg kg$^{-1}$ wet weight decaBDE).

The results of vitellogenin (VTG) measurements in fish indicate several areas where moderate oestrogenic effects in male fish occur, i.e., where VTG levels between 1,000 and $1 \times 10^6$ ng ml$^{-1}$ plasma are measured. VTG production was more pronounced in bream (*Abramis brama*) than in flounder (*Platichthys flesus*). In the estuarine and marine environment, flounder mostly had low plasma VTG levels, but somewhat elevated levels were found at a few sites, including the industrialized port of Amsterdam harbour and an offshore spawning area, northwest of the Dutch Wadden Sea islands. Intersex (ovotestis) was observed in bream at a few sites but not in any of the flounder examined. Results of *in vitro* and *in vivo* assays and possible relationships between chemical and biological effect parameters are currently being analysed. The final report is available in September 2001.

The results for VTG and ovotestis in male flounder observed in Dutch estuaries and coastal waters compare well to those reported earlier in flounder from UK estuaries. These studies, together with those reported for viviparous blenny (*Zoarces viviparus*) in the UK, clearly indicate that oestrogenic effects may exist in some estuaries and coastal zones.

The ACME emphasized that additional ICES Member Countries should consider conducting similar field studies assessing oestrogenic effects using flounder (or closely related species, e.g., the American starry flounder, *Platichthys stellatus*) and/or viviparous blenny in their estuarine and coastal waters. In particular, the wide distribution of the flounder would allow a spatial comparison to be made among major estuaries within a large part of the ICES area.

### COMPREHEND

This EU programme includes partners from the UK, France, the Netherlands, Sweden, Norway, Finland, and Switzerland. The Norwegian Institute for Water Research (NIVA) has responsibility for the marine part of the programme, which includes effluent studies with Atlantic cod (*Gadus morhua*), method validation for vitellogenin in cod, and studies on sex change in the hermaphroditic cuckoo wrasse (*Labrus bimaculatus*). Effluent studies have indicated that vitellogenin in cod has a similar sensitivity to this response in salmonids. The validation of cod vitellogenin includes a seasonal study, studies on temperature and salinity effects, as well as a study on the effects of food availability. The seasonal study has been finalized, whereas most of the other studies still remain to be done. Preliminary results indicate that there are no major seasonal differences in the ability of low to moderate doses of 17β-oestradiol and 4-nonylphenol to induce vitellogenin synthesis in cod. An overview can be found at http://www.ceh.ac.uk/comprehend.

### Other issues of endocrine disruption

A research paper described vitellogenin-like proteins in mussels, induced by oestradiol and nonylphenol treatment. Based on histological observations of gonadal tissues, oyster (*Crassostrea gigas*, *Crassostrea virginica*) and the blue mussel (*Mytilus edulis*) are known to contain a vitellin-like protein with synthesis presumably under oestrogen mediation (e.g., 17β-oestradiol). Typical invertebrate steroids such as ecdysone have only rarely been reported, while there is good evidence for the presence and biosynthesis of vertebrate-type sex steroids such as progesterone and testosterone from precursors in the ovotestis (Le Blanc *et al.*, 1999). Biochemical studies of such proteins are rare and techniques to measure vitellin-like proteins in molluscs appear to be lacking. This vitellin-like protein should, in theory, possess characteristics similar to fish and amphibian vitellogenins, which contain glycogen, phosphate, lipids, calcium and zinc ligands.

No specific bioassays or biomarkers have been developed to detect endocrine disruption in molluscs (with the exception of imposex/intersex in gastropods). An attempt has been made recently on clam in order to measure the level of vitellogenin-like proteins in soft-shell clams (*Mya arenaria*) and to obtain information on potential (anti-) oestrogenic effects resulting from exposure to the mixture of contaminants in the field (Blaise *et al.*, 1999). However, given the fact that so many species of gastropods are affected by TBT, and given the endocrine nature of the response, this system is a likely candidate for assay development.

A project will soon be initiated in France to evaluate the reasons for juvenile mortality of the oyster *Crassostrea gigas*. This multidisciplinary project will be conducted along the Atlantic coasts and will include physiology, pathology, genetic, and ecotoxicology approaches. More specifically, vitellogenin-like proteins will be explored as potential biomarkers.

Activities were described which are directed towards the development of two-generational fish tests for endocrine disruption and reproductive toxicology within the framework of the Organisation for Economic Cooperation and Development (OECD). Three species have been brought forward as candidates for such a test, i.e., Japanese medaka, fathead minnow, and zebrafish. The current status is that all three species have been accepted. Work has been completed or is under way for all three species to develop protocols for the tests. Endpoints include hatching success, embryonic development, sex ratio, gonadal development, vitellogenin induction (measured on whole-body homogenates), growth, and maturation.

WGBEC was made aware of a report commissioned by EC DG Environment on a priority list of substances with the potential to act as endocrine disruptors (BKH/TNO, 2000). The report aimed to identify a standardized procedure to identify possible endocrine-disrupting contaminants, with limited data available. This report has been criticized by others because of the selection procedure. Because persistence and/or HPV have been included as a requirement for selection, many relevant contaminants are not included. Alkylphenols is one group of substances that were not included.

*Need for further research or additional data*

The ACME is aware that a number of studies on endocrine disruption in the marine and estuarine environments are under way worldwide, and it is important that these studies be continued in order to establish the causes of the observed effects, and whether the problem is increasing or decreasing in extent.

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## 6.3 Studies of Sediment Processes related to Contaminant Exposure

*Request*

This is part of the continuing ICES work on the review and update of information on sediment chemistry, and physical, biological, and chemical processes that may influence the concentrations of metals and organic contaminants in sediments, their exchange with the water phase, and the exposure of biota.

*Source of the information presented*

The 2001 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS) and ACME deliberations.

*Status/background information*

The ACME noted that the 2001 WGMS meeting considered a document on sediment-water interactions, where the application of new technical tools to sediment-water exchange studies, presently a subject of research, is considered and future possibilities are outlined. This document points out that, to be able to estimate the environmental risk of sediment-associated contaminants, it is important to have information on:

1) the freely dissolved concentration in equilibrium with the sediment;
2) the desorption rate from the sediment;
3) the fraction in the sediment that is exchangeable with the water phase.

One developing technique which shows promise is the use of Semi-Permeable Membrane Devices (SPMDs), which are passive devices for sampling dissolved contaminants in the water column. These devices are deployed for periods of weeks to months, and ideally reach an equilibrium with the dissolved contaminant concentrations in the water. Also, they act to some degree as integrators of the average concentration during the exposure period. The use of these devices is not without difficulties, however, as the equilibrium reached and the rate of attaining it is dependent on a number of factors, and is particularly influenced by the flow rate of the water body in which it is placed. For this reason, techniques have been developed which involve the addition of surrogate standards to the triolein within the sampling device before deployment. The rate of loss of this compound from the sampling device is also related to the flow rate of the local water body, and so the remaining fraction at recovery can be determined and used to calibrate the rate of uptake of the contaminants accumulated from the water mass. These samplers are primarily designed to collect lipophilic, predominantly organic, contaminants, and experience gained during current deployments is allowing the means of calibration and the interpretation of the data produced to be further refined. They are often deployed alongside organisms such as mussels, which act as active samplers of the water column, but the two are not really equivalent as SPMDs accumulate dissolved contaminants whereas mussels are filter-feeders and also accumulate contaminants from ingested particles. As SPMDs can be suspended close to the sediment surface in still or flowing water, they may also be useful in studying sediment-water exchange processes in the future.

In the discussion, the ACME noted the ongoing research activities and looked forward to receiving further information in future years as the studies progress.

**References**

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## 6.4 Methods to Define Sediment Quality Criteria

*Request*

This is part of continuing ICES work on methods and tools to assist in the assessment of sediment quality, and the implications for marine environmental programmes both in ICES and within the regulatory Commissions.

*Source of the information presented*

The 2001 reports of the Working Group on Marine Sediments in Relation to Pollution (WGMS) and the Working Group on Biological Effects of Contaminants (WGBEC), and ACME deliberations.

*Status/background information*

The terms of reference for the 2001 WGMS meeting included to review methods to define sediment quality criteria, taking account of experience in The Netherlands, USA, and Canada. In order to initiate cooperation between WGMS and WGBEC, the review was to be made available to WGBEC before its meeting.

According to this, WGMS prepared a document in which the main advantages and drawbacks of several different approaches for setting sediment quality guidelines (SQGs) are briefly outlined. The document is based on the review paper by Chapman (1989), and the approaches considered are: background sediment chemistry, water quality criteria, sediment/water equilibrium partitioning, sediment bioassays, effects range and effects level approach (i.e., Effects Range—Low/Effects Range—Median (ERL/ERM) and Probable Effects Level/Threshold Effects Level (PEL/TEL)), Apparent Effects Threshold (AET), and Sediment Quality Triad.

Considerations and advice by ICES on the issue of sediment quality criteria have been provided over many years. Meetings of a special study group and joint meetings of WGMS and WGBEC have been held, where both general and technical aspects have been discussed in depth in order to develop a conceptual framework within which sedimentological and biological effects monitoring procedures could be coordinated and combined to provide a more comprehensive assessment of sediment quality. The detailed, comprehensive work produced was reviewed by ACME and can be found in its reports (ICES, 1989, 1990, 1992, 1994a). Within this framework, a specific, comprehensive review on approaches for setting sediment quality criteria is included in the 1994 ACME report (ICES, 1994b). Guidance is also found in extensive documents—including a large number of references—on the integration of chemical and biological measurements, including specific recommendations for marine sediments in the 1995 and 1996 ACME reports (ICES, 1995, 1996).

Furthermore, very recent advice on Background and Reference Concentrations—one of the approaches for setting sediment quality guidelines—can be found in the 2000 ACME report. This item has been considered within ICES in relation to the outcome of two OSPAR/ICES Workshops on Background/Reference Concentrations for nutrients and contaminants, and a HELCOM Workshop on the same subject for the Baltic Sea area. The ACME stressed the importance of a clear definition of terms, and a clear explanation on how the different values are derived, as well as emphasizing that the differences in natural ranges that may occur in different areas should be taken into account (ICES, 2000).

The document prepared at the 2001 WGMS meeting provides a brief overview of the approaches reviewed by Chapman (1989). Several of these approaches were considered too simplistic, while others required a large amount of data, particularly on the toxicity of contaminants to sediment-dwelling organisms. Of these methods, the ERL/ERM was considered to be the most promising on which to develop SQGs. But it was noted that the ERL/ERM methodology has been developed for use with North American sediments and benthic organisms, and will need to be validated before deployment in other areas. It was considered important to establish that the North American SQGs are appropriate for other sediments and other local fauna, and it was pointed out that the only way to do this is to analyse data from samples for which there are matching contaminant and biological data.

This material was further reviewed and discussed by WGBEC at its 2001 meeting. WGBEC observed that there were two categories of methods: one category focuses on the determination of levels of any given contaminant in sediments that would be expected to cause biological effects (background chemistry, water quality criteria, equilibrium partitioning, ERL/ERM, PEL/TEL, AET). The second category comprises methods that may be used to assess the toxicity of sediments directly (sediment bioassay, sediment quality triad). Although of obvious relevance to managers, there are clear conceptual problems with all types of assessment criteria (the first category) since they do not take sufficient account of the complexity of sediments as a habitat and matrix. WGBEC was of the opinion that the issue will need to be tackled in more detail, and that a suitable forum could be a joint meeting between WGMS and WGBEC.

WGBEC also pointed out that the category of methods used to develop assessment criteria (i.e., “convert chemistry to biology”) has some inherent weaknesses. They include:

a) there are few data available on whole sediment tests;

b) data are available only for a very limited range of robust organisms;

c) there are major difficulties in estimating bioavailability from chemical and physical properties;

d) where field data are used to derive criteria, problems occur in quantifying the contribution from each contaminant and distinguishing this from natural factors (requires that “all” parameters are determined).

WGBEC considered it necessary to validate methodologies of biological testing before their use in monitoring programmes. To develop validated biological testing protocols, more background information is necessary to interpret toxicity responses. With regard to the standardization and validation, well-defined validation procedures should be applied to consider robust sediment toxicity techniques. The methods have to be validated according to a strict protocol of accuracy, repeatability, sensitivity, detection limits, and analytical error. The last point means that the availability of the toxicological effects is influenced by many confounding factors, such as grain size, salinity, organic matter, and concentrations of sulphides and ammonia. For all bioassays, an interlaboratory intercalibration should be performed before implementation in monitoring programmes.

The WGBEC discussions also highlighted the recurrent request for more sensitive endpoints than immobilization or death in sediment bioassays. Therefore, WGBEC encouraged studies on biomarker-type endpoints for organisms that are used in such bioassays, and noted that more extensive use of less robust organisms than the 10–15 species now used would be advisable.

In the discussion of the above material, the ACME fully supported the comments by WGBEC concerning the weaknesses of the different approaches, as well as on the need for methods validation according to a strict protocol. The ACME agreed that this issue needs to be developed in greater detail.

*Need for further research or additional data*

The ACME encourages further progress and development of the joint work initiated by WGMS and WGBEC on this issue.

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ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 34–36.

# 7 FISH DISEASE ISSUES

## 7.1 Trends in Diseases of Wild and Farmed Fish and Shellfish Stocks

*Request*

This is part of continuing ICES work to consider new developments with regard to fish and shellfish diseases.

*Source of the information presented*

The 2001 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and ACME deliberations.

*Status/background information*

The ACME reviewed the relevant sections of the WGPDMO report providing information from 2000 on new trends in the occurrence of diseases in wild fish stocks based on national reports and new information obtained on the M74 syndrome in Baltic salmon and on *Ichthyophonus hoferi* infection in wild fish species.

Special attention was drawn to the new trends in the distribution of the following diseases in wild and farmed fish, shellfish, and mollusc stocks:

Viral Haemorrhagic Septicaemia virus (VHSV). In recent years, marine VHSV has been isolated from a large number of marine fish species in the North Sea, Skagerrak, Kattegat, and the Baltic Sea, as well as along the Pacific coasts of the USA and Canada. In 2000, marine VHSV was isolated for the first time from dead and moribund mummichog (*Fundulus heteroclitus*) and three-spined stickleback (*Gasterosteus aculeatus*) in New Brunswick, Atlantic Canada.

The first outbreaks of Viral Haemorrhagic Septicaemia (VHS) occurred in sea-reared rainbow trout in Finland in 2000. There might be a possible link with wild fish such as herring, which show a high prevalence of VHSV infection in the Baltic Sea.

The toxic alga, *Pfiesteria piscicida*, has been suspected of causing dermal ulcers in menhaden (*Brevoortia tyrannus*). However, it was only detected in 12 of 486 water samples (using a gene probe) from rivers draining into Chesapeake Bay, an area in which fish dermal ulcers had previously been attributed to *P. piscicida*. A highly significant relationship between the presence of dermal ulcers and reduced immunoglobulin levels was observed in a study of 315 menhaden. This observation supports other work that showed that the relationship between *P. piscicida* and dermal ulcers was weaker than previously believed.

The prevalence of liver nodules in dab (*Limanda limanda*) and flounder (*Platichthys flesus*) in the central and southern North Sea has decreased over the past 5–6 years and a similar observation has been made for flounder in the Gulf of Finland. A significant decline in the prevalence of microscopic hepatic lesions in English sole (*Parophrys vetulus*) indicates the efficacy of a clean sediment cap placed over contaminated sediments in Eagle Harbor, Washington State, USA, six years earlier.

Intersex conditions were observed for the first time in viviparous blenny (*Zoarces viviparus*) collected from the Tyne estuary, UK.

The prevalence of skin ulcers in cod (*Gadus morhua*) from the southern Baltic Sea showed an increasing trend, approaching maximum levels reported in 1998.

Lobster (*Homarus americanus*) mortality, reported in 1999 in Long Island Sound, USA, did not continue in 2000. In addition to the *Paramoeba* sp. originally reported as the probable cause, other environmental issues may be involved (see below).

Giant sea scallop (*Placopecten magellanicus*) mortalities of unknown origin are spreading along the lower north shore of the Gulf of St. Lawrence, Canada.

## M74 syndrome in Baltic salmon

A decreasing trend in M74 prevalence in salmon in most river systems in the Baltic Sea area was recorded in 2000 compared to 1999. However, the disease prevalence in most rivers is significantly higher than in 1998, when the prevalence reached a tolerable level. The prevalence of female salmon with 100 % fry mortality in salmon rivers monitored in Finland and Sweden during 2000 varied between 10–45 %. However, these figures are an underestimation as they only include female salmon with 100 % fry mortality. Partial mortality due to M74 occurs at all levels and the real disease prevalence is considerably higher. Moreover, in Sweden decreased thiamine levels were recorded in offspring from apparently normal salmon females in the absence of the M74 syndrome.

The prognosis for the 2001 hatch is still preliminary. A Finnish prognosis for the River Tornionjoki indicates an increase in disease prevalence; a Swedish prognosis for River Dalälven indicates a slight decrease. At present, there are no verified reports of M74 in salmonids in European areas outside the Baltic Sea. In Iceland, however, the mortality in turbot fry showing M74 symptoms was significantly reduced using thiamine baths, indicating that thiamine deficiency may also be a problem in non-salmonids.

Recent research projects in Sweden exposing salmon to thiamine antagonists, such as pyrithiamine, oxythiamine and amprolium, induced histopathological alterations typical for M74 fry and high fry mortalities. Utilizing these models makes it possible to study the pathogenesis of M74.

Ongoing research will focus on the role of environmental pollutants and oxidative stress in modulating the kinetics of thiamine in salmon. Exposure of rainbow trout to environmental pollutants in the laboratory activated the antioxidant enzyme systems but had no effect on the thiamine levels of the fish.

Finnish work has focused on the level of thiaminase activity in the prey fish species (sprat (*Sprattus sprattus*) and herring (*Clupea harengus*)) of Baltic salmon as well as on thiaminase activity in the intestinal tract of salmon. It was demonstrated that the concentration of thiaminase in Baltic herring varies on a wide scale. About 30 % of the herring had a thiaminase concentration at the same high level as in the salmon gastrointestinal contents.

Screening for thiaminase-producing or thiaminolytic bacteria in the intestinal tract of salmon and Baltic herring has so far given negative results.

Work is currently being carried out in Finland in order to evaluate the role that algae and cyanobacteria blooms may play in the thiamine/thiaminase balance of organisms in the food chain of Baltic salmon.

## *Ichthyophonus hoferi*

*Ichthyophonus hoferi* infection continues to persist at a low prevalence in the European herring stocks examined, i.e., in herring from Icelandic waters, the Kattegat, the northern North Sea, the Barents Sea and the Norwegian Sea, without any indication of an epizootic.

In Pacific herring (*Clupea pallasi*) in Puget Sound, the prevalence of *Ichthyophonus* was 60–70 %. At three months of age, 5–6 % of the fish were infected.

In Chinook salmon (*Oncorhynchus tshawytcha*) from the Yukon River, 30 % of the fish sampled were infected by *Ichthyophonus*. The prevalence dropped to 10 % at the terminal spawning time, suggesting significant mortality.

## The role of *Paramoeba* infection and other factors in the mass mortality of lobsters on Long Island, USA

High mortalities were reported in lobster (*Homarus americanus*) in the late summer and fall of 1999 in Long Island Sound, USA, suspected to be associated with environmental factors, including contaminants. Although localized mortalities had occurred in 1990, 1991, 1993, 1997, and 1998, the 1999 mortalities were much more severe and widespread. They were associated with the following conditions and events:

1) A dramatic increase in population abundance in the mid- to late 1990s, which reached a peak in 1998 that was 3–4 fold higher than the mean for the previous decade.
2) Heavy harvest pressure, as indicated by the deployment of approximately half a million traps, each baited weekly with approximately 1.5 kg of menhaden (*Brevoortia* sp.).

3) Unusually high summer temperatures. The year 1999 was the warmest of the decade, and the decade of the 1990s was the warmest on record. *Homarus americanus* is at the southern end of its temperature range in Long Island Sound. This range is set by the highest temperatures, which occur during summer.

4) Application of pesticides, specifically methoprene, around the western end of the Sound, where most of the mortalities occurred. This was an effort to kill mosquito vectors of West Nile Virus, which was found for the first time in and around New York City in the summer of 1999 and caused the death of several people.

5) The passing of Hurricane Floyd in mid-September, which caused heavy rain and runoff. Most of the mortality is thought to have occurred after Floyd.

The following findings were reported from samples of dead and dying lobsters, and of water, from the affected area:

- No unusual concentrations of contaminants (volatile and semi-volatile organics, organochlorine pesticides, chlorinated herbicides, and heavy metals) were found in either water or tissue.
- No toxic algae were found.
- Tests for *Gaffkemia* sp. were negative.
- A *Paramoeba* sp. was found in the tissues (mostly nerve tissues) of dead and dying lobsters; however, no prevalence data are available.

A trawl survey by the State of Connecticut in April–May 2000 found the following:

- Lobster density had decreased 40 % from the 1998 peak (a decline that began in 1999), but was still the third highest since the survey began in 1986.
- Lobster density was highest in the western end of the Sound where mortalities had been greatest the previous summer and where densities and fishing effort are typically highest.

The status as of early 2001 was as follows:

- The *Paramoeba* sp. is still found in lobsters, including those with no signs of distress, but no statistics are available and unusual mortalities have not been reported.
- Summer temperatures in 2000 were at or below average.
- A number of research projects have recently been funded to examine hypotheses about causes of the mortality, including the *Paramoeba* infection and a series of environmental factors, and to develop stress-related indices for lobster.

*Need for further research or additional data*

ICES Member Countries should continue to monitor the development of disease trends in wild and farmed finfish and shellfish stocks. The following disease problems are particularly of concern:

- The increasing prevalence of skin ulcerations in Baltic cod should be considered, as they may contribute to increased mortality and, hence, have an impact on the fishery.
- The first indication of an outbreak of VHS in farmed rainbow trout in Finland associated with an infection source originating from the wild fish population should be considered. The high prevalence of marine VHSV in herring and sprat, especially in the Baltic Sea, may create a serious hazard for the marine fish farming industry in this area.
- The high prevalence of *Ichthyophonus hoferi* infection in Chinook salmon in Pacific USA may have an impact on the stock level.

The aetiology of the M74 syndrome is still unclear and the disease remains a serious threat to wild salmon populations in the Baltic Sea. Therefore, it is still important that ICES Member Countries continuously monitor salmonid populations for the occurrence of M74 or M74-like reproductive disorders. In light of the recent trend of seriously increasing disease prevalence, the ACME emphasizes the urgent need for increased research efforts regarding the causes of this disease.

The persistence of *Ichthyophonus* in European herring stocks makes it necessary to continue the monitoring of the prevalence of the infection in the herring stocks.

*Recommendations*

ICES recommends that:

1) in order to solve the regulatory problems associated with VHS being a notifiable disease, Member Countries should direct efforts towards the characterization of marine and freshwater strains of VHSV and their links to pathogenicity;
2) Member Countries should continue to monitor salmonid as well as non-salmonid populations for the occurrence of reproductive disorders similar to the M74 syndrome;
3) Member Countries should continue to monitor the prevalence of *Ichthyophonus hoferi* infection in herring as part of the fish stock assessment work.

### 7.2 Progress in Work on Fish Disease Data Assessment

*Request*

This is part of continuing ICES work to develop and apply appropriate statistical methods to analyse and assess ICES fish disease prevalence data in combination with other types of relevant data in the ICES Marine Data Centre.

*Source of the information presented*

The 2001 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and ACME deliberations.

*Status/background information*

During its past three meetings, the ACME has reviewed progress made by WGPDMO with regard to the statistical analysis of wild fish disease prevalence data submitted to the ICES Marine Data Centre by ICES Member Countries on an annual basis (ICES, 1999, 2000a, 2000b). Recent activities have focused on the analysis of disease data in combination with other types of environmental and fishery data held in the ICES Marine Data Centre.

At the 2000 ICES Annual Science Conference, a paper was presented that provides an updated overview of current work and information on the relationship between the prevalence of externally visible diseases (lymphocystis, epidermal hyperplasia/papilloma, acute/healing skin ulcerations) of dab (*Limanda limanda*) from the North Sea and a wide range of potentially explanatory factors. These include contaminants in water, sediments and biota, nutrients in water, general hydrographic parameters, and catch per unit effort as a measure of population density (Wosniok *et al.*, 2001). For this purpose, a previous analysis focusing only on one area in the southeastern North Sea (including the German Bight) (ICES, 1999, 2000a) was extended to cover areas in the central (including the Dogger Bank) and the northwestern North Sea (including the Firth of Forth). The time span considered covered up to two decades, depending on the availability of relevant data.

The statistical analysis was carried out by means of logistic modelling, involving a newly applied interpolation technique for missing data, based on a Gaussian kernel smoother and generalized cross-validation and a bootstrap procedure to account for the effects of using interpolated values.

The results of the multivariate analysis revealed a number of significant relationships between the disease prevalence and the potentially explanatory factors considered, including contaminants. Within an area, a few factors were identified with a consistent effect on the prevalence of at least two of the three diseases. However, none of these factors exerted the same effect in all three areas, not even for one of the diseases. Therefore, there was no clear indication for the existence of a single or a few underlying factors that drive the disease prevalence in all areas in the same way. Among other possible explanations, the authors attributed this to the following:

- The disease prevalence can be affected by various factors inducing the same change in prevalence (concept of a multifactorial disease aetiology/ pathogenesis).

- The effects of factors might differ between areas (e.g., contaminants may be present but the levels in some areas may be below a toxicologically relevant threshold concentration, or fish may have different tolerance levels due to adaptation, genetic predisposition, etc.).
- The availability of data differs between areas (e.g., if contaminant data are not available, no effects can be attributed to contaminants).

When reviewing this paper, the WGPDMO identified some shortcomings leading to problems in the analysis and subsequent interpretation of results:

- There is still a striking lack of environmental data, particularly for contaminants, in the ICES Marine Data Centre. Even if data interpolation is considered feasible, it cannot replace real observed values and, therefore, may introduce a considerable bias and lead to misleading results and interpretation.
- The ICES fish disease database is not complete because some of the historic data held by ICES Member Countries have not yet been submitted to ICES.
- Many of the potentially explanatory factors included in the analysis were highly correlated, possibly leading to ambiguous or erroneous conclusions. Cause-effect relationships between single factors and disease prevalence might be obscured by strong spurious statistical relationships with other factors that co-vary with the causal factor.

*Need for further research or additional data*

The ACME endorsed the view of WGPDMO that considerable progress has been made over the past years with respect to the analysis and assessment of the ICES fish disease data. It emphasized that the results of the statistical analyses carried out using the ICES data have suggested that several relationships between the disease prevalence and potentially explanatory factors exist. It pointed out the importance of continuing this work, particularly in the light of the application of a more ecosystem-based approach aiming at an understanding of the relationship between environmental factors and the variation in disease prevalence.

However, as in previous years, a lack of data in the ICES Marine Data Centre was noted, particularly regarding contaminants data. Corresponding to concern already expressed, the ACME pointed out that ICES Member Countries should again be encouraged to submit their data to the ICES Marine Data Centre in order to facilitate a more comprehensive statistical analysis.

*Recommendations*

ICES strongly encourages Member Countries to submit their national environmental data, in particular contaminants data and historic fish disease data, to the ICES Marine Data Centre in order to facilitate a more comprehensive and holistic analysis of ICES fish disease data. An expanded database will also be crucial for more general ecosystem-based assessments on the occurrence of biological effects of contaminants and other environmental factors affecting the quality of the marine ecosystems in the ICES area.

**References**

ICES. 1999. Statistical analysis of fish disease prevalence data from the ICES Environmental Data Centre. *In* Report of the ICES Advisory Committee on the Marine Environment, 1998. ICES Cooperative Research Report, 233: 297–327.

ICES. 2000a. ICES data for a holistic analysis of fish disease prevalence. *In* Report of the ICES Advisory Committee on the Marine Environment, 1999. ICES Cooperative Research Report, 239: 193–209.

ICES. 2000b. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 81–82.

Wosniok, W., Lang, T., Dethlefsen, V., Feist, S.W., McVicar, A.H., Mellergaard, S., and Vethaak, A.D. 2000. Analysis of ICES long-term data on diseases of North Sea dab (*Limanda limanda*) in relation to contaminants and other environmental factors. ICES CM 2000/S:12. 15 pp.

## 7.3 Spatial and Temporal Trends in Parasites of Wild Fish and Potential Association with Environmental Factors

*Request*

This is part of continuing ICES work to review trends in the occurrence of diseases and parasites of wild marine fish in relation to effects of environmental factors.

*Source of the information presented*

The 2001 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and ACME deliberations.

*Status/background information*

At its 2000 meeting, the ACME reviewed work carried out by WGPDMO to evaluate the usefulness of fish parasites as indicators of environmental change. It was emphasized that, as a basis for a more comprehensive evaluation of the use of parasites as indicators, existing data sets on parasites of wild fish must be compiled and analysed in order to obtain a better impression of the extent of local and temporal variations in occurrence and the impact of environmental factors.

Based on this recommendation, a report on spatial and temporal trends in the occurrence of selected grossly visible parasites of North Sea dab (*Limanda limanda*) and whiting (*Merlangius merlangus*) was prepared intersessionally and reviewed at the 2001 WGPDMO meeting.

The report contains information on temporal variation in the prevalence of the dab parasites *Acanthochondria cornuta* (Crustacea, Copepoda) and *Stephanostomum baccatum* (Digenea) and the whiting parasites *Lernaeocera branchialis*, *Clavella adunca* (both Crustacea, Copepoda), *Diclidophora merlangi* (Monogenea), and *Cryptocotyle lingua* (Digenea) in three areas (the German Bight, Dogger Bank, and Firth of Forth) for the period 1985–2000. The data were obtained in the German long-term fish disease monitoring programme carried out on an annual or biannual basis. The data presented in the report were intended to be used as examples, from which a thorough assessment of the feasibility of studies on fish parasites as indicators of environmental change could be made.

The analysis of the data set revealed the following results:

- There is evidence that none of the parasites of dab and whiting considered in the study is restricted to certain areas of the North Sea. However, significant differences in prevalence were detected among the areas, indicating the existence of differences in the environmental conditions and/or the structure/dispersion of the communities of intermediate or definite hosts, affecting the abundance of the parasites. Pronounced examples of spatial variation are the high prevalences of *Lernaeocera branchialis* and, to a lesser degree, of *Cryptocotyle lingua* in whiting from the German Bight and the high prevalence of *Stephanostomum baccatum* in dab from the Firth of Forth area.
- Patterns of temporal change in prevalence did not reveal any clear long-term trends but were significantly different between parasites and areas, indicating that there were no major underlying environmental factors affecting the parasite prevalence in the same way in all areas.
- The mean length of the fish in the samples examined had a major impact on the prevalences of the parasites recorded. For an assessment of spatial and temporal variation, this length-dependence has to be taken into account and further statistical and demographic methods have to be developed in order to achieve this.

In the discussion of the working document, WGPDMO noted that for most of the parasites considered, sufficient data series exist for a more thorough analysis of possible effects of environmental change on the occurrence of the parasites. It will be necessary to consider a wide range of host-specific and site-specific factors, including biotic and abiotic variables. For such an approach, data maintained in the ICES Marine Data Centre may be used (e.g., oceanographic, contaminant, and stock assessment data).

WGPDMO took note of additional studies carried out in UK estuaries, which incorporate the assessment of spatial and seasonal differences in parasitic fauna in flounder, viviparous blenny (*Zoarces viviparus*), and sand goby (*Gobius* sp.) and their effects on the hosts as indicators of environmental change. Results from this study will also be reported to WGPDMO at its 2002 meeting.

WGPDMO expressed its concern that, due to the complexity of the interactions between parasites, their hosts and the environment, it will be difficult to establish clear cause-effect relationships between the occurrence of parasites and environmental factors. It was felt that this particularly will be the case for parasites with complex life cycles, involving different host species, and if large geographical areas are being monitored. The effort and resources needed to obtain a better understanding of the relationships will be enormous and it is doubtful whether such studies can be incorporated into routine monitoring programmes.

If parasites are to be included in monitoring programmes, the selection of parasites and host species will depend on the objectives of the programme. For regular long-term monitoring covering large areas, conspicuous parasites such as those considered in the working document are suitable since they can be recorded within existing fish disease monitoring programmes without any major additional efforts. For temporally and spatially restricted studies, an assessment of changes in the whole parasitic fauna may be more appropriate.

WGPDMO emphasized that the results of a number of studies have clearly indicated that environmental change may cause changes in the abundance and diversity of parasites of wild fish. However, before regular studies on parasites of wild fish can generally be recommended for monitoring purposes, further targeted research is required.

*Need for further research or additional data*

The ACME agreed that studies on parasites of marine organisms may be a useful tool for environmental monitoring. However, it emphasized that the identification of cause-effect relationships in most cases is complicated and requires significant resources.

To improve the predictive capacity of parasites as bio-indicators, further targeted research is required. This may involve laboratory studies on the susceptibility of individual parasites and their life cycle stages to environmental variables as well as studies on environmental factors that influence the susceptibility of fish to parasites.

Furthermore, studies on the distribution of intermediate hosts and their response to environmental change are needed. Multivariate statistical analyses should be carried out combining existing parasite and environmental data series to generate cause-effect hypotheses. Based on existing and developing knowledge, criteria should be carefully defined to select the parasites that can be used as bio-indicators of environmental change and the marine fish species suitable for this type of monitoring.

*Recommendations*

ICES encourages Member Countries to continue ongoing research on the relationship between spatial and temporal changes in the occurrence of fish parasites and the variation of environmental factors, and on the usefulness of parasites of wild marine fish as indicators of environmental change.

# 8 INTRODUCTIONS AND TRANSFERS OF MARINE ORGANISMS

## 8.1 Status of Ongoing Introductions and Accidental Transfers of Marine Organisms

*Request*

ICES Member Countries may request ICES to review proposed introductions and transfers of marine organisms for mariculture purposes. These proposals receive in-depth review by the Working Group on Introductions and Transfers of Marine Organisms (WGITMO), with final review by the ACME. WGITMO also keeps under review the progress of such introductions and reports the outcome to the ACME.

No new requests for review of proposed introductions were received in 2001, but the status of ongoing introductions and transfers was reviewed.

*Source of the information presented*

The 2001 report of the Working Group on Introductions and Transfers of Marine Organisms (WGITMO) and ACME deliberations.

*Status/background information*

The ACME reviewed the WGITMO report and agreed to present the information contained below.

### 8.1.1 Status of existing controlled introductions

**Fish**

Since the early 1980s, there has been considerable interest in the culture of Atlantic salmon (*Salmo salar*) on the west coast of British Columbia, Canada. In 2000 alone, 2.5 million quarantined Atlantic salmon eggs were imported into British Columbia from a health-certified farm in Washington State, USA.

Juvenile Atlantic salmon were first observed in the wild in 1996. Since then, a total of 359 juveniles have been captured in ten different river or lake systems. The majority of the discoveries were assumed to be escapees from hatcheries and lake-pen rearing sites. However, in 1998 twelve juvenile Atlantic salmon were recovered from the Tsitika River on the northeast coast of Vancouver Island. These fish were subjected to otolith microstructure analysis using a double-blind test and were found to be of wild origin. These are the only fish to be tested in this fashion. In subsequent surveys in 1999, populations of juvenile Atlantic salmon that were believed to be feral were discovered in the Adam River and Amor de Cosmos Creek. In extensive surveys in British Columbia, juvenile Atlantic salmon were recovered again in Amor de Cosmos Creek and in the Tsitika River. These findings may have serious implications for both native species and the aquaculture industry.

*Recommendations*

ICES notes with concern that non-native Atlantic salmon apparently can reproduce in the wild and recommends that surveys be continued to assess the long-term survival of these populations.

**Seaweeds**

Japanese kelp (*Undaria pinnatifida*) was originally introduced to France for cultivation in 1983. By 1990, eight sites were listed as farming areas. Initial reports concluded that several years after introduction, the alga had colonized only some areas close to the original farming sites, while at other sites small and fluctuating populations had developed. These studies concluded that *Undaria* did not have a detrimental impact on the environment (ICES, 1994). By 1997, natural sublittoral *Undaria* populations were reported to have decreased significantly, especially in the northern part of Brittany. In southeastern France, limited long-line culture still existed, but no negative impacts were reported.

At the same time, attached plants were found on the south coast of England and the Isle of Wight. Plants also had been found in Jersey and the Channel Isles, but were regarded as new introductions rather than natural spreading from the original site (ICES, 1997).

Recent reports from both Belgium and the Netherlands indicate that *Undaria* has again increased its range and intensity. In the Eastern Scheldt, *Undaria* covers areas of five to six acres; here, it grows on the Japanese oyster *Crassostrea gigas,* but also attaches to mussels on mussel plots. Because of the slippery texture of kelp, it is difficult for small boats to dredge the oysters and fishermen have to spend time in cleaning up the plots before dredging becomes possible.

The transport of small *Crassostrea gigas* (with attached *Undaria*) from oyster plots in the Eastern Scheldt into Lake Grevelingen may have been responsible for its introduction to that site.

In Italy, *Undaria* has been present since 1992 in the Chioggioa sector near the fish market and sites where imported seafood (mainly shellfish) are handled. Both container water and water from the fish food products are discharged directly into the lagoon canals. *Undaria* is competing with *Sargassum muticum* and *Desmarestia viridis,* two other large brown algae.

Subsequently, *Undaria* was reported in 1998 in the Mar Picollo of Taranto, also arriving by means of the oysters imported from France. It is monitored monthly to investigate its life cycle and propagation.

In the urban centre of Venice, the spread of *Undaria* has been more rapid. The autochthonous species in the areas covered by *Undaria* have decreased in biomass, but no extinction of species has occurred. The competition for space is dominated by *Undaria*. Some of the local algal species succeed in overgrowing it, but are lost when it detaches from the substrate (usually in July). For a few months the other algae find a bare substrate to settle on, but are overgrown when *Undaria* returns. The competition for light has damaged further photophilous species that were already jeopardized by the increase in turbidity of lagoon waters.

The ACME noted with concern the continued role of shellfish transfers as vectors of this species.

**References**

ICES. 1994. Report of the ICES Advisory Committee on the Marine Environment, 1994. ICES Cooperative Research Report, 204: 65.

ICES. 1997. Report of the ICES Advisory Committee on the Marine Environment, 1997. ICES Cooperative Research Report, 222: 96.

### 8.1.2 Selected examples of current invasions, their consequences and significance

**North American lobster (*Homarus americanus*)**

Several ICES Member Countries have reported increased problems with imports of live seafood, particularly the North American lobster (*Homarus americanus*), because of the potential genetic impact on the native species.

In Sweden, the demand for live European lobsters (*Homarus gammarus*) is exceeding the supply so there is an interest in the import of live American lobsters (*Homarus americanus*). The yearly import of live American lobsters to Sweden is about 150 to 200 tonnes.

The imported American lobsters are sometimes kept in cages on the Swedish west coast, although this is illegal. There are severe risks that the lobsters can accidentally escape from the cages. During autumn 2000, there were observations on the Swedish west coast of lobsters that did not resemble the European lobster. A DNA identification is now being performed to decide whether the specimens caught are hybrids or American lobsters.

The American lobster (*Homarus americanus*) was discovered in Norway in 1999. During 2000 a network of collecting stations was established in southern Norway. In December 2000, 24 lobsters were collected and five of them were confirmed to be *H. americanus* when studied by genetic tools. In addition to the five confirmed *H. americanus*, three specimens had morphological features resembling the American lobster. Circumstantial evidence indicated that the lobsters had been released. The captured specimens were all found in close vicinity to cities with airports.

In 1999, two lobsters showing aberrant morphological characters from the native *Homarus gammarus* were delivered to the aquarium of Drøbak, Norway. Both were shown by morphological and genetic analyses to be specimens of the American lobster.

Belgium has also expressed concern about escapement of this species.

Laboratory studies have shown that males of the American lobster can reproduce with females of the European lobster. The hybrids have shown a high survival and growth rate and females can also reproduce; thus, there is a potential risk that the hybrids may out-compete the European lobster. There is also a risk that the American lobster can transfer parasites and diseases to the European lobster.

*Recommendations*

To reduce the spreading of the American lobster into European waters, it is important to give information to both consumers and producers about the risks of keeping lobsters alive. Stricter regulations of live imports of seafood could also be a way of reducing risks. A problem with stricter regulations is that they are often in conflict with the free trading of goods.

**Toxic alga (*Cochlodinium polykrikoides*)**

*Cochlodinium polykrikoides,* a major fish and shellfish killer in Korea, was identified for the first time on 30 July 1999 as a bloom-forming organism in the northern part of Clayoquot Sound on the west coast of Vancouver Island, Canada. A bloom in a more northerly inlet, Quatsino Sound, moved east into Holberg Inlet causing the death of maricultured fish worth about $2 million. Cells of *Cochlodinium* have rarely been reported in water samples taken from the west coast of Vancouver Island prior to 1999. This implies that *Cochlodinium polykrikoides* may have been present on the coast for many years and simply overlooked, or that it is a recently introduced species. In August 1999, a sampling cruise of selected inlets along the west coast of Vancouver Island indicated higher concentrations of *Cochlodinium,* mainly in Nootka Sound and Esperanza Inlet, both of which are inlets for ships taking on cargo at Gold River and Tahsis, respectively. Such cargo ships taking on ballast water in Korea during a *Cochlodinium* bloom would probably have viable cysts in the water being discharged prior to lading cargo at these ports. Although this is circumstantial evidence of an introduced species, the distribution of *Cochlodinium* appears to be increasing. In 1999, *Cochlodinium* was observed on the east side of Vancouver Island in only one out of eight sites monitored, at Simoom Sound in the Queen Charlotte Strait. By comparison, in 2000 seven out of sixteen sites monitored on the east side of the island contained *Cochlodinium*, even those at the north end of the Strait of Georgia. It would appear, therefore, that the species is spreading southwards down the east side of Vancouver Island. If this distribution increases in future years, it might be deduced that *Cochlodinium polykrikoides* was introduced to the Canadian coast in ballast water from a cargo ship.

*Recommendations*

The ICES Code of Practice on Introductions and Transfers of Marine Organisms should be reviewed and updated as a **matter of priority** in the light of issues associated with importation and transfers of species intended for such purposes as the aquarium trade, the bait industry, or for immediate consumption, that can result in the release into the wild of such species and any accompanying organisms, including pests, parasites, and disease agents. The review should take account of the interim guidelines of the Convention on Biological Diversity (CBD).

## 8.2 Databases related to Non-indigenous Species

*Request*

This is part of ongoing ICES work to review the status of databases on introduced species that have been developed on a regional basis, in order to improve communication and the dissemination of information within and between ICES Member Countries and also with other organizations.

*Source of the information presented*

The 2001 report of the Working Group on Introductions and Transfers of Marine Organisms (WGITMO) and ACME deliberations.

*Status/background information*

The ACME noted that WGITMO prepared a list of databases on introduced and transferred species. These databases represent valuable sources of information to scientists in ICES Member Countries. This list is reproduced here to bring it to the attention of the wider scientific community.

1) Bulletin Board for marine pests (e-mail): marine-pests@hba.marine.csiro.au

2) Information for the Baltic Region: http://www.ku.lt/nemo/mainnemo.htm

3) Information for the Mediterranean Region: http://www.ciesm.org (Atlas Preview) including site for *Rapana* information http://www.ciesm.org/atlas/Rapana venosa.html/ http://com.univ-Mrsfr/gisposi/gisposi.htm

4) The GIS Posidonie bibliographic database on the spread of the tropical alga *Caulerpa taxifolia* in the Mediterranean Sea is now available at the following web address: http://www.com.univ-Mrsfr/basecaul [in French]

5) UNESCO-IOC Project Global Directory of Marine (and Freshwater) Professionals: http://ioc.unesco.org/glodir/default.htm

6) Centre for Research on Introduced Marine Pests (CRIMP) (Australia). A database of non-indigenous species established in Australian waters was compiled by CRIMP. The folder contains more than 75 records including taxonomical remarks on the species (picture), area of origin, the current distribution, associated effects/impacts on the environment and economy (Furlani, 1996). Distribution information available at: http://www.ml.CSIRO.au/~spinks/CRIMP/index.html

7) Database on identification material (Inger Wallentinus) and material from Kristina Jansson (not available on the Internet):

Jansson, K. 1994. Alien Species in the Marine Environment. Introductions to the Baltic Sea and the Swedish West Coast. Swedish Environmental Protection Agency, 68 pp.

1) Russian Group on Aquatic Alien Species (GAAS), located at the Russian Academy of Sciences: http://www.zin.ru/projects/invasions/

2) GISP website: http://jasper.stanford.edu/gisp/invfeatures.htm

3) List of top 100 invasive species: www.issg.org with overview at www.issg.org/database/welcome

4) IUCN Guidelines for the prevention of biodiversity loss caused by invasive species: http://iucn.org/themes/ssc/pubs/policy/invasivesEng.htm

5) Norwegian database: http://www.naturforvaltning.no/

6) Database for the North Sea (not available on the Internet):

Reise, K., Gollasch, S., and Wolff, W.J. 1999. Introduced marine species of the North Sea coasts. Helgoländer Meeresunters., 52: 219–234.

14) Alien species in Finland: http://www.vyh.fi/luosuo/lumo/lumonet/aliens.htm

15) Canadian Biodiversity Information Network (CBIN): http://www.ec.gc.ca/ecs/biodiv/biodiv.html

16) The Smithsonian Environmental Research Center (SERC), Edgewater, MD, USA, in collaboration with scientists around the world have developed an international database of researchers and research studies in the field of aquatic invasions, the Aquatic Invasions Research Directory (AIRD): http://invasions.si.edu/aird.htm

17) Intergovernmental Oceanographic Commission (IOC); Harmful Algal Blooms. Via the IOC's Home Page you can find information on IOC's Harmful Algal Blooms Programme (HAB) and the IOC Science and Communication Centre on Harmful Algae: http://www.unesco.org/. Electronically available documents include reports from meetings and workshops, the newsletter Harmful Algae News, and access to IOC's databases, e.g., HABDIR - IOC Harmful Algae Bloom Expert Directory.

18) Nature Conservancy (1998): America's Least Wanted: Alien Species Invasions of U.S. Ecosystems (with links to organizations involved): http://www.consci.tnc.org/library/pubs/dd/toc.html.

19) Alien species of crayfish in Europe (University of Firenze, Italy): http://www.unifi.it/.

20) Exotic Phytoplankton from Ship's Ballast Water. Risk of Potential Spread to Mariculture Sites on Canada's East Coast. A summary of Canadian activities, some case histories of introduced species and shipping studies are included at: http://www.maritimes.dfo.ca/science/mesd/he/ballast.html.

21) "Harmful Non-Indigenous Species in the United States": http://www.ota.nap.edu/pdf/1993idx.html.

22) US Great Lakes, Exotic species in the Great Lakes: http://www.great-lakes.net/.

23) Woods Hole Oceanographic Institution lists a page on harmful algae: http://habserv1.whoi.edu/hab/.

24) Zebra Mussel links: http://www.science.wayne.edu/~jram/zmlinks.htm, http://www.nfrcg.gov/zebra.mussel/.

25) Inventory of non-native species along the British coasts (not available on the Internet):

Eno, N.C. 1996. Non-native Marine Species in British Waters: Effects and Controls. Aquatic Conservation: Marine and Freshwater Ecosystems, 6: 215–228.

Eno, N.C., Clark, R.A., and Sanderson W.G. (eds.) 1997. Non-native Marine Species in British Waters: a Review and Directory. Joint Nature Conservation Committee, 152 pp. http://www.jncc.gov.uk/marine/dns/

26) FAO—Food and Agriculture Organization, the FAO Database on Introductions of Aquatic Species (DIAS): http://www.fao.org/waicent/faoinfo/fishery/statist/fisoft/dias/index.htm

27) NAS – Non-indigenous Aquatic Species (U.S.). The NAS information resource for the United States Geological Survey. Located at the Florida Caribbean Science Center, this site has been established as a central repository for accurate and spatially referenced biogeographic accounts of non-indigenous aquatic species: http://www.nfrcg.gov/nas/nas.htm-http://nas.er.usgs.gov/.

28) Overview of the study on non-indigenous species in the Gulf of Mexico ecosystem: Work contained herein identifies exotic and non-indigenous species in the Gulf of Mexico ecosystem and research needs for these species. Gulf of Mexico Program: http://lionfish.ims.usm.edu/~musweb/invaders.html.

29) The Sea Grant Nonindigenous Species Site (SGNIS). The Sea Grant Nonindigenous Species Site is a project of the National Sea Grant College Program, produced by the Great Lakes Sea Grant Network: http://www.sgnis.org/.

30) The Nonindigenous Aquatic Species Program of the Florida Carribean Science Center. It tracks the status and distribution of introduced aquatic organisms and provides this information in a timely manner for research, management and education: http://www.fcsc.usgs.gov/Nonindigenous_Species/nonindigenous_species.html.

## 8.3 Progress in Research and Management on Ballast Water and Other Ship Vectors

*Request*

This is part of the continuing ICES work to keep under review new information concerning research and management on ballast water and other ship vectors of marine organisms.

*Source of the information presented*

The 2001 report of the ICES/IOC/IMO Study Group on Ballast and Other Ship Vectors (SGBOSV) and ACME deliberations.

### Assessment of types of ship vectors

Shipping is certainly a vector of very great importance for species invasions globally, but it is difficult to prove that a species was introduced by shipping, although this is very likely in many cases. The relationship between hull fouling versus dispersal by ballast water or sediment as vectors needs to be better estimated, especially in the future when a ban on TBT in antifouling paints may increase dispersal on the hulls, particularly if more species-specific antifouling paints (based on chemicals inhibiting settling for certain important fouling organisms, e.g., barnacles) are developed.

It is becoming clear that increasing attention needs to be paid to fouling communities on ships' hulls and in sea chests. Recently undertaken summaries of non-native species in, e.g., the North Sea and certain areas of Australia and the USA have revealed the importance of hull fouling as a vector for invasions, as historically the number of non-native species likely to have been introduced by hull fouling of ships is greater than ballast water-mediated introductions. However, it is important to note that in some cases it remains unclear whether the species could have arrived as adult individuals in ship's fouling or as larvae in the ballast water. Further, it is unclear whether hull fouling is currently the most important vector of species introductions or whether it was more important in the past (wooden sailing ships).

The movement of heavily fouled vessels and other marine platforms is of growing concern. Examples include exploratory platforms, the movement of swim docks, and the movement of vessels that have been anchored for long periods of time in one region.

To estimate the relative importance of shipping as a vector, it is necessary to have better quantitative estimates on the role of other vectors. Furthermore, a particular species (e.g., the Japanese kelp *Undaria pinnatifida*) may have been introduced by several vectors (in this case, both shipping and aquaculture, unintentionally as well as intentionally), making it difficult to estimate the relative importance of each vector. Drifting might in many cases be the main vector for further dispersal (secondary introduction) from the first point of introduction, and could probably be an important vector of species dispersal.

An assessment of different types of ship vectors, with specific attention to determining which of these vectors have been quantitatively sampled in recent years, was undertaken. It was agreed that no data exist to assess the relative importance of vessel types, voyage lengths, voyage routes, seasonal changes, and other pertinent variables to assess future species invasions.

To further demonstrate the importance of vectors for species invasions, details on the most likely vector of introduction for recent species invasions were compiled. The most common introducing vectors are ballast water, hull fouling, and the secondary spread of previously recorded invasions from neighbouring areas. However, it has to be noted that for many newly recorded species the transportation vector remains unknown, as several vectors seem likely for certain species invasions.

### Ballast water control and management technologies

It has so far been concluded that no single or simple solution exists for shipboard treatment of ballast water. However, a combination of techniques might be at least partially effective and feasible in terms of economic and shipboard constraints. With current technology, these would most likely comprise some form of mechanical removal of organisms followed by a physical or chemical treatment method.

Ballast water management procedures have been investigated to a certain extent, but insufficient research has been carried out to assess the effectiveness of applicable ballast water treatment techniques. Shipboard treatment of ballast water is considered preferable to land-based reception/treatment facilities. Particular emphasis should therefore be placed on the evaluation of potential options for shipboard treatment that should be undertaken by future SGBOSV meetings with the aim of contributing to relevant related working groups (e.g., IMO Marine Environment Protection Committee, Ballast Water Working Group). In close cooperation with, and possibly by inviting experts from, relevant authorities (e.g., IMO and the International Chamber of Shipping (ICS)), SGBOSV should continue to assess currently implemented and planned ballast water control and management technologies.

A quarantine system does not provide an absolute barrier to prevent the introduction of unwanted non-indigenous species. It is also assumed that no single treatment process is likely to achieve the required inactivation or removal of unwanted organisms. A two-stage approach seems to be most likely. After an initial (e.g., mechanical) treatment process, an additional (e.g., physical) treatment process or a technique involving manipulation of the environmental conditions within the ballast tank could provide a solution.

At this stage, various methods of ballast water treatment and management have been put forward (see the IMO Assembly Resolution A.868(20)) and are described as a "tool box" from which the most practical (easy and safe to apply, not damaging existing ship installations such as ballast tank coating, isolators and sealing rings), cost effective, safe and environmentally sound combination should be selected.

To date, three different types of techniques to treat ballast water onboard ships have been suggested: (a) mechanical technologies; (b) physical treatments; and (c) chemical treatments.

Mechanical technologies are based on particle size or specific weight to separate or remove organisms and/or sediment mechanically from the water. Methods that have been considered include filtration, cyclonic separation, centrifugation, continuous deflective separation, sedimentation/flotation, high pressure pumping, and ballast exchange.

Physical treatment techniques use different susceptibilities of organisms to render them harmless: electrolytically generated copper and silver ions, ultraviolet radiation, removal of oxygen, heat treatment, cooling treatment, electric pulse and pulse plasma techniques, acoustic systems, and magnetic fields.

Chemical treatment technologies have been discussed, but the potential negative effects of long-term accumulation of residuals are of concern. Methods include hypersalination/salinity adjustment, chlorination, ozonation, antifouling compounds inside ballast tanks, pH adjustment, and the addition of chlorine dioxide, peroxide, sodium and calcium hypochlorite as well as other biocides.

The option to use land-based facilities to treat ballast water has not been excluded from the theoretical tool box, but might only be an option to treat smaller volumes of ballast water. One of the main concerns is the need for pipework of enormous dimensions. Alternatively, reception facilities may be installed on a treatment vessel that could then be moved from ship to ship to collect and treat the ballast water.

### Ballast management

Management strategies, techniques, and approaches of ballast water uptake should receive more research effort, specifically in relation to minimizing the uptake of organisms within donor regions. The IMO Assembly Resolution 868(20) "Guidelines for the Control and Management of Ship's Ballast Water to Minimize the Transfer of Harmful Aquatic Organisms and Pathogens" lists precautionary practices to reduce the number of organisms taken onboard by pumping in the ballast water (e.g., avoid ballasting at night when bottom-dwelling organisms may rise up in the water column or in very shallow water, where propellers may stir up sediment). Further approaches in this regard should receive the benefit of detailed feasibility and practicability studies.

Similar strategies should be explored more thoroughly relative to where ballast is released within an estuary or harbour, if it was not successfully exchanged in the open ocean. For example, every effort should be made to minimize or prohibit the release of ballast water in close proximity to mariculture or aquaculture activities.

The mid-ocean exchange of ballast water is believed to be currently the most reliable method of minimizing the risk of transfer of unwanted organisms. Compared with coastal waters, deep ocean waters contain fewer organisms and species occurring in open ocean waters are generally not able to survive in coastal zones and vice versa. If safety permits, all the ballast water should be released until suction is lost. Stripping pumps or eductors should be used, if possible. Where the flow-through method is employed in open ocean by pumping ballast water into the tank or hold and allowing the water to overflow, at least three times the tank volume should be pumped through the tank. This method is non-polluting and inexpensive in comparison to other potential treatment and management measures. Where open-ocean exchange is not possible, requirements developed within regional agreements may be applicable, particularly in areas within 200 nautical miles from shore.

#### *Additional comments*

The ACME noted that SGBOSV will conduct an assessment of the effectiveness of the mid-ocean exchange of ballast water based on the results of several ongoing ballast water programmes (e.g., the GloBallast Programme and activities at the Smithsonian Environmental Research Center (SERC)) and shipping studies that review ballast water exchange relevant to species composition and numbers of individuals in the ballast water before and after the exchange.

## 8.4 Standardized Format for Collating Data on Non-native Species and the Method and Fate of Introduction

*Request*

This is part of continuing ICES work on issues related to introductions and transfers of marine organisms.

*Source of the information presented*

The 2001 report of the Working Group on Introductions and Transfers of Marine Organisms (WGITMO) and ACME deliberations.

*Status/background information*

At its 2001 meeting, WGITMO agreed on a reporting format for the collection of data on non-native species or unexpected occurrences of species. Reports should include details on the species, biogeography and range expansion, method of introduction, relative abundance and distribution in the invaded region, life history, impact, possible benefit, control measures and management options, mitigation in the invaded country, further likely areas of colonization, similar species in the area of invasion, reference material, and references.

The reporting format is indicated below:

**Species**

- taxonomic group;
- generic and specific name;
- common name(s) as appropriate (different languages);
- identification;
- include the best available drawing or picture of the species (refer to web-pages).

**Biogeography and expansion**

- date of first record (possibly back-calculated if adult species found that was probably introduced at an earlier life stage) or from museum material of earlier collections and locality (see distribution map) including close-up insert(s) in world maps;
- date of deliberate introduction;
- natural range (continent, country, region);
- primary/secondary inoculation. If secondary, indicate source if known;
- range expansion in ICES Member Countries.

**Method of introduction**

- give details according to ICES list of dispersal vectors;
- list more than one vector if appropriate.

**Relative abundance and distribution in invaded region**

- habitat;
- biomass;
- densities: numbers, mass occurrences or individuals (occasional records);
- list nearest population.

**Life history**

Provide paragraph(s) on life history, including (as appropriate), but not limited to the following: lethal temperatures, temperature tolerance, temperature range required for reproduction, longevity, resting stages, asexual reproduction, known predators, grazers, survival in other habitats, tolerances, habitat, larval duration, trigger of spawning, etc.

**Impact and Benefit**

Provide table and fill in as appropriate (example used below: *Undaria pinnatifida*):

**Impact:** (* = possibly harmful, ** = harmful, *** = very harmful, ? = not known, $ = beneficial)

| **Resources/environment** | | | **Uses of the sea** | | |
|---|---|---|---|---|---|
| Commercial stocks | $ | Commercially harvested or farmed in some areas. | Fisheries | * | Algal canopy may hinder fishermen spotting abalone. |
| Other biota | * or $ | Competing with other seaweeds. Eaten by many grazing animals. | Aquaculture | ** or $ | Fouling on lines, cages, also growing on molluscs or competing for space. Used to feed abalone. |
| Human health | $ | Nutritional value when eaten. | Water abstractions | ? | May grow on openings of water intakes. |
| Water quality | $ | Takes up nutrients (as all plants) which are removed if harvested. | Aquatic transport | ** | Fouling on boats, buoys, etc., including costs for cleaning. |
| Habitat modification | * or $ | Large canopies change habitat, reduce light and water movements. Provides shelter for animals. | Tourism | * | Detached plants can accumulate on beaches (similar to native species). |

Other impacts, such as hybridization, should be added.

**Control measures and management options**

The mitigation in the invaded country and other information, as outlined in the following paragraphs for *Undaria pinnatifida,* should be added wherever possible:

Since the microscopic gametophytes are very tolerant and not visible to the naked eye, eradication is extremely difficult and manual eradication, tried in Italy, has not been successful. Studies on the effects of herbicides and antifouling paints have shown that some antifouling paints are effective in stopping zoospore germination or cause gametophyte mortality, while some herbicides are not. Patches not painted (e.g., covered by supporting structures during painting) or single corroded plates may develop dense lumps of sporophytes. Ships' hulls should only be cleaned out of the water and the organisms dumped out of the reach of the sea. Since sporophytes have been found surviving and growing on the hulls for voyages of over 4000 km, they should be removed before sporophylls are developed (in some cases sporophylls are small and difficult to see) to avoid seeding of other areas. If fertile, detached plants should be kept in containers when removed to avoid release of zoospores, because slightly dried sporophylls which are reimmersed in water release zoospores very quickly. As pontoons, towed buoys or drifting objects such as ropes, plastics, etc., also contribute to the dispersal, they should preferably be taken out of water and cleaned more thoroughly than simply by scraping off plants or be disposed of, when carrying *Undaria* plants.

Gametophytes can survive temperatures around 30 °C for up to 10–40 days and, thus, high temperature treatment is needed for cleaning hulls, and one must be reassured that the hot water penetrates into crevices and other openings. Gametophyte survival in small moist crevices in the hulls, anchor wells, etc., is possible even during dry docking as well as transportation on land for days up to at least about a month. Since they can stand darkness for more than seven months, ballast transport is a likely vector, especially as the gametophytes may form thick-walled resting stages, with a potential of surviving also in the sediment. Exposure to UV light can be effective on growing gametophytes, although it is not known if this affects the thick-walled resting stages.

Farming of *Undaria* should not be considered in areas where it does not yet grow, nor should lines and supporting structures in aquaculture be moved from sites with *Undaria* to areas where it does not grow. Proper quarantine treatment is needed in aquaculture to prevent unintentional introductions with molluscs. Movements of molluscs from *Undaria*-infested areas to algal-free areas should be avoided.

Information on colonized sites should be distributed and great care taken not to perform scientific experiments in the field or in open flow-through systems in areas where the species does not yet occur. Also, material brought in for demonstrations should be carefully disposed of on land, especially when plants with sporophylls are used.

### Further likely areas of colonization

### Similar species in area of invasion

### Reference material

- indicate if reference material exists; if possible, where this is stored (identification number);
- details on the taxonomist who confirmed the identification;
- details on the collector.

### References

- include taxonomic identification literature;
- refer to web-pages and other sources of information for further information (further reading).

# 9 MARINE BIOLOGICAL COMMUNITIES, PROCESSES, AND RESPONSES

## 9.1 Benthos Issues

*Request*

This is part of continuing ICES work on benthos ecology issues.

*Source of the information presented*

The 2001 report of the Benthos Ecology Working Group (BEWG) and ACME deliberations.

*Status/background information*

**Progress in the North Sea Benthos Project**

The ACME noted that, since the BEWG meeting in 2000, an intersessional meeting had been held among the participating institutes during the North Sea Symposium in Wilhelmshaven, Germany in early May 2000. At this meeting, the possibilities of harmonization of sampling were discussed and the end products of the North Sea Benthos Project (NSBP) were agreed upon.

The 2001 meeting of BEWG reviewed the progress in national surveys made during 2000. In general, a significant sampling effort had been realized by the different North Sea countries. In the year 2001, continued sampling will be conducted in order to cover areas not yet sampled in 2000. These areas include the Borkum Riff and Amrum Bank area (Germany), parts of the Belgian Continental Shelf, and areas off the English east coast.

The ACME noted that the BEWG had agreed that the Flanders Marine Institute should collate and store the data from the NSBP. The ACME expressed concern that the separate construction of a new database to handle data from the NSBP should not proceed in isolation from development of the biological community database at ICES, which is designed to service future needs. A workshop concerning this database was suggested in the autumn of 2001 in Ostend to discuss the treatment of differences in the data sets from the different countries. A second workshop is planned in 2002 to discuss and carry out the data analysis.

The goals and end products of the North Sea Benthos Project, as formulated at the Wilhelmshaven meeting, are:

- the goals are to produce a report for publication in the *ICES Cooperative Research Report* series, and articles for publication in the *ICES Journal of Marine Science.*

- End products will include:

  1) an overall comparison with the results from the 1986 North Sea Benthos Survey;

  2) comparison of 1986–2000 data in relation to the North Atlantic Oscillation and other environmental influences (e.g., the input of nutrients);

  3) testing of the applicability of the EUNIS habitat classification system as developed by the European Environmental Agency;

  4) investigation of the relationship between the benthos (large and long-lived species) and bottom trawling intensity.

BEWG agreed that these end products should be reconsidered during the workshops to be held under the coordination of the Flemish Marine Institute. Further progress will be reported at the 2002 meeting of BEWG.

*Recommendations*

The ACME took note of the positive development of the survey and recommended that the analysis of data should include proper mapping of the data.

Guidelines for sampling and objective community description of epibiota of soft sediments and hard bottom sub-strata, including QA matters

The ACME noted that progress had been made with the preparation of these guidelines on sampling and community description of subtidal epifauna, including quality assurance procedures. It is intended that the BEWG will review these guidelines at its 2002 meeting and approve them for publication in the *ICES Techniques in Marine Environmental Sciences* (TIMES) series.

## 9.2 Phytoplankton Ecology Issues

*Request*

This is part of the continuing ICES work of coordinating quality assurance activities and reporting on the results of new or improved methods and their implications for monitoring programmes.

*Source of the information presented*

The 2001 report of the Working Group on Phytoplankton Ecology (WGPE) and ACME deliberations.

*Status/background information*

At its 2001 meeting, the WGPE discussed the results of the Study Group on an ICES/IOC Microplankton Protists List (SGPHYT) to compile a checklist of microplankton protists. At present, a HELCOM checklist has been drafted, which will be the basis for expansion to the entire ICES area based on previous preparatory work of the WGPE. Future use of the Internet as a Virtual Taxonomy Centre is considered as a good forum for phytoplankton QA work. Checklists will form the basis for the ICES databases on phytoplankton communities.

Scientific and political disagreements on how enhanced nutrient inputs affect phytoplankton communities still form the basis of numerous discussions on how to assess and control eutrophication. A dominant issue in such discussions is the extent to which phytoplanktonic systems should be considered in terms of biomass (chlorophyll *a*) or as a community of species of which some reach dominance and cause algal blooms. Both top-down (grazers) and bottom-up (physics, nutrients) control mechanisms are proposed to explain the phenomena observed in the field. To discuss the natural and anthropogenic forcing on planktonic systems and their possible role in ecosystem changes, a workshop has been proposed for March 2002.

As a consequence of improved interdisciplinary exchange, WGPE and the Working Group on Zooplankton Ecology (WGZE) jointly discussed phytoplankton-zooplankton interactions and the possibilities to model these interactions. A first outcome of this discussion is a proposal that a workshop be held to integrate field and process-oriented studies with modelling exercises.

The ACME appreciates the efforts of WGPE and WGZE to work intensively on interdisciplinary topics that enhance the quality of future advice on planktonic systems.

*Need for further research or additional data*

The ACME endorses the recommendation of the WGPE to hold a Workshop on the Role of Anthropogenic Forcing in Planktonic Ecosystem Change in the Hague in March 2002 and to consider and review plans for a Workshop on Modelling Phytoplankton-Zooplankton Interactions in 2003. The ACME suggested that these activities be merged with those of the new Study Group on Modelling Physical/Biological Interactions (SGMPBI) to encourage future interdisciplinary studies.

The ACME recommends that the interdisciplinary work of WGZE and WGPE should have two foci: 1) eutrophication effects of anthropogenic nutrient inputs, and 2) plankton as food for juvenile and adult planktivorous fish.

## 9.3 Progress in Understanding the Dynamics of Harmful Algal Blooms, including Implementation of GEOHAB

*Request*

This is part of the continuing ICES work to support research and collect information on this issue, owing to the health and economic problems associated with the worldwide occurrence of harmful and/or toxic phytoplankton blooms.

*Source of the information presented*

The 2001 report of the ICES/IOC Working Group on Harmful Algal Bloom Dynamics (WGHABD) and ACME deliberations.

*Status/background information*

The ACME noted that the WGHABD is a joint ICES/IOC enterprise which has been extended by the recent GEOHAB (Global Ecology and Oceanography of Harmful Algal Blooms) research programme under the supervision of IOC/SCOR. The work of WGHABD contributes to the general issue of environmental and ecosystem assessment.

The ACME welcomed the continued efforts of WGHABD to update the mapping exercise and long-term trend studies of harmful algal blooms (HABs) based on collation and assessment of national reports and contributions. This information is available as part of the ICES Environmental Status Report, at the ICES website under http://www.ices.dk/status/decadal (see also Section 10.6, below).

Part of the work of WGHABD is to improve the HAB database by modification of the harmful event report forms, which also allow input from IOC countries outside the ICES geographical area. This harmful algae event database (HAEDAT) summarizes information on a regional, temporal, and species basis and is available through the web.

The ACME expressed appreciation for the work of WGHABD to evaluate and assess new methods such as remote sensing and *in situ* optical sensing technology to understand the dynamics of HABs and to investigate the potential sensitivity of HABs to climate changes, including the use of historical data sets and fossil records. These efforts to incorporate new and existing technologies to further improve the possibilities to monitor HABs and their effects are strongly supported.

The ACME has endorsed the active support of ICES in the implementation of the GEOHAB research programme (see ICES, 2000). GEOHAB could be a central activity of the WGHABD with special emphasis on the Baltic sea region as a model area to address the problem of HAB dynamics in brackish water systems.

WGHABD proposed the organization of a Workshop on Real-Time Observation Systems applied to Harmful Algal Bloom Dynamics Studies and Global Ecosystem Functioning, to be co-sponsored by regional programmes such as GEOHAB, GLOBEC, and GOOS. This workshop should encourage and encompass other activities within ICES to strengthen links in the fields of quality assurance, modelling, monitoring, and general understanding of the causes of harmful algal blooms.

*Need for further research or additional data*

The ACME endorsed the proposal of the WGHABD to prepare a Workshop on Real-Time Observation Systems Applied to Harmful Algal Bloom Dynamics Studies and Global Ecosystem Functioning as part of the strategy to improve future monitoring techniques for HABs, and agreed that co-sponsorship from regional programmes should be sought.

### Reference

ICES. 2000.GEOHAB: SCOR-IOC Programme on Global Ecology and Oceanography of Harmful Algal Blooms. *In* Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 189–190.

## 9.4 Statistical Analysis of Biological Community Data

*Request*

This is part of the continuing ICES work to provide advice on the development of effective methods for designing monitoring strategies and assessing monitoring data.

*Source of the information presented*

The 2001 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) and ACME deliberations.

*Status/background information*

Characteristic features in biological community data ("little creature data")

Both planktonic and benthic marine communities are most often characterized by skewed distribution in abundances in the sense that most species occur in low numbers and only a few in large densities. There is also a temporal and spatial variation in species abundance and biomass. The seasonal variation in species abundance and biomass can be quite considerable in temperate coastal environments. It is known that environmental factors (temperature, waves, currents, etc.) to a large extent determine community structure. Spatial and seasonal variability complicates statistical treatment of the data and environmental factors such as those named above should be included in the statistical analyses.

**Overview of the methods used to analyse biological community data**

Biological community data are usually characterized by a large species-station data matrix. In order to reduce this complex information in *n* (number of species) dimensions, several tools have been developed and used in the display and interpretation of these data.

**Stages in the analysis of biological community data**

For practical reasons, it is convenient to categorize possible analyses of biological community data into four main stages:

1) Representing communities by graphical description of the relationship between the biota in the various samples. This includes a pure description rather than an explanation or testing and the emphasis is on reducing the complexity of the multivariate information in typical species-samples matrices. In other words, to obtain some form of low-dimensional picture of how the samples of biological communities are interrelated.
2) Discriminating sites/conditions on the basis of biotic composition. The purpose here is that of hypothesis testing in order to examine whether there are "proven" community changes between groups of samples identified *a priori*, for example, demonstrating differences between control sites and impacted sites.
3) Determining levels of "stress" or disturbance by attempting to construct biological measures, which are indicative of disturbed conditions. These measures may be absolute measures ("this feature is indicative of pollution") or relative criteria ("under impact, this coefficient is expected to decrease in comparison with control levels").
4) Linking to environmental variables and examining issues of causality of any changes. This is done either by letting the biological data "tell their own story" and then examining whether any associated environmental variables from the same sample-area can be related to the biotic pattern or by relating the environmental variables directly to the biotic pattern in the same ordination. The extent to which the identified "explanation" by the environmental variables is actually causing the observed biological community can only really be determined by experiments, either in the field or through laboratory studies.

## Different types of methods to display and analyse biological community data

### Diversity indices and indicators[1]

A widely used type of method to indicate community characteristics is diversity indices, for example, the Shannon-Wiener index. The Shannon-Wiener index is defined as:

$H = -\sum p_i \log_2 (p_i)$ (summation from 1 to $n$)

where $p_i$ is the number of specimens of a species divided by the total number of specimens of all species in the sample.

The Shannon-Wiener index ranges from 0 when only one species is present, to $\log_2 n$, when all $n$ species are equally abundant. The use of a prior selected indicator species, which is assumed to respond to a particular environmental change, also gives rise to univariate analysis. The interpretation of these diversity indices and indicator species is based on the assumption that environmental changes influence these measurements in a certain way. Caution should be taken when evaluating the environmental quality of a habitat based on diversity indices. A high diversity, for example, is not necessarily an indication of a pristine or "good" quality of a habitat. Several studies have shown that an intermediate disturbance results in a higher diversity than either less or more disturbed situations (Connell, 1978; Huston, 1979). It should be emphasized that similar indices at different sites do not indicate that the species compositions are similar.

### Distributional methods

Distributional techniques are a type of method that summarizes the set of species counts for a single sample by a curve. An example is the k-dominance curves (Lambshead *et al.,* 1983), which rank the species in decreasing order of abundance. The abundance of a species as a percentage of the total abundance is then plotted cumulatively against the species rank. A further development based on k-dominance is the so-called ABC-method (abundance-biomass comparison) (Warwick, 1986), where k-dominance curves for both abundance and biomass are plotted together on the same figure. Another type of distributional technique is the species abundance distributions in which species are categorized into geometrically scaled abundance classes and a histogram showing the number of species in each abundance class is presented. The interpretation of these curves is based on empirical evidence that these curves change shape or position in relation to each other according to environmental disturbance. As for the univariate methods, information about species compositions cannot be deduced from this technique—two sites can have similar distributional curves without having any species in common.

### Multivariate methods

These methods are based on comparisons of the species occurrences and abundance in different samples. Either implicitly or explicitly, all of these methods are based on some kind of similarity measurement between samples. These similarity measures are then used for classification or clustering of samples into groups which are mutually similar or used for an ordination plot in which samples are "mapped" in such a way that the distances between pairs of samples are a reflection of their relative dissimilarity in species composition. There is a large variety of methods used to analyse biological community data and only a few examples will be mentioned here. The Principal Component Analysis (PCA) is one of these methods with a long history. The interpretation of the results of this analysis is often based on the assumption that species abundance is linearly related to environmental variables (e.g., temperature, salinity, etc.). Correspondence analyses are another type of method that is based on the assumption that species abundance is related unimodally to environmental variables. Finally, a third method is the non-metric Multi-Dimensional Scaling (n-MDS), which is based on ranking of the similarities (Bray-Curtis) between sites. This method, which is widely used at present, is not based on any assumption of any particular species abundance response to environmental variables.

## Limitations of these methods

There are obvious limitations in every method used for the analysis of biological community data, in the sense that variations in $n$ dimensions are reduced to a few dimensions or even to one single number. The basic assumptions for

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[1] Indicators are quantitative or qualitative information, which help to explain how the quality of the environment changes over time or varies spatially. Indicators are linked to policy questions, which should be answered by the indicator, e.g., by comparing with a target value. Indices refer to aggregations of data or indicators, to a calculation method, or a complex formula. Indices are developed in order to limit the information that decision makers and other interested parties have to absorb; they aim to condense the information in the data in an appropriate way.

many ordination methods are that species abundance follows specific patterns in relation to environmental gradients (linear, unimodal, or even multimodal). The relationship between species abundance and environmental gradients is usually unknown, which means that we cannot make sure that the basic assumptions are fulfilled. The n-MDS has in this respect some advantages, as it is without these constraints.

The use of simple measurements of biological community structure (diversity indices, indicator species or groups) as an indication of the state of the environment should be handled with caution. Although, from a management perspective, it is helpful to use a very simple expression of the environmental quality, the constraints in the use of such measurements should be emphasized.

**Data available at the WGSAEM meeting**

HELCOM phytoplankton data on biomass aggregated to family level or higher were available at the WGSAEM meeting. These data were from the Baltic Proper, the Kattegat, and the Belt Sea. The data covered the time period from 1979–2000, although this time period was not covered on all stations. Phytoplankton data from the Danish waters were also available from 1994 and 1995. These data were on species level.

The sampling frequency showed a rather uneven distribution throughout the year (Table 9.4.1). The data available from the two stations BMP H2 and BMP H3 fall mainly into four more or less distinct intervals of the year: March, May–June, August–September, and November. The distribution of observation times over seasons varies between years.

**Table 9.4.1.** Monthly distribution of samplings in the years 1979–2000 (total and stations BMP H2 and BMP H3).

| Month | All stations | BMP H2 | BMP H3 |
|---|---|---|---|
| | (1979–2000) | (1979–1996) | |
| 1 | 39 | | |
| 2 | 106 | | |
| 3 | 356 | 6 | 2 |
| 4 | 230 | 2 | 1 |
| 5 | 569 | 24 | 11 |
| 6 | 157 | 4 | 10 |
| 7 | 210 | | |
| 8 | 432 | 12 | 9 |
| 9 | 146 | 2 | 2 |
| 10 | 273 | 1 | 1 |
| 11 | 430 | 24 | 19 |
| 12 | 46 | | |

Plots of the observed biomass over time revealed a very fluctuating pattern, with no clear apparent long-term trend. Strong peaks in the biomass of Cyanophyta were observed. The statistical distributions of values show a very clear seasonal variation for dinoflagellates (Figure 9.4.1), somewhat less clear for Cyanophyta, and almost none for diatoms. WGSAEM discussed several transformations of the data in order improve the analysis of data. The overall distribution appears to be reasonably log-normally distributed when the zero values are not included. Power transformation is in general preferable because of the large frequency of 0-values. If log-transformed, there is still a group of values close to zero even if zero values are excluded from the data (Figures 9.4.1 and 9.4.2).

All transformations that achieve more symmetrical distributions will result in strong categorization for low values, due to the limited numerical resolution in the data. It was suggested that these highly fluctuating data should be treated in a way that only values above a certain threshold (occurrence of blooms) should be included in the analysis.

Some preliminary general linear models (GLM) on log-transformed data from the two stations were analysed to determine the extent to which the seasonal variation could be accounted for. For dinoflagellates, the analysis resulted in a model that can be written

$$\log(\text{Biomass})_{i(s)} = \text{Mean} + (a \cdot y_i + b \cdot y_i^2) + (c_s + d_s \cdot t_i)$$

Here $s$ denotes seasonal interval within the year (see above), $y_i$ is year, and $t_i$ is time within the year for observation $i$.

The term $c_s$ is the mean for seasonal interval $s$ (see above), and $a$, $b$, and $d_s$ are regression coefficients.

The two terms in parentheses represent a quadratic regression on year, and independent regressions within each seasonal interval defined by the data. This model was able to account for about 60 % of the total variance, and indicated a significant non-linear trend, with reduction during the first half of the series and increase in the later part of the series. The seasonal effect had the largest unique contribution to the reduction in variance. Currently, zeros are not included in the model and therefore the results might be biased.

Since season is such an important factor, and given the small-scale temporal variation (i.e., short-term peaks) that dominate these kinds of data, it might be more effective to include meteorological data directly as explanatory variables instead of merely adapting empirical seasonal variability. This could improve the predictive power of the model.

**Figure 9.4.1.** Observations for dinoflagellates shown against time of year. (Zero values not shown.)

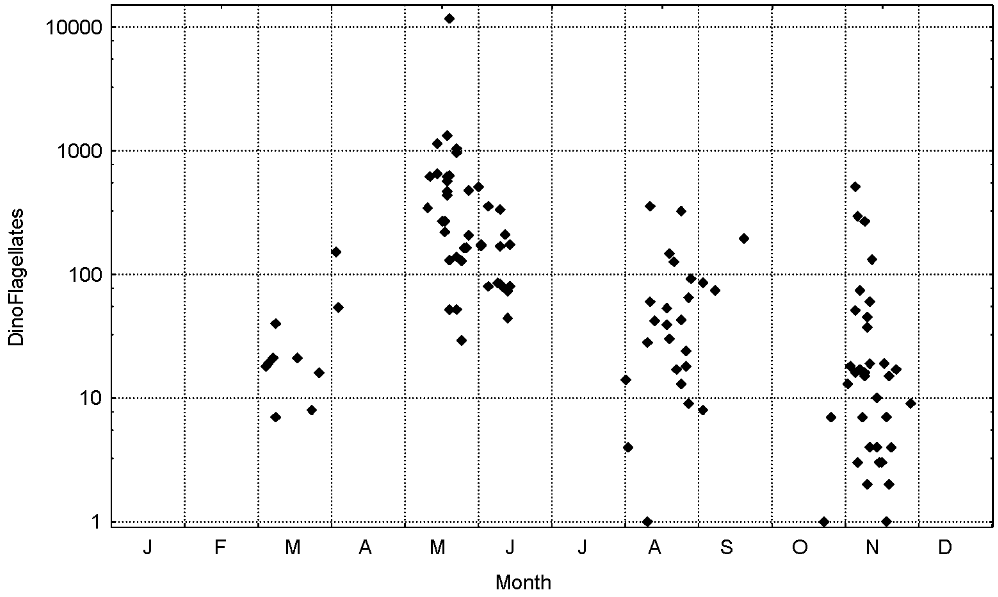


**Figure 9.4.2.** Distribution of cyanobacteria at station BMP H3. Observe the large number of samples close to zero. (Zero values are excluded.)

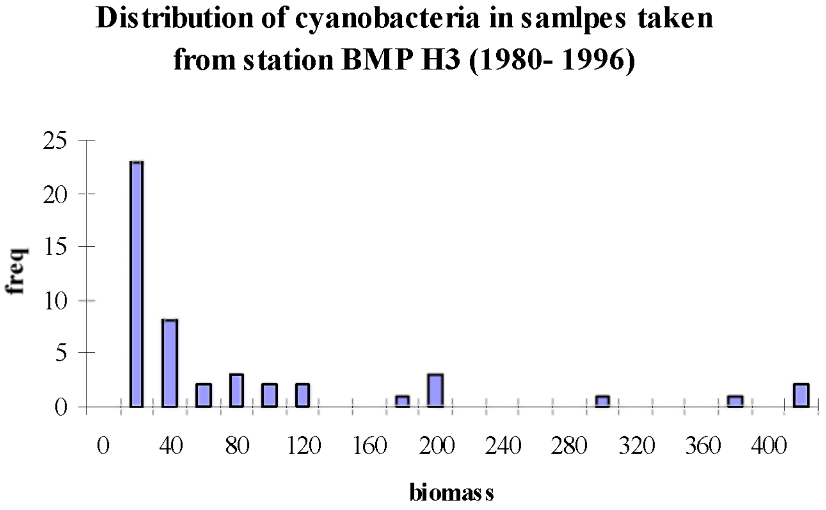
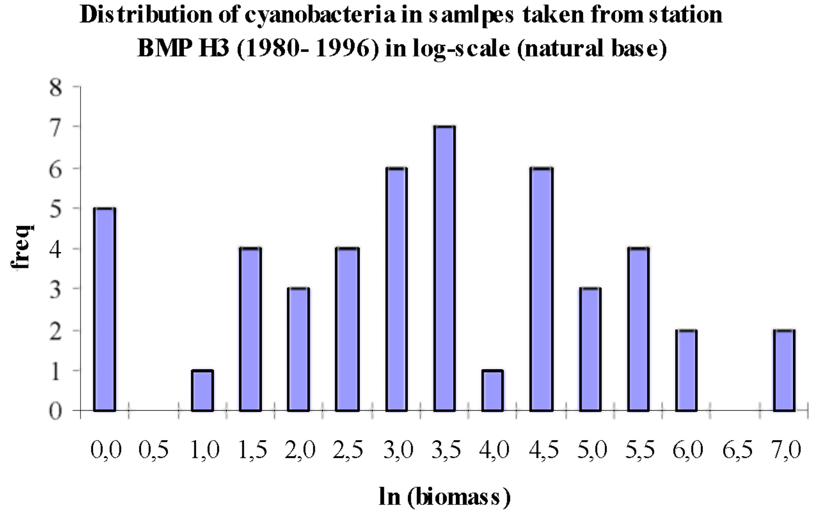


**Figure 9.4.3.** Same data as in Figure 9.4.1 on a log-scale (natural base).



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Warwick, R.M. 1986. A new method for detecting pollution effects on marine macrobenthic communities. Marine Biology, 92: 557–562.

## 9.5 Monitoring of Seabirds

*Request*

This is part of continuing ICES work on the role and interactions of seabirds in marine ecosystems.

*Source of the information presented*

The 2001 report of the Working Group on Seabird Ecology (WSGE) and ACME deliberations.

*Status/background information*

Marine birds are considered prominent members of the marine community and their numbers are considered relatively easy to survey. The WGSE presented information on current population sizes of seabirds, wildfowl, and waders compared to their historical abundance. Emphasis is placed on species that breed or winter around the North Sea, where the most recent and most complete information is available. In some cases, however, information between countries is incompatible.

Definite differences, including increases and decreases in numbers of seabirds, were shown for some species (Table 9.5.1), but it was also noted that for some, such as the European Shag, numbers in the North Sea are relatively variable within wide limits (Figure 9.5.1). For most species, the number of individuals was increasing. Exceptions include declines in Manx shearwater in Shetland due to introduced mammals; declines in Arctic skua in Orkney and Shetland; and substantial declines in black-legged kittiwake and localized declines in other species.

Where available, the data for migratory waterfowl in the North Sea showed the numbers to be stable or increasing for most species over recent years. Similarly, the numbers for wader species were stable or increasing.

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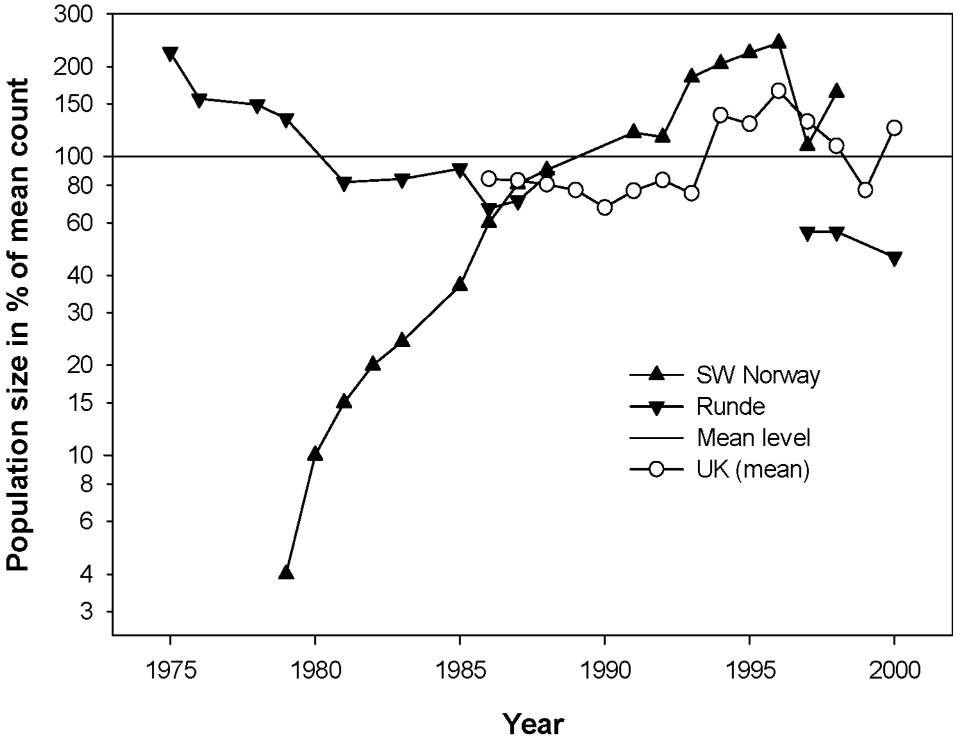
**Table 9.5.1.** Population figures for seabirds on North Sea coasts. Wintering counts are of individuals; breeding data are nesting pairs, except for auks which are individuals. Breeding data are from Dunnet *et al.* (1990) for all species except northern gannet, the sources here being Murray and Wanless (1997) and Thompson *et al.* (1996); winter data are from Skov *et al.* (1995) and are modelled estimates based on known average densities in winter months in different areas of the North Sea. Recent (approximately the past decade) trends of breeding populations (where known or suspected) are indicated. German trends are from Hälterlein *et al.* (2000).

| **Species** | **Wintering population** | **Breeding population** | **Breeding trend** |
|---|---|---|---|
| Northern fulmar | 3,744,000 | 307,599 | = |
| Manx shearwater | 500 | ca. 250 | = |
| European storm-petrel | 0 | low 1000s | |
| Leach's storm-petrel | 0 | low 100s? | |
| Northern gannet | 157,800 | 60,326 | + |
| Great cormorant | 14,315 | 2,222 | + |
| European shag | 29,115 | 19,804 | + |
| Arctic skua | 0 | 3,194 | − |
| Great skua | 1,000 | 7,303 | + |
| Mediterranean gull | 0 | ca.150 | + |
| Little gull | 5,370 | 40 | + |
| Black-headed gull | ? | 129,342 | = |
| Mew gull | 175,530 | 73,332 | |
| Lesser black-backed gull | 15,315 | 49,311 | + |
| Herring gull | 971,700 | 237,114 | = |
| Yellow-legged gull | ? | 10s | + |
| Great black-backed gull | 299,900 | 24,436 | + |
| Black-legged kittiwake | 1,032,690 | 415,427 | − |
| Gull-billed tern | ? | < 100 | ?- |
| Sandwich tern | 0 | 30,547 | = |
| Roseate tern | 0 | 36 | − |
| Common tern | 0 | 61,487 | = |
| Arctic tern | 0 | 74,729 | = |
| Little tern | 0 | 2,335 | |
| Common guillemot | 1,562,400 | 680,434 ind. | + |
| Razorbill | 324,000 | 73,115 ind. | + |
| Black guillemot | 6,595 | 23,741 ind. | = |
| Little auk | 852,690 | 0 | |
| Atlantic puffin | 26,000 (early winter),<br>74,600 (late winter) | 225,957 ind. | + |

**Figure 9.5.1.** Standardized abundance of nesting pairs of European shags at two Norwegian and five UK colonies (data from Lorentsen (2000) and the UK Seabird Colony Register).



# 10 ENVIRONMENTAL ASSESSMENT

## 10.1 Approach to Risk Assessment Methodology for the Marine Environment

*Request*

This is new work regarding risk assessment methodologies in relation to marine contaminants.

*Source of the information presented*

The report of the 2001 meeting of the Marine Chemistry Working Group (MCWG) and ACME deliberations.

*Status/background information*

The ACME took note of the MCWG discussion on the EU approach to risk assessment, which utilizes both measured and model-predicted data for exposure. These models have been developed for certain types of compounds (mainly lipophilic substances) and the predictions of the environmental distribution for other types of chemicals is more uncertain. The importance of using measured data was stressed as a means of validating the model outputs. Some comments were made to a draft document on developing a common EU/OSPAR approach on risk assessment methodology for the marine environment, but it was not fully reviewed. In many cases, there will be a paucity of high quality data from extended monitoring programmes available for use in an assessment, and again the importance of using all suitable measured data was stressed. The filtering of outliers was also considered to present potential dangers, as an increasing concentration of a pollutant often first becomes apparent from the presence of elevated values—at that stage indistinguishable statistically from apparent "positive outliers". Further developments are expected in the future, both within EU/OSPAR and in a proposed GESAMP working group on hazard assessment of contaminants in the marine environment in relation to both the quality of seafood for human consumption and also risk to the marine ecosystem.

## 10.2 Guidelines for Screening and Evaluation of Data Prior to Assessment

*Request*

Item 2.1.1 of the 2001 Work Programme from the OSPAR Commission:

Data preparation methods: Consider means of including temporal trend data with various degrees of QA (e.g., "fuzzy" data sets (cf. SIME 99/3/25)).

Item 2 of the 2001 requests from the Helsinki Commission: To annually review the quality of data starting 2001 with a test case by SGQAC reviewing contaminants data for thematic assessment.

*Source of the information presented*

The 2001 reports of the Marine Chemistry Working Group (MCWG), the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), and the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM), and ACME deliberations.

*Status/background information*

Three working papers on this topic were discussed (attached as Annexes 8, 9, and 10). All of them had been discussed at the meeting of WGSAEM. The first (Annex 8), which had earlier been discussed also by MCWG, considered criteria for accepting or rejecting data for trend studies on the basis of QA information, with examples based on data on concentrations of contaminants in marine biota. In particular, the paper showed that setting QA targets that are too stringent can lead to the rejection of data that can still be useful for trend detection. Further, that criteria based on observed P- and Z-scores could be misleading if applied without care. Finally, the paper suggested that one way of dealing with variable analytical quality would be to down-weight data points with poorer QA.

The second and third papers (Annexes 9 and 10) described the technical details of a weighted trend analysis. Both papers used the same underlying model for the analysis. Annex 10 gave details of various tests, including an overall trend and a contrast between the mean at the start and the end of the series. It also examined how the trend assessment is affected by different patterns of missing years, and also contrasted weighted and un-weighted analyses when an observation with poor QA occurs at the start or at the middle of a ten-year series. Annex 9 compared the effectiveness of different weighting strategies in terms of the trend likely to be detected when different numbers of years at the start of the series have poor QA. Rejection of data (equivalent to zero weight) was universally poor in terms of the effectiveness of detecting a linear trend.

Drawing on the comments made by MCWG and WGSAEM during their meetings, the ACME agreed to the following statements concerning these procedures:

1) Whilst the down-weighting of valid though old (and therefore not fully quality controlled to today's standards) data was regarded as a valid treatment, any weighting strategy needs to be considered with care. For example, it may be tempting to down-weight historic data with poor (or no) analytical quality, but to delete modern data with poor analytical quality. However, this would invoke Green's paradox, arising when a laboratory has consistent but poor analytical quality throughout the monitoring period, in which case only the historic data would be used in the assessment.
2) The process of accepting data which are quality-assured to a lower standard than is currently required could be seen to present a dubious message to analysts and their managers. Certainly, if misinterpreted, the weighting procedure could be seen as a method to rescue poor analytical practice. However, the process of accepting data should guarantee that this will not be the case. Trend detection will be most effective when performance in routine analyses and QA programmes is perfect. However, in terms of trend detection, deleting data with poor QA may make a bad situation worse.
3) Ideally, clear criteria for data acceptability should be established within each collaborative monitoring programme at inception so as to ensure that all data are "fit for purpose". In practice, however, criteria for data acceptability are developed when the data are first assessed. A quantitative framework should be developed, based on the objectives of the study, which can be applied in advance of the work programme—e.g., to ensure that the analytical performance of the participating laboratories, considered as a group, would be sufficiently good that meaningful trends in the environment (both spatial and temporal) are not distorted or obscured. This framework should account for different levels of environmental variability in relation to the precision of the chemical analysis. If the chemical analysis is very precise in relation to the environmental variability or biological variation, then there will be more gain in allowing less precise analytical data in the assessment. Thus, it is expected that in situations of very high environmental variability, taking into account data of poor QA might increase the power of the trend detection considerably, which is not expected to be the case in situations with low environmental variation.
4) There may be a danger that apparent trends resulting from improvements in analytical methods (e.g., due to an increase in recovery, or a lowering of the limit of detection) may be interpreted as environmental changes. If this change is so large as to distort meaningful trends in contaminant concentrations, the data should be deleted. A more effective approach for trend detection might be to include the data and attempt to model these changes in analytical performance. This would, however, be difficult to apply within a large trend assessment.
5) The ACME considered that there needed to be clarification about what could be done ideally, and what could be done in practice—both in requirements for new data and what was recorded in historic data. Therefore, developing more realistic examples of the application of these techniques to environmental trend data, using data from the ICES database, and evaluating the outcome, would provide a basis for further discussions in and between the Working Groups.
6) QA screening and the exploitation of QA data are an important topic that would benefit from further discussion between MCWG and WGSAEM, and with the managers of collaborative programmes such as those of HELCOM and OSPAR.
7) For the purposes of assessment groups such as OSPAR, a workable procedure for both QA screening (and weighting of analysis, if incorporated) needs to be simple, transparent, agreed, and compatible with the data available.

The ACME further considered the following points:

The use of quality assurance information to evaluate data acceptability should ideally incorporate a number of types of analyses which, taken together, give a full picture of the performance of a laboratory both day-by-day and over the long term. These should include the batchwise analysis of laboratory reference materials (routinely used to develop quality control charts), the periodic analysis of certified reference materials, and periodic participation in laboratory proficiency schemes and intercomparison studies in which blind samples are distributed. There are also problems with weighting of data when there are different types of QA information available in different years. For example, what would be a suitable weighting strategy based on a mixture of in-house analyses of laboratory reference materials and the results of

QUASIMEME comparative exercises? Another focus for future work should be on the treatment of possible matrix effects, particularly when the laboratory and/or certified reference material does not represent the same matrix as the material sampled.

If data are to be rejected from assessments on the basis of QA performance, a suitable criterion should be developed. A more formal link between the targets, e.g., for P- and Z-scores, for the underlying within- and between-batch standard deviations at a laboratory, and a test to see if these have been met, would provide a more consistent basis for defining and rejecting unacceptable data. Different levels may be set for laboratory evaluation and for data assessment purposes. Targets for analytical quality focus on noise in measurements, whereas targets for trend detection focus on noise in the data, which is a combination of both analytical and environmental variability.

To move forward, the ACME considers that there needs to be further development of appropriate screening and weighting tools that would lead towards a protocol that could be adopted for, e.g., the OSPAR trend assessments. To begin this process, WGSAEM would require an overview of the QA information available in the ICES database. WGSAEM would also require a subset of trend data, together with the corresponding QA information, to both develop and demonstrate possible screening and weighting procedures. This subset should be of sufficient length to provide the full range of QA horrors that will inevitably arise.

Further, the ACME noted that there are many QA initiatives with statistical implications taking place (cf. the SGQAC work) that have implications for QA data collection and its role in collaborative assessments. This could allow an opportunity to step back and consider QA methods currently in use and those being developed.

Finally, the ACME noted that OSPAR has proposed an assessment of trends in contaminants in sediments for 2002. This will require appropriate evaluation and use of QA data.

*Need for further research or additional data*

a) The ACME agreed to promote further discussion on issues of data acceptability and quality assurance, involving both MCWG and WGSAEM, along with data generators and assessors. For example, there should be further interaction on QA screening and weighting procedures between MCWG and WGSAEM. This should be in the context of a specific programme, e.g., an OSPAR assessment of trends in contaminants in biota, or the SGQAC evaluation of COMBINE programme data.

b) The ICES Secretariat should examine with OSPAR whether there is a requirement for MCWG and WGSAEM to develop protocols for the most appropriate use of QA data and relevant techniques for data acceptability and weighting, and provide appropriate guidance to the Working Groups in advance of their meetings in 2002.

c) There should be intersessional interaction between the ICES Secretariat and WGSAEM to obtain an overview of the QA data available in the ICES database.

d) There should be intersessional interaction between the ICES Secretariat and WGSAEM to identify and provide a subset of trend data, together with the corresponding QA information, for the development of screening and weighting procedures.

e) The ICES Secretariat should facilitate future studies by providing remote access to the ICES database for future WGSAEM meetings, so that data can be more readily investigated.

*Recommendations*

ICES recommends to OSPAR and HELCOM to take note of these aspects of data treatment during assessments, and the effects of straightforward data rejection when applied criteria are not met. It would greatly facilitate the development of protocols for data acceptability and weighting within the trend assessments if a dialogue were to be developed between the regulatory commissions and ICES in advance of their forthcoming data assessments. This dialogue could possibly take place during a special workshop on this topic.

### 10.3 Workshop on the Scientific Basis for Ecosystem Advice in the Baltic

*Request*

This is part of ongoing ICES work to develop an ecosystem approach to environmental and resource management.

*Source of the information presented*

The 2000 report of the Study Group on the Scientific Basis for Ecosystem Advice in the Baltic (SGBEAB) and ACME deliberations.

*Status/background information*

The ACME was informed that a recommendation to hold a Workshop on "The Scientific Basis for Ecosystem Advice in the Baltic" in 2001 was put forward by the Study Group on the Scientific Basis for Ecosystem Advice in the Baltic (SGBEAB) that met in June 2000. Having considered the report of the SGBEAB at the 2000 Annual Science Conference, the Baltic Committee noted that ecosystem advice must be based on a wide scientific knowledge of the systems. ICES does not have access to a wide basis at present. To improve this in the area of the Baltic Sea, a closer cooperation with the existing independent scientific organizations was recommended. The Baltic Committee was informed that the Baltic Marine Biologists (BMB) and the Conference of Baltic Oceanographers (CBO) welcome ICES participation in the scientific conference organized by the BMB, CBO, and Baltic Marine Geologists (BMG) on 24–29 November 2001. Therefore, it was decided that the ICES workshop should be held just after the conference, from 30 November to 1 December in Stockholm. According to the proposal by the SGBEAB, among other presentations there, an ICES speaker should deliver an overview on the main needs expressed by clients to ICES.

In the brackish Baltic Sea, where a number of ecological subsystems and corresponding local populations of fish and other animals exist, the main problems are the high load of nutrients and toxic substances as well as intense exploitation of fish resources, particularly piscivorous fish (cod and salmon). The fishery results in changes in the composition and abundance of fish. It exploits adult and young commercial fish, but also by-catches non-target species, marine mammals, and seabirds.

SGBEAB has suggested that, in the future, ICES advice in the Baltic Sea should be based on a wide range of background information, including:

1) background information on meteorological and hydrological conditions (exchange processes, inputs to the Baltic);
2) nutrients, productivity, and toxic algal blooms:
3) contaminants (anthropogenic substances);
4) evaluation of the biomass and the production of the main prey used by intensively exploited fish stocks;
5) assessments of fish stocks (herring, cod, sprat) by their natural populations;
6) evaluation of the condition of seabirds and marine mammals;
7) evaluation of the state of the Baltic Sea ecosystem.

The planned Workshop on the Scientific Basis for Ecosystem Advice in the Baltic (WKSBEAB) should develop the corresponding basis. According to the SGBEAB suggestion, in addition to the ICES speaker, viewpoints of the local governments, HELCOM and the International Baltic Sea Fisheries Commission (IBSFC), as well as scientific analyses on the condition of the cod stock and the Baltic food web, should be presented. Also, specific topics from an ecosystem perspective looking at the present state of the knowledge, future work needed, and the ability to give advice that will meet the managerial needs, should be considered during the Workshop.

### 10.4 Environmental Indicators

*Request*

This is part of ongoing activities to develop scientifically sound ways of assessment of the marine environment.

*Source of the information presented*

The 2001 report of the Study Group on Ecosystem Assessment and Monitoring (SGEAM) and ACME deliberations.

*Status/background information*

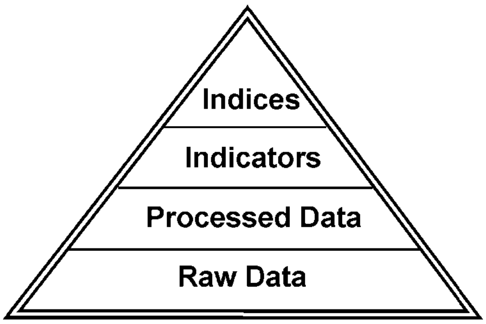
The ACME noted various approaches to the development of indicators for the assessment of the marine environment that can be helpful for policymakers and managers. Particular attention has been paid to the developments by the OECD, the European Environment Agency (EEA), HELCOM, and the Global International Waters Assessment (GIWA).

The term "indicator" has been given various definitions, but generally it refers to a measure of something. The OECD defined indicator as:

*A parameter, or a value derived from parameters, which points to / provides information about / describes the state of a phenomenon / environment / area with a significance extending beyond that directly associated with a parameter value* (OECD, 1993).

The relationship of indicators to the information on which they are based is illustrated in Hammond's information pyramid (Hammond, 1995) (Figure 10.4.1). Basically, data or information is processed, then refined to form indicators. In this case, indices refer to aggregations of indicators or processed data. Indices are developed in order to limit the amount of information that decision-makers and other interested parties have to absorb. By their nature, indices and indicators are less informative than their indicator or data components, respectively, since the process of aggregation dampens the impact of the individual indicators and data. The use of indices and indicators must therefore be made cautiously.

**Figure 10.4.1.** The information pyramid (Hammond, 1995).



Generally speaking, the information available from scientific papers and environmental periodic assessments (Quality Status Reports) is at the "processed data" level and, as such, might be too voluminous and complicated, and therefore not very useful to decision-makers. Thus, strong pressure is put on experts to identify the problem and indicate effects in a descriptive and quantifiable way in the form of indicators or even indices. Indices represent the most integrated information with the least amount of detail. Indices can also be expressed as classes, e.g., from first to fifth, from "no known impact" through "slight impact", "moderate impact" to "severe impact" (GIWA, 2001).

The OECD has developed a systematic framework for environmental indicators commonly referred to as "pressure-state-response" (OECD, 1993), which is based on the following causality chain:

"Human activities exert pressures on the environment ("pressure") and change its quality and the quantity of natural resources ("state"). Society responds to these changes through environmental, general economic and sectoral policies (the "societal response"). The latter form a feedback loop to pressures through human activities" (OECD, 1993).

Indicators of pressure (P) can also be called indicators of driving forces or stressors. The original cause of pressure on the marine environment is sometimes created far from the sea. A causal chain analysis is needed to identify the original source of pressure. Pressure indicators include general social and economic indicators related to wealth, population and other demographics, as well as more specific indicators relating to the consumption and use of natural resources.

State (S) indicators are needed to properly assess the state of the marine ecosystem. This knowledge comes through research and monitoring. State indicators are measures of the state of environmental quality.

Response (R) indicators should help in the decision-making process, in developing regulatory standards, and in identifying the actions needed. Response indicators include government policies and regulatory efforts, as well as societal responses through individual and collective actions. These response activities usually result in changes in the pressure indicators, thus closing the loop.

The ACME also noted the EEA effort to develop a "Driving force-Pressure-State-Impact-Response" (DPSIR) framework of indicators to assess the environmental status of the European seas. In the EU-funded project EUROCAT (European catchments and their ecological effects on coastal seas), indicators to describe the effects of inputs (nutrients and contaminants) will be developed for a series of European catchment areas; the rivers Vistula, Elbe, Rhine, Humber, Po, and Axios are part of this project. Indicators to be used will be on different levels, including parameters to describe the state of the environment as well as processes. The ACME will follow the outcome of this project with great interest.

The ACME is of the opinion that, due to the complicated nature of ecosystems, indicators cannot perfectly represent the state of the environment or the complex interrelationships between the natural environment and anthropogenic activities. Indicator systems need to strike a balance between sophistication, as measured by the number of indicators and degree of functional representation, and simplicity and cost considerations. Very sophisticated systems including a large amount of data and models may be a more accurate reflection of environmental conditions, but decision-makers may not be able to make use of them without clear scientific advice, for example, from ICES.

Ultimately, the success of indicator-based assessments will depend on parallel developments of other issues related to ecosystem health, such as Ecological Quality Objectives (EcoQOs) and progress on developing systems of background/reference values.

Results of indicator-based assessments will depend, even more than "traditional" assessments, on the availability of data. This is one more reason why ICES Member Countries should be urged to provide environmental data to the ICES Marine Data Centre.

*Need for further research or additional data*

The ACME advises ICES to become involved in indicator development, and to cooperate in relevant ongoing and upcoming efforts, including those of the EEA, GIWA, and HELCOM.

Indicator development efforts should be fully integrated with ongoing environmental assessments, including HELCOM Periodic Assessments, OSPAR Quality Status Reports, and GIWA Scoping and Scoring Methodology.

ICES should take a proactive stance in working on indicators describing environmental status (State indicators) in the context of socio-economics (Pressure) and decision-making (Response).

**References**

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EEA. 2001. Testing of indicators for the Marine and Coastal Environment in Europe. Part 1. Eutrophication and Integrated Coastal Zone Management. 46 pp. Part 2. Hazardous Substances. 41 pp. EEA, Copenhagen.

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### 10.5 Review of Recent Environmental Assessments and Production of Environmental Quality Status Reports

*Request*

This is part of continuing ICES work to review and advise on effective methods to conduct environmental assessments and prepare quality status reports.

*Source of the information presented*

The 2001 report of the Study Group on Ecosystem Assessment and Monitoring (SGEAM) and ACME deliberations.

*Status/background information*

Recent developments within the work of the Global International Waters Assessment (GIWA) (see also Section 14.3) and the Global Environment Facility (GEF) Baltic Sea Regional Project were considered by SGEAM. In considering the relevance of GIWA, SGEAM noted that socio-economic assessment aspects form an important component, in line with the framework for the management of marine ecosystems previously outlined by SGEAM with reference to integrated comprehensive assessments. A proposed scoring system for environmental and socio-economic aspects for 22 issues associated with the five major concerns identified for the Baltic Sea was discussed. SGEAM felt that, although the details of the preliminary criteria and scores may merit further discussion, the general approach used by GIWA should be considered by ICES when deriving indices for comprehensive integrated assessments of geographical regions, such as the environmental assessments undertaken within OSPAR and HELCOM. However, despite the approval of the GIWA concept, SGEAM noted a challenge in moving from conservative quantitative sciences organized in a sectoral manner to the multidisciplinary integration of results required by comprehensive assessments. ICES should determine the extent to which it can contribute to a GIWA-related assessment in all science areas, and also give increased priority to the identification and development of relevant indicators of the status of important components of the ecosystem.

The objective of the GEF Baltic Sea Regional Project is to introduce ecosystem-based assessments to strengthen the management of the Baltic Sea coastal and marine environments. The Baltic Sea is now an ecosystem under extreme stress, and the coastal states have initiated a Joint Comprehensive Environmental Action Plan (JCP) to aid long-term restoration of the ecological balance in the region. The proposed project supports the JCP, initially during the period 2001–2006, and will be coordinated by HELCOM.

An assessment of the Northern Seas undertaken by ICES for the Nordic Council of Ministers was reviewed by SGEAM. The area covered was the Baltic Sea, the North Sea, the Northeast Atlantic, areas of the Arctic without permanent ice cover (e.g., the Barents Sea) and West Greenland, and the report provides information on the effects of fisheries on fish stocks and marine ecosystems. The impact of environmental conditions on fish stocks is also considered, along with contaminant concentrations and disease occurrence in fish and shellfish. SGEAM concluded that the report provided a good summary of current knowledge, the important issues were focused on, and it represented a good balance between style and layout as well as scientific substance. SGEAM felt that the report can be considered as providing a significant step towards arriving at an integrated assessment involving fish, fisheries, and relevant environmental factors. Such an assessment can be readily updated, and could be maintained on an annual basis and made available via electronic means.

SGEAM reviewed the OSPAR Quality Status Report (QSR) 2000 and, as the full report of the HELCOM Fourth Periodic Assessment of the State of the Environment of the Baltic Marine Area, 1994–1998, was not yet available, a short "popular" version was discussed. SGEAM noted an inconsistency in the level of detail reported under each of the identified "issues" in the QSR 2000. The regional Quality Status Reports (e.g., Region II, greater North Sea) provide a great deal of useful monitoring and assessment data, although references to the sources of the data are lacking in most cases. The fisheries issue admits that current management measures to regulate fish stocks are not working: "although effective in some fisheries, overall these measures have had limited effectiveness, given the existing over capacity of some European fishing fleets". Overall, SGEAM felt that the present emphasis and progress made within ICES Working Groups on ecosystem-level processes has not been reflected in the "key" sections of the QSR 2000 and, in particular, in the recommendations for future research and development. Integrated reporting and assessment need to be underpinned by integrated monitoring. This not only applies within a single monitoring programme, where more than one determinand is being measured, but integration is also required between different sectoral monitoring programmes.

The short-form version of the HELCOM assessment was felt to be a well-illustrated and informative leaflet. SGEAM noted shortcomings, however, in the information presented despite some positive developments being made over earlier assessment documents. Some important issues were absent, such as biological effects of harmful substances in the lower portions of the food chain, coastal fish and biodiversity issues. There is no discussion of the offshore commercial Baltic Sea salmon fishery, although this is one of the key causes for the critical situation of this species. This fishery may also contribute one of the major threats to the local harbour porpoise population. Also, with regard to mariculture, the report concludes that its impact on the Baltic marine environment is negligible, although several studies have shown that nutrients from fish farms have resulted in eutrophication of areas in the Finnish archipelago.

SGEAM noted that ICES was contributing to the development of Ecological Quality Objectives (EcoQOs) for marine mammals and seabirds in the North Sea through its Working Groups. Considerable further development of EcoQOs is necessary before they are ready for adoption and implementation by management bodies, and SGEAM recommended that ICES give a high priority to this work within its core science programme.

An integrated ecosystem approach to the assessment and management of the marine environment necessitates an understanding of how the ecosystem works in order to identify which attributes need to be monitored and why. SGEAM recognizes that, in order to evaluate the consequences of various management scenarios, realistic ecosystem models coupled to useable management tools need to be developed. The challenge of such ecosystem modelling is how to handle (numerically) the links between all the defined (separately modelled) cause/consequence processes. Examples of such modelling tools are available from Sweden and Canada.

In noting the SGEAM comments concerning the treatment of fisheries and mariculture issues in the HELCOM Fourth Periodic Assessment, the ACME pointed out that ICES had contributed this chapter to the assessment report. At its 2000 meeting, the ACME had reviewed extensive material for this chapter prepared by a number of ICES Working Groups. However, owing to the small number of pages allocated to this chapter in the Fourth Periodic Assessment Report, only a small amount of this material was actually included in the chapter. The ACME included some of the additional material in its 2000 report; see ICES (2000) for details.

### Reference

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 144–145.

## 10.6 ICES Environmental Status Report

*Request*

During the past few years, several ICES Working Groups have agreed to contribute to an ICES Environmental Status Report, which will be updated annually or more frequently, depending on the subject matter. The Environmental Status Report is published on the ICES website (http://www.ices.dk/status) as material becomes available.

### 10.6.1 Oceanographic conditions

*Source of the information presented*

The 2001 report of the Working Group on Oceanic Hydrography (WGOH) and ACME deliberations.

*Status/background information*

The North Atlantic Oscillation (NAO) Index continued to recover to positive values up to and including winter 2000 (winter—December through February—is defined by the year of the January), though with some indication of an eastward shift in the NAO dipole pattern. The result was that most parts of the area under review showed moderate or warm conditions in 2000. However, the climatic data set for winter 2001 showed the second lowest NAO Index since 1979, which means that the NAO Index has undergone a sharp return to negative conditions.

Surface temperatures off West Greenland were relatively warm during the summer of 2000 due to mild atmospheric conditions. Stronger inflows of polar water were noted.

Ocean conditions in the Northwest Atlantic cooled slightly during 2000 relative to 1999 values, but were near or above normal in most areas. Sea-ice extent also increased slightly over the light ice conditions of 1999. An increased southward transport of polar waters was noted on the Labrador shelf.

The surface waters of the Labrador Sea were observed to be slightly cooler, fresher, and denser in the summer of 2000 compared to 1999. More convection and overturning took place in the Labrador Sea during the 2000 winter than in recent years, but not as intensely as during the early 1990s.

In Icelandic waters, 2000 revealed in general relatively high temperatures and salinities as in the past 2–3 years, following the very cold years of 1995 and 1996, although temperatures were also cooler than in 1999 in this area.

The annual mean air temperature over the southern Bay of Biscay during 2000 remained at nearly the same value as during the preceding two years. Surface waters were slightly cooler and fresher than in previous years.

Early 2000 saw a peak in the temperature of surface waters in the Rockall Trough, caused by an influx of unusually warm water into the region. By the spring of 2000, the temperature had dropped somewhat, though it remained above the long-term mean.

2000 was the sixth warmest year since 1971 in the North Sea, in terms of annual mean sea surface temperature. All months were warmer than average, except for June and July. There was evidence of a large input of fresh water from the Baltic Sea.

Since 1996, temperatures have been increasing in the southern and central Norwegian Sea. In 2000 the warming continued at the southern section, while a cooling occurred at the central section. In the northern Norwegian Sea, the temperature since 1996 has been close to the long-term average.

The temperature in the Barents Sea decreased from 1 °C above average during early winter to 0.2 °C in the autumn. In the eastern Barents Sea, the temperature stayed high during the whole year.

A larger than normal inflow of Atlantic water has resulted in warmer and more saline conditions in the eastern Greenland Sea.

**Prognosis**

The NAO in the winter 2000/2001 was found to have undergone a further rapid reversal to negative values. We can therefore expect warming in the Northwest Atlantic and cooling in the east.

The full ICES Annual Ocean Climate Status Summary for 2000/2001 is available on the ICES website at http://www.ices.dk/status.

### 10.6.2 Zooplankton monitoring results

*Source of the information presented*

The 2001 report of the Working Group on Zooplankton Ecology (WGZE) and ACME deliberations.

*Status/background information*

The WGZE ongoing activity to compile information from zooplankton monitoring by ICES Member Countries and make scientific information accessible to the public forms part of the annual edition of the summary status report on zooplankton monitoring results in the ICES area. The preparation of this summary has been given priority in the work of WGZE. A new version will be available for the ICES Annual Science Conference, and will also be available via the ICES website and in the WGZE annual report.

### 10.6.3 Harmful algal blooms

*Source of the information presented*

The report of the ICES-IOC Working Group on Harmful Algal Bloom Dynamics (WGHABD) and ACME deliberations.

*Status/background information*

As part of its ongoing activity, the WGHABD has produced an annual edition of the decadal maps of harmful events related to phytoplankton blooms in ICES Member Countries, which have been presented for some years on the web (http://www.ices.dk/status). The maps indicate the presence of toxins or observations of animal/plant mortality, regardless of the level of toxicity. The types of events covered are: amnesic shellfish poisoning (ASP); ciguaterra fish poisoning (CFP); diarrhetic shellfish poisoning (DSP); neurotoxic shellfish poisoning (NSP); paralytic shellfish poisoning (PSP); and other toxic effects, such as cyanobacterial toxin poisoning. Earlier results of this compilation activity were presented in the annual ACME report (ACME, 1999).

**Reference**

ICES. 1999. Report of the ICES Advisory Committee on the Marine Environment, 1998. ICES Cooperative Research Report, 233: 250–262.

### 10.6.4 Fish disease prevalence

*Source of the information presented*

The 2001 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and ACME deliberations.

*Status/background information*

At its 2001 meeting, WGPDMO evaluated the progress in the intersessional development of maps of marine fish and shellfish diseases as a contribution to the ICES Environmental Status Report.

The maps prepared in 2000, illustrating temporal trends of the diseases lymphocystis, epidermal hyperplasia/papilloma, and skin ulcerations in dab (*Limanda limanda*) from the North Sea and English Channel, the spatial distribution of the oyster diseases *Bonamia ostreae*, *Marteilia refringens,* and *Perkinsus marinus,* and the spatial distribution of marine Viral Haemorrhagic Septicaemia virus (VHSV) covering all ICES countries, have been updated where new developments have been recorded.

Diseases of dab have been selected because they are used in national marine environmental monitoring programmes carried out by ICES Member Countries bordering the North Sea and have been recommended for inclusion in the OSPAR Joint Assessment and Monitoring Programme (JAMP). Data used were extracted from the ICES Environmental Data Centre.

The diseases of shellfish have been selected as they are some of the most important diseases in oyster culture, and the marine VHS has been selected as it may be an emerging disease problem. WGPDMO members have provided the data for these maps. The maps on the spatial distribution of *Bonamia ostreae, Marteilia refringens,* and marine VHSV have been updated, as new developments have occurred.

Updated maps have been produced for presentation in the web-based ICES Environmental Status Report at http://www.ices.dk/status. Proposals for improving the information in the form of short descriptions of the specific diseases accompanied by proper illustrations were given by WGPDMO and will be implemented in due course.

# 11 ADVICE AND STANDARD DATA PRODUCTS FOR DEVELOPING THE COMMON PROCEDURE FOR IDENTIFICATION OF THE EUTROPHICATION STATUS OF THE MARITIME AREA

*Request*

Item 3.1 of the 2000 Work Programme from the OSPAR Commission: provision of advice and standard data products for the purposes of developing the Common Procedure for the Identification of the Eutrophication Status of the Maritime Area and contributing to further intersessional work.

*Source of the information presented*

Report prepared by the ICES Oceanographer and ACME deliberations.

*Status/background information*

The data available for this study are those currently residing in the ICES oceanographic database. Some of these data arrive there via the ICES Environmental Data Reporting Format and these are specifically delivered as part of the data collected for the OSPAR monitoring programmes. Other data (the majority) arrive as part of the country and project oceanographic data submissions to ICES and are not delivered in any specific format. It is assumed that all of these data are available to OSPAR for the purpose of this study even though some are delivered with restrictions to their use.

Most data are for the North Sea, but a few data from the Irish Sea are also presented as maps. A full set of maps is available at www.ices.dk/ocean/project/ospar. In addition to the maps requested by OSPAR, maps of nitrite have been prepared because of the strong signal related to this parameter in the southeastern North Sea, in particular.

The choice of time period was dictated initially by a combination of the available data, and the variability of climate conditions prevailing since 1980. These conditions are typified by changes in the winter North Atlantic Oscillation (NAO) Index (Figure 11.1). Initially two periods were chosen, 1986–1989 and 1995–1999, these periods being chosen in order to capture non-exceptional NAO-index periods as far as possible. The addition of the period 1991–1994 encompasses a sustained period of high index values. Periods of high index tend to be characterized by high rainfall and strong westerly winds, and low index winters tend to be associated with cold, anti-cyclonic type weather. All things being equal, the first and last periods should have produced relatively similar climatic conditions, but this can only be confirmed by a much more detailed assessment, especially with regard to rainfall and freshwater release.

As well as climatic factors, data distribution changes have an influence on property distributions. A telling factor is the almost complete lack of Norwegian nutrient data since 1995, but other factors include the very irregular sampling of ammonium. Thus, the dissolved inorganic nitrogen (DIN) maps generally show a very limited distribution. In the case of the Irish Sea, as no ammonium has been measured prior to 1995, and subsequently only few measurements have been made, nitrate+nitrite maps were produced in place of the DIN maps. In addition to these distribution maps, an attempt has been made to discern trends by preparing "difference" maps. These show the changes that have occurred from one period to the other and should be compared with the analysis of specific area and riverine trends as described below. A cursory check shows that the two methods do not produce conflicting information, but this will have to be confirmed by a more rigorous comparison.

No attempt has been made to produce maps with respect to the coasts of Spain, France, Portugal, or Ireland (other than the east coast) owing to the paucity of data from these areas, especially in the coastal areas, that are available from the ICES oceanographic database. The database is best populated with Spanish data, but this is from a very small region off Santander and few of these data are from the area of the coastal salinity gradient.

Linear regression analyses of plots of winter nutrient concentrations versus salinity for major North Sea estuaries and coastal waters were performed. The regression values at salinity 30 for each successive year were used to construct time series of salinity-normalized winter nutrient concentrations. A selection of the trend products has been prepared. These are not entirely for the requested localities. The Channel has so far not been included because of poor, irregular sampling in this area. However, the Scheldt has been included as this river and estuary constitutes the best data coverage that is available. The trends have been calculated as a five-year running mean, partly to coincide with the approximate period of averaging in the mapping products, and partly because in most cases there was not nearly enough data to attempt annual or biennial averaging. Furthermore, no trend values for DIN were obtained, $NO_3$+$NO_2$ trends being acquired instead. This has the advantage that a common set of trends was acquired for all requested areas, as there was no ammonium data available from the Humber or Thames estuaries at salinities of less than about 25.

In all cases, the trend figures assumed a significant linear relation between salinity and the required property. These calculations were done over the period mentioned above, and the value of the property at a salinity of 30 was calculated. It is clear from these plots that linear regression fails in a number of cases and some caution will have to be placed on any interpretation. This will apply, in particular, to the English estuaries, where irregular sampling in space and time limits the ability of such calculations. It should also be noted that the calculation does not apply to the Skagerrak or Kattegat over the salinity range for which there are data. In the case of the Kattegat, salinity values do not reach 30, and for this area an analysis based on straight averaging during the winter quarter is included for comparison.

Figures 11.2 and 11.3 present composite diagrams designed to summarize the products described above. From this it is evident that the Thames has consistently higher concentration values than the other locations, whereas the Kattegat has the lowest concentrations. The Scheldt river shows most obviously a reduction trend.

The ACME has previously advised that there is a need to move from concentrations to fluxes in consideration of eutrophication (ICES, 1992, 1994).

The nutrient-salinity relationship for the major North Sea rivers and estuarine systems offers a basis for this. The salinity scale corresponds to a (non-linear) scale dilution factor. With knowledge of riverine freshwater input, this again corresponds to a progressively increasing volume of water with increasing salinity.

Combined with the nutrient data, this provides a basis for calculating volumes and fluxes of water and nutrients.

*Recommendations*

The ACME recommends that the estimation of pools and fluxes of water and nutrients should be conducted in further development of the OSPAR Common Procedure for the Identification of the Eutrophication Status of the Maritime Area. This will allow an ecologically meaningful comparison between nutrient inputs and fluxes in the receiving coastal water masses.

## References

ICES. 1992. Report of the ICES Advisory Committee on Marine Pollution, 1992. ICES Cooperative Research Report, 190: 36–37.

ICES. 1994. Report of the ICES Advisory Committee on the Marine Environment, 1993. ICES Cooperative Research Report, 198: 22.

**Figure 11.1.** Two-year running mean of NAO Index 1980–2000. High index values imply strong westerly air streams over northern Europe.

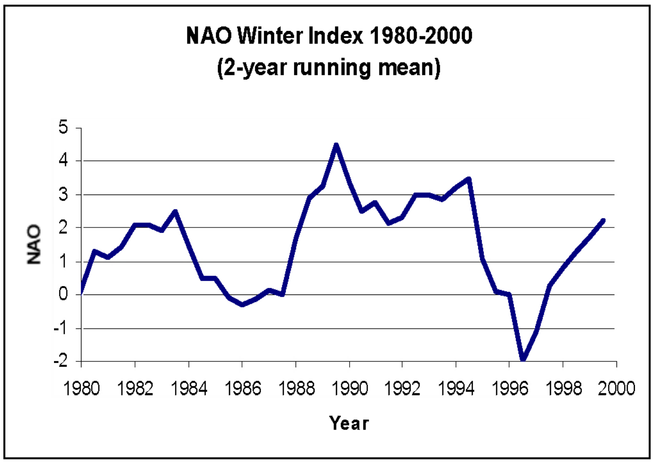


**Figure 11.2.** River/area trend composites for nitrate at salinity 30 for the period 1980–2000.

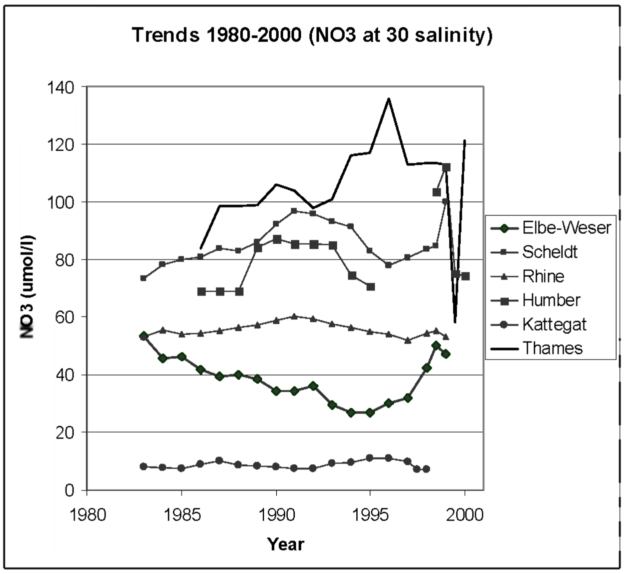
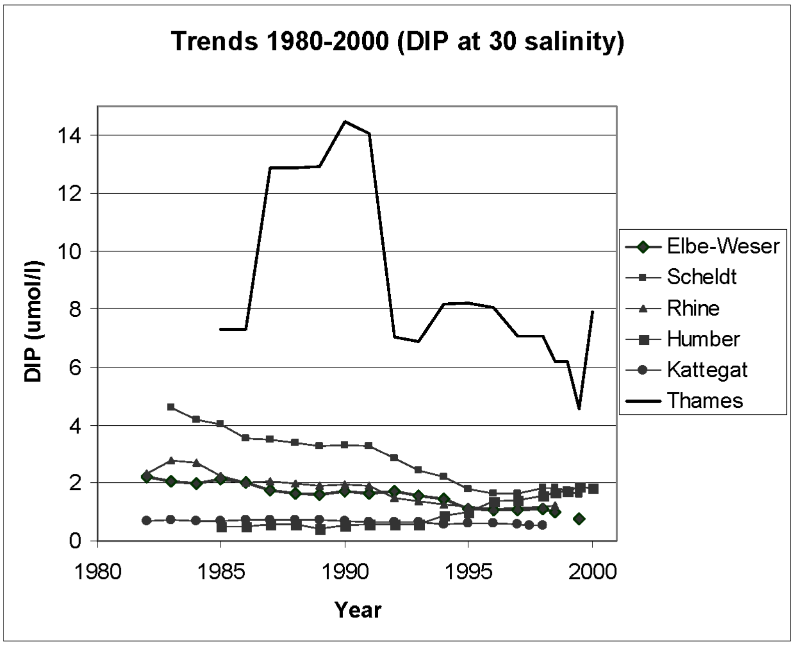


**Figure 11.3.** River/area trend composites for dissolved inorganic phosphorus at salinity 30 for the period 1980–2000.



# 12 ISSUES RELATED TO MARICULTURE

## 12.1 Interactions Between Seabirds and Aquaculture

*Request*

This is part of continuing ICES work to keep under review environmental issues relating to mariculture.

*Source of the information presented*

The 2001 report of the Working Group on Seabird Ecology (WGSE) and ACME deliberations.

*Status/background information*

A review was prepared by the WGSE to depict the interactions between mariculture and seabirds. With the large increase in mariculture activities over the past few decades, various concerns have been raised regarding a variety of potential environmental impacts, including the interactions of seabirds with mariculture facilities.

Mariculture can provide new feeding opportunities for some birds, and so can create a local increase in bird numbers. Increases in bird numbers at fish farms may lead to problems for fish farmers. Birds may eat or damage stock, may represent a nuisance or be a vector of disease. These problems may cause significant costs to fish farmers both in direct financial terms, and in terms of time spent in trying to reduce bird problems. The impacts of birds on fish farming can lead to farmers taking action against perceived bird problems, while farming itself may have some negative impacts on birds. Direct negative effects of mariculture on seabirds (defined here as marine birds and shorebirds) have been thought to arise mainly from loss of habitat, harvest of young marine animals for culture that may represent natural food of some seabirds, disturbance of birds by fish farm workers, and killing of birds (either deliberately or accidentally). It should be noted that enhancing food supply to wildlife is not necessarily a positive effect, since increases in some animal populations can have negative impacts on others, and can lead to populations becoming dependent on artificial feeding opportunities.

**Enhancing food supplies**

There are several cases where mariculture provides food for seabirds to an extent that certainly influences the pattern of distribution of the seabirds and may in some cases increase their population size. As an example, common eiders specialize in feeding on mussels. Farmed mussels grown on suspended rope cultures are attractive to the eiders because the shells tend to be thin and they have a high energy content compared to wild mussels found intertidally. Because the mussels are grown in high densities, the eiders develop the habit of flocking at unprotected mussel farms where they can rapidly deplete the standing stocks.

Attraction of birds to aquaculture and impacts on fish farming profitability

Where aquaculture attracts large numbers of birds, the activities of the birds may present a serious impact on the profitability of farming as a result of birds taking product or interfering with the functioning of the farm. The main perceived impacts on farming are depredations of fish by cormorants and herons, and depredations of mussels by sea ducks.

Few studies in the ICES area have quantified the costs, but studies in other areas have shown significant financial impact.

**Disturbance of birds by mariculture activities**

Mariculture can cause disturbance to wildlife by major modification of habitat, such as removal of habitat required for resting or feeding sites. It can also cause local disturbance through minor alterations to habitat. For example, oyster culture on intertidal areas involves the addition of racks, stakes, culture bags, marker poles, and other equipment onto open tidal flats. Some birds are attracted onto such structures, however, most species of shorebirds tend to avoid oyster culture plots, preferring to feed on open areas of tidal flats. Since shorebird numbers are influenced by the amount of food in their wintering sites, loss of open foraging habitat to mariculture is likely to have a negative impact on shorebird populations.

### Persecution of birds by fish farmers

Many forms of mariculture attract certain birds to feed on the high concentrations of food being cultivated. If no action is taken, birds can have devastating effects on the viability of farms. Farmers generally adopt one or more of three strategies: they may invest in costly structures to exclude wildlife from farms (Brugger, 1995; Ross and Furness, 2000); they may reduce the numbers of birds by shooting them or by other means (Belant *et al.,* 2000); or they may employ non-lethal deterrents that scare birds away from the area (Mott and Boyd, 1995; King, 1996), but many non-lethal methods have not been successful (Mott and Boyd, 1995; Russel *et al.,* 1996; Ross and Furness, 2000).

*Additional comments*

The material presented here, along with a longer review, will be published as a chapter in an *ICES Cooperative Research Report* with the tentative title “Seabirds as Monitors of the Marine Environment”.

### References

Belant, J.L., Tyson, L.A., and Mastrangelo, P.A. 2000. Effects of lethal control at aquaculture facilities on populations of piscivorous birds. Wildlife Society Bulletin, 28: 379–384.

Brugger, K.E. 1995. Double-crested cormorants and fisheries in Florida. Colonial Waterbirds, 18: 110–117.

King, D.T. 1996. Movements of double-crested cormorants among winter roosts in the Delta Region of Mississippi. Journal of Field Ornithology, 67: 205–211.

Mott, D.F., and Boyd, F.L. 1995. A review of techniques for preventing cormorant depredations at aquaculture facilities in the southeastern United States. Colonial Waterbirds, 18: 175–180.

Ross, B.P., and Furness, R.W. 2000. Minimising the impact of eider ducks on mussel farming. University of Glasgow, Glasgow, UK. 54 pp.

Russel, I.C., Dare, P.J., Eaton, D.R., and Armstrong, J.D. 1996. Assessment of the problem of fish-eating birds in inland fisheries in England and Wales. Directorate of Fisheries Research, Lowestoft. 130 pp.

## 13 EFFECTS OF EXTRACTION OF MARINE SAND AND GRAVEL ON MARINE ECOSYSTEMS

*Request*

This is part of continuing ICES work on ecosystem effects of marine aggregate extraction.

*Source of the information presented*

The 2001 report of the Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT) and ACME deliberations.

*Status/background information*

The ACME reviewed and accepted several sections of the report of the Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT) containing information and discussions on the effects of marine sand and gravel extraction on marine ecosystems, including quantities of material extracted, impacts on biota, and the effect of turbidity caused by dredging. Approaches to environmental impact assessment were also reviewed.

The ACME noted that draft ICES Guidelines on the Management of Marine Sediment Extraction were considered, with a view to producing a draft set of ICES guidelines at the next meeting of WGEXT. These Guidelines are intended to replace both the ICES Code of Practice on Commercial Extraction of Marine Sediments and the ICES Guidelines for Environmental Impact Assessment of Marine Aggregate Dredging.

The ACME decided to present the information below, summarizing this material.

### 13.1 Current Marine Extraction Activities and Results of Assessment of their Environmental Effects

The ACME took note of the status of marine extraction and dredging activities in ICES Member Countries, as reported to WGEXT. Particular emphasis was given to a review of approaches to environmental impact assessment and related environmental research, as summarized in the paragraphs below.

**Belgium**

Marine aggregate (sand and gravel) extraction figures for Belgium in 2000 are:

| Dredging area | Amount ($m^3$) |
|---|---|
| Zones 1 and 2 | 1,901,000 |

In 2000 a total of 1,901,000 $m^3$ of sand was extracted, predominantly from extraction zone 2 on the Belgian continental shelf and, from the end of 2000, from extraction zone 1. This is an increase of approximately 12 % from 1999. Sixteen licensees are currently involved, with a total licensed amount of 6,350,000 $m^3$. As in previous years, most of the sand was extracted from the northern part of the Kwintebank. Three further applications are under consideration. Until the end of 2000, only zone 2 was licensed.

The amount of material extracted for beach replenishment projects for 2000 was:

| Dredging area | Material | Amount ($m^3$) | Beach |
|---|---|---|---|
| De Poortjes (Access channel to port of Oostende) | sand | 260,000 | De Haan |

**Canada**

The extraction of marine minerals does not take place in Canadian offshore areas. The Canadian federal government, under the leadership of Natural Resources Canada, continues to move forward in assessing the potential for the development of a framework to permit and control marine mining through a project termed OMMI (Offshore Minerals Management Initiative) which began in 1998. The Provinces of British Columbia, Nova Scotia, and Newfoundland continue to express a strong interest in furthering this activity. Government advisory groups have been established and meetings have been conducted on the east and west coasts of Canada. Documents have been prepared on the socio-economic implications, technological assessment, a public consultation and communication strategy, and a strategic environmental assessment.

Consultations are planned with focus groups in the late spring to early summer of 2001. These will be conducted through web-based technologies and designed to receive feedback on risks and opportunities associated with marine mining. Factual background information on environmental, socio-economic, and technical resource aspects will be made available to assist participants in discussions.

The marine mineral extraction industry continues to express interest in mining for offshore placers and aggregates, but the absence of a legislative framework remains a deterrent to further investment and investigation. Preliminary marine mineral assessment projects have been completed for areas off the east coast of Canada on the Scotian Shelf and Grand Banks of Newfoundland which have identified potential resources. These projects have been co-sponsored by the federal government and the provincial governments of Nova Scotia and Newfoundland.

### Denmark

The extraction of marine sand and gravel represents 10–20 % of the total production of materials for construction and reclamation in Denmark. The production of construction aggregates has remained stable over the past five years. However, the production of coarse aggregates has been decreasing slightly. The dredging of sand fill for land reclamation has increased markedly over the past ten years to meet the demand from several large construction works in coastal areas.

Between 1989 and 1993, more than $9 \times 10^6$ $m^3$ of sand fill and till were dredged for the construction of the Great Belt Bridge and tunnel project.

During the construction of the fixed link between Denmark and Sweden, $1.3 \times 10^6$ $m^3$ were dredged, with losses from the dredger spillways of only 2.8 %. In the same period, $7 \times 10^6$ $m^3$ of dredged materials comprising glacial till and limestone were reused for reclamation and as hydraulic fill in ramps for the bridge and tunnel.

A major enlargement of the harbour of Århus required more than $8 \times 10^6$ $m^3$ of sand fill. The construction works started in the autumn of 1998 and were completed in 2000. A total of $8 \times 10^6$ $m^3$ was dredged from two areas in Århus Bight. The spill from the dredging operations was 3.7 %.

The consumption of sand for beach nourishment at the west coast of Jutland increased significantly from 40,000 $m^3$ in 1980 to more than $3.5 \times 10^6$ $m^3$ in 1998. Consumption in the coming years is forecast to be $2.5 \times 10^6$ $m^3$ per year.

No detailed forecast for the future extraction of sand has been prepared. In general, it can be noted that the extraction varies in line with the development of the national economy. Several major construction works have increased the demand for sand fill considerably since 1995. These projects finished during 2000 and the demand is expected to decrease. However, a further enlargement of Århus Harbour is expected to take place from 2002 and will require up to $7 \times 10^6$ $m^3$ of sand fill. A project for the construction of a major container terminal near Stigsnæs, southern Sjælland, is in preparation. The project will require $5.5 \times 10^6$ $m^3$ of sand fill from areas in the vicinity of the construction area. The construction start is waiting the necessary financing.

It is expected that the total marine extraction of construction aggregates in Denmark will remain at the current level over the next five years, perhaps with a slight decrease in the dredging of coarse aggregates due to an expected slow decline in the construction industry.

### Finland

Sand and gravel extraction from Finnish coastal areas has been negligible in recent years. Since 1996, no major marine sand or gravel extraction activities have been reported. However, the Harbour of Helsinki has permission from the Water Rights Court to extract 8 million $m^3$ of gravel off Helsinki for harbour construction purposes, but the extraction has not yet started. The Forest and Park Service, manager of state-owned sea areas, has applied for permission to extract sand off Helsinki for another 8 million $m^3$. The Environmental Impact Assessment of this application is under way. The Forest and Park Service, in cooperation with the Geological Survey of Finland, has surveyed six other possible areas for future use.

## France

Marine aggregate extraction (sand and gravel) figures for France in 2000 were:

| Dredging area | Amount |
|---|---:|
| Normandy | 444,000 $m^3$ |
| Britanny | 38,000 $m^3$ |
| Atlantic coast | 1,945,000 $m^3$ |
| Total | 2,427,000 $m^3$ |

For siliceous aggregate, a conversion rate of 1.6 t $m^{-3}$ has been used.

The amount of aggregate extraction has remained stable in France for many years.

For the period 1991–1998, the production (excluding maintenance dredging of navigation channels) was (in million $m^3$):

| 1991 | 1992 | 1993 | 1994 | 1995 | 1996 | 1997 | 1998 |
|---:|---:|---:|---:|---:|---:|---:|---:|
| 2 | 1.9 | 1.9 | 2.5 | 2.5 | 2.3 | 2.6 | 2.6 |

(Data: National Organisation of Aggregates Industries)

Shell and maerl extraction in France in 2000 was:

| Dredging area | Material | Amount |
|---|---|---:|
| North Britanny | maerl | 215,000 $m^3$ |
| North Britanny | shelly sands | 143,000 $m^3$ |
| West Britanny | maerl | 2,700 $m^3$ |
| West Britanny | shelly sands | 26,700 $m^3$ |
| South Britanny | maerl | 82,000 $m^3$ |
| Total | | 469,400 $m^3$ |

For calcareous aggregate, a conversion rate of 1.3 t $m^{-3}$ has been used.

## Germany

Marine aggregate extraction (sand and gravel) figures for Germany in 2000 were:

| Dredging area | Amount |
|---|---|
| North Sea | 1,673,723 $m^3$ |
| Baltic Sea | 1,296,986 $m^3$ |

The amount of material extracted in Germany for beach replenishment projects in 2000 was:

| Dredging area | Material | Amount |
|---|---|---|
| Westerland II | Sand | 1,673,723 $m^3$ |
| Baltic Sea | Sand | 1,110,719 $m^3$ |

## Ireland

Non-aggregate (e.g., shell, maerl, boulders, etc.) extraction figures for 2000/2001 was:

| **Dredging area** | **Material** | **Amount** |
|---|---|---|
| Bantry Bay | Maerl | 16,000 t |
| Dingle Bay | Broken Rock | 45,000 t |
| Kilmore Quay | Broken Rock | 12,900 t |
| Foynes | Broken Rock | 46,000 t |

A license to extract 5,000 tonnes per year of "dead" *Lithothamnion* shell (maerl) was first issued in 1994. In January 2000, a ten-year license to extract up to 16,000 tonnes per year was granted.

Dingle Harbour Commissioners dredged 6,000 tonnes of silt/sand and 45,000 tonnes of broken rock, which were stored underwater to be reused. There are approximately 1,300 tonnes of rock remaining to be dredged.

The Department of the Marine (Engineering Section) disposed of 4,780 tonnes of sand/silt, and 12,900 tonnes of broken rock at sea from dredging at Kilmore Quay.

Shannon Foynes Port Company dredged and disposed of 685,000 tonnes of silt, 82,000 tonnes of clay/gravel, and stored 46,000 tonnes of rock underwater to be reused.

The amount of material extracted for beach replenishment projects in 2000/2001 was:

| **Dredging area** | **Material** | **Amount** |
|---|---|---|
| Codling Bank, Irish Sea | Gravel | 234,767 $m^3$ |
| Dingle, Co. Kerry | Broken Rock | |

In terms of beach replenishment schemes, extraction for 2000/2001 for Ireland was confined to gravel from the Codling Bank for coastal protection works at Bray, Co. Wicklow.

**The Netherlands**

Sand extraction in 2000

The amount of sand extracted from the Dutch sector of the North Sea in 2000 was as follows:

| **Dredging area** | **Amount** |
|---|---|
| Euro-/Maas access-channel to Rotterdam | $6.8 \times 10^6$ $m^3$ |
| IJ-access-channel to Amsterdam | $4.8 \times 10^6$ $m^3$ |
| Dutch Continental Shelf | $13.8 \times 10^6$ $m^3$ |
| Total sand extraction | $25.4 \times 10^6$ $m^3$ |

The main uses for the extracted sand are for beach nourishment and for landfill. In 2000, approximately $7.6 \times 10^6$ $m^3$ was used for beach nourishment and approximately $17.8 \times 10^6$ $m^3$ was used mainly for landfill, while a small quantity was used by the concrete and building industries in Belgium and the southwest Netherlands.

Gravel extraction in 2000

In 2000, there was no extraction of gravel in the Dutch part of the North Sea. The Dutch policy on the extraction of surface minerals, as contained in the Structure Plan (Major Rivers Delta Plan) for Surface Minerals, precludes extraction on the Claever Bank until gravel extraction carried out to lower the winter bed of the River Maas has ceased. This policy is expected to result in a peak in the extraction of gravel in the southeast of the Netherlands (Limburg).

## Shell extraction

On the basis of the National Policy Note and EIA for shell extraction (15 December 1998), there are maximum permissible amounts defined from 1999 onwards.

The total amount (in $m^3$) of shells extracted from the Wadden Sea, North Sea, and Internal Waters between 1994 and 2000 was as follows:

Total amount of shells extracted from the Wadden Sea and sea-inlets of the North Sea.

| **Dredging area** | **1994** | **1995** | **1996** | **1997** | **1998** | **1999*** | **2000*** |
|---|---|---|---|---|---|---|---|
| Wadden Sea | 125,755 | 102,503 | 93,670 | 64,938 | 107,933 | 104,255 | 97,706 |
| Sea-inlets | 79,715 | 68,666 | 55,025 | 70,998 | 52,007 | 102,787 | 114,790 |
| Total | 205,470 | 171,169 | 148,695 | 135,936 | 160,000 | 207,042 | 212,496 |

*From 1999 the permissible amounts are: 90,000 $m^3$ for the Wadden Sea; 120,000 $m^3$ for the sea-inlets; thus, 210,000 $m^3$ in total.

Total amount of shells extracted from Zeeland and the North Sea (in $m^3$).

| **Dredging area** | **1994** | **1995** | **1996** | **1997** | **1998** | **1999**** | **2000**** |
|---|---|---|---|---|---|---|---|
| Eastern Scheldt | 5,575 | 300 | 750 | 0 | 0 | 0 | 0 |
| Western Scheldt | 4,158 | 26,850 | 21,025 | 28,340 | 16,600 | 3,250 | 13,750 |
| Voordelta | 6,750 | 20,505 | 22,500 | 48,415 | 55,285 | 31,075 | 31,875 |
| Rest of the North Sea | 0 | 0 | 0 | 0 | 0 | 47,550 | 27,043 |
| Total | 16,483 | 47,655 | 44,275 | 76,755 | 71,885 | 81,875 | 72,668 |

**From 1999 the permissible amounts are 0 $m^3$ for the Eastern Scheldt; 40,000 $m^3$ for the Western Scheldt; 40,000 $m^3$ for the Voordelta; and unlimited for the rest of the Dutch sector of the North Sea.

### Norway

No sand and gravel extraction took place on the Norwegian shelf in 2000. Carbonate sand extraction in 2000 remained similar to previous years, at around 80,000 tonnes.

### Poland

Marine aggregate (sand and gravel) extraction figures for Poland in 2000 are:

| **Dredging area** | **Amount** |
|---|---|
| Slupsk Bank | 280,000 m$^3$ |
| Jastarnia field | 167,000 m$^3$ |
| Rozewie field | 74,000 m$^3$ |
| Wladyslawowo fairway | 126,000 m$^3$ |
| Vistula Lagoon, Krynica Morska and Kadyny pits | 172,400 m$^3$ |

The uses of this aggregate are as follows:

- Slupsk Bank—extraction of gravel for export to Germany;
- Jastarnia and Rozewie fields (open sea north of Hel Peninsula)—extraction of medium-grained sand for beach nourishment;
- Wladyslawowo fairway—fine-grained sand from fairway used for beach nourishment;
- Vistula Lagoon (Krynica Morska and Kadyny pits)—fine sand, slightly clayey used for land reclamation.

There is no extraction activity in the Polish EEZ of the Baltic Sea.

The amount of material extracted in Poland for beach replenishment projects in 2000 was:

| **Dredging area** | **Material** | **Amount** |
|---|---|---|
| Rozewie field | medium sand | 74,000 m$^3$ |
| Jastarnia field | medium sand | 167,000 m$^3$ |
| Wladyslawowo fairway | fine sand | 126,000 m$^3$ |

### Sweden

There have been no permits for marine extraction in Sweden since 1995. The last permission was for the dredging of new stretches of part of the Flint shipping channel between Saltholm Island and the coast of Scania in connection with the building of the Øresund Link between Sweden and Denmark. All the material dredged was used for the construction of artificial islands south of Saltholm Island on the Danish side of the Sound. The amount extracted within the Swedish EEZ was 2,500,000 m$^3$.

The Swedish Geological Survey (SGU) is still considering one application for marine extraction off the coast of Scania in the southwestern Baltic. The city of Ystad has applied for a ten-year permission to dredge 500,000 m$^3$ of sand from the Sandhammaren bank. All the material will be used for beach nourishment. The coast of Scania is subject to serious erosion.

### United Kingdom

Marine aggregate (sand and gravel) extraction figures for the UK in 2000 (includes aggregate and material for beach replenishment and fill contract) are:

| Dredging area | Amount (tonnes) |
|---|---|
| Humber | 3,811,044 |
| East Coast | 10,541,378 |
| Thames | 854,483 |
| South Coast | 5,694,002 |
| Southwest Coast | 1,793,768 |
| Northwest Coast | 316,090 |
| Rivers and Miscellaneous | 46,120 |
| Total | 23,056,885 |

The conversion factors used are 1.66–1.73 tonnes $m^{-3}$ for aggregate, and 1.5 tonnes $m^{-3}$ for sand.

Licenses especially for fill contracts and beach replenishment were as follows:

| | |
|---|---|
| Contract fill | 213,471 tonnes |
| Beach replenishment | 2,159,074 tonnes |

With regard to non-aggregate (e.g., shell, maerl, boulders, etc.) extraction figures for the UK in 2000, there was no calcareous seaweed (i.e., maerl) extracted from Crown Estate licenses during 2000.

**United States of America**

Marine aggregate (sand and gravel) extraction figures for 2000 are:

| Dredging area | Amount |
|---|---|
| New York Harbor | 1,100,000 $m^3$ |

The only commercial marine sand mining operation is currently extracting material from the main shipping channel into New York Harbor (the Ambrose Channel). This sand is fairly fine-grained. It is mixed with crushed rock to provide a suitable aggregate used primarily for highway construction.

The amount of material extracted for beach replenishment projects in 2000 was:

| Dredging area | Material | Amount |
|---|---|---|
| New Jersey Continental Shelf | sand | 360,125 $m^3$ |
| New York Continental Shelf | sand | 1,848,000 $m^3$ |
| Maryland Continental Shelf | sand | 1,340,340 $m^3$ |

On the Northeast Atlantic coast of the United States (above 37 °N), about 3.5 million $m^3$ of marine sand was dredged for beach replenishment in 2000.

## Approaches to Environmental Assessment

### Canada

Although no marine mining presently takes place in Canadian waters, harbour dredging and port maintenance are a major activity. A large research project has been undertaken to assess the effects of dredge spoil disposal in the Bay of Fundy off St. John, New Brunswick. A variety of high-resolution seismic, side-scan, and multibeam tools have been used and have identified periodic slumping of the dredged muddy sediments into deeper water. Measurements of contaminants and sediment transport have determined net movements of material to the west.

Cooperative projects to assess the effects of seabed trawling and clam dredging on seabed habitat are in the final stages of data assessment, conclusions, and write-up. Some of these results can be applied to potential seabed mining activities as the technology is similar to that applied in seabed mining. These projects are being conducted jointly between Fisheries and Oceans Canada and the Geological Survey of Canada. Results of these surveys will be a quantitative and qualitative assessment of the effects of bottom fishing gear on seabed alteration, biodiversity, community complexity, and ecosystem reoccupation and recovery.

In order to effectively manage living marine resources in a sustainable fashion, a need exists to understand broader natural links between the habitat and fisheries. In the case of demersal fish, it is essential to understand how different life stages utilize benthic habitats and associated epibenthic organisms; what kinds of habitat are required to support them; how these habitats are spatially distributed; how much of these habitats is required to support sustainable fish communities, and how vulnerable these habitats or species associations are to human disturbance.

A new project will be initiated in 2001 to define and map essential fish habitat on the Scotian Shelf within the Eastern Scotian Shelf Integrated Management (ESSIM) area, primarily within the boundaries of an area closed to mobile groundfish gear since 1987 and in adjacent fished areas. This is a pilot study year of a potential four-year project. The dominant demersal fish species in this area is haddock, but cod and various flatfish species are also abundant. Upon completion of the 2001 pilot study, a formal proposal for continued funding will be sought.

### Denmark

In Denmark, the National Forest and Nature Agency is responsible for administration of marine aggregate dredging. All new licensed areas are subjected to a Government View Procedure including public and private involvement.

### Recent research or environmental impact studies

#### Øresund Link

The construction of the Øresund Link began in 1995 and was completed on 1 July 2000. A total amount of $14.2 \times 10^6$ $m^3$ was dredged during the project, with an average spill of 4.1 %. Only minor effects were demonstrated during the construction works. A final report on the environmental impact was published in 2000. The report compares environmental objectives and criteria defined by the authorities with the actual environmental status in the area. The observed effects are in accordance with the forecasts and within the acceptable environmental limits set up by the authorities. The conclusions from monitoring programmes and the documentation for the fulfillment of the so-called Zero Solution for the water exchange between the Kattegat and the Baltic Sea are summarized in the Tenth Semi-Annual Report from the Authorities.

The amount of sand fill required for the construction of the Link was dredged from Kriegers Flak in the Baltic Sea. Before commencement of the project, a detailed resource assessment and an environmental impact assessment of the dredging of sand fill was carried out on Kriegers Flak in the Baltic by the Øresund Consortium. The assessment was prepared in accordance with the EC Directive 85/337.

During the project, $1.3 \times 10^6$ $m^3$ of sand fill was dredged from Kriegers Flak, with a spill of 2.8 %. Sediment spill and the environmental impact of the dredging activities were monitored in detail during the dredging operations, and a final report on the findings was finished in April 2000. The results show, in accordance with the EIA, that there were no environmental impacts outside 1000 m from the dredging area.

#### The Harbour of Århus

A major enlargement of the Harbour of Århus has required dredging of $8 \times 10^6$ $m^3$ of sand fill. Based on prospecting carried out by the Harbour, two areas in Århus Bight were selected for dredging. Due to the size of the project, the Harbour was requested to carry out an environmental impact assessment in accordance with the EC Directive 85/337 as part of the application. Based on the assessments, acceptable spill limits for the two areas were set at 6 % and 7 %, respectively. The spill should be measured for every tenth cargo. Besides that, the Harbour has set up a monitoring programme to ensure that the environmental impact is within the limits stated in the permission.

Results from monitoring the bottom fauna after the dredging of approximately $8 \times 10^6$ $m^3$ of sand show that the changes outside the dredging areas are very small and of the same magnitude as in the reference area. The results in both the impact area and the reference area document a significant and parallel increase in the number and abundance of species

The Harbour of Århus is preparing a new EIA for dredging up to 7 × $10^6$ $m^3$ of sand fill for a further enlargement of the harbour. The sand fill will be dredged from three areas in the Bay of Århus. Two of the areas have been used in the first part of the project. The EIA will be published during 2001.

Stigsnæs

An Environmental Impact Assessment undertaken in accordance with the EC Directive 85/337 was carried out in 2000 for a proposal to construct a Container Terminal Hub near Stigsnæs, Western Zealand. The project includes dredging of 5.6 × $10^6$ $m^3$ of sand fill in a very environmentally sensitive area. To fulfill the environmental requirements, direct pumping from the dredging site and the use of sedimentation basins is expected to be necessary. It is expected that permission will be given during 2001.

North Sea

The Danish Coastal Authority (DCA) has applied for four new dredging areas in the North Sea to be used for dredging of sand for beach nourishment in the next ten years. The application covers dredging of up to 30 × $10^6$ $m^3$. The application is based on an Environmental Impact Assessment in accordance with the EC Directive 85/337. During 2001, DCA will publish a separate Environmental Impact Assessment for both onshore and nearshore nourishment.

Marine windmill parks

Environmental Impact Assessments for dredging operations necessary for the construction of marine windmill parks have been carried out for parks on Horns Rev in the North Sea, south of the island of Læsø, and in Femer Belt.

### France

IFREMER commenced a research project in 2001 designed to investigate the effects of marine aggregate extraction on coastal stability. The research project is due to run for five years and will include sediment transport studies and morphodynamic modelling.

Recent environmental impact studies

The study of sand deposition continued in Dieppe in 2000 to determine the maximum distance at which the impact of over-sanding could be detected in the direction of prevailing currents (eastwards). Samples collected from five stations, located between 500 m and 2500 m from the dredging site, did not show any evidence of impact (either negative or positive), in contrast to the situation observed in 1999 when a negative impact was detected eastwards and a positive one northwards and westwards.

### Germany

Regeneration of sediment extraction sites in the North Sea and Baltic Sea

In March 1999, the Federal Maritime and Hydrographic Agency (BSH) initiated a three-year research project on the sedimentological processes which control the refilling of sediment extraction sites along the North Sea and Baltic Sea coasts. Four extraction sites within coastal waters of the North Sea and Baltic Sea are being investigated. The project is being funded by the Federal Ministry of Education and Research.

Westerland II is a sand extraction site used for coastal protection off the island of Sylt. The Tertiary sands and gravels are extracted by anchor dredging from 10–12 m deep pits in a water depth of 15 m. Since the beginning of the extraction in 1984, the site has been regularly echo-sounded and these data are used to evaluate the behaviour of the adjacent sea floor. The pits act as a sediment trap for fine-grained material which accumulates in their deeper parts. A single sediment extraction was performed in 1994 near the island of Pellworm (Wadden Sea) for a dike protection in 1 m water depth. The pit was stable for several years, but has almost completely refilled since 1999.

There is very large activity along the Baltic Sea coast of Mecklenburg-Vorpommern to extract sand and gravel from shallow waters for coastal protection and industrial use, respectively. At Graal-Müritz, one sand extraction took place in 2000 for coastal protection of a near-coastal section. Trailer dredgers extracted 362,000 $m^3$ of mobile sands from an area which is characterized by a sand thickness of 2–4 m.

In the Tromper Wiek, both gravelly sands for industrial use and sands for coastal protection are extracted from water depths of 10–20 m. Gravelly sands are sieved onboard the anchor dredgers and the sandy fraction is returned to the sea with the overflow. The behaviour of this mobile sediment and the stability of the pits are of major interest at this site. The main aims of the project are:

- to evaluate the influence of shore-parallel and shore-normal sediment transport on the physical refilling of extraction sites;
- to estimate the duration of refilling in shallow waters (10–20 m water depth); and
- to estimate the size of seabed areas involved in the sediment delivery.

**Ireland**

Approaches and guidelines to Environmental Impact Assessment are currently under review and will be developed in line with future policy regarding the issue of licenses for aggregate extraction.

**The Netherlands**

The Ministry of Transport, Public Works and Water Management carried out an Environmental Impact Assessment for an area off the coast of the province of Zuid-Holland to support the policy on deep extraction for concrete sand. The EIA was published in April 2001 for public consultation. This study has a general character and focuses on the environmental impact of the extraction of sand for concrete (to a maximum of 40 million tonnes) from a depth of 5 m to 30 m below the seabed. Particular attention has been given to the handling of the cover layer of lower-quality sand. The results of the environmental impact assessment suggest either a refill of the pit with the sand from the cover layer, or a combination of extraction for concrete sand with extraction of fill-sand for land reclamation projects. Proposals for large-scale extraction (> 10 million $m^3$) or deep extraction (> 2 m) to gain concrete sand must be accompanied by an EIA that is more specific than the general EIA mentioned above.

An EIA for land reclamation in relation to the enlargement of Rotterdam harbour will be completed in 2001. The EIA considers the effects of extraction of about 400 million $m^3$ of fill-sand. This EIA is a general one to support the decision-making process for the land reclamation scheme. A general area was chosen for the sand extraction. A more specific EIA will be undertaken to consider the definitive detailed proposals.

An EIA will be undertaken in 2001 to support a license application for the extraction of concrete sand from the Cleaverbank area.

**United Kingdom**

Inshore seabed characterization in the inshore zone – Thames Estuary

Work on bringing together into a common digital format, information on the seabed characterization of the Outer Thames Estuary (from the Deben Estuary to Dungeness) was completed in 2000 and the report will be published shortly. The aim of the work has been to:

- collate information on coastal processes and coastal change within the sector;
- provide an overview of sediment transport processes across the sector;
- provide the geoscientific information in a format accessible to a wide range of users;
- collate information on the marine aggregate resources of the sector.

The majority of the information is held on digital maps, which were digitized in Microstation and translated into MapInfo for wider usage.

The second theme has been to consider briefly the various habitat classification systems being developed and to examine the use and application of geological data, maps, and interpretation to the assessment and mapping of marine habitats. This has involved close consultation between the British Geological Survey (BGS) and the Centre for Environment, Fisheries and Aquaculture Science (CEFAS).

BGS is carrying out a detailed geological interpretation of an area of seabed in the eastern English Channel off Shoreham. This area of seabed has been intensively studied by CEFAS under the project "Mapping of gravel biotopes and an examination of the factors controlling the distribution, type and diversity of their biological communities".

CEFAS has collected a wide range of data sets from this area, including acoustic, biological and video data, and from this information has produced biotope maps of the region (seabed habitats and associated communities). BGS is currently re-interpreting the side-scan sonar data, collected by CEFAS during this work, and combining this information with other acoustic data sets they hold. The final geological interpretation will be compared with the biotope maps produced by CEFAS to establish how useful a detailed understanding of the geology of a region is for mapping and understanding the spatial distributions of benthic communities. A final report is expected later in 2001.

### Assessment of rehabilitation of the seabed following marine aggregate dredging

This four-year field-based study seeks to enhance the understanding of the processes leading to the physical and biological recovery of the seabed following dredging. The project is now in its second year. In accordance with its work programme, CEFAS has produced a draft literature review. Pilot surveys at a number of licensed dredging areas were undertaken in 2000 as a basis for the development of an action plan for future survey work.

### Procedural guidelines for the conduct of benthic studies at aggregate dredging sites

This one-year project is being undertaken to provide guidelines for conducting benthic studies in relation to EIAs associated with applications for Dredging Permissions or as part of a programme to monitor the effects of dredging. The guidelines will be published later in 2001.

### Scoping the assessment of sediment plumes from dredging

The report from the CIRIA project on "Scoping the assessment of sediment plumes arising from dredging" was published in 2000. Its bibliographic reference is:

John, S.A., Challinor, S.L., Simpson, M., Burt, T.N., and Spearman, J. 2000. Scoping the assessment of sediment plumes from dredging. CIRIA publication C547. ISBN 0 86017 547: 2.

### Southern North Sea Sediment Transport Study Phase II

This two-year research project commenced in June 2000. The purpose of this research is to improve understanding of the southern North Sea sediment transport system and its impact on the eastern English coastline between Flamborough Head and the River Thames. Information to be obtained includes sediment sources, transport pathways, volume of sediment, areas of deposition, and offshore features. Phase I of the project was completed in 1996. It included a literature review, the creation of a database, and the creation of a concept for a sediment transport model. Phase II will address the gaps in information identified in Phase I. It will update the database and amend the transport model to take account of further information provided since Phase I. The contract is due to be completed by summer 2002.

### Cumulative Impact Studies

The objective of this four-year study is to distinguish natural changes from dredging-induced changes to allow a scientific evaluation to be made regarding multiple extraction activities.

The programme has involved biological and environmental sampling of dredging sites to allow predictions of the cumulative impacts of future dredging projects. The desk-based portion of the study has so far involved the collection of data on the relevant licensed areas, Electronic Monitoring System (EMS) data, the analysis of aerial surveillance data, and consultation with relevant organizations. Field investigations have also been carried out on active license areas. Further steps will include the establishment of referenced stations for further monitoring and further investigation of fisheries data.

## 13.2 Progress on Methods to Assess Localized Impacts from Aggregate Extraction on Fisheries

The ACME reviewed a description of how Geographic Information Systems (GIS) can be used to analyse spatially referenced data to answer specific questions about the regional distribution of fisheries resources. Mapping systems such as GIS provide efficient electronic data storage and retrieval facilities that allow information to be routinely updated and predictions modified in the light of new information. The techniques described can be applied to other spatially referenced data such as habitat structure and distribution of invertebrate assemblages.

## Using GIS to assess the regional sensitivity of fisheries to human impact

### Introduction

There is an increasing need to assess the broad-scale impacts of human activity on the marine environment. The recent development of the Strategic Environmental Assessment process in the offshore oil and gas industry, and the continuing concerns over the "in-combination" effects of marine aggregate extraction licenses on commercial fisheries, highlight the need to describe resource vulnerability on the scale of regional seas. This material describes how Geographic Information Systems (GIS) can be used to analyse spatially referenced data to answer specific questions about the regional distribution of fisheries resources. Mapping systems such as GIS provide efficient electronic data storage and retrieval facilities that allow information to be routinely updated and predictions modified in the light of new information. They also provide a framework for understanding the more complex mechanisms that are responsible for structuring marine communities (Ligdas, 1996; Meaden, 1996; Rubec *et al.*, 1998). While the interests here relate only to demersal fish resources and their commercial exploitation, the techniques described can be applied to other spatially referenced data such as habitat structure and distribution of invertebrate assemblages.

Licenses for marine aggregate extraction require the applicant to assess the site-specific environmental impact of dredging, with reference to any nearby biological resources that may be at risk. For fisheries this involves detailed descriptions of the distribution of nursery areas, spawning areas, and any migration routes in the vicinity of the application, and an assessment of the likely contribution that the area makes to the catch of commercial fisheries which operate in the area. Evaluating the potential effects of several dredging applications in the same region will, however, require a broad-scale approach which uses similar information but covers a wider area. The techniques that need to be adopted for this type of analysis are not yet clearly described. A method is outlined here which uses GIS to identify and quantify the spatial extent of areas that are intensively used by fish for spawning, and which may therefore be considered potentially sensitive to marine aggregate extraction.

### Methods

The GIS software MapInfo was used to build a database of individual maps, which describe the known spawning areas of commercially exploited fish species, and the distribution of some shellfish species, around the coastal waters of the British Isles. These maps were based on existing information obtained from a range of sources over many years, but were based heavily on the charts published in Coull *et al.* (1998). Although the primary areas of concern are within the UK 200-mile limit, the charts include most of the North Sea and Celtic Sea.

Maps of spawning areas for sixteen different species (Table 13.2.1) were digitized in a vector format. This format stores the outline of a mapped spawning area as a series of joined $x$ and $y$ coordinates. The digitizing process creates electronic maps of geographically referenced polygons from paper map references. Any information concerning the polygon, such as the species it represents, or timing of the spawning season, is stored in an attribute table. This table also stores data describing the importance of each area in terms of spawning intensity. In this example, the attribute table contains a value of zero (to describe the absence of spawning) or 1 (to describe the presence of spawning). This is useful in more advanced analyses because it provides a method for comparing spawning areas of different intensity, and allows different levels of sensitivity to be allocated to different species.

Before these vector plots can be overlaid to assess the combined distribution of fish spawning, they must be converted to a raster or grid-file format. This process converts a vector plot to a grid by dividing the area up into many small cells. Each cell in these new grid-files has a numeric value taken from the attribute table (i.e., 0 or 1), depending on whether the species is present or absent from that position.

A derivative map is produced from the combination of several such grid-files describing the spawning distribution of fish species. Each cell in the derivative map describes the combined total of species which spawn within that cell. A stylized illustration showing the principle behind this is provided in Figure 13.2.1. The value of overlaying and combining maps using GIS in this way is that the same cell in each "layer" can be queried to show which species contribute to the total spawning intensity at that position (Figure 13.2.2).

Discussion

The example shown in Figure 13.2.2 is a preliminary output from this process for the Eastern Channel. The areas of greatest intensity of shading represent those locations that support the most fish and shellfish species. Although this example uses only a small range of benthic species, the GIS user can choose which species to include based on their vulnerability to specific activities, the timing and duration of sensitive periods, and the relative importance of species in terms of their economic or conservation value. The degree of overlap between these intensively used zones and individual licensed aggregate areas, or any other type of human impact, can be used to assess the potential impact of individual site-specific activities on sensitive areas. On a regional scale, the total vulnerability of these intensively used zones can also be assessed, since the GIS process allows the user to calculate their total area and the proportion of each aggregate extraction license or application area which encroaches sensitive regions. Knowing how much of a particular resource coincides with aggregate licenses is the first step towards evaluating whether dredging will adversely affect the resource.

Future developments of this technique will explore the potential conflict of interest between fishing fleets and marine aggregate extraction. There is often a perception by fishers that they are excluded from their traditional fishing grounds where these coincide with aggregate extraction activities, either because of the disturbance caused during dredging, or perhaps by secondary effects on the habitat.

Where a number of licenses occur in the same region, the combined effects of this "exclusion" can cause considerable local concern. Although of importance in offshore waters, this effect can be more marked in local inshore waters where fleets are composed of small day boats with limited range.

It is important to remember that these techniques rely entirely on good quality data describing the distribution of fish spawning grounds, or the seasonal distribution of fisheries. Obtaining and updating these data is being undertaken in parallel with further developments in the GIS approach.

Acknowledgement

The ACME expresses its appreciation to R. Stocks, S. Freeman, and S. Rogers, Centre for Environment, Fisheries and Aquaculture Science (CEFAS), Lowestoft, UK, for this material on the use of GIS to assess the sensitivity of fisheries to human impact.

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Meaden, G.J. 1996. Potential for geographical information systems (GIS) in fisheries management. Computers in Fisheries Research, pp. 41–79.

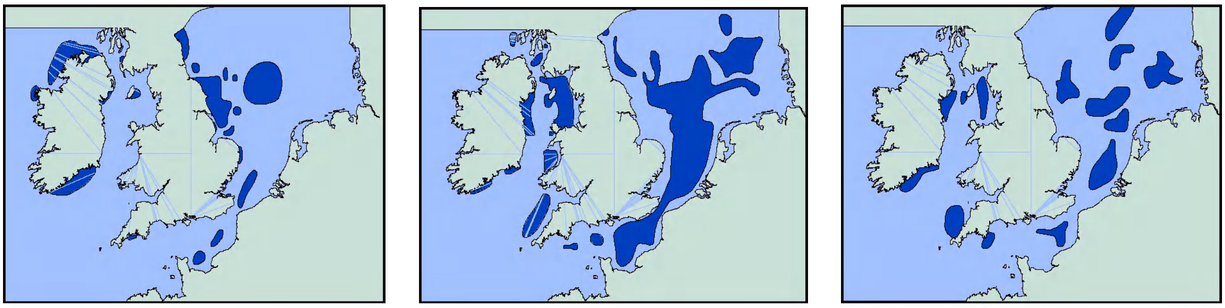
Rubec, P.J., Coyne, M.S., McMichael, R.H., and Monaco, M.E. 1998. Spatial methods being developed in Florida to determine essential fish habitat. Fisheries, 23: 21–25.

**Table 13.2.1.** List of species currently available in GIS format, and whether the maps refer to spawning or nursery grounds, or species presence.

| | Species | Spawning | Nurseries | Presence |
|---|---|---|---|---|
| 1. | Bass (*Dicentrarchus labrax*) | ✓ | ✓ | |
| 2. | Black bream (*Spondyliosoma cantharus*) | ✓ | ✓ | |
| 3. | Cod (*Gadus morhua*) | ✓ | ✓ | |
| 4. | Edible crab (*Cancer pagarus*) | | | ✓ |
| 5. | Haddock (*Melanogrammus aeglefinus*) | | | |

| | | | | |
|---|---|---|---|---|
| 6. | Herring (*Clupea harengus*) | ✓ | ✓ | |
| 7. | Lemon sole (*Microstomus kitt*) | ✓ | ✓ | |
| 8. | Mackerel (*Scomber scombrus*) | ✓ | ✓ | |
| 9. | Nephrops (*Nephrops norvegicus*) | | | ✓ |
| 10. | Plaice (*Pleuronectes platessa*) | ✓ | ✓ | |
| 11. | Sandeel (*Ammodytes marinus*) | ✓ | ✓ | |
| 12. | Scallop (*Pecten maximus*) | | | ✓ |
| 13. | Sole (*Solea solea*) | ✓ | ✓ | |
| 14. | Sprat (*Sprattus sprattus*) | ✓ | ✓ | |
| 15. | Turbot (*Psetta maxima*) | ✓ | | |
| 16. | Whiting (*Merlangius merlangus*) | ✓ | ✓ | |

**Figure 13.2.1.** Stylized illustration of the derivative mapping technique using GIS. Regional cumulative sensitivity maps can be produced by combining overlying cell values from individual species grid files.



A: Herring spawning B: Plaice spawning C: Cod spawning

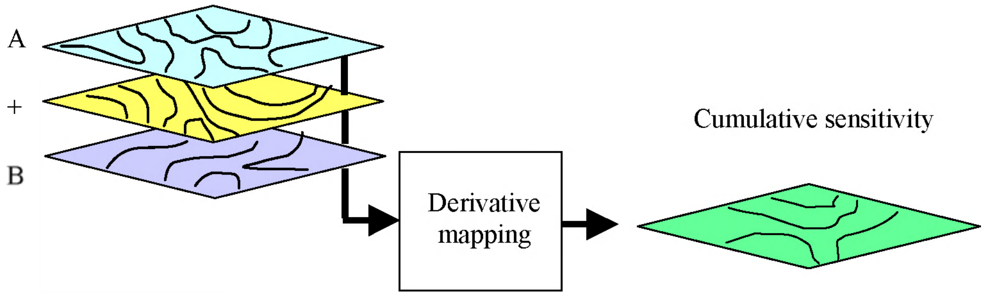
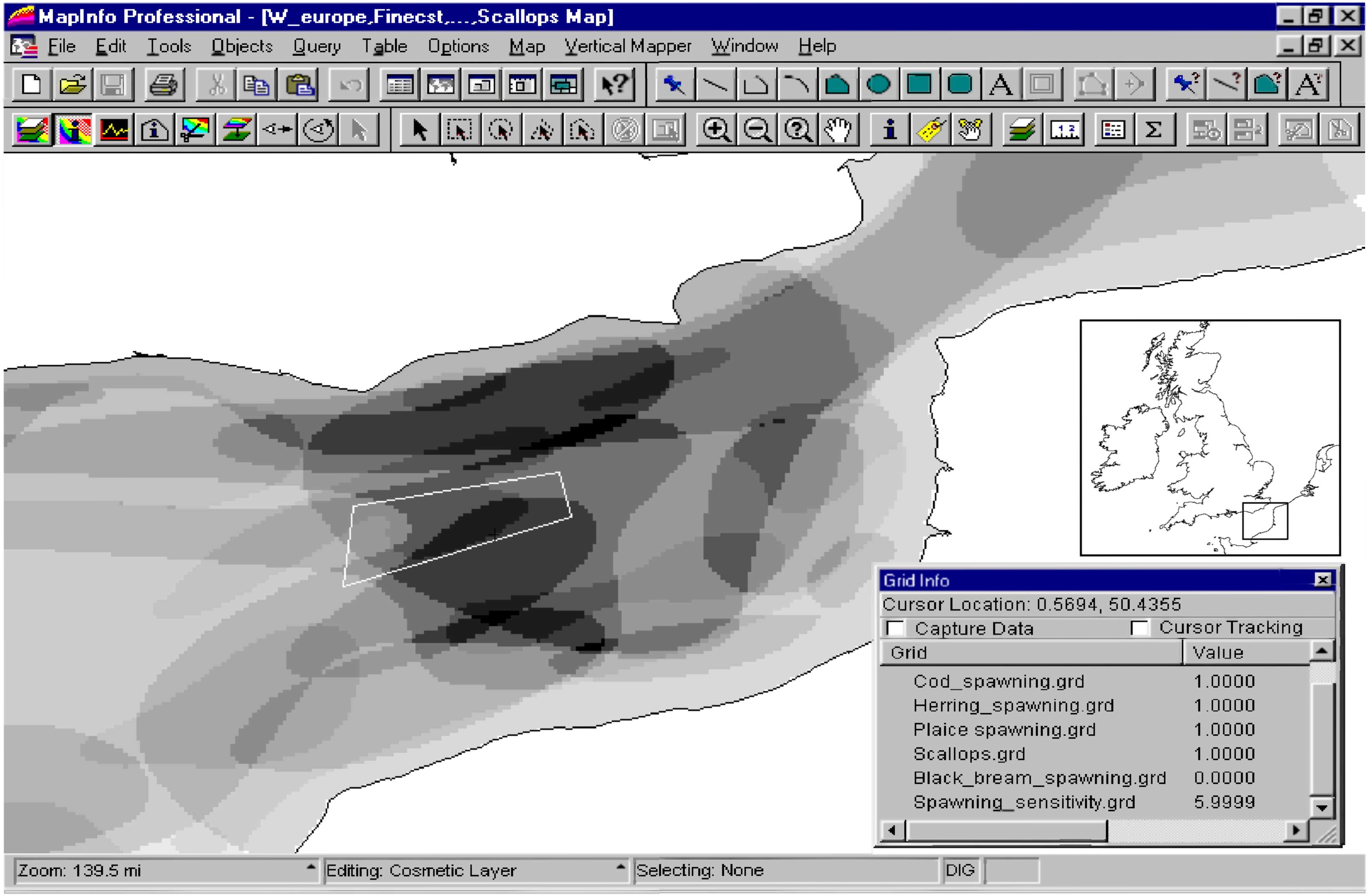


**Figure 13.2.2.** A cumulative sensitivity map of the eastern English Channel. Shaded areas show sensitivity from low (light grey) to high (dark grey) derived from the number of species spawning in the area. The white polygon represents a hypothetical dredging license application area and the cursor (white cross) is used to retrieve information at chosen geographical coordinates. Selecting a location produces a "Grid Info" dialogue box that gives information about the top spawning sensitivity layer and the species contributing to the total sensitivity. Individual species information comes from spatially co-occurring cells in data layers positioned beneath the visible spawning sensitivity map.



Cursor Location: 0.5694, 50.4355

☐ Capture Data ☐ Cursor Tracking

| Grid | Value |
|---|---|
| Cod_spawning.grd | 1.0000 |
| Herring_spawning.grd | 1.0000 |
| Plaice spawning.grd | 1.0000 |
| Scallops.grd | 1.0000 |
| Black_bream_spawning.grd | 0.0000 |
| Spawning_sensitivity.grd | 5.9999 |

Zoom: 139.5 mi

Editing: Cosmetic Layer

Selecting: None

DIG

# 14 GLOBAL PROGRAMMES

## 14.1 Global Ocean Ecosystem Dynamics (GLOBEC) Programme

*Request*

This is part of continuing ICES work on marine ecosystems issues.

*Source of the information presented*

The 2000 report of the Working Group on Cod and Climate Change (WGCCC), a progress report from the ICES/GLOBEC Coordinator, and ACME deliberations.

*Status/background information*

GLOBEC is the only current international global change programme in which ICES plays a major part, as set out in a Memorandum of Understanding with IOC, SCOR, and IGBP. ICES is a regional co-sponsor, with responsibility for the Cod and Climate Change, which is the North Atlantic regional programme. Following the decision by the ICES Council in 2000 "to continue to support the ICES/GLOBEC office by covering the indirect costs, provided that there are sufficient external funds to cover the direct costs (salary, travel etc.)", the programme has continued and the Coordinator has a contract that runs to the end of March 2002.

The Steering Group for the ICES-GLOBEC North Atlantic Programme and Regional Office (SGNARO) was re-established by the ICES Bureau at its January 2001 meeting, with Dr Scott Parsons as Chair, taking into account a resolution from the Oceanography Committee at the 2000 Statutory Meeting. The purpose of SGNARO is to identify strategic goals for GLOBEC research and a strategic approach for the GLOBEC Office. The future of the ICES/GLOBEC office, and the issue of whether the work that it supports on environment-fisheries interactions should be maintained within the ICES Secretariat, has been under review and discussion for several years.

The plan for future work by WGCCC is included in the International GLOBEC Implementation Plan (IGBP Report 47, 1999) and on the International GLOBEC website:
http://www.pml.ac.uk/globec/Structure/RegProgs/ICES%20CCC/futureplans_icesccc.htm). It was updated by WGCCC in 2000. The main focus over the next 3–5 years will be on synthesis and on the application of the results to management concerns.

During the past year, a great deal of work has been presented on cod growth (ICES CM 2000/C:12) and this is also the subject of one of the Theme Sessions at the 2001 Annual Science Conference. These studies will be published as an *ICES Cooperative Research Report*. The report of the Workshop on Gadoid Stocks in the North Sea during the 1960s and 1970s was published as ICES (2001). Preparation is in hand for a workshop on transport processes during the early life of cod, using coupled physical/biological models.

The issue of how information about the environment (in a broad sense) can be used to improve the management of fisheries and the marine ecosystem has been the subject of many papers, meetings, and groups over the past year and the GLOBEC programme has contributed to this area of work in many ways.

The ICES/GLOBEC Newsletters provide further information about progress at regional and national levels and are intended to help with coordination and planning. They are regularly circulated to about 250 scientists and can all be viewed on the ICES website at http://www.ices.dk/newslet/.

GLOBEC is currently the largest internationally coordinated programme in biological oceanography and will run for at least five more years. ICES has a specific scientific role, as well as a regional role, within the programme and should continue to support relevant research. The regional role is to facilitate exchange of information, data and results (via the web, Newsletter, Theme Sessions, Symposia) and to help with the coordination of GLOBEC-related research (via Working Groups, Workshops, Study Groups, etc.).

As a long-established application-oriented organization, ICES can play a valuable role in the formulation and implementation of marine science programmes in collaboration with the International Geosphere-Biosphere Programme (IGBP), the European Science Foundation (ESF), and other bodies.

**Reference**

ICES. 2001. Report of the Workshop on Gadoid Stocks in the North Sea during the 1960s and 1970s. The Fourth ICES/GLOBEC Backward-Facing Workshop, 1999. ICES Cooperative Research Report, 244.

### 14.2 Global Ocean Observing System (GOOS)

*Request*

This is part of the continuing work of ICES on issues related to monitoring the marine environment.

*Source of the information presented*

The 2001 report of the ICES/IOC Steering Group on GOOS (SGGOOS) and ACME deliberations.

*Status/background information*

GOOS is a permanent global system for observations, modelling, and analysis of marine and ocean variables to support operational ocean services worldwide. It is a parallel programme to the Global Climate Observing System (GCOS) and the Global Terrestrial Observing System (GTOS), which were all designed in response to the need for sustainable development as proclaimed by the UN Rio Conference in 1992. GOOS will provide accurate descriptions of the present state of the oceans, including living resources, continuous forecasts of the future conditions of the sea for as far ahead as possible, and serve as the basis for forecasts of climate change.

In 1997, an ICES Steering Group on GOOS (SGGOOS) was formed in order to prepare an action plan for how ICES should take an active and leading role in the further development and implementation of GOOS at a North Atlantic regional level, with special emphasis on operational fisheries oceanography. SGGOOS reported to the 1998 Annual Science Conference, recommending that ICES should initiate a regional GOOS component and that a workshop should be convened to take these ideas forward. This workshop took place in 1999 in Bergen, where a draft design and implementation plan was conceived. This had three essential components:

1) to promote global/regional linkages in a GOOS context;

2) to promote the ICES Annual Ocean Climate Status Summary as a contribution to GOOS;

3) to design and implement a regional GOOS in the North Sea.

In order to develop these suggestions further, the SGGOOS was re-established in 1999 as a joint ICES/IOC Steering Group on GOOS, with a joint Chair. The terms of reference for this group were to develop further the ICES-GOOS Implementation. During its meeting, these three components were discussed in greater detail.

**Global and regional linkage**

Links between the relevant national representatives to GOOS and the members of the Steering Group remain poorly developed, which means that ICES interests are not being conveyed to the various GOOS Committees at national, regional, and global levels. Different actions were proposed to improve the communication between IOC-GOOS, EuroGOOS, and ICES. It was noted in particular the importance of collaboration between ICES and EuroGOOS, especially with respect to GOOS issues in northern European GOOS developments. Issues include the sharing of data and the exploitation of the expertise across these organizations in the generation of appropriate products.

Only a few ICES Member Countries participated in the Steering Group, in spite of the fact that an appeal for additional members had been made to ACME members. The western Atlantic was represented at this meeting by Canada alone. In future, efforts should be made to ensure the participation of the USA as well as to balance European participation.

**The ICES Annual Ocean Climate Status Summary (IAOCSS)**

SGGOOS recommended that ICES, with guidance from IOC, should develop a clearly defined and identified sub-set of the ICES Standard Stations and Sections, presently provided by ICES Member Countries to prepare the IAOCSS, into an ICES regional Repeat Hydrographic Programme. This will allow the ICES Oceanographic Data Centre to serve as a

Regional Data Centre which rapidly collates and disseminates a low-resolution, preliminary data set targeted at the international GOOS climate community.

In order to do this, it is necessary to examine in detail the national data policies with respect to allowing the rapid-transmission data set to be submitted in a timely way to the ICES data centre. Secondly, it is necessary to identify which of the ICES Standard Stations and Sections are already nominated as national contributions to GOOS. Finally, ICES should prepare a document describing the set of national GOOS contributions that will form the ICES Repeat Hydrographic Programme (I-RHP), for submission to ICES-GOOS in 2002 in time for ICES-GOOS to nominate the I-RHP as a regional, multi-national Ocean Observing System and a contribution to the Global Climate Observing System (GCOS).

ICES should develop further the IAOCSS as a data product produced by an ICES Working Group, for a mainly ICES customer base, but at the same time being openly available via the web. A closer partnership between different Working Groups (e.g., WGOH, WGPE, WGCCC, WGZE) in order to link ocean climate with ecosystem variability and produce integrated status summaries should be considered.

### A Regional Operational Observing System for the North Sea

SGGOOS recognized the need for further planning before progress on this item can be made, with an emphasis on addressing whether collectively there is the potential of servicing a wide range of customers in a more effective manner. Connections have to be remade between the varied disciplines monitoring in the North Sea, including fisheries ecology. There is a problem of different physical and temporal scales that must be addressed by a North Sea operational system. In terms of spatial scale, physically there are arguments to include the entire Northwest European Shelf, and adjacent enclosed seas. In terms of fish stocks, there are distinct sub-areas that should be treated independently. Politically, there is a focus on the North Sea; physically, there is a focus on the Northwest Shelf. A nested approach may therefore be required, as well as consideration of how to deal with open boundaries.

A further workshop to develop these issues was thought to be necessary. SGGOOS therefore made a proposal for a strategic workshop to be held in Bergen, Norway, 5–7 September 2001, co-sponsored by IOC, ICES, OSPAR, the North Sea Conferences, and EuroGOOS. The title of the workshop is "Towards a North Sea GOOS Component for Ecosystem Assessment and Management".

The workshop will aim to:

- agree a strategy for a coordinated and harmonized observation network in order to progress the development of an ecosystem approach to North Sea management;
- develop the strategy in order to increase the efficiency and cost effectiveness of current national and international monitoring systems through the implementation of a pilot North Sea Ecosystem GOOS project which will integrate fisheries and oceanographic data.

The aim is to present the resulting strategic plan to the Fifth North Sea Conference in March 2002.

SGGOOS is also preparing a brochure on the partnership between GOOS and ICES as a contribution to the ecosystem approach to management. The brochure will discuss why GOOS is important for ICES, which potential GOOS products will be useful to ICES, and how can ICES contribute to GOOS.

## 14.3 Global International Waters Assessment (GIWA)

*Request*

This is part of ICES activity related to reviewing assessment methodologies of the marine environment.

*Source of the information presented*

The 2001 report of the Study Group on Ecosystem Assessment and Monitoring (SGEAM) and ACME deliberations.

*Status/background information*

The ACME took note of the Global International Waters Assessment (GIWA), funded by the Global Environment Facility (GEF), UNEP, and other donors. GIWA objectives are to develop a comprehensive, strategic framework for the identification of priorities for remedial and mitigatory actions in international waters, designed to achieve significant environmental benefits at national, regional, and global levels.

The assessment will be organized into 66 sub-regions as basic units, grouped into nine mega-regions. A number of these sub-regions cover the ICES area and are similar to the designations for so-called Large Marine Ecosystems (LMEs). Five environmental concerns were selected:

1) Freshwater shortage;
2) Pollution;
3) Habitat and community modification;
4) Unsustainable exploitation of fisheries and other living resources;
5) Global change.

These concerns cover 22 different environmental issues. For example, Pollution covers:

- Microbiological;
- Eutrophication;
- Chemical;
- Suspended solids;
- Solid wastes;
- Thermal;
- Radionuclides;
- Spills.

The results of the GIWA project should give a global picture of the quality of international waters, which will facilitate the identification of areas for GEF intervention.

The ACME noted that socio-economic assessment aspects form an important component of the GIWA project; this is also in accordance with the framework for an ecosystem approach to the management of marine ecosystems by ICES.

Examples of the GIWA approach (GIWA Scoping Methodology, criteria for scoring environmental impacts) related to the selected issues of eutrophication, chemical pollution, and exploitation of living resources are given below.

**Eutrophication**

*Eutrophication, including harmful algal blooms, refers to artificially enhanced primary productivity in receiving water basins related to the increased availability or supply of nutrients.*

Score 0 = No known Impact

No known impact is determined when the following criteria are met:

- No visible effects on the abundance and distributions of natural living resources in the area;
- No increased frequency of hypoxic conditions and/or fish mortality events and/or harmful algal blooms associated with enhanced primary production;
- No evidence of periodically reduced dissolved oxygen or fish and zoobenthos mortality;
- No evident abnormality in the frequency of harmful algal blooms.

Score 1 = Slight Impact

"Slight" impact is determined when one or more of the following criteria are met or exceeded:

- Increased abundance of epiphytic algae; or
- A statistically significant trend in decreased water transparency associated with algal production as compared with long-term (> 20 year) data sets; or
- Measurable shallowing of the depth range of macrophytes.

Score 2 = Moderate Impact

"Moderate" impact is determined when one or more of the following criteria are met or exceeded:

- Increased filamentous algal production resulting in algal mats; and/or
- Medium frequency (< once per year) of large-scale hypoxia and/or fish and zoobenthos mortality events and/or harmful algal blooms.

Score 3 = Severe Impact

"Severe" impact is determined when one or more of the following criteria are met or exceeded:

- High frequency (> 1 event per year), or intensity, or large areas of periodic hypoxic conditions, or high frequencies of fish and zoobenthos mortality events or harmful algal blooms;
- Significant changes in the littoral community;
- Presence of hydrogen sulphide in historically well-oxygenated areas.

**Chemical pollution**

*Chemical pollution refers to the adverse effects of chemical contaminants released to standing or marine water bodies as a result of human activities. Chemical contaminants are here defined as compounds that are toxic and/or persistent and/or bioaccumulating.*

Score 0 = No known Impact

No known impact is determined when the following criteria are met:

- No known or historical levels of chemical contaminants except background levels of naturally occurring substances;
- No fisheries closures or advisories due to chemical pollution;
- No incidence of fisheries product tainting;
- No unusual fish mortality events.

If there are no available data, use the following criteria:

- No use of pesticides;
- No sources of PCDD/PCDF;
- No regional use of PCBs;
- No Bleached Kraft Pulp Mills using chlorine bleaching;
- No use or sources of contaminants listed in footnote 6 [not included here].

Score 1 = Slight Impact

“Slight” impact is determined when one or more of the following criteria are met or exceeded:

- Chemical contaminants are below threshold limits defined for the country or region (e.g., by a regional or national Commission);
- Restricted area advisories regarding chemical contamination of fisheries products.

If there are no available data, use the following criteria:

- Some use of pesticides in small areas;

  or

- Presence of small sources of PCDD/PCDF (e.g., incineration plants or small Bleached Kraft Pulp Mills using chlorine;

  or

- Some previous and existing use of PCBs and limited amounts of PCB-containing wastes, but not in amounts invoking local concerns;

  or

- Presence of other contaminants described in the UNEP Global Plan of Action for the Protection of the Marine Environment from Land-Based Activities.

Score 2 = Moderate Impact

“Moderate” impact is determined when one or more of the following criteria are met or exceeded:

- Chemical contaminants are above threshold limits defined for the country or region (e.g., by a regional or national Commission);
- Large area advisories by public health authorities concerning fisheries product contamination, but without associated catch restrictions or closures;

  or

- High mortalities of aquatic species near outfalls.

If there are no available data, use the following criteria:

- Large-scale use of pesticides in agriculture and forestry;

  or

- Presence of major sources of PCDD/PCDF such as large municipal or industrial incinerators or large Bleached Kraft Pulp Mills using chlorine as a bleaching agent;

  or

- Considerable quantities of waste PCBs in the area with inadequate regulation and some public concerns;

  or

- Presence of considerable quantities of other contaminants described in the UNEP Global Plan of Action for the Protection of the Marine Environment from Land-Based Activities.

Score 3 = Severe Impact

“Severe” impact is determined when one or more of the following criteria are met or exceeded:

- Chemical contaminants are above threshold limits defined for the country or region (e.g., by a regional or national Commission);

- Public health and public awareness of fisheries contamination problems, with associated reductions in the marketability of such products either through the imposition of limited advisories or by small-area closures of fisheries;

or

- Large-scale mortalities of aquatic species.

If there are no available data, use the following criteria:

- Indications of health effects resulting from use of pesticides;

and/or

- Known emissions of PCDD/PCDF from either incinerators or chlorine bleaching of pulp, with attendant advisories on mollusc or crustacean consumption or large-area fisheries closures;

and/or

- Known contamination of the environment or foodstuffs as a result of poor waste management of PCB-containing wastes;

and/or

- Known contamination of the environment or foodstuffs as a result of poor waste management of other contaminants described in the UNEP Global Plan of Action for the Protection of the Marine Environment from Land-Based Activities.

**Over-exploitation**

*Over-exploitation refers to the capture of fish, shellfish or marine invertebrates at a level that exceeds the maximum sustainable yield of the stock.*

Score 0 = no known impact

- No harvesting exists catching fish (with commercial gear for sale or subsistence).

Score 1 = slight

"Slight" impact is determined when one or more of the following criteria are met or exceeded:

- Commercial harvesting exists but there is no evidence of over-exploitation.

Score 2 = moderate

"Moderate" impact is determined when one or more of the following criteria are met or exceeded:

- One stock is exploited beyond MSY (maximum sustainable yield) or is outside safe biological limits.

Score 3 = severe

"Severe" impact is determined when one or more of the following criteria are met or exceeded:

- More than one stock is exploited beyond MSY or is outside safe biological limits.

Below is a selected example of GIWA socio-economic impacts related to pollution:

1) Increased risks to human health;
2) Increased costs of human health protection;

3) Loss of water supplies (e.g., potable water);
4) Increased costs of water treatment;
5) Costs of preventive medicine;
6) Costs of medical treatment;
7) Costs of clean-up;
8) Loss of tourism or recreational values;
9) Loss of aesthetic values;
10) Loss in fisheries;
11) Costs of increased fisheries product processing;
12) Change in fisheries value;
13) Reduced options for aquaculture development;
14) Risk to aquaculture;
15) Loss of property values;
16) Costs of weed control;
17) Loss of wildlife sanctuaries;
18) Costs of increased navigational clearance, navigational survey or dredging activities;
19) Increased costs of fish surveillance in the case of toxin incidence;
20) Costs of reduced fish marketability due to aesthetic perceptions;
21) Loss of protected areas;
22) Reduction in options of other uses of fresh water;
23) Potential for international conflicts;
24) Loss of reservoir storage capacity;
25) Damage to equipment (e.g., particle impacts);
26) Increased costs of coastal protection from waves/storm surges/erosion;
27) Costs of cleaning intakes;
28) Endangerment of species;
29) Increased costs of animal protection (especially endangered species);
30) Displacement of valued species;
31) Avoidance of amenities and products due to perceptions of effects of contamination;
32) Costs of public reassurance;
33) Maintenance of monitoring and radiological protection activities for public reassurance purposes;
34) Costs of preventive measures (e.g., tanker design/construction);
35) Costs of contingency measures;
36) Costs of litigation;
37) Costs of insurance;
38) Costs of disruption to shipping, marine reserve and marine scientific activities during survey and clean-up of spills.

In noting the above, the ACME advises that ICES become involved in the GIWA development and regularly review GIWA progress on water assessments related to the ICES area.

The general approach used by GIWA should be considered by the ICES entities that may eventually be charged with developing indices for comprehensive integrated assessments of geographic "regions", such as the environmental assessments of OSPAR and HELCOM.

The ACME underlines that ICES should determine the extent to which it can contribute to a GIWA-related assessment in all science areas.

**Reference**

GIWA. 2001. GIWA Methodology – Introduction and Scoping/Scaling. GIWA, Kalmar, Sweden.

# 15 DATA HANDLING

## 15.1 Handling of Data on Contaminants in Marine Media

*Request*

Item 3 of the 2001 Work Programme from the OSPAR Commission: to carry out data handling activities relating to:

3.1 contaminant concentrations in biota and sediments;

3.2 measurements of biological effects.

Contract from the Helsinki Commission (HELCOM) to serve as a Thematic Data Centre for the Cooperative Monitoring in the Baltic Marine Environment (COMBINE) Programme data for a three-year period beginning on 1 July 1998, and extended for a second three-year period.

Contract from the Arctic Monitoring and Asssessment Programme (AMAP) to serve as Thematic Data Centre for the marine component from 1998–1999, extended to 2000–2001.

*Source of the information presented*

Progress report from the ICES Marine Data Centre and ACME deliberations.

*Status/background information*

### 15.1.1 The ICES data and information products

Over a period of approximately five years, the ICES Bureau has expressed concern at continuing difficulties surrounding the handling of data and the preparation of information products within the ICES Secretariat. As a result of this concern, the Bureau authorized the appointment of a Database Manager with the aim of establishing an integrated solution to the database problems in the Secretariat. The Bureau has endorsed a plan for the database development and the overall goals are stated as follows:

To provide user-friendly, seamless, and dynamic access to all ICES products (data, documentation, and information) associated with both the scientific and administrative sides of the Secretariat. This goal will be met by;

a) employing web technology to provide the interface between the Secretariat and users (primarily marine scientists concerned with ICES activities);

b) developing as far as possible, and desirable, common database solutions to meet all Secretariat data, information, and administrative needs;

c) instigating an active training programme to raise the capability of all Secretariat members, in particular those currently concerned with database activities, in order to enhance the availability of resources;

d) ensuring that all future recruitment of staff focuses on the need for relevant IT skills;

e) employing a Web/database manager to provide the necessary technical and managerial skills.

The main development work to be tackled urgently will be to restructure the ICES databases in a uniform way. The possible benefits of Relational Database Management Systems such as SQL or Oracle will be investigated in this regard.

### 15.1.2 Databases on contaminants in marine media, biological effects of contaminants, and fish diseases

The environmental data held by the ICES Data Centre includes the following types:

1) contaminants in marine invertebrates, fish, birds, and mammals (approximately 330,000 records);

2) contaminants in sea water (approximately 280,000 records);

3) contaminants in marine sediments (approximately 80,000 records);
4) biological effects of contaminants (approximately 4000 records);
5) fish disease prevalence data (approximately 80,000 records).

There seems to be a downward trend in the number of data submissions. This decrease will hopefully be reversed as a result of the development of a more flexible data exchange format, e.g., the possibility to submit files containing comma-separated values.

Since mid-1998, ICES has served as the Thematic Data Centre (TDC) for HELCOM under a three-year contract. A new three-year contract has now been signed with HELCOM. Under this contract, ICES functions as the TDC for the COMBINE Programme (oceanographic, biological, and contaminants) data. This activity, as well as the inclusion of older data, is expected to increase the flow of data substantially.

### 15.1.3 Handling of data for the Arctic Monitoring and Assessment Programme (AMAP)

ICES has continued to serve as the Thematic Data Centre for the marine component of AMAP under a 1998 contact that has been prolonged to cover the period 1999–2001 as well. During 2001, there has been increased activity as a result of the preparation of the second AMAP Assessment Report.

### 15.1.4 On-line access to data inventories

Access to dynamic/query inventories of the environmental data in the ICES Marine Data Centre can be established through an interface on the ICES website [http://www.ices.dk/env]. The interface allows the user to retrieve information about present holdings of contaminants and biological effects data. These inventories will be expanded in order to satisfy the needs of the different Commissions. It should be noted, however, that not all the data in the ICES Marine Data Centre are visualized by this web interface, as some laboratories have not given permission for their data to be included in this inventory.

### 15.1.5 CoastBase

ICES is a partner in the CoastBase Project, which is funded by the EC within the Fifth Framework Programme. The aim of the CoastBase Project is to increase the accessibility of data and metadata in order to improve policy making and cooperation along the European coasts by making a prototype of a data warehouse. Data products from both the environmental and the oceanographic databases are considered for inclusion in this prototype. A first version of the prototype was demonstrated in May 2001.

### 15.1.6 Outcome of the ICES/OSPAR Workshop on Data Submission and Data Exchange with the ICES Environmental Data Centre

An OSPAR/ICES Workshop on Data Submission and Data Exchange with the ICES Environmental Data Centre took place on 8–9 February 2001 at ICES Headquarters in Copenhagen under the chairmanship of Prof. Hein Rune Skjoldal. The workshop was attended by representatives from the following countries:

- Belgium, Denmark, Finland, France, Germany, Ireland, the Netherlands, Norway, Portugal, Sweden, and the United Kingdom;

and from the following intergovernmental organizations:

- Arctic Monitoring and Assessment Programme (AMAP); European Environment Agency – European Topic Centre on Marine and Coastal Environment (EEA/ETC-MCE); United Nations Environment Programme Mediterranean Action Plan (UNEP-MAP).

The objectives of the workshop were to address all relevant issues relating to data transfer and exchange between OSPAR Contracting Parties and the ICES environmental databases, taking into account the related needs and arrangements of AMAP, HELCOM, and the EEA. In doing so, it was intended that the workshop examine and attempt to solve the problems related to the submission of data to the ICES environmental databases, and identify the principal structural needs of OSPAR relating to data exchange with the ICES environmental databases.

The workshop discussed several problems in relation to the exchange of data and made a list of recommendations. These are contained in the report from the workshop, which can be found on the ICES website at: http://www.ices.dk/env/index.htm under the heading "Data Workshop Report".

### 15.1.7 ICES Environmental Data Reporting Format

As an outcome of the OSPAR/ICES Workshop on Data Submission and Data Exchange, the ICES Marine Data Centre has initiated the development of a conversion program in order to accept data in the form of comma-separated ASCII files and change these into the existing version 2.2 environmental data format. The first version of the conversion program has been developed and a suggested structure of the comma-separated ASCII files was distributed for comments among the participants of the workshop in March 2001. The ICES Marine Data Centre has received several constructive comments on this development and the conversion program will be elaborated in order to cover these comments as far as possible.

*Need for further research or additional data*

In line with the recommendations from the OSPAR/ICES Workshop on Data Submission and Data Exchange with the ICES Environmental Data Centre, there is a need to continue to upgrade/modernize and integrate the ICES databases, taking into account the advantages and potential of all available programming language options including XML.

Furthermore, there is a need to revise the ICES Environmental Data Reporting Formats and to resolve problems experienced with the existing format. However, changes should be made as far as possible in one single large step, and not as a series of small revisions.

Finally, there is a need to consider the development of a library of useful assessment tools that can be demonstrated to be of value in preparing products for data held at ICES.

*Recommendations*

ICES encourages Member Countries to promote openness and free access to environmental data and information to the extent possible. This should include a re-examination of their data policies with regard to data release.

ICES further recommends Member Countries to submit data collected in relation to monitoring programmes as well as other relevant data, as these data submissions are of prime importance for the development of future data products from the ICES Marine Data Centre.

## 15.2 Handling of Nutrient Data for the OSPAR Commission

*Request*

Item 3 of the 2001 Work Programme from the OSPAR Commission: to carry out data handling activities relating to:

3.3 the implementation of the Nutrient Monitoring Programme.

*Source of the information presented*

Report from the ICES Oceanographer and ACME deliberations.

*Status/background information*

The position (as of November 2001) concerning the delivery of nutrient data to the oceanographic database in the ICES Marine Data Centre is provided in Table 15.2.1.

**Table 15.2.1.** Status of submission and implementation of OSPAR-relevant data to the ICES oceanographic database (November 2001).

| **Country** | **Nutrient data identified as OSPAR (until year shown)** | **Other nutrient data (until year shown)** |
|---|---|---|
| Belgium | 2000 | 1999 |
| Denmark | - | 2000 |
| France | 1992 | 1998 |
| Germany | 1999 | 1999 |
| Ireland | - | 1992‡ |
| Iceland | - | 1999 |
| Netherlands | 1997 | 2000 |
| Norway | - | 2000 |
| Portugal | - | 1990 |
| Spain | - | 1999* |
| Sweden | - | 2001 |
| UK | 1995 | 2001 |

* not yet implemented; ‡ only year.

As indicated in Table 15.2.1, some of these data have been submitted via the ICES Environmental Data Reporting Format and these are specifically delivered as part of the data collected for the OSPAR monitoring programmes. Other data (the majority) arrive as part of the country and project oceanographic data submissions to ICES and are not delivered in any specific format. It is assumed that all of these data are available for the OSPAR Nutrient Monitoring Programme even though some are delivered with restrictions to their use.

Table 15.2.2 provides, in a more detailed way, information on what nutrient data are available in the period 1995–2001 on a country-by-country basis. This table makes use of information provided to ICES by means of the Cruise Summary Report (ROSCOP) database and from the contents of the oceanographic database. In the case when no ROSCOP has been received, but data have, then a ROSCOP entry is created by ICES.

ROSCOP is the system used globally to provide information on all research vessel cruises. In particular, it provides information about what has been collected and this information is normally provided immediately after each cruise. Consequently, it provides an independent source of information about the existence of data, thus allowing it to be an effective data tracking system. In the table, the numbers given in the "Cruises" rows are number of cruises available in the ROSCOP database, and the "Data" rows give the number of actual cruises for which data have been provided.

Based on the information contained in Table 15.2.2, the situation with regard to the submission of nutrient data to ICES can be summarized below:

Belgium: Almost all Belgian nutrient data are provided via the Environmental Data Reporting Format and are for the area immediately adjacent to the Belgian coast and estuaries. 1997 and 1998 submissions appear (almost) complete and a significant fraction of information about cruises has been submitted up until 2000.

Denmark: Most of the shortfall in Danish data submissions arise from Faroese cruises. There is limited information from 1998 onwards. Apart from that, it is believed that data submissions are fairly complete, and include some "Counties" data.

France: Much ROSCOP information is available via the French Data Centre SISMER. This shows that only a small fraction of the cruises collecting nutrient data have provided these data to ICES.

**Table 15.2.2.** Number of cruises collecting nutrient data and number of cruises for which nutrient data have been submitted to ICES in the period 1995–2001 (November 2001).

| | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 |
|---|---|---|---|---|---|---|---|
| Belgian Cruises | 22 | 14 | 27 | 25 | 14 | 10 | 0 |
| Belgian Data | 10 | 6 | 25 | 25 | 6 | 4 | 0 |
| Danish Cruises | 22 | 17 | 35 | 18 | 7 | 7 | 3 |
| Danish Data | 15 | 11 | 21 | 12 | 5 | 5 | 0 |
| French Cruises | 21 | 23 | 31 | 33 | 29 | 18 | 0 |
| French Data | 4 | 3 | 3 | 1 | 0 | 0 | 0 |
| German Cruises | 78 | 64 | 50 | 51 | 34 | 19 | 7 |
| German Data | 28 | 25 | 21 | 20 | 3 | 0 | 0 |
| Icelandic Cruises | 11 | 3 | 24 | 6 | 4 | 0 | 0 |
| Icelandic Data | 0 | 3 | 4 | 4 | 4 | 0 | 0 |
| Irish Cruises | 1 | 1 | 5 | 3 | 0 | 0 | 0 |
| Irish Data | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Dutch Cruises | 23 | 23 | 16 | 2 | 1 | 2 | 0 |
| Dutch Data | 23 | 23 | 16 | 2 | 1 | 1 | 0 |
| Norwegian Cruises | 39 | 37 | 44 | 41 | 30 | 35 | 12 |
| Norwegian Data | 23 | 20 | 25 | 21 | 17 | 23 | 0 |
| Spanish Cruises | 25 | 13 | 7 | 0 | 0 | 0 | 0 |
| Spanish Data | 18 | 1 | 0 | 0 | 0 | 0 | 0 |
| Swedish Cruises | 19 | 19 | 17 | 19 | 45 | 16 | 9 |
| Swedish Data | 18 | 18 | 17 | 19 | 45 | 1 | 1 |
| Portuguese Cruises | 0 | 1 | 2 | 0 | 0 | 0 | 0 |
| Portuguese Data | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| UK Cruises | 32 | 25 | 17 | 14 | 9 | 22 | 3 |
| UK Data | 17 | 19 | 11 | 11 | 6 | 13 | 2 |

Germany: ROSCOP information is almost complete owing to the efforts of the German Data Centre (DOD). There is a very large number of cruises, but the percentage of these cruises providing nutrient data to ICES is low (approximately 30 %). Of these, the majority will be data provided via the Environmental Data Reporting Format and via the Data Centre's own procedures. Data up to 2000 have been received, but due to various problems it has not been possible to place them in the database.

Iceland: Very few Icelandic ROSCOP forms are provided and most of the data submitted are in connection with other research projects, mainly in the Norwegian Sea. It is not possible to assess the scale of the shortfall.

Ireland: Very few ROSCOPs and data are received. This does not reflect the very large level of activity that is known to exist.

Netherlands: Very few ROSCOPs are provided to ICES so the full scale of any shortfall is difficult to assess. Many of the data received in this period arrive via the Environmental Data Reporting Format, but some data arrive via ICES projects (e.g., the IBTS surveys). Data up to 2000 have been received, but due to various problems it has not been possible to place them in the database.

Norway: The submission of ROSCOP information is thorough, lending credibility to the figures. There is a very large number of cruises, but with a very significant shortfall in the amount of nutrient data submitted. Most data are submitted by one institute, which is not the main potential provider. The shortfall represents about 30 % of the total number of stations held by ICES, and is therefore quite serious.

Spain: Information from Spain is limited. ROSCOP information and data arrive mainly from one survey of Santander. There has been a prolonged delay in entering these data into the database owing to various difficulties.

Sweden: ROSCOPs and data are provided routinely and efficiently and cover most of the government-financed data sources. Some data from university sources are missing.

Portugal: Hardly any information is available and no data at all are available for this period.

UK: Like France and Germany, the UK is a nearly complete supplier of ROSCOP information, lending credibility to the figures, especially for pre-1997. Most of the data that are available are from the research/monitoring activities of the two Fisheries Research Institutes.

### 15.3 Development of Biological Community Databases

*Request*

Item 3.4 of the 2001 Work Programme from the OSPAR Commission: to carry out data handling activities relating to data on phytobenthos, zoobenthos, and phytoplankton species.

Contract from HELCOM to serve as a Thematic Data Centre for COMBINE Programme data for a three-year period beginning on 1 July 1998. This contract has been renewed for another three-year period, from 1 July 2001.

*Source of the information provided*

Progress report from the ICES Marine Data Centre and ACME deliberations.

*Status/background information*

In 1997 OSPAR and HELCOM requested ICES to make preparations for establishing databases on phytoplankton, zooplankton, phytobenthos, and zoobenthos community measurements. Specifically, the Commissions requested ICES to prepare reporting formats and data-entry/data-screening software for data on these parameters. The work is coordinated from the ICES Secretariat, but is also based on input from several Working Groups and individual scientists.

The ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements related to Eutrophication Effects (SGQAE) and the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB) have reviewed the final draft of the ICES Biological Data Reporting Format. These groups made several suggestions to the reporting format and these suggestions have been incorporated into the reporting format as far as possible.

The first release of this format, in spring 2000, revealed some serious inconsistencies in the linking of the various records and was therefore withdrawn. An improved version was subsequently released and can be found on the ICES website at: http://www.ices.dk/env/index.htm, under "Reporting Formats" and then "Biological Communities". This new release also includes the possibility to submit data as comma-separated ASCII files. The development of the relational database is essentially complete. Data submissions can be accepted from autumn 2001.

A possible change to a more flexible format for both the contaminants data and the biological community data will be considered in order to ease the submission of data from national databases to the ICES Marine Data Centre.

### 15.4 Development of Reporting Format for Biological Effects Measurement Data

*Request*

Item 6 of the 2000 Work Programme from the OSPAR Commission, as stated in detail in the text below.

*Source of the information provided*

The 2001 report of the Working Group on Biological Effects of Contaminants (WGBEC) and ACME deliberations.

*Status/background information*

As a part of the work programme for OSPAR, ICES was asked to expand the Environmental Data Reporting Format to include all the reporting parameters required for each of the biological effects techniques adopted by OSPAR, where these reporting formats have not already been developed. In so doing, this work was to be undertaken in three stages:

Stage 1: the development of reporting formats for:

- P4501A1 (EROD)
- PAH metabolites
- DNA adducts
- Liver histopathology
- Liver nodules
- TBT (intersex, imposex)

Stage 2: the development of reporting formats for:

- Metallothionein
- ALA-D
- Bioassays
- Fish reproductive success

Stage 3: the development of reporting formats for:

- TBT shell thickening
- Lysosomal stability
- Antioxidant enzymes

The different measurements of biological effects of contaminants described and discussed in the monitoring guidelines of the OSPAR Coordinated Environmental Monitoring Programme (CEMP) have been compiled, and the relevant volumes of the *ICES Techniques in Marine Environmental Sciences* have been reviewed in order to check details of the relevant measurements. These measurements have been compared with the existing ICES Environmental Reporting Formats and the relevant ICES codes (see ICES, 2000).

WGBEC has been asked to consider whether the listing of measurements is appropriate for inclusion in the reporting format. Furthermore, WGBEC was asked to consider whether any relevant and applicable measurement, data parameter, or metadata is lacking on this list. This issue has been on the agenda of WGBEC both in 2000 and 2001. However, a key requirement preceding the development of the reporting formats is agreement on the complete methodology for each technique. As shown by the WGBEC review of progress in the Biological Effects Quality Assurance in Monitoring Programmes (BEQUALM) project, several of the measurement techniques may be modified based on the experience gained in their use in BEQUALM. At the end of 2001, more information on the quality assurance requirements for the biological effects techniques in the CEMP will become available as a result of the BEQUALM project.

The ICES Environmental Data Reporting Format will be expanded to include data on the CEMP biological effects measurements. It should be emphasized, however, that the revision of the ICES Reporting Formats will not occur until the BEQUALM project is finalized, since data will only be submitted to ICES after the quality assurance procedures have been established successfully. It cannot be excluded that the experience gained in the course of the project might possibly lead to a need for a further revision of the details of the data field requirements of biological effects measurements to be reported to ICES.

## Reference

ICES. 2000. Report of the ICES Advisory Committee on the Marine Environment, 2000. ICES Cooperative Research Report, 241: 243–248.

## ANNEX 1

## AN OVERVIEW OF THE STATUS AND MONITORING OF THE “ERIKA” OIL SPILL

### The nature of the pollutant

The pollutant released in the “Erika” oil spill was heavy fuel oil No. 2, designated internationally as fuel oil No. 6. This insoluble and highly viscous product has a characteristic smell. Heavy fuel oil is a residue from the distilling of crude oil, and additives facilitate the mixture of heavy residues from distillation. This heavy fuel oil is used mainly for industrial combustion and in very high power slow diesel engines on ships. The composition of “Erika” oil was a mixture of hydrocarbons (alkanes: 15 %, cycloalkanes: 45 %, aromatics: 25 %; and non-hydrocarbon compounds: 15 %). The oil contained around 25 % heavy products and 50 % PAHs. The physico-chemical characteristics of “Erika” oil indicate that degradation is slow in the natural environment. The soluble fraction is low, and the impact on the fauna is likely to be severe.

### The extent of the pollution

The “Erika” spill was generally characterized by a small amount of oil leakage into the sea that, nonetheless, caused pollution over a wide geographical area and for a long period of time. The range of pollution was large because the tanker sank at some distance from the coast. Other contributing factors were the ocean currents in the region, poor weather conditions after the disaster, the composition of the product, and continuing slight leakage from the wreck. The degree of the impact was not directly correlated with pollutant tonnage. The “Erika” contained 30,000 tonnes, of which 25,000 tonnes have leaked into marine waters. Despite this apparently low volume compared to the 200,000 tonnes lost from the “Amoco Cadix” in 1978, the effects are likely to be very severe, as the composition of the fuel oil is more toxic than that of crude oil.

### Effects on health

A short-term epidemiological study showed health problems occurring in volunteers participating in the cleaning of polluted sites, namely neurotoxic (headache, dizziness), respiratory, gastrointestinal, cutaneous, and mucosal disorders.

Quality criteria were established by the French committee of experts from the AFSSA (French Agency for the Safety of Food). Based on the contamination levels of Σ16 PAHs observed between 1994 and 1997 under the French national monitoring network RNO, a control value (500 $\mu g\ kg^{-1}$) and an exclusion value (1000 $\mu g\ kg^{-1}$) were established.

### Impacts in the environment

#### Natural sites along the coast

The coastal areas affected were varied: mud flats, cliffs, rocky coasts with coves, sand dunes, and beaches. The pollution showed different forms, depending on the amount of pollutant deposited and the nature of the shoreline. Cliffs were polluted by patches of oil on the rocky substrate and spray from heavy swells. Beaches were polluted by pellets, droplets, and sheets several tens of square metres in size that were partly buried in the sand. Around 200,000 tonnes of oil-polluted waste have been collected and stored. The Total Company has estimated a cost of 200 million French francs for processing this waste (consisting of sand, seaweed, collection materials, plastic nets, etc.).

#### Sea salt production

The three hundred producers in the region set up earthen barriers at the entry to salt marshes to prevent polluted ocean waters from penetrating into channels. The inability to harvest salt in 2000 caused a financial loss for the producers, and additional costs were involved to restore operations in ponds dried up for several months, and to eliminate the freshwater fauna that had developed in the absence of sea water.

#### Impact on tourism

A loss of around 5.3 million overnight stays was recorded in coastal communities.

Fauna

300,000 birds wintering in the Bay of Biscay and some from Greenland were killed (mainly guillemots, black scoters, gannets, and razorbilled auks).

Fisheries and aquaculture resources

Little oil was found in trawl nets, and no massive deaths of species were observed, particularly sole, young eels, and whiting, which ordinarily live in the areas affected by the oil spill. There is still uncertainty about the capacity of the fish to reproduce. Monitoring has been initiated in sole spawning and nursery zones. The first observations indicate that some nursery zones have been contaminated. Fish populations and benthic populations near the wreck site are being monitored.

The sales of wholesale fish merchants and fishmongers were affected by the distrust of customers. The damage reported by fishermen concerned mainly contamination of stationary fishing devices (lobster pots, fixed nets), and loss of income due to immobilization of boats because of floating barriers intended to prevent oil from penetrating into harbours. Some losses were due to the confiscation and destruction of polluted catches by veterinary services (for example, 500 kg of spider crabs).

Shellfish

The damage experienced by the shellfish-farming industry was considerable because of administrative bans on the marketing of shellfish during the Christmas period when demand is very great in France. The psychological effect of the disaster contributed to reducing consumer sales. Eighty-five percent of shellfish farmers experienced a 30 % to 60 % drop in turnover. Ninety-five percent of the shellfish-farming zones were closed in the Loire Atlantic (north and south of the Loire estuary). On-shore fishing was also affected by the ban on shellfish gathering on tidal flats and rocky areas.

Monitoring programme on biological effects of contaminants

Chemical monitoring

A monitoring programme was initiated within the national network. More frequent PAH analyses were performed monthly at 43 points, and the profile of sixteen PAHs was enlarged to include sulphated, methylated, and nitrogenous compounds. This survey showed that shellfish were contaminated by PAHs shortly after the wreck. The mean Σ16 PAH concentrations calculated over the one-year survey (December 1999–December 2000) were between 230–620 ng $g^{-1}$ (two to four times higher than the mean recorded from the RNO). The maximum concentration levels (890–5200 ng $g^{-1}$) expressed as Σ16 PAH were from five to eighteen times higher in bivalves after the spill. The profile of PAHs and bile metabolites will be analysed in juveniles of sole.

Monitoring of biological effects

A monitoring programme involving the monitoring of a battery of biomarkers was also initiated in 2000 on juveniles of sole (*Solea solea*) and mussel (*Mytilus edulis*).

Juvenile sole were collected during three sampling cruises in February, July, and September 2000. Ten fish were analysed in four nursery zones for biomarker analysis and pools of ten fish were collected for biochemical analysis on the same cohort. A battery of biomarkers recommended for biomonitoring was analysed in liver and muscle (see Table A1.1).

**Table A1.1.** Biomarkers measured in sole (*Solea solea*).

| **Method** | **Tissue** | **Mechanism** |
|---|---|---|
| EROD | liver | detoxication |
| AChE | muscle | neurotoxicity |
| MXR | liver | inducible transport of xenobiotics |
| FACIM | liver | DNA damage |

| | | |
|---|---|---|
| COMET assay | blood cells | DNA integrity |
| DNA adducts | liver | DNA damage |
| PAH metabolites | bile | PAH exposure |

EROD: ethoxyresorufin-*O*-deethylase; AChE: acetyl-cholinesterase; MXR: multi-xenobiotic resistance.

The first biomarkers analysed in juvenile sole (EROD and DNA adducts) showed a decrease of the signal in samples collected from February to September. EROD activity showed a significant increase after the arrival of the spilled fuel oil on the shoreline in February and a decrease in July and September. A very high level of adducts was observed in all zones during the three periods. The profile showed a typical radioactive diagonal and two other spots. This profile showed bitumen-type contamination, i.e., the presence of PAHs, but also of thiophene-type derivatives. Particularly intense spots were observed during the cruise conducted in February. This same spot was still very intense during the cruise in July, but greatly reduced during the cruise in September. Otoliths and size will be compared with biomarkers in order to check a possible mixing of cohorts in July and September that could explain the rapid decrease of DNA adducts.

Mussels were collected on a monthly basis for a one-year period along the entire 400 km of coast affected by the oil spill. In 2000 and 2001, this programme on mussels was targeted on the most affected area, i.e., North Vendée and Loire Atlantique (north and south of the Loire estuary). The mussels were dissected in the IFREMER laboratory and stored in liquid nitrogen. The tissues were then sent to different laboratories for biomarker analysis. A battery of biomarkers was analysed in mussel gills and digestive gland (see Table A1.2).

**Table A1.2.** Biomarkers used in blue mussels (*Mytilus edulis*).

| **Method** | **Tissue** | **Mechanism** |
|---|---|---|
| Benzo[*a*]pyrenehydroxylase (BPH) | digestive gland | detoxication |
| AChE | gills | neurotoxicity |
| GST | gills | detoxication |
| Catalase | gills | oxidative stress |
| MDA (malonedialdehyde) | gills | oxidative stress |
| MXR | gills | multi-xenobiotic resistance |
| DNA adducts | gills | DNA damage |

AChE: acetylcholinesterase; GST: glutathion-*S*-transferase(s); MXR: multi-xenobiotic resistance.

The initial results obtained with BPH and AChE demonstrate that biological effects were impacted by a massive first pollution for three months after the wreck of “Erika”. During 2000, successive phases of pollution episodes (under the influence of high tidal ranges), caused recurrent PAH pollution. The variations of the BPH and AChE activities seem to be in relation to the quite heterogeneous contamination levels by PAHs.

Acknowledgement

This paper was prepared by Dr T. Burgeot, IFREMER, Nantes, France.

# ANNEX 2

## NORMALIZATION OF CONTAMINANT CONCENTRATIONS IN SEDIMENTS

This annex provides guidance on the application of methods to normalize contaminant concentrations in sediments. It is intended to replace Technical Annex 2 of the Guidelines for the Use of Sediments in Marine Monitoring Programmes (ICES, 1994).

## 1. INTRODUCTION

Normalization is defined here as a procedure to correct contaminant concentrations for the influence of the natural variability in sediment composition (grain size, organic matter, and mineralogy). Most natural and anthropogenic substances (metals and organic contaminants) show a much higher affinity to fine particulate matter compared to the coarse fraction. Constituents such as organic matter and clay minerals contribute to the affinity to contaminants in this fine material.

Fine material (inorganic and organic) and associated contaminants are preferentially deposited in areas of low hydrodynamic energy, while in areas of higher energy, fine particulate matter is mixed with coarser sediment particles, which are generally not able to bind contaminants. This dilution effect will cause lower and variable contaminant concentrations in the resulting sediment. Obviously, grain size is one of the most important factors controlling the distribution of natural and anthropogenic components in sediments. It is, therefore, essential to normalize for the effects of grain size in order to provide a basis for meaningful comparisons of the occurrence of substances in sediments of varying granulometry and texture within individual areas, among areas, or over time.

When analysing whole sediment (i.e., <2 mm fraction) for spatial distribution surveys, the resulting maps give a direct reflection of the seabed sediments. However, in areas with varying grain size distributions, a map of contaminant concentrations will be closely related to the distribution of fine-grained sediments, and any effects of other sources of contaminants, for example, anthropogenic sources, will be at least partly obscured by grain size differences. Also in temporal trend monitoring, differences in grain size distribution can obscure trends. If samples used for a spatial survey consist predominantly of fine material, the influence of grain size distribution is of minor importance and may probably be neglected.

## 2. NORMALIZATION PROCEDURES

Two different approaches to correct for variable sediment composition are widely used:

1) Normalization can be performed by relating the contaminant concentration with components of the sediment that represent its affinity for contaminants, i.e., binding capacity. Such co-factors are called normalizers (see Section 4, below). Simple contaminant/normalizer ratios or linear regression can perform normalization. Another procedure takes into account the coarse fraction containing natural metal concentrations in the crystal structure before the normalization is performed. Using multiple regression and also combinations of co-factors can be identified as normalizers.
2) Isolation of the fine fraction by sieving (e.g., <20 µm, <63 µm) can be regarded as a physical normalization to reduce the differences in sediment granulometric compositions and is applicable to both metals and organic contaminants (Ackermann *et al.*, 1983; Klamer *et al.*, 1990). Consequently, the coarse particles, which usually do not bind anthropogenic contaminants and thus dilute their concentrations, are removed from the sample. Then, contaminant concentrations measured in these fine fractions can be directly compared. Subsequently, the differences in sediment composition due to geochemical nature remaining after sieving can be further corrected for by the use of co-factors. Thus, sieving is a first powerful step in normalization.

## 3. LIMITATIONS OF NORMALIZATION

Clearly, normalization procedures may not apply equally well to all elements at all sites; especially important in this respect are elements that participate in diagenetic reactions. In cases where there is a lack of full understanding of the geochemical processes operating, care should be taken when normalizing for grain size differences. These processes can create important natural enrichment of metals at the sediment surface, as a result of the surficial recycling of oxihydroxides, or deeper in the sediment as the result of co-precipitation of the metals with sulphides (see, e.g., Gobeil *et al.*, 1997), which cannot be accounted for by normalization.

## 4. NORMALIZATION WITH CO-FACTORS

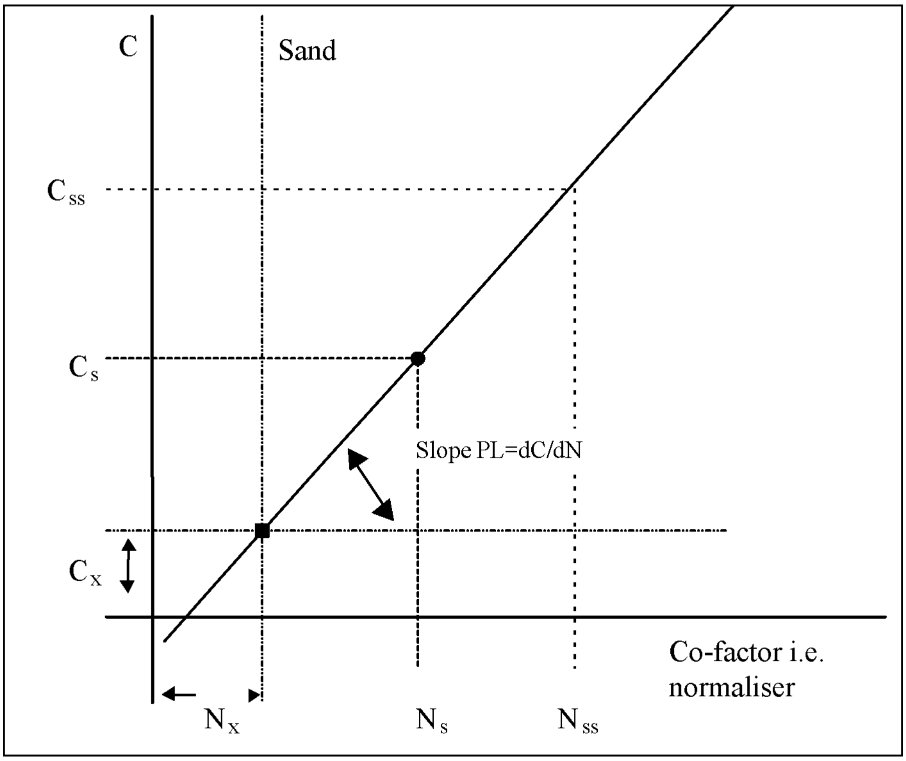
Normalization by calculation with the content of a certain grain-size fraction such as <2 µm (clay), <20 µm, and <63 µm can be used. This normalization technique is based on the fact that the binding capacity of the sediments can be related to the content of fines (primary) in the sediments.

As the content of fines is represented by the contents of major elements of the clay fraction such as aluminium (Windom *et al.*, 1989) or trace elements enriched in that fraction such lithium (Loring, 1991), these can also be used as a co-factor (secondary).

Both aluminium and lithium behave conservatively as they are not significantly affected by, for example, early diagenetic processes or strong redox effects frequently observed in sediments. Problems may occur in cases where the sediment is derived from glacial erosion of igneous rocks, with significant amounts of aluminium present in feldspar minerals contributing to the coarse fraction. In such cases, lithium may be preferable (Loring, 1991).

Organic matter, usually represented by organic carbon, is the most common co-factor for organic contaminants due to their strong affinity to this sediment component. However, trace metals can be also normalized using the organic carbon content (Cato, 1977, 1989). Care has to be taken when normalizing with organic carbon because organic matter is not a conservative component of sediments; for example, concentrations may vary seasonally.

**Figure A2.1.** Relation between the contaminant *C* and the co-factor *N* (see text).



## 5. THEORY

The general model for normalization taking into account the possible presence of contaminants and co-factors in the coarse material is given in Figure A2.1. $C_x$ and $N_x$ represent the contaminant and the co-factor contents, respectively, in pure sand. These "intercepts" can be estimated from samples without fines and organic material. The line of a regression between the contaminant and the co-factor will originate from that point. That means that regression lines of sample sets with a different contamination level and consequently different slopes will have this point in common (i.e., turning point). When this turning point is known, only one sample is required to estimate the slope. This allows determination of the contaminant content for any agreed (pre-selected) co-factor content ($N_{ss}$) by interpolation or extrapolation. The slope for a sample with a contaminant content $C_s$ and a co-factor content of $N_s$ can be expressed as follows:

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x}$$

The extrapolation to an agreed co-factor content, $N_{ss}$, follows the same slope:

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x} = \frac{C_{ss} - C_x}{N_{ss} - N_x}$$

Rewriting gives the contaminant content, $C_{ss}$, that is normalized to $N_{ss}$:

$$C_{ss} = (C_s - C_x)\frac{N_{ss} - N_x}{N_s - N_x} + C_x$$

Results of different samples normalized to the agreed $N_{ss}$ can be compared directly.

Normalization by this model can be applied with different co-factors. Here, primary and secondary co-factors can be distinguished. A primary co-factor like clay or organic carbon is not present in the coarse fraction and consequently has no intercept ($N_x = 0$). Al and Li are present in the coarse fraction and therefore are considered to be secondary co-factors. Provided that $N_x$ and $C_x$ are known, the model allows recalculation of total samples to a co-factor content usually found in sieved fractions, either <20 µm or <63 µm. However, such an extrapolation for a coarse-grained sample will be associated with a large error due to the uncertainty of the intercepts and the parameters analysed. For a more fine-grained sample, the uncertainty of the normalized result is much lower than for normalization of a sieved fraction to the agreed co-factor content and will result in a more accurate result. The model presented also applies to the normalization of organic contaminants using organic carbon, but in that case the intercepts $N_x$ and $C_x$ will not differ significantly from zero.

Principally, the result allows comparison of data on total and sieved samples, irrespective of the sieving diameter, but the error has to be taken into account. Through propagation of errors, the standard error of the result can be calculated from the analytical variation and the natural variation of the intercept $N_x$. Results can therefore always be reported with a standard deviation.

## 6. CONSIDERATIONS ON CO-FACTORS

The **clay content** is the most important co-factor for trace metals. In the model above, the $N_x$ will be zero for clay and only the intercept due to the content of the trace metal in the coarse fraction ($C_x$) has to be taken into account. However, current intercomparison exercises do not include this variable. At present, other variables such as aluminium or lithium are used to represent the clay content.

The **aluminium** content in the sandy fraction may vary from area to area. For some areas, aluminium contents in the sandy fractions are found at the same level as found in the fines (Loring, 1991) and therefore the intercept $N_x$ becomes very high. In equation (3), this implies that the denominator is the result of subtracting two large numbers, that is the normalizer content in the sample ($N_s$) and the normalizer content in only sand ($N_x$). Consequently, due to their individual uncertainties, the result has an extremely high error. Obviously, normalization with low intercepts is more accurate. Much lower intercepts are found if partial digestion methods are used that digest the clay minerals, but not the coarse minerals. Using partial digestion, the spatial variability of the results of aluminium analyses in the sandy fraction has been found to be much smaller than with total methods. Although normalizing fine-grained material will always give more accurate results, an error calculation will identify whether the use of coarse samples (and total methods, e.g., HF, X-ray fluorescence) will still allow the requirements of the programme to be met.

For most areas, the **lithium** content in the sandy fraction is much lower than in the fine fraction. In addition, results from partial digestion and total methods do not differ significantly. There is only little spatial variability of the lithium content in the sandy fraction. Generally, compared to aluminium, more accurate normalized data can be expected using lithium.

As for clay, no intercept ($N_x$) applies for organic matter, which usually is represented by **organic carbon**. Organic matter will also occur in the coarse fraction but is then still a co-factor that contributes to the affinity for contaminants, whereas the aluminium in the coarse fraction does not. Furthermore, organic matter in a sample is not always well defined as it can be composed of material with different properties. The most variable properties will be found in the organic matter present in the coarse fraction, that means not associated with the fines. In **fine sediments** or in the sieved fine fractions, the majority of the organic matter is associated with the mineral particles and it is assumed to be better defined than in the total sample. In addition, the nature of the organic matter may show spatial variation. For samples with low organic carbon content close to the detection limit, the normalization using this co-factor suffers from a large relative error. This results from the detection limit and the insufficient homogeneity that cannot be improved due to the limited intake mass for analysis.

For further interpretation of data, the **proportion of fines** determined by sieving can be useful. Provided that there are no significant amounts of organic matter in coarse fractions, the proportion can be used as a normalizer. The error in the determination of fines has to be taken into account and will be relatively high for coarse samples.

## 7. CONSIDERATIONS ON CONTAMINANTS

Almost all trace metals, except mercury and in general also cadmium, are present in the coarse mineral matrix of samples. The metal concentrations show a spatial variability depending on the origin of the sandy material. As for aluminium, with partial digestion (no HF) lower values are measured in the sand compared to total methods. This implies that partial digestion results in lower intercepts (the turning point is closer to zero). However, the partial digestion must be strong enough so that the clay will be totally digested, and the aluminium content measured remains representative for the clay. It was demonstrated that for fine material similar results are obtained for partial and total methods (QUASH/QUASIMEME).

In general, the correlation of the organic contaminants with organic carbon has no significant intercept. Obviously, a normalized result from a coarse sample will show a large error as, due to the dilution by sand, the concentrations are often close to or even below the detection limit. At present, for PAHs organic carbon is usually applied for normalization. It should be recognized, however, that due to the possible presence of undefined material, for example soot or ash, elevated PAH concentrations may occur in specific fractions that may have limited environmental significance. Although this needs further investigation, existing results indicate that PAH concentrations in the sieved fractions were not significantly affected.

## 8. ISOLATION OF FINE FRACTIONS FOR ANALYSES

Samples must be sieved over 2 mm mesh as soon as possible after sampling to remove large detritus and benthic organisms. Otherwise, during further sample handling such as storage, freezing or ultrasonic treatment, this biotic material will deteriorate and become part of the sediment sample. Until the final sieving procedure that isolates the fines, the sample can be stored at 4 °C for about one week and up to three months when frozen at −20 °C, although direct wet sieving is preferred. For prolonged storage, it should be considered to freeze-dry the samples. In that case, contamination and losses of contaminants during freeze-drying have to be checked. Air-drying is not appropriate due to high contamination risks. In addition, samples may be difficult to be disintegrated and mineral structures may be affected.

To isolate the fine-grained fractions, either the fraction <63 µm or <20 µm, a wet sieving procedure is required (freeze-dried samples will have to be resuspended using ultrasonic treatment). Sea water, preferably from the sampling site, should be used for sieving, as it reduces the risk of changes in the sample, i.e., contamination or losses through leaching. Furthermore, sea water supports the settling of fine particles after the sieving. If water from the sampling site is not available, then sea water from an unpolluted site, diluted with deionized water to the required salinity, can be used. The amount of water used for sieving should be kept to a minimum and water can be reused for sieving subsequent batches. Sediments should be agitated during sieving, in order to prevent clogging of the mesh and to disintegrate agglomerates of fines.

The currently most efficient sieving method pumps sea water over a sieve that is clamped onto a vibrating table. The water passing the sieve is led to a flow-through centrifuge that retains the sieved particles and the effluent of the centrifuge is returned to the sieve by a peristaltic pump. Large sample amounts, up to 500 g, can be handled easily. Alternatively, small portions, 20–60 g, can be sieved by a manual system using an 8-cm sieve in a glass beaker placed in an ultrasonic bath. Particles can be isolated from the water passing the sieve by batch-wise centrifugation. The upper water can be reused for a subsequent batch of sediment. In case of sandy samples, when large amounts of sediments have to be sieved, removal of the coarse material by pre-sieving over, e.g., a 200 µm mesh can facilitate the sieving process.

To prevent contamination, it is recommended to use large sample amounts for sieving. No significant contamination or contaminant losses were detected when at least 25 g of fine fraction was isolated (QUASH).

Isolated fine fractions must be homogenized thoroughly, preferably by a ball mill, as centrifugation produces inhomogeneous samples due to density differences in different grain size fractions.

More information about the sieving procedures is available on a video produced by the QUASH Project (QUASH, 1999).

## 9. RECOMMENDATIONS

1) For both temporal trend and spatial monitoring, it would be ideal to analyse samples with equal composition. This could be confirmed by determination of the co-factors Al, Li, organic carbon, and grain size distribution. However, this situation will not always occur, particularly not in spatial surveys.
2) New temporal trend programmes should be carried out by the analysis of fine sediments or a fine-grained fraction, isolated by sieving. Existing temporal trend programmes could be continued, provided that assessment of the data indicates that the statistical power of the programme is adequate for the overall objectives.
3) Contaminant concentrations in whole sediments can be subjected to normalization using co-factors for organic matter, clay minerals, etc., taking into account the presence of both co-factors and target contaminants in the mineral structure of the sand fraction of the sediment. Taking into account these non-zero intercepts of regressions of contaminant concentrations with co-factors, normalization to pre-selected co-factor content will reduce the variance arising from different grain sizes. Normalized values for sandy sediments will have greater uncertainties than for muddy sediments. The propagated error of the variables used for normalization may be unacceptably high for sandy sediments if both contaminant and co-factor concentrations are low, particularly when approaching detection limits. In that case, in order to draw reliable maps, alternative procedures, such as sieving, need to be used to minimize the impact of this error structure.
4) Variance arising from grain size differences can be reduced in a direct way by separation of a fine fraction from the whole sediment. Spatial distribution surveys of the concentrations of contaminants in separated fine fractions can be used to prepare maps, which will be much less influenced by grain size differences than maps of whole sediment analyses. There will still be some residual variance arising from differences in the composition (mineralogy and organic carbon content) of the sediments.
5) The natural variance of sample composition will be smaller in the fraction <20 µm than in the fraction <63 µm. Therefore, the fraction <20 µm should be preferred over the fraction <63 µm. However, separation of the fraction <20 µm can be considerably more laborious than the separation of the fraction <63 µm and might be an obstacle to its wide application. For this practical reason, the fraction <63 µm is nevertheless an acceptable compromise for both temporal trend and coordinated large-scale spatial surveys.
6) The preferred approach for preparing maps of the spatial distribution of contaminants in sediments consists of two steps: analyses of contaminants in fine sediments or in the fraction <63 µm followed by normalization of analytical results using co-factors (cf. Section 4, above). Current scientific knowledge indicates that this procedure minimizes the variances arising from differences in grain size, mineralogy, and organic matter content. Application of this two-tiered approach to fractions <20 µm gives results that can be directly compared to results found by normalization of concentrations measured in fractions <63 µm. This should give the most consistent and comparable data sets over the ICES/OSPAR area. Maps of contaminant levels in fine sediments should be accompanied by mapping the co-factors in the whole sediments.
7) In order to clarify aspects of data interpretation, analytical data for field samples should be accompanied by information on limits of detection and long-term precision. In order to contribute to environmental assessment, data for field samples should include the grain size distribution of the original samples.

## 10. REFERENCES

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# ANNEX 3

## THE LOESS SMOOTHER FOR MONTHLY DATA: INCORPORATION OF SEASONALITY

## 1 INTRODUCTION

This report focuses on the incorporation of a seasonality term in the LOESS smoother. For general background and theory on smoothers used for assessments of contaminant time series, the reader is referred to Fryer and Nicholson (1999), and for the basic theory for fitting and making inference about smoothers to the textbook of Hastie and Tibshirani (1990).

## 2 DEFINITION

Assume that the samples are taken monthly or biweekly and let $y_i$ ($i = 1,\ldots,n$) denote the observation at time $x_i$. Express $x_i$ in units of a year, i.e., the difference of one day equals 1/365.25. Then the smoother matrix $S$ of the LOESS smoother is constructed from a series of weighted regressions constructed for each time $x_t$ using any data that fall within a range $x_t \pm \Delta_t$. The weight of the observation $y_i$ in the local regression for time $x_t$ is determined by the distance between time $x_i$ and time $x_t$,

$$w_{ti} = \begin{cases} \left(1-\left(\dfrac{|x_t - x_i|}{\Delta_t}\right)^3\right)^3 & \text{for } 0 \le \dfrac{|x_t - x_i|}{\Delta_t} \le 1 \\ 0 & \text{otherwise} \end{cases}.$$

The width of $\Delta_t$ controls the amount of smoothing, and according to the proposal of Nicholson and Fryer (1999) for the LOESS smoother without seasonality, one may choose $\Delta_t$ to include data from a fixed span of years, i.e.,

$$\Delta_t = \max\left\{\frac{\text{span}+1}{2}, \text{span - min}\{\text{t - 1, n - t}\}\right\}.$$

Then, writing

$$X = \begin{pmatrix} 1 & x_1 & \sin 2\pi x_1 & \cos 2\pi x_1 & \sin 4\pi x_1 & \cos 4\pi x_1 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & x_n & \sin 2\pi x_n & \cos 2\pi x_n & \sin 4\pi x_n & \cos 4\pi x_n \end{pmatrix}$$

for the design matrix of the regression model with a seasonal component of second order, $Y = \begin{pmatrix} y_1 \\ \vdots \\ y_n \end{pmatrix}$ for the vector of observations, and $W_t = \begin{pmatrix} w_{t1} & 0 & \cdots & 0 \\ 0 & w_{t2} & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & w_{tn} \end{pmatrix}$

for the corresponding diagonal matrix of weights, the value of the smoother in year $x_t$ is given by $S_t^{'}Y$, where $S_t^{'}$ is the $t$th row of $X\left(X'W_tX\right)^{-1}X'W_t$. The resulting smoother matrix is denoted $S = \begin{pmatrix} S_1^{'} \\ \vdots \\ S_n^{'} \end{pmatrix}$.

Alternatively one may avoid local weighting, applying the weight function

$$w_{ti} = \begin{cases} u_i & \text{if there are not more than } k \text{ observations between } x_t \text{ and } x_i \\ 0 & \text{otherwise} \end{cases}$$

## 3 TESTS

Tests for the linear trend, for the non-linear trend, for the difference between the level at start and end of the time series, and for confidence limits can be obtained by straightforward extensions of the case without seasonality. A test for the seasonality may be obtained as follows: Let $K_{error}$ denote the square matrix defined by the quadratic form

$$SS_{error} = Y'(I-S)'(I-S)Y =: Y'K_{error}Y$$

and $K_{season}$ the square matrix defined by the quadratic form

$$SS_{season} =$$
$$Y'(I-S_{noseason})'(I-S_{noseason})Y - Y'(I-S)'(I-S)Y$$
$$=: Y'K_{season}Y\ ,$$

where $S_{noseason}$ denotes the smoother matrix for the LOESS smoother without seasonality.

Let the test statistic $F_{season} = \dfrac{SS_{season}/df_1}{SS_{error}/df_2}$, where

$$df_1 = \frac{\mathrm{tr}(K_{season})^2}{\mathrm{tr}(K'_{season}K_{season})},\quad df_2 = \frac{\mathrm{tr}(K_{error})^2}{\mathrm{tr}(K'_{error}K_{error})}$$

Under the null hypothesis (that there is no non-linear trend), the distribution of

$$\frac{\dfrac{\mathrm{tr}(K_{error})}{\mathrm{tr}(K'_{error}K_{error})}}{\dfrac{\mathrm{tr}(K_{season})}{\mathrm{tr}(K'_{season}K_{season})}} F_{season}$$

can be approximated by an F distribution with ($df_1$, $df_2$) degrees of freedom. Therefore, the null hypothesis (that there is no seasonal effect) can be rejected if

$$F_{season} > \frac{\dfrac{\mathrm{tr}(K_{season})}{\mathrm{tr}(K'_{season}K_{season})}}{\dfrac{\mathrm{tr}(K_{error})}{\mathrm{tr}(K'_{error}K_{error})}} F(df_1, df_2, 1-\alpha).$$

## 4 EXAMPLE

The time series of the ortho-phosphate concentration (in mg $l^{-1}$) measured monthly at Herbrum/Ems from 1984–1997 is presented in Figure A3.1. All calculations presented in the following example are performed on the original scale, since on the log scale the distribution of the data is highly left-skewed. According to Figure A3.1, it appears that in the first fifteen months levels are clearly below the peaks in the months after that. However, this is not reflected in the trend obtained with the LOESS smoother based on the annual mean concentration data. This is demonstrated in Figure A3.2 for the LOESS smoother with a span of seven years, and even with a span of five years this is not reflected in the calculated trend (see Figure A3.3). Another disadvantage of the method is the negative lower confidence limit at the end of the time series. This is partly due to the fact that at the start of the time series there is considerable variability in the series.

**Figure A3.1.** Time series of ortho-phosphate concentrations (in mg $l^{-1}$) measured monthly at Herbrum/Ems from 1984–1997.

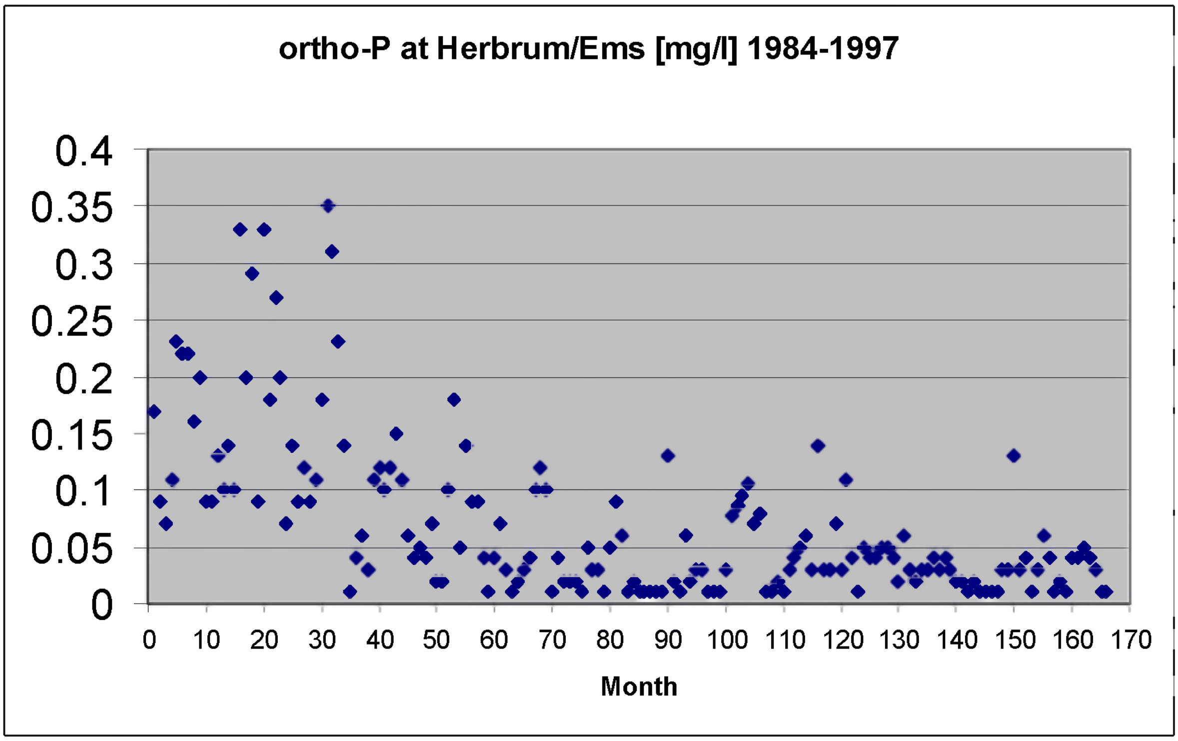


**Figure A3.2.** Trend in ortho-phosphate (in mg $l^{-1}$) at Herbrum/Ems from 1984–1997 obtained with the LOESS smoother with a span of seven years based on annual mean concentration data.

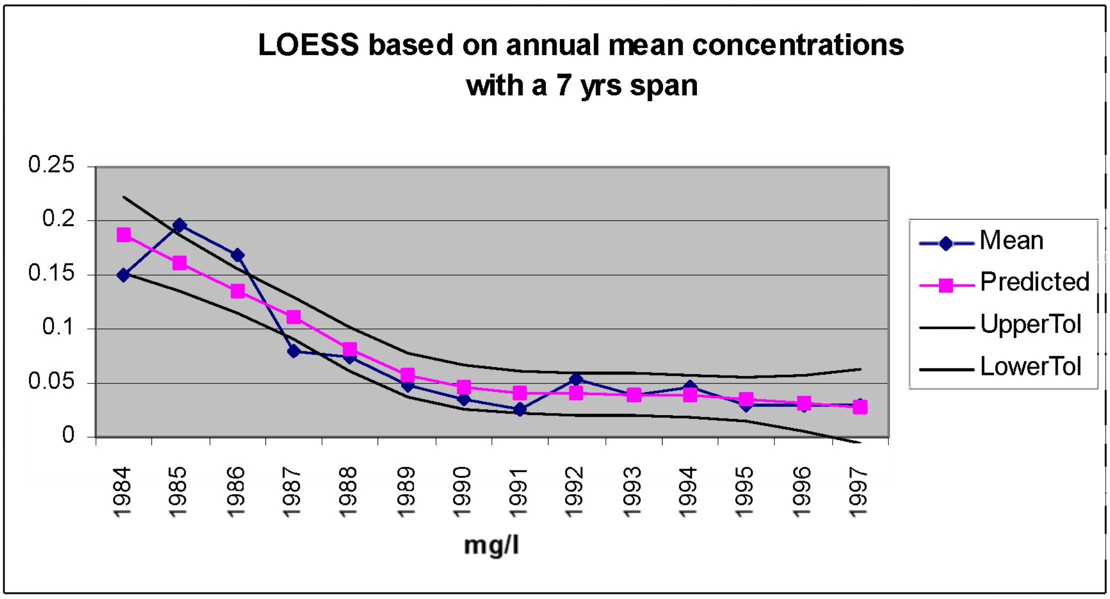
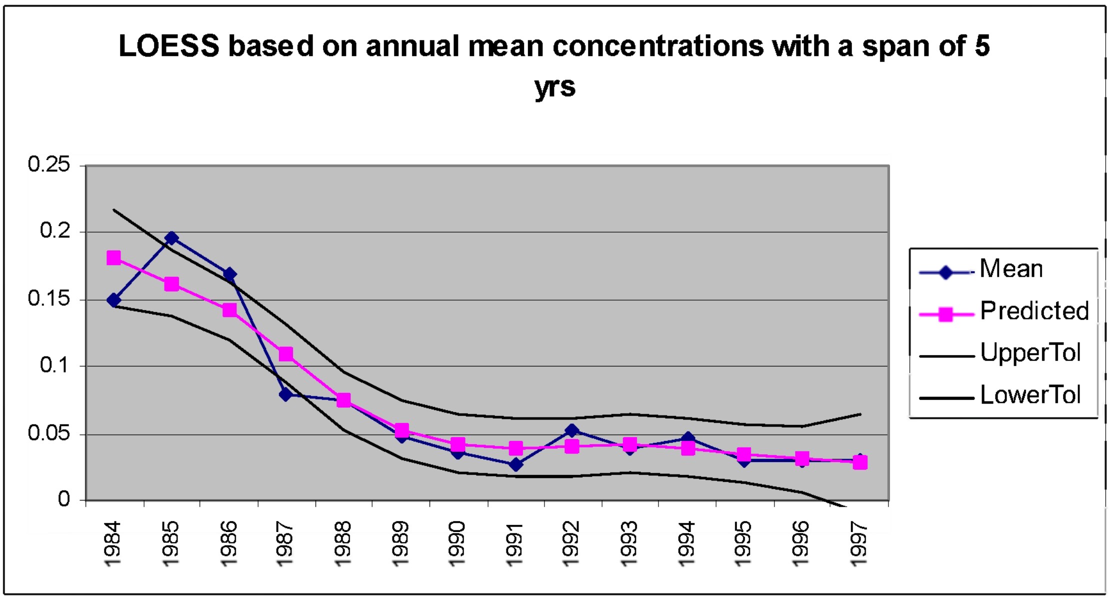
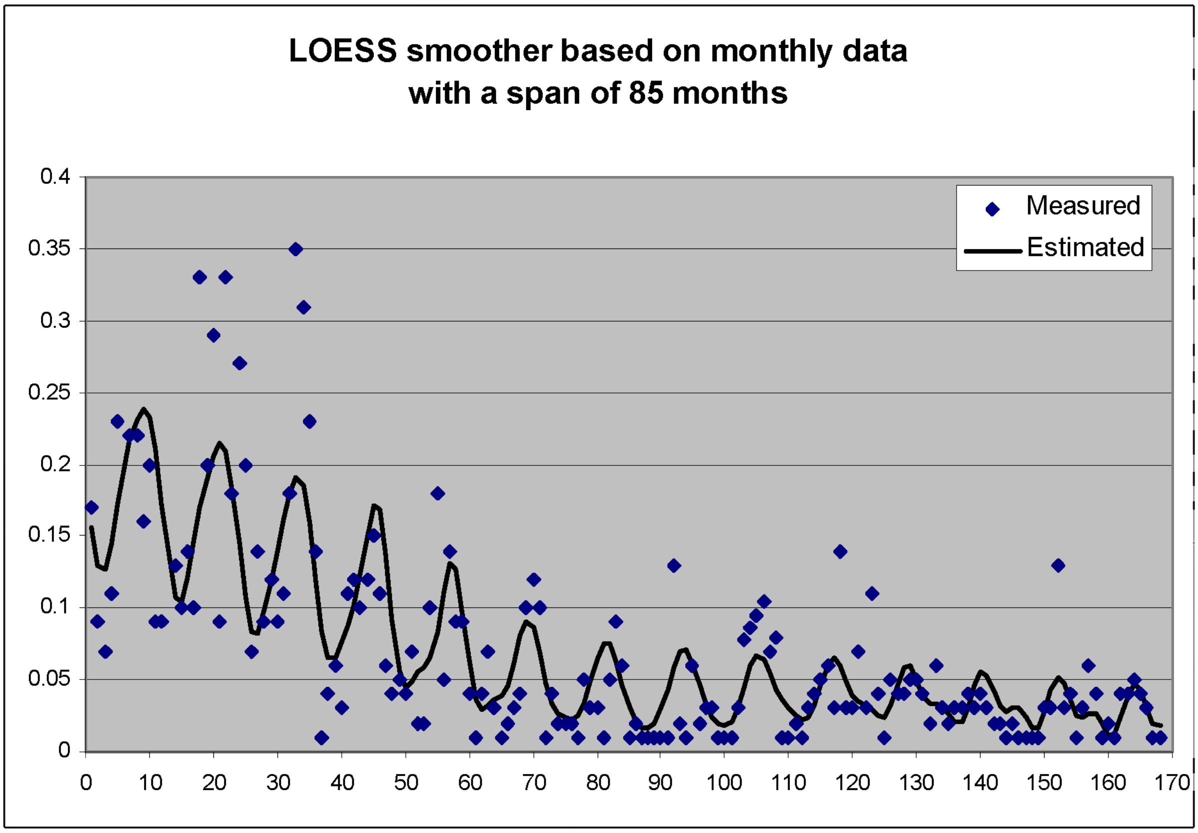


**Figure A3.3.** Trend in ortho-phosphate (in mg $l^{-1}$) at Herbrum/Ems from 1984–1997 obtained with the LOESS smoother with a span of five years based on annual mean concentration data.



Some improvement is possible by applying a LOESS smoother based on monthly data. The fit of the smoother with a span of 85 months is presented in Figure A3.4.

**Figure A3.4.** Trend in ortho-phosphate (in mg $l^{-1}$) at Herbrum/Ems obtained with a LOESS smoother with a span of 85 months based monthly data.



From that fit, estimated mean concentrations and corresponding confidence bands can simply be derived. The result is presented in Figure A3.5.

Obviously the confidence range is considerably smaller than for the smoother based on annual data. Even better results with regard to the flexibility of the trend curve can be obtained with a span of 49 months; see Figure A3.6.

**Figure A3.5.** Estimated mean concentrations of ortho-phosphate (in mg $l^{-1}$) at Herbrum/Ems based on monthly data, as calculated with a span of 85 months.

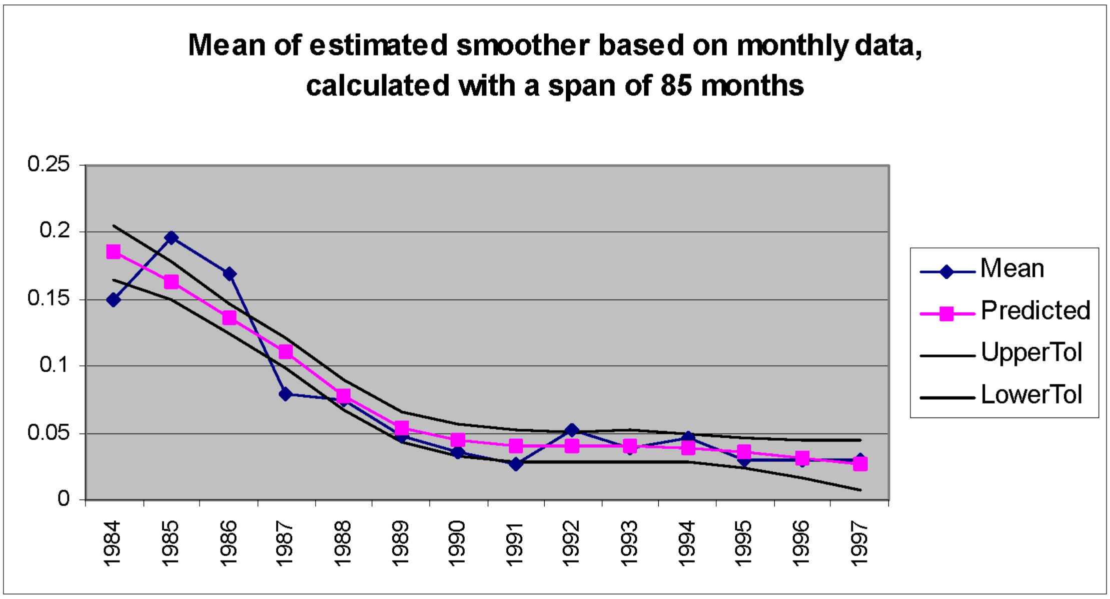
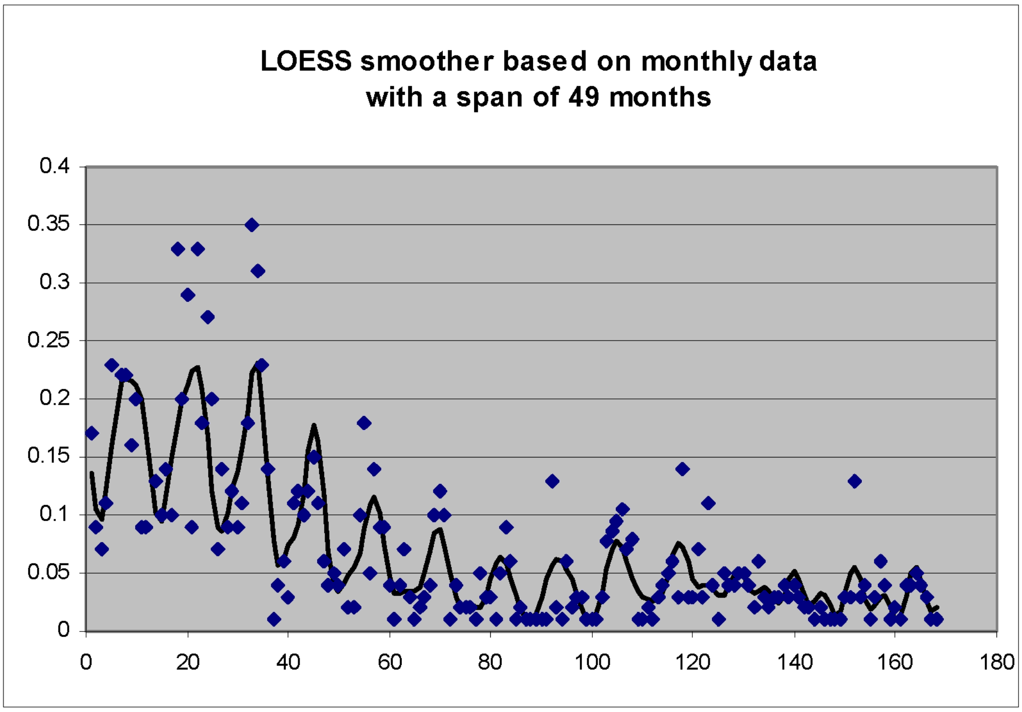


**Figure A.3.6.** Trend in ortho-phosphate (in mg $l^{-1}$) at Herbrum/Ems obtained with a LOESS smoother with a span of 49 months based on monthly data.



## 5 CONCLUSIONS

The analysis of monthly data with the LOESS smoother offers the advantage that the confidence range is smaller than for the LOESS smoother based on annual data. Secondly, the analysis of monthly data offers the possibility to reduce the span from five to four years. This might be especially relevant if anthropogenic changes are assumed to become effective within a few years.

## 6 ACKNOWLEDGEMENT

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# ANNEX 4

## CERTIFIED REFERENCE MATERIALS FOR ORGANIC CONTAMINANTS, TRACE METALS AND NUTRIENT COMPOUNDS, FOR USE IN MARINE MONITORING

The following comments apply to these tables:

a) The compiled tables are for information. Although every effort has been made to ensure that these tables are accurate, users of CRMs should consult vendors for full and accurate information;

b) Certified calibration materials and standards are not included;

c) These tables do not purport to be complete and all the CRMs listed may not be commercially available.

Additional information can be found at the following websites:

NIST (USA), National Institute of Standards and Technology: http://ts.nist.gov/ts/htdocs/230/232/232.htm

BCR (EC), Bureau of Community Reference, now EC Institute for Reference Materials and Measurements (IRMM): www.irmm.jrc.be/mrm.html

NRC (Canada), National Research Council for National Measurement Standards (INMS):

www.cm.inms.nrc.ca/ems1.htm

IAEA (UN), International Atomic Energy Agency: www.iaea.org/programmes/nahunet/e4/nmrm/index.

LGC (UK), Laboratory of the Government Chemist: www.lgc.co.uk/products/products.htm

USGS (USA), U.S. Geological Survey: http://minerals.cr.usgs.gov/geo_chem_stand/index.html

RTC (USA), Resource Technology Corporation: http://www.rt-corp.com/catallog/99solph.htm

DHI (Denmark), Danish Hydraulic Institute, Water and Environment: www.dhi.dk

NIES (Japan), National Institute for Environmental Standards http://www.nies.go.jp

The IAEA provides a very comprehensive and searchable database for natural matrix reference materials.

### Acknowledgement

This material was compiled by Dr J. de Boer, Netherlands Institute for Fisheries Research, IJmuiden, The Netherlands, and E. McGovern, Marine Institute, Dublin, Ireland, on behalf of the Marine Chemistry Working Group, and Dr P. Woitke, German Environmental Agency, Berlin, Germany, for the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea.

### Reference

de Boer, J., and McGovern, E. 2001. Certified Reference Materials for organic contaminants for use in monitoring of the aquatic environment. Trends in Analytical Chemistry, 20(3): 140–159.

**Table A4.1.** Currently available CRMs for marine monitoring programmes (January 2001).

| **Matrix** | **Certified values for** | **Material** | **Name** | **Manufacturer** |
|---|---|---|---|---|
| Sediment | New batch in prep. | BCR 277R | Trace elements in estuarine sediment | BCR (Belgium) |
| Sediment | 2 Sn-species | BCR 462 | Coastal sediment | BCR (Belgium) |
| Sediment | 2 Hg-species | BCR 580 | Estuarine sediment | BCR (Belgium) |
| Sediment | 10 Metals | MURST-ISS-A1 | Antarctic sediment | BCR (Belgium) |
| Sediment | 14 Metals | HISS-1 | Marine sediment | NRC (Canada) |
| Sediment | 20 Metals | MESS-3 | Marine sediment | NRC (Canada) |
| Sediment | 19 Metals, 3 Sn-species | PACS-2 | Marine sediment | NRC (Canada) |
| Sediment | 18 Metals | SRM 1646A | Estuarine sediment | NIST (USA) |
| Sediment | 9 Metals | SRM 1944 | New York/New Jersey sediment | NIST (USA) |
| Sediment | 39 Metals | IAEA 356 | Marine sediment | IAEA (Austria) |
| Sediment | 23 Metals | GBW 07313 | Marine sediment | NRCCRM (China) |
| Sediment | 9 Metals | GBW 07314 | Offshore marine sediment | NRCCRM (China) |
| Sediment | 56 Metals | GBW 07315 | Marine sediment | NRCCRM (China) |
| Sediment | 56 Metals | GBW 07316 | Marine sediment | NRCCRM (China) |
| Sediment | 19 Metals | LGC6137 | Estuarine sediment | LGC (UK) |
| Sediment | 20 Metals | LGC6156 | Harbour sediment | LGC (UK) |
| | | | | |
| Sediment | in prep. (PAHs) | SRM 1941b | Organics in marine sediment | NIST (USA) |
| Sediment | 24 PAHs, 29 PCBs | SRM 1944 | New York/New Jersey sediment | NIST (USA) |
| Sediment | 7 PCBs | LGC6114 | Harbour sediment | LGC (UK) |
| Sediment | PAHs, Organo-Cl | IAEA 383 | Marine sediment | IAEA (Austria) |
| Sediment | PAHs, Organo-Cl | IAEA 408 | Marine sediment | IAEA (Austria) |
| Sediment | 10 PCBs | NRCC-HS-1 | Marine sediment | NRC (Canada) |
| Sediment | 10 PCBs | NRCC-HS-2 | Marine sediment | NRC (Canada) |
| Sediment | 20 PAHs | NRCC-HS-3B | Harbour sediment | NRC (Canada) |
| Sediment | 20 PAHs | NRCC-HS-4B | Harbour sediment | NRC (Canada) |
| Sediment | 16 PAHs | NRCC-HS-5 | Marine sediment | NRC (Canada) |
| Sediment | 16 PAHs | NRCC-HS-6 | Marine sediment | NRC (Canada) |
| Sediment | 13 PAHs | SES-1 | Spiked estuarine sediment | NRC (Canada) |
| Sediment | PCBs | CS-1 | Marine sediment | NRC (Canada) |
| | | | | |
| Biota | 9 Metals | BCR 278R | Mussel tissue | BCR (Belgium) |
| Biota | 6 Metals | BCR 279 | Sea lettuce | BCR (Belgium) |
| Biota | 11 Metals | BCR 414 | Plankton | BCR (Belgium) |
| Biota | 10 Metals | BCR 422 | Cod muscle | BCR (Belgium) |
| Biota | 2 Hg-species | BCR 463 | Tuna fish | BCR (Belgium) |
| Biota | 2 Hg-species | BCR 464 | Tuna fish | BCR (Belgium) |
| Biota | 3 Sn-species | BCR 477 | Mussel tissue | BCR (Belgium) |
| Biota | 3 As-species | BCR 627 | Tuna fish tissue | BCR (Belgium) |
| Biota | 10 Metals | MURST-ISS-A2 | Antarctic krill | BCR (Belgium) |
| Biota | 17 Metals and species | DOLT-2 | Dogfish liver | NRC (Canada) |
| Biota | 14 Metals, Methyl-Hg | DORM-2 | Dogfish muscle | NRC (Canada) |
| Biota | 17 Metals | LUTS-1 | Lobster hepatopancreas | NRC (Canada) |
| Biota | 15 Metals, Methyl-Hg | TORT-2 | Lobster hepatopancreas | NRC (Canada) |

**Table A4.1.** continued

| **Matrix** | **Certified values for** | **Material** | **Name** | **Manufacturer** |
|---|---|---|---|---|
| Biota | 21 Metals | SRM 1566b | Oyster tissue | NIST (USA) |
| Biota | 2 Hg-species | SRM 1974a | Organics in mussel tissue | NIST (USA) |
| Biota | 6 Metals, Methyl-Hg | SRM 2977 | Mussel tissue | NIST (USA) |
| Biota | 25 Metals | IAEA-140/TM | *Fucus* (sea plant homogenate) | IAEA (Austria) |
| Biota | 20 Metals | GBW08571 | Mussel | NRCCRM (China) |
| Biota | 19 Metals | GBW08572 | Prawn | NRCCRM (China) |
| Biota | 27 Metals | NIES-CRM-09 | Sargasso seaweed | NIES (Japan) |
| Biota | 3 Sn-species | NIES-CRM-11 | Fish tissue | NIES (Japan) |
| Biota | 6 PCBs | BCR 349 | Cod liver oil | BCR (Belgium) |
| Biota | 6 PCBs | BCR 350 | Mackerel oil | BCR (Belgium) |
| Biota | 18 PCDDs, PCDFs, PCBs | CARP-1 | Fish (carp) | NRC (Canada) |
| Biota | 24 PCBs, 14 Pesticides | SRM 1588a | Organics in cod liver oil | NIST (USA) |
| Biota | 27 PCBs, 15 Pesticides | SRM 1945 | Organics in whale blubber | NIST (USA) |
| Biota | PAHs, PCBs, Pesticides | SRM 1974a | Organics in mussel tissue | NIST (USA) |
| Biota | PAHs, PCBs, Pesticides | SRM 2974 | Organics in freeze-dried mussel tissue | NIST (USA) |
| Biota | PAHs, PCBs, Pesticides | SRM 2977 | Mussel tissue | NIST (USA) |
| Biota | PAHs, PCBs, Pesticides | SRM 2978 | Mussel tissue | NIST (USA) |
| Biota | PAHs, PCBs, Pesticides | IAEA-140/OC | *Fucus* (sea plant homogenate) | IAEA (Austria) |
| | | | | |
| Water | 6 Metals | BCR 403 | Trace elements in sea water | BCR (Belgium) |
| Water | 4 Metals | BCR 505 | Trace elements in estuarine water | BCR (Belgium) |
| Water | Hg | BCR 579 | Coastal sea water | BCR (Belgium) |
| Water | 12 Metals | CASS-4 | Nearshore sea water | NRC (Canada) |
| Water | 10 Metals | NASS-5 | Open ocean sea water | NRC (Canada) |
| Water | 11 Metals | SLEW-3 | Estuarine water | NRC (Canada) |
| Water | 6 Metals | LGC6016 | Estuarine water - metals | LGC (UK) |
| Water | $NO_3$, $NH_4$, $PO_4$ | QCWW1A | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | $NH_4$, $PO_4$ | QCWW2.1 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | $NO_3$ | QCWW2.2 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | TN, TP | QCWW3 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | DOC, TOC | QCWW4 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | DOC, TOC | QCWW4a | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | BOD | QCWW5 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | $NO_3$, $NH_4$, $PO_4$ | QCRW1 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |
| Water | TN, TP | QCRW2 | Nutrients (Concentrate in ampoule) | DHI (Denmark) |

**Table A4.2a.** Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

| **Code** | **MURST-ISS-A1** | **HISS-1** | **MESS-3** | **PACS-2** |
|---|---|---|---|---|
| ***Organization*** | BCR | NRC | NRC | NRC |
| ***Country of origin*** | Belgium | Canada | Canada | Canada |
| ***Matrix*** | Antarctic sediment | Marine sediment | Marine sediment | Harbour sediment |
| ***Units*** | µg $g^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| **[±] *expressed as*** | no information | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) |
| ***UNITS OF ISSUE*** | 75 g | 100 g | 50 g | 65 g |
| ***FORM*** | | Freeze-dried | Freeze-dried | Freeze-dried |
| | | | | |
| | | | | |
| Aluminium | 6.71 ± 0.33 % | 0.73 ± 0.05 % | 8.59 ± 0.23 % | 6.62 ± 0.32 % |
| Antimony | 4.41 ± 1.06 | (0.13)* | 1.02 ± 0.09 | 11.3 ± 2.6 |
| Arsenic | 0.538 ± 0.027 | 0.801 ± 0.099 | 21.2 ± 1.1 | 26.2 ± 1.5 |
| Beryllium | 42.1 ± 3.4 | 0.129 ± 0.023 | 2.30 ± 0.12 | 1.0 ± 0.2 |
| Cadmium | 6.87 ± 0.31 | 0.024 ± 0.009 | 0.24 ± 0.01 | 2.11 ± 0.15 |
| Calcium | 2.44 ± 0.07 % | 1.14 ± 0.10 % | 1.47 ± 0.06 % | 1.96 ± 0.18 % |
| Chromium | 21.0 ± 2.9 | 30.0 ± 6.8 | 105 ± 4 | 90.7 ± 4.6 |
| Cobalt | 446 ± 19 | (0.65)* | 14.4 ± 2.0 | 11.5 ± 0.3 |
| Copper | 9.56 ± 1.05 | 2.29 ± 0.37 | 33.9 ± 1.6 | 310 ± 12 |
| Iron | 53.3 ± 2.7 | 0.246 ± 0.009 % | 4.34 ± 0.11 % | 4.09 ± 0.06 % |
| Lead | | 3.13 ± 0.40 | 21.1 ± 0.7 | 183 ± 8 |
| Lithium | | 2.83 ± 0.54 | 73.6 ± 5.2 | 32.2 ± 2.0 |
| Magnesium | | 0.075 ± 0.016 % | (1.6 %)* | 1.47 ± 0.13 % |
| Manganese | | 66.1 ± 4.2 | 324 ± 12 | 440 ± 19 |
| Mercury | | (0.01)* | 0.091 ± 0.009 | 3.04 ± 0.20 |
| Molybdenum | | (0.13)* | 2.78 ± 0.07 | 5.43 ± 0.28 |
| Nickel | | 2.16 ± 0.29 | 46.9 ± 2.2 | 39.5 ± 2.3 |
| Phosphorus | | 0.332 ± 0.013 % | (0.12 %)* | 0.096 ± 0.004 % |
| Potassium | | 0.050 ± 0.007 | (2.6 %)* | 1.24 ± 0.05 % |
| Selenium | | 0.016 ± 0.002 | 0.72 ± 0.05 | 0.92 ± 0.22 |
| Silver | | 0.373 ± 0.026 % | 0.18 ± 0.02 | 1.22 ± 0.14 |
| Sodium | | 96.9 ± 11.2 | (1.6 %)* | 3.45 ± 0.17 % |
| Strontium | | (0.06)* | 129 ± 11 | 276 ± 30 |
| Sulphur | | (0.11)* | (0.19 %)* | 1.29 ± 0.13 % |
| Thallium | | 0.076 ± 0.004 % | 0.90 ± 0.06 | (0.6)* |
| Tin | | 6.80 ± 0.78 | 2.50 ± 0.52 | 19.8 ± 2.5 |
| Titanium | | 4.94 ± 0.79 | 0.44 ± 0.06 % | 0.443 ± 0.032 % |
| Vanadium | | | 243 ± 10 | 133 ± 5 |
| Zinc | | | 159 ± 8 | 364 ± 23 |

**Table A4.2b.** Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

| **Code** | **SRM 1646A** | **SRM 1944** | **LGC6137** | **LGC6156** |
|---|---|---|---|---|
| ***Organization*** | NIST | NIST | LGC | LGC |
| ***Country of origin*** | USA | USA | UK | UK |
| ***Matrix*** | Estuarine sediment | Waterway sediment | Estuarine sediment | Harbour sediment |
| ***UNITS*** | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| **[±] *expressed as*** | Conf. interval (95 %) | Conf. interval (95 %) | No information | No information |
| ***UNITS OF ISSUE*** | 70 g | 50 g | 50 g | 5 x 50 g |
| ***FORM*** | Freeze-dried | Freeze-dried | Extractable metals | Extractable metals |
| | | | | |
| Aluminium | 2.297 ± 0.018 % | 5.33 ± 0.49 % | 1.90 % | 1.90 % |
| Arsenic | 6.23 ± 0.21 | 18.9 ± 2.8 | 12.4 | 38.3 |
| Barium | 0.148 ± 0.007 | 8.8 ± 1.4 | 82 | 4.1 |
| Beryllium | 0.519 ± 0.02 % | 266 ± 24 | 1.0 | 2.9 |
| Cadmium | 40.9 ± 1.9 | 3.53 ± 0.16 % | 5.11 | 4.30 % |
| Calcium | 10.01 ± 0.34 | 330 ± 48 | 47 | 111 |
| Chromium | 2.008 ± 0.039 % | 505 ± 25 | 13.7 | 28.3 |
| Cobalt | 11.7 ± 1.2 | 76.1 ± 5.6 | 31.6 | 2400 |
| Copper | 0.388 ± 0.009 % | 656 ± 75 | 3.07 % | 7.20 % |
| Iron | 234.5 ± 2.8 | | 73.0 | 1685 |
| Lead | 0.027 ± 0.001 % | | 42.5 | 0.9425 % |
| Lithium | 0.864 ± 0.016 % | | 1.11 | 553 |
| Magnesium | 0.193 ± 0.028 | | 665 | 10.1 |
| Manganese | 40.00 ± 0.16 % | | 0.34 | 19.9 |
| Mercury | 0.741 ± 0.017 % | | 31.5 | 61 |
| Molybdenum | 0.352 ± 0.004 % | | 0.501 | 0.546 % |
| Nickel | 0.456 ± 0.021 % | | 0.742 | 2.01 % |
| Phosphorus | 44.84 ± 0.76 | | 47.0 | 145 |
| Potassium | 48.9 ± 1.6 | | 231 | 91.5 |
| Selenium | | | | 3530 |
| Silicon | | | | |
| Sodium | | | | |
| Sulphur | | | | |
| Tin | | | | |
| Titanium | | | | |
| Vanadium | | | | |
| Zinc | | | | |

**Table A4.2c**. Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

| **Code** | **GBW 07313** | **GBW 07314** | **GBW 07315–3** | **GBW 07316** |
|---|---|---|---|---|
| ***Organization*** | NRCCRM | NRCCRM | NRCCRM | NRCCRM |
| ***Country of origin*** | China | China | China | China |
| ***Matrix*** | Marine sediment | Offshore sediment | Marine sediment | Marine sediment |
| ***UNITS*** | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| [±] ***expressed as*** | No information | No information | No information | No information |
| ***UNITS OF ISSUE*** | 50 g | 50 g | 50 g | 50 g |
| ***FORM*** | | | | |
| | | | | |
| Aluminium | 7.2778 % | 13.070 % | 6.04 % | 4.08 % |
| Antimony | 1.85 | (1.4)* | 2.0 | 1.3 |
| Arsenic | (5.8)* | 10.3 | 7.1 | 4.6 |
| Barium | 0.44 | 425 | 3100 | 2500 |
| Boron | 125 | (73)* | 125 | 84 |
| Cadmium | 1.2221 % | 0.2 | (0.25) | (0.3) |
| Calcium | 82 | 4.3100 % | 4.10 % | 16.14 % |
| Cerium | 9.4 | (78)* | 82 | 55 |
| Caesium | 58.4 | (8.2)* | 6.8 | 4.5 |
| Chromium | 76.7 | 86 | 59 | 38 |
| Cobalt | 424 | 14.2 | 81 | 53 |
| Copper | 4.602 % | 31 | 357 | 231 |
| Iron | 29.3 | 5.3600 % | 37 | 22 |
| Lead | 60 | 25 | 51 | 1.22 % |
| Lithium | 2.0388 % | 2.5000 % | 1.81 % | 3099 |
| Magnesium | 3257 | 0.048 | 4570 | 0.13 |
| Manganese | 7.2 | (0.64)* | 0.95 | 5.7 |
| Mercury | 150 | 34.3 | 14 | 108 |
| Molybdenum | 1963 | 2.4800 % | 167 | 1441 |
| Nickel | 2.449 % | 0.16 | 2096 | 1.34 % |
| Phosphorus | 25.1795 % | 28.9430 % | 1.93 % | 14.75 % |
| Potassium | 3.5685 % | 150 | 23.85 % | 2.79 % |
| Selenium | 267 | (103.1)* | 3.29 % | 2340 |
| Silicon | 4 016 | 87 | 298 | 69 |
| Silver | 112 | | 3660 | 142 |
| Sodium | 160 | | 101 | |
| Strontium | | | 137 | |
| Titanium | | | | |
| Vanadium | | | | |
| Zinc | | | | |

**Table A4.2d**. Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

| **Code** | **MAG-1** | **CRMPR-96961** | **CRM015–050** | **CRM016–05** |
|---|---|---|---|---|
| ***Organization*** | USGS | RTC | RTC | RTC |
| ***Country of origin*** | USA | USA | USA | USA |
| ***Matrix*** | Marine sediment | Sediment | Sediment | Sediment |
| ***UNITS*** | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| **[±]** ***expressed as*** | Uncertainty | Uncertainty | No information | No information |
| ***UNITS OF ISSUE*** | 30 g | | 50 g | 50 g |
| ***FORM*** | | | | |
| | | | | |
| Aluminium | 8.68 ± 0.17 % | (2.7896)* | 0.92 % | 0.892 % |
| Antimony | 0.96 ± 0.1 | 8.0 ± 0.5 | 6.6 | 6.48 |
| Arsenic | (9.2)* | (128.6)* | 83 | 79.3 |
| Barium | 480 ± 43 | (0.3)* | (8.6)* | (13)* |
| Boron | 140 ± 6 | 2.3934 ± 0.1915 % | 2.3463 % | 0.47 |
| Cadmium | 0.20 ± 0.03 | (33.3)* | 14.3 | 2.2646 % |
| Calcium | 0.98 ± 0.07 % | (7.4)* | 6.04 | 14.5 |
| Cerium | 88 ± 9 | 17 ± 1 | 16.1 | 5.96 |
| Caesium | 8.6 ± 0.7 | 2.1506 ± 0.0860 % | 1.7070 % | 15.5 |
| Chromium | 97 ± 8 | (15.4)* | 15.04 | 1.6831 % |
| Cobalt | 20 ± 2 | (1.3890 %)* | 1.3611 % | 14.1 |
| Copper | 30 ± 3 | 208.1 ± 12.5 | 183.4 | 1.3246 % |
| Iron | 4.8 ± 0.4 % | (0.1)* | 0.1 | 180 |
| Lead | 24 ± 3 | (18.6)* | 1.16 | 0.11 |
| Lithium | 79 ± 4 | 0.73 ± 0.04 | 17.5 | (0.97)* |
| Magnesium | 1.8 ± 0.1 % | (0.4080)* | 0.2074 % | 16.7 |
| Manganese | 759 ± 68 | 79 ± 4 | (1)* | 0.1958 % |
| Mercury | (0.02)* | | (491)* | (1)* |
| Molybdenum | (1.6)* | | 0.0400 % | (347)* |
| Nickel | 53 ± 8 | | (62)* | (0.7)* |
| Phosphorus | 700 ± 90 | | 22.1 | 0.0292 % |
| Potassium | 2.95 ± 0.15 % | | 69.9 | (61)* |
| Selenium | 23.52 ± 0 % | | | 22.5 |
| Silicon | (0.08)* | | | 69.7 |
| Silver | 2.84 ± 0.09 | | | |
| Sodium | 150 ± 15 | | | |
| Strontium | 0.45 ± 0.04 % | | | |
| Titanium | 140 ± 6 | | | |
| Vanadium | 130 ± 7 | | | |
| Zinc | | | | |

**Table A4.3.** Reference materials for trace metal species in marine sediments.

| Code | CRM 462 | PACS-2 | CRM 580 |
|---|---|---|---|
| ***Organization*** | BCR | NRC | BCR |
| ***Country of origin*** | Belgium | Canada | Belgium |
| ***Matrix*** | Coastal sediment | Harbour sediment | Estuarine sediment |
| ***UNITS*** | µg kg$^{-1}$ | mg kg$^{-1}$ | µg kg$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight |
| **[±]** ***expressed as*** | Expanded uncertainty (coverage factor k = 2) | Confidence interval (95 %) | Expanded uncertainty (coverage factor k = 2) |
| ***UNITS OF ISSUE*** | 25 g | 65 g | 50 g |
| ***FORM*** | Air-dried | Freeze-dried | |
| | | | |
| Tributyltin (as Sn) | 22 ± 6 | 0.98 ± 0.13 | |
| Dibutyltin (as Sn) | 35 ± 6 | 1.09 ± 0.15 | |
| Monobutyltin (as Sn) | | 0.45 ± 0.05 | |
| Total Mercury | | | 132 ± 3 mg kg$^{-1}$ |
| MeHg | | | 75.5 ± 3.7 |

**Table A4.4a.** Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

| Code | BCR 278R | BCR 279 | BCR 414 | BCR 422 |
|---|---|---|---|---|
| ***Organization*** | BCR | BCR | BCR | BCR |
| ***Country of origin*** | Belgium | Belgium | Belgium | Belgium |
| ***Matrix*** | Mussel tissue | Sea Lettuce | Plankton | Cod muscle |
| ***UNITS*** | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| **[±]** ***expressed as*** | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) |
| ***UNITS OF ISSUE*** | 8 g | 35 g | 5 g | 7 g |
| ***FORM*** | Freeze-dried | | Freeze-dried | |
| | | | | |
| Arsenic | 6.07 ± 0.13 | 3.09 ± 0.20 | 6.82 ± 0.28 | 21.1 ± 0.5 |
| Cadmium | 0.348 ± 0.007 | 0.274 ± 0.022 | 0.383 ± 0.014 | 0.017 ± 0.002 |
| Chromium | 0.78 ± 0.06 | 13.14 ± 0.37 | 23.8 ± 1.2 | 1.05 ±0.07 |
| Copper | 9.45 ± 0.13 | 13.48 ± 0.36 | 29.5 ± 1.3 | 5.46 ± 0.30 |
| Iron | 2.00 ± 0.04 | 0.593 ± 0.032 | 3.97 ± 0.19 | 4.95 ± 0.49 |
| Iodine | 7.69 ± 0.23 | 51.3 ± 1.2 | 299 ± 12 | 0.085 ± 0.015 |
| Lead | 0.196 ± 0.009 | | 0.276 ± 0.018 | 0.543 ± 0.028 |
| Manganese | 1.84 ± 0.10 | | 18.8 ± 0.8 | 0.559 ± 0.016 |
| Mercury | 83.1 ± 1.7 | | 1.75 ± 0.1 | 1.63 ± 0.07 |
| Nickel | | | 8.1 ± 0.18 | 19.6 ± 0.5 |
| Selenium | | | 112 ± 3 | |
| Vanadium | | | | |
| Zinc | | | | |

**Table A4.4b.** Reference material for trace metal species in marine biota.

| Code | BCR 463 | BCR 464 | BCR 477 | BCR 627 |
|---|---|---|---|---|
| ***Organization*** | BCR | BCR | BCR | BCR |
| ***Country of origin*** | Belgium | Belgium | Belgium | Belgium |
| ***Matrix*** | Tuna fish | Tuna fish | Mussel tissue | Tuna fish |
| ***UNITS*** | µg $g^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| **[±]** ***expressed as*** | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) |
| ***UNITS OF ISSUE*** | 15 g | 15 g | 14 g | 10 g |
| ***FORM*** | Freeze-dried | Freeze-dried | | |
| | | | | |
| Total Mercury | 2.85 ± 0.16 | 5.24 ± 0.10 | | |
| MeHg | 3.04 ± 0.16 | 5.50 ± 0.17 | 2.20 ± 0.19 | 52 ± 3 µmol $kg^{-1}$ |
| TBT - $Sn(C_4H_9)_3^{+}$ | | | 1.54 ± 0.12 | 2.0 ± 0.3 µmol $kg^{-1}$ |
| DBT - $Sn(C_4H_9)_2^{2+}$ | | | 1.50 ± 0.28 | 4.8 ± 0.3 |
| MBT - $Sn(C_4H_9)^{3+}$ | | | | |
| Arsenobetaine | | | | |
| Dimethylarsinic acid | | | | |
| Total arsenic | | | | |

**Table A4.4c.** Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

| **Code** | **MURST-ISS-A2** | **SRM 1566b** | **SRM 2977** | **IAEA-140/TM** |
|---|---|---|---|---|
| ***Organization*** | BCR | NIST | NIST | IAEA |
| ***Country of origin*** | Belgium | USA | USA | Austria |
| ***Matrix*** | Antarctic krill | Oyster tissue | Mussel tissue | *Fucus* |
| ***UNITS*** | $\mu g\ g^{-1}$ | $\mu g\ g^{-1}$ | $\mu g\ g^{-1}$ | $\mu g\ g^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight |
| [±] ***expressed as*** | Conf. interval (95 %) | Uncertainty | No information | Uncertainty |
| ***UNITS OF ISSUE*** | 0.5 g | 25 g | 10 g | 14 g |
| ***FORM*** | Freeze-dried | Freeze-dried | Freeze-dried | |
| | | | | |
| Aluminium | | 197.2 ± 6.0 | | (1184)* |
| Antimony | 5.02 ± 0.40 | 7.65 ± 0.65 | 4 0.179 ± 0.003 | 0.103 ± 0.022 |
| Arsenic | 0.73 ± 0.06 | 0.0838 ± 0.0020 % | 9.42 ± 0.52 | 44.3 ± 2.2 |
| Bromine | 0.110 ± 0.010 | 2.48 ± 0.08 | 2.27 ± 0.13 | 567 ± 96 |
| Calcium | 65.2 ± 2.3 | 0.371 ± 0.009 | 23.93 ± 0.29 | 1.2730 ± 0.1782 % |
| Cadmium | 56.6 ± 2.3 | 71.6 ± 1.6 | 6.06 ± 0.24 | 0.537 ± 0.038 |
| Cobalt | 1.11 ± 0.09 | 205.8 ± 6.8 | 69.3 ± 4.2 | 0.876 ± 0.131 |
| Chromium | 4.12 ± 0.10 | 0.308 ± 0.009 | | 10.4 ± 0.8 |
| Copper | 1.28 ± 0.12 | 0.1085 ± 0.0023 % | | 5.05 ± 0.30 |
| Iron | 7.37 ± 1.13 | 18.5 ± 0.2 | | 1256 ± 38 |
| Lithium | 66.0 ± 2.0 | 0.0371 ± 0.0013 | | 2.29 ± 0.34 |
| Lead | | 0.0132 ± 0.0007 | | 2.19 ± 0.64 |
| Magnesium | | 1.04 ± 0.09 | | 0.9070 ± 0.0907 |
| Manganese | | 0.652 ± 0.009 % | | 56.1 ± 2.2 |
| Mercury | | 3.262 ± 0.145 | | 0.038 ± 0.006 |
| MeHg (as Hg) | | 2.06 ± 0.15 | | 0.000626 ± 0.000106 |
| Molybdenum | | 0.666 ± 0.009 | | 2.65 ± 0.37 |
| Nickel | | 0.3297 ± 0.0053 % | | 3.79 ± 0.42 |
| Potassium | | 0.6887 ± 0.0140 % | | 3.1100 ± 0.2488 % |
| Rubidium | | 0.0367 ± 0.0043 | | 16.4 ± 2.30 |
| Selenium | | 0.577 ± 0.023 | | (0.079)* |
| Silver | | 424 ± 46 | | (0.078)* |
| Sodium | | | | 3.2000 ± 0.6720 % |
| Strontium | | | | 750 ± 98 |
| Sulfur | | | | 0.299 ± 0.063 |
| Thorium | | | | 0.73 ± 0.08 |
| Uranium | | | | 3.67 ± 0.48 |
| Vanadium | | | | 47.3 ± 1.9 |
| Zinc | | | | |

**Table A4.4d.** Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

| **Code** | **DOLT-2** | **DORM-2** | **LUTS-1** | **TORT-2** |
|---|---|---|---|---|
| ***Organization*** | NRC | NRC | NRC | NRC |
| ***Country of origin*** | Canada | Canada | Canada | Canada |
| ***Matrix*** | Dogfish liver | Dogfish muscle | Lobster hepatopancreas | Lobster hepatopancreas |
| ***UNITS*** | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Wet weight | Dry weight |
| **[±] *expressed as*** | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) |
| ***UNITS OF ISSUE*** | 25 g | 30 g | 6 x 10 g | 35 g |
| ***FORM*** | | | Slurry (85 % water) | Vacuum dried |
| | | | | |
| Aluminium | 25.2 ± 2.4 | 10.9 ± 1.7 | | |
| Arsenic | 16.6 ± 1.1 | 18.0 ± 1.1 | 2.83 ± 0.13 | 21.6 ± 1.8 |
| Calcium | 20.8 ± 0.5 | 0.043 ± 0.008 | 203 ± 33 | 26.7 ± 0.6 |
| Cadmium | 0.24 ± 0.05 | 0.182 ± 0.031 | 2.12 ± 0.15 | 0.51 ± 0.09 |
| Cobalt | 0.37 ± 0.08 | 34.7 ± 5.5 | 0.051 ± 0.006 | 0.77 ± 0.15 |
| Chromium | 25.8 ± 1.1 | 2.34 ± 0.16 | 0.079 ± 0.012 | 106 ± 10 |
| Copper | 1103 ± 47 | 142 ± 10 | 15.9 ± 1.2 | 105 ± 13 |
| Iron | 0.22 ± 0.02 | 0.065 ± 0.007 | 11.6 ± 0.9 | 0.35 ± 0.13 |
| Lead | 6.88 ± 0.56 | 3.66 ± 0.34 | 0.010 ± 0.002 | 13.6 ± 1.2 |
| Magnesium | 2.14 ± 0.28 | 4.64 ± 0.26 | 89.5 ± 4.1 | 0.27 ± 0.06 |
| Manganese | 0.693 ± 0.053 | 4.47 ± 0.32 | 1.20 ± 0.13 | 0.152 ± 0.013 |
| Mercury | 0.20 ± 0.02 | 19.4 ± 3.1 | 0.0167 ± 0.0022 | 0.95 ± 0.10 |
| MeHg (as Hg) | 6.06 ± 0.49 | 1.40 ± 0.09 | 0.0094 ± 0.0006 | 2.50 ± 0.19 |
| Molybdenum | 0.608 ± 0.032 | 0.041± 0.013 | 0.200 ± 0.034 | 5.63 ± 0.67 |
| Nickel | (0.13)* | (0.004)* | 948 ± 72 | 45.2 ± 1.9 |
| Potassium | 85.8 ± 2.5 | (0.023)* | 0.641 ± 0.054 | (0.04)* |
| Selenium | | 25.6 ± 2.3 | 0.580 ± 0.049 | 1.64 ± 0.19 |
| Silver | | 16.4 ± 1.1 | 2.46 ± 0.28 | 180 ± 6 |
| Strontium | | 0.248 ± 0.054 | 12.4 ± 0.8 | |
| Thallium | | | | |
| Tin | | | | |
| Vanadium | | | | |
| Zinc | | | | |
| Arsenobetaine (as As) | | | | |
| Tetramethyl-arsonium (as As) | | | | |

**Table A4.4e.** Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

| **Code** | **GBW08571** | **GBW08572** | **NIES-CRM-09** | **NIES-CRM-11** | **SRM 2976** | **SRM 2974** |
|---|---|---|---|---|---|---|
| ***Organization*** | NRCCRM | NRCCRM | NIES | NIES | NIST | NIST |
| ***Country of origin*** | China | China | Japan | Japan | USA | USA |
| ***Matrix*** | Mussel | Prawn | Sargasso seaweed | Fish tissue | Mussel tissue | Mussel tissue |
| ***UNITS*** | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ | µg g$^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight |
| **[±]** ***expressed as*** | Uncertainty | Uncertainty | Uncertainty | Uncertainty | Uncertainty | Uncertainty |
| ***UNITS OF ISSUE*** | 12 g | 8 g | 10 g | 20 g | 25 g | 8 g |
| ***FORM*** | | | | | Freeze-dried | Freeze-dried |
| | | | | | | |
| Aluminium | (231)* | 1310 ± 39 | (215)* | | | |
| Arsenic | 6.1 ± 1.2 | 1.42 ± 0.07 | 115 ± 9 | 2.4 ± 0.1 | 13.3 ± 1.8 | |
| Barium | 1110 ± 44 | 4.29 ± 0.73 | (270)* | 1.3 ± 0.1 | | |
| Bromine | 4.5 ± 0.6 | (13.5)* | 13400 ± 536 | (6.3)* | | |
| Calcium | 0.94 ± 0.07 | 3040 ± 61 | 0.15 ± 0.02 | | | |
| Cadmium | 0.57 ± 0.08 | 0.023 ± 0.004 | 0.12 ± 0.01 | | 0.82 ± 0.16 | 176 ± 13 µg kg$^{-1}$ |
| Cobalt | 7.7 ± 1.0 | (0.029)* | (0.2)* | | | |
| Chromium | 221 ± 15 | 0.24 ± 0.06 | 4.9 ± 0.2 | | | |
| Copper | 1.96 ± 0.12 | 4.66 ± 0.28 | 187 ± 6 | | 4.02 ± 0.33 | 77.3 ± 3.1 µg kg$^{-1}$ |
| Fluorine | 1970 ± 217 | 5.31 ± 0.42 | 1.35 ± 0.05 | | | |
| Iron | 10.2 ± 1.8 | 19.8 ± 0.4 | 6500 ± 325 | | 171.0 ± 4.9 | |
| Lead | 0.067 ± 0.008 | 0.298 ± 0.021 | 21.2 ± 1.1 | | 1.19 ± 0.18 | |
| Magnesium | (0.6)* | 1600 ± 48 | (0.04)* | | | |
| Manganese | 1.03 ± 0.14 | 1.96 ± 0.16 | 61000 ± 183 | | | |
| Mercury | 4240 ± 212 | 0.201 ± 0.004 | 24 ± 2 | | 61.0 ± 3.6 µg kg$^{-1}$ | |
| MeHg (as Hg) | | | | | 27.8 ± 1.1 µg kg$^{-1}$ | |
| Molybdenum | 3.65 ± 0.18 | 5970 ± 119 | | | | |
| Nickel | 5820 ± 175 | 1.52 ± 0.05 | | | | |
| Potassium | 12.8 ± 1.3 | 3810 ± 114 | (0.05)* | | | |
| Ruthenium | 138 ± 11 | 40.6 ± 3.7 | 0.31 ± 0.02 | | | |
| Selenium | | 60.8 ± 1.8 | 17000 ± 850 | | 1.80 ± 0.15 | |
| Silver | | | 1000 ± 30 | | | |
| Sodium | | | 1 ± 0.1 | | | |
| Strontium | | | 15.6 ± 1.2 | | | |
| Tin | | | | | | |
| Vanadium | | | | | | |
| Zinc | | | | | 137 ± 13 | |
| TBT (as Sn) | | | | | | |
| TPhT (as Sn) | | | | | | |

**Table A4.5.** Reference materials for trace metals in sea water. Values preceded by an asterisk (*) are non-certified.

| **Code** | **BCR 403** | **BCR 505** | **BCR 579** | **CASS-4** |
|---|---|---|---|---|
| ***Organization*** | BCR | BCR | BCR | NRC |
| ***Country of origin*** | Belgium | Belgium | Belgium | Canada |
| ***Matrix*** | Sea water | Estuarine water | Coastal sea water | Nearshore sea water |
| ***UNITS*** | nmol kg$^{-1}$ | nmol kg$^{-1}$ | ng kg$^{-1}$ | µg l$^{-1}$ |
| **[±]** ***expressed as*** | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) | Conf. interval (95 %) |
| ***UNITS OF ISSUE*** | 2 litres | 1 litre | 1 litre | 500 ml |
| ***FORM*** | Acidified | Acidified | Acidified | Acidified |
| | | | | |
| Arsenic | | | | 1.11 ± 0.16 |
| Cadmium | 0.175 ± 0.018 | 0.80 ± 0.04 | 1.85 ± 0.20 | 0.026 ± 0.003 |
| Cobalt | 3.9 ± 0.4 | 29.4 ± 1.5 | | 0.026 ± 0.003 |
| Chromium | 0.117 ± 0.025 | 24.1 ± 2.0 | | 0.144 ± 0.029 |
| Copper | 103 ± 20 | 172 ± 11 | | 0.592 ± 0.055 |
| Iron | 4.4 ± 0.4 | | | 0.713 ± 0.058 |
| Lead | 25.7 ± 2.9 | | | 0.0098 ± 0.0036 |
| Manganese | | | | 2.78 ± 0.19 |
| Mercury | | | | 8.78 ± 0.86 |
| Molybdenum | | | | 0.314 ± 0.030 |
| Nickel | | | | 1.18 ± 0.16 |
| Vanadium | | | | 0.381 ± 0.057 |
| Zinc | | | | |

| **Code** | **NASS-5** | **SLEW-3** | **LGC6016** | |
|---|---|---|---|---|
| ***Organization*** | NRC | NRC | LGC | |
| ***Country of origin*** | Canada | Canada | UK | |
| ***Matrix*** | Open ocean sea water | Estuarine water | Estuarine water | |
| ***UNITS*** | µg l$^{-1}$ | µg l$^{-1}$ | µg kg$^{-1}$ | |
| **[±]** ***expressed as*** | Conf. interval (95 %) | Conf. interval (95 %) | no information | |
| ***UNITS OF ISSUE*** | 500 ml | 500 ml | 50 ml | |
| ***FORM*** | Acidified | Acidified | | |
| | | | | |
| Arsenic | 1.27 ± 0.12 | 1.36 ± 0.09 | | |
| Cadmium | 0.023 ± 0.003 | 0.048 ± 0.004 | 101 | |
| Cobalt | 0.011 ± 0.003 | 0.042 ± 0.010 | 190 | |
| Chromium | 0.110 ± 0.015 | 0.183 ± 0.019 | 196 | |
| Copper | 0.297 ± 0.046 | 1.55 ± 0.12 | 976 | |
| Iron | 0.207 ± 0.035 | 0.568 ± 0.059 | 186 | |
| Lead | 0.008 ± 0.005 | 0.0090 ± 0.0014 | 75 | |
| Manganese | 0.919 ± 0.057 | 1.61 ± 0.22 | | |
| Molybdenum | 9.6 ± 1.0 | (5.1)* | | |
| Nickel | 0.253 ± 0.028 | 1.23 ± 0.07 | | |
| Vanadium | 0.102 ± 0.039 | 2.57 ±0.31 | | |
| Zinc | | 0.201 ± 0.037 | | |

## Relevant Certified Reference Materials for Nutrients, for Use in Marine Monitoring

**Table A4.6a.** Certified Reference Materials for nutrients in surface water. (RW = Recipient Water). Recommended also for the control of analyses of mineral nutrients in marine water samples. They are to be diluted 100 times with sea water.

| **Code** | **QC RW1** | **QC RW2** |
|---|---|---|
| ***Organization*** | DHI Water & Environment<br>(e-mail: refmat@dhi.dk) | DHI Water & Environment<br>(e-mail: refmat@dhi.dk) |
| ***Country of origin*** | Denmark | Denmark |
| ***Matrix*** | Water | Water |
| ***UNITS*** | µg $l^{-1}$ | µg $l^{-1}$ |
| **[±] *expressed as*** | ± 95 % CI (according to ISO 5725) | ± 95 % CI (according to ISO 5725) |
| ***UNITS OF ISSUE*** | Set 10 or 50 ampoules,<br>10 ml/ampoule | Set 10 or 50 ampoules,<br>10 ml/ampoule |
| ***FORM*** | | |
| **NUTRIENTS** | | |
| Nitrate-N | 100 | |
| Ammonium-N | 100 | |
| Orthophosphate-P | 100 | |
| Total Nitrogen (TN) | | 250 |
| Total Phosphorus (TP) | | 200 |
| COD (Cr) | | |
| BOD | | |
| TOC (NVOC) | | |

**Table A4.6b** Certified Reference Materials for nutrients, recommended mainly for waste water (WW = Waste Water).

| **Code** | **QC WW1A** | **QC WW2.1** | **QC WW2.2** | **QC WW3** | **QC WW4, 4A** | **QC WW5** |
|---|---|---|---|---|---|---|
| ***Organization*** | DHI Water & Environment (e-mail: refmat@dhi.dk) | DHI | DHI | DHI | DHI | DHI |
| ***Country of origin*** | Denmark | Denmark | Denmark | Denmark | Denmark | Denmark |
| ***Matrix*** | Water | Water | Water | Water | Water | Water |
| ***UNITS*** | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ |
| **[±] *expressed as*** | ± 95 % CI | ± 95 % CI | ± 95 % CI | ± 95 % CI | ± 95 % CI | ± 95 % CI |
| ***UNITS OF ISSUE*** | | | | | | |
| ***FORM*** | | | | | | |
| **NUTRIENTS** | | | | | | |
| Nitrate-N | 5.0 | | 1.0 | | | |
| Ammonium-N | 1.0 | 10 | | | | |
| Ortho-phosphate-P | 1.5 | 5.0 | | | | |
| Total Nitrogen (TN) | | | | 7.5 | | |
| Total Phosphorus (TP) | | | | 1.5 | | |
| COD (Cr) | | | | | 500, 50 | |
| BOD | | | | | | 200 |
| TOC (NVOC) | | | | | 200, 20 | |

COD: Chemical Oxygen Demand; BOD: Biological Oxygen Demand; TOC: Total Organic Carbon.

# ANNEX 5

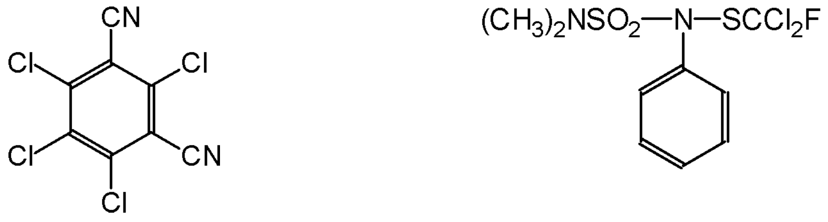
# THE AQUATIC FATE AND EFFECTS OF ANTIFOULING PAINT BOOSTER BIOCIDES

## 1 INTRODUCTION

In the late 1980s a ban on the use of triorganotins (TOTs) as biocidal additives in antifouling paints, used on small boats (< 25 m), led to the development of alternative organic antifouling biocides to boost the performance of alternative formulations. In the small boat sector of the antifouling paint market, these compounds are typically added to copper-based paints in order to improve their efficacy, however, they are also added to tributyltin (TBT)-based paints used on larger vessels.

The International Maritime Organization (IMO) Marine Environment Protection Committee (MEPC) has proposed a total ban on the use of organotins as biocides in antifouling paints to be introduced in 2003. As organotin antifoulants are phased out, greater attention is being paid to the remaining biocides. It is estimated that worldwide, around eighteen compounds are used as biocidal additives in professional and amateur antifouling products. This review will focus on the eight booster biocides in common use (Figure A5.1), since little or no data are available for the other compounds.

**Figure A5.1.** Chemical structures of the eight most common antifouling paint booster biocides in use.

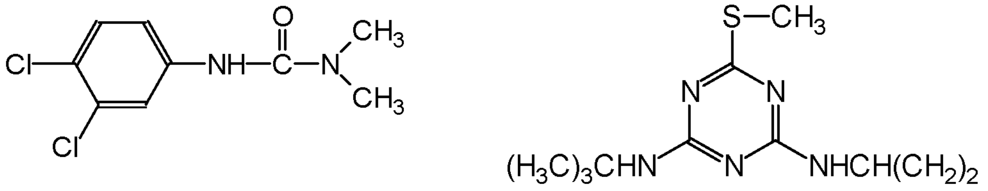


chlorothalonil

(2,4,5,6-tetrachloro-isophthalonitrile)

dichlofluanid

(*N*′-dimethyl-*N*-phenylsulphamide)

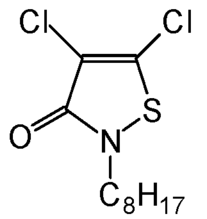


diuron

(1-(3,4-dichlorophenyl)-3,3-dimethylurea)

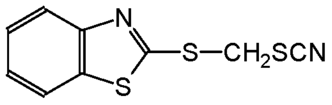
Irgarol 1051

(*N*′-tert-butyl-*N*-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine)



SeaNine 211

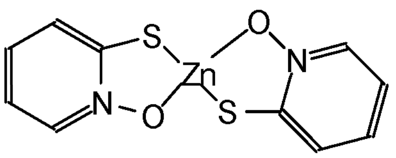
(4,5-dichloro-2-*n*-octyl-3-(2H)-*iso*thiazolin-3-one)



TCMTB

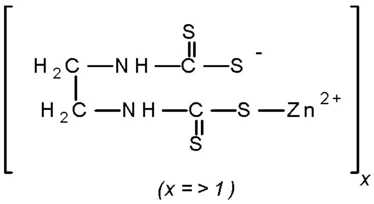
(2-(thiocyanomethylthio)-benzothiazole)

**Figure A5.1.** Continued.



zinc pyrithione

(*bis*(1-hydroxy-2(1H)-pyridethionato-O,S)-T-4 zinc)



Zineb

(zinc ethylene*bis*-(dithiocarbamate))

The fate and behaviour of any compound released into the environment is subject to a number of complex processes. The processes most likely to affect the fate and behaviour of booster biocides are transport, transformation, degradation, cross-media partitioning, and bioaccumulation. The group of compounds collectively termed booster biocides vary considerably in their chemical and physical characteristics (Table A5.1). Consequently, the processes that control their fate and behaviour will differ and will inevitably lead to differences in environmental persistence and likely harm to non-target species. A common misconception is that very little is known about the fate and behaviour of these compounds. Reviews on the fate and effects of Irgarol 1051 (Hall *et al.*, 1999), chlorothalonil (Caux *et al.*, 1996), SeaNine 211 and ZPT have been performed (Madsen *et al.*, 2000) and data from these papers are used to complement this review. Although we are far from completely understanding the overall threat that they may pose to the aquatic environment, preliminary data are available on the basic mechanisms that regulate environmental fate. In order to provide a point of reference for the data currently available, this report reviews data on the release, occurrence, transport, transformation, degradation, cross-media transfer, volatilization, bioaccumulation, and aquatic toxicology of organic antifouling paint booster biocides currently available in the public domain.

**Table A5.1.** Physico-chemical properties of common antifouling paint booster biocides.

| Biocide | Log $K_{ow}$ | $K_{oc}$ (soil) | $K_{oc}$ (marine sediments) | $K_d$ | Solubility (mg $l^{-1}$) | Calculated Log $K_{oc}$* |
|---|---|---|---|---|---|---|
| **Chlorothalonil** | **4.0** | **1,300–14,000** | | | **0.9** | **3.8** |
| **Dichlofluanid** | **3.7** | | | | **1.3** | **3.5** |
| **Diuron** | **2.8** | **251–1010** | | | **35** | **2.6** |
| **Irgarol 1051** | **3.95** | **820** | **990** | **3.49** | **7** | **3.7** |
| **SeaNine 211** | **2.8** | **7865** | **15441** | | **14** | **2.6** |
| **TCMTB** | **3.3** | **282–2270** | | **27** | **10.4** | **3.1** |
| **Zinc pyrithione** | **0.9** | **10633** | **10633** | | **8** | **0.7** |
| **Zineb** | **0.8** | **1230** | | | **0.07–10** | **0.6** |

* Log $K_{oc}$ = log $K_{ow}$ − 0.21 (Karickhoff, 1981).

## 2 OVERVIEW OF AVAILABLE DATA

### Release from the paint surface

An important factor in assessing the environmental risk posed by biocidal antifouling additives is the rate at which the compound is released from the paint surface. Many regulatory bodies, including the UK Health and Safety Executive (HSE) and the US Environmental Protection Agency (US EPA), request release rate data generated using laboratory-based protocols. This forms part of a risk assessment performed during the registration process (e.g., The UK Control of Pesticides Regulations, 1986 and European Commission Biocidal Products Directive 98/8/EC).

Two standardized protocols are currently employed to generate release rate data. The US EPA has adopted the American Society of Testing Materials (ASTM) method (D5108–80), whilst the UK HSE and many other European regulatory bodies have adopted the International Standards Organisation (ISO) method (ISO/DIS 15181–1,2) for assessing leach rates under standard conditions. Both test systems consist of a polycarbonate cylinder painted with the candidate paint.

The cylinder is rotated in a baffled beaker containing synthetic sea water at 60 rpm and concentrations of biocide are measured periodically to calculate the release in terms of micrograms of active ingredient released from each square centimetre of painted surface per day ($\mu$g cm$^{-2}$ day$^{-1}$). The method is designed to allow close control of pH, temperature, and salinity and provide a comparable laboratory measurement for different formulations.

If laboratory-based release rate measurements are to be used in environmental risk assessments, then they need to be representative of actual environmental conditions. A study commissioned by the UK HSE showed that the ISO protocol could be used to obtain a release rate for a number of booster biocides (Table A5.2) (Thomas and Waldock, 1999; Thomas *et al.*, 1999a, 2001a). When these data were compared with those determined using a flume system, designed to simulate environmental conditions, the release rates determined using the flume were consistently lower than those obtained using the ISO method for all biocides, other than dichlofluanid and TCMS pyridine. It was observed that changes in salinity, temperature, vessel speed, pH, and the concentration of suspended particulate matter had very little or no effect on the release rate of all biocides tested. The effects of longer-term changes (three months) in temperature and salinity on Irgarol 1051 release was more pronounced, with an increased Irgarol 1051 release of 0.4–2.0 $\mu$g cm$^{-2}$ day$^{-1}$ when the temperature was increased (15–25 °C).

**Table A5.2.** Comparison of biocide release rates from antifouling coatings.

| Biocide | Alternative trade name | Release Rate ($\mu$g cm$^{-2}$ day$^{-1}$) | |
|---|---|---|---|
| | | ISO test system | Flume system |
| **Cuprous oxide** | | **25–40**[a] | **18.6±6.5** |
| **TBT** | | **1.5–4.0**[a] | **1.6** |
| **Irgarol 1051** | | **5.0** | **2.6**[b] |
| **Diuron** | | **3.3** | **0.8** |
| **Dichlofluanid** | **Preventol A4, Euparen** | **0.6** | **1.7** |
| **Zinc pyrithione** | **Zinc Omadine** | **3.3** | **-**[c] |
| **SeaNine 211** | **Sea-Nine 211, DCOI** | **2.9** | **3.0** |
| **TCMTB** | **Busan** | **-**[c] | **0.9** |
| **TCMS pyridine** | **Densil S** | **0.6** | **3.8** |

Table reproduced from Thomas and Waldock (1999)[a]Obtained from Thomas *et al.* (1999a) for comparison. [b]Mean of two data points. [c]No data available.

## 3 OCCURRENCE

### Irgarol 1051

The *s*-triazine herbicide Irgarol 1051 was the first booster biocide to gain prominence as an environmental contaminant. The presence of Irgarol 1051 was reported in 1993 in the surface waters of marinas on the Côte d'Azur, France by Readman *et al.* (1993) at concentrations of up to 1700 ng l$^{-1}$. Since 1993, the occurrence of Irgarol 1051 has been reported in a number of other European countries, Japan, and Australia (Table A5.3). Irgarol 1051 is not currently used in the US or Canada.

**Table A5.3.** Summary of Irgarol 1051 occurrence data.

| Region | Irgarol 1051 concentration (ng l$^{-1}$) | | | References |
|---|---|---|---|---|
| | Marinas | Estuaries | Coastal | |
| **Côte d'Azur, France** | **5–1693** | | **< 5–48** | **Readman *et al.*, 1993** |
| **Southeast England** | **52–500** | **4–190** | **< 2–11** | **Gough *et al.*, 1994** |
| **Côte d'Azur, France** | **14–640** | | **< 105–17** | **Tolosa *et al.*, 1996** |
| **Northwest Sweden** | **30–400** | | **n.d.** | **Dahl and Blanck, 1996** |
| **Western Scheldt, NL** | | **1.6–10** | | **Steen *et al.*, 1996** |
| **Lake Geneva, Switzerland** | **3–148** | | | **Tóth *et al.*, 1996** |
| **Humber, Northeast UK** | **169–682** | **< 1–39** | | **Zhou *et al.*, 1996** |
| **Mediterranean, Spain** | **7–325** | | | **Ferrer *et al.*, 1997** |
| **Plymouth Sound, UK** | **26–107** | **9–24** | **< 1–1** | **Scarlett *et al.*, 1997** |
| **Japan** | **13–264** | | | **Liu *et al.*, 1999a** |
| **North Sea, Germany** | **11–440** | | | **Biselli *et al.*, 2000** |
| **Sas van Gent and Schaar van Ouden, NL** | | **5–42** | | **Hall *et al.*, 1999** |
| **Stockholm Archipelago, Sweden** | **5–130** | | **4–6** | **Haglund *et al.*, 2001** |
| **Southern Coast, UK** | **< 1–1421** | **< 1–32** | **< 1–1** | **Thomas *et al.*, 2001b** |

In the UK, Irgarol 1051 has been found in areas of high boating activity on the Southeast Coast, the Humber estuary, Plymouth Sound, Southampton Water, and the Crouch estuary (Table A5.3). Similar concentrations have been reported in the Mediterranean. Other areas of Europe where the occurrence of Irgarol 1051 has been reported include Lake Geneva, Switzerland; the west coast of Sweden; Stockholm Archipelago, Sweden; the Western Scheldt, The Netherlands; Sas van Gent and Schaar van Ouden, The Netherlands; and the Baltic Sea and North Sea marinas of Germany. Two studies have been conducted outside Europe. Scarlett *et al.* (1999) studied the Irgarol 1051 concentration in coastal water seagrasses from Queensland, Australia, and reported concentrations of up to 118 ng g$^{-1}$ wet weight leaf tissue. Liu *et al.* (1999a) studied water concentrations at marinas and ports in Japan and Canada. In Japanese waters, concentrations of between 13 ng l$^{-1}$ and 264 ng l$^{-1}$ in marinas, up to 20 ng l$^{-1}$ in ports, and up to 142 ng l$^{-1}$ in fishery harbours have been reported. It has also been reported that concentrations of up to 500 ng l$^{-1}$ have been found within Bermudan waters (Scarlett *et al.*, 1999).

### Diuron

Diuron (dichlorophenyl dimethylurea), a phenylurea herbicide, has been in use since the 1950s. Predominantly this use has been associated with weed control in non-agricultural applications. Several studies have investigated the impact of non-antifouling use on diuron release into the aquatic environment (Albanis *et al.*, 1994); however, the assessment of inputs from antifouling applications has been restricted to three studies. Dahl and Blanck (1996) reported diuron concentrations in Swedish marinas of between 10 ng $l^{-1}$ and 100 ng $l^{-1}$. A study of marinas on the Spanish Mediterranean coast reported similar concentrations (10–100 ng $l^{-1}$), whilst a study in the UK reported much higher concentrations in marinas (4–6742 ng $l^{-1}$) (Thomas *et al.*, 1999b, 2001b). This study also reported diuron concentrations of between 5 ng $l^{-1}$ and 226 ng $l^{-1}$ in water samples collected from estuaries, between 1 ng $l^{-1}$ and 45 ng $l^{-1}$ in coastal waters, and < 8 ng $l^{-1}$ offshore.

### SeaNine 211

Only one study has reported the environmental occurrence of SeaNine 211. R.J.C.A. Steen (pers. comm.) reported the monitoring of SeaNine 211 in a Danish harbour following the application to two Danish naval vessels of antifouling paint containing this biocide. It was reported that there was a strong decline in SeaNine 211 concentration as a function of the distance from the ship. Concentrations ranged from 283 ng $l^{-1}$ near the ship, rapidly declining to < 5 ng $l^{-1}$. A study by Thomas *et al.* (1999b, 2001b) did not detect SeaNine 211 in marinas on the south coast of the UK in 1998.

### TCMTB

Environmental data are available from the study of point discharges relating to the use of TCMTB as a fungicidal agent in seed coatings and timber treatments (Walsh and O'Halloran, 1997). Few studies have assessed its occurrence due to antifouling use. Thomas (1998) reported that no TCMTB was found in UK marinas, whilst Ferrer and Barceló (1999) found that the same was also true for Mediterranean marinas.

### Dichlofluanid, chlorothalonil, TCMS pyridine, and copper/zinc pyrithione

All the studies that have assessed the occurrence of dichlofluanid, chlorothalonil, TCMS pyridine, and zinc pyrithione in the aquatic environment through their use as antifouling paint booster biocides have failed to demonstrate their presence.

Thomas (1999) and Thomas *et al.* (1999b) looked for copper/zinc pyrithione, dichlofluanid, chlorothalonil, and TCMS pyridine concentrations in UK marinas.

Concentrations of these biocides were found to be below the limits of detection for the methods employed (< 5 ng $l^{-1}$). Ferrer and Barceló (1999) also reported the absence of dichlofluanid and chlorothalonil in waters collected from Mediterranean marinas.

## 4 CHEMICAL TRANSFORMATION

The only biocide that is known to have the potential for chemical transformation is zinc pyrithione (ZPT). ZPT is the zinc chelate of 2-pyridinethiol-1-oxide (Figure A5.2). It has been reported that ZPT can transchelate with other cationic metals (e.g., $Cu^{2+}$). Copper pyrithione (CPT), with the lowest dissociation constant, would be likely to be the most abundant (Turley *et al.*, 2000).

## 5 DEGRADATION

A summary of the degradation half-lives ($t_{½}$), mode of degradation, and principal degradation products for the eight booster biocides used in the UK is presented in Table A5.4. Only one study published to date has compared the relative degradability of booster biocides. Callow and Willingham (1996) studied the disappearance of SeaNine 211, Irgarol 1051, diuron, and chlorothalonil from natural sea water, containing the diatom *Amphora coeffeaeformis.*

The study concluded that SeaNine 211 was easily degraded, whilst chlorothalonil was unlikely to persist in the water column. The study also concluded that Irgarol 1051 and diuron were not easily degraded after eight weeks. A similar study assessed the effects of SeaNine 211 and ZPT degradation on their acute toxicity to *Arcartia tonsa* (Madsen *et al.*, 2000). It was demonstrated that both biocides are rapidly detoxified by either rapid degradation or partitioning to sediments.

**Figure A5.2.** Transchelation of zinc pyrithione to copper pyrithione.

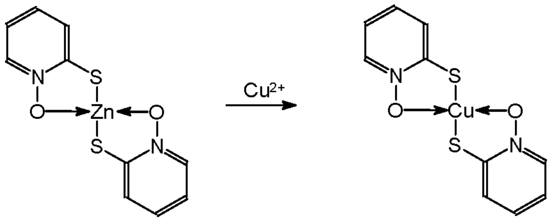


**Table A5.4.** Degradation data for antifouling paint booster biocides.

| Biocide | Half-life in natural sea water | Principal mode of degradation | Principal degradation products |
|---|---|---|---|
| Chlorothalonil | 1.8 days | Biotic degradation | 4-hydroxy-2,5,6-trichlorisophthalonitrile, 5-cyano-4,6,7-trichloro-2H-1,2-benzisothiazol-3-one |
| Dichlofluanid | 18 h | - | - |
| Diuron | - | Biotic degradation | 3-(3,4-dichlorophenyl)-1-methylurea and dichlorophenyl urea |
| Irgarol 1051 | 100 days | - | GS26575<br>CGA234575<br>CGA234576 |
| SeaNine 211 | < 24 h | Biotic degradation | N-(octyl)carbamic acid |
| TCMTB | 740 h | Hydrolysis | 2-mercaptobenzothiazole (MBT),<br>2-(methylthio)benzothiazole (MTBT) |
| Zinc pyrithione | < 24 h | Photolysis | 2-pyridine sulphonic acid |
| Zineb | 96 h | Hydrolysis | ethylenethioura (ETU), DIDT, ethylene diisothiocyanate (EDI) |

### Irgarol 1051

Irgarol 1051 is not considered to be easily degraded in natural sea water and has a half-life ($t_{½}$) of about one hundred days (Scarlett *et al.*, 1997; Ciba Geigy, 1995). Four studies have reported the degradation of Irgarol 1051 (Liu *et al.*, 1997, 1999b; Okamura *et al.*, 1999; Hall *et al.*, 1999). Biodegradation (Liu *et al.*, 1997), photodegradation (Okamura *et al.*, 1999), and chemical hydrolysis (Liu *et al.*, 1999b) of Irgarol 1051 all result in *n*-dealkylation to yield 2-methylthio-4-tert-butylamino-6-amino-s-triazine (GS26575) as the principal degradation product (Figure A5.3). Research suggests that GS26575 may be a stable degradation product of Irgarol 1051 (Liu *et al.*, 1997; Okamura *et al.*, 2000b), implying a potential for accumulation. However, Hall *et al.* (1999) reported a rapid decline in GS26575 concentration within a marine mesocosm study, and very little partition to the sediment phase; these authors suggested a similar half-life to that of Irgarol 1051.

The presence of GS26575 has also been reported in Japanese (Okamura *et al.*, 2000b), Spanish (Ferrer and Barceló (1999), and UK marinas (Thomas *et al.*, 2000).

## Diuron

Diuron is also considered to be relatively persistent in sea water (Callow and Willingham, 1996), with no half-life data available. Aerobic degradation of diuron is reported to result in the formation of 1-(3,4-dichlorophenyl)-3-methylurea and 1-(3,4-dichlorophenyl)urea, whilst anaerobic degradation in sediments results in the formation of 1-(3-chlorophenyl)-3,1-dimethylurea (Ellis and Camper, 1982) (Figure A5.4).

**Figure A5.3.** Degradation of Irgarol 1051.

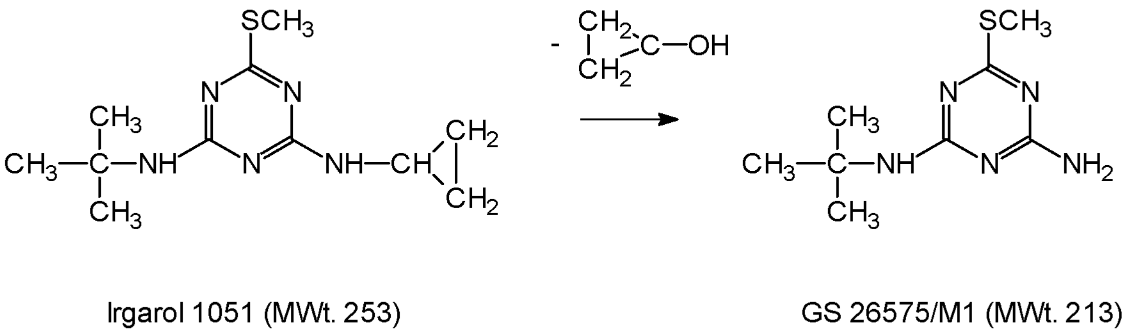
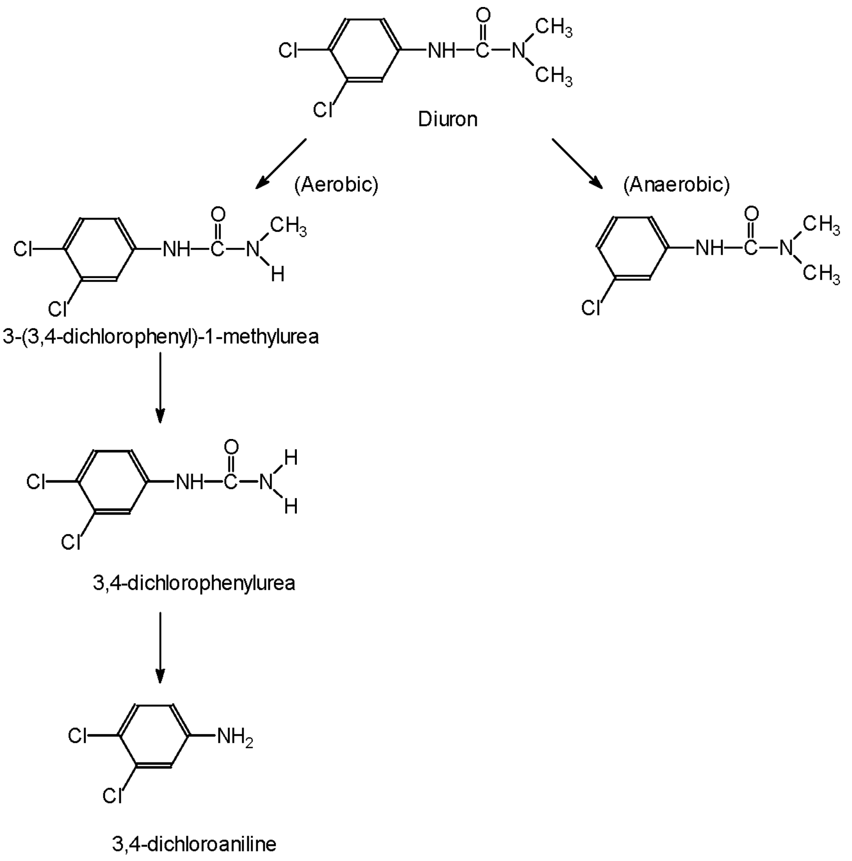


**Figure A5.4.** Proposed degradation pathway for diuron under aerobic and anaerobic conditions (Ellis and Camper, 1982).



SeaNine 211

SeaNine 211 degrades rapidly in natural sea water (Callow and Willingham, 1996) and sediment (A.H. Jacobson, pers. comm.; Environment Australia, 1999). Degradation half-lives have been determined for SeaNine 211 in a number of environmental matrices (Table A5.5).

Biological degradation is considered to be over 200 times faster than hydrolysis or photolysis (Willingham and Jacobson, 1996; Jacobson *et al.*, pers. comm.). Biodegradation involves cleavage of the isothiazolone ring and subsequent oxidation of alkyl metabolites. The primary degradation products are N-octyl oxamic acid, 4,5-dichloro-thiazole and N-octyl carbamic acid (Figure A5.5).

**Figure A5.5.** Proposed metabolic pathway for SeaNine 211 under aerobic conditions (Environment Australia, 1999).

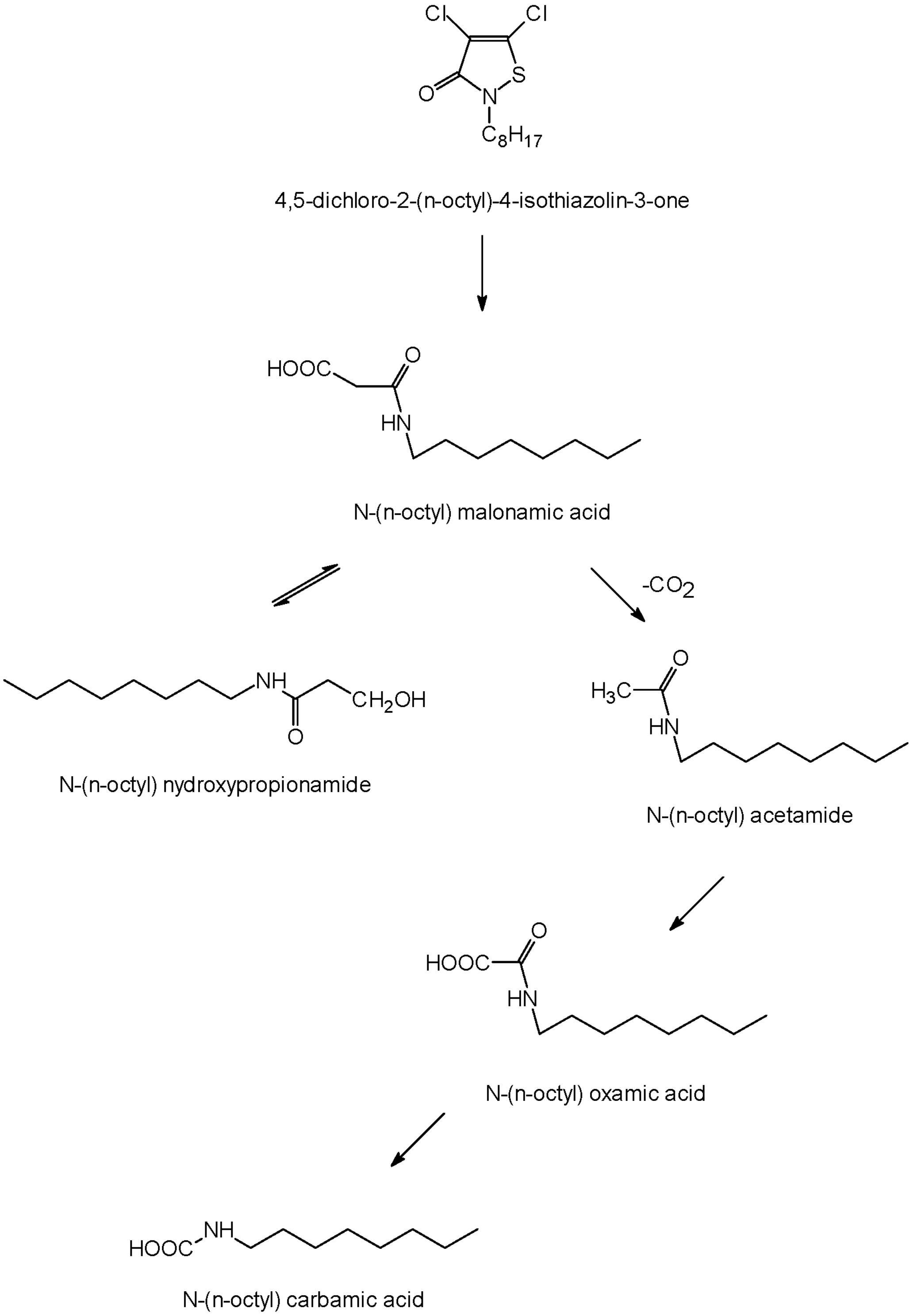


**Table A5.5.** Summary of SeaNine 211 half-lives in various environmental matrices.

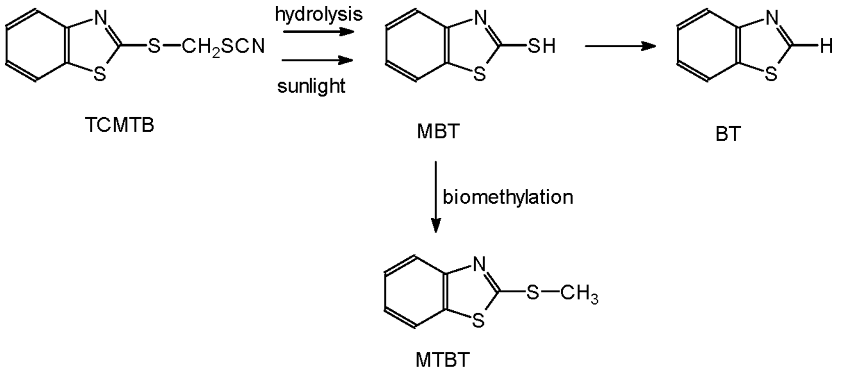
| **Matrix** | **Half-life (h)** |
|---|---|
| Photolysis | 322 |
| Hydrolysis | |
| pH 5 | 216 |
| pH 7 | > 720 |
| pH 9 | 288 |
| Aerobic aquatic microcosm (25 °C) | < 1 |
| Anaerobic aquatic microcosm (25 °C) | < 1 |
| Sea water | < 24 |
| Synthetic sea water | > 720 |
| Synthetic sea water + algae | < 3 |
| Reagent water | > 720 |

Reproduced from Willingham and Jacobson (1996).

## TCMTB

TCMTB is considered unlikely to persist in the environment (Brownlee *et al.*, 1992). Laboratory experiments have shown that TCMTB rapidly degrades to 2-mercaptobenzothiazole (MBT) and 2-(methylthio)benzothiazole (MTBT). This probably occurs through hydrolysis, followed by biological methylation (Figure A5.6). The half-life of TCMTB in natural sea water has been reported as 740 h. TCMTB is also degraded rapidly (< 0.5 h) by photolysis (Brownlee *et al.*, 1992).

**Figure A5.6.** Proposed degradation pathway for TCMTB (Brownlee *et al.*, 1992).



## Zinc pyrithione and copper pyrithione

Zinc pyrithione (ZPT) is rapidly degraded in natural sea water, with a reported half-life of < 24 h (Turley *et al.*, 2000). ZPT photolysis is extremely rapid ($t_{½}$ < 1 h), whilst, by contrast, hydrolysis half-lives range from 96–120 days. Both aerobic and anaerobic biotic degradation also appear to be very rapid ($t_{½}$ < 2 h). The primary degradation product of ZPT has been reported to be 2-pyridine sulfonic acid with $Zn^{2+}$ released into the aqueous phase. Copper pyrithione (CPT) is also rapidly degraded in natural sea water with a reported half-life of 0.5 h (Turley *et al.*, 2000).

Dichlofluanid

Only one study has reported on the degradation of dichlofluanid. Callow and Finlay (1995) reported on a bioassay method to measure the degradation of antifouling biocides. In natural sea water at 25 °C, degradation was complete after 72 h and a half-life of 18 h was calculated.

Chlorothalonil

Degradation half-lives of between 4 h and 150 h have been reported for chlorothalonil in natural fresh water (Davies, 1987) and between 1.8 days and 8 days in natural estuarine water and sediment water test systems (Walker *et al.*, 1988). A bioassay system to measure the degradation of antifouling biocides showed much slower degradation in natural sea water at 25 °C, reporting a half-life of approximately 8 weeks (Callow and Willingham, 1996).

Zineb and Mancozeb

Zineb is known to degrade rapidly, through hydrolysis, to 5,6-dihydro-3H-imidazo (2,1-c)-1,2,4-dithiazole-3-thione (DIDT), ethylene diisothiocyanate (EDI), and ethylenethiourea (ETU) (Hunter and Evans, 1991; HSDB, 1997). A half-life of 96 h has been reported at pH 10 and a temperature of 20 °C (Klisenko and Vekshtein, 1970). Mancozeb is considered to have a similar degradation rate to that of Zineb.

Thiram

It is reported that Thiram is rapidly broken down by hydrolysis and photodegradation, especially under acidic conditions. No conditions were reported (Extoxnet, 2000).

## 6 SEDIMENT/WATER PARTITIONING

The partitioning of contaminants between aquatic compartments has implications for other fate mechanisms discussed within this review. The ability of a compound to partition between compartments is determined by its adsorption coefficient ($K_d$) and partition coefficient related to organic carbon ($K_{OC}$). It is considered that organic contaminants with a $K_d < 10^5$ exist mainly in the dissolved phase (Duinker, 1986). Another factor, specific to antifouling paint biocides, is that the biocides may become incorporated into sediments as paint particles from boats and ships that have been hosed down prior to repainting. In such cases, the $K_d$ and $K_{OC}$ have very little influence on the presence of booster biocides in sediments.

Irgarol 1051

A $K_d$ of 3100 l kg$^{-1}$ and a $K_{OC}$ of between 251 l kg$^{-1}$ and 63,095 l kg$^{-1}$ have been reported for Irgarol 1051 (Tolosa *et al.*, 1996; Biselli *et al.*, 2000), which suggest that Irgarol 1051 will mainly be associated with the dissolved phase. Calculations using the Mackay fugacity model estimate that 4.4 % of the Irgarol 1051 present in marina waters will partition to sediments (Rogers *et al.*, 1996). Irgarol 1051 has been reported in sediments collected from marinas in the UK (< 10–132 ng g$^{-1}$, 1993; < 1–30 ng g$^{-1}$) (Gough *et al.*, 1994; Thomas *et al.*, 1999b, 2001b), Switzerland (2.5–8 ng g$^{-1}$) (Tóth *et al.*, 1996), Sweden (< 10 ng g$^{-1}$) (Hall *et al.*, 1999), and Germany (< 1–220 ng g$^{-1}$) (Biselli *et al.*, 2000). Two studies have also reported the determination of the Irgarol 1051 metabolite GS26575 in sediments. Thomas *et al.* (2000) reported GS26575 concentrations of < 0.4–5 ng g$^{-1}$ in UK marinas, whilst Hall *et al.* (2000) reported concentrations < 10 ng g$^{-1}$.

Diuron

Diuron is relatively soluble in water (35 mg l$^{-1}$), with a log $K_{OW}$ of 2.8. Diuron is reported to have a $K_d$ of 8.9 ± 13.4 l kg$^{-1}$ (Table A5.1) (House *et al.*, 1997), which suggests that diuron will be predominantly found in the dissolved phase and only weakly adsorbed to sediments. Thomas *et al.* (2000) reported the presence of diuron in an enclosed UK marina (1420 ng g$^{-1}$). However, this was thought to be due to the presence of paint particles within the sample.

SeaNine 211

SeaNine 211 also has a reported log $K_{OW}$ of 2.8 and a solubility of 14 mg $l^{-1}$. A $K_d$ of 625 l $kg^{-1}$ has been reported for SeaNine 211 in aquatic sediments (Table A5.1). However, SeaNine 211 has also been reported to bind strongly and essentially irreversibly to sediment (Willingham and Jacobson, 1996).

TCMTB

A study to assess the sediment/water partitioning of TCMTB failed to determine any partition coefficients since the TCMTB completely degraded to MTBT. The same study calculated a log $K_{OC}$ of 2.74 and a $K_d$ of 27 for a sediment containing 5 % organic carbon (Brownlee *et al.*, 1992).

Dichlofluanid

No reported data were found on the partitioning of dichlofluanid.

Zinc pyrithione

ZPT is considered to bind strongly to sediments; however, due to its short half-life, the influence of partition on the fate of ZPT is considered insignificant (Turley *et al.*, 2000).

Chlorothalonil

The adsorption of chlorothalonil to sediments is considered to be an important route of removal from the dissolved phase (Davies, 1987; Walker *et al.*, 1988). Once bound to the sediment, chlorothalonil is thought to be biodegraded.

Zineb

It is reported that Zineb rapidly absorbs to sediments, leading to faster degradation rates (HSDB, 1997).

## 7 VOLATILIZATION

The ability of a compound to partition across the air-water interface is determined by its air-water partition coefficient, referred to as Henry's law constant. Henry's law constant was only available for chlorothalonil. Estimated constants for other biocides suggest that for all the biocides listed in Table A5.6, volatilization is not an important fate mechanism.

## 8 BIOACCUMULATION

There have been very few reports of studies relating to the biological uptake and bioaccumulation of booster biocides. Biological uptake of Irgarol 1051 has been shown to occur in freshwater macrophytes (Tóth *et al.*, 1996), with bioconcentration factors (BCFs) of up to 30,000 times, and within marine macrophytes (Scarlett *et al.*, 1997, 1999). Predicted BCFs of 75 and 22 calculated for diuron suggest that the compound would not appreciably bioaccumulate in aquatic organisms (Kenaga, 1980). Bioaccumulation of SeaNine 211 in fish is considered to be very low (< 1 % parent compound) (Willingham and Jacobson, 1996). Metabolism of SeaNine 211 is considered to be rapid, with the metabolites being associated with proteins. Both Zineb and Thiram are reported not to bioaccumulate (HSDB, 1997; Verschueren, 1996). No pertinent data were available for any of the other biocides.

## 9 TRANSPORT

There are three main processes that can transport a chemical within the aquatic environment: bulk transport with dispersion, sedimentation, and diffusion. Bulk transport with dispersion refers to the dispersion and dilution of a compound in a body of water. Sedimentation refers to the transport of a compound whilst it is associated with bottom and suspended sediments, and diffusion refers to the movement of molecules from areas of high concentration to areas of low concentration. Very little information on these three processes is available for antifouling paint booster biocides. From the occurrence data described above, it appears that these compounds mainly occur in areas of high boating activity and/or limited water exchange and that, as they are transported to offshore areas, dilution plays an important role since the concentrations of booster biocides in offshore waters are low (Thomas *et al.*, 1999b).

Another potential transport route for booster biocides is through the mechanical disposal of dredged material from harbours, docks, and marinas. This route is dependent on the fate mechanisms discussed, such as cross-media partition and persistence. Harbour, dock, and marina sediments may also contain antifouling paint particles that will continue to release active biocides. The disposal of sediments contaminated in such a way may facilitate the transport of biocides into other previously unaffected areas.

**Table A5.6.** Measured and estimated Henry's law constant for selected booster biocides.

| **Biocide** | **Henry's law constant (atm $m^3$ $mol^{-1}$)** | **Vapour pressure (atm @ 25 °C)** | **Solubility (mol $m^{-3}$)** | **References** |
|---|---|---|---|---|
| Chlorothalonil | $2 \times 10^{-7}$ | - | - | Caux *et al.*, 1996 |
| Dichlofluanid | †$9.5 \times 10^{-8}$ | $3.7 \times 10^{-10}$ | $3.9 \times 10^{-3}$ | HSDB, 1997 |
| Diuron | †$2 \times 10^{-6}$ | $3.6 \times 10^{-7}$ | 0.18 | HSDB, 1997 |
| Irgarol 1051 | †$2.5 \times 10^{-8}$ | $8.7 \times 10^{-10}$ | 0.035 | Hall *et al.*, 1999 |
| SeaNine 211 | †$5.1 \times 10^{-7}$ | $9.7 \times 10^{-9}$ | 0.019 | Australian EPA, 1999 |
| TCMTB | †$2.7 \times 10^{-7}$ | $1.17 \times 10^{-8}$ | 0.044 | HSDB, 1997 |
| Thiram | †$3.1 \times 10^{-7}$ | $2.3 \times 10^{-8}$ | 0.075 | HSDB, 1997 |
| Zinc pyrithione | Non- volatile | - | - | Madsen *et al.*, 2000 |

† Estimated from Henry's law constant ($H$) = P/S; where P = vapour pressure (atm) and S = solubility in water (mol $m^{-3}$).

## 10 AQUATIC TOXICOLOGY

As would be expected from a group of compounds that differ both in physico-chemical properties and modes of toxic effect, the toxicity of each compound is also very different (Table A5.7a–f). Aquatic toxicity data are available for many of the commonly used biocides (e.g., Irgarol 1051 and diuron) as well as the most recently developed biocides (e.g., SeaNine 211 and zinc pyrithione). Examples of toxicity data for Irgarol 1051, diuron, SeaNine 211, zinc pyrithione, and chlorothalonil are presented in Table A5.7a–f. Much of the data are public domain data that have previously been submitted to regulatory authorities for risk assessments. These data are generally based upon acute toxicity tests performed on a small number of species that allow comparative risk assessments to be performed. Chronic data are limited. An example by Dahl and Blanck (1996) showed that Irgarol 1051 had chronic effects on periphyton communities at concentrations in the range 0.06–0.25 µg $l^{-1}$. Such studies are occasional, whilst very few data are available on the toxicity of the products of degradation. No data are available on whether any of these compounds disrupt the endocrine system of organisms or whether they have joint modes of action. However, current projects (see below) are addressing these issues.

Two projects that are currently addressing the gaps in the data available are the multi-agency, EU-funded, "Assessment of antifouling agents in coastal environments" project (ACE) (www.pml.ac.uk/ace/) and the UK Ministry of Agriculture, Fisheries and Food (MAFF)-funded project "Fate and bioavailability of antifouling booster biocides in harbour, dock and marina dredge material" (www.maff.gov.uk/research/summary/obj2.htm).

## 11 CONCLUSIONS

Due to the wide range of environmental properties exhibited within the group of antifouling paint booster biocides included in this review, it is clear that the fate and behaviour of each one will differ considerably. Data are available for the biocides most commonly used in Europe and North America (Irgarol 1051, SeaNine 211, zinc pyrithione), whilst very little or no data are available for other biocides. Gaps in the data available also make it difficult to accurately predict equilibrium values for water, sediment, and biota at sites where regulators may wish, for example, to protect sensitive environments close to moored vessels. From the degradation data, it appears that chlorothalonil, dichlofluanid, SeaNine 211, zinc pyrithione, and Zineb degrade rapidly ($t_{½}$ < 4 days), whilst Irgarol 1051 and diuron seem more persistent. However, very few data are available on the fate, behaviour, and toxicity of the products of degradation, although data are available on the comparative phytotoxicity of Irgarol 1051 and GS26575 (Okamura *et al.*, 2000). Chlorothalonil, dichlofluanid, SeaNine 211, and Zineb are reported to have a high affinity for particulate material.

Few data are available on the biological uptake of booster biocides or their degradation products, although BCF data are available for risk assessments performed by national regulatory bodies (e.g., UK HSE, US EPA, and Australian EA). All the above-mentioned properties have an important role in the transport and migration of these compounds from their point of release and more information is required to underpin risk assessments.

The other large gap in our understanding is the fate of these compounds when associated with particulate paint waste. In the UK, it is still common practice for small boats to be scrubbed down and repainted on the banks of estuaries. In such cases, the complex science involved in understanding partition, degradation, and transformation becomes a secondary need to that of tracking the movement of particles. Each particle becomes a new site for release of the biocide and the release rate within a sediment is likely to be very different from that of a painted hull. Current research programmes at CEFAS are aimed at predicting the movement of particle-associated biocides, and providing better information on the release of actives from complex media and the subsequent fate and effects of released products. These studies complement on-going work on TBT release from contaminated sediments and will allow the risk posed by each of these compounds to be fully assessed, and so determine whether they offer a safe alternative to triorganotin antifoulants.

## 12 ACKNOWLEDGEMENT

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**Table A5.7a.** Aquatic toxicology data for Irgarol 1051.

| **Species** | **Parameter, Endpoint** | **Exposure time** | **Result (ng l$^{-1}$)** | **Reference** |
|---|---|---|---|---|
| Algae | | | | |
| ***Anabaena flos-aquae*** | Growth, EC50 | 72–120 h | 2070–> 2870 | Hall *et al.*, 1999 |
| ***Selenastrium caprocornutum*** | Growth, EC50 | 72–120 h | 1460–1580 | Hall *et al.*, 1999 |
| ***Dunaliella tertiolecta*** | Growth, EC50 | 120 h | 560 | Hall *et al.*, 1999 |
| ***Isochrysis galbana*** | Growth, EC50 | 120 h | 440 | Hall *et al.*, 1999 |
| ***Skeletonema costatum*** | Growth, EC50 | 72–120 h | 357–430 | Hall *et al.*, 1999 |
| ***Chlorococcum* sp.** | Growth, EC50 | 120 h | 420 | Hall *et al.*, 1999 |
| ***Navicula pelliculosa*** | Growth, EC50 | 72–120 h | 58–136 | Hall *et al.*, 1999 |
| ***Selenastrum capricornutum*** | Growth, EC50 | 72 h | 3680 | Hall *et al.*, 1999 |
| ***Scenedesmus subspicatus*** | Growth, EC50 | 72 h | 4030 | Hall *et al.*, 1999 |
| ***Lemna gibba*** | Growth, EC50 | 4–14 days | 1780–> 5860 | Hall *et al.*, 1999 |
| Periphyton communities | Community structure (EC50) | 21 days | 1390 | Dahl & Blanck, 1996 |
| | Long-term photosynthesis (EC50) | 21 days | 1210 | Dahl & Blanck, 1996 |
| | Community structure (NOEC) | 21 days | 64 | Dahl & Blanck, 1996 |
| | Long-term photosynthesis (NOEC) | 21 days | 64 | Dahl & Blanck, 1996 |
| ***Closterium ehrenbergii*** | Growth, EC50 | 5 days | 2500 | Okamura *et al.*, 2000b |
| Macroalgae | | | | |
| ***Enteromorpha intestinalis*** | Growth, EC50 | 72 h | 2500 | Scarlett *et al.*, 1997 |
| ***Porphyra yezoensis*** | LC50 | 4 days | 5,000,000 | Okamura *et al.*, 2000b |
| ***Eisenia bicyclis*** | Growth, EC50 | 7 days | 5900 | Okamura *et al.*, 2000b |
| ***Zostera marina*** | Photosynthesis, EC50 | 10 days | 2500 | Scarlett *et al.*, 1999 |
| Fish | | | | |
| ***Oncorhynchus mykiss*** | LC50 | 96 h | 790,000 | Hall *et al.*, 1999 |
| | Hatchability (NOEC) | | 184,000 | Hall *et al.*, 1999 |
| | Survival (NOEC) | 60 days | 184,000 | Hall *et al.*, 1999 |
| | Growth (NOEC) | 60 days | 4020 | Hall *et al.*, 1999 |
| ***Menidia beryllina*** | LC50 | 96 h | 1,580,000 | Hall *et al.*, 1999 |
| ***Lepomis macrochirus*** | LC50 | 96 h | 2,600,000 | Hall *et al.*, 1999 |
| ***Crypnodon variegatus*** | LC50 | 96 h | 3,500,000 | Hall *et al.*, 1999 |
| Molluscs | | | | |
| ***Crassostrea virginica*** | EC50 | 48 h | 3,200,000 | Hall *et al.*, 1999 |
| Crustaceans | | | | |
| ***Daphnia magna*** | EC50 | 48 h | 5,300,000 | Hall *et al.*, 1999 |
| ***Daphnia pulex*** | LC50 | 24 h | 5,700,000 | Okamura *et al.*, 2000b |
| ***Thamnocepharus platyurus*** | LC50 | 24 h | 12,000,000 | Okamura *et al.*, 2000b |
| ***Artemia salina*** | LC50 | 24 h | > 40,000,000 | Okamura *et al.*, 2000b |
| ***Mysidopsis bahia*** | LC50 | 96 h | 400,000 | Hall *et al.*, 1999 |
| | Growth (NOEC) | 28 days | 110,000 | Hall *et al.*, 1999 |
| | Survival (NOEC) | 28 days | 260,000 | Hall *et al.*, 1999 |
| | Reproduction (NOEC) | 28 days | 260,000 | Hall *et al.*, 1999 |

NOEC: no observed effect concentration; LC50: lethal concentration to 50%; EC50: median effective concentration

**Table A5.7b.** Aquatic toxicology data for GS26575.

| **Species** | **Endpoint** | **Exposure time** | **Result (ng l$^{-1}$)** | **Reference** |
|---|---|---|---|---|
| Algae | | | | |
| *Skeletonema costatum* | EC50 | 72–120 h | 8,110–16,150 | Hall *et al.*, 1999 |
| *Closterium ehrenbergii* | EC50 | 5 days | 8300 | Okamura *et al.*, 2000b |
| Macroalgae | | | | |
| *Porphyra yezoensis* | LC50 | 4 days | 6,500,000 | Okamura *et al.*, 2000b |
| *Artemia salina* | LC50 | 24 h | > 40,000,000 | Okamura *et al.*, 2000b |
| Crustaceans | | | | |
| *Daphnia magna* | EC50 | 48 h | 5,300,000 | Hall *et al.*, 1999 |
| *Daphnia pulex* | LC50 | 24 h | 5,700,000 | Okamura *et al.*, 2000a |
| *Thamnocepharus platyurus* | LC50 | 24 h | 12,000,000 | Okamura *et al.*, 2000a |

Table A5.7c. Aquatic toxicology data for SeaNine 211 (Madsen *et al.*, 2000).

| Species | Parameter, Endpoint | Exposure time | Result (ng l$^{-1}$) |
|---|---|---|---|
| Algae | | | |
| *Selenastrium caprocornutum* | Growth, EC50 | 120 h | 32,000 |
| *Skeletonema costatum* | Growth, EC50 | 96 h | 13,900–26,000 |
| Fish | | | |
| *Lepomis macrochirus* | LC50 | 96 h | 17,000–29,000 |
| *Oncorhynchus mykiss* | LC50 | 96 h | 2,700–7,700 |
| *Cryprinodon variegatus* | LC50 | 96 h | 17,000 |
| Molluscs | | | |
| *Crassostrea virginica* | Growth, EC50 | 48 h | 6,900–24,000 |
| *Mussel* | LC50 | 96 h | 850,000 |
| Crustaceans | | | |
| *Daphnia magna* | Immobilization, EC50 | 48 h | 5,200–21,600 |
| *Panaeus aztecus* | LC50 | 96 h | 12,400 |
| *Mysidopsis bahia* | LC50 | 96 h | 4,700 |

**Table A5.7d.** Aquatic toxicology data for zinc pyrithione (Madsen *et al.*, 2000).

| **Species** | **Parameter, Endpoint** | **Exposure time** | **Result (ng l$^{-1}$)** |
|---|---|---|---|
| Algae | | | |
| ***Selenastrium caprocornutum*** | Growth, EC50 | 72 h & 120 h | 28,000 |
| Fish | | | |
| ***Lepomis macrochirus*** | LC50 | 96 h | 21,000 |
| ***Oncorhynchus mykiss*** | LC50 | 96 h | 3,200 |
| ***Cryprinodon variegatus*** | LC50 | 96 h | 400,000 |
| ***Ictalurus punctatus*** | LC50 | 96 h | 35,000 |
| Molluscs | | | |
| ***Crassostrea virginica*** | LC50 | 96 h | 22,000 |
| Crustaceans | | | |
| ***Daphnia magna*** | Immobilization, EC50 | 48 h | 6,300 |
| ***Mysidopsis bahia*** | LC50 | 96 h | 4,700 |

EC50: median effective concentration; LC50: lethal concentration to 50%

**Table A5.7e.** Aquatic toxicology data for diuron (Verschueren, 1996).

| Species | Parameter, Endpoint | Exposure time | Result (ng $l^{-1}$) |
|---|---|---|---:|
| Algae | | | |
| ***Isochrysis galbana*** | Growth, EC50 | 10 days | 10–20 |
| ***Monochrysis lutheri*** | Growth, EC50 | 10 days | 10 |
| ***Phaedactylum tricornutum*** | Growth, EC50 | 10 days | 10 |
| ***Chlorococcum* sp.** | Growth, EC50 | 10 days | 10–20 |
| Fish | | | |
| ***Salmo gairdneri*** | LC50 | 96 h | 6,500,00 |
| ***Oncorhynchus mykiss*** | LC50 | 48 h | 4,300,000 |
| ***Lepomis macrochirus*** | LC50 | 96 h | 5,800,000 |
| Crustaceans | | | |
| ***Daphnia magna*** | LC50 | 24 h | 1,400,000 |
| ***Daphnia pulex*** | LC50 | 24 h | 1,400,000 |
| ***Gammarus lacustris*** | LC50 | 96 h | 160,000 |
| ***Gammarus fasciatus*** | LC50 | 96 h | 700,000 |

**Table A5.7f.** Aquatic toxicology data for chlorothalonil (Caux *et al.*, 1996).

| Species | Parameter, Endpoint | Exposure time | Result (ng $l^{-1}$) |
|---|---|---|---|
| Algae | | | |
| ***Selenastrum capricornutum*** | Growth, EC50 | 7 days | 8,500,000 |
| Fish | | | |
| ***Oncorhynchus mykiss*** | LC50 | 24–96 h | 10,500 – 9,200,000 |
| Crustaceans | | | |
| ***Daphnia magna*** | LC50 | 48 h | 97,000 |

EC50: median effective concentration; LC50: lethal concentration to 50%

# ANNEX 6

## BIOCONCENTRATION AND HAZARD ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS (VOCS)

In order to evaluate the possible consequences of the volatile organic compound (VOC) concentrations found in marine organisms, one can use the hazard assessment proposed by van Leeuwen *et al.* (1992). However, the model hinges on the applicability of the Equilibrium Partitioning Theory (EPT). According to the EPT, concentrations of chemicals, such as VOCs, in organisms originate from those in the water column through a process of physico-chemical partitioning. That is, the EPT assumes passive partitioning of a chemical compound between the aqueous phase and a lipid or a lipid-like organic phase (van Leeuwen *et al.,* 1992). The resulting partition coefficient, which is equal to the ratio of the concentrations in the organism ($C_{org}$) and the water ($C_w$), is called the Bioconcentration Factor (BCF):

$$BCF = C_{org} / C_w \ . \qquad [1]$$

This partition coefficient is supposed to be an intrinsic property of the compound and can, as a result, be related to its octanol-water partition coefficient, $K_{ow}$. Neely *et al.* (1974) and, subsequently, several other authors (Isnard and Lambert, 1988; Connell and Hawker, 1988; Banerjee and Baughman, 1991) demonstrated that BCF and $K_{ow}$ are linearly related according to:

$$\text{Log BCF} = a \log K_{ow} + b \qquad [2]$$

with *a* the regression coefficient and *b* the y intercept. The data obtained during the present study were compared with the average water concentrations reported by Dewulf *et al.* (1998) for the southern North Sea and BCFs were calculated for all VOCs. Plotting the logarithm of these BCFs against log $K_{ow}$ indeed resulted in the linear relationship ($r = 0.42$) predicted by Equation 2. This becomes especially evident when the data for higher $K_{ow}$ values reported by Neely *et al.* (1974) are included in the picture (Figure A6.1). The larger number of data points, spread over a larger $K_{ow}$ range, results in a much better correlation ($r = 0.94$). Moreover, the observed slope is essentially the same as the one reported by these authors. However, plotting the average of the BCFs reported in the literature resulted in a slope that is lower than those obtained with our data and those of Neely *et al.* (1974) (Figure A6.1). This suggests that the BCFs reported in the literature are somewhat too low, especially for the VOCs with a log $K_{ow}$ of less than 2.8. One explanation could be the use of nominal instead of actual concentrations. BCFs reported in the literature are often the result of laboratory experiments in open systems and nominal concentrations can easily be too high due to the high volatility of the compounds of interest (Crookes *et al.*, 1993). Even so, the observed relationship indicates that VOC concentrations in the water column are indeed reflected in the organisms and suggests that the EPT can be applied.

On the basis of the above observations one may conclude that the hazard assessment of van Leeuwen *et al.* (1992) can be used. These authors used Quantitative Structure-Activity Relationships (QSARs), the extrapolation of toxicity data, and equilibrium partitioning to assess the effects of narcotic industrial pollutants such as the target compounds of this study. The extrapolation of toxicity data generated by QSARs was used to derive safe levels for water. The QSARs in their study were expressed as:

$$\log \text{NOEC} = a' \log K_{ow} + b' \qquad [3]$$

where NOEC is the no-observed-effect concentration, *a'* the regression coefficient, and *b'* the y intercept. These concentrations were derived from literature data or, if no chronic toxicity data were available, they were estimated from acute toxicity data using acute/chronic ratios. The safety level was arbitrarily set at 95 %. This implies that a threshold concentration is calculated which is unlikely to cause harm to 95 % of the aquatic community. This calculated concentration, HC5, is the hazardous concentration that will affect, at most, 5 % of the species. The $HC5_w$ for the water column was calculated from:

$$HC5_w = C_w \times (1+1.85 \times 10^{-6} K_{ow}) \qquad [4]$$

where $HC5_w$ is the total concentration in the water phase (including suspended matter) and $C_w$ is the concentration in the water column for a given $K_{ow}$ that is unlikely to harm 95 % of the population, calculated on the basis of the QSARs as given in Equation 3. The proportionality constant, *a'*, relates to the average suspended matter concentrations in the area and their organic carbon content (van Leeuwen *et al.,* 1992). The internal tissue concentration, ITC or $HC5_{org}$, for the organisms was calculated from

$$HC5_{org} = 0.05 \times HC5_w \times K_{ow} \qquad [5]$$

where a lipid content of about 5 % weight in the organism is assumed. Table A6.1 compares the calculated $HC5_{org}$ values and the average concentrations in the different organisms and tissues. The results show that, in no case, is the $HC5_{org}$ for the monocyclic aromatic hydrocarbons (MAHs) and chlorinated hydrocarbons (CHCs) exceeded. Most probably, this would have been true also for ethylbenzene if an $HC5_{org}$ had been available. Moreover, the observed averages are several orders of magnitude lower than the $HC5_{org}$. However, the present results still cause concern because the hazard assessment does not take into account synergistic, and thus more damaging, effects. Despite the often high results, no definite statements can, as yet, be made concerning long-term effects such as carcinogenicity or immunosuppression. The number of data is too limited and the calculation of the HC5 is one approach amongst several and needs to be further evaluated. What is clear, however, is that additional research, especially with regard to the long-term consequences of small doses of VOCs, is urgently required.

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**Figure A6.1.** Plot of the log of BCFs calculated for the present study, BCFs reported in the literature, and BCFs reported by Neely *et al.* (1974) against log $K_{ow}$.

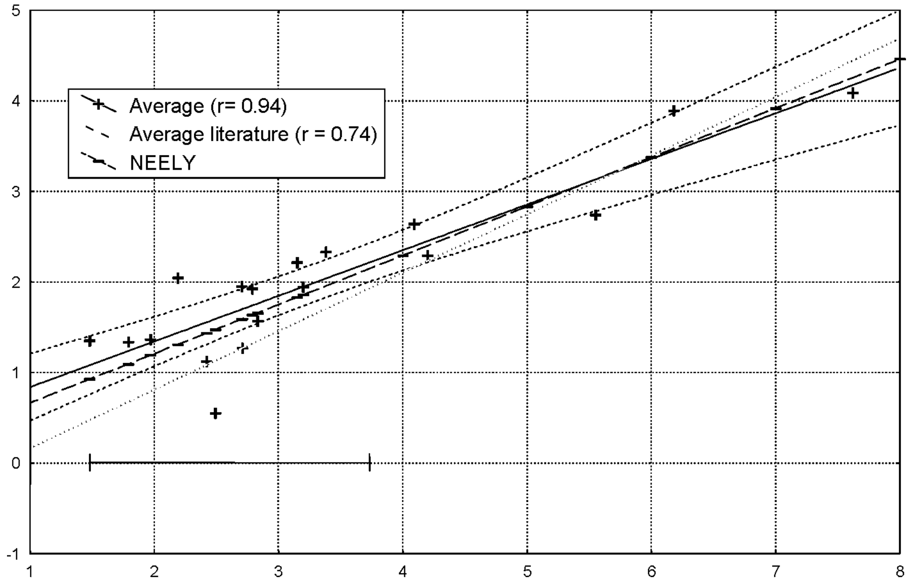

**Table A6.1.** Comparison of the average tissue concentrations in pg $g^{-1}$ of the present data set and the proposed safety level (HC5).

| **Compound** | ***Crangon crangon*** | ***Mactra stultorum*** | ***Mya truncata*** | ***Spisula* species** | ***Limanda limanda* liver** | ***Limanda limanda* muscle tissue** | ***Merlangius merlangus* liver** | ***Merlangius merlangus* muscle tissue** | **HC5** |
|---|---|---|---|---|---|---|---|---|---|
| **MAHs** | | | | | | | | | |
| Benzene | 700 | 2,500 | 550 | 2,000 | 14,000 | 500 | 5,800 | 800 | $5.2\times10^6$ |
| Toluene | 900 | 21,000 | 3,200 | 1,600 | 4,800 | 950 | 1,500 | 1,000 | $5.9\times10^6$ |
| Ethylbenzene | 9,800 | 2,500 | 2,400 | 2,200 | 11,000 | 1,500 | 5,200 | 2,600 | na |
| *m*- & *p*-Xylene | 9,700 | 3,000 | 3,500 | 2,500 | 11,000 | 1,500 | 6,300 | 3,200 | $6.4\times10^6$ |
| *o*-Xylene | 4,100 | 1,600 | 1,300 | 1,600 | 6,000 | 700 | 3,600 | 1,500 | $6.5\times10^6$ |
| | | | | | | | | | |
| **CHCs** | | | | | | | | | |
| 1,1-Dichloroethane | 40 | nd | nd | 60 | nd | 140 | 5 | 100 | $6.7\times10^6$ |
| Chloroform | 1,100 | 700 | 400 | 2,600 | 3,200 | 5,400 | 2,800 | 2,000 | $8.1\times10^6$ |
| Tetrachloromethane | 8 | 5 | 5 | 20 | 200 | 450 | 43,000 | 70 | $9.8\times10^6$ |
| 1,2-Dichloroethane | 300 | 900 | 300 | 400 | 900 | 300 | 550 | 500 | $6.7\times10^6$ |
| 1,1,1-Trichloroethane | 40 | 20 | 6 | 30 | 200 | 50 | 400 | 100 | $8.8\times10^6$ |
| Trichloroethylene | 70 | 80 | 20 | 60 | 200 | 200 | 13,000 | 400 | $8.7\times10^6$ |
| Tetrachloroethylene | 200 | 200 | 60 | 200 | 1,200 | 500 | 1,300 | 350 | $9.7\times10^6$ |

nd = not detected; na = not available.

## ANNEX 7

## DIOXINS AND DIOXIN-LIKE CBs IN FISH AND FEED AND THE CURRENT STATUS OF LEGISLATION IN THE EU

The term “dioxins” refers to a group of polychlorinated, planar aromatic substances with similar structures, chemical and physical properties. This group of compounds consists of dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) of which seven dioxin congeners and ten furans in particular are extremely resistant to biological and chemical degradation processes and, consequently, persist in the environment and accumulate in the food chain. A limited number of polychlorinated biphenyls (PCBs) contain similar chemical, physical, and toxicological properties as the group of seventeen dioxins and are therefore referred to as “dioxin-like CBs”.

Since the Belgian dioxin crisis in 1999, the European Commission has put a lot of effort into the evaluation of the potential risks of intake of dioxins (PCDDs, PCDFs) and dioxin-like CBs by the consumption of food. The data available on the occurrence of these contaminants in feed and food were collected and evaluated (Anon., 2000a, 2000b). Currently, discussions on new maximum residue limits for PCDDs, PCDFs and dioxin-like PCBs are taking place at national levels and in the European Union (Liem *et al.*, 2000). In November 2000, the EU adopted a new tolerable weekly intake (TWI) for the total intake of dioxins and dioxin-like CBs at a maximum level of 7 pg TEQ $kg^{-1}$ bw (Anon., 2000c). This TWI is based on the WHO-TDI (Tolerable Daily Intake) of 1–4 pg $kg^{-1}$ bw $day^{-1}$.[a]

The purpose of this paper is to summarize the available information on (i) the available data on the occurrence of dioxins and dioxin-like CBs in fish and fish products, and (ii) current legislation within the EU member states on contamination of fish and fish products.

### Dioxins and dioxin-like CBs in fish, fish oil, and fishmeal

The biochemical and toxic response to dioxins in animals and humans depends on the planar or nearly planar conformation and the geometrical size of the different congeners, with 2,3,7,8-TCDD being the most toxic compound. As the toxicity of the different congeners varies, toxic equivalency factors (TEFs) are used to express the total concentrations and exposures in toxic equivalents of 2,3,7,8-TCDD (TEQ). The I-TEQ values are based on the international TEFs (I-TEF) issued by NATO/CCMS in 1988. For dioxin-like CBs the PCB-TEFs, as published by Ahlborg *et al.* (1994), have been used. Recently the WHO has re-evaluated the toxicity of dioxins and dioxin-like CBs and established WHO-TEFs for seven dioxins, ten furans, and eleven dioxin-like CBs (van den Berg *et al.*, 1998). WHO-TEFs and I-TEFs are listed in Appendix 1.

### Dioxins and dioxin-like CBs in fish

Concentrations of dioxins and dioxin-like CBs in fish and fish products vary considerably, which is due to the difference in fish species, fat content, and the geographical differences (Anon., 2000a). Many species contain dioxins and dioxin-like CBs at levels below 1 pg I-TEQ $g^{-1}$ and 1 pg PCB-TEQ $g^{-1}$ wet weight, respectively (Appendix 2). In some fish species such as crab (Norway), Mediterranean tuna, eel, and cod liver, higher concentrations have been found. Baltic herring shows a comparable total-TEQ to that of North Sea herring (4–6 pg $g^{-1}$), but Baltic salmon showed a relatively high TEQ of 16 pg $g^{-1}$. Serious gaps in data on the dioxin-like CBs hinder the drawing of overall conclusions on the contamination of fish with dioxin-like CBs. Time trends are rarely available. In general, the PCB contribution to the total-TEQ is higher than the contribution of PCDDs and PCDFs together. However, ratios vary strongly, depending on species and location.

In a recent Dutch study on the contamination of fish and shellfish with dioxins and dioxin-like CBs, similar results were obtained (Leonards *et al.*, 2000). Many species contain dioxins at levels below 1 pg $g^{-1}$ WHO-TEQ but in some fish and shellfish species such as eel, mussels, cod, and herring originating from Dutch fresh waters or the southern North Sea, higher levels were found (Appendix 3). Levels of dioxins of approximately 17 pg WHO-TEQ per gram of product were found in cod liver from the North Sea (Appendix 3). The total-TEQ (PCDD/Fs and CBs) ranged from 0.03 pg TEQ $g^{-1}$ product (tuna from Sri Lanka) to 88.7 pg TEQ $g^{-1}$ product (cod liver, southern North Sea). The level of contamination depends highly on the origin of the fish: freshwater fish were more contaminated than fish from the North Sea.

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[a] Based on new scientific information, the SCF amended, in May 2001, the t-TWI of 7 pg TEQ $kg^{-1}$ bw to 14 pg TEQ $kg^{-1}$ bw (Anon., 2001).

Concentrations of 0.7–10.7 pg TEQ $g^{-1}$ product (PCDD/Fs) were found in cultured fish. No consistent relation was found between the PCDD/F TEQ and the dioxin-like CB TEQ.

Dioxins and dioxin-like CBs in fish oil and fishmeal

Fish is frequently used as a raw material for the production of animal feed and can be identified as an important source of dioxins in foodstuffs. Although few dioxin analyses have been carried out, the available data are relatively consistent. The data show a clear difference in contamination levels between fishmeal and fish oil originating from the (south) Pacific (Chile and Peru) and those originating from the European waters, with average concentrations in the latter being approximately eight-fold higher. Table A7.1 shows levels of dioxins and dioxin-like CBs in fishmeal and fish oil from European waters and the Pacific (Anon., 2000b).

Contaminated fishmeal used as fish feed can lead to an accumulation of the contaminants in the cultured fish. In particular, this can become a problem with relatively highly contaminated fishmeal or oil from European waters. A reduction of the dioxin content in cultured fish may be obtained by 1) the use of fish originating from clean areas such as the Pacific, 2) partly replacing fishmeal and oil by vegetable feeding stuffs, or 3) applying cleaning techniques such as filtration or distillation.

**Table A7.1.** Levels of dioxins and dioxin-like CBs in fishmeal and fish oil originating from Europe and the Pacific, expressed as the range of occurrence (low–mean–high) (Anon., 2000b).

| | **Europe** | | **Pacific** | |
|---|---|---|---|---|
| | Dioxins only[1] | Dioxins and PCBs[2] | Dioxins only[1] | Dioxins and PCBs[2] |
| **Fishmeal** (ng WHO-TEQ $kg^{-1}$ dry matter) | 0.04–1.2–5.6 | 0.18–6–28.2 | 0.02–0.14–0.25 | 0.11–0.7–1.26 |
| **Fish oil** (ng WHO-TEQ $kg^{-1}$ fat) | 0.7–4.8–20 | 3.5–24–100 | 0.16–0.61–2.6 | 0.8–3–13 |

[1] TEQ based on the contribution of PCDDs and PCDFs.

[2] TEQ based on the contribution of PCBs, PCDDs and PCDFs.

**Effects of cooking**

The actual human intake of dioxins and PCBs through the consumption of fish is influenced by the commonly used cooking practices. Removal of the toxic substances may occur by volatilization, extraction in the cooking oil, or by discarding the fat drippings and removal of the (contaminant-rich) skin.

Several studies (Zabik *et al.*, 1992, 1996; Zabik and Zabik, 1995; Salama *et al.*, 1998; Schecter *et al.*, 1998; Wilson *et al.*, 1998) reported reductions of PCBs and PCDD/Fs, depending on the cooking process applied. Zabik *et al.* (1996) reported a reduction of 40 % in the sum of PCBs through smoking of lake trout, whereas baked, char-boiled, and salt boiled showed reductions of approximately 15 %. In another study, the total amount of PCBs in boiled blue crab was reduced by 25–36 % compared with the raw material (Zabik *et al.*, 1992). Salama *et al.* (1998) studied reductions of PCBs in Atlantic bluefish filets and found reductions with smoking and microwave baking of 65 % and 60 %, respectively. Skin-off charbroiling, skin-on charbroiling, pan-frying, and convection oven baking showed reductions of 46 %, 37 %, 27 %, and 39 %, respectively.

The sum of the congeners of PCDDs and dioxin-like CBs in catfish was reduced by 43 % and 32 % wet weight, respectively (Schecter *et al.*, 1998). The amount of PCDFs, however, was increased by 67 %, caused by an increase of the congener OCDF, for which no explanation was given. Reductions are presumably an effect of the reduction of the fat in the sample. Zabik and Zabik (1995) showed PCDD reductions through cooking of skin-on fillets of about 40 % to 80 % for different species. Cooking of skin-off fillets showed increased reductions. Finally, Wilson *et al.* (1998) reviewed the available data from different studies and reported average PCB mass reductions of 28 %, 68 %, 28 %, 48 %, and 30 %, respectively, for baking, boiling, broiling, frying, and smoking, but data from different studies were inconsistent and showed significant ranges. Microwaving was applied in one study and reported to cause a 26 % reduction of PCBs (Wilson *et al.*, 1995).

It is rather complicated to take the effect of cooking into account when assessing the human exposure, as cooking methods vary (temperature, cooking time, etc.) and differ between species and tissues. Moreover, cooking methods differ geographically and, in practice, this step is not controlled as with the laboratory experiments. Besides, the available data are not consistent and show gaps. Therefore, although a tendency towards a reduction of the PCB and dioxin content of fish due to cooking processes may be extracted from the literature, it is difficult to express a quantitative reduction for all species and cooking methods, which, for the time being, hampers the inclusion of cooking factors into an overall risk assessment.

Present regulations on dioxins and dioxin-like CBs in fish and feed

Recently, the WHO re-evaluated the toxicology of dioxins and recommended a TDI of 1–4 pg TEQ $kg^{-1}$ body weight (including dioxin-like PCBs) (van Leeuwen *et al.*, 2000). It was stressed that the upper range of the TDI of 4 pg TEQ $kg^{-1}$ bw should be considered as a maximum tolerable daily intake on a provisional basis and that the ultimate goal is to reduce human intake levels below 1 pg TEQ $kg^{-1}$ bw $day^{-1}$. Based on the WHO re-evaluation, the EU recently established a group TWI for PCDDs, PCDFs, and dioxin-like CBs of 7 pg WHO-TEQ $kg^{-1}$ bw (Anon., 2000c)[a]. The total intake of dioxins and dioxin-like CBs from the diet in the EU countries is currently equivalent to 1.2–3.0 pg WHO TEQ $kg^{-1}$ bw $day^{-1}$ (Anon., 2000c). A considerable proportion of the European population will exceed the above-mentioned group TWI. The contribution of fish to the daily intake of dioxins in the EU countries ranges from 2 % (Netherlands) to 63 % (Finland), depending on the composition of the diet and the contamination of the fish consumed (Anon., 2000a).

**Table A7.2.** Present regulations on concentrations of dioxins and dioxin-like PCBs in fish in European countries (Anon., 2000a).

| **Country** | **Dioxins (PCDDs, PCDFs)** | **Dioxin-like PCBs** | **Other CBs (non-dioxin-like)** |
|---|---|---|---|
| Austria, Belgium, Denmark, Finland, Germany, Greece, Ireland, Italy, Luxembourg, Norway, Portugal, Spain, Sweden, United Kingdom | No explicit guidelines on maximum level of dioxins in fish | No explicit guidelines on maximum level of dioxin-like CBs in fish | Sweden: CB 153 (0.1 mg $kg^{-1}$ wet weight)<br>Germany: congener- specific limits for CBs 28, 52, 101, 138, 153 and 180 (0.008–0.6 mg $kg^{-1}$ fat or whole weight basis) |
| Netherlands | Eel: 8 pg WHO-TEQ $g^{-1}$ product[1] | Limit for CB 118 (wet weight basis)[2], in eel: 0.40 mg $kg^{-1}$, in fish liver: 1.2 mg $kg^{-1}$, in other fish: 0.08 mg $kg^{-1}$ | Congener-specific limits for CBs 28, 52, 101, 138, 153 and 180 (0.04–2.0 mg $kg^{-1}$ wet weight for fish and fish liver) |

[1]Anon., 2000d.

[2]Anon., 1984.

Present regulations within European countries with respect to the concentrations of PCDDs, PCDFs, and PCBs in food from different origins are diverse. Several countries have not set national limits, whereas regulations in other countries are mainly in force on milk, milk products and pork, beef, poultry and eggs. Recently, the Netherlands has enforced a regulation on the maximum allowable concentrations of dioxins (only) in eel (Anon., 2000d). The Dutch Ministry of Agriculture, Nature Management and Fisheries is currently evaluating the possibilities of setting group limits on the maximum allowable concentrations of PCDD/Fs and dioxin-like CBs in fish.

In Sweden, Germany, and the Netherlands, tolerance levels in fish are valid for indicator CBs. The single dioxin-like CB included in the tolerance levels in the Netherlands is CB 118 (Table A7.2). Although other European countries currently have no legislation in force on concentrations of dioxins or dioxin-like PCBs in fish (see Table A7.2), it is the intention of the EU to regulate maximum allowable concentrations in different types of food and feed, including fish and fish products, in the near future.

**Acknowledgement**

This report was prepared by Dr S.P.J. van Leeuwen and Dr J. de Boer, Netherlands Institute for Fisheries Research, IJmuiden, The Netherlands.

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[a] Based on new scientific information, the SCF amended, in May 2001, the t-TWI of 7 pg TEQ $kg^{-1}$ bw to 14 pg TEQ $kg^{-1}$ bw (Anon., 2001).

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## APPENDIX 1: TEF-VALUES FOR DIOXINS, FURANS AND PCBS

| | WHO-TEF values[1] | I-TEF values[2] |
|---|---|---|
| **Dioxins (PCDDs)** | | |
| 2,3,7,8-TCDD | 1 | 1 |
| 1,2,3,7,8-PeCDD | 1 | 0.5 |
| 1,2,3,4,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 0.01 |
| OCDD | 0.0001 | 0.001 |
| **Furans (PCDFs)** | | |
| 2,3,7,8-TCDF | 0.1 | 0.1 |
| 1,2,3,7,8-PeCDF | 0.05 | 0.05 |
| 2,3,4,7,8-PeCDF | 0.5 | 0.5 |
| 1,2,3,4,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDF | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 | 0.01 |
| OCDF | 0.0001 | 0.001 |
| **PCBs** | | |
| **Non-*ortho* CBs** | | |
| CB 77 | 0.0001 | 0.0005 |
| CB 81 | 0.0001 | - |
| CB 126 | 0.1 | 0.1 |
| CB 169 | 0.01 | 0.01 |
| **Mono-*ortho* CBs** | | |
| CB 105 | 0.0001 | 0.0001 |
| CB 114 | 0.0005 | 0.0005 |
| CB 118 | 0.0001 | 0.0001 |
| CB 123 | 0.0001 | 0.0001 |
| CB 156 | 0.0005 | 0.0005 |
| CB 157 | 0.0005 | 0.0005 |
| CB 167 | 0.00001 | 0.00001 |
| CB 189 | 0.0001 | 0.0001 |
| **Other CBs** | | |
| CB 180 | - | 0.00001 |

[1] van den Berg *et al.*, 2000.

[2] NATO/CCMS, 1988.

# APPENDIX 2: NATIONAL AVERAGE CONCENTRATIONS OF DIOXINS AND RELATED PCBs IN REPRESENTATIVE SAMPLES OF FISH AND FISH PRODUCTS (ANON., 2000a) FROM 1995 TO 1999 I-TEF VALUES HAVE BEEN USED.

| Country | Species | Latin name | PCDD/F (pg TEQ g$^{-1}$ product) | PCB (pg TEQ g$^{-1}$ product) |
|---|---|---|---|---|
| Denmark | Alaska pollack | | 0.01 | |
| | Carp | *Cyprinus carpio* | 0.74 | |
| | Catfish | *Anarchinas lupus* | 0.52 | |
| | Coalfish | *Pollachius virens* | 0.07 | |
| | Cod | *Gadus morhua* | 0.05 | |
| | Eel | *Anguilla anguilla* | 1.64 | |
| | Haddock | *Melanogrammus aeglefinus* | 0.04 | |
| | Hake | *Merluccius merluccius* | 0.03 | |
| | Halibut | *Hippoglossus hippoglossus* | 0.46 | |
| | Herring | *Clupea harengus harengus* | 0.79 | |
| | Mackerel | *Scomber scombrus* | 0.29 | |
| | Plaice | *Pleuronectes platessa* | 0.28 | |
| | Redfish | *Sebastes marinus* | 0.23 | |
| | Salmon (cultured) | *Salmo salar* | 0.43 | |
| | Sardine | *Sardina pilchardus* | 0.43 | |
| | Trout | *Salmo trutta* | 0.43 | |
| | Trout (cultured) | *Oncorhynchus mykiss* | 0.26 | |
| | Tuna | *Thunnus thynnus* | 0.01 | |
| | Fish mixture | - | 0.29 | |
| | Sea fish mixture | - | 0.48 | |
| Finland | Trout (cultured) | *Oncorhynchus mykiss* | 0.74 | 1.49 |
| France | Sea fish mixture | - | 0.63 | |
| | Seafood mixture | - | 1.41 | |
| Italy | Anchovy | *Engraulis encrasicolus* | 0.35 | |
| | Clam | | 0.10 | |
| | Mackerel | *Scomber scombrus* | 0.86 | |
| | Mussel | *Mytilus edulis* | 0.17 | |
| | Norway lobster | *Homarus gammarus* | 0.12 | |
| | Red mullet | *Mullus surmuletus* | 0.44 | |
| | Squid | | 0.18 | |
| Norway | Crab | | 10.2 | |
| Sweden | Cod | *Gadus morhua* | 0.13 | 0.23 |
| | Herring | *Clupea harengus harengus* | 0.73 | 1.11 |
| | Herring (Baltic) | *Clupea harengus harengus* | 3.18 | 1.33 |
| | Pike | *Esox lucius* | 0.90 | 0.67 |
| | Salmon (Baltic) | *Salmo salar* | 7.04 | 9.12 |
| | Salmon (cultured) | *Salmo salar* | 1.04 | 1.16 |
| | Trout (cultured) | *Oncorhynchus mykiss* | 0.81 | 1.14 |
| | Fish mixture | - | 0.39 | 0.55 |
| UK | Cod | *Gadus morhua* | 0.03 | 0.07 |
| | Dietary supplements | - | 3.55 | 14.2 |
| | Eel | *Anguilla anguilla* | 1.55 | 8.39 |
| | Haddock | *Melanogrammus aeglefinus* | 0.03 | 0.03 |
| | Herring | *Clupea harengus* | 2.10 | 6.24 |
| | Mackerel | *Scomber scombrus* | 0.61 | 2.50 |
| | Plaice | *Pleuronectes platessa* | 0.25 | 0.48 |
| | Salmon | *Salmo salar* | 0.71 | 2.39 |
| | Trout (cultured) | *Oncorhynchus mykiss* | 0.24 | 0.87 |
| | Whiting | *Merlangius merlangus* | 0.03 | 0.11 |

# APPENDIX 3: RESULTS OF A DUTCH STUDY ON DIOXINS, FURANS AND PCBs IN FISH AND FISH PRODUCTS FROM FRESH AND MARINE WATER SOURCES (LEONARDS *ET AL.*, 2000) WHO-TEF VALUES HAVE BEEN USED.

| **Species** | **Latin name** | **Location** | **TEQ-concentrations (pg TEQ g$^{-1}$ product)** | | |
|---|---|---|---|---|---|
| | | | **PCBs** | **PCDD/Fs** | **ΣTEQ PCB+PCDD/Fs** |
| Anchovy | *Engraulis encrasicolus* | Italy | 7.9 | 0.6 | 8.5 |
| Bass | *Dicentrarchus labrax* | France | 13.8 | 1.0 | 14.8 |
| Blue whiting | *Micromesistius poutassou* | Atlantic Ocean | 0.52 | 0.11 | 0.63 |
| Trout (cultured) | *Oncorhynchus mykiss* | Cultured | 0.7 | 0.2 | 0.9 |
| Grey gurnard | *Eutrigla gurnardus* | North Sea | 1.9 | 1.4 | 3.3 |
| Herring | *Clupea harengus* | The Channel | 1.77 | 1.46 | 3.23 |
| Herring | *Clupea harengus* | North Sea | 1.12 | 1.31 | 2.43 |
| Herring | *Clupea harengus* | The Channel | 3.9 | 1.8 | 5.7 |
| Herring | *Clupea harengus* | The Channel | 1.8 | 2.1 | 3.9 |
| Hake | *Merluccius merluccius* | Celtic Sea | 0.4 | 0.05 | 0.4 |
| Halibut | *Hippoglossus hippoglossus* | Cultured | 0.5 | 0.2 | 0.7 |
| Horse mackerel | *Trachurus trachurus* | Celtic Sea | 2.13 | 0.57 | 2.70 |
| Cod | *Gadus morhua* | Silverpit | 0.22 | 0.07 | 0.29 |
| Cod | *Gadus morhua* | North Sea | 0.5 | 0.3 | 0.8 |
| Cod liver | *Gadus morhua* | North Sea | 71.6 | 17.1 | 88.7 |
| Coalfish | *Pollachius virens* | North Sea | 0.8 | 0.1 | 1.0 |
| Coalfish (black) | *Rachycentron canadum* | Northern North Sea | 0.2 | 0.1 | 0.3 |
| Dab | *Limanda limanda* | North Sea | 0.84 | 0.54 | 1.38 |
| Eel | *Anguilla anguilla* | Yssel Lake (Enkhuizen) | 32.8 | 3.9 | 36.7 |
| Eel | *Anguilla anguilla* | Yssel Lake (Staveren) | 14.56 | 3.11 | 17.7 |
| Eel | *Anguilla anguilla* | Yssel Lake (Medemblik) | 7.48 | 2.14 | 9.6 |
| Eel | *Anguilla anguilla* | Yssel Lake (Urkerhoek) | 18.55 | 3.63 | 22.2 |
| Eel | *Anguilla anguilla* | Yssel Lake (Staveren) | 7.33 | 1.39 | 8.7 |
| Eel (cultured) | *Anguilla anguilla* | Netherlands | 8.18 | 2.54 | 10.7 |
| Eel (cultured) | *Anguilla anguilla* | Italy | 3.13 | 0.77 | 3.89 |
| Eel (cultured) | *Anguilla anguilla* | Netherlands | 7.2 | 2.2 | 9.4 |
| Eel (cultured) | *Anguilla anguilla* | Italy | 5.4 | 0.7 | 6.1 |
| Haddock | *Melanogrammus aeglefinus* | North Sea | 0.1 | 0.1 | 0.2 |
| Haddock liver | *Melanogrammus aeglefinus* | North Sea | 25.6 | 17.5 | 43.1 |
| Mackerel | *Scomber scombrus* | South of Ireland | 1.60 | 0.63 | 2.23 |
| Mackerel | *Scomber scombrus* | Skagerrak | 1.0 | 0.3 | 1.3 |
| Mackerel | *Scomber scombrus* | Atlantic Ocean | 1.0 | 0.3 | 1.3 |
| Mussel | *Mytilus edulis* | Eastern Scheldt | 2.03 | 1.47 | 3.50 |
| Mussel | *Mytilus edulis* | Western Wadden Sea | 1.20 | 1.10 | 2.30 |
| Pikeperch | *Stizostedion lucioperca* | River Nieuwe Merwede, Netherlands | 2.7 | 1.1 | 3.8 |
| Pikeperch | *Stizostedion lucioperca* | River Lek, Netherlands | 2.5 | 1.3 | 3.7 |
| Pikeperch | *Stizostedion lucioperca* | River Amer, Netherlands | 1.8 | 0.9 | 2.7 |
| Pikeperch | *Stizostedion lucioperca* | River Rhine, border, Netherlands | 2.3 | 0.8 | 3.1 |
| Pikeperch | *Stizostedion lucioperca* | River Waal, Netherlands | 4.0 | 1.5 | 5.5 |
| Pilchard | *Sardina pilchardus* | The Channel | 6.3 | 1.6 | 7.9 |

**Appendix 3.** continued

| **Species** | **Latin name** | **Location** | **TEQ-concentrations (pg TEQ g$^{-1}$ product)** | | |
|---|---|---|---|---|---|
| | | | **PCBs** | **PCDD/Fs** | **ΣTEQ PCB+PCDD/Fs** |
| Plaice | *Pleuronectes platessa* | North Sea | 0.23 | 0.25 | 0.48 |
| Redfish | *Sebastes marinus* | Northern North Sea | 1.6 | 0.8 | 2.4 |
| Salmon | *Salmo salar* | Norway | 2.0 | 1.3 | 3.3 |
| Salmon | *Salmo salar* | Norway | 2.94 | 1.36 | 4.31 |
| Salmon | *Salmo salar* | Scotland | 2.78 | 1.14 | 3.93 |
| Salmon | *Salmo salar* | Scotland | 2.6 | 1.4 | 4.1 |
| Sardinella | *Sardinella uarita* | Africa | 0.08 | 0.02 | 0.10 |
| Sea devil | *Lophius piscatorius* | Northern North Sea | 0.2 | 0.1 | 0.3 |
| Shrimps | *Crangon crangon* | Wadden Sea-west, Netherlands | 0.93 | 1.02 | 1.95 |
| Shrimps | *Crangon crangon* | Wadden Sea (Sylt) | 0.57 | 0.76 | 1.33 |
| Shrimps | *Crangon crangon* | Western Scheldt | 0.5 | 0.6 | 1.1 |
| Shrimps | *Pandalus borealis* | Norway | 0.1 | 0.1 | 0.2 |
| Sole | *Solea solea* | North Sea | 0.18 | 0.15 | 0.32 |
| Sprat | *Sprattus sprattus* | North Sea | 3.1 | 2.5 | 5.6 |
| Squid | *Loligo* spp. | North Sea, Dutch coast | 2.0 | 1.2 | 3.1 |
| Swordfish | *Xiphias gladius* | Italy | 3.4 | 0.5 | 3.9 |
| Tuna | *Thunnus thynnus* | Sri Lanka | 0.02 | 0.01 | 0.03 |
| Tuna (Bonito) | *Thunnus thynnus* | Italy | 9.0 | 0.7 | 9.8 |
| Tuna | *Thunnus thynnus* | France | 3.5 | 0.6 | 4.2 |
| Turbot | *Psetta maxima* | North Sea, Dutch coast | 2.4 | 0.8 | 3.3 |
| Whiting | *Merlangius merlangus* | North Sea | 0.17 | 0.07 | 0.24 |
| Yellow gurnard | *Trigla lucerna* | North Sea | 2.4 | 1.5 | 4.0 |
| Silversmelt | *Argentina silus* | Atlantic Ocean | 0.54 | 0.40 | 0.94 |

# ANNEX 8

# CRITERIA FOR SCREENING DATA FOR ANALYTICAL QUALITY IN CONTAMINANT TREND STUDIES

## SUMMARY

Although targets for laboratory QA are important, failure to meet these targets does not mean that data generated by the laboratory are worthless. In contaminant trend studies, when the level of environmental variability is low, meaningful trends can still be detected even when levels of analytical variability are high. Conversely, when the level of environmental variability is high, trend detection is poor regardless of the level of analytical variability.

A simple way to use data with poor underlying QA is to down-weight the corresponding data in the statistical analysis. Such data are easily identified in the analysis, and the analysis provides more effective trend detection than simply rejecting the data.

The informal use of *P* and Z scores to categorize data as, e.g., *satisfactory* can be misleading, with more data than expected apparently meeting targets for precision, and fewer than expected apparently meeting targets for bias. Modified rules are described which maintain a fixed probability of incorrectly concluding that targets have not been met.

## 1 INTRODUCTION

In its 2000 report, the Marine Chemistry Working Group commented that, although laboratory QA is regarded as absolutely necessary, it is unclear how this information can be incorporated into, e.g., the determination of temporal trends and questioned what is the best approach to take into account the performance of laboratories in intercomparison exercises.

They provided a review of different national criteria for signifying that performance at a particular laboratory is adequate—for example, for the UK, that 80 % of the laboratory means are within the limit value of a maximum tolerable bias as set by the organizer of the proficiency test. However, none of these criteria were based on any quantitative justification that, in some sense, data generated by the laboratory would be fit for their purpose. Further, there was no explicit guidance on how these criteria could be used to accept/reject data submitted to international assessments.

Nicholson (1994), Nicholson and Jones (1996), and Fryer *et al.* (1999) showed that in trend studies, targets for analytical quality can be constructed based on the levels of environmental variability and the magnitude of the trend considered worth detecting. However, this approach still leaves the problem of how to deal with data submitted by laboratories that have not demonstrated satisfactory performance.

This is not a small problem, especially when assessing time series where data quality in early years may not have been measured or may have been poorer than in subsequent years. For example, in the 1998 OSPAR assessment of contaminant trends in marine organisms, a considerable amount of data was rejected on QA grounds. The following table shows the percentage of annual observations of trace metals lost for the four countries experiencing the highest losses. The table also shows the reasons the data were rejected as a percentage of the total number of losses.

| | **Germany** | **Netherlands** | **Norway** | **Iceland** |
|---|---|---|---|---|
| % Deleted | 45 | 41 | 27 | 24 |
| QA absent | 87 | 68 | 47 | - |
| Poor QA (Z and/or P scores > 2) | 6 | 30 | 53 | 100 |
| Undocumented Reference Materials | 7 | 2 | - | - |

In this paper, it will be demonstrated that:

- When considered in relation to the levels of environmental variability, data that fail targets for analytical quality may still be useful for trend detection (Section 2).
- A simple strategy for dealing with variable QA is to down-weight poor-quality data in the statistical assessment of trend. This is demonstrated for trends in mercury in fish (Section 3).
- Rejection rules based on the QUASIMEME definition of *satisfactory P* and *Z* scores can be misleading. Modified rules are suggested (Section 4).

## 2 THE EFFECT OF ENVIRONMENTAL AND ANALYTICAL VARIABILITY ON TREND ASSESSMENTS

In this section, we demonstrate how the relative size of environmental and analytical variation affects the detection of a temporal trend. We assume that the contaminant index constructed at time $t$, $y_t$, is made up of four components as follows

$$y_t = f(t) + e_t + b_t + w_t$$

where $f(t)$ is the trend signal, and $e_t$, $b_t$, and $w_t$ are noise components due to the <u>e</u>nvironment (including sampling), analytical variability <u>b</u>etween time periods, and analytical variability <u>w</u>ithin the time period, respectively. Further, we will assume that these noise terms are independent, and Normally distributed with mean zero and variances $\sigma_e^2$, $\sigma_b^2$, and $\sigma_w^2 / R$, respectively. $R$ is the number of replicate analyses, equal to the number of animals if analyses are made on individual animals.

The component $b_t$ is commonly referred to as *bias*, and the standard deviation $\sigma_w$ as *precision*. Here we assume that bias varies from time period to time period.

The following table gives some guidance on the likely values of environmental variability for mercury in fish muscle. They are taken from Nicholson *et al.* (1997), who summarized environmental variation (including sampling) seen in OSPAR assessments for three groups corresponding to *Low, Medium,* and *High* levels of variability. The values shown below assume that the annual index of mercury concentration is calculated as the back-transformed mean log-concentration measured individually in 25 fish.

| **Group** | **Environ-mental** St. Dev. % | **Detectable trend %** analytical St. Dev. = 0 % | **Detectable trend %** analytical St. Dev. = 12.5 % | **Detectable trend %** analytical St. Dev. = 25 % |
|---|---|---|---|---|
| Low | 9.7 | 3.9 | 6.5 | 11.2 |
| Medium | 26.2 | 11 | 12 | 15 |
| High | 52.4 | 21 | 22 | 24 |

The performance of a temporal trend programme can be measured by the detectable trend (Nicholson *et al.,* 1997), the linear trend (% change per year) that would be detected after ten years with a power of 90 % using a test at the 5 % significance level. The final three columns of the table give the detectable trend for three levels of analytical variability: $\sigma_w = \sigma_b = 0$ %, $\sigma_w = \sigma_b = 12.5$ %, and $\sigma_w = \sigma_b = 25$ %.

As would be expected, the effect of increasing analytical noise is greatest for the group with *Low* environmental variation. However, in that group, even with $\sigma_w = \sigma_b = 25$ % (where analytical variability is about 2.5 times greater than environmental variability), trends of the order of 10 % are still detectable. At *High* levels of environmental variation, the effect of increased analytical variability is small, with little change in the detectable trend.

## 3 DOWN-WEIGHTING OBSERVATIONS WITH POORER ANALYTICAL QUALITY

An alternative to rejecting data with unsatisfactory QA is to down-weight them in the statistical assessment of the trend. This is demonstrated below using weighted linear regression to assess the trend.

Figure A8.1 shows a realization of a simulated decreasing trend in the log-concentration of mercury over ten years. The trend has been subjected to the level of environmental variation from the *Low* group defined in Section 2. The underlying trend is a decrease of 3.9 % per year, i.e., the *detectable trend* in this group when there is zero analytical noise.

In the final five years, an additional component of low-level analytical variability has been added with $\sigma_w = \sigma_b = 6.25$ %. In the first five years, however, a higher level of analytical noise with $\sigma_w = \sigma_b = 25$ % has been added. In the figure, this difference in QA status is indicated by different plotting symbols, with solid circles indicating poorer QA.

Three fitted lines are shown. The solid line is an unweighted regression line, i.e., where all the data have equal weight. The dotted line is from a weighted regression, where the first five years have been down-weighted by 50 %. The short dashed line is an unweighted regression line fitted to the data from the last five years, i.e., where the data from the first five years have been deleted.

Judged informally, the weighted line is slightly flatter than the unweighted line, due to the higher concentrations observed in the early years being down-weighted. However, it still captures the essence of the underlying trend. There is little suggestion of any trend in the line fitted to only the last five years.

## 4 IDENTIFYING ANALYTICAL QUALITY FROM *P* AND *Z* SCORES

For any weighting strategy, including rejection, the QA status of the data must be inferred. This is commonly done using *P* and *Z* scores derived from the results of interlaboratory exercises. They are usually interpreted as indicators of *precision* and *bias*, respectively. However, as shown below, uncritical interpretation of these scores could be misleading, since both are dependent on the number of replicate analyses made in the exercise, and the *Z* score is a function of both precision and bias.

This may not matter if the scores are used informally to compare performance between laboratories within an interlaboratory exercise. However, it is important if the scores are intended to provide an objective basis for rejecting data. Formulae for deriving formal rules are derived below.

### Definition of *P* and *Z* Scores

Typically, for an experiment to assess analytical performance for some determinand at concentration $\mu$, laboratory $i$ reports a series of $n$ results, $x_{i1}, x_{i2}, \ldots, x_{in}$, measured in a circulated sample. These can be summarized by the sample mean ($\bar{x}_i$) and standard deviation ($s_i$), used to define

$$P_i = {s_i}/{\sigma_{w(\text{target})}}$$

and

$$Z_i = {\bar{x}_i - \mu}/{\sigma_{b(\text{target})}}$$

where $\sigma_{w(\text{target})}$ and $\sigma_{b(\text{target})}$ are targets for $\sigma_w$ and $\sigma_b$ (Wells *et al.*, 1993). Alternative robust estimators are discussed by Cofino and Wells (1994).

## Assessment of Data Quality on the Basis of $P \leq 2$ and $Z \leq 2$

Common assessment criteria for interpreting the significance of $P$ and $Z$ scores are that absolute values $\leq 2$ indicate that performance is *satisfactory* (Cofino and Wells, 1994). This is based on the assumption that $Z$ has a standard Normal distribution when $\sigma_b = \sigma_{b(\text{target})}$ (Wells *et al.*, 1993), with the implication that the probability (significance level) of incorrectly rejecting the hypothesis of *satisfactory* analytical performance is approximately 5 %. However, it is simple to show that the actual significance levels for these rules is given by

$$\Pr[|P| \leq 2] = \Pr\left[\chi^2_{n-1} \leq \left. 4(n-1)\sigma^2_{\text{w(target)}} \middle/ \sigma^2_{\text{w}} \right.\right]$$

and

$$\Pr[|Z| \leq 2] = \Pr\left[\chi^2_1 \leq \left. 4\sigma^2_{\text{b(target)}} \middle/ \sigma^2_{\text{b}} + \sigma^2_{\text{w}} / n \right.\right]$$

where $\chi^2_{df}$ is a chi-squared variate with *df* degrees of freedom. Thus, the significance of $P$ scores depends on the value of $n$ (in addition to $\sigma_w$), and the significance of $Z$ scores depends on both $n$ and $\sigma_w$ (in addition to $\sigma_b$).

Values of $n$ used in practice tend to be small, typically in the range 2 to 5 (e.g., Pedersen and Cofino, 1994; Dixon and Gardner, 1998). The following table shows how $n$ affects the probabilities of getting $P$ or $Z$ scores greater than 2 when the underlying values of $\sigma_w$ and $\sigma_b$ equal their targets $\sigma_{w(\text{target})}$ and $\sigma_{b(\text{target})}$, and when $\sigma_{w(\text{target})} = \sigma_{b(\text{target})}$.

| ***n*** | **Pr[\|P\| > 2]** | **Pr[\|Z\| > 2]** |
|---|---|---|
| 2 | 0.05 | 0.10 |
| 3 | 0.02 | 0.08 |
| 4 | 0.01 | 0.07 |
| 5 | 0.01 | 0.07 |
| ∞ | 0.01 | 0.05 |

The significance level for $P$ scores decreases rapidly with $n$, so when $n > 2$, more data than expected will apparently meet the targets for precision. For $Z$ scores, the significance level decreases from double the notional value of 5 % when $n = 2$, to 5 % when $n = \infty$, so fewer data than expected will apparently meet the targets for bias.

Another way of looking at this is to consider the values of $\sigma_w$ and $\sigma_b$ for which the true significance level of the criteria $|P| \leq 2$ and $|Z| \leq 2$ is 5 %. Assuming $\sigma_w = \sigma_b$ and $\sigma_{w(\text{target})} = \sigma_{b(\text{target})} = \sigma_{(\text{target})}$, the following table shows the approximate values of $\sigma_w^2$ and $\sigma_b^2$ that satisfy $\Pr[|P| \leq 2] = 0.95$ and $\Pr[|Z| \leq 2] = 0.95$ for $n = 2$ and $n = \infty$.

| **n** | $\boldsymbol{\sigma_w^2}$ | $\boldsymbol{\sigma_b^2}$ |
|---|---|---|
| 2 | $\sigma^2_{(\text{target})}$ | $\sigma^2_{(\text{target})}/2$ |
| ∞ | $4\sigma^2_{(\text{target})}$ | $\sigma^2_{(\text{target})}$ |

When $n = 2$, $\Pr[|P| \leq 2] = 0.95$ when $\sigma_w^2 \approx \sigma^2_{(\text{target})}$ as expected. However, $\Pr[|Z| \leq 2] = 0.95$ when $\sigma_b^2 \approx \sigma^2_{(\text{target})}/2$, so we are actually aiming for a more demanding target for bias. Only when $n$ is very large does $\Pr[|Z| \leq 2] = 0.95$ when $\sigma_b^2 \approx \sigma^2_{(\text{target})}$, but then the actual target for $\sigma_w^2$ is too liberal.

## Alternative Assessment Criteria based on *P* and *Z* Scores

Alternative criteria based on $P$ and $Z$ scores can be constructed which correctly control the probability of incorrectly concluding that results are not *satisfactory*. For example, it is simple to show that $\Pr[|P| \le k_P] = 0.95$ implies

$$k_P = \sqrt{\frac{\sigma_{\mathrm{w}}^2}{\sigma_{\mathrm{w(target)}}^2} \times \frac{\chi_{n-1}^2(0.95)}{n-1}}$$

whereas $\Pr[|Z| \le k_Z] = 0.95$ implies

$$k_Z = \sqrt{\frac{\sigma_{\mathrm{b}}^2 + \sigma_{\mathrm{w}}^2/n}{\sigma_{\mathrm{b(target)}}^2} \times \chi_1^2(0.95)}\ .$$

Thus, assuming $\sigma_{w(\mathrm{target})} = \sigma_{b(\mathrm{target})} = \sigma_{(\mathrm{target})}$, we can maintain the correct 5 % significance level if we define performance to be *satisfactory* if $|P| \le k_P$ and $|Z| \le k_Z$, where

$$k_P = \sqrt{\frac{\chi_{n-1}^2(0.95)}{n-1}}$$

and

$$k_Z = \sqrt{\frac{n+1}{n}\chi_1^2(0.95)}\ .$$

The table below gives the appropriate values of $k_P$ and $k_Z$ for different values of $n$.

| ***n*** | ***k_P*** | ***k_Z*** |
|---|---|---|
| 2 | 2.0 | 2.4 |
| 3 | 1.7 | 2.3 |
| 4 | 1.6 | 2.2 |
| 5 | 1.5 | 2.1 |
| ∞ | 1.0 | 2.0 |

These rules could easily be extended to a three-tier system, e.g., with QA performance classified as *satisfactory*, *questionable*, and *unsatisfactory*. For example, suppose *unsatisfactory* corresponds to $\sigma_w > 2\sigma_{(\mathrm{target})}$ and $\sigma_b > 2\sigma_{(\mathrm{target})}$. Then if $n = 2$, classifying data based on the following rules:

| ***satisfactory*** | ***questionable*** | ***unsatisfactory*** |
|---|---|---|
| $P \le 2$ | $2 < P \le 4$ | $4 < P$ |
| $Z \le 2.4$ | $2.4 < Z \le 5$ | $5 < Z$ |

provides a maximum probability of approximately 5 % that standard deviations less than or equal to their targets would be mislabelled as *questionable* or *unsatisfactory*, and that standard deviations less than twice their targets are mislabelled as *unsatisfactory*.

If these extended rules were incorporated into a QA-weighted trend assessment, data classified as *questionable* would be down-weighted. Data classified as *unsatisfactory* could either be further down-weighted or rejected.

## 5 DISCUSSION

We have looked at the interaction between analytical variability and environmental variability, and considered the implications of accepting or rejecting data with different levels of analytical quality. In particular, we have shown that data of poorer quality might still be useful for trend assessments. This does not, of course, imply that targets for laboratory performance should be looser. Trend detection will be most effective when analytical variability is as low as possible. However, our results have shown that although minimum targets of, e.g., 12.5 % may be useful for motivating improvements in laboratory performance, they may be excessive when used to filter out unworthy data.

Further, our results show that informal assessments of *P* and *Z* scores can be a misleading way of rejecting data. A better solution is to define appropriate rules taking the number of replicate analyses into account.

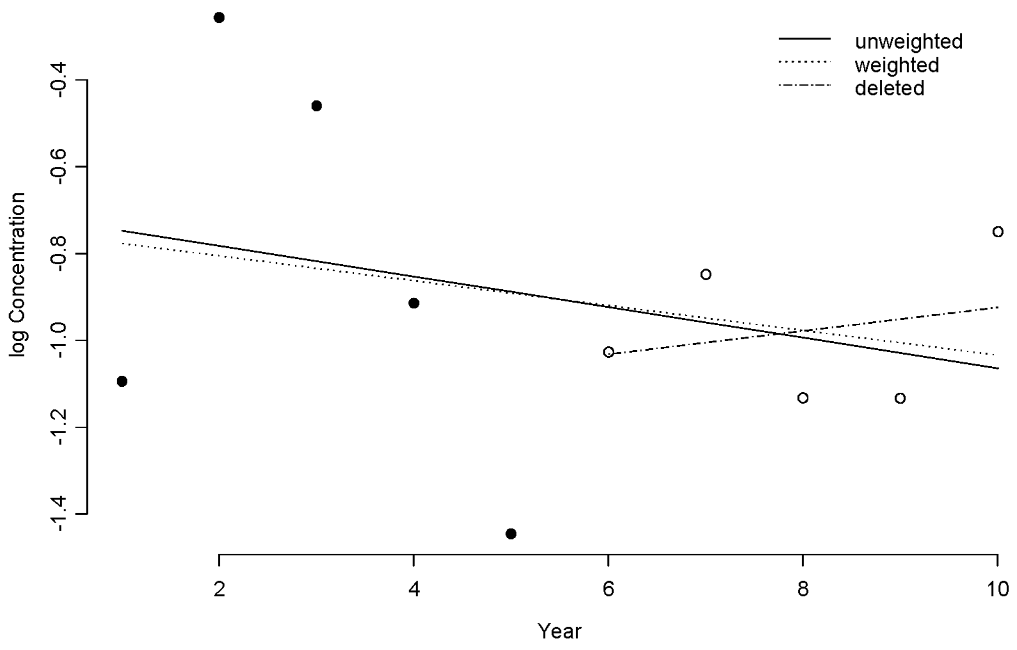
The weighting approach appears to offer a useful compromise between ignoring high analytical variability and rejecting data. In particular, the weighting approach is likely to have greater power than rejection because it retains more degrees of freedom. It would be simple to extend the weighting approach so that extremely poor data are rejected and questionable data are down-weighted. The visual presentation of QA status in a trend plot allows the inferior quality of some data points to be identified, and would assist in the interpretation of possible QA-related outliers.

The method of trend assessment used here for demonstration was linear regression. However, the weighting procedure could be extended to other assessment models such as smoothers (cf. Fryer and Nicholson, 1999).

The weighting used in the example was a fixed, crude approximation of the optimum weighting based on the levels of environmental variability typically observed in mercury time series.

If this statistical basis was abandoned, the weighting could be seen as a simple heuristic device to reduce the contribution of questionable data to the analysis. In this case, other non-quantitative information could contribute to some index of quality. For example, Dobson *et al.* (1999) suggested an index of fitness for data generated at a laboratory based on the answers to eighteen questions concerning QA/QC. This could easily be extended to incorporate other equally important qualities, such as the extent to which sampling guidelines have been followed, climatic anomalies, or any other variations in conditions known to affect the monitored signal.

**Figure A8.1.** Example of trend assessment with down-weighting of data with poor QA (solid circles).



## 6 ACKNOWLEDGEMENT

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# ANNEX 9

# WEIGHTING PROCEDURES FOR ASSESSING TREND DATA OF VARIABLE QUALITY

## 1 INTRODUCTION

There are many reasons why the quality of trend monitoring data may vary in time. Some factors, such as changes in analytical variability or fluctuations in sample sizes may have a direct effect on the variance of a contaminant index. Others, such as *ad hoc* modifications to the sampling guidelines, may have a less quantifiable effect, and are more difficult to deal with in an objective way.

Weighting the data offers one way of incorporating such information into formal assessments of trends, assuming that appropriate weights can be constructed. These may be derived intuitively based on some subjective measurement of data quality. For example, Dobson *et al.* (1999) suggested an index of fitness for data generated at a laboratory based on the answers to eighteen questions concerning QA/QC. This could easily be extended to incorporate other equally important factors, such as the extent to which sampling guidelines have been followed, annual climatic anomalies, or any other variations in conditions known to affect the monitored signal.

However, weights can be generated more formally when data quality is reflected in changes in the underlying components of variance. Here we consider one such example, where there is information from inter-laboratory experiments about changing analytical accuracy over time. We show how this information can be incorporated into trend assessments using weighted regression models, specifically when trend is estimated using a linear smoother. This is described in Section 2. In Section 3, we use a simple application of the EM algorithm (Dempster *et al.,* 1977) to estimate the optimum weights. This is demonstrated using a synthetic example in Section 4. In Section 5, we consider various non-optimal weighting strategies, including a special case where data are rejected (i.e., given a weight of zero) when analytical variability is above some threshold.

## 2 WEIGHTED TREND ASSESSMENTS

For any weighting strategy, we can consider annual contaminant indices $\mathbf{y} = (y_1, y_2 \ldots y_T)'$ observed in years $t_1, t_2 \ldots t_T$ such that $\mathbf{y}$ has a multivariate normal distribution with

$$E[\mathbf{y}] = (f(t_1), f(t_2), \ldots f(t_T))'$$

and

$$V[\mathbf{y}] = \psi^2\mathbf{V}$$

where $f(t)$ is a smooth function of $t$ and

$$\mathbf{V} = \mathrm{diag}(v_1, v_2, \ldots v_T)$$

i.e., the $y_t$ are independent. We also define $\mathbf{W}$, a known weighting matrix given by

$$\mathbf{W} = \mathrm{diag}(w_1, w_2, \ldots w_T).$$

We will consider estimators of $f(t)$ of the form

$$\hat{\mathbf{f}} = \mathbf{A}\mathbf{y}$$

where $\mathbf{A}$ is a known $T{\times}T$ smoothing matrix. We follow Fryer and Nicholson (1999) and make inferences about trends by comparing three hypotheses about $f(t)$. We will differ by incorporating $\mathbf{W}$ into $\mathbf{A}$. The three hypotheses are:

$$H_0: f(t) = \mu$$

$$H_1: f(t) = \mu_0 + \mathrm{b}t$$

and

$H_2$: $f(t)$ = unspecified smooth function of time.

These hypotheses correspond to three smoothing matrices.

Under $H_0$, we have

$$\hat{\mathbf{f}} = \mathbf{Ky}$$

where **K** is constructed such that all values in the $i$th column are given by $w_i \big/ \sum_{t=1}^{T} w_t$ .

Similarly, under $H_1$, we can write

$$\hat{\mathbf{f}} = \mathbf{Ly}$$

where

$$\mathbf{L} = \mathbf{X}(\mathbf{X}'\mathbf{W}\mathbf{X})^{-1}\mathbf{X}'\mathbf{W}$$

and **X** is the design matrix for linear regression of $y_t$ on $t$.

Under $H_2$, a modified version of the LOESS smoothing matrix **S** is constructed by multiplying the relevant elements of **W** by the tri-cube weights in the weighted regression used to calculate the individual values of $\hat{\mathbf{f}}$ . Then

$$\hat{\mathbf{f}} = \mathbf{Sy} .$$

The residual sum of squares for a smoothing matrix **A** is given by $\mathbf{y}'\mathbf{R}_A\mathbf{y}$ with

$$df_A = \mathrm{tr}(\mathbf{R}_A\mathbf{W}^{-1})$$

degrees of freedom, where tr(.) denotes the trace of a matrix,

$$\mathbf{R}_A = (\mathbf{I} - \mathbf{A})'\mathbf{W}(\mathbf{I} - \mathbf{A})$$

and **I** is the $T \times T$ identity matrix.

Tests of trends can be made using F statistics calculated from the differences between appropriate residual sums of squares. For example,

$$F = \frac{\mathbf{y}'(\mathbf{R}_K - \mathbf{R}_S)\mathbf{y} / (df_K - df_S)}{\mathbf{y}'\mathbf{R}_S\mathbf{y} / df_S}$$

can be compared with an F distribution on ($df_K - df_S$) and $df_S$ degrees of freedom, and this provides a test of significance of the overall trend ($H_0$ versus $H_2$). See Fryer and Nicholson (1999) for details of the full analysis of variance and a discussion of this test and expressions for alternative degrees of freedom.

This test is only correct when $\mathbf{W} = \mathbf{V}^{-1}$. When $\mathbf{W} \neq \mathbf{V}^{-1}$, $\hat{\mathbf{f}}$ will still be an unbiased estimator of **f** (assuming that the correct model has been fitted), but will no longer have minimum variance. Further, confidence limits and tests of significance could be misleading. In the following section, we derive estimates of the optimum weighting when **V** is unknown.

## 3 ESTIMATION OF THE OPTIMUM WEIGHTS

When the source of variation in data quality is analytical variation and this has been measured in interlaboratory experiments, it is possible to estimate **V** and hence the optimum weights. The estimation procedure must allow for both the (unknown) environmental variability and analytical variability. We do this using a simple application of the EM algorithm (Dempster *et al.*, 1977; McLachlan and Krishnan, 1997), which consists of an iterative two-stage procedure.

To derive this procedure, suppose the variance at time $t$ is

$$\psi^2 v_{\mathrm{t}} = \sigma_e^2 + \sigma_{at}^2$$

where $\sigma_e^2$ is the unknown and constant environmental variance (including sampling variability), and $\sigma_{at}^2$ is the known but variable total analytical variance (including within- and between-time variability). Equating

$$\psi^2 = \sigma_e^2$$

and

$$v_t = 1 + \frac{\sigma_{at}^2}{\sigma_e^2}$$

the optimum weights are given by

$$w_t = v_t^{-1} = \frac{\sigma_e^2}{\sigma_e^2 + \sigma_{at}^2}\ .$$

The EM algorithm treats the $w_t$ as missing data, and consists of a Maximizing stage, where conditional on $w_t$, $\sigma_e^2$ is estimated by maximizing the likelihood of **y**, and an Estimation stage where the $w_t$ are updated. This cycle continues until the change in the likelihood is negligible.

Apart from constants, the log-likelihood is given by

$$\log Likelihood = -\tfrac{1}{2}T\log\sigma_e^2 - \tfrac{1}{2}\sigma_e^{-2}\sum\nolimits_{t=1}^{T} w_t(y_t - f(t))^2$$

If $f(t)$ is estimated using a smoothing matrix S, then conditional on **W** the log-likelihood is maximized by

$$\hat{\sigma}_e^2 = \frac{1}{T}\sum\nolimits_{t=1}^{T} w_t(y_t - \hat{f}(t))^2 = T^{-1}\mathbf{y}'\mathbf{R}_{\mathrm{S}}\mathbf{y}$$

giving a value of

$$\log Likelihood = -\tfrac{1}{2}T(\log\hat{\sigma}_e^2 + 1)\ .$$

In practice, it makes more sense to use the unbiased estimator of $\sigma_e^2$ taking into account the degrees of freedom lost in fitting the smoother. Hence at the $k$th iteration, the maximization stage can be written

$$\hat{\sigma}_e^2(k) = \frac{1}{df_{\mathrm{S}_{(k-1)}}}\sum\nolimits_{t=1}^{T} w_t(k-1)(y_t - \hat{f}_{(k-1)}(t))^2$$

where, e.g., $w_t(k-1)$ denotes estimates obtained at iteration $k-1$, and the estimation stage as

$$\hat{w}_t(k) = \frac{\hat{\sigma}_e^2(k)}{\sigma_e^2(k) + \sigma_{at}^2}.$$

## 4 EXAMPLE

To demonstrate the method, we simulated data consisting of log concentrations of mercury with T = 15 years from a Normal distribution with

$\mu(t) = \mu_0$ with $\mu_0 = -0.69$ $t = 1986–1990$

$\mu(t) = \mu_0 - \beta(t-1990)$ with $\beta = 0.037$ $t = 1991–2000$

$\sigma_e = 0.097$

$\sigma_{at} = 0.278$ $t = 1986–1995$

and

$\sigma_{at} = 0.116$ $t = 1996–2000$

i.e., data with a constant concentration of 0.5 mg $\text{kg}^{-1}$ for five years followed by an underlying downward trend of approximately 4 % per year for ten years, and a higher level of analytical variability in the first ten years compared to the last five years.

For a starting value of $\sigma_e^2$ and hence **W**, the un-weighted residual variance was assumed to be an estimate of $\sigma_e^2 + \overline{\sigma}_a^2$. Then a starting value of $\hat{\sigma}_e^2(0) = 0.048$ was obtained by subtraction.

Figure A9.1a shows the track of the log-likelihood levelling off after 25 iterations. The final unbiased estimate of $\sigma_e^2$ is $\hat{\sigma}_e^2(25) = 0.079^2$. Figure A9.1b shows log concentrations plotted against year with the corresponding estimated smoother. The following table gives the corresponding analysis of variance, showing a non-significant overall trend, but a significant linear trend.

| **Effect** | **df** | **ss** | **mss** | **F** | **p value** |
|---|---|---|---|---|---|
| Time | 3.78 | 0.0583 | 0.01541 | 2.49 | 0.110 |
| Linear | 1 | 0.0569 | 0.05690 | 9.21 | 0.012 |
| Non-linear | 2.78 | 0.0014 | 0.00051 | 0.08 | 0.961 |
| Residual | 10.22 | 0.0631 | 0.00618 | | |

## 5 COMPARISONS WITH ALTERNATIVE WEIGHTING STRATEGIES

In some situations, data quality may be measured by some non-variance based indicator, or simply categorized as, e.g., *Good*, *Poor*, or *Bad*. An intuitively weighted analysis can be made using weights based on these indicators. For example, Nicholson *et al.* (2001) considered a simple weighting scheme of 1 for *Good* data and 0.5 for *Poor* data.

These categories were defined in terms of the QUASIMEME targets for analytical variability of within-batch ($\sigma_w$) and between-batch ($\sigma_b$) standard deviations of 12.5 % (Wells *et al.,* 1993). They argued that this approach would be better than deleting *Poor* data, the current practice followed in OSPAR assessments of contaminants in biota.

However, if data quality is determined by variance heterogeneity, these *ad hoc* weighting procedures are not optimal. Their performance will depend on how close the weightings are to the inverses of the appropriate variances, determined by the relative values of environmental and analytical variability. We will explore the consequences of different weighting strategies using some historic estimates of environmental variability of mercury in fish with different amounts of superimposed analytical variability.

The following table gives historic levels of environmental variability in mercury summarized by Nicholson *et al.* (1997). The third column shows the corresponding detectable trend when $\sigma_w = \sigma_b = 0$ %, i.e., the linear trend (% change per year) that would be detected after ten years with a power of 90 %, for a test at the 5 % significance level. For simplicity, we have assumed that the test would be based on linear regression (i.e., not the smoother). The final two columns show the optimum weights that would be used at time $t$ if $\sigma_w = \sigma_b = 6.25$ % or $\sigma_w = \sigma_b = 25$ %, respectively.

| Group | Environmental standard deviation | Detectable trend % | $w_t = \dfrac{\sigma_e^2}{\sigma_e^2 + \sigma_{at}^2}$ | |
|---|---|---|---|---|
| | $\sigma_e$ | $\sigma_w = \sigma_b = 0$ % | $\sigma_w = \sigma_b = 6.25$ % | $\sigma_w = \sigma_b = 25$ % |
| Low | 0.097 | 3.9 | 0.698 | 0.126 |
| Medium | 0.262 | 11 | 0.944 | 0.514 |
| High | 0.524 | 21 | 0.985 | 0.809 |

The values of the weights assume that the annual index of mercury concentration is calculated as the back-transformed mean log-concentration measured individually in 25 fish. The values for the *Low* group were used to generate the data for the example analysed in Section 4.

To give some indication of the sensitivity of weighted regression to the choice of weight, consider data for the final ten years from example 1, where the first $n$ years have *Poor* data quality ($\sigma_w = \sigma_b = 25$ %) and the final $10 - n$ years have *Good* data quality ($\sigma_w = \sigma_b = 6.25$ %). We compare the different weighting strategies using the detectable trend. This can be computed by writing $\mathbf{B} = (\alpha, \beta)'$ and noting that an arbitrary weight matrix $\mathbf{W}$ gives

$$\hat{\mathbf{B}}_{\mathrm{W}} = (\mathbf{X'WX})^{-1}\mathbf{X'y}$$

for which

$$V[\hat{\mathbf{B}}_{\mathrm{W}}] = \sigma^2 (\mathbf{X'WX})^{-1}\mathbf{X'WVWX}(\mathbf{X'WX})^{-1}.$$

If we assume that $\mathbf{V}$ is known and there is an unbiased estimate of $\sigma^2$ with $T-2$ degrees of freedom, the detectable trend is obtained from a non-central F-distribution on 1 and $T-2$ degrees of freedom with non-centrality parameter given by $\beta^2 / V[\hat{\beta}_{\mathrm{W}}]$.

Figures A9.2a, b, and c show for the *Low*, *Medium*, and *High* group, respectively, how the detectable trend changes with increasing $n$. This is done for four weighting strategies:

1) optimum-weighted regression: $\mathbf{W} = \mathbf{V}^{-1}$;

2) intuitive-weighted regression using a weight of 100 % for *Good* years and 50 % for *Poor* years: $\mathbf{W} = \mathrm{diag}(0.5, 0.5,.. 1, 1,..)$;

3) un-weighted regression: $\mathbf{W} = \mathbf{I}$;

4) rejection of *Poor* years: $\mathbf{W} = \mathrm{diag}(0, 0,.. 1, 1,..)$ with appropriate reduction in the degrees of freedom to allow for the missing values.

In each figure, the line for rejection (strategy 4) has been curtailed as it heads off approximately linearly into the stratosphere, indicating the huge inefficiency of this option.

We see that, by definition, optimum weighting (strategy 1) is better than no weighting (strategy 3). Intuitive-weighting (strategy 2) does well in the *Medium* group, where the 50 % weighting is close to the optimum, and better than no weighting (strategy 3) when the level of environmental variability is *Low*.

Intuitive-weighting does less well than no weighting when the level of environmental variability is *High*. For this group the optimum weighting is close to 100 %, the implicit weights in the no-weighting strategy. However, in this group the effect of increasing the number of *Poor* years has little effect on the *detectable trend*, which is largely determined by the high value of $\sigma_e$ (note the changes of scale for the y-axis between these figures).

## 6 DISCUSSION

We have shown how a simple weighting strategy can be used to incorporate historical information about laboratory analytical quality into trend assessments. This could, of course, be extended to incorporate information about other components of variance. Note that this is not an *a posteriori* procedure for minimizing the influence of possible outliers. It is an *a priori* way of using known information about the veracity of individual data points to control their influence, regardless of whether in some sense they appear anomalous.

One weakness in the method is the assumption that the values of the analytical components of variance are known. In reality, these are very poorly estimated in interlaboratory experiments with teeny-weeny degrees of freedom. A more intuitive weighting strategy may capture the spirit of these estimates without giving them an undeserved appearance of accuracy. For example, we could group these estimates into, e.g., *Good*, *Average*, and *Poor*, and allocate either an average or a notional value to each category, similar to the procedure used by Nicholson *et al.* (2001).

Another approach would be to incorporate some model for the variances into the assessment. For example, we might assume that analytical variability develops as a function of time to be estimated from the data using some parametric or non-parametric model. This approach has the advantage that missing QA data could be interpolated from the model. A simple example would be to label data as *Historic* or *Current*, and assume different analytical quality in each period. A more sophisticated approach would be to estimate the function using a smoother (cf. Carrol and Rupert, 1988). This analysis could also be weighted to reflect the precision of different interlaboratory experiments.

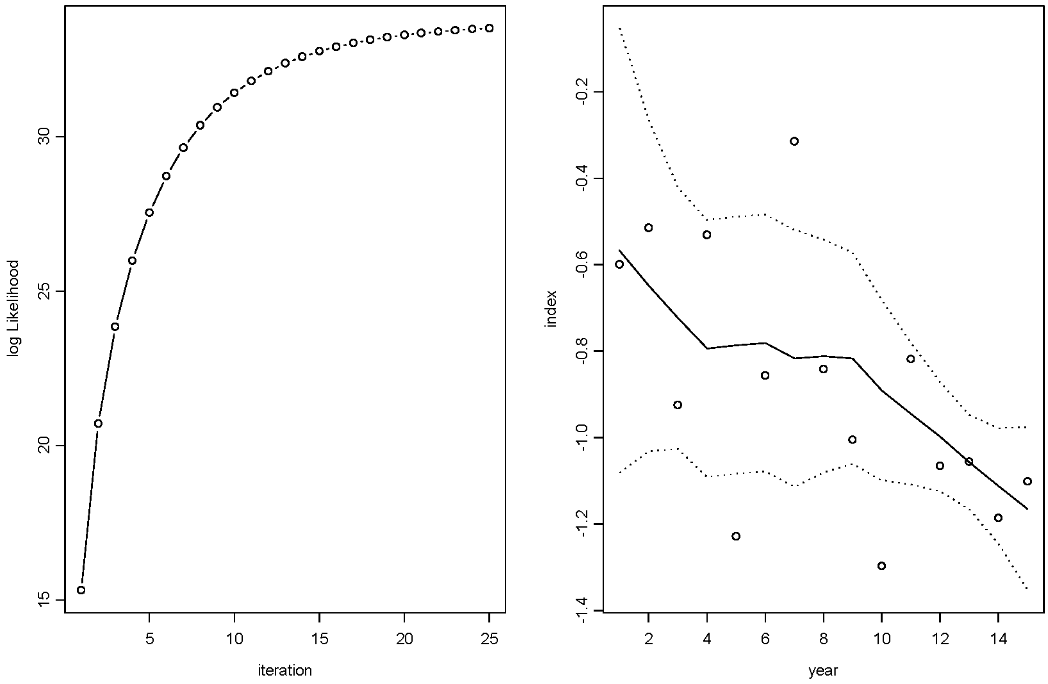
A further weakness in the method is the assumption that measurements with poor or absent QA are unbiased. If the lack of quality control corresponds to a period of constant bias, then including these points in the trend assessment will induce a spurious trend.

The results of comparing different weighting strategies are somewhat tentative. First of all, they assume that **V** is known and that there is an unbiased estimate of $\sigma^2$, neither of which would be true in practice. Secondly, for the optimum weighting strategy, we have also assumed that the true weights are used. Although using $\hat{\mathbf{V}}$ is asymptotically fully efficient, further assessment of the method with small data sets is required. However, there is at least sufficient indication that even with levels of analytical variation that would be considered very high (i.e., $\sigma_w = \sigma_b = 25$ %) by QUASIMEME standards, data rejection strategies are very inefficient.

## 7 ACKNOWLEDGEMENT

This paper was prepared by M. Nicholson (CEFAS, Lowestoft, UK) and R. Fryer (FRS Marine Laboratory, Aberdeen, UK).

**Figure A9.1a, b.** Example of weighted trend assessment using the EM algorithm to estimate the optimal weights given the components of analytical variance.



**8**

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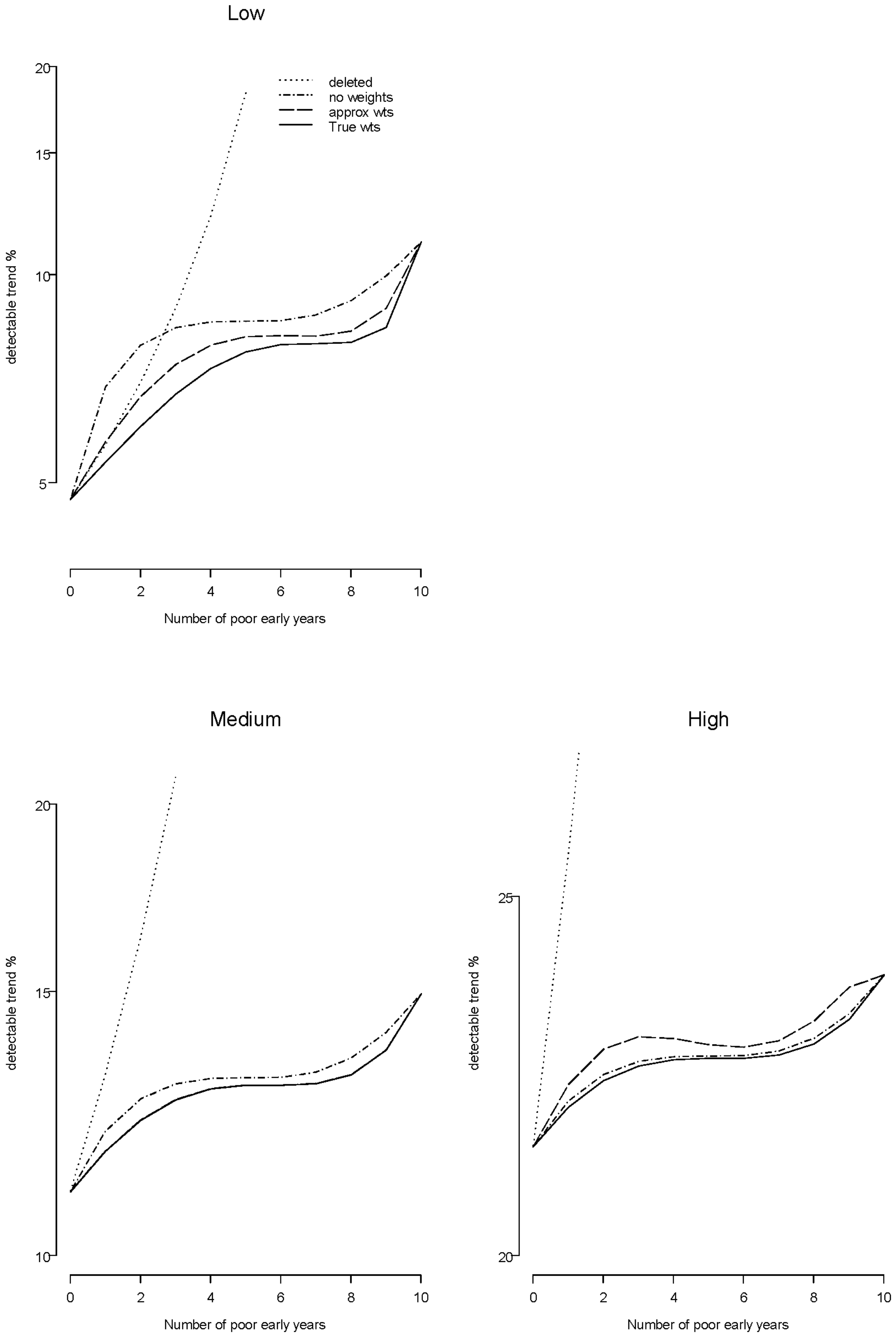
Wells, D.E., Cofino, W.P., Quevauviller, P., and Griepink, B. 1993. Quality assurance of information in marine monitoring: A holistic approach. Marine Pollution Bulletin, 26: 368–375.

**Figures A9.2a, b, and c.** Example of the change in detectable trend with increasing number of early years with poor data quality for the *Low*, *Medium*, and *High* environmental variability groups, respectively. Note the different scale for the y-axis in each figure. Key: deleted = strategy 4; no weights = strategy 3; approx wts = strategy 2; True wts = strategy 1.



# ANNEX 10

# THE LOESS SMOOTHER: INCORPORATION OF UNCERTAINTY DATA AND THE BEHAVIOUR WITH MISSING VALUES

## 1 THE LOESS SMOOTHER OPTIMIZED FOR VARYING UNCERTAINTY AND MISSING OBSERVATIONS

This report focuses on extensions of the Trend-y-tector with regard to the treatment of missing values and the incorporation of uncertainty data. For general background and theory on the smoothers used for assessments of contaminant time series, the reader is referred to Fryer and Nicholson (1999), and for the basic theory for fitting and making inference about smoothers to the textbook of Hastie and Tibshirani (1990).

### 1.1 Definition

An extended version of the LOESS smoother taking into account missing values and the relative uncertainty of the observations may be constructed as follows.

Let $y_i$ ($i = 1,\ldots,n$) denote the observation for year $x_i$ and let $u_i$ denote the "uncertainty weight" of the observation, with $u_i = 0$ in case of missing observations and otherwise reciprocal to the squared length of the corresponding standard error.

The smoother matrix $S$ of the LOESS smoother is constructed from a series of weighted regressions constructed for each year $x_t$ using any data that fall within a range $x_t \pm \Delta_t$. The weight of the observation $y_i$ in the local regression for year $x_t$ is determined by the uncertainty weight $u_i$ and by the distance between year $x_i$ and year $x_t$,

$$w_{ti} = \begin{cases} u_i\left(1-\left(\dfrac{|x_t - x_i|}{\Delta_t}\right)^3\right)^3 & \text{for } 0 \le \dfrac{|x_t - x_i|}{\Delta_t} \le 1 \\ 0 & \text{otherwise} \end{cases}.$$

The width of $\Delta_t$ controls the amount of smoothing, and Nicholson and Fryer (1999) choose $\Delta_t$ to include data from a fixed span of years, i.e.,

$$\Delta_t = \max\left\{\frac{\text{span}+1}{2}, \text{span} - \min\{\mathrm{x_t} - \mathrm{x_1}, \mathrm{x_n} - \mathrm{x_t}\}\right\}$$

and, with a span of seven years (span = 7),

$$\Delta_t = \begin{cases} 4 & \text{for} \quad 4 \le t \le n-3 \\ 5 & \text{for} \quad t = 3 \text{ or } t = n-2 \\ 6 & \text{for} \quad t = 2 \text{ or } t = n-1 \\ 7 & \text{for} \quad t = 1 \text{ or } t = n \end{cases}.$$

Then, writing $X$ for the design matrix of the simple linear regression model,

$$X = \begin{pmatrix} 1 & x_1 \\ 1 & x_2 \\ \vdots & \vdots \\ 1 & x_n \end{pmatrix},$$

$Y$ for the vector of observations,

$$Y = \begin{pmatrix} y_1 \\ \vdots \\ y_n \end{pmatrix},$$

and $W_t$ for the corresponding diagonal matrix of weights,

$$W_t = \begin{pmatrix} w_{t1} & 0 & \cdots & 0 \\ 0 & w_{t2} & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & w_{tn} \end{pmatrix},$$

the value of the smoother in year $x_t$ is given by $S_t^{'}Y$ ,

where $S_t^{'}$ is the $t$th row of

$$X(X'W_tX)^{-1}X'W_t.$$

In case of equidistant observations with identical uncertainty weights, the resulting smoother matrix $S = \begin{pmatrix} S_1^{'} \\ \vdots \\ S_n^{'} \end{pmatrix}$ equals the smoother currently implemented in the Trend-y-tector. Otherwise, the extended LOESS smoother can be quite different from the standard LOESS smoother.

### 1.2 Examples

**Missing values**

If there are ten equidistant observations with identical uncertainty, and if the second observation is missing, the smoother matrix based on a span of seven years is:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.787 | 0 | 0.311 | 0.084 | −0.064 | −0.089 | −0.029 | 0 | 0 | 0 |
| 0.547 | 0 | 0.299 | 0.159 | 0.035 | −0.025 | −0.015 | 0 | 0 | 0 |
| 0.323 | 0 | 0.277 | 0.214 | 0.132 | 0.049 | 0.005 | 0 | 0 | 0 |
| 0.077 | 0 | 0.297 | 0.267 | 0.213 | 0.12 | 0.026 | 0 | 0 | 0 |
| 0 | 0 | 0.172 | 0.231 | 0.227 | 0.203 | 0.133 | 0.035 | 0 | 0 |
| 0 | 0 | 0.042 | 0.145 | 0.206 | 0.216 | 0.206 | 0.145 | 0.042 | 0 |
| 0 | 0 | 0 | 0.042 | 0.145 | 0.206 | 0.216 | 0.206 | 0.145 | 0.042 |
| 0 | 0 | 0 | 0.011 | 0.06 | 0.123 | 0.172 | 0.202 | 0.223 | 0.209 |
| 0 | 0 | 0 | −0.01 | −0.018 | 0.025 | 0.111 | 0.209 | 0.3 | 0.383 |
| 0 | 0 | 0 | −0.025 | −0.082 | −0.077 | 0.028 | 0.199 | 0.388 | 0.569 |

The second column corresponds to the second observation and is therefore vanishing. Neighboring observations have higher weights than in cases without missing observations. It should be noted that the span is seven years regardless of the number of missing observations in that span.

**Varying uncertainty**

If there are ten equidistant observations with uncertainty weights 1,1,1,0.25,1,1,1,1,1,1, the smoother matrix based on a span of seven years is

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.57 | 0.391 | 0.204 | 0.009 | −0.071 | −0.079 | −0.025 | 0 | 0 | 0 |
| 0.388 | 0.313 | 0.229 | 0.034 | 0.047 | −0.004 | −0.007 | 0 | 0 | 0 |
| 0.22 | 0.243 | 0.229 | 0.051 | 0.156 | 0.083 | 0.018 | 0 | 0 | 0 |
| 0.05 | 0.172 | 0.246 | 0.064 | 0.246 | 0.172 | 0.05 | 0 | 0 | 0 |
| 0 | 0.061 | 0.198 | 0.066 | 0.259 | 0.229 | 0.149 | 0.039 | 0 | 0 |
| 0 | 0 | 0.065 | 0.051 | 0.265 | 0.249 | 0.21 | 0.128 | 0.032 | 0 |
| 0 | 0 | 0 | 0.012 | 0.164 | 0.223 | 0.224 | 0.204 | 0.136 | 0.037 |
| 0 | 0 | 0 | 0.003 | 0.063 | 0.128 | 0.175 | 0.203 | 0.222 | 0.206 |
| 0 | 0 | 0 | −0.003 | −0.021 | 0.02 | 0.108 | 0.208 | 0.301 | 0.386 |
| 0 | 0 | 0 | −0.025 | −0.082 | −0.077 | 0.028 | 0.199 | 0.388 | 0.569 |

The fourth column corresponds to the fourth observation with reduced weight 0.25 and is therefore considerably down-weighted, whereas neighboring columns are up-weighted. Weights are chosen so that any linear trend in the observations will be represented as a linear trend in the smoother curve.

### Non-equidistant observations

If there are ten observations in the years 1,3,5,7,9,10,11,12,13,14 with constant uncertainty weights, the smoother matrix based on a span of seven years is

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.831 | 0.302 | −0.098 | −0.035 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.365 | 0.335 | 0.234 | 0.066 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.04 | 0.285 | 0.348 | 0.285 | 0.04 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0.314 | 0.402 | 0.225 | 0.059 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0.29 | 0.313 | 0.242 | 0.13 | 0.026 | 0 | 0 |
| 0 | 0 | 0 | 0.077 | 0.297 | 0.267 | 0.213 | 0.12 | 0.026 | 0 |
| 0 | 0 | 0 | 0 | 0.172 | 0.231 | 0.227 | 0.203 | 0.133 | 0.035 |
| 0 | 0 | 0 | 0 | 0.065 | 0.129 | 0.176 | 0.204 | 0.221 | 0.205 |
| 0 | 0 | 0 | 0 | −0.022 | 0.019 | 0.106 | 0.208 | 0.302 | 0.388 |
| 0 | 0 | 0 | 0 | −0.092 | −0.091 | 0.015 | 0.193 | 0.392 | 0.583 |

Due to the bi-yearly sampling frequency in years 1–9, the weights for single observations are higher than in the remaining years. This is especially relevant for the first year, for which the first observation has a dominating weight. Note also that due to the fixed seven-year span, the number of observations taken into account for the years 1–11 is smaller than for the remaining years.

## 2 TREND TESTS BASED ON THE EXTENDED LOESS SMOOTHER

### 2.1 Analysis of Variance of the Sum of Squares

Tests based on the extended smoother are partly different from the corresponding tests based on the un-weighted smoother. Since the observations are weighted, the sums of squares have to be weighted, too:

$$SS_{total} = \sum_{t=1}^{n} u_t \left(y_t - \bar{y}\right)^2$$

$$SS_{linerror} = \sum_{t=1}^{n} u_t \left(y_t - \left(a + bx_t\right)\right)^2$$
$$= Y'\left(U - UX\left(X'UX^{-1}\right)X'U\right)Y$$

$$SS_{error} = \sum_{t=1}^{n} u_t\left(y_t - z(x_t)\right)^2 = Y'(I - S')U(I - S)Y$$

where $\bar{y} = \left(\sum_{t=1}^{n} u_t y_t\right) / \left(\sum_{t=1}^{n} u_t\right)$ denotes the weighted arithmetic mean of the observation vector,

$U$ denotes the diagonal matrix of uncertainty weights,

$$U = \begin{pmatrix} u_1 & 0 & \cdots & 0 \\ 0 & u_2 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & u_n \end{pmatrix},$$

and $a$ and $b$ denote the regression coefficients calculated by weighted regression:

$$\begin{pmatrix} a \\ b \end{pmatrix} = (X'UX)^{-1} X'UY .$$

The corresponding degrees of freedom are

$$df_{total} = n - 1$$

$$df_{linerror} = n - 2$$

$$df_{error} = n - tr(2S - SUS'U^{-1})$$

where $df_{error}$ is determined by the mean value of $SS_{error}$ under the assumption that the covariance matrix of Y equals $\sigma^2 U^{-1}$:

$$\begin{aligned} E[SS_{error} / \sigma^2] &= E\left[\left(Y'(I - S')U(I - S)Y\right) / \sigma^2\right] \\ &= tr\left[(I - S')U(I - S)U^{-1}\right] \\ &= tr(I) - 2tr(S) + tr\left(SUS'U^{-1})\right), \end{aligned}$$

where $I$ denotes the identity matrix. $SS_{error} / \sigma^2$ is not exactly chi-squared distributed, but its distribution can be approximated by a chi-squared distribution with $df_{error}$ degrees of freedom.

Note: In case of missing values some diagonal entries of $U$ are vanishing. In that case, the inverse does not exist and therefore for the calculation the zero elements on the diagonal should be replaced by ones. This does not affect the resulting sums of squares.

The total sum of squares $SS_{total}$ can be split into three components

$$SS_{total} = SS_{lin} + SS_{nonlin} + SS_{error}$$

where

$$SS_{lin} = SS_{total} - SS_{1inerror}$$

with $df_{total} - df_{nonlin} = 1$ degree of freedom and

$$SS_{nonlin} = SS_{linerror} - SS_{error}$$

with $df_{linerror} - df_{error}$ degrees of freedom.

These sums of squares can be used for several trend tests and confidence intervals.

### 2.2 Testing the Contrast between the Estimated Level at the Start and End of the Time Series

The contrast $z(n) - z(1)$ between the estimated level at the start and the end of the time series can be tested with the test statistic

$$t = \frac{z(n) - z(1)}{s\sqrt{\sum_{i=1}^{n}(S_{1i} - S_{ni})^2}},$$

where $s$ denotes the residual standard deviation of the extended smoother:

$$s = \sqrt{\frac{1}{df_{error}} SS_{error}} = \sqrt{\frac{1}{df_{error}} \sum_{t=1}^{n} u_t (y_t - z(x_t))^2} .$$

Under the null hypothesis, the test statistic $t$ can be considered t-distributed with degrees of freedom $df_{error} = n - tr(2S - SUS'U^{-1})$.

### 2.3 Testing the Linear Trend

The linear trend can be tested with the test statistic

$$t = \frac{b}{s}\sqrt{\sum_{t=1}^{n} u_t (x_t - \bar{x})^2}$$

with $df_{error} = n - tr(2S - SUS'U^{-1})$ degrees of freedom and the weighted regression coefficient $b$ for the slope (according to Section 2.1, above).

### 2.4 Testing the Non-linear Trend

Let $K_{error}$ denote the square matrix defined by the quadratic form

$$SS_{error} = Y'(I - S)'U(I - S)Y =: Y'K_{error}Y$$

and $K_{nonlin}$ the square matrix defined by the quadratic form

$$SS_{nonlin} = Y'(I - L)'U(I - L)Y - Y'(I - S)'U(I - S)Y \begin{array}{l} = Y'U(I - L)Y - Y'(U - S'U - US + S'US)Y \\ = Y'(2US - S'US - UL)Y =: y'K_{nonlin}y \end{array}$$

with regression matrix $L = X(X'UX)^{-1}X'U$.

Let the test statistic

$$F^*_{nonlin} = \frac{SS_{nonlin} / df_1}{SS_{error} / df_2} = \left( \frac{SS_{linerror}}{SS_{error}} - 1 \right) \frac{df_2}{df_1},$$

where

$$df_1 = \frac{\operatorname{tr}(K_{nonlin})^2}{\operatorname{tr}\left(K'_{nonlin} K_{nonlin}\right)}, \quad df_2 = \frac{\operatorname{tr}(K_{error})^2}{\operatorname{tr}\left(K'_{error} K_{error}\right)}.$$

Under the null hypothesis (that there is no non-linear trend), the distribution of the test statistic can be approximated by an F distribution with ($df_1$, $df_2$) degrees of freedom. Therefore, the null hypothesis can be rejected if

$$F^*_{nonlin} > \frac{\dfrac{\operatorname{tr}(K_{nonlin})}{\operatorname{tr}\left(K'_{nonlin} K_{nonlin}\right)}}{\dfrac{\operatorname{tr}(K_{error})}{\operatorname{tr}\left(K'_{error} K_{error}\right)}} F(df_1, df_2, 1 - \alpha),$$

where $F(df_1, df_2, 1-\alpha)$ denotes the $(1 - \alpha)$-quantile of the F distribution with ($df_1$, $df_2$) degrees of freedom.

## 3 FURTHER ASPECTS OF MISSING VALUES, OUTLIERS, AND UNCERTAINTY

### 3.1 Missing Values

How many missing observations are acceptable? In order to answer this question, one may compare the variances of the LOESS trend with and without missing observations. Generally, the covariance matrix of the LOESS trend based on smoother matrix $S$ can be written

$\mathrm{Cov}(Z(1),\ldots,Z(n)) = \sigma^2 SS'$,

and the variance of $Z(t)$ equals the $t$th diagonal element of $\sigma^2 SS'$. Figure A10.1 presents the variances of the LOESS smoother for 10 years with and without missing observations, respectively. Variances are given in units of $\sigma^2$, and according to the first figure (year 1) the variance of the estimated trend is approximately 0.53 $\sigma^2$ if there are no missing observations. If the second and the fourth observations are missing, the respective variance is 0.76 $\sigma^2$. This is an increase of the estimation variance for the first year by 44 %. The maximum increase is attained for the fourth year with 63 %.

The variances depend on the number and position of missing observations. In the case of ten years with two missing observations within the interval from the second to the ninth year, the maximum increase of the variance is obtained if the observations of both the second and the third years or of both the eighth and the ninth years are missing. In that case, the maximum increase of the variance is approximately 81.5 %; see Figure A10.2.

**Figure A10.1.** Variance (in units of $\sigma^2$) of LOESS smoother, second and fourth observations missing.

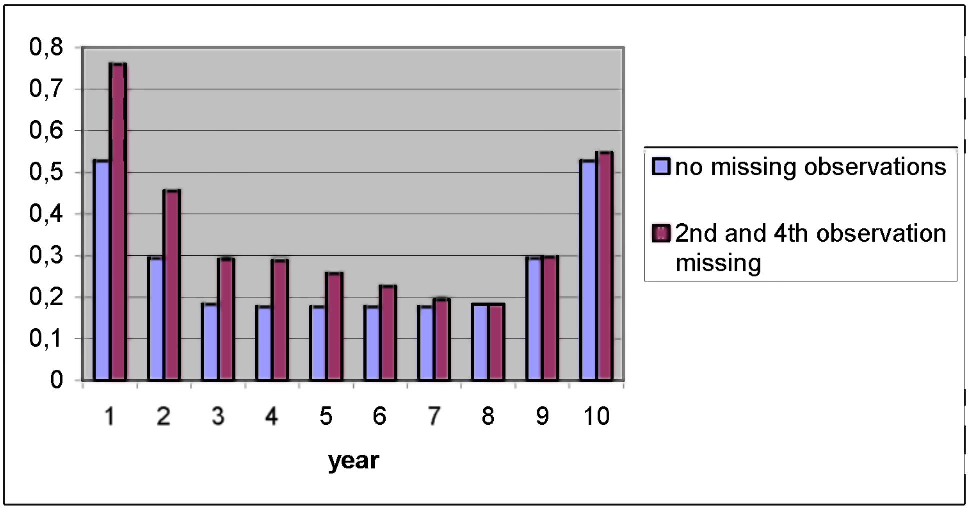
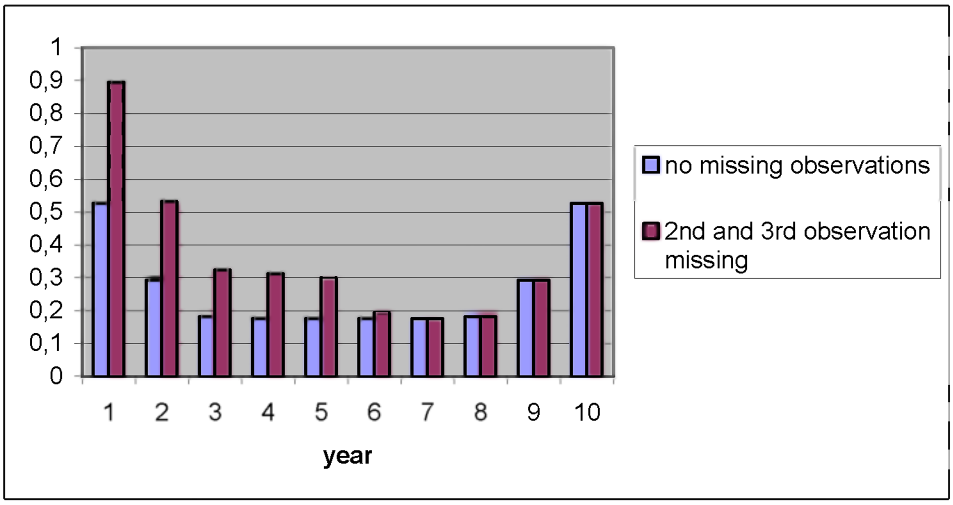


**Figure A10.2.** Variance (in units of $\sigma^2$) of LOESS smoother, second and third observations missing.



If there are no subsequent missing observations, the maximum increase of the variance will be 63 %. This may be considered acceptable, especially if the first two or the last two years do not contain any missing observation. Under that circumstance, the maximum variance of $Z(t)$ is $0.623\sigma^2$, which is only slightly higher than in the case without missing observations.

Both the distance between the missing observations and the minimum distance to the start or end of the time series determine the variance of the LOESS smoother. Table A10.1 contains the percentage increase of the average variance of $Z(t)$ for $n = 10$. If there are missing observations close to the start or the end of the time series or if there are subsequent missing values, considerable increase of the average variance is to be expected.

### 3.2 Effect of Outliers

If there are outlying values with reduced uncertainty weights, considerable effects of the weighted LOESS smoother can be observed. Effects depend on the position of the outlier within the time series. At the beginning or the end of the series, an outlier bends the trend line of the unweighted LOESS smoother into the direction of the outlier, whereas the weighted LOESS smoother is almost unaffected. This is demonstrated in Figure A10.3, where the uncertainty weight of the first observation is 1/9 of the weight of the remaining observations.
Outliers in the middle of the series may cause an artificial quadratic trend. This is demonstrated in Figure A10.4. Again, the weighted LOESS smoother is almost unaffected by the outlier.

**Table A10.1.** Increase of average variance of LOESS smoother for two missing observations (*n* = 10).

| | | Minimum distance of missing observation to the first or the last observation of the time series | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| Distance between missing observations | 1 | 37.9 % | 23.7 % | 22.9 % | 26.8 % |
| | 2 | 29.0 % | 21.4 % | 20.8 % | |
| | 3 | 26.7 % | 19.4 % | 17.1 % | |
| | 4 | 25.7 % | 17.2 % | | |
| | 5 | 24.5 % | 18.9 % | | |
| | 6 | 26.5 % | | | |
| | 7 | 33.9 % | | | |

**Figure A10.3.** Effect of an outlier in the first year on simulated concentrations of a contaminant (e.g., in µg l$^{-1}$).

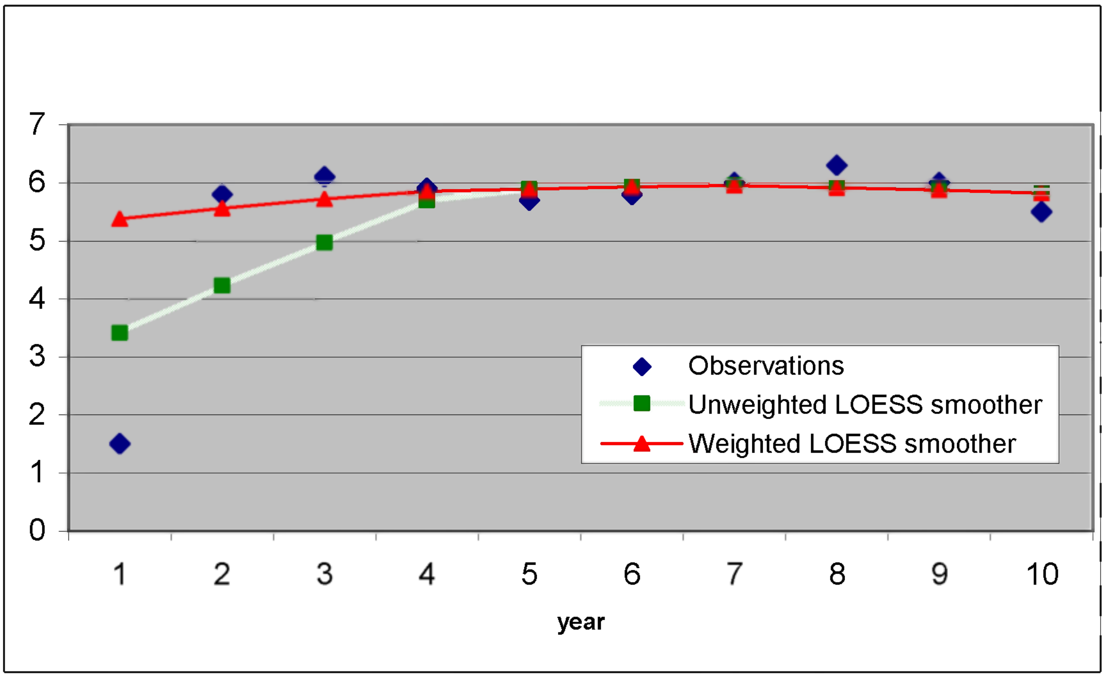
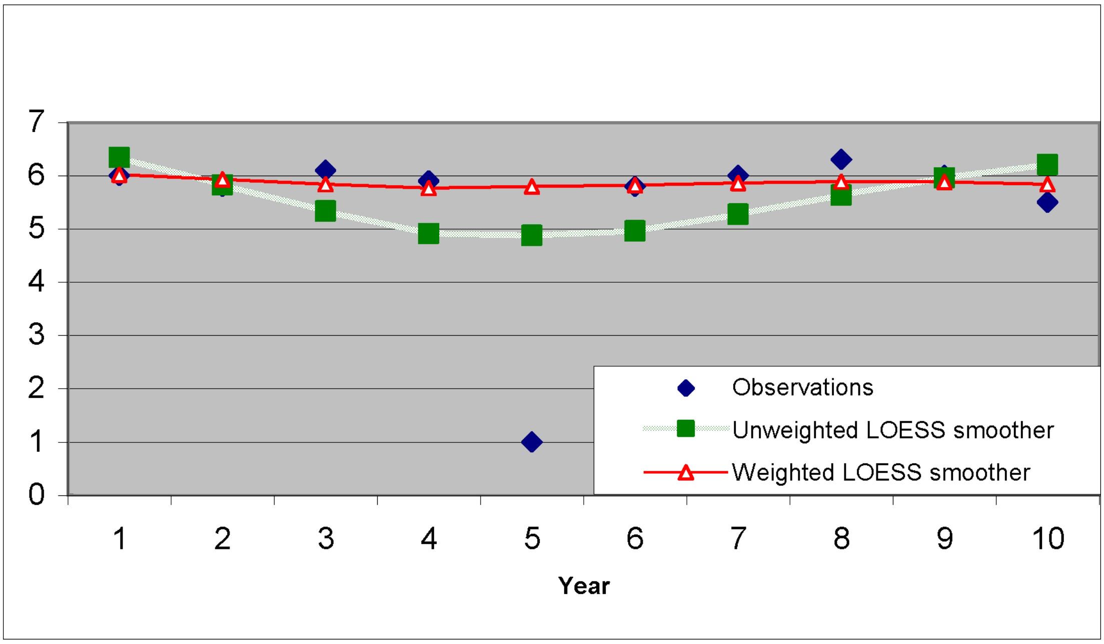


**Figure A10.4.** Effect of an outlier in the fifth year on simulated concentrations of a contaminant (e.g., in µg $l^{-1}$).

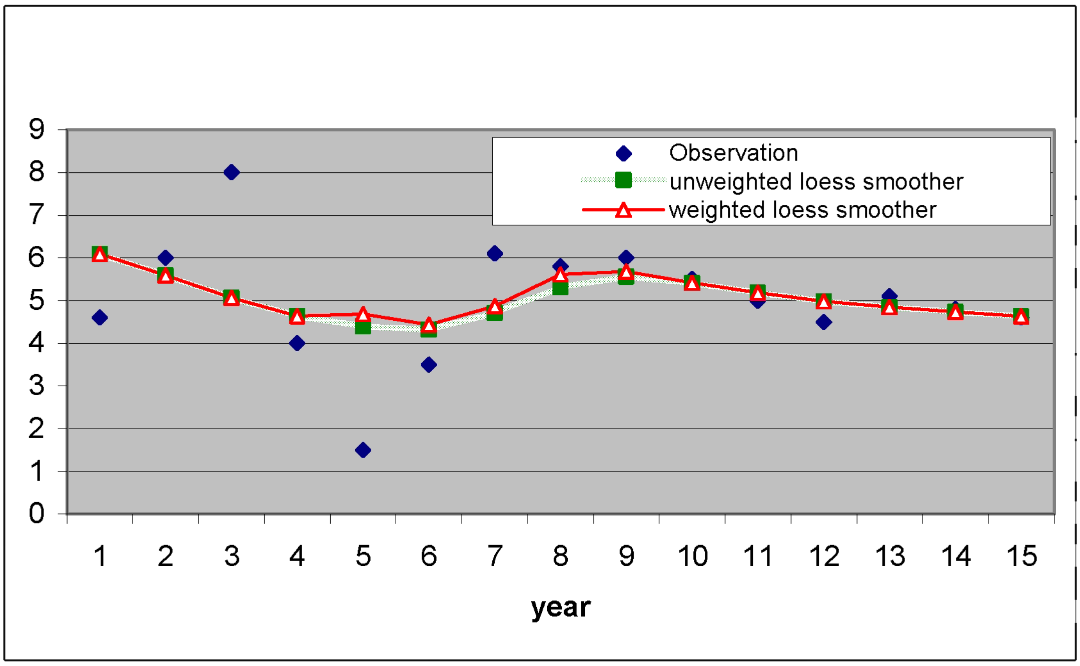


## 3.3 Effect of Local Weighting

Due to the principle of local regression, the weighted LOESS smoother accounts for uncertainties locally. Assuming that in the first half of the time series the uncertainty is much higher than in the second half (e.g., in case of substantial improvement of sampling procedure or analytical method), it would be sensible to apply a higher level of smoothing in the first half, and a reduced level in the second half of the series. This is only partially reflected in the weighted LOESS smoother.

For the time series presented in Figure A10.5, the uncertainty weight in years 1–7 is 1/9, and in the remaining years 8–15 the uncertainty weight is 1. Differences between the weighted and the unweighted LOESS smoother are small. Apparently the level of smoothing at the start and end of the time series is the same and both smoothers are not satisfyingly smooth in the first half of the time series. This is due to the estimation principle, which is based on a fixed seven-year span.

**Figure A10.5.** Example with reduced uncertainty standard deviation in years 8–15, based on simulated concentrations of a contaminant (e.g., in µg $l^{-1}$).



## 3.4 Calculation of Uncertainties of Mean Concentrations

Varying uncertainties may affect the estimated trend and test results considerably, and it is a prerequisite to calculate uncertainties in an appropriate way. In order to give an idea of such a calculation, an example is presented on how to perform the calculations.

Table A10.2 contains annual arithmetic mean concentrations and standard deviations of the concentrations of lead in water (ng $l^{-1}$) at Lobith/Rhine. Calculations are based partly on monthly and partly on bi-weekly measurements. In a comprehensive analysis of the data, it turned out that seasonal variation and runoff effects are small and hence can be neglected.

**Table A10.2.** Mean and standard deviation of Pb in water (ng $l^{-1}$) at Lobith/Rhine.

| **Year $x_t$** | **Samples $n_t$** | **Arithmetic mean $m_t$** | **Standard deviation $s_t$** | **Uncertainty weight $u_t$** |
|---|---|---|---|---|
| 1984 | 23 | 5,696 | 3,673 | 1,704 |
| 1985 | 26 | 6,962 | 3,293 | 2,397 |
| 1986 | 27 | 6,878 | 2,895 | 3,221 |
| 1987 | 25 | 4,936 | 1,838 | 7,402 |
| 1988 | 26 | 4,338 | 1,684 | 9,165 |
| 1989 | 26 | 5,008 | 1,757 | 8,424 |
| 1990 | 14 | 5,886 | 1,209 | 9,570 |
| 1991 | 13 | 6,692 | 2,015 | 3,201 |
| 1992 | 13 | 5,115 | 1,575 | 5,242 |
| 1993 | 12 | 5,500 | 3,401 | 1,037 |
| 1994 | 26 | 4,273 | 1,984 | 6,604 |
| 1995 | 26 | 3,698 | 2,426 | 4,418 |

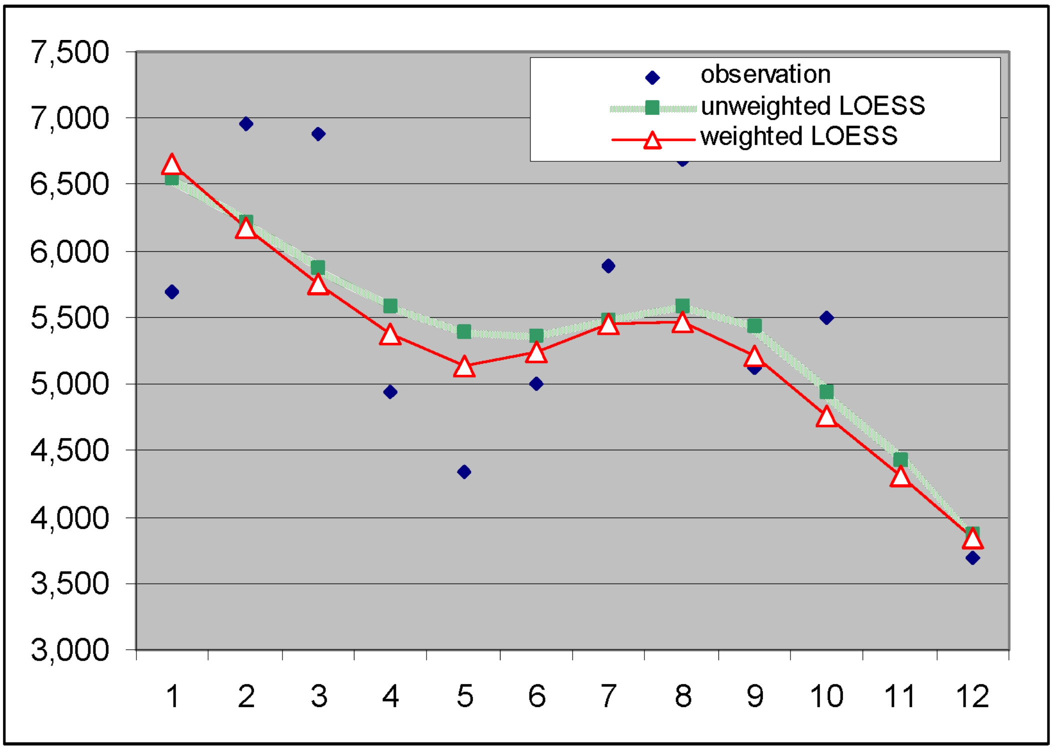
The Bartlett test statistic applied to the annual standard deviations equals 46.7 and exceeds the critical value 24.7 at the 99 % significance level. Therefore, it can be concluded that the within-year variance cannot be considered constant. Under that circumstance and under the assumption that there is no other source of uncertainty, the standard deviation of the arithmetic mean can be calculated $\sqrt{\frac{s_t^2}{n_t}}$, and the corresponding uncertainty weight equals $u_t = \frac{n_t}{s_t^2}$. These uncertainty weights are represented in Table A10.2. The corresponding weighted LOESS smoother and the unweighted LOESS smoother are represented in Figure A10.6.

The corresponding degrees of freedom for the residual variance are 8.184 and the residual variance equals

$$s^2 = \frac{1}{df_{error}} SS_{error} = \frac{1}{df_{error}} \sum_{t=1}^{n} u_t \left(y_t - z(x_t)\right)^2$$
$$= 2.702$$

However, if the model assumptions do hold and if the total standard deviations $s_t$ of the observations equal the standard deviations calculated, the expected value of the residual variance will be 1. Under the assumptions just mentioned, the distribution of $SS_{error}$ can be approximated by the chi-squared distribution with $df_{error}$ degrees of

**Figure A10.6.** Pb concentrations (in ng l$^{-1}$) at Lobith/Rhine from 1984 to 1995.



freedom. Therefore, if $SS_{error}$ exceeds the 95 % quantile of the chi-squared distribution with $df_{error}$ degrees of freedom, it can be concluded that either the model assumptions do not hold or the estimated standard deviations $s_t$ do not comprise all sources of uncertainty. Since $SS_{error}$ = 22. 0 > 15.5 exceeds the critical value, it can be concluded that in fact there might be other sources of uncertainty, such as inter-annual variation, or systematic short-term fluctuations (autocorrelation) which cannot be reflected properly by the seven-year smoother.

Inter-annual variation may be caused, e.g., by biological or climatic processes, and the crucial point is that, by definition, the inter-annual variation cannot be assessed by analyses based on within-year variations. It can only be assessed by comparisons between years.

For the example, there are two options. One could apply another smoother with a lower degree of smoothing, e.g., a LOESS smoother with a span of five years. This might be appropriate if it is supposed that there are anthropogenic changes that become effective within a few years.

Another option is to recalculate the uncertainty weights taking into account an additional inter-annual variance component $\sigma^2_{\text{inter}}$, e.g., calculating the uncertainty weights $u_t = \dfrac{1}{\sigma^2_{\text{inter}} + s_t^2 / n_t}$. Then $\sigma^2_{\text{inter}} = 0$ would imply the old formula $u_t = \dfrac{n_t}{s_t^2}$, and $\sigma^2_{\text{inter}} \to \infty$ would imply constant uncertainty weights, i.e., $\sigma^2_{\text{inter}} > 0$ implies some compromise between constant weights and varying uncertainties. The problem is how to determine $\sigma^2_{\text{inter}}$ in an appropriate way, and this should be the subject of further consideration. Accounting for an additional inter-annual variance component might be necessary, especially if the concentration level is considerably affected by biological processes or in case of strong seasonal variation.

### Acknowledgement

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# ANNEX 11

## *ACME/ACMP ADVICE BY TOPIC FOR THE YEARS 1990–2001*

Numbers in the table refer to sections of the present report and of the ACMP or ACME reports from 1990 to 2001, in reverse chronological order. From 2001, relevant sections from the report of the Advisory Committee on Ecosystems (ACE) are also listed.

*Signifies major advice on that topic.

| **Topic** | **Sub-topic** | **2001** | **2000** | **1999** | **1998** | **1997** | **1996** | **1995** | **1** |
|---|---|---|---|---|---|---|---|---|---|
| Monitoring | Strategy | | | | | | | 5.1 | *A |
| | Programme evaluation | | 6.7 | | | | | | |
| | Statistical methods for design | 4.6.2;4.6.3<br>;<br>4.6.4 | 6.6.2 | 5.6 | | | | | |
| | Benthos | | 6.8.1 | | | | 6.1.2;<br>11.1;<br>*Ann. 8 | | |
| | NSTF/MMP | | | | | | | | |
| | Sediments/guidelines | 4.5.1;<br>*Ann. 2 | | | 4.6;<br>*Ann. 2 | 4.5;<br>*Ann. 1 | 5.5;<br>*Ann. 4 | | |
| | Sediment data normalization | 4.5.1;<br>*Ann. 2 | 6.5.1;<br>Ann. 1 | 5.5 | | 4.5.2 | 5.5.1 | | |
| | Sediment sensitivity, variance factors | | | | | | | 5.6 | |
| | Metals/sediments | | | | | | 9.5 | 5.6 | |
| | Matrix tables<br>▪ general (JMP) | | | | | | | | |
| | ▪ organic | | | | | | | | |
| | ▪ NSTF | | | | | | | | |
| | Substances that can be monitored | | | | | | | | |
| | ▪ organic | | | 5.4 | 4.5 | | 5.4 | 6.6 | |
| | ▪ inorganic | | 6.4 | 5.4 | 4.5 | 4.2 | | | |
| | Use of seaweeds | | | | | | | | |
| | Use of seabird eggs | | | 13.2; Ann.<br>7 | 4.7.5 | | | | |
| | Spatial monitoring | 4.6.2;4.6.4 | 6.6.3 | | | *4.7.2 | | 5.3 | |
| | JAMP/JMP guidelines | | | | | 4.1 | 5.2;5.4 | 5.4 | |
| | BMP guidelines | | | | | | 5.1.2 | 5.4 | |
| | AMAP | 4.4 | 6.3 | 5.2 | 4.4 | | 5.1.3 | | |
| | Effects of nutrient enrichment | | | 12.1 | | | 9.1 | 5.8 | |
| | Monitoring PAHs | | | | 4.2;<br>*Ann. 1 | 4.4.1;4.<br>5;<br>*Ann. 1 | | | |
| Assessment | Statistical methods | 4.6.1;<br>Ann. 3,10 | | | 4.7.1 | | | | |
| | Combined effects of contaminants | | | 5.1.5 | 11.2 | | | | |
| | Biological community data | 9.4 | | | | | | | |
| | Data screening prior to assessment | 10.2;<br>Ann. 8,9 | | | | | | | |
| Temporal trend monitoring | Strategy/objectives | | | | | | *4;<br>Ann. 1 | | *<br>*An |
| | Guidelines | | | | | | 4.4 | | 4; |
| | Data analysis | | | | 4.7.4 | 15.2 | | | 5 |
| | Nutrients | | | | | | 5.7 | | |
| | Fish/JMP/JAMP | 4.6.5 | | 5.6.4 | | | 5.6 | | |
| | Fish/CMP | | | | | | 5.6 | | |
| | Biota/BMP | | | | | | | 7.3 | |
| | Biological effects | | | | 4.1 | | | | |
| | Mussels | | | | | | | | |
| | Pooling | | | | | | | | |

| Topic | Sub-topic | 2001 | 2000 | 1999 | 1998 | 1997 | 1996 | 1995 | 1 |
|---|---|---|---|---|---|---|---|---|---|
| | Precision | | 6.6.5 | | | | | | 5 |
| | Sediments | | | | | | 4.3;<br>5.5.3 | | |
| | Statistical requirements | | | | 4.7 | | | 4.3 | |
| Integration of biological/ chemical measurements | Sediment quality | 6.3;6.4 | | | | | 5.2.2 | 4.2;<br>Ann. 2 | 5 |
| Biological effects monitoring | Monitoring strategy | | | | | | *5.3 | 4.1;<br>*Ann. 1 | |
| | Statistical design | | | | 4.1* | 4.31 | | | |
| | Methods | 4.1 | 6.1.2 | 5.1.1 | | 4.3.2 | 5.3.2 | Ann. 1 | |
| | Molecular techniques | | | | | | | *5.2 | |
| | Pathology | | | | | 4.3.3 | 5.3.3 | 8.4 | 9 |
| | Workshop results | 4.1.1 | 6.1.4 | | | | 5.3.2 | | |
| | Source of variability | | 6.1.1;<br>6.6.4 | 5.1.2 | | | | | |
| | Data analysis<br>▪ general | | | | | | | | |
| | ▪ EROD | | | | | | | | |
| | ▪ oyster bioassay | | | | | | | | |
| | Endocrine disruption | | 9.6 | | | | | | |
| Baseline studies | ICES Baseline TM/SW | | | | | | | | |
| | Contaminants in<br>▪ Baltic sediments | | | 5.2 | 4.3 | 6.1 | 7.1 | 7.1 | 7 |
| | ▪ North Sea sediments | | | | | | | | |
| | HCH in sea water | | | | | | | | |
| Regional assessments | Guidelines | | | | | | | | |
| | Preparation plans/reviews | 10.5 | 18.4;<br>Ann. 9 | | | | | | |
| | North Sea QSR | | | | | | | | |
| | Baltic Sea | | | | | | 7.2 | 7.2 | 7 |
| | Baltic fish | | 18.2 | | | | 7.3 | 7.2 | 7 |
| | Canadian waters | | | | | | | | |
| | Nutrient trends–North Atlantic | | | | | | | | |
| Quality assurance | Philosophy | | | | | | | | |
| | Reference materials | 5.6;<br>Ann. 4 | 7.5;<br>Ann. 4 | | 5.6 | 4.2 | | | *6 |
| | Oxygen in sea water | | | | | *Ann. 3 | | | |
| | Nutrients | | | | | 5.7 | | | |
| | Quality/comparability<br>▪ organic contaminants | | | 5.4 | 4.5 | | | *6.6 | *6 |
| | Lipids | | | | | | | 6.4 | 6 |
| | NSTF | | | | | | | | |
| | Biological effects techniques | 5.3 | 7.3 | 7.4 | 5.4 | 5.3 | *6.2;<br>*Ann. 5 | 6.2 | |
| | Sediment quality criteria | | | | | | | | |
| | QA of sampling | | 7.7 | 7.6 | 5.7 | 5.10 | | | |
| | QA info. in data bank | 5.5 | | | | 16.1.1 | | | 6. |
| | Chemical measurements–Baltic Sea | 5.4 | 7.4 | 7.5 | 5.5 | 5.4 | 6.3 | 6.3 | 6 |
| | Biological measurements | 5.1;5.2 | 7.1; 7.2 | 7.1; 7.2 | 5.1; 5.2 | 5.1; 5.2 | 6.1 | 6.1 | 6 |
| | Fish disease monitoring | 5.3 | | | 8.2 | 5.3.2 | *Ann. 6 | | |
| | Use of QA data | 10.2 | | | | | | | |

| Topic | Sub-topic | 2001 | 2000 | 1999 | 1998 | 1997 | 1996 | 1995 | 19 |
|---|---|---|---|---|---|---|---|---|---|
| Intercomparison exercises | Status | | | Ann. 8 | | Ann. 10 | Ann. 10 | Ann. 7 | An |
| | Nutrients/sea water | | | | | | 6.4 | 6.5 | 6 |
| | Hydrocarbons in biota | | | | | | | 6.7 | |
| | PAHs/standards | | | | | | | | |
| | PCBs/CBs in biota | | | | | | | 6.6; 6.7 | 6.3; |
| | Organochlorines in biota | | | | | | | 6.6; 6.7 | |
| | CBs/standards | | | | | | | | |
| | CBs in sediments | | | | | | | 6.6 | 6 |
| | Metals in<br>▪ sea water | | | | | 5.5 | 6.5 | | |
| | ▪ SPM | | | | | | | | 6 |
| | Dissolved oxygen in sea water | | | | | | | | |
| | Oyster embryo bioassay | | | | | | | | |
| | EROD | | | | | | | | |
| Methods | DO in sea water | | | | | *Ann. 3 | | | |
| | Sediment normalization | 4.5.1;<br>*Ann. 2 | 6.5.1;<br>Ann. 1 | | | | | | 5 |
| | Organic carbon measurements | | | | | 4.6;<br>Ann. 2 | | | |
| | Zooplankton studies | | 6.8.3 | | | | | | |
| Algal blooms | Primary production methods | | | | | | | | |
| | Initiating factors | | | | | | | | |
| | Dynamics | | | | 10.2 | 9.2 | | | 8 |
| | Exceptional blooms | 9.3 | 6.8.2;<br>Ann. 3 | 12.2;<br>Ann. 2 | Ann. 3 | Ann. 8 | | | |
| | Phycotoxins/ measurements | | | | | | | | |

| **Topic** | **Sub-topic** | **2001** | **2000** | **1999** | **1998** | **1997** | **1996** | **1995** | **19** |
|---|---|---|---|---|---|---|---|---|---|
| Fish diseases and related issues | Relation to pollution | | | | 8.2 | 8.3 | 5.3.3 | 8.4 | 9 |
| | Survey methods | | | | | 7.2 | | | |
| | Diseases in wild fish | 7.1 | 9.1 | 10.1 | | | | | |
| | Baltic fish | | 9.4;<br>*Ann. 6 | | | 7.2 | | 8.1; 8.2;<br>8.3 | 9 |
| | Data analysis | 7.2 | 9.2 | 10.2;<br>Ann. 5 | 8.1;<br>*Ann. 8 | 7.1 | 8.2 | | 9 |
| | M74 in Baltic salmon | 7.1 | 9.3 | 10.3 | 8.3 | 6.2 | 7.4 | 7.4 | 9 |
| Mariculture | Interactions | 12 | 14.1 | 15.2 | | | 15.1 | 14 | 1 |
| | Escape of fish—effects | | 15.1 | | 14.2 | 14.1 | | | |
| | Nutrient inputs/Baltic | | 14.2 | | | | | | |
| | Use of chemicals | | 14.1.2 | 15.2 | | 14.2 | | | |
| Introductions and Transfers | Code of Practice | | | | | | 14.2 | 13.1 | 14 |
| | Accidental transfers, including via ships | 8.1.2;<br>8.3 | 10.1.2;<br>10.2 | 11.1 | 9.1; 9.2 | 13.2 | 14.4;<br>*Ann. 9 | 13 | 14 |
| | Genetically modified organisms | | | 15.1 | 9.3 | | 14.5 | | |
| | On-going introductions | 8.1.1 | 10.1.1 | | | 13.1 | 14.1 | | |
| | Baltic Sea | | | 11.1 | 9.3 | | 14.3 | | |
| Marine mammals | Contaminants/effects | | 13.2 | 14.1 | 12.2;<br>*Ann. 10 | 11.4 | 5.4.2;<br>13.3;<br>13.4 | | |
| | Seal epidemic 1988 | | | | | | | | |
| | Baltic marine mammal stocks | | *13.1 | 14.2 | | 11.1 | 13.1 | | 10 |
| | Populations/N. Atlantic | ACE 4.6 | | | | | | | 10 |
| | Pathogens | | | | | | | | |
| | Impact of fisheries | ACE 3 | | | 12.1;<br>*Ann. 9 | 11.2;<br>11.3 | 13.2 | | |
| Seabirds | Diet, food consumption | | | 13.1;<br>*Ann. 6 | | | | | |
| | Use in contaminant monitoring | | | 13.2;<br>*Ann. 7 | | | | 5.3 | |
| | Effects of contaminants | | 12.1 | | | | | | |
| | Populations | ACE 4.8 | | | | | | | |
| Overviews | Mercury | | | | 7.1;<br>*Ann. 4 | | | | |
| | Hormone disruptors | 6.2 | | | 7.4;<br>Ann. 6 | | Ann. 2 | | |
| | HCB | | | | | | | | |
| | Lindane (γ-HCH) | | | | | | | | |

| **Topic** | **Sub-topic** | **2001** | **2000** | **1999** | **1998** | **1997** | **1996** | **1995** | **19** |
|---|---|---|---|---|---|---|---|---|---|
| Overviews (cont.) | Tris(4-chlorophenyl) methanol/methane | 6.1.1 | 8.1 | | | | 10;<br>*Ann. 7 | | |
| | Benzene/ alkylated benzenes | | | | | | | 10.2;<br>*Ann. 5 | |
| | Chlorinated alkanes | | 8.1 | | | | | 10.1;<br>Ann. 4 | |
| | PBBs and PBDEs | 6.1.2 | | 9.2;<br>*Ann. 4 | | | | | |
| | PCDDs and PCDFs | 6.1.5;<br>*Ann. 7 | | | | | | | |
| | PCDEs | | | | | 8.1;<br>*Ann. 6 | | | |
| | TBT | | | 9.2;<br>*Ann. 3 | | | | | |
| | Octachlorostyrene | | | | | | | | |
| | Toxaphene | | | | | 8.1;<br>*Ann. 5 | | | 12 |
| | Atrazine | | | | | | | | 12 |
| | Irgarol 1051 | 6.1.3;<br>*Ann. 5 | | | | 8.1;<br>*Ann. 4 | | | |
| | Antifouling booster biocides | 6.1.3<br>*Ann. 5 | | | | | | | |
| | Volatile organic contaminants | 6.1.4;<br>Ann. 6 | | | | | | | |
| Classification/ assessment tools | Human health | | | | | | | | |
| | Hazardous substances | | | | 11.1 | | | 12.3 | |
| | Background concentrations | | 6.2 | | | 15.1 | | 12.1 | |
| | Ecological Quality Objectives—North Sea | ACE 4 | 18.6 | 17.2 | | | | | |
| | Ecotoxicolgical reference values | | | | | | | 12.2 | |
| | Environmental indicators | 10.4 | | 17.1 | | | | | |
| Sand/gravel extraction | Code of Practice | | | | | | | | |
| | Effects | 13 | 16 | 8.1 | 6.1 | *6.3 | | | |
| | Environmental impact assessment | 13 | | 8.1 | | | | *15 | *1 |
| Modelling | Radioactive contaminants/Baltic Sea | | | | | | | | |
| | Use in monitoring and assessment | | | | | | | | 1 |

| Topic | Sub-topic | 2001 | 2000 | 1999 | 1998 | 1997 | 1996 | 1995 | 19 |
|---|---|---|---|---|---|---|---|---|---|
| Data banks and management | Nutrients | 15.2 | 20.2 | 19.2 | 15.2 | 17.2 | 16.1.2 | | |
| | Contaminants | 15.1 | 20.1 | 19.1 | 15.1 | 17.1 | 16.1.1;<br>16.3 | 17 | 2 |
| | NSTF | | | | | | | | |
| | ICES format | 15.1 | 20.1.10;<br>20.5 | 19.1 | | | 16.6 | | |
| | ICES databases | 15.1 | 20.1 | 19.1 | | | | | |
| | Biological database | 15.3 | 20.3 | 19.3 | 15.1.3 | 17.3;<br>17.4 | | | 11<br>An |
| | AMAP | 15.1 | 20.1.3 | 19.1.3 | | 17.1.1 | 16.2 | | |
| Ecosystem effects of fishing | General | | 18.1 | | | *12 | 12 | | 1 |
| | Effects of disturbance on benthos | | 5 | | 10.4 | 9.3 | 11.2 | 9;<br>Ann. 3 | 11 |
| | Seabird/fish interactions | | 12.2 | 4 | | 10 | | | 1 |
| | Changes in abundance of non-target fish species | | | | *13.3 | | | | |
| | Models and metrics | | 18.5 | | 13.4.1 | | | | |
| | Effects on level of predation on benthos by fish | | | | 13.4.2 | | | | |
| | Impact on size/age and spatial distributions of target fish | | | | 13.1 | | | | |
| | Discards | | *11 | | 13.2 | | | | |
| Inputs of contaminants and nutrients | Riverine inputs (gross) | | | | 4.7.2;<br>4.7.3 | *4.7.1 | | | |
| | Trend detection methods | 4.6.1;<br>Ann. 3 | *6.6.1;<br>*Ann. 2 | *6;<br>*Ann. 1 | | | | | |
| | Atmospheric inputs | | | | | 4.7.1 | | | |
| ICES Environmental Report | Oceanographic conditions | 10.6.1 | 18.3.1 | 8.4.1 | 6.2.1 | | | | |
| | Zooplankton | 10.6.2 | | | 6.2.2 | | | | |
| | Harmful algal blooms | 10.6.3 | 18.3.2 | 8.4.2;<br>Ann. 2 | 6.2.3;<br>Ann. 3 | | | | |
| | Fish disease prevalence | 10.6.4 | 18.3.3;<br>Ann. 8 | | | | | | |

| **Topic** | **Sub-topic** | **2001** | **2000** | **1999** | **1998** | **1997** | **1996** | **1995** | **19** |
|---|---|---|---|---|---|---|---|---|---|
| Special topics | Context of ACMP advice | | | | | | | | |
| | Nutrient trends/eutrophication in OSPAR area | 11 | | | | Ann. 9 | | | |
| | Nutrients and eutrophication | | | | 10.1 | 9.1 | 9.1 | 5.8 | |
| | Sediments—Baltic | | | 5.2 | 4.3 | 6.1 | 7.1 | 7.1 | 7 |
| | Sediments (bioavailability) | | | | | | 9.3 | 4.2;<br>Ann. 2 | 5 |
| | Bioaccumulation of contaminants | | | | | 8.2;<br>*Ann. 7 | | | |
| | Oil spill studies | Ann. 1 | | | | | | | |
| | Coastal zone fluxes | | | | | | | | |
| | Influence of biological factors on contaminant concentrations | | | | 7.2;<br>Ann. 5 | | | | |
| | Discharge of produced water by offshore platforms | | | | 7.6;<br>Ann. 7 | | | | |
| | North Sea Benthos Survey | 9.1 | | | | | | 9 | |
| | GLOBEC | 14.1 | 19.1 | 18.1 | 16.2 | | | | |
| | GOOS | 14.2 | 19.2 | 18.2 | 16.1 | 16 | | | |
| | GIWA | 14.3 | | | | | | | |
| | Marine habitat classification/ mapping | ACE 5 | 17 | 16 | | | | | |
| | Toxicity of dredged material | | 8.4 | | | | | | |

# ANNEX 12

## TITLES OF RECENTLY PUBLISHED ICES COOPERATIVE RESEARCH REPORTS

| No. | Title |
|---|---|
| 222 | Report of the ICES Advisory Committee on the Marine Environment, 1997 |
| 223 | Report of the ICES Advisory Committee on Fishery Management, 1997 (Part 1 and Part 2) |
| 224 | Ballast Water: Ecological and Fisheries Implications |
| 225 | North Atlantic-Norwegian Sea Exchanges: The ICES NANSEN Project |
| 226 | Report on the Results of the ICES/IOC/OSPARCOM Intercomparison Programme on the Determination of Chlorobiphenyl Congeners in Marine Media—Steps 3a, 3b, 4 and Assessment |
| 227 | Tenth ICES Dialogue Meeting |
| 228 | Report of the 11th ICES Dialogue Meeting on the Relationship between Scientific Advice and Fisheries Management |
| 229 | Report of the ICES Advisory Committee on Fishery Management, 1998 (Part 1 and Part 2) |
| 230 | Working Group on Methods of Fish Stock Assessment—Reports of Meetings in 1993 and 1995 |
| 231 | Status of Introductions of Non-Indigenous Marine Species to North Atlantic Waters 1981–1991 |
| 232 | Diets of Seabirds and Consequences of Changes in Food Supply |
| 233 | Report of the ICES Advisory Committee on the Marine Environment, 1998 |
| 234 | Report of the Workshop on Ocean Climate of the NW Atlantic during the 1960s and 1970s and Consequences for Gadoid Populations |
| 235 | Methodology for Target Strength Measurements (with special reference to *in situ* techniques for fish and micronekton) |
| 236 | Report of the ICES Advisory Committee on Fishery Management, 1999 (Part 1 and Part 2) |
| 237 | Seventh Intercomparison Exercise on Trace Metals in Sea Water |
| 238 | Report on Echo Trace Classification |
| 239 | Report of the ICES Advisory Committee on the Marine Environment, 1999 |
| 240 | Report of the Young Scientists Conference on Marine Ecosystem Perspectives |
| 241 | Report of the ICES Advisory Committee on the Marine Environment, 2000 |
| 242 | Report of the ICES Advisory Committee on Fishery Management, 2000 (Part 1) |
| 243 | Report of the 12th ICES Dialogue Meeting (First Environmental Dialogue Meeting) |
| 244 | Report of the Workshop on Gadoid Stocks in the North Sea during the 1960s and 1970s. The Fourth ICES/GLOBEC Backward-Facing Workshop |
| 245 | The Annual ICES Ocean Climate Status Summary 2000/2001 |
| 246 | Report of the ICES Advisory Committee on Fishery Management, 2001 (Part 1, Part 2 and Part 3) |
| 247 | Effects of Extraction of Marine Sediments on the Marine Ecosystem |

# ACRONYMS

| | |
|---|---|
| ACE | Advisory Committee on Ecosystems |
| ACFM | Advisory Committee on Fishery Management |
| AchE | acetylcholinesterase |
| ACIA | Arctic Climate Impact Assessment |
| ACME | Advisory Committee on the Marine Environment |
| ACMP | Advisory Committee on Marine Pollution |
| ADI | acceptable daily intake |
| AET | apparent effects threshold |
| AFSSA | French Agency for the Safety of Food |
| AHH | aryl hydrocarbon hydroxylase |
| AI | artificial intelligence |
| AIRD | Aquatic Invasions Research Directory |
| ALA-D | δ-aminolevulinic acid dehydratase |
| AMAP | Arctic Monitoring and Assessment Programme |
| ANOVA | analysis of variance |
| AQC | analytical quality control |
| ARC | Aquatic Restoration and Conservation |
| ASC | Annual Science Conference (ICES) |
| ASC | Assessment Steering Committee (AMAP) |
| ASCOBANS | Agreement on Small Cetaceans of the Baltic and North Sea |
| ASE | accelerated solvent extraction |
| ASG | Assessment Steering Group (AMAP) |
| ASMO | Environmental Assessment and Monitoring Committee (OSPAR) |
| ASP | amnesic shellfish poisoning |
| ATHN | 7-acetyl-1,1,3,4,4,6-hexamethyltetrahydro-naphthalene |
| ATP | adenosine triphosphate |
| AUV | automated underwater vehicle |
| BACI | before/after comparison impact |
| BCF | bioconcentration factor |
| BCPS | bis-*p*-chlorophenyl sulfone |
| BCR | European Commission Community Bureau of References |
| BDE | bromodiphenylether |
| BECPELAG | ICES/IOC Sea-going Workshop on Biological Effects of Contaminants in Pelagic Eosystems |
| BEEP | Biological Effects of Environmental Pollution in Monitoring and Coastal Ecosystems |
| BEQUALM | Biological Effects Quality Assurance in Monitoring Programmes |
| BEWG | Benthos Ecology Working Group |
| BFG | Institute of Hydrology (Koblenz, Germany) |
| BFR | brominated flame retardants |
| BGS | British Geological Survey |

| | |
|---|---|
| BMB | Baltic Marine Biologists |
| BMG | Baltic Marine Geologists |
| BMP | Baltic Monitoring Programme (HELCOM) |
| BOD | biological oxygen demand |
| BP | before present |
| BPH | benzo[*a*]pyrene hydroxylase |
| B/RC | background/reference concentrations |
| BSH | Federal Maritime and Hydrographic Agency (Germany) |
| BSPAs | Baltic Sea Protected Areas |
| BW | body weight |
| CAFF | Conservation of Arctic Flora and Fauna |
| CAU | Christian-Albrechts-Universität zu Kiel (Germany) |
| CBs | chlorobiphenyls |
| CBD | Convention on Biological Diversity |
| CBIN | Canadian Biodiversity Information Network |
| CBO | Conference of Baltic Oceanographers |
| CCA | canonical correspondence analysis |
| CDEs | chlorodiphenylethers |
| CD-ROM | compact disc: read-only memory |
| CEFAS | Centre for Environment, Fisheries and Aquaculture Science (UK) |
| CEMP | Coordinated Environmental Monitoring Programme (OSPAR) |
| CFP | ciguatera fish poisoning |
| CHBs | chlorinated bornanes |
| CHCs | chlorinated hydrocarbons |
| CIEM | Conseil International pour l'Exploration de la Mer |
| CIL | Cambridge Isotope Laboratories (USA) |
| CIRIA | UK-based research association concerned with improvingthe performance of all involved in construction and the environment |
| CMACS | Centre for Marine and Coastal Studies in Liverpool |
| CMDGC | comprehensive multidimensional gas chromatography |
| CITES | Convention on International Trade in Endangered Species |
| CMP | Cooperative ICES Monitoring Studies Programme |
| COD | chemical oxygen demand |
| COMBINE | Cooperative Monitoring in the Baltic Marine Environment (HELCOM) |
| COMPREHEND | EU project on endocrine disruptors |
| CORINE | EEA Coordination of Information on the Environment |
| CPR | Continuous Plankton Recorder |
| CPT | copper pyrithione |
| CPUE | catch per unit effort |
| CRIMP | Centre for Research on Introduced Marine Pests (Australia) |
| CRMs | certified reference materials |
| CTD | conductivity–temperature–density |

| | |
|---|---|
| CUSUM | **Cu**mulative **Sum** |
| CV | coefficient of variation |
| CYP | cytochrome P450 |
| DBT | dibutyltin |
| DCA | Danish Coastal Authority |
| DCM | dichloromethane |
| DDE | dichlorodiphenylethylene |
| DDT | dichlorodiphenyltrichloroethane |
| ∑DDT | total DDT |
| DES | diethylstilbestrol |
| DETR | Department of the Environment, Transport and the Regions (UK) |
| DG | Directorate General |
| DGTs | diffusive gradients in thin films |
| DIFFCHEM | OSPAR Working Group on Diffuse Sources |
| DIN | dissolved inorganic nitrogen |
| DMA | dimethylarsenic |
| DNA | deoxyribonucleic acid |
| DO | dissolved oxygen |
| DOC | dissolved organic carbon |
| DPP | differential pulse polarography |
| DPSIR | driving forces-pressure-state-impact-responses |
| DR-CALUX | dioxin-responsive chemical-activated luciferase |
| DSP | diarrhetic shellfish poisoning |
| DST | diarrhetic shellfish toxin |
| DTA | direct toxicity assessment |
| DYNAMEC | Ad Hoc Working Group on the Development of a Dynamic Selection and Prioritisation Mechanism for Hazardous Substances (OSPAR) |
| EAC | ecotoxicological assessment criteria |
| EC | European Commission |
| ECD | electron capture detection |
| ECE LRTAP | Economic Commission for Europe Long-Range Transboundary Air Pollution Convention (UN) |
| EcoQO | ecological quality objective |
| ED | endocrine disruptor |
| EDCs | endocrine-disrupting chemicals |
| EDI | ethylene diisothiocyanate |
| EDMAR | UK Programme on endocrine disruption |
| EEA | European Environment Agency |
| EEZ | Exclusive Economic Zone |
| EI | electron impact ionization |
| EIA | environmental impact assessment |
| ELISA | enzyme-linked immunosorbent assays |
| EMD | evaporative mass detector |

| | |
|---|---|
| EMS | Electronic Monitoring System |
| ENDS | Environmental Data Services (UK) |
| ENSO | El Niño Southern Oscillation |
| EOC | elemental organic carbon |
| EOCl | extractable organic chlorine |
| EPA | Environmental Protection Agency (USA) |
| EPT | Equilibrium Partitioning Theory |
| EQG | environmental quality guidelines |
| EQS | environmental quality standard |
| ER-CALUX | oestrogen-responsive chemical-activated luciferase |
| ERL/ERM | Effects Range—Low/Effects Range—Median |
| EROD | ethoxyresorufin-*O*-deethylase |
| ESB | Environmental Specimen Bank (Germany) |
| ESE | enhanced solvent extraction |
| ESF | European Science Foundation |
| ETC/MCE | European Topic Centre on Marine and Coastal Environment |
| ETU | ethylenethiourea |
| EU | European Union |
| EUC | Eutrophication Committee (OSPAR) |
| EUNIS | European Nature Information System |
| EUROCAT | European catchments and their ecological effects on coastal seas |
| EUROSTAT | Statistical Office of the European Communities |
| EU-SMT | EU Standards, Measurement and Testing |
| FAO | Food and Agriculture Organization |
| FDA | fluresein diacetate |
| FDE | Fish Disease Data Entry Program |
| FID | flame ionization detection |
| FMO | flavin-containing mono-oxygenase |
| FRS | Fisheries Research Service (UK) |
| FTZ | Research and Technology Centre of Kiel University (Germany) |
| GAAS | Russian Group on Aquatic Alien Species |
| GABA | γ-aminobutyric acid |
| GAM | general additive model |
| GC | gas chromatography |
| GCOS | Global Climate Observing System |
| GC/ECD | gas chromatography/electron capture detection |
| GC/MS | gas chromatography/mass spectrometry |
| GEF | Global Environment Facility |
| GESAMP | Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection |
| GEOHAB | Global Ecology and Oceanography of Harmful Algal Blooms (IOC-SCOR) |
| GIS | Geographical Information System |

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| GIWA | Global International Waters Assessment |
| GLM | general linear model |
| GLOBEC | Global Ocean Ecosystem Dynamics Programme |
| GOOS | Global Ocean Observing System |
| GPC | gel permeation chromatography |
| GPX | glutathione peroxidase |
| GSI | gonadosomatic index |
| GST | glutathion-*S*-transferase(s) |
| HAB | harmful algal bloom |
| HAE | harmful algal event |
| HAEDAT | Harmful Algal Event Database |
| HARP | Harmonized Reporting Procedures (OSPAR) |
| HELCOM | Helsinki Commission (Baltic Marine Environment Protection Commission) |
| HPLC | high performance liquid chromatography |
| HRMS | high resolution mass spectrometry |
| HSP | heat-shock protein(s) |
| IASC | International Arctic Science Committee |
| IBSFC | International Baltic Sea Fisheries Commission |
| IBTS | International Bottom Trawl Survey |
| ICES | International Council for the Exploration of the Sea |
| IFREMER | Institut Français de Recherche pour l'Exploitation de la Mer |
| IfM | Institut für Meereskunde, Kiel, Germany |
| IGBP | International Geosphere-Biosphere Programme |
| IJC | International Joint Commission (Canada and the USA) |
| IMM | Intermediate Ministerial Meeting (North Sea) |
| IMO | International Maritime Organization |
| IMPACT II | EU-funded project on the impact of bottom trawls on the North Sea and Irish Sea benthic ecosystems |
| INPUT | Working Group on Inputs to the Marine Environment (OSPAR) |
| IOC | Intergovernmental Oceanographic Commission |
| IOS | Initial Observing System (GOOS) |
| IOW | Institute of Baltic Sea Research (Warnemünde, Germany) |
| IPCC | Intergovernmental Panel on Climate Change |
| ISA | Infectious Salmon Anaemia |
| ISE | Intersex Sequence Index |
| ISO | International Organization for Standardization |
| ITIS | Interagency Taxonomic Information System (USA) |
| ITM | Institute of Applied Environment Research (Sweden) |
| IUCN | International Union for the Conservation of Nature and Natural Resources |
| IWC | International Whaling Commission |
| JAMP | OSPAR Joint Assessment and Monitoring Programme |
| JGOFS | Joint Global Ocean Flux Study (IGBP) |

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| JMP | OSPAR Joint Monitoring Programme |
| JNCC | Joint Nature Conservation Committee (UK) |
| LD | lethal dose |
| LGC | Laboratory of the Government Chemist (UK) |
| LIFE | EC conservation programme |
| LMR | Living Marine Resources Panel (GOOS) |
| LOES | National Investigation into Oestrogenic Compounds in the Aquatic Environment (Dutch acronym) |
| LOESS | statistical smoother |
| LOWESS | statistical smoother |
| LOI | loss-on-ignition |
| LPS | Laboratory Performance Scheme (QUASIMEME) |
| LRMs | laboratory reference materials |
| LRMS | low resolution mass spectrometry |
| MA | Marketing Authorisation |
| MAFF | Ministry of Agriculture, Fisheries and Food (UK) |
| MAHs | monocyclic aromatic hydrocarbons |
| MarLIN | Marine Life Information Network (UK) |
| MAST | Marine Science and Technology Programme (EC) |
| MBT | monobutyltin |
| MCWG | Marine Chemistry Working Group |
| MDA | malone dialdehyde |
| MDGC | multidimensional gas chromatography |
| MDR | multidrug resistance |
| MDS | multi-dimensional scaling |
| MEDPOL | Monitoring and Research Programme of the Mediterranean Action Plan |
| MeHg | methyl mercury |
| MFO | mixed-function oxidase |
| MMA | monomethylarsenic |
| MMHg | monomethylmercury |
| MMP | Monitoring Master Plan (NSTF) |
| MON | Working Group on Monitoring (OSPAR) |
| MONAS | Monitoring and Assessment Group (HELCOM) |
| MPA | Marine Protected Area |
| mRNA | messenger ribonucleic acid |
| MS | mass spectrometry |
| MSD | mass selective detector |
| MSY | maximum sustainable yield |
| MT | metallothionein |
| MTBT | (methylthio)benzothiazole |
| mtDNA | mitochrondrial DNA |
| MXR | multixenobiotic resistance |

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| NAO | North Atlantic Oscillation |
| NCI | negative chemical ionization |
| NCM | Nordic Council of Ministers |
| NERC | National Environmental Research Council |
| NIES | National Institute for Environmental Standards (Japan) |
| NIHS | National Institute of Health Science (Japan) |
| NILU | Norwegian Institute for Air Reearch |
| NIST | U.S. National Institute of Standards and Testing |
| NIVA | Norsk instittutt for vannforskning [Norwegian Institute for Water Research] |
| NMBAQC | National Marine Biological Analytical Quality Control Scheme (UK) |
| NMR | nuclear magnetic resonance |
| NOAA | National Oceanic and Atmospheric Administration (USA) |
| NOAEC | no observable adverse effects concentration |
| NOAEL | no observable adverse effects level |
| NODC | National Oceanographic Data Center (USA) |
| NOEL | no observable effects level |
| NORWECOM | **Norw**egian **Eco**logical **M**odel |
| NOWESP | North-West European Shelf Programme (EU MAST Project) |
| NPE | nonylphenol |
| NRC | National Research Council (Canada) |
| NRPA | Norwegian Radiation Protection Agency |
| NRR | neutral red retention |
| NSBP | North Sea Benthos Project |
| NSP | neurotoxic shellfish poisoning |
| NSTF | North Sea Task Force |
| NWRI | National Water Research Institute (Canada) |
| OCs | organochlorines |
| OCPs | organochlorine pesticides |
| OECD | Organisation for Economic Cooperation and Development |
| OIE | Office International des Epizooites |
| OM | oxidizable matter |
| OPs | organophosphates |
| OSPAR | OSPAR Commission |
| PAHs | polycyclic aromatic hydrocarbons |
| PAMP | Post-Authorisation Monitoring Programme (Scotland) |
| PAR | photosynthetic available radiation |
| PBBs | polybrominated biphenyls |
| PBDEs | polybrominated diphenylethers |
| PBTs | persistent, bioaccumulative, toxic compounds |
| PCA | principal component analysis |
| PCBs | polychlorinated biphenyls |

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| PCDDs | polychlorinated dibenzo-*p*-dioxins |
| PCDEs | polychlorinated diphenylethers |
| PCDFs | polychlorinated dibenzofurans |
| PCNA | proliferating cell nuclear antigen |
| PCNs | polychlorinated naphthalenes |
| PCP | pentachlorophenol |
| PCR | polymerized chain reaction |
| PCTs | polychlorinated terphenyls |
| PD | project directory |
| PEEK | polyetheretherketone |
| PEL/TEL | Probable Effects Level/Threshold Effects Level |
| PERC | Plymouth Environment Research Centre |
| PFC | plaque-forming cell |
| PHAHs | polyhalogenated aromatic hydrocarbons |
| PICES | North Pacific Marine Science Organization |
| PICT | pollution-induced community tolerance |
| PNEC | predicted no-effect concentration |
| POC | particulate organic carbon |
| POPs | persistent organic pollutants |
| PROD | pentoxyresorufin-*O*-deethylase |
| PSP | paralytic shellfish poisoning |
| PSU | practical salinity unit |
| PTFE | polytetrafluorethene |
| PTS | persistent toxic substances |
| QA | quality assurance |
| QC | quality control |
| QPID | Quality Peak Identification Database |
| QSARs | quantitative structure-activity relationships |
| QSR | quality status report |
| QUASH | Quality Assurance of Sampling and Sample Handling (EC) |
| QUASIMEME | Quality Assurance of Information for Marine Environmental Monitoring in Europe |
| RIA | radioimmunoassay |
| RIKZ | Rijksinstituut voor Kust en Zee [National Institute for Coastal and Marine Management] |
| RMs | reference materials |
| RPSI | Relative Penis Size Index |
| ROSCOP | Cruise Summary Report |
| ROV | remotely operated vehicle |
| RQSR | regional Quality Status Report |
| RUBIN | Rutin för Biologiska Inventeringar |
| RV | research vessel |
| SACs | special areas of conservation |

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| SAR | species at risk |
| SCAN | European Scientific Committee on Animal Nutrition |
| SCF | EC Scientific Committee on Food |
| SCOOP | Scientific Cooperation (EU SCOOP) Task 3.2.5 (on dietary intake of dioxins and related PCBs in the EU) |
| SCOR | Scientific Committee on Oceanic Research |
| SEPA | Scottish Environment Protection Agency |
| SERC | Smithsonian Environmental Research Center |
| SFE | supercritical fluid extraction |
| SFG | scope for growth |
| SG | Study Group |
| SGBEAB | Study Group on the Scientific Basis for Ecosystem Advice in the Baltic |
| SGBOSV | ICES/IOC/IMO Study Group on Ballast and Other Ship Vectors |
| SGDIB | Study Group on Estimation of the Annual Amount of Discards and Fish Offal in the Baltic Sea |
| SGEAM | Study Group on Ecosystem Assessment and Monitoring |
| SGGOOS | Steering Group on GOOS |
| SGMHM | Study Group on Marine Habitat Mapping |
| SGNARO | Steering Group for the ICES-GLOBEC North Atlantic Programme and Regional Office |
| SGNIS | Sea Grant Nonindigenous Species Site |
| SGPHYT | Study Group on an ICES/IOC Checklist of Phytoplankton |
| SGSEA | Steering Group for a Sea-going Workshop on Pelagic Biological Effects Methods |
| SGQAB | ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea |
| SGQAC | ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea |
| SGQAE | ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements related to Eutrophication Effects |
| SIM | selected ion monitoring |
| SIME | Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (OSPAR) |
| SNBF | Swedish National Board of Fisheries |
| SOAEFD | Scottish Office Agriculture, Environment and Fisheries Department |
| SOAER | State of the Arctic Environment Report |
| SOD | superoxide dismutase |
| SOPs | Standard Operating Procedures |
| SP | solid phase |
| SPM | suspended particulate material |
| SPMDs | semi-permeable membrane devices |
| SPME | solid-phase micro-extraction |
| SQGs | sediment quality guidelines |
| SQL | structured query language |
| SRMs | standard reference materials |
| STP | sewage treatment plant |
| TALs | total annual loads |

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| TBA | tetrabutylammonium |
| TBPS | tertiary butylbicyclophosphorothionate |
| TBT | tributyltin |
| TCDD | tetrachlorodibenzo-*p*-dioxin |
| TCMTB | 2-(thiocyanomethylthio)-benzothiazole |
| TCPM | *tris*(4-chlorophenyl)methanol |
| TCPMe | *tris*(4-chlorophenyl)methane |
| ΣTCP | TCPM + TCPMe |
| TDC | Thematic Data Centre |
| TDI | tolerable daily intake |
| TE | toxic equivalent |
| TEF | toxic equivalency factor |
| TEQ | toxic equivalent |
| TIE | toxicity identification evaluation |
| TIMES | *ICES Techniques in Marine Environmental Sciences* |
| TIP | training and intercalibration programme |
| TMA | trimethylarsenic |
| TMAP | Trilateral Monitoring and Assessment Programme (Wadden Sea) |
| TN | total nitrogen |
| TOC | total organic carbon |
| TON | total organic nitrogen |
| TOSC | total oxyradical scavenging capacity |
| TOT | triorganotins |
| TP | total phosphorus |
| TPT | triphenyltin |
| TWI | tolerable weekly intake |
| UAF | University of Alaska, Fairbanks |
| UK | United Kingdom |
| UN | United Nations |
| UNEP | United Nations Environment Programme |
| UNCED | World Commission on Environment and Development |
| UNESCO | United Nations Educational, Scientific, and Cultural Organization |
| U.S. | United States |
| USA | United States of America |
| USEPA | United States Environmental Protection Agency |
| UV | ultraviolet |
| VDSE | Vas Deferens Sequence Index |
| VEN | viral erythrocytic necrosis |
| VHSV | viral hæmorrhagic septicæmia virus |
| VIC | Voluntary International Contaminant Monitoring in Temporal Trends (OSPAR) |
| VMD | Veterinary Medicines Directorate (UK) |

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| VOCs | volatile organic compunds |
| VPC | Veterinary Products Committee (UK) |
| VTG | vitellogenin |
| WCRP | World Climate Research Programme |
| WFD | Water Framework Directive |
| WGAGFM | Working Group on the Application of Genetics in Fisheries and Mariculture |
| WGBAST | Baltic Salmon and Trout Assessment Working Group |
| WGBEC | Working Group on Biological Effects of Contaminants |
| WGCCC | Working Group on Cod and Climate Change |
| WGECO | Working Group on Ecosystem Effects of Fishing Activities |
| WGEIM | Working Group on Environmental Interactions of Mariculture |
| WGEXT | Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem |
| WGHABD | ICES/IOC Working Group on Harmful Algal Bloom Dynamics |
| WGITMO | Working Group on Introductions and Transfers of Marine Organisms |
| WGMDM | Working Group on Marine Data Management |
| WGMMHA | Working Group on Marine Mammal Habitats |
| WGMMPD | Working Group on Marine Mammal Population Dynamics and Trophic Interactions |
| WGMS | Working Group on Marine Sediments in Relation to Pollution |
| WGOH | Working Group on Oceanic Hydrography |
| WGPDMO | Working Group on Pathology and Diseases of Marine Organisms |
| WGPE | Working Group on Phytoplankton Ecology |
| WGSAEM | Working Group on the Statistical Aspects of Environmental Monitoring |
| WGSE | Working Group on Seabird Ecology |
| WGZE | Working Group on Zooplankton Ecology |
| WHO | World Health Organisation |
| WKSBEAB | Workshop on the Scientific Basis for Ecosystem Advice in the Baltic |
| WKQAC | Second ICES/HELCOM Workshop on Quality Assurance of Chemical Procedures for the COMBINE and PLC-4 Programmes |
| WOCE | World Ocean Circulation Experiment |
| WWW | world wide web |
| XML | EXtensible Markup Language |
| ZPT | zinc pyrithione |
| ZRP | zona radiata protein |