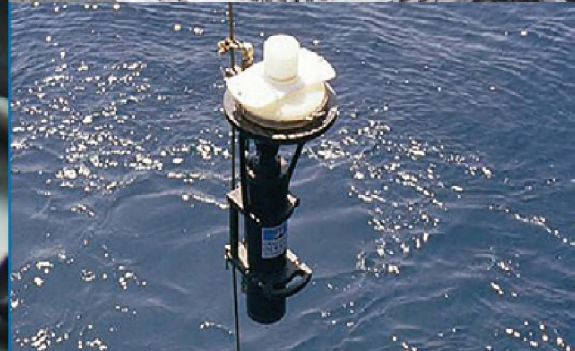
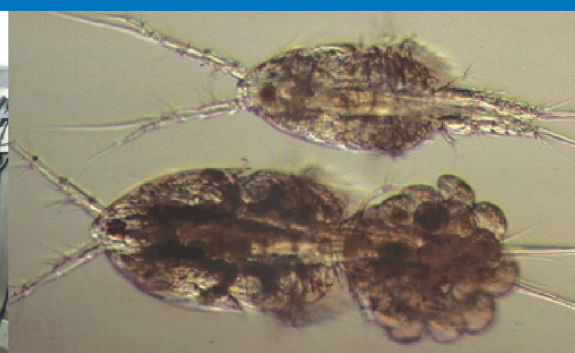


Position Paper 16

Monitoring Chemical Pollution in Europe's Seas

Programmes, Practices and Priorities for Research

November 2011



Marine Board-ESF

The Marine Board provides a pan-European platform for its member organisations to develop common priorities, to advance marine research, and to bridge the gap between science and policy in order to meet future marine science challenges and opportunities.

The Marine Board was established in 1995 to facilitate enhanced cooperation between European marine science organisations (both research institutes and research funding agencies) towards the development of a common vision on the research priorities and strategies for marine science in Europe. In 2011, the Marine Board represents 34 Member Organisations from 20 countries. The marine Board provides the essential components for transferring knowledge for leadership in marine research in Europe. Adopting a strategic role, the Marine Board serves its member organisations by providing a forum within which marine research policy advice to national agencies and to the European Commission is developed, with the objective of promoting the establishment of the European Marine Research Area.

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Monitoring Chemical Pollution in Europe's Seas

Programmes, Practices and Priorities for Research

Marine Board-ESF Position Paper 16

This position paper is based on the activities of the Marine Board Working Group on Existing and Emerging Chemical Pollutants (WGPOL) which convened in Brussels (28-29/01/2008; 5-6/06/2008; 30-31/03/2009) and in Oslo (14-15/12/2009) with financial support from the Research Council of Norway (RCN).

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Foreword

The oceans and seas are of major strategic importance to Europe, both economically and socially. European marine and coastal waters provide transport routes for shipping, extractable sand and gravel, space and resources for aquaculture production, access to subsea oil and gas, food for human consumption and a backdrop for recreation and tourism. The increasing human activities taking place at sea and the ever-increasing demands for marine space and resources place tremendous pressures on the marine environment and the goods and services it provides.

A recent poll¹ of more than 10,000 citizens from ten European countries found that pollution is the primary concern of the public at large, when considering the issues that threaten the marine environment. Such public concern is not misplaced and is supported by scientific evidence. Human pollution is one of the main pressures affecting the marine environment today. About 30,000 of the chemicals currently on the EU market have a production volume of higher than one tonne per year and many have been on the market for more than 20 years. These substances can, and often do, end up in rivers, estuaries and seas with potentially damaging effects on marine organisms, ecosystems and processes.

Knowledge on the impacts of chemicals in the marine environment, together with a number of high impact marine pollution events such as the oil spills from the *Exxon Valdez* (Alaska, 1989), *Sea Empress* (Wales, 1996), and *Prestige* (Galicia, 2002), have resulted in the development and progressive implementation of policies and measures to protect the marine environment from chemical pollution. This includes monitoring programmes aimed at assessing the health of marine ecosystems and the effects of the measures taken to protect them. However, it is clear that existing regulatory frameworks and large international monitoring programmes do not address the full range of potentially damaging pollutants, and completely overlook many of the “new” pollutants which have entered use in recent years. In addition, until today, the monitoring of European seas has been largely based on the measurement of chemical concentrations in water, sediments and biota. As such, current programmes are failing to take sufficiently sophisticated approaches to determine the true impacts of chemicals on individuals, populations and whole marine ecosystems. It is for these reasons that the Marine Board-ESF set-up a working group of experts in 2008 with the following specific objectives:

1. Review existing monitoring and assessment frameworks and practices and assess the need to evaluate the relevance of substances currently

being monitored and/or assessed in the marine environment;

2. Review the recent literature on new and emerging chemicals in the marine environment to provide examples of substances of concern and assess the need (and appropriate mechanisms) to incorporate them into existing and future monitoring and assessment programmes;
3. Examine existing methods used to evaluate the impacts/risks of chemicals in marine systems and, based on recent scientific knowledge, propose improved procedures and identify future research and development needs.

This position paper, *Monitoring Chemical Pollution in Europe's Seas – Programmes, Practices and Priorities for Research*, presents the work and conclusions of the Marine Board Working Group on Existing and Emerging Chemical Pollutants (WGPOL). It provides an overview of the existing monitoring and assessment frameworks (Chapter 2), a critical evaluation of current monitoring practices (Chapter 3), and examples of emerging chemicals of concern and mechanisms used to include them in monitoring programmes (Chapter 4). Two case studies are also presented, focusing on particular pollutant groups or sources which are of concern. The first case study addresses the accidental or deliberate release of hydrophobic substances with low water solubility from shipping; the second addresses the environmental risks posed by chemicals released by the off-shore oil industry.

On behalf of the Marine Board, we would like to sincerely thank all of the members of the working group who so willingly gave their time and expertise to support the production of this important position paper. Their work has been crucial to highlight the importance of adequate monitoring of marine pollutants and in providing a clear set of research priorities and recommendations to further improve the assessment and monitoring of existing and emerging chemicals in European marine waters. Our special thanks goes to the Working Group co-Chairs, Patrick Roose and Colin Janssen, and to Jan-Bart Calewaert of the Marine Board Secretariat for his diligent support to the Working Group and his work in finalising this report. We also thank Alain Abarnou, Jacob de Boer, Jan Boon, Ian M Davies and Gerhard Dahlmann for their invaluable comments and suggestions. Finally, the Board is very grateful to the Research Council of Norway (RCN) for its generous contribution of funding to support this initiative.

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¹ See the results of the poll of the FP7 CLAMER project (Climate Change and European Marine Ecosystem Research) at www.clamer.eu.

Executive Summary

Since the industrial revolution, the impact of human activities on marine environments and ecosystems has increased markedly, affecting the intrinsic health of marine waters and the goods and services they provide. One of the main human pressures affecting the marine environment results from chemical pollution: the release and subsequent effects of chemicals and particles from industrial, agricultural and municipal waste, into riverine, transitional and marine waters. Some marine pollutants can cause harmful effects on aquatic species and wildlife and, in turn, cause serious negative impacts on the structure and functioning of ecosystems, the goods and services they provide, and ultimately on human prosperity and health.

Monitoring the health of the marine environment is essential to measure and understand human pressures and impacts against a backdrop of natural variation, and to assess whether measures taken to protect the environment and to sustainably manage maritime activities are effective. Monitoring is also important to support research, mainly to validate and improve models and, more generally, to reduce the level of uncertainty associated with our knowledge of marine ecosystems.

Over the years, a number of programmes and regulatory measures have been developed and implemented at various geographical scales to monitor, control and reduce the pressures and impacts of chemical substances in European marine waters. However the approach, legal framework, complexity and extent of implementation varies considerably between programmes. Meanwhile, the EU Water Framework Directive (WFD) and the EU Marine Strategy Framework Directive (MSFD) will play an increasingly important role in the regulation and control of marine pollution.

Monitoring of marine waters can be done in many different ways and generally requires considerable resources. Today, monitoring of chemicals in the marine environment is largely carried out at national level, with the goal of complying with international agreements. Most monitoring efforts focus on a limited list of widely recognized substances measured mainly by chemical concentrations in water, sediment and biota. However, a number of substances of concern which are either found in the marine environment, or known to enter it, are not routinely monitored or assessed. The level of knowledge and awareness of the presence and potential impacts of such new and emerging marine pollutants is still very limited. To be genuinely effective, monitoring programmes will need to take into account a continually expanding list of chemical pollutants, the impact that different pollutants can have on organisms, ecosystems and processes, and to attribute efforts and resources according to the perceived risk. It is clear that until a

more scientifically robust and sophisticated approach is adopted, existing monitoring programmes are only providing a part of the picture.

This report has been produced by the Marine Board Working Group on Existing and Emerging Chemical Pollutants (WGPEL) first convened in 2008 and tasked to examine the assessment and monitoring of existing and emerging chemicals in the European marine and coastal environment. The Working Group considered (i) existing monitoring/assessment frameworks; (ii) current monitoring practices; and (iii) new and emerging chemicals of concern and the mechanisms used to include them in current monitoring programmes.

The primary conclusions and recommendations of this position paper are:

1. Fully implement state of the art environmental risk assessment procedures (combining exposure and effect assessment) to evaluate the full impact of chemical substances on the different compartments of coastal and open sea systems.
2. Further improve the coordination, cooperation and harmonization between existing monitoring efforts and those under development, to avoid duplication of effort, loss of expertise and a reduced willingness to fulfil the obligations towards regional conventions.
3. Ensure that the development and implementation of monitoring programmes for the assessment of chemicals in marine and coastal environment are based on a science-based and dynamic process.
4. Apply more resources targeted at developing appropriate approaches, tools and practices (education and training) to improve the acquisition and management of monitoring data.

In addition to the above main recommendations, two further recommendations have been identified on the basis of two specific case studies which form part of this paper and which focus on the release, effects and monitoring of (i) hydrophobic and insoluble chemicals in the marine environment from merchant shipping; and (ii) chemicals released by the offshore oil-industry in the North Sea. These case studies highlighted the need to:

5. Develop a consistent, pan-European or regional (legal) framework/regulation which covers the activities of the oil and gas industry at sea. At the same time, more information and research is needed on the release and the effects of chemicals arising from offshore oil and gas activities.
6. Develop and apply state-of-the-art environmental risk assessment procedures (combining exposure and effect assessments, including on human health) to evaluate the impact of noxious liquid substances listed under MARPOL Annex II on the different compartments in coastal and open sea ecosystems.

1. Introduction

What is the problem?

European marine and coastal waters support a wide range of important socio-economic activities. They provide commercial highways for the shipping industry, extractable sand and gravel, areas for aquaculture production, a source of wild fish for human consumption and important recreational opportunities. To be able to maintain these functions in the future, it is essential that the biodiversity, resources and environmental quality of European marine ecosystems are conserved, protected and sustainably managed.

Unfortunately, the intense human activity which takes place in and around Europe and the ever-increasing human demands on marine and coastal resources and services place tremendous pressure on the marine ecosystem. Fisheries over-exploitation, pollution, maritime activities, oil and gas extraction all have very significant impacts in addition to a range of phenomena such as global warming, sea level rise, invasive alien species and harmful algal blooms which show alarming trends in their magnitude and/or frequency. The significance of these impacts and changes must be properly understood and their causes and consequences addressed.

One of the main pressures affecting the marine environment today results from chemical pollution: the release and effects of chemicals, particles, industrial, agricultural and residential waste, in marine environments. Worldwide, the production of chemicals is increasing with a total production volume expected to double in comparison with 2000 levels by 2024 (see Figure 1.1). About 100,000 chemicals are available on

the EU market. About 30,000 of these chemicals have a production volume higher than one tonne per year and have been on the market for more than 20 years. Some of these substances end up in the marine environment, which may result in harmful effects on aquatic species and wildlife and, ultimately, human health, mainly through food web transfer.

The occurrence of marine pollutants is the result of direct releases (e.g. from shipping), land-based river run-off or atmospheric deposition, all of which contribute significantly to marine pollution. Contamination of the marine environment by chemical substances gives rise to considerable concern as it may result in serious adverse effects on the structure and functioning of ecosystems, the goods and services they provide, and on human health. Unwanted chemical substances may, for example, reduce biodiversity and productivity in marine ecosystems, resulting in a reduction and depletion of human marine food resources.

Chemicals can cause not only direct intoxication and obvious effects such as death of marine biota, but they can also cause more subtle adverse effects such as impairment of the reproductive, hormone and immune systems. As stated by Paracelsus (16th century) it is “the dose (concentration) that determines if a substance is a poison”. From this it follows that for chemicals which are toxic at very low concentrations, release into the marine environment should be prevented at all costs. Other substances - which may not cause a direct effect - may cause indirect impacts through food-chain transfer.

If we are not able to protect the environment from chemical pollution, ecosystems may falter and cease

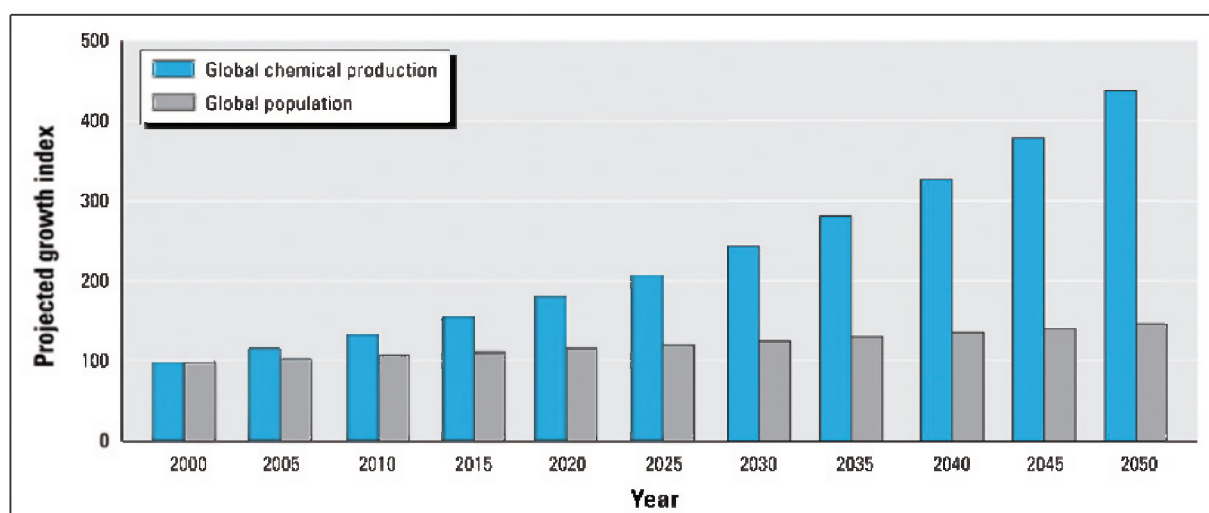


Figure 1.1. Global chemical production is projected to grow at a rate of 3% per year, rapidly outpacing the global population growth. On this trajectory, chemical production will double by 2024, indexed to 2000. (From Wilson and Schwarzman, 2009)

1. Introduction

to support us. This awareness, reinforced by some high impact pollution events in the past (e.g. Bhopal, 1984; Seveso, 1976; Torrey Canyon, 1967; Amoco Cadiz, 1978; and Exxon Valdez, 1989), has resulted in the development of policies and measures to protect the marine environment from chemical pollution, including monitoring programmes aimed at assessing the health of marine ecosystems and the effects of the measures taken to protect them.

What can be done about it?

Monitoring the health of the marine environment is essential because it helps us to measure and understand man-made changes against a background of natural variation. It also allows an assessment of whether measures taken to protect the environment are effective.

In this context, monitoring refers to the repeated measuring of: (i) the quality of the marine environment and of its components (water, sediments and biota); (ii) natural and anthropogenic activities and inputs which may adversely affect the quality of the marine environment; and (iii) the effects of these activities and inputs.

Monitoring is not only needed to define status and trends, but is also important for the purposes of research, mainly to validate and improve models and, more generally, to reduce the level of uncertainty associated with our knowledge of marine ecosystems. Monitoring also raises important questions for both science and policy such as: why is a certain area polluted? Where does the contamination come from? How can the situation be resolved?

Monitoring of the marine environment can be done in many different ways and generally requires considerable resources. Chemical monitoring of the marine environment involves examination of water and sediment samples using analytical chemical techniques. The results provide information on the type and concentrations of compounds present in these compartments. Biological monitoring involves the use of plant, animal, and/or microbial indicators to assess presence of chemicals in marine organisms (biological monitoring) and/or the effects of chemicals on marine organisms (biological effects monitoring). To date, the monitoring of European seas has been largely based on the measurement of chemical concentrations in water, sediments and biota. However, while essential, monitoring of marine pollution in European seas solely based on chemical analysis does not provide any indication of deleterious effects on biota.



Figure 1.2. Sampling organic pollutants at sea with a high-volume sampling system

Monitoring frameworks

Following the Second World War, the rapid development of the chemical industry gave rise to an enormous diversity of novel products and a concurrent increase in pollutant emissions. The general awareness of the risks (to the environment and to man) of large-scale contamination grew throughout the second half of the 20th century, as a number of incidents drew world-wide attention to the dangers of these developments. For example, in the late 1950s, the adverse environmental impacts of the pesticide DDT and its metabolites were first linked with decreased population sizes of brown pelicans, bald and white-tailed eagles and other wild birds in North America and in the Baltic. In 1961, a crippling and sometimes fatal, disease was found to be related to industrial mercury discharges in Minamata (Japan). Since then, scientists have shown that, even in the open ocean, large fish sometimes contain high concentrations of mercury (Roose and Brinkman, 2005). Other well-known examples include the chemical accidents of Bhopal (1984) and of Seveso (1976) and the large oil spills (e.g. Torrey Canyon, 1967; Amoco Cadiz, 1978; and Exxon Valdez, 1989) that gave rise to the extensive monitoring programmes of dioxins and polycyclic aromatic hydrocarbons (PAHs) in the environment.

The general awareness caused by these and other incidents has led to the development of policy measures to reduce or eliminate the release of contaminants into the environment in general, and the marine environment in particular. The implementation of these policies required observation and assessment of the evolving situation in the field and hence large scale-monitoring programmes were developed.

There are currently a number of international frameworks and regulatory measures in place to monitor, control and reduce pressures and impacts of chemical substances on the European marine environment. National marine monitoring programmes have also been implemented for a long time in most European coastal countries and normally provide the primary source of information for international programmes. At the same time, new regulatory devices such as the EU Water Framework Directive (WFD) and the EU Marine Strategy Framework Directive (MSFD) are in their infancy. The key questions which should be addressed are whether: (i) current (and potentially also new) regulatory frameworks or large international monitoring programmes incorporate the most recent scientific developments and/or relevant scale in their assessment schemes; and (ii) these types of data allow a science-based evaluation of the risks posed by chemicals to marine ecosystems and/or to humans exposed via marine exposure routes.

Monitoring of chemicals in the marine environment is largely limited to a list of *well-known* substances measured by individual countries in order to comply with international agreements. However, there are a number of substances of concern which are either found in the marine environment or known to enter it, which are not routinely monitored or assessed. Scientific evidence for the presence and potential impacts of new and emerging substances is growing (Chapter 4).

For the purpose of this position paper an “emerging substance of concern” is defined as a chemical or anthropogenic material which is of growing scientific concern but which is currently not extensively monitored under international programmes such as HELCOM, OSPAR, UNEP and the Water Framework Directive (Chapter 2). In this context, it is important to consider the following questions: how do we know if some of the emerging chemicals of concern which are not yet routinely monitored really pose a considerable risk? Also, if they are found, how can they be included in routine monitoring programmes? What are the procedures? Is this systematic, or *ad hoc*? Is it based on the same criteria as those initially used for establishing the existing priority lists?

Overall, the major questions to be addressed are: (i) is there a need to evaluate the importance and relevance of the substances presently being (chemically) monitored; and (ii) should systematic monitoring be performed of new and emerging substances? Realising the importance of these questions, the Marine Board-ESF decided to set up a Working Group of experts in 2007 to investigate these questions and to deliver a position paper.

Aims of this position paper

This position paper is the outcome of the activities of the Marine Board Working Group on Existing and Emerging Chemical Pollutants (WGPOL) and provides an overview of the existing monitoring/assessment frameworks (Chapter 2), a critical evaluation of current monitoring practices (Chapter 3), and examples of emerging chemicals of concern and the mechanisms used to include them in current monitoring programmes (Chapter 4). In addition, this position paper presents two case studies evaluating the current knowledge and monitoring practices of potentially harmful substances in the marine environment. The first case study (Chapter 5) deals with accidental or deliberate releases of hydrophobic substances with low water solubility from shipping; the second one (Chapter 6) with the environmental risks posed by chemicals released by the off-shore oil industry.

This position paper is primarily intended to inform those responsible for the development and funding of marine scientific research in the context of monitoring tools, equipment and programmes, sustainable development and risk assessment of chemicals, at national, regional, European and international levels. The position paper should also inform the science community on what research priorities need to be addressed to strengthen and advance this type of marine research as well as stimulate networking and the development of common views of expert scientists, potentially leading to new approaches and collaborative projects.

2. Existing programmes for assessment and monitoring of the marine environment

2.1 Introduction

Monitoring activities over several decades have revealed the ubiquitous presence of organic micro-contaminants and trace metals in all compartments of the marine environment (water, sediment and biota). Furthermore, the eutrophication status of an area and the occurrence of harmful algal blooms are routinely evaluated by monitoring nutrient and shellfish toxin levels. In addition to the large-scale international and regional programmes, most European countries conduct national monitoring programmes which generally focus on the same parameters. These national monitoring programmes are nearly always the primary data source for the international programmes.

In recent years, European and other international organizations have been extending their lists of priority hazardous substances. Techniques based on biological effects are finding their way into various programmes and assessment methodologies are rapidly maturing.

This chapter aims to provide an overview of relevant programmes and approaches used for the monitoring and assessment of chemicals in the European marine environment.

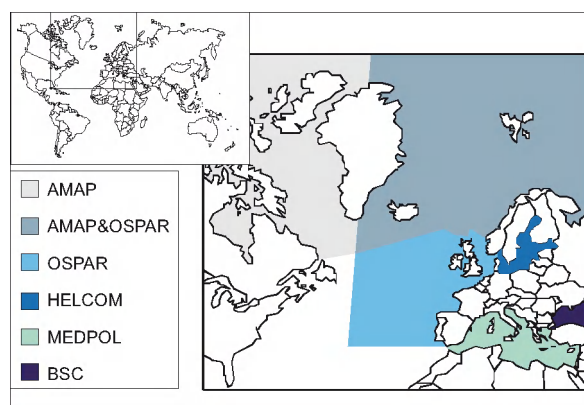


Figure 2.1. Regional Marine Conventions/Commissions and Programmes relevant for the monitoring of the European marine environment; the programmes are given by their acronyms (from Roose, 2010)

2.2 Existing frameworks and legislation

2.2.1 Global conventions

2.2.1.1 United Nations Environment Programme

Monitoring activities on a global scale are linked through the United Nations Environment Programme (UNEP). UNEP was established as a follow-up to the 1972 Stockholm Conference on the Human Environment, as the environmental component of the UN system (see www.unep.org). Through UNEP, a basis was created for comprehensive coordinated action within the UN on the problems of the human environment. UNEP attempts to nurture partnerships with other UN bodies, the scientific community and organisations such as OSPAR.

UNEP has several water-related programmes. For example, the Regional Seas Programme (RSP), initiated in 1974 as a global programme, includes 15 regions and more than 140 coastal states and territories (Figure 2.2). It is an action-oriented programme focusing not only on the mitigation or elimination of the consequences of environmental degradation, but also on its causes. The focus has gradually shifted from the protection of the marine environment from pollution towards the overall sustainable development of the coastal and marine environment through integrated management. UNEP is responsible for the secretariat set up to implement the 1995 Global Programme of Action (GPA) for the Protection of the Marine Environment from Land-based Activities.

UNEP is also one of the implementing agencies for the Global Environment Facility (GEF). This is an independent international financing entity with the long-term goal of ensuring progress towards global environmental security. The UNEP portfolio of GEF-funded activities in international waters includes global assessments, trans-boundary diagnostic analyses (TDAs) of shared water bodies, support for the implementation of strategic action programmes for marine and freshwater areas, and support for integrated management of shared freshwater bodies. Because water issues play an important and increasing role in international development cooperation, GEF has designated international waters as one of its four focal areas.

The Global International Waters Assessment (GIWA), led by UNEP and 50% funded by GEF, provides the information needed for GEF's work in this particular area. The aim of GIWA is to produce a comprehensive and integrated global assessment of international waters, specifically the ecological status and the causes of environmental problems in sixty-six water bodies around



Figure 2.2. Overview of the Regional Seas Programme

the world, and the key issues and problems facing the aquatic environment in transboundary waters. The assessment is designed not merely to analyse the current problems but also to develop scenarios of the future condition of the world's water resources and analyse policy options with a view to providing sound, science-based advice to decision makers and managers. In the near future, GIWA activities will be linked and coordinated with monitoring programmes such as OSPAR and HELCOM described elsewhere in this section.

UNEP should be seen as a facilitator and does not play the same role as organisations such as OSPAR and HELCOM. UNEP's role to create the conditions that make marine monitoring feasible through capacity building projects, technical and scientific advice (e.g. in the form of technical guidelines) and by bringing together organisations that have common goals.

In the period 2001-2002, the feasibility of establishing a regular global process for assessing the marine environment was explored by the UN. As a preparatory stage towards the establishment of this regular process, the Assessment of Assessments (AoA) was launched in 2005. The actual work was undertaken by a Group of Experts and supported from a secretariat drawn from the two lead agencies, the United Nations Environment Programme (UNEP) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO.

The AoA assembled information on existing marine assessments and submitted this to a critical appraisal. Furthermore, it identified a framework and options to build the regular process.

The AoA was published in 2009 and represents the most comprehensive initiative undertaken to date by the UN to better coordinate ocean governance.

2.2.1.2 International Convention for the Prevention of Pollution from Ships (MARPOL)

The MARPOL Convention is the most important international convention aimed at the prevention of marine pollution caused by operational or accidental shipping activities. It is a combination of two treaties adopted in 1973 and 1978 and updated by amendments in more recent years.

In 1973, the International Convention for the Prevention of Pollution from Ships (MARPOL) was adopted by the International Maritime Organisation (IMO) as the result of growing concerns over threats to the marine environment from transported mineral oil and non-oil products. It covered pollution by oil, chemicals, harmful substances in packaged form, sewage and garbage. The MARPOL 1978 Protocol was adopted at a Conference on Tanker Safety and Pollution Prevention (February 1978) which was held in response to a number of tanker accidents during 1976 and 1977. As the 1973 MARPOL Convention had not yet entered into force, the 1978 MARPOL Protocol absorbed the parent Convention. The combined instrument is referred to as the International Convention for the Prevention of Marine Pollution from Ships, 1973, as modified by the Protocol of 1978 (MARPOL 73/78). It entered into force on 2 October 1983 (Annexes I and II).

MARPOL contains 6 annexes, concerned with preventing different forms of marine pollution from ships:

- Annex I – Oil
- Annex II – Noxious Liquid Substances carried in Bulk
- Annex III – Harmful Substances carried in Packaged Form
- Annex IV – Sewage
- Annex V – Garbage
- Annex VI – Air Pollution

A summary of the instruments described in the MARPOL annexes is given in Table 2.1.

Instrument	Entry into force	Contracting States	Share of world tonnage (%)
MARPOL 73/78 (Annex I/II)	02-Oct-83	149	99.01
MARPOL 73/78 (Annex III)	01-Jul-92	132	95.76
MARPOL 73/78 (Annex IV)	27-Sep-03	123	81.62
MARPOL 73/78 (Annex V)	31-Dec-88	138	96.98
MARPOL Protocol 1997 (Annex VI)	19-May-05	56	83.46

Table 2.1. Status of the MARPOL instruments as on 31st of July 2009

2. Existing programmes for assessment and monitoring of the marine environment

Since 2005, 161 countries are party to this agreement. A country that becomes party to MARPOL must accept Annex I and II, while Annexes III and VI are voluntary annexes.

For more information see www.imo.org/conventions

2.2.1.3 The Stockholm Convention

The Stockholm Convention (2001) is a global treaty which has been signed by 152 governments and which is aimed at protecting human health and the environment from persistent organic pollutants (POPs). In implementing the Convention, governments have to take measures to eliminate or reduce the release of POPs into the environment (see www.pops.int). POPs are chemicals which remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. POPs circulate globally and may cause damage wherever they occur. The Stockholm Convention identified twelve priority POPs: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and toxaphene.

It is possible to add new substances to this list. In May 2009 an agreement was reached to add nine additional POPs: alpha hexachlorocyclohexane; beta hexachlorocyclohexane; chlordecone; hexabromobiphenyl; hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether); gamma-hexachloro cyclohexane (lindane); pentachlorobenzene; perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride; tetrabromodiphenyl ether and pentabromodiphenyl ether (also known as commercial pentabromodiphenyl ether). The agreement entered into force on 26 August 2010 for 151 of the 152 Parties to the Stockholm Convention². One more compound, endosulfan, was added to the list in April 2011 bringing the total number of POPs listed under the Stockholm Convention to 22. Two more (hexabromocyclododecane, and short-chained chlorinated paraffins) are currently under review.

The Stockholm Convention on POPs and other international agreements state that monitoring activities should be established to verify the effective implementation of the conventions and the decrease of environmental levels of persistent pollutants. Some monitoring activities are already in place but, as different methodologies are used, comparison of the data can be difficult. To improve the situation a guidance document



Figure 2.3. Signatories of the International Convention for the Prevention of Pollution from Ships (MARPOL) 73-78 (2005)

has been developed³ with support from the Stockholm Convention Secretariat.

2.2.1.4 Other international conventions and organisations

It is not within the scope of this paper to review all the international conventions and organisations that deal directly or indirectly with priority chemicals. Nevertheless, some deserve particular mention.

For instance, the **Rotterdam Convention** promotes shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals. The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. The ultimate goal is to protect human health and the environment from potential harm. It also contributes to the environmentally sound use of those hazardous chemicals⁴. The Convention entered into force in 2004.

The **Basel Convention** deals with the Control of Transboundary Movements of Hazardous Wastes and their Disposal (www.basel.int). The Convention has 175 Parties and aims to protect human health and the environment against adverse effects resulting from the generation, management, transboundary movements and disposal of hazardous and other wastes. It is claimed to be the most comprehensive global environmental agreement on hazardous and other wastes. It came into force in 1992.

Local Authorities International Environmental Organisation (**KIMO**) is an International Environmental Organisation founded by local municipalities with a shared concern for the state of the environment. KIMO has identified what it considers to be pressing environmental issues which it addresses through diplomatic action, demonstration projects and research⁵.

2. See <http://chm.pops.int/Programmes/New%20POPs/Overview/tabid/667/language/en-US/Default.aspx>; and <http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/language/en-US/Default.aspx>

3. See www.pops.int/documents/meetings/cop_3/meetingdocs/inf14/GMP%20Guidance%20CD/Guidance.pdf

4. See www.pic.int

5. See www.kimointernational.org

2.2.2 Regional conventions

2.2.2.1 AMAP

The Arctic Monitoring and Assessment Programme (AMAP), was established in 1991 and is aimed at implementing certain components of the Arctic Environmental Protection Strategy (AEPS). Its primary focus is to (i) provide reliable and sufficient information on the status of, and threats to, the Arctic environment; and (ii) provide scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions relating to contaminants (www.amap.no). The Arctic Council, established in 1996 by the eight Arctic countries (CA, DK, FI, IS, NO, RU, SE, and the US), coordinates AMAP activities.

AMAP was conceived as a programme which integrates both monitoring and assessment activities in relation to pollution issues and provides information and reports on the state of the Arctic environment. The *AMAP Trends and Effects Monitoring Programme* is designed to monitor the levels of pollutants and their effects in all compartments of the Arctic environment. Contaminants covered by the programme include metals, radioactive substances, PCBs, hexachlorobenzene (HCB), dioxins (PCDDs and PCDFs), pesticides (aldrin, chlordane, dieldrin, DDT, endrin, heptachlor, mirex, and toxaphene), PAHs, OTINs, short-chain chlorinated paraffins (SCCPs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA), perfluorooctanol sulphonic acid and its salts (PFOS) and polychlorinated naphthalenes (PCNs).

There are five sub-programmes, which deal with atmospheric, terrestrial, freshwater, and marine environments, and human health. Reviews from these programmes are produced every three to five years.

2.2.2.2 Barcelona Convention

In 1976, 16 Mediterranean countries and the EU adopted the Barcelona Convention for the Protection of the Mediterranean Sea Against Pollution, overarching the Mediterranean Action Plan (MAP), approved one year earlier (www.unepmap.org/). The Barcelona Convention was amended in 1996, entered into force on 2005 and is now including all 21 Mediterranean countries (AL, DZ, BA, HR, CY, EG, ES, FR, GR, IL, IT, LB, LY, MT, MC, MA, SI, SY, TN, TR) and the EU. In the framework of the Barcelona Convention, seven Protocols have been adopted by the contracting parties:

- Protocol for the protection of the Mediterranean Sea against pollution from Land-based Sources and Activities or LBS (adopted 1980, amended 1996, in force 2008);
- Specially protected areas (adopted 1995, in force 1999);



Figure 2.4. Geographic coverage of the Arctic Monitoring and Assessment Programme (AMAP)

- Pollution from ships and aircrafts (adopted 1976, amended 1995);
- Pollution from offshore activities (adopted 1994, in force 2011);
- Transboundary movements of hazardous substances (adopted 1996, in force 2008);
- Preventing and combating pollution from ships in case of emergency (adopted 2002, in force 2004); and
- ICZM (adopted 2008, in force 2011).

Marine pollution monitoring is been implemented in the Mediterranean region in the framework of the LBS Protocol under coordinated of the Programme for the Assessment and Control of Pollution in the Mediterranean region (MEDPOL), which was established on 1974.

During the initial phases of the programme, the main aim was the establishment of a network of institutions involved in marine pollution work and the collection of information concerning the levels of pollution in the Mediterranean Sea, through research and monitoring. In the 1990s, national monitoring programmes were established in many Mediterranean countries and coordinated MEDPOL Phase III (1996-2005) and Phase IV (2006-2013). Also during MEDPOL Phase III and IV emphasis shifted from pollution assessment to pollution assessment and control, in the framework of the Strategic Action Programme.

2. Existing programmes for assessment and monitoring of the marine environment



Figure 2.5. Map showing the parties of the Barcelona Convention

The monitoring activities cover heavy metals in marine biota and sediment (mainly mercury and cadmium), halogenated hydrocarbons in marine biota and sediment (mainly PCBs and DDTs), and nutrients and chlorophyll-a in seawater. Data is generated by the National monitoring programmes of the Mediterranean countries and are reported to MEDPOL and uploaded in the MEDPOL marine pollution database. In parallel, MEDPOL provides assistance in the formulation and implementation of regional and national action plans addressing pollution from land-based sources and activities. It also formulates and carries out capacity-building programmes on the technical and management aspects of contaminants analysis and data treatment. Furthermore, the contracting Parties to the Barcelona Convention have decided (2008) to gradually apply an ecosystem approach to the management of human activities in the Mediterranean and to revise the MAP monitoring programme in order to generate data for 11 Ecological Objectives, including pollution and biodiversity. The ECAP Ecological Objectives are very close to the MSFD 11 Descriptors for the definition of Good Environmental Status (GES). The new integrated MAP monitoring programme is under preparation and expected by 2012.

2.2.2.3 Bucharest Convention

The Convention on the Protection of the Black Sea Against Pollution (the Bucharest Convention), was signed in Bucharest in April 1992, and ratified by the legislative assemblies of all six Black Sea countries (BG, GE, RO, RU, TR and UA) in early 1994 (www.blacksea-commission.org). To support the implementation of the convention (www.blacksea-commission.org/_commission.asp), the Black Sea Commission (BSC) was established.

The convention targets: (i) the control of land-based sources of pollution; (ii) the control of dumping of waste; and (iii) the establishment of a framework for joint actions in the case of incidents such as oil spills. Specifically for the assessment and monitoring of pollutants, two *State of Environment of the Black Sea* reports were prepared and published in 2001 and 2008, respectively, for the periods of 1996-2000 and 2001-2006/2007. It is based on data collected through the coordinated pollution monitoring and assessment programmes. The organic micropollutants (OMPs) considered by the programme include organotins, organohalogen compounds such as DDT, DDE, DDD, PCBs, persistent organo-P compounds, and, persistent substances with proven toxic carcinogenic, teratogenic or mutagenic properties.

2.2.2.4 HELCOM

The Baltic Marine Environment Protection Commission or the Helsinki Commission, is the governing body of the Convention on the Protection of the Marine environment of the Baltic Sea Area, signed in 1992 (www.helcom.fi). HELCOM's main goal is to protect the marine environment of the Baltic Sea from all sources of pollution, and to restore and safeguard its ecological balance. The present contracting parties to HELCOM are DE, DK, EE, EC, FI, LV, LT, PL, RU and SE. The set-up is very similar to



Figure 2.6. HELCOM marine area and the Baltic Sea catchment area

that of OSPAR, and many of the OSPAR principles such as “best environmental practices”, “best available technologies” and “the polluter pays” principle have been adopted and applied by HELCOM.

Monitoring and assessment are an integral part of the convention, according to which “emissions from both point sources and diffuse sources into water and air should be measured and calculated in a scientifically appropriate manner by the Contracting Parties”. Every five years, the Commission publishes a “Periodic Assessment of the State of the Environment of the Baltic Marine Area” based on monitoring activities performed in the area. Recently, a prioritisation of OMPs was carried out, based on recent developments and existing lists such as those of OSPAR, the WFD and UNEP POP (Füll, 2002). The complete list is given in Appendix II and discussed in Chapter 3.

2.2.2.5 OSPAR

The Oslo Convention (1972), also called the Convention for the Prevention of Marine Pollution by Dumping from Ships and Airplanes, entered into force in 1974. The Convention regulated dumping operations involving industrial waste, dredged material and sewage sludge. The Paris Convention, or Convention for the Prevention of Marine Pollution from Land-Based Sources, was established in 1974 and came into force in 1978. Its principal aim was to prevent, reduce and, if necessary, eliminate pollution within the Convention area from land-based sources, which are discharges from rivers, pipelines, the coast, but also offshore installations and the atmosphere.

The tasks set forth in both Conventions were originally handled by two individual commissions: the Oslo Commission and the Paris Commission. In 1978, both commissions established a Joint Monitoring Programme, the JMP, obliging contracting parties to initiate monitoring activities for a number of parameters in their water bodies.

In the 1980s, the policy of the Oslo and Paris Commissions evolved according to changes in environmental policy in Western Europe, as those voiced at the Ministerial Conferences for the Protection of the North Sea (Roose and Brinkman, 2005). It was soon recognised that the existing Oslo and Paris Conventions did not adequately control some of the many sources of pollution, and that a revision was needed. This resulted, not in a revision of the initial conventions, but more importantly, in the merger of both commissions into a new convention, the Convention for the Protection of the Marine Environment of the North-East Atlantic or OSPAR (www.ospar.org). The new Convention was opened for signature at the Ministerial Meeting of the Oslo and Paris Commissions, in September 1992.

The key objective of the strategy is the cessation of discharges, emissions and losses of hazardous substances by 2020 with the aim of achieving concentrations in the marine environment close to background values for naturally occurring substances and close to zero for man-made synthetic substances. To monitor environmental quality throughout the north-east Atlantic, a Joint Assessment and Monitoring Programme (JAMP) has been established, which has recently been revised (OSPAR, 2003). An overview of the substances monitored in the context of the JAMP is given in Chapter 3 and in Appendix II.

2.2.2.6 UNECE

In this overview, it is important to include one of the international fora where the Persistent Organic Pollutants (POPs) discussions actually began, namely, the United Nations Economic Commission for Europe (UN-ECE). UN-ECE comprises eastern and western Europe, Canada and the United States of America. The UN-ECE initiatives on POPs began in 1992 with the establishment of a Task Force on POPs under the framework of the Convention on Long-Range Transboundary Air Pollution (CLRTAP) (Lerche *et al.*, 2002). In 1996 a Preparatory Working Group was formed by the executive body to start negotiations on a POP Protocol. At the Fourth Pan-European Environmental Ministerial Conference in Aarhus, Denmark (June 1998), the UN-ECE POP Protocol was signed by 33 member states and the European Union (www.unece.org/env/lrtap/status/98pop_st.htm). In 2009, the protocol was signed by 36 parties and ratified by 29 of them. The objective of the protocol is “to control, reduce or eliminate discharges, emissions and losses of persistent organic pollutants” (Article 2). The chemical substances included in the UN-ECE POP Protocol are characterised as being persistent, bioaccumulating and toxic organic compounds prone to long-range atmospheric transport. The original convention protocol included sixteen priority substances (aldrin, chlordane, chlordecone, dieldrin, DDT, dioxins, endrin, furans, heptachlor, hexachlorobenzene, hexachlorocyclohexane (including lindane), hexabromobiphenyl, mirex, PCBs, PAHs, and toxaphene). More substances can be added to the protocol through a procedure specifically developed for this purpose. Several substances or groups of substances have been suggested and on the 18th of December 2009, seven new substances were added to the protocol (even new substances: hexachlorobutadiene, octabromodiphenyl ether, pentachlorobenzene, pentabromodiphenyl ether, perfluorooctane sulfonates, polychlorinated naphthalenes and short-chain chlorinated paraffins).

2. Existing programmes for assessment and monitoring of the marine environment

2.2.3 European Union legislation

Early European water legislation began in 1975 by setting standards for rivers and lakes used for drinking water abstraction. This resulted in binding quality targets for drinking water in 1980. The main emission control element was the Dangerous Substances Directive (76/464/EEC). This directive identified different water bodies (e.g. fish waters, shellfish waters, bathing waters and ground waters) and established two lists of substances considering the degree of hazard they pose to the aquatic environment. During the following decade, the 76/464/EEC Directive was developed further through five different daughter directives and their amendments that set up emission limit values and quality objectives for specific pollutants included in the first list (82/176/EEC, 84/156/EEC, 83/513/EEC, 84/149/EEC and 86/280/EEC).

A second phase of water legislation resulted in the adoption in 1991 of the Urban Waste Water Treatment Directive (91/271/EEC) and the Nitrates Directive (91/676/EEC), which addressed water pollution by nitrates from agriculture. Other legislative results of these developments were EC proposals for action on a new Drinking Water Directive, which reviewed the quality standards and, where necessary, tightened them (adopted in 1998) and a Directive for Integrated Pollution and Prevention Control, which addressed pollution from large industrial installations (adopted in 1996).

While EU actions such as the Drinking Water Directive and the Urban Waste Water Directive can be considered milestones, it became clear that European water policy needed to address problems in a coherent and integrated way, i.e. not separated into sectors or topics such as drinking water and wastewater. This became the basis for a new European water policy, which was developed through an open consultation process involving all interested parties and which eventually resulted in the Water Framework Directive 2000/60/EC2 (WFD).

2.2.3.1 Water Framework Directive

In 1997, the EC proposed a European Parliament and Council Directive establishing a framework for Community action in the field of water policy, entitled the Water Framework Directive or WFD.

The WFD, which was adopted in September 2000, should “contribute to the progressive reduction of emissions of hazardous substances to water” with the ultimate aim “to achieve the elimination of priority hazardous substances (PHS) and contribute to achieving concentrations in the marine environment near background values for naturally occurring substances” (European Commission, 2000). The WFD essentially combines the efforts in protecting groundwater and all surface waters on land and in the territorial waters of



Figure 2.7. Overview of the Water Framework Directive and related environmental protection legislation in Europe (from Mänpää *et al.*, 2006)

the EU member states, and therefore also transitional (e.g. estuarine) and coastal marine waters. This holistic approach to monitoring not only overlaps regionally but also thematically with programmes carried out by the existing Marine Environmental Conventions described below.

The WFD provides the major common principles that must prevail when adopting new policies to protect and improve the quality of the aquatic environment. A combined approach for point and diffuse sources is adopted, based on emission limit standards for the control of pollution at source, as well as environmental quality standards to guarantee good ecological water status. It also established a list of priority substances presenting a significant risk to the aquatic environment, in addition to a set of control measures. An overview of how the WFD interacts with or substitutes existing policies is given in Figure 2.7.

2.2.3.2 Marine Strategy Framework Directive

While the European Commission recognises that progress has been made in certain areas, e.g. in reducing nutrient inputs or pollution from hazardous substances, in particular inorganic trace elements (heavy metals), it is also clear that the state of the marine environment has been deteriorating significantly over recent decades (European Commission, 2005) and that the existing policy framework has not delivered the high level of protection of the marine environment that is needed.

In light of the increasing concerns in relation to the state of Europe's oceans and seas, the EU's 6th Environment Action Programme⁶ included a commitment to develop a Thematic Strategy for the protection and conservation of the marine environment with the overall aim “to promote

6. <http://ec.europa.eu/environment/newprg/index.htm>

Information Box 2.1 – Monitoring under the Water Framework Directive (WFD)

The Water Framework Directive (WFD) identifies three types of monitoring: (i) surveillance monitoring; (ii) operational monitoring; and (iii) investigative monitoring.

Surveillance monitoring provides information for assessment of the status of a river basin, and for the development of future monitoring programmes, and serves to monitor long-term changes under natural conditions and changes resulting from anthropogenic activity. In practical terms, surveillance monitoring is not continuous (intermittent periods), but is thorough. For the entire set of priority pollutants a monthly sampling scheme is foreseen for a period of one year during a management cycle.

Operational monitoring is undertaken to assess the status of water bodies that are at risk of failing to meet

the environmental objectives and to assess changes resulting from programmes of measures. Operational monitoring is continuous and follows the same frequency as surveillance monitoring. Although it is only intended for specific cases, it has severe implications both in time and effort.

Investigative monitoring is carried out if reasons for non-compliance with threshold levels are unknown, or surveillance monitoring indicates that the objectives will not be met and operational monitoring is not yet established, or to investigate the impact of accidental pollution.

For more information on monitoring in the frame of the Water Framework Directive: http://ec.europa.eu/environment/water/water-framework/index_en.html

sustainable use of the seas and conserve marine ecosystems". In 2002, the European Commission published a Communication entitled "Towards a strategy to protect and conserve the marine environment" (European Commission, 2002), which sets out objectives and related actions to address the declining quality of European marine waters (European Commission, 2004a). This Communication represented the first step in the development of a European Marine Strategy for the protection and conservation of the marine environment. To achieve the objective of this strategy, it was considered that a binding legal commitment was required under the form of a Marine Strategy Directive, ambitious in its scope but not overly prescriptive in its tools.

After a long development and approval process, the Directive establishing a Framework for Community Action in the field of Marine Environmental Policy (Marine Strategy Framework Directive or MSFD) was adopted on June, 17 2008 (Directive 2008/56/EC). With this Directive, the European Commission aims to install a strong, integrated EU policy on marine protection in order to achieve a good environmental status of marine ecosystems by the year 2020 at the latest. In this context the term "good environmental status" means "the environmental status of marine waters where these provide ecologically diverse and dynamic oceans and seas which are clean, healthy and productive within their intrinsic conditions, and the use of the marine environment is at a level that is sustainable, thus safeguarding the potential for uses and activities by current and future generations." Currently, 11 "good environmental status" descriptors have been identified which will be used to assess this.

Information Box 2.2 – Monitoring under the Marine Strategy Framework Directive

The establishment and implementation of a monitoring programme for ongoing assessment and regular updating of its targets is foreseen 6 years after entry into force except where otherwise specified in the relevant Community legislation. This policy must initially be based on an assessment or evaluation of the state of the marine environment, and the implementation of the latter must be followed by observation and assessment of what has, and has not, been achieved. Existing regional-seas monitoring and assessment programmes should be used as far as possible for new developments on EU and pan-European levels. Likewise, in developing existing EU measures – especially the EC Water Framework Directive – attention should be given to the links to both the pan-European and the regional-seas level (European Commission, 2004b).

More information is available from http://ec.europa.eu/environment/water/marine/index_en.htm

2. Existing programmes for assessment and monitoring of the marine environment

The Strategy has been prepared following an extensive consultation process⁷ from 2002 through 2004 including all EU Member States, candidate countries, the European Parliament, the European Economic Area (EEA) States (Norway and Iceland), the various, mainly regional, international organisations engaged in different sectoral aspects of the marine environment such as OSPAR, ICES and IMO (International Maritime Organisation), with environmental NGOs (non-governmental organisations), and with various sectoral industry associations. Coordination with existing programmes is thus an inherent part of the MSFD. From the outset, it has been recognised that the regional marine conventions/commissions and programmes, described in this Chapter play an important role at the interface between marine research and policy. They offer regional marine assessments that provide a scientific basis for policy making and also advise on the requirements and measures necessary to protect the marine environment.

7. EC MSFD Consultation evaluation report is available at http://ec.europa.eu/environment/water/consult_marine.htm

The MSFD states: “In order to achieve the coordination referred to in Article 5(2), Member States shall, where practical and appropriate, use existing regional institutional cooperation structures, including those under Regional Sea Conventions, covering that marine region or subregion” (Directive 2008/56/EC, adopted 17 June 2008).

According to the MSFD, Marine Strategies shall apply an ecosystem-based approach (see Information Box 2.3) to the management of human activities, while enabling the sustainable use of marine goods and services. This is in line with policies of the existing regional conventions which almost uniformly adhere to the ecosystem approach as well. The specific parameters which constitute this approach (e.g. Ecological Quality Objectives versus Environmental Quality Standards) may differ but the principles are the same. This constitutes a break with the classical comparison against a fixed set of objectives but also poses a new challenge on interpretation and assessment. It has also been recognized that monitoring and assessment have a vital role when the

Information Box 2.3 – The Ecosystem Approach

An ecosystem is a dynamic complex of plant, animal and micro-organism communities and their non-living environment interacting as a functional unit at different spatial scales. The marine environment is both an ecosystem and an interlocking network of ecosystems. Our understanding of the interactions within marine ecosystems and the collective effects of human activities on them is limited.

The notion of “Ecosystem Approach” was first used in the early 1980’s, but gained wide acceptance at the Earth Summit in Rio in 1992 as a key underpinning concept of the Convention on Biological Diversity (CBD). It was later described as “a strategy for the integrated management of land, water and living resources that promotes conservation and sustainable use in an equitable way.” It is considered as the main tool to work coherently towards a holistic approach to address the problems posed by the pressures and impacts of human activities on the (marine) environment.

In the context of marine pollution, the Ecosystem Approach entails that the state of the ecosystem itself is used as a measure by which to identify, plan and implement management actions needed to combat pollution from all sources and to promote protection, as well as sustainable use and development, of the environment (HELCOM, 2006). This differs from earlier sector-by-sector approach.

Following the commitment of the North Sea States in 2002 in Bergen (Norway) to implement the ecosystem approach, the HELCOM and OSPAR Commissions adopted a joint Statement towards an Ecosystem Approach to the Management of Human Activities (JMM, 2003). For the purpose of their Conventions, OSPAR and HELCOM define the ecosystem approach as “the comprehensive integrated management of human activities based on the best available scientific knowledge about the ecosystem and its dynamics, in order to identify and take action on influences which are critical to the health of marine ecosystems, thereby achieving sustainable use of ecosystem goods and services and maintenance of ecosystem integrity”.

During their 15th Meeting (Spain, 2008), the Contracting parties to the Barcelona Convention decided to gradually apply an Ecosystem Approach to the management of human activities in the Mediterranean region and agreed on a road map for its implementation in the Mediterranean.

For more information on the ecosystem approach and the 10 principles and 12 operational guidance points on the Ecosystem Approach adopted by the Convention on Biological Diversity, see: www.cbd.int/ecosystem/

For information about the ecosystem approach in the context of the OSPAR Convention see: www.ospar.org/content/content.asp?menu=00430109150000_000000_000000

ecosystem approach is applied to the management of human activities affecting the marine environment.

The role and the impact of the MSFD is only gaining momentum. It can be expected that the MSFD will become the driving force for most monitoring and assessment related activities in the marine environment at the European level.

2.2.3.3 REACH and other relevant EU regulations

A number of industrial chemicals have been evaluated in the EU Existing Chemicals Programme (Council Regulation EEC 793/93). The Member States have, to date, conducted approximately 140 risks assessments to prioritise substances or groups of substances. To support these exercises, a Technical Guidance Document⁸ (TGD) was developed in the mid 1990s and updated in 2003 (Anonymous, 2003). The TGD contains a chapter on how to conduct risk assessments for the marine environment. It also defines and provides cut-off values for the classification of substances. The latter allows a system which is based on hazard (see also Information Box 3.2 on concepts of risk and hazard) whereby chemicals are classified as persistent, bioaccumulating and toxic compounds (PBTs) or as very persistent and very bioaccumulating substances⁹ (vPvBs). It was, however, soon realized that the process of conducting comprehensive risk assessments was too slow and cumbersome to manage a major part of the tens of thousands of chemicals on the market.

A new European legislation named Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), was therefore introduced in 2006¹⁰. REACH requires that industry bears most of the responsibilities of assessing and managing the risks posed by chemicals and provides appropriate safety information to users. In parallel, it foresees that the European Union can take additional measures on highly dangerous substances, where there is a need for complementing action at EU level. REACH also created the European Chemicals Agency (ECHA) with a central coordination and implementation role in the overall process.

To facilitate the transition to the REACH system, the registration provisions will be applied in a step-wise fashion to introduce substances. For this purpose, a series of registration deadlines have been established according to the different tonnage ranges. In addition, certain substances of high concern (i.e. potentially carcinogenic, mutagenic or toxic to reproduction substances; persis-

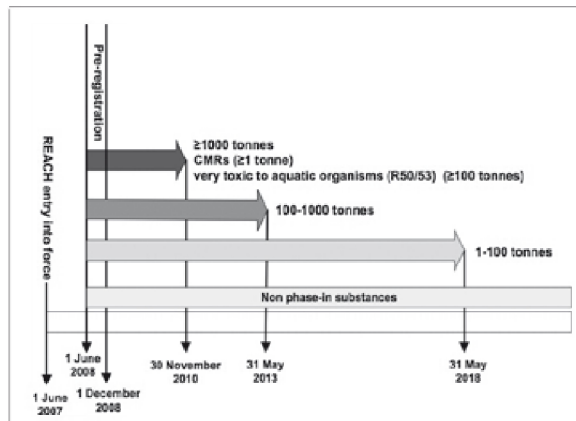


Figure 2.8. Time frame of the EC REACH Directive

tent, bioaccumulative and toxic (PBT) substances; very persistent and very bioaccumulative (vPvB) substances; and/or substances that are potentially dangerous to health or the environment and that are used in dispersive ways), will also need to be registered early.

Risks posed by biocides are assessed under a special legislation called the Biocides Directive¹¹. Active substances must be assessed and those that can be authorized are placed on a “List of active substances with requirements agreed at community level for inclusion in biocidal products” (Annex I). Member States shall authorise the biocidal products in accordance with the rules and procedures set in Annex VI of the Directive. They can only authorise products which contain active substances included in Annex I. A biocidal product authorised in one Member State shall be authorised upon application also in other Member States unless there are specific grounds to derogate from this principle of mutual recognition.

Medicines can be authorised in the European Union by using either the centralised authorisation procedure or national authorisation procedures (EC Regulation No 726/2004). The European Medicines Agency (EMA) is responsible for the centralised procedure. This procedure results in a single marketing authorisation that is valid across the European Union, as well as in the EEA/EFTA states of Iceland, Liechtenstein and Norway.

In addition to the above mentioned regulations, the EU also has Food Quality Standards in which the maximum concentration of potential contaminants in marine food-products are stipulated. This type of legislation will not be discussed here as it is outside of the scope of this report.

8. See <http://ecb.jrc.ec.europa.eu/tgd/>

9. For more information see <http://ecb.jrc.ec.europa.eu/esis/index.php?PGM=ora>

10. For more information see http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm

11. See http://ec.europa.eu/environment/biocides/pdf/dir_98_8_biocides.pdf

2. Existing programmes for assessment and monitoring of the marine environment

2.3 Critical considerations on existing monitoring programmes and regulations

The **Arctic Monitoring and Assessment Programme (AMAP)** has produced comprehensive and scientifically sound assessments of contaminants in the Arctic environment, describing contaminant levels, trends and effects. An AMAP assessment can therefore not be considered as a formal environmental risk assessment, but rather as a compilation of current knowledge. The emphasis is very much on science as the basis for relevant policy development. Indeed, the setup is much like a scientific programme and there seems to be no legally binding obligations such as those under the WFD or strict guidelines such as those proposed by OSPAR. Specific to the AMAP programme is the assessment of human health through the study of dietary intake and body burdens.

The **Black Sea Commission** provides the basis for proper marine monitoring via an integrated monitoring and assessment programme for the black Sea region (BSIMAP) (www.blacksea-commission.org/_bsimap.asp), and all the Black Sea countries have national monitoring programmes but only some of them are in line with the full objectives of BSIMAP. A recent Report prepared by the BSC (2010) for the EEA on the improvements to the regular reporting process on the state of the Black Sea environment (www.blacksea-commission.org/_publ-BSDiagnosticReport2010.asp) has shown that there is also a high volume of ecosystem quality data outside the Black Sea Information System (BSIS) which has not been part of the regular reporting system. According to the same report, monitoring of contaminants in biota, sediments (BSC, EEA, MSFD indicators) and their effects (MSFD indicator) are studied in the Black Sea sporadically, but the data are not sufficient for regional assessments yet. In order to improve the regional monitoring and reporting system, programmes should be better integrated and coordinated among different organizations at the national level. Capacity-building and active collaboration with the European Commission and other international bodies are also clear priorities.

The **Barcelona Convention** and its LBS Protocol provide the legal basis for the implementation of a coordinated monitoring programme of the Mediterranean marine environment. However, while national monitoring programmes are implemented in a coordinated manner in a number of Mediterranean countries, many spatial and temporal gaps still exist in other areas and as such the full implementation of a coordinated and well-developed regional monitoring programme, like that of

HELCOM and OSPAR, has yet to be realized. Emphasis has therefore been mainly on capacity-building and setting up the conditions that will eventually result in the full implementation of a sustainable monitoring programme for the Mediterranean. To this end, capacity-building has focussed on analysis of contaminants and guidelines have been developed covering various aspects of marine monitoring. Monitoring of the biological effects of contaminants and eutrophication monitoring are included in the MEDPOL Programme as pilot studies and a number of Mediterranean laboratories have the capacity to apply appropriate techniques. Periodic assessments on the state of the Mediterranean marine and coastal environment are prepared by MAP and thematic pollution assessments are prepared by MEDPOL. Recently, a State of Environment and Development Report (MAP/Blue Plan, 2009) and an initial Integrated Assessment Report at regional and sub-regional level, including pollution and biodiversity (MAP, 2011), have been prepared for the Mediterranean region.

The **Baltic Marine Environment Protection Commission or the Helsinki Commission (HELCOM)** has a well-developed and coordinated monitoring programme that shows large similarities with that of OSPAR. Both organisations have relied on the same scientific advice from the International Council for the Exploration of the Seas (ICES). HELCOM provides a standardized set of instructions, guidelines and common procedures (HELCOM COMBINE Manual) that deals with sampling, sample handling, analysis, quality assurance, data handling, data reporting and interpretation. This has resulted in high quality assessments focused, on potential impacts and trends for specific contaminants. HELCOM has put less emphasis on biological effect assessment techniques in comparison to other organisations although individual contracting parties have incorporated biological methods in their routine monitoring programmes. Specific for HELCOM is the development of Indicator Fact Sheets that provide information on the recent state of, and trends in, the Baltic Sea. HELCOM has also developed Ecological Quality Objectives (EcoQOs), associated indicators and target levels for these indicators. These objectives are used as central tools for identifying and striving towards a healthy ecosystem. As such the HELCOM approach can be considered as an ecosystem approach. Finally, although contracting parties are required to meet their HELCOM obligations, there are no legal sanctions if this does not happen. This often results in gaps in the datasets which can, in turn, weaken the quality and reliability of the assessments.

The **Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR)** has (with the JAMP) a well-developed monitoring and assessment programme with many similarities to that of HELCOM. The level of coordination is high, particularly for the Coordinated Environmental Monitoring Programme (CEMP), which can be considered as exemplary. The CEMP can be described as that part of monitoring within JAMP where the national contributions overlap and are coordinated. The CEMP has guidelines, quality assurance tools and assessment tools for all its mandatory parameters (which include both chemical and biological effects techniques). Although OSPAR has identified a rather extensive set of priority chemicals through the DYNAMEC process, only a limited number of substances are part of the CEMP (see Chapter 3). Important here is that the three elements above (guidelines, quality assurance and assessment tools) have to be in place before monitoring is undertaken. Additionally, sufficient information is required to determine that the chemical in question needs to be monitored on a routine basis. Data reporting is also co-ordinated and quality assured. OSPAR has taken, with its assessment tools, the next step in data assessment by using novel statistical approaches to test against a set of reference values such as Background Assessment Concentrations and Environmental Assessment Criteria. OSPAR also has well-defined statistical tools for temporal trend analysis that take the quality of the used data into account. This has resulted in innovative and high quality assessments that are published at regular intervals and describe the spatial distribution and trends of contaminants in the OSPAR area.

OSPAR periodically performs general assessments of the current knowledge of the health status of the sea, assessing the impact of humans on hydrodynamics, chemistry, habitats and biota, and provide a basis for implementing the ecosystem approach. These assessments are published in the form of Quality Status Reports (QSRs) of the North-East Atlantic and its sub-regions, the latest of which appeared in 2010¹². Like HELCOM, OSPAR has also developed Ecological Quality Objectives (EcoQOs) for the implementation of the ecosystem approach. However, also in this case there are no legal sanctions if contracting parties do not meet their obligations.

The **Water Framework Directive (WFD)** and the **Marine Strategy Framework Directive (MSFD)** overlap both regionally and thematically with programmes carried out by the existing marine environmental conventions. This holds both risks and opportunities. If insufficiently coordinated, the current situation could

easily result in an unnecessary duplication of monitoring efforts or even a reduction of the marine monitoring obligations for the conventions in favour of the much more stringent legal obligations of the European directives. Also, some contracting parties of the marine conventions are not EU member states and as such have no legal obligations to comply with the directives.

Although the requirements of the WFD relating to quality of the measurements, data reporting, setup and regional coordination are of a high level, certain aspects have not been conceived and are thus suboptimal for marine environmental monitoring. The choice of water as the primary matrix for hydrophobic contaminants monitoring is just one example. In contrast, the MSFD has, from the outset, supported coordination with existing programmes, recognising that they play an important role at the interface between marine research and policy, both in the context of regional marine assessments and the development of measures for marine management. It is highly important to build on the valuable experience that has already been gained through these regional programmes. Overlaps between the WFD and the MSFD have been dealt on the basis that the MSFD will not deal with matters already handled by the WFD for coastal and transitional waters. Coordination will, therefore, only be possible for substances or matrices not covered by the WFD or in marine waters beyond the 12-mile zone. Controversially, it is precisely in the coastal zone that most of the monitoring for the marine conventions already takes place. EU member states will, therefore, be obliged to comply with WFD for their coastal waters which may have a negative impact on their commitment to international and regional marine conventions. Nevertheless, certain aspects remain compatible such as the WFD requirement for trend monitoring and the possibility of measuring contaminants in biota and sediment, the preferred matrices in most marine conventions and programmes.

2.4 Conclusions and recommendations

Monitoring and assessment are vital to the evaluation of the impact of human activities on the marine environment, particularly with regard to contaminants. It seems imperative that any policy regarding the marine environment is initially based on a science-based assessment or evaluation of the state of that environment. Also, the practical implementation of a policy must be followed by observation and assessment of the evolving situation in the field. Evaluating the policy against its achievements and shortcomings through an assessment process allows adjustments to be made as required. Ideally, such

12. <http://qsr2010.ospar.org/en/index.html>

2. Existing programmes for assessment and monitoring of the marine environment

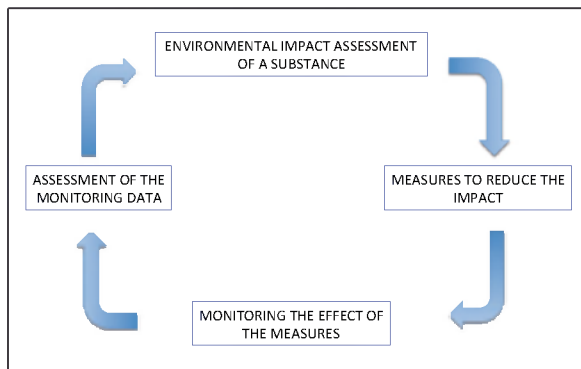


Figure 2.9. Monitoring the marine environment for chemical pollutants must be an iterative process: the plan-do-assess-revise cycle.

a cycle must be continuously repeated (see Figure 2.9). As monitoring and assessment are fundamental to a sound policy, they must be correctly designed from the start and rigorously implemented. Yet, at the same time there should be a feedback mechanism that allows timely modification of an existing monitoring programme if new scientific information becomes available. Such adaptive management is a critical component of the Ecosystem Approach.

Over the years, monitoring programmes have been developed and initiated at various national and international levels. The principles described in the paragraph above are embedded in most programmes but the degree to which they are applied in practice varies considerably. Clearly, there is also a need to coordinate the efforts of the various programmes.

The MSFD in particular requires harmonisation in terms of monitoring and assessment for specific issues. The long-term commitment of many European countries towards various marine monitoring programmes has resulted in important datasets and innovative approaches for monitoring and assessment of results. It is precisely this extensive experience that provides the opportunities for the MSFD while at the same time avoiding pit-falls like duplication of effort. This will require much greater cooperation than has been hitherto achieved. The development of the permanent process for a Global Marine Assessment, under the United Nations, and other UN processes such as those of the UN Environment Programme, can also play an important role in fostering better synergies between various monitoring programmes.

Furthermore, it is important to note that the development of a monitoring programme and its implementation are different processes, each requiring different expertise, resources and commitment from the parties involved.

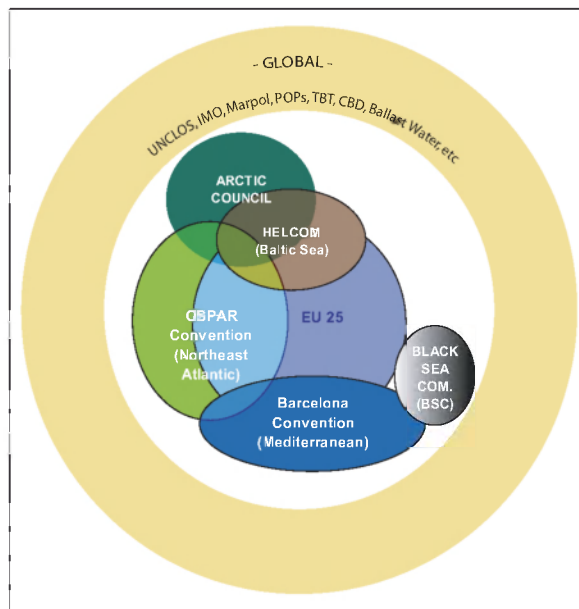


Figure 2.10. Institutional frameworks for the protection of Europe's seas and oceans. (Source: European Commission, 2006)

Although monitoring programmes have been able to demonstrate specific problems and trends associated with pollutants, most are far from perfect. Data collection and reporting is often incomplete, which hampers the assessment processes. For the WFD, countries are obliged by law to meet the requirements described in the directive. This gives the WFD considerably more leverage compared to other programmes, which will influence the amount and quality of data reported by the different parties. The MSFD will have a similar legal status and thus similar improved capacity.

There is also a continuous need to address common technical questions associated with all aspects of monitoring. Over the past decade these discussions have been ongoing within the various commissions and organisations but there is a definite need to involve all parties (including the European Commission, marine conventions, Member and Associated States and relevant marine science organisations) in the discussions. For assessments, these can include methodologies such as trend analysis techniques and other statistical evaluation methods. For monitoring, these can include the temporal and spatial distribution of sites to be monitored, selection of appropriate matrices, sampling methodology and analytical methodology. For both monitoring and assessment, data handling is important, and there will be a growing interest from different sectors in techniques of data exchange and the creation and management of relevant databases.

A fundamental difficulty for an efficient science-policy interface arises from the fact that research and policy have different agendas and operate on different time-scales. Whereas policy tends to focus on the short-term perspective, science focuses on long-term goals and challenges. Moreover, while policy tries to involve the development of acceptable compromises, the scientific community aims to establish objective scientific facts. This ambiguity is also reflected in the current monitoring programmes.

On the one hand there is a clear need for more data, both in terms of quantity (e.g. spatial and temporal distribution of data points) and quality (e.g. number of organic micropollutants determined) if we are to understand the status of the marine environment. Given the natural variability, lack of data is often disastrous for a proper evaluation of trends in the natural environment. On the other hand, collecting more data requires greater resources and this inevitably meets practical and budgetary constraints. Nevertheless, it is arguable that, in certain instances, the potential consequences of decisions outweigh the costs of obtaining the right information.

While there are initiatives underway which improve harmonization for data collection and distribution (e.g. EMODNET and NORMAN) it is clear that there needs to be more coordination, cooperation and harmonization between WFD/MSFD and regional monitoring programmes (e.g. OPAR, HELCOM and Barcelona Convention) to avoid duplication of effort, loss of expertise and to prevent a reduction of obligations for the regional conventions.

Summary Box 2.1 – Recommendations regarding existing and emerging monitoring programmes

1. For both monitoring and assessment there is a need for ICT-TOOLS, better data management, the creation of databases and techniques for data exchange.
2. Some regional programmes have not yet reached the level of maturity needed for appropriate assessments of the state of the marine environment. There is a need for capacity building measures and greater funding and collaboration to bring all regional programmes to an adequate standard.
3. Some regional programmes impose no legal sanctions when contracting parties do not meet their obligation which leads to gaps in datasets. This needs to be addressed.
4. There is a need to move towards full implementation of the ecosystem approach to monitor and assess the health of the marine environment.
5. There is a clear need for more (comparable) data both in terms of quality and quantity to understand the state of the marine environment and to follow its evolution over time.
6. To allow for science-based decision making, more efforts are needed to improve the interface between science and policy, overcoming barriers such as differences in timescales, objectives, methods and language.
7. There is a strong need for coordination, cooperation and harmonization between the EU (WFD/MSFD) and regional (e.g. OSPAR, HELCOM, Barcelona Convention) monitoring programmes to avoid duplication of effort, loss of expertise and to prevent a reduction of obligations for the regional conventions.

3. Current monitoring

3.1 Introduction

Monitoring of the health of the marine environment has been ongoing for several decades at both national and international levels. Although initially focused on measuring the concentrations of chemicals in abiotic media or organisms, the last decade has seen an increasing focus on effect-oriented parameters in monitoring programmes. There has been little change in the range of chemical substances which have been monitored in recent decades. Monitoring still focuses on the “legacy” organochlorines, the polynuclear aromatic hydrocarbons and several metals and metal-containing compounds. This is illustrated in Table 3.1 which summarises the main contaminants that are being measured in some well established, long-term marine monitoring programmes. There are several reasons for this. Initially, the analytical tools were either not available to increase the number of analysed substances, or the costs were prohibitive. With the rapid development of chemical analytical tools during the 1990’s, scientists began exploring the marine environment for the presence of a much larger number of substances. Simultaneously, organisations were evaluating threats to the marine environment, not solely through the detection of substances, but also based on their properties and production volumes. At the same time, biological effect assessment techniques became available and were applied to evaluate the potential adverse effects caused by these contaminants.

Unfortunately, international organisations are sometimes slow to adopt novel techniques and approaches and their acceptance for routine use often takes longer than it should. Also, marine monitoring is very costly which can restrict the further development of these programmes.

Although analyses of chemical contaminants are essential, monitoring of marine pollution in European

seas solely based on chemical analysis is considered insufficient since it does not provide any evidence of whether or how chemicals affects marine organism or ecosystems (Cajaraville *et al.*, 2000; Allan *et al.*, 2006; Letcher *et al.*, 2010). Organisms are exposed in their natural environment to a multiplicity of chemical (and physical) stressors caused by anthropogenic activities. These stressors can interact in complex ways that, even at very low levels, may elicit adverse effects.

This chapter aims at giving an overview of the current practices in marine environmental monitoring programmes in Europe, focusing on the selection of substances, chemical and biological (effects) techniques as well as the assessment procedures. It also summarizes and evaluates the approaches used in European programmes and discusses the development of integrated monitoring frameworks.

3.2 Chemical monitoring

3.2.1 European Union legislation Substances of concern

Chemical monitoring is usually targeted towards detecting and measuring compounds that are on an official priority list developed by responsible organisations. These lists were initially compiled in a rather non-systematic way, and many of these compounds were those linked to a pollution event or selected after their (sometimes accidental) detection at elevated levels in the environment. In the absence of well-directed and/or targeted selection procedures, many chemicals of genuine concern may be overlooked. On the other hand, it is clear that it is impossible to determine concentra-

Table 3.1. Overview of some major well-established international monitoring programmes and the contaminants and matrices they measure (after Roose and Brinkman, 2005)

Organisation or programme ¹	Start of the programme	Parameters ^{2,3}	Sample types
AMAP	1978	HM, PCBs, PAHs, OCPs	biota, sediment, water, human tissue
HELCOM	1979	HM, PCBs, PAHs, OCPs, OTINs	biota, sediment, water
NS&T	1986	HM, PCBs, PAHs, OCPs	biota, sediment
IMW	1965	HM, PCBs, PAHs, OCPs	biota (bivalves)
OSPAR	1978	HM, PCBs, PAHs, OCPs, OTINs	biota, sediment

¹ AMAP: Arctic Monitoring and Assessment Programme; HELCOM: The Baltic Marine Environment Protection Commission or the Helsinki Commission; NS&T: NOAA's National Status and Trends (NS&T); The IMW (International Mussel Watch) (actually started in 1991-1992, but data were already available since 1965 from earlier programmes); OSPAR: Oslo and Paris conventions.

² Not all parameters measured during entire period;

³ HM: heavy metals; PCBs: polychlorinated biphenyls; PAHs: polycyclic aromatic hydrocarbons; OCPs: organochlorine pesticides; OTINs: organotin.

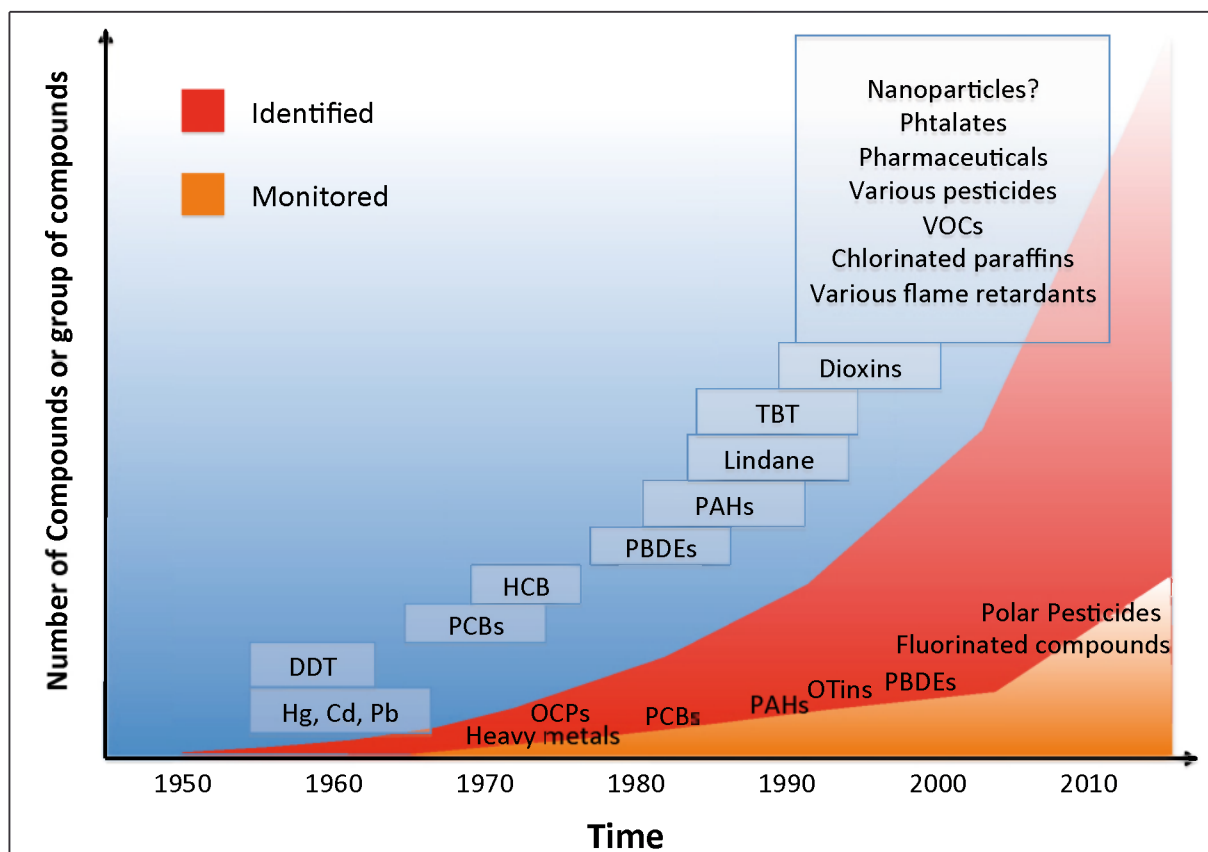


Figure 3.1. Timeline illustrating the time lag between discovery and routine monitoring of chemical substances or groups of substances. The Y-axis is a rough estimate indicating the number of substances/groups of substances. The X-axis is a time line covering the last decades. The names on the timeline are an estimate for the period their presence in the marine environment was first reported (orange) and when monitoring started at a national or international level (red). The list of chemicals illustrated here is not exhaustive. (Cd = cadmium, Pb = lead, Hg = mercury, DDT = p,p'-DDT and metabolites, PCBs = polychlorinated biphenyls, HCB = hexachlorobenzene, TBT = tributyltin, Otins = Organotins including TBT, VOCs = Volatile Organic Compounds, PBDEs = Polybrominated Diphenyl Ethers, SCCPs = Short Chained Chlorinated Paraffins)

tions in the marine environment of the approximately 250,000 man-made chemicals (OSPAR, 2000). Over the years this concern has led to the development of criteria for determining chemicals which may have negative impacts on the marine environment. Not surprisingly, different approaches have led to slightly or even significantly different lists of chemicals of concern selected for monitoring (Roose and Brinkman, 2005).

3.2.1.1 Selection criteria

There are several criteria that can be used for selecting potentially harmful substances. One of the first serious attempts to develop a procedure to select potentially harmful chemicals was instigated by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection or GESAMP, an Advisory Committee on Protection of the Sea in 1990 (GESAMP,

1990). They based their selection procedure on criteria such as the octanol/water partition coefficient (K_{ow}) or bioconcentration potential, acute toxicity, persistence, production volume and use of a chemical compound. The resulting list of potentially harmful substances contained mainly low molecular-weight (MW) (C1-C3) chlorinated alkanes such as chlorinated methanes (e.g. dichloromethane, trichloromethane also known as chloroform and tetrachloromethane), medium-MW compounds such as chlorinated benzenes, phenols and toluenes, PCBs and PCDDs/Fs. In addition, an extensive list of compounds was identified for which insufficient data were available to allow for assessment and selection.

Almost simultaneously, the threat of hazardous substances was recognized at the Third International Conference on the Protection of the North Sea (1990), identifying more than 200 potentially hazardous

3. Current monitoring



Figure 3.2. Meeting of GESAMP 38 in Monaco, 9-13 May 2011. The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection or GESAMP has played an important role in advancing international marine monitoring as an Advisory Committee of the United Nations on Protection of the Sea.

substances¹³. Subsequently, at the Fourth International Conference on the Protection of the North Sea (1995) which delivered the Esjberg Declaration, the need for further development of criteria for defining and prioritising hazardous substances which require action was identified¹⁴.

The OSPAR Convention was charged with implementing the targets of the Esjberg Declaration, and a dynamic selection and prioritisation mechanism, DYNAMEC, was developed (OSPAR, 2000) (see Information Box 3.1).

The OSPAR list played an important role during the selection of priority substances for the WFD. The basic procedure used for the WFD was the Combined Monitoring-based and Modelling-based Priority Setting (COMMPS) procedure. Similar to the OSPAR definition, hazardous substances are “substances or groups of substances that are toxic, persistent and have the potential to bioaccumulate, and other substances or groups of substances that give rise to an equivalent level of concern”. During the initial step of the COMMPS procedure, priority substances were again selected from among the list of hazardous substances. This was based on evidence regarding the intrinsic hazard, widespread environmental contamination and other proven factors which may indicate the possibility of widespread contamination. Next, exposure indices (based both on surface water monitoring and on modelling data) and effect indices were calculated. This finally led to a risk-based priority index, essentially achieved by multiplying both effect and exposure indices. This list was then

Information Box 3.1 – DYNAMEC system

In response to its strategy concerning hazardous substances, the OSPAR Commission developed a dynamic selection and prioritisation mechanism, DYNAMEC, to select priority substances. Hazardous substances are defined as (groups of) compounds that are persistent, toxic and liable to bioaccumulate (PTB), or give rise to an equivalent level of concern through, *e.g.*, synergistic effects or degradation into hazardous substances. The approach was holistic, *i.e.* OSPAR used the chemical universe as a starting point and looked at those chemicals with highly hazardous properties resulting in a general threat to the aquatic environment, based on the following criteria:

- strong indications of risk for the marine environment;
- widespread presence in one or more compartments of the marine environment;
- potential threat to human health via consumption of seafood; and
- presence of diverse sources or pathways to the marine environment.

After the initial selection, the compounds were ranked based on an algorithm. Final selection of substances for priority action was done by a group of experts. In addition, data on direct and indirect effects and production volumes and use were also taken into account. Calculated exposures and monitored concentrations were also considered. The initial selection led to a total of 80 substances or groups of substances, divided into five categories. Eventually, 15 were selected as substances for priority action and another twelve as candidates for prioritisation. The list of substances was updated in subsequent years. After the recent additions of PFOS, and the (pentabromo) methyl ester of 2-propenoic acid, the list now contains 47 chemicals for priority action.

For more information consult the DYNAMEC manual available at:

www.ospar.org/documents/DBASE/Publications/p00256_New%20DYNAMEC%20Manual.pdf

13. See Ministerial Declaration of the 3rd International Conference on the Protection of the North Sea (1990)

14. See Ministerial Declaration of the 4th International Conference on the Protection of the North Sea, 1995

Table 3.2. Overview of the main selection criteria used for selecting potentially harmful substances as applied by major marine monitoring programmes and frameworks.

WFD: Water Framework Directive; AMAP: Arctic Monitoring and Assessment Programme; HELCOM: Baltic Marine Environment Protection Commission or the Helsinki Commission; MEDPOL: Programme for the Assessment and Control of Pollution in the Mediterranean region; OSPAR: Convention for the Protection of the Marine Environment of the North-East Atlantic; UNEP POP: UNEP Global Monitoring Programme for Persistent Organic Pollutants

Programme Criterion	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UN-ECE POP
Persistence	X	X	X	X	X	X	X
Bioaccumulation	X	X	X	X	X	X	X
Toxicity	X	X	X	X	X	X	X
Production volume and use	X			X		X	
Presence in the environment	X	X	X	X			
Modelling	X						
Long-range transport		X			X		X

submitted for expert judgement and selection of priority substances. The procedure resulted in a list of 33 priority substances (see Appendix II).

The OSPAR and EU approaches, which are clearly related, provided the basis for priority setting under HELCOM (Füll, 2002). As a result, a very similar list of 42 substances or substance groups was agreed by HELCOM (see Appendix II).

Priority setting has by no means been limited to Europe. On a global scale, similar criteria are being used or developed in many national and international fora such as AMAP (2004), UNEP (2001), UNECE-POP (Lerch *et al.*, 2002), the US-EPA in its new chemicals programme (Moss *et al.*, 2000), and Environment Canada in its Domestic Substances List (DSL) Categorization and Screening Program¹⁵.

Although this overview should not be considered to be complete, the examples allow to summarise the most common selection criteria:

- Persistence;
- Bioconcentration/Bioaccumulation capacity;
- Toxicological risk towards humans and/or the environment;
- Production volume;
- Current use and application;
- Occurrence far away from known sources or potential for long range transport;
- Widespread occurrence.

The extent to which these criteria have been applied by the organisations mentioned in Chapter 2 is sum-

marised in Table 3.2. However, the true challenge for further work is not the identification of the criteria as such, but the proper weight that each factor should be given in the assessment. The effect of this weighting has led to considerable differences in “priority substances” as discussed in the next section.

3.2.1.2 Comparing the lists

Roose and Brinkman (2005) have made a comprehensive overview of the substances selected and considered by the WFD, OSPAR, HELCOM, BSC, MEDPOL and UNEP-POP. As can be observed from Table 3.1 and Appendix II, the “legacy” organochlorines and inorganic trace elements, are the most common compounds on the list. Although there is much overlap in the selected substances, there are also several striking differences. Surprisingly, not a single compound appears on all lists. Tributyltin (TBT) is common on all lists with the exception of UNEP-POP, but that list is restricted to organic pollutants and organometals are often not considered as belonging to that group.

The actual numbers of substances considered in the various programmes clearly differ. For example, more developed programmes from the Northern hemisphere (WFD, OSPAR, HELCOM, AMAP) consider a much larger variety of priority substances and these programmes are also not solely focused on the “legacy” contaminants. This is due, to a large extent, to the more stringent selection criteria and the broader ambitions of these programmes. However, not all the substances on even the most extensive lists are necessarily routinely monitored (see Appendix II for an overview). OSPAR’s coordinated environmental monitoring programme, for example, is restricted to only a limited number of substances.

15. Green Lane, Environment Canada’s website: Existing substances evaluation: Domestic Substances List Categorization and Screening Program. Available from: <http://www.ec.gc.ca/cceb1/ese/eng/dslprog.htm>.

3. Current monitoring

Given the fact that nearly every programme has identified Persistence-Bioaccumulation-Toxicity (PBT) criteria as one element of their selection process, it is obvious that this explains, to a certain extent, both the similarities and differences in the lists of priority substances identified by the different programmes.

Persistence is often expressed as the half-life of a chemical in the environment and the cut-off values used in the various programmes vary considerably. For example, UN-ECE and UNEP have set their criterion at a half-life of >2 months in water whereas GESAMP already considers a compound as persistent if it has a half-life of >1 week.

Bioconcentration is often approximated by the compound's K_{ow} value or expressed by its bioconcentration factor (BCF). Also here differences can be quite important. GESAMP considers compounds with a $\log K_{ow}$ of more than 3 as being "bioaccumulative" whereas OSPAR has set its value at equal to, or larger than, 4. The latter organisation also uses, when available, a BCF of equal to, or larger than, 500 whereas the COMMPS procedure sets the cut-off at 100. In this regard, it is important to consider the often large uncertainty of the values of factors (such as K_{ow}). Sometimes, literature reviews show around one order of magnitude differences for these values.

The use of the "Toxicity" criterion also exhibits considerable variance among the different programmes. Some programmes apply cut-off values related to acute effects (e.g. Lethal Concentrations LC_{50} ¹⁶ and Effect Concentration EC_{50} ¹⁷) or chronic (no) effect levels (e.g. No Observed Effect Concentrations $NOECs$ ¹⁸). Vaguely defined criteria like "Potential to adversely affect human health and/or the environment" are also used (e.g. UNEP). When cut-offs are used, the differences between various programmes can be considerable. However, there seems to be an evolution towards more restrictive cut-off values. In 1990, GESAMP used EC_{50} or LC_{50} values of <10 mg L⁻¹ as its selection criterion. Several years later, OSPAR set its value at <1 mg L⁻¹ for EC_{50} or LC_{50} s and ≤0.1 mg L⁻¹ for $NOECs$.

Differences of a factor of ten in cut-off values of PBT criteria are not uncommon and there seems to be no

general consensus. Despite these differences in cut-off values, a large number of substances are commonly selected in the different programmes, including most of the legacy contaminants.

If other factors such as production volume and use are taken into consideration, different priority substances begin to appear. This is partly due to the fact that expert judgement seems to play an important role in each selection process. For example, PCBs, PCDFs and PCDDs were eliminated in the final step of the COMMPS procedure based on expert judgement. Although the initial COMMPS selection procedure included most of them (even as top-ranking substances), they were not considered as priority substances because there is no current production or usage of these substances, or use is strictly regulated or forbidden. Exclusion from a list of priority substances is, therefore, not necessarily based on PBT criteria only. Similarly, in the OSPAR selection process a number of substances received a lower priority although they have rankings in terms of persistency, bioaccumulation and toxicity that indicate equal concern to that of other substances on the list. However, because they are used exclusively in closed systems as an intermediate in the production of other substances, or because there is no current production or use in the OSPAR states, these substances received a lower priority. In this approach both hazard potential and probability of exposure are taken into account which illustrates a movement from a purely hazard-based approach towards more risk-based approaches (see Information Box 3.2 for concepts of risk and hazard).

Another example of the discrepancies between the priority substances selected for monitoring by different organisations concerns PAHs. PAHs were not selected for the UNEP-POP list because they do not bioaccumulate in fish. Nonetheless, PAHs should be considered as high-priority environmental pollutants owing to their high persistence and potential carcinogenic and mutagenic effects. Although they are rapidly metabolised in vertebrates, they do bioaccumulate in invertebrates such as bivalves and can accumulate in sediments. Moreover, large quantities still reach the marine environment. As such, they are recognised as priority hazardous substances by AMAP, OSPAR, WFD and HELCOM.

The data set to which selection criteria are applied is also important. The COMMPS procedure for the WFD applied a monitoring-based exposure scoring but relied exclusively on the freshwater data for this. As a result, a prominent group in that selection is the so-called "modern" pesticides. Most of them are well known and a lot of freshwater studies have been conducted on these substances. Also, many of the pesticides (see Appendix II) are already monitored in the freshwater environment,

16. LC stands for "Lethal Concentration". LC_{50} values refer to the concentration of a chemical in air or water that kills 50% of the test population of a test organisms in a given period of time.

17. EC stands for "Effect Concentration". An EC_{50} value or half maximal effective concentration refers to the concentration of a drug, antibody or toxicant which induces a response halfway between the baseline (no effect) and maximum effect after some specified exposure time.

18. In ecotoxicology, $NOECs$ refer to the highest tested dose or concentration of a substance (i.e. a drug or chemical) or agent (e.g. radiation), at which no adverse effect (e.g. alteration of morphology, functional capacity, growth, development or life span) is found in exposed test organisms where higher doses or concentrations resulted in an adverse effect.

Information Box 3.2 – Risk versus hazard

A hazard can be defined as “a property or situation that in particular circumstances could lead to harm” or more shortly “the potential to cause harm” (Royal Society, 1992). Risk on the other hand is used to reflect the “chance of disaster” in everyday life, or the likelihood that someone or something would be harmed by a hazard. In the process of risk assessment the most commonly accepted definition for risk is “the combination of the probability or frequency of occurrence of a defined hazard and the magnitude of the consequences of the occurrence” (Royal Society, 1992).

The distinction between hazard and risk can be illustrated by a simple example. A large number of chemicals have hazardous properties. Potassium dichromate for example is a highly toxic carcinogenic chemical and as such hazardous. However, it is used in some techniques to analyse exhaled breath for alcohol content. For this application it is sealed in a tube, and does not become airborne when air is drawn over it. Therefore while it is a highly hazardous substance, its use in this case does not present any risk to the user.

For more information consult:
www.eea.europa.eu/publications/GH-07-97-595-EN-C2/chapter1h.html
www.agius.com/hew/resource/hazard.htm

hence their selection. However, many of the modern pesticides (e.g. the phenylurea pesticides diuron and isoproturon, the triazines atrazine and simazine and the anilide alachlor) are semi-polar and it remains to be seen if they will pose a serious threat to the marine environment, as they do not have a tendency to accumulate (e.g. in sediments). On the other hand, the more fat-soluble pesticides such as chlorpyrifos, chlorfenvinphos, trifluralin and dicofol have a much greater potential to form a *sink* in marine systems in similar ways to the old organochlorines.

Specific local conditions may warrant the inclusion of certain substances on monitoring lists. Acrylonitrile, aramite, isobenzene and kelevan all appear on the HELCOM list and have been selected with the particular situation of the Baltic in mind. This region-specific approach has not been used by either DYNAMEC or COMMPS. Nevertheless, in the Baltic, there are certain physical, chemical and biological features which may increase the vulnerability of this ecosystem to anthropogenic chemicals, which differ from the marine or freshwater environments addressed in the OSPAR and EU frame-

works. This is also the case for the Mediterranean and the Black Sea.

Although persistence and bioaccumulation are important factors in the selection process, these have certainly not provided the basis for selection of the many volatile organic compounds (VOCs) which are listed for monitoring (see Appendix II) (e.g. benzene, 1,2-dichloroethane, dichloromethane, trichlorobenzenes and trichloromethane). Nonetheless, these are mostly well-known atmospheric contaminants and important industrial compounds with a high annual production, which is an important consideration (Huybrechts *et al.*, 2003). Simply put, even though a low log K_{ow} will not lead to excessive bioconcentration, a sufficiently large input may still result in levels that cause concern. Studies showed the general presence of several VOCs in the tissue of marine organisms belonging to different trophic levels (Weigel *et al.*, 2001). Body concentrations of 1,000 times that of the surrounding water have been reported. The bioconcentration factors calculated from these data were generally higher than those reported in the literature, possibly due to the continuous exposure of the organisms to low or very low levels of these compounds in the water column.

Finally, different selection procedures can result in the selection of chemicals that are indeed not an obvious choice. This does not mean that the rationale behind their selection is at fault. It may indicate, for example, a potential substance of concern for which there is, at present, insufficient data available. Acquiring this information is key to further assessment, but is not always done in a timely fashion. For instance, clotrimazole was selected through the DYNAMEC procedure on the basis of its resistance to biodegradation and its toxicity. However, little is known about the presence in, or impact on, the marine environment of this pharmaceutical which is mainly used for treatment of dermatological and gynaecological fungal infections. Little effort has been put into demonstrating its presence or absence in the marine environment. It is not because a chemical has been earmarked as a substance of concern that it exhibits a wide distribution in the marine environment and/or that it is routinely monitored. Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/Fs), for example, have been recognised as important contaminants and while they are found on most lists of priority chemicals, they are not routinely monitored. On the contrary, OSPAR recently highlighted the lack of data for these compounds in the marine environment, which is mainly a result of the high costs involved in their ultra-trace level determination. The same is true for the more toxic non-ortho and mono-ortho Chlorinated Biphenyls (CBs 77, 81, 105, 118, 126, 169, 114, 123, 156, 157, 167 and 189). Although most monitoring programmes require or

3. Current monitoring

suggest the analysis of individual congeners such as the “ICES seven” (CBs 28, 52, 110, 118, 138, 153, 180), only a few programmes have included the former. Although the concentrations of these CBs typically are 1,000-fold less than those of the so-called indicator CBs, their toxicity is some 1,000-fold higher.

The inclusion of radionuclides in various monitoring programmes may be mainly driven by perception rather than science-based environmental concerns. Essentially all contemporary practices involving significant quantities of radionuclides are regulated (GESAMP, 2001). AMAP, HELCOM and OSPAR have been monitoring their presence in their regional environment and have, so far, not been able to demonstrate that there is cause for concern. According to the OSPAR Quality Status Report 2010, much of the earlier efforts were focused on radionuclides from the nuclear sector where significant improvements in environmental levels have been observed (OSPAR, 2010). More recently, nuclides from the non-nuclear sector are also being considered, but this has not lead to different conclusions (OSPAR, 2010). Nevertheless, as these contaminants engender strong public opinion, this issue will probably continue to be prominent in environmental reviews at all levels. This leads to a key question which holds for this and possibly other groups of contaminants: if the presence of a contaminant in the marine environment cannot be demonstrated (in long-term monitoring series) should it be continued to be monitored? It is suggested that it may be wise to re-assess the current lists of substances of concern in the context of our current knowledge on their presence in the marine environment.

3.2.2 Analytical methods and quality assurance

3.2.2.1 Analytical methods

Developments in analytical science have been an important driver of environmental research. The rapid development of chemical analytical tools during the 1990s resulted in an ever-broadening scope of substances that can be detected and measured and which are often found in the environment. Determining chemicals in marine matrices poses quite a challenge, as levels tend to be much lower than those in terrestrial/freshwater systems. As a result, the entire chain of processes, from sampling at sea through the preparation steps that lead to the final analysis, is considerably more demanding.

Nevertheless, analytical and instrumental developments have boosted the search for ever lower concentrations of chemicals in recent years. These developments are characterised by numerous attempts to find procedures



Figure 3.3 Marine scientist preparing samples in the laboratory

which are less time-consuming, use less solvent and/or enable miniaturisation. In the field of gas chromatography-mass spectrometry (GC-MS), the leading technique for the analysis of low-polarity chemicals, developments such as time-of-flight MS, MS/MS techniques based on ion trap (ITMS) and triple quadrupole instruments have allowed the detection of substances at levels previously not possible. It is safe to state that detection limits have decreased by several orders of magnitude since the early seventies. Furthermore, selectivity has also tremendously improved and novel techniques such as comprehensive multidimensional GC are starting to unravel complex mixtures.

Similarly, developments in liquid chromatography (LC) – mass spectrometry (LC-MS) have broadened the analytical spectrum by allowing the detection of more polar organic substances at very low ng L⁻¹ levels. Some substances such as PFOSs for instance, have even been determined in seawater at the very low pg L⁻¹ levels.

A typical advantage of most modern analytical procedures is that they have been designed as multi-residue approaches. That is, if in the near future one or more related substances are added to priority monitoring lists, no further method development will be required.

The availability of high-end methods does not necessarily mean that they can immediately be applied for routine purposes such as monitoring. It generally takes some time for a new method to become established and this nearly always results in a discrepancy between

the time of the first discovery of a compound and the more extensive data gathering e.g. through monitoring. Finally, the relevance of being able to detect very small quantities of a given substance should be taken into consideration. Detection limits should be linked to risk assessment which in turn should result in a sensible policy as far as monitoring is concerned.

3.2.2.2 Quality assurance

The quality assurance (QA) of analytical measurements is receiving increasing attention and will continue to be an important aspect of monitoring. Since many years, the marine environmental chemistry community has contributed significantly to improve the quality assurance in monitoring, for example by organising and participating in intercomparison exercises of contaminants in marine samples (water, sediment or biota) within various frameworks (e.g. ICES-MCWG, QUASIMEME programme, exercises organised by the Marine Environment Laboratories of the International Atomic Energy Agency).

One of the daughter directives to the WFD has defined minimum performance criteria for analytical methods and there is a general tendency to demand compliance with ISO 17025 for laboratories that are involved in routine monitoring. Today, many laboratories are either accredited or, in the absence of accreditation, are routinely processing procedural blanks, analysing reference materials and participating in inter-comparison exercises. On the other hand, the increased attention to QA does imply that the analytical performance is under control and that potential problems are readily identified and the analytical performance is quantified. De Boer and Law (2003) showed that the performance of laboratories in proficiency testing schemes (PTS) has not greatly changed in recent years. Even for a well-known compound such as CB 153, the average inter-laboratory coefficient of variation on measurements is about 30%. The situation is even worse for compounds such as lindane. Also, there is a well-known inverse relation of the concentration of the analytes and the coefficient of variation. Since marine chemists will continually be confronted with ever-lower analyte concentrations, the QA requirements for many of the compounds included in current monitoring programmes will certainly become more demanding. The clear demands of the WFD daughter directive are certainly evidence of this.

As its name suggests, currently, the QUASIMEME project/programme (Quality Assurance of Information for Marine Environmental Monitoring in Europe) is playing a principal role in the context of quality assurance, but the question can be posed if this will suffice in the future. At present, there is no framework nor directive dealing with QA for marine environmental monitoring in Europe.

Furthermore an particularly in relation to emerging substances, CRMs are often not available. Yet, method validation and interlaboratory exercises should be considered as mandatory requirements for environmental monitoring. This will need to be addressed at the national, European and international level.

3.3 Biological effects monitoring

3.3.1 Biological effects methods

The European Water Framework Directive (WFD) is an important tool to achieve “good ecological and chemical status” by 2015 in inland, transitional and coastal waters and offers the potential for the incorporation of biological tools in its monitoring programme and to integrate both chemical and ecological parameters.

Because of the absence of clear scientifically quantifiable relationships between chemicals in tissue and adverse effects on the organisms, it is crucial to measure effects directly. Methods which have been developed and used for this purpose range from quantifying embryonic aberrations in fish larvae, through biochemical, physiological or tissue changes, to identification of overt disease and clear organismal effects such as reductions in reproduction or death.

The main species used in European monitoring programmes are fish (e.g. dab, flounder, Atlantic cod, red mullet, eelpout), mussels and gastropods.

In recent decades, several biomarkers (molecular, biochemical, cytological, immunological and physiological effects) have been developed and applied in monitoring programmes performed in various European coastal areas (Cajaraville *et al.*, 2000; van der Oost *et al.*, 2003; Handy *et al.*, 2003; ICES, 2007; Hylland *et al.*, 2008). The OSPAR/ICES WKIMON/SGIMC working groups¹⁹ have recently summarised guidance documents on the use of biological measurements in marine monitoring programmes. These include assessment of EROD (7-ethoxyresorufin O-deethylase) activity, PAH-bile metabolite concentrations, DNA adduct concentrations, fish disease assessments including histopathological studies, vitellogenin (VTG) concentrations, δ -aminolevulinic acid dehydratase activity (ALA-D), acetyl cholinesterase (AChE) inhibition, metallothionein (MT) concentrations, assessment of reproductive success in fish, lysosomal stability measurements, scope for growth assessment in mussels and water and sediment bioassays with various species.

19. For more information see ICES website www.ices.dk

3. Current monitoring



Figure 3.4. Mussels are often used to measure the biological effects of pollution in the marine environment.

As mentioned above, a range of techniques have been developed for measuring biological effects of contaminants. An inventory and review of available techniques has been developed by ICES working groups and a suite of biomarkers suitable for incorporation into monitoring programmes has now been identified (ICES WGBEC, 2008).

3.3.2 Selection of methods

Over the past decades, a growing number of scientists have suggested requirements for biological effects methods to be used in monitoring (e.g. McCarthy, 1990; Peakall and Walker, 1994; Stegeman *et al.*, 1992). Suggested selection criteria generally include aspects such as contaminant specificity, simplicity of analysis, cost, applicability across different species and ecological relevance. The latter criterion is crucial as the method/marker should provide information on the health status of the organism. Although the above are clearly desirable characteristics, not all are fulfilled for most of the available techniques. Clearly, vital properties would be contaminant specificity, or at least knowledge of confounding factors, and some knowledge of response patterns (sigmoid dose-response, bell-shaped dose-response, threshold response). The remaining characteristics are either unrealistic (e.g. applicability across different species), or may be applicable subject to further development (e.g. simplicity and cost). ICES WGBEC (2005) identified three main criteria for methods to be recommended for monitoring programmes: (i) contaminant specificity (single substances or wider range); (ii) a known concentration-response relationship between exposure and response; and (iii) documented usefulness for monitoring activities.

For any method to fulfil these three criteria, particularly criterion (iii), there is a need to integrate research components in monitoring activities. Such integration can be done by including some testing techniques in monitoring programmes, as has been done for the Norwegian offshore water column monitoring programme (see Chapter 6). A final important component, rarely referred to in the open scientific literature, is the need for quality assurance procedures.

3.3.3 Analytical methods and quality assurance

Biological effects methods have been used in national and international programmes during the past two decades. A limited number of methods have been identified as useful for marine monitoring and have been applied in regional programmes such as MEDPOL and OSPAR.

As with chemistry programmes, quality assurance (QA) is an essential component of biological effects monitoring programmes. There has been some activity in this area over the past decade. Some EU-projects have conducted intercalibration exercises for selected methods (e.g. BEEP, COMPREHEND) and there have been regional activities, e.g. in MEDPOL. There has, furthermore, been a long-term activity on quality assurance of biological effects methods offered through the BEQUALM programme²⁰. Like QUASIMEME for chemical analyses, BEQUALM has offered intercalibrations of selected methods on a regular basis. However, there is a clear need to expand on the number of methods and the frequency of intercalibrations offered through that programme or elsewhere.

3.3.4 Assessment criteria

For most biomarkers, the use of particular species, sex, age/size classes, sampling time of year etc., are recommended in the standard operational procedures to minimise variation of the results (ICES WGBEC, 2005). Furthermore, background responses should be known before biological effect parameters can be integrated in the assessments. The general philosophy is that elevated biomarker levels compared to a background response indicate exposure to, or effects of, one or more hazardous substances (ICES WGBEC, 2005). Background responses can, therefore, be used as a basis for defining the distinction between “background” and “exposed” (background response is defined as the upper level of natural variation and response).

A crucial issue for setting values for background responses for biological effects techniques is the selection

²⁰. For more information see www.bequalm.org

of reference sites. The selection of reference sites to determine background responses has often been based on the existence of available data, e.g. related to the knowledge of low point source inputs, or from offshore sites as used in the United Kingdom for some biomarkers in fish studies, or from northern reference locations as in Norway. Furthermore, differences in responses between more or less sensitive species and non-linear dose-response relationships should be taken into account when the levels of biological effects are assessed (ICES, 2005).

The growing knowledge base on biological effects techniques has led their increased use in marine monitoring programmes. For example, guidelines for assessing the effects of organotins in molluscs (imposex and intersex) have been in place for more than a decade.

Although methods range from those that are contaminant-specific to those which may respond to many contaminants, there is a need for a more comprehensive effort in unravelling whether there are critical responses that are not yet covered. Immunotoxic responses appear to be one area with limited coverage, while there is also a need for further research on methods to detect reproductive and developmental toxicity of contaminants.

Despite suggestions to the contrary, it has become increasingly clear that responses need to be interpreted on a species-specific basis, and that methods and assessment frameworks need to take species-specific responses into account. It has been suggested that some methods are generally applicable to all species, e.g. lysosomal membrane stability, but this still needs to be corroborated by experimental studies exposing different organisms simultaneously. Although some quality assurance systems for biological effects methods are available (e.g. BEQUALM), marine ecotoxicologists in Europe need to sign up to these programmes to ensure the quality of the obtained results.

Recently, the most robust, well-established and quality assured biological effects methods have been included in an assessment framework (OSPAR WKIMON) that aims to address contaminant impacts in marine ecosystems in an integrated manner.

An overview of the biological effects monitoring recommended by relevant international organisations and which include quality assurance procedures can be found in Appendix III. This Appendix also highlights the biological effects monitoring implemented in individual European countries. In some cases, biological effects monitoring is conducted independent of chemical monitoring.

In contrast, OSPAR have produced guidelines for the integrated monitoring of biological effects- and chemical measurements (see also Information Box 3.3).

3.3.4.1 Integrated assessment

Different tools for biomarker data integration and interpretation have been proposed with the aim of developing integrated effect-based indices. Such indices comprise different biological effects which reflect pollution induced effects at several levels of biological organization and rank different stages of pollution-induced stress.

A two-tiered approach has been suggested in the Mediterranean region for wide-scale biomonitoring using caged organisms (mussels or fish). An early-warning, sensitive, low-cost biomarker (e.g. lysosomal membrane stability, LMS) and survival rate is used in Tier 1. Tier 2 tests for a battery of biological effects, and uses only organisms sampled at sites in which LMS changes are significant and where there is no mortality. This provides a simple but comprehensive assessment of pollutant-induced stress.

The increasing number of potential stressors present as complex mixtures in the European seas and coastal waters calls for novel strategies to assess the potential adverse biological effects of these contaminants (Cajaraville *et al.*, 2000; Broeg *et al.*, 2005). This assessment of the adverse effects should be based on a battery of selected biological effect essays that cover different mechanisms of action and combined with chemical analyses to detect short-term as well as long-term ecologically relevant effects. This can also provide insight on the relationships between environmental stressors and ecological effects (Handy *et al.*, 2003; Galloway *et al.*, 2004; Broeg *et al.*, 2005; ICES WGBEC, 2008).

Although useful as tools to increase our understanding of mechanisms and to identify possible biomarkers of contaminant stress, toxicogenomics, toxicoproteomics and toxicometabolomics are currently research tools and, as such, cannot yet be recommended for inclusion in monitoring programmes. It should be noted, however, that such methods used in conjunction with established biological effects techniques in monitoring programmes can yield important new insights.

It is recommended that future European monitoring programmes should include both chemical analyses and biological effects measurements. Biomarkers to be included should be those which are fully validated in terms of their ecological relevance and for which monitoring guidelines, quality control procedures and assessment tools are in place.

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Information Box 3.3 – The Integrated Approach

In recent years, working groups under ICES/OSPAR (i.e. WKIMON, SGIMC, WGIMC) have developed an integrated assessment framework for the use of biological effects measurements in environmental monitoring and assessment and which meet the objectives of the OSPAR Strategy for Hazardous Substances. The integrated approach is based on recommendations of sets of measurements that can be used to investigate the effects of contaminants on fish (dab, flounder, haddock, cod, red mullet) and/or mussels.

An integrated programme that includes both chemical measurements and biological effects measurements as well as different matrices and support data will increase the value of the individual measurements. For example, biological effects measurements will contribute to the assessment of measured concentrations of contaminants in biota and sediments. On the other hand, biological effects measurements in combination with chemical measurements will provide an enhanced assessment due to improved ability to identify the substances contributing to the observed effects.

It is known that specific contaminants or groups of contaminants have characteristic biological effects. The ability of organotin compounds to induce imposex or intersex in gastropods is a good example of these substance specific effects. While it is theoretically possible for other substances to disrupt the hormonal systems of snails in a similar way, it is generally accepted that TBT and other organotins are the primary marine contaminants responsible for these effects.

While a range of subcellular responses can be linked more or less specifically to certain hazardous substances, measurements of whole organism effects are much less contaminant-specific. On the other hand, the latter are often more closely linked to potential effects at the population level. The integrated framework described above comprises components that provide both types of information.

For more information see:
www.ospar.org/content/content.asp?menu=00900301090135_000000_000000

3.4 Assessment and evaluation of approaches and methods

Monitoring data will ultimately need to be compared with a set of criteria representing the status of the environment, irrespective whether one is dealing with chemical measurements, biological monitoring or biological effects monitoring. The WFD for instance, has clearly set the goals for chemical measurements in the proposed Environmental Quality Standards (EQS) values. EU member states are expected to demonstrate that the concentration of priority substances does not exceed the EQS in order to prove a good environmental status. However, no guidelines exist on how to compare the measured concentrations with the EQS. Also, the WFD states that it should be demonstrated that the situation in a water body is not deteriorating, but again no advice is given on how this should be achieved.

Marine monitoring programmes have faced the same challenges as the texts of these strategies contain statements such as “the levels of contaminants should be... at background levels for naturally occurring substances and close to zero for man-made substances” or “they should not cause harm to the environment” (see among others www.ospar.org). The latter is often translated in concentration levels derived from ecotoxicological experiments, food safety standards or by some other means. Also, every programme aims to prove that the situation is not deteriorating. As a result, trend analysis has been an essential element of all marine monitoring programmes and is also embedded in the non-deterioration principle of the WFD. The statistical methodology for this has reached a state of maturity in recent years. The most advanced approach to these questions has been developed by OSPAR with OSPAR trend assessments are based on an annual sampling programme for a given region. The statistics have mainly been developed by scientists active in the ICES working group on statistical aspects of environmental monitoring.

To assess progress towards the objectives of the OSPAR Hazardous Substances Strategy, two assessment tools have been developed: Background Concentrations (BCs) and the associated Background Assessment Criteria (BACs) and Environmental Assessment Criteria (EACs) (OSPAR, 2004).

Background Concentrations (BCs), formerly Background Reference Concentrations (BRCs), are intended to represent the concentrations of certain hazardous substances that would be expected in the North-East Atlantic if certain industrial developments had not happened. They represent the concentrations of those substances at “remote” sites, or in “pristine” conditions based on contemporary or historical data respective-

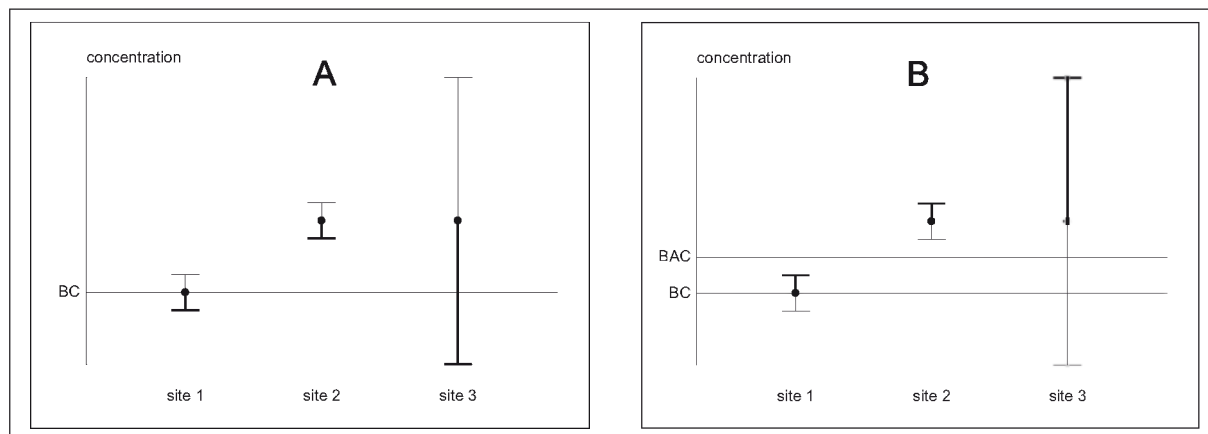


Figure 3.5. Graphical illustration of the brown test and the modified green test for environmental concentrations from three hypothetical sites (courtesy Patrick Roose)

ly, in the absence of significant mineralization and/or oceanographic influences.

However, how is it possible to quantify near background and close to zero? And how is it possible to test whether the objective has been met? To address these concerns, OSPAR introduced Background Assessment Criteria (BACs). BACs are statistical tools defined in relation to the background concentrations (BCs), which enable precautionary testing of whether mean observed concentrations can be considered to be near background concentrations. Essentially, it is a test that assumes one can establish a Background Assessment Concentration (BAC) below which concentrations can be considered near background. The assumption is that the mean concentration is above background unless there is statistical evidence to show that it is near background. In this test, concentrations are near background if the upper confidence limit is below the BAC. For example, the concentrations at sites 2 and 3 in Figure 3.5 (B) are above background and the concentrations at site 1 are near background.

OSPAR BACs have been calculated based on the residual variability of the data in the CEMP dataset and on the basis of QA information provided by contracting parties (OSPAR, 2005). The BCs themselves have a somewhat different history. For xenobiotic compounds, the BC is assumed to be zero as the substance is normally not present in the environment. For substances with a natural background (i.e. for which some trace levels are naturally present in the environment) such as metals, they are either derived from deep core sediment data representing deposition layers of pre-industrial times for sediments or consensus low values for organisms. The approach has been successfully used in recent OSPAR assessments (OSPAR, 2008).

For the assessment of the potential effects of hazardous substances, Environmental Assessment Criteria (EACs), formerly ecotoxicological assessment criteria, are used. Their main purpose is to identify potential areas of concern and chemicals which should be considered as priority substances. Regardless of similarities with EQS, EACs should not be used as firm standards or as triggers for remedial action (as opposed to the EQS). EACs suffer from the same shortcomings as other ecotoxicological criteria such as lack of sufficient ecotoxicological data, species-specific data and the use of pragmatic assessment factors to extrapolate laboratory to field responses. However, EACs are not the only OSPAR tool for the assessment of effects of contaminants. The OSPAR CEMP also contains actual field biological effect monitoring. For the effects of tributyltin (TBT), for example, a set of guidelines and assessment tools has been developed. The latter is particularly interesting because the effect of TBT on certain species of marine snails occurs at levels that cannot be measured chemically (ICES WGBEC, 2005).

An approach similar to the BAC has recently been suggested for biological effects techniques (BETs). OSPAR has been actively working towards that goal in recent years through a series of workshops in collaboration with ICES (ICES/OSPAR Workshops on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-sea Areas 2005-2007). This work has resulted in guidelines for integrated chemical and biological effects monitoring and proposals for assessment criteria for a number of BETs (ICES, 2007). This approach links chemistry with the health of the ecosystem which is also one of the objectives of the WFD. WFD related organisations or institutions may well benefit, in a later stage, from these developments.

3.5 Conclusions and recommendations

Summary Box 3.1 – Recommendations regarding current practices in marine environmental monitoring programmes in Europe

1. Selection criteria for priority substances to be monitored in the marine environment need to be harmonised between the different regulatory/assessment/monitoring frameworks. These criteria should not be exclusively hazard-based but also need to incorporate risk considerations.
2. Not all chemicals which appear on the lists of substances of concern in even the more developed monitoring programmes are effectively or routinely monitored. Monitoring programmes should increase monitoring effort to include a higher number of compounds which are identified as substances of concern on their lists.
3. There is a need to develop more low-cost, high-capacity analytical tools with low detection limits. At the same time, with ever lower analyte concentrations, there is a need for stricter quality assurance requirements.
4. There is a clear need to expand on the number of methods offered through programmes which provides regular intercalibrations for selected biological effects methods. At the same time, more ecotoxicologists need to develop and use quality assurance programmes for biological effects methods to assure the quality of the obtained results.
5. To advance biological effects monitoring, there is a need for more comprehensive efforts to assess critical responses that are not covered. For example, immunotoxic responses appear to be one area with limited coverage.
6. Monitoring should be science-based. There is a need to move towards fully implementing a science-based approach to the monitoring and assessment of the health of the marine environment taking into account regional differences.
7. Monitoring should be risk based. There is a need to move to fully implementing a risk-based approach to the monitoring and assessment of chemicals in the marine environment, including both hazard and exposure elements to be taken into account.
8. Monitoring should be a dynamic process. There is a need to periodically re-assess the current list of substances of concern in the marine environment – to remove (or at least reduce the monitoring effort for) chemicals which are no longer present or at levels which cause no concern to the health of the marine environment.
9. There is a need to develop novel strategies to assess potential adverse biological effects of mixtures of multiple-stressors. This needs to be based on a battery of biological effects at different levels of biological organization and combined with chemical analyses to detect short-term as well as long-term ecologically relevant effects. In this way, relationships between environmental stressors and ecological effects will be established. To achieve this, more research is needed on new techniques such as genomics and proteomics which are not yet ready for inclusion in long-term monitoring efforts.
10. Future European monitoring programmes should include both chemical and biological effects measurements selected on the basis of the results of earlier spatial integrated chemical-biological effects programmes. Bioassays including biomarkers to be used should be those where monitoring guidelines, quality control procedures and assessment tools are already in place and fully validated.
11. Currently, there is a strong focus on measurements. There is a need for more data interpretation and assessment, for example from data mining, and more analysis using existing data on geographic patterns.

4. Emerging substances of concern

4.1 Introduction

For the purpose of this position paper, the working group defined an “emerging substance of concern” as a chemical or anthropogenic material which is of growing scientific concern but currently not extensively monitored in international programmes. The concern may be due to new hazard information for earlier identified compounds (re-emerging) or due to the discovery of new substances in the environment for which a potential risk cannot be excluded. This pragmatic definition reflects the fact that there is considerable variation in the existing priority contaminant lists of HELCOM, OSPAR, UNEP and the Water Framework Directive, as summarised in Chapter 2 of this report.

Concern about emerging substances (also termed “emerging contaminants” or “emerging pollutants”) in marine ecosystems is often driven by progress in analytical chemistry applied to environmental samples. Increases in the sensitivity of these methods together with other advances in environmental surveillance methods resulted in the identification of previously undefined contaminants in aquatic environments. Together with research in freshwater and estuarine ecosystems, marine investigations have led to the identification of various types of emerging contaminants including, for example, halogenated flame retardants, endocrine disruptors, pharmaceuticals and personal care products (PPCPs) (Daughton and Ternes, 1999; Smital *et al.*, 2004; Richardson *et al.*, 2005; le Farré *et al.*, 2008). Some of these chemical classes which have been identified as organic micropollutants are likely to become (or remain) priority target chemicals for the North Sea area (Roose and Brinkmann, 2005).

The emerging contaminants debate also reflects scientific concerns that may be raised for older classes of chemicals or materials where new (eco) toxicity data suggest a potential for long-term adverse effects in marine biota. Examples include the endocrine disrupting properties of alkylphenols (Servos, 1999; Porte *et al.*, 2005; Ricciardi *et al.*, 2008) or the growing concern on the transport of persistent organic pollutants by plastics (Rios *et al.*, 2007; Teuten *et al.*, 2007 and 2009). In such cases, new information may warrant a revised marine environmental assessment of such a chemical (or class of chemicals), taking into account potential long-term effects in marine taxa, not included in freshwater environmental risk assessments (Leung *et al.*, 2001; Wheeler *et al.*, 2002). The emerging toxicity profile of a chemical may also reflect new mode-of-action observations from *in vitro* or *in vivo* toxicity studies in mammals or other model organisms (e.g. zebrafish) (Debenard *et al.*, 1994; Zapata *et al.*, 2003; de Wolf *et al.*, 2005; Zon and Peterson, 2005).

Based on the combined drivers of analytical chemistry and emerging toxicity profiles highlighted above, certain classes of chemicals are increasingly featured within the peer-reviewed literature (e.g. pharmaceuticals and personal care products). Concern has also recently been expressed about chemicals expected to be released into the seas from historical munitions disposal (Glasby 1997a; Brewer and Nakayama, 2008; Chauhan *et al.*, 2008). Glasby (1997b) reported unpublished Russian predictions that corrosion of munitions canisters dumped after World War II will lead to maximal leakage periods in the middle of the 21st century. Finally, the emerging contaminants debate also needs to reflect growing concern about marine litter, especially plastics, and its potential effects on marine life (Derraik, 2002; Browne *et al.*, 2007; Teuten *et al.*, 2009). With respect to emerging contaminants, attention continues to focus on persistent, bioaccumulative and toxic chemicals, and as scientific knowledge advances, the scope of concern goes beyond what is currently covered under the internationally agreed programmes (le Farré *et al.*, 2008). The complex range of exposure and toxicity scenarios underlines the need to be vigilant about both existing and new chemicals, and their risks for marine wildlife and human health.

When considering emerging substances of concern, it is important to keep in mind that the marine environment is not isolated from terrestrial and freshwater sources of pollutants. The occurrence of marine pollutants is not only the result of direct releases into the marine environment from activities at sea (e.g. from shipping), but also land-based sources which contribute considerably to marine pollution through river run-off and atmospheric deposition.

The aim of this chapter is to demonstrate in a non-exhaustive manner that there are a number of chemicals of concern which are currently not being routinely monitored and assessed in the existing programmes/frameworks. It also addresses some of the weaknesses in current approaches for selecting the chemicals to be monitored. The chapter is not aimed at listing, setting priorities or assessing the environmental risks of new and emerging substances.

4. Emerging substances of concern

4.2 Emerging substances

4.2.1 Endocrine disruptors

This is a group of chemicals not structurally related but effect related. The European Commission's 1996 Weybridge workshop defined an endocrine disruptor as "an exogenous substance which causes adverse effects in an organism, or its progeny, subsequent to changes in the endocrine system" (European Commission, 1996).

Over the past 30 years, numerous scientific reports have revealed that hormonal disturbances do occur in marine animals exposed to certain contaminants. The best documented case is that observed in molluscs exposed to organotin compounds released from anti-fouling paints. Effects were noted first in oyster (*Crassostrea gigas*) populations in the Arcachon Bay, France, in the late 1970s (Alzieu *et al.*, 1982, 1986 and 2000). Here it was noted that oyster shells developed lamellated chambers and spatfall decreased. In the 1980s the condition of imposex (superimposition of male features such as penis in females) was observed with increasing frequency in marine gastropods exposed to tributyl tin (TBT). It was found that female dogwhelks (*Nucella lapillus*) are sterilized by blockage of the oviduct at exposure concentrations as low as 1 or 2 ng L⁻¹. Since then, the mechanism of action and occurrence of this phenomenon has been intensively studied (Matthiessen and Gibbs, 1998; Depledge and Billinghamurst, 1999; Castro *et al.*, 2007).

The extensive range of chemicals which are capable of disrupting the endocrine systems of animals can be categorized as follows: (i) environmental oestrogens (e.g. bisphenol A, methoxychlor, octylphenol) and nonylphenol; (ii) environmental anti-oestrogens (e.g. dioxin, endosulphan and tamoxifen); (iii) environmental anti-androgens (e.g. DDE, procymidone, vinclozolin); (iv) chemicals that reduce steroid hormone levels (e.g. fenarimol and ketoconazole); (v) chemicals that affect reproduction primarily through effects on the central nervous system (e.g. dithiocarbamate pesticides, methanol); and (vi) chemicals with multiple mechanisms of endocrine action (e.g. phthalates, tributyltin) (Depledge and Billinghamurst 1999; Roepke *et al.*, 2005; Henley and Korach 2006; Castro *et al.*, 2007; Jensen and Leffers, 2008).

Endocrine-disrupting chemicals have received much attention in recent years and are recognised by all programmes except UNEP. This is especially the case for "new" substances such as alkylphenols but has also resulted in renewed interest for some "old" organochlorines such as DDT and its metabolites.

There is a high level of international concern regarding developmental and reproductive impacts on marine



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Figure 4.1. Dog whelk *Nucella lapillus*. The term "imposex" refers to "a superimposition of male features in females" in response to chemical pollutants and was first described in dog whelk *Nucella lapillus*. Biological effects assessment in molluscs has been successfully used to identify endocrine disruptors in marine environments.

organisms from exposure to chemicals with endocrine disrupting properties. Hence, these chemicals represent an important group of emerging contaminants. The increasing number of OECD test guidelines being developed to identify chemicals with endocrine disrupting properties will likely further contribute to a better understanding of the actual impacts of these chemicals and the extent of the problem (Gourmelon and Ahtianen, 2007). Nonetheless, further research is needed to identify which of these endocrine disruptor substances warrants monitoring on a much larger scale than at present.

4.2.2 Organo-halogenated contaminants of concern

OSPAR has recently widened its scope of concern to include the following emerging contaminants: brominated flame retardants (including polybrominated diphenylethers (PBDEs), tetrabromobisphenol A (TBBP-A); hexachlorobutadiene; pentachlorobenzene and short-chain chlorinated paraffins (SCCPs).

Brominated flame retardants (particularly the brominated diphenyl ethers (BDEs) and hexabromocyclododecane (HBCD)) have been widely detected in the European marine environment (OSPAR, 2004). Environmental compartments studied include the atmosphere, water, sediments, sewage sludge and a variety of biological samples. Law *et al.* (2006) reported that the input of BDEs (especially BDE209) into the Baltic Sea through atmospheric deposition now exceeds that of PCBs by almost a factor of 40. Sewage sludge samples from both industrial and domestic locations show similar concen-

trations of BDEs, HBCD and tetrabromobisphenol-A (TBBP-A), indicating that a major source is diffuse leaching from products into wastewater streams from users, households and industries. BDEs are widely distributed in fish collected from various geographic regions, including those from European high mountain lakes. This reflects the long-range atmospheric transport and deposition of these substances. A temporal trend study in archived freeze-dried mussels from the Seine estuary, France, indicated an exponential increase in BDE concentrations during the period 1982-1993, which levelled off in 1999 and 2001 and then began to decrease after 2002 (Johansson *et al.*, 2006). HBCD was detected in liver and blubber samples from harbour seals and harbour porpoises from the Wadden and North Seas. Tanabe (2008) summarized various studies related to temporal trends of brominated flame retardants (BFRs) in coastal waters of Japan and South China. Archived marine mammal fat tissues and dated sediment cores were used to evaluate temporal trends of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in relation to their usage in the region. The results from this study indicated that environmental concentrations of these BFRs in Japan and South China increased significantly during the last decades. PBDE levels in marine mammals and sediments from Japan, after showing peak concentrations in the 1990s, appear to have levelled off in recent years. This is in accordance with the discontinued usage of tetra- and octa-BDEs in Japan in the 1990s. Furthermore, in recent years HBCD concentrations in marine mammals from Japanese waters appear to exceed those of PBDEs, presumably reflecting increasing use of HBCDs over PBDEs.

Apart from the well-known PBDE's and BFRs mentioned above, other BFRs, produced in lower volumes, have also been found in the marine environment. Examples are pentabromotoluene (PBT), decabromodiphenylethane (DBDPE), 2,4,6-tribromotoluene (TBT) and 2,4,6-tribromoanisole (TBA) (de Boer, 2009). PBT and DBDPE, for example, have been found in Arctic samples remote from sources of contamination (de Wit *et al.*, 2010). Their presence in the Arctic is quite disturbing and an indication of their potential for long-range atmospheric transport. They tend to accumulate in top predators. Increasing anthropogenic use will, in all likelihood, lead to increasing environmental concentrations. There is thus a need to improve our knowledge of the prevalence and potential adverse effects of these compounds.

Finally, regulatory authorities and industrial producers have promoted the development of larger molecular weight BFR polymers. BFR polymers are considered relatively harmless since, as large molecules, they are less likely to be released from end use products, thus

preventing their dispersion in the environment. However, these BFR polymers may contain low molecular weight molecules such as "free" monomer units, by-products, and/or impurities (Han *et al.*, 2001). These compounds may have a high potential for migrating from the polymer matrix if they are not chemically bound to the backbone of the material. Therefore, polymeric BFRs may, in this way, be a source of emerging brominated organic compounds to the environment (Gouteux *et al.*, 2008). This example demonstrates how attempts at solving one problem can lead to another.

Next to BFRs, there is a considerable group of halogenated compounds that have been identified as priority substances but which in the context of this report should be considered as "emerging", as they are not routinely monitored. Medium and Short Chained Chlorinated Paraffins (SCCPs) are a good example of compounds which fit in this category. They are ubiquitous in the environment and tend to behave in a similar way to persistent organic pollutants (POPs) (Bayen *et al.*, 2006). Although SCCPs were selected through the OSPAR DYNAMEC and the EU COMMPs procedure, these substances should still be considered as emerging substances. This is mainly because of the shortage of environmental monitoring data caused by the lack of sensitive, quantitative analytical procedures. Nevertheless, they have been found in a variety of water bodies and sediments, and also in fish and marine mammals (OSPAR, 1997, Bennie *et al.*, 2000, Bayen *et al.*, 2006).

There are more compounds that could be considered in this category such as polychlorinated naphthalenes (Bidleman *et al.*, 2010) for example, but addressing them all would go beyond the scope of this document. Nevertheless, based on the growing evidence of the presence and potential effects of the organohalogenes discussed above, some of these substances should be assessed further and included in routine monitoring programmes.

4.2.3 Perfluorinated compounds

Perfluorinated compounds (PFCs) are globally distributed anthropogenic contaminants. PFCs, such as perfluorooctane sulphonate (PFOS), have been industrially manufactured for over 50 years and their production and use has increased considerably since the early 1980s. The main producer of PFOS voluntarily ceased its production in 2002. Furthermore the large-scale use of PFOS has been restricted. PFOS has been used in many industrial applications such as fire fighting foams and consumer applications such as surface coatings for carpets, furniture and paper. Following the restrictions placed on its production, the main uses of PFOS

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are in fire fighting foam, metal plating, photographic and semiconductor industries. PFCs are released into the environment during the production and use of products containing these compounds. The first global production, emission and environmental inventory for PFOS has recently been published (Paul *et al.*, 2009). Although PFCs have been present in the environment for decades, concern about their potential environmental effects has been raised only in the last decade. Currently there is a lot of uncertainty surrounding their exact environmental fate, accumulation patterns and possible effects.

Perfluorinated is a term used to describe molecules in which all the hydrogens have been replaced with fluorine. About 350 polyfluorinated compounds of different chemical structures are known. The most widely known are perfluorooctane sulphonate (PFOS; C₈F₁₇SO₃) and perfluorooctanoic acid (PFOA; C₈F₁₅O₂) which are chemically stable and thus may be persistent (substance dependent). PFCs do not accumulate in lipid but instead accumulate in the liver, gall bladder and blood, where they bind to proteins. Therefore, for body burden monitoring in fish, analysis of the liver is recommended.

PFCs were recently added to the Stockholm convention list of POPs. PFOS was added to the OSPAR List of Chemicals for Priority Action in 2003 owing to its persistence, bioaccumulation and toxicity, but analysis is not yet required for the OSPAR Co-ordinated Environment Monitoring Programme (CEMP). Although PFCs are not currently a requirement of most international monitoring programmes, there have been an increasing number of publications on the presence of PFCs in the marine environment, covering a wide range of matrices and locations. PFCs have been detected worldwide, including the Arctic and Antarctic Oceans, in almost all matrices of the environment.

For monitoring purposes, the high-volume chemicals PFOS and PFOA are considered the most important PFCs and are, therefore, the most frequently measured PFCs in environmental monitoring. Additionally, it has been suggested that long-chained PFCs (\geq C₈) should be included in analysis due to their bioaccumulative potential. High concentrations of PFOS and PFOA have been found in food, human blood and human milk. PFOS is generally the most abundant compound in biota and sediment. Compared to other POPs such as CBs, PFCs are found in higher ambient concentrations.

High concentrations of PFCs have been found in marine mammals. A screening project in Greenland and the Faroe Islands indicated high biomagnification of PFCs, with elevated concentrations in polar bear liver (1300 $\mu\text{g kg}^{-1}$). PFOS was the main PFC detected in the biota samples, except for minke whale (*Balaenoptera acutorstrata*) and long-finned pilot whale (*Globicephala*

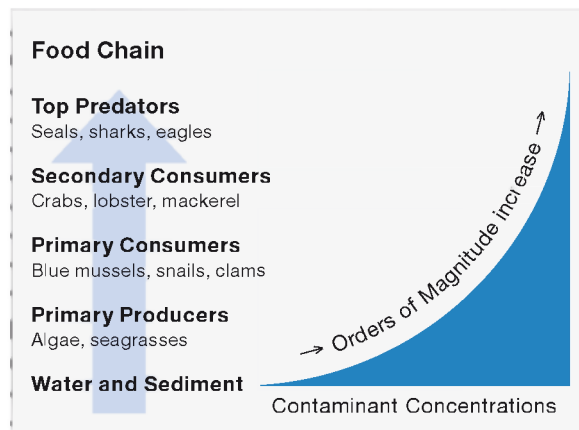


Figure 4.2. Biomagnification refers to the process whereby the tissue concentrations of a contaminant increase as it passes up the food chain through two or more trophic levels.

melas) which had higher levels of PFOA than of PFOS. A time trend study on archived ringed seal liver samples (1983–2003), showed increasing concentrations for all PFCs, from approximately 30 $\mu\text{g kg}^{-1}$ wet weight (median concentration) to 100 $\mu\text{g kg}^{-1}$ wet weight for ringed seals from East Greenland. In the UK, a study on stranded and by-catch harbour porpoise liver (1992 and 2003), found PFOS at concentrations ranging from <16 up to 2,420 $\mu\text{g kg}^{-1}$ wet weight; PFOA was not detected. There is a decreasing trend going from south to north.

Although there are an increasing number of reports on the occurrence of these compounds in the marine environment, including in marine biota, few studies are available on the ecotoxicological and potential ecological effects of these substances. As such, the occurrence of environmental impacts and environmental risk arising from the presence of these chemicals has yet to be established. However, because of their intrinsic properties and world-wide occurrence it is recommended that trends in environmental concentrations are monitored on a routine bases.

4.2.4 Antifouling paint booster biocides

There is a globally recognized need for effective antifoulants to prevent the settlement and growth of marine organisms on submerged structures, such as ship's hulls, oil rig supports, buoys and aquaculture systems. For several decades, tributyltin (TBT) compounds were the most widely used active ingredients in paint formulations. However, as described in 4.2.1 above, TBT has been regulated internationally since 1990 due to its severe impact on aquatic organisms (see review by Antizar-Ladislao, 2008). Many countries banned the use of TBT-based paints on small vessels (<25 m) and

in 2003, the International Maritime Organization (IMO) announced a ban on the use of TBT as an antifouling agent on all ships (Konstantinou and Albanis, 2004). Nonetheless, there are still localised concerns over the continued presence and impacts of TBT in some European coastal ecosystems (Berge *et al.*, 2005; Smith *et al.*, 2006; Sousa *et al.*, 2009).

Organic booster biocides were recently introduced as alternatives to organotin compounds in antifouling products. These replacement products are generally based on copper metal oxides and organic biocides. Commonly used biocides in today's antifouling paints are: Irgarol 1051, diuron, Sea-nine 211, dichlofluanid, chlorothalonil, zinc pyrithione, TCMS (2,3,3,6-tetrachloro-4-methylsulfonyl) pyridine, TCMTB [2-(thiocyanomethylthio) benzothiazole], and zineb. A number of studies have demonstrated the presence of these biocides in coastal environments around the world as a result of their increased use (notably in Australia, the Caribbean, Europe, Japan, Singapore and the United States) (Konstantinou and Albanis 2004; Carbery *et al.*, 2006). For example, Thomas *et al.* (2002) reported that Irgarol 1051, the Irgarol 1051 degradation product GS26575, diuron, and three diuron degradation products (1-(3-chlorophenyl)-3,1-dimethylurea (CPDU), 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU) and 1-(3,4-dichlorophenyl)urea (DCPU)) were all detected in marine surface waters and some sediments in the UK. A preliminary study of biocide input during both normal use and foreshore hull hosing showed that the latter operations may currently be a significant point source input of biocides. Field based measurements and laboratory experiments showed that Irgarol 1051 and diuron persist in the water column because of their low adsorption affinity to sedimentary material and high resistance to degradation. Other biocides such as chlorothalonil, dichlofluanid, and Sea-Nine 211 were all found to be less persistent and rapidly removed from the water column. In terms of effects assessment, Bellas (2006) reported that booster biocides may be ranked from highest to lowest toxicity to marine invertebrate embryo-larvae as follows: chlorothalonil > Sea-Nine 211 > dichlofluanid = tolylfluanid > Irgarol 1051. Risk assessments indicate that the predicted levels of chlorothalonil, Sea-Nine 211 and dichlofluanid in marinas represent a risk to marine invertebrates, whilst the risk due to Irgarol 1051 was low (Bellas, 2006). In summary, there is an on-going need to assess the environmental pathways and potential impacts of antifoulant paints using booster biocides.

Finally, non-eroding silicone-based coatings can effectively reduce fouling of ship hulls and are an alternative to biocidal and heavy metal-based antifouling paints. They consist of a silicone resin matrix and may contain unbound silicone oils (1-10%). If these oils leach



Figure 4.3. Ship hull hosing

out, they can have impacts on marine environments. Polydimethylsiloxanes (PDMS), the most widely used silicon-based organic polymers, are persistent, adsorb to suspended particulate matter and settle into sediment where they may inhibit pore water exchange. Although PDMS do not bioaccumulate in marine organisms and soluble fractions have low toxicity to aquatic and benthic organisms, undissolved silicone oil films or droplets can cause physical-mechanical effects such as trapping and suffocation of organisms. These “new” effects are not covered by current assessment schemes. PDMS illustrate that very low water solubility and bioavailability do not necessarily preclude damage to marine environments (Nendza, 2007).

In conclusion, despite the ban on TBT, continued monitoring is essential because of their very high toxicity and historic burden (including sources such as hull hosing) on the marine environment. Alternative antifouling substances need to be further evaluated using risk assessment techniques to fully determine their potential impacts on the marine environment.

4.2.5 Human and veterinary pharmaceuticals

Pharmaceuticals are a class of emerging environmental contaminants that are extensively and increasingly being used in human and veterinary medicine. These chemicals are designed to have a specific mode of action, affecting the activity of e.g. an enzyme, ion channel, receptor or transporter protein (Halling-Sørensen *et al.*, 1998; Gunnarsson *et al.*, 2008).

The first reports of pharmaceuticals in marine environments date back some twenty years (Peele *et al.*, 1981). More recently, Buser (1998), Weigel (2002) and others reported the presence of clofibric acid (a cardiovascular drug metabolite) throughout the North Sea

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sampling area. Several medicinal drugs were found to be ubiquitous in the river Elbe and its tributaries (including antibiotics, carbamazepine, diclofenac, ibuprofen, metoprolol, phenazone, and paracetamol) (Wiegel *et al.*, 2004). Clotrimazole, dextropropoxyphene, erythromycin, ibuprofen, propranolol, tamoxifen and trimethoprim were detected in UK coastal waters (Thomas and Hilton, 2004) and in UK estuaries (Roberts and Thomas, 2006) at concentrations ranging from 4 to 2370 ng L⁻¹. The results of this study show that concentrations of some pharmaceutical compounds are effectively reduced during their passage through a tertiary wastewater treatment works, whilst others are sufficiently persistent to end up in estuaries and coastal waters. Concerns have also been raised over the presence of pharmaceuticals (including antibiotics) and personal care products in coastal waters of South East Asia (Richardson *et al.*, 2005; Gulkowska *et al.*, 2007).

Compared with terrestrial and freshwater organisms, there is a lack of experimental data on the impacts of pharmaceuticals in marine and estuarine species. However, there is experimental evidence that selected pharmaceuticals have the potential to cause sub-lethal effects in a variety of organisms. For example, under laboratory conditions, tamoxifen (a selective oestrogen receptor mediator) is known to cause developmental toxicity in sea urchin embryos (Pagano *et al.*, 1994; Roepke *et al.*, 2005). Other experimental studies have shown that hormonally active chemicals affect copepod populations (Hutchinson *et al.*, 1999; Kusk and Wollenberger 2007). More recently, Porsbring *et al.* (2009) studied the impact of the pharmaceutical, clotrimazole, on marine microalgal communities, whereby concentrations of 10-100 nmol L⁻¹ and higher caused large reductions in community growth, and changed community pigment profiles in a concentration-dependent manner. These authors also noted that OSPAR (2005) estimated a risk quotient exceeding 2 for low tide marine scenarios.

Direct and indirect impacts of antibiotic pharmaceuticals are also of concern in marine environments. For example, Näslund *et al.* (2009) studied the effect of ciprofloxacin on the marine sediment bacterial community structure and on pyrene degradation. They concluded that antibiotic substances in marine ecosystems can pose a potential threat to bacterial diversity, nutrient recycling and removal of other chemical pollutants. Although there are large gaps in the current knowledge on the potential impacts of human and veterinary pharmaceuticals on marine and estuarine species, recent work on the mode-of-action of pharmaceuticals in aquatic species suggests this is a cost-effective approach for environmental risk assessment of these substances (Smítal *et al.*, 2004; Gunnarsson *et al.*, 2008).

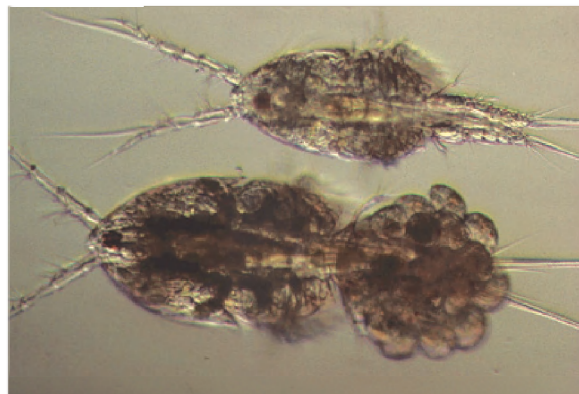


Figure 4.4. Microscopic image of the marine copepod *Tisbe battagliai*. Experimental studies with these marine copepods have been used to assess population impacts of pharmaceuticals and other potentially toxic substances.

Although data on the occurrence of pharmaceuticals and antibiotics in the marine environment is becoming more available, the true extent of the potential risks posed by this group of contaminants cannot, at present, be assessed, mainly due to the lack of effect data. However, it is clear that these substances should not be neglected and it is therefore recommended that increased research (biological effects, survey and possible monitoring) should be performed to allow a full assessment of the risks of these chemicals to the marine environment.

4.2.6 Personal care products

Potential risk of personal care products received considerable scientific attention in the late 90s, following reports of their presence in the aquatic environment and biota (Yamagishi *et al.*, 1981 and 1983). Several studies showed that synthetic musks are widespread in marine and freshwater environments and bioaccumulate in fish and invertebrates. (Rimkus and Wolf, 1995; Bester *et al.*, 1998; Rimkus, 1999; Gatermann *et al.* 2002).

Musk ingredients are substances used by the fragrance industry for their musky scent in a wide range of consumer products. Synthetic musks are generally divided into three groups of substances with similar properties but different chemical structures: nitromusks, polycyclic musks and macrocyclic musks. The main nitromusks are musk xylene and musk ketone. The main polycyclic musks are Galaxolide (HHCB) and Tonalide (AHTN).

The musk xylene group and other musks were added to the OSPAR List of Chemicals for Priority Action in 1998. Nitromusks are not produced in Europe and production in Europe of AHTN and HHCB is concentrated at one (inland) plant in the EU for each substance respectively

(OSPAR, 2004). Musk xylene and musk ketone and the two main polycyclic musks (AHTN and HHCB) have been included in priority lists under the EC existing substances regulation (ESR). Because acute and chronic toxicity thresholds for musks in invertebrate and fish species are much higher than the environmentally measured levels (Balk and Ford, 1999), the OSPAR marine risk assessment (OSPAR, 2004) concluded that the industrial use of musk xylene, musk ketone, AHTN and HHCB should not be considered a concern. Even if trade effluents are locally discharged into the marine environment without proper treatment, no impact is to be expected. Unlike the point releases generated by industrial use, the use of these substances in consumer products causes a more diffuse emission pattern, probably covering the whole OSPAR Convention area. Nevertheless, the risk ratios for the various consumer use scenarios also indicate that there is no reason for concern.

Nakata *et al.* (2009) recently studied the presence of personal care products in the marine environment. The authors identified benzotriazol organic UV filters such as UV-320 (2-(3,5-di-*t*-butyl-2-hydroxyphenyl)-benzotriazole), UV-326 (2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole), UV-327 (2,4-di-*t*-butyl-6-(5-chloro2H-benzotriazol-2-yl) phenol), and UV-328 (2-(2H-benzotriazol-2-yl)-4,6-di-*t*-pentylphenol).

These substances were detected in marine organisms collected from the Ariake Sea, off western Japan. Relatively high concentrations of several hundred nanograms per gram (soft body tissue, muscle tissue) on a lipid weight basis were found in the investigated species. There are also indications that marine mammals and seabirds accumulate UV-326, 328 and UV-327. Benzotriazole UV filters were also detected in surface sediments from the Ariake Sea, at the average concentrations of several ng/g (dry wt.). The results suggest a significant bioaccumulation of UV filters through the marine food-webs and a strong adsorption to sediments. Hence, they display strong characteristics for selection as candidate contaminants and the authors underline the need for further investigation.

PCPs comprise a large group of very diverse chemicals. Although a full risk assessment of some of these has been performed (e.g. musks), for most PCPs there is little data on their occurrence and their effects in the marine environment. However, there is reason for concern. Siloxane, used in PCP, was found in the Arctic (Warner *et al.*, 2010) which is generally considered to be an omen for the widespread distribution of a chemical. Therefore, it is recommended that more research on this group of substances is performed to enable a comprehensive assessment of their potential risks.

4.2.7 Micro plastics and litter

Marine litter, including plastics, is an issue of rapidly growing concern across the globe (Arthur *et al.*, 2009; Thompson *et al.*, 2009). Global plastic production has increased from 5 million tonnes in the 1950s to over 230 million tonnes in 2005 (Plastics-Europe, 2006). This production volume, coupled with their high durability has led to widespread accumulation of discarded plastic in the aquatic and terrestrial environment. Studies in the Pacific region have reported significant quantities of plastic debris on beaches from Hawaii to New Zealand and large volumes of floating plastic debris in major ocean currents (reviewed by Thompson *et al.*, 2009). Plastic debris accumulating in the marine environment is fragmenting into smaller pieces, thereby increasing the potential for ingestion by marine animals and/or interfering with their functioning (Derraik, 2002). A study of archived plankton samples from the northeast Atlantic showed that the abundance of microscopic plastics in the water column has increased significantly in the last 40 years. Similar particles were also found on beaches throughout the United Kingdom. Microplastic particles appear, therefore, to be a widespread contaminant that has accumulated across a range of habitats (Thompson *et al.* 2004; Browne *et al.*, 2007).



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Figure 4.5. Sorting of marine litter on UK research vessel Cefas Endeavour

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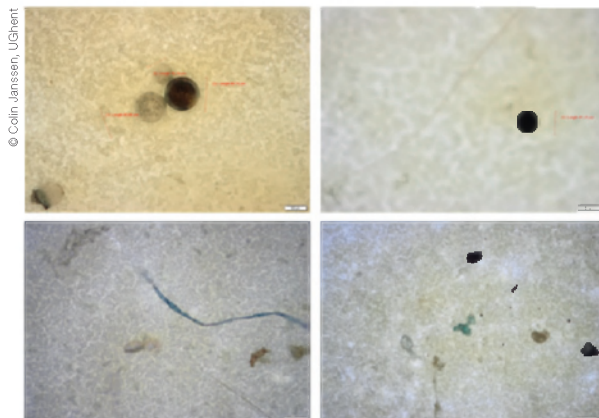


Figure 4.6. Micro-plastics detected in filtered seawater samples

Several marine species have been shown to ingest and accumulate plastic particles in their tissues (Eriksson and Burton 2003; Browne *et al.*, 2008). A number of recent workshops held in Europe (Thompson *et al.*, 2009) and North America (Arthur *et al.*, 2009) have underlined the major knowledge gaps in understanding the spatial and temporal trends in plastic pollution of marine ecosystems, together with a need to evaluate the effects of such pollution on marine organisms.

Plastic polymers are composed of repeating subunits called monomers. As reviewed by Browne *et al.* (2007), polyvinylchloride, polystyrene and polycarbonate have been shown to release toxic monomers that have been linked in some studies with cancer and reproductive abnormalities in humans, rodents, and invertebrates. Monomers are not the only chemicals that could be potentially transferred from plastics upon uptake by organisms. A range of chemical additives are incorporated into plastic, including catalysts (e.g. organotins), antioxidants (nonylphenol) and flame retardants (polybrominated diphenyl ethers). In addition to chemicals used in its manufacture, plastic has been shown to adsorb and concentrate hydrophobic contaminants (e.g. polychlorinated biphenyls, dichlorodiphenyl trichloroethane, and nonylphenol) from the marine environment at concentrations several orders of magnitude higher than those of the surrounding seawater (Mato *et al.*, 2001; Rios *et al.*, 2007).

Plastic litter, in particular micro-plastic litter, is a growing issue which needs to be urgently addressed. The available data is too sparse to allow a comprehensive assessment of the magnitude and impact of this contamination in marine ecosystems. There is an urgent need for (i) validated methods to assess the occurrence and effects of microplastics; and (ii) routine monitoring and/or surveys.

4.2.8 Organophosphate esters

Due to concerns about the presence of brominated flame retardants (BFR) in the environment, restrictions have been placed on their manufacture and use. Therefore, there has been a shift in the flame retardants on the market. One particular class of chemicals which represent a possible substitute for BFRs are organophosphate esters (OPs), which are used as flame retardants. In Western Europe, the use of OPs has increased to 91,000 tonnes yr^{-1} in 2006 (Reemtsma *et al.*, 2008). It is thought that this will increase further due to the increased restrictions on the use of polybrominated diphenyl ethers. OPs include chlorinated alkylphosphates such as tris-(2-chloro,1-methylethyl)-phosphate (TCPP) and tris-(2-chloro-, 1-chloromethylethyl)-phosphate (TCEP), and non chlorinated OPFRs such as triphenyl phosphate. Chlorinated OPs are mainly used as flame retardants in a multitude of applications such as polyurethane foam (PUF) and polyvinylchloride (PVC), paints, textiles and electronic equipment. Non-chlorinated OPs are mainly used as plasticisers.

Despite their widespread use in electronics, fabrics, and wall insulation, comparatively little is known about OPs and their presence in the environment. There is limited knowledge also on the toxicity of OPs, although some are suspected carcinogens (WHO, 1998). OPs have been identified in environmental samples, although studies are scarce. A number of studies were carried out in the 1970s and 1980s in which OPs were found to degrade in the environment and, therefore, most studies were abandoned (Reemtsma *et al.*, 2008). However, in recent years there has been increased interest in this contaminant group as they have been detected in the indoor environment and new information indicates they may be more persistent than first believed (Reemtsma, 2008; Carlsson, 1997; Stapleton, 2009). As with many substances already discussed, there is an urgent need for more comprehensive data on their occurrence (survey and monitoring) and effects of OPs on marine biota.

4.2.9 Nanoparticles

Nanotechnology is a major area of scientific, technological and economic activity across diverse fields such as electronics, engineering, marine technology, medicine and pollution remediation. As summarised by Ju-Nam and Lead (2008), nanoparticle research involves the study of materials on the nanoscale level, i.e. between approximately 1 and 100 nm in size. In general, NPs can be categorised into carbon-based materials such as fullerenes and carbon nanotubes and inorganic nanoparticles including those based on metal oxides (e.g. zinc oxide, iron oxide, titanium dioxide and cerium oxide), metals (e.g. gold, silver, titanium and iron) and

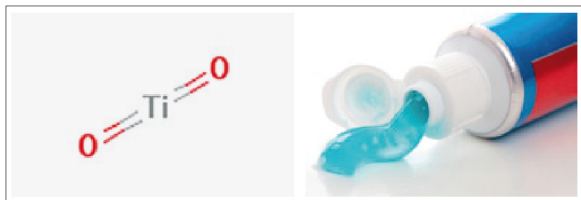


Figure 4.7. Researchers are currently investigating the effects of various nanoscale particles, including titanium dioxide (figure left) on marine ecosystems. Titanium dioxide is used as a whitener in many products, from toothpaste to candy to cosmetics. Observations indicate that nanoscale particles may have important indirect impacts on aquatic organisms by varying the toxicity of coexisting pollutants on top of potential direct effects.

quantum dots (e.g. cadmium sulfide and cadmium selenide).

There are, however, few published data available on potential impacts of man-made nanoparticles on human and ecosystem health. The surface properties and very small size of nanoparticles provide surfaces that may bind and transport toxic chemical pollutants, as well as possibly being toxic in their own right by generating reactive radicals.

Although there is a wealth of evidence for the harmful effects of nanoscale combustion-derived particulates (“ultrafines”), the release of manufactured nanoparticles into the aquatic environment is largely an unknown and is an important area for research (Moore, 2006; Handy *et al.*, 2008; Ju-Nam and Lead, 2008). A potentially significant hazard associated with marine organisms exposed to nanoparticles is the potential for nanoparticles to affect the bioavailability of chemical toxicants and enhance their uptake into cells and organisms (for example, the pharmaceutical industry is seeking to use nanoparticles to improve the delivery of drugs to target tissues (Panyam and Labhasetwar, 2003). There are only a few reported *in vivo* studies on the effects of nanoparticles on marine organisms. Scarano and Morelli (2003) studied the properties of phytochelatin-coated metallic nanocrystallites formed in marine phytoplanktonic alga, concluding that uptake by endocytotic routes was a probable major mechanism of entry into cells. Complementary to *in vivo* approaches, several *in vitro* studies have recently been published giving valuable insights into the cellular mechanisms of toxicity. For example, Koehler *et al.* (2008) observed uptake of glass wool nanoparticles into the gills and hepatopancreas of marine mussels while Moore *et al.* (2009) studied the *in vitro* cellular toxicity of C60-fullerene and carbon nanotubes within the lysosomal compartment of phagocytic blood cells (haemocytes) from marine mussels (*Mytilus galloprovincialis*). They showed that high-concentration aqueous suspensions of carbon nanoparticles (C60-

fullerene 1 – 10 g L⁻¹) induced cytotoxicity in circulating phagocytic haemocytes, which are a key component of the molluscan immune system. Moore and co-workers concluded that their findings were consistent with the hypothesis that C60-fullerene is cytotoxic on uptake into the endocytic-lysosomal system and that cell injury may be mediated by generation of reactive oxygen species (ROS). Additionally, it should be recognized that nanoparticles may enhance the toxicity of other chemical substances (Baun *et al.*, 2008).

Given the rapidly increasing incorporation of nanoparticle-based technologies into modern life, and concomitant likely environmental dispersion of these materials, there is a need for an in-depth assessment of the fate and the *in vivo* effects of the most common nanoparticles in the marine environment.

4.2.10 Leakage from weapons disposal

Following World Wars I and II, large quantities of conventional munitions and chemical weapons, including phosphorus incendiary devices, mustard gas and other chemical warfare agents, were dumped in European waters. Figure 4.8 gives an overview of locations of

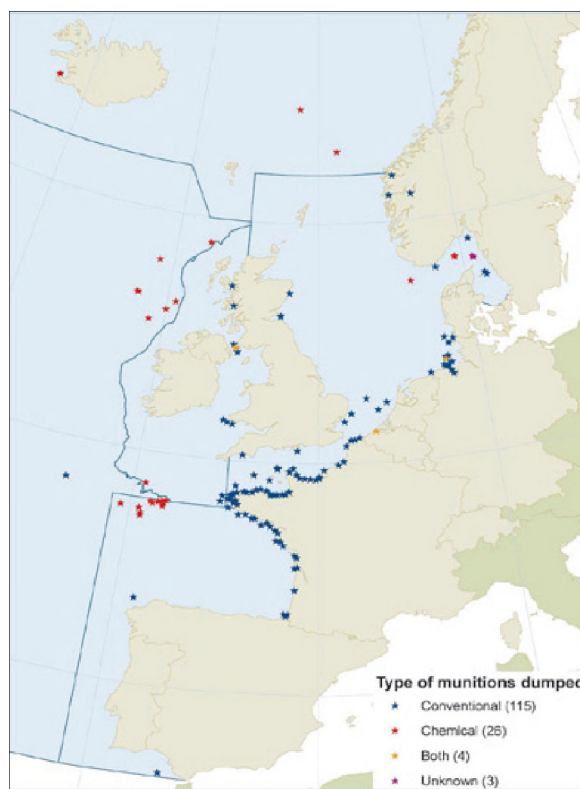


Figure 4.8. Location of known munitions dumping sites and type of munitions dumped (from OSPAR, 2009)

4. Emerging substances of concern

munitions dumpsites in the OSPAR region. However, in many cases the locations are inaccurate because the original records have been lost; dumping took place outside of designated areas and/or the movement of munitions through natural processes (Beddington and Kinloch, 2005).

Since the fall of the Berlin Wall in 1989, more information has become available on the vast quantities of chemical weapons present in Europe at the end of World War II. Estimates suggest that in excess of one million tonnes of munitions were dumped in the northern Irish Sea, 168,000 tonnes in the Skagerrak, and 300,000 tonnes in the North Sea (OSPAR, 2009). Large quantities of chemical warfare agents were dumped in the Baltic Sea after 1945. For example, 32,000 tonnes of munitions, including 11,000 tonnes of chemical warfare agents, were dumped into the Bornholm Basin and 2000 tonnes of munitions, including 1,000 tonnes of chemical warfare agents, in the Gotland Basin (Glasby, 1997a). Russian scientists predict leakage of chemical agents from their corroding canisters, with a peak release in the middle of the 21st Century (Glasby, 1997b). Post-Soviet models for the White Sea predict that mustard gas from dumped chemical weapons could reach concentrations of 10 mg L⁻¹ in the overlying seawater if the canisters were physically disturbed (e.g. by anchors, drilling rigs or strong storms). In 1990, up to 20 million starfish were washed ashore along the White Sea coast over a one month period of strong storms. It has been suggested that this mortality even may have been due to the release of chemical warfare agents (Glasby, 1997b).

The Paardenmarkt, a shallow sand flat with water depth of 1.5 – 5.5 m, off the coast of Belgium, is estimated to harbour about 10,000 tonnes of toxic ammunition dumped after the First World War. Missiaen (2002) stated that, despite past research, very little is known about the migration and impact of toxic agents in the marine environment. A subsequent Belgian study at the Paardenmarkt site showed that dispersion of Yperite and the arsenic-containing irritants CLARK I and II is restricted to the immediate vicinity of the shells and that these materials do not form a serious threat to their wider surroundings (Francken *et al.*, 2009).

Large quantities of chemical warfare agents were also dumped in the Mediterranean Sea after 1945, leading to rusting munitions and bomb fragments being subsequently caught in fishing nets. As a direct result, over 200 Italian fishermen were hospitalized between 1946 and 1996 (Amato *et al.*, 2006). In fact, chemical weapons disposal at sea occurred from 1946 until the signing of the London Convention in 1972 (Bearden 2007; Brewer and Nakayama 2008). Although the convention, which was established through the UN International Maritime

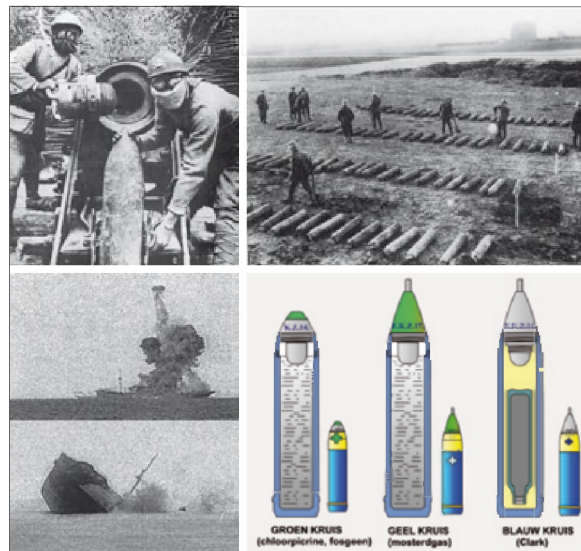


Figure 4.9. After World War I and II, large quantities of ammunition were dumped in European waters, often close to densely populated coastal areas (courtesy Renard Centre of Marine Geology of the Ghent University)

Organization (IMO), forbade further dumping, it did not establish criteria for site identification, monitoring, or reporting. Brewer and Nakayama (2008) noted that despite considerable and ongoing debate within IMO and efforts to create databases, very little of this information has been made available to marine scientists and policy makers.

Of the spectrum of chemical warfare agents produced during World War II, bis-(2-chloroethyl) sulphide (mustard gas) and dichloro-(2-chlorovinyl)arsine (lewisite) are thought to be the main threats to the marine environment (Amato *et al.*, 2006; Chauhan *et al.*, 2008). Amato *et al.* (2006) noted that mustard gas and lewisite (log K_{ow} of 1.37 – 2.41 and 2-3, respectively) are regarded as persistent in water and produce toxic metabolites via hydrolysis (e.g. arsenic compounds) which could affect benthic ecosystems. Given the limited data available (Nipper *et al.*, 2002), a UK study also recommended assessment of the persistence, bioaccumulation and toxicity properties of these chemicals in order to establish the risks that they pose (Beddington and Kinloch, 2005; Amato *et al.* 2006).

From the above and given the predicted near-term leakage of World War II weapons dumped at sea, an integrated survey approach for the analysis of biota, sediment and water should be considered for priority areas of the European marine environment.

4.3 Marine hazard and risk assessment

As discussed previously in this report, chemicals are included in some monitoring and assessment lists but not in others for a range of scientific and other reasons (see Chapters 2 and 3). The approach common to most programmes prioritizing chemicals is the evaluation of their POP or PBT properties and/or evidence of their long-range transport (UNEP, 2001; Muir and Howard, 2006; Brown and Wania, 2008). Appendix IV summarizes the criteria used by various organisations or countries for identifying chemicals which have intrinsic properties that give cause for concern about their potential to damage the environment or human health based on persistence, bioaccumulation and toxicity.

Although this approach is useful for the prioritisation and selection of substances to be monitored, it cannot be considered as a risk assessment of these compounds. Indeed, as indicated above, these approaches are mainly based on the intrinsic properties of the substance and, as such, do not consider all processes involved in the exposure and effects assessment, i.e. the two main pillars of an environmental risk assessment.

The procedures for conducting a marine risk assessment are described in the Technical Guidance Document (TGD), published by the EU (Anonymous, 2003). However, a risk assessment for the marine environment has only been performed for a limited number of substances regulated under the Existing Substances Regulation and, more recently, the REACH regulation. It should be recognized that the procedures recommended in the TGD for a marine risk assessment do contain a number of assumptions which, through the absence of specific knowledge on marine environments, have a limited scientific bases. One example is the proposed extrapolation (assessment) factors used to extrapolate laboratory-derived ecotoxicity data to a predicted no effect concentration for the environment (PNEC). For the marine environment these factors are 10 times higher (more stringent) than those used for the freshwater environment. This difference is based on the unproven assumption that marine systems are more sensitive than their freshwater counterparts.

In general, it can be concluded that considerable research effort is needed to refine existing procedures and methods used in marine risk assessments.

4.4 Conclusions and recommendations

The pragmatic definition of an emerging substance of concern used in this report, i.e. a chemical or anthropogenic material which is of growing scientific concern but where the substance is currently not extensively monitored in international programmes, results in a list of substances that can hardly be considered “emerging” in a strict sense. PBDEs, SCCPs and TBT are good examples. Concerns about their presence in the marine environment date from the 1980s and early 1990s. However, they have only recently been taken up in some – and not all – routine monitoring programmes. Still other substances have yet to even attain this status, although they have been identified as “priority” pollutants through the various selection procedures.

Identification and selection does not automatically result in monitoring. The reasons for this vary. Quite often, additional monitoring obligations will be met with great reluctance by the parties involved, primarily because of the associated costs. At the same time, there is a similar reluctance to give up monitoring of well-established contaminants for which there may be very good reasons for postponing monitoring.

The advent of the WFD has dramatically changed the situation for monitoring in European coastal waters. As the directive obliges member states to assess the chemical status in territorial waters (up to 12 miles offshore), the presence or absence of a significantly larger number of substances in the marine environment will need to be investigated.

In addition to the substances discussed in this chapter, all of which have been discussed in the peer reviewed literature, there is a growing list of substances that can truly be considered to be “emerging” in the sense that there is little or no previous evidence of their occurrence. These include, for example, substances that are used in place of those for which use has been banned or seriously restricted, e.g. anti-fouling substances and flame retardants. As they will retain most of the properties of the substances they replace, the question of the environmental risk associated with these new substances should immediately be addressed. On the other hand, the appearance of novel substances in the peer-reviewed literature is almost entirely the result of the diligence of environmental chemists. As analytical methods become ever more powerful, the scope of substances for which our environment can be screened becomes larger.

This may lead to the question of why these substances are not picked up by the selection/prioritisation procedures described above. Short-chain chlorinated

4. Emerging substances of concern

paraffins (SCCPs) were picked up even though analysis was unfeasible. However, some of these are probably truly novel with production only starting up due to their necessity as replacement products. Others were simply not picked, owing to the limitations of the selection criteria. Until recently, few people have considered nanoparticles or personal care products to be a potential problem for the environment. Selection criteria are heavily relying on PBT properties and these compounds clearly are not identified using this procedure.

It is clear that other approaches are needed. Indeed, brominated flame retardants (BFRs) will not be the last group of chemicals to be found to occur in the environment and as a consequence in our food. The vast number of chemicals that we produce and need for modern living for all sorts of purposes from fire safety to pharmaceutical applications will continue to contribute to the spectrum of chemical residues present in the marine environment and ultimately in our food. Knowledge on existing classes of chemicals and modern analytical and toxicological techniques should help us make an inventory of the associated risks in an early stage, long before those residues reach levels of concern. (de Boer, 2009).

The EU defines “pollution” as “the direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly dependant on aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment”. More or less the same definition has been used by GESAMP. Bearing this definition in mind, the present approaches for identifying and selecting (e.g. PBT) “pollutants” is clearly inadequate. As indicated earlier, a more comprehensive, science-based risk assessment procedure is needed to identify and manage chemicals of concern in the marine environment. Indeed, the establishment of the presence of a chemical compound in the marine environment means little if the level of risk cannot be properly established. Analytically, low levels of many of the compounds considered in this paper, can be determined even on a routine basis. Yet, what do these levels mean? What is the risk for the marine environment? What is the effect of exposure to the complex mixtures the chemists have been able to demonstrate? These are questions that deserve at least as much attention as the search for still more substances.

Summary Box 4.1 – Recommendations regarding monitoring of emerging substances of concern

1. There is a clear need for a more rapid identification of ‘new’ substances in the marine environment, followed by more extensive surveys and eventually, if needed, comprehensive monitoring.
2. Improved procedures are required to allow a more rapid inclusion of ‘new’ substances into existing monitoring frameworks programmes.
3. Urgent research is needed on:
 - a. Biological effects of ‘new’ substances and the development of validated biological effects assessment methods;
 - b. Sensitive analytical procedures, which can be applied routinely for ‘new’ substances.
4. Direct research into well-chosen, specific aspects of fundamental marine ecology and impact of substances on marine systems is needed to reduce major uncertainties associated with marine risk assessments.
5. There is a need for the development of approaches (and subsequent policy) to assess the risks of environmentally relevant mixtures of (new and existing) contaminants. This approach should, in the long-term, replace single substance assessment and regulation.

5. Case study: Environmental impact of hydrophobic chemicals with low water solubility released from merchant shipping

5.1 Introduction

Aside from the chemicals released from land-based facilities entering the marine environment through atmospheric or freshwater input, there are also direct releases from maritime activities such as shipping. Mineral oil spills²¹ for example, including accidental spills and chronic oil pollution (illegal discharges and unreported small spills), can cause considerable damage in the marine environment and usually involve wildlife casualties. Within Europe there is a long history of marine mineral oil pollution (Clark, 2001).

While wildlife hazards due to mineral oil incidents are widely recognised and frequently published, little factual information is available on the effects of noxious substances other than mineral oil, including hydrophobic chemicals with low water solubility, on the marine environment. A hazardous and noxious substance is any substance other than mineral oil which, if introduced into the marine environment, is likely to create hazards to human health, to harm living resources and marine life, to damage amenities, or to interfere with other legitimate uses of the sea.

Although the amount of mineral oil released into the marine environment has fallen substantially in recent decades, even today there are still at least thousands of illegal spills detected per year in European waters (Joint Research Centre, European Commission; Camphuysen 2007). Mineral oil-related mass mortality events affecting marine wildlife still occur on an annual basis (Camphuysen, 1995 and 1997; Schmitt, 2006; GESAMP, 2007; Camphuysen, 2008; Verstraete *et al.*, 2008; Heubeck and Mellor, 2009). However, in the past decades discharges and strandings of hydrophobic substances other than mineral oil or mineral oil products and their effects on marine wildlife have become more prominent than before (e.g. Timm and Dahlmann, 1991; Camphuysen *et al.*, 1999; Hak, 2003). This either indicates an increase in discharges of these substances, or that discharges and strandings of such substances have received more attention following a steady decline in chronic mineral oil pollution of our seas and oceans. Most important, however, is that our understanding of the source(s) of these pollutants and their environmental impacts is far from complete. The relative contributions of non-mineral oil substances affecting marine wildlife, their chemical composition, as well as their impacts on the marine environment and wildlife are not well understood and, as shown in this chapter, have rarely been studied.

The aim of this chapter is to provide an overview of observed and anticipated impacts of hydrophobic chemicals with low water solubility released by merchant shipping on European marine ecosystems and wildlife.

The regulatory framework for the release of hydrophobic chemicals with low water solubility in the marine environment from shipping has recently been refined within the International Convention for the Prevention of Pollution from Ships (MARPOL), more specifically under its Annex II (Noxious Liquid Substances in Bulk). The hydrophobic substances with low water solubility that are currently listed within MARPOL Annex II²² are selected by the Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (EHS) of the Group of Experts on Scientific Aspects of Marine Environmental Protection (GESAMP), an advisory body, established in 1969, that advises the United Nations (UN) on the scientific aspects of marine environmental protection. Many of the hydrophobic substances other than mineral oil or mineral oil products involved in observed discharges and strandings in the past decades are listed under MARPOL Annex II on Noxious Liquid Substances transported in bulk. In this chapter we provide examples on the effects of substances in each of four categories of hazardousness on marine biota (MARPOL Annex II categories of hazardousness are explained below). Apparent trends in the frequency and/or scale of releases of hydrophobic chemicals with low water solubility in European seas and the possibilities for efficient spill responses are investigated.

5.2 Expected effects of noxious substances on the marine environment

Many kinds of potentially harmful chemicals are found in environments used by wildlife. There are numerous synthetic compounds that became environmental contaminants through human use and application. These chemicals may cause direct intoxication and death, but they may also cause adverse effects on wildlife through the impairment of their biological systems, such as the reproductive and immune systems. In general terms: dosage alone determines poisoning (see also Chapter 1). For some chemicals, their toxicity is such that the release from ships into the marine environment should be prevented at all cost.

For many substances, the anticipated adverse effects

21. Mineral oil: crude oil and all mineral oil products

22. International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk - IBC Code

5. Case study: Environmental impact of hydrophobic chemicals with low water solubility released from merchant shipping

on biota are not that clear. Apart from intoxication, substances may affect wildlife health in different ways, and the substances would need to be placed in subcategories to provide a more insightful overview of likely environmental effects. A better understanding of the kind of environmental impacts that result from different types of substances is crucial to facilitate a more effective spill response in case of accidents or illegal discharges of these substances.

Noxious substances can have a variety of direct and delayed effects on marine flora and fauna. With declining acuteness, these are:

- direct toxic effects after ingestion, inhalation, or skin contact;
- loss of waterproofing and insulation leading to hypothermia and exhaustion;
- mechanical defects (locomotion);
- weight loss, starvation (e.g. when the digestive system or foraging capabilities are affected);
- disease or impaired disease resistance (i.e. susceptibility to infectious disease);
- reduced immunologic function;
- pathological changes in tissue (e.g. inflammation of gastrointestinal lining, malformations, atrophy or accumulation of fluids);
- physiological disruptions (e.g. altered endocrine function, liver and kidney disorders, altered blood chemistry, blood disorders, impaired salt gland function, etc);
- reduced growth and development;
- food chain effects (through bioaccumulation); and
- impaired reproduction.

Amongst others, non-anticipated effects may occur with substances that readily float, that tend to form a mousse (mixed with seawater) and are slow in solidification after discharge, somewhat similar to mineral oil and mineral oil products. The loss of waterproofing and insulation (hypothermia, exhaustion), mechanical defects (locomotion), weight loss, and starvation are symptoms to be expected in marine megafauna such as seabirds and marine mammals. These are by no means the only effects of noxious liquids on marine biota, but certainly the most visible and most easily detectable. Other anticipated effects may resemble those effects of other forms of chemical pollution such as the effects of polychlorinated biphenyls (PCBs) or organochlorines (OCs) in the marine environment. In these cases, it is much harder to observe an impact. Necropsies of casualties and the chemical analysis of samples are required to find and study any effects (e.g. disease and toxic effects, pathological changes), whereas delayed impacts on the environment and marine flora and fauna (reduced growth and development, impaired reproduction, food chain effects) are most likely to either go completely

undetected, or are unlikely to be linked with certainty to a specific discharge. At least some of these chemicals are likely to also significantly affect microbes, such as algae, bacteria, archaea and viruses and therefore the so-called microbial foodweb because very specific micro-environmental conditions surrounding their cells are required for their proper functioning.

In conclusion, many *in situ* effects are very difficult to detect, leading to biased results following differences in the “visibility” (or likelihood of detection) of environmental effects. For example, frequent reports of immobilized and dead or dying charismatic megafauna following a spill may receive disproportional attention, whereas more obscure or subtle effects of ingestion and intoxication will go unnoticed, most certainly so when such effects are not actively investigated. Potential hazards to human health are not further considered in this chapter, but several of the examples of environmental effects of hydrophobic chemicals with low water solubility presented in this chapter do include reported cases of short- and long-term effects on humans.

5.3 MARPOL Annex II

In 1973, the International Convention for the Prevention of Pollution from Ships (MARPOL) was formulated by the International Maritime Organisation (IMO) as result of the growing concerns regarding the threats of transported mineral oil and non-oil products to the marine environment (see also Section 2.2.1.2). The convention was modified by the Protocol of 1978 (MARPOL 73/78) and amended from time to time. MARPOL 73/78/97 consists of a Convention text, two Protocols and six Technical Annexes that regulate preventive measures regarding the following main categories of substances:

- Oil (Annex I);
- **Noxious Liquid Substances in Bulk (Annex II);**
- Harmful Substances Carried by Sea in Packaged Forms (Annex III);
- Sewage (Annex IV);
- Garbage (Annex V); and
- Air Pollution (Annex VI).

The implementation of Annex II of the MARPOL 73/78 Convention aims to control pollution by Noxious Liquid Substances (NLS) by ships from operational or accidental causes (www.imo.org/conventions). Annex II entered into force on 6 April 1987 and details the discharge criteria and measures for the control of pollution by noxious liquid substances carried in bulk (IMO, 2009).

The work on the revision of MARPOL Annex II and the IBC Code commenced almost 15 years ago in an attempt to reassess the risks and hazardousness of released

substances in the marine environment. Subsequently some >800 substances were evaluated and included in a revised list appended to the Convention. It concluded with the adoption of a revised MARPOL Annex II by the Marine Environmental Protection Committee (MEPC 52) in October 2004 and the adoption of the revised IBC Code by both MEPC and the Maritime Safety Committee (MSC 79) in December 2004²³. The revised requirements have entered into force and took effect from 1 January 2007.

In general, the discharge of residues of noxious liquid substances carried in bulk is allowed only to reception facilities unless certain concentrations and conditions (which vary with the category of substances) are complied with. The residues of moderately hazardous substances are permitted to be discharged into the sea but only (i) in limited quantities; (ii) under the waterline; (iii) at least 12 miles offshore; (iv) with 25 meters or more of water under the keel; and (v) at a speed of not less than 7 knots. So-called “non-hazardous” substances are unregulated and have no discharge criteria at present (GESAMP, 2002; IMO, 2006). No discharge is allowed, of any sort, within the Antarctic.

5.3.1 Pollution categories under the revised MARPOL Annex II list of substances

Substances were originally evaluated following a five-category system under MARPOL Annex II of pollution/safety hazards (A, B, C, D and an Appendix III which lists products to which the IBC Code does not apply). IMO re-categorized substances, for which they received the necessary information for evaluation under the mandatory GESAMP/EHS procedures utilising Global Harmonized System (GHS) principles²⁴. During the GESAMP EHS review process, mostly with a numerical rating (0 to 6 or 0 to 3), 13 different aspects of potential hazard to the environment were evaluated for all substances. These aspects can be grouped as issues regarding:

- the aquatic environment (Columns A and B);
- human health (Columns C and D); and
- interference with other uses of the sea (Column E).

These aspects comprise:

- bioaccumulation (A1) and biodegradation (A2) properties;
- acute (B1) or chronic (B2) aquatic toxicity;
- acute mammalian toxicity from oral (C1), dermal (C2) or inhalation (C3) contact;
- skin (D1) and eye irritation (D2);
- long-term health effects (D3);

- tainting (E1);
- physical effects on wildlife and benthic habitats (E2); and
- interference with Coastal Amenities (E3).

The rating scales begin at 0 (“practically non-hazardous” or “negligible hazard”) and run to a maximum of 3 to 6, indicating more severe hazards. Non-numerical ratings apply for A2, D3, E1 and E2. Under MARPOL Annex II of pollution and/or safety hazards has been revised to essentially four categories: X, Y, Z, and OS (Table 5.1).

The GESAMP hazard profile forms the basis for the evaluation of carriage requirements for all bulk noxious liquid substances (NLS) cargoes (see Figure 5.1). Substances which have not been re-evaluated by IMO are not permitted to be carried by ships.

The noxious liquid substances transported in bulk listed under MARPOL Annex II (revised list; IMO/MEPC, 2007) are very diverse and have highly different properties and characteristics. MARPOL Annex II substances do not always enter into the marine environment on their own, but are often released mixed with cleaning agents or other solutions when cleaning a vessel’s hold. The use of cleaning additives, however, should also be recorded on board (Appendix 2 to MARPOL Annex II, List of items to be recorded). Tank cleaning additives are evaluated by the Sub-Committee on Bulk Liquids and Gases (BLG) in order to protect the marine environment from adverse effects related to their use.

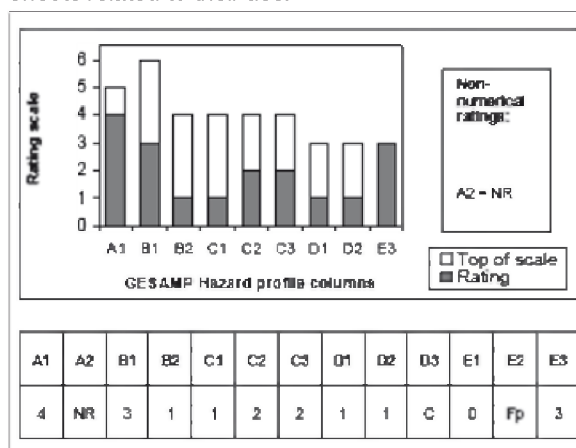


Figure 5.1. Graphical (top) and tabular (bottom) illustration of revised GESAMP hazard profile for a given substance X, with a high potential to bioaccumulate (A1), is not readily biodegradable (A2), has a moderate acute (B1) and low chronic (B2) aquatic toxicity, has a low oral (C1) and moderate dermal (C2) and inhalation (C3) toxicity to mammals, is mildly irritating to the skin (D1) and eyes (D2), is potentially carcinogenic (D3), is not liable to taint seafood (E1), is a floating substance liable to form persistent slicks on the sea surface (E2), and forms a significant physical hazard to onshore and offshore amenities (E3). (From GESAMP 2002; reproduced with permission)

23. www.imo.org;

www.imo.org/About/mainframe.asp?topic_id=848&doc_id=4405

24. www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html

5. Case study: Environmental impact of hydrophobic chemicals with low water solubility released from merchant shipping

Table 5.1. MARPOL Annex II categories of noxious liquid substances in bulk, evaluated under GESAMP/EHS procedures utilising GHS principles. Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (EHS) of the Group of Experts on Scientific Aspects of Marine Environmental Protection (GESAMP), is an advisory body, established in 1969, that advises the United Nations (UN) system on the scientific aspects of marine environmental protection

Category	Substances	Examples
X	substances presenting a major hazard , to either marine resources or human health and, therefore, justify the prohibition of the discharge into the marine environment	mostly low molecular weight hydrocarbons, chlorinated compounds, aromatic compounds including phenols, phthalates, fatty acids and esters, amines, amides, ethers, phosphates and metal-contaminated compounds.
Y	substances presenting a hazard , to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment,	products defined as “floaters” and “persistent floaters”. Vegetable oils (including acid oil distillates and other products derived from these oils) are specified and have been upgraded from the old Appendix III of the IBC Code (i.e. not particularly hazardous to the marine environment) to this category Y.
Z	substances presenting a minor hazard to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment,	mostly relatively highly volatile and/or water soluble substances
OS	other substances (OS) presenting no harm to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment	include slurries of clays, coal, glucose solution, hydrogenated starch hydrolysate, lecithin, molasses, non-noxious liquids, sorbitol solution, hydrolysed vegetable protein solution, and water

The chemical nomenclature of substances listed in the various documents used by industry, based on the revisions of MARPOL Annex II, are often highly confusing from a chemical point of view (see for example Intertanko, 2006). This is a consequence of the procedures regarding the transport of commercial chemicals. The procedure starts with the request of a shipping company to transport a certain substance or mixture of substances indicated by their product or trade name. Such a product or trade name is straightforward and prevents misunderstandings in the commercial shipping branch, but can be confusing if the MARPOL Annex II list of substances is compared with inventories of polluting and hazardous chemicals used by other organisations. IUPAC names, traditional names, incomplete names, product names, mixtures of chemicals, etc. are being used in an inconsistent manner in the MARPOL Annex II list. Because of this, the same chemical or suite of chemicals can be found listed more than once, even in different categories. It is therefore recommended to also indicate the IUPAC names of the individual substances as well as their corresponding CAS and ICSC numbers, as much as possible, to limit misinterpretations, or to use the formal lists (IMO/MEPC, 2007).

5.4 Examples of environmental effects of MARPOL Annex II substances

5.4.1 MARPOL Annex II Category X substances presenting a major hazard

Published examples of environmental effects of MARPOL Annex II category X substances include cases which strongly resemble mineral oil spills. Several of these cases involved spills of nonylphenol (Engelen 1987, Averbek 1990, Zoun 1991, Zoun *et al.* 1991a and 1991b). One example was a spill, or a series of spills, which took place between December 1988 and March 1989 resulting in several thousands of seabirds washing ashore in The Netherlands. The seabirds were contaminated with a sticky substance, subsequently identified as nonylphenol (Zoun, 1991). The mortality was caused by a combination of toxicity and immobilising effects on the affected seabirds. As with (mineral) oiled seabirds, their plumage had lost insulating properties and their livers were in many cases degenerated and necrotic. Several other substances were also found on

the affected birds, including vegetable oils, ethylester and 2-hydroxy-1-(hydroxymethylethyl)hexadecanoic acid. Concurrently, similar spills were witnessed in the German Bight with “nonylphenol” identified as an important aspect of the external contamination (Averbeck, 1990; Timm and Dahlmann, 1991).

A similar event occurred in December 1990 north of the Frisian islands in the North Sea. This event was only noticed because Northern Gannets (*Morus bassanus*) started washing ashore, covered in a sticky substance (Zoun and Boshuizen, 1992). While cleaning the gannets, personnel from rehabilitation centres along the coast suffered from serious irritation of the mucousal membranes of the eyes and the upper respiratory tract. A chemical analysis of feather samples revealed the presence of lubricating oil, but additional investigations were done to explain the health problems reported. Gas liquid chromatography combined with mass spectrometry (GC/MS) was applied to demonstrate the presence of dodecylphenol, a toxic compound that – like other phenols – irritates the eyes, skin, respiratory tract and the alimentary tract. After resorption, it initially stimulates and later on depresses the central nervous system, leading to death from respiratory or heart failure. In the form of calciumdodecylphenolate (not specifically listed under Annex II), dodecylphenol is used as an additive in lubricating oil for ship engines. In the presence of moisture, it decomposes to dodecylphenol and calciumhydroxide (Timm and Dahlmann, 1991). Both dodecylphenol and lubricating oil are hydrophobic and therefore easily adhere to feathers, affecting heat insulation and water repellence of exposed seabirds. In severe cases these effects result in death from hypothermia or exhaustion, but in the described case, it was concluded that dodecylphenol had markedly contributed to the mortality among gannets as a result of intoxication. This example also indicates that chemical transformations of the substances discharged and exposed to the environmental conditions have to be taken into account when assessing the actual impact on the marine environment.

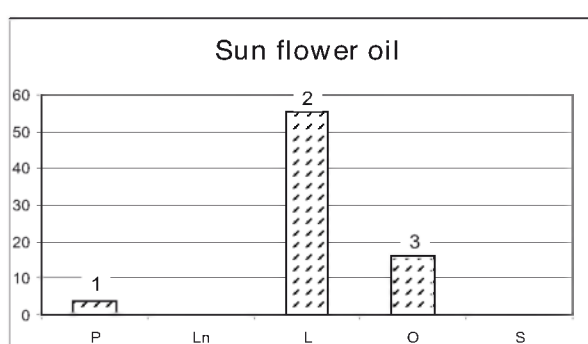
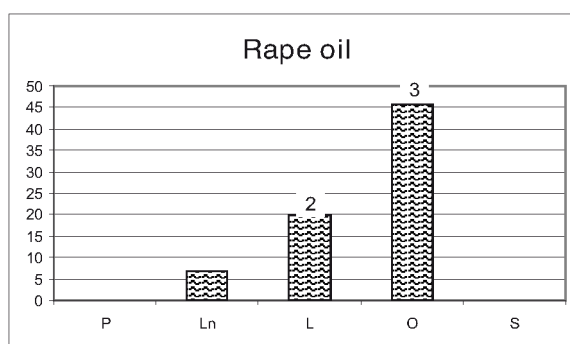
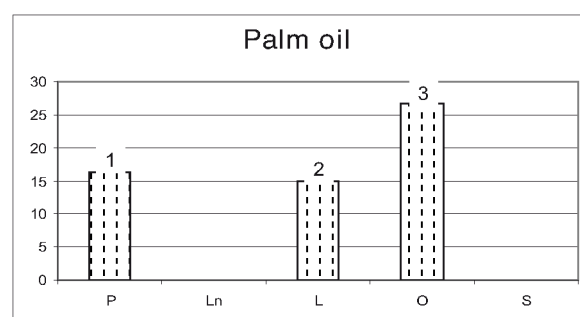
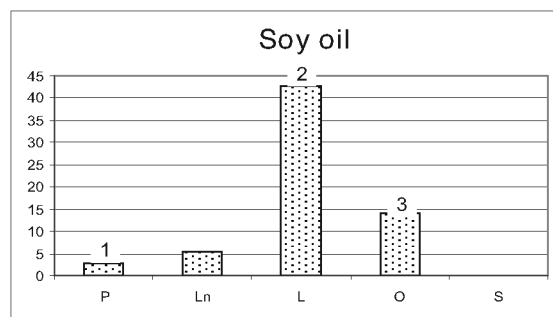
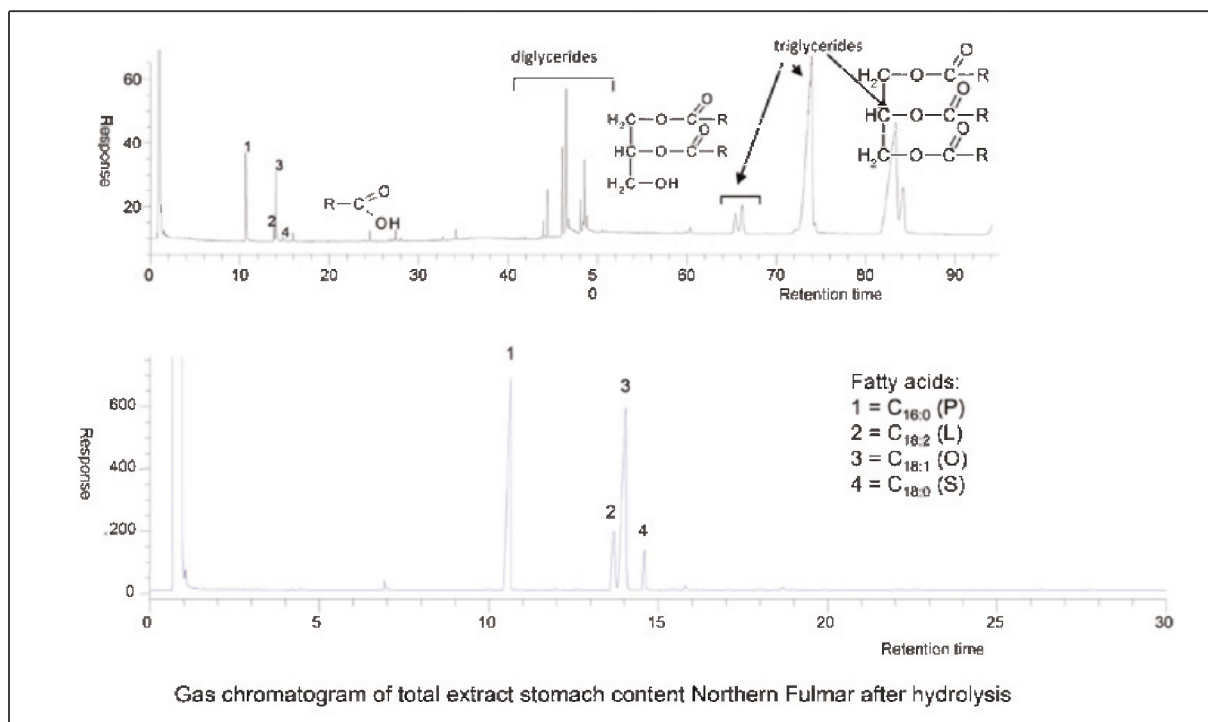
5.4.2 MARPOL Annex II Category Y substances presenting a hazard

Engelen (1987) reported an event affecting hundreds of seabirds in the Wadden Sea after a discharge of linseed oil. Given the species affected, Common Guillemots (*Uria aalge*), a marine species, and Common Eiders (*Somateria mollissima*), an inshore species, it was obvious that some slicks had entered the Wadden Sea from the North Sea, affecting different types of seabirds in the process. Hundreds of kilograms of the substance were found on beaches, more or less solidified, whereas the affected birds were covered in a highly sticky substance

that contained linseed oil (90%) and other unknown substances. The incident resembles, in many aspects, other reported incidents which involved toxic substances (or additives), except that irritation of the eyes or the upper respiratory tract in humans handling the casualties was not reported. The effect on birds was first and foremost immobilisation, followed by hypothermia, exhaustion and (certainly in the absence of human intervention) starvation. A very low proportion of the birds received in rehabilitation centres survived. Cleaning these birds required unusually aggressive cleaning agents which hampered a full recovery of the affected birds.

Another example represents a diet study of Northern Fulmars (*Fulmarus glacialis*), routinely performed to assess levels of plastic particle ingestion, as a monitoring project to evaluate spatial and temporal patterns on plastic pollution of seas and oceans (Ryan *et al.*, 2009). So called “unknown substances” are frequently encountered in the stomachs of these surface feeding seabirds. As with plastics, these substances are probably mistaken for suitable food by the birds and some of these hydrophobic substances (notably the vegetable oils and their products) are indeed edible, but not necessarily harmless. In this monitoring project, dead Northern Fulmars are collected during beached bird surveys and the stomach contents are examined during a necropsy. Unidentified fatty substances in the proventriculus are frequently found and routinely collected. In the illustrated example (Figure 5.2), a bright yellow substance was found to contain fatty acids (C_{16} , $C_{18:2}$, $C_{18:1}$ and $C_{18:0}$), traces of monoglycerids, C_{16} , $C_{18:1}$ and $C_{18:0}$ diglycerids and triglycerids (Baas *et al.* unpubl. data). The fatty acid composition of the di- and triglycerids as analysed after hydrolysis suggested that slightly decomposed palm oil had probably been consumed. The cause of death could not be identified, but the presence of this substance in the stomach of the bird suggests that it was either difficult to digest resulting in a mal-functioning stomach, or harmful for the animal by deregulation of the digestive tract. This example is also interesting, because the partial decomposition of a category Y-substance (palm oil) after exposure to the marine environment results in potentially hazardous diglycerids and triglycerids, which are not listed under Annex II.

5. Case study: Environmental impact of hydrophobic chemicals with low water solubility released from merchant shipping



Fatty acid compositions of triglycerides of vegetable oils 1 = C_{16:0} (P) 2 = C_{18:2} (L) 3 = C_{18:1} (O) 4 = C_{18:0} (S)

Figure 5.2. Gas chromatogram of a total extract of the stomach content of Northern Fulmar before and after hydrolysis (top 2 panels) and fatty acid composition of triglycerides of vegetable oils (bottom panels)

5.4.3 MARPOL Annex II Category Z substances presenting a minor hazard

Camphuysen *et al.* (1999) reported on a mass stranding of seabirds in the North Sea in December 1998. Hundreds of birds washed ashore alive in Zeeland (SW Netherlands), covered in a whitish, sticky substance, and were transported to a rehabilitation centre. About 10 days later, more (dead) casualties washed ashore further to the north on Texel and along the mainland coast, again covered in a glue-like substance (Figure 5.3). Common Guillemots, Northern Fulmars and Common Scoters (*Melanitta nigra*) were the most numerous birds affected in this incident. Both strandings were temporarily (10 days) and geographically separated (ca. 120 km apart), but were apparently caused by a single source of pollution. At least 1,100 seabirds were affected by this substance, soon identified as polyisobutylene (PIB; $C_4H_8)_n$. PIB is known as a non-toxic, non-aggressive substance, used for example to manufacture chewing gum and cello tape. However, volunteers cleaning the birds reported serious discomfort and dizziness. Moreover, the soft parts of the birds found dead (bill, eye, throat, feet, webs) appeared to dissolve in the substance within a few days time. Apart from these aspects, possibly resulting from the effects of an unidentified cleaning agent associated with this discharge, the birds were completely immobilised after contacting the substance at sea and died either instantly, or with some delay after having lost the insulating properties of their plumage.

5.4.4 MARPOL Annex II Other Substances (OS) presenting no harm to marine resources

There are no studies reporting effects on marine biota of any of the substances listed in this category. However, it should be noted that a discharge of for example lecithin, one of the substances listed, followed by decomposition as described above, would result in potentially harmful compounds (diglycerides and triglycerides) after environmental exposure (Figure 5.4). Furthermore, the physical state of harmful substances is another factor to consider. Upon discharge many liquid or semi-liquid hydrophobic substances such as vegetable oils and their products can become solid under the environmental conditions (e.g. lower temperature, evaporating of cleaning agents). Once solid they are not further diluted and can serve as food for birds (as described) or even fish and other megafauna.



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Figure 5.3. Razorbill *Alca torda*, fresh but with soft parts dissolved, totally covered in polyisobutylene (PIB; $C_4H_8)_n$, Texel, December 1998

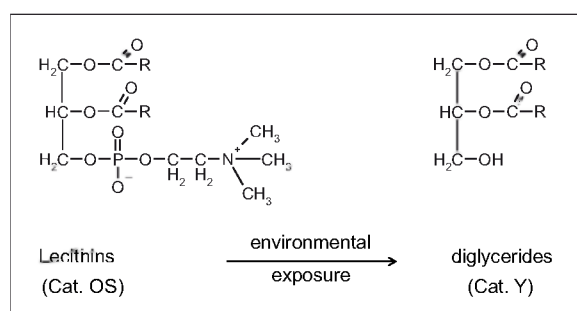


Figure 5.4. Decomposition of lecithin following environmental exposure

5.4.5 Unknown substances

A final example represents a discharge into the marine environment of a substance which was never adequately characterised. In January 2007, seabirds washed ashore that were completely smothered into a green, sticky mass. An estimated 20-28 tonnes of the substance were observed on beaches of Noord-Holland, Texel and Vlieland, until a violent storm washed the coast clean of (visible) pollutants. Samples of affected birds taken included Common Guillemots, Razorbills, *Alca torda*, and Northern Fulmars, indicating an offshore rather than a nearshore spill. During necropsies, conducted at the Royal Netherlands Institute for Sea Research, it appeared that the birds had died at least some days earlier (confirming the offshore nature of the spill), but were still fairly fresh and must have died instantly as a result of smothering effects (Figure 5.5) and inhalation of the substance (respiratory tract filled with green substance).

A sinister aspect of the spill was that the rather fresh carcasses of the birds, covered in this substance, dissolved at a high rate, except where dense layers of feathers covered the body (Figure 5.6). The source of the spill was never traced. The substance turned out to be a chemical mix, but with high concentrations of sulphur, strontium, arsenic, and copper, and traces of

5. Case study: Environmental impact of hydrophobic chemicals with low water solubility released from merchant shipping



Figure 5.5. Common Guillemot *Uria aalge*, fresh but smothered in an unidentified green substance, Texel, January 2007



Figure 5.6. Common Guillemot *Uria aalge*, fresh but smothered in an unidentified green substance and with loosening skin and dissolving soft parts, Texel, January 2007

4-tert-butylphenol (CAS 98-54-4) and 4-(1,1-dimethylpropyl)phenol (CAS 80-46-6). People working with the casualties suffered from serious irritation of the upper respiratory tract. A final conclusion of the chemical analysis of the substance(s) involved regarding the origin and effect of this event has never been published.

5.4.6 Conclusions from the presented examples

The regulations under MARPOL 73/78 Annex II are such that spills of “unwanted” noxious substances into the marine environment (X, Y, Z) are either strictly prohibited or essentially very small, distant from the nearest coast and in very low concentrations (IMO 2006; see also below). Discharges at low concentrations cannot be fully prevented, and some permitted discharges can still have some impact on the marine environment. However, the quantities reported in each of the above case studies suggest that discharges took place well above permitted levels, and in the absence of any masters of vessels reporting an accident at sea, they have to be regarded as illegal spills. The presented cases are nevertheless interesting, because they show that the effect of discharges of noxious liquid substances on the marine environment *can* be substantial, no matter the categorisation of the substance released (X, Y, Z, or even OS). The case studies also clearly highlight the fact that substantial discharges do occur frequently, despite international regulations and conventions.

Most studies reported effects of noxious substances on marine wildlife that are superficially similar to the effects of mineral oil spills on marine biota. Sometimes the effects were aggravated due to immediate toxic effects, or due to the aggressive nature of components of the substances released (some were additives to a substance of

lesser concern). In essence the effects were smothering and immobilisation leading to immediate death or starvation and death (generally highly visible effects). These effects were found *only* because the casualties washed ashore. Any spill with casualties further offshore or under conditions that would not favour a (mass-) stranding would have gone unnoticed. The frequency of ingestion of hydrophobic substances by marine wildlife is not well known and investigated only in a few taxa (e.g. Ryan *et al.*, 2009). The effects of ingestion are completely unknown. The last case study highlights some of the main problems of these and similar spills:

- uncertainties about the origin, nature and chemical composition of the substances spilled or their environmentally transformed products (at least for those involved in clean-up and response; including scientific investigations of the casualties);
- the absence of a monitoring protocol in which all details about cause and effects are logged; and
- the absence of a final publication reviewing all details and accumulated information.

5.5 Impact assessments

Categorizations ranging from “hazardous” to probably “not-hazardous” (X, Y, Z and OS) were based on a variety of properties, including biodegradability, toxicity, effects on human (and mammalian) health, and the tendency to float or sink. Effects on marine wildlife such as captured in the presented studies (Section 5.4) are not particularly well covered in this procedure, illustrating the unexpected effects of substances that are regarded as relatively harmless according to the IMO/GESAMP evaluation criteria. One reason for the unexpected side-effects may be the introduction of cleaning agents leading to mixtures that are lethal to marine biota, or that the intro-

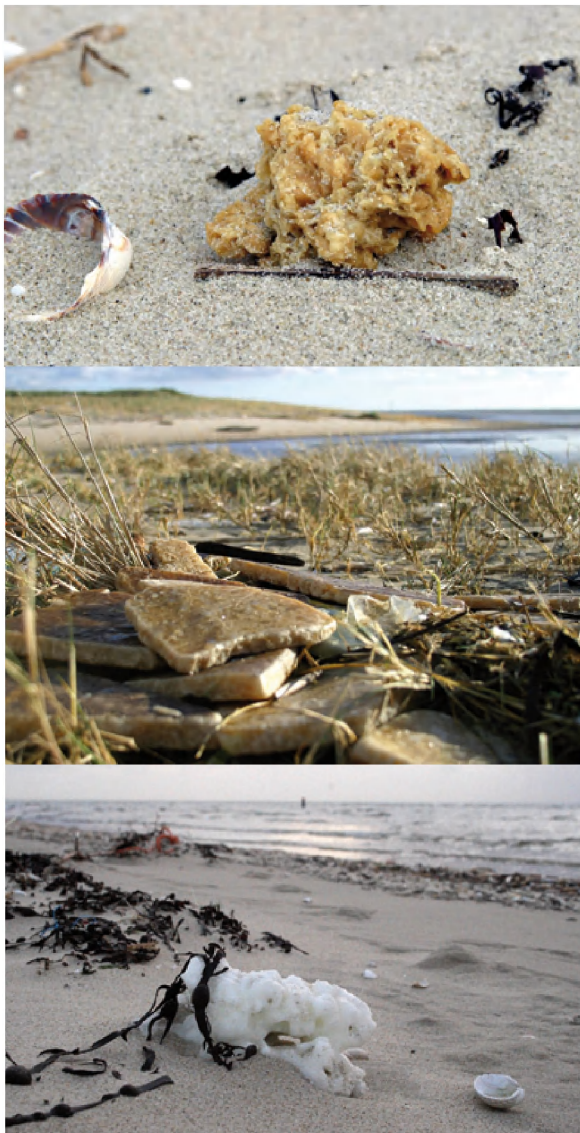


Figure 5.7. Solidified fatty substances on beaches

duction into seawater triggers a chemical process which changes the properties of the substance (Section 5.4.4). There is clearly a need for more thorough knowledge on the effects of noxious substances of all categories on the marine environment. This highlights the need to perform impact assessments in case of spills.

In the GESAMP hazard evaluation procedure, the likelihood for immediate physical effects on wildlife and benthic habitats (other than intoxication) are tested under artificial conditions during a limited period and listed under just one column (E2, properties as persistent floater, floater or sinking substances). The environmental

effects of many of these floating hydrophobic chemicals with low water solubility in the actual marine environment are therefore not always predictable. We therefore recommend to perform tests in more realistic conditions (e.g. in marine mesocosms).

Mineral oil impact assessments have been conducted on a regular basis in only relatively few countries and sea areas, producing highly biased information regarding the scale and possible impact of spills within Europe (Camphuysen, 2007). It is wrong to assume that mineral oil spills have not affected the marine environment in the absence of study reports following an event. However, even in some areas known to hold highly sensitive wildlife populations and experiencing both chronic mineral oil pollution and accidental spills, baseline data needed to perform an impact assessment have never been collected. Most published studies report only the immediate impact of these spills, not the longer lasting or delayed effects at the population-level. A serious complication is that many offshore spills affect wintering wildlife, migrating animals or immatures. Population-level effects are often found (and are thus searched for) in rather distant or even unidentified breeding grounds (migrants), or with considerable delay (when mostly immatures are affected, effects will be diluted and not visible before normal recruitment into the breeding stock).

With regard to the impact assessment of other hydrophobic chemicals with low water solubility, the situation within Europe is even worse. The examples given earlier in this chapter mostly originate from reports produced in countries bordering the southern North Sea. While this area is widely known as a relatively polluted area (chronic pollution from shipping, as a result of a network high density traffic lanes), there is no reason to believe that other, similar sea areas are better off. McKelvey *et al.* (1980) reported for example that “Within the period of our records, spills of vegetable oils at Vancouver harbour have caused greater losses of birds than spills of petroleum oils. Because most vegetable oils are edible their potential danger to aquatic birds, fish, or marine mammals may go unnoticed and sites of storage and transshipment of vegetable oils may be overlooked in oil spill contingency planning”.

The above statement reflects the absence of systematic studies and monitoring programmes elsewhere in Europe, other than monitoring projects to study the effects of mineral oil pollution (e.g. Camphuysen, 1995 and 1997; Schmitt, 2006; GESAMP, 2007; Camphuysen, 2008; Verstraete *et al.*, 2008; Heubeck and Mellor, 2009) and projects to study the effects of litter (Ryan *et al.*, 2009). New initiatives to raise preparedness for mineral oil spills in Europe and to develop protocols on how to handle affected wildlife (dead or alive; including scientific

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impact assessments of spill), all refer to the effects of mineral oil and seldom, if at all, mention noxious liquids such as addressed under MARPOL Annex II (www.oiled-wildlife.eu, Camphuysen *et al.*, 2007). Given the nature of some of the noxious liquid substances and the potential effects on human health, guidelines for spill responses should be provided also outside the context of shipping and harbour authorities. While the general public was involved in all of the presented studies (see Section 5.4), clear-cut information on the nature of substances involved was either absent or available rather late.

5.6 Monitoring the adverse effects of noxious substances

It is clear that regulatory frameworks may not always incorporate the most recent scientific developments and/or relevant scale in their assessment schemes to allow a (recent) science-based evaluation of the risks posed by hydrophobic chemicals with low water solubility, to open marine and coastal ecosystems. The following main shortcomings can be identified:

- (i) Monitoring of substances is mostly limited to mineral oil products plus a list of “hazardous” chemicals measured by international organisations. However, both the effects of most hydrophobic chemicals with low water solubility on marine wildlife and their occurrence as pollutants are insufficiently known;
- (ii) Where the potential risks of these substances for marine wildlife and habitats are incompletely understood, the true impact on the marine environment cannot be evaluated.

To achieve significant steps forward in combating chronic pollution of the marine environment by noxious liquid substances (notably hydrophobic chemicals with low water solubility), research is needed (i) into the chemical composition and source of pollutants currently causing environmental damage; (ii) concrete descriptions of the types of damage (risk of external fouling, entanglements, ingestion and/or intoxication of marine biota); and (iii) whether legislative measures can be taken to improve the current situation. The coupling of such research with existing monitoring programmes sampling stranded seabirds (beached bird surveys) and marine mammals would provide further insight in the sources of pollution as well as their substance-specific effects on marine wildlife.

5.6.1 Beached bird surveys as indicators of chronic pollution

Beached bird surveys, conducted according to internationally agreed standard protocols (Camphuysen and Dahlmann 1995, Camphuysen and Heubeck 2001, www.oiledwildlife.eu), are widely used to monitor trends in chronic mineral oil pollution in the marine environment. Around the North Sea, beached bird surveys have demonstrated a steady decline in chronic mineral oil pollution, concurrent with other monitoring tools such as aerial surveys (Camphuysen, 1998; Anonymous, 1993; ITOFF, 2008), remote sensing techniques (satellite data; Joint Research Centre, European Commission), and logs of harbour reception facilities. From species-specific differences in mineral oil-rates measured during beached bird surveys, it is demonstrated that the situation in nearshore environments has improved more than in off-shore areas. This is in accordance with expectations set by distance-to-the coast-limits under MARPOL Annex I.

Unfortunately, beached bird surveys have never been structurally improved by coupling the censuses with a systematic sampling programme of contaminants found on and in seabirds or beaches, despite some promising results reported in pilot studies (Vauk *et al.*, 1987; Dahlmann *et al.*, 1994). “Unknown” substances were rarely analysed and identified in qualified laboratories. Unknown “fatty substances” were usually briefly described, but many substances affecting the plumage of seabirds were simply overlooked. In Dutch Beached Bird Surveys, one of the longest and most consistent running programmes in Europe, “unknown substances” have been logged as “non-mineral oils” since 1977 (see Figure 5.8). Reported cases represent a minimum, because many substances are hard to detect visually. Since 1977, however, up to 33 reports of contaminated seabirds were received per year, with a maximum of 411

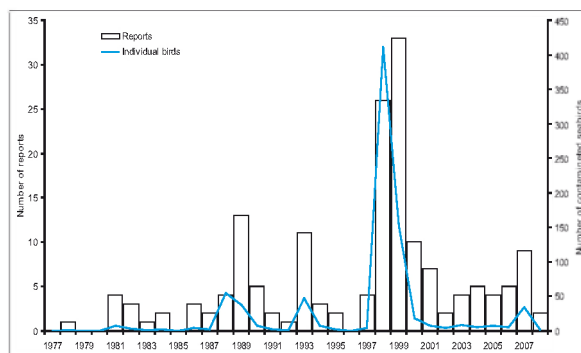


Figure 5.8. Number of reports and total number of contaminated seabirds found during routine beached bird surveys in The Netherlands, 1977-2008: all substances excluding (presumed) mineral oil (Dutch Seabird Group, National Beached Bird Surveys, unpubl. data)

Table 5.2. Beached bird surveys reporting the presence of birds contaminated with non-mineral oils including unknown substances (positive reports), the number of affected birds (n) and their relative abundance (n km⁻¹ surveyed), Dutch Beached Bird surveys, 1977-2009, Dutch Seabird Group (NZG/NSO), unpubl. data

Beached bird surveys, The Netherlands (NZG/NSO)			Positive reports		Affected birds	Relative abundance
	surveys (n)	km surveyed	n	%	n	n km ⁻¹
1977-1981	563	4,077	5	0.9%	8	0.002
1981-1986	1,596	11,245	7	0.4%	8	0.001
1986-1991	1,079	7,842	25	2.3%	104	0.013
1991-1996	746	5,396	16	2.1%	56	0.010
1996-2001	1,246	7,291	74	5.9%	587	0.081
2001-2006	1,569	7,897	20	1.3%	30	0.004
2007-2012	640	2,609	10	1.6%	35	0.013
	7,439	46,356	157	2.1%	828	0.018

contaminated seabirds in anyone year of survey. The frequency of beached birds contaminated with substances other than mineral oils is more or less stable, in contrast with the sharply declining levels of mineral oil pollution found on stranded seabirds (Camphuysen, 1998), with a non-significant trend of increase with time (Table 5.2). Identified substances include polyisobutylene, nonylphenol, dodecylphenol, palm oil, linseed oil, sunflower oil, various other vegetable oils, alcohols, green, blue, silvery, white, orange and red paint, paraffins, and some other substances listed in the case studies earlier in this chapter.

Based on samples taken during beached bird surveys in Germany, it was concluded in the early 1990s, that “other products than mineral oil are normally only a minor cause of death of seabirds... [but] there is a broad range from ‘harmless’ vegetable oils up to the very toxic nonylphenol and dodecylphenol, the mere presence of which as a form of marine pollution requires action.” (Timm and Dahlmann, 1991).

Following the revision of MARPOL Annex II, it is required to establish monitoring programmes to study the effects of more stringent legislation resulting from this international agreement. Monitoring programmes are required (i) during inspections of vessels in harbours; (ii) during visual or remote sensing surveys at sea; and (iii) to study the environmental impacts of noxious liquid substances legally or illegally discharged or accidentally spilled. It should be noted that beached bird surveys are potentially a highly cost-effective source of information regarding the occurrence and effect of hydrophobic chemicals with low water solubility (and some environmental effects) in the marine environment, but only when coupled to systematic sampling and chemical analysis of samples (feather mixtures, stomach contents and beach samples).

5.6.2 Diet studies as indicators of chronic pollution

Most case studies have dealt with external effects of noxious substances (notably hydrophobic insoluble chemicals). In most cases, the substances must have been at least near-fluid (liquids) to be able to adhere to the plumage of seabirds. Volatile fractions disappear usually within days after a discharge, often gradually reducing the toxicity of the dumped materials. Weathering, wear and biodegradation over time may result in the solidification of substances. Paraffin, stearin and palm oil are examples of substances that are frequently found as solid blocks littering shorelines (Figure 5.9). The often observed peck marks suggest that marine wildlife has been eating from these blocks. Diet studies of marine biota often result in lengthy lists of prey items, including clearly unwanted objects or substances (Auman 1998, Baird and Hooker 2000, Cooper *et al.*, 2004; Camphuysen *et al.*, 2008). There is extensive literature on many aspects of ingestion of marine litter in surface feeding seabirds, marine mammals and marine fish, suggesting that marine organisms frequently, and in some cases consistently, mistake plastics and other foreign objects for suitable prey (Day *et al.*, 1985; Moser and Lee, 1992). Solidified hydrophobic chemicals with low water solubility are among those items (paraffin, stearin, palm oil and other vegetable oils and their transformation products). Some marine species routinely regurgitate pellets to reject any slowly or indigestible prey items (Figure 5.9), others - try to- fully digest prey, including foreign objects and substances swallowed incidentally. There are multiple reports of gizzard contents comprising worn and weathered, half-digested plastic, wood, and other materials. Also, there are multiple reports of marine birds that produced boluses to feed their offspring containing all the accumulated plastics in their proventriculus. Hydrophobic substances and plastics

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Figure 5.9. Lump of paraffin mixed with bones of the marine fish whiting (*Merlangius merlangus*), suggesting a marine origin, regurgitated by Herring Gull (*Larus argentatus*)

may adsorb other highly toxic hydrophobic micropollutants such as PCB's, alkylphenols thereby considerably enhancing potential harmful effects. We can only guess about the physiological consequences of such digestive processes, but it is likely that these components are absorbed by organism, leading to physiological disruptions and possible delayed effects such as growth and development reductions, impaired reproduction and food chain effects.

Solidification is not a prerequisite for ingestion. Some surface feeding seabirds, such as Storm-Petrels “drink” oily substances from the sea surface (BWPi, 2006), and these substances could include hydrophobic and insoluble chemical liquids listed under Annex II.

Van Franeker and Meijboom (2002) studied marine litter from ingested foreign objects in Northern Fulmars (*Fulmarus glacialis*) as part of diet studies of Fulmarine seabirds (tube-noses, Procellariiforms taxonomically related to Northern Fulmars) in the North Sea, the Arctic and the Antarctic, and recorded pollutants (industrial or chemical waste remains) in considerable detail. Substances ranked under pollutants included slags (re-

mains of incineration ovens, often pumice like material), tar (solidified hydrocarbons), chemicals (paraffin-like materials or sticky substances arbitrarily judged to be of chemical origin), condoms, plastics, and feather-lumps (excessive amounts of ingested feathers indicating excessive preening of feathers sticky with oil or chemical pollutants). Some of these substances are relevant for the topics addressed in this chapter, others are not or not directly, but in the absence of a chemical analysis of substances encountered, a clear distinction cannot be made. The chemical composition of substances should never be judged by eye only. Recent studies on Laysan albatrosses (*Phoebastria immutabilis*) have further highlighted the immense scale of the issue of plastic ingestion by marine birds (Jordan, 2009). These studies, however, highlight the frequency of ingestion of foreign objects and substances by marine wildlife that seemingly mistake them for suitable prey. In the same way, discharges and accidental spills of hydrophobic chemicals with low water solubility may pose a similar potential hazard for marine biota. The accumulation of substances and foreign materials in the digestive tract of marine biota is a relatively novel and currently under-estimated toxicological issue that urgently requires further investigations (cause and effect studies).

5.7 Conclusions and recommendations

Many of the substances listed under categories X and Y are, much like mineral oils, biodegradable, or are volatile, leading to reduced effects with time after a discharge at sea. Ballast water introduced in cargo tanks should contain very low concentrations (less than 1 ppm of the substance previously carried) before it may be discharged into the sea under specified, set conditions (with reference to ship's speed, water depth, and distance to land). Given the observed effects on marine biota of substances listed in each of the hazard categories (the examples provided include only the visible impacts on top-predators), the possibility to release any substance or item at sea should be questioned and certainly deserves a new debate.

Important remaining questions and conclusions are:

- MARPOL Annex II States that no discharge of residues containing noxious substances is permitted within 12 miles of the nearest land. The rationale for this is not sufficiently clear. While a minimum distance from the nearest land for any discharge to be permitted may deal with human health issues, such a restriction does not minimise any hazardous effects on the marine environment itself. Most of the case-studies reported in this report involve seabirds not

commonly found in near-shore waters and highly vulnerable to offshore spills. The same holds for marine mineral oil pollution, where distance restrictions have always been questioned by ecologists working on these issues.

- Only the Antarctic is a Special Area under MARPOL Annex II, and the discharge of any noxious liquid substance in that region is prohibited. However, there are numerous particularly sensitive areas worldwide, including recognised areas such as coral reefs (Great Barrier) and the Wadden Sea. In analogy with the prevention of marine oil pollution, evaluations of the spatial and temporal patterns in sensitivity of sea areas should be conducted using a similar strategy as developed with Oil Vulnerability Indices coupled with censuses of marine biota (e.g. Carter *et al.*, 1993; Begg *et al.*, 1997).
- We are unaware of monitoring programmes measuring even the immediately visible effects of noxious liquids in the marine environment. We were unable to trace any standard protocol to deal with affected wildlife during spills of these substances. In the absence of detailed studies, it is highly unlikely that environmental impacts and the effects on human health of the release of noxious liquids in the marine environment will be detected, if these are not self-evident. In the absence of impact assessments, it is unlikely that (further) suggestions for the improvement of the existing situation can be formulated.

It is increasingly recognised that even substances of less concern should not be discharged into the sea in unlimited amounts and under uncontrolled conditions (GESAMP, 2002). Recent reports on scale of occurrence and impact of plastics in the marine environment (macro- and micro-plastics), call for further research and mitigation measures.

Summary Box 5.1 – Recommendations regarding the impact of hydrophobic chemicals with low water solubility released from merchant shipping on European marine ecosystems and wildlife

From this chapter, there is a clear need to:

1. Evaluate the importance (e.g. frequency and quantity of release) and environmental effects of *all* substances (X, Y, Z, or OS) presently being transported and/or being discharged, accidentally, legally or illegally;
2. Identify and assess the chemical composition and (possible) chemical reactions of substances or mixtures of substances when they enter marine environments (i.e. including permitted additives or cleaning agents used during operational discharges and otherwise non-hazardous substances). This should be tested in the GESAMP hazard evaluation procedure in more realistic conditions (e.g. by using marine mesocosms);
3. Further classify substances listed, incorporating vital substance-specific issues such as highlighted in studies of the direct and delayed effects on 'marine wildlife', benthic habitats and estuaries (smothering, immobilization, intoxication, etc)
4. Initiate monitoring programmes of new and emerging substances which have been shown to enter marine environments within the MARPOL context;
5. Develop and apply state of the art environmental risk assessment procedures (combining exposure and effect assessments, including human health) to evaluate the impact of noxious liquids listed under MARPOL Annex II on the different compartments of coastal and open sea ecosystems;
6. Develop and apply state of the art spill response protocols to minimise the effects on the marine environment and specific biota during an accidental spill or illegal discharges of noxious liquid substances;
7. Make use of the IUPAC names of the individual substances as well as their corresponding CAS and ICSC numbers mandatory to limit misinterpretations, or use the formal lists (IMO/MEPC 2007); and
8. Assess ecotoxicological aspects of (micro-) plastic ingestion by marine organisms.

6. Case study: Environmental impact of chemicals released by the offshore oil-industry

6.1 Introduction

There is an increasing production of oil and gas from offshore installations world-wide and this is also the case for European waters. While the main marine production areas in Europe are currently located in the North Sea and Norwegian Sea, activities in the north are increasing. In addition, other European marine areas are being exploited for hydrocarbons, including the Chara Sea, Barents Sea, the Adriatic (Mediterranean) Sea, the Black Sea, the Atlantic and (to a limited extent) the Baltic Sea.

The offshore oil and gas industry comprises many and varied activities. Environmental impacts from offshore oil and gas exploitation activities can arise from the following:

- Physical placement such as anchoring of rig or platform and pipeline construction;
- Drilling activity and cuttings discharges;
- Discharge of produced waters including production chemicals;
- Pipeline discharges such as pigging and dewatering;
- Jetting;
- Spills;
- Atmospheric emissions, i.e. flaring and fugitive emissions; and
- Decommissioning.

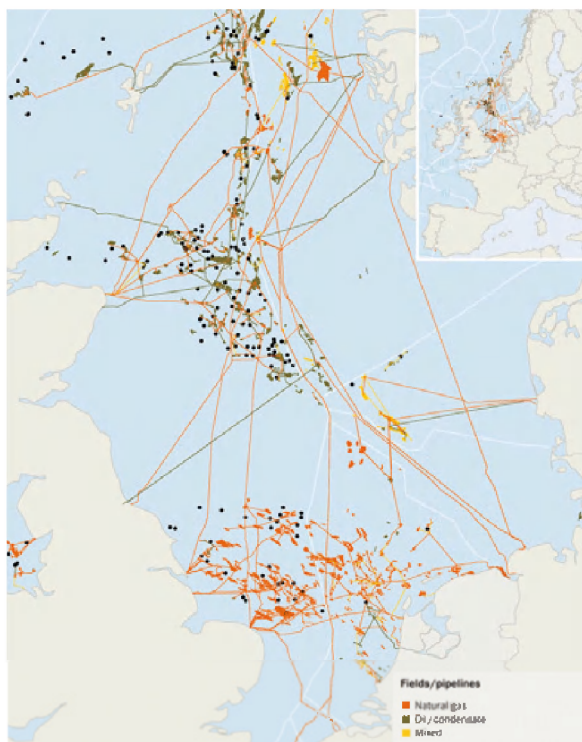


Figure 6.1. Location of offshore oil and gas exploitation facilities in the OSPAR region (from OSPAR QSR 2010)

This chapter focuses on monitoring related to discharges from drilling and production activities as they are expected to have the largest environmental impacts. Irregular inputs due to maintenance such as pipeline discharges or jetting (release of accumulated sediment from platforms) or spills may have serious environmental consequences but they are not assessed as part of routine monitoring programmes. Atmospheric inputs, mainly due to flaring, may be substantial. Although the inputs are mainly greenhouse gases such as carbon dioxide, the inputs also include e.g. polycyclic aromatic hydrocarbons.

There is limited monitoring of quantities and consequent inputs to marine ecosystems. Reports indicate that 730 offshore installations were discharging to the marine environment in the NE Atlantic area in 2007, a figure that has increased almost constantly from 1984 onwards (OSPAR, 2009). The majority of these installations are operating in the North Sea (Figure 6.1.)

The aim of this chapter is to present current frameworks and practices for the monitoring of chemicals released by the off-shore oil-industry, highlighting the need for the development and implementation of a framework for integrated monitoring and assessment in relation to the offshore oil and gas industry. This includes providing a brief outline of activities in European seas and the types of inputs and strategies chosen to monitor benthic and pelagic environments. Finally, the chapter aims to identify knowledge gaps and areas that require further research.

The chapter will focus on the North Sea area as the most intensely operated area within European waters and hence the area where there has been the most extensive research and monitoring activity.

6.2 Chemicals introduced through offshore activities

Inputs from installations vary depending on the activity being carried out. These can be categorised under the headings of drilling, cementing, completion/work-up and production. Drilling discharges include water based mud cuttings, such as bentonite, barite and mica. Drill cuttings from production sites using water-based muds contain organic material and will generally cause local effects on benthic fauna due to burial or oxygen consumption (see e.g. Schaanning *et al.*, 2008). In addition, components of the cuttings have been shown to affect marine organisms (Cranford *et al.*, 1999). Drill cuttings may also include chemicals such as biocides, corrosion inhibitors, shale inhibitors, scale inhibitors, viscosifi-

ers, etc. Cementing chemicals are intended to remain in place long-term. Discharges to the marine environment during the drilling process tend to be through the discharge of wash-water. Cement additives include antifoams, thinners, biocides, viscosifiers etc. Completion or work-up chemicals may include brines, detergents and corrosion inhibitors. Production chemicals include gas hydrate inhibitors, biocides, corrosion inhibitors and hydrogen sulphide scavengers.

Some of the chemical substances used in the offshore industry are assumed to have limited environmental impact (PLONOR substances²⁵), including substances such as cellulose, gypsum (calcium sulphate) and calcium chloride. However, many others are, or may contain, chemicals expected to cause adverse impact in the marine environment. Such chemicals may be classified under various headings, depending on which regulations are being applied. Table 6.1 gives an indication of the quantities of chemicals discharged in the NE Atlantic area in 2007 (OSPAR, 2009).

Produced water is a complex matrix that generally contains natural components such as polycyclic aromatic hydrocarbons, a range of unidentified hydrocarbons, organic acids and metals as well as a range of chemicals that are added in varying amounts to aid the production process, such as H₂S scavengers, scale inhibitors and biocides. Highly variable between wells, some produced waters also contain radioactive isotopes, e.g. ²²⁶Ra. The composition of produced water varies from well to well and over time in individual wells.

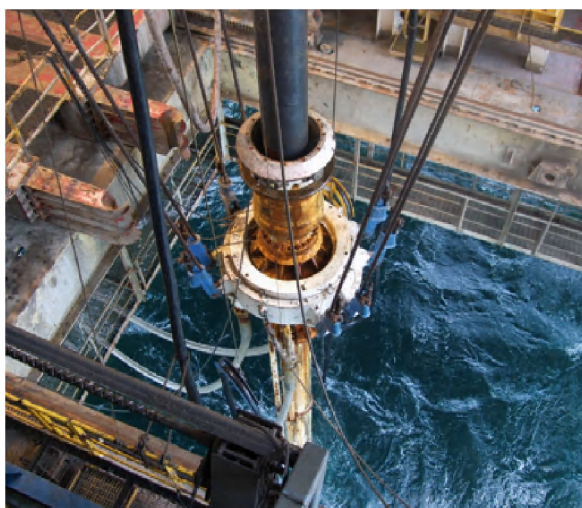


Figure 6.2. Riser and slip joint of a semisubmersible oil rig which carries oil and gas to the surface while drilling

25. Substances considered to Pose Little Or NO Risk to the marine environment; OSPAR 2004 Summary Record (OSPAR 04/23/1, Annex 9, updated 2008).

Table 6.1. Details of chemical discharges from offshore oil and gas installations in the OSPAR area in 2007. The numbers represents discharges to the North Sea. Data from OSPAR (2009)

Number of installations with discharges to sea and emissions to air	730*
Quantity of produced water discharged to the sea	401,516,892 m ³
Dispersed oil discharged in produced and displacement waters	5,021 tonnes
Dissolved oil discharged in produced and displacement waters	4,575 tonnes
Quantity of chemicals discharged with LC ₅₀ or EC ₅₀ <1 mg l ⁻¹	1.115 tonnes
Quantity of chemicals discharged with biodegradability <20% in 28 days	727 tonnes
Quantity of chemicals meeting two out of three PBT** criteria	1,332 tonnes

* includes 85 drilling installations

**The principles of Persistence (P), Bioaccumulation (B) and Toxicity (T) as an indicator of hazard has become part of various international initiatives undertaking prioritisation of potentially harmful substances in the environment. Given PBT characteristics can be indicated by chemical properties, many organisations, including the EU, have developed PBT threshold criteria to identify such chemicals. As such PBT assessment has become in many cases a core feature of marine risk assessment.

6.3 Existing frameworks and legislation

MARPOL 73/78 (International Convention for the Prevention of Marine Pollution from Ships, 1973, modified by the Protocol of 1978), covering pollution by oil, chemicals, harmful substances in packaged form, sewage and garbage was the primary regulation concerning discharges from offshore platforms.

In addition to national regulation and codes of practise to control discharges and emissions from the offshore industry in many countries, current EU environmental legislation applying to the offshore industry in EU states includes:

- Council Directive 2003/87/EC establishing a scheme for greenhouse gas emission allowance trading within the Community (and amending Council Directive 96/61/EC);
- Council Directive 97/11/EC (amending Directive 85/337/EEC) on the assessment of the effects of certain public and private projects on the environment;
- Council Directive 92/43/EEC on the Conservation of natural habitats and of wild fauna and flora;
- Council Directive 96/61/EC concerning integrated pollution prevention and control;

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Figure 6.3. Offshore oil platform with support ships

- Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

European coastal countries are also party to one or more of the following regional conventions: the OSPAR Convention, the Helsinki Convention and the Barcelona Convention.

Annex VI of the Helsinki Convention states that “The Contracting Parties undertake to prevent and eliminate pollution from offshore activities by using the principles of Best Available Technology and Best Environmental Practice as defined in Annex II.” HELCOM Recommendation 18/2 includes measures for monitoring requirements, oil in produced water and discharge of chemicals of concern, as listed in Annex I of the Convention.

Article 5 of the OSPAR Convention on pollution from offshore sources states “The contracting parties shall take, individually and jointly, all possible steps to prevent and eliminate pollution from offshore sources in accordance with the provisions of the convention, in particular as provided for in Annex III”.

The many decisions, recommendations and guidelines set out by OSPAR aim to minimise the adverse impact on the marine environment through delivering environmental goals, substituting harmful chemicals and the aim of zero harmful discharge by 2020.

For OSPAR contracting parties, OSPAR is the chief source of environmental regulation for offshore oil and gas industry. A list of relevant decisions and recommendations are included in Appendix V of this report. The OSPAR guidelines for monitoring the impacts of offshore industry provide details of comprehensive monitoring approaches, including biological and chemical monitoring for the sediment and water column compartment.

6.4 Environmental impact and risk assessment of oil industry chemicals in the North Sea

6.4.1 Background

The North Sea has, over the last four decades, become the centre of one of the world’s most productive oil and gas industries. Considerable quantities of natural gas were first found in the Groningen area of The Netherlands in 1959. This was followed by the discovery of gas in 1965 in the UK West Sole field; production from this field commenced in 1967. In 1969, the first oil was discovered in Norwegian waters in the massive Ekofisk field. The first North Sea oil was brought ashore from the Ekofisk field in 1971. This was followed in 1975 by the Argyll and Forties fields (UK).

The North Sea has been subject to extensive drilling and production in the past decades. Benthic surveys of the North Sea in the 1980s (Davies *et al.*, 1984) revealed the environmental damage caused by the discharge of cuttings contaminated with oil-based mud.

In the 1980s there were suggestions that contaminants could be responsible for high incidences of abnormalities in fish embryos found in the southern North Sea (von Westernhagen *et al.*, 1987 and 1989). An extensive fish disease monitoring activity that started in the late 1970s (Lang, 2002a), while demonstrating decreases in some diseases, also observed increases in others (Dethlefsen *et al.*, 1987; Wosniok *et al.*, 1999; Lang and Wosniok, 2003). It is, however, challenging to establish direct links from such observations to contaminant exposure because of the multifactorial etiology of diseases and embryonic aberrations. There is some concern as to possible impacts of offshore gas and oil activities on North Sea fish populations and recent data for sublethal health-related measurements (biomarkers) indicate that fish populations in areas with high produced water inputs are affected by contaminants in the discharges (Hylland *et al.*, 2006b).

As mentioned in Section 6.3, different phases of oil and gas prospecting and production will affect all parts of marine ecosystems. Monitoring of benthic systems has primarily focused on the composition of soft sediment communities and levels of selected contaminants. Pelagic monitoring near platforms has been done using caged organisms and to some extent, passive samplers. In addition, there have been some specific studies and regional assessments that address issues that are relevant to both benthic and pelagic systems (e.g. Hylland *et al.*, 2006b).

6.4.2 Environmental impact and risk assessment

As described in Section 6.3, offshore activities are expected to impact benthic and pelagic ecosystems, the former primarily as a result of drilling, and the latter mainly during the production phase. Benthic impacts in the vicinity of platforms have been monitored since the 1970s (see e.g. Gray *et al.*, 1999). This has resulted in revised use of chemicals, including a ban of discharge of oil-based mud and improved monitoring guidelines. Produced water monitoring was initiated in the Norwegian sector of the North Sea in the late 1990s (Utvik *et al.*, 1999) and has since then been developed as an integrated chemical and biological monitoring activity following the international BECPOLAG workshop in 2001 and 2002 (Hylland *et al.*, 2002a,b; 2006a). A guideline document that includes both benthic and pelagic monitoring of offshore activities was developed by OSPAR (2004). The main species used have been Atlantic cod and blue mussels.

Different strategies have been chosen by the North Sea countries involved in oil and gas production. Most countries require monitoring for benthic impacts and chemical analyses of the effluent from each platform (in Norway, twice a year), but the approach described here for water column monitoring has only been fully implemented in the Norwegian sector of the North Sea.

6.4.2.1 Benthic monitoring

The main impacts on benthic ecosystems will arise during the drilling phase, although it is to be expected that some components in produced water, if released, will associate with particles and sediment to the sea-floor. As mentioned above, benthic offshore monitoring programmes have been developed using soft-bottom macrofauna composition in addition to chemical analyses of sediment and determination of non-contaminant factors that may affect species composition (e.g. particle size, organic material) (see Renaud *et al.*, 2008 for an overview).

The strategy chosen in Norway was initially focused on individual fields, but has since 1996 been based on 11 regions from Spitsbergen in the north to the central North Sea (not all of which are currently monitored due to a lack of activity). Monitoring is performed on rotation between regions. This general strategy has later been adopted by OSPAR (2004). A distinction is made between field-specific monitoring, with a focus on a specific production area (Figure 6.4) and wide-area (regional) monitoring with sampling sites selected in a region with no particular reference to offshore activities in the region.

Figure 6.5. provides an examples of total hydrocarbon concentrations in sediments around different platforms. Data for total hydrocarbon in sediments clearly show

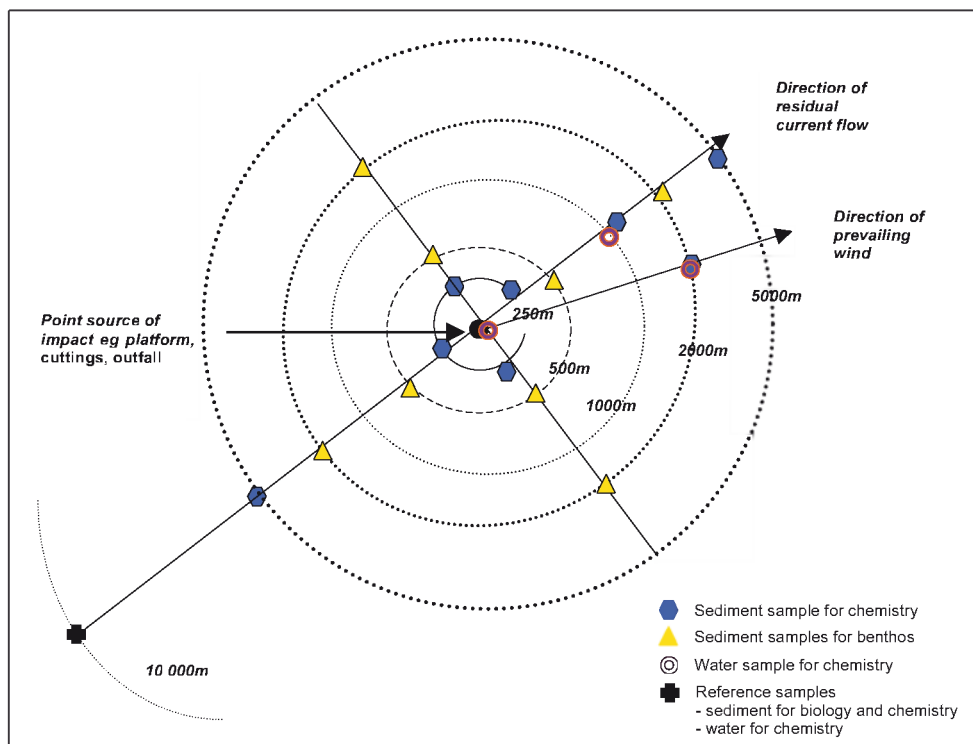


Figure 6.4.
Illustration of a typical sampling plan for a benthic impact assessment

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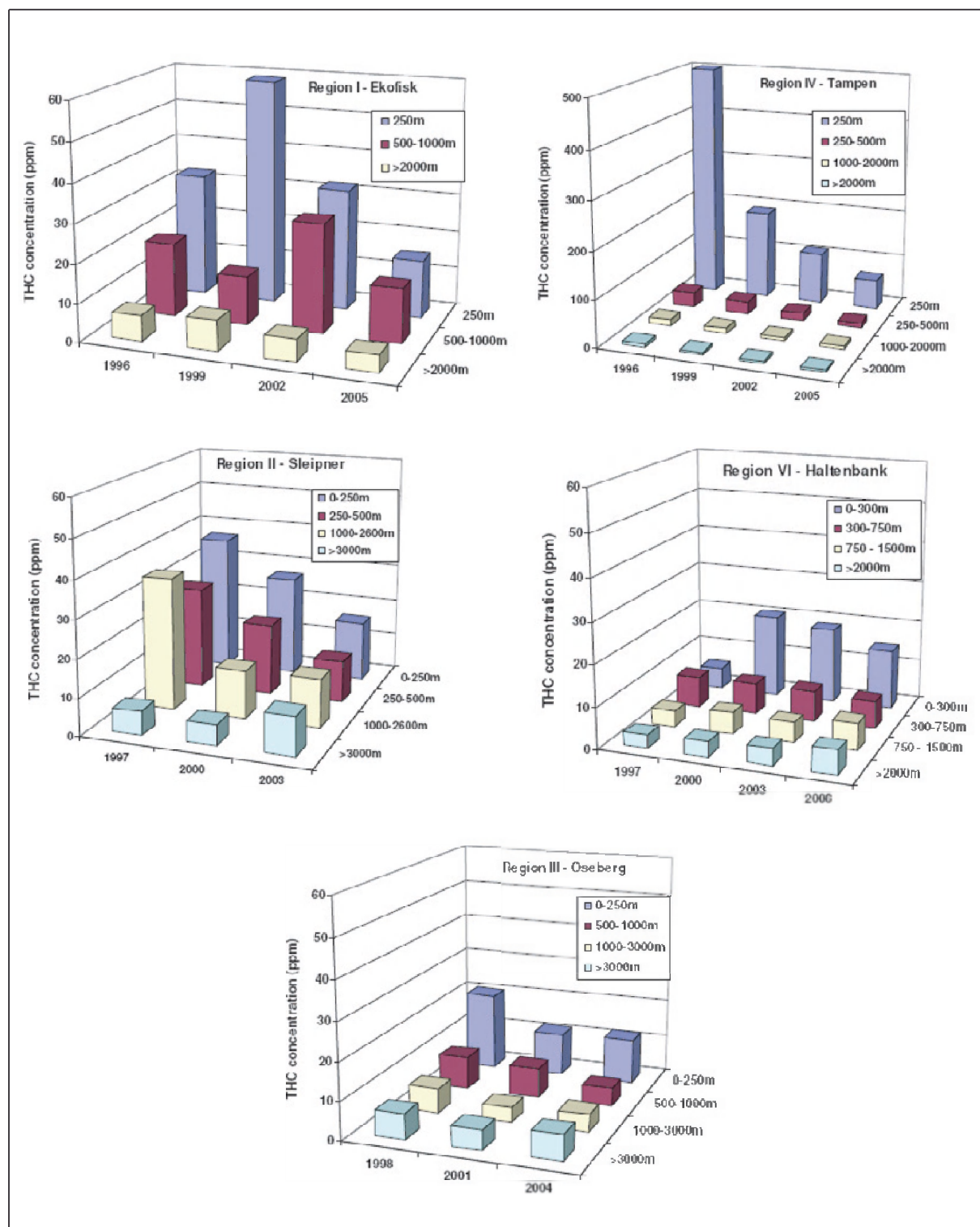


Figure 6.5. Median total hydrocarbon (THC) in sediment sampled in different years in different distances from the indicated platforms (from Renaud *et al.*, 2008); note different scale for Region IV compared to the others

that concentrations decrease away from platforms and that the general tendency is towards decreasing concentrations over time.

For most of the fields there is large interannual variation in species composition. Any differences between locations close to the platforms and reference locations have generally been found within the year group in the analyses (Renaud, 2008). A substantial fauna recovery over time has been seen as a result of the switch from oil-based to water-based drilling fluids in 1993. At present effects on the benthic community structure are rarely found beyond 500 m distance from a cuttings discharge position (see Figure 6.6).

6.4.2.2 Pelagic monitoring

6.4.2.2.1 Background

Large volumes of produced water are generated at oil and gas production platforms. Where technically feasible, produced water is reinjected (i.e. pumped back into the reservoir). The volume of produced water released for each tonne of gas or oil produced will increase over the lifetime of the platform as the ratio of water to oil/gas increases. Although the chemical composition of produced water is analysed and reported twice annually in some areas (e.g. Norwegian and UK sectors of the North Sea) it is challenging to predict possible environmental impacts, not least due to dilution, partitioning and transformation processes in the receiving seawater. Although produced water is the main effluent released from production platforms, there may be other waste inputs as a result of maintenance (e.g. jetting). It is unlikely that benthic communities will be strongly affected by produced water inputs and benthic monitoring is therefore not generally viewed as a relevant assessment of produced water inputs.

6.4.2.2.2 Monitoring approaches

The following approaches have been used to evaluate the environmental impact of produced water (Table 6.2).

(i) Modelling – chemical analysis of produced water and model toxicity

As mentioned above, regular chemical analyses of produced water from each platform are a requirement in most countries. Using discharge volumes, concentrations in the surrounding seawater can be estimated (modelled), compared with toxicity levels determined in the laboratory and extrapolated to ecosystem level (generally using PNEC – predicted no effect concentration – calculations).

Although inputs from any one platform may vary over time, the composition of such effluents is generally thought to be sufficiently stable to enable spatial modelling of discharge concentrations. Wind and

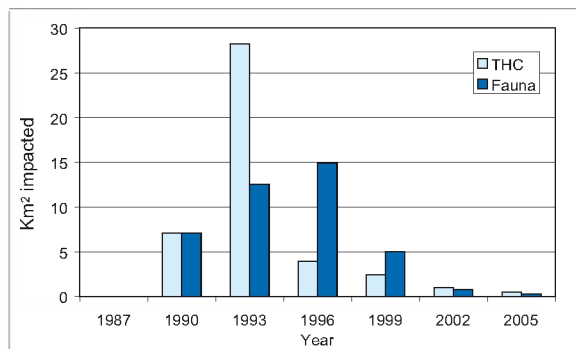


Figure 6.6. Temporal change in estimated areas (km²) of THC contamination and fauna adverse effects around the Gyda field, southern North Sea, from 1987 (baseline survey) to 2005 (from Bakke *et al.*, in press)

current data is available and a 3D dispersion model, DREAM²⁶, has been developed that can be run for each platform or production area to predict concentrations in the surrounding seawater (see e.g. Johnsen *et al.*, 1998). The output from the model has been compared to back-calculated concentrations of components from caged mussels. Sometimes observed and modelled concentrations correspond well (Durrell *et al.*, 2006; Utvik *et al.*, 1999), while in other cases the correspondence has been less clear (Utvik and Gärtner, 2006).

The CHARM (Chemical Hazard and Risk Management) calculator is used in all countries to estimate the risk associated with the discharge of oilfield chemicals.

(ii) Model inputs and measure toxicity (in extracts of produced water and/or seawater)

A problem with chemical analyses is its specificity: one only finds what one looks for. There are many unknown components in any complex effluent such as produced water. To circumvent this problem the toxicity of produced water or surrounding seawater can be assessed directly using various bioassays following an extraction of the effluent, seawater or passive samplers (see e.g. Tollefsen *et al.*, 2007; Vethaak, 2006). In addition to providing a direct value for toxicity, bioassay-based measurements can assist in the selection of endpoints in other types of monitoring studies using *in situ* caging and/or field sampling. Bioassays may also be included in bioassay-directed fractionation and toxicity identification procedures to determine the identity of toxicologically active compounds in the effluents (Thomas *et al.*, 2004 and 2006).

One problem with using produced water for toxicity

26. DREAM: Dose Related Effects Assessment Model

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Table 6.2. Overview of approaches used to assess environmental impacts of offshore effluents

Approach	Advantage(s)	Disadvantage(s)	Reference(s)
(i) exposure and/or effect modelling	reproducible, direct link to risk assessment	no direct link to environmental impact	Johnsen <i>et al.</i> , 1998 Utvik and Gärtner, 2006 Neff <i>et al.</i> , 2006
(ii) <i>in situ</i> extracts (produced water, seawater, passive samplers) combined with bioassays	identify specific mechanisms and substances; sensitive and reproducible; possible to test systems not otherwise included (e.g. early life stages in fish)	no direct relationship to intact organisms, metabolism or bioavailability	Tollefsen <i>et al.</i> , 2006 Thomas <i>et al.</i> , 2004, 2006
(iii) caging	reflects local exposure over exposure period; can use organisms with desirable characteristics (e.g. blue mussel and locally relevant fish species)	“semi-natural” exposure situation; food availability unknown; limited to selected species; exposure at one point	Hylland <i>et al.</i> , 2004 Hylland <i>et al.</i> , 2006d Hylland <i>et al.</i> , 2008
(iv) field sampling	high ecological relevance	difficult to assess area integrated over (but large); high natural variability (needs large sample numbers)	Hylland <i>et al.</i> , 2006b Lang, 2006

studies is the volatility and biodegradability of some components. Laboratory studies have, however, explored mechanisms of toxicity and bioavailability of produced waters from different platforms following transport of large volumes of produced water to land-based facilities (Casini *et al.*, 2006; Meier *et al.*, 2007 and 2008). In addition, recent studies have used simulated produced water in chronic exposure studies (Holth *et al.*, 2008 and 2009a,b). A final option which has not been fully investigated is the exposure of organisms to diluted produced water on the platform itself. Such studies would make it possible to perform chronic studies with selected concentrations of produced water and relevant organisms. Produced water can be modified following even short-term storage and it is therefore difficult to do such studies in land-based facilities.

(iii) Caging - integrated chemical and biological assessment of organisms caged at different locations near the platform(s)

It is clearly challenging to determine the exposure period for organisms sampled in the produced water plume and consequently assess the true effects of this exposure. One way around that problem is to deploy organisms in cages moored in the vicinity of the platforms. As an additional advantage, it provides an opportunity to use organisms with a known history (e.g. from aquaculture) and to select organisms that have desirable properties.

The modification of produced water components

following release to the sea is a process which is challenging to model. Direct assessment of possible impacts can either use caging of organisms or collection of natural populations. Caged organisms have a known exposure history and clearly represent exposure in a certain period of time and at a single location. There are two main advantages associated with the use of caging: (i) the exposure remains natural while it allows some level of control; and (ii) the organisms can be selected (species and origin). Individuals may therefore be selected from unpolluted and unstressed populations and measurements made from the population or even the same individuals (blood, hemolymph) prior to and after deployment (Hylland *et al.*, 2004 and 2006). For the purpose of offshore monitoring in the North Sea, blue mussels have been deployed at multiple sites for spatial monitoring (e.g. to determine the area of influence), supplemented by the use of caged fish at a few sites (for endpoints not available in mussel, e.g. estrogenicity and other vertebrate related endpoints). Results from the BECPÉLAG workshop clearly showed the utility of using caged organisms (see e.g. Aas *et al.*, 2006; Bilbao *et al.*, 2006a, Danischewski, 2006). Experience from the last decade of pelagic monitoring in the Norwegian sector of the North Sea has identified some issues, e.g. the challenge involved in ensuring that caged organisms will be exposed, decided by the direction and depth of the effluent plume.

(iv) Field sampling – integrated chemical and biological assessment of organisms collected from surrounding seawater or seafloor

Natural populations of pelagic organisms in the sea receiving produced water will be exposed to varying concentrations and for varying time periods. On the other hand, any effluent-related impact at the population level is clearly serious from an ecological point of view. Such studies need to be designed carefully to provide the information needed, not least in terms of replication and spatial considerations.

Although clearly the most environmentally relevant of all approaches, field sampling of organisms also has its draw-backs. It may not always be possible to sample the species, size range or sex required at all sites. Sampling of natural populations should always be complemented with an assessment of general condition (e.g. condition index for fish), migratory behaviour and hydrographical data, especially water temperature. The main issue with field sampling is of course the limited information available concerning exposure. Field studies have, however, indicated large-scale environmental impacts that may be linked to offshore activities (see e.g. Bilbao *et al.* 2006b; Hylland *et al.* 2006b).

6.4.2.2.3 Monitoring framework

There has been a focus on integrating chemical and ecotoxicological analyses in developing a monitoring framework for the Norwegian sector of the North Sea. The initial screening for appropriate methods was done by the BECP ELAG workshop. The methods suggested following the workshop retained links to the original contaminant-specific and general monitoring guidelines published by OSPAR (JAMP, 1998 a,b), but also included methods that target putative effects of components known to be present, such as polycyclic aromatic hydrocarbons (PAHs) and alkylphenols (APs). This approach is not necessarily optimal as components in the different effluents are largely unknown (other than the above) and a larger range of methods should have been used to identify effects of other components or interactions. The original list of methods included in the monitoring framework accepted by Norwegian operators and national authorities also included methods that reflect more general health effects, e.g. histology (Table 6.3 and Table 6.4).

In addition to a range of core methods, an important component of the programme consists of the possibility to include novel methods. One recently included method that appears to reflect effects caused by offshore effluents is micronucleus formation, quantified in mussel hemocytes and in selected cells from cod.



Figure 6.7. Sampling with research vessel Walther Herwig III near the Statfjord B platform during the BECP ELAG workshop

6.4.2.2.4 Local and regional programmes

The Norwegian offshore monitoring programme for produced water originally adopted elements from the existing programme for benthic monitoring, i.e. a separation between local and regional impacts. Local impact surveys have been based on caging studies with Atlantic cod and blue mussel, whereas the regional programmes have been based on wild-caught fish.

The integration of chemistry and biology in the local impacts programme was initiated by the BECP ELAG workshop in 2001 and has since covered three different production areas (Tampen, Troll and Ekofisk). Results from the initial three campaigns were reported in Hylland *et al.* (2008). Although sublethal contaminant-related responses were observed for both caged cod and mussels in 2001 (e.g. Bilbao, 2006; Danischewski, 2006; Smolders *et al.*, 2006; Aas *et al.*, 2006), limited effects have been seen in the subsequent campaigns (Hylland *et al.*, 2008). This can partly be explained by lower exposure levels as cages were not positioned at locations where the main plume eventually ended up (positions were selected using data from previous years). A second factor that added to lower exposure levels was seasonal differences in hydrography: most produced water effluents will rise to the surface (higher temperature than surrounding seawater) and will be diluted in the upper layer, which is generally much shallower in spring than in autumn. Lower exposure levels were thus documented through accumulation of PAHs in blue mussels and PAH metabolites in cod bile (Hylland *et al.*, 2008).

The aim of the regional monitoring campaigns carried out in 2002 and 2005, was to clarify whether any produced water-related components could be detected in fish fillet and to identify any produced water related

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Table 6.3. Core methods for effects monitoring using fish (Atlantic cod) included in the monitoring framework established for the Norwegian offshore sector (and later adopted by OSPAR)

Method	Tissue/matrix	Reference
cytochrome P4501A activity (EROD) activity	liver	Stagg and McIntosh (1996)
glutathione S-transferase (GST) activity*	liver	Habig <i>et al.</i> (1974)
DNA adduct concentration	liver	Reichert <i>et al.</i> (2001)
vitellogenin concentration*	blood plasma	Scott and Hylland (2002)
Histopathology	liver	Bilbao <i>et al.</i> (2006a)
delta-aminolevulinic acid dehydratase activity (ALA-D)**	red blood cells	Hylland (2004)
acetyl cholinesterase (AChE) activity**	muscle	Bocquené and Galgani (1998)
PAH-metabolite concentration	bile	GC or HPLC
metal (Cd, Hg, Pb) concentration	liver	accredited analytical method

* until the present there has not been clear responses in this parameter;

** proposed, but has not yet been implemented in Norwegian monitoring activities.

Table 6.4. Core methods for effects monitoring using blue mussel included in the monitoring framework established for the Norwegian offshore sector (and later adopted by OSPAR)

Method	Tissue/matrix	Reference
benzo(a)pyrene hydroxylase (BaPH) activity **	hepatopancreas	Michel <i>et al.</i> (1994)
acetyl cholinesterase (AChE) activity	hepatopancreas	Bocquené and Galgani (1998)
Lysosomal stability	hematocytes	Lowe <i>et al.</i> (1995)
histopathology	hepatopancreas	Bilbao <i>et al.</i> (2006a)
PAH concentration*	whole mussel	accredited analytical method
lipid content	whole mussel	accredited analytical method
metal (Cd, Hg, Pb) concentration	whole mussel	accredited analytical method

* the PAH-compounds to be analysed should be those on EPA's "list of 16 compounds". PAHs should be quantified by GC/MS according to JAMP Guideline Agreement 1999-01, Technical Annex 3. In some instances, total 2-6 ring parent and branched PAH analysis might be desirable. NPDs are the sum of naphthalene, phenanthrene/anthracene, dibenzothiophene and their C₁C₃ alkyl-homologues;

** in the Norwegian sector there has now been a change to pyrene hydroxylase, which appears more sensitive to the components in offshore effluents.

sublethal responses in commercial fish species. The programme had a focus on gadiids, i.e. Atlantic cod (*Gadus morhua*), haddock (*Melanogrammus aeglefinus*) and saithe (*Pollachius virens*). Fish were sampled by trawling in three areas of the North Sea in 2002 and additionally in the Norwegian and Barents Seas in 2005 and 2008.

Not surprisingly, concentrations of produced water related components (PAHs and alkylphenols) were below or at detection limits in all but a few samples of fish tissues. Both PAHs and alkylphenols are readily metabolised by fish and their metabolites were quantified in bile. While there were no clear patterns for cod and saithe, there was a consistent increase in both PAH bile metabolites and DNA adducts in haddock from areas with high pro-

duction activity (Tampen) compared to the reference area (Egersund Bank) (Grøsvik *et al.*, 2007; Klungsøyr *et al.*, 2003; Hylland *et al.*, 2006b). A second interesting observation has been the different lipid profile of haddock at Tampen compared to haddock from reference areas (Grøsvik *et al.*, 2007; Hylland *et al.*, 2006b). The differences were larger than would be expected simply from differences in feeding regime between the regions. Some differences were also observed in enzymes involved in protection against oxidative stress in the same fish and it could be speculated that oxidative stress linked to environmental factors associated with oil production could have caused increased lipid peroxidation and shifts in the relative ratios of membrane lipids.

6.5 Conclusions and recommendations

Benthic community analyses are clearly useful to monitor effects during drilling and to assess recovery after drilling has ended, but will provide little information about environmental impacts caused by oil or gas production (i.e. inputs of produced water).

Many of the methods used in pelagic monitoring are not sufficiently sensitive to detect the low levels of contaminants in seawater some distance from the platform. One of the promising methods tested in addition to core methods was micronucleus formation in both caged fish and blue mussels (see Barsiene *et al.*, 2004 and 2006). For example, results from both 2003 and 2004 indicated that micronucleus formation was increased even at low produced water concentrations, demonstrating exposure to substances that cause chromosome breaks.

Gaps of knowledge

There is still limited knowledge of possible environmental impact of substances present in offshore effluents. Recent studies have shown that substances present in high concentrations in effluents, e.g. naphthenic acids, may affect marine organisms (Thomas *et al.*, 2009).

There is a need to develop methods that are sufficiently sensitive to identify and quantify effects, if any, of produced water inputs. At the moment there is only knowledge of possible effects in a limited number of species, hence there is a need for broader assessment of the possible sensitivity of other species. There is very little knowledge of the possible sensitivity of pelagic invertebrates (both meso- and holoplankton) and bird species that feed on plankton (e.g. fulmars).

Challenges and opportunities

There are still challenges in understanding the toxicity of effluents from offshore platforms, both related to exposure and to their potential environmental toxicity. Although diluted in large volumes of seawater, there is evidence that produced water inputs do cause effects in both caged and wild-caught organisms. While the use of caging for local impact monitoring and field-collection for regional assessments appear reasonable, there remain two main challenges: (i) determination of the area influenced by any single platform or group of platforms; and (ii) developing sufficiently sensitive methods to detect impact at the low exposure levels present in the sea outside the immediate vicinity of platforms.

It is clear that the approach to select locations for caging is critical and that a larger number of cages need to be deployed to provide better estimates for the expo-

sure area. In this context, variability due to differences in hydrography (i.e. depth of pycnocline) needs to be addressed.

Monitoring and regulation

There is a need to be clear about objectives and appropriate methodology in monitoring environmental impacts from offshore activities: benthic monitoring is useful to monitor environmental effects during drilling or to monitor remediation, but any monitoring of produced water impacts should focus on the water column (e.g. caging).

The current use of caging has been found to provide useful information for local monitoring, but has suffered from a low number of deployed cages and difficulties in predicting both stratification and the direction of the plume. A larger number of cages need to be used (presumably limited to mussels as test organisms), and the cages must be positioned as for benthic monitoring, not according to modelling of last years' plume.

Previous experience has shown that both chemical and biological data are useful for assessment purposes supporting the benefits of an integrated chemical and biological approach.

Research and development

It has become increasingly clear that a range of substances in produced water may affect marine organisms through mechanisms other than acute toxicity. There is a need for a more comprehensive effort in clarifying different modes of action and possible environmental impacts.

More knowledge is needed about confounding factors for environmental effects of offshore discharges, including seasonality (e.g. primary production) and interactions with UV radiation.

There is limited knowledge about any effects of offshore discharges on invertebrate larvae or different zooplankton species. Full life-cycle studies should be performed with a range of marine taxa.

6. Case study: Environmental impact of chemicals released by the offshore oil-industry

Summary Box 6.1 – Recommendations regarding Environmental impact/risk assessment of chemicals released by the offshore oil-industry

From this chapter, there is a clear need to:

1. Harmonise methodologies for monitoring offshore environmental impacts in different countries.
2. Establish integrated monitoring programmes that include core methods used on a regular (annual) basis as well as appropriate testing methods.
3. Accrue and use knowledge of environmental interactions that may affect the impact of offshore discharges (seasonality, turbidity, stratification, UV, etc).
4. Develop and apply methods that can be deployed to monitor possible impacts of offshore effluents on sensitive life pelagic life stages, i.e. invertebrate and fish larvae.
5. Develop a regulatory framework which allows for a greater transparency with regard to chemicals used in both drilling and production operations, as well as analytical methods with which to quantify their presence in marine matrices and biota.

7. Conclusions and recommendations

This report is the result of the activities of a Marine Board Working Group of experts initiated in 2008 and tasked to develop a Strategic position paper on the assessment and monitoring of existing and emerging chemicals in the European marine and coastal environment. The need to mandate a Working Group on this topic came from the recognition that (i) existing regulatory frameworks or large international monitoring programmes to control and reduce pressures and impacts on the marine environment or (ii) new ones being developed (e.g. EU Marine Strategy Directive), may not always incorporate the most up to date scientific developments and/or relevant scale in their assessment schemes to allow a recent science-based evaluation of the risks posed by chemicals to marine and coastal systems.

The WG was established to:

1. Review existing monitoring/assessment frameworks and practices and assess the need to evaluate the relevance of substances currently being monitored and/or assessed in the marine environment;
2. Review recent literature on new and emerging chemicals in the marine environment to provide examples of substances for which there is cause for concern and assess the need (and appropriate mechanisms) to incorporate them in existing and future monitoring and assessment schemes; and
3. Review existing methods used to evaluate the impact/risks of chemicals in marine systems and, based on recent scientific knowledge, propose improved procedures and identify future research and development needs.

The findings of the Working Group in addressing these tasks are developed in chapters one through four which constitute the core of this position paper. Each of these chapters contains a clear set of conclusions and recommendations related to (i) existing monitoring/assessment frameworks (Chapter 2); (ii) current monitoring practices (Chapter 3); and (iii) new and emerging chemicals of concern and the mechanisms used to include them in current monitoring programmes (Chapter 4). This chapter presents the priorities under the umbrella of four main overarching recommendations which have been identified and need to be addressed. These are:

1. There is a clear need to fully **implement state of the art environmental risk assessment procedures** (combining exposure and effect assessment) to evaluate the impact of the substances on the different compartments of coastal and open sea systems.

While there is a trend to incorporate more methods to evaluate biological effects of chemical substances in existing monitoring/assessment programmes, the potential risks of chemicals in the marine environment are mainly assessed through the use of (exclusively) chemical techniques (chemical concentrations in water, sediment and biota). As such, the true impact of these substances cannot be evaluated. The risks of potentially harmful substances in the marine environment can only be evaluated by fully implementing a risk-based approach to the monitoring and assessment of chemicals, including both hazard (effect) and exposure assessment. A risk-based approach should be implemented, or at least be jointly considered with other criteria, when ranking and selecting “substances of concern” for the marine and coastal environment.

There is an imbalance between the data available on the presence, concentrations and body burdens of chemicals (exposure data) and data and knowledge on their actual effects in the different compartments of the marine and coastal environment. It is recommended that future European monitoring programmes should include both chemical analyses and biological effects measurements. Bioassay methods, including biomarkers, to be included should be those for which validated monitoring guidelines, quality control procedures and assessment tools have been developed. There is a clear need for the further development, evaluation and validation of efficient biological effects assessment tools.

There is a lack of current knowledge on how to deal with (i) mixtures, (ii) environmental interactions that modulate the bioavailability of chemicals, and (iii) the effects of additional stressors on the ecotoxicity of anthropogenic chemicals. Research is urgently needed on the effects of mixtures to allow science-based risk assessment and central concepts need to be introduced into policy to move beyond the current focus on individual substances. There is a need to develop novel strategies to assess potentially adverse biological effects of mixtures of multiple-stressors. This should be based on a battery of biological effect assessment methods at different levels of biological organisation and combined with chemical analyses to detect short-term as well as long-term ecologically relevant effects, thus providing knowledge on the relationships between environmental stressors and ecological effects. To achieve this, more research is needed on the application of both conventional and new techniques such as genomics and proteomics. The latter are, due to the current lack of knowledge on the ecological relevance of these endpoints, not yet ready for inclusion in long-term monitoring efforts.

7. Conclusions and recommendations

2. There is a **strong need for coordination, cooperation and harmonization** between the various existing monitoring efforts and those under development, to avoid duplication of effort, loss of expertise and a reduced willingness to fulfil the obligations towards regional conventions.

Comparison of the current monitoring programmes discussed in this position paper revealed that there are considerable differences between them in terms of goals, approaches and methods. While they consider the same environment, selection of chemicals, normalisation procedures, assessment tools and matrix selection often differ considerably. This ultimately leads to different substances being monitored, incompatible datasets and incomparable assessments. Clearly, harmonisation of the methodology, approaches and concepts of monitoring is required. This pertains to the entire chain of procedures, from planning and sampling at sea to the final assessment of the data, i.e. the assessment of the state of the marine environment.

There is also a strong need to coordinate the efforts of the various programmes in order to avoid duplication and wastage of resources. This has been recognised to a certain extent: the recent EC Marine Strategy Framework Directive (MSFD) specifically requires harmonisation in terms of monitoring and assessment for specific issues, and regional conventions such as OSPAR and HELCOM are actively exploring ways to harmonise their methodologies and assure compatibility with the requirements of the MSFD. Other ongoing initiatives such as EMODNET and NORMAN focus on harmonization of data collection and distribution. An improvement in efforts towards harmonization is urgently needed.

The long-term commitment of many European countries towards marine monitoring programmes has resulted in, among others, important datasets and innovative approaches for monitoring and assessment of the state of the marine environment. It is precisely this extensive experience that provides the basis for future development. However, this requires much more cooperation and common vision and methods than has existed to date.

Finally, it should be recognized that there are regional differences, both in the natural (background) concentrations of some substances (e.g. naturally occurring metals) and the sensitivity of local ecosystems. These differences should be taken into account when developing new and harmonised monitoring schemes. In the long-term, while individual monitoring programmes may

require different approaches, a harmonized approach towards monitoring should be achieved in the European marine environment.

3. The development and implementation of monitoring programmes for the assessment of chemicals in the marine and coastal environment **should be a science-based and dynamic process.**

In this report it has been shown that actual monitoring is often limited to a common, historical set of chemicals for which there is an international consensus. Also, monitoring is often a rigid process. Once a chemical is selected for monitoring it is likely to remain on the list for a long time, even if it is no longer present in the environment or is present at levels that pose little or no risk to the health of the marine environment. At the same time, many new and emerging substances are not routinely monitored and/or assessed. There is a clear and substantial time lag between the scientific observations and consensus concerning the danger of certain chemicals (or group of chemicals) and their inclusion in a routine monitoring programme.

Therefore, there is a clear need to evaluate the importance and relevance of the substances presently being (chemically) monitored and the methods used to evaluate environmental impacts. Monitoring should be a dynamic process, constantly evaluating its own performance in terms of methods, substances evaluated, the toxicological and ecological relevance of the effects methods employed, confounding factors, assessment criteria and other procedural aspects. Figure 7.1 presents a decision-scheme for the selection and monitoring of new and emerging substances developed by the working group. Such a system should allow for the inclusion of new compounds and the discontinuation of monitoring (or a reduced effort) for substances that are no longer relevant. The selection mechanism should be science-based and time lags between discovery and monitoring should be reduced as much as possible. Often, a lack of scientific background (e.g. (eco) toxicological data) and/or the necessary analytical tools will hamper the process. This could be addressed through a structural mechanism, whereby research in these fields is initiated and supported on a long-term basis. Future monitoring should also be interdisciplinary and take into account advances across the relevant disciplines. Ideally, chemical, biological, and biological effects monitoring should be integrated to the largest possible extent and take into consideration other observations, e.g. from physical oceanography. There is a need to be able to account for confounding, non-substance related factors such as turbidity, stratification and time of sampling. Finally, a

sound underlying statistical basis is necessary at the different levels of programme design, chemical and biological assessment methods and data interpretation.

One way forward may be to develop a tiered system that starts with a constant vigilance for the discovery of unknown compounds present in the marine environment. Once detected, analytical methods can be developed and a one-off survey can be organised to obtain insight into the extent of the problem. For the latter, a sound statistical basis is a prerequisite. Further monitoring, if deemed necessary, will then require the development of assessment tools and methods that allow robust routine monitoring backed by appropriate Quality Assessment and Quality Control procedures. This approach is already used in Japan and Sweden, and advocated by OSPAR, but requires investment of significant resources and budgetary support. Finally, novel potential problems such as micro-plastics or nanoparticles will require a totally different approach, highlighting the need for more research on the behaviour, effects and monitoring options for novel pollutants.

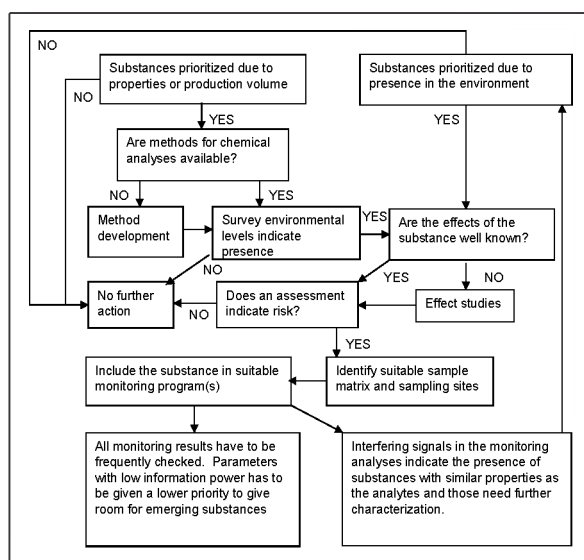


Figure 7.1. Decision-scheme developed by the Working Group for the selection and monitoring of new and emerging substances

4. More resources should be targeted at developing appropriate approaches, tools and practices (education and training) to **improve acquisition and management of monitoring data.**

Monitoring results in huge quantities of data. The quality and management of that data is of the utmost importance. Furthermore, science will benefit from data that is easily exchanged and comparable. At present, the large international schemes approach this in different ways, although initiatives are underway to improve harmonization. For instance, OSPAR and HELCOM both use ICES as the repository of their data. The data is stored in a well-defined structure, uniform format and is easily accessible. The EU is exploring ways to directly link relevant datasets in the various European data centres through a web-based interface. Yet, in general scientists still encounter significant difficulties when trying to assess or obtain data in an international or national database. Clearly, data should be protected for unwanted access and unwarranted use, but there is real value in allowing scientists to perform data mining and analysis beyond the scope of monitoring programmes.

In-depth examination of data from monitoring programmes will sometimes reveal substantial gaps in time-series and spatial coverage. Most pollution data is limited to coastal areas, partly because the problem is most serious there, but also because of the expense involved in monitoring beyond coastal boundaries. Marine monitoring is expensive, and without strict legally binding mechanisms, individual countries may opt not to meet their obligations. This problem should be addressed and solved at a supra-national level.

In addition to the above main recommendations, the following key recommendations have been identified drawing from two specific case studies presented in Chapters 5 and 6 on the release, effects and monitoring of (i) hydrophobic and insoluble chemicals in the marine environment from merchant shipping (Chapter 5); and (ii) chemicals released by the offshore oil-industry in the North Sea (Chapter 6). While specific recommendations are listed at the end of both chapters, these case studies revealed that:

5. There is a need to **develop a consistent pan-European or regional (legal) framework/regulation which covers oil and gas industry activities at sea.** At the same time, **more information and research is needed on the release and the effects of chemicals arising from offshore oil and gas activities.**

7. Conclusions and recommendations

The information on the release and the effects of chemicals arising from offshore oil activities is limited and the risks to the marine environment resulting from the release of “typical” oil-industry related chemicals are poorly understood. A high number and large quantity of often unknown chemicals in complex mixtures originating from offshore oil and gas activities in Europe enter in the marine environment, with largely unknown consequences.

Efforts and applied practices to monitor the release and effects of chemicals from the off-shore oil and gas industry in Europe vary from country to country as there is no consistent Pan-European legal framework/regulation which covers chemicals from oil and gas industry activities at sea. Some guidelines exist, but not all countries follow them rigorously.

Traditionally, during the drilling phase, existing monitoring efforts have mainly been oriented towards the benthic environment, as effects are mostly expected in that compartment. Because of changes in drilling practices, however, the impacts on benthos during drilling have reduced considerably and hence there is less need for benthic monitoring. At the same time, activities are shifting more and more into deeper waters and it is recommended that water monitoring is also carried out during the drilling phase. Benthic monitoring will remain relevant to assess the recovery process, but not necessarily to evaluate the effects on the benthic environment as such. A reduction in benthic monitoring will allow resources to become available for more intensive “produced water” monitoring.

During the production phase, there is an impact from produced water. While the composition, potential toxicity and effects of produced water is poorly understood, evidence suggests that the potential adverse effects from produced water related compounds are a cause for concern. Hence, there is a need for more extensive produced-water monitoring and assessment and guidelines on how this should be achieved. Therefore, more resources need to be allocated to the development of tools and techniques and to set up relevant monitoring initiatives. More research is needed to overcome a number of complicating factors such as high dilution of the produced water and the changes in plume direction.

Information on the release and effects of hydrophobic chemicals with low solubility from shipping is limited and the risks to the marine environment resulting from their release are, therefore, poorly understood. To be able to assess and manage the actual risks linked to release of these substances there is a need to:

- Evaluate the importance (e.g. frequency and quantity of release) and environmental effects of all substances (X, Y, Z, or OS of MARPOL Annex II) presently being transported and/or discharged, accidentally, legally or illegally;
- Identify and assess the chemical composition and (possible) chemical reactions of substances or mixtures of substances when they enter marine environments (thus including permitted additives or cleaning agents used during operational discharges, also of otherwise non-hazardous substances), in the GESAMP hazard evaluation procedure under more realistic conditions, for example by using marine mesocosms;
- Initiate monitoring programmes of new and emerging substances which have been shown to enter marine environments within the MARPOL context.

6. There is a **need to develop and apply state of the art environmental risk assessment procedures** (combining exposure and effect assessments, including human health) **to evaluate the impact of noxious liquid substances listed under MARPOL Annex II** on the different compartments in coastal and open sea ecosystems.

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List of acronyms and abbreviations

ACH : acetyl cholinesterase	DSL : Domestic Substances List	ICSC : International Chemical Safety Cards
AEPS : Arctic Environmental Protection Strategy	DYNAMEC : Dynamic Selection and Prioritisation Mechanism	IL : Israel
AHTN : Tonalide	DZ : Algeria	IMO : International Maritime Organisation
AL : Albania		IMW : International Mussel Watch
ALA-D : Delta-aminolevulinic acid dehydratase activity	EACs : Environmental Assessment Criteria	IOC : Intergovernmental Oceanographic Commission
AMAP : Arctic Monitoring and Assessment Programme	EC : Effect Concentration	IS : Iceland
AoA : Assessment of Assessments	EC : European Commission	IT : Italy
	ECHA : European Chemicals Agency	ITMS : Ion Trap-Mass Spectrometry
BA : Bosnia and Herzegovina	EcoQOs : Ecological Quality Objectives	IUPAC : International Union of Pure and Applied Chemistry
BACs : Background Assessment Criteria	EE : Estonia	
BaPH : Benzo(a)pyrene hydroxylase	EEA : European Economic Area	JAMP : Joint Assessment and Monitoring Programme
BCF : Bioconcentration Factor	EEC : European Economic Community	JMP : Joint Monitoring Programme
BCs : Background Concentrations	EG : Egypt	
BECPELAG : Biological Effects of Contaminants in Pelagic Ecosystems	EHS : Evaluation of the Hazards of Harmful Substances Carried by Ships	KIMO : Kommunenes Internasjonale Miljøorganisasjon; Local Authorities International Environmental Organisation
BEEP : Biological Effects of Environmental Pollution	EMEA : The European Medicines Agency	
BEQUALM : Biological Effects Quality Assurance in Monitoring Programmes	EMODNET : European Marine Observation and Data Network	LB : Lebanon
BFRs : Brominated Flame Retardants	EQS : Environmental Quality Standards	LBS : land-based sources
BG : Bulgaria	EROD : 7-ethoxyresorufin O-deethylase	LC : Lethal Concentration
BLG : Bulk Liquids and Gases	ES : Spain	LC-MS : Liquid Chromatography-Mass Spectrometry
BRCs : Background Reference Concentrations	EU : European Union	LMS : Lysosomal Membrane Stability
BSC : Black Sea Commission		LT : Lithuania
	FI : Finland	LV : Latvia
CA : Canada	FR : France	LY : Libya
CAS : American chemical society		MA : Morocco
CBD : Convention on Biological Diversity	GC-MS : Gas Chromatography-Mass Spectrometry	MAP : Mediterranean Action Plan
Cd : Cadmium	GE : Georgia	MARPOL : International Convention for the Prevention of Pollution from Ships
CEMP : Coordinated Environmental Monitoring Programme	GEF : Global Environment Facility	MC : Monaco
CHARM : Chemical Hazard and Risk Management	GESAMP : Group of Experts on Scientific Aspects of Marine Environmental Protection	MEDPOL : Programme for the Assessment and Control of Pollution in the Mediterranean region
CLRTAP : Long-Range Transboundary Air Pollution	GHS : Global Harmonized System	MEPC : Marine Environmental Protection Committee
COMMPs : Combined Monitoring-based and Modelling-based Priority Setting	GIWA : Global International Waters Assessment	MSC : Maritime Safety Committee
CPDU : 1-(3-chlorophenyl)-3,1-dimethylurea	GPA : Global Programme of Action (GPA)	MSFD : EU Marine Strategy Framework Directive
CY : Cyprus	GR : Greece	MT : Malta
	GST : Glutathione S-transferase	MT : Metallothionein
DBDPE : Decabromodiphenylethane		MW : Molecular Weight
DCPMU : 1-(3, 4-dichlorophenyl)-3-methylurea	HBCD : Hexabromocyclododecane	
DCPU : 1-(3, 4-dichlorophenyl)urea	HCB : Hexachlorobenzene	NGOs : Non-Governmental Organizations
DDT : dichlorodiphenyltrichloroethane	HELCOM : Helsinki Commission	NLS : Noxious Liquid Substances
DE : Germany	Hg : Mercury	NO : Norway
DK : Denmark	HHCB : Galaxolide	NOAA : National Oceanic and Atmospheric Administration (US)
DREAM : Dose Related Effects Assessment Model	HM : Heavy Metals	NOECs : No Observed Effect Concentrations
	HR : Croatia	
	ICES : International Council for the Exploration of the Seas	

List of acronyms and abbreviations

NORMAN: Network of reference laboratories for monitoring and biomonitoring of emerging environmental pollutants	SCCPs: Short Chained Chlorinated Paraffins
OCPs: Organochlorine Pesticides	SE: Sweden
OPs: Organophosphate Esters	SGIMC: Study Group on Integrated Monitoring of Contaminants
OS: Other Substances	SI: Slovenia
OSPAR: Convention for the Protection of the Marine Environment of the North-East Atlantic	SSCPs: Short-chain Chlorinated Paraffins
OTIN: Organotins	SY: Syrian Arab Republic
PAHS: Polycyclic Aromatic Hydrocarbons	TBA: 2,4,6-tribromoanisole
Pb: Lead	TBBPA: Tetrabromobisphenol-A
PBDEs: Polybrominated Diphenyl Ethers	TBT: Tributyltin
PBT: Pentabromotoluene	TCEP: tris-(2-chloro-, 1-chloromethylethyl)-phosphate
PBTs: Persistent, Bioaccumulating and Toxic compounds	TCMTB: 2-(thiocyanomethylthio) benzothiazole
PCBs: Polychlorinated biphenyls,	TCPP: tris-(2-chloro,1-methylethyl)-phosphate
PCDDs: Polychlorinated dibenzodioxins	TDA: trans-boundary diagnostic analysis
PCDFs: Polychlorinated dibenzofurans	TGD: Technical Guidance Document
PCNs: Polychlorinated naphthalenes	TN: Tunisia
PDMS: Polydimethylsiloxanes	TR: Turkey
PFCs: Perfluorinated compounds	UA: Ukraine
PFOS: perfluorooctane sulphonate	UN-ECE: United Nations Economic Commission for Europe
PHS: Priority Hazardous Substances	UNEP: United Nations Environment Programme
PIB: Polyisobutylene	UNESCO: United Nations Educational, Scientific and Cultural Organization
PIC: Prior Informed Consent	US: United states
PL: Poland	UV-320: 2-(3,5-di-t-butyl-2-hydroxyphenyl)-benzotriazole
PLONOR: Pose Little or No Risk	UV-326: 2-(3-t-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole
PNEC: Predicted No Effect Concentration	UV-327: 2,4-di-t-butyl-6-(5-chloro2H-benzotriazol-2-yl) phenol
POPs: Persistent organic Pollutants	UV-328: 2-(2H-benzotriazol-2-yl)-4,6-di-t-pentylphenol
PPCPs: Pharmaceuticals and Personal Care Products	VOCs: Volatile Organic Compounds
PTS: Proficiency Testing Schemes	vPvBs: very Persistent and very Bioaccumulating substances
PUF: Polyurethane foam	VTG: Vitellogenin
PVC: Polyvinylchloride	WFD: EU Water Framework Directive
QA: quality assurance	WG: Working group
QSRs: Quality Status Reports	WG POL: Marine Board Chemical Pollutants Working Group
QUASIMEME: Quality Assurance of Information for Marine Environmental Monitoring in Europe	WKIMON: Workshop on Integrated Monitoring
RCN: Research Council of Norway	
REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals	
RO: Romania	
RSP: Regional Seas Programme	
RU: Russia	

Appendix I. Members of the Marine Board Working Group on existing and emerging chemical pollutants

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Appendix II. Overview of (groups of) substances selected by international organisations

Table Appendix II. Overview of (groups of) substances selected by international organisations

WFD: Water Framework Directive; **AMAP:** Arctic Monitoring and Assessment Programme; **BSC:** Black Sea Commission; **HELCOM:** Baltic Marine Environment Protection Commission or the Helsinki Commission; **MEDPOL:** Programme for the Assessment and Control of Pollution in the Mediterranean region; **OSPAR:** Convention for the Protection of the Marine Environment of the North-East Atlantic; **UNEP POP:** UNEP Global Monitoring Programme for Persistent Organic Pollutants. Compounds in table are those selected as priority substances, which does not mean that they are actually monitored.

“Old” organochlorines	WFD¹	AMAP	BSC	HELCOM	MEDPOL⁶	OSPAR	UNEP POP⁷
Aldrin				X	X		X
Chlordane		X		X	X		X
DDTs		X	X	X	X		X
Dieldrin		X		X	X		X
Endosulphan		X ²	X				X
Endrin		X		X	X		X
Heptachlor		X		X	X		X
Hexabromobiphenyl				X			X
Hexachlorobenzene	XX	X			X		X
Hexachlorocyclohexane isomers (HCH)	XX		X ⁸	X	X	X	X
Mirex		X		X	X		X
PCBs		X	X	X	X	X	X
PCDDs		X		X	X	X	X
PCDFs		X		X	X	X	X
Polychloronaphthalenes (PCNs)		X				X	
Polychlorinated terphenyls				X			
Toxaphene (OSPAR: heptachloronorborene)		X		X	X	X	X
“New” pesticides	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Acrylonitrile				X			
Alachlor	X			X			
Aramite				X			
Atrazine	X ²						
Chlordecone				X			X
Chlordimeform				X			
Chlorfenvinphos	X						
Chlorpyrifos	X ²						
Dicofol						X	
Diuron	X ²						
Ethyl O-(p-nitrophenyl) phenyl phosphonothionate (EPN)						X	
Flucythrinate						X	
Fluoroacetic acid and derivatives				X			
Isobenzane				X			
Isodrin				X		X	
Isoproturon	X ²						
Kelevan				X			
Methoxychlor						X	

“New” pesticides	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Morfamquat				X			
Nitrophen				X			
Pentachlorophenol (PCP)	X ²		X ⁹	X	X	X	
Quintozene				X			
Simazine	X ²						
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)				X			
Tetrasul						X	
Trifluralin	X ²					X	
VOCs	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
1,2,3-Trichlorobenzene	X					X	
1,2,4-Trichlorobenzene	X					X	
1,2-Dibromomethane				X			
1,2-Dichloroethane	X						
1,3,5-Trichlorobenzene	X ²					X	
Benzene	X						
Dichloromethane	X						
Trichloromethane	X			X			
PAHs	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Polycyclic aromatic hydrocarbons	XX ³	X	X ¹⁰	X	X	X	
Anthracene	X ²					X	
Fluoranthene	X ⁴	X				X	
Naphthalene	X ²	X				X	
“New” organohalogens	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Brominated flame retardants	XX ⁵	X				X	
1,3,5-tribromo-2-(2,3-dibromo-2-methylpropoxy)-benzene						X	
Hexabromocyclododecane (HBCD)		X					
Hexachlorobutadiene	XX						
Hexachlorocyclopentadiene (HCCP)						X	
Pentabromoethylbenzene		X				X	
Pentachloroanisole		X				X	
Pentachlorobenzene	XX						X
2-Propenoic acid, (pentabromo)methyl ester						X	
Short-chain chlorinated paraffins (SCCPs)	X	X		X		X	
Tetrabromobisphenol A (TBBP-A)		X				X	

Appendix II. Overview of (groups of) substances selected by international organisations

Endocrine disruptors	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Nonylphenol/ethoxylates (NP/NPEOs)							
and related substances	XX			X		X	
Octylphenol	X ²					X	
Phthalates: dibutylphthalate, diethylhexylphthalate (DEHP)	X ²			X		X	
Other organic chemicals	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
1,5,9-Cyclododecatriene						X	
2,4,6-Tri-tert-butylphenol						X	
3,3'-(ureylenedimethylene) bis(3,5,5-trimethylcyclohexyl)-diisocyanate						X	
4-(dimethylbutylamino)-diphenylamin (6PPD)						X	
4-tert-Butyltoluene						X	
Clotrimazole						X	
Cyclododecane						X	
Diosgenin						X	
Hexamethyldisiloxane (HMDS)						X	
Musk xylene				X		X	
Neodecanoic acid, ethenyl ester						X	
Perfluorooctanol sulphonic acid and its salts (PFOS)		X				X	X
Triphenyl phosphine						X	
Metals and related compounds	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Cadmium	XX	X	X	X	X	X	
Lead and organic lead compounds	X ²		X	X	X	X	
Mercury and organic mercury compounds	XX	X	X	X	X	X	
Nickel and its compounds	X	X	X ¹¹		X		
Organic tin compounds	XX	X		X	X	X	
Selenium and its compounds		X		X			
Radionuclides	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	UNEP POP
Tritium						X	
Cs-137		X	X ¹⁰			X	
Tc-99						X	
Pu-239,240		X				X	

1 For the WFD: WFD identifies priority (X) and priority hazardous (XX) substances, in principal all compounds have to be monitored on a monthly basis as soon as the EQS is not met.

2 This priority substance is subject to a review for identification as possible "priority hazardous substance".

3 Benzo(a)pyrene, benzo(b) and benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene.

4 Fluoranthene is on the list as an indicator of other, more dangerous Polycyclic Aromatic Hydrocarbons.

5 Only pentabromobiphenylether

6 For MEDPOL: Marked in blue the parameters actually monitored

7 For UN-POP: Monitoring within this convention is not mandatory

8 Lindane, optional in Water, mandatory in Sed and Biota

9 Group name "Phenols Chlorinated" is included in the BSC monitoring program as optional parameter. Individual compounds are not specified. The same for detergents.

10 Monitoring is optional for this compound(s)

11 Monitoring in sediment and biota is optional for this compound(s)

Appendix III. Biological effects monitoring recommended by different international organizations

Table Appendix III. Overview of (groups of) substances selected by international organisations

QA: Quality Assurance; **WFD:** Water Framework Directive; **AMAP:** Arctic Monitoring and Assessment Programme; **BSC:** Black Sea Commission; **HELCOM:** Baltic Marine Environment Protection Commission or the Helsinki Commission; **MEDPOL:** Programme for the Assessment and Control of Pollution in the Mediterranean region; **OSPAR:** Convention for the Protection of the Marine Environment of the North-East Atlantic; **ICES:** International Council for the Exploration of the Sea; **UNEP:** UNEP Global Monitoring Programme for Persistent Organic Pollutants

Water and Sediments	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
Benthic community analysis	B	X					X	X	
Whole sediment bioassays	B						X	X	
Sediment pore-water and/or elutriate bioassays							X	X	
Water bioassays							X	X	
Eco-assays		X							
Mussels	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
Stress						X			
Lysosomal membrane integrity (including NRR)	O/B/U		X		?	X	X	X	X
Lipofuscin lysosomal accumulation						X			
Peroxisome proliferation						X			
Scope for growth	Q/O		X					X	
Acetylcholinesterase (AChE) inhibition	O				?	X		X	X
Metallothionein (MT) concentration	O		X		?	X			
Histopathology					?			X	
Genotoxic damage					?	X			
Micronucleus formation					?	X			
DNA damage	B		X		?	X			
Gastropods	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
Imposex/intersex	Q/B		X		X		X-M	X	
Fish	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
Lysosomal Stability					?	X	X	X	
Liver Neoplasia/ Hyperplasia/ Nodules	B				X		X-V	X	
Externally Visible Fish Diseases	B				X		X-V	X	
Reproductive Success in Fish	B				X		X	X	
Acetylcholinesterase (AChE) induction	O				?		X	X	X

Appendix III. Biological effects monitoring recommended by different international organizations¹

Fish	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
Metallothionein induction	B		X		?		X	X	X
ALA-D inhibition	B		X				X	X	
CYP1A and/or EROD induction	B		X		X	X	X	X	X
Bulky DNA formation	B					X	X	X	
PAH metabolites	Q				?		X	X	
Liver pathology	B		X		X		X	X	
Intersex					?			X	
Vitellogenin induction	B						X	X	
Lipofuscin lysosomal accumulation						X			
Micronucleus formation					?	X			
<i>In vitro</i> assays (cells)	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
CALUX								X	
YES gene assay								X	
YAS gene assay								X	
Birds									
Reproductive effects					X				
CYP1A- EROD			X						
Thyroxin (T4 and T4 to T3 ratio) in blood			X						
Hepatic vitamin A			X						
DNA adducts			X						
Marine Mammals	QA	WFD	AMAP	BSC	HELCOM	MEDPOL	OSPAR	ICES	UNEP
Reproductive effects					X				
CYP1A- EROD			X						
Thyroxin (T4 and T4 to T3 ratio) in blood			X						
Hepatic vitamin A			X						
DNA adducts			X						
Immunoglobulin concentrations (both IgG and IgM)			X						
DNA adducts			X						
Immunoglobulin concentrations (both IgG and IgM)			X						

1 For Quality Assurance: B=BEQUALM; Q=QUASIMEME; O= Other (EU projects BEEP; COMPREEND); U=UNEP MEDPOL.

2 For OSPAR: V=Voluntary; M=Mandatory

3 For HELCOM: X=Monitored by HELCOM partners as part of COMBINE programme (see also www.helcom.fi/groups/monas/CombineManual/PartD/en_GB/main) and ?=Application is presently evaluated within the BONUS+ BEAST project (www.bonusportal.org/research_projects/research_projects/beast/)

4 For MEDPOL: The biological effects component of the programme is in the pilote phase, but it is not to be considered as a monitoring programme in place / Lysosome Membrane Stability is the preferred bioindicator measured.

Appendix IV. Persistence, bioaccumulation and toxicity criteria for identifying substances of concern and safety net procedures

This appendix summarizes the Persistence (P), Bioaccumulation (B) and Toxicity (T) criteria used by various organisations or countries for identifying chemicals which have intrinsic properties that give cause for concern about their potential to damage the environment or human health based on persistence, bioaccumulation and toxicity. Although this approach is useful for the prioritisation and selection of substances to be monitored, it cannot be considered as a risk assessment of these compounds. These approaches are mainly based on the intrinsic properties of the substance and, as such, do not consider all processes involved in the exposure and effects assessment, i.e. the two main pillars of an environmental risk assessment.

Persistence (P), bioaccumulation (B) and toxicity (T) criteria for identifying substances of concern:

- $P = t_{1/2} \text{ water} > 2 \text{ months}$ or $t_{1/2} \text{ soil/sediment} > 6 \text{ months}$
- $B = \log K_{ow} > 4$ ($K_{ow} > 10,000$) or Bioconcentration Factor (BCF) > 500 where data are available. If experimental BCF is < 500 , $\log K_{ow}$ does not apply.
- $T = \text{Acute } L(E)C50 < 1 \text{ mg L}^{-1}$ or long term $NOEC < 0.1 \text{ mg L}^{-1}$ OR category 1 or 2 carcinogen, mutagen or reprotoxin and category 3 mutagens.
- OR evidence of endocrine disrupting effects.

Very Persistent (vP) and very bioaccumulative (vB) criteria for identifying substances of concern:

- $vP = t_{1/2} \text{ water} > 2 \text{ months}$ or $t_{1/2} \text{ soil/sediment} > 6 \text{ months}$
- $vB = \log K_{ow} > 5$ ($K_{ow} > 100,000$) or Bioconcentration Factor (BCF) > 5000 where data are available. If experimental BCF is < 5000 , $\log K_{ow}$ does not apply.

In addition to the criteria above, and to assist in prioritizing the consideration of chemicals, the UK government (2008) recommends the following criteria for substances of highest concern:

- $P = t_{1/2} \text{ marine water} > 60 \text{ days}$, fresh water $> 40 \text{ days}$ or $t_{1/2} \text{ marine /sediment} > 180 \text{ days}$, freshwater sediment $> 120 \text{ days}$.
- $B = \log K_{ow} > 4.5$ or Bioconcentration Factor (BCF) > 2000 where data are available. If experimental BCF < 2000 , $\log K_{ow}$ does not apply.
- $T = \text{Acute lethal (effect) concentration } L(E)C50 < 0.1 \text{ mg L}^{-1}$ or long term no observable effect concentration, $NOEC < 0.01 \text{ mg L}^{-1}$ OR category 1 or 2 carcinogen, mutagen or reprotoxin, and category 3 mutagens and reprotoxins
- OR evidence of endocrine disrupting effects.

Certain European authorities and OSPAR have also adopted a “safety net procedure” for chemicals that do not meet the PBT or vPvB criteria but where there are reasons to believe that the chemicals raise equivalent concerns. Given here as an example, the UK government’s Advisory Committee on Hazardous Substances (ACHS) advised that the following types of organic substances or scenarios could be subject to the safety net procedure:

- Substances that are very toxic (vT) to organisms in the aquatic or terrestrial compartments: For example, substances with acute toxicity $L(E)C50 < 0.1 \text{ mg L}^{-1}$, $NOEC < 0.01 \text{ mg L}^{-1}$ ($L(E)D50 < 0.1 \text{ mg kg}^{-1}$, $NOED < 0.01 \text{ mg kg}^{-1}$). Such substances may not be sufficiently persistent or bioaccumulative to meet the PBT criteria, but due to their potent toxicity may still be a cause for concern, especially if they are continually released to the environment.
- Substances which are actually or potentially very bioaccumulative (vB) by whatever mechanism (not necessarily just lipophilic compounds, but also those that accumulate in bone, bind to proteins etc). These may include, for example, substances with a $BCF > 10,000$ or substances with a $\log K_{ow} > 6$, respectively. Note - BCFs must be determined in typical environmental concentrations to give an accurate indication. Bioaccumulation factors should also be used where available. These substances (especially if actually found in biota) may be of concern due to their bioaccumulation, even if their persistence and toxicity do not meet the standard EU TGD criteria. Substances with a very high $\log K_{ow}$, however, may have reduced bioavailability to organisms as they may sorb very strongly to soils and sediments, and may not be freely available in water. Substances which are both bioaccumulative and toxic (i.e. B and T) also may be a cause for concern, especially if the substances are released regularly (i.e. the input load is greater than the degradation removal).
- Organic substances that may persist in the environment for many years ($t_{1/2} > 10 \text{ years}$), or for shorter periods where evidence suggests that adverse effects to the environment and human health may occur. Evidence of potential adverse effects may be identified by measurement via testing, by modelling predictions, or by monitoring. Adverse effects may include interference with biogeochemical cycles or toxicity to humans or other organisms.
- Substances that may cause adverse effects measured, or detected, as novel toxicity endpoints. Such substances may cause sub-lethal effects that might result in population level effects for exposed species, and could include endocrine-disrupting chemicals, for example. Further scrutiny on a case by case basis may be required to determine whether or not a particular substance should be included in the safety net.
- The safety net will consider additional substances identified on other appropriate priority lists such as OSPAR, which apply to the UK as a consequence of our European and/or international commitments. If these

Appendix IV. Persistence, bioaccumulation and toxicity criteria for identifying substances of concern and safety net procedures

substances comply with one or other of the proposed safety net criteria, they will be retained. If not, they will be considered further to determine if they require inclusion in the safety net due to some unforeseen potential hazard or whether they should not form part of the safety net list.

- Substances that are very toxic to organisms in either the aquatic or terrestrial compartments. Toxicity thresholds for inorganic substances could be those with acute toxicity of $L(E)C50 < 0.1 \text{ mg L}^{-1}(\text{Kg})$, or point estimate (or $\text{NOEC/D}) < 0.01 \text{ mg L}^{-1}(\text{Kg})$.
- Substances that are actually or potentially very bioaccumulative in organisms, by whatever mechanism. These may include, for example, substances with a $\text{BCF/BAF} > 5,000$. The UK government points out that to eliminate the bioaccumulation concern, then BCF/BAF data should only be used if the experiments were conducted at environmentally relevant concentrations. Finally, chemicals identified under the safety net criteria would require case-by-case consideration by the ACHS prior to the Chemicals Stakeholder Forum's consideration for risk management.

Appendix V. OSPAR Decisions, Recommendations and Guidelines relevant to offshore oil and gas industry

- OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic – Annex 3;
- OSPAR Decision 98/3 on the disposal of disused offshore installations;
- OSPAR Decision 2000/3 on the Use of Organic-Phase Drilling Fluids (OPF) and the Discharge of OPFcontaminated cuttings;
- OSPAR Recommendation 2003/5 to promote the use and implementation of Environmental Management Systems by the Offshore Industry;
- OSPAR Guidelines 2004/11 for Monitoring the Environment Impact of Offshore Oil and Gas Activities;
- OSPAR Decision 2005/1 and Recommendations 2000/4 and 2005/3 for a Harmonised Mandatory Control System for the use and reduction of the discharge of offshore chemicals;
- OSPAR Recommendation 2006/4 amending OSPAR Recommendation 2001/1 for the Management of Produced Water from Offshore Installations.

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