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Metal contamination of sediments and statutory quality objectives

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METAL CONTAMINATION OF SEDIMENTS AND STATUTORY QUALITY OBJECTIVES

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EXECUTIVE SUMMARY

Under the Water Resources Act 1991 all controlled waters may be subject to a system of classification. At present there is no suitable classification for estuarine or coastal waters but the NRA has developed outline schemes dividing water quality into four classes based on water and sediment quality, and biological and aesthetic criteria.

This report proposes a classification scheme for the sediment component of the schemes for estuarine and coastal waters based on existing levels of List I and List II metals (Hg, Cd, Cu, Pb, Cr, Zn, Ni, As) in UK estuarine and coastal sediments. The scheme is designed to reflect the extent of contamination from natural and anthropogenic sources and is not intended to relate directly to any biological effects which may result. However, the relative toxicity of List I and List II metals is considered when deriving the overall classification.

Three options were assessed, both for the establishment of class thresholds for each individual metal and for the combination of individual metal classes to form a single metal sediment classification. To obtain a more normal distribution of zones over the classification, it is proposed that class thresholds be based on the 15:50:85 percentiles of the concentration distribution for each metal. An overall classification may then be obtained by weighting List I metals against List II and obtaining a weighted mean.

A single sampling strategy for estuarine and coastal waters is proposed. It was necessary to base the initial class boundaries on the 100 µm size fraction due to limitations in available data. It is therefore recommended that, for the first survey, both the 100 µm and <63 µm size fractions are analysed and subsequent classifications standardised to the <63 µm fraction.

The scheme is severely constrained because of the lack of comparable data from a truly representative sample of UK estuaries and coastal waters and it is considered essential that the class boundaries are reviewed in the light of subsequent data collected for the scheme.

KEY WORDS

Metals, Sediments, UK Estuarine and Coastal Waters, Statutory Quality Objectives

1. INTRODUCTION

Sections 82 and 83 respectively of the Water Resources Act 1991 require that all controlled waters may be subject to a system of classification and the Statutory Water Quality Objectives (SWQOs) may be set in relation to such waters by the Secretary of State for the Department of the Environment (DoE). Similar powers are laid down in Scotland (Schedule 23 Sections 30A to 30E of the Water Act 1989 which amended the Control of Pollution Act 1974).

In 1991 the NRA published their initial proposals for SWQOs (NRA 1991) comprising three elements, namely:

- achievement of relevant use-related environmental quality objectives (EQOs), i.e. compliance with relevant environmental quality standards (EQSs);
- achievement of target class of relevant classification scheme;
- compliance with EC directives.

Following a period of public consultation, the proposals have been rearranged into (NRA 1992):

- different Use Classifications (UCs) for setting targets relating to the actual or proposed use of the water, on a statutory basis i.e. Statutory Water Quality Objectives; plus
- a General Quality Assessment (GQA) scheme, for assessing general overall progress on a periodic basis.

These new proposals have now been passed to the Department of the Environment (DoE) for consideration.

At present, no classification scheme exists for coastal waters and the existing National Water Council (NWC) scheme for estuaries is considered unsuitable for a statutory scheme because of its subjectivity and the limited determinands it covers. In 1990, a sub-group of the NRA Water Quality Survey Group proposed a framework for a new tidal waters classification scheme which has components relating to sediment accumulation of persistent toxic substances, and water, aesthetic and biological quality. They also proposed that coastal waters be separated into two zones (NRA 1991):

- nearshore waters, extending from the landward limit to a line 200 metres offshore from the spring tide low water mark; and
- offshore waters, extending from the 200 metre line to the Three Nautical Mile Limit

The proposals for estuaries and coastal waters have not been altered since the publication of the consultation document.

This document reports the research undertaken to develop the contaminated sediment component of the proposed classification scheme.

2. PROJECT OBJECTIVES

The overall objective of the project as written in the PIA was:

To establish typical concentrations of EC Dangerous Substances Directive List I and List II metals (in particular mercury (Hg), cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr), zinc (Zn), nickel (Ni) and arsenic (As)) in sediments within UK estuarine and coastal waters. To utilise these data as a basis for classifying such waters into four classes based on the extent of sediment contamination: background, elevated, substantially elevated and grossly elevated.

The specific objectives of the project were:

(a) to review by means of a desk study, available information on List I and List II metals in surface sediments from UK estuarine and coastal waters. Comparability between sites of different granulometric composition should be ensured and any metal for which there are insufficient data to form the basis of the classification scheme identified;

(b) the data gathered should then be utilised to establish a typical "uncontaminated" background level for each metal. An incremental classification scheme should then be developed, based on multiples of the background levels, to represent three further classes: elevated, substantially elevated and grossly elevated;

(c) the implications of the scheme should be illustrated for a representative cross section of the UKs estuaries and coastal waters;

(d) a standardised sampling and analysis strategy should be defined such that data are comparable despite differences in granulometric composition between sites.

3. GENERAL APPROACHES AND CONSIDERATIONS FOR CLASSIFICATION SCHEMES

There are number of general options for the form or basis of classification schemes:

- a quantitative comparison of contaminant or determinand levels;
- differences in quality related to effects;
- assessment of anthropogenic impacts;
- allowance for natural or background quality.

The aim of the classification scheme would be to gain a quantitative comparison of sediment quality within the estuaries and coastal waters of England and Wales. Ideally as well as a giving a direct comparison of quality, be it in a 'snap-shot' of time, the scheme would give a comparative assessment of anthropogenic impact against natural or background quality. For example, there are large differences in geology around the coasts of England and Wales which is reflected in a large variation in background sediment contaminant concentrations. These differences may confound or mask anthropogenic impacts. A comparison of quality resulting from anthropogenic sources would serve to highlight more readily problem areas and direct more efficiently control measures required to improve the situation. Such an approach has been developed for the biological assessment of river quality using the RIVPACS model which aims to predict the structure of macrobenthic river communities expected in 'clean' situations from a range of measured physicochemical parameters. Observed community parameters are then compared with those predicted to obtain an indication of possible impact.

Particulate metals from natural and anthropogenic sources accumulate together and therefore it is difficult to determine which proportion of the sedimentary load is natural and which is anthropogenically derived. This is due mainly to the variation in sedimentary loads, depending on the mineralogy of the area and the grain size distribution. Such natural variability of trace metal levels in sediments can be compensated for by the use of normalisation techniques, thus allowing anthropogenic contributions to the metal load to be identified and calculated.

There are several techniques which have been used to normalise for the effects of grain size and mineralogy on sediment-metal levels. These include:

- granulometric normalisation approach;
- absolute metal concentrations in specific size fraction approach;
- geochemical normalisation approach;
- integrated approaches to normalisation.

There are also options for the definition of the quality/class thresholds in a GQA. They can, for example, be based on:

- simple statistical rules;
- multiples of 'background' levels;
- proportion of maximum levels;
- defined 'effects';
- anthropogenic impacts.

A common problem of assessment or classification schemes is how to set threshold values between classes when, in effect, one is attempting to classify a continuum of quality with generally no natural cut-off points between classes or quality. An approach to this is to set threshold values between classes based on simple statistical rules so that a certain or desired proportion of the total estuary or coastal water population appears in certain classes. For example, it might be decided that average quality estuaries should predominate and most would, therefore, appear in Classes 2 and 3 (in a four class classification). Alternatively class thresholds could be based on defined 'effects' or standards. For example in the case of sediment contaminants it could be based on measured toxic effects as defined by a specific ecotoxicological test, or, if they existed, sediment EQSs. Class boundaries could then perhaps be based on levels of measured effect e.g. chronic against acute concentrations and/or biological community effects, or on multiples of EQSs. Another approach is to set thresholds to reflect degrees of contamination in relation to maximum observed values, multiples of background (if these can be determined) or minimum observed values.

The classification should aim to quantify or at least account for the following sources of variability in sediment contaminant concentrations:

1. Spatial: from small scale (metres) to differences within an estuary or coastal zone, or geographic differences. Within an estuary variability may reflect the location of sources of the contaminants (e.g. rivers, industrial discharges). Fine sediments also tend to accumulate in upstream zones of estuaries and therefore gross metal concentrations may be higher in these areas. Geographic differences may reflect differences in mineralogy and geochemistry as well as differences in anthropogenic inputs.

2. Temporal: these are likely to manifest themselves over relatively long time periods compared to water quality determinands. Sediments act as integrators of impact of metal concentrations and therefore changes are likely to happen over many years, both in relation to sediment movement patterns and as pollution control measures are introduced.

3. Granulometry: it is well established that metals preferentially associate with different size fractions of sediment, particularly with the fine sediment. The comparison of sediments within estuaries and between estuaries and coastal sites therefore requires due allowance for this (i.e. the data are generally normalised to standard size fractions).

4. Anthropogenic and natural source of contaminants: many sediments have high contaminant concentrations arriving from natural rather than anthropogenic sources. Ideally the classification would reflect anthropogenic factors only. The separation of anthropogenic contamination from natural can be attempted, as described earlier, through normalisation methods that rely on comparison with marker/conservative elements.

5. Sampling and analytical methods: such as use of grabs or divers, types of grab, analytical methods acid digestions XRF etc. Different types of grab could potentially achieve different penetration within the sediment leading to different layers being sampled and hence potential differences in concentration. Different acid leaches would remove different proportions of the adsorbed contaminant and methods such as X-ray fluorescence would give gross rather than net values.

Sampling and monitoring for classification would, therefore, have to cope with the inherent variability associated with tidal waters particularly in estuaries and to some extent coastal waters.

Once the GQA has been formulated, the accuracy of the assessment of quality is affected by:

- amount of sampling done;
- accuracy of instrumentation/analytical methods used to produce determinands;
- statistical form of all data relevant to the classification rules;
- statistical form of estuary classification rules themselves;
- how close the estuary is in truth to a Class boundary.

The more sampling undertaken the more accurately will the classification of sites be. However, there would have to be a trade off between what is desirable and what is affordable. For all levels of sampling, standard methods and procedures with appropriate AQC would be required to obtain standardised, directly comparable, data. Decisions would also be required on how data are combined in deriving the measure of quality, for example, would mean, median or percentile values be used. The statistical form of the classification rules how the estuary or coastal zone population is divided into the different classes. There are also likely to be problems associated with those sites that are in truth to a class boundary, there will always be difficult decisions taken and particular sites may change class from one assessment to another based on only small changes in the summary statistic.

4. DERIVATION OF THE CLASSIFICATION SCHEME

4.1 Sources of data

All the NRA regions and RPBs in Scotland were approached, as primary sources of recent data and in addition some Regional Councils in Scotland and other organisations. Literature searches and reviews were carried out at the start of the study, however the data available were found to be relatively old and tended to be incompatible with each other. By far the largest collection of comparable data was held by the Plymouth Marine Laboratory, and this was eventually obtained for the purposes of this study.

Although most laboratories now analyse the <63 µm sediment fraction this was not so in the past. As a result data were received for total sediment, <2 mm, <100 µm and <90 µm sediment fractions in addition to the <63 µm fraction. The problems this presents can be illustrated using data obtained from the outer Thames estuary. A comparison of the metal levels determined in the <90 µm and <63 µm sediment fractions indicates that, as may be expected, metal concentrations were generally higher in the <63µm fraction than in the <90 µm fraction. For three of the four metals (Hg, Pb and Zn) a statistical relationship between the metal levels in the two fractions could be found, whereas for cadmium the relationship was not statistically significant. The ratios between the <63 and <90 µm fraction are shown below:

	<90 µm	<63 µm
Cd	0.59	1
Hg	0.4	1
Pb	0.56	1
Zn	0.54	1

It is likely that this relationship would be different for different geographic locations and for other metals not included in this comparative study. Little information could be found covering the relationship between metal levels in different sediment size fractions, and therefore it was not possible to determine factors by which data from different fractions could be corrected. The inconsistencies between different data sets in the sediment size fraction analysed means that it is difficult to realistically combine data obtained from the NRA regions and the extensive PML dataset. Therefore, for the purposes of this study the PML data alone have been used.

4.2 Manipulation of database

The ideal database would have contained data from each estuary and coastal water to be classified from samples taken in the same time frame and collected and analysed by the same methodology. As the best available database was not established on this basis, several methods were used in an attempt to obtain as representative a picture as possible of the range and frequency of sediment concentrations in England and Wales. The database was, therefore, examined and manipulated in four ways to assess the options for deriving the classification. These were:

- giving equal weight to each sample;
- deriving a summary statistic for each site;
- deriving a summary statistic for each estuary;
- dividing estuaries and coastal areas into zones, and deriving a summary statistic for each zone.

The PML database is an amalgam of the estuarine metal contamination studies undertaken over the last 20 years or so. The various studies that make up the database had a number of objectives that focused on an assessment of benthic invertebrates as analytical indicators of metal contamination. Monitoring was, therefore, not the primary objective although most estuaries appear to have been visited. Studies have historically concentrated on the most polluted areas with clean sites represented by small amounts of data. The database reflects this with large numbers of samples from the polluted estuaries and only few samples from the cleaner estuaries. The dataset cannot be thought of as a continuous record, but rather as a series of snapshots of a large number of estuaries. (Bryan *et al.* 1992)

The first stage of the manipulation involved a simple assessment of the entire population of samples, to gain some idea of likely contaminant levels and the sampling distribution throughout the UK. At this stage all samples were considered equally to produce an overall distribution. Table 4.1 shows the number of samples taken for each of the metals, together with some basic summary statistics. All of the metals are characterised by skewed distributions with the vast majority of samples having values well below the mean.

Table 4.1 Summary statistics for each metal

Metal	Number of samples	Mean	Median	St Dev	Min	Max	25%ile	75%ile
Cd	836	1.0295	0.570	1.8046	0.0030	27.600	0.264	1.0745
Cr	859	52.57	40.60	57.53	4.60	826.00	31.10	54.20
Cu	993	317.2	60.0	717.0	2.8	4779.1	31.3	257.5
Zn	994	500.7	234.2	841.6	26.4	6095.6	135.8	434.0
Pb	990	231.6	101.5	769.2	1.8	9305.0	56.8	183.0
Hg	567	0.9099	0.4790	1.1814	0.0130	8.940	0.210	0.9600
Ni	880	30.083	28.150	19.514	3.200	413.00	21.666	36.500

This very simple assessment takes no account of the geographical location of sampling, nor the number of times a site was sampled through time. This means that particular estuaries and sites within estuaries which have been sampled more frequently will bias any metal classifications. Since the majority of these are the most heavily polluted it is important to account for this. However, there are a number of simple techniques which may be applied when designing the classification to reduce this bias.

Before the classification system can be derived, a statistic to represent the area or unit to be classified must be selected. For example, if a number of samples are taken at a particular site, one value (a summary statistic) is required to represent that site. The median was chosen as the most appropriate statistic in favour of the mean, due to the skewed nature of the data, as being more representative of the large number of samples below the mean. The use of the mean as a threshold value between Classes 2 and 3, for example, would lead to more sites falling in the "less contaminated" classes. Equally a number of other statistical parameters could be considered, for example the maximum value at a a site or the minimum value at a site.

Assessing the median value for each metal for each site is not a task that lends itself readily to electronic calculation, especially for a large database such as this one. Therefore one metal, cadmium, was chosen upon which to model the classification. A second smaller database was produced containing the median, maximum and the number of samples taken at each site sampled for cadmium. This second database removed an element of the bias associated with treating all samples equally, as any one particular site is now represented by one statistic. It does not, however, remove the bias associated with many of the sampling sites being located within one particular estuary or part of an estuary. This is important to consider because if sampling is concentrated around "hotspots" of high contamination the overall class of an estuary could be adversely affected, and therefore would not be representative of overall sediment quality.

It is possible to reduce this bias by choosing a suitable resolution of the area to be classified. A range of methods can be adopted in order to achieve this. One option explored in this study was to produce a single value for an estuary. The site statistics were grouped by estuary, using, as far as possible, estuarine regions used in previous water quality surveys. For example, Southampton Water and its tributaries (Hamble and Itchen) were each treated as separate estuaries. This produced a further database containing values for the median concentrations and the number of samples taken for each estuary sampled.

There are potentially some difficulties associated with the estuary resolution approach. Many systems are complex and metals may not act conservatively, leading to the possibility that one or two high site statistics could result in an entire estuary being classified in one band whilst a much better representation would be to subdivide an estuary into appropriate zones and classify each of them separately. The NRA have previously adopted an approach of dividing estuaries into smaller zones for water quality classification. Inspection of any water quality map will illustrate this clearly, with different areas of the same estuary being shaded different colours. There are a number of criteria by which an estuary may be divided into zones including salinity, area, distance from head etc. Within the constraints of the project and the available data (e.g. no salinity data was available for estuaries sampled by PML) it was only possible to divide an estuary along its length. Each estuary was, therefore, subdivided into three zones of approximately equal length; inner, middle and outer. Thus up to three values could result for each estuary. The more complex systems, such as the Fal (Cornwall) which has several estuaries in the same system, were divided to have one common outer zone and a number of mid and inner zones (one for each composite estuary) as illustrated in Figure 4.1.

4.3 Temporal trends and variability.

The database contains information from 1968-1990 and therefore there could potentially be evidence of the temporal variation associated with the data. There is an obvious need to consider this variation and identify any possible trends. Unfortunately, the data contained within the database does not allow for a comprehensive temporal assessment.

The majority of the sites have only been visited once, when they would have been analysed for the suite of metals (Figure 4.2). Very few sites have more than ten values for any one particular determinand and no site had more than 20 samples taken. Figure 4.2 clearly illustrates that over 80% of the data is more than six years old and more than 50% predates the 1980s. None of the sites have a complete temporal dataset and therefore temporal trends can not easily be determined. However, in order to illustrate the importance of temporal variability, two sites on the Mersey estuary for which there are a number of samples were considered. Figures 4.3 and 4.4 reveal distinct temporal trends, with a decrease in sediment contamination over the last few years for all metals at both the sites. Ideally the classification would be based on the most recent data on samples taken within the same time frame. The presence of distinct temporal trends in the data leads to the likelihood of estuaries and coastal waters moving into a better quality class when classified using a new database, than when classified according to the present dataset.

The derivation of the classification does not therefore take into account temporal changes.

4.4 Determination of class boundaries

As there were no data that allowed normalisation to take into account natural contamination (Section 3), the classification was based on the observed gross concentrations only.

The derivation of the scheme will be illustrated by the example of cadmium. A population of 219 values was analysed, one for each estuarine zone. Section 4.2 details options for both choosing a statistic and choosing the resolution of the area (estuary, zone or site) on which the classification could be based. Here a number of options are put forward for deciding class thresholds. Potentially many combinations of statistic and resolution could be used as the basis of a classification scheme, e.g. maximum metal value to represent a site, estuary or zone. There was not scope within the project to illustrate how determination of class boundaries would affect all of these and one combination is chosen to illustrate options for determination of class boundaries: median value for each estuarine zone. The derivations below are detailed using the cadmium data and overall summaries presented for other metals. Despite the removal of the bias relating to sampling programme there remained a high skew in the distribution of metal values (Figure 4.5).

Very few zones have high cadmium values with the majority being much lower.

The present NWC scheme for estuarine water quality has four classes A-D so it would appear sensible to adhere to this number of classes. For all the options considered here there are four classes 1-4, with 1 being least-contaminated and 4 most-contaminated. The distribution of cadmium can now be used to determine the class thresholds, here again there are a number of options that can be applied. Three have been selected and used to derive classification schemes, namely:

1. To divide the distribution into non-equal quartiles and set thresholds based on the 15-50-85 percentiles. With respect to the 219 zones that have cadmium values this results in 34, 76, 75 and 34 in Classes 1 to 4 respectively.

2. To divide the distribution into quartiles and set thresholds based on the 25-50-75 percentiles, so that there are an equal number of zones in each class. For cadmium this is: 55, 54, 55, 55 respectively.

3. To determine the thresholds based on a percentage of the maximum value of the distribution, in the case of cadmium 8.69 $\mu g\ kg^{-1}$. Due to the highly skewed nature of the distribution the following thresholds were chosen 2.5, 5 and 10% of maximum value. Applying these thresholds to the cadmium dataset resulted in 64 Class 1, 54 Class 2, 60 Class 3 and 41 Class 4 estuarine zones.

The assignment of zones to a class can be illustrated by drawing on examples from the database. For an example, Option 2 above, using the 25% median and 75% quartiles as class boundaries, was applied to a specific case. The sediment of the inner zone of the Dart estuary has a median cadmium value of 0.45 $\mu g\ g^{-1}$. If this value is compared with the summary statistics in Table 4.2 it falls between the median value, 0.37 $\mu g\ g^{-1}$ and the 75 percentile value of 0.7 $\mu g\ g^{-1}$ and is, therefore, allocated to Class 3. Taking the inner zone of the Dart example again and applying the classification thresholds suggested in Option 3, based on the percentage of the maximum value 8.69 $\mu g\ g^{-1}$ observed, it lies between the 10% and 5% class boundaries and is also assigned to Class 3. Table 4.3 reiterates these examples for the middle and outer Dart and additionally illustrates class assignment based on Options 1 and 3.

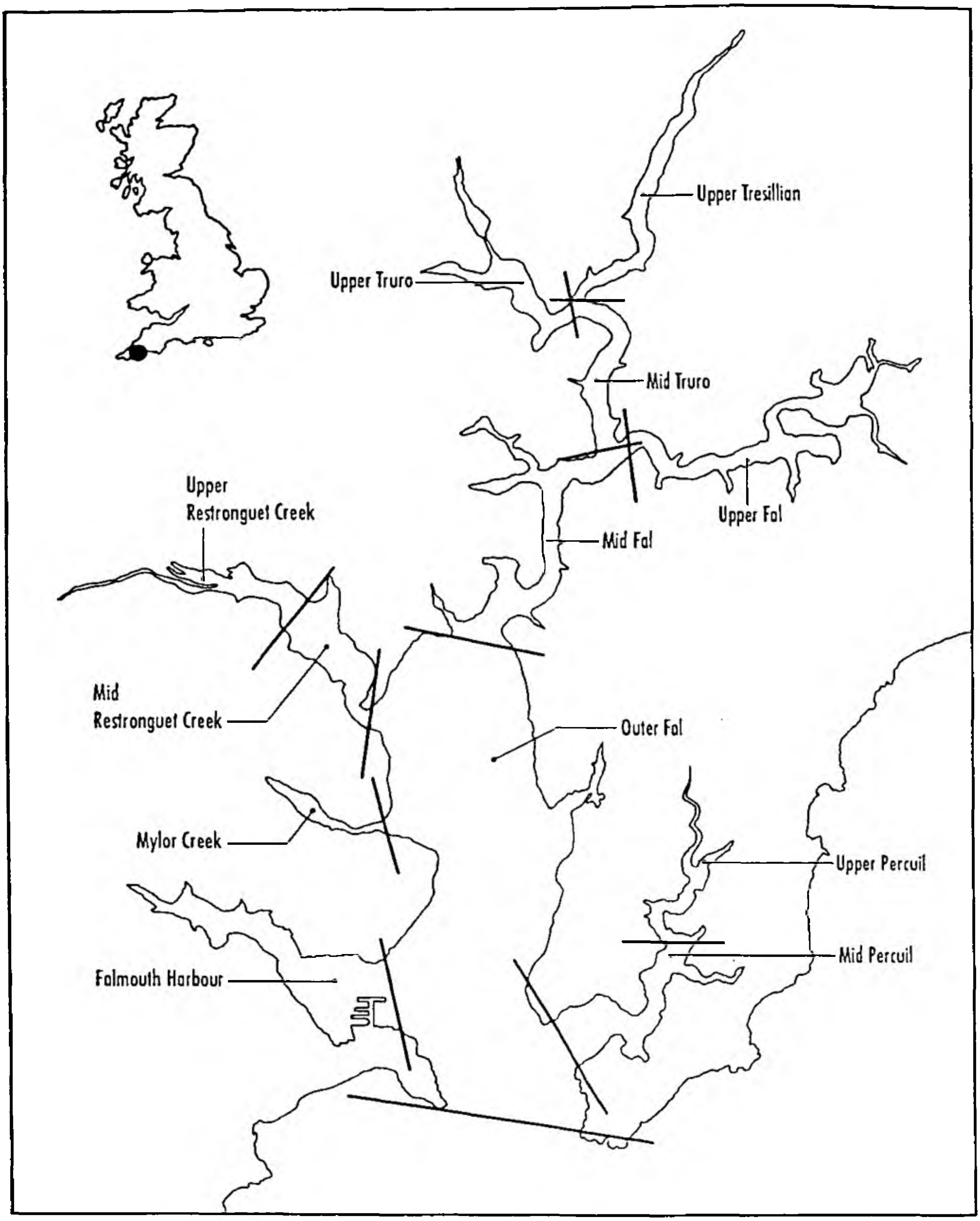

Figure 4.1 Example of spatial divisions within a complex estuary

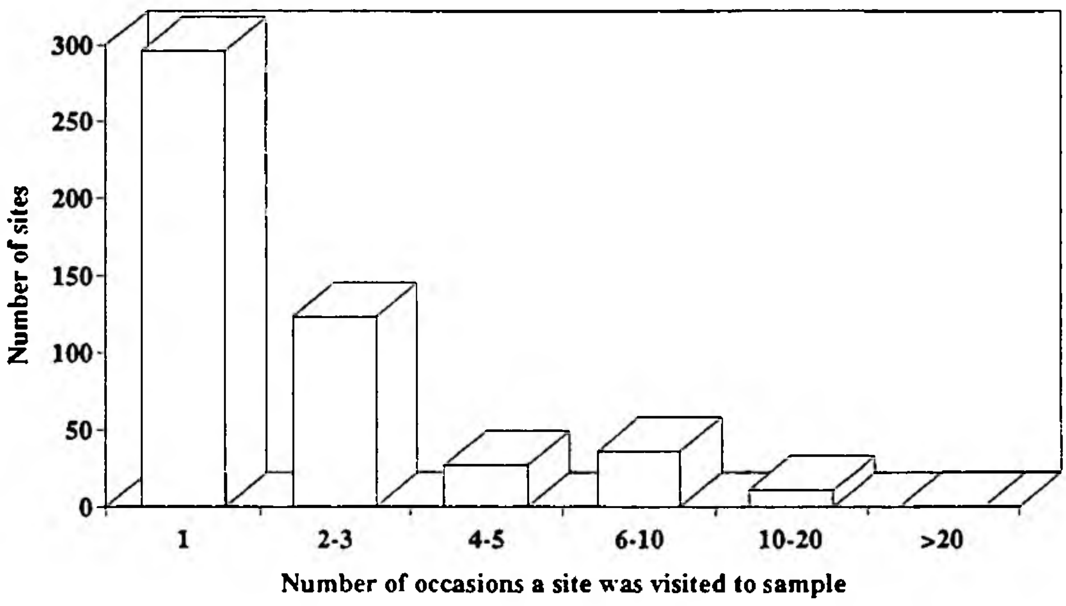

Figure 4.2 Sampling frequency for metals in sediments

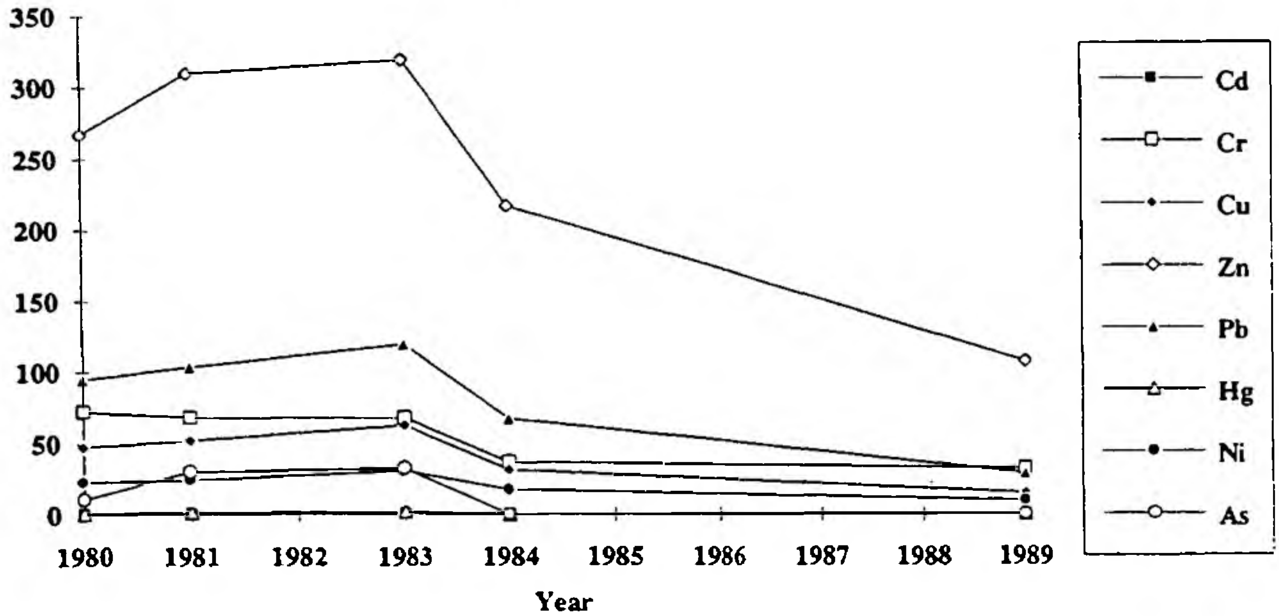

Figure 4.3 Metal concentrations at Egremont (Mersey) 1980-1989

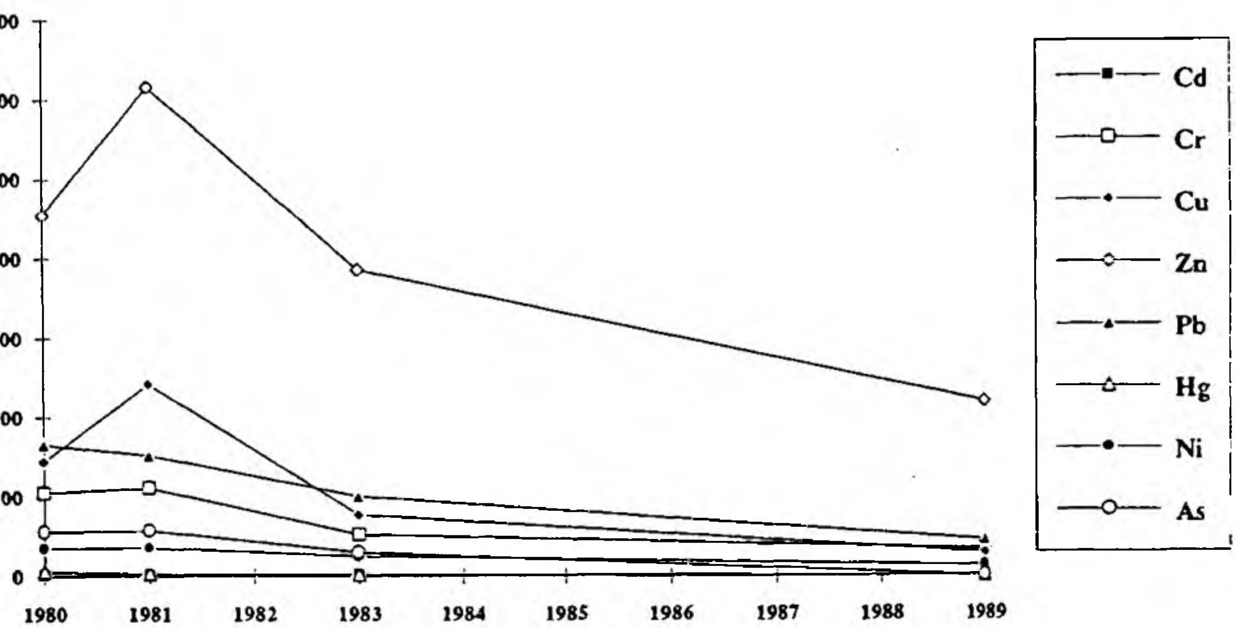

Figure 4.4 Metal concentrations at Widnes (Mersey) 1980-1989

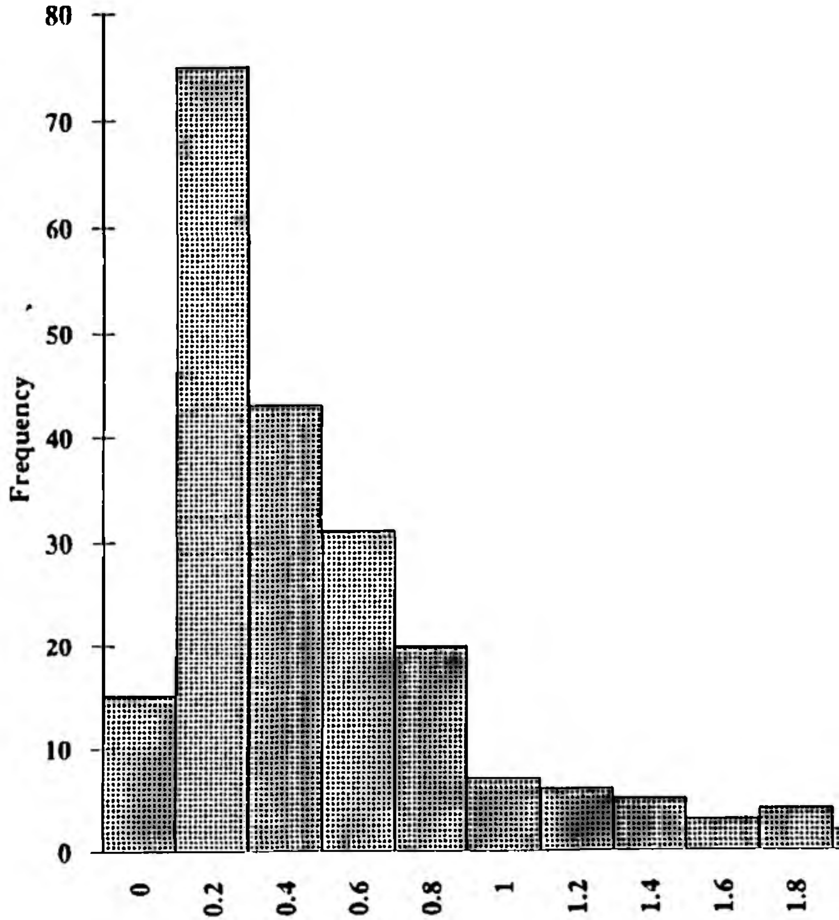

Figure 4.5 Distribution of Cadmium values (zone statistic)

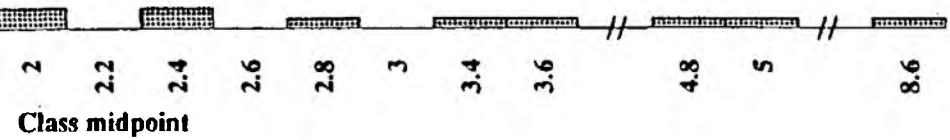
2
2.2
2.4
2.6
2.8
3
3.4
3.6
4.8
5
8.6
Class midpoint

Table 4.2 Summary statistics for cadmium (mg kg^{-1} dry weight)

Number of zones	Mean	StDev	Se mean	Min	Max	Percentiles of distribution					% of maximum		
						0.15	0.25	0.5	0.75	0.85	2.5	5	10
219	0.62	0.88	0.06	0.02	8.69	0.15	0.19	0.37	0.7	0.9	0.22	0.43	0.87

Table 4.3 Assignment of Cadmium values to classes for the Dart Estuary

	Zone	Cd	Option 1 15-50-85	Option 2 25-50-75	Option 3 2.5-5-10%	NWC
Dart	IN	0.450	3	3	3	A
	MID	0.730	3	4	3	A
	OUT	0.060	1	1	1	A

Following the selection of the criteria on which the classification boundaries would be set, based on cadmium, all estuarine and coastal zones were classified by these three options for each metal. Table 4.4 gives the classification boundaries for each metal whilst Table 4.5 summarises the number of zones falling into the different classes.

It can be seen that Option 3 (proportion of the maximum) gives a very variable distribution of the number of zones in each class for the different metals. For example, whereas cadmium and mercury gives an approximately even distribution of zones between classes, zinc gives a normal distribution, copper, lead and arsenic a highly skewed distribution towards Class 1, and nickel and chromium highly skewed to Classes 3 and 4. If this approach was adopted then there is a potential shortcoming in that the overall classification (Section 4.5) may always default down to same metal, that is chromium and nickel.

Table 4.4 Classification boundaries for each metal

Metal/Class	Option 1	Option 2	Option 3
Cd			
1/2	0.15	0.19	0.22
2/3	0.37	0.37	0.43
3/4	0.9	0.7	0.87
Cr			
1/2	27	30	17
2/3	37	37	33
3/4	58	49	67
Cu			
1/2	15	19	84
2/3	32	32	167
3/4	100	59	335
Zn			
1/2	80	96	73
2/3	96	96	145
3/4	300	259	290
Pb			
1/2	30	41	78
2/3	58	58	156
3/4	150	106	312
Hg			
1/2	0.1	0.16	0.17
2/3	0.34	0.34	0.34
3/4	0.85	0.58	0.67
Ni			
1/2	17	20	4
2/3	25	25	8
3/4	35	34	16
As			
1/2	7.5	8.7	58
2/3	12.2	12.2	117
3/4	30	23.2	233

Table 4.5 Resultant class distributions for individual metals based on three classification options

Metal/Class	Option 1	Option 2	Option 3
Cd			
1	34	55	64
2	76	54	54
3	75	55	60
4	34	55	41
Cr			
1	33	55	11
2	77	55	71
3	76	55	114
4	33	55	24
Cu			
1	34	56	184
2	78	56	18
3	78	56	10
4	34	56	12
Zn			
1	34	56	27
2	78	56	83
3	78	56	75
4	34	56	39
Pb			
1	31	56	137
2	81	56	54
3	81	56	26
4	31	56	7
Hg			
1	29	54	56
2	79	54	52
3	74	54	59
4	34	54	49
Ni			
1	32	55	0
2	78	55	2
3	74	57	26
4	38	55	194
As			
1	34	53	200
2	73	54	7
3	73	54	1
4	35	54	7

4.5 Combined metal classification

A further requirement of the scheme is to produce a combined classification that, in some way, incorporates all of the individual metal classifications. Once again a number of potential options are possible. The three considered have all been illustrated using the 15-50-85 percentile individual classifications, although the combinations below could equally have been carried out on any of the other classifications suggested in Section 4.4. The three options/methods for obtaining an overall classification proposed are:

A: taking an average of the individual metal classifications;

B: defaulting to the worst List I class;

C: weighting the List I classes by a factor of ten compared to List II and then obtaining an overall average.

As before it is easiest to illustrate the derivation of the combined metal classifications by drawing on specific examples from the database. Table 4.6 below shows metal classifications for each of the individual metals for three estuaries Tees, Red and Restronguet Creek and the resulting combined classifications based on the three options. Classification for all the estuarine zones examined in the study are displayed in Appendix A.

Option A: Average of all classes

(Cd class + Cr class + Cu class + Zn class + Pb class + Hg class + Ni class + As class)/8

for the Inner Tees this equates to

(4+4+4+4+4+4+3+4)/8 = 3.875 = Class 4

and for the Outer Tees:

(3+4+3+3+3+4+3+4)/8 = 3.375 = Class 3

Option B: Default to worst List I class and ignore List II values

For the Inner Restronguet Creek :

Hg is Class 3 and Cd is Class 4. Defaulting to the worst of these leads to an overall classification of Class 4.

For the Outer Tees:

Hg is Class 4 and Cd is Class 3. Defaulting to the worst of these leads to an overall classification of Class 4

Table 4.6 Examples of the combined classification

		Cd	Cr	Cu	Zn
Tees	IN	4	4	4	4
Tees	MID	*	*	*	*
Tees	OUT	3	4	3	3
Red	IN	2	1	4	2
Restronguet Ck	IN	4	1	4	4
Restronguet Ck	MID	4	2	4	4

Pb	Hg	Ni	As	Op.A	Op.B	Op.C	NWC
4	4	3	4	4	4	4	C-D
*	4	*	3	4	4	4	C-D
3	4	3	4	3	4	3	B
1	1	1	4	2	2	2	C
4	3	3	4	3	4	3	B
4	3	3	4	4	4	4	B

Option C : Weighted average ((10*List I + List II)/26)

(10(Cd class)+10(Hg class)) + Cr class + Cu class + Zn class + Pb class + Ni class + As class)/26

For the Outer Tees this equates to:

((10*3)+(10*4)+4+3+3+3+3+4)/26 = 3.46 = Class 3

For the Inner Restronguet Creek:

((10*4)+(10*3)+1+4+4+4+3+4)/26 = 3.46 = Class 3

Table 4.7 below summarises the number of zones within each class for each of the options.

Table 4.7 Class distribution of estuarine and coastal zones based on proposed combined metal classification options

Class	Option A	Option B	Option C
1	25	20	25
2	81	72	93
3	114	92	99
4	20	54	23

Options A and B tend to result in more zones being classified into Classes 3 (most) and 4, while Option C gives a more normal distribution with the most estuaries occurring in Classes 2 and 3. Option C would, therefore, seem to be the most favoured option and it is perhaps also scientifically more justifiable as cadmium and mercury are generally considered to be more toxic (in the water column) than List II metals.

5. ITERATIONS

Following the derivation of the classifications for each individual metals, and the development of methods for the combination of the schemes, iterations were performed to determine the effect of the boundaries on classification assigned to estuaries by the current NWC system. Table 5.1 below gives details of the median metal values and subsequent individual metal classes, based on Option 1 (15-50-85 percentiles) for three estuarine zones.

Table 5.1 Mean metal concentrations and individual metal classifications for three estuarine zones, based on Option 1

	Cd	Cr	Cu	Zn	Pb	Hg	Ni	As
Mid Yealm								
Conc. (mg kg^{-1})	0.14	31	30	88	50	1.2	26	7.1
Class achieved based on Option 1	1	2	2	1	2	4	3	1
Mid Tamar								
Conc. (mg kg^{-1})	0.91	48	319	392	167	0.87	45	97.
Class achieved based on Option 1	4	3	4	4	4	4	4	4
Inner Tamar								
Conc. (mg kg^{-1})	1.1	42.7	412	477	194	0.86	50.7	109
Class achieved based on Option 1	4	3	4	4	4	4	4	4

As already discussed these data can be used to develop a combined classification scheme. For example, considering the Mid Yealm zone, if the combined classification is based on Option B, then the overall classification becomes Class 4, due to the high mercury value. The combined classifications for the three estuarine zones are given in Table 5.2. In each case the individual metal classifications were obtained using Option 1.

Table 5.2 Combined classifications for three estuarine zones

	NWC	Option A	Option B	Option C
Mid Yealm	A	2	4	2
Mid Tamar	A	4	4	4
Inner Tamar	A	4	4	4

All three of these options for combination show very few Class 1 estuaries and most estuaries fall into Classes 2 or 3. Adoption of any of these options would result in a large divergence from the current NWC classification, in which the vast majority of estuaries are in Classes A and B. For several zones, the classification has moved from the cleanest class to the most contaminated with the great majority being downgraded by at least one class. Table 5.3 summarises the changes in class which would result following the adoption of each method of combination.

Table 5.3 Number of zones changing in class from existing NWC water quality scheme to a proposed metal sediment classification

Classification	Number of classes changed				
Option	-3	-2	-1	0	+1
Option A	9	73	88	48	5
Option B	25	75	85	34	3
Option C	10	61	103	45	4

The number of zones classified by each option in Table 5.3 are not the same, this is because some zones lacked either cadmium or mercury data.

6. SAMPLING STRATEGY

It is suggested that each defined subzone of an estuary and area of coastal waters is sampled with a degree of replication for the purposes of classification. The sample sites should be selected where they are believed to reflect general sediment quality of that zone - existing information might help in this selection. It is likely that there will be steep concentration gradients around known sources of contaminants. Sampling too close to these point sources may, therefore, distort the overall assessment of sediment quality. The number of sites per unit area of classification would depend on the desired precision of defining differences in sediment concentrations on a small and large spatial scale. Replication is required in order to account for some of the large heterogeneity that is likely to be found on a small spatial scale.

For example, a statistically designed sediment sampling survey was undertaken in the Thames estuary to examine the components of error associated with sampling for metals at a predetermined location (ap Rheinallt *et al.* 1989). It was found that both subsampling error (two subsamples from the same grab) and re-grab (multiple grabs from the same site) errors were large, indicating considerable small-scale variability, but re-visit error (by sailing away and returning in between sampling) was not usually significant. Replication at each site would reduce this error: for a given number of samples per site, the expected reduction in error is greatest if single samples are taken from each of a number of grabs on a single visit. Though it is difficult to be definitive about the number of replicates needed (as this is likely to differ between locations and between metals) it is suggested that four replicates are taken. In the case of the Thames estuary this would have reduced the standard deviation around the mean concentration by 57%.

It is proposed that for the first classification survey that samples are taken and analysed for both the <100 µm and <63 µm size fractions. The classification would be run on both and if results between the two were not significantly different, for subsequent surveys only the <63 µm size fraction need be used. If resources allow, it is also recommended that other elements such as lithium and aluminium are simultaneously analysed so that the possibility of basing the classification on anthropogenic impacts alone is further examined. In this case the whole sediment sample would be analysed.

7. FAVOURED SCHEME

The alternatives for the choice of summary statistic to represent the data are discussed in Sections 4.2. In this study the estuaries for which there are data have been divided into zones, on a geographical basis, and the median value of the metal level at each site within that zone calculated. The median was chosen as the summary statistic as being more representative of a large number of samples below the mean.

The options for the derivation of classification schemes for each individual metal are discussed in Section 4.4. The preferred option is Option 1, to divide the distribution into non-equal quartiles and set thresholds based on the 15-50-85 percentiles. This results in a normal distribution of estuarine zones (not of concentration) over the classification. Options 2 and 3 would result in an equal distribution over all classes and a skewed distribution towards the uncontaminated respectively. However, it should be recognised that the selection of classification method is, in part, a political decision, and that the threshold levels set must remain constant for future years, if any change in classification is to be meaningfully monitored. If the thresholds are set incorrectly, no change in classification may be seen in contaminated estuary, despite measures to improve the level of metal contamination in the sediment. This is also a major shortcoming of the inability to correct for natural concentrations. Zones with naturally high metal levels may always remain in "poor" classes in spite of pollution control measures to improve water, and thereby sediment, quality. The preferred option outlined above is judged to be the most sensitive to changes in metal levels, particularly over the Class 3/4 boundary.

The most favoured option for combining the individual metal classifications is Option C, to take the weighted average of the individual classifications with List I metals receiving a weighting of 10. This method is preferred because it introduces a measure of biological relevance to the scheme, in addition to giving a more normal distribution of the classes achieved. The next preferred option would be Option A, the straight average of all metal classifications, as this takes into account all metals, and is not merely restricted to List I as Option B.

8. CONCLUSIONS AND RECOMMENDATIONS

The options for the derivation of a classification scheme for List I and List II metals (namely mercury, cadmium, chromium, copper, nickel, lead and zinc) are discussed in Section 4, with the preferred option being outlined in Section 7 above. The implications of each option on the current classification of estuaries are discussed in Section 5.

Conclusions drawn through this study are:

1. The proposed classification has been based on observed concentrations of List I and List II metals in <100 µm sediment fraction collected between 1969 and 1990.

2. It was not possible to base the classification on anthropogenic metal contamination as no data for the application of normalisation methods were available.

3. The classification was highly biased towards data from estuaries as opposed to coastal waters, the database contained 1060 data points for estuaries and 68 for coastal sites.

4. For most metals, concentrations were highly skewed by some sites having very high levels - this would potentially bias class thresholds towards high levels. In an attempt to obtain a more normal distribution of sites between classes the data were summarised by median values rather than mean or maximum values for sites, estuaries or zones of estuaries.

5. The database could have been potentially biased by the number of samples taken from particular estuaries or coastal waters, or by the frequency of sampling - options to account for this were tested: giving equal weight to each sample; deriving a summary statistic for each site; deriving a summary statistic for each estuary; and, dividing estuaries and coastal zones into zones and deriving a summary statistic for each zone. The latter option was adopted.

6. There were temporal trends within the databases - these were ignored in the classification. This implies that the distribution of estuaries are likely to move towards better classes when subsequently reclassified.

7. A number of options were assessed for the establishment of class thresholds: 15:50:85 percentiles of the concentration distribution; 25:50:75 percentiles; and, 2.5%, 5% and 10% of maximum values. The first option was the favoured option.

8. A number of options were assessed for the combination of individual metal classes into a single metal sediment classification: a simple average of class; defaulting to the worst List I metal class; and, weighting List I metals against List II and obtaining a weighted mean. The latter was the favoured option.

9. The favoured scheme was tested on the estuary database divided into zones and the resultant class compared against the current NWC class. It was found that 78% of the zones dropped by at least one class, 20% remained the same and only 2% went up by one class.

Following these conclusions this report recommends the following:

1. That the classification is based on median concentrations derived from the estuary and coastal water database divided into zones or units of classification. The class thresholds should be established on 15:50:85 percentiles of the concentration distribution and the overall metal class should be derived from a weighted (to List I metals) average.

2. When estuaries and coastal waters are sampled for classification purposes, samples should be analysed for <63 µm and <100 µm size fractions: the subsequent classification should be standardised to the <63 µm fraction.

3. Data should also be obtained at the same time on conservative elements so that the classification can be subsequently revised to allow for natural 'background' levels of metals - the classification would be more robust if it were to be based on anthropogenic contamination only.

4. The sampling strategy should also incorporate a degree of sample replication at each site.

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APPENDIX A - COMBINED CLASSIFICATION

	Grid ref	Zone	Cd	Cr	Cu
Aberystwyth	sn582812	COAST	3	1	2
Adur	tq206058	IN	2	2	2
Adur	tq217048	OUT	2	2	2
Alde	tm403562	IN	2	3	2
Alde	tm425495	MID	1	3	2
Aln	nu243108	OUT	1	2	2
Ang Dulas	sh480885	COAST	2	2	4
Ang Holy Island	sh281783	COAST	2	2	2
Ang Malltraeth	sh406686	COAST	2	4	3
Ang Menai North	sh588729	COAST	3	3	2
Ang Menai South	sh476627	COAST	2	2	2
Ang Red Wharf	sh529809	COAST	2	3	2
Avon	st563740	IN	3	3	3
Avon	st524763	MID	3	3	3
Axe	sy256917	IN	2	2	2
Axe	sy255906	MID	1	2	1
Axe	sy253902	OUT	2	1	1
Beaulieu	su390023	IN	*	3	2
Beaulieu	su407003	MID	*	*	*
Blackwater	tl860066	IN	2	2	2
Blackwater	tl995082	MID	1	3	2
Blythe	tm454755	IN	1	3	2
Blythe	tm501750	OUT	1	2	2
Bridgwater Bay n	st110667	COAST	3	3	3
Bridgwater Bays1	ss972471	COAST	2	3	3
Bridgwater Bays2	st007447	COAST	*	1	1
Bridgwater Bays3	st029436	COAST	2	3	2
Bridgwater Bays4	st072435	COAST	3	3	3

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
4	4	2	3	1	3	3	3	B
1	1	2	1	2	2	2	2	A
1	2	2	1	3	2	2	2	A
2	2	2	3	2	2	2	2	A
2	2	2	3	2	2	2	2	A
1	2	2	2	2	2	2	2	A
4	2	2	2	2	3	2	2	NA
2	2	2	2	3	2	2	2	A
2	2	2	2	2	2	2	2	A-B
2	3	3	2	2	3	3	3	A
2	2	2	2	1	2	2	2	A
3	2	2	3	1	2	2	2	NA
2	2	3	3	2	3	3	3	A
3	3	3	4	1	3	3	3	B
2	2	*	2	*	2	2	2	A
1	1	*	2	*	1	1	1	A
2	1	2	1	1	1	2	2	A
2	2	2	2	3	2	2	2	A
*	*	2	*	3	3	2	2	A
2	2	2	2	2	2	2	2	A
1	1	2	2	3	2	2	2	A
2	2	2	3	2	2	2	2	A
1	2	2	2	2	2	2	2	A
3	3	3	4	2	3	3	3	NA
3	3	3	3	2	3	3	3	NA
1	1	*	1	*	1	*	1	NA
3	3	1	2	2	2	2	2	NA
3	3	3	4	2	3	3	3	NA

	Grid ref	Zone	Cd	Cr	Cu
Butley	tm392476	MID	1	3	2
Camel	sw986731	IN	2	2	4
Camel	sw934755	OUT	3	1	3
Cartmel	sd318830	IN	1	1	1
Cartmel	sd314777	MID	1	1	1
Chichester Hbr	su833029	IN	1	3	3
Christhbr	sz183920	OUT	*	*	*
Cleddau	sn018078	MID	3	2	2
Cleddau E		IN	3	2	2
Cleddau W	sm978118	IN	3	3	2
Clwyd	sj000799	IN	3	4	3
Clwyd	sh998810	OUT	3	3	3
Clyde	ns462723	IN	3	4	3
Clyde	ns424739	MID	3	4	3
Clyde	ns281827	OUT	3	4	2
Colne	tm025233	IN	2	3	3
Colne	tm075163	MID	2	3	2
Conwy	sh787718	IN	4	2	2
Conwy	sh788778	MID	3	3	2
Coquet	nu259052	OUT	1	2	2
Cornwall Par	sx085528	COAST	1	1	3
Cornwall Porth	sw625256	COAST	4	*	4
Cree	nx473573	MID	3	2	1
Crouch	tq853964	IN	2	3	2
Crouch	tq994956	OUT	2	3	2
Cumbria Harring	nx989253	COAST	4	4	3
Cumbria Mary	ny033367	COAST	3	3	2
Cumbria W.Haven	nx972183	COAST	4	4	3
Cumbria Work	nx994291	COAST	4	3	3
Dart	sx807603	IN	3	*	3

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
2	2	2	3	2	2	2	2	A
3	2	2	3	4	3	2	2	A
1	2	*	1	*	2	3	3	A
1	1	2	1	1	1	2	1	A
1	1	2	1	1	1	2	1	A
3	2	*	3	*	3	1	2	A
*	*	3	*	3	3	3	3	A
2	2	2	3	2	2	3	2	A
3	2	2	3	2	2	3	2	A
3	2	2	3	2	3	3	3	A
3	3	4	3	3	3	4	3	A
3	3	4	3	3	3	4	3	A
3	3	4	3	3	3	4	3	C
3	4	2	3	2	3	3	3	B
2	3	2	2	2	3	3	3	A
2	3	3	3	3	3	3	3	B
2	2	3	3	3	3	3	3	A
3	2	2	2	1	2	4	3	A
3	3	2	2	1	2	3	2	A-B
1	2	1	2	2	2	1	1	A
2	1	*	1	*	2	1	1	NA
4	4	*	4	*	4	4	4	NA
2	2	1	2	2	2	3	2	A
2	2	2	2	3	2	2	2	A
2	2	3	2	3	2	3	2	A
3	3	3	3	3	3	4	3	NA
3	3	3	3	3	3	3	3	NA
3	3	3	4	4	4	4	4	NA
3	3	3	4	3	3	4	3	NA
2	4	*	*	*	3	3	3	A

	Grid ref	Zone	Cd	Cr	Cu
Dart	sx847567	MID	3	3	3
Dart	sx875524	OUT	1	2	2
Deben	tm280493	IN	2	2	2
Deben	tm287452	MID	2	3	2
Deben	tm307414	OUT	2	3	2
Dee Hoylake	sj216897	COAST	4	3	3
Dee Solway	nx676514	IN	3	2	1
Dee Solway	nx667495	MID	2	2	1
Dee Wales	sj291704	IN	4	4	3
Dee Wales	sj252814	MID	3	3	3
Dee Wales	sj222847	OUT	1	1	1
Dovey	sn668973	IN	3	2	2
Dovey	sn663971	MID	3	2	2
Dovey	sn632963	OUT	3	2	2
Duddon	sd187685	MID	2	2	1
Dwyryd	sh600379	MID	1	1	1
Dwyryd	sh567375	OUT	2	1	2
Erme	sx627490	IN	2	2	2
Esk (Cumbria)	sd088943	IN	2	2	1
Esk (Cumbria)	sd084966	MID	2	2	1
Esk (Yorks)	nz901104	IN	3	3	3
Exe	sx967875	IN	3	3	3
Exe	sx974844	MID	3	2	2
Exe	sx979791	OUT	3	2	2
Fal	sw877407	IN	3	1	4
Fal	sw827384	MID	3	2	4
Fal	sw833363	OUT	3	2	4
Fal hbr	sw797342	OUT	2	3	4
Fishguard Bay	sm962373	COAST	3	2	2
Fleet	nx574545	MID	2	2	1

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
3	3	4	4	3	3	4	3	A
2	2	*	2	*	2	1	1	A
2	2	3	2	3	2	3	2	B
2	2	3	2	2	2	3	2	A
2	2	2	3	2	2	2	2	A
3	3	4	3	3	3	4	4	NA
1	1	1	1	1	1	3	2	A
1	1	1	1	2	1	2	1	A
4	3	4	2	4	4	4	4	A
4	3	4	3	3	3	4	3	A-B
1	1	2	1	1	1	2	1	A-B
3	3	2	3	3	3	3	3	A
3	4	1	3	2	3	3	2	A
3	4	2	3	2	3	3	3	A
1	1	2	1	1	1	2	2	A
2	1	1	1	1	1	1	1	A
2	2	1	2	1	2	2	2	A
2	2	3	3	1	2	3	2	A
2	2	2	2	2	2	2	2	A
1	2	2	1	2	2	2	2	A
3	3	4	4	3	3	4	3	A
3	3	3	3	2	3	3	3	A
2	2	2	2	2	2	3	2	A
2	2	*	2	*	2	3	3	A
3	2	2	1	4	3	3	3	C
4	4	3	3	4	3	3	3	A-B
4	3	3	2	4	3	3	3	A
4	4	*	4	*	4	2	3	B
3	3	2	2	3	3	3	3	NA
1	1	1	2	1	1	2	1	A

	Grid ref	Zone	Cd	Cr	Cu
Forth	ns895895	IN	2	4	3
Forth	ns926840	MID	2	4	3
Forth	nt053802	OUT	2	4	3
Forth Firth1	nt190774	COAST	4	3	3
Forth Firth2	nt336732	COAST	3	2	3
Forth Firth3	nt469804	COAST	2	2	2
Forth Firth4	nt659787	COAST	1	1	1
Fowey	sx106558	IN	2	2	4
Fowey	sx127554	MID	2	2	4
Frome	sy944875	MID	*	*	*
Gannel	sw813607	IN	4	2	4
Gannel	sw804607	MID	4	1	3
Gannel	sw790613	OUT	3	2	3
Ghead Dmpin	ns098460	COAST	4	4	4
Ghead Dmpmid	ns085462	COAST	3	4	3
Ghead Dmpout	ns042478	COAST	2	4	3
Gwendrath	sn396064	IN	3	2	2
Hayle	sw547364	IN	3	3	4
Helford	sw722256	IN	4	3	4
Helford	sw735275	MID	1	3	4
Helford	sw762266	OUT	2	1	3
Holesbay	sz000911	MID	4	4	3
Holkham Bay	tf916447	OUT	3	3	2
Holy Island	nu082427	COAST	1	2	1
Humber	ta027235	MID	*	4	3
Humber	ta233187	OUT	3	4	3
Humbers	tf457935	COAST	3	4	3
Iow Medina	sz504912	IN	*	*	*
Iow Medina	sz509928	OUT	*	*	*
Iow Newtown	sz423904	MID	*	*	*

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
3	3	4	4	3	3	4	3	C
3	3	4	4	3	3	4	3	B
3	3	4	3	3	3	4	3	A
4	3	4	4	3	4	4	4	C
3	2	3	3	2	3	3	3	B
2	2	3	2	2	2	3	2	B
1	1	1	2	2	1	1	1	A
3	3	3	3	4	3	3	3	A
3	3	*	2	*	3	2	2	A
*	*	4	*	3	4	4	4	A
4	4	4	4	4	4	4	4	A
3	4	*	2	*	3	4	4	A
3	4	1	3	4	3	3	2	A
4	4	4	4	4	4	4	4	C
3	3	3	4	3	3	3	3	C
3	3	3	4	3	3	3	3	C
2	2	2	2	2	2	3	2	A
4	4	2	3	4	3	3	3	A
4	3	3	3	3	3	4	3	A
3	3	*	3	*	3	1	2	A
3	2	*	3	*	2	2	2	A
3	3	4	3	2	3	4	4	A
2	2	2	3	3	3	3	3	A
1	1	1	2	1	1	1	1	A
3	3	3	4	4	3	3	3	A-B
3	3	3	4	4	3	3	3	A-B
3	3	3	4	4	3	3	3	NA
*	*	3	*	3	3	3	3	C
*	*	3	*	3	3	3	3	A
*	*	1	*	3	2	1	1	A

	Grid ref	Zone	Cd	Cr	Cu	Zn	Pb
low Wootton	sz548925	IN	*	*	*	*	*
Irvine Bay	ns313386	COAST	*	*	*	*	*
Kent	sd479810	MID	1	1	1	1	1
Langstone Hbr	su674034	IN	2	3	2	3	2
Largs Bay	ns207543	COAST	*	*	*	*	*
Looe	sx253540	OUT	1	2	3	2	3
Looe E	sx251553	IN	2	2	3	3	3
Looe E	sx247557	MID	2	2	3	2	3
Looe w	sx233547	IN	2	2	3	3	4
Looe W	sx238544	MID	1	2	3	2	4
Loughor	ss564983	IN	3	4	3	3	3
Loughor	ss537960	MID	3	4	2	2	2
Loughor	sn485004	OUT	3	4	2	2	2
Lune	sd453617	IN	2	1	1	1	1
Lune	sd447563	OUT	2	2	1	1	2
Lychett Bay	sy973911	MID	4	3	2	3	2
Lymington	sz329960	IN	1	1	2	2	3
Lynher	sx382593	IN	3	*	4	4	4
Lynher	sx408570	MID	2	3	4	4	4
Lytham St Anne	sd335272	COAST	2	1	1	2	1
Mawddach	sh655175	MID	2	1	3	2	2
Mawddach	sh623156	OUT	2	1	2	2	2
Mersey	sj513836	IN	4	4	3	4	3
Mersey	sj474807	MID	4	4	4	4	4
Mersey	sj340862	OUT	3	4	3	3	3
Morecambe Bay	sd451653	OUT	1	1	1	1	1
Mylor	sw806359	IN	4	3	4	4	4
N.West (Lune)	sd456586	MID	*	1	1	1	1
Neath	ss732935	IN	4	3	3	3	3
Neath	ss720928	OUT	4	3	3	4	3

Hg	Ni	As	Option A	Option B	Option C	NWC
2	*	3	3	2	2	C
2	*	1	2	2	2	C-D
2	1	2	1	2	1	A
*	2	*	2	2	2	A
1	*	2	2	1	1	B-C
2	3	2	2	2	2	A
2	4	2	3	2	2	A
2	3	3	3	2	2	A
2	4	3	3	2	2	A
2	3	2	2	2	2	A
2	3	3	3	3	3	A
2	2	3	3	3	3	A
2	3	3	3	3	3	A
2	1	1	1	2	2	A
2	1	1	2	2	2	A
3	2	2	3	4	3	A
3	1	2	2	3	2	B
3	4	4	4	3	3	A3
*	*	*	3	2	3	A
2	1	1	1	2	2	B
2	2	2	2	2	2	A
1	2	1	·2	2	2	A
4	3	4	4	4	4	D
4	3	4	4	4	4	C-D
4	2	4	3	4	3	B-C
1	1	1	1	1	1	A
4	3	4	4	4	4	B
2	1	1	1	2	2	A
4	4	3	3	4	4	B
4	4	3	4	4	4	B

	Grid ref	Zone	Cd	Cr	Cu
Nene	tf493267	MID	2	3	2
Newport Bay	sn062395	COAST	2	1	1
Nith	nx994680	OUT	*	*	*
Orwell	tm196391	IN	2	3	2
Orwell	tm246380	MID	*	*	*
Otter	sy075823	OUT	2	2	2
Oulton Broad	tm528931	OUT	3	*	*
Ouse	tf599236	MID	2	3	2
Parrett	st262425	OUT	3	4	3
Percuil	sw862346	MID	2	3	4
Plym	sx508554	IN	4	1	3
Plym	sx504544	MID	4	2	4
Plymouth Sound	sx440503	OUT	2	2	3
Poole Hbr	sz029860	OUT	3	3	2
Portsmouth Hbr	su582053	IN	4	3	3
Ramehead	sx380470	COAST	1	2	3
Red	sw582423	IN	2	1	4
Restronguet ck	sw794388	IN	4	1	4
Restronguet ck	sw813375	MID	4	2	4
Rhymney	st227775	MID	4	4	3
Ribble	sd425269	OUT	3	3	2
Rye	tq925206	IN	1	2	1
Rye	tq940194	MID	1	2	1
S Water	su404110	IN	3	3	4
S Water	su432075	MID	3	3	4
S Water	su467034	OUT	*	*	*
S Water Hamble	su495092	IN	2	2	3
S Water Hamble	su489059	MID	2	2	2
S Water Itchen	su436146	IN	3	3	4
S Water Itchen	su434101	MID	3	3	3

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
2	2	2	2	3	2	2	2	B
2	1	2	2	2	2	2	2	B
*	*	1	*	1	1	1	1	A
2	2	2	2	2	2	2	2	C-D
*	*	2	*	3	3	2	2	A
2	2	3	2	2	2	3	2	A
*	*	4	3	3	3	4	3	A
2	3	2	2	3	2	2	2	A-B
3	3	*	4	*	3	3	3	B
4	3	*	3	*	3	2	2	A
3	2	3	1	4	3	4	3	A
4	4	*	1	*	3	4	4	A
2	4	3	2	1	2	3	2	A
2	2	3	2	3	3	3	3	A
3	3	*	2	*	3	4	4	A
2	2	*	2	*	2	1	1	NA
2	1	1	1	4	2	2	2	C
4	4	3	3	4	3	4	3	B
4	4	3	3	4	4	4	4	B
4	3	3	4	2	3	4	3	B
3	3	3	2	2	3	3	3	B
1	1	1	1	3	1	1	1	A
1	1	1	1	3	1	1	1	A
4	3	4	2	2	3	4	3	A
2	2	3	2	3	3	3	3	A-B
*	*	2	*	*	2	2	2	A-B
2	3	3	2	3	3	3	3	A
2	2	2	1	3	2	2	2	A
3	4	3	2	2	3	3	3	A
3	4	3	2	2	3	3	3	A

	Grid ref	Zone	Cd	Cr	Cu
Salcombe	sx747433	IN	2	2	3
Severn	so666019	IN	3	3	3
Severn	st612963	MID	3	3	3
Severn	st301485	OUT	3	4	3
Solente	sz308916	COAST	*	*	*
Solente low	sz650888	OUT	*	*	*
Solentw low	sz355893	OUT	*	*	*
Solway	ny282649	IN	2	2	1
Solway	ny232628	MID	1	1	1
Solway	ny147654	OUT	1	1	1
Stour	tm112322	IN	2	4	3
Stour	tm162320	MID	2	2	2
Stour	tm272343	OUT	2	3	2
Swansea Bay	ss664921	OUT	3	1	2
Taf	sn300129	IN	3	2	2
Taf	sn305109	OUT	3	2	2
Taff	st187739	MID	4	4	3
Tamar	sx435686	IN	4	3	4
Tamar	sx436627	MID	4	3	4
Tamar	sx462538	OUT	2	2	4
Tavy	sx475650	IN	*	*	4
Tavy	sx462636	MID	3	3	4
Taw	ss560327	IN	3	3	3
Taw	ss516335	MID	3	3	2
Tawe	ss631912	OUT	2	4	3
Tees	nz502214	IN	4	4	4
Tees	nz511255	MID	*	*	*
Tees	nz558264	OUT	3	4	3
Teifi	sn164468	IN	2	1	1
Teifi	sn167483	OUT	2	2	1

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
2	3	4	3	2	3	4	3	A
3	3	3	3	2	3	3	3	A-B
3	3	3	4	2	3	3	3	A-B
3	3	3	4	2	3	3	3	A-B
*	*	2	*	3	3	2	2	A
*	*	3	*	3	3	3	3	A
*	*	3	*	3	3	3	3	A
1	2	1	2	2	2	2	2	A
1	1	1	1	1	1	1	1	A
1	1	1	1	1	1	1	1	A
2	2	3	3	3	3	3	3	A
1	2	2	2	3	2	2	2	A
2	2	2	3	3	2	2	2	A-B
3	3	3	2	3	3	3	3	A
2	2	2	2	3	2	3	2	A
2	2	1	3	1	2	3	2	A
4	3	3	4	2	3	4	3	A
4	4	4	4	4	4	4	4	A
4	4	4	4	4	4	4	4	A
3	3	3	3	4	3	3	3	A
3	4	*	*	*	4	*	4	A
4	4	3	4	4	4	3	3	A
3	2	3	3	2	3	3	3	A
3	2	3	3	3	3	3	3	A
3	3	3	4	3	3	3	3	A
4	4	4	3	4	4	4	4	C-D
*	*	4	*	3	4	4	4	C-D
3	3	4	3	4	3	4	3	B
2	1	1	2	2	2	2	2	A
2	1	1	2	2	2	2	2	A

	Grid ref	Zone	Cd	Cr	Cu
Teign	sx880723	IN	4	2	3
Teign	sx903724	MID	4	2	3
Teign	sx926724	OUT	3	2	2
Thames	tq801692	OUT	3	3	3
Tiddy	sx364572	IN	2	3	4
Torbay	sx909632	COAST	1	1	1
Torridge	ss462246	IN	3	2	3
Torridge	ss466289	MID	3	2	2
Torridge	ss453308	OUT	2	2	2
Tresillian	sw862457	MID	3	1	4
Truro	sw833438	IN	4	2	4
Tweed	nt996526	COAST	1	3	2
Twyi	sn386137	IN	3	2	2
Twyi	sn367129	MID	3	2	2
Twyi	sn358108	OUT	3	2	2
Tyne	nz226627	IN	*	3	3
Tyne	nz291823	MID	4	3	3
Tyne	nz339655	OUT	4	3	3
Urr	nx836548	MID	2	2	1
Usk	st314831	MID	4	3	3
Wash	tf563574	OUT	2	3	2
Waveney	tg473052	IN	2	3	2
Waveney	tg510088	MID	1	3	2
Waveney	tg526053	OUT	1	3	1
Welland	tf344338	IN	3	4	3
Witham	tf381391	MID	2	3	2
Wye	st546920	MID	3	3	3
Wyre	sd378398	IN	3	3	2
Wyre	sd358436	MID	2	2	2
Wyre	sd341468	OUT	2	2	2

Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
4	4	3	3	4	3	4	3	A
4	3	2	3	3	3	4	3	A
2	3	2	2	3	2	3	2	A
2	3	3	2	3	3	3	3	A-B
4	4	3	4	4	4	3	3	A
1	1	*	1	*	1	1	1	NA
3	2	3	3	2	3	3	3	A
2	2	3	3	2	2	3	3	A
2	2	2	3	3	2	2	2	A
4	3	3	2	4	3	3	3	A
4	4	3	2	4	3	4	3	B
2	2	3	3	2	2	3	2	A
2	2	1	2	1	2	3	2	B
2	2	2	2	2	2	3	2	A
3	2	1	2	2	2	3	2	A
2	3	4	3	3	3	4	4	A-C
4	3	3	4	3	3	4	3	B-C
4	4	3	3	3	3	4	3	A-B
1	2	1	2	2	2	2	2	A
3	3	3	4	2	3	4	3	B
3	3	2	3	3	3	2	2	A
2	3	3	3	2	3	3	3	A
2	2	2	2	1	2	2	2	A
1	2	2	2	2	2	2	2	B
3	3	2	4	4	3	3	3	A
2	2	2	2	3	2	2	2	A
3	3	3	4	2	3	3	3	A
3	3	4	2	1	3	4	3	B
2	2	4	2	1	2	4	3	B
2	2	3	1	2	2	3	2	B

	Grid ref	Zone	Cd	Cr	Cu	Zn	Pb	Hg	Ni	As	Option A	Option B	Option C	NWC
Yealm	sx546502	IN	1	3	3	2	3	3	4	4	3	3	2	A
Yealm	sx539476	MID	1	2	2	2	2	4	3	1	2	4	2	A
Yealm	sx531475	OUT	1	1	1	1	1	*	2	*	1	1	1	A

Notes:
- COAST - Coastal
- IN - Inner zone
- MID - Middle zone
- OUT - Outer zone
- NWC - Present classification under National Water Council system