



Marine Pollution Monitoring Management Group

The Group Co-ordinating Sea Disposal Monitoring

**Final Reports of the
Metals Task Team and the
Organics Task Team**

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Number 49

**Marine Pollution Monitoring
Management Group**

The Group Co-ordinating Sea Disposal Monitoring

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and
The Organics Task Team**

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This report was written by S. M. Rowlatt B.Sc. PhD, CEFAS Burnham Laboratory (Chairman of the GCSDM Metals Task Team), and I. M. Ridgeway B.Sc. PhD, Scottish Environment Protection Agency (SEPA) (Chairman of the GCSDM Organics Task Team). Further copies of the report may be obtained from CEFAS Burnham Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex CM0 8HA.

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FOREWORD

The Group Co-ordinating Sea Disposal Monitoring (GCSDM), a sub-group of the Marine Pollution Monitoring Management Group (MPMMG), was set up in 1987 in order to co-ordinate the monitoring work carried out at sewage-sludge disposal sites. To help achieve its aims, the GCSDM established a number of specialist Task Teams to review the existing procedures used for the monitoring of sewage-sludge disposal sites and to define sediment quality criteria which could be employed to ensure that such waste disposal does not cause undesirable effects.

Two of the initial Task Teams, established in 1988, were the Metals Task Team and the Organics Task Team. These were charged, respectively, with reviewing the monitoring of metal and organic contaminants at sewage-sludge disposal sites; their remits were later extended to include a similar review of dredged material disposal sites. The work of each of these Task Teams extended over a period of six years, to 1994 and included the development of numerical Sediment Quality Standards. The completion of their work occurred at a time when major advances were being made in the development of sediment bioassays and a second report covering the work of the Sediment Bioassay Task Team, established in 1992, will be published alongside this report. In due course, the use of biological techniques may supersede the numerical approaches developed by the Metals and Organics Task Teams, but for the present it is recommended that both should run in parallel.

This document contains the final reports of the Metals and Organics Task Teams. It gives details of their work, their findings and the resulting recommendations as approved by the GCSDM.

METALS TASK TEAM

FINAL REPORT (A summary of work 1988-1994)

EXECUTIVE SUMMARY

The original remit of the Metals Task Team was to review the procedures presently used for monitoring metal contamination at sewage-sludge disposal sites and to make recommendations to the GCSDM accordingly. A review was carried out of the methods used for the collection of sediments at sewage-sludge disposal sites and an intercomparison scheme was devised in order to assess the comparability of the sediment chemical data produced in site surveys.

The scheme consisted of four phases: comparison of sieving techniques by different laboratories; comparison of digestion procedures; intercomparison of the analysis of a standard solution and; a complete analysis comparison. On the basis of the resulting information, the Task Team concluded that valuable improvements would result from both more effective monitoring and also from a single, uniform methodology being used throughout the country. The following is a summary of the Task Team's findings and recommendations:

- Sediment samples from disposal sites should be collected using a non-contaminating grab, such as a Day grab with stainless steel jaws.
- Sediments from sewage-sludge disposal sites should be freeze-dried and sieved through a 63 µm sieve. This fraction should then be digested using *Aqua Regia* and the metals extracted, measured using the analyst's preferred method.
- To provide the necessary quality assurance data (QA), it is recommended that internal reference material (IRM) is analysed at the same time as the unknown sample.
- The results of the intercomparison exercise indicated that the laboratories concerned are all capable of producing analytical data on samples from disposal sites that would be of broadly comparable quality and therefore of a suitable standard to allow comparison across and between disposal sites. However, any new contractor would not necessarily achieve the same standard and would need to demonstrate ability by analysis of appropriate intercomparison materials.
- The Task Team has defined a range of metal concentrations, termed 'Action Levels'. If metal concentrations higher than the 'Action Level' are detected at a disposal site, further studies are recommended to assess their environmental significance.
- Sediments from dredged material disposal sites should be freeze dried and sieved through a 2 mm sieve. This fraction should be digested using hydrofluoric acid (HF) and the metals extracted, measured using the analysts preferred method. The data should be normalised, aluminium or lithium being the preferred normalisers.
- Disposal operations at dredged material sites vary considerably. The Task Team have therefore recommended criteria to allow the selection of those sites likely to require monitoring for sediment metals. The proposals are for guidance only and would, in many cases, mean that monitoring of the disposal site is not required.
- At dredged material sites where monitoring is required, only site specific 'no change' standards are recommended and measurements should be made in relation to a reference site.

1. INTRODUCTION

In the UK, all sewage-sludge disposal sites are monitored to check the extent of chemical contamination. Surveys are undertaken across the area which is likely to be affected by the sludge.

In 1987, much of this work was carried out by various Water Authorities, Purification Boards, MAFF (Ministry of Agriculture, Fisheries and Food), IRTU (Industrial Research and Technology Unit, Northern Ireland) and the Scottish Office. There had, at that time, been little concerted attempt either to check the quality of the data obtained by different groups or to harmonise the approaches used in data collection and interpretation.

In order to remedy these deficiencies in relation to metals in sediments, the Group Co-ordinating Sea Disposal Monitoring (GCSDM) established a Task Team to review present procedures, to arrange for a check on the intercomparability of the produced data, and to advise accordingly. The work of the Task Team extended from a consideration of sewage-sludge disposal sites to include the definition of sediment standards at disposal sites and of the sampling and analytical methods to be used at dredged material disposal sites.

This report summarises the Task Team's work and conclusions. It opens with a discussion of the topics dealt with by the group when considering sewage-sludge disposal sites; the sampling and analysis of sediments at sewage-sludge disposal sites, an intercomparison exercise for sediment metal analysis and standards for sediment metals at sewage-sludge disposal sites. The remaining topics covered by this report are the sampling and analysis of sediments at dredged material disposal sites and standards for sediment metals at dredged material disposal sites.

2. SAMPLING AND ANALYSIS AT SEWAGE-SLUDGE DISPOSAL SITES

The Task Team reviewed the methods used for the collection of sediments at sewage-sludge disposal sites. On the basis of this review and an intercomparison exercise (see Section 3), the following approach was decided to be most appropriate.

Samples should be collected using a grab with close-fitting and non-contaminating jaws (e.g. a Day grab with stainless steel jaws). The surface 0-1 cm of the sediment should be sampled using a non-contaminating scoop and the samples stored frozen until analysis.

On return to the laboratory, the sediment samples should be freeze-dried and sieved through a 63 µm sieve to extract the fine fraction. This fraction should then be digested using *Aqua Regia*. The metals extracted by this acid should then be measured using the analyst's

preferred method, generally atomic absorption spectrophotometry or ICP/MS (inductively coupled plasma/mass spectrometer).

In order to provide the necessary Quality Assurance (QA) data, it is recommended that internal reference material (IRM) is analysed at the same time as the unknown samples.

3. INTERCOMPARISON EXERCISE FOR SEDIMENT METAL ANALYSIS

3.1 Introduction

The method recommended by the Task Team for the measurement of metals in sediments involves freeze-drying the sediment, sieving at 63 µm through a plastic sieve, digestion in *Aqua Regia* and analysis of the digest using the analyst's preferred method (see Section 2).

The Team decided that despite the use of the same methods there would still be an element of uncertainty in the comparison of sediment chemical data produced by different laboratories. In order to assess the comparability of the sediment chemical data produced in sewage-sludge disposal site surveys, an intercomparison scheme was devised by the Metals Task Team.

The scheme included 4 phases:

- Phase 1. Sieving comparison

Individual laboratories sieved and subdivided sediment samples which were then analysed centrally.

- Phase 2. Digestion comparison

A sediment sample was collected, sieved and sub-divided centrally and then digested in individual laboratories. The digest was split, one half analysed centrally and one half in the participating laboratories.

- Phase 3. Standard solution intercomparison.

After phase 2 it was decided that there was some doubt concerning the analytical stage. Therefore, a standard solution was distributed and analysed by the participating laboratories.

- Phase 4. Complete analysis comparison

A sediment sample was collected and split centrally. It was then sieved, digested and analysed by the participating laboratories.

The laboratory codes used in this section are given in Table 1.

Table 1. Laboratory codes used in this report

Code	Laboratory
SOAEFD	Scottish Office Agriculture, Environment and Fisheries Department
MAFF	Ministry of Agriculture, Fisheries and Food (CEFAS, Burnham Laboratory)
WRc	WRc
WE	Wallace Evans
IRTU	Industrial Research and Technology Unit, Northern Ireland
LRC	Lothian Regional Council
DOE/NI	Department of the Environment, Northern Ireland
UCNW	University College North Wales
DAFS	Department of Agriculture and Fisheries for Scotland

3.2 Phase 1. Sieving comparison

Sub-samples of freeze-dried sediment were distributed to the six participating laboratories during October 1988. Participants sub-divided the sample into six portions and sieved through a 63 μm mesh. The sieved portions were then sent to Water Research Centre (WRc) for *Aqua Regia* digestion and analysis.

Results for Cr, Ni, Cu, Zn, As, Cd and Pb are presented in Table 2. The results for chromium were obtained by flame atomic absorption spectrometry (AAS) using an air-acetylene flame as nitrous oxide-acetylene was unavailable at the time of analysis. This means that Cr results may be negatively biased by up to about 30%. In spite of this, the results are valid for comparative purposes.

Apart from copper, the mean laboratory results for each metal were distributed within about $\pm 5\%$ of the mean of all laboratories (Table 3). For some elements, the results of one or more laboratory were significantly different (95% CI) from the mean of all laboratories - though this should not be taken to imply that the mean of all laboratories was in fact the 'correct' result. The only clear pattern that could be observed was that for each metal, the WRc result was the lowest. This may be a reflection of a smaller degree of contamination or the use of an oversize sieve in the WRc set. The data do not, however, allow any firm conclusions to be made.

Initially, it was suspected that the differences between laboratories could have stemmed from differences in the sieving procedure, namely whether a plastic or metal meshed sieve was used. Details of the type of sieve used are given in Table 4. No link could be made between the type of sieve and observed variations in the results.

Table 2. Summary of results of sieving intercomparison

All results in $\mu\text{g g}^{-1} \pm 95\%$ confidence limits
*** = Significantly different from the mean of all laboratories (95% CI)

Chromium		
IRTU	270.17	± 5.33
MAFF	282.17	± 7.78
LRC	274.67	± 4.18
DAFS	284.00	± 5.10 ***
UCNW	273.67	± 2.63
WRc	261.60	± 3.37 ***
Mean	274.38	± 8.59
Nickel		
IRTU	48.75	+ 0.87
MAFF	48.65	± 0.80
LRC	48.25	± 0.92
DAFS	48.57	+ 0.64
UCNW	49.08	± 1.03
WRc	47.78	± 0.89
Mean	48.51	± 0.52
Copper		
IRTU	215.67	± 2.54
MAFF	219.17	± 4.27
LOTHIAN	216.17	± 3.41
DAFS	234.00	± 11.58
UCNW	254.50	± 2.64 ***
WRc	207.67	± 1.44
Mean	224.53	± 17.88
Zinc		
IRTU	489.67	± 7.99
MAFF	509.50	± 10.68
LRC	494.00	± 7.42
DAFS	514.83	± 7.64 ***
UCNW	500.83	± 2.04
WRc	473.67	± 3.23 ***
Mean	497.0	± 15.54
Arsenic		
IRTU	21.45	± 0.55
MAFF	21.55	± 0.43
LRC	21.81	± 0.70
DAFS	22.28	± 0.58 ***
UCNW	21.25	± 0.44
WRc	20.35	± 0.42 ***
Mean	21.45	± 0.68
Cadmium		
IRTU	3.82	± 0.08
MAFF	3.85	± 0.08
LRC	3.89	± 0.12
DAFS	3.96	± 0.08
UCNW	3.94	± 0.04
WRc	3.76	± 0.08 ***
Mean	3.08	± 0.08
Lead		
IRTU	235.50	± 4.24
MAFF	240.67	± 8.37
LRC	233.67	± 4.18
DAFS	242.50	± 7.88
UCNW	229.83	± 3.08
WRc	218.33	+ 1.44 ***
Mean	233.42	± 9.16

Table 3. Range of laboratory results expressed as a percentage of the mean of all laboratories

Chromium	95.4 - 103.5%
Nickel	98.5 - 101.2%
Copper	92.5 - 113.4%
Zinc	95.3 - 103.4%
Arsenic	94.9 - 103.9%
Cadmium	97.2 - 102.3%
Lead	93.5 - 103.9%

Table 4. Type of sieve used in Phase 1 of the intercomparison exercise.

Laboratory	Sieve type
IRTU	Stainless steel
MAFF	Plastic
LRC	Stainless steel
DAFS	Plastic
UCNW	Stainless steel
WRc	Plastic

For several metals, the standard deviations of results varied significantly between participants. In general, large standard deviations were associated with high results (Table 2). Such differences could not be attributed to analytical variations, as all of the analysis was performed at one laboratory. This suggests, though not conclusively, that contamination occurred during sieving at some laboratories.

3.3 Phase 2. Digestion comparison

Sub-samples of freeze-dried sediment were distributed to the participating laboratories. Each laboratory digested 4 g of sediment using *Aqua Regia* for various metals (Cd, Cr, Cu, Pb, Ni, Zn and Hg in some cases), Nitric/sulphuric for mercury and Nitric/sulphuric/V₂O₅ for arsenic. An aliquot of each digest was sent to the WRc for comparative analysis.

Results for Hg, Cd, Cr, Cu, Ni, Zn, and Pb are presented in Table 5 and a summary of some metals is given in Table 6.

This stage of the exercise showed that digestion and analysis by individual laboratories gave results

frequently more than 10% away from the mean of all laboratories and in one case, more than 35% away from the mean. This degree of variation was greater than that shown by central analysis (generally <5%).

Therefore, an additional phase was added to this intercomparison study. For this, standard solutions were distributed and analysed by individual laboratories (see Phase 3 below).

3.4 Phase 3. Standard solution intercomparison

The object of this additional phase (see above) was to test the analytical procedures used at various laboratories. Therefore, two mixed metal standard solutions, as detailed in Table 7, were distributed to all participating laboratories.

The comparative data for this exercise are shown in Table 8. The results using the *Aqua Regia* standard solution show only 2 instances of deviance greater than 15% from the mean of all laboratories. In contrast, the results using the nitric acid standard solution show several instances of deviance greater than 25% from the mean of all laboratories. One laboratory shows a deviance greater than 15% for all metals. This suggests some difficulty analysing a possibly unfamiliar matrix.

The results were considered generally acceptable by the group, although UCNW (University College North Wales) did appear to fall >20% away from the mean of all laboratories more frequently than expected. It was expected that this laboratory would pay some attention to its analytical procedures.

3.5 Phase 4. Complete analysis comparison

Sediment samples were distributed, together with a standard solution, to all participating laboratories. The sediments were sieved, digested and analysed by individual laboratories.

The results of this work are listed in Table 9. Zinc appears to be the most and lead the least uniform across the laboratories. Most results, if UCNW is excluded, fall within 20% of the overall mean. This was the level of acceptability used in the SEDMON (JMG/NSTF/ICES) international exercise. It was considered acceptable by the Task Team and is of a suitable standard for monitoring at sewage-sludge disposal sites to allow comparison across and between disposal sites.

Table 5. Comparison of the analysis of sediment digests

All results are in $\mu\text{g g}^{-1}$ for the sediment as supplied

WRc Analysis: results obtained for the analysis at WRc of the digest solutions prepared by each laboratory

Lab Analysis: results obtained by each laboratory for their own digest solutions

* 5-10% away from mean

** 10-15% away from mean

*** >15% away from mean

	WRc Analysis			Lab analysis		
	Mean	95%CL	% mean of labs	Mean	95%CL	% mean of labs
Cadmium						
WRc	4.89	0.04	100.0	4.89	0.04	93.1*
MAFF	5.04	0.06	103.1	5.4	0.06	102.9
LRC	4.90	0.07	100.2	5.83	0.28	111.0**
IRTU	4.73	0.04	96.7	4.63	0.14	88.2**
UCNW	-	-	-	5.52	-	105.1*
DAFS	-	-	-	5.58	-	-
Mean of labs	4.89			5.25		
std. dev.	0.13 (RSD 2.6%)			0.49 (RSD 9.3%)		
Copper						
WRc	276.1	1.0	100.5	276	1.0	93.2 *
MAFF	281.9	4.2	102.7	323	12	109.1 *
LRC	274.1	5.3	99.8	311	16.1	105.1 *
IRTU	266.4	1.5	97.0	264	2.4	89.1 **
UCNW	-	-	-	308	-	104.1
DAFS	-	-	-	308	-	-
Mean of labs	274.6			296		
std. dev.	6.4 (RSD 2.3%)			25.1 (RSD 8.5%)		
Chromium						
WRc	379.9	16.6	-	380	16.6	95.3
MAFF	-	-	-	460	6	115.4***
LRC	-	-	-	403	22.7	101.1
IRTU	-	-	-	345	3.3	86.6 **
UCNW	-	-	-	405	-	101.6
DAFS	-	-	-	-	-	-
Mean of labs				399		
std. dev.				39.6 (RSD 9.9%)		
Lead						
WRc	281.8	8.8	102.8	282	8.8	93.8 *
MAFF	291.3	8.2	106.3	335	5	111.4 **
LRC	247.1	16.2	90.2	250	30.6	83.2 ***
IRTU	275.9	4.2	100.7	260	5.0	86.5 **
UCNW	-	-	-	376	-	125.1 ***
DAFS	-	-	-	290	-	-
Mean of labs	274.0			300.6		
std. dev.	19.0 (RSD 6.9%)			53.4 (RSD 17.8%)		
ex LRC	283, 7.8, (2.7%)					
Nickel						
WRc	47.0	0.9	102.0	47.0	0.9	98.5
MAFF	46.1	0.6	100.0	49.8	0.4	104.4
LRC	44.7	0.4	97.0	45.4	0.9	95.2
IRTU	46.4	0.7	100.7	48.7	0.4	102.1
UCNW	-	-	-	65	-	136.3 ***
DAFS	-	-	-	49.5	-	-
Mean of labs	46.1			47.7 (ex UCNW)		
std. dev.	1.0 (RSD 2.2%)			1.9 (RSD 4.0%)		
Zinc						
WRc	599.8	10.9	100.8	600	10.9	
MAFF	609.9	11.1	102.5	693	5	115.6
LRC	589.8	9.4	99.1	672	25.6	113.9
IRTU	580.6	7.6	97.6	550	13.1	94.8
UCNW	-	-	-	647	-	-
DAFS	-	-	-	664	-	-
Mean of labs	595.0			632.4		
std. dev.	12.6 (RSD 2.1%)			57.6 (RSD 9.1%)		
Mercury						
WRc	-	-	-	-	-	-
MAFF	-	-	-	1.57	0.05	-
LRC	-	-	-	1.58	0.24	-
IRTU	-	-	-	1.83	0.19	-
UCNW	-	-	-	-	-	-
DAFS	-	-	-	-	-	-
Mean of labs	-			-		
std. dev.	-			-		

Table 6. Range of laboratory results in the digestion intercomparison. Data expressed as a percentage of the mean of all laboratories

	WRc analysis	Lab analysis
Cadmium	96.7-103.1	88.2-111.0
Chromium	-	86.6-115.4
Copper	97.0-102.7	89.1-109.1
Lead	90.2-106.3	83.2-125.1
Nickel	97.0-102.0	95.2-104.4 (ex UCNW)
Zinc	97.6-102.5	94.8-115.6

Table 7. Standards used in Phase 3 of the intercomparison exercise

Solution 1: Mixed Standard - 0.1 M HNO₃

Solution 2 : Mixed Standard - Aqua Regia (concn. as per digest)

Metal	Concentration Range (mg l ⁻¹)
Cd	0.2 - 0.5
Ni	2 - 5
Pb,Cu,Cr	5 - 10
Zn	15 - 20

Table 8. Results of the standard solution intercomparison

* 10-20% away from the nominal

** 20-30% away from the nominal

*** >30% away from the nominal

Laboratory	Aqua Regia		0.1M HNO ₃	
	Concentration found	%Difference from nominal	Concentration found	%Difference from nominal
Chromium (mg l⁻¹)				
Nominal	9.50		9.50	
SOAEFD	11.9	25.3 **	12.3	29.5 **
IRTU	9.76	2.7	9.59	0.9
LRC	9.85	3.7	9.77	2.8
MAFF	10.8	13.7 *	10.3	8.4
WE	9.74	2.5	9.8	3.2
UCNW	7.76	-18.3 *	6.00	-36.8 ***
WRc 1	9.70	2.1	9.77	2.8
WRc 2	(9.70)		(9.80)	
Mean	9.93	4.5	9.65	1.5
Cadmium (mg l⁻¹)				
Nominal	0.450		0.450	
SOAEFD	0.458	1.8	0.468	4.0
IRTU	0.438	-2.6	0.460	2.2
LRC	0.451	0.2	0.453	0.7
MAFF	0.434	-3.6	0.448	-0.4
WE	0.451	0.2	0.449	-0.2
UCNW	0.443	-1.6	0.297	-34.0 ***
WRc 1	0.455	1.1	0.457	1.6
WRc 2	(0.450)		(0.462)	
Mean	0.447	-0.1	0.456	1.3
Copper (mg l⁻¹)				
Nominal	9.50		9.50	
SOAEFD	9.10	-4.2	9.40	-1.1
IRTU	9.81	3.3	9.63	1.4
LRC	10.7	11.3*	10.8	13.5 *
MAFF	9.08	-4.4	9.16	3.6
WE	10.1	5.9	9.94	4.6
UCNW	8.10	-14.7*	7.18	-24.4 **
WRc 1	9.51	0.1	9.60	1.1
WRc 2	(9.64)		(9.83)	
Mean	9.49	-0.1	9.39	-1.2
Lead (mg l⁻¹)				
Nominal	9.50		9.50	
SOAEFD	9.82	3.4	9.78	2.9
IRTU	9.59	0.9	9.66	1.7
LRC	10.8	13.7	10.9	14.7 *
MAFF	10.2	7.4	10.8	13.7 *
WE	9.96	4.8	9.74	2.5
UCNW	9.21	-3.1	7.95	-16.3 *
WRc 1	9.65	1.6	9.65	1.6
WRc 2	(9.58)		(9.74)	
Mean	9.89	4.1	9.78	3.0

Table 8. Results of the standard solution intercomparison - continued

Laboratory	<i>Aqua Regia</i>		0.1M HNO ₃	
	Concentration found	%Difference from nominal	Concentration found	%Difference from nominal
Nickel (mg l⁻¹)				
Nominal	4.50		4.50	
SOAEFD	4.68	4.0	4.74	5.3
IRTU	4.59	2.0	4.58	1.8
LRC	4.88	8.4	5.17	14.9 *
MAFF	3.95	-12.2	4.20	-6.6
WE	4.60	2.2	4.86	8.0
UCNW	4.16	-7.6	3.55	-21.1 **
WRc 1	4.60	2.2	4.63	2.9
WRc 2	(4.60)	(4.66)		
Mean	4.49	-0.1	4.53	0.7
Zinc (mg l⁻¹)				
Nominal	19.0		19.0	
SOAEFD	19.1	0.4	19.8	4.2
IRTU	19.1	0.7	19.4	2.2
LRC	21.1	11.1*	21.4	12.6 *
MAFF	19.3	1.6	19.5	2.6
WE	18.8	-1.1	18.4	-3.2
UCNW	21.0	10.5*	15.4	-18.9 *
WRc 1	19.1	0.5	19.5	2.6
WRc 2	(19.1)		(19.3)	
Mean	19.6	3.3	19.1	0.3

Notes: 1. Both solutions were prepared at the same nominal concentrations from certified standard solutions.
 2. UCNW reported results with and without background correction. All data presented for UCNW is without background correction.
 3. WRc 1 - Solution analysed at WRc 11/04/91
 WRc 2 - Solution analysed at WRc 09/07/91
 Only result from WRc 1 included in mean of all laboratories.

Table 9. Comparison of the complete sediment analysis procedure

All results in µg g⁻¹

Laboratory	Cr	Cr % of mean	Cu	Cu % of mean
Clyde RPB				
IRTU	32.60	111.45	10.80	99.54
LRC	26.50	90.60	10.10	93.09
MAFF	35.40	121.03	12.60	116.13
UCNW	21.30	72.82	9.80	90.32
SOAEFD	30.10	102.91	12.20	112.44
WE	29.60	101.20	9.60	88.48
Mean of labs	29.25		10.85	
Laboratory	Pb	Pb % of mean	Ni	Ni % of mean
Clyde RPB				
IRTU	23.40	91.11	14.10	91.46
LRC	21.90	85.27	14.40	93.41
MAFF	21.00	81.77	14.80	96.00
UCNW	34.50	134.33	17.50	113.51
SOAEFD	31.70	123.43	17.70	114.81
WE	21.60	84.10	14.00	90.81
Mean of labs	25.68		15.42	
Laboratory	Hg	Hg % of mean	Zn	Zn % of mean
Clyde RPB				
IRTU	0.09	81.25	66.00	103.99
LRC			58.60	92.33
MAFF	0.08	73.21	65.60	103.36
UCNW	0.17	147.32	57.20	90.13
SOAEFD	0.11	100.00	76.00	119.75
WE	0.11	98.21	57.40	90.44
Mean of labs	0.11		63.47	

3.6 Conclusions of intercomparison study

- For the sieving comparison, laboratory results were generally comparable to within about $\pm 5\%$ of the mean of all results for each metal, except copper. However, small but significant differences were observed between laboratories. The best comparability was for nickel, the worst for copper.
- For several metals in the sieving comparison, the standard deviations of results varied significantly between laboratories. As such differences could not be attributed to analytical variations, contamination problems may have been experienced in some of the participating laboratories.
- No significant differences could be found between laboratories using plastic or stainless steel sieves.
- Analysis by individual laboratories resulted in greater variation than by one central laboratory. The degree of variation was examined using standard solutions and laboratories informed of possible problems.
- Comparison of the complete analytical procedure showed that all laboratories except one exhibited levels of variability that were internationally acceptable (Table 10).

Table 10. Range of laboratory results in the complete analysis expressed as a percentage of the mean of all laboratories

Element	Range
Chromium	72.8-121.0
Copper	88.5-116.1
Lead	81.8-134.3
Nickel	90.8-114.8
Zinc	90.1-119.8
Mercury	73.2-147.3

4. STANDARDS FOR SEDIMENT METALS AT SEWAGE-SLUDGE DISPOSAL SITES

4.1 Sediment quality criteria

The GCSDM has defined two Environmental Quality Objectives (EQOs) relevant to sediments at disposal sites and suggested the basis for setting standards (MAFF, 1989):

(i) General ecosystem conservation

Objective: Maintenance of environmental quality so as to protect aquatic life and dependent non-aquatic organisms, such that the ecosystem is typical of coastal water with those physical characteristics and latitude.

Basis of standard: Grain-size, carbon/nitrogen and toxic substances to be below levels of effect, and within any Environmental Quality Standard (EQS) set by relevant legislation.

(ii) Preservation of the natural environment

Objective: Outwith the immediate disposal zone, the quality of the receiving environment will be indistinguishable from that of the adjacent estuarine or marine environment.

Basis of standard: Minimal percentage change over background levels of metals and other contaminants. No continuing upward trends after 'steady-state' is achieved.

4.2 Methods used for setting sediment standards

Several different approaches have been used for setting sediment standards. These are listed in this section together with the advantages and disadvantages of each method (Chapman, 1989).

(i) Background sediment chemistry

The background sediment chemistry approach is based on a comparison of concentrations of metals in contaminated sediments with those in reference, uncontaminated sediments.

Advantages

- can be implemented using available data.
- does not require toxicity testing or detailed chemical reasoning.

Disadvantages

- difficult to define reference sediments.
- highly site-specific.
- gives no indication of likely biological effects.
- very subjective and difficult to defend.

(ii) Water Quality Criteria (WQC)

The water quality criteria approach measures the concentration of metals in the interstitial waters of sediments and compares the values with accepted water quality standards.

Advantages

- makes use of well-established toxicological database.

Disadvantages

- difficult to measure interstitial water quality.
- does not relate to mixtures.
- no use if there are no relevant WQC.

(iii) Sediment/water quality equilibrium [Equilibrium Partitioning Approach (EPA)]

This approach combines EPA water quality criteria together with equilibrium partitioning calculations to obtain sediment metal concentrations that give rise to water concentrations equivalent to the Water Quality Standard.

Advantages

- makes use of well-established toxicological database.
- makes use of organic carbon.
- makes use of chemical equilibria which are often well-known.
- a large amount of experimental work which supports this approach has been carried out (largely in the US).

Disadvantages

- synergistic and antagonistic effects are not considered.
- some partition coefficients are uncertain.
- only strictly valid for non-polar organic compounds.
- data do not relate to mixtures.
- sensitive to sediment type.
- water quality criteria are set for pelagic not benthic species.
- may underestimate toxicity to benthos.

(iv) Sediment bioassay

Sediment bioassays may be used in two ways. Firstly, test animals may be exposed to a range of sediments from clean to heavily contaminated areas. The response of the organism considered to be unacceptable is related to the sediment composition, which is then taken as the standard. Secondly, animals may be exposed to a range of spiked sediments. Again, the response of the organism considered to be unacceptable may be related to the sediment composition which is then taken as the standard. In this second case a dose-response curve is developed.

Advantages

- good for identifying problem sediments.
- deals with synergism in real-world sediments.
- does not require prior knowledge of mechanisms of uptake.

Disadvantages

- uncertainty over the cause of any effects seen.
- difficult to implement with a wide range of organisms.
- may not reflect chronic effects.
- massive amount of work to examine mixtures and dosages which can occur.

(v) Screening level concentration

This is a field-based approach that estimates the highest concentration of a contaminant that can be tolerated by approximately 95% of the benthic infauna.

Advantages

- suitable for any chemical component.
- can use existing databases.
- does not require prior knowledge of mechanisms.

Disadvantages

- large amount of field data required.
- values are sensitive to the accuracy of field data used in the calculation.
- assumes that chemicals evaluated are responsible for all of any observed effects on benthos.

(vi) Apparent effects threshold (AET)

This approach uses field data on chemical concentrations in sediments and at least one indicator of bioavailability/bioeffects (e.g. sediment bioassays, benthic infaunal community structure, bottom-fish histopathological abnormalities, bioaccumulation) to determine the concentration of a particular contaminant above which statistically significant biological effects (relative to a reference site) are always expected.

Advantages

- utilises existing databases
- can be used to develop criteria for any contaminant using any effects measure provided it can be statistically evaluated
- does not require prior knowledge of mechanisms
- because biological effects always occur above AET it is non-contradictory

Disadvantages

- requires large database of field measurements
- can be influenced strongly by unknown toxic compounds
- may not reflect chronic effects
- assumes that chemicals evaluated are responsible for all of any observed effects on benthos.

(vii) Sediment Quality Triad

This approach is based on correspondences between 3 measures; sediment chemistry to determine contamination, sediment bioassays to determine toxicity and *in situ* bioeffects to determine alteration of resident communities.

Advantages

- uses a combination of three different measures.
- does not require prior assumptions about mechanisms.
- can be used for any contaminant.
- accounts for both acute and chronic effect.

Disadvantages

- requires a large database.
- can be strongly influenced by unmeasured compounds.
- statistical criteria have not yet been developed.
- methodology not yet developed.

4.3 Metals Task Team standards

It is considered that the two EQOs set by GCSDM are best approached in different ways. Firstly, for 'ecosystem maintenance' standards, a method which ensures that interstitial water concentrations do not exceed a 'safe' level will protect the ecosystem. This has been achieved using the Equilibrium Partitioning method of Pavlou and Weston (1984). Sediment standards calculated by this method are, by definition, 'the concentration in the sediment which ensures that the concentration in the interstitial water does not exceed the published EPA Water Quality Criteria'. The sediment concentrations have had to be modified in some cases taking account of other data or expert knowledge.

Secondly, for 'no-change' standards, methods have been used to calculate the metal concentration in sediments and observe that concentration through time.

4.4 Standards based on the Equilibrium Partitioning method

While there are many problems associated with the definition of standards it is recognised that waiting for all the technical problems to be solved will serve no useful environmental purpose. It is considered better to produce standards now which can reasonably be expected to protect the environment and refine them later as knowledge permits rather than delay environmental protection until high accuracy standards are possible.

The following discussion firstly assesses the aims of setting standards, proposes a method and defines a set of values.

Setting standards for sediment metals

Before setting out to determine a 'standard', 'criterion', 'guideline' or 'action level' it is important to state clearly what is to be achieved using that value. For example, when the value is exceeded, management action may be initiated to close or restrict input to a disposal site or discharge. Alternatively, exceedance may require further scientific studies to be initiated to investigate, chemically or biologically, the availability of the metallic contaminants in the sediment to organisms. Management action, if necessary, would be based on the results of the further studies.

Once the use has been clearly stated it is possible to assess the accuracy with which the value should be defined and the size of the safety factors to be built into it. For example, a value designed only to flag potential problems could err significantly on the side of caution without risking serious consequences of false positive values, while one defined for management decision making would need to be more accurate to provide adequate environmental protection but still avoid unnecessary actions being taken as a result of false positives. In the case of management decision-making it is doubtful whether the necessary level of accuracy is at present achievable.

The Metals Task Team only considered the definition of concentrations which initiate further investigation. These concentrations are termed 'action levels'.

Action level

Several methods for defining standards have been suggested, notably in the American literature (e.g. Chapman, 1989). The more important of these are outlined above in Section 4.2.

The Task Team used the equilibrium partitioning approach which combines distribution coefficients with carbon concentrations to calculate the sediment metal concentration corresponding to the relevant EPA water quality criterion (Pavlou and Weston, 1984). The method is based on the relationship of the metal concentration in sediment adjusted for dependence on organic matter and the concentration in water:

$$K_{OC} = C_{S/OC} / C_{IW}$$

Where: K_{OC} = organic carbon normalised partition coefficient
 $C_{S/OC}$ = sediment concentration normalised to organic carbon
 C_{IW} = interstitial water concentration

The sediment action level is then calculated according to:

$$C_{S/OC} = K_{OC} \cdot C_{IW\text{ std}}$$

Where: $C_{IW\text{ std}}$ = water quality standard

The values of K_{OC} and $C_{IW\text{ std}}$ used in this paper are the same as those of Pavlou and Weston (1984).

This technique is rather simplistic and makes a number of assumptions about the geochemical processes operating in sediments but the Task Team considered that it is appropriate for use as a first stage in assessing sediments. However, it must be noted that while this approach is effective for non-polar hydrophobic organic chemicals it has been criticised when used with metals

(Chapman, 1989) partly because partitioning is dependent on many phases rather than just organic matter and in some cases organic matter is far from being the controlling phase. Also, it only takes account of metal absorbed by organisms from water rather than that absorbed from particulates. More sophisticated methods are being developed but are not yet available.

The action levels were calculated on the basis of this simple method. The values together with the exceptions below are listed in Table 11.

Alteration of action levels to meet practical constraints

Distribution coefficient data are not available for all metals and in some cases the results produced are unacceptable for practical reasons (e.g. they are far below average shale concentrations). In these cases action levels have been set on other bases.

As no suitable data were available to calculate action levels for chromium and nickel, values of 100 mg kg⁻¹ at 1% carbon were chosen.

The calculated value for cadmium was 8 mg kg⁻¹ which, on the basis of experience, was considered too high particularly as it is a List 1 substance with potential for bioaccumulation. The action level was set at 2 mg kg⁻¹.

In contrast to cadmium the value for mercury was considered too low. It was 0.007 mg kg⁻¹, significantly below the average shale value of 0.4 mg kg⁻¹ (Table 11); it was therefore set at 0.4 mg kg⁻¹.

Of course the sediment concentration at which effects occur may be much higher if the nature of the sediment limits the toxicity of a component. For example sulphides may limit the availability of contaminant

metals to biota as the result of the formation of insoluble metal sulphides. Circumstances may change and possibly as the result of a storm or of anthropogenic activity (e.g. dredging) the sulphides could be oxidised and the metals released, giving rise to toxic effects. Thus it is appropriate to consider, when defining sediment action levels, the worst case, i.e. to assume that all the metal in a sediment is capable of participating in equilibrium reactions.

Comparison with other values

For comparison it is of interest to consider the lowest possible value for an action level, viz the average natural concentrations of metals. As such values represent the natural situation, it can be presumed that they are generally non-toxic. The average composition of shale (Krauskopf, 1967) and the composition of pre-industrial sediments from cores give an indication of natural concentrations (Table 11).

Two factors tend to limit the value of a comparison of action levels and average shale and deep core metal concentrations. Firstly there is an unknown degree of diagenetic decomposition of organic matter in both shale and cores which introduces a large element of uncertainty into the carbon values and therefore into metal:carbon ratios, a key element of action levels. Secondly, core concentrations are likely to be site-specific and not always amenable to comparison with regional values.

Despite the limitations of such comparisons they are nonetheless of interest. The calculated action levels at 1% carbon are, with the exception of cadmium, about 1-2.5 times average shale (the calculated cadmium is approximately 25 times average shale). This suggests that, in general, the proposed action levels are not dramatically higher than background concentrations. This observation is supported by the core data; the proposed action levels are 3-5 times higher than the Liverpool Bay core samples.

Chromium and nickel action levels (where no calculations are possible at present) are set at similar values to the shale concentrations but are nonetheless 3 and 5 times higher than the Liverpool core respectively.

Given the present state of uncertainty associated with some of the methods currently available and the limited UK dataset suitable for use in the others it would seem appropriate to attempt a comparison of the action levels with the results of other methods. Table 12 shows a range of standards, guidelines and background values. While it is difficult to compare an organic carbon dependent variable (the action level) with the absolute values of most other techniques, it should be noted that the present values at 1% organic carbon are similar to the ER-L values of Long and Morgan (1990). These values are at the lower end of the range in which Long and Morgan expect effects to occur.

Table 11. Action levels compared with the pre-industrial background in a core from Liverpool Bay (mg kg⁻¹)

Metal	Shale	Liverpool core	Calculated action level	Metals T/T action level
Cadmium	0.3		7.7	2
Chromium	100	29	N/A	100
Copper	57	6.9	34	40
Lead	20	13	33	40
Mercury	0.4		0.007	0.4
Nickel	95	18	N/A	100
Zinc	80	57	190	200

N/A = Not applicable

Table 12. Various quality values (mg kg⁻¹)

Metal	ER-L	ER-M	EP chronic	Puget AET Amphipod	Puget AET Oyster	Puget AET benthic	Puget AET Micro	Metals T/T
Cadmium	5	9	7.7	6.7	9.6	5.8	9.6	2
Chromium	80	145						100
Copper	70	390	34	800	390	310	390	40
Lead	35	110	33	700	660	300	530	40
Mercury	0.15	1.3	0.007	2.1	0.59	0.88	0.41	0.4
Nickel	30	50		120	39	49	28	100
Zinc	120	270	190	870	1600	260	1600	200

ER-L Effects Range Low: The concentration above which adverse effects may be observed in sensitive life stages or species.

ER-M Effects Range Median: The concentration above which adverse effects would almost always be observed

EP Equilibrium Partitioning value

AET Apparent Effects Threshold The concentration above which biological effects are always expected when considering:

Amphipod: amphipod toxicity

Oyster: oyster larval bioassay

Benthic: benthic communities

Micro: Microtox

UK sewage-sludge disposal sites

Figures 1-3 show the values for action levels plotted with values at and around sewage-sludge disposal sites. The data shown in Figures 1 and 2 relate to analyses of the fine (<63 µm) fraction of sediments. Those in 3 are from analyses of the <2 mm fraction of sediment. It

should be noted that because this method deals with the relationship between two variables it is largely independent of grain-size although it must be recognised that grain-size dependent variations in the mineralogy or character of organic matter may have an influence on the applicability of the method.

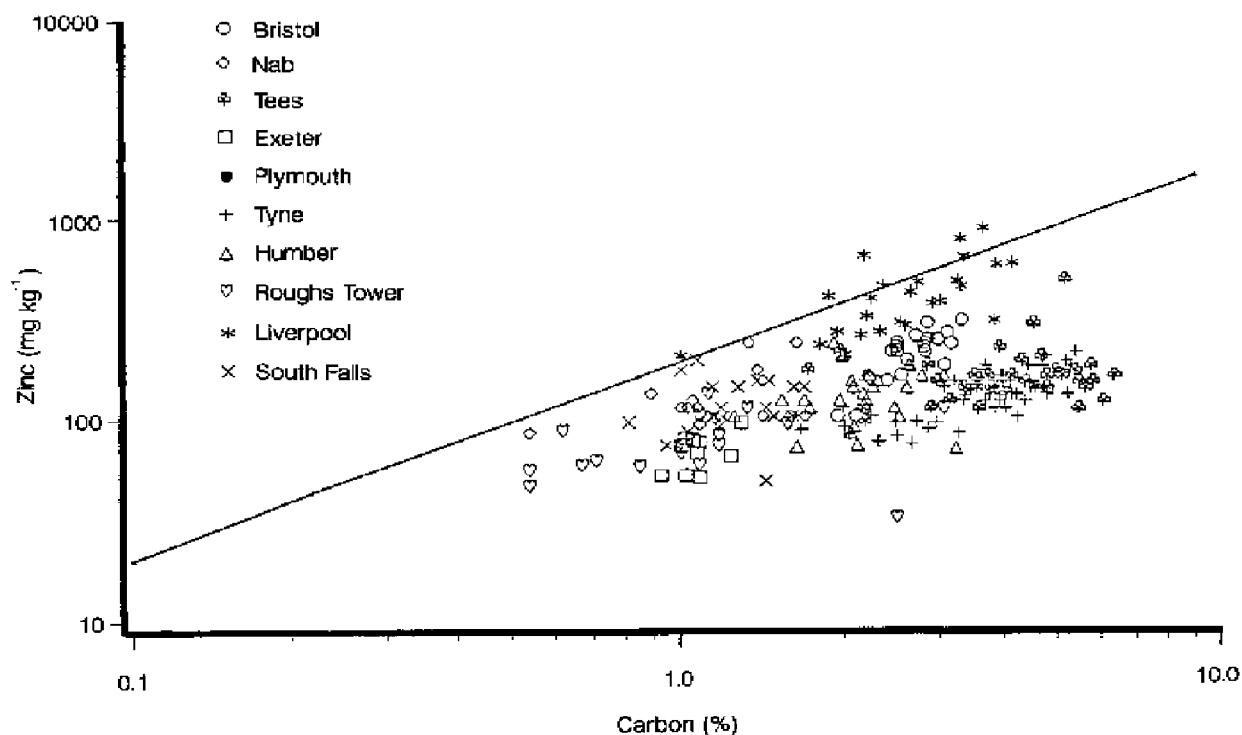


Figure 1. The relationship between zinc (mg kg⁻¹) and carbon (%) in the <63 µm fraction of sediments at and around various sewage-sludge disposal sites off the English coast. The line indicates the proposed action level

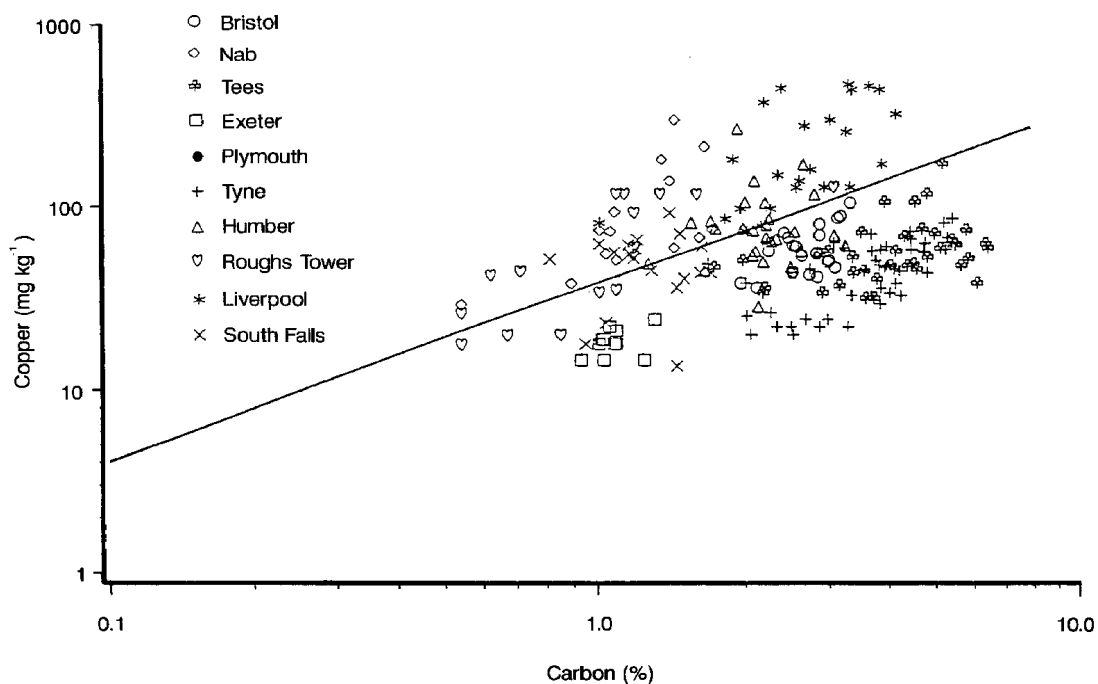


Figure 2. The relationship between copper (mg kg^{-1}) and carbon (%) in the $<63 \mu\text{m}$ fraction of sediments at and around various sewage-sludge disposal sites off the English coast. The line indicates the proposed action level

In the case of zinc (Figure 1), all samples except for a few from Liverpool Bay fall on the 'no action' side of the action level. In the case of copper (Figure 2), some samples from Roughs, South Falls and Humber are above the action level as are most from Liverpool Bay, indicating the need for further study in this area. All the samples from St Abbs Head (Figure 3) are below the action level.

Previous work based on expert judgement had already identified Liverpool Bay as such an area and while this procedure does not add to the cause of environmental protection in this case, the observation does give a degree of confidence that the method is effective.

The question arises whether this technique is appropriate for high-organic sediments. Those at Garroch Head (the only accumulating disposal site around UK) contain a maximum of about 10% organic carbon corresponding to mercury and cadmium action levels of 4 and 20 mg kg^{-1} respectively.

Conclusion

There is a need for values with which to assess the significance of metals in marine sediments, particularly at disposal sites. Robust methods for the calculation of such values are not yet available, but this should not prevent the definition of provisional values designed to protect the marine environment.

This Metals Task Team has defined action levels which are concentrations of metals above which detailed

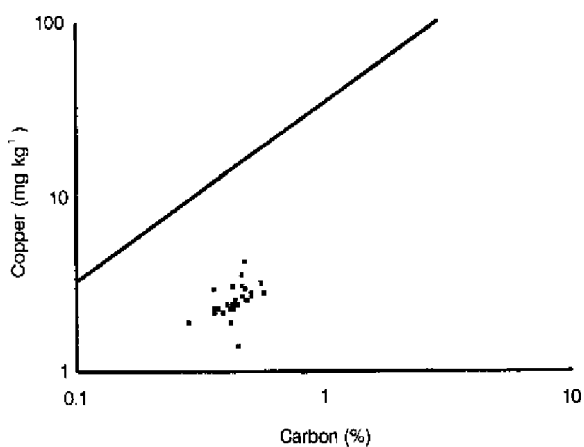


Figure 3. The relationship between copper (mg kg^{-1}) and carbon (%) in the $<2 \text{mm}$ fraction of sediments at and around the St Abbs Head sewage sludge disposal site. The line indicates the proposed action level

studies should be carried out to assess their biological significance. A simple equilibrium partitioning scheme is described for screening sediments at sewage-sludge disposal sites to identify areas where such studies should be carried out.

Many aspects of the approach will be improved with developments in scientific knowledge (e.g. K_{oc} values). In particular the performance of the method at high carbon concentrations needs further study.

4.5 Standards based on limited change

When waste is deposited at a disposal site and the material reaches the seabed there will almost certainly be a change in the quality of the sediment at the seabed. This change is likely to be most pronounced in the early stages of an on-going operation, it will then reach an equilibrium. A standard based on limited change in this 'equilibrium' period will ensure that the quality of the seabed at the disposal site will not become worse. Of course, the standard based on Equilibrium Partitioning (see above) which is designed to protect the ecosystem will also have to be met.

4.5.1 Measuring change

The following section provides two examples of the approach to measuring change in sediment and setting 'no-change' standards.

4.5.2 Tyne

Introduction

In order to improve the water quality of the Tyne estuary, changes were made in the Tyneside sewerage system in the late 1970s. Among these changes were the installation of new collection sewers and treatment facilities, these resulted in the production of quantities of primary settled sewage sludge which is deposited at sea off the River Tyne. The operation started at a low level in 1978 and increased to an annual deposition of approximately 500 000 wet tonnes in 1984, since when it has varied little.

The seabed at the sewage-sludge disposal site consists of soft muddy sand and the water is 50 m deep. The tidal streams run approximately parallel with the coast with maximum velocities of 40 cm s^{-1} .

During the early stages of operation regular monitoring was undertaken with a view to detecting any effects of disposal as soon as they occurred. The monitoring programme was primarily aimed at assessing the condition of the seabed and its associated fauna, although the area was also examined for water and fish quality as part of nation-wide monitoring programmes. The present discussion deals with studies of spatial and temporal changes in surface sediment quality. The temporal component of this work has been carried out since 1987.

Methods

Seabed samples were collected in line with GCSDM guidelines. A 0.1 m^2 Day grab was used to sample the seabed. Immediately after collection a surface scrape of the sediment was taken for bacterial analysis. *E. coli* were enumerated using the membrane filtration procedure described by West (1988).

Sub-samples of the surface 0-1 cm of the sediment were stored frozen for later chemical and physical analysis. On return to the laboratory the sediments were defrosted and sieved at $63 \mu\text{m}$ to extract the fine fraction. The fines were sub-divided and the carbon content of one sub-sample determined instrumentally, after pre-treatment with sulphurous acid to remove any carbonates present. Another sub-sample was digested with *Aqua Regia* and the metals mercury, copper, chromium, nickel, lead and zinc determined using atomic absorption spectrophotometry (Harper *et al.*, 1989).

Results and Discussion

The area of sludge settlement as indicated by faecal bacteria is at and to the south-east of the disposal site (Figure 4). This figure also shows areas of sediment impacted by the outflow of the River Tyne and coastal outfalls, both of which contain sewage bacteria.

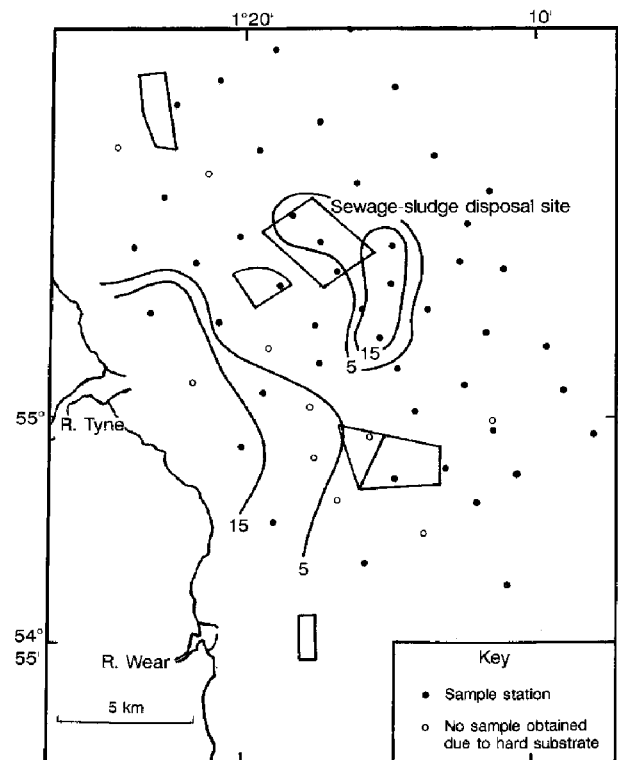


Figure 4. Distribution of *E. coli* in the sediments around the Tyne sewage-sludge disposal site, May 1988

The examples given in Figures 5(a-c) show that there is a general reduction in trace metal and carbon concentrations with distance from the shore and that the outflow of the River Tyne affects sediment composition. However, with the possible exception of chromium, there is no evidence of accumulation of either metals or carbon at the disposal site. In the

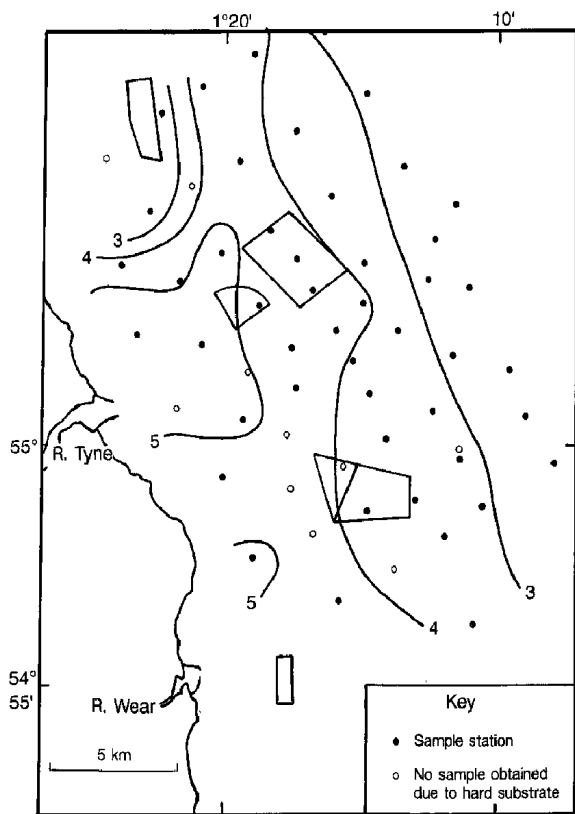


Figure 5(a). Distribution of organic carbon (%) in the <63 μm fraction of sediments around the Tyne sewage-sludge disposal site, May 1988

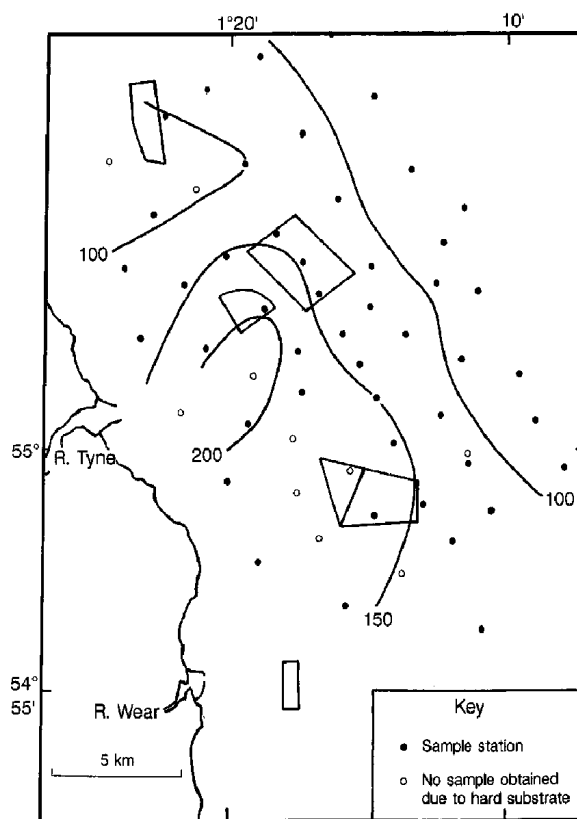


Figure 5(c). Distribution of zinc (mg kg^{-1}) in the <63 μm fraction of sediments around the Tyne sewage-sludge disposal site, May 1988

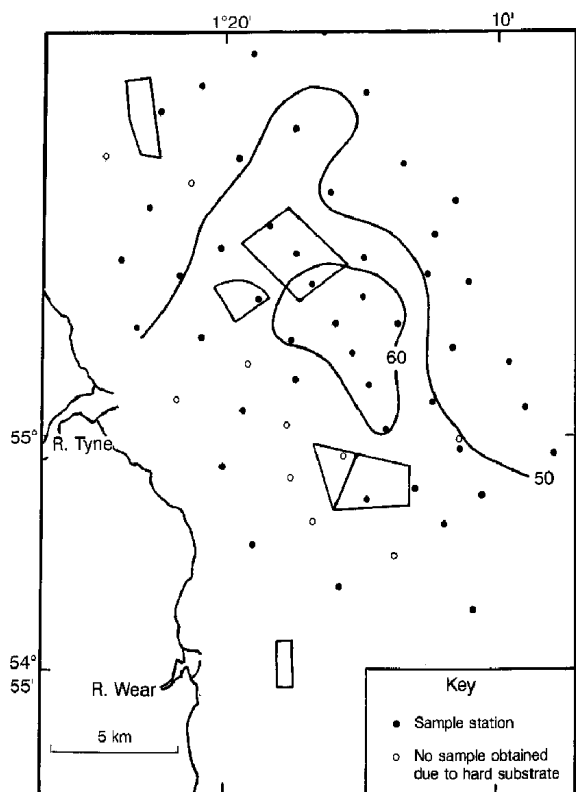


Figure 5(b). Distribution of chromium (mg kg^{-1}) in the <63 μm fraction of sediments around the Tyne sewage-sludge disposal site, May 1988

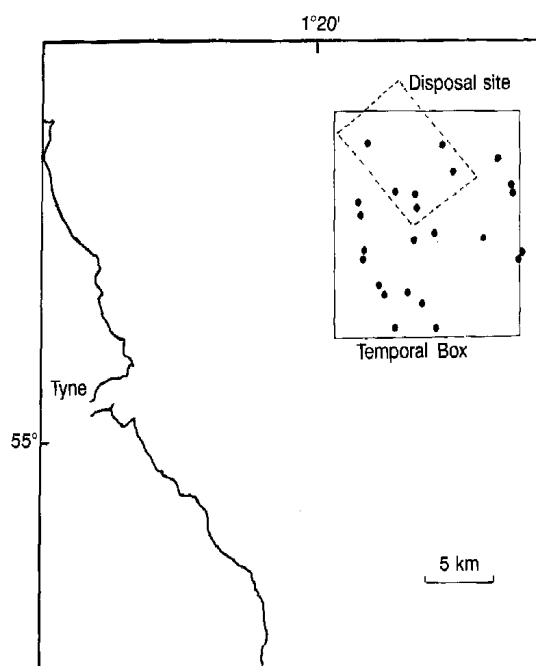


Figure 6. Sampling grid used to assess temporal changes in sediment quality off the Tyne

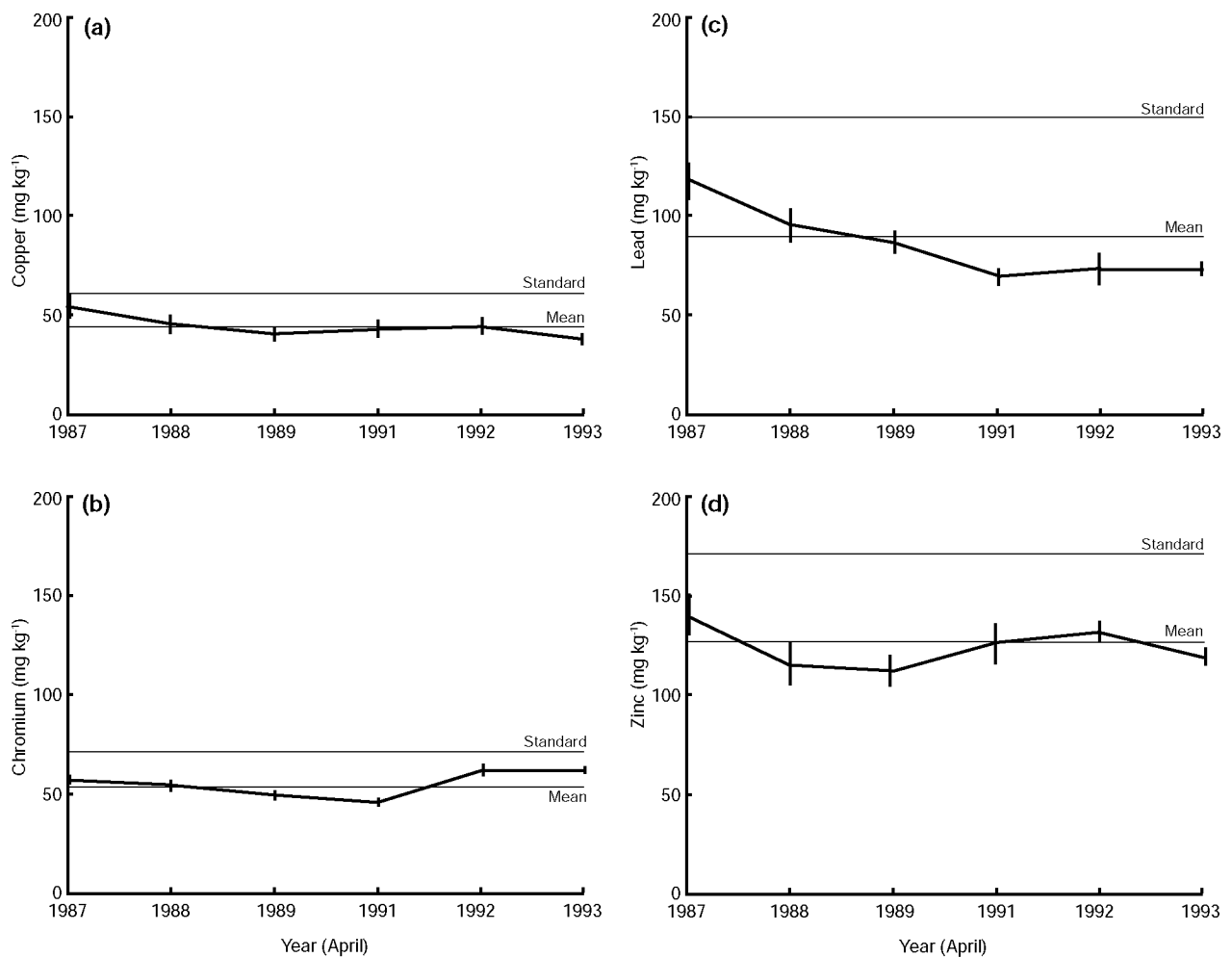


Figure 7. Time-series of concentrations (mg kg⁻¹) of (a) copper; (b) chromium; (c) lead; and (d) zinc in the <63 μm fraction of sediments collected at the Tyne sewage-sludge disposal site (mean concentration ± S.E.). Metals Task Team 'no-change' standards shown on chart

context of the riverine inputs to the nearshore zone it should be noted that the Tyne drains a catchment which includes the heavily mineralised Pennines as well as industrial sources of contamination and the elevated levels of metals cannot be ascribed wholly to man-made contamination.

In order to assess any changes in sediment quality with time a system has been set up based on a stratified random design (Figure 6) in which sediment samples collected in different years can be compared. The samples are collected from an area centred on the zone of initial settlement defined by the faecal bacteria discussed earlier and is designed to detect changes in sediment quality brought about if there is an accumulation of sludge. This design meets the requirements of GCSDM for a 'no-change' standard. This sampling system supersedes an earlier design based on transect sampling which was liable to reflect a component of the general offshore trend of decreasing metal concentrations.

For most elements there is little year to year variation in the results (Figures 7(a-d)).

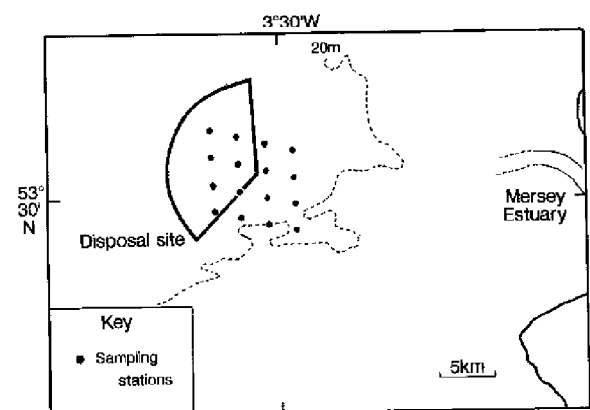


Figure 8. Sewage-sludge disposal site and sediment sampling grid in Liverpool Bay

4.5.3 Liverpool Bay

Introduction

Each year about 1.5 million wet tonnes of sewage sludge are deposited at a designated site in Liverpool Bay (Figure 8) by North West Water Ltd (formerly the North West Water Authority). MAFF (CEFAS, Burnham Laboratory) has studied the area since the 1970s to determine any effects on water, sediment or fish quality.

This work has included the analysis of sediment samples collected near the disposal site (Figure 8), where effects on sediment chemistry have been observed (Norton *et al.*, 1984 and unpublished data).

Methods

Sediment samples were collected using a 0.1 m² Day grab. Samples of the surface 0-1 cm of the sediment were stored frozen for later chemical and physical analysis. On return to the laboratory the sediments were defrosted and sieved to extract the fine fraction. While the 90 µm sieve was not in accord with GCSDM advice, it was used in preference to the 63 µm sieve to ensure consistency with earlier work.

The fines were sub-divided and the carbon content of one sub-sample determined instrumentally, after pretreatment with sulphurous acid to remove any carbonates present. Another sub-sample was digested with *Aqua Regia* and the metals mercury, copper, chromium, nickel, lead and zinc determined by atomic absorption spectrophotometry (Harper *et al.*, 1989).

Results and Discussion

Concentrations of trace metals in the sediments exhibit highly non-normal distributions and are therefore described using non-parametric measures. Figure 9(a-c) shows the median and range of concentrations of mercury, zinc and chromium from 1980 to 1990. The most notable feature of the time series is the absence of any marked trend over the decade of study. Figure 9(d) shows carbon data presented in the same manner as the metal data. This shows a consistent median value during the period 1983 to 1990, although it appears the concentrations may have been slightly lower in the early

years of the decade. The concentration ranges show considerable overlap between all years suggesting that this small difference is of little significance.

When considering data from this sandy area, it must be recognised that the <90 µm fraction in general represents less than 5% of the total sediment and that, when considered on a whole sediment basis, the concentrations of metals are very low.

It is known that sediments in the vicinity of the disposal site contain higher concentrations of several metals (e.g. copper, mercury, zinc and lead) than sediments further away (Norton *et al.*, 1984) and it seems reasonable to conclude that there has been some accumulation of metal contaminants in the area as a direct consequence of the sewage-sludge disposal operation. However, the fact that there has been no increase during the last 10 years indicates that the system is in a steady state and has been so for at least the last decade.

4.6 No-change action levels

The above data show the changes in sediment metal concentrations at the Tyne and Liverpool Bay disposal sites. In order to show the data graphically, the Tyne data have been dealt with using parametric statistics while the Liverpool Bay data have required the use of non-parametric measures.

The Metals Task Team, after examining this information, together with some from the Garroch Head disposal site decided that standards should be set on the basis of a Shewart chart using the standard errors calculated on the basis of 5 year's data. Two standard errors should be

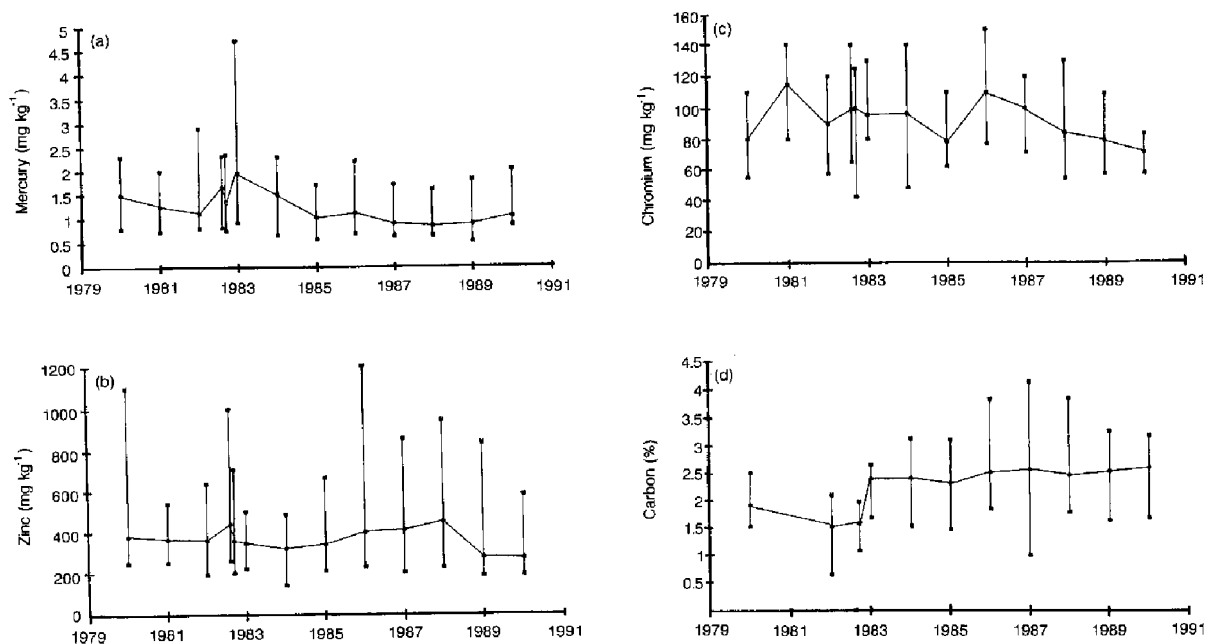


Figure 9. Time series of concentrations of carbon and metals in the <90 µm fraction of sediments collected near the Liverpool Bay sewage-sludge disposal site: (a) mercury; (b) zinc; (c) chromium; and (d) carbon. Bars show median value and range

taken as the warning level and 3 as the Action Level. Figures 7(a-d) illustrate this approach in the case of the Tyne. These figures demonstrate that the sediment metal concentrations at the Tyne have not exceeded the 'no-change' action level. Of course, this approach is equally applicable to skewed data such as that from Liverpool Bay although it may be necessary to log-transform the data.

4.7 Calculation of 'no-change' standards

The following advice is provided to assist with the development of a 'no-change' standard using a control chart survey design.

1. The data should be as homogeneous as possible, i.e. it should have been derived from a consistent approach to sampling, preparation and analysis.
2. As the basic hypothesis is that conditions (i.e. metal concentrations) within the sampling unit are stable, the actual sampling format is immaterial. The important point is that the sampling strategy shall not have changed during the period of the study.
3. The points to be plotted on the control chart, and used for the establishing of the chart, should be the mean values of the metal concentrations for each of the surveys selected.
4. When establishing the chart, the data should be examined for any temporal trend, for example by regression analysis. If a clear trend is found, then the control chart approach is not appropriate, as the fundamental assumption is that conditions are stable. A different approach would be necessary if a temporal trend was present.
5. The control chart may apply to the whole sampling area (e.g. St Abbs Head or Bell Rock), or to only part of it (e.g. the central area of the disposal site, or an annulus at some distance from the centre).
6. The control chart may be set up using actual concentrations, or may be set up using transformed (e.g. log transformed) data, if that increases the approximation of the data to normality. It would be possible to set up control chart limits on non-normal data, assuming a degree of skewness, but these would have presentational difficulties (apparent and obvious, greater tolerance of increases in concentration than of decreases).
7. If the control chart is set up on only a limited amount of data, it would be advantageous to include each new set in the set used to establish the chart, provided there was no indication of temporal trend.
8. The control limits could be set up using standard deviations (in the usual way) or using t-distributions. The latter method takes into account the uncertainty in the estimate of the variance of the distribution of the annual means, and results in wider limits. For example, the t-distribution, equivalent to a 2-sigma warning limit, based on five data points, would be approximately 2.8 sigma. A precautionary approach would suggest using the standard deviation only, but bearing in mind the inherent uncertainties in the positions of the warning and action limits.

5. SAMPLING AND ANALYSIS AT DREDGED MATERIAL DISPOSAL SITES

5.1 Sampling and analysis

Samples of sediment should be collected from the disposal site and a reference site nearby. The reference site should be close enough to be affected by the same general influences as the disposal site, but not so close as to be affected by the disposal operation.

The samples should be collected using a grab with close-fitting and non-contaminating jaws (e.g. a Day grab with stainless steel jaws). The surface 0-1 cm of the sediment should be sampled using a non-contaminating scoop. The samples should be stored frozen until analysis.

On return to the laboratory the sediment samples should be freeze-dried, sieved at 2 mm and completely digested using hydrofluoric acid. The metals extracted should then be measured using the analyst's preferred method, generally atomic absorption spectrophotometry or ICP/MS.

In most cases, only a standard range of contaminants should be analysed; mercury, cadmium, copper, chromium, nickel, lead and zinc. In addition to these contaminants, one or more normalisers should be measured; aluminium, lithium or scandium.

5.2 Interpretation of data

The data from dredged material disposal sites should be normalised using the following procedure.

Normalisation requires the use of a non-contaminant element associated with clay minerals to account for mineralogical variations. Two potential normalising elements are aluminium and lithium. Both of these elements are present in clay minerals and each may act as a surrogate for the clay mineral fraction.

Several methods of normalisation are possible, ranging from the use of simple metal/normaliser ratios to more complex methods based on regression analysis. As some metal/normaliser regressions have significant intercepts on the metal axis, the simple metal/aluminium ratio can lead to spuriously high values at low normaliser concentrations. Therefore it is generally preferable to use a method less sensitive to the effects of an intercept value. One such technique is based on a metal/normaliser regression model with calculation of residuals about the regression line (Figure 10).

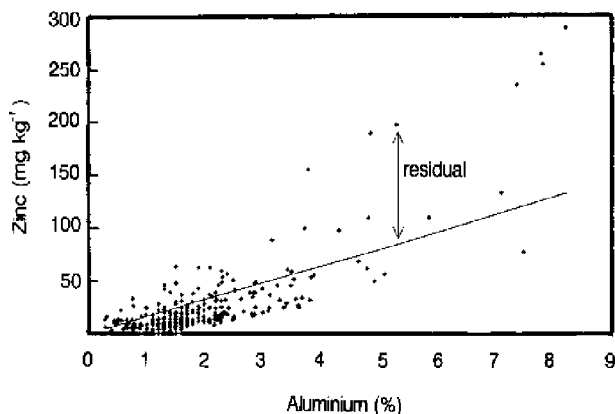


Figure 10. Method of calculation of residuals about metal/aluminium relationships using the relationship between lead and aluminium concentrations in sediments from the western North Sea

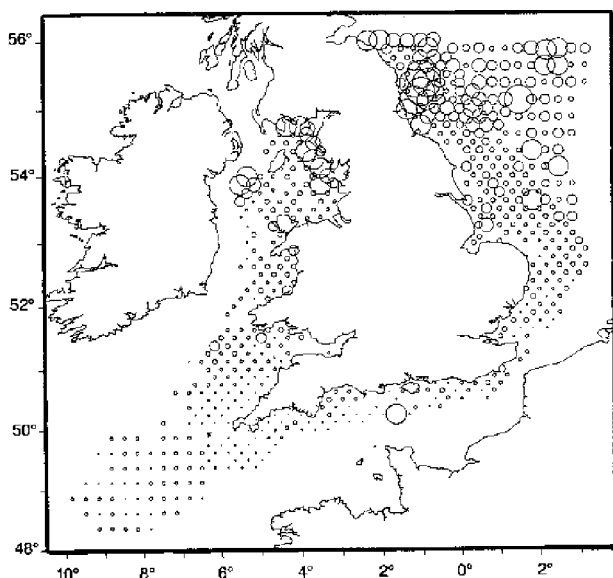


Figure 11. Residual values around the relationship between aluminium and lithium in sediments expressed as percentile groups with boundaries set at 99, 95, 90, 75, 50, 25, 10, 5 and 1 per cent. The highest percentile groups are represented by the largest circles

Various authors have favoured different normalisers. For example, Windom (1986), working in Florida, preferred aluminium, while Middleton and Grant (1990), in the Humber used rubidium. Loring (1991) recommended the use of lithium in areas with sediments derived by glacial processes where aluminium may be present in feldspars in the sand-sized sediment fraction. Figure 11 shows aluminium normalised against lithium and indicates an excess of aluminium in the northern North Sea and suggests that the effect described by Loring affects UK data. However, an examination of sediment lead concentrations in the North Sea (Figure 12) showed little difference in the final results obtained using lithium and aluminium as normalisers, indicating that any such effect is only minor. As, firstly, there was little difference in the overall distribution patterns produced using these two normalisers and secondly, aluminium is more widely accepted as a normaliser, aluminium is therefore generally preferred to lithium.

6. STANDARDS FOR SEDIMENT METALS AT DREDGED MATERIAL DISPOSAL SITES

The disposal operations at dredged material disposal sites vary considerably, depending on the reason for dredging and the nature of the material to be cleared (including the local geology). For example, maintenance dredging at Liverpool to permit access for ships generally yields mud and sand while capital dredging at Felixstowe for the construction of docks produces a range of material from stiff London clay to rock. As well as ranging from fine sediment to coarse rock and massive clay, it can also range from clean to contaminated material.

As well as yielding a range of different materials the type of dredging operation also affects the frequency with which the material is deposited at the disposal site. For example, dock construction generally produces a large quantity of waste in a short period of time and the operation may never be repeated, while channel maintenance can produce waste regularly (possibly even daily).

These variations in the quality of material and the frequency of disposal make monitoring rather more problematic than in the case of sewage-sludge disposal sites where a consistent type of material is deposited regularly and in most cases frequently (more often than daily).

There are more than 120 dredged material disposal sites around UK, about 80 of which are in use at any one time. Monitoring at all sites would be an extremely time-consuming exercise and therefore the Metals Task Team have recommended criteria to allow those sites suitable for monitoring to be selected. The Task Team

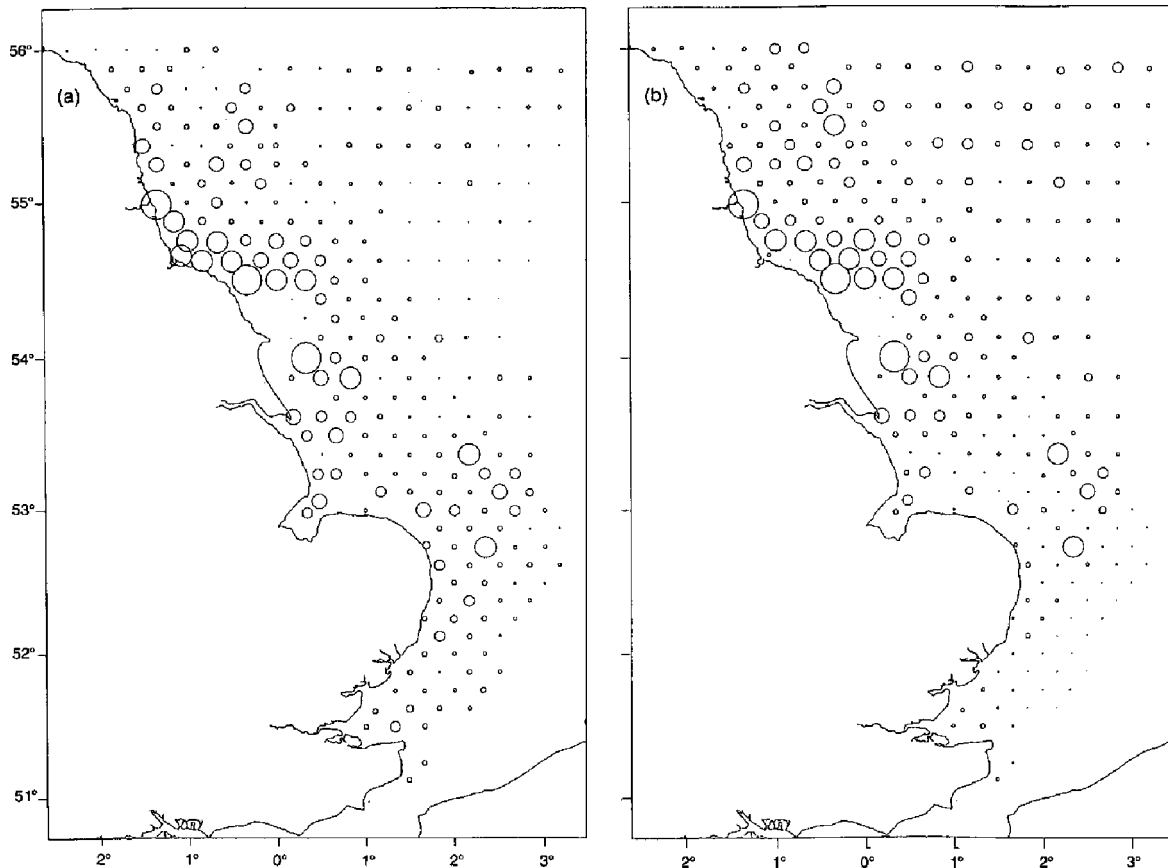


Figure 12. Residual values around the relationship between lead and two normalisers, (a) aluminium and (b) lithium, in sediments from the North Sea. Data expressed as percentile groups with boundaries set at 99, 95, 90, 75, 50, 25, 10, 5 and 1 per cent. The highest percentile groups are represented by the largest circles

felt that a simple cut-off value is inappropriate and therefore made the following proposal which should be used as a guide only rather than as a rigid prescription. At disposal rates greater than 15 000 tonnes per annum monitoring of sediment metals is recommended, and at annual rates below 15 000 tonnes per annum where no positive result had occurred with a biotest of the waste, no monitoring of sediment metals is required. It should be noted that this guidance would, in many cases, mean that monitoring of the disposal site is not required.

Where monitoring is required, only site-specific 'no change' standards should be used. The team felt that measurements should be made in relation to a reference site.

7. RECOMMENDATIONS

- Sediment samples for monitoring purposes at sewage-sludge disposal sites should be collected using a grab and on return to the laboratory should be freeze-dried and sieved through a 63 μm sieve to extract the fine fraction. This fraction
- should then be digested using *Aqua Regia* and the metals extracted measured using the analyst's preferred method, generally atomic absorption spectrophotometry or ICP/MS.
- In order to provide the necessary QA data, it is recommended that internal reference material is analysed at the same time as the unknown samples.
- Based on the results of the intercomparison exercises, it is apparent that the laboratories concerned are all capable of producing analytical data on samples from disposal sites that would be of broadly comparable quality and therefore of a suitable standard to allow comparison across and between disposal sites. It is equally apparent that any new contractor would not necessarily achieve the same standard.
- A set of 'Action Levels' is proposed for sediment quality at disposal sites. Exceedance of these levels would trigger further study to assess their environmental significance rather than automatic management action.

- Sediment samples for monitoring purposes at dredged material disposal sites should be collected using a grab and on return to the laboratory should be freeze-dried and sieved at 2 mm and completely digested using hydrofluoric acid. The metals extracted should then be measured using the analyst's preferred method, generally atomic absorption spectrophotometry or ICP/MS. The data should be normalised, aluminium or lithium being the preferred normalisers.
- The Task Team proposed the following guidance for use at dredged material disposal sites. At disposal rates greater than 15 000 tonnes per annum monitoring of sediment metals is recommended, and at annual rates below 15 000 tonnes per annum where no positive result had occurred with a biotest of the waste, no monitoring of sediment metals is required. It should be noted that this guidance would, in many cases, mean that monitoring of the disposal site is not required.
- At dredged material disposal sites where monitoring is required, only site-specific 'no change' standards should be used. The team felt that measurements should be made in relation to a reference site, until such time as biological testing for sediments is a proven and generally adopted technique.

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ANNEX 1. Membership of the Metals Task Team

Team Chairman

Dr S M Rowlatt MAFF, DFR (now CEFAS)

Team Members

Dr D Harper AEA Technology

Mr S Blake WRc

Dr J Towner EAG Ltd

Dr J Webster Lothian Regional Council

Dr I Davies SOAEFD

Dr P C Head North West Water

Dr E Donaldson IRTU

ORGANICS TASK TEAM

FINAL REPORT (A summary of work 1988-1994)

EXECUTIVE SUMMARY

The Task Team on Organics (TTO) was tasked specifically to concentrate on organic contaminants likely to be of concern. Those compounds appearing on the Red List were given highest priority but other important contaminants, for example Polycyclic Aromatic Hydrocarbons (PAHs), were also considered. These aims were realised through literature reviews, consultation with relevant experts in the field of marine monitoring, the tasks teams own extensive experience and with a series of intercomparison exercises. The principal findings are summarised below:

- Field variance was shown to be highly significant (30% on average) and must be taken into account when planning monitoring strategies and interpreting survey data.
- Some guidance has been given with respect to minimising field variance effects but further research is required in this area.
- Recommendations on the collection and storage of samples for subsequent organic analysis have been provided.
- The results of several intercomparison exercises indicated a number of problems common to many laboratories. These included use of inappropriate analytical columns, poor calibration, poor chromatography and inadequate sample clean-up.
- Protocols for sample preparation and analysis have been recommended which should help analysts avoid the common pitfalls associated with the analysis of organic contaminants in marine sediments.
- Laboratories involved in monitoring marine sediments are strongly recommended to participate in the National Marine Analytical Quality Control (NMAQC) Scheme.
- It was recommended that marine disposal licences for polychlorinated biphenyls (PCBs) contain a requirement for congener-specific reporting of information rather than on a formulation basis.
- Long term analysis of reference materials indicated significant analytical variance ranging from 14-24% for PCBs and 25-79% for organochlorine compounds (OCPs). In view of this it was recommended that AQC compliance become a condition of licence for dischargers and their agents. Quality Criteria covering organochlorine analyses have been proposed.
- After consideration of a number of different approaches the use of the Equilibrium Partitioning (EP) theory was finally chosen as the most scientific approach currently available for defining Sediment Quality Standards.
- It was recognised that this approach is at best a model which can supply some interim quality criteria for some compounds. To reflect this it was deemed appropriate to call the values derived in this way 'Sediment Action Levels'.
- Sediment Action Levels have been recommended for a variety of List I and List II organic compounds. Users of this information should however be fully aware of the limitations of this approach. Empirical testing of the derived values is now required with refinement as necessary.
- Where data allowed, comparison of the proposed Sediment Action Levels with actual levels reported at sites around the UK indicated reasonable agreement between predicted and observed effects.

- The use of Sediment Action Levels alone is insufficient. Development of other approaches is required in order to derive viable sediment quality criteria for compounds whose behaviour cannot be predicted by the EP approach. All of these approaches should then be combined with biological assessments as part of an integrated disposal area management scheme.
- The task team concluded that the sampling and analysis protocols recommended for monitoring sludge disposal sites would be equally valid for dredge material disposal sites. The Sediment Action Levels proposed for sludge dumping sites should, in principle, also be valid for dredge material disposal sites.
- Where there is a risk that dredged materials may be contaminated with potentially toxic components then such material should be monitored and risk assessments made prior to disposal, especially if the disposal is to a near-shore or controlled site.

In conclusion, although there are still many uncertainties to be resolved, the work of the GCSDM-TTO has provided a number of recommendations which should aid those responsible for the management of marine disposal sites.

1. INTRODUCTION

The Group Co-ordinating Sea Disposal Monitoring - Task Team on Organics (GCSDM-TTO) was set up in June 1989 to consider the problems associated with the potential contamination of the sediments in and around sewage-sludge disposal sites by organic chemicals. All sewage-sludge disposal sites are routinely monitored in the UK, and have been for some time. However, concern was expressed as to the suitability and reliability of these monitoring programmes. Furthermore, could standards be set to ensure that such disposal methods would not cause detrimental effects on the surrounding environment? To address these questions, the team was given the following remit;

- (i) To conduct suitable intercomparison exercises for the determination of trace organic compounds in sediments to allow the production of detailed guidance on procedures to be followed, and possible pitfalls, for analytical techniques used in monitoring programmes.
- (ii) To develop environmental quality standards (EQSs) against which to judge the results of analyses of sediments and whether or not the Environmental Quality Objectives are met.

In 1993, following increased international interest in dredged material disposal, the team's remit was extended as follows;

- (iii) To determine whether the analytical guidelines and standards derived for sewage-sludge disposal sites would be equally applicable for dredged material disposal sites and if not to recommend suitable alternatives.

This report provides a broad outline of the work undertaken by the GCSDM-TTO to meet these objectives and summarises their results and key conclusions.

2. ANALYTICAL PROCEDURES

To ensure effective monitoring it is essential to know that the samples taken will be representative, that the analytical methods employed will have the required accuracy, specificity, sensitivity, and reproducibility and that appropriate quality control steps are taken. All of these factors were carefully considered.

2.1 Sampling strategies

Taking representative samples is a crucial part of any monitoring exercise. Care must be taken to ensure that the samples are taken from the right location, that the correct layer of sediment is sampled (normally surface), and that the samples are not contaminated during collection and subsequent analysis.

If the results of such sediment monitoring exercises are to be compared with environmental quality standards it is imperative that the levels of uncertainty associated with such measurements are defined. Field variance alone can be substantial, the coefficient of variance may range from 20-50% depending on the properties and location of the site. Multiple sampling is recommended if statistically valid data are to be produced, and this has obvious cost implications. The most cost-effective policy when monitoring a disposal site would be to pool samples rather than analyse them individually, and analyse a number of such pools. Each pool should consist of a small number of samples bulked together (e.g. 5) and homogenised, from which one or two sub-samples would then be analysed. These limitations must be taken into account by those responsible for the design of monitoring programmes. Detailed discussion documents and a paper published in 1994 (Kelly *et al.*) were presented to the task team outlining field variance effects, however, it was beyond the scope of the team to investigate the extent of such effects or to provide more specific guidance. Further research on these aspects is required.

To minimise the risks of sample contamination and/or sample losses during collection and storage prior to analysis the following approach was considered to be the most appropriate for organics work:

- (i) Use a stainless steel Day Grab for sample collection ensuring that the cables/rope, shackles and grab are degreased before use and rinsed between stations.
- (ii) The top 1 cm fraction of sediment should be collected using a teflon scoop and transferred to a solvent-washed Beatson jar, sealed with an aluminium foil-lined cap, and frozen (preferably in a blast freezer if available). They should then be kept frozen until required for preparation for analysis.

2.2 Intercomparison exercises

A variety of analytical procedures is used by the different authorities monitoring organic compounds in sediments and sludges, however, the general approaches are broadly similar. Although a primary consideration of the GCSDM-TTO was to harmonise procedures to some extent it was not considered necessary or appropriate to impose standard methods. However, comparability and reliability of results were key issues and a series of intercomparison exercises were undertaken to assess the validity of the methods in use.

Four exercises were carried out in all and they concentrated on PCBs and OCPs. The first two exercises were designed to test the ability of participating laboratories to resolve, identify and

quantify PCBs and OCPs from solutions which were provided. The latter two exercises were more complicated and involved the analysis of real samples, both wet and dry sediments, where the participating laboratories used their own methodologies and standards. Initially, participants were drawn from the task team members but some consistently failed to make returns because of other priorities and others struggled to meet the deadlines so that the resultant statistical base used in assessing the results proved inadequate. To resolve this problem a questionnaire was circulated to determine the level of interest of other laboratories likely to be involved in sediment analysis. As a result, samples were distributed to twenty-one laboratories for the fourth exercise.

Results from the initial two exercises carried out in 1990 and 1991 highlighted some common problems. Whilst some of the results were within 10% of the expected values, quantitation of components at lower levels proved to be more variable. The principal causes were non-linearity of electron capture (ECD) detectors (which became very noticeable where single point calibrations were used), use of external rather than internal standard calibration techniques and use of inappropriate column dimensions and/or phases which lead to poor chromatographic resolution and misidentification problems. Results from exercise three indicated that the chromatography was much improved but some calibration problems at lower levels were still evident. Inadequate clean-up was also highlighted as a problem for some laboratories. Eighteen laboratories returned results for the final exercise. Despite providing clear guidelines with respect to column selection, multi-level calibration, use of internal standards and advice on the need for sample clean-up, only four of the participating laboratories used pairs of columns of the recommended specifications. Many participants used columns that were too short or too wide a bore or of an inappropriate liquid phase. Two laboratories used external calibrations and five used single point calibrations. As a consequence results were incomplete even for the solutions provided. Errors in standard preparation, inadequate calibration techniques, poor choice of columns and poor chromatography remained common problems. Inadequate sample clean-up and use of contaminated chromatographic systems were also highlighted. Laboratories using Gas Chromatography Mass Spectrometer (GCMS) systems were no less prone to some of these problems and there was a definite degradation in the quality of quantitative data at the trace level where GCMS techniques were used. In addition, one laboratory using GCMS reported significant false-positive results for several OCP compounds.

The data obtained from the intercomparison exercises provides a very realistic view of the current proficiency of the major UK laboratories involved in the environmental monitoring field to analyse trace organic components in marine sediments. There is an obvious need for some laboratories to revise their protocols and

a requirement for further intercomparison exercises to ensure that improvements are achieved. This task will be continued under the auspices of the National Marine Analytical Quality Control (NMAQC) Scheme and the Scheme Manager will be advised of relevant GCSDM-TTO recommendations.

2.3 Analytical protocols

Based on the combined experience of task team members, a review of current literature and the results of the inter-comparison exercises, the following guidelines are recommended for the analysis of organics in marine sediments.

- (i) Samples should be air-dried to constant weight at ambient temperatures in clean air.

Initially either freeze-drying or air-drying were considered acceptable and results of comparative tests that had been carried out at some laboratories indicated that there was little difference between the two options. Recent work at the Centre for Environment, Fisheries and Aquaculture Science (CEFAS) (formerly MAFF, DFR) indicates that losses of PCBs and OCPs may occur on freeze-drying depending on the extent of compound chlorination and lipid content of the samples. Alcock and Jones (1993) reported some losses of PCBs during the freeze-drying of sludges. Other supporting evidence has not yet appeared in the open literature, therefore the team cannot categorically rule out the use of freeze-drying but feel there is sufficient doubt to recommend that samples be air-dried.

It is important to note that in situations where the monitoring of more volatile organic components is required, sediments should be analysed wet and suitable precautions taken to prevent volatile losses e.g. use of Kuderna-Danish apparatus or purge-and-trap systems.

- (ii) Large pebbles should be removed and the samples dry sieved (unless wet sample analysis is required) through a 1 mm stainless steel mesh and homogenised.
- (iii) The fractionated sediment should be analysed and organic carbon determined, using standard methods, in addition to the determinands of interest. Normalisation of the results relative to organic carbon allows more reliable intercomparison of data for contaminant levels at different sites. In areas where there is a high incidence of coal particles (e.g. north-east coast of England), such normalisation would not work and alternative procedures may need to be considered e.g. normalisation to aluminium.

- (iv) The recommended standard methods for organic carbon analysis are either the chromic acid wet-oxidation technique (e.g. Strickland and Parsons, 1972, Buchanan, 1984) or use of a CHN elemental analyser (e.g. Parker, 1983). When using the latter, carbonates must be removed prior to analysis (e.g. by fuming with HCl). The wet-oxidation technique is recommended if the sediments are coarse sands, especially if large quantities of shell debris are present in the sample.
- (v) Organic contaminants are extracted from the ground, sieved material using Soxhlet apparatus. The solvent cycling time should be ≈ 20 cycles per hour. There is a choice of solvents, polar ones such as DCM or mixtures such as Hexane/Acetone (60:40 v/v) are recommended since extraction is complete after 4 hours. Hexane is less efficient and extraction takes 24 hours using it alone. Super critical fluid extraction techniques may be suitable providing they meet the necessary AQC requirements.
- (vi) All sample extracts should be put through a clean-up. For PCBs and OCPs alumina column clean-up is essential.
- (vii) Sulphur removal is generally necessary and a choice of techniques is available. Mercury is not recommended due to the hazards involved. Activated copper filings (i.e. HCl washed followed by distilled water and solvent washes) can be added at the Soxhlet stage. This technique has the advantage of being both quick and simple, the filings are simply added until they no longer turn black. For those samples having a higher sulphur content Jensens reagent (Jensen *et al.*, 1977) is recommended. It is highly efficient and is generally added post-clean-ups.
- In terms of the analytical conditions a variety of different columns, types of sample injection, temperature programmes, etc. can be used in the final analysis. However to minimise analytical errors analysts are strongly advised to note recommendations (viii) to (xxii) shown below;
- (viii) Columns should be 50-60 m long with an internal diameter of ≈ 0.25 mm and a film thickness of $0.25 \mu\text{m}$ or $0.15 \mu\text{m}$ to achieve the required resolution of components.
- (ix) For PCBs/OCPs 5% phenyl methyl silicone columns are advised e.g. DB-5, SE-54, BP-5, etc. Confirmation on a second more polar column e.g. OV-1701 or equivalent is advised where analysis is by ECD but should not be necessary if GCMS used.
- (x) Use either helium or hydrogen as a carrier gas. Hydrogen is considered ideal.
- (xi) Well maintained, clean systems are essential.
- (xii) The systems in use should be optimised for maximum resolution of the determinands of interest, e.g. congeners 28/31 and 149/118 in the case of PCBs. Optimisation of initial column temperature and subsequent ramping rates are important as is optimisation of injector temperature when using split/splitless injectors. It should be remembered that even when looking for a limited range of components in a sample co-elution problems may still exist and the analyst should ensure that the target peaks are free from interference from non-target peaks.
- (xiii) Automated injection systems are recommended as they can improve reproducibility.
- (xiv) The linear range of the ECD should be checked for each component.
- (xv) Certified standards should be used for preparing stock solutions and working standards. It should be noted that some proprietary mixtures are unreliable. All standards should be made up on a gravimetric basis.
- (xvi) Multi-point calibrations with an internal standard must be used. Responses that deviate by $\pm 10\%$ for any component in the system should be checked thoroughly.
- (xvii) Independent standards, preferably from a separate source/supplier should be used to check calibration data.
- (xviii) Certified Reference Materials (CRMs) such as the Canadian Reference Sediments (e.g. HS-1) containing PCBs/OCPs should be run occasionally. It is advisable to prepare an in-house reference material which should be run with each batch of samples.
- (xix) A duplicate sample and blank should be run with each batch.
- (xx) Internal standards should be used. DCBE Nos 6 and 16 are recommended but iodobenzene and octachloronaphthalene are acceptable, although some problems have been noted with the latter when using 'on-column' injection.
- (xxi) Participation in the NMAQC scheme or other appropriate scheme is advisable to demonstrate adequate analytical performance.

(xxii) For practical purposes it is easier to analyse PCBs in terms of congeners. Congener data can be used to estimate formulation data but the reverse is prone to greater errors. In view of this it was recommended that marine disposal licences for PCBs should contain a requirement for congener-specific reporting of information rather than on a formulation basis. To maintain continuity both congener and formulation data should be provided initially, with the formulations gradually being phased out.

Further guidance on the optimisation of systems for PCB analyses can be found in the reports published by ICES (e.g. ICES, 1995).

2.4 Analytical Quality Control

Although recommendations on the steps that should be followed for Analytical Quality Control (AQC) are provided in Section 2.3 (xvii) to (xxi), there is a need to ensure that proper control procedures are implemented and can be clearly demonstrated by those organisations which are responsible for monitoring marine sediments and ensuring there are no adverse environmental effects. Laboratories normally do this routinely, however, the questionnaire returns in March 1992 indicated that some of the larger discharging organisations appeared reluctant to incorporate some of the recommendations into their standard operating procedures (SOPs). Whilst most accepted the need to incorporate AQC measures into their methodologies (and most have their own protocols set up) there was little interest shown in participating in the NMAQC scheme. Some organisations considered it inappropriate given that they monitor sludge rather than sediments.

Spatial and temporal trend monitoring of trace organic contaminants in the environment becomes meaningless unless the variances associated with the measurements are known. Analytical variance can be highly significant as illustrated by the following example - consider two sets of survey data for Lindane produced by a laboratory with moderate to good analytical quality control measures in place;

Survey 1 Results : 5.9, 6.9, 7.9, 8.9, 10.9 $\mu\text{g l}^{-1}$ giving a mean of 8.1 $\mu\text{g kg}^{-1}$, a standard deviation of 1.9 and a coefficient of variation of 23.8%.

Survey 2 Results : 6.9, 7.9, 8.9, 9.9, 10.9, 11.9, 12.9 $\mu\text{g l}^{-1}$ giving a mean of 9.9 $\mu\text{g kg}^{-1}$, a standard deviation of 2.2 and a coefficient of variation of 21.8%.

Applying a t-test yields a result of $t = 1.49$ which is not significant at the 95% confidence limit, therefore the mean results of 8.1 and 9.9 $\mu\text{g kg}^{-1}$ although 22% different are not significant statistically because of the

high variance. It is easy to imagine what the variability would be like without adequate AQC measures. Collation of data provided for the analysis of certified reference materials by laboratories routinely monitoring marine sediments indicated that variability ranged from 14-24% for PCBs and 25-79% for OCPs.

In view of the importance of AQC measures, the team concluded that positive action should be taken to ensure this requirement was met. The most suitable means of achieving this was considered to be making AQC compliance, and participation in an appropriate scheme such as the NMAQC scheme, a condition of any disposal licence which is granted. Organisations were encouraged to do this voluntarily but this approach proved largely unsuccessful because of the financial implications. The recommended quality criteria for the analysis of organochlorine compounds, including PCBs, are detailed in full in Appendix I. The analytical requirements, the need for using standard operating procedures, method performance requirements and reporting conditions are clearly stated.

3. SEDIMENT QUALITY CRITERIA

In 1989, the GCSDM proposed a number of Environmental Quality Objectives (EQOs) designed to protect the marine environment (MAFF, 1989). Sediment Quality was a key issue in two of these; ecosystem maintenance and preservation of environment. Standards are required in order to monitor for compliance with such objectives and the GCSDM-TTO was asked to consider standards which might be set in relation to organic contaminants in sediments.

3.1 Comparison of approaches

The setting of Environmental Quality Standards (EQSs) for organic contaminants in sediments is very complex due in part to the lack of information available on impact assessments or the concentrations of compounds in the sediments. Moreover, difficulties associated with analytical and field variance further complicate matters. Despite these obvious problems it was recognised that guidance levels of some kind were required even if based on less than perfect methods. Refinements could be made at a later date taking advantage of technical advances or other knowledge as/when they become available. A variety of different approaches were considered (see Long and Morgan, 1990 for useful review) and are outlined below.

3.1.1 Background Approach

This approach is widely used in the UK. Levels of contaminant are monitored for either no-change, or for a significant change over time relative to a reference value.

Advantages

- minimal data needs, easily implemented with available data.
- no detailed chemical knowledge or toxicity testing required.

Disadvantages

- very subjective and difficult to defend.
- likely to be site-specific, therefore cannot set universal standards.
- gives no indication of likely biological effects.
- difficult to define reference conditions.

3.1.2 Spiked-sediment Bioassay Approach

Involves the exposure of organisms to spiked sediment under controlled conditions with subsequent evaluation of LC₅₀ or similar value.

Advantages

- useful for identifying contaminated sediments.
- synergistic effects are taken into account.
- knowledge of uptake mechanisms is not required.

Disadvantages

- chronic effects may not be evident.
- difficult to isolate cause of any effects seen.
- tests may only be possible with limited range of organisms.
- labour-intensive to assess mixtures and dosages that may occur.

3.1.3 Screening Level Concentration (SLC) Approach

Utilises field data and matches sediment concentrations of contaminants with benthic faunal data to statistically arrive at a concentration that has a minimal effect.

Advantages

- utilises existing databases.
- prior knowledge of mechanisms not required.
- suitable for any chemical component.

Disadvantages

- requires large amount of field data.
- sensitive to accuracy of field data
- assumes that chemicals evaluated are responsible for all of any observed effects on the benthos.

3.1.4 Apparent Effects Threshold (AET) Approach

This approach also utilises data from matched sediment chemistry/faunal sets to estimate the concentration

above which statistically significant effects always occur.

Advantages

- utilises existing databases.
- prior knowledge of mechanisms not required.
- suitable for any chemical component using any effects measure providing it can be evaluated statistically.
- non-contradictory as biological effects always occur above AET.

Disadvantages

- requires large amount of field data.
- chronic effects may not be shown.
- assumes that chemicals evaluated are responsible for all of any observed effects on the benthos.

3.1.5 Bio-effects/Contaminant Co-occurrence Analysis (COA) Approach

Another statistical approach using field collected data but utilises means and standard deviations calculated for sediment concentrations observed to have an effect. The advantages and disadvantages of this approach are essentially the same as those for the SLC and AET approaches (see Sections 3.1.3 and 3.1.4).

3.1.6 Equilibrium Partitioning (EP) Approach

In this approach standards are set at the concentration in sediment which, in equilibrium with surrounding water, gives rise to a concentration in water equal to the water quality criterion.

Advantages

- utilises well established toxicological database.
- takes account of organic carbon levels.
- utilises data on chemical equilibria which are often well defined.
- significant experimental work has been conducted, mainly in the United States, which supports many of the assumptions this approach makes.

Disadvantages

- synergistic and antagonistic effects are not considered.
- some contaminants may be irreversibly bound to the sediments.
- water quality criteria are set for pelagic not benthic organisms.
- may underestimate toxicity to benthos.
- some partition coefficients are uncertain.
- sensitive to sediment type.

3.2 Principles of Equilibrium Partitioning

Although the Equilibrium Partitioning (EP) Approach has its drawbacks, it was ultimately recognised as providing the most practicable scientific approach of all the options considered. Consequently, the GCSDM-TTO concentrated on this approach and utilised it in an attempt to derive meaningful sediment quality standards (see Section 3.3).

The EP approach was developed by Pavlou and Weston (1984) on behalf of the US EPA. The approach defines the safe level, i.e. the concentration below which benthic organisms would suffer no harmful effects, as:

“The concentration in the sediment, in equilibrium with the surrounding water, which does not lead to a breach of the relevant water quality criteria.”

A significant amount of work has been carried out since 1984, principally in the US but also in other countries such as the Netherlands, which has produced further data to support the approach (e.g. review by Di Toro, 1989 and Di Toro *et al.*, 1991). The following points in particular help to corroborate some of the assumptions inherent in the application of the EP method:

- (i) Available data indicate that benthic species are not uniquely sensitive to toxic effects of chemicals. Therefore, there is some validity in deriving sediment criteria from water quality criteria.
- (ii) For organic carbon contents >0.2% the dissolved free concentration of chemical in the pore water is proportional to the organic carbon normalised total sediment concentration.
- (iii) For a number of chemicals, the concentration response curve for biological effect has been shown to be correlated with the pore water concentration and not the total sediment concentration.
- (iv) Evidence from tissue concentrations indicates that the bioavailability of chemicals is positively correlated with the organic carbon content of the sediments.

The technique requires three pieces of information to allow the derivation of a numeric standard for the chemical of interest by applying the following equation;

$$C_{sed} = K_{oc} \times C_{w/cr} \times TOC$$

where:

- C_{sed} is the sediment standard for the component of interest ($\mu\text{g g}^{-1}$)
- K_{oc} is the partition coefficient normalised to organic carbon
- $C_{w/cr}$ is the relevant water quality standard ($\mu\text{g ml}^{-1}$)
- TOC is the fractional organic carbon content of the sediment (i.e. 10% organic-C in the sediment gives a $TOC = 0.1$).

For non-ionic organic compounds it is possible to use regression equations to produce theoretical estimates of K_{oc} from K_{ow} (octanol/water partition coefficient) measurements made in the laboratory. A variety of such regression equations for several different classes of organic compounds were reported by Pavlou and Weston (1984). Caution is advised when using such equations as the difference between measured and predicted values could result in the derived value for C_{sed} varying by factors of 10 or more. The use of empirically derived K_{oc} values is always preferable.

3.3 Proposed Sediment Action Levels

In order to satisfy fully the Environment Quality Objectives, a dual approach to setting sediment standards is required. A ‘no measurable-change’ clause is necessary to ensure that sites already contaminated do not get any worse. Advice on how to calculate such standards is detailed in the final report of the GCSDM-Metals Task Team and need not be repeated here. In conjunction with the ‘no-change’ clause, any criteria based on Equilibrium Partitioning (EP) will also have to be met.

Table 1 shows the ‘Sediment Action Levels’ that the GCSDM-TTO have derived using the EP approach for a variety of priority organic pollutants. Volatile organic compounds were not considered initially because of their tendency to disappear during treatment prior to and during sludge disposal, however, they may pose more of a problem where dredge materials are concerned. Therefore, Table 2 shows some Action Levels for volatiles. The term ‘Sediment Action Levels’ is considered to be more appropriate than ‘Sediment Quality Standards’ given the limitations associated with the EP approach (see below). It also highlights the fact that some action is required by managers if the values are exceeded, whether it be to restrict further inputs to a site or initiate more detailed investigations.

Table 1. Sediment Action Levels for organic contaminants

Substance	Water Quality Criterion ($\mu\text{g l}^{-1}$)	$\log K_{ow}$	K_{oc}	Sediment Action Level ($\mu\text{g g}^{-1}\text{-oc}$)
Lindane	0.02		1950	0.04
Endrin	0.005	4.56	7210	0.036
ppDDT	0.001*		160000	0.16
ppDDE	0.01	5.69	29700 (b)	0.297
HCB	0.10		2000	0.20
HCB	0.03		37200	1.11
Aldrin	0.01	5.0 (a)	12500 (b)	0.125
Total PCB as Arochlor	0.014*		314000 (c)	4.40
Total PCB as ICES 7				2.31 (d)
PCB-28				0.279
PCB-31				0.192
PCB-52				0.300
PCB-101				0.285
PCB-118				0.334
PCB-153				0.474
PCB-105				0.117
PCB-138				0.292
PCB-156				0.045
PCB-180				0.348
Trifluralin	0.10		13800	1.38
Dichlorvos	0.04	1.4	138(b)	0.006
Atrazine & Simazine	2.0		162 (e)	0.324
Azinphos methyl	0.04	1.87	248 (b)	0.01
Malathion	0.02		1780	0.036
Dieldrin	0.01	4.56 - 5.48	7210 - 22800	0.07 - 0.23
TCB (Total)	0.40	3.8	2300 (f)	0.92
PCP	2.00		24000	48
Endosulfan	0.003	3.83	4170 - 5750	0.013 - 0.017
Fenitrothion	0.01	3.38	1450 - 2000	0.014 - 0.02
Tributyl Tin	0.002	3.2-3.84	717 - 2480 (f)	0.001 - 0.005
Triphenyl Tin	0.008	3.2-3.84	717 - 2480 (f)	0.006 - 0.02
Fluoranthene	8*		45000	360
Anthracene	150*	4.5	7400 - 25100	1100 - 3770
Benz[a]anthracene	150*	5.6	37000 - 39800	5800 - 5970
Benzo[b]fluoranthene	150*	6.5	300000 - 501000	75000 - 75200
Benzo[k]fluoranthene	150*	6.8	631000 - 840000	94600 - 125000
Benzo[g]perylene	150*	7.1	1800000 - 2000000	270000 - 299000
Benzo[a]pyrene	150*	6.0	300000 - 2000000	45000 - 299000
Chrysene	150*	5.9	77000 - 79400	11500 - 11900
Phenanthrene	150*	4.5	9300 - 25100	1400 - 3770

Notes:

* US Chronic Value used

(a) $\log K_{ow}$ value unrealistic, hexane/water co-efficient used in preference

(b) K_{oc} calculated from equation: $\log K_{oc} = 0.544 \log K_{ow} + 1.377$

(c) Mean K_{oc} value for mixture of Arochlors 1242, 1254 and 1260 has been used these being the most common mixtures encountered in UK waters.

(d) Sum total for 7 ICES congeners (28,52,101,118,138,153,180). Individual PCB congener water quality criteria are not available.

Values for individual congeners are therefore calculated on a percentage basis in terms of their maximum concentration in any Arochlor mixture

(e) Mean K_{oc} value for Atrazine + Simazine

(f) K_{oc} calculated from equation: $\log K_{oc} = 0.843 \log K_{ow} + 0.158$

The equations used to calculate K_{oc} values were taken from a paper by Pavlou, P.S. and Weston, D.P., 1984. Initial Evaluation of alternatives for development of sediment related criteria for toxic contaminants in Marine Waters (Puget Sound). Prepared by JRB Associates for EPA, EPA Report No. 910/9-83-117

The values in the table represent the latest revision as of October 1994 and as such may differ slightly from those published prior to this date

Table 2. Sediment Action Levels for volatile organic compounds

Substance	Water Quality Criterion ($\mu\text{g l}^{-1}$)	$\log K_{ow}$	K_{oc}	Sediment Action Level ($\mu\text{g g}^{-1}\text{-oc}$)
1,2-Dichloroethane	10	1.45	32.4	0.324
1,1,1-Trichloroethane	10*	2.47	178	0.178
1,1,2,2-Tetrachloroethane	10*	2.39	79.4	0.790
Chloroform	12	1.95 ⁽¹⁾	63.4 ⁽²⁾	0.761
Carbon Tetrachloride	12	2.64 ⁽¹⁾	242 ⁽²⁾	2.90
Benzene	10*	2.11 ⁽¹⁾	55 ⁽³⁾	0.550
Chlorobenzene	10*	3.79 ⁽¹⁾	2530 ⁽³⁾	25.3
Perchloroethylene	10	2.53	363	3.63

Notes:

* A Water Quality Criterion of 10 has been assumed for these compounds.

⁽¹⁾ = $\log K_{ow}$ data taken from Mackay, D., 1982 : Correlation of Bioconcentration Factors. *Environ. Sci. Technol.*, 16:274-278

⁽²⁾ = K_{oc} calculated using the equation; $\log K_{oc} = 0.843 \log K_{ow} + 0.158$

⁽³⁾ = K_{oc} calculated using the equation; $\log K_{oc} = 0.989 \log K_{ow} - 0.346$

The equations used to calculate K_{oc} values were taken from a paper by Pavlou, P.S. and Weston, D.P., 1984. *Initial Evaluation of alternatives for development of sediment related criteria for toxic contaminants in Marine Waters (Puget Sound)*. Prepared by JRB Associates for EPA, EPA Report No. 910/9-83-117

After consultation with other experts in the field of marine monitoring, including ecotoxicologists, and based on the task teams own experiences, it is clear that the Equilibrium Partitioning Approach is at best a model which can supply us with Interim Action Levels for some organic contaminants. This in itself is an improvement on the current situation in the UK, but it emphasises the urgent need to test and improve the model by carrying out proper field evaluations. Realistic sediment quality criteria can only be derived by combining theoretical principles with empirical testing. The Sediment Action Levels produced for PAHs provide a perfect example of the problems that can occur when relying on theoretical principles alone to develop standards. Table 3 shows data on PAH effects levels in fish, based on the occurrence of liver neoplasias, which have been reported in the open literature. Sediments from six sites in the USA have been considered. Two of these sites; President Point and Sinclair Inlet, were considered no-effect sites. The other four; Duwamish Waterway, Eagle Harbour, Everett Harbour and Mukilteo, showed evidence of liver neoplasias with varying frequencies. The data indicate that detrimental effects occur at concentrations between 10 and 100 times lower than the proposed Sediment Action Levels for fluoranthene and anthracene and between 400 and 17 600 times lower in the case of benz[a]anthracene and benzo[a]pyrene. Clearly the EP approach does not appear to work for PAHs. Two problems may have contributed to this;

- (i) PAHs are not found singly in sediments but in assemblages of tens/hundreds of compounds depending on the source (fossil fuel combustion/oil/creosote).
- (ii) The equilibrium partitioning model extrapolates from acute toxicity, whereas many PAHs are also carcinogenically active.

Alternative approaches are obviously required in such cases. Agencies in Canada and the US are developing other models to take account of such problems but information from these projects is not yet available.

The values shown in Table 1 therefore represent only the first part of the process for defining sediment criteria, it is now up to other groups to test and refine these Action Levels. The schematic diagram shown below indicates the sort of refinement process that could be followed.

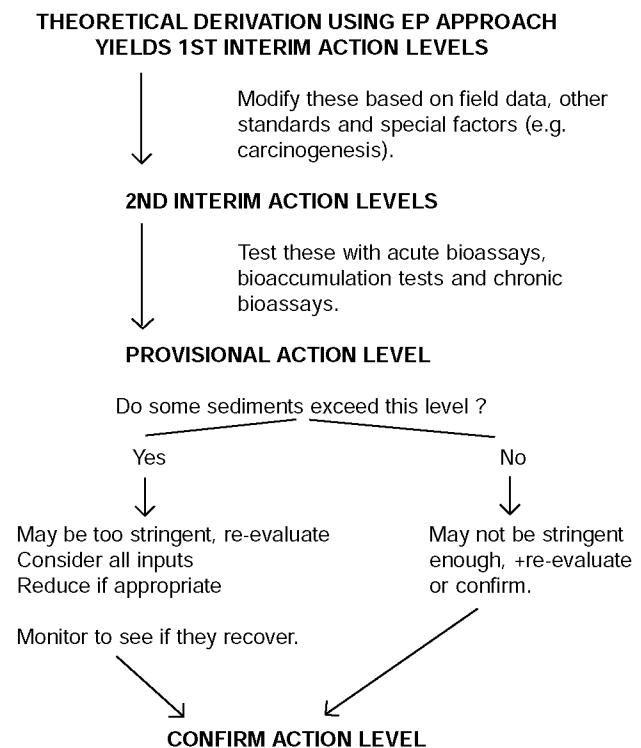


Table 3. PAH effects levels in fish

Occurrence of hepatic neoplasia in fish and associated sedimentary PAH concentrations

Compound	Safe concentration ($\mu\text{g l}^{-1}$)	K_{oc}	Safe concentration ($\mu\text{g g}^{-1} \text{ oc}$)	Actual concentration ($\mu\text{g g}^{-1} \text{ dry wt oc}$) (all assuming 1% organic carbon)	Reference	Site
Fluoranthene	8	45000	360	22 (no effect)	Malins <i>et al.</i> , 1985(a)	President Point
				200 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo
				470 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo
				180 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour
				2500 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour
				32 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour
				850 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour
				1100 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour
				150 (neoplasms)	Varanasi <i>et al.</i> , 1987	Everett Harbour
				89 (neoplasms)	Varanasi <i>et al.</i> , 1987	Duwamish Waterway
				12 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet
				15 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet
				Anthracene	150	7400/25100
20 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo				
51 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo				
58 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour				
1200 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour				
12 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour				
340 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour				
570 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour				
36 (neoplasms)	Varanasi <i>et al.</i> , 1987	Everett Harbour				
14 (neoplasms)	Varanasi <i>et al.</i> , 1987	Duwamish Waterway				
9.2 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet				
8.7 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet				
Benz[a]anthracene	150	37000/39800	5800/5970			
				45 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo
				120 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo
				110 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour
				520 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour
				13 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour
				200 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour
				230 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour
				250 (neoplasms)	Varanasi <i>et al.</i> , 1987	Everett Harbour
				29 (neoplasms)	Varanasi <i>et al.</i> , 1987	Duwamish Waterway
				14 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet
				21 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet
				Benzo[a]pyrene	150	300000/2000000
17 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo				
55 (neoplasms)	Malins <i>et al.</i> , 1985(a)	Mukilteo				
110 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour				
210 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour				
19 (neoplasms)	Malins <i>et al.</i> , 1985(b)	Eagle Harbour				
62 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour				
64 (neoplasms)	Varanasi <i>et al.</i> , 1987	Eagle Harbour				
<0.5 (neoplasms)	Varanasi <i>et al.</i> , 1987	Everett Harbour				
26 (neoplasms)	Varanasi <i>et al.</i> , 1987	Duwamish Waterway				
22 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet				
30 (no effect)	Varanasi <i>et al.</i> , 1987	Sinclair Inlet				

Malins, D. C., Kraha, M. M., Brown, D. W., Rhodes, L. D., Myers, M. S., McCain, B. B. and Chan, S. L. (1985(a)). *Toxic chemicals in marine sediment and biota from Mukilteo, Washington: relationships with hepatic neoplasms and other hepatic lesions in English sole (Parophrys vetulus)*

Malins, D. C., Kraha, M. M., Myers, M. S., Rhodes, L. D., Brown, D. W., Krone, C. A., McCain, B. B. and Chan, S. L. (1985(b)). *Toxic chemicals in sediments and biota from a creosote-polluted harbour: relationships with hepatic neoplasms and other hepatic lesions in English sole*

Varanasi, U., Brown, D. W., Chan, S. L., Landahl, J. T., McCain, B. B., Myers, M. S., Schiewe, M. H., Stein, J. E. and Wever, D. D. (1987). *Etiology of tumors in marine fish. Final Report: Interagency agreement YO1 CP40607. Environmental Conservation Division, National Marine Fisheries*

With sludge disposal at sea due to cease in 1998 the sediments in the disposal areas provide a unique test bed for carrying out studies of this nature. Appropriate management action would be required to ensure that resources are available to do this and that the programme is properly planned and implemented.

In the absence of any other criteria there is no doubt that the Equilibrium Partitioning Approach is a useful tool with which to assess the status of marine sediments, more so than the subjective approaches presently used. However, it is also recognised that it has its drawbacks and so should not be considered in isolation. Professional judgement and experience still have a role to play and biological effects should be carefully studied. The 'Sediment Action Levels' should be derived and used with caution. Users must be aware of the limitations associated with the approach. The principal ones are summarised below;

- (i) Normalisation to organic carbon content becomes difficult in areas where substantial amounts of coal residues are present.
- (ii) Pore water is important but not the only route of uptake of pollutants by the biota.
- (iii) The possibility of synergistic and antagonistic effects is not considered.
- (iv) Some contaminants will be irreversibly bound to the sediments.
- (v) Many of the water quality criteria have been set for pelagic rather than benthic organisms. Therefore, it is especially important that biological assessments are carried out to confirm the model predictions.
- (vi) There is evidence to suggest that where there is a high suspended load in the overlying water column the partitioning coefficients may change significantly which could invalidate any standards set.
- (vii) There is a paucity of data on partition coefficients for the substances of interest to UK legislating authorities. Whilst the US authorities have put a lot of effort into such measurements they are generally interested in substances of little relevance to the UK situation. Theoretical estimates of the relevant coefficients can be utilised but often the difference between measured and predicted values is highly significant and could affect derived 'sediment action levels' by factors of 10 or more. Empirical measurements for the substances of interest are therefore essential.
- (viii) Long term carcinogenic effects and the possibility of bioaccumulation are largely ignored.
- (ix) There is strong evidence to suggest the EP approach does not work for PAHs. The same may be true of other pollutants e.g. polar organic compounds or those which under certain circumstances may enter the environment in granular form such as TBT in paint chips, rather than in solution. Obviously an alternative approach is required for these compounds.
- (x) Some benthic organisms may burrow into anaerobic conditions and this could lead to more problems than the model predicts.

3.4 Application to existing sites

In practice two procedures can be used to evaluate monitoring data using 'Sediment Action Levels'. The first is a simple numerical approach based on the calculation of normalised concentrations. For example; consider a comparison of two stations at a disposal site for the contaminant pp-DDT. On analysis the following results are obtained:

Station A: Sediment Organic Carbon = 15%,
pp-DDT = 0.020 $\mu\text{g g}^{-1}$

Station B: Sediment Organic Carbon = 15%,
pp-DDT = 0.120 $\mu\text{g g}^{-1}$

Normalising to organic carbon gives 0.133 and 0.800 $\mu\text{g DDT g}^{-1}\text{-oc}$ at A and B respectively. The 'Sediment Action Level' for DDT (see Table 1) is 0.16 $\mu\text{g DDT g}^{-1}\text{-oc}$ indicating that Station A is at 83% of this level, whereas Station B is at 500%. Effects on benthic organisms would be expected at site B but not site A using the EP approach.

The second approach is a graphical one and probably more useful when dealing with a large number of data points. The carbon content of the sediment at each sampling station should be plotted against the corresponding level of the contaminant of interest. A line can be superimposed on the plot indicating the 'Sediment Action Level' at various organic carbon levels. An example of such a plot is given in Figure 1 using the data for Stations A and B above. The status of the site as a whole, or individual stations, can be easily assessed using this procedure, stations lying to the excess side of the line may require further assessment.

Comparison of the proposed 'Sediment Action Levels' with actual levels reported at sites around the UK is difficult. Data on organic contaminants in sediments at disposal sites are few and there is little which links concentrations of a particular organic component directly with effects levels in benthic organisms. From the limited data that are available, the proposed values for Lindane, Dieldrin and PCBs do however seem to be realistic. More research is required before comments can be made on the validity of the values produced for other components.

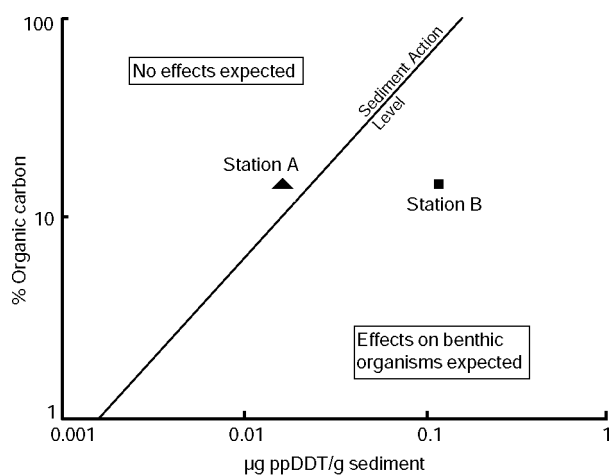


Figure 1. Graphical use of Sediment Action Levels using DDT as an example

The GCSDM-TTO was very keen to encourage other organisations involved in sediment monitoring activities to use the 'Sediment Action Levels' that have been derived. Initially this was done on a voluntary basis, mostly by task team members. To raise awareness of the team's efforts to a wider audience, a paper was published in *Marine Pollution Bulletin* (Webster and Ridgway, 1994). Metal and organic contaminant data at two UK sea disposal sites were compared with the derived 'Sediment Action Levels'. Good agreement was found between predicted and observed effects although it should be noted that some of the action levels presented have now been revised. The paper has certainly stimulated some interest with 37 requests for further information received so far (USA 18, Canada 5, UK 3, Europe 7, Others 4). Of the UK requests, two are applying the approach to their monitoring data. Feedback has been received from one of these for sediments in the Mersey Estuary. Preliminary indications for HCB, Lindane, Dieldrin, ppDDE and some metals are that predicted and observed effects are broadly similar suggesting that the model is useful for these components.

3.5 Future requirements

Despite the limitations that apply to this technique, there is sufficient evidence to suggest that it merits further investigation by workers in the field of marine monitoring. As outlined in Section 3.3 the 'Sediment Action Levels' that have been derived can only be considered as interim measures. Validation of these values is now required using a combination of empirical testing and by comparison with existing data sets where available. Monitoring organisations should be encouraged to use this approach and to provide feedback on its effectiveness. In the first instance this would probably have to be on a voluntary basis but could also be realised through the marine disposal licensing scheme.

Development of other approaches will be necessary if viable standards are to be derived for organic contaminants whose behaviour cannot be predicted using the Equilibrium Partitioning approach (e.g. poorly soluble compounds, PAHs). The Environment Agency, formerly the National Rivers Authority (NRA), is currently investigating the use of Direct Toxicity Assessments (DTA) as a means of control for complex discharges. Once fully developed, the DTA approach should provide very useful information which can then be used in conjunction with the EP approach and biological assessments as part of an integrated sediment management system. It is now widely recognised that, when dealing with such complex systems as sediments where there are still many unknowns, an integrated approach is the only way forward (EPA, 1992).

Accurate analysis is crucial to any monitoring programme, particularly if the results are then going to be compared against numerical standards, therefore efforts must continue to ensure that appropriate techniques are used and that adequate quality control can clearly be demonstrated. Many laboratories will do this as a matter of course, however, participation in appropriate schemes such as the NMAQC should be encouraged and in the case of marine disposal it is recommended that this be a condition of licence.

Further research is required into the effects of field variance and the strategies that can be employed to minimise these effects. Ultimately a guidance document should be produced as an aid to managers responsible for developing sediment monitoring programmes.

4. DREDGED MATERIAL DISPOSAL SITES

Following consultation with experts directly involved with dredged material disposal and monitoring, the GCSDM-TTO concluded that, in principle, the recommendations made with respect to the monitoring of sediments in sewage-sludge disposal areas would be equally applicable for dredged material disposal sites. The protocols recommended for sampling and analysis would also be valid. However, due to the physical disruptions and other associated problems that occur at dredged material disposal sites, it is recommended that where monitoring is considered necessary it should be carried out at locations immediately adjacent to the disposal area and/or at the final deposition sites in cases where dispersive disposal sites are utilised. Not all dredged materials will require monitoring but ideally those that do should be monitored and assessed prior to disposal especially if disposal is at a near-shore site or in shellfish waters. It was the Task Team's opinion that, providing these recommendations are followed, the proposed 'Sediment Action Levels' for sediments in sewage-sludge disposal areas would be equally applicable to most dredged material disposal sites. It was recognised, however, that for quasi-shoreline disposal other factors

may cause significant effects that are not predicted by the model used. No data are available for the levels of organic contaminants in relation to the biological effects at such sites, therefore it was not possible to provide guidance to cover these circumstances.

The current situation with regard to organic contaminants in dredged materials was reviewed by the GCSDM-TTO. At present no dredged material sites or operators are limited by the specification of organic compounds in licences although it is understood that some are not permitted to dredge certain locations within their licensed areas because of the presence of organic contaminants. Both MAFF and the Scottish Office Agriculture, Environment and Fisheries Department (SOAEFD) considered it unlikely that this would change significantly in the short term. However, both authorities do consider factors such as the concentration, load, disposal sites and alternatives for disposal prior to granting a licence.

The Marine Laboratory in Aberdeen (MLA) have taken onboard the suggestion that licensing authorities should work towards a requirement to provide organic data as part of the licensing process. Since January 1993, they have requested that PCB data should be provided in advance of licensing certain operations and have arranged to monitor samples from selected marine disposal operations. MAFF operate a similar policy for certain dredged materials (not sands) and sewage sludges.

Few dredged material sites are presently monitored on a regular basis, but the MLA are programming surveys of all regularly used disposal sites in Scottish waters. It is hoped the surveys will help to identify the level of contamination at such sites and the radius of effects. Unfortunately the programme will mainly concentrate on heavy metals. MAFF are considering the feasibility of introducing self-monitoring on a site-specific basis. In areas where ship building/breaking activities have taken place it may be particularly relevant to look at PCB levels.

Disposal site surveys for organic contaminants are likely to become a requirement in the future at certain sites. The recommendations made by the GCSDM-TTO on sampling and analytical protocols, including participation in proficiency schemes such as the NMAQC and the interim 'Sediment Action Levels', should prove invaluable to those responsible for the management of disposal sites.

5. SUMMARY OF RECOMMENDATIONS

The key recommendations arising from the work of the GCSDM-TTO are summarised below. Cross-references to sections and/or relevant page numbers of this report have been made in some instances to aid clarity and/or avoid unnecessary duplication.

5.1 Sampling and analysis

- Further research is required into field variance effects and the strategies that can be employed to minimise these effects. Ultimately a guidance document should be produced as an aid to managers responsible for developing sediment monitoring programmes.
- To reduce field variance effects the analysis of pooled rather than individual samples is advised (see Section 2.1 for details).
- In situations where dredged material disposal sites require monitoring it is recommended that the monitoring be carried out at locations immediately adjacent to the disposal area and/or at the final deposition site in cases where dispersive sites are utilised.
- If it is considered necessary to monitor dredged material this should ideally be carried out prior to disposal especially if disposal is at a near-shore site or in shellfish waters.
- Use a stainless steel Day Grab for sample collection ensuring that the cables/rope, shackles and grab are degreased before use and rinsed between stations.
- The top 1 cm fraction of sediment should be collected using a teflon scoop and transferred to a solvent-washed Beatson jar, sealed with an aluminium foil-lined cap, and frozen (preferably in a blast freezer if available). Samples should then be kept frozen until required for preparation for analysis.
- Samples should be air-dried to constant weight at ambient temperatures in clean air. It is important to note that in situations where the monitoring of more volatile organic components is required, sediments should be analysed wet and suitable precautions taken to prevent volatile losses e.g. use of Kuderna-Danish apparatus or purge-and-trap systems.
- Large pebbles should be removed and the samples dry sieved (unless wet sample analysis is required) through a 1 mm stainless steel mesh and homogenised.
- The fractionated sediment should be analysed and organic carbon determined, using standard methods, in addition to the determinands of interest. Normalisation of the results relative to organic carbon allows more reliable intercomparison of data for contaminant levels at different sites. In areas where there is a high incidence of coal particles (e.g. north-east coast

- of England), such normalisation would not work and alternative procedures may need to be considered e.g. normalisation to aluminium.
- The recommended standard methods for organic carbon analysis are either the chromic acid wet-oxidation technique (e.g. Strickland and Parsons, 1972, Buchanan, 1984) or use of a CHN elemental analyser (e.g. Parker, 1983). When using the latter, carbonates must be removed prior to analysis (e.g. by fuming with HCl). The wet-oxidation technique is recommended if the sediments are coarse sands, especially if large quantities of shell debris are present in the sample.
 - Organic contaminants are extracted from the ground sieved material using Soxhlet apparatus. The solvent cycling time should be ≈ 20 cycles per hour. There is a choice of solvents, polar ones such as DCM or mixtures such as Hexane/Acetone (60:40 v/v) are recommended since extraction is complete after 4 hours. Hexane is less efficient and extraction takes 24 hours using it alone. Super critical fluid extraction techniques may be suitable providing they meet the necessary AQC requirements.
 - All sample extracts should ideally be put through a clean-up. For PCBs and OCPs alumina column clean-up is essential.
 - Sulphur removal is generally necessary and a choice of techniques is available. Mercury is not recommended due to the hazards involved. Activated copper filings (i.e. HCl washed followed by distilled water and solvent washes) can be added at the Soxhlet stage. This technique has the advantage of being both quick and simple, the filings are simply added until they no longer turn black. For those samples having a higher sulphur content Jensens reagent (Jensen *et al.*, 1977) is recommended. It is highly efficient and is generally added post-clean-ups.
 - Analytical columns should be 50-60 m long with an internal diameter of ≈ 0.25 mm and a film thickness of 0.25 μm or 0.15 μm to achieve the required resolution of components.
 - For PCBs/OCPs 5% phenyl methyl silicone columns are advised e.g. DB-5, SE-54, BP-5, etc. Confirmation on a second more polar column e.g. OV-1701 or equivalent is advised where analysis is by ECD but should not be necessary if GCMS used.
 - Use either helium or hydrogen as a carrier gas. Hydrogen is considered ideal.
 - Well maintained, clean systems are essential.
 - The systems in use should be optimised for maximum resolution of the determinands of interest, e.g. congeners 28/31 and 149/118 in the case of PCBs. Optimisation of initial column temperature and subsequent ramping rates are important as is optimisation of injector temperature when using split/splitless injectors. It should be remembered that even when looking for a limited range of components in a sample co-elution problems may still exist and the analyst should ensure that the target peaks are free from interference from non-target peaks.
 - Automated injection systems are recommended as they can improve reproducibility.
 - The linear range of the ECD should be checked for each component.
 - Certified standards should be used for preparing stock solutions and working standards. It should be noted that some proprietary mixtures are unreliable. All standards should be made up on a gravimetric basis.
 - Multi-point calibrations with an internal standard must be used. Responses that deviate by $\pm 10\%$ for any component in the system should be checked thoroughly.
 - Independent standards, preferably from a separate source/supplier should be used to check calibration data.
 - Certified Reference Materials (CRMs) such as the Canadian Reference Sediments (e.g. HS-1) containing PCBs/OCPs should be run occasionally. It is advisable to prepare an in-house reference material which should be run with each batch of samples.
 - A duplicate sample and blank should be run with each batch.
 - Internal standards should be used. DCBE Nos. 6 and 16 are recommended but iodobenzene and octachloronaphthalene are acceptable, although some problems have been noted with the latter when using 'on-column' injection.
 - Marine disposal licences for PCBs should contain a requirement for congener-specific reporting of information rather than on a formulation basis. To maintain continuity both congener and formulation data should be provided initially with the formulations gradually being phased out.

- AQC compliance, and participation in an appropriate scheme such as the NMAQC scheme, is considered imperative. Consideration should be given to making this a condition of any disposal licences which are granted. Appendix 1 provides full details of the recommended quality criteria that should be applied for the analysis of organochlorine compounds, including PCBs.

5.2 Sediment Quality Criteria

- A dual approach to setting sediment standards is required. A 'no measurable-change' clause is necessary to ensure that disposal sites already contaminated do not get any worse. In conjunction with the 'no-change' clause, specific criteria which have been derived will also have to be met.
- The Equilibrium Partitioning Approach is recommended as providing the most practicable scientific approach for deriving sediment quality criteria. These criteria should be termed 'Sediment Action Levels' and should be derived and used with caution. Users must be aware of the limitations associated with the approach (see Sections 3.2 and 3.3).
- Tables 1 and 2 show the proposed Sediment Action Levels for a variety of organic compounds. They are applicable to both sewage sludge and dredge material disposal sites. These are at best interim values therefore there is an urgent need to carry out proper field evaluations. Realistic quality criteria can only be derived by combining theoretical principles with empirical testing.
- The use of Sediment Action Levels alone is insufficient. Development of other approaches is required in order to derive viable sediment quality criteria for compounds whose behaviour cannot be predicted by the EP approach (e.g. PAHs). All of these approaches should then be combined with biological assessments as part of an integrated disposal area management scheme.
- With sludge disposal at sea due to cease in 1998 the sediments in the disposal areas provide a unique test bed for carrying out field trials to assess the validity of the Sediment Action Levels, how quickly sites recover and other related studies. Appropriate management action would be required to ensure that resources are available to do this and that the programme is properly planned and implemented.
- Monitoring organisations should be encouraged to follow the recommendations of the GCSDM-TTO and to provide feedback on its effectiveness. This would probably have to be on a voluntary basis but could also be realised through the marine disposal licensing scheme.

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ANNEX 1. Marine waste disposal monitoring recommended quality criteria for the analysis of organochlorine compounds

A1. Analytical requirements

The minimum standards for systems to be used for the analysis of organochlorine compounds in marine waste disposal monitoring samples are set out below. Any system of analysis is acceptable, providing that it can be demonstrated to equal or better the standards described.

A1.1 Limits of detection

Limits of detection which are appropriate to the samples being analysed shall be specified in the Standard Operating Procedure (SOP) for the method, and shall in any case not exceed one tenth of the proposed sediment action level for each compound or group of compounds.

A1.2 Detection performance

The system shall be capable of detecting each compound of interest in a standard at a concentration not exceeding the limit of detection which is to be quoted, and shall meet the performance criteria defined in the SOP for the method.

A1.3 Quantification

Compounds shall be quantified individually. PCBs shall be determined in accordance with the terms of an appropriate licence; otherwise, the minimum set of congeners to be determined shall be IUPAC numbers 28, 52, 101, 118, 153, 138, and 180.

A1.4 Calibration

Calibration shall be multi-level, comprising a minimum of three points, and shall take account of the linear range of the analytical method. If quantification is intended outside the linear range, then additional calibration levels shall be included such that the maximum deviation of the calibration curve from the true response curve does not exceed 10%. The calibration curve shall not be extrapolated to the origin unless it can be demonstrated to be linear over this range.

A1.5 Standards

A1.5.1 Standard solutions for calibration and analytical quality control shall be prepared from the certified, pure materials.

A1.5.2 Calibration standards must be verified against an independent set of standards. The materials for preparing calibration and AQC solutions shall therefore be obtained from independent sources, where this is possible.

A2. Standard operating procedures

A2.1 All analysis shall follow a written standard operating procedure (SOP).

A2.2 If for any reason any deviation from the SOP is unavoidable, then it shall be fully documented and reported with the analytical results.

A2.3 The SOP shall be made available for inspection on request.

A3. Method performance

A3.1 Method Blanks shall give rise to results for each compound which are less than the quoted limit of detection.

A3.2 Method precision shall not exceed 25% and shall be determined by calculation from control chart data. No fewer than six data points shall be used for this determination, and the number of points considered and the period covered shall be quoted with any statement of the method precision.

(Note: the minimum of six data points does not apply when the method is first used. It is not expected that fewer than six points will be used more than six months after a regular analysis is begun).

A3.3 Method bias

A3.3.1 For PCBs, method bias shall be assessed by the analysis of a certified reference material (CRM).

A3.3.2 In the absence of a suitable CRM for organochlorine compounds, accuracy may be determined either by participation in intercalibration exercises or by the analysis of a spiked sample.

A3.3.3 Method bias shall be less than 30%, and therefore the results of individual analysis of a CRM shall be within $\pm 80\%$ of the certified value.

A3.4 A control chart shall be maintained in order to provide the precision data specified in A3.2 above, and to demonstrate that the method continues to perform to an acceptable standard.

A4. Reporting of results

In addition to the analytical data, the following information shall be reported:-

A4.1 With the first application for licence:

A4.1.1 The proposed SOP.

A4.1.2 Analytical instrument type and operating conditions.

A4.1.3 Limits of detection of the analytical method.

A4.2 With each batch of analytical data to be reported:

A4.2.1 Results of analysis of the method blank.

A4.2.2 Method precision and the number of data points used in its calculation.

A4.2.3 Method accuracy and means of determination.

A4.2.4 Details of any documented deviations from the SOP.

ANNEX 2. Membership of the Organics Task Team 1989 - 1994

Team Chairmen

Mr R. J. Vincent	Thames Water plc	1989-90
Mr S. Scott	Thames Water plc	1990-91
Dr I. M. Ridgway	Forth River Purification Board (now Scottish Environment Protection Agency (SEPA))	1991-94

Team Secretary

Mr H. R. Rogers	Water Research Centre	1989-94
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Team Members

Mr C. Allchin	MAFF, DFR (now CEFAS)	1989-94
Mr R. Law	MAFF, DFR (now CEFAS)	1989-94
Mr J. Webster	Lothian Regional Council	1989-94
Dr E. Donaldson	DoED(NI)/IRTU	1989-94
Mr W. A. McCrum	North West Water Ltd.	1989-90
Mr M. Tombs	North West Water Ltd.	1990-94
Dr A. Kelly	SOAEFD	1989-93
Dr P. Balls	SOAEFD (by correspondence only)	1994
Mr D. Yeoman	Strathclyde Regional Council	1989-92
Mr M. Cunningham	Strathclyde Regional Council	1992-94
Mr S. Scott	Thames Water plc	1991-94
Dr D. Hillier	Thames Water plc	1994
Dr B. Crathorne	Water Research Centre	1989
Dr C. Watts	Water Research Centre	1993-94
Mr B. Wibberly	Wessex Water plc	1989-92
Mr M. G. Firth	NRA Yorkshire Region (now Environment Agency North East Region)	1991-93
Mr M. Daniels	NRA Yorkshire Region (now Environment Agency North East Region)	1993-94
Miss S. Owen	Northumbrian Water plc	1994



The Centre for Environment, Fisheries & Aquaculture Science
Lowestoft Laboratory, Pakefield Road
Lowestoft, Suffolk NR33 0HT UK
Tel: +44 (0) 1502 562244
Fax: +44 (0) 1502 513865

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