

# Estimation of background reference concentrations for metals in UK freshwaters

by

Water Framework Directive - United Kingdom Technical Advisory Group (WFD-UKTAG)

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# Executive summary

This report provides estimates of ambient background concentrations (ABCs) for several metals and one metalloid in UK freshwaters. ABCs are defined as concentrations representing low anthropogenic inputs, rather than natural backgrounds.

Specifically, this report aims to:

- Establish a practical methodology for the use of freshwater monitoring data to estimate ABCs for UK hydrometric areas and water bodies, as defined under the Water Framework Directive.
- Collate freshwater monitoring data from England, Wales, Scotland and Northern Ireland for dissolved concentrations of copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), zinc (Zn) and arsenic (As).
- Where possible, estimate ABCs from these data for individual hydrometric areas.
- Outline uncertainties in the methodology and discuss options for how ABCs may be used in a compliance assessment framework and what may be done when too few quality data are available for the derivation of hydrometric area-specific ABCs.

The methodology used to derive environmental quality standards (EQSs) for the Water Framework Directive (WFD) (2000/60/EC) uses assessment factors to account for uncertainty for chemicals with limited ecotoxicity data. This approach is reasonable and appropriate in chemical risk assessment when iteration and refinement are possible. However, when deriving EQS, which are effectively pass/fail limit values, this approach can lead to values so low that they are not detectable by routine analytical methodologies, or that cause UK-wide surface water compliance failures with limited relevance to potential environmental risk.

This issue is especially relevant for those metals for which concentrations in the water column can vary over orders of magnitude because of natural geological variability and low level anthropogenic inputs. Single value generic metal EQSs are therefore largely impractical to implement on a country-wide scale, and are of limited regulatory value.

A Dutch policy solution to the issue of implementing single metal EQSs in waters with variable background metal concentrations is the added risk approach (ARA). It assumes that the effects of naturally occurring background metal concentrations may be desirable; that is, the ecosystem has developed because of the metals that are present.

The ARA can be defined as:

*(Specific) Quality Standard = Specific Background + (Generic) Quality Standard*

where the (generic) quality standard is corrected to take account of local or regional background concentrations to derive a (specific) quality standard.

The key issue when implementing the ARA is the determination of a natural or ambient background metal concentration. Numerous methodologies exist to perform this derivation process, but there is insufficient accepted scientific evidence to justify selecting one of these methodologies over any other.

In this project we have taken a pragmatic approach to the estimation of ABCs by using a low percentile (for example, 5th or 10th) of the distribution of monitoring data for a

dissolved metal for a specific WFD hydrometric area. This approach is relatively precautionary, but is reasonable when used in a suitable tiered regulatory framework, given that the monitoring data will likely include contributions from natural and anthropogenic (point and diffuse) metals sources.

A tiered approach towards compliance assessment has been proposed for metals in which biotic ligand models may be applied. Such an approach may also be considered for metals where *no* correction for bioavailability is possible. In such cases, failure of the quality standard would potentially trigger an investigation of the background concentrations relevant to the assessment site.

Employing the derived ABCs within a tiered risk assessment approach will allow any further efforts to refine ABCs, either at the level of the whole hydrometric area or individual water bodies, to be targeted according to risk. If a location for which an uncertain ABC has been derived is not considered to be at risk then further consideration of the reliability of the ABC would not be necessary, provided that there is confidence that the uncertainty is not too large (which could result in an unprotective risk characterisation).

We consider the ABCs derived within this report appropriate for application within a tiered approach towards compliance assessment. The derived ABCs are relatively conservative values. This means that they are unlikely to overestimate the relevant ABC for any individual water body greatly. However, it also means that in some localised areas, higher background concentrations may be applicable.

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# 1 Introduction

## 1.1 Report structure

This report estimates values that may be applied as ambient background concentrations (ABCs) for several metals and one metalloid in freshwaters in the UK. ABCs are defined as concentrations representing low anthropogenic inputs, rather than natural backgrounds.

Specifically, this report aims to:

- Establish a practical methodology for the use of freshwater monitoring data to estimate ABCs for UK hydrometric areas and water bodies, as defined under the Water Framework Directive.
- Collate freshwater monitoring data from England, Wales, Scotland and Northern Ireland for dissolved concentrations of copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), zinc (Zn) and arsenic (As).
- Estimate values from these data which may be applied as ABCs for individual hydrometric areas.
- Outline uncertainties in the methodology and discuss options for how ABCs may be used in a compliance assessment framework and what may be done when too few quality data are available for the derivation of hydrometric area specific ABCs.

In this introductory section of the report we briefly describe the EQS-setting process in the Water Framework Directive (WFD) and outline why ABCs are important for metals and metalloids. At the end of this section we introduce the rationale behind the use of 'added risk'.

In Section 2 we outline the challenges encountered when using monitoring data to estimate ABCs, and describe the methodological options available for dealing with these challenges, giving examples of how each of these options affects ABC estimation. Finally, we state the uncertainties in the methodological options and provide recommendations on how monitoring data should be used to estimate ABCs.

In Section 3 we briefly describe the datasets we used for estimating ABCs and how the data were collated, outlining any specific difficulties with the datasets.

In Section 4 we provide estimations of hydrometric area delineated ABCs from the monitoring data for copper, iron, manganese, nickel, zinc and arsenic.

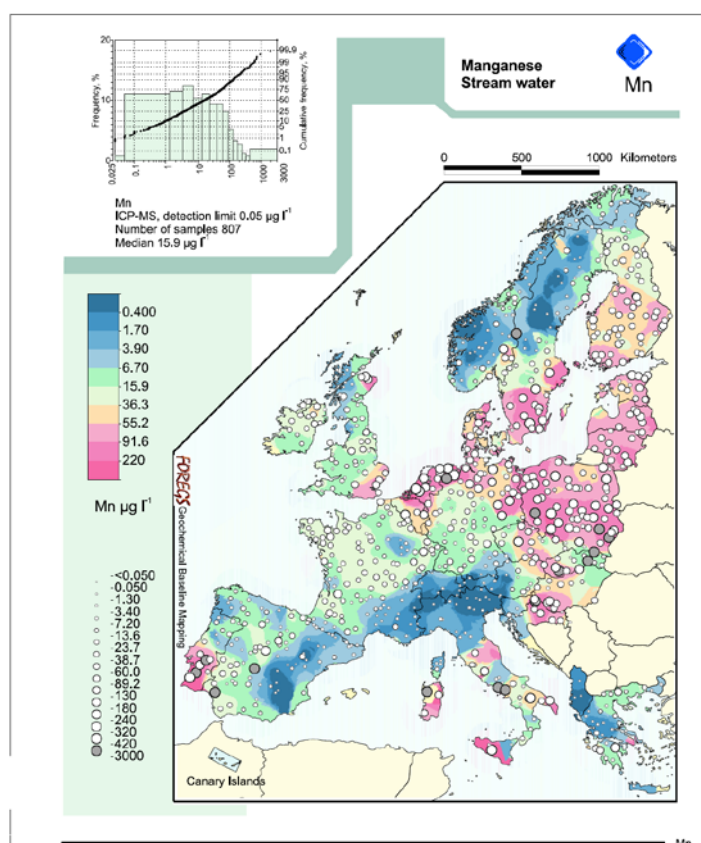
In Section 5 we outline options for the use of ABCs in the context of a regulatory framework and provide options to address the situation where it has not been possible to estimate ABCs because of lack of data.

Finally, in Section 6 we draw conclusions from the previous sections and make recommendations for taking forward the methodology for estimation and use of ABCs in the context of the WFD.



## 1.2 EQS values for metals and metalloids and the Water Framework Directive

It is widely recognised that metals present significant regulatory challenges compared with organic chemicals (Adams and Chapman, 2007). As naturally occurring elements, metals are an intrinsic part of the environment. Furthermore, because of the effects of variable underlying geology, historic anthropogenic inputs and numerous low level diffuse sources, the concentrations of metals in the environment, including freshwaters, are spatially highly variable. An example of this variability is shown in Figure 1.1, which displays concentrations of manganese in pristine, unimpacted freshwaters in the EU. It can be clearly seen that manganese concentrations in the UK cover the complete range of concentrations measured across the EU, indicating the significant variability across the UK.



**Figure 1.1 Concentrations of manganese in stream water across the EU from the FOREGS Programme<sup>1</sup>**

The methodology used to derive EQSs for the Water Framework Directive (EC, 2000), as outlined by Lepper (2005), uses assessment factors to account for uncertainty for those chemicals where the ecotoxicity data are limited. This approach is reasonable and appropriate in chemical risk assessment when iteration and refinement are possible. However, when deriving EQS, which are effectively pass/fail limit values, this approach can lead to values so low that they are not detectable by routine analytical methodologies, or that could result in UK-wide surface water compliance failures (with limited relevance to potential environmental risk).

This issue is especially relevant for those metals for which concentrations in the water column can vary over orders of magnitude because of natural geological variability and

<sup>1</sup> [http://www.gsf.fi/publ/foregsatlas/maps/Water/w\\_icpms\\_mn\\_edit.pdf](http://www.gsf.fi/publ/foregsatlas/maps/Water/w_icpms_mn_edit.pdf) [accessed December 2008].

low level anthropogenic inputs (such as in Figure 1.1). Single value generic metal EQS are therefore largely impractical on a country-wide scale, and are of limited regulatory value.

Therefore, it is clear that attempting to reflect metal environmental risks, such as those from manganese, across the whole of the UK by setting a single EQS is both impractical and technically flawed. Difficulties with metals regulation have been recognised by the European Commission, who has provided an opportunity in the Daughter Directive on Priority Substances to consider metal speciation, (bio)availability and backgrounds when addressing compliance issues (EC, 2008). Metal-specific guidance is now available for the assessment of environmental risks, which accounts for speciation, (bio)availability and naturally occurring backgrounds (ICMM, 2007). However, this guidance is limited if the metal under consideration is relatively data-poor or if the understanding of its aquatic fate and behaviour is not well developed. This means that for most metals and metalloids there is insufficient information to enable consideration of speciation and (bio)availability issues. Therefore, if the goal is to derive a practical metric by which to assess freshwater compliance under the WFD, accounting for natural background concentrations in freshwaters may be the only realistic option available for metals with limited ecotoxicity, fate and behaviour data.

If the range and magnitude of metal ABCs in freshwaters is understood it becomes possible to gauge the reality of a proposed EQS derived using WFD-compliant methodology. For example, an EQS for manganese of  $0.007 \text{ mg}\cdot\text{l}^{-1}$  was previously proposed for use across the UK (Environment Agency, 2007). By considering the range of manganese ABCs across the UK it is likely that this value will approximate to the 25th percentile (Environment Agency, 2008a) of concentrations of manganese in surface waters, effectively meaning that 75 per cent of UK waters will fail to comply. This raises the question of whether, in reality, 75 per cent of UK freshwaters are adversely affected by manganese. If this is not the case, then it is likely that the proposed EQS is not environmentally relevant.

### 1.3 How might ambient background concentrations be estimated?

Having identified that there is a need to consider ABCs for several metals and metalloids, the next step is to establish how this can be undertaken in a practical and evidence-based way.

The determination of 'natural' metal background in environmental media is fraught with a number of technical, practical and political difficulties (ICMM, 2007). The reality is that in Europe there are probably very few, if any, surface waters containing only 'natural' concentrations of metals. Therefore, the usual or 'ambient' concentration of a metal in surface waters consists of both a natural geochemical fraction and an anthropogenic fraction (International Organization for Standardization (ISO), 2005). In this context, the term 'anthropogenic fraction' refers to moderate diffuse inputs into the water, not the inputs from local point sources that generally result in a much elevated concentration. In this report, we have used the term 'ambient background concentration' or 'ABC' to mean the same as the ISO-defined term 'usual background concentration'.

The key aim of this project is to provide estimates of ABCs for arsenic, copper, iron, manganese, nickel and zinc in freshwaters that are relevant for use at Water Framework Directive spatial scales. Specifically, this will be achieved by:

- Using a low percentile (for example, 5th or 10th) of the distribution of monitoring data for a metal for a specific hydrometric area.

- Considering groundwater data in hydrometric areas in which there are insufficient surface water monitoring data.
- Using expert judgement to recommend situations in which 'read across' from other hydrometric areas may be reasonable, based on geology or proximity.

Taking a low percentile of monitoring data for a particular area, such as a hydrometric area, may be viewed as providing a relatively conservative estimate of the background concentration. The monitoring data will include contributions from both natural and anthropogenic sources. Distinguishing between natural contributions and large numbers of small point source discharges, such as sewage discharges, is not possible. Taking a low percentile of such a dataset is intended to remove, or at least reduce, the effect of point source discharges on the derived background concentrations.

The possibility of using general freshwater monitoring data to derive ABCs may depend on whether potential issues or problems are expected within the catchment as a result of the metals of interest. Where there are no significant discharges of a contaminant identified within a catchment there may be very little, or no, monitoring data available. On the other hand, in catchments where issues or potential problems are expected there may be much more monitoring data available. This means that, to an extent, the derived background concentrations could reflect the pressures identified on a particular catchment. For example, hydrometric area 17 (Almond Group in Scotland) has only limited monitoring data for several trace elements (arsenic, copper, nickel and zinc), but has more extensive monitoring of iron and manganese. This mix of monitoring data may reflect the identified pressures on the catchment (Section 4).

In The Netherlands, current methodology involves the use of geometric mean values (90th percentiles are used for groundwaters (van Vlaardingen et al., 2005)). However, this is an area of active discussion, and Fraters et al. (2001) suggest that the median would be more appropriate as the mean may include a significant anthropogenic component. This is because the measured environmental concentrations are mostly log normally distributed and the median therefore represents a typical value, whereas the mean is likely to overestimate the typical values by including a small number of very high values.

A recent report from the British Geological Survey, commissioned by the Environment Agency (Environment Agency, 2008a), used several techniques on a relatively limited spatial dataset to derive ABCs for metals. The ABCs were derived from the 50th and 90th percentiles of restricted data (outliers removed) delineated on the basis of catchments, river basin districts and geology/topography. A tiered approach of options was used for the estimations. This is a reasonable approach for spatially limited datasets, but is likely to be too complicated for application across the whole of the UK. It is also unclear how the use estimates based on the 50th and 90th percentiles for streams compared with hydrometric area monitoring data for rivers. Where datasets with reasonable methods of detection were used, the limits of detection (LODs) were 'generalised' (and seem to have been used at face value), but for some metals (chromium, lead and zinc) up to a quarter of all samples were below the LOD. The authors acknowledge that this introduces a significant amount of uncertainty into subsequent background concentration estimation.

In cases where either 50th or 90th percentiles of a dataset are used for the derivation of background concentrations, it is important that the datasets employed do not contain monitoring data that are likely to be influenced by anthropogenic emissions. Monitoring undertaken in small headwater streams, above any sewage treatment works, are likely to be appropriate for such a purpose. These sampling locations are, however, unlikely to be representative of typical compliance assessment points.

## 1.4 Using ambient background concentrations: The added risk approach

The added risk approach (ARA) is the most widely recognised policy-based approach for regulating naturally occurring substances in environmental matrices. The ARA is a Dutch policy solution to the issue of implementing single metal EQS in waters, soil and sediments with variable background metal concentrations (Crommentuijn et al., 1997). It assumes that the effects of naturally occurring background metal concentrations may be desirable; that is, the ecosystem has developed because of the metals that are present (Muysen and Janssen, 2001; ICMM, 2007).

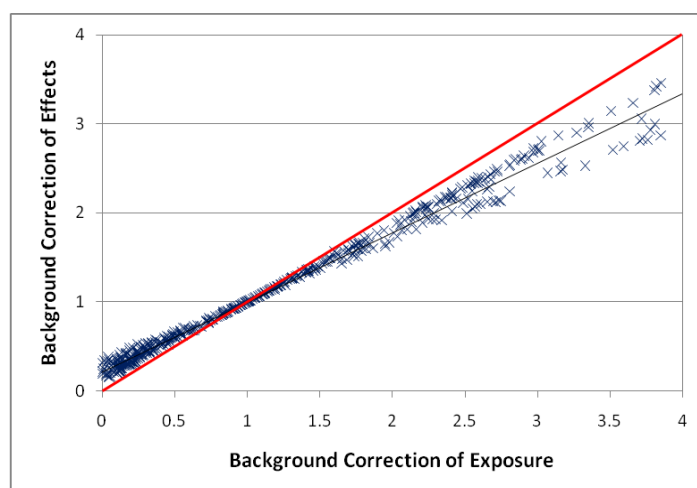
The ARA approach can be defined as:

$$\text{(Specific) Quality Standard} = \text{Specific Background} + \text{(Generic) Quality Standard}$$

where the (generic) quality standard is corrected to take account of local or regional background concentrations to derive a (specific) quality standard (Lepper, 2005).

This implies that the background concentration should be added to the quality standard in order to derive the relevant compliance limit, and is effectively correcting for the background concentration on the effects side of the assessment. Alternatively, the background concentration could be subtracted from the monitored concentrations to allow comparison against a single EQS value, which is an approach that applies the background correction to the exposure side of the assessment. The two approaches do result in slightly different risk characterisation ratios because of changes to either the predicted environmental concentration (PEC) or predicted no-effect concentration (PNEC) used, but do not affect the conclusions drawn regarding compliance. When the risk characterisation ratio is unity both approaches provide the same outcome, and the conclusion on risk is the same. This can be seen in Figure 1.2, in which background correction to the effects side results in lower risk characterisation ratios, but identical conclusions. Whichever method is applied, it is important to maintain consistency.

The ARA is not without its detractors, who suggest that it is conceptually flawed because added and background metals will behave as a single pool, and exposed organisms will not distinguish between them. The ARA also relies on the ability to determine natural background concentrations of metals.



**Figure 1.2 Risk characterisation ratios for different background corrections for an example dataset from UK freshwaters (n = 499); the red line shows a 1:1 relationship**

## 2 Methods of derivation for ambient background concentrations

The aim of this project is to derive ABCs that can be applied in undertaking compliance assessments of EQS for several trace metals. These ABCs are intended to provide a generic ABC that can be applied to all water bodies within a hydrometric area and is suitable for application during the initial tiers of a tiered approach to compliance assessment (Section 5.1). For the ABCs to be applicable in the screening stages of a tiered approach, it is important that they are relatively conservative so as to minimise the chances of erroneous passes of the quality standard. The following sections set out how the appropriate procedures for deriving the ABCs were developed.

### 2.1 How many data are needed to estimate ambient background concentrations?

Different regulatory, political and non-technical drivers result in a variable number of samples in monitoring datasets, with some datasets having no data for some elements, or having less than 20 samples over a 5-year period. Following the removal of obvious outliers and pollution incidents, the number of samples falls further.

The ABCs of metals to be estimated in this project are intended to represent individual hydrometric areas within the UK. A hydrometric area is a grouping of catchments for monitoring and reporting purposes. Within each hydrometric area there are generally several water bodies, each representing a coherent sub-unit in the river basin district, and usually identified on the basis of geographical and hydrological determinands (EC, 2003a). The number of water bodies within each hydrometric area will vary, but can be in the region of tens (for example, Anglesey) to many hundreds (such as the Thames Region).

We recommend that ABCs should initially only be estimated for those hydrometric areas where there are at least as many samples available as there are water bodies in the area. Raising this criterion (for example, by estimating ABCs only for hydrometric areas where there are 10 times as many data points as water bodies) would provide considerably greater confidence in the derived ABCs, but it would also limit the number of hydrometric areas for which they can be derived.

Ideally, the number of data required for the derivation of an ABC within a hydrometric area would be related to the number of water bodies within the hydrometric area. If the data are treated in this way then large hydrometric areas with large numbers of water bodies would require more extensive datasets than small hydrometric areas with limited numbers of water bodies.

On average there should ideally be a minimum of five monitoring data for each water body in a hydrometric area. A hydrometric area with only 10 water bodies should have at least 50 data for each metal considered. A large hydrometric area containing 100 water bodies should have a minimum of 500 data points for adequate derivation of an ABC. While a requirement for a larger amount of monitoring data would result in more reliable ABCs being derived, in many cases only relatively limited monitoring data are available. In cases where the number of water bodies within the hydrometric area is

unknown, a minimum of 100 data points are required to ensure that the derived ABCs are adequately representative.

There will be considerable uncertainty in deriving ABCs for hydrometric areas containing only a very small number of water bodies, such as some of those in Northern Scotland, and also for hydrometric areas with limited monitoring data. However, in many cases these areas are likely to be subject to more limited pressures than more frequently monitored areas.

As the ABCs are derived as a low percentile of the monitoring data for each hydrometric area, larger datasets provide much greater confidence in the resulting ABC estimates. For example, in a dataset of 20 data points, only a single point will lie below the 5th percentile, whereas in a dataset of 100 data points, there would be 5 points below the 5th percentile. Applying a single cut-off value for the number of data required per hydrometric area will therefore penalise small hydrometric areas with relatively few data and may not ensure that adequate data are actually available for very large hydrometric areas. For this reason, we recommend that datasets with less than 50 data points should not be included for derivation of ABCs, unless they are from a hydrometric area with less than 10 water bodies. This should ensure that there are adequate numbers of data for the derivation of ABCs in large hydrometric areas, without penalising small hydrometric areas.

## 2.2 How do we deal with limits of detection?

Several methodologies are available for dealing with values reported as LODs when analysing and processing monitoring data, with no acceptance of any single methodology (Larson et al., 1997; Grunfeld, 2005; Mumford et al., 2006). Furthermore, many methods for dealing with single, limited datasets are impractical when deriving ABCs for 6 elements for over 100 hydrometric areas from three datasets.

Relatively recent advances in metals analyses have meant that significant improvements in detection levels have occurred over the last five years, with most regulatory laboratories using inductively coupled plasma mass spectroscopy (ICPMS). However, many still frequently use the less sensitive inductively coupled plasma with optical emission spectroscopy (ICPOES) when reporting requirements do not demand low levels of detection. It is common to find the reporting limits defined by a particular regulation described in regulatory data sets as LODs, when clearly this is not the case, as sensitive methods of detection would result in values significantly lower than these reported LODs. The datasets used in this project have been selected from the last five years of freshwater monitoring in order to reduce the presence of variable LODs, although this has still not been entirely successful.

Datasets containing data reported as less-than values are known as censored datasets. It is a relatively common practice to substitute those results reported as a less-than value (that is, less than the LOD or reporting limit) with a single value, such as one half of the censoring value. This approach is typically taken because it is simple, although it may introduce a bias in any resulting descriptive statistics.

When deriving low percentiles of a dataset, censorship of the data at a level below the required percentile will not affect the calculation of the value of that percentile. Estimations based on the 10th percentile of a distribution, for which more than 10 per cent of the data are censored, are likely to be inaccurate. This issue can be further complicated by datasets that include multiple reporting limits or LODs.

## 2.2.1 Comparing approaches to taking account of the limits of detection

Using freshwater monitoring data from the Scottish Environment Protection Agency (SEPA) for hydrometric area 84 (the Clyde), we have illustrated six options for dealing with LODs to estimate a robust ABC (Table 2.1). The Clyde hydrometric area is typical of many of the datasets we are dealing with. However, we have ignored our initial recommendation in Section 2.1, in regard to size of datasets, in order to have enough data to provide reasonable examples (the Clyde has 59 separate water bodies).

Option 1 derives a low percentile value for a dataset, where that percentile is below the LOD or reporting limit for the analytical method. Options 2 to 6 use various different approaches for handling data reported as less-than values; that is, they may be excluded, fixed to one of the reporting limits or halved. Options 5 and 6 retain some of the information about the distribution of data points reported as less-than values by maintaining the distinction between different LOD values.

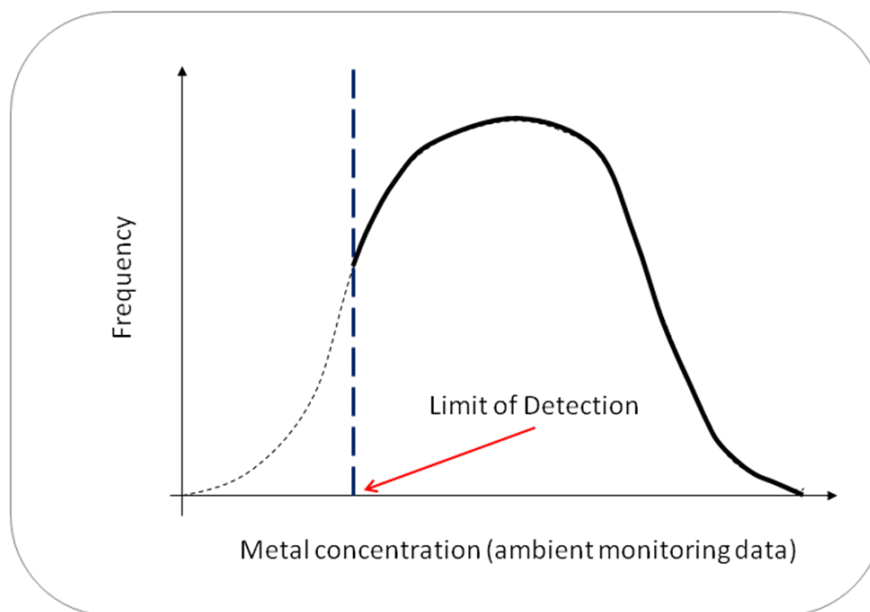
**Table 2.1 Options for treating limits of detection for estimation of ambient background concentrations**

Option	Basis of methodology	Possible influence of the 5th and 10th percentiles?
1. Extrapolation	Estimate true value of 5th and 10th percentiles by extrapolation from reported data.	Possibly higher than true values, but capable of deriving values that are below the LOD.
2. LOD Removal	All the data listed as <LOD are excluded from estimation of the 10th to 90th percentiles.	Reduces the dataset and produces percentiles that are likely to be high relative to the true values. Estimates cannot be lower than the LOD.
3. LODs set to lowest	All the <LODs are set to the lowest LOD in the dataset.	Precautionary approach where there are multiple LODs, generally leading to relatively low and similar 5th and 10th percentiles.
4. LODs set to highest	All the <LODs are set to the highest LOD in the dataset.	Not precautionary, but (as with Option 3) possibly leading to similar 5th and 10th percentiles.
5. LOD as reported value	All the <LODs are treated as measured data at the recorded LOD.	Depends on how many measured data are available in the distribution tail and what proportion of the dataset is recorded as LODs. May handle datasets with multiple reporting limits better than other methods.
6. LOD is halved	All the values recorded as <LODs are halved and then treated as measured data.	Generally, this should produce a strong downward bias.

Option 2 will produce an upward bias to the results, by effectively removing the lowest recorded portion of the data (Helsel, 2006). The worst practice when dealing with non-detects is to exclude or delete them. This produces a strong upward bias in all subsequent measures of location such as means and medians. Options 3, 4 and 5 should have a smaller upward bias to the data, although this will depend on the number and range of different LODs within the dataset.

## 2.2.2 Extrapolation of low percentiles of censored datasets

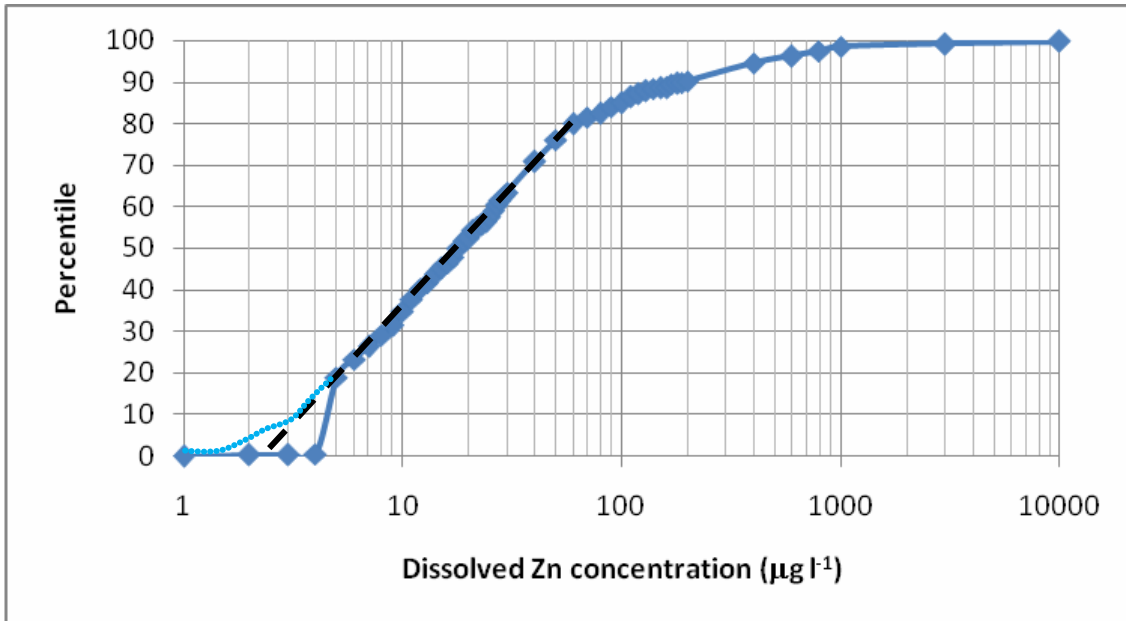
In some datasets there may be a relatively high proportion of data reported as a less-than value. This may be either the LOD or the reporting limit for the analysis, but the effect on the data is the same. Also, in some cases there may be multiple LODs used within a single dataset. Less-than values can be treated in various ways, which can result in differences between the estimates of the background concentration from the dataset.



**Figure 2.1 Example of a censored dataset**

By using information about the distribution of the data for the portion of the dataset where results are all above the LOD, it is possible to provide an estimate of a percentile that lies below the LOD (Helsel, 1990; 2005). An example of a hypothetical dataset censored in this way is shown in Figure 2.1. By using information about the available data distribution it is possible to make refined estimates of the censored portion of the distribution. This may be simply performed by extrapolation from a linear portion of the graph, although doing so tends to slightly overestimate the true value of the unknown data, as shown in Figure 2.2, where the black line indicates the extrapolation and the dotted pale blue line indicates possible non-linearity in the data.

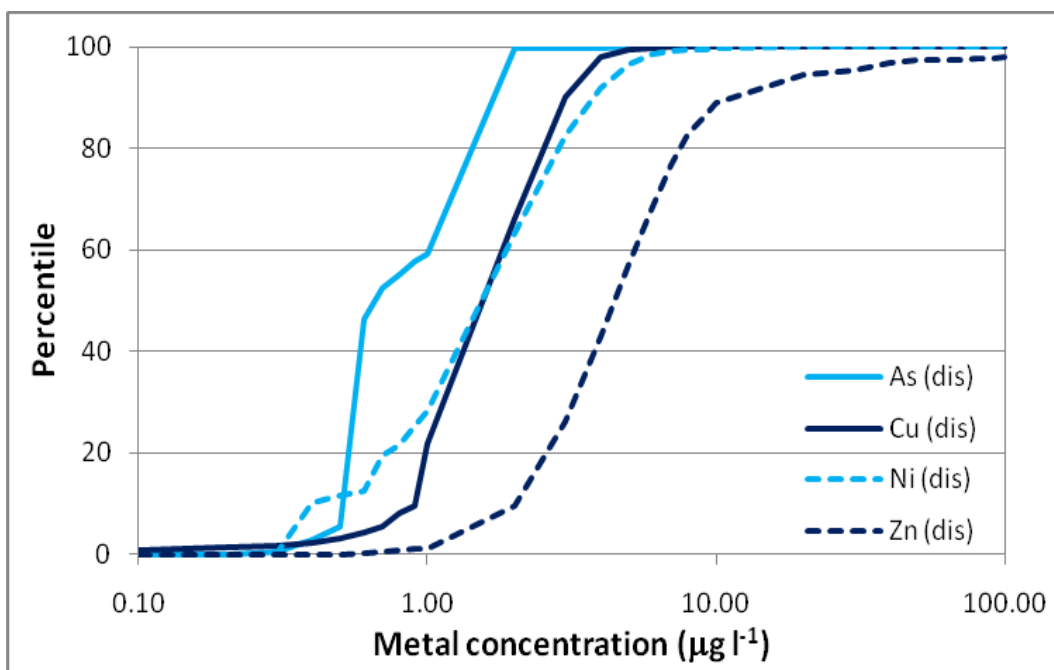




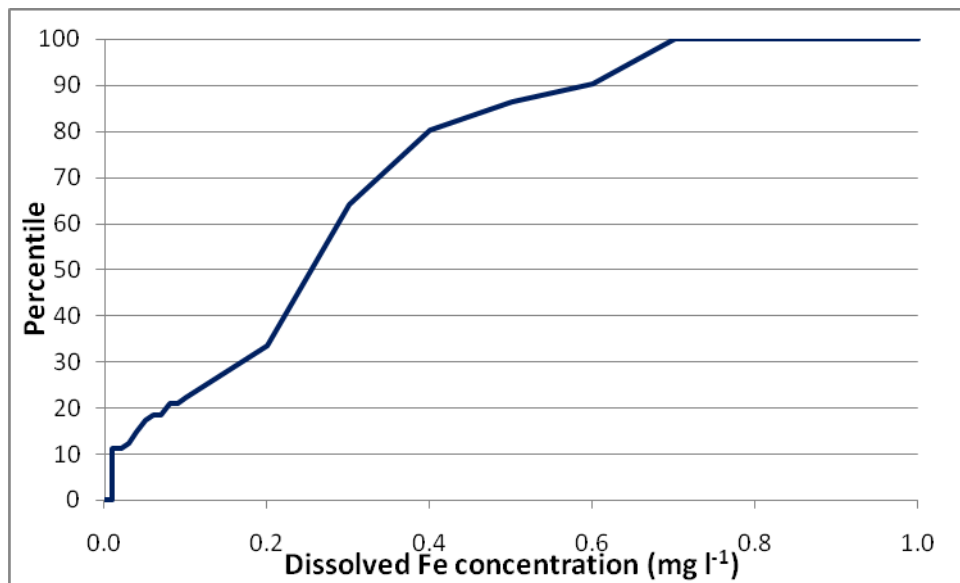
**Figure 2.2 Extrapolation of dissolved zinc concentrations in the Mersey**

A missing percentile of the dataset can be estimated by extrapolation from a linear portion of log transformed metal concentrations against percentiles (for log normally distributed data), as in Figure 2.2. This approach works best for the central portion of the dataset, and is likely to be less accurate towards the extremes of the distribution. Estimates of the 10th percentile by this method are therefore likely to be more accurate than estimates of the 5th percentile.

Using SEPA monitoring data for hydrometric area number 84 (the Clyde) as an example, cumulative frequency distributions of data are shown in Figure 2.3 for arsenic, copper, nickel and zinc, and in Figures 2.4 and 2.5 for iron and manganese, respectively.

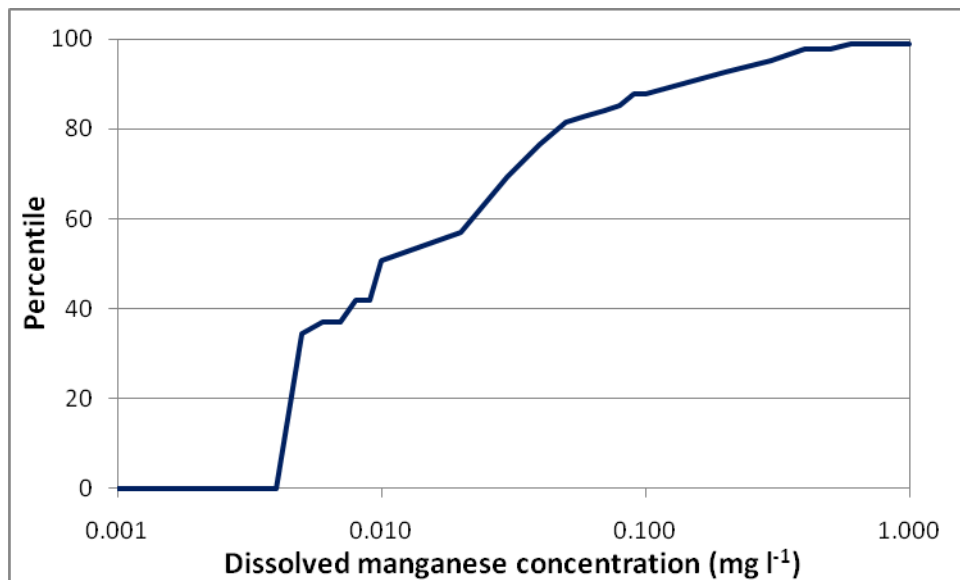


**Figure 2.3 Distribution of reported dissolved arsenic, copper, nickel and zinc data in the Clyde hydrometric area**



**Figure 2.4 Distribution of reported dissolved iron data in the Clyde hydrometric area**

The distribution of dissolved iron and manganese data do not follow a log normal distribution, in contrast to the other metals.



**Figure 2.5 Distribution of reported dissolved manganese data in the Clyde hydrometric area**

The results from the extrapolation of these data in Figures 2.2 to 2.5 are shown as Option 1 in Table 2.1, and are compared with the other methodologies in Figure 2.6 (Section 2.2.3).

### 2.2.3 Manipulation of the limit of detection

There are several methods for manipulating LOD values. These include replacing the values with zeros, excluding the data (Zhao et al., 2007), setting the values at the detection limits (Larson et al., 1997) or assuming a measured value of half the LOD (Paustenbach, 2001). Tables 2.2–2.7 give the results of the analysis of the Clyde data for six metals using a number of options for the treatment of LODs. The results from the analysis were calculated using Microsoft Excel and UnCensor 5.1<sup>2</sup>.

Option 2 calculates the 5th and 10th percentiles, after removing any data recorded as LODs. Option 3 sets all the data recorded as LOD to the lowest LOD for the respective element in the dataset before calculating the 5th and 10th percentiles of the distribution. Option 4 sets all the values recorded as LODs at the highest LOD in the dataset before calculating the percentiles. Option 5 treats recorded LODs as measured values when calculating the percentiles. Option 6 takes the recorded values of the LODs, halves them, and treats the resulting values as if they were measured data when calculating the percentiles. The datasets for Option 2 are obviously reduced in size compared with those for Options 3–6.

**Table 2.2 Analysis of arsenic data from the Clyde hydrometric area ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Number		231	776	776	776	776
%LODs used in calculation	46	0	70	70	70	70
Mean		0.696	0.764	0.565	0.931	0.485
Standard deviation		0.517	0.358	0.294	0.321	0.332
Coefficient of variation (%)		74	47	52	34	68
Variance		0.268	0.128	0.087	0.103	0.110
95% Confidence interval on mean		0.632–0.761	0.739–0.789	0.545–0.585	0.908–0.953	0.463–0.508
5th Percentile	0.110	0.335	0.497	0.497	0.497	0.475
10th Percentile	0.130	0.402	0.510	0.510	0.541	0.475

The dataset for arsenic has a high percentage of LODs for Options 1 and 3–6. The effect of this can be seen in the resulting values of the respective 5th and 10th percentiles, which are very similar or the same. The relatively high coefficient of variation for Option 2 gives an indication of the spread of the data about the mean, which decreases when the LODs are included. Option 1 gives especially low percentiles compared with Options 3–6 (that is, compared with those options that include the LODs in some way). However, the influence of the LODs (at 70 per cent of the complete dataset) introduces such a significant level of uncertainty into the percentile determinations that we would not recommend the use of a dataset in which greater than 30 per cent of the data are expressed as LODs.

<sup>2</sup> Virginia Institute Of Marine Science (VIMS). [http://www.vims.edu/env/research/software/vims\\_software.html](http://www.vims.edu/env/research/software/vims_software.html) [accessed December 2008].

**Table 2.3 Analysis of copper data from the Clyde hydrometric area ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Number		699	776	776	776	776
%LODs used in calculation	22	0	10	10	10	10
Mean		1.886	1.781	1.709	1.793	1.740
Standard deviation		0.902	0.917	1.009	0.901	0.964
Coefficient of variation (%)		48	51	59	50	55
Variance		0.813	0.841	1.019	0.812	0.929
95% Confidence interval on mean		1.820– 1.953	1.718– 1.845	1.639– 1.779	1.730– 1.856	1.670– 1.810
5th Percentile	0.760	0.720	0.654	0.100	0.746	0.475
10th Percentile	0.820	0.950	0.950	0.257	0.950	0.475

From Table 2.3 it is clear that the dataset for copper has relatively few LODs, when compared with the dataset for arsenic, and has a reasonable number of measured data. The coefficients of variation for Options 2–6 are all fairly similar. This dataset is characterised by having multiple LODs, which has greatly influenced the estimated 5th percentiles in Options 3–6. Nevertheless, four of the options (1–3 and 5) have delivered very similar 5th and 10th percentiles and the regulatory reality is that there is probably not a substantial difference between the values produced by each of these options, aside from Options 4 and 6.

**Table 2.4 Analysis of iron data from the Clyde hydrometric area ( $\text{mg}\cdot\text{l}^{-1}$ )**

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Number		74	81	81	81	81
%LODs used in calculation	22	0	9	9	9	9
Mean		0.428	0.391	0.392	0.392	0.392
Standard deviation		0.379	0.381	0.81	0.81	0.381
Coefficient of variation (%)		86	97	200	200	97
Variance		0.143	0.145	0.145	0.145	0.145
95% Confidence interval on mean		0.344– 0.510	0.312– 0.470	0.312– 0.470	0.312– 0.470	0.312– 0.469

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
5th Percentile	0.067 <sup>1</sup>	0.037	0.009	0.009	0.009	0.0045
10th Percentile	0.078 <sup>1</sup>	0.057	0.010	0.010	0.010	0.010

<sup>1</sup> Or 0.012 and 0.038 assuming iron concentrations to be normally distributed. This makes quite a significant difference to the extrapolated 5th and 10th percentiles, meaning that there is little certainty surrounding extrapolations for iron (in this case at least) because of the data distribution (that is, uncertainty about whether it is truly normal or log normal).

The iron dataset (Table 2.4) is characterised by very few samples at the LOD and a relatively low total number of samples (n = 81). All the options have high coefficients of variation, with the lowest for Option 2, which has excluded the LODs. The 5th and 10th percentiles for Options 3–6 are all highly influenced by the LODs. Option 1 is unreliable as the distribution of the data is not clear and we have had to assume a log normal distribution. We do not recommend estimating an ABC from these data owing to the low number and variability of these data.

**Table 2.5 Analysis of manganese data from the Clyde hydrometric area (mg l<sup>-1</sup>)**

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Number		55	81	81	81	81
%LODs used in calculation	37	0	32	32	32	32
Mean		0.101	0.070	0.070	0.070	0.0692
Standard deviation		0.279	0.234	0.234	0.234	0.234
Coefficient of variation (%)		276	334	334	334	338
Variance		0.078	0.055	0.054	0.054	0.0548
95% Confidence interval on mean		0.031–0.163	0.022–0.113	0.022–0.113	0.022–0.113	0.0215–0.112
5th Percentile	0.001	0.006	0.005	0.005	0.005	0.0025
10th Percentile	0.002	0.008	0.005	0.005	0.005	0.0025

Table 2.5 gives the analysis for the manganese data and, as is the case for iron, there are relatively few samples. Unlike iron, however, a greater number of the samples are recorded as LODs (>30 per cent). The paucity of measured data at the tail of the distribution is clear from the fact that Options 3–5 deliver the same values for the 5th and 10th percentiles and Option 6 is simply half these values. Option 1 has a higher percentage of LODs and gives 5th and 10th percentiles that are highly uncertain. The coefficients of variation are relatively high for Options 2–5 compared with some of the data for the other elements, and we would not recommend taking the estimates for any of the options as ABCs of manganese.

**Table 2.6 Analysis of nickel data from the Clyde hydrometric area ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Number		658	774	774	774	774
%LODs used in calculation	28	0	15	15	15	15
Mean		2.188	1.933	1.917	1.962	1.897
Standard deviation		1.459	1.478	1.494	1.450	1.515
Coefficient of variation (%)		67	76	78	74	80
Variance		2.128	2.185	2.231	2.103	2.294
95% Confidence interval on mean		2.080– 2.298	1.833– 2.033	1.816– 2.017	1.863– 2.060	1.795– 1.999
5th Percentile	0.620	0.689	0.370	0.370	0.670	0.185
10th Percentile	0.690	0.876	0.383	0.370	0.670	0.335

There is a reasonable amount of monitoring data for nickel in the Clyde hydrometric area and a relatively low number of samples recorded as LODs (Table 2.6). However, it is clear from coefficients of variation that the data are very widely spread. There is a clear lack of measured data at the tail of the distribution as shown by Options 3–5, which give very similar, or the same, values for the 5th and 10th percentiles. When the LOD data are excluded in Option 2, the 5th and 10th percentiles are substantially different (and similar to Option 1). Option 6 provides percentiles that are the lowest derived and perhaps offer a reasonable estimate of ABCs of nickel.

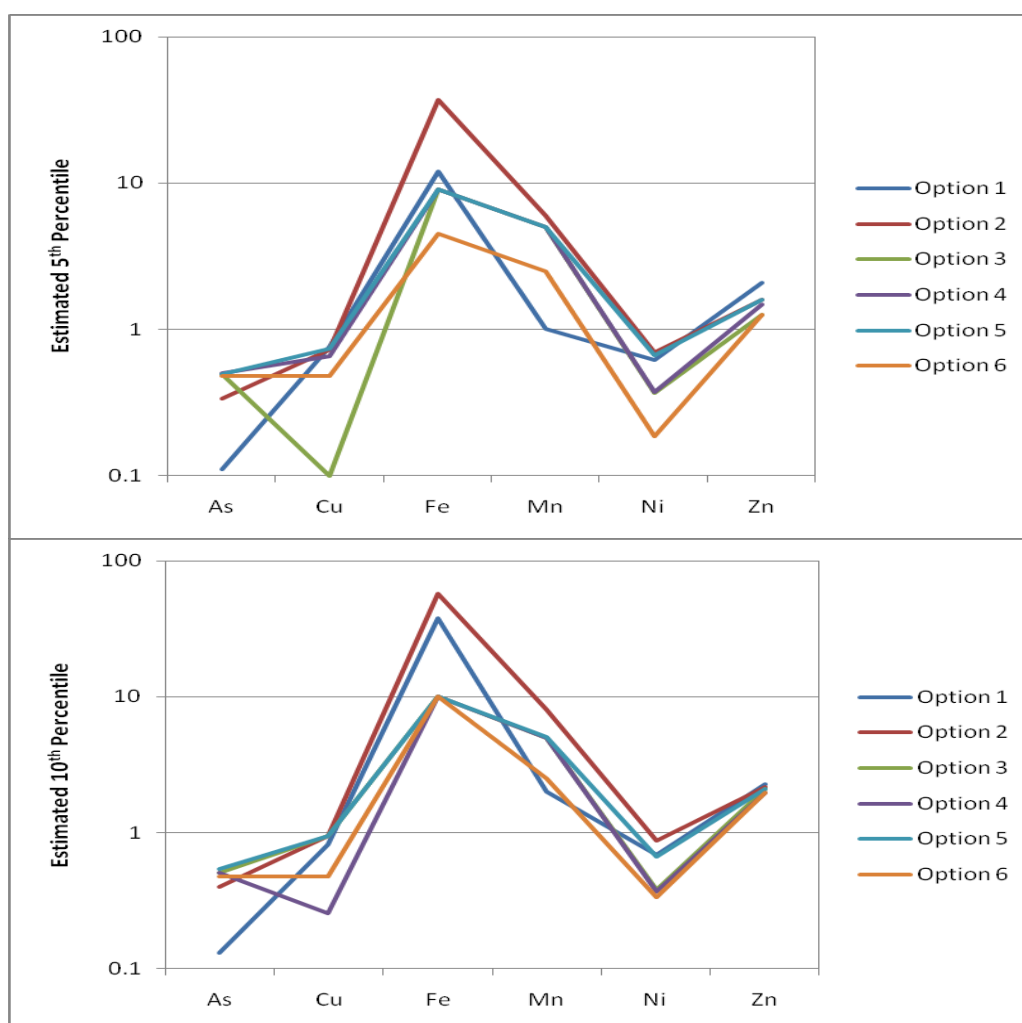
**Table 2.7 Analysis of zinc data from the Clyde hydrometric area ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
Number		747	764	764	764	764
%LODs used in calculation	26	0	2	2	2	2
Mean		8.72	8.56	8.54	8.58	8.54
Standard deviation		18.66	18.49	18.49	18.48	18.49
Coefficient of variation (%)		213	216	216	216	216
Variance		348	342	342	342	342
95% Confidence interval on mean		7.52– 9.90	7.38– 9.71	7.36– 9.69	7.40– 9.73	7.37– 9.70

	Option 1	Option 2	Option 3	Option 4	Option 5	Option 6
5th Percentile	2.08	1.59	1.47	1.25	1.60	1.25
10th Percentile	2.27	2.19	2.09	1.96	2.10	1.96

Table 2.7 shows the analysis of monitoring data for dissolved zinc in the Clyde hydrometric area. This dataset has the lowest percentage of LODs of all the metals assessed. Options 2–6 provide similar percentiles, whereas Option 1 is less precautionary. The coefficients of variation are relatively high but the means from all the methods are very similar.

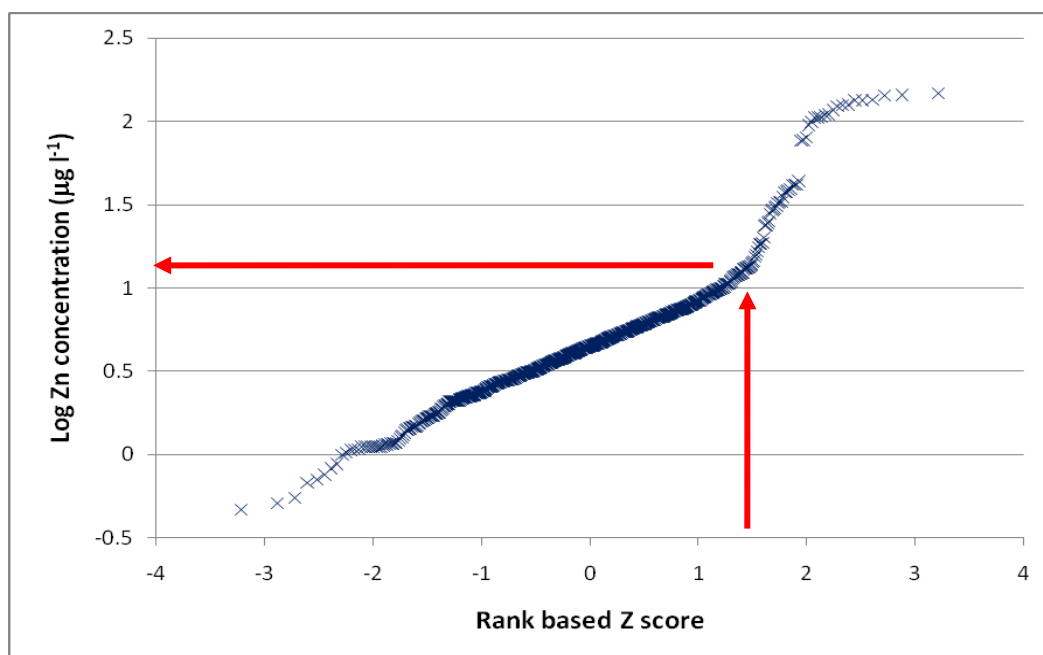
Overall we recommend Option 5 or 6 as being the most suitable to use for estimation of the ABCs on a hydrometric area basis. The relative performance of all the different options for all the metals is shown in Figure 2.6 for the estimates of both the 5th and the 10th percentiles.



**Figure 2.6 Performance of different options for deriving 5th and 10th percentiles**

An alternative approach has been applied to distinguish between background and contaminated samples on the basis of their concentration in soils (Davies, 1983; Environment Agency, 2008b). This approach identifies a change in the gradient of a plot of the rank scores (representation of cumulative frequency distribution) against logarithmically transformed metal concentration. In the example for zinc in the Clyde

hydrometric area, shown in Figure 2.7, this inflection occurs at a zinc concentration of approximately 10 to 13  $\mu\text{g}\cdot\text{l}^{-1}$  dissolved zinc.



**Figure 2.7 Inflection between impacted and unimpacted zinc measurements**

Making a distinction between impacted and unimpacted measurements is likely to be more useful in deriving site- or water body specific ABCs than in deriving default ABCs for an entire hydrometric area. This is because treatments of the upper end of the dataset have a limited effect on the derivation of percentiles from the lower end. However, this methodology also has a number of drawbacks:

- It generates a single mean value and a single percentile range for the whole database instead of site-specific values (not such an issue for this project).
- It assumes that only the population representing the lowest metal concentrations is 'uncontaminated'. This may be too simplistic. There may be several populations in the whole dataset, with more than one (that is, the lowest concentration) population being associated with the relatively 'uncontaminated' category (Environment Agency, 2008b).

An ABC derived in this way would be likely to include many small, localised emissions, such as those from sewage treatment works and diffuse sources of emissions, and therefore may not ensure an adequate level of protection.

### 2.3 Is it possible to extrapolate 'total' to 'dissolved' metal concentrations?

The proposed EQS for zinc is set on the basis of dissolved concentrations, whereas the current statutory EQS for zinc is set on the basis of total concentrations. As a result there are very limited monitoring data for dissolved zinc in some regions of the UK. Background concentrations need to be expressed in the same form as the quality standard, so also need to be derived on the basis of dissolved zinc concentrations.

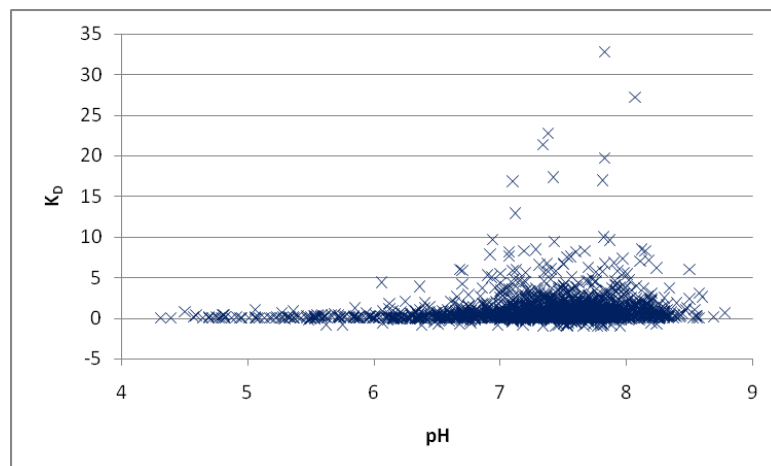


A matched dataset from Southwest Scotland, including pH, suspended solids, dissolved organic carbon (DOC), total organic carbon (TOC), dissolved zinc, and total zinc, was assessed for parameters that influence the partition coefficient ( $K_D$ ) of zinc (Zn).

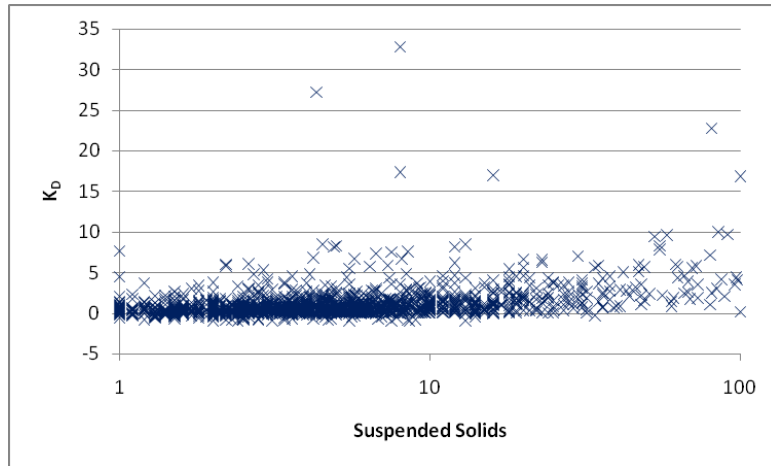
$K_D$  is defined as: 
$$\frac{[\text{total Zn}] - [\text{dissolved Zn}]}{[\text{dissolved Zn}]}$$

A  $K_D$  value was calculated for each matched set of total and dissolved zinc monitoring data. Figures 2.8 to 2.11 show the calculated  $K_D$  values as a function of pH, suspended solids, DOC, and the estimated copper PNEC (which is used here as a general surrogate for metal availability). There is no clear effect attributable to any of these parameters, at least when considered individually, although the highest  $K_D$  values are observed between pH values of approximately 7 and 8.

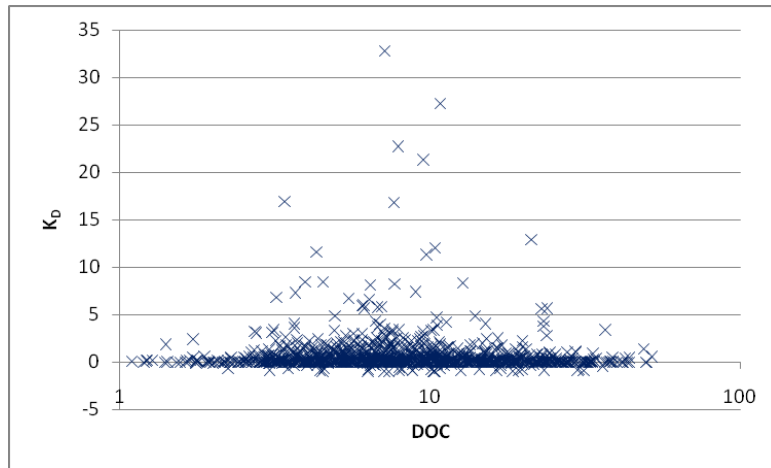
The estimated copper PNEC was considered as a possible factor for describing the variation in zinc  $K_D$  values because of the importance of copper/DOC binding when calculating the bioavailability of copper. High estimated copper PNEC values might be associated with low dissolved zinc concentrations. It may not be possible to accurately describe the partitioning behaviour of zinc between the dissolved and particulate fractions (as defined by filtration through a 0.45  $\mu\text{m}$  membrane).



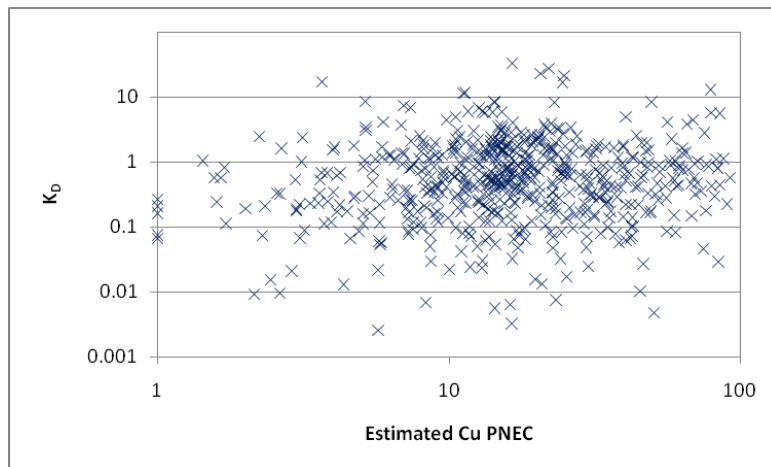
**Figure 2.8**  $K_D$  as a function of pH



**Figure 2.9  $K_D$  as a function of suspended solids concentration**



**Figure 2.10  $K_D$  as a function of DOC concentration**

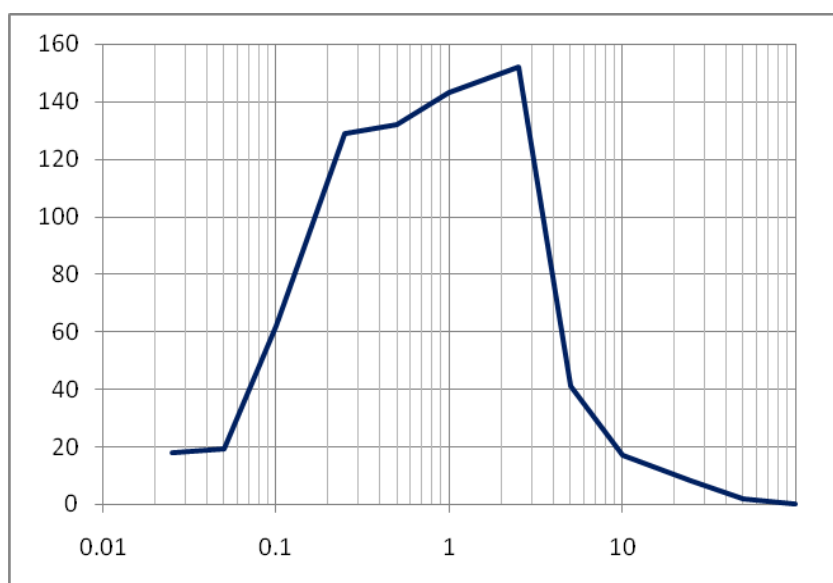


**Figure 2.11  $K_D$  as a function of estimated copper PNEC**

$K_D$  does not vary consistently as a function of pH, suspended solids, DOC, TOC, particulate organic carbon, or the estimated copper PNEC for the local conditions.

None of these parameters can be used to improve the reliability of  $K_D$  estimates alone for the correction of total zinc concentrations. Therefore, we do not recommend the estimation of dissolved metal concentrations from measured total concentrations.

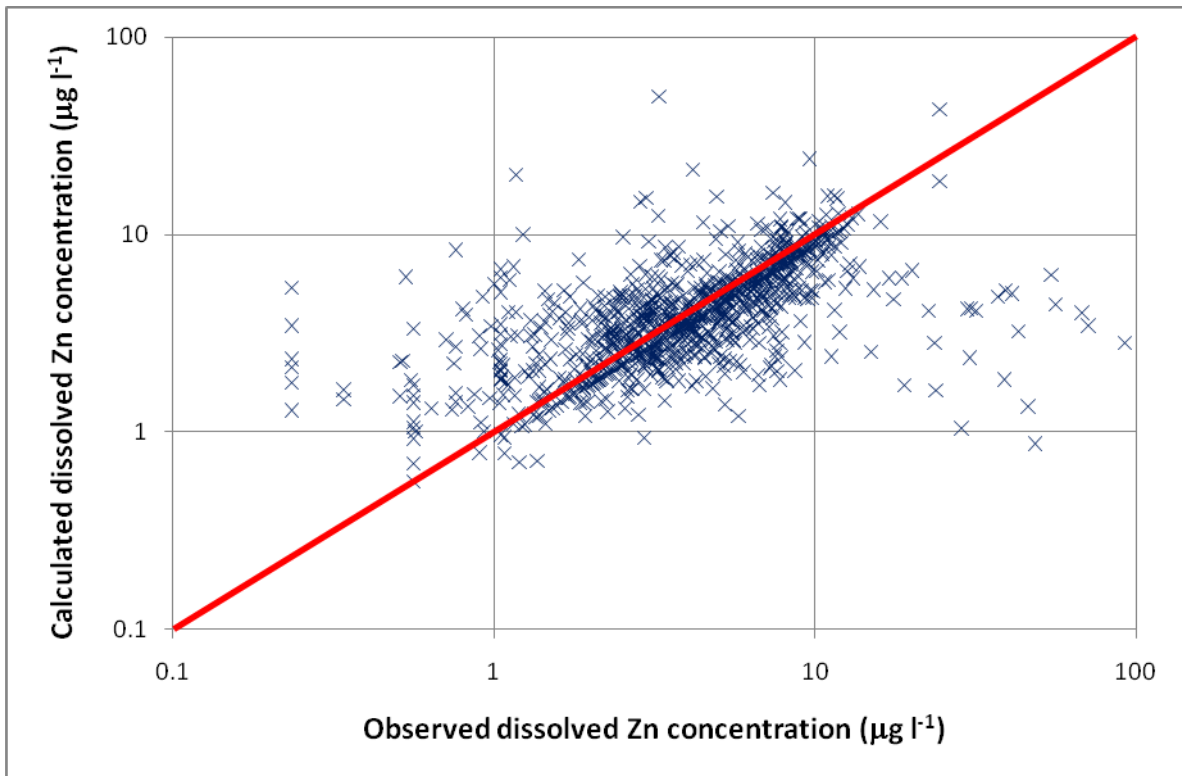
Figure 2.12 shows the frequency distribution of calculated  $K_D$  values for zinc in Scottish surface waters. Typical  $K_D$  values for zinc vary between approximately 0.3 and 3, with a value of approximately 1 being generally representative. Excluding those  $K_D$  values that are calculated as  $\leq 0$  (that is, those where the dissolved zinc concentration is apparently greater than the total zinc concentration) gives a dataset of 743  $K_D$  values with a geometric mean of 0.43 and a 50th percentile of 0.48. The distribution of  $K_D$  values is log normal, suggesting that using either the 50th percentile value or the geometric mean will provide a better indication of typical conditions than the mean value (of 1.17).



**Figure 2.12 Frequency distribution of calculated  $K_D$  values for zinc in Scottish surface waters**

When estimating from data where only total zinc has been analysed, it can be assumed that approximately 70 per cent of total zinc is present as dissolved zinc (that is, a  $K_D$  value of 0.43). In the majority of cases, this is likely to be accurate to within around a factor of approximately three.

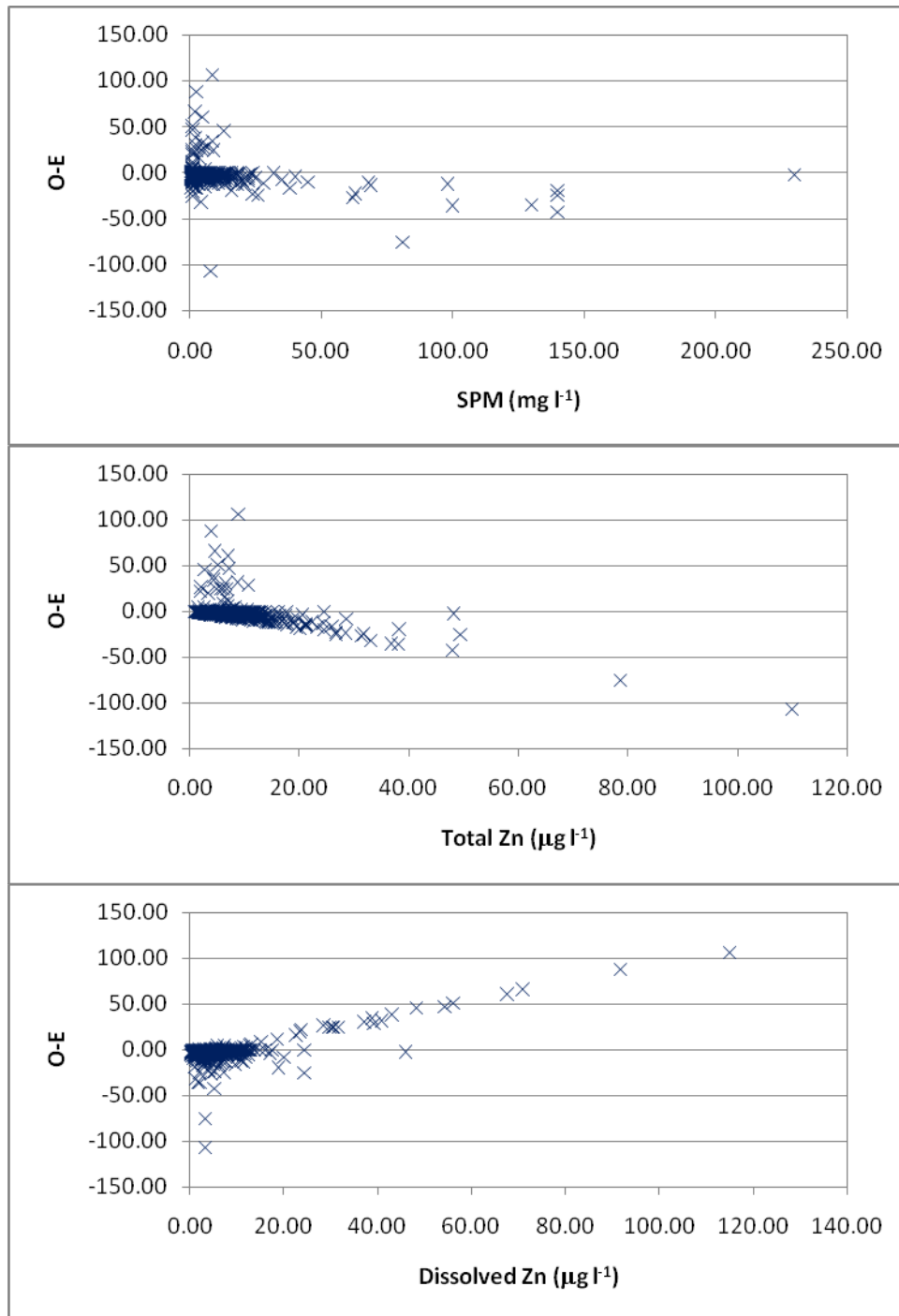
Alternatively, the partitioning equations provided by the EU Technical Guidance Document (EC, 2003b) may be applied to estimate the dissolved concentration of zinc from a measured total concentration. These equations apply a suspended matter–water partition coefficient ( $l \cdot kg^{-1}$ ) and the concentration of suspended solids ( $kg \cdot l^{-1}$ ) to calculate the dissolved zinc concentration ( $\mu g \cdot l^{-1}$ ). These calculations were performed using both the  $K_p$  value from the zinc Risk Assessment (Dutch National Institute for Public Health and the Environment (RIVM), 2004) of  $110,000 l \cdot kg^{-1}$  and using a fitted  $K_p$  value from the measured data. A comparison of the observations and predictions of dissolved zinc concentrations using the fitted  $K_p$  value of  $152,141 l \cdot kg^{-1}$  is shown in Figure 2.13. While acceptable predictions can be made in many cases, there would be considerable uncertainty in the application of such models to the derivation of ABCs.



**Figure 2.13 Performance of predictions of dissolved zinc from total zinc**

The standard deviation in the predictions of dissolved zinc concentrations from total zinc concentrations in Figure 2.13 is approximately  $7.7 \mu\text{g}\cdot\text{l}^{-1}$ . This means that approximately 95 per cent of estimates of the dissolved zinc concentration will be accurate to within around  $15 \mu\text{g}\cdot\text{l}^{-1}$ . The 95th percentile of dissolved zinc concentrations in the dataset that was used for this testing is only  $11.5 \mu\text{g}\cdot\text{l}^{-1}$ , indicating that in most cases the error will be greater than the result.

Examination of the residuals from these calculations indicates that dissolved zinc concentrations tend to be overestimated at high concentrations of suspended particulate matter and high total zinc concentrations, and underestimated when the measured dissolved zinc concentrations are high. These results are shown in Figure 2.14. The residual errors did not vary consistently as a function of either DOC or TOC concentrations in the samples.



**Figure 2.14 Errors in dissolved zinc calculations as a function of suspended particulate matter, total zinc concentrations and dissolved zinc concentrations; Observed–estimated concentrations, negative values indicate overestimation of dissolved zinc relative to measurements**

Given the uncertainties surrounding the calculation of dissolved zinc concentrations from total zinc concentrations, even when specific information on the suspended solid concentrations is available, we do not recommend applying such corrections for the estimation of ABCs for dissolved zinc from total zinc monitoring data.

## 2.4 Recommendations

It is clear that a single methodology for dealing with LODs is unlikely to suit all metals or all datasets and the fundamentally important factor is the quality of the dataset.

While there are numerous methods for dealing with LODs that could potentially be used for the freshwater monitoring datasets collated in this project, there is little definitive technical evidence available to facilitate the choice of one over another.

We have outlined above the implications of using some of these methods. Based on this analysis we propose that the following rules be used when estimating ABCs from monitoring data. We have applied these rules throughout the rest of this project, when defining ABCs.

**Table 2.8 Options for calculating ABCs from monitoring data**

Question	Rule
What is the minimum amount of monitoring data required to estimate an ABC for a hydrometric area?	There should be at least as many sampling points as there are water bodies represented by the estimated ABC (if it is possible to establish how many water bodies are in a hydrometric area).
When is a dataset not useable for determining ABCs?	When more than 30 per cent of the data have been reported as less-than values.
What approach should be adopted for handling LODs?	Options 5 and 6 should be used most of the time, with 6 being slightly more precautionary, although the difference is not generally large.
	If less than 5 per cent of the data are reported as LODs, use Option 2, 5 or 6. Option 2 does involve exclusion of some data, which is not usually a preferred approach. However, at these low percentages this will not lead to substantial differences to the estimates.
	Options 3 and 4 should not be used.
Can total metal concentrations in freshwaters be used to derive dissolved metal concentrations?	Not reliably. Any efforts to derive ABCs for dissolved metal from total metal concentrations will be subject to considerable uncertainty (at least three times greater than for ABCs derived from dissolved metal data).

There are some options available in the absence of adequate data to derive an ABC:

- Pool data across several adjacent hydrometric areas. These need to have broadly comparable geology, land use and hydromorphology.
- Adopt an ABC from an adjacent hydrometric area.
- Derive a reasonable worst case UK ABC for use in cases where neither of the above options is viable. This might be based on a low percentile of the whole

UK data, or on a statistic of the derived ABCs (for example, the geometric mean of all derived ABCs). This can be verified against other monitoring data for the UK, such as FOREGs.

### 3 Data collation

There are 111 hydrometric areas in the UK and these are split between 15 river basin districts, two of which are shared with the Republic of Ireland (Figure 3.1.). One of these river basin districts (the Solway Tweed district) is shared between England and Scotland, where different environmental regulatory agencies operate.



**Figure 3.1 River basin districts in the UK and Ireland (WFD UKTAG)**

In some cases the data are reported as either less than the LOD or less than a reporting limit. In cases where a large proportion of the data are reported as less-than values, the dataset is not considered appropriate for the derivation of ABCs. In cases where the desired percentile is lower than the proportion of less-than values in the dataset the result can only be given as less than the LOD or reporting limit, unless extrapolation techniques are applied. In such cases, both the 5th and 10th percentiles of the data will be recorded as 0.5 times the LOD. In these cases the derived ABCs are subject to considerable uncertainty, as their values are defined by the treatment of those data that have been reported as less-than values.



Because the current statutory EQS values for some of the metals considered in this report are based on total concentrations (for example, zinc), there are relatively few dissolved monitoring data available for certain metals. The current statutory EQS values for each of the metals in question are shown in Table 3.1. The LODs or reporting limits currently employed by the analytical laboratories of the regulatory agencies are adequate for assessing compliance against these EQS values.

**Table 3.1 Environmental quality standards for trace metals in the UK**

<b>Metal</b>	<b>Current statutory annual average EQS</b>
As (dissolved)	50 $\mu\text{g}\cdot\text{l}^{-1}$
Cu (dissolved)	1 to 28 $\mu\text{g}\cdot\text{l}^{-1}$ (hardness banded)
Fe (dissolved) <sup>1</sup>	1 $\text{mg}\cdot\text{l}^{-1}$
Mn (dissolved) <sup>2</sup>	30 $\mu\text{g}\cdot\text{l}^{-1}$
Ni (dissolved)	50 to 200 $\mu\text{g}\cdot\text{l}^{-1}$ (hardness banded)
Zn (total) <sup>3</sup>	8 to 500 $\mu\text{g}\cdot\text{l}^{-1}$ (hardness banded)

<sup>1</sup> A standard of 1  $\text{mg}\cdot\text{l}^{-1}$  (total Fe) is applied for classification purposes in Scotland.

<sup>2</sup> There is no statutory EQS for manganese.

<sup>3</sup> Values also depend on fishery status (salmonid or cyprinid).

### 3.1 Northern Irish monitoring data

Northern Ireland has nine hydrometric areas in three river basin districts. Two of these river basin districts are shared with the Republic of Ireland. The monitoring data for Northern Ireland were provided for this project for a period between 1999 and 2008. Matched data were provided for samples sorted into individual hydrometric areas.

Extensive monitoring data were available for dissolved copper, but there were very few measurements of other dissolved metals. All of the available dissolved arsenic data were reported as less than the LOD or less than the reporting limit of 1  $\mu\text{g}\cdot\text{l}^{-1}$ . Furthermore, there were no monitoring data for manganese and only between 90 and 100 data points for iron and nickel, respectively, for the period between 1999 and 2008 for the whole of Northern Ireland. All zinc concentrations were reported as total concentrations, for assessment of compliance against the current statutory EQS. As discussed in Section 3.1 above, it was therefore not possible to use these zinc data to estimate ABCs.

### 3.2 Scottish monitoring data

Scotland has 45 hydrometric areas in two river basin districts. Monitoring data for Scotland were provided as matched data (that is, physico-chemical determinands for the same site, taken at the same time) for individual samples. The dataset covered three years of monitoring activity between 2005 and 2007. The metal concentrations were sorted into individual hydrometric areas prior to further processing, to derive ABCs for each hydrometric area (see Section 4.2).

The coverage of metals monitoring data was variable, with some hydrometric areas having very few matched data points for certain metals, and other hydrometric areas having many hundreds.

There were very limited dissolved metal monitoring data for iron and manganese across Scotland. For zinc, the reporting requirements of the current statutory EQS

(which is for total rather than dissolved zinc) meant that the useable data available for this metal were also limited.

### 3.3 England and Welsh monitoring data

England and Wales have >60 hydrometric areas in 11 river basin districts. Monitoring data for England and Wales, like Scotland, were provided as matched data (that is, physico-chemical determinands for the same site), taken at the same time for individual samples.

The dataset covered 10 years of monitoring activity between 1998 and 2008. The metal concentrations were sorted into individual hydrometric areas prior to further processing, to derive ABCs for each hydrometric area (Section 4.3).

The coverage of metals monitoring data was, as with the Scottish dataset, variable, with some hydrometric areas having very few matched data points for certain metals (just tens), and other hydrometric areas having hundreds of thousands. Minimum data requirements were especially poor for nickel and arsenic (fewer than six hydrometric areas). No metal fulfilled all the minimum data requirements for all hydrometric areas.

# 4 Estimation of ambient background concentrations

Having collated all the recent UK monitoring data for dissolved concentrations of copper, iron, manganese, nickel, zinc and arsenic, these were arranged into hydrometric areas. Data for each metal in each hydrometric area were assessed in order to extract the following information:

- Total number of data (to compare with minimum requirement).
- Number of less-than values (to compare with maximum allowable).
- Value of the lowest LOD or reporting limit.
- The 5th and 10th percentiles of the data distribution (following conversion of less-than values into 0.5 times the reported value).

The conversion of less-than values into 0.5 times the reported value is not an ideal treatment of the data but is both practical and transparent and in accordance with current Environment Agency treatment of less-than data. Where fewer than five per cent of the data are reported as less-than values, the treatment of these data has no substantial effect on the derived percentiles (Option 6).

The following sub-sections provide a summary of the estimated ABCs for hydrometric areas in the UK.

## 4.1 Northern Ireland ambient background concentrations

The estimated ABCs for Northern Ireland are shown in Table 4.1. As discussed in Section 3.2, there were few monitoring data available for metals, and only the copper dataset for Northern Ireland exceeded the minimum data requirements for the estimation of ABCs (five monitoring data for each water body in a hydrometric area).

The extrapolation method was used for the estimation of many of the copper ABC values for the Northern Ireland hydrometric areas. This method was used to assess the usefulness of the approach, although it is considered to be too time-consuming for routine application in the derivation of ABC values.

**Table 4.1 Estimated ABCs for copper in Northern Ireland from monitoring data collected between 1999 and 2008 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Belfast Lough and East Down	2,393 (45)	1.00	2.00
Bush and North East Coast	1,437 (264)	0.35 <sup>2</sup>	0.40 <sup>2</sup>
Erne	5,097 (33)	0.66 <sup>2</sup>	0.74 <sup>2</sup>
Foyle	5,097 (498)	0.52 <sup>2</sup>	0.60 <sup>2</sup>
Lough Foyle	1,505 (91)	0.77 <sup>2</sup>	0.86 <sup>2</sup>
Lough Melvin	3,52 (35)	0.49 <sup>2</sup>	0.56 <sup>2</sup>
Lough Neagh and Lower Bann	8,716 (361)	0.94 <sup>2</sup>	1.05 <sup>2</sup>
Lough Swilly	91 (0)	2.00	3.00

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Mourne and South Armagh	1,975 (215)	0.77 <sup>2</sup>	0.87 <sup>2</sup>

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

<sup>2</sup> Calculated using the extrapolation method (Option 1) described in Section 2.2.2.

## 4.2 Scottish ambient background concentrations

Ambient background concentrations were derived for Scottish hydrometric areas where the number of data points was at least five times the number of water bodies in the hydrometric area (Tables 4.2 to 4.6).

**Table 4.2 Estimated ABCs for arsenic in Scotland from monitoring data collected between 2005 and 2007 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Shin Group	58 (0)	0.11	0.12
Spey	217 (0)	0.07	0.08
Deveron Group	58 (0)	0.27	0.29
Don (Aberdeenshire)	50 (0)	0.23	0.24
Dee (Aberdeenshire)	168 (0)	0.07	0.09
Cree	412 (117)	0.50	0.51
Lock Alsh Group	35 (0)	0.06	0.07

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.3 Estimated ABCs for copper in Scotland from monitoring data collected between 2005 and 2007 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Shin Group	60 (8)	0.20	0.22
Spey	274 (33)	0.31	0.47
Deveron Group	77 (8)	1.63	1.82
Don (Aberdeenshire)	66 (13)	0.29	0.34
Dee (Aberdeenshire)	169 (14)	0.15	0.23
Earn	66 (3)	0.67	0.71
Esk	90 (15)	0.46	0.68
Annan	104 (22)	0.63	0.71
Nith	59 (9)	0.69	0.85
Dee	348 (64)	0.10	0.15
Cree	410 (114)	0.20	0.40
Doon Group	151 (28)	0.31	0.43
Irvine and Ayr	329 (12)	0.95	1.15
Clyde	776 (77)	0.65	0.95
Leven	113 (14)	0.62	0.71
Firth of Clyde	28 (2)	0.53	0.70
Loch Alsh Group	31 (6)	0.13	0.13

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.4 Estimated ABCs for iron and manganese in Scotland from monitoring data collected between 2005 and 2007 ( $\text{mg}\cdot\text{l}^{-1}$ )**

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
<b>Fe</b>			
Almond Group	138 (0)	0.03	0.06
<b>Mn</b>			
Almond Group	141 (0)	0.01	0.02

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.5 Estimated ABCs for nickel in Scotland from monitoring data collected between 2005 and 2007 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Shin Group	58 (9)	0.07	0.07
Spey	215 (28)	0.13	0.13
Deveron Group	58 (0)	0.52	0.80
Don	51 (0)	0.27	0.39
Dee	167 (36)	0.13	0.13
Esk	90 (17)	0.37	0.37
Nith	59 (15)	0.37	0.37
Cree	410 (119)	0.37	0.37
Doon Group	150 (41)	0.37	0.37
Irvine and Ayr	324 (32)	0.37	0.67
Clyde	774 (116)	0.37	0.38

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.6 Estimated ABCs for zinc in Scotland from monitoring data collected between 2005 and 2007 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Findhorn Group	45 (13)	1.10	2.00
Deveron Group	77 (14)	2.10	2.28
Dee	181 (47)	2.10	2.10
Tay	354 (41)	0.65	0.70
Earn	52 (9)	0.65	0.65
Esk	89 (6)	0.81	1.03
Annan	101 (14)	1.10	1.12
Nith	58 (0)	2.30	2.56
Dee (Galloway)	347 (13)	1.67	2.10
Cree	401 (15)	2.10	2.28
Doon Group	150 (10)	1.12	1.51
Irvine and Ayr	324 (8)	1.65	2.06
Clyde	764 (17)	1.47	2.09
Leven	109 (15)	1.12	1.29
Firth of Clyde Group	27 (0)	2.07	2.44
Fyne Group	23 (1)	1.08	1.19
Add Group	23 (1)	1.37	1.57
Aire and Etive	95 (6)	1.05	1.24

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

### 4.3 England and Wales ambient background concentrations

ABCs were derived for English and Welsh hydrometric areas where the number of data points was at least 100 per hydrometric area and where no more than 30 per cent of the dataset was reported as limit of detection (Tables 4.7 to 4.11).

**Table 4.7 Estimated ABCs for arsenic in England and Wales from monitoring data collected between 1998 and 2008 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Blackwater, Chelmer	Thames	529(118)	0.50	0.50
Tamar	South West	447(36)	0.50	1.20
Fal	South West	1377(64)	1.00	1.38
Camel	South West	1,695(63)	1.20	2.00
Tone, Parrett	South West	330(89)	0.50	0.50

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.8 Estimated ABCs for copper in England and Wales from monitoring data collected between 1998 and 2008 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Tweed	North East	737(30)	0.55	0.65
Coquet, Wansbeck	North East	3,553(20)	1.07	1.25
Tyne	North East	3,192(18)	0.95	1.12
Wear	North East	4,039(14)	1.28	1.50
Tees	North East	3,066(28)	1.02	1.21
Hull	North East	3,860(89)	0.66	0.80
Ouse, Humber	North East	34,364(391)	1.00	1.23
Ouse, Humber	Midland	476(0)	1.70	2.10
Ouse, Humber	North West	120(1)	1.44	1.51
Trent	North East	106(0)	6.50	7.14
Trent	Midlands	108,428(215)	1.92	2.23
Ancholme	Anglian	1,957(560)	0.50	1.10
Witham	Anglian	1,866(328)	1.10	1.25
Witham	Midland	193(0)	1.44	1.82
Welland	Anglian	1,419(318)	0.50	1.20
Nene	Anglian	1,707(172)	1.25	1.25
Great Ouse	Anglian	10,260(1269)	0.50	1.25
Gipping	Anglian	929(214)	1.05	1.25
Stour	Anglian	1,098(200)	1.25	1.25
Blackwater, Chelmer	Anglian	2,322(301)	1.25	1.25
Blackwater, Chelmer	Thames	960(44)	0.50	1.00
Lee	Thames	4,170(643)	1.20	1.25
Thames	Thames	30,525(6385)	0.70	1.20
Medway, Stour	Southern	28,667(7020)	1.25	1.25
Fal	South West	12,104(3133)	1.25	1.25
Camel	South West	8,849(2282)	1.25	1.25
Severn	Midland	76,374(634)	1.01	1.36
Taff	Wales	13,001(3072)	0.50	0.50
Tawe, Neath	Wales	10,723(2840)	0.50	0.50
Loughor	Wales	8,594(1195)	0.50	0.50
Rheidol, Ystwyth	Wales	5,401(996)	0.50	0.50

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Clwyd, Conwy	Wales	5,079(1396)	0.50	0.50
Anglesey	Wales	2,134(109)	0.50	1.15
Dee	Wales	13,911(2802)	0.50	0.50
Dee	North West	122(0)	1.75	2.05
Weaver	North West	9,508(48)	1.60	2.06
Mersey	North West	20,805(133)	1.13	1.41
Douglas	North West	3,578(9)	1.65	2.06
Ribble	North West	6,754(38)	1.05	1.28
Lune	North West	6,616(214)	0.56	0.68
Leven, Kent	North West	6,077(582)	0.25	0.52
Derwent	North West	305(1)	1.58	1.84
Eden	North West	4,436(263)	0.25	0.60
Lyne, Esk	North West	1341(83)	0.25	0.57

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.9 Estimated ABCs for iron in England and Wales from monitoring data collected between 1998 and 2008 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Tyne	North East	1,030(30)	1.02	1.19
Wear	North East	1,253(26)	1.40	1.70
Tees	North East	453(83)	1.04	1.25
Ouse, Humber	North East	10,658(839)	15.00	34.00
Trent	Midlands	19,403(4816)	15.00	15.00
Bure, Waveney	Anglian	1,898(555)	15.00	15.00
Gipping	Anglian	408(38)	1.20	1.25
Blackwater, Chelmer	Thames	530(46)	1.00	1.30
Medway, Stour	Southern	4,256(778)	15.00	15.00
Arun, Ouse, Cuckmere	Southern	1,849(162)	15.00	31.00
Piddle, Frome	South West	322(72)	15.00	15.00
Exe	South West	610(53)	15.00	32.00
Dart	South West	673(65)	15.00	30.00
Tamar	South West	732(57)	1.40	2.00
Fal	South West	1,450(157)	1.25	1.25
Camel	South West	1,798(388)	1.25	1.25
Torridge, Taw	South West	811(36)	30.00	40.00
Severn	South West	126(31)	15.00	15.00
Wye	Wales	2,713(115)	8.10	14.00
Usk	Wales	2,515(72)	13.00	19.00
Taff	Wales	3,934(37)	32.00	46.00
Tawe, Neath	Wales	3,077(85)	0.50	0.50
Loughor	Wales	1,929(65)	0.50	0.50
Tywi	Wales	4,331(153)	9.60	18.00
Cleddau	Wales	877(53)	1.50	19.00
Teifi	Wales	573(1)	42.00	52.00
Rheidol, Ystwyth	Wales	766(13)	0.50	0.50
Dovey	Wales	2,225(170)	5.00	9.00
Glaslyn	Wales	1,803(110)	10.00	14.00
Clwyd, Conwy	Wales	845(28)	0.50	0.50
Anglesey	Wales	590(8)	1.10	1.30
Dee	Wales	2,311(78)	15.00	34.00
Weaver	North West	338(23)	15.00	41.00
Mersey	North West	2,010(75)	36.00	59.00

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Douglas	North West	1,394(6)	1.90	2.30
Ribble	North West	1,963(87)	32.00	53.00
Lune	North West	142(3)	0.55	0.67
Duddon	North West	462(19)	34.00	53.00
Lyne, Esk	North West	139(8)	0.51	0.62

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.10 Estimated ABCs for manganese in England and Wales from monitoring data collected between 1998 and 2008 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Tyne	North East	313(0)	1.03	1.20
Wear	North East	526(45)	1.41	1.67
Ouse, Humber	North East	1,443(78)	5.00	15.00
Trent	Midlands	1,800(157)	5.00	11.00
Bure, Waveney	Anglian	384(59)	5.00	5.00
Medway, Stour	Southern	1,747(201)	5.00	5.00
Arun, Ouse, Cuckmere	Southern	698(10)	11.00	18.00
Fal	South West	877(49)	1.25	1.25
Torridge, Taw	South West	536(120)	5.00	5.00
Tone, Parret	South West	234(20)	5.00	10.00
Severn	Midlands	710(192)	5.00	5.00
Wye	Wales	1,321(104)	5.00	5.70
Usk	Wales	866(44)	7.40	13.00
Taff	Wales	1,132(35)	5.00	11.00
Tawe, Neath	Wales	1,683(43)	0.50	0.50
Loughor	Wales	712(4)	0.50	0.50
Tywi	Wales	3,952(271)	3.00	5.00
Angelsey	Wales	206(2)	1.15	1.36
Cleddau	Wales	680(93)	1.50	4.00
Teifi	Wales	403(26)	9.80	15.70
Rheidol, Ystwyth	Wales	490(52)	0.50	0.50
Dovey	Wales	1,722(185)	4.60	5.50
Glaslyn	Wales	1,260(157)	4.50	5.00
Clwyd, Conwy	Wales	558(96)	0.50	0.50
Dee	Wales	1,407(145)	5.00	5.00
Mersey	North West	1,002(4)	28.70	41.80
Douglas	North West	214(1)	1.80	2.30
Ribble	North West	507(111)	5.00	5.00
Lyne, Esk	North West	139(39)	0.52	0.65

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

**Table 4.11 Estimated ABCs for zinc in England and Wales from monitoring data collected between 1998 and 2008 ( $\mu\text{g}\cdot\text{l}^{-1}$ )**

Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Tyne	North East	689(1)	1.10	1.30
Wear	North East	927(78)	1.50	1.70
Tees	North East	419(124)	1.10	1.30
Ouse, Humber	North East	6,885(759)	2.50	2.50
Trent	Midlands	8,716(661)	2.50	5.80
Great Ouse	Anglian	4,217(673)	2.50	2.50



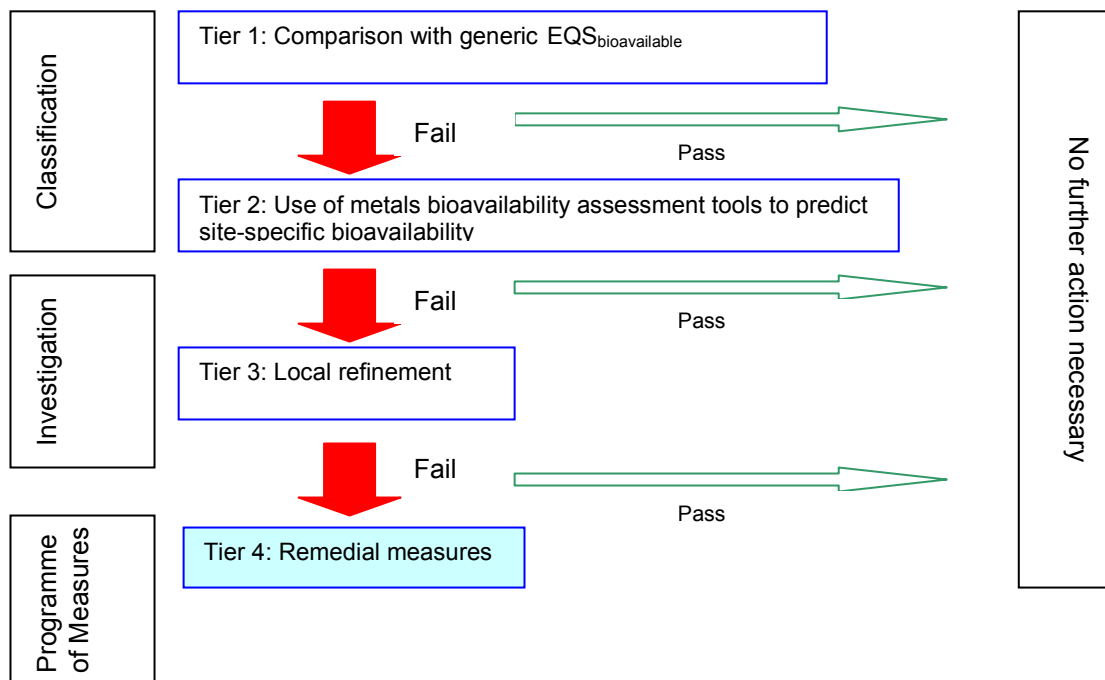
Hydrometric area	Region	Number of data <sup>1</sup>	5th Percentile	10th Percentile
Lee	Thames	1,135(152)	1.25	1.25
Thames	Thames	8,686(1981)	2.50	2.50
Avon	South West	331(73)	2.50	2.50
Piddle, Frome	South West	251(39)	2.50	4.80
Tamar	South West	612(56)	1.90	2.50
Fal	South West	1197(16)	1.25	1.25
Camel	South West	976(33)	1.25	1.25
Torridge, Taw	South West	758(216)	2.00	2.50
Tone, Parrett	South West	308(70)	2.50	2.50
Frome, Bristol, Avon	South West	556(125)	2.50	2.50
Severn	South West	155(3)	13.40	15.00
Severn	Midlands	10,459(1878)	2.50	2.50
Wye	Wales	1,365(149)	2.10	2.50
Usk	Wales	501(59)	3.40	5.00
Taff	Wales	1,693(171)	2.50	2.50
Tawe, Neath	Wales	903(71)	0.50	0.50
Loughor	Wales	511(16)	0.50	0.50
Tywi	Wales	3,901(260)	2.50	3.00
Cleddau	Wales	449(72)	1.50	2.70
Teifi	Wales	585(24)	4.10	5.20
Angelsey	Wales	413(9)	1.20	1.40
Dovey	Wales	1,755(75)	3.70	5.00
Glaslyn	Wales	1,414(109)	2.80	4.10
Clwyd, Conwy	Wales	575(91)	0.50	0.50
Dee	Wales	1,431(95)	2.50	3.30
Weaver	North West	402(73)	2.50	2.50
Mersey	North West	2,178(237)	2.50	2.50
Ribble	North West	1,120(180)	2.50	2.50

<sup>1</sup> The number of values given as <LOD is shown in parenthesis.

# 5 The use of ambient background concentrations

## 5.1 Ambient background concentrations within a compliance framework

A tiered approach towards compliance assessment for metals has been proposed (Environment Agency, 2009) and refined (Figure 5.1), in which metals bioavailability assessment tools may be applied. Such an approach may also be considered for metals where no correction for bioavailability is possible. In such cases the compliance assessment would be made at Tier 1, and Tier 2 would not apply. Failure of the quality standard would then potentially trigger an investigation of the background concentrations relevant to the assessment site.



**Figure 5.1 Tiered approach to compliance assessment**

The ABCs derived within this report are relatively conservative. These estimates may be used as part of the above tiered approach. Because the ABCs have been derived over a relatively large area, there may be localised water bodies for which higher ABCs would be appropriate. This might be anticipated in water bodies where mining activities have been undertaken in the past, or where there are high metal concentrations owing to the local geology.

In cases where the PNECs from which the quality standards were derived are based on the results of tests conducted with minimal background concentrations of the metal of interest, it may be appropriate to treat the PNEC as a  $PNEC_{add}$  (that is, a PNEC to which a background concentration should be added). Where there is an appreciable

background concentration of the metal of interest in the culture and control medium of the test waters, it will be necessary to calculate the  $PNEC_{add}$  by correcting the toxicity report data for their background concentrations. It will also be necessary to consider the relative levels of the PNEC and the background concentration in the culture and control media, to assess whether or not the levels may be considered as appreciable (ICMM, 2007). For example, background concentrations of less than 10 per cent of the PNEC might be considered sufficiently low for the PNEC not to require further correction for conversion into a  $PNEC_{add}$ .

Where conservative estimates of the relevant ABCs are available they may be applied at the first tier of the assessment, by addition to the  $PNEC_{add}$ . It is unlikely that any water bodies will require a specific ABC that is lower than the generic ABC derived for the whole hydrometric area, as in this case a very low percentile of the dataset has been used.

In some cases, where the majority of metals monitoring is undertaken at locations that are likely to experience problems (that is, the likelihood of failure prompted the monitoring in the first place), the ABCs estimated in this report could be biased towards values that are higher than the true values. This may be a relatively common factor in regulatory datasets, although it is generally difficult to test whether or not this is the case because of a lack of other comparable datasets.

If sites fail the assessment at Tier 3, then it may be appropriate to undertake more detailed local investigations of the ABC for the water body in question, especially if the local geology indicates potentially elevated background concentrations (for example, evidence of historic mining activities may be considered as an indicator of metal rich geology). An alternative approach toward the derivation of ABCs may be undertaken where they are derived on a more localised scale than at the hydrometric area level. The refined ABCs would then be applied in future compliance assessments.

## 5.2 Action when there is no ambient background concentration

Initially, it may be reasonable to undertake an assessment in accordance with the tiered approach outlined in Section 5.1 without taking account of background concentrations. If the compliance assessment does not result in a conclusion of potential risk, there will be no requirement for further action. Only where the definitive compliance assessment results in a conclusion of potential risk (failure of the quality standard) will further action be needed. For water bodies lying within hydrometric areas for which it has not been possible to derive a background concentration, further work may be required to characterise the ABC relevant to the hydrometric area and/or the water body in question, as a first stage of risk management. The outcome of investigations into relevant ABCs for particular water bodies or hydrometric areas would then provide an input of the ABC that should be applied in future compliance assessments. In some cases, such local consideration of ABCs may not be considered important, owing to the magnitude of the risk characterisation ratio.

An alternative approach may be to derive a generic hydrometric area ABC for each metal, based on national or UK data, and apply this where data are insufficient. This generic ABC may be derived as an average of the calculated ABCs, such as the mean, the geometric mean, or the median.

Where it has not been possible to derive an ABC for a hydrometric area, consideration may be given to reading across ABCs from adjacent hydrometric areas, especially where there are similarities between the local geology and land cover. Grouping of data

from several adjacent hydrometric areas to combine data would be expected to produce similar results.

# 6 Conclusions and recommendations

## 6.1 Conclusions

ABCs have been derived on a hydrometric area basis for between 1 and 45 out of 111 hydrometric areas in the UK for arsenic, copper, iron, manganese, nickel, and zinc. It has not been possible to derive an ABC for each of the hydrometric areas because of lack of data or because a large proportion of the reported concentrations were below the LOD. Where the available monitoring data were judged to be adequate, ABCs were derived as either the 5th or the 10th percentile of the data.

There are a number of difficulties to be overcome in deriving ABCs on the basis of current regulatory monitoring data in the UK:

- Analytical methods (such as total or dissolved metal), LODs and reporting limits are appropriate to the requirements of the current statutory EQS and not necessarily to those of revised EQS under the WFD.
- Monitoring tends to be focused towards areas of greater anticipated exposure.
- ABCs must be derived as a low percentile of the dataset, to avoid significant influences from local emissions, which might make them over-precautionary.
- A significant proportion of the data are reported as less-than values.
- Some hydrometric areas have inadequate data for derivation of ABCs.
- In some cases, both the 5th and 10th percentiles are reported as 0.5 times the LOD owing to the treatment of data reported as less-than values.

Reading across ABCs from adjacent hydrometric areas or, alternatively, pooling data from several adjacent hydrometric areas, may allow provisional ABCs to be derived for those hydrometric areas where no derivation has been possible in the present study.

Employing the derived ABCs within a tiered risk assessment approach (see Section 5.1) will allow any further efforts to refine ABCs, either at the hydrometric area or water body scale, to be targeted according to the level of identified risk. If a location for which an uncertain ABC has been derived is not considered to be at risk, then it would not be necessary to consider the reliability of the ABC further, provided that there is confidence that it is not too large (which would result in an unprotective risk characterisation).

For the assessment of an EQS based on a  $PNEC_{add}$ , a more conservative approach in the absence of a reliable ABC for a water body or hydrometric area would be to undertake an initial compliance assessment without taking account of the background concentration (or assuming a zero background concentration). Only in cases where risks are identified would it be necessary to consider the relevant ABC in more detail. It is likely that the background concentrations will only influence the risk characterisation where the identified risks are marginal.

## 6.2 Recommendations

We consider that the ABCs derived within this report are appropriate for application within a tiered approach towards compliance assessment (see Section 5.1). The derived ABCs are relatively conservative values. This means that they are unlikely to overestimate the relevant ABC greatly for any individual water body. However, it also means that, in some localised areas, higher background concentrations may be applicable.

Furthermore, if backgrounds are applied to the bioavailable PNEC, as is likely with zinc, then they need also to be bioavailability-corrected. In other words, it is necessary to make the assumption either that the background has the same bioavailability as the added value, or that it is not bioavailable, and not correctable, and needs to be applied separately from bioavailability corrections to the total dissolved concentrations.

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# List of abbreviations

ABC	ambient background concentration
ARA	added risk approach
DOC	dissolved organic carbon
EQS	environmental quality standard
EU	European Union
$K$	partition coefficient
LOD	limit of detection
PEC	predicted environmental concentration
$PNEC_{add}$	predicted no-effect
TOC	total organic carbon
UK	United Kingdom
WFD	Water Framework Directive
Zn	zinc