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# Determination of Metal Background Reference Concentrations: Feasibility Study

Science Report – SC050063

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SCHO0408BNZB-E-P

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**Author(s):**
Dr E. Louise Ander, Dr Susan Casper

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**Research Contractor:**
British Geological Survey
Kingsley Dunham Centre,
Keyworth, Nottingham.
NG12 5GG

**Environment Agency's Project Manager:**
Dr Susan Casper, Science Department,

**Steering Group:**
John Batty (EA), Bruce Brown (EA), Alwyn Hart (EA), Chris Johnson (BGS), Ben Klinck (BGS), Graham Merrington (EA), Adam Peters (SEPA), Hugh Potter (EA), Catherine Tomlin (EA)

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# Science at the Environment Agency

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Steve Killeen

Steve Killeen

**Head of Science**

# Executive summary

New water quality standards proposed by the EU Water Framework Directive (WFD) for metals that are 'specific or other polluting' substances form the background to this project, whose purposes are two-fold: to compare natural concentrations of metals in UK waters with the proposed standards; and to establish what this entails for the 'added risk' approach to water quality assessment advocated by the WFD. This report then makes a series of recommendations based on the consequences of applying these standards to the UK regulatory regime.

The 'added risk' approach allows that ecosystems may be adapted or acclimatised to certain concentrations of metals in surface waters as a result of their natural abundance, and that these background concentrations can therefore be taken into account when setting water quality standards. The assumption is that background concentrations do not adversely affect the ecology; or for example, the ecology of a particular site is different to that expected (the 'norm' or 'reference condition') because organisms have been exposed to long-term, naturally high (or low) metal concentrations. This project was a feasibility study to examine whether it would be possible to determine relevant metal background reference concentrations (MBRCs) for application with the added risk approach, and to set out the options and frameworks for doing so.

The study compared natural background concentrations of nine metals (aluminium, arsenic, chromium, copper, iron, manganese, nickel, lead, zinc) in stream water in England and Wales with the proposed WFD standards. We found a range of natural background concentrations for these metals, highlighting the difficulty of using a single value for a background concentration.

Analysis of the large dataset of stream water metal concentrations held by the British Geological Survey (BGS) (G-BASE project) showed that, for some metals, there would be widespread failure to meet the proposed WFD standards. In terms of the magnitude of failure for the different metals studied, we determined that there would be:

- more than 75 percent failure for iron, arsenic and manganese;
- more than 20 percent failure for aluminium, zinc and nickel (depending on the value of the standard used);
- less than five percent failure for copper, chromium and lead.

The data suggest that the proposed standards for iron, manganese and arsenic might be over-protective, and could be expected to generate additional work arising from compliance failure simply because of high natural background concentrations. However, existing standards for iron and arsenic are probably not protective enough, as they are rarely exceeded by natural background concentrations.

Our study has therefore demonstrated the value of using the 'added risk' approach, where applying a background concentration appropriate to the local environment could prevent large-scale failure in meeting a standard, simply because natural background concentrations of the metals were high.

Our recommendations for the use of the added risk approach are summarised as:

Chromium and Lead – added risk approach is not required.

Copper – use of added risk with a single MBRC value (Cu MBRC = 1.6 µg/l).

Aluminium, arsenic, iron, manganese, nickel and zinc – use of added risk with derived MBRC.

MBRCs have been generated at a national scale, at a river basin district scale, and based on WFD typology (characterised for all catchments under the WFD) as ‘default’ options for application (and are included in this report), but can also be established at increasingly local scales where data is available to generate statistically robust values. We have also developed a decision framework for deriving an appropriate MBRC value for use in the added risk approach depending on the requirements for a particular metal, relevance of MBRC values to the local environment, and available data.

During the course of this project, there have been a number of alterations to the numerical values of the proposed standards, and not all of the proposed standards have yet been formally accepted, so there may well also be further future changes. As a result, we have aimed to present the data in this report in such a way that it will remain useful in providing an indication of the probable extent of failures, and need for the added risk approach for specific metals, should the standards be amended again.

This study also looked at the relationship between stream water metal concentrations and geological units, stream water pH, conductivity and organic carbon concentrations to help explain regions with high background concentrations. Such relationships can help to understand where failure to meet a given standard might be attributable to prevailing natural conditions, and could indicate where a locally derived MBRC might be more appropriate. This approach could also be used as part of a further assessment in response to compliance failure.

A comparison of BGS G-BASE data in England and Wales with data recently released for Northern Ireland was also carried out. Although the highly contrasting geological and geographical environments of the two regions made direct comparison difficult, it offered a valuable means of comparing, for example, MBRCs generated for WFD typologies. For default (national-scale) MBRCs, aluminium, iron, and manganese levels were generally higher in Northern Ireland. For trace elements (arsenic, copper, nickel, lead and zinc but not chromium), MBRCs were typically slightly higher in England and Wales, although generally more consistent between the two sets.

The findings of this study demonstrate that it is possible to select MBRCs where there are data poor catchments, though it must be accepted that there is little substitute for ‘real’ data. The BGS baseline sampling programme is scheduled for completion in the south of England, and at the moment there are no plans to revisit sites already sampled for stream sediment in order to collect stream water. This particularly affects the north of England and Scotland, and to a lesser extent Wales and the west of England where ICP-MS analysis is not available. The paucity of data may affect future similar work.

The results of this project provide a strong case for amending proposed WFD standards for arsenic, iron, and manganese, and for implementing a compliance regime that will allow background concentrations of metals to be taken into account. Without these, there is a substantial risk of widespread failure to meet some standards, in some cases simply because of natural background levels. It is also unlikely to be cost-effective or even appropriate to try to reduce metal concentrations in water bodies failing WFD standards, where a substantial part of the metal comes from a natural rather than anthropogenic source.

# Acknowledgements

The authors would like to thank all members of the steering board for their contributions and advice, and John Batty and Graham Merrington in particular for their patience with our requests for further information. In addition, we would like to thank Dr Mark Cave and Dr Simon Chenery (BGS) for their advice with the statistical analysis of data.

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# 1 Introduction

As part of the implementation of the Water Framework Directive (WFD), UK TAG (the UK's Technical Advisory Group on the Water Framework Directive) has been developing new or revised water quality standards for both Priority Substances (Annex X) and Specific Pollutants (Annex VIII), which will eventually replace existing Environmental Quality Standards (EQSs) in the Dangerous Substances Directive. This work is being completed in phases, and has to date focussed on the development of Predicted No-Effect Concentration (PNEC) thresholds, which after further consultation, and consideration of how the standards could be implemented in practice, may be adopted as final EQSs for the WFD.

Part of the process in developing such standards for the WFD considers whether there are likely to be naturally occurring background concentrations of the substance in question to which biota may be acclimatised, and whether this needs to be taken into account when applying the standard. Discounting background levels as part of applying the standard is called the Added Risk Approach (ARA), whilst applying the standard without discounting the background is called the Total Risk Approach.

This report looks at nine metals for which UKTAG has developed new proposed standards for surface waters for the WFD, and examines the feasibility of determining background concentrations for these metals in order to apply the added risk approach. As a feasibility study, it will look at options for the development and use of background concentrations for these metals, will examine the implications of data availability, and will make recommendations as far as possible within its scope, but it cannot make any final decisions on implementation, and does not claim to be fully comprehensive. In other words, depending on the choice of options or routes preferred, more work may be required to develop fully the background concentrations required for implementation – for example if these are to be geographically or geologically specific.

## 1.1 Metal Background Reference Concentrations (MBRCs)

It is widely recognised in the environmental science community that the variability of any naturally occurring substance can be substantial. This tends to be particularly true in the case of the variation in metal concentrations in surface waters across the UK, because of the underlying substantial variation in bedrock geology from which they may be derived. These naturally occurring concentrations are referred to as the 'background', irrespective of their actual concentrations. Unfortunately, this variation means that the definition of a single value for the metal background concentration, that could be applied for example in the added risk approach, may be extremely difficult, and potentially scientifically invalid. In this report we have attempted to highlight cases where we consider use of a single value MBRC may be justified, and options for the development of more specific MBRCs (e.g. restricted by WFD typology, geology, or geography) that could be used more robustly within the added risk approach, or in highlighting reasons for compliance failures.

The literature reveals some interchangeable use of the terms 'background' and 'baseline', to mean alternatively 'ambient concentration' and 'concentration indicative of low anthropogenic impact'. As this project supports the WFD *Priority and Other Specific Polluting Substances* (POSPS) programme, this report uses the Analysis and Monitoring of Priority Substances (AMPS) Working Group's definition of background concentration:

> *"The background concentration of target metals in the aquatic ecosystems of a river basin, river sub-basin, or river basin management area, is that concentration in the present or past corresponding to very low anthropogenic pressure."*

In practical terms, for the UK this effectively defines background concentrations for metals as ambient concentrations at sites of low anthropogenic impact, which in most cases will be low order streams (excluding areas where headwater streams may be impacted by mining activity – see section 4.1). It is rare to find large river courses which have not been the site of human settlement and associated industrial activities for many hundreds, if not thousands, of years, so this effectively precludes their inclusion from an assessment of un-impacted sites.

Much of the river water quality data held by the Environment Agency reflects the role of the Agency in implementing pollution control measures, and monitoring sites are often at locations likely to be impacted by anthropogenic activities. For this reason the primary data source used in this project is the British Geological Survey (BGS) G-BASE data which is systematically acquired from low order streams, spatially distributed throughout the catchment. However, further detailed examination of Environment Agency data may prove useful in areas where overall data availability is low, or for 'ground-truthing' exercises.

The project aims to:

- Develop generic or 'default' metal background reference concentrations (MBRCs) for nine metals based on the most suitable available data, and look at options for developing more specific MBRCs that could be used within a compliance regime.
- Examine the probability of water bodies failing to meet the proposed standards as a result of natural background concentrations, and the reduction in such failures that could be expected from applying the added risk approach.
- Suggest a possible tiered approach which could be applied in the event of water quality failures to establish (using a weight-of-evidence approach) whether the failure is likely to be due to natural rather than anthropogenic sources of metal concentrations.

We have attempted to present data in a way that maintains its usefulness beyond the lifetime of the project, and in the event of any changes in the standards proposed; and to illustrate a method of dealing with compliance in a way that is transparent and defensible in both data rich and data poor areas.

Nine metals of interest were included in this study, namely three minor elements and six trace elements. The minor elements (with natural environmental concentrations typically in the range 10 to 5,000 µg/l) were aluminium (Al), iron (Fe) and manganese (Mn). The trace elements (with environmental concentrations generally below 50 µg/l) were arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). (For the sake of brevity, in this report arsenic is included in the catchall term of 'metals', although it is actually a metalloid).

As the project was initiated by the Environment Agency, a large part of the work focused on England and Wales, although there was some consideration of the applicability of the work to Northern Ireland and Scotland.

## 1.2 Existing and proposed standards

Existing regulatory standards are shown in Table 1.1 alongside the proposed new WFD standards. The proposed standards used in this report were correct at the time of writing, but some are still under review and have not been finalised. A summary of the latest available proposed standards for copper, nickel and lead, and their relationship to the data, are presented in Appendix 3[1], in keeping with the presentation methods used elsewhere in this report. It should be noted that where the change in standard is large in comparison to the natural abundance of the metal, the requirement to use the ARA may be reconsidered.

Table 1.1 gives the proposed long-term and short-term standards. The long-term standards offer the most sensible comparison with background concentrations (reflecting long-term protection of the ecosystem, rather than any short-term additional acceptable input), and these values were used in this report.

**Table 1.1: Existing and proposed standards for the nine metals of interest[2].**

| Metal | Existing standard[#](µg/l) | Proposed standard[##](µg/l) | |
|---|---|---|---|
| | | Long-term | Short-term |
| Aluminium (Al) | 1,000 | 25 | n/a |
| Iron (Fe) | 1,000 (AA) | 16 | 41 |
| Manganese (Mn) | 30 (AA) - 300 (MAC) | 7 | 24 |
| Arsenic (As) | 50 (AA) | 0.5 | 8.0 |
| Chromium (Cr) | 5 - 50* | Cr(III): 4.7 | 32 |
| | | Cr(VI): 3.4 (SSD) | |
| | | Cr(VI): 0.47(det) | 2.0 |
| Copper (Cu) | 1 - 28 | 8.2 | n/a |
| Nickel (Ni) | 50 - 200* | 4.9 - 35.6[++] | n/a |
| Lead (Pb) | 4 - 20* | 6 | n/a |
| Zinc (Zn) | 8 - 125* | 7.8 (SSD) | |
| | | 1.7 (det) | 3.2 |

[#] Existing standards are statutory EQS for List II substances, with the exception of aluminium and manganese, which are Environment Agency non-statutory standards. Ranges denote that the existing standard used for compliance assessment is dependent on other factors such as water hardness. AA = annual average; MAC = maximum acceptable concentration.

* The standards used here are the EQS List II salmonid standards, as most protective of the freshwater environment. These are the standards used for comparison with proposed standards in Figure 3.4. The equivalent cyprinid standards are Cr, 150-250 µg/l; Ni, 50-250 µg/l; Pb, 50-250 µg/l; and Zn, 75-500 µg/l. For copper, the salmonid and cyprinid standards are identical.

[##] For chromium and zinc, different standards have been proposed depending on their determination by species sensitivity distribution (SSD) or deterministic (det) methods. Both have been included here for completeness, but current opinion is that the SSD standard will be implemented, so it is this value that is used in the remainder of the report.

[++] The nickel standard is given as a range, the precise standard being dependent on a range of factors (not available at the time of writing).

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[1] This Appendix is apparently out of sequence because it was a very last minute addition to the report as a result of very recent proposals for new alternative standards. As a result it was not justifiable to re-order the sequence and change all other following table and figure numbers.

[2] The proposed standards have changed several times during this project. Those in Table 1.1 represent the latest information available at the time the majority of the project work was undertaken. For further information and updates, see Appendix 3.

# 2 Data resources

## 2.1 Spatial data availability

The river basin districts (RBDs) of England and Wales are shown in Figure 2.1. These are the primary reporting units of the WFD, and thus were used as the initial basis for all subdivision of datasets in this report. Catchment polygon files at the sub-RBD level were not available for this project as a national dataset, because of difficulties with licensing. Thus, where catchment-scale data were used, these were derived within the project. National-scale data could be applied to the approaches described following resolution of licensing issues.

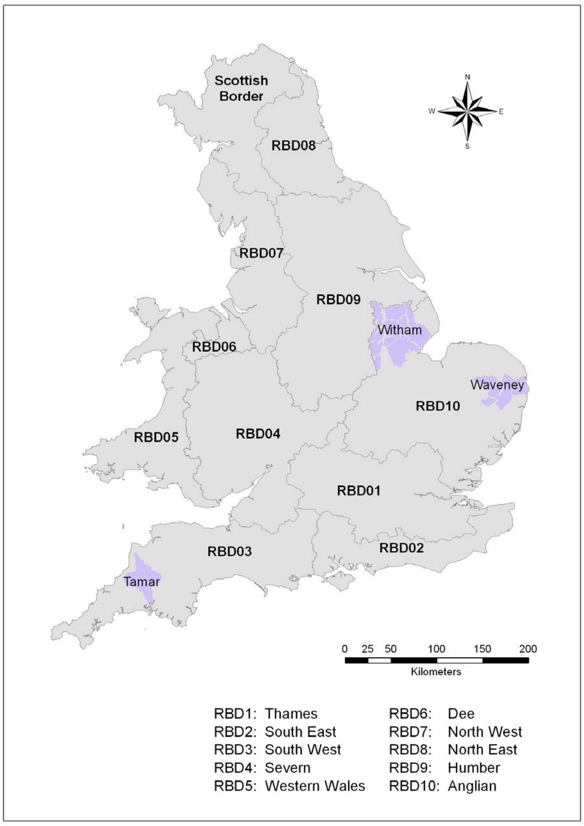


**Figure 2.1: Water Framework Directive River Basin Districts in England and Wales.** Catchments used in Section 5.2 are shown for the Tamar, Witham and Waveney.

Another national dataset fundamental to RBD reporting is that of geological typologies, of which there are four classes: siliceous, calcareous, salt and peat. The distribution of these, in relation to the RBDs, is shown in Figure 2.2. These categories are greatly simplified from British Geological Survey (BGS) mapping of the bedrock and superficial (glacial and post-glacial) geological formations. Where these formations are important in understanding sub-RBD and sub-geological typology variations in stream water chemistry, the extent of their outcrop is indicated in Figure 2.2. Some RBDs are dominated by one geological typology, such as the calcareous typology in RBD10. Salt and peat typologies are of limited spatial extent in England and Wales. Metalliferous mining areas were considered in this report as a source of potentially elevated stream water metal concentrations. The location of sample data within areas affected by metalliferous mining is shown in Figure 2.2. These data are also identified within a subset of the RBDs, and on a subset of geological typologies.

The BGS G-BASE (*Geochemical Baseline Survey of the Environment*) project has systematically collected geochemical data suitable for determining background concentrations of metals in stream waters; some background on the project is given in Section 2.2. In order to determine any large contrasts between background concentrations in catchments and those in higher order rivers, sampling data collected by the Environment Agency in Eastern England and BGS in the Tamar river catchment were also used. The location of these catchments is shown in Figure 2.1.

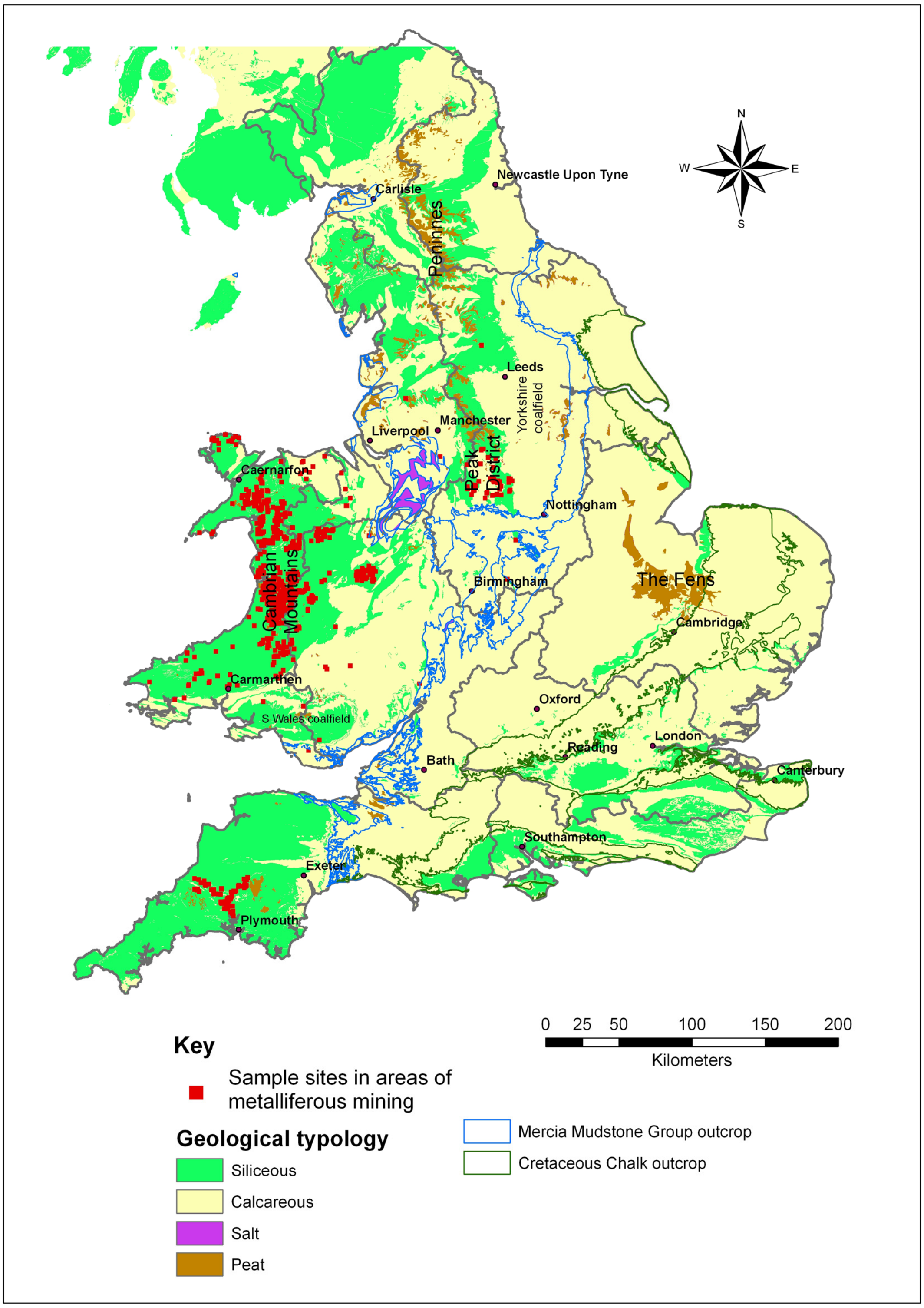


**Figure 2.2: Water Framework Directive geological typology in England and Wales (including known G-BASE samples sites which occur in metalliferous mining areas). Grey boundaries represent River Basin Districts (RBDs).**

## 2.2 The BGS G-BASE project

The G-BASE project is a UK-wide, systematic geochemical survey being undertaken by the BGS. Further information on the aims and methods of the project has recently been published (Fordyce et al., 2005; Johnson et al., 2005). The project was initially conceived as a mineral reconnaissance programme of research, sampling only stream sediments. However, as social values and analytical capabilities have evolved a greater range of sample media are now collected, including stream waters.

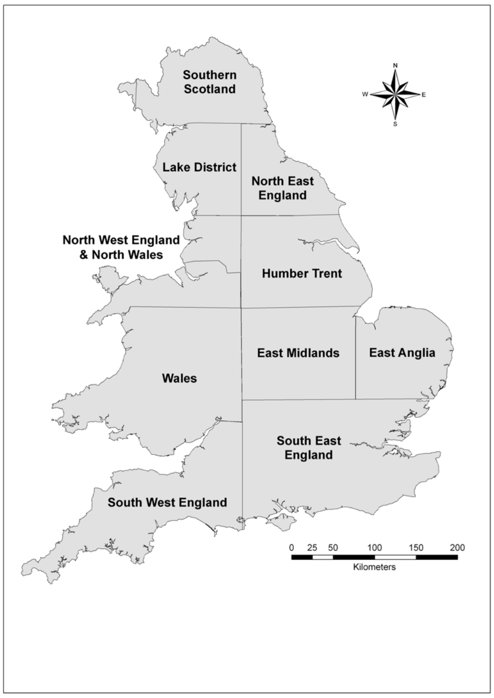


**Figure 2.3: G-BASE atlas areas in England and Wales.**

G-BASE collects stream channel samples (water and sediment) primarily from first and second order streams. The aim is to represent natural conditions in these sub-catchments as closely as possible. The resulting stream water data are thus suitable for establishing background values. The sampling strategy is to provide an average sampling density of one stream sample per 1.5 km$^2$. This density varies on a local scale, increasing in areas with a high density of small streams, and decreasing in areas where stream density is low. The consequence of this is that many upland areas have higher sample numbers, reflected in RBDs such as those including Welsh and Peak District mountains. Lower sample numbers are associated with RBDs with large areas of permeable geological formations, such as the Chalk; an example of this is RBD10 (Anglian). Urban areas are avoided in the sampling strategy, as they will be affected by anthropogenic activities.

Figure 2.3 shows the atlas areas of the G-BASE project within England and Wales. These are the administrative units of the project, which also frequently coincide with the implementation of improved analytical methods. Thus, whilst stream water pH, conductivity, bicarbonate and fluoride concentrations were measured from the start of the project, it was only possible to determine a wide range of analytes after 1989. This has resulted in variable coverage of different analytical techniques through England and Wales, shown in Figure 2.4. This figure represents a generalised summary which is correct for most elements; where variations in data availability occur, they are accurately reported in the inset map for each element in Figure 3.1(a-i).

In Wales and West England, samples have been analysed by inductively coupled plasma - atomic emission spectrometry (ICP-AES), and since 1994, by inductively coupled plasma - mass spectrometry (ICP-MS) as well. These techniques have generated a large suite of trace element data, with trace elements most accurately determined by ICP-MS. There are 24,000 samples with ICP-AES data and a subset of 10,000 samples with ICP-MS data. The improved (lower) detection limits of ICP-MS make this the preferable analytical method for the metals studied in this report (with the exception of iron and manganese), and ICP-MS data are thus used wherever available.

Figure 2.4 therefore shows the limitation of the G-BASE dataset for the purposes of this project, with incomplete coverage of England and Wales and of data generated by ICP-MS. Completeness of data also varies at the RBD level.

Publications fully describing the sampling, analysis and interpretation of data are available for all the northern atlases, although only Wales and Humber Trent include comprehensive analysis of stream waters (British Geological Survey, 1999; BGS *in prep.*). A report is also available on data from the Tamar (Devon/Cornwall) catchment (Rawlins *et al.*, 2003). Whilst data from East Midlands and East Anglia areas were used in this project, they are newly released and have not yet been published.

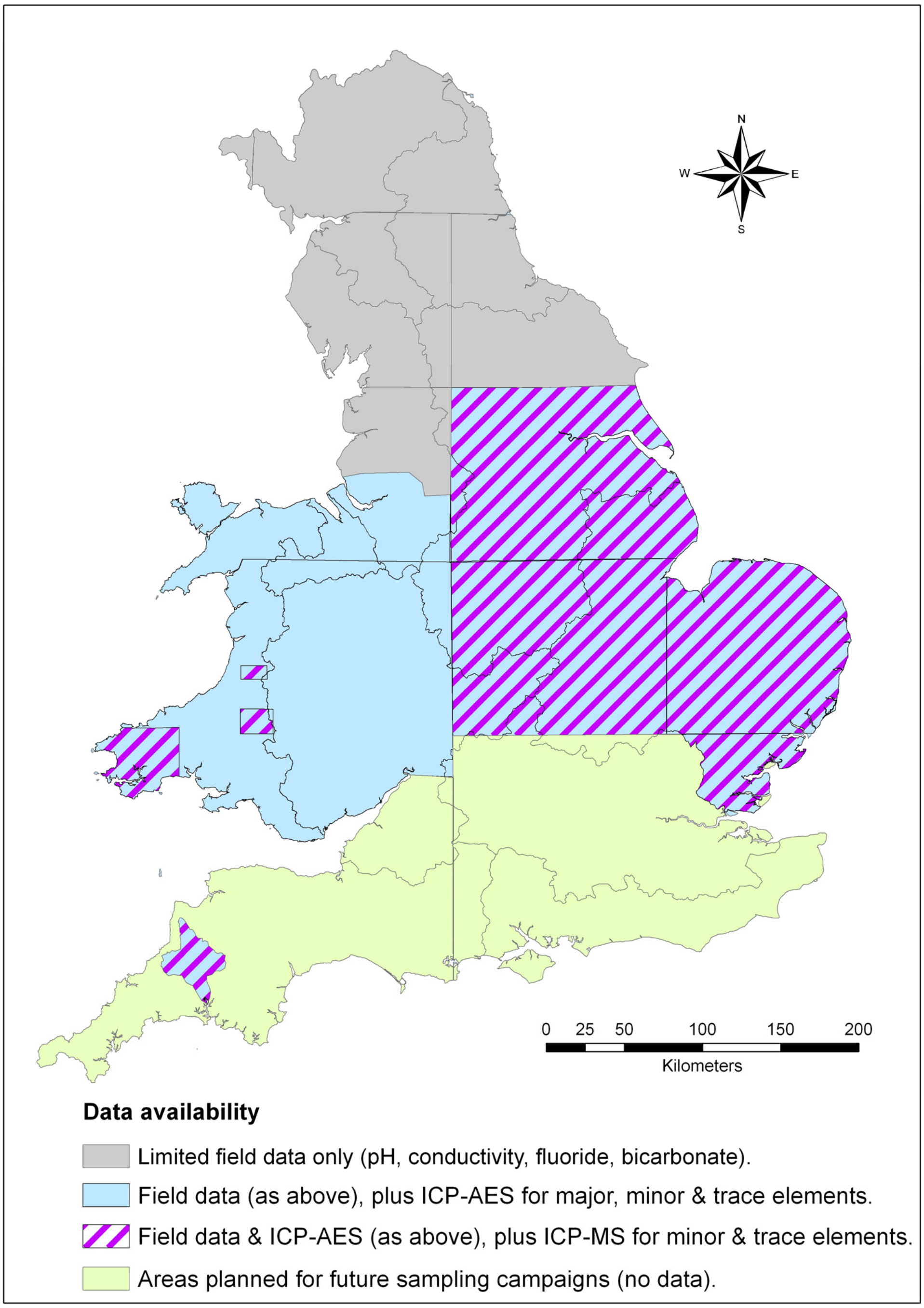


**Figure 2.4: G-BASE data availability summarised by G-BASE atlas area and Water Framework Directive river basin district (grey lines).**

# 3 Default MBRCs and assessment standards

## 3.1 Distribution of metal concentrations

### 3.1.1 Geochemical maps of metal concentration distributions

Maps of the concentrations of the nine metals of interest to this project are shown in Figure 3.1(a-i). These figures show how the metals vary in different regions where data are available. Maps are also included so that any later assessment of local areas where MBRCs might need to be set higher than default can be partly validated by these maps. Data are presented in a standard percentile format, which relates only to the values contained within that dataset and not to any external drivers, such as water quality standards. The use of percentiles also avoids assumptions about data distribution in the classification (for example, whether or not it is normally distributed).

Concentrations over the 75th percentile are shown in orange/red colours; those which fall between the 50th-75th percentile are in yellow, the 25th-50th percentile in green, and below the 25th percentile, in shades of blue. Where values are below the detection limit for more than five percent of the data, this limits the total number of classes that can be shown. In this case, this lowest class is represented by a different shade of blue (for example, compare Figure 3.1d (arsenic) with Figure 3.1e (chromium)) to highlight that this may encapsulate data occurring within several shades of blue/green in other geochemical maps.

Where ICP-AES and ICP-MS data are shown on the same map (aluminium, chromium, nickel, lead and zinc), ICP-AES measurements are associated with much higher detection limits. This means that large areas of data measured by this method are generally below the detection limit. However, these data are shown on the image to demonstrate where information is available, but are represented by a dark grey colour in order to distinguish them from the lower concentration data measured by ICP-MS. The rest of the ICP-AES dataset is plotted according to percentile values of the ICP-MS dataset, ensuring direct equivalence in the colours used across the surveyed area.

The mapped data (Figure 3.1a-i) also shows voids within the mapped areas, which are caused by one of two factors. Firstly, some regions have a natural paucity of stream networks caused by the permeable geological formations of that area. Examples of this are the western edge of the Chalk outcrop in East Anglia, North Lincolnshire/South Yorkshire, and the Carboniferous Limestone of the Peak District. The Chalk of East Anglia is covered by glacial till deposits across much of its outcrop away from the western edge; it is these clayey sediments which allow a higher density stream network to form than would otherwise be expected from the extent of the Chalk. Other areas with no data are associated with major urban centres such as Birmingham, Manchester, Liverpool, Nottingham and Sheffield; these areas are not sampled as part of the programme because they do not represent baseline hydrological conditions.

Mining areas are sampled as part of the regional programme, although spoil/adit drainage is avoided. The natural baseline concentration in these areas will be higher than in the unmineralised areas (this is the basis of mineral exploration using geochemistry), although past mining activities may have further increased the concentration of many of the metals studied. This project cannot determine specifically all sites likely to have related mining activity although some of the mineralised areas can be seen on some of the metal concentration maps (for example Figure 2.2 and Figure 3.1). However, the project has removed potentially affected sample sites from the data used by intersecting the BGS G-BASE data layer with the available BGS dataset on mine locations in order to reduce the influence of any such sites on the MBRC developed (Section 4). It should also be recognised that some of the chemical processes which lead to the increased concentrations of some metals in mined areas are entirely natural and may also occur in non-mineralised areas, for example increased concentrations of aluminium and iron at low pH values (Section 3.2). The influence of any local anomalies from mining sources is also diminished by using the median as the statistical measure of background, rather than the mean. The median is considered an appropriate measure of background concentration as it is not, for example, as conservative as the 10th percentile, but within the regulatory regime could be considered in general more protective than the 90th percentile of the background concentration (as a statistical population) where there is incomplete data coverage. In addition, the median is less likely to be influenced by outliers in the population, such as data points that are impacted by anthropogenic mining activity.

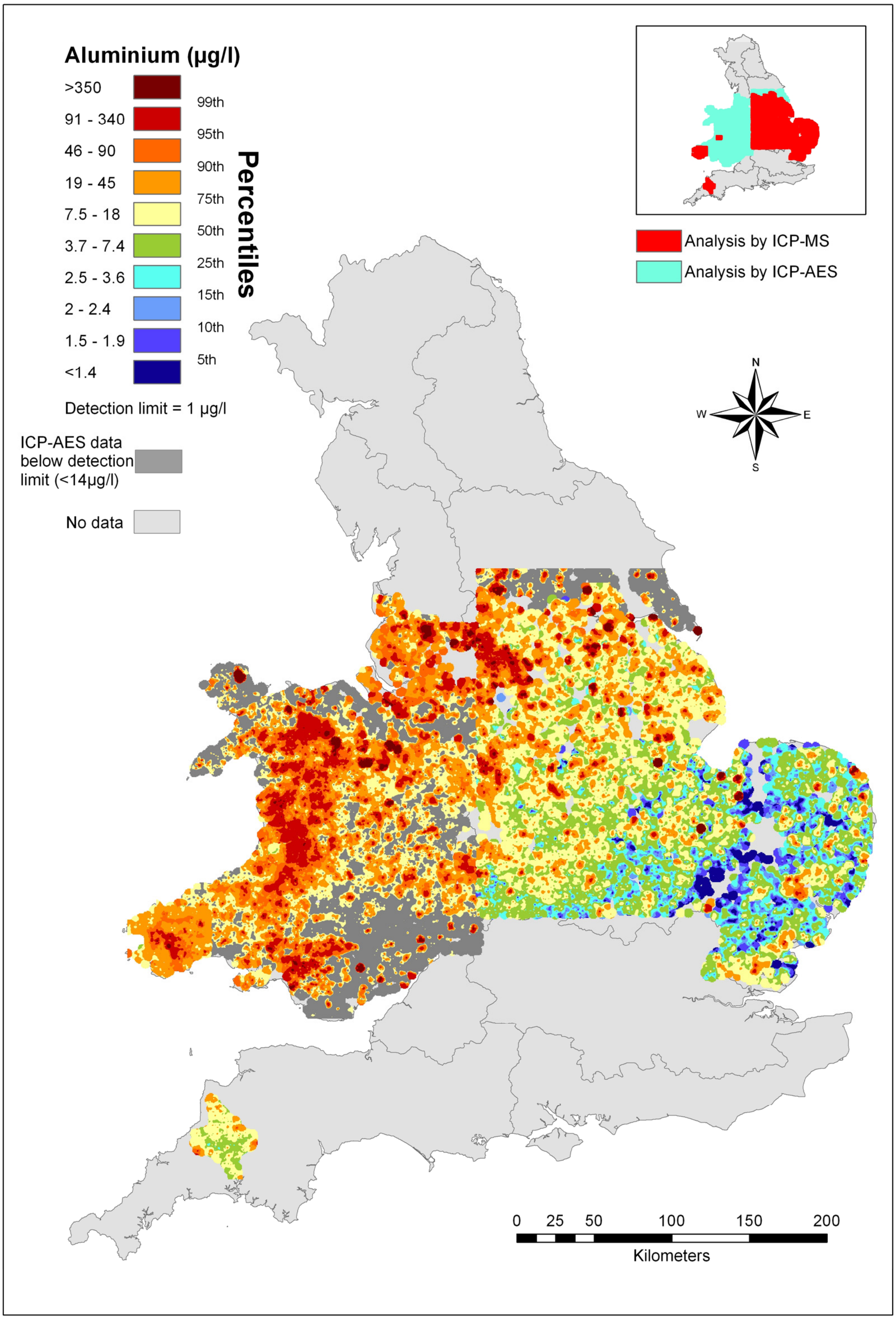


Figure 3.1a: Concentration of aluminium in stream waters (both ICP-AES and ICP-MS data shown).

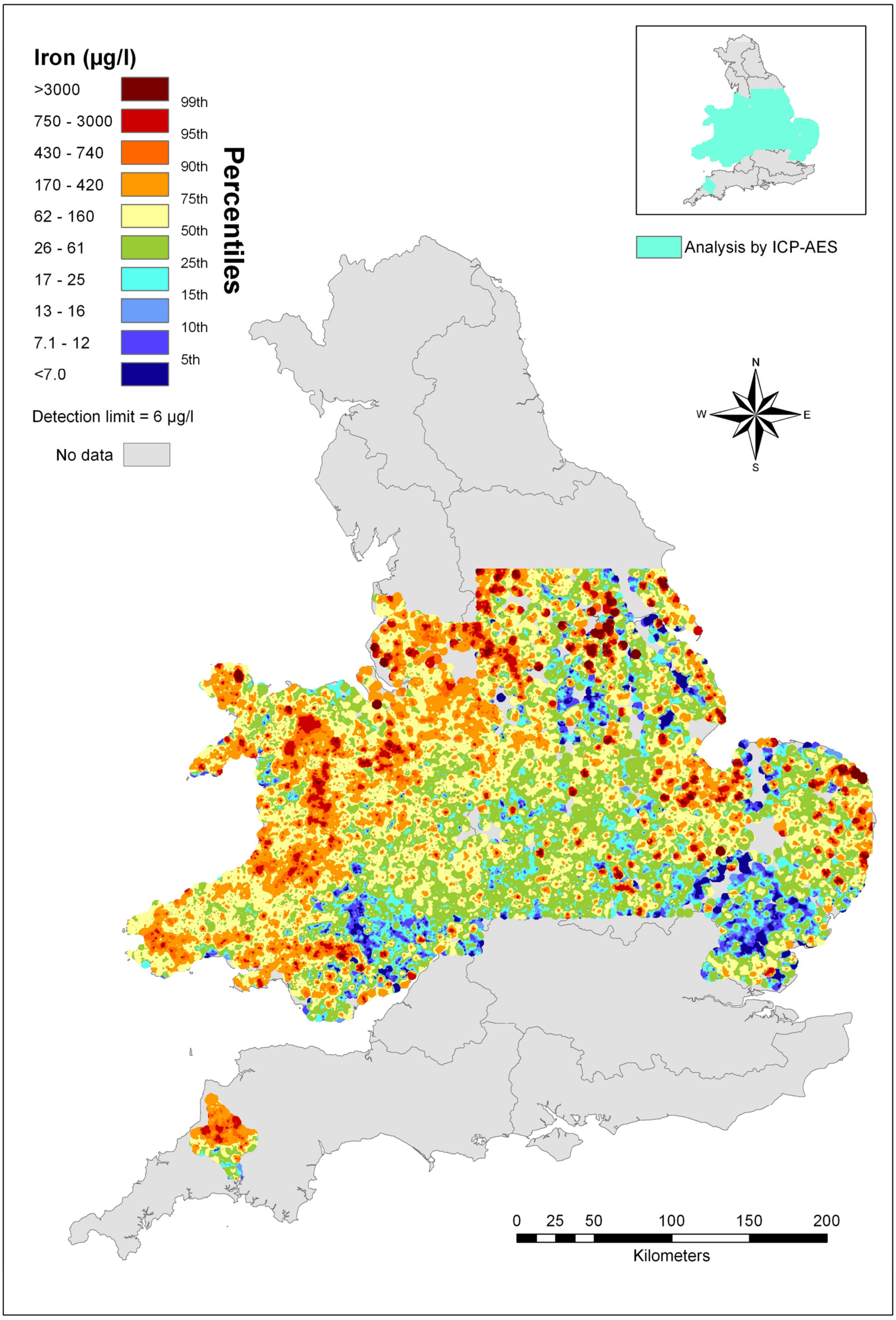


**Figure 3.1b: Concentration of iron in stream waters (ICP-AES data).**

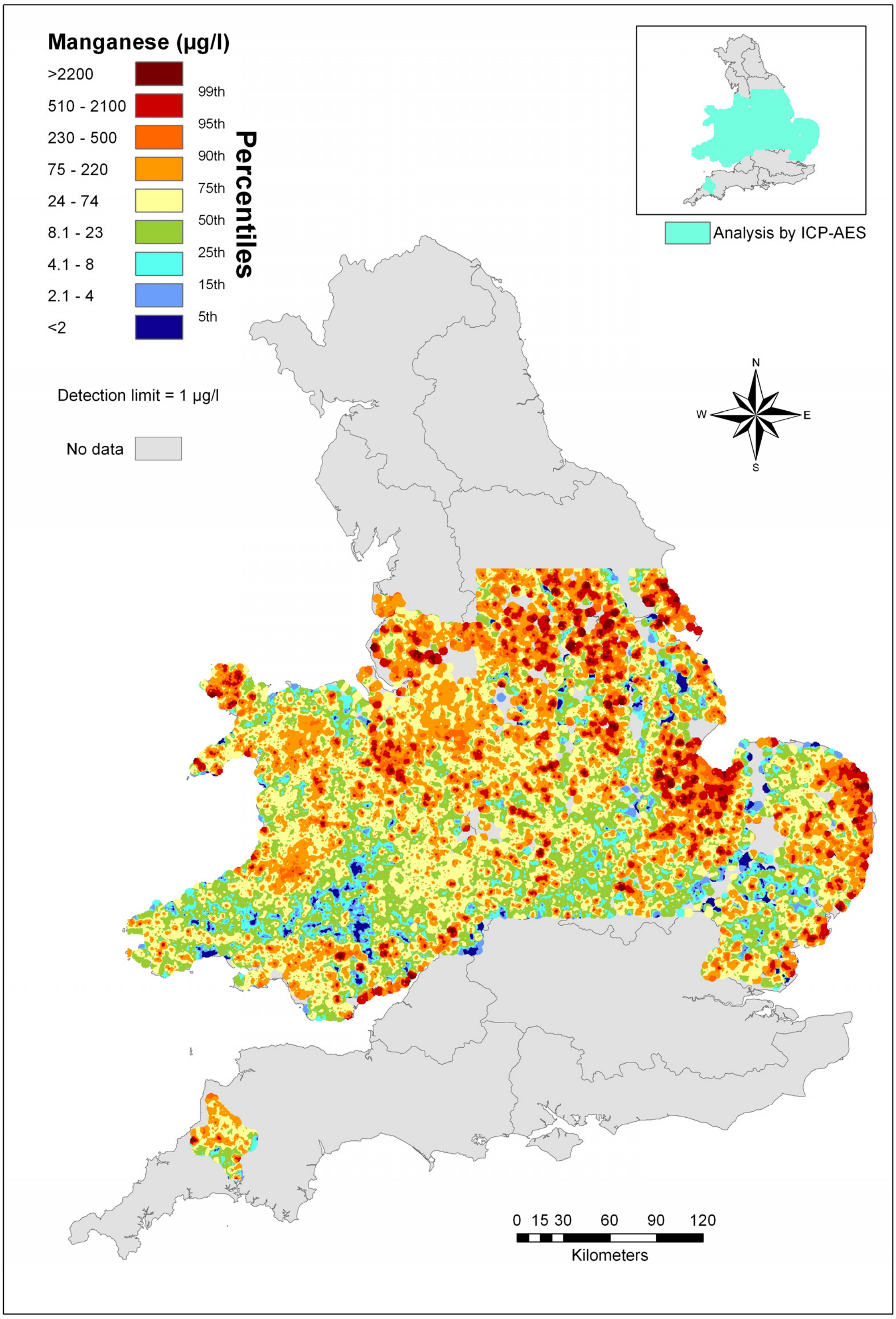


Figure 3.1c: Concentration of manganese in stream waters (ICP-AES data).

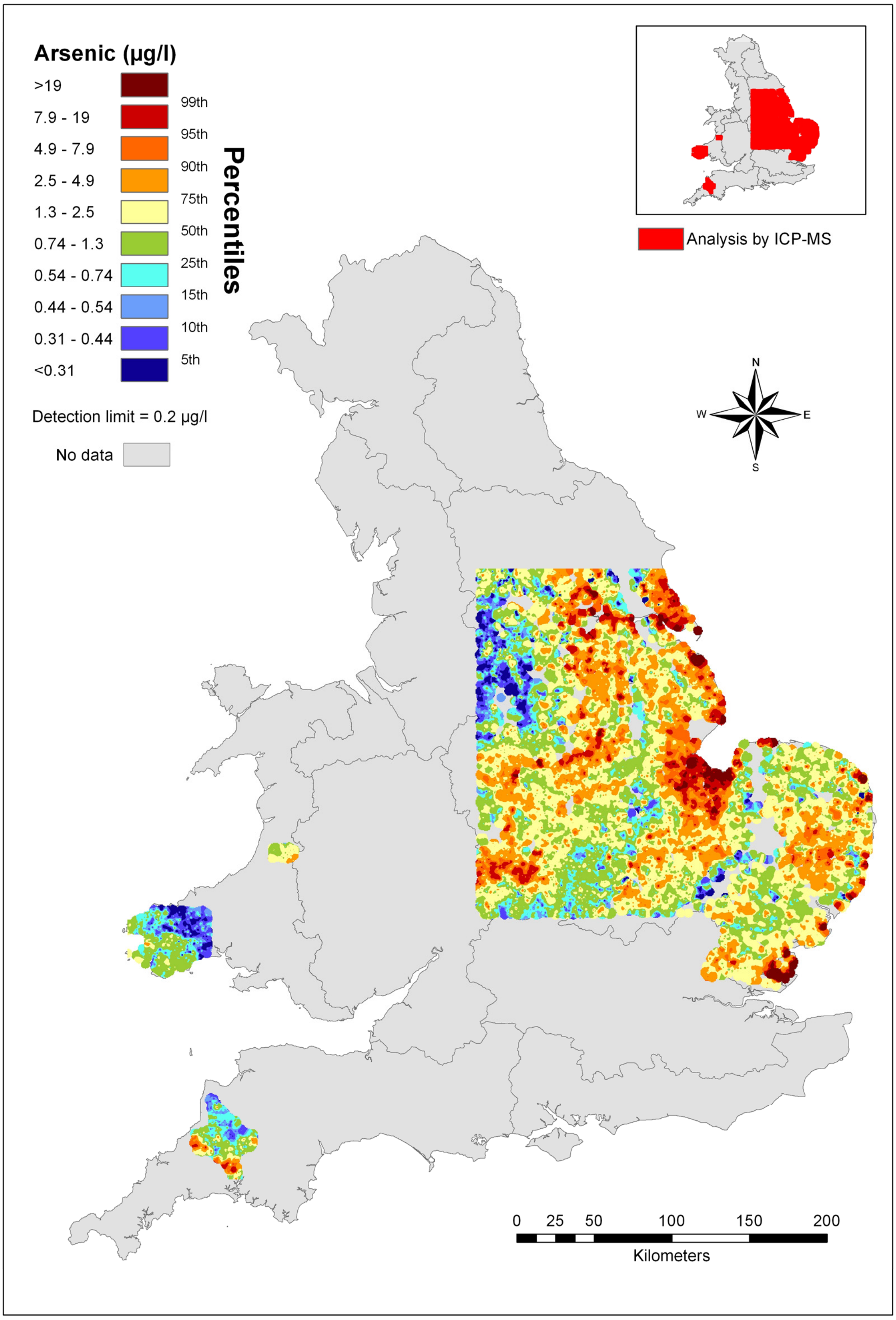


Figure 3.1d: Concentration of arsenic in stream waters (ICP-MS data).

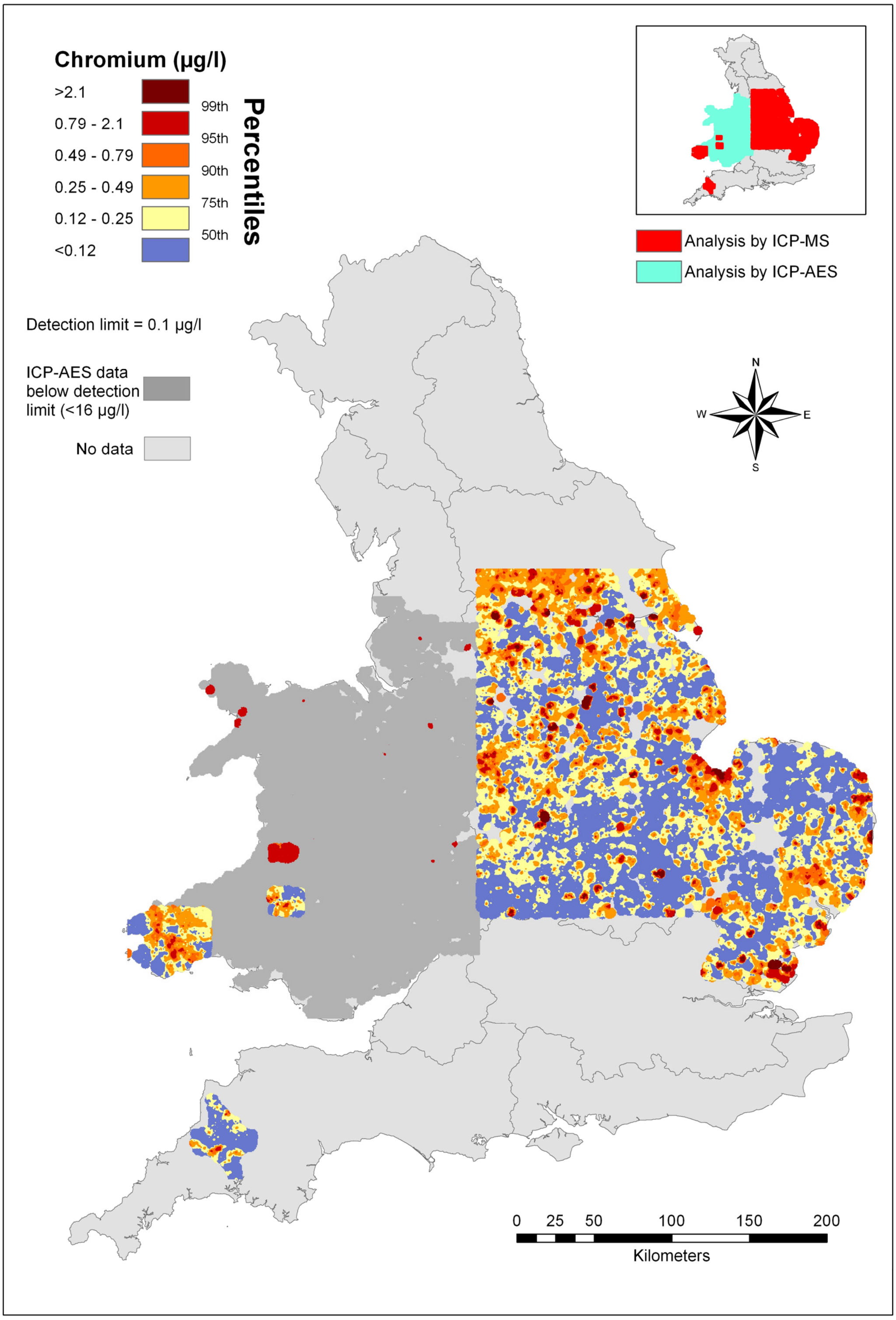


**Figure 3.1e: Concentration of chromium in stream waters (both ICP-AES and ICP-MS data shown).**

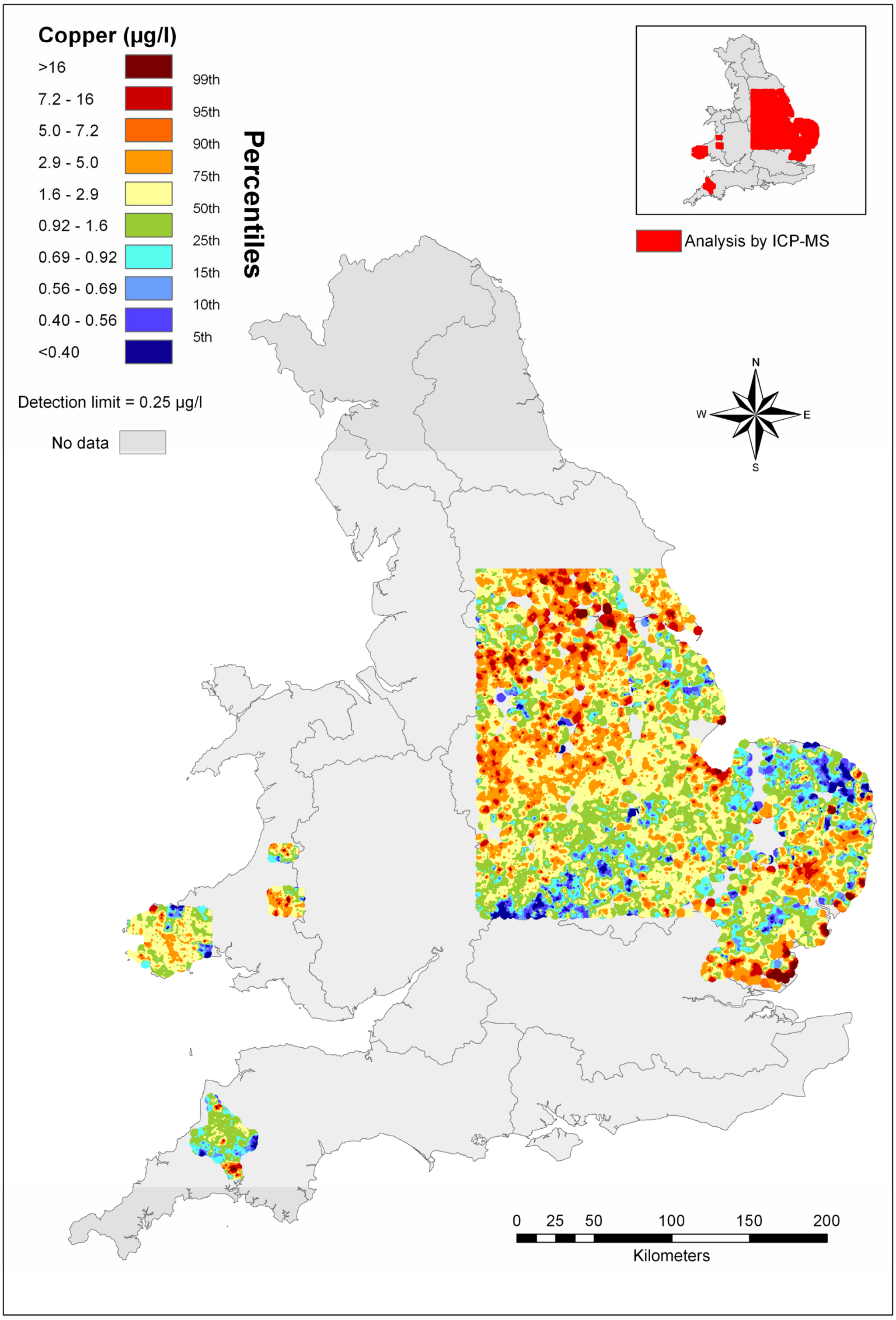


Figure 3.1f: Concentration of copper in stream waters (ICP-MS data).

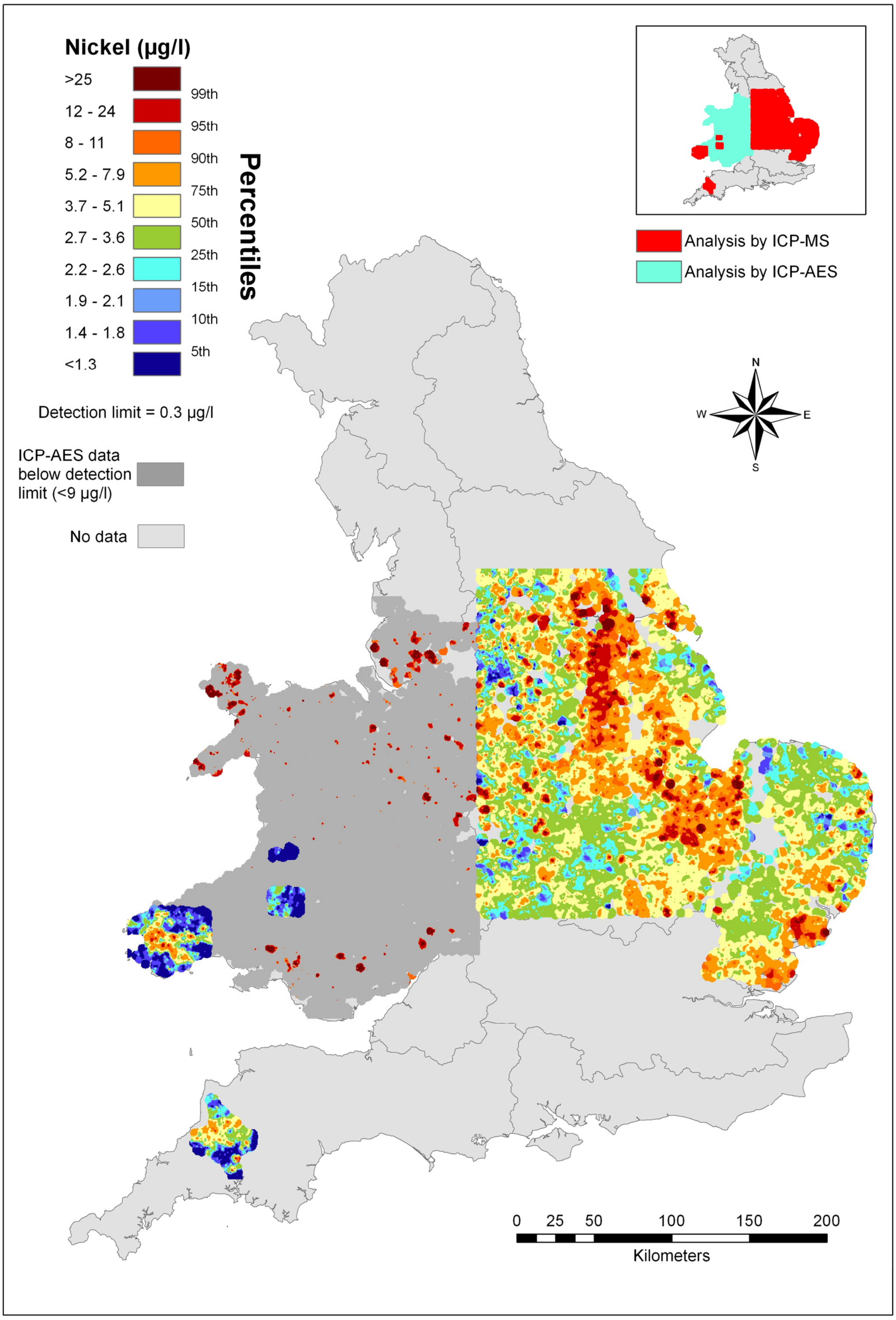


**Figure 3.1g: Concentration of nickel in stream waters (both ICP-AES and ICP-MS data shown).**

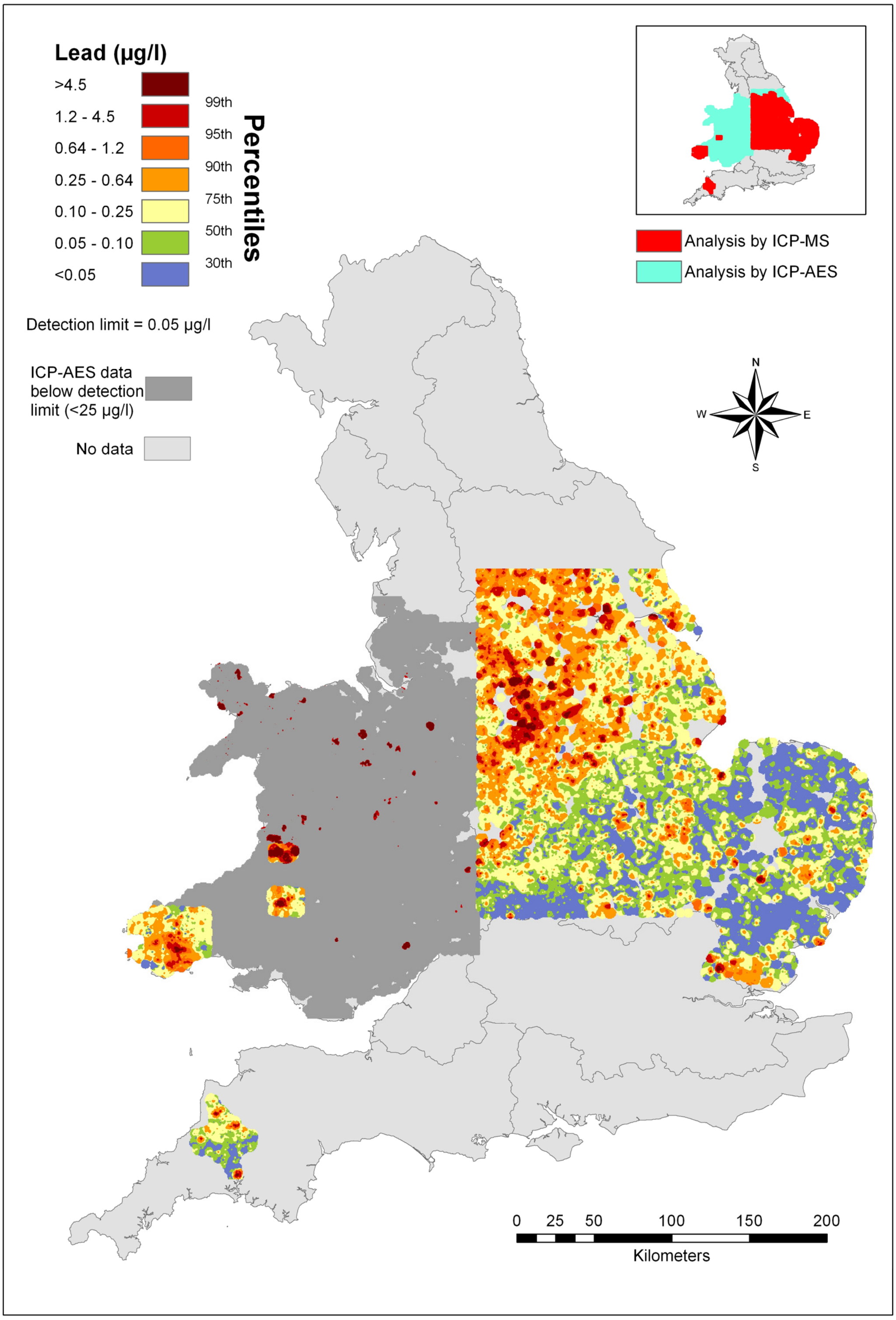


Figure 3.1h: Concentration of lead in stream waters (both ICP-AES and ICP-MS data shown).

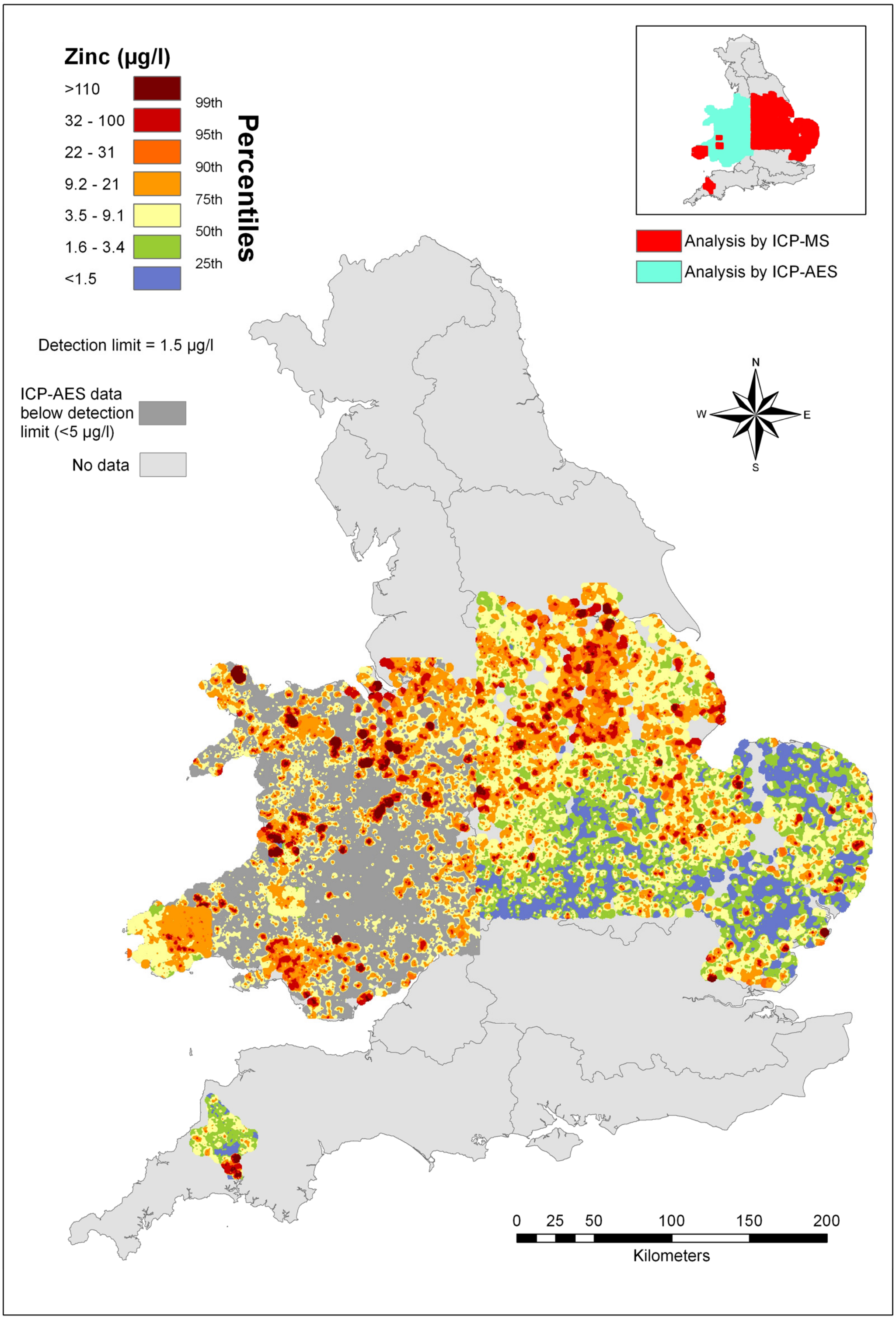


Figure 3.1i: Concentration of zinc in stream waters (both ICP-AES and ICP-MS data shown).

### 3.1.2 Factors influencing the distribution of metal concentrations in stream water – statistical analysis

Available data on factors which may influence and be used to predict stream water metal concentrations, such as geology, stream water pH and concentration of dissolved organic carbon, were statistically analysed to ascertain their relative influence. The analysis provided a description of geochemical variation in stream waters (shown in Figures 3.1(a-i)), and illustrated, for example, where geology might be a good underlying descriptor of the variation in metal concentrations. The aim was to identify the best association of stream water metal concentration with an environmental parameter with which to develop more localised MBRCs that could potentially be used in the absence of metal data. These analyses built upon the findings of geochemical surveys that such variations can be explained by geological and terrain factors (British Geological Survey, 1999; BGS *in prep.*).

The primary statistical methods used were exploratory data analysis and analysis of variance (ANOVA). Exploratory data analysis, using formal tests of normality and dataplots such as shown in Figures 3.2 and 3.3, confirmed that the data were not normally distributed and were generally not log-normally distributed, although all the metals more closely approximated this distribution. Statistical methods based on continuous variables, such as factor analysis and principle component analysis, were not used at this stage because they do not allow direct comparison with categorical geological and land use classification factors. Transformation of categorical data into indicator variables (other than that already undertaken for the WFD typology scheme) was also not feasible because of the large numbers of categories in geological mapping.

The data used included the parameters of land use, geological data at various scales and some key physico-chemical variables commonly measured in stream waters (pH, conductivity and dissolved organic carbon). More unusual variables (such as other trace elements) were not examined, as there was no advantage to describing factors which would not be routinely or easily measured.

The characteristics of underlying geology were included in the ANOVA analysis in three ways. The first two related to WFD typology, as the characterisation of geology according to the WFD typology itself (WFD data), and WFD typology with a distinction between upland and lowland peat areas ($WFD_p$ data). The third characterisation of geology was based on the BGS bedrock to superficial mapping (PM (parent material) datasets).

The physico-chemical variables pH, conductivity and dissolved organic carbon were included in the ANOVA analysis by classifying them according to concentration. These parameters are important indicators of the overall geochemical environment and exert a strong control on the solubility of metals. The parameters are themselves strongly related to the geological environment, with a high proportion of their variance being explained by WFD, $WFD_p$ and PM 250/50 geological classifications. They also reflect terrain controls (such as altitude, rainfall) and intensity of agricultural land use (for example, whether acid soils are limed), which are superimposed on the geological classes. Measurement of pH and conductivity in stream waters is widespread and inexpensive, increasing the usefulness of any predictions made using these data. Categorisation of the geochemical data allowed direct incorporation into the ANOVA analysis, and thereby a direct comparison with existing categorical data. All metal data were log(10) transformed for the ANOVA analysis, in order to more closely approximate a log-normal population (variations from which ANOVA is reasonably robust to). Further study of the data using digital catchment boundaries (which were not available to this project) could be expected to increase the variance explained within RBDs, and may lead to different factors being identified as most useful in explaining differences between RBDs. This should increase the amount of variance explained using direct correlations of numerical data (e.g. pH and aluminium).

Table 3.1 summarises the ANOVA analysis. The statistical output shows that land use classes do not explain much of the variation in the geochemical data. The land use category is thus not considered any further in the national scale data.

**Table 3.1: ANOVA analysis of geological and geochemical data for the metals of interest.**

| Category | Al[#] | Al[##] | Fe | Mn | As | Cr | Cu | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| | Percentage variance explained | | | | | | | | | |
| Land use | 9 | 10 | 5 | 2 | 12 | 1 | 1 | 9 | 5 | 1 |
| WFD | 13 | 22 | 20 | 3 | 29 | 2 | <1 | 16 | 8 | 9 |
| WFD$_p$ | 14 | 31 | 20 | 3 | 31 | 3 | 3 | 22 | 15 | 9 |
| Solid (625k) | 17 | 30 | 17 | 10 | 32 | 9 | 13 | 20 | 26 | 23 |
| Solid (250k) | 20 | 34 | 22 | 15 | 36 | 11 | 14 | 26 | 30 | 28 |
| Solid (50k) | 16 | 30 | 19 | 12 | 33 | 10 | 13 | 23 | 26 | 24 |
| PM (250/625) | 16 | 24 | 18 | 15 | 31 | 8 | 12 | 24 | 18 | 23 |
| PM (50/50) | 18 | 32 | 21 | 15 | 36 | 12 | 15 | 26 | 28 | 25 |
| PM (625/50) | 18 | 31 | 20 | 14 | 36 | 11 | 16 | 24 | 27 | 25 |
| PM (250/50) | 21 | 35 | 24 | 18 | 38 | 13 | 17 | 29 | 32 | 29 |
| pH (category) | 27 | 27 | 21 | 13 | 7 | 7 | 5 | 1 | 14 | 19 |
| Conductivity (category) | 20 | 18 | 8 | 12 | 33 | 5 | 9 | 34 | 7 | 15 |
| Organic C (category)* | 2 | 4 | 16 | 20 | 31 | 15 | 25 | 24 | 7 | 10 |

* Organic carbon data only available for a subset of Fe and Mn data (Figure 2.4). P-values are <0.01 in all ANOVA analyses shown in this table. [#] ICP-AES data [##] ICP-MS data used (Figure 2.4).

Note on the derivation of categories in Table 3.1: Landuse is derived from the on-site record of landuse made when the BGS samples are collected. The categories between WFD and PM 250/50 relate to various scales of geological mapping. Those from WFD to Solid (50k) have a systematic increase in detail. Those that are prefixed by ‘PM’ indicate where solid geological units are overlain with superficial geological units (where they occur). The union of these datasets to give a combined image is named according to the scale of the solid to the drift. Thus, ‘PM 50/50’ takes the 1:50,000 data at both scales. WFD$_p$ is derived by discriminating between low-lying (generally coastal) peat deposits, such as the Fens, and those that occur in upland areas (such as the Peak District); the other standard WFD typologies are in no way affected by this reclassification. Categorisation of the continuous variables of pH, conductivity and organic carbon were undertaken using the percentile class breaks at five, 10, 15, 25, 75, 90 and 95 per cent. Bicarbonate concentrations are not independent of pH, and thus were not included after a preliminary inspection of the data found pH to be the more useful (and widely measured) parameter. This method effectively normalises data measured on very different numerical scales to an internally consistent scale. The interquartile range is taken as one category, due to the small change in numerical values it encompasses in relation to the overall concentration range.

The ANOVA analysis showed that very little of the variance in any parameter could be explained by WFD typologies alone, although for elements with a strong contrast between upland and lowland peat, WFD$_p$ was a more effective predictor for aluminium (in the regions with ICP-MS data), nickel and lead and to a much lesser extent, arsenic, chromium and copper. However, WFD typology is a primary category for the implementation of the WFD in catchments, and where suggestions for a hierarchical approach are made in Section 7, WFD typology is cited wherever possible in order to aid application, should this be operationally employed.

The geological categorisation which explained the greatest variance in geochemical data was the combination of 1:250,000 bedrock mapping with the 1:50,000 superficial mapping overlain, referred to here as PM250/50. Where similarity in the variance was explained by the PM250/50 categorisation and other scales of data tested (such as PM50/50), the PM250/50 scale was preferable because it provided fewer data classes to consider, and was therefore simpler overall, and for those metals which greatest need for an ARA is identified (Section 7) this is the most effective descriptor (iron, manganese and arsenic).

A comparative assessment of pH, conductivity and dissolved organic carbon is also given in Table 3.1. The total variance of metal distribution data could be explained in part by several of these variables, alluding to the complex relationships that control the metal distributions. In general, of the variables tested the geological categories, particularly PM250/50, explained the largest proportion of variance in geochemical data, and could therefore be viewed as the best predictor of such data. Dissolved organic carbon explained more of the variance in distribution data for manganese, chromium, and copper (although only by a narrow margin for manganese and chromium) and was therefore the most important controlling factor for these metals. However, particularly for manganese and chromium, the similarity with the geological class 'PM 250/50' meant that geological variation would still make the most useful descriptor, partly because the geological data are more widely available than dissolved organic carbon data.

For copper, the relative influence of dissolved organic carbon to geology was much greater, although the overall variance explained by the factors considered here was lower than for other elements. For copper, it would be useful to examine organic carbon as a predictor, but this is currently of limited use because of the lack of available spatial data, which would restrict application at the larger scale. Using the geological variables for copper would also be consistent with the treatment of other metals.

The ANOVA analysis demonstrated, as might be expected, a key dependence of the distribution of stream water metal concentrations on underlying geology. Although associations of the metal concentration distribution with other physico-chemical parameters such as pH and dissolved organic carbon were found, these parameters in turn would be influenced by the underlying geology. Thus, it would be reasonable to determine more localised MBRCs based on their association with geology; this would also provide a mechanism to predict appropriate MBRCs in the absence of metal data, based on geology already characterised for the WFD.

### 3.1.3 Graphical summary of data distribution ('box and whisker')

Figure 3.2(a-b) shows the metal data summarised as a 'box and whisker' plot, which provides a graphical summary of the data distribution. The main components of each figure are based on percentile classifications, with the mean concentration also shown. In every case, the mean concentration is close to or exceeds the 75th percentile of the dataset, which indicates that the data are highly skewed, and that mean concentrations (and standard deviations) are highly biased by outliers compared to the median. This report therefore adopted the median to represent background concentrations; however, if the data were used to derive alternative background values based on the mean or standard deviation, the influence of outliers would need to be considered.

The detection limit is also displayed, in order to show why the plots for some elements (such as chromium) are truncated; this gives a good indication of the natural abundance of the metals in relation to the detection limit and proposed standards. For example, ICP-AES is an appropriate method for iron and manganese, while the natural abundance of chromium is low compared to the ICP-MS detection limit. Clearly, any proposed standards that are set too close to the detection limit of the best routinely available method will require developments in analytical techniques in order to assess compliance. The data also illustrate the relative position of standards to the data distribution and give an immediate indication of the likely scale of compliance failure. For instance, if the proposed standard were to be equal to the median, 50 per cent of samples would fail, due largely to the background concentration. Thus, where most of the data population falls above the proposed standard(s), there is likely to be a large number of failures for these metals, as illustrated for iron, manganese and arsenic. The summary statistics for these are compiled in Table 4.3.

### 3.1.4 Data population distributions for each metal ('probability plot')

Figure 3.3(a-i) shows the data plotted in terms of population distribution, with each plot truncated at its detection limit. Unlike the 'box and whisker' plot, these graphs do not reduce the data to a summary, but plot every data point and give a more detailed visual description of the data population structure. Plotting data on a probability scale against concentration shows whether the data are from one (normally distributed) population or not. A normal distribution would form a straight line when plotted by this method. The graphs show that all of the metals deviate from a straight line, suggesting that they are multimodal (formed of several different populations). This is a sensible outcome, given that the geochemical maps clearly show spatial variations in data, suggesting discrete populations.

Probability plots also permit the range of background data to be ascertained. This natural variability in concentration appears to be large, covering three orders of magnitude for trace elements and over four orders of magnitude for minor elements. At the highest concentration of each plot, individual data points can be discriminated because the outliers are fewer in number and so do not coalesce on the plot like the bulk of the population. These outliers are the data which skew the dataset and cause a high mean compared to the median. Whilst the plot gives no indication of the cause of these outliers, it does allow an estimate of the concentration at which they appear to deviate from the rest of the data population. There is a long history of using these plots to establish background concentrations based on the work in the mineral exploration industry. Generally the approach there is to use values such as the 97th or 99th percentile (the approximate equivalent to the mean plus either two or three standard deviations of a log-normal data population) to discriminate the background from the high concentration mineralised zone (e.g. Sinclair, 1976).

Existing and proposed standards are also plotted on these graphs. The intersection of the standard concentration with the data points provides an estimate of the proportion of sites which will exceed the standard (from the y-axis), and indicates the potential effect of the proposed standards. The shape of the distribution close to the proposed standard further indicates what effect even a minor change would have on the number of samples passing/failing the standard. The steeper the curve, the more samples will be encapsulated in a given change of concentration. The graphs also allow a very immediate inspection of the effect of any changes in proposed standards (to either higher or lower concentrations), in relation to the likely failures in the areas of England and Wales where data has been collected.

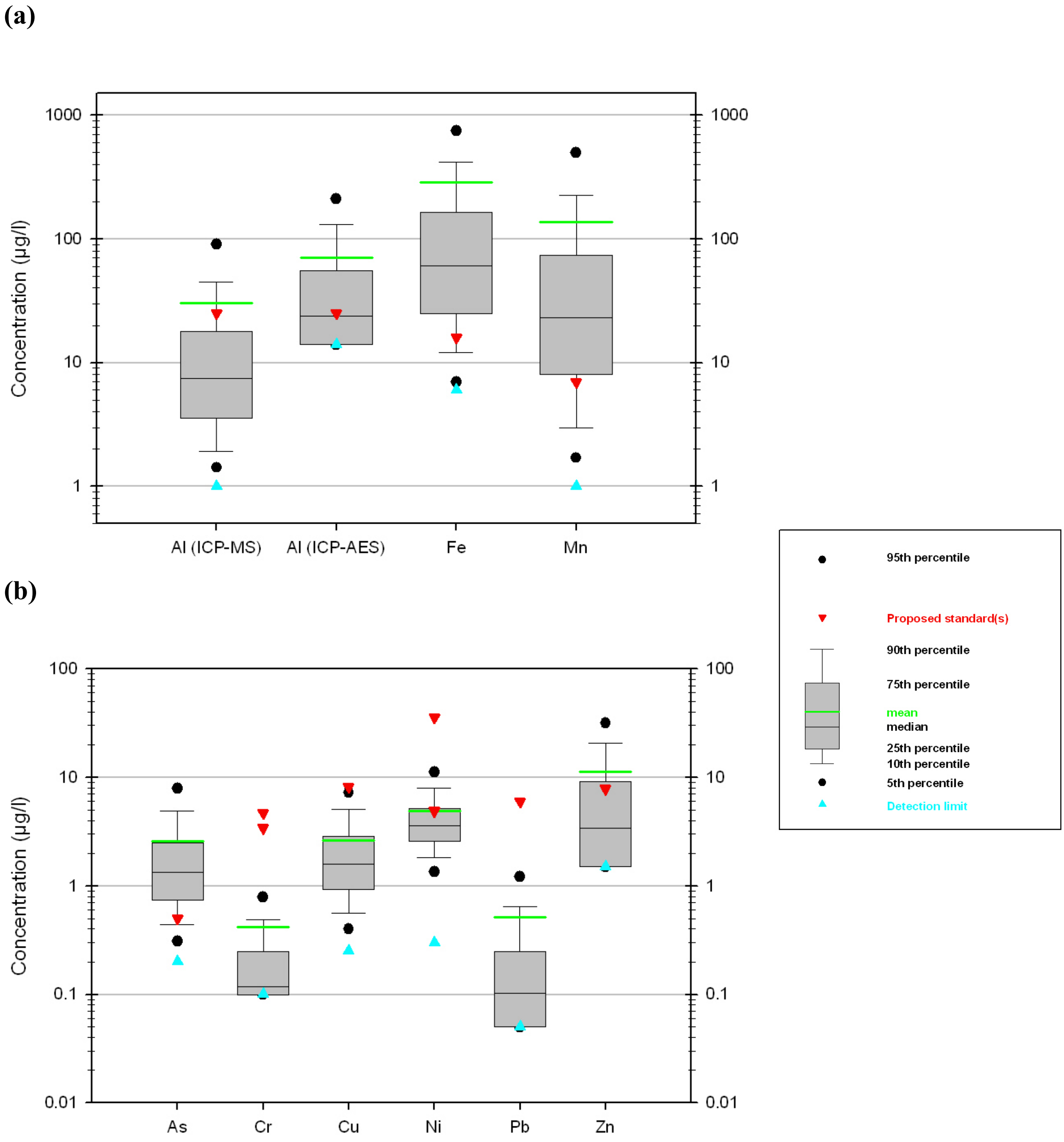


**Figure 3.2: Boxplot summaries of the stream water data:**
**(a) minor elements (Al, Fe, Mn);**
**(b) trace elements (As, Cr. Cu, Ni, Pb, Zn).**
(Note that concentrations are shown on a $\log_{10}$ scale).

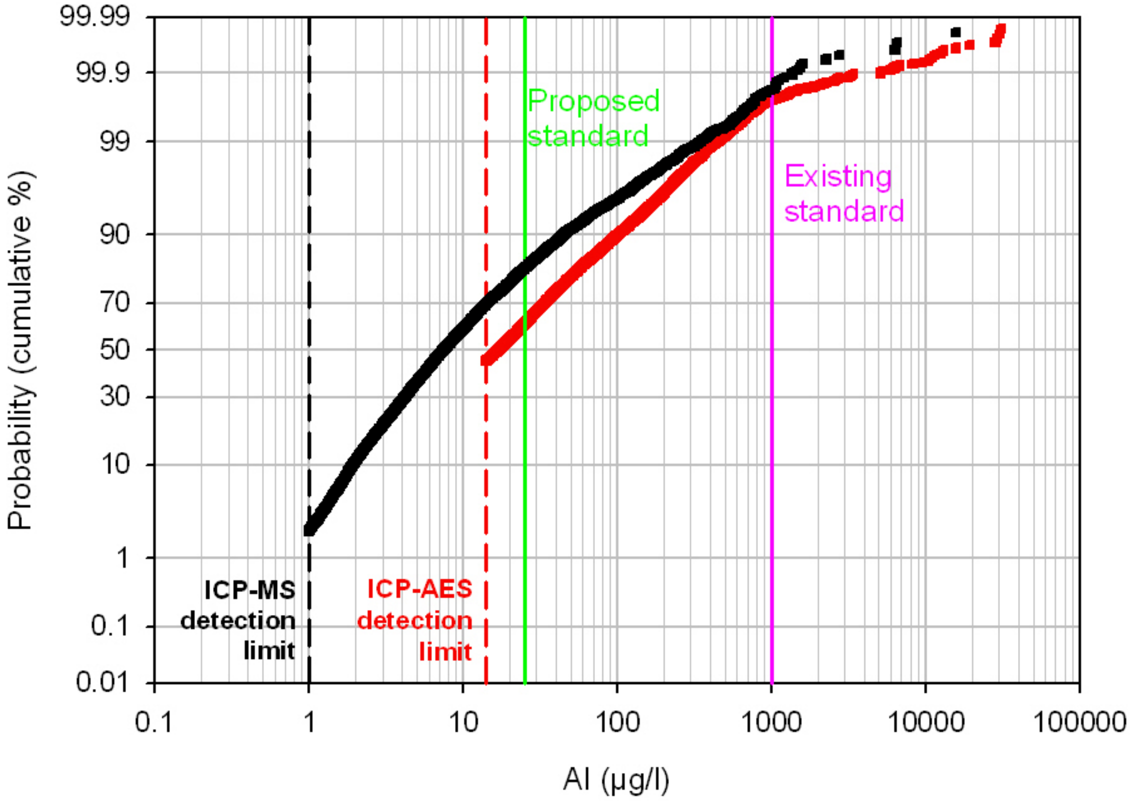


Figure 3.3a: Probability plot of aluminium in stream waters (both ICP-AES and ICP-MS data shown).

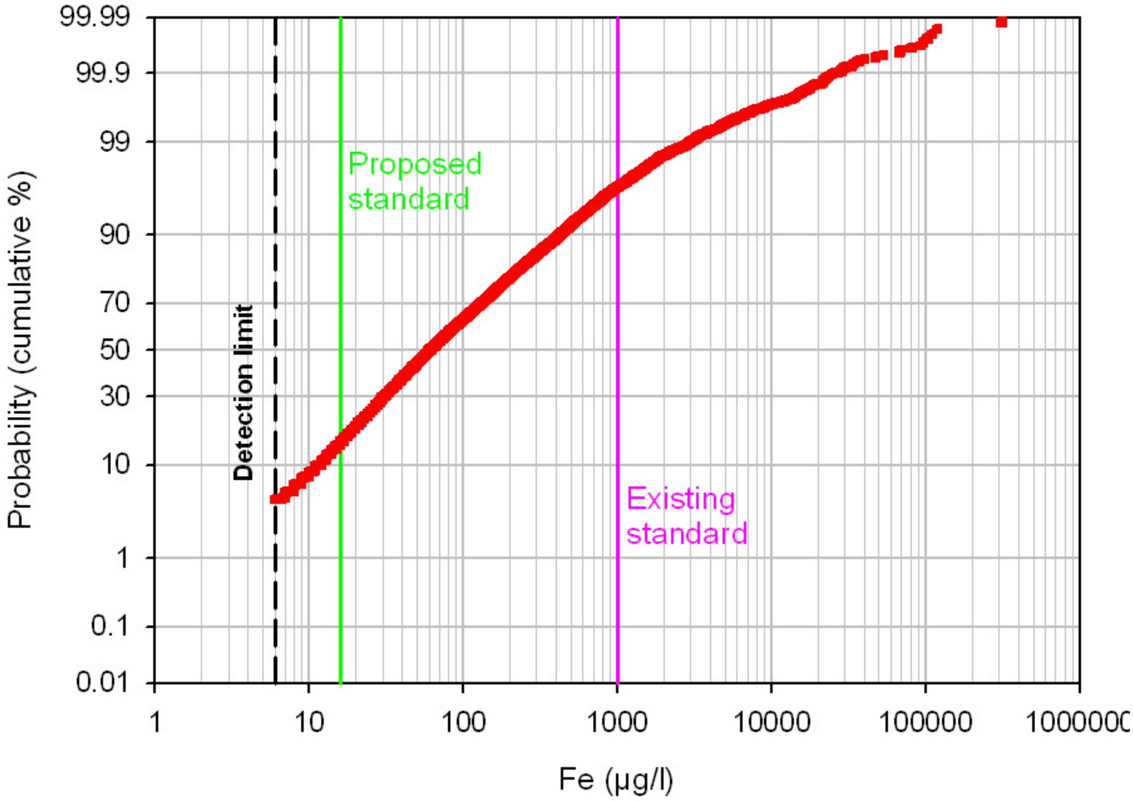


Figure 3.3b: Probability plot of iron in stream waters (ICP-AES data).

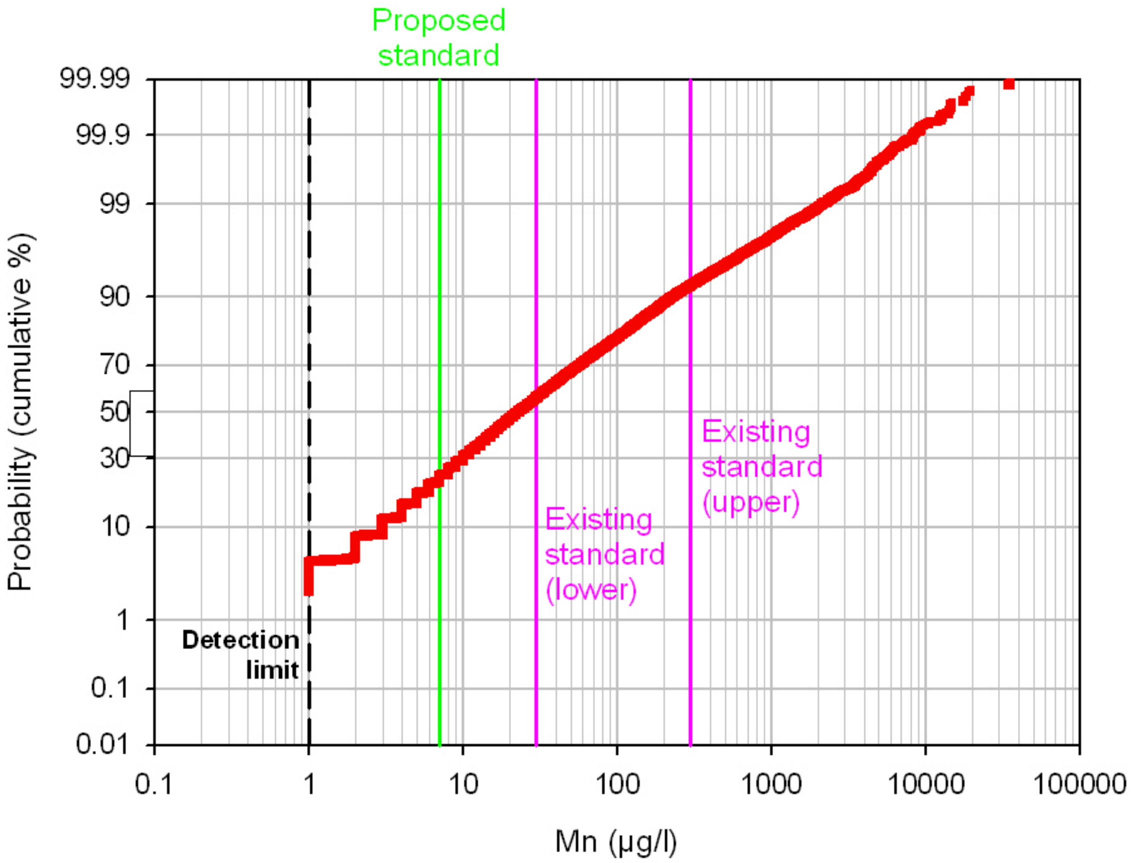


Figure 3.3c: Probability plot of manganese in stream waters (ICP-AES data).

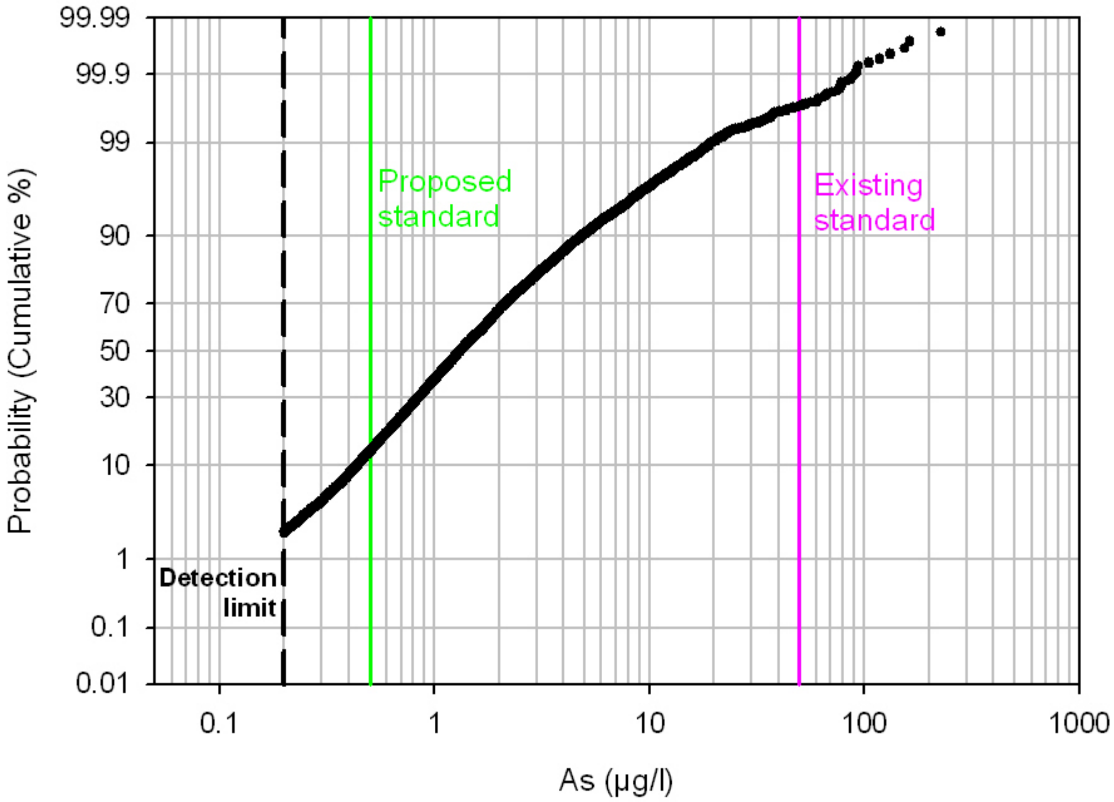


Figure 3.3d: Probability plot of arsenic in stream waters (ICP-MS data).

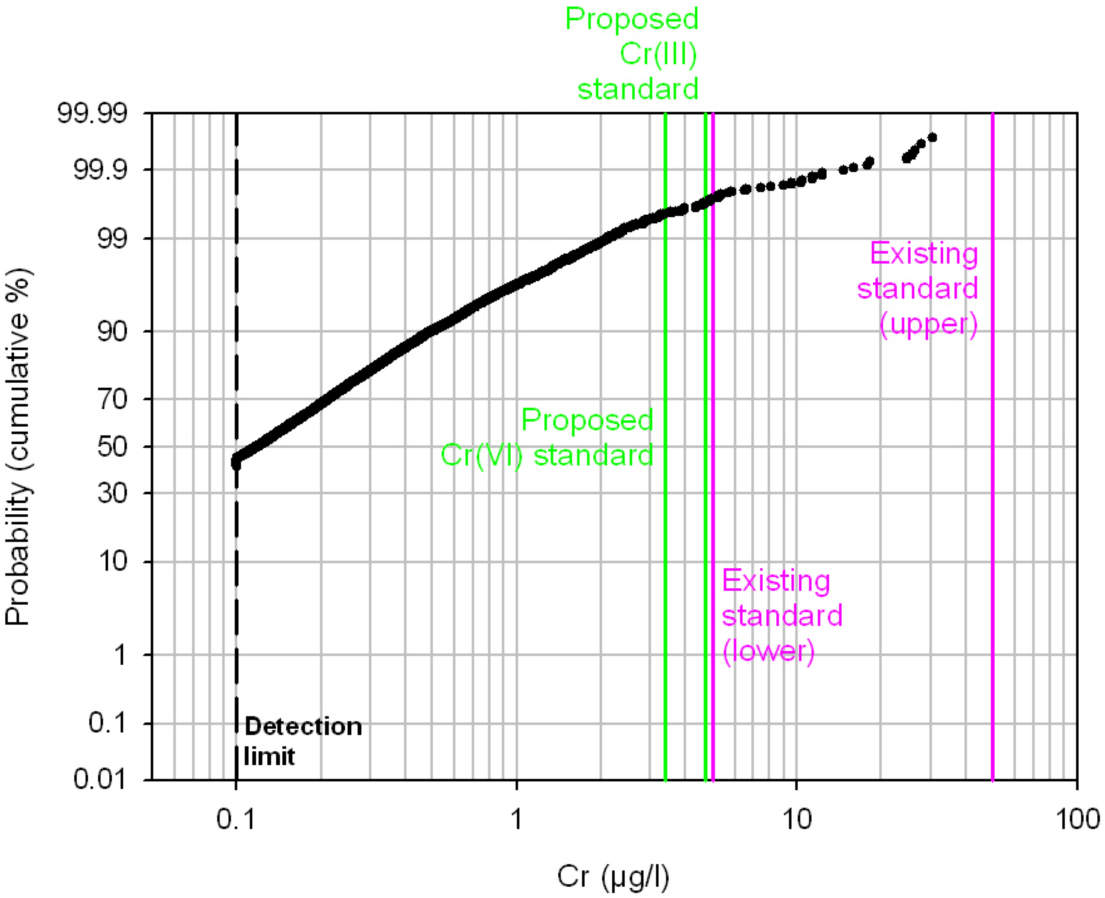


Figure 3.3e: Probability plot of chromium in stream waters (ICP-MS data).

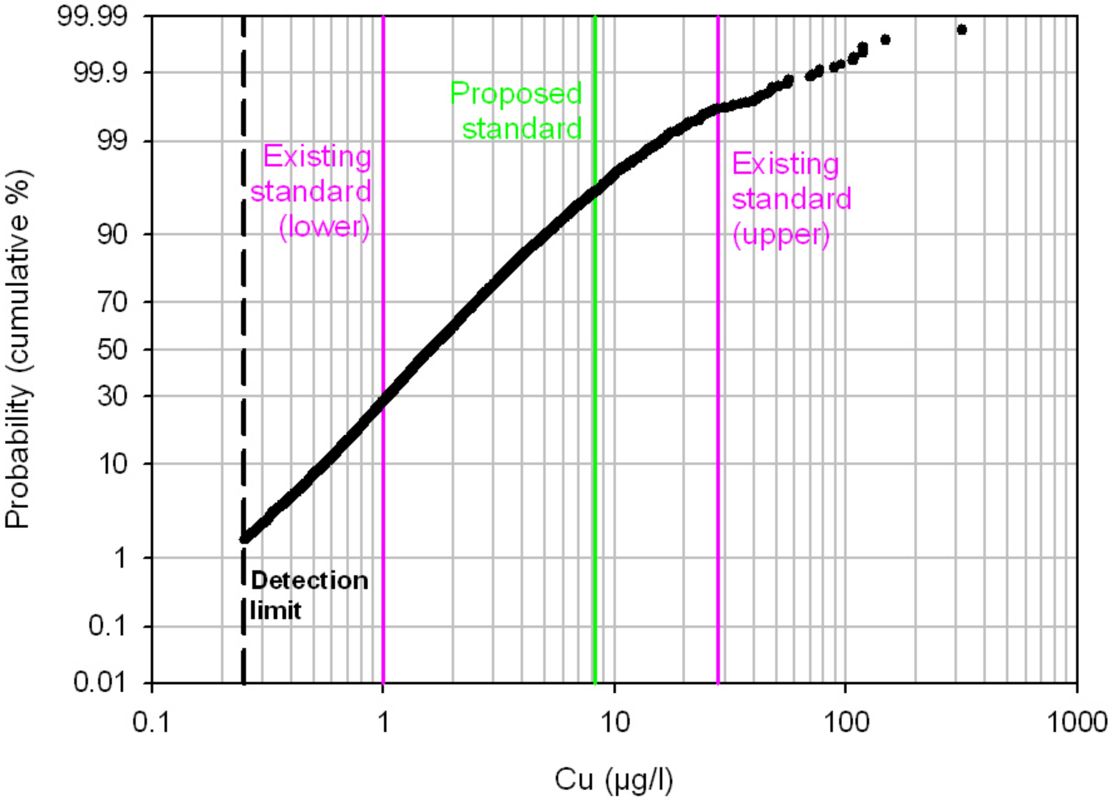


Figure 3.3f: Probability plot of copper in stream waters (ICP-MS data).

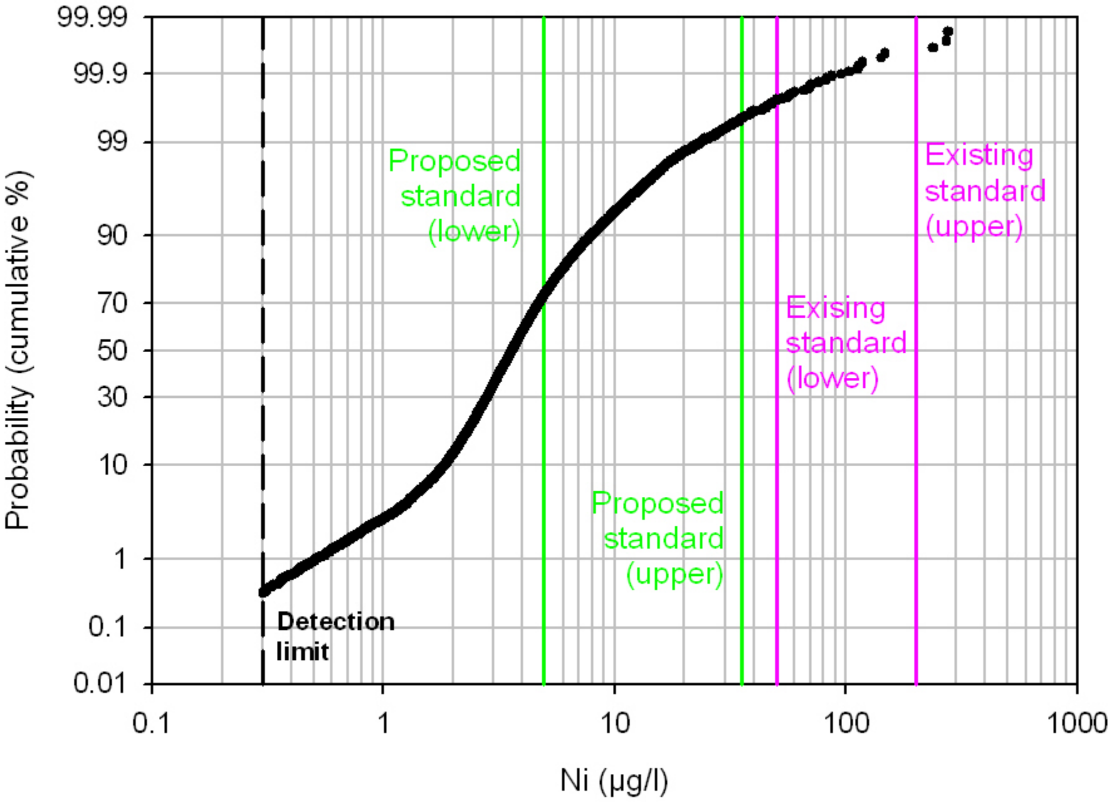


Figure 3.3g: Probability plot of nickel in stream waters (ICP-MS data).

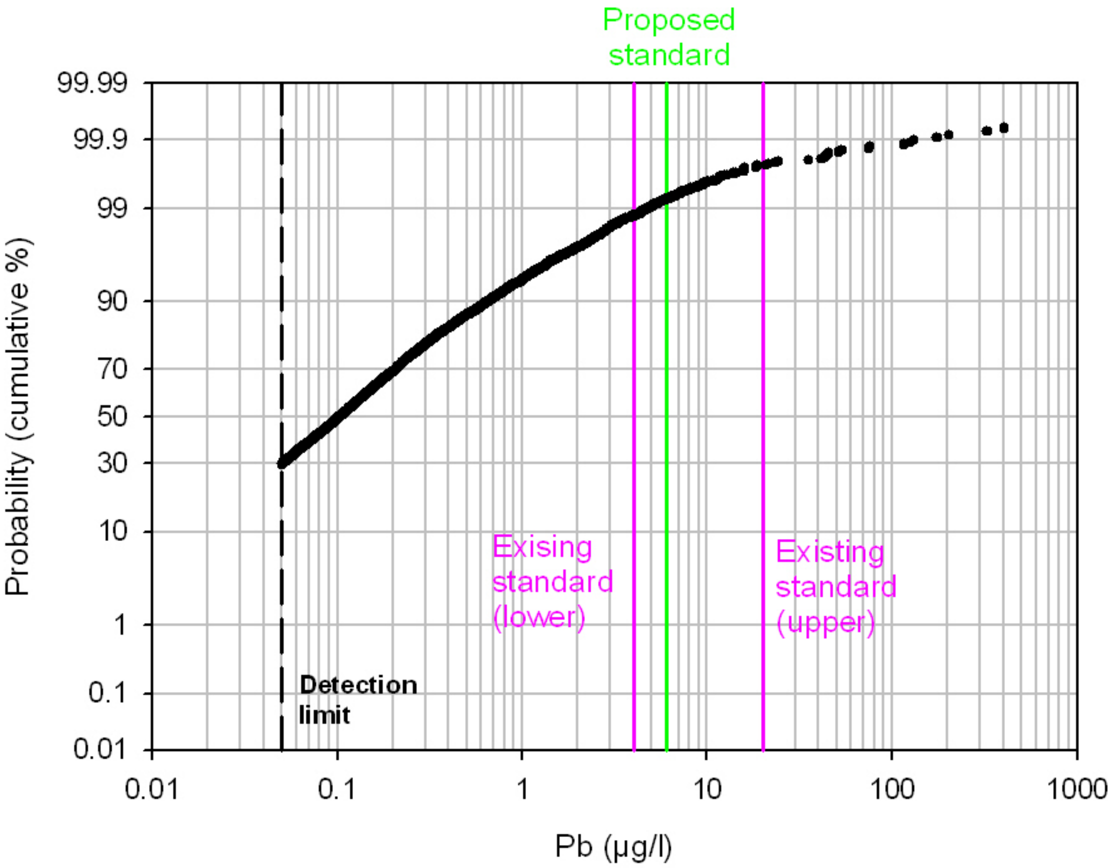


Figure 3.3h: Probability plot of lead in stream waters (ICP-MS data).

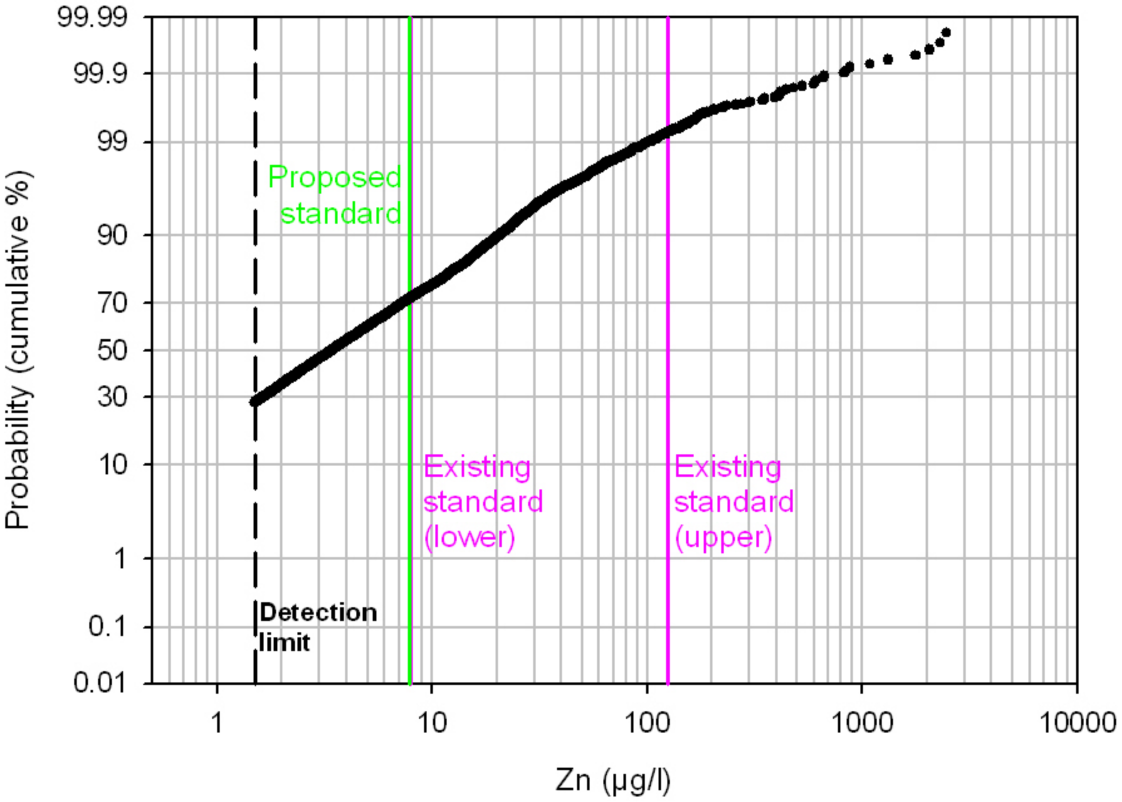


**Figure 3.3i: Probability plot of zinc in stream waters (ICP-MS data).**

## 3.2 Summary (by metal) of the influences on geographical variation in concentration

### 3.2.1 Aluminium

A substantial proportion of variance in the aluminium data can be explained by geological factors and pH (Table 3.1). Aluminium is an abundant element in many rock-forming minerals (with the exception of calcite), and aqueous concentrations are generally limited by solubility controls rather than source abundance, with factors such as low pH promoting higher concentrations of aluminium in solution. These geological controls can be seen in Figure 3.1a, with concentrations generally higher over the siliceous lithologies of Wales and the Peak District and lower over the calcareous lithologies of the east of England. The data in Wales, western England and the north of the Humber Trent area (ICP-AES) are plotted according to the percentile classes of the rest of the dataset (by ICP-MS). This results in a larger area of the map appearing in yellow/red colours in Wales, because the detection limit of the ICP-AES method lies above the median of the overall dataset, but concentrations are higher due to the larger span of upland areas in Wales than over the ICP-MS mapped region. These higher concentrations are a result of the effects of terrain being superimposed on the underlying lithology.

The WFD regions identified as ‘organic’ are best classified into upland and lowland peat regions ($WFD_p$). This is because the major geochemical characteristics of the lowland Fens of the Humber Levels and the Fenland of East Anglia are quite different to those of the upland peat areas described above. These low-lying areas have high conductivity and are associated with much higher pH values and lower aluminium solubility. The greater differentiation associated with the use of ‘PM 250/50’ in explaining the variance relates to a higher resolution in the geological classes than afforded by the $WFD_p$ class. However, pH is very influential, and these factors could be used to help explain compliance failure due to natural processes. If the data from areas of ICP-AES analysis is considered (Wales and the West Midlands) it can be seen that the pH category does explain more of the variance in the aluminium data (Table 3.1) than the geological category of ‘PM250/50’. Possible future work using more localised catchment data (see recommendation in Section 8) may also find that pH has a more closely defined influence within these spatially restricted subsets of the whole dataset.

Mineralisation may be contributing to higher concentrations of the metal because of the reduction in pH associated with sulphide oxidation. This process may be the cause of some of the elevated concentrations shown in Figure 3.1a in areas such as the mid-Wales orefield, or the south Yorkshire and south Wales coalfields. Whilst the process could affect other mining regions, there is no evidence of extensive areas of elevated concentrations in the south of the Tamar catchment or over the Peak District mineralisation (which is carbonate-hosted, restricting aluminium solubility through the buffering of pH). External drivers of aqueous pH, such as atmospheric acid deposition or agricultural liming may increase or decrease (respectively) dissolved aluminium.

### 3.2.2 Iron

Iron concentrations vary systematically across the mapped region, but these variations are not as strongly constrained by WFD typologies as aluminium, as is borne out by the ANOVA results. The variations can be explained by more detailed geological classification, such as ‘PM 250/50’ for example, where the contrast between the north and south of the Tamar catchment reflects the change in dominant formations in that area (and are not related to the mining activity in the southern part of the catchment). The relative importance of pH and dissolved organic carbon also reflects solubility controls on iron.

A major control on iron solubility that is not quantified within the G-BASE dataset is redox potential. Oxidising waters generally have lower iron concentrations, as the dominant iron species in such waters is insoluble. Conversely, in more reduced waters (especially of low pH), iron solubility is much higher. As with all the metals considered in this study, complexation of dissolved iron with other solutes may be important maintaining high concentrations in solution. Dissolved organic carbon (DOC) is recognised to complex with iron species, and may promote high concentrations in solution, in conjunction with the mechanisms described above. The distribution of DOC measured by BGS in stream waters is shown in Figure 7.4, whilst in addition DOC-rich waters may be expected in peaty areas as are found in upland Wales. Thus, high iron concentrations are found in the upland areas of mid- and North Wales, the Peak District and the Tamar catchment. Higher concentrations are also found in the low-lying areas of the Fens, Humber Levels and Broads. These areas are associated with greater dissolved organic carbon. The lowest concentrations are seen in the edges of the Chalk outcrop in Yorkshire/Lincolnshire and Norfolk/Cambridgeshire and the outcrop of the Devonian in South East Wales. These higher pH waters are associated with more calcareous formations, and low concentrations of dissolved organic carbon and iron both indicate well-oxidised stream waters. The map indicates that moderate concentrations are found over a wide swathe of central England and the Welsh Borders, where most samples within the interquartile range occur.

### 3.2.3 Manganese

There are large similarities between the geochemical images for iron and manganese, and similar factors are involved in the mobility of these metals. However, a smaller proportion of variance in the data is explained by geological factors than is the case for iron, and dissolved organic carbon appears to have a greater influence (although not by a large amount compared to ‘PM 250/50’). This is not necessarily a direct relationship; rather, dissolved organic carbon is a better descriptor of lower-oxygen stream waters in which manganese is more soluble. Manganese differs from iron in that its solubility increases before that of iron as the redox potential decreases, although soluble reduced species dominate at a similar pH to iron. The increased areas of high concentrations can be seen along low-lying coastal regions on the east and west coasts and in upland areas associated with low redox (Eh) peaty drainage.

### 3.2.4 Arsenic

The stream water data for arsenic (Figure 3.1d) is strongly controlled by geological factors, as shown by the results of the ANOVA analysis. These are most clearly defined by the high concentrations associated with low-lying coastal regions along the east coast. The large area of the Fens forms a particularly striking feature of high arsenic concentrations. High concentrations are also associated with the Mercia Mudstone outcrop. Low concentrations are found in the siliceous regions for which there is data, including the Peak District, Pembrokeshire and the upper Tamar catchment. Low concentrations are associated with streams flowing on the edge of the Chalk outcrop, and the outcrop of the Jurassic Lias and Oxford Clay sediments. Mineralisation may also contribute to high arsenic concentrations, such as can be observed in the south of the Tamar catchment, where mining for copper and arsenic was conducted on a large scale in the past, and mining wastes contribute even further to the total arsenic mobilised in the catchment.

Increased detail in the WFD ‘calcareous’ category that is afforded by ‘PM 250/50’ is probably the cause of the greater amount of variance explained. High variance related to conductivity and organic carbon reflects the descriptions applied above. Comparative study of the soil, stream sediment and stream water data for the Humber-Trent mapping region reveals no real relationship between the concentration of arsenic in the solid phase samples and that in stream waters, indicating that factors controlling solubility are more important in controlling the aqueous concentration of arsenic than the source abundance.

### 3.2.5 Chromium

The boxplot summary (Figure 3.2) shows that the natural abundance of chromium is low compared to the detection limit of ICP-MS analysis, and is below the detection limit of ICP-AES in almost every sample. This is reflected in the interpolated image (Figure 3.1e), where even the ICP-MS data can only be discriminated above the median concentration. High concentrations relate to regions with high dissolved organic carbon, which is reflected in the results of the ANOVA analysis. This result is close to the variance explained by the geological categorisation of ‘PM 250/50’. Data in the lowest class that is mapped are ‘noisy’, with a great deal of scatter. This arises from the numerical proximity of the class interval to the detection limit. These data are associated with higher uncertainties, simply as a result of this proximity to the detection limit. The variations related to organic carbon (excluding Pembrokeshire) appear to be controlled entirely by the influence of Quaternary sediments and terrain controls, without any relationship to solid geology. It is not clear if such an explanation also applies to the data from Pembrokeshire, in the absence of dissolved organic carbon data.

Samples with only ICP-AES data which are above the detection limit are isolated and suggest a non-background population, and so are not helpful in the consideration of background concentrations.

### 3.2.6 Copper

Copper concentrations have the least relationship to geological categorisation, with the WFD typologies accounting for less than one per cent of the variance in the data. Dissolved organic carbon is a better predictor of copper concentrations, and this relationship is strongest in East Anglia, although the region of high copper concentrations around the Fenlands is much more constrained than is the area of high dissolved organic carbon. Additionally, the area of low copper concentrations associated with the outcrop of the Jurassic Lias and Oxford Clay sediments, is also associated with low dissolved organic carbon. Otherwise, the relationship does not appear to be that strong by visual inspection, although of all the indicators available, organic carbon explains the most variance in the copper data (Table 3.1). This is to be expected from the recognised role of DOC in complexing copper in solution, increasing its solubility (Langmuir, 1997). Copper solubility increases with lower pH as well as complexation with organic ligands. However, the region for which copper data are available does not include any large areas of siliceous formations with low pH, which may account for the apparent lack of relationship between copper and pH.

Mineralisation in the south of the Tamar catchment, where extensive copper mining activity took place, can be clearly seen in the high copper concentrations around Gunnislake.

### 3.2.7 Nickel

Variations in nickel concentrations are large between areas where there is ICP-MS data. Variance in the nickel data is mostly explained by conductivity, but is also related to the geological categorisation ‘PM 250/50’. The relationship with conductivity arises from high concentrations in the high conductivity Mercia Mudstone Group and low-lying areas of eastern England, such as the Humber Levels, the Fens and the South Suffolk/North Essex coast. High concentrations are also observed in the Carboniferous Crackington formation (argillaceous sediments) of the Tamar catchment and over various Ordovician and Carboniferous formations of Pembrokeshire, but these variations are clearly independent of conductivity in those areas. Low nickel concentrations found in the Peak District are associated with low conductivity stream waters, and the low concentrations across North Norfolk are associated with relatively low conductivity values.

Localised anomalies seen in the ICP-AES data are sufficiently spatially constrained to suggest they should be investigated as potential local anthropogenic contamination. This is because they are relatively isolated, and do not form an area of geological or geographical coherence that would be more reflective of background concentrations. The distribution of nickel in the ICP-MS data (Figure 3.1g) does exhibit this sort of coherence in certain areas, where concentrations are controlled by geological and other water quality factors. Most of the ICP-AES data are below the detection limit, rendering the data of little value in further discussion of background concentrations in relation to proposed standards. However, Appendix 3 provides summary statistics for an alternative standard which has been proposed for nickel, and in this case the ICP-

AES detection limit is well below the proposed standard – thus making all these data useful in the comparison of proposed standards.

### 3.2.8 Lead

The natural abundance of lead is moderate compared to the detection limit of ICP-MS, as shown in Figure 3.2, which results in the lowest 30 per cent of the data being included in that category on Figure 3.1h. Concentrations of lead are poorly described by WFD typologies, but a much better description of the variance is derived from the geological classification 'PM 250/50'. This can be seen in the mapped data (Figure 3.1h), where little variation systematic with the siliceous and calcareous classes can be seen, whilst higher concentrations are observed through the English Midlands, with low concentrations across East Anglia, the exception being the area of eastern Essex in the south-most region of the mapped data.

Higher concentrations are found in the lead and zinc mining district of mid-Wales and the Peak District. Higher concentrations can also be seen in the Coal Measures of Yorkshire and around Coventry. The only samples with measurable lead in the ICP-AES region clearly reflect anomalous samples, with the background concentration falling below 25 µg/l; no further useful information on background concentrations can be obtained from these measurements.

Whilst the solubility of lead is known to be greatly affected by a number of factors, including pH and dissolved organic carbon, these do not provide a satisfactory explanation of the variance in the lead data (as shown by the ANOVA analysis).

### 3.2.9 Zinc

Zinc concentrations were measured over most of the normal ICP-MS region, but some early analyses failed quality control checks and were not released, hence the lower sample numbers in the north of the Humber-Trent region. The ICP-MS detection limit is moderate compared to the natural abundance of zinc; thus, 25 per cent of the data are below the detection limit and cannot be plotted as separate class intervals on the map. The majority of the ICP-AES data are below the detection limit, and are therefore not useful for establishing a background concentration.

Concentrations of zinc vary across the mapped region (Figure 3.1i). Little of the variation appears to arise from WFD typologies, but the 'PM 250/50' classification explains far more of the variation. This failure of the WFD typologies is likely to arise from the large variation within calcareous and siliceous typologies, such as the Tamar catchment (siliceous). Concentrations are low or only moderately elevated above the detection limit over large areas of eastern and central England and much of the northern part of the Tamar catchment. Higher concentrations are found in some of the Fens of Lincolnshire, Cambridgeshire and Norfolk. High concentrations are also seen along the Mercia Mudstone outcrop,

Concentrations are high in the mineralised zone of the Tamar catchment, and downstream of the Peak District mineralisation. Mining activities in the Welsh orefields and the South Wales coalfield are reflected in the high (measurable) concentrations in the ICP-AES data from these regions. Some of the high concentrations in the Sherwood Sandstone outcrop in North Nottinghamshire are also linked to deep coal mining and industrial activities (British Geological Survey, *in prep.*).

The geochemical behaviour of zinc is affected by pH, particularly in the liberation of zinc from ore minerals. Once in solution, zinc is more soluble than many other trace elements at neutral pH because of the high solubility of its carbonate phases, and it is thus prone to be present in high concentrations. The pH and conductivity categories explain moderately large amounts of the variance, and may be useful in addition to the geological classification to explain failures in compliance from natural background concentrations.

## 3.3 Comparison of background concentrations with current and proposed standards

In order to explore the relevance of including metal background concentrations in water quality assessments, a series of maps shown in Figures 3.4(a-i) compare metal stream water concentrations directly with existing and proposed standards. These maps show the areas which are likely to fail to meet the proposed standards, primarily because of high background concentrations. These comparisons suggest the likely effect of applying the proposed standards, and indicate where the ‘added risk’ approach might be applied or the case made for amending the standard.

The restricted geographical nature of the data and consequences of this for extrapolation to the whole of the UK is discussed further in Sections 6 to 8. The data used in these maps are identical to those used in Figures 3.1(a-i), with the same application of dark grey to ICP-AES data below the detection limit.

Figures 3.4(a-i) have been prepared with the following format:

> Map ‘i’ in each pair represents the comparison with the *existing* standard. This is simply represented in terms of samples that do or do not exceed the value of the standard. Where the standard is expressed as a relationship with hardness (chromium, copper, nickel, lead and zinc) these maps report either ‘pass’ (green) or ‘fail’ (brown). The rest of the standards relate only to the concentration of the metal. These are represented by: pale blue denoting data below the detection limit; pale green measurable data that fall below the value of the standard and data above the standard are shown in brown. Where the ICP-AES data do not provide useful information in relation to the standard (due to their respective concentrations), these data have not been plotted (chromium, nickel, lead).
>
> Map ‘ii’ in each pair shows the geographical location of samples that fall above or below the *proposed* standard. The pale blue and green colours represent those areas where data are below the detection limit or lowest proposed standard respectively. Areas shown in brown exceed the proposed standard, and where there is a range of possible standard values (nickel) two shades of brown are used to indicate the best to worst case scenarios (in the absence of confirmation of the contextual conditions). These colours are directly comparable to those used in map ‘i’. Where the ICP-AES data do not provide useful information in relation to the standard (due to their respective concentrations), these data have not been plotted (chromium, nickel, and lead).

Areas of brown shading on these maps illustrate the areas where water bodies are most likely to fail the standard as a result of background concentrations of metals. With respect to the proposed standards, large areas of brown show that widespread failure is likely. However, this comparison takes no account of the way in which the regulatory regime might be applied, for example as a strict ‘pass/fail’ of the standard, with an allowance of ‘no deterioration’, or the application of ‘added risk’. Thus, it does not necessarily indicate *actual* failure, nor does it assess whether the standard represents the level of ecosystem protection advocated by the WFD.

In these maps, regionally significant areas of failure should be given close attention, because localised isolated high concentrations are likely to relate either to anomalous local conditions or to isolated anthropogenic influences, which are beyond the scope of a regional assessment. It is the areas that are geographically and geologically coherent that represent a potential problem in terms of widespread, naturally derived, high concentrations in relation to the proposed standard.

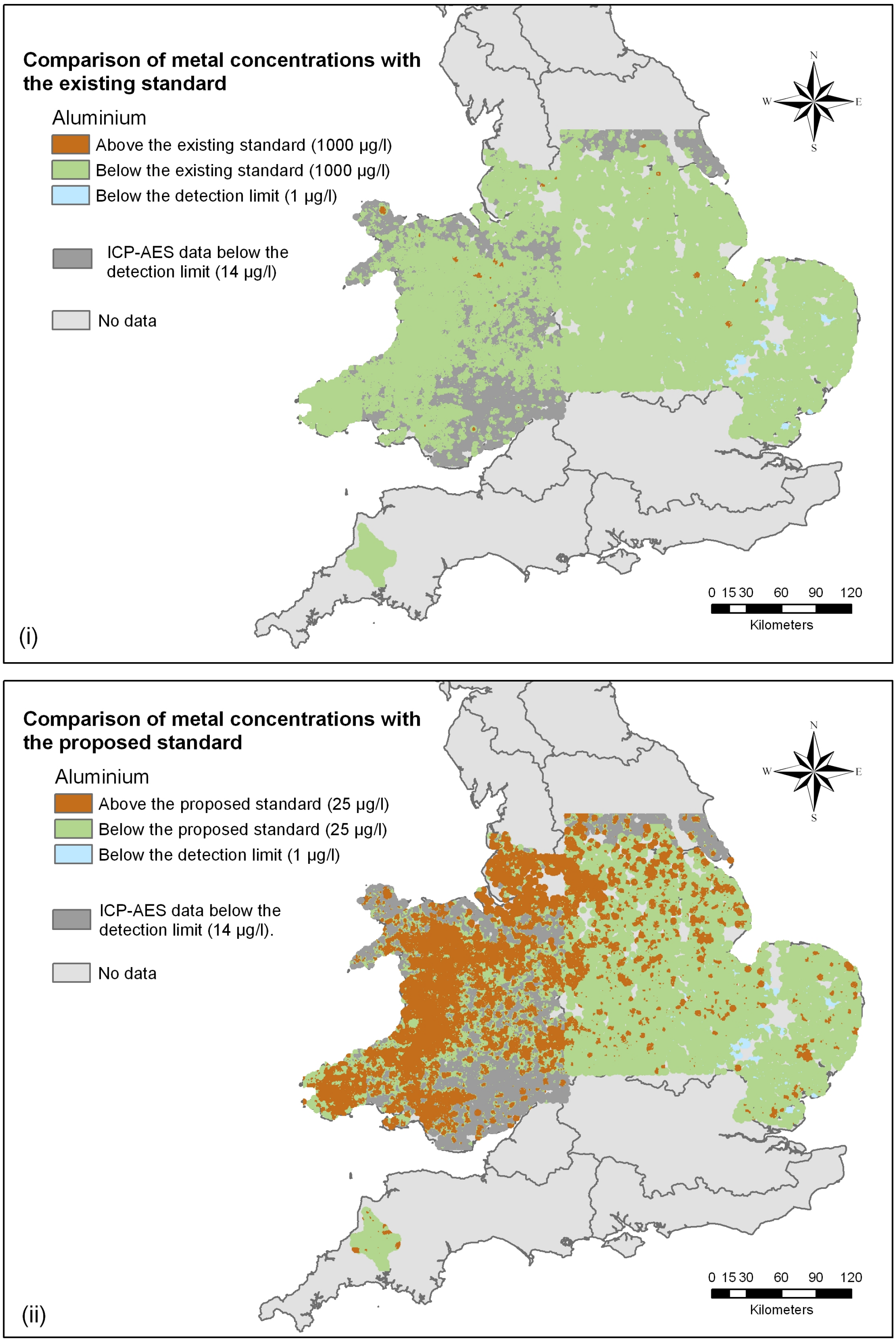


**Figure 3.4a: Comparison of aluminium concentrations with (i) existing standards, and (ii) proposed standards.**

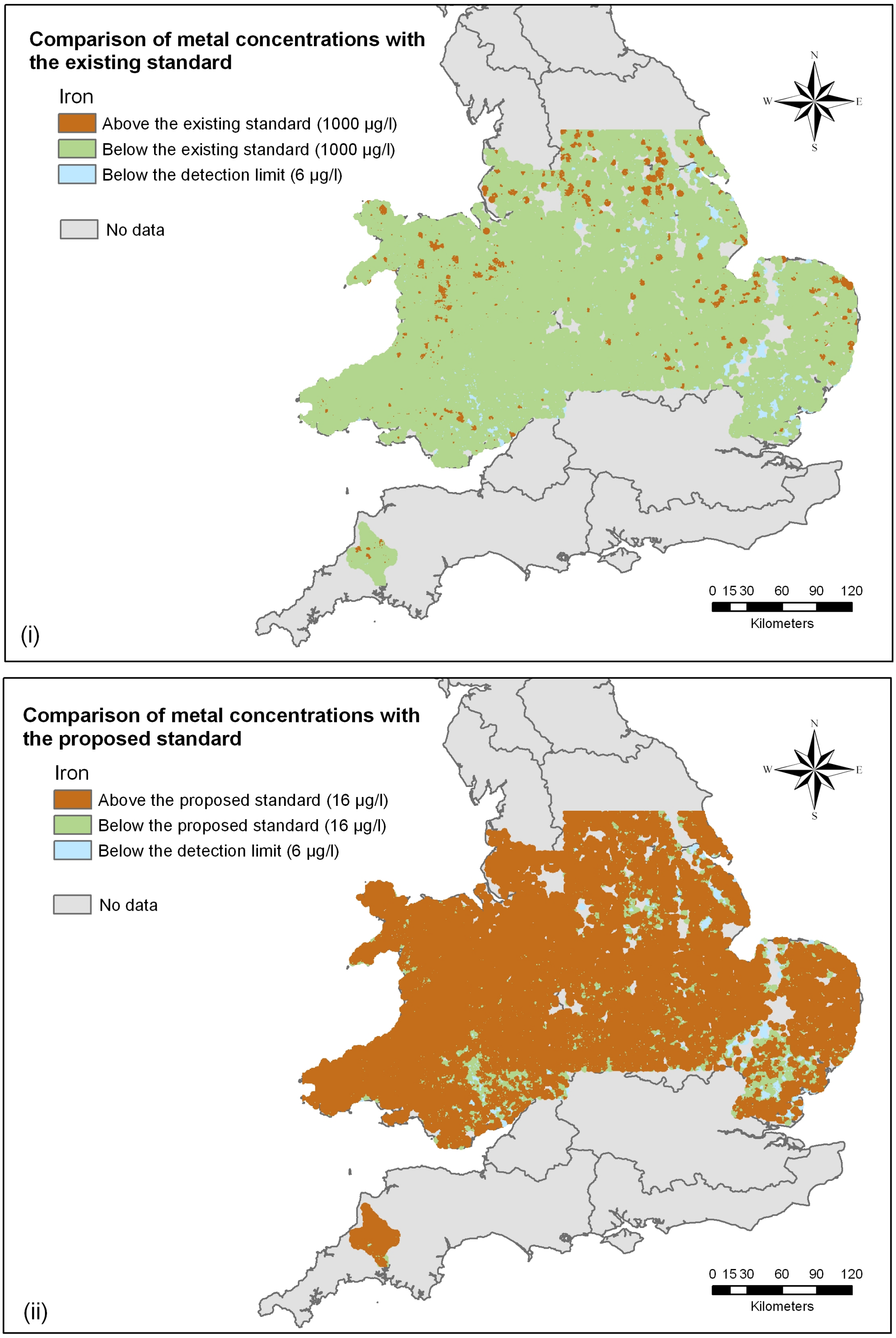


**Figure 3.4b: Comparison of iron concentrations with (i) existing standards, and (ii) proposed standards.**

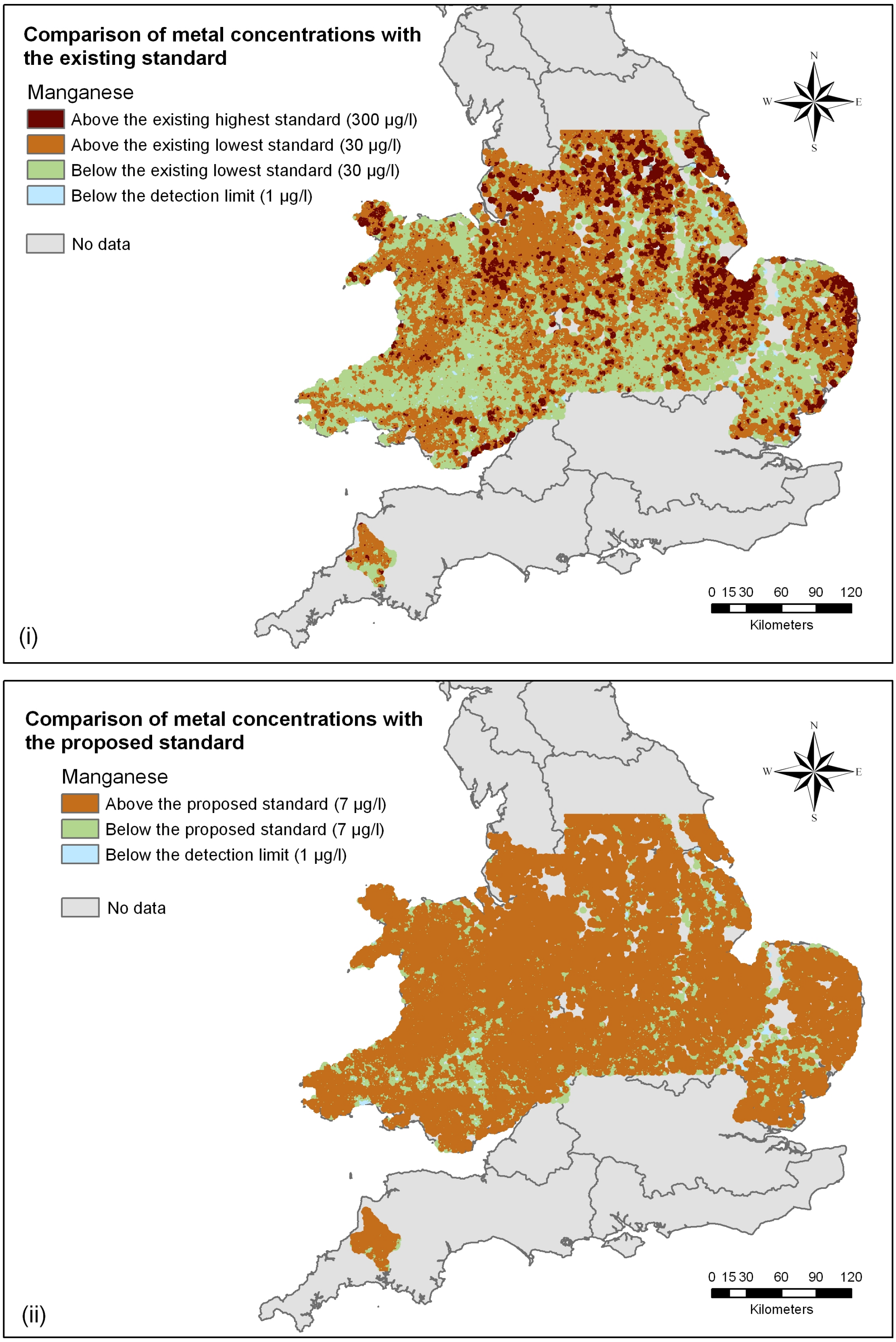


**Figure 3.4c: Comparison of manganese concentrations with (i) existing standards, and (ii) proposed standards.**

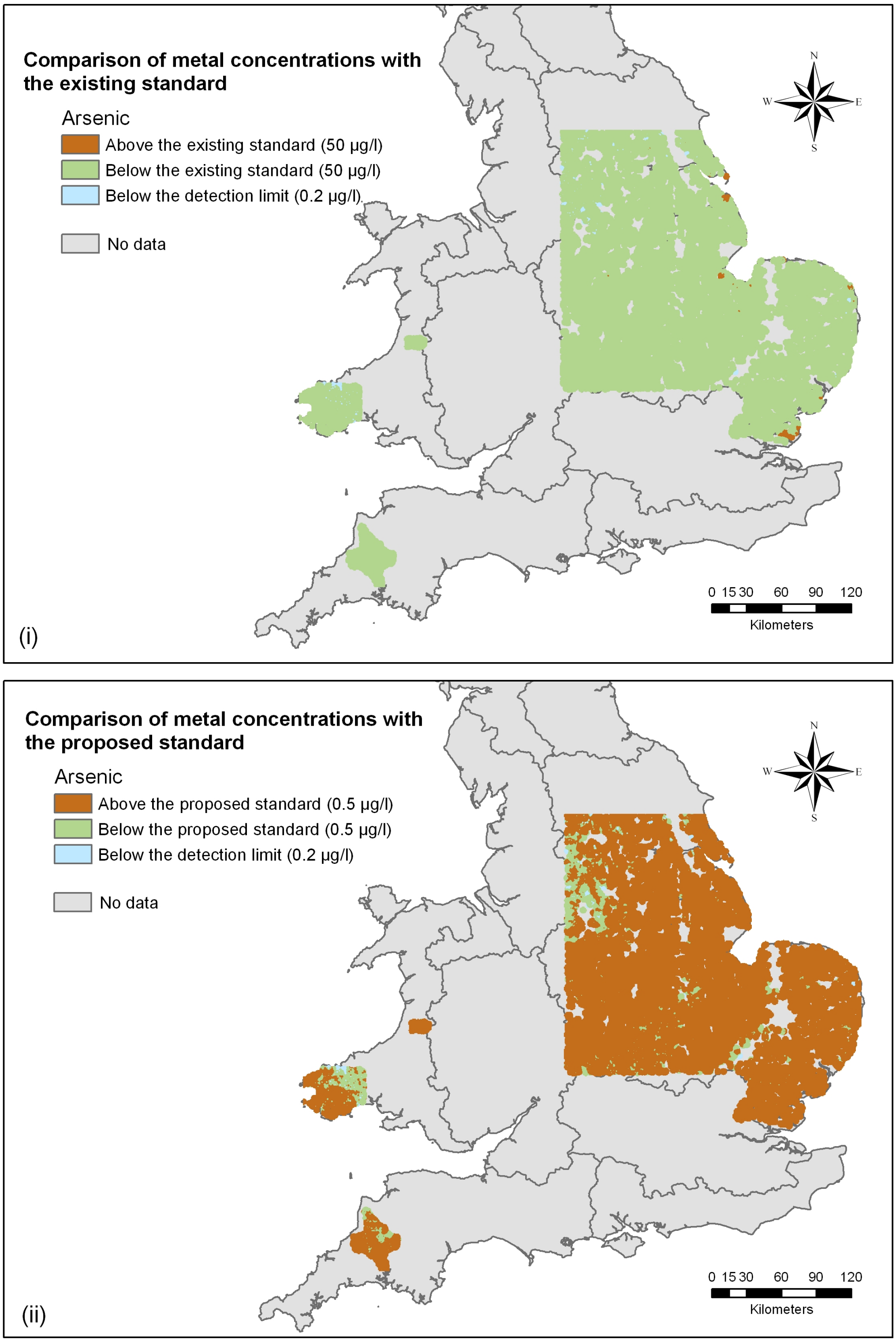


**Figure 3.4d: Comparison of arsenic concentrations with (i) existing standards, and (ii) proposed standards.**

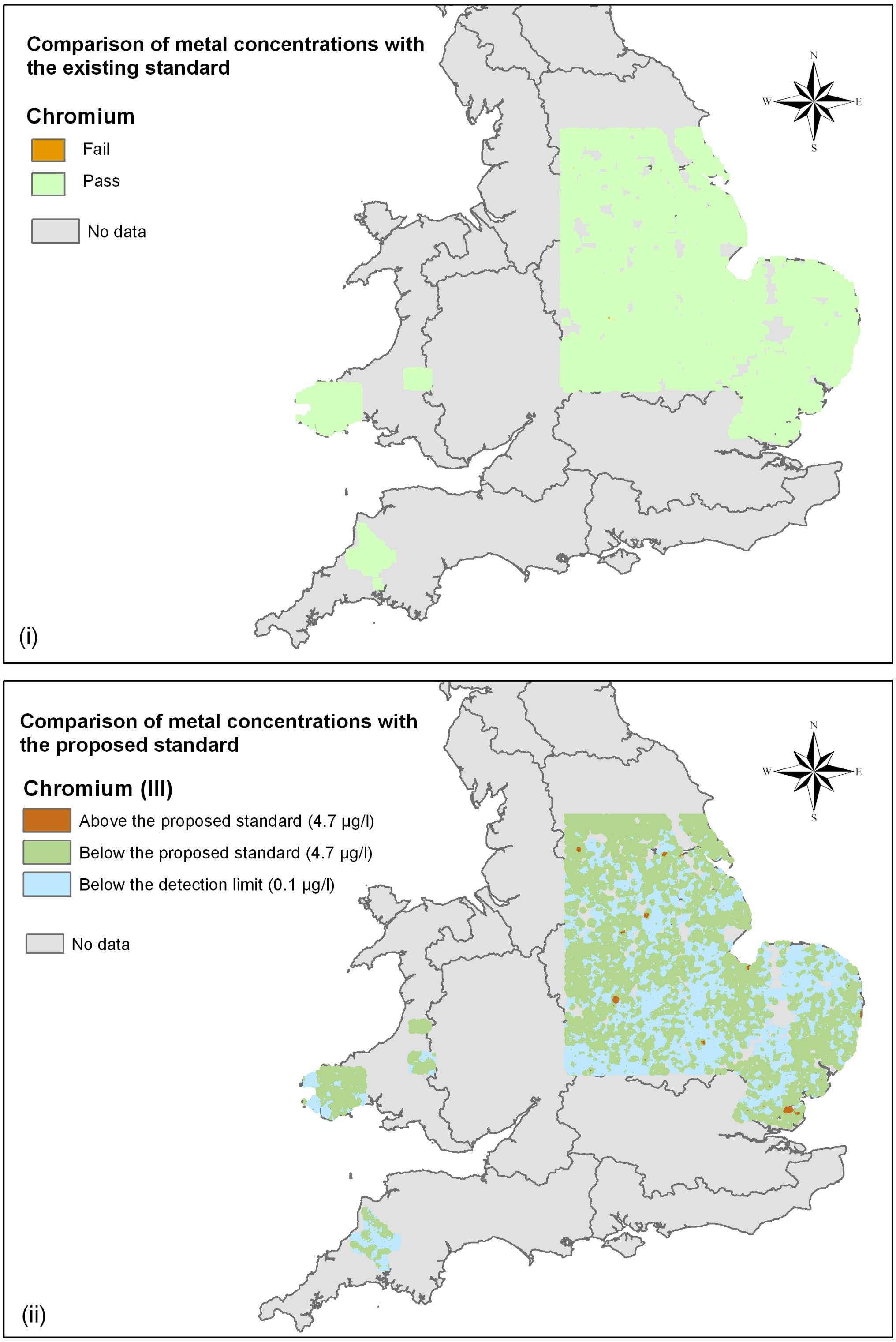


**Figure 3.4e1: Comparison of chromium concentrations with (i) existing standards, and (ii) proposed standards for Cr(III).**

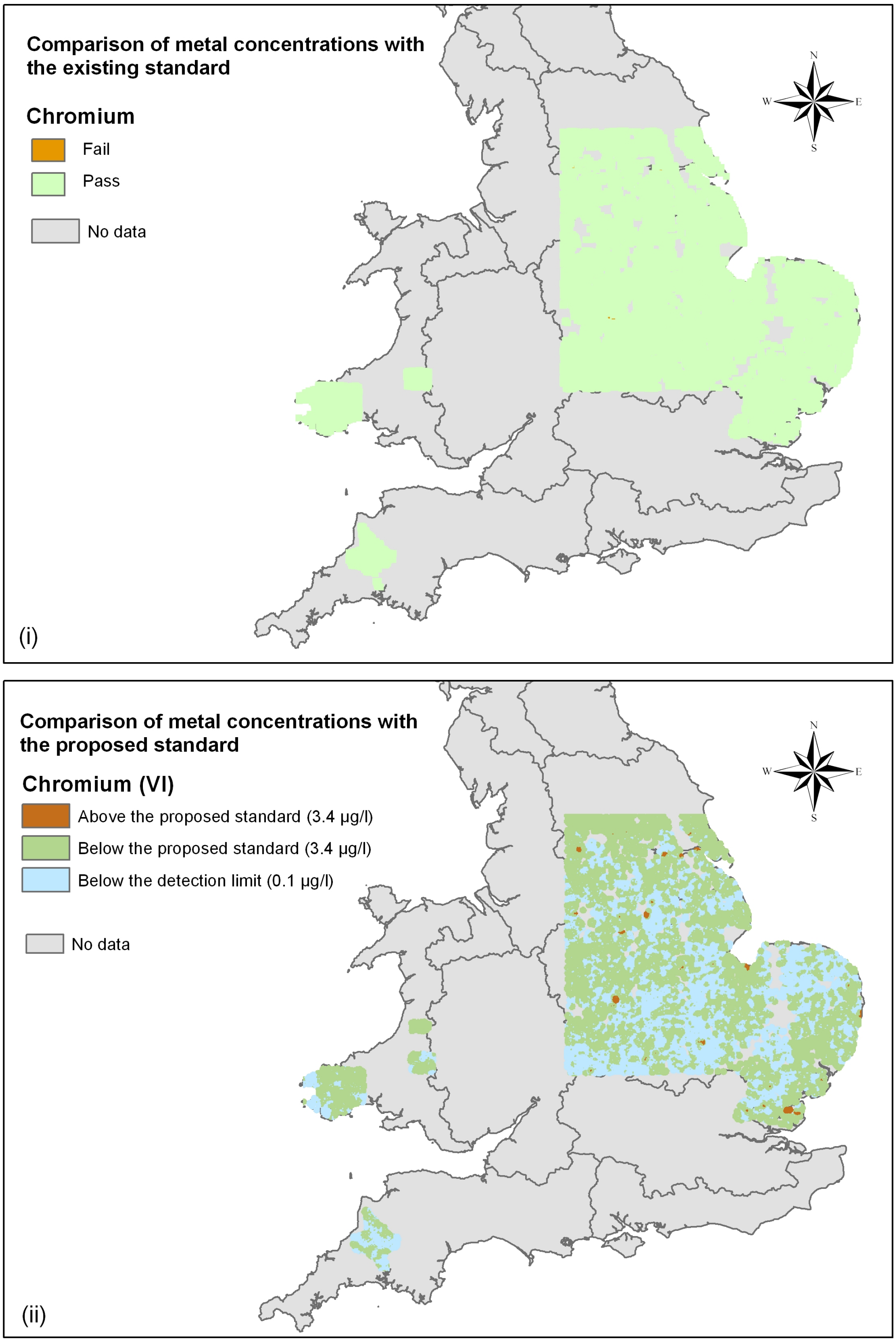


**Figure 3.4e2: Comparison of chromium concentrations with (i) existing standards, and (iii) proposed standards for Cr(VI).**

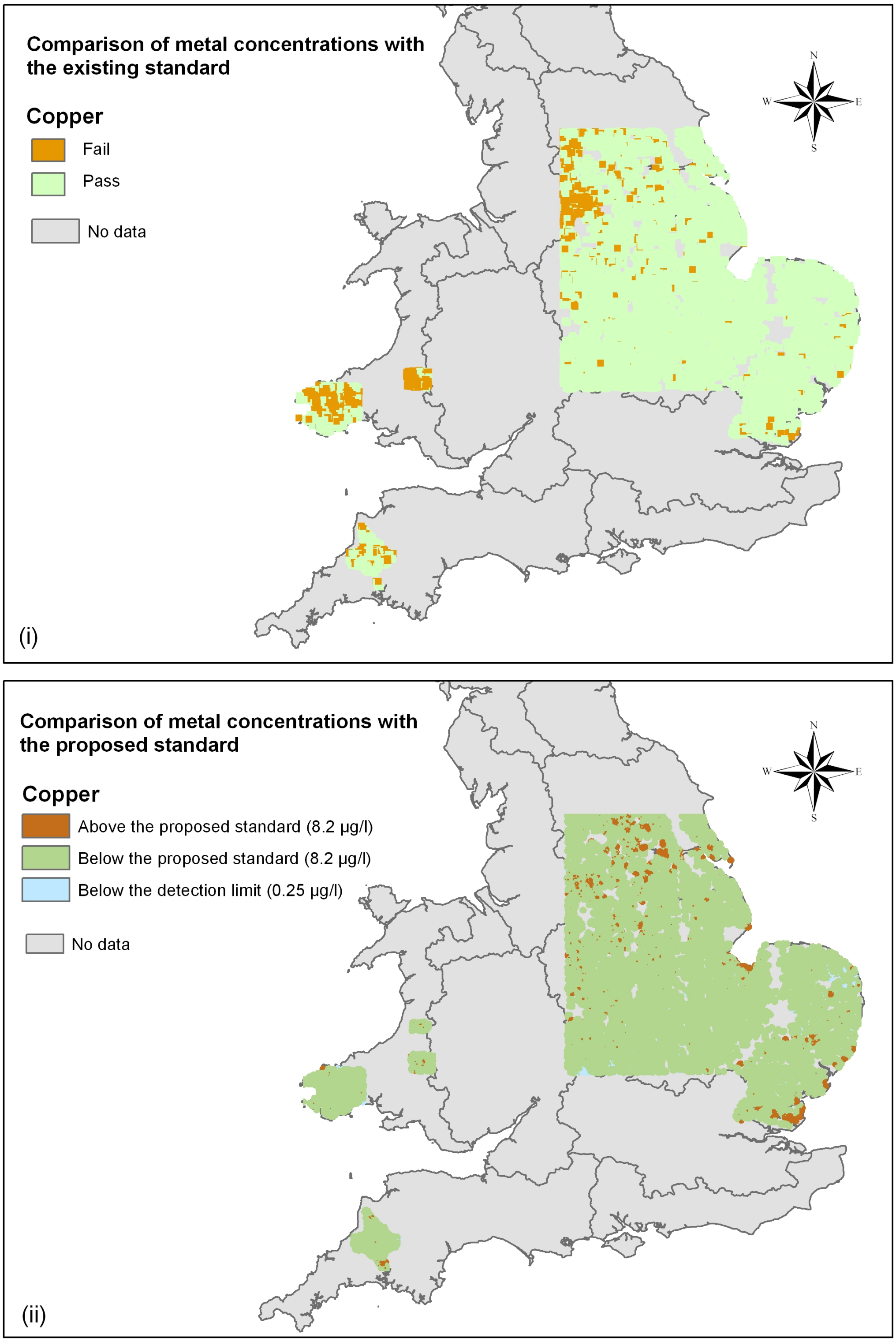


Figure 3.4f: Comparison of copper concentrations with (i) existing standards, and (ii) proposed standards.

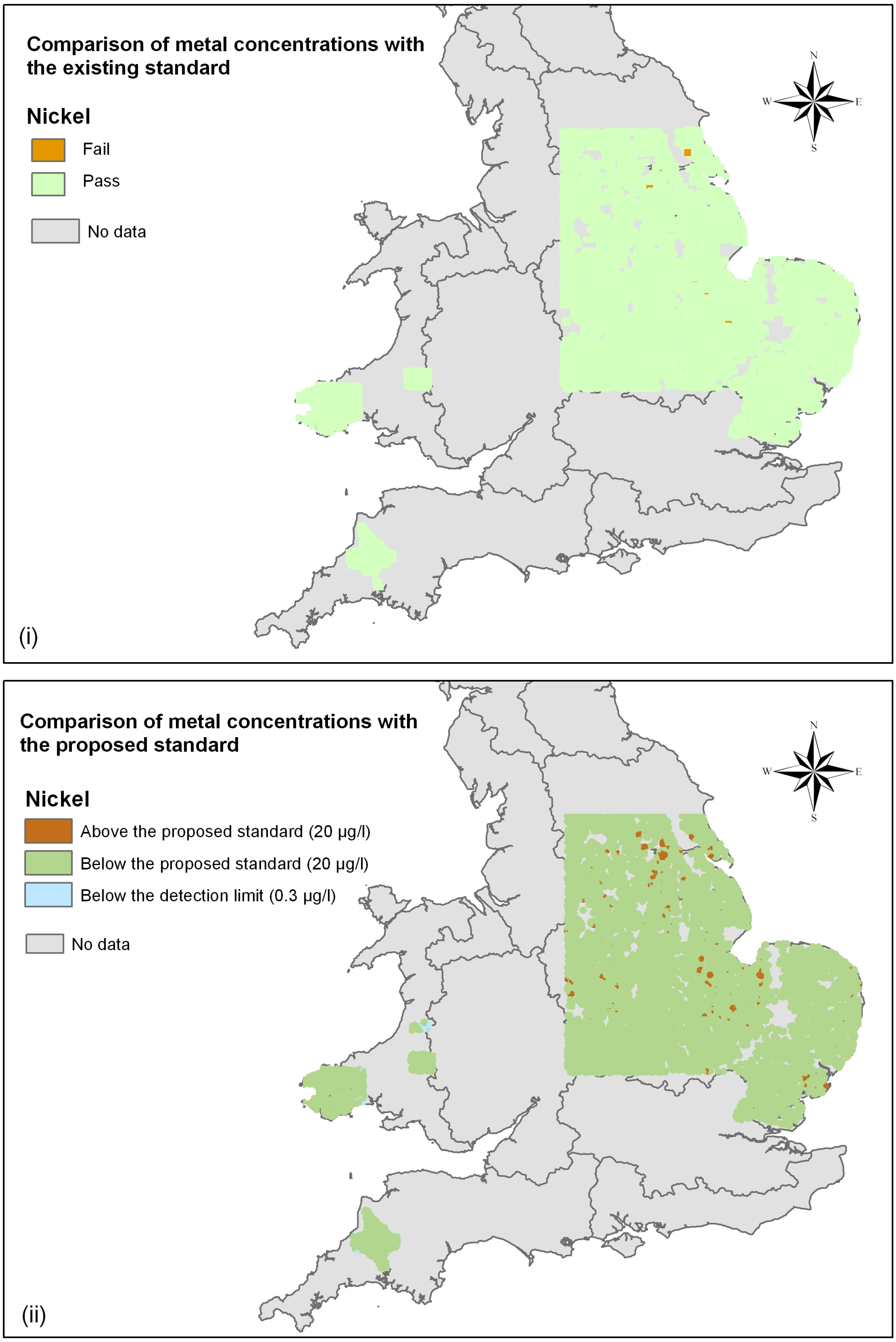


**Figure 3.4g: Comparison of nickel concentrations with (i) existing standards, and (ii) proposed standards**

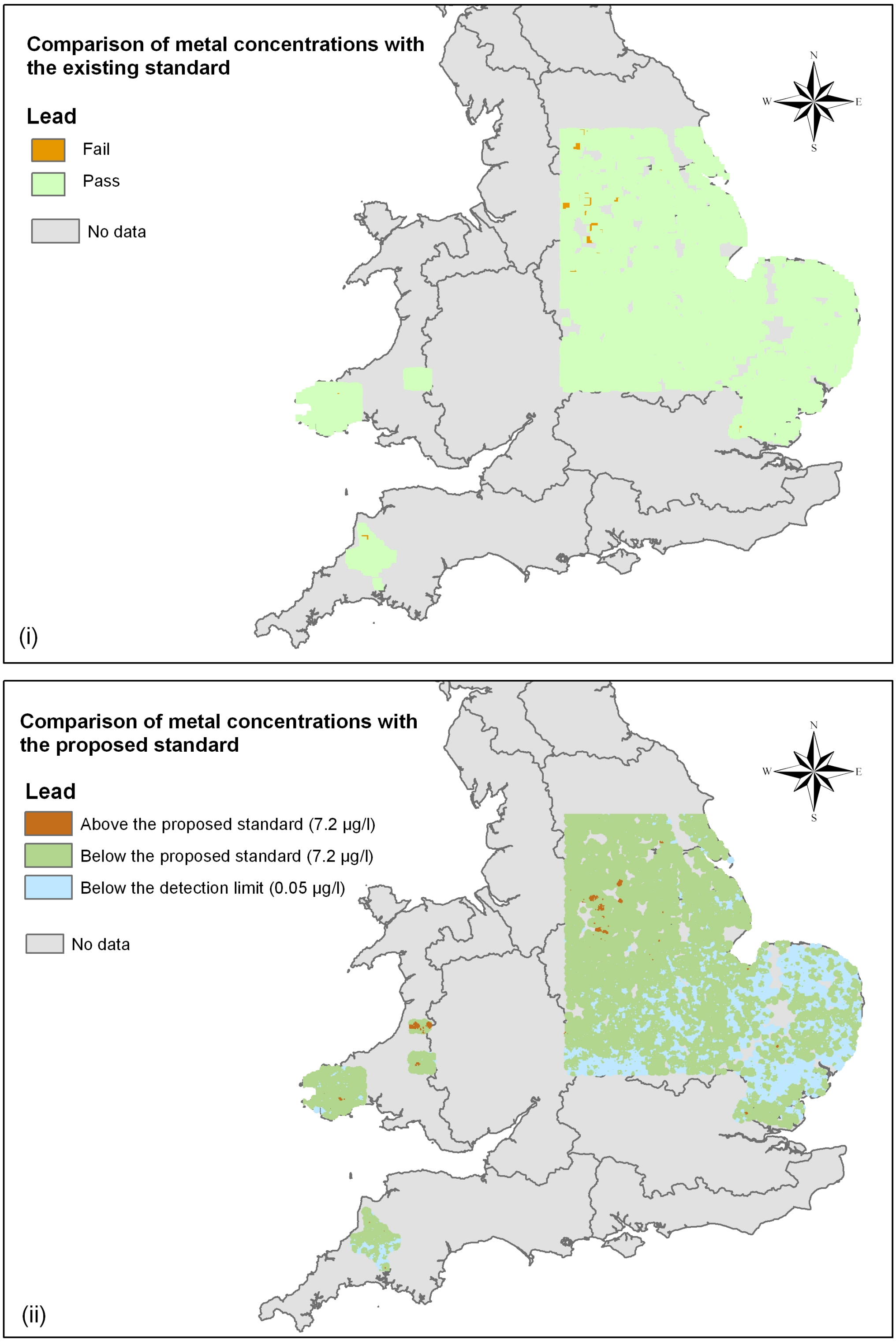


**Figure 3.4h: Comparison of lead concentrations with (i) existing standards, and (ii) proposed standards**

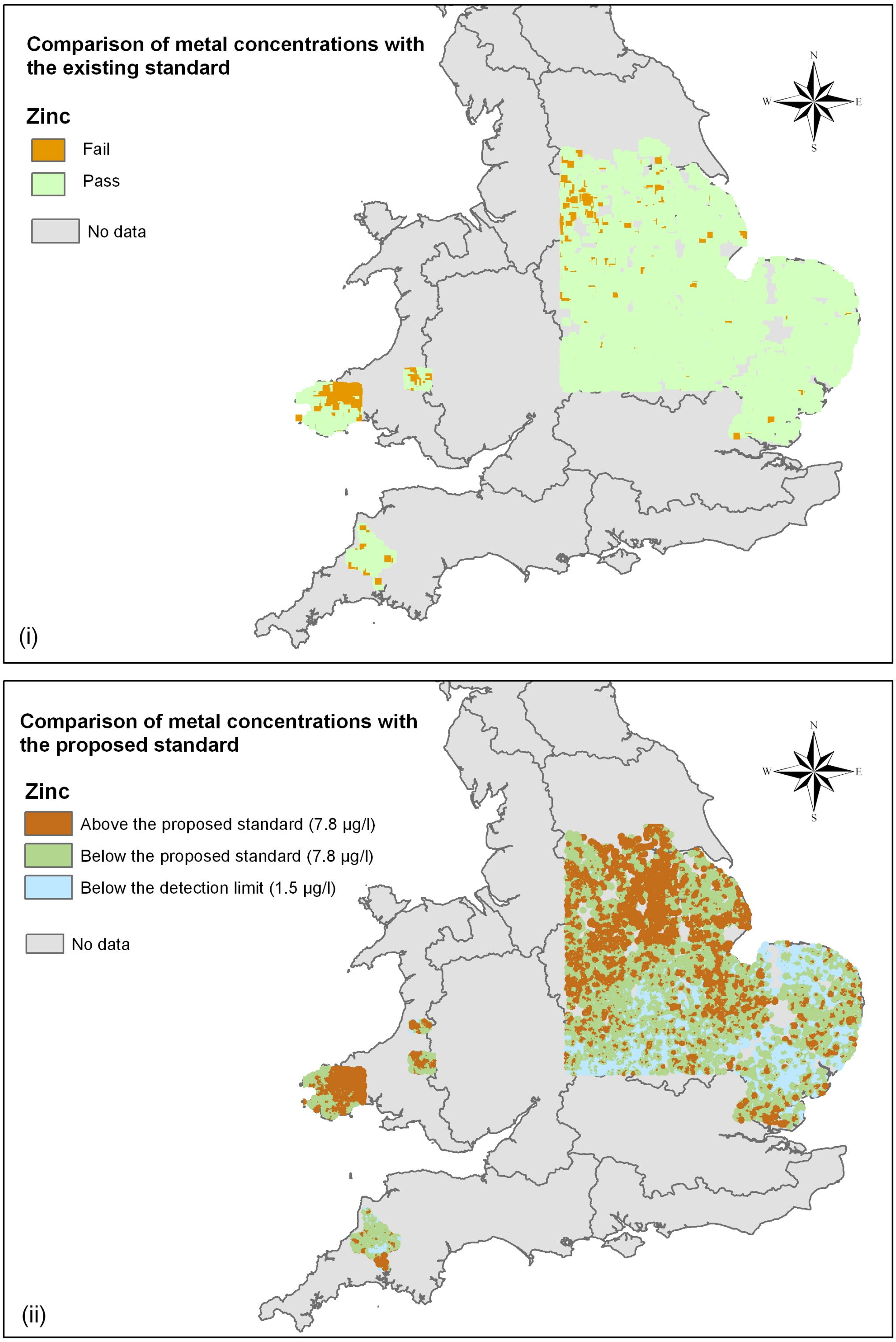


**Figure 3.4i: Comparison of zinc concentrations with (i) existing standards, and (ii) proposed standards**

**Aluminium**, in common with iron and arsenic, is rarely (<1%) high enough in concentration to fail the existing standard. The proposed standard is exceeded more frequently, and the distribution of failures is related to upland regions as described in Section 3.2.1. These failures could be dealt with by a hierarchical approach looking at geological factors and geochemical variables to assess whether natural processes were responsible. The probability distribution of the data, where intersected by the proposed standard (Figure 3.3a), confirms that a substantial proportion of background concentration data are above the proposed standard. By comparison, the existing standard appears to fall at the point of a major break in population (for ICP-AES data), such that the outliers above this point do not appear to form part of the main data population, and would merit further consideration as ‘failures’ of the standard.

**Iron** and **arsenic** both show a large discrepancy between existing and proposed standards. Current standards are passed by most of the sample data (>97%), which suggests that present standards may not be sufficiently protective. Proposed standards, by comparison, could cause significant problems, with potential failure of both in more than 80 per cent of cases due almost entirely to natural background concentrations, which cannot be controlled. Establishing whether the ‘added risk’ approach could be applied might be useful here.

**Manganese** concentrations fail the existing standard in 67 per cent of cases, which can be explained by the geological and geochemical factors described in Section 3.2.3. The proposed standard is failed in more than 75 per cent of samples, and as for iron and arsenic, could cause significant problems with compliance assessment.

**Chromium** (as chromium(III) or chromium(VI)) and **lead** do not present problems of significantly failing to meet existing or proposed standards (≤1%). Those failures which do occur are so localised that it would be appropriate to further investigate the source of these elevated concentrations, to establish if they were linked to contamination.

The existing **copper** standard is failed by 11 per cent of samples, whilst the proposed standard is rarely exceeded. The proposed standard is failed by only four per cent of samples, and these failures tend to be isolated cases, suggesting that anthropogenic influences should be investigated.

**Nickel** concentrations are rarely high enough to fail the existing standard (<1%), but the proposed standards lead to a moderate number of failures, which occur in known geological and geochemical domains. However, the proposed standard is a range, where the specific value applied in compliance assessment will be based on other stream water conditions, which are not yet fully defined. When these conditions can be applied to the data, the number of failures might be reduced.

Failures of **zinc** increase between the current (7%) and proposed (28%) standards. Where there are regional exceedances of the proposed standard, in several areas geological and geochemical factors may explain these. This knowledge could be used to assess whether the failures were due to natural background levels or required further investigation.

# 4 Metal background reference concentrations

## 4.1 Development of 'default' MBRCs

### 4.1.1 Data restrictions

The data used up to this point were G-BASE data which had passed BGS quality control procedures and were applied in the first phase of the project to produce the maps shown in the preceding sections. However, this data may have contained a small proportion of outliers representing anthropogenically affected samples. Whilst it was useful to retain all sample data for completeness of presentation in the preceding section, for the second stage of this work − to develop numerical MBRCs − retaining a large number of outlier concentrations could substantially affect both the mean and highest percentile classes of the data.

This project used the median as the statistical measure of background concentration, which is reasonably robust to outliers, and could reasonably be expected not to be greatly altered by the removal of outliers and statistical re-analysis of the data. But, since a different statistical measure of background concentration (such as the mean) might be used in future, it was decided to generate MBRC values using a 'restricted' dataset, in which the recognised outliers (of urban and mining origin) were removed. This restricted dataset is henceforth referred to as restricted-MBRC (or r-MBRC) data. An alternative approach, based on an assumption of a log-normal data population, is to use the geometric mean. However, given that the data do not conform perfectly to a log-normal population and the median is even more robust as a measure of central tendency, it has been decided not to use the geometric mean in this report.

Outliers in the data may be caused by samples taken in urban or industrial areas. Whilst the G-BASE project seeks to avoid such areas in its sampling programme, a limited number of samples are recorded as being close to such areas. These 468 samples were thus removed from the overall dataset (of 24,000 samples), and were not used further in this study. This sample data cannot however be used to independently assess urban background concentrations as they are not spatially coherent and do not encapsulate major built-up areas.

Mining activities could further enhance regionally anomalous metal concentrations, as described for the orefields of Wales, the Tamar catchment and the Peak District. Samples from these areas could have substantially higher concentrations of some elements, and were therefore removed from the dataset. A BGS database of areas of mining activities was used to identify and remove 900 samples from the overall dataset, although only 120 of these affected the ICP-MS dataset (from the Tamar and Peak District regions). This dataset of samples from mining areas is referred to as 'mining-MBRC' and is used in later sections of this report, with most samples coming from the WFD typology 'siliceous'. This approach was assessed for its potential to determine background concentrations in areas with known historical mining activity.

However, 'mining-MBRC' samples were selected by location rather than by element. Thus, for example, if using this dataset to develop an arsenic-mining MBRC, further restriction might be needed to identify data points in arsenic-mining impacted areas from the whole dataset. Mining-MBRCs in Table 4.4 represent the whole dataset, which for the reasons described above may need refinement for further use. But, use of the median value would diminish the influence of low outliers (non-mining impacted) and might represent a reasonable guideline value for the areas sampled, recognising that these areas do not cover all those that are known to exist in the UK. One recommendation for future work is further development of MBRCs related to mining pressures. Such an approach could make use of specific EA data from sampling at past mining sites, and allow further refinement in relation to the composition of the orebody.

### 4.1.2 Statistical descriptors of the restricted dataset

The concentration for every fifth percentile of the r-MBRC dataset is shown in Tables 4.1a and 4.1b, along with the minimum, maximum and mean concentrations for each metal. The level of detail in the tables should allow ready comparison of any changed proposed standards, with (to the nearest five per cent) level of compliance failures in the r-MBRC data. These tables also permit the future choice of a percentile class other than the median to be used for the background concentration if required. The percentile data are sufficiently robust to outliers (and drawn from such a large population) that even the removal of the maximum value in each dataset does not affect the 95th percentile value. This suggests that even if a small number of anthropogenically affected samples (as outliers), have been missed by the screening process described above, they will not affect the use of the data presented in Tables 4.1a and 4.1b.

The median, highlighted in both tables, was adopted as the ‘default’ MBRC in later sections of this report, being the most nationally relevant value for the background concentration of each metal. As such, it could potentially be used in the absence of other relevant available data, or as a value against which to compare more local data (such as RBD- and catchment-scale data, discussed in Section 5).

In terms of their use for deriving a background value for water quality standards, higher percentile values, such as the 75th percentile value, would result in (25 per cent) less of the data exceeding background concentrations. The use of a lower percentile value would be more protective, but this could create substantially more work in determining failures resulting from natural concentrations rather than anthropogenic input.

In common with the approach taken throughout this report, data are reported to two significant figures, which is considered appropriate, given the scale of variation observed in natural background concentrations.

**Table 4.1a: Statistical summary of r-MBRC dataset concentrations for the minor elements: aluminium, iron and manganese (µg/l).**

| Element | | Aluminium (ICP-AES) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|---|---|
| Minimum | | <14 | <1 | <6 | <1 |
| Percentiles | 5 | <14 | 1.4 | 6.7 | 1.5 |
| | 10 | <14 | 1.9 | 11 | 3.0 |
| | 15 | <14 | 2.4 | 16 | 4.0 |
| | 20 | <14 | 3.0 | 20 | 6.0 |
| | 25 | <14 | 3.6 | 25 | 8.0 |
| | 30 | <14 | 4.2 | 30 | 10 |
| | 35 | <14 | 4.8 | 36 | 12 |
| | 40 | <14 | 5.6 | 42 | 15 |
| | 45 | <14 | 6.4 | 50 | 18 |
| | 50 | 16 | 7.4 | 59 | 22 |
| | 55 | 19 | 8.6 | 70 | 27 |
| | 60 | 23 | 10 | 84 | 34 |
| | 65 | 27 | 12 | 100 | 43 |
| | 70 | 32 | 14 | 130 | 55 |
| | 75 | 39 | 18 | 160 | 72 |
| | 80 | 49 | 22 | 210 | 100 |
| | 85 | 65 | 30 | 280 | 140 |
| | 90 | 93 | 43 | 420 | 230 |
| | 95 | 160 | 86 | 740 | 500 |
| Maximum | | 110,000 | 26,000 | 310,000 | 19,000 |
| Mean | | 56 | 30 | 290 | 140 |

**Table 4.1b: Statistical summary of r-MBRC dataset concentrations for the trace elements: arsenic, chromium, copper, nickel, lead and zinc (µg/l).**

| Element | | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|---|
| | Minimum | <0.2 | <0.1 | <0.25 | <0.3 | <0.05 | <1.5 |
| Percentiles | 5 | 0.31 | <0.1 | 0.41 | 1.4 | <0.05 | <1.5 |
| | 10 | 0.44 | <0.1 | 0.56 | 1.9 | <0.05 | <1.5 |
| | 15 | 0.54 | <0.1 | 0.70 | 2.2 | <0.05 | <1.5 |
| | 20 | 0.64 | <0.1 | 0.82 | 2.4 | <0.05 | <1.5 |
| | 25 | 0.74 | <0.1 | 0.93 | 2.6 | <0.05 | <1.5 |
| | 30 | 0.84 | <0.1 | 1.1 | 2.8 | 0.05 | 1.6 |
| | 35 | 0.94 | <0.1 | 1.2 | 3.0 | 0.06 | 1.9 |
| | 40 | 1.1 | <0.1 | 1.3 | 3.2 | 0.07 | 2.3 |
| | 45 | 1.2 | 0.10 | 1.4 | 3.4 | 0.09 | 2.8 |
| | 50 | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| | 55 | 1.5 | 0.14 | 1.8 | 3.8 | 0.12 | 4.0 |
| | 60 | 1.7 | 0.16 | 2.0 | 4.1 | 0.14 | 4.9 |
| | 65 | 1.9 | 0.18 | 2.2 | 4.4 | 0.17 | 5.9 |
| | 70 | 2.1 | 0.21 | 2.5 | 4.7 | 0.20 | 7.2 |
| | 75 | 2.5 | 0.24 | 2.9 | 5.1 | 0.24 | 9.0 |
| | 80 | 3.0 | 0.29 | 3.3 | 5.7 | 0.30 | 12 |
| | 85 | 3.7 | 0.36 | 4.0 | 6.5 | 0.41 | 15 |
| | 90 | 4.9 | 0.46 | 5.0 | 7.9 | 0.62 | 20 |
| | 95 | 7.9 | 0.72 | 7.2 | 11 | 1.1 | 31 |
| | Maximum | 260 | 1,400 | 150 | 1,000 | 400 | 1,800 |
| | Mean | 2.6 | 0.38 | 2.6 | 4.9 | 0.39 | 9.6 |

### 4.1.3 Comparison of default MBRC values

The median is a reliable indicator of the central tendency of datasets, and in line with current thinking, could thus be adopted from Tables 4.1a and 4.1b to represent the most widely applicable background reference concentrations, denoted r-MRBCs, for England and Wales.

The G-BASE data has also been used to generate a further set of 'default' MBRCs based on WFD typology, shown in Table 4.2a and table 4.2b, recognising that underlying geology has a significant influence on metal concentrations in stream water. This would enable the selection of a geology-specific MBRC for areas where the geology or WFD typology was known, including all river basins. This typology-based MBRC would be more indicative of background concentrations for a specific area, although the degree to which this would result in a significantly different value would depend on individual elements.

It can be seen from Table 4.2a that the median value of chromium, copper and lead do not vary substantially with WFD typology, suggesting that adoption of a single MBRC value for these elements (if an added risk approach is required) would be appropriate. One caveat is that future study at a more local scale may establish specific catchments where a more local MBRC would be more representative of background conditions. The values for the other metals (Table 4.2a and Table 4.2b) show more variation with WFD typology (as a proxy for geology) and suggests that the WFD typology specific MBRCs are likely to be more representative of background metal concentrations. However, this needs to be taken in context of the standard applied in that if the variation in the values for the different typologies is not significant in comparison with the standard value, a single value for the MBRC (e.g. the median of the overall dataset), may well be sufficient. Later work (Section 5) suggests that a localised catchment approach is generally the most robust, partly because the spatial restriction automatically takes underlying geology into account in determining the background concentration at a given location. However, sufficient data is not always available at the local scale to determine an appropriate MBRC, in which case the WFD typology 'default' values presented in this section may be applied.

The generation of different values for the default MBRC could be used in a hierarchical approach to compliance, or to consider the reasons for individual failure. For example, if a water body failed to meet the standard, the nationally applicable default (r-MBRC) could be taken into account, and if the water body still failed, consideration could be given to whether the underlying geology had a sufficiently substantive effect to warrant a typology-specific MBRC. If the water body still failed to comply, this could trigger a higher level of assessment involving a local MBRC (if sufficient local data were available to generate one), or a specific site assessment. Such a hierarchical approach is discussed further in Section 8.

Another data source which could be used to set MBRCs is the EuroGeoSurveys (previously the Forum of European Geological Surveys or FOREGS) project (Salminen *et al.*, 2005; De Vos and Tarvainen, 2006). Median values of this pan-European dataset (collected at a sampling density of one per 100 km$^2$) for metal concentrations in stream water are given in Tables 4.2a and 4.2b, and compared with r-MBRCs and typology-specific MBRCs described above.

European dataset median values are close to r-MBRC values for iron, manganese, lead and zinc. The data for arsenic, copper and nickel are somewhat higher in the r-MBRC dataset, whilst those for aluminium and chromium are much higher in the European dataset. Thus, if European values were adopted as background concentrations, the problem of potentially large scale failure for arsenic would be exacerbated, although it is likely that iron and manganese would not be greatly altered.

**Table 4.2a: Comparison of r-MBRC median, geological typology median and European survey median concentration values (µg/l) for the minor elements.**

| | Aluminium | Iron | Manganese |
|---|---|---|---|
| European+ | 18 | 67 | 16 |
| r-MBRC | 7.4 | 59 | 22 |
| r-MBRC: WFD Siliceous | 18 | 120 | 25 |
| r-MBRC: WFD Calcareous | 6.3 | 41 | 19 |
| r-MBRC: WFD Salt | n/a | 140 | 66 |
| r-MBRC: WFD Peat | 12 | 120 | 81 |
| r-MBRC: WFD Peat (lowland) | 6.8 | 72 | 56 |
| r-MBRC: WFD Peat (upland) | 142 | 304 | 105 |

+ (Salminen *et al.*, 2005); r-MBRC values quoted for Al by ICP-MS analysis.

**Table 4.2b: Comparison of r-MBRC median, geological typology median and European survey median concentration values (µg/l) for the trace elements.**

| | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| European | 0.63 | 0.38 | 0.88 | 1.9 | 0.093 | 2.7 |
| r-MBRC | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| r-MBRC: WFD Siliceous | 0.61 | 0.14 | 1.6 | 2.9 | 0.16 | 5.1 |
| r-MBRC: WFD Calcareous | 1.5 | 0.11 | 1.6 | 3.7 | 0.09 | 2.8 |
| r-MBRC: WFD Salt | n/a | n/a | n/a | n/a | n/a | n/a |
| r-MBRC: WFD Peat | 1.6 | 0.15 | 1.6 | 5.5 | 0.13 | 7.4 |
| r-MBRC: WFD Peat (lowland) | 2.0 | 0.13 | 1.4 | 6.6 | 0.064 | 6.1 |
| r-MBRC: WFD Peat (upland) | 0.63 | 0.31 | 3.5 | 2.7 | 0.82 | 14 |

Whilst the WFD typology has been shown to be of limited use for some elements, the median values for each geological typology are included in Tables 4.2a and 4.2b, because it is a fundamental unit of the WFD approach. If a tiered approach were adopted, it would probably be better to use a level of detail similar to those of ‘PM 250/50’ (see Section 3.1.2), rather than as broad a description as the WFD typologies. This approach is explored in Section 7, with further detail included in Appendix 1. The use of the typologies is still a relevant approach, because this can be used where we do not have the data to support the more detailed approaches (‘PM 250/50’ and/or restriction by geographical scale).

As would be expected from the results of the ANOVA analysis, the WFD typologies give rise to varying amounts of distinction between typology categories. Aluminium concentrations vary little between the r-MBRC median and calcareous typology (which contains the greatest number of samples), whilst these are different to the siliceous and peat typologies which are themselves similar. Iron concentrations are lower in the calcareous typology, with all other classes being much higher in concentration and more similar to each other. Manganese concentrations are lower in the calcareous and siliceous typologies than in peat and salt. The $WFD_p$ data split between lowland and upland peats are shown, since these improved the description of variance within the ANOVA analysis. As expected, concentrations of minor elements are higher in the upland peat sites compared with the lowland sites.

The variation in background concentrations for trace elements is reasonably well described by the use of WFD geological typologies. Arsenic concentrations are lower in the siliceous typology than in the overall dataset, and other typologies, whilst concentrations of nickel and zinc are higher in peat typologies. A systematic difference is evident between upland and lowland peat sites for arsenic and nickel (for which upland < lowland), and copper and zinc (for which upland > lowland). While most of the geological typology data are within the interquartile range of the dataset, exceptions include the data for arsenic in streams over the siliceous typology (where the median is below than the overall dataset 25th percentile) and data for nickel in streams over the organic typology (where the median is above the overall dataset 75th percentile). Overall, the data show a benefit in using a typology-specific MBRC, where substantial variations in typology-specific MBRCs have the greatest implications for compliance failure.

## 4.2 Use of r-MBRC and proposed standards in an 'added risk' approach

Default MBRCs generated so far have been based on median values of the datasets used, and whilst the median is a reliable statistical descriptor, by definition 50 per cent of samples within the dataset will exceed this value. Thus, if used as a measure of background, half the samples will automatically exceed the background value, mostly from natural causes.

Other studies have used different figures for setting the point at which samples no longer form part of the main data population, such as the use of probability plots of the type shown in Figure 3.3 (Sinclair, 1976). In any case, geochemists recognise 'background' (or 'baseline' where background equates to the geochemical baseline in the absence of any anthropogenic contamination) as a concentration range rather than a single figure, which fits with the understanding of data populations (Edmunds *et al.*, 2003). While MBRCs have been generated as single values in this report for clarity and simplicity, this does not preclude the generation of a range of background values, depending on how these would be applied. Indeed, a range could be used to infer a level of confidence in a risk assessment, depending on how close the actual stream water metal concentration was to the upper or lower end of the range encompassing the background concentration plus the standard.

Figures 3.1(a-i) have already shown exceedances of existing and proposed standards in the (unrestricted) dataset. Table 4.3 shows the number of samples from the r-MBRC dataset which exceed these standards, confirming that the greatest expected compliance failure would occur for iron, manganese and arsenic. Table 4.3 also indicates the degree of compliance failure where background concentration is taken into account in the 'added risk' approach.

**Table 4.3: Comparison of r-MBRC data with the proposed standard and proposed standard plus background**

| Element | Standard | r-MBRC (median) | Standard + r-MBRC | Samples > standard | Samples > (standard + r-MBRC) |
|---|---|---|---|---|---|
| | µg/l | µg/l | µg/l | % | % |
| Aluminium (ICP-MS) | 25 | 7.4 | 32 | 18 | 14 |
| Aluminium (ICP-AES) | 25 | 16 | 41 | 37 | 24 |
| Iron | 16 | 59 | 75 | 84 | 43 |
| Manganese | 7 | 22 | 29 | 76 | 43 |
| Arsenic | 0.5 | 1.3 | 1.8 | 87 | 37 |
| Chromium: Cr(III) | 4.7 | 0.12 | 4.8 | <1 | <1 |
| Chromium: Cr(VI) | 3.4 | 0.12 | 3.5 | <1 | <1 |
| Copper | 8.2 | 1.6 | 9.8 | 4 | 3 |
| Nickel (low)* | 4.9 | 3.6 | 8.5 | 28 | 9 |
| Nickel (high)* | 35.6 | 3.6 | 39 | <1 | <1 |
| Lead | 6 | 0.10 | 6.1 | 1 | 1 |
| Zinc | 7.8 | 3.4 | 11 | 28 | 21 |

* A range of possible standards exist for Ni; here, the lowest and highest values are used for comparative purposes.

The most recent available updated standards available for copper, nickel, and lead are given in Appendix 3 (Table A3.1).

Applying the background plus the proposed standard shows promise for iron, manganese and arsenic, as this reduces the extent of failure to a more manageable level. Figures 4.1(a-c) map the location of these continuing failures, along with the areas that would no longer fail. This approach could be extended to any metal in stream water.

In these figures, the first map compares geochemical data with the proposed standard, reproduced here from Figures 3.4b – 3.4d, for ease of cross-comparison. The second map compares the data with the r-MBRC median added to the proposed standard (as shown in Table 4.3). In each case, the r-MBRC median exceeds the proposed standard. These maps include all the data (not just the sites used in the r-MBRC approach), in order to provide complete information, and the fact that any site exclusions would only apply for specific metals.

In the second map, dark purple areas show which data exceed the r-MBRC median plus the proposed standard. These areas would still fail if the r-MBRC median was incorporated into the WFD assessment. But, where they are spatially coherent regions explainable by geochemical conditions in stream waters (Section 3), they could be assessed by a tiered approach for failure due to natural conditions, and the use of a higher percentile statistic for the MBRC value (see Section 7).

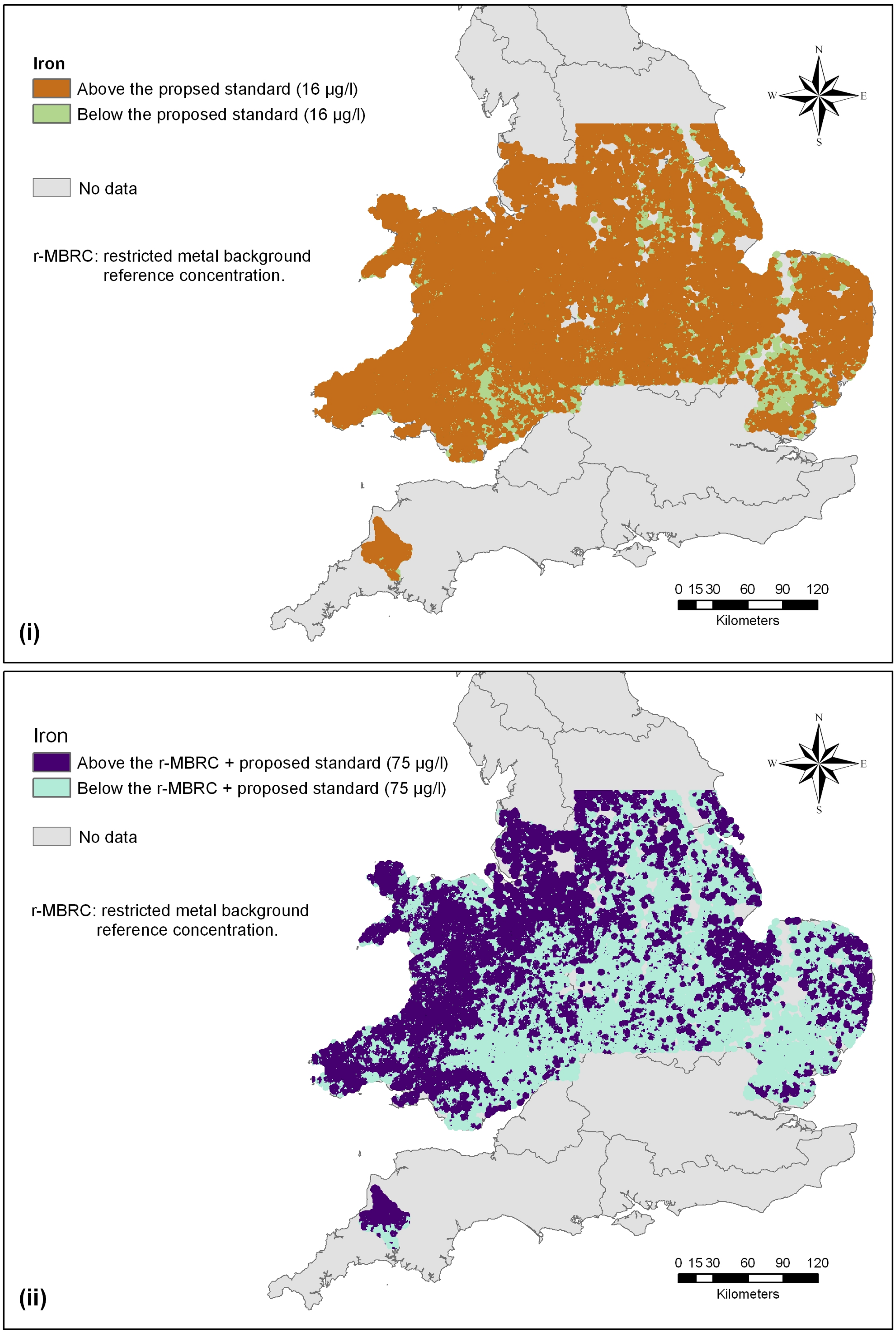


**Figure 4.1a: Comparison of iron concentrations with (i) the proposed standard, and (ii) the added-risk approach, using the proposed standard plus the r-MBRC.**

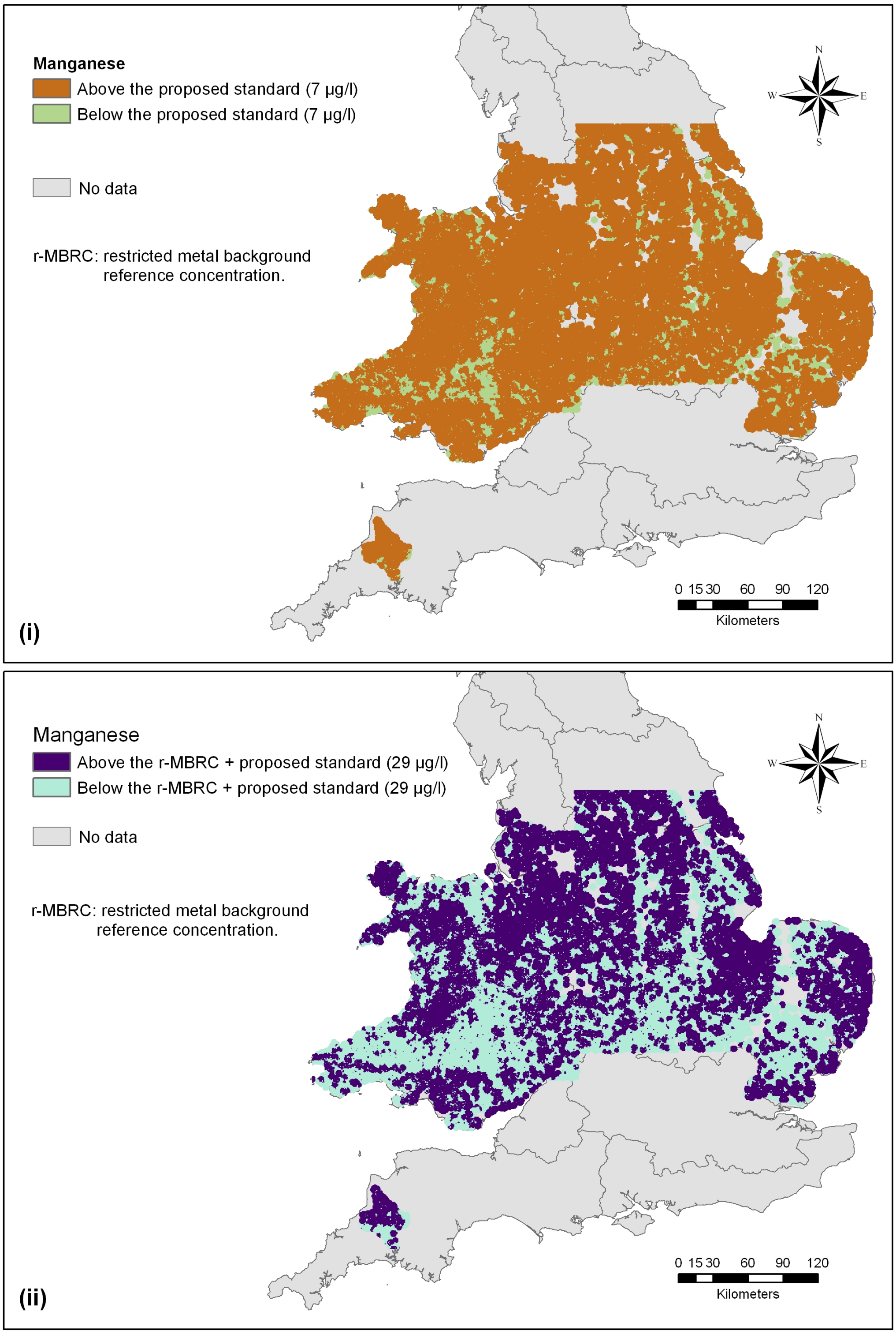


**Figure 4.1b: Comparison of manganese concentrations with (i) the proposed standard, and (ii) the added-risk approach, using the proposed standard plus the r-MBRC.**

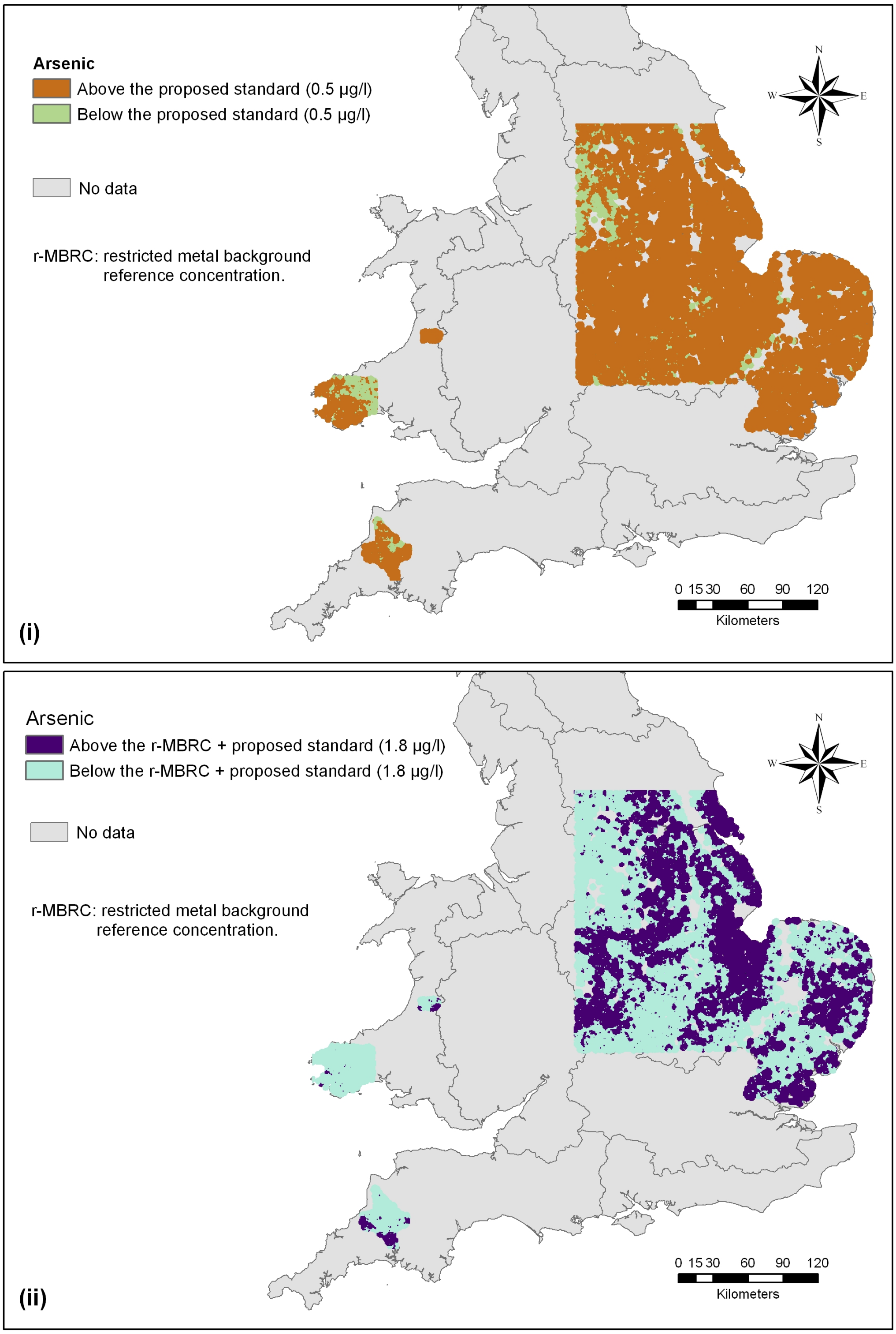


**Figure 4.1c: Comparison of arsenic concentrations with (i) the proposed standard, and (ii) the added-risk approach, using the proposed standard plus the r-MBRC.**

Although the addition of background concentration to the proposed standard substantially reduces the extent of potential compliance failure, these metals would likely remain problematic if a ‘pass/fail’ compliance regime were adopted.

### 4.2.1 Mining-MBRC median concentrations

Median concentrations for the mining-MBRC dataset are summarised in Table 4.4a and 4.4b for comparison with r-MBRC values. These could be used as background concentrations for areas where mining has taken place, to indicate where failure might arise from geochemical processes associated with mining and mine waste. We reiterate the consideration of sample sites selected purely on location, and not on the composition of minerals in the orefield, which is borne out by the mining-MBRC median for nickel. None of the mineralised areas sampled are associated with nickel mineralisation, and the mining-MBRC for nickel is actually lower than the r-MBRC because the highest concentrations, found in the survey thus far, are related to other geological and geochemical environments. Systematic variations in the relative abundance of the trace elements in other orefields would be expected to be reflected in whether they are elevated in stream waters (or not) in any specific area.

**Table 4.4a: Mining-MBRC median values for minor elements (all concentrations in μg/l)**

| | Aluminium (ICP-AES) | Aluminium (ICP-MS)^ | Iron | Manganese |
|---|---|---|---|---|
| r-MBRC | 16 | 7.4 | 59 | 22 |
| Mining-MBRC* | 39 | 9.4 | 81 | 25 |
| Mining-MBRC*: WFD Siliceous (n = 870) | 41 | 9.8 | 85 | 25 |
| Mining-MBRC*: WFD Calcareous (n = 40) | <14 | 5.7 | 45 | 15 |
| Mining-MBRC*: WFD Salt (n = 0) | n/a | n/a | n/a | n/a |
| Mining-MBRC*: WFD Peat (n = 70) | 66 | 8.9 | 80 | 41 |

* See Section 4.1.1 for more details on the restrictions associated with these data.

^ Sample numbers for this method are the same as those in Table 4.4b.

**Table 4.4b: Mining-MBRC median values for trace elements (all concentrations in μg/l)**

| | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| r-MBRC | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| Mining-MBRC* | 0.83 | <0.1 | 1.3 | 2.1 | 0.13 | 5.4 |
| Mining-MBRC*: WFD Siliceous (n = 100) | 0.86 | <0.1 | 1.2 | 1.7 | 0.10 | 4.7 |
| Mining-MBRC*: WFD Calcareous (n = 20) | 0.73 | 0.12 | 1.6 | 4.2 | 0.27 | 6.1 |
| Mining-MBRC*: WFD Salt (n = 0) | n/a | n/a | n/a | n/a | n/a | n/a |
| Mining-MBRC*: WFD Peat (n = 5) | 1.0 | 0.18 | 3.4 | 19 | 0.95 | 19 |

* See Section 4.1.1 for more details on the restrictions associated with these data.

The mining-MBRC is above the r-MBRC for zinc and lead, which is consistent with lead and zinc mineralisation in the Peak District (mostly calcareous) and some ores of the Tamar (mostly siliceous) catchment. Aluminium measured by ICP-AES is also one of the largest differentials between the two median concentrations; this reflects the low pH environment across most of the Welsh orefields, which may be exacerbated by sulphide oxidation processes (acid mine drainage), thereby increasing aluminium concentrations. These are also the largest areas of sampling associated with approximately 800 samples, suggesting that values are more reliable than for some other mining-MBRC categories. Other metals do not show a great deal of variation between r-MBRC and mining-MBRC values. In the case of arsenic and copper, which were mined in the south Tamar catchment, this is probably due to lower concentrations in Peak District mining area stream waters, and high natural background concentrations in eastern England which are not associated with mining. This illustrates the need for further refinement of mining-MBRC values.

# 5 Development of local MBRC values

The fact that, for some metals, background concentrations might exceed not only the proposed standards, but also concentrations in the 'added risk' approach (median plus standard) encourages examination of the data at more local scales.

Unlike earlier sections of this report where the whole dataset was used, data in many of the tables in this section include the sample numbers alongside median concentrations. Low numbers of samples occur in some sections, with a large disparity in sample numbers between some subsections. Sample numbers are thus a check on the reliability of the data, so that important decisions are not made based on very small or localised, datasets. One limitation of the G-BASE dataset is that it is incomplete (Figure 2.4), so care should be taken in cross-referencing information to set concentrations for a river basin district (RBD). This is further illustrated in the RBD-specific maps in Appendix 1.

## 5.1 MBRC values by river basin district

River basin districts (RBDs) are a fundamental reporting unit of the WFD, so defining background concentrations for these areas (where possible) may be a useful indicator of possible compliance problems with proposed standards. Equally, generating localised MBRCs for specific RBDs may enable a more realistic MBRC to be used in the 'added risk' approach, or to provide evidence for the underlying reasons for compliance failure.

RBDs are shown in Figures 2.1 and 2.4, and indicate that not all RBDs are fully covered by G-BASE data, and some have no data at all. Tables 5.1a and 5.1b give overall MBRCs for each RBD, and Tables 5.2a and 5.2b give WFD typology-specific MBRCs for each RBD, where sufficient data exist to calculate these. There are some 'gaps' in the tables where not all typologies are available in each district, or specific analytical data are not available as a result of sampling limitations discussed previously (Section 2).

**Table 5.1a: The r-MBRC data (median values) by river basin district, minor elements (all concentrations in µg/l)**

| r-MBRC | Aluminium (ICP-AES) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|---|
| Default | 16 | 7.4 | 59 | 22 |
| RBD01 (Thames)^ | 9.1 | 4.5 | 26 | 11 |
| RBD03 (South West)^ | 9.7 | 7.9 | 260 | 41 |
| RBD04 (Severn)^ | 19 | 6.0 | 52 | 18 |
| RBD05 (Western Wales) | 28 | 32 | 100 | 19 |
| RBD06 (Dee) | 42 | n/a | 150 | 37 |
| RBD07 (North West)^ | 38 | 61 | 150 | 71 |
| RBD09 (Humber)^ | 12 | 12 | 51 | 34 |
| RBD10 (Anglian) | 4.6 | 4.5 | 38 | 19 |

RBDs 02, 08 and 'Scottish Border' have no ICP-AES data
^ RBDs which are incompletely sampled (Figure 2.4)

**Table 5.1b: The r-MBRC data (median values) by river basin district, trace elements (all concentrations in µg/l)**

| r-MBRC | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| Default | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| RBD01 (Thames)^ | 0.98 | <0.1 | 0.81 | 3.5 | <0.05 | <1.5 |
| RBD03 (South West)^ | 0.64 | <0.1 | 1.0 | 3.0 | 0.08 | 1.9 |
| RBD04 (Severn)^ | 1.4 | <0.1 | 1.2 | 3.1 | 0.06 | <1.5 |
| RBD05 (Western Wales) | 0.57 | 0.21 | 1.8 | 1.9 | 0.20 | 11 |
| RBD07 (North West)^ | 0.42 | 0.17 | 2.7 | 2.3 | 0.36 | 6.9 |
| RBD09 (Humber)^ | 1.5 | 0.16 | 2.2 | 3.8 | 0.20 | 6.0 |
| RBD10 (Anglian) | 1.5 | <0.1 | 1.3 | 3.8 | 0.06 | 2.1 |

RBDs 02, 06, 08 and 'Scottish Border' have no ICP-MS data

^ RBDs which are incompletely sampled (Figure 2.4)

Differences in the median concentrations of the RBDs are evident, although these variations are not systematic between the different elements. Concentrations are generally lower in RBDs 01, 03, 04 and 10 for aluminium, chromium, lead and zinc, with these elements having higher concentrations in RBD07. Arsenic concentrations are highest in RBDs 04, 09 and 10 and lowest in RBD07. Nickel concentrations do not appear to vary by RBD classification.

**Table 5.2a: MBRC values for the minor elements, classified by WFD geological typology within each RBD (all concentrations in µg/l)**

| r-MBRC | WFD typology (sample numbers) | Aluminium (ICP-AES) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|---|---|
| RBD01 (Thames)[^] | Calcareous* (211) | 9.1 | 4.5 | 26 | 11 |
| RBD03 | Siliceous (390) | 9.6 | 7.8 | 273 | 42 |
| (South West)[^] | Calcareous (13) | 13 | 14 | 40 | 12 |
| RBD04 | Siliceous (2200) | 30 | n/a | 142 | 26 |
| (Severn)[^^] | Calcareous (4200) | 14 | 6.0 | 35 | 15 |
| | Salt (16) | 28 | n/a | 118 | 64 |
| | Peat (33) | 42 | n/a | 96 | 53 |
| | WFD$_p$ – lowland peat (14) | 15 | n/a | 80 | 57 |
| | WFD$_p$ – upland peat (19) | 100 | n/a | 97 | 50 |
| RBD05 | Siliceous (3500) | 31 | 33 | 101 | 19 |
| (Western Wales)[^^] | Calcareous (760) | 16 | 30 | 72 | 12 |
| | Peat[++] (50) | 100 | n/a | 169 | 67 |
| RBD06 | Siliceous (490) | 49 | n/a | 160 | 36 |
| (Dee) | Calcareous (200) | 28 | n/a | 109 | 29 |
| | Salt (12) | 27 | n/a | 188 | 67 |
| | Peat[++] (7) | 60 | n/a | 112 | 70 |
| RBD07 | Siliceous (100) | 29 | 43 | 96 | 36 |
| (North West)[^^] | Calcareous (140) | 27 | 27 | 137 | 68 |
| | Salt (40) | 26 | n/a | 142 | 89 |
| | Peat (57) | 133 | 173 | 343 | 129 |
| | WFD$_p$ – lowland peat (6) | 39 | n/a | 231 | 91 |
| | WFD$_p$ – upland peat (51) | 167 | 173 | 343 | 129 |
| RBD09 | Siliceous (550) | 14 | 22 | 135 | 39 |
| (Humber)[^] | Calcareous (3000) | 11 | 10 | 46 | 32 |
| | Peat (118) | 87 | 82 | 394 | 123 |
| | WFD$_p$ – lowland peat (38) | 6 | 14 | 50 | 117 |
| | WFD$_p$ – upland peat (75) | 127 | 131 | 734 | 125 |
| RBD10 | Siliceous (180) | 0.45 | 4.6 | 37 | 19 |
| (Anglian) | Calcareous (3800) | 4.5 | 4.3 | 37 | 18 |
| | Peat[+] (300) | 10 | 6.0 | 72 | 52 |

RBDs 02, 08 and ‘Scottish Border’ have no ICP-AES data.

[^] RBDs which are incompletely sampled (Figure 2.4).

[^^] RBDs which have less ICP-MS data than ICP-AES data (see Figure 2.4).

* All samples are from the ‘calcareous’ WFD typology.

[+] All samples are WFD$_p$ lowland peat.

[++] All samples are WFD$_p$ upland peat.

**Table 5.2b: MBRC values for the trace elements, classified by WFD geological typology within each RBD (all concentrations in µg/l)**

| r-MBRC | WFD typology | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|---|
| RBD01 (Thames)^ | Calcareous* (202) | 0.98 | <0.1 | 0.81 | 3.5 | <0.05 | <1.5 |
| RBD03 | Siliceous (390) | 0.63 | <0.1 | 1.0 | 3.0 | 0.078 | 1.9 |
| (South West)^ | Calcareous (13) | 4.9 | 0.42 | 1.1 | 1.0 | <0.05 | 2.1 |
| RBD04 | Siliceous (5) | n/a | <0.1 | 1.8 | 1.1 | 0.26 | 5.6 |
| (Severn)^# | Calcareous (790) | 1.4 | <0.1 | 1.2 | 3.1 | 0.06 | <1.5 |
| RBD05 (Dee)# | Siliceous (510) | 0.53 | 0.21 | 1.8 | 2.0 | 0.18 | 12 |
| | Calcareous (140) | 0.75 | 0.18 | 1.7 | 1.6 | 0.26 | 8.0 |
| | Peat++ (2) | n/a | 0.27 | 2.3 | 3.2 | 0.69 | 19 |
| RBD07 | Siliceous (80) | 0.31 | 0.13 | 2.2 | 1.9 | 0.26 | 5.5 |
| (North West)^ | Calcareous (10) | 0.39 | <0.1 | 4.1 | 3.1 | 0.17 | 12 |
| | Peat++ (50) | 0.63 | 0.26 | 4.3 | 2.7 | 0.98 | 17 |
| RBD09 | Siliceous (540) | 0.56 | 0.18 | 2.1 | 3.2 | 0.30 | 5.3 |
| (Humber)^ | Calcareous (2750) | 1.8 | 0.16 | 2.3 | 3.9 | 0.17 | 5.7 |
| | Peat (113) | 1.1 | 0.25 | 2.6 | 3.2 | 0.56 | 14 |
| | WFD$_p$ – lowland peat (38) | 2.7 | 0.16 | 2.3 | 9.2 | 0.17 | 17 |
| | WFD$_p$ – upland peat (75) | 0.61 | 0.40 | 3.2 | 2.6 | 0.75 | 13 |
| RBD10 (Anglian) | Siliceous (180) | 1.3 | <0.1 | 1.2 | 4.0 | <0.05 | 2.4 |
| | Calcareous (3800) | 1.5 | <0.1 | 1.3 | 3.7 | 0.056 | 1.9 |
| | Peat+ (300) | 1.9 | 0.13 | 1.4 | 6.5 | 0.056 | 5.3 |

RBDs 02, 06, 08 and 'Scottish Border' have no ICP-MS data.
^ RBDs which are incompletely sampled (Figure 2.4).
# RBDs 4 and 5 have less arsenic data than is available for other elements (see Figure 3.4).
* All samples from RBD 1 are from the 'calcareous' WFD typology.
+ All peat within WFD$_p$ lowland peat.
++ All peat within WFD$_p$ upland peat.

Tables 5.2a and 5.2b reveal substantial differences in MBRC values for different typologies (notably the peat typologies), and between river basin districts. This shows that more localised and typology-specific MBRCs would be useful for the 'added risk' approach, depending on the degree of difference between the MBRC and proposed standard. The more similar the scale of the MBRC and standard, the greater effect the choice of values given in the tables above would have.

Data classified by WFD typology within the RBDs include the previously described WFD$_p$ split between upland and lowland peat bodies. Substantial differences can be seen for most metals, the main exceptions being chromium (where data are only just above the detection limit) and copper (as may be expected from the ANOVA analysis).

Concentrations of mining-MBRC median values are classified by RBD in Tables 5.3a and 5.3b. These show more clearly the influence of the ore-bodies in the regions considered, and may be more appropriate background concentrations in such areas than ‘default’ values. For example, the Humber region (RBD09) encompassing the Peak District lead-zinc mineralisation has substantially higher background concentrations for both lead and zinc than default r-MBRC values (particularly for lead). Considerable variation within WFD typologies is also visible, in this case especially for zinc. The data also indicate the influence of pH on aluminium and iron concentrations in stream waters, even where mining activity has taken place, since these are generally lower over the calcareous lithologies than in other categories. This shows the influence of pH on stream water concentrations of some metals over and above the impact of natural abundance.

**Table 5.3a: Mining-MBRC data (median values) by river basin district for the minor elements (all concentrations in μg/l)**

| | WFD typology | Aluminium (ICP-AES) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|---|---|
| r-MBRC | All (22,000) | 16 | 7.4 | 59 | 22 |
| Mining-MBRC | All (937) | 39 | 9.4 | 81 | 24 |
| Mining-MBRC: RBD03 (South west) | All (71) | 7.3 | 7.4 | 35 | 10 |
| Mining-MBRC: RBD04 | All (205) | 55 | * | 124 | 31 |
| (Severn) | (1) Siliceous (195) | 55 | * | 125 | 32 |
| | (2) Calcareous | 8.9 | * | 41 | 6.0 |
| | (4) Peat (5) | 197 | * | 85 | 24 |
| Mining-MBRC: RBD05 | All (601) | 45 | 27 | 75 | 24 |
| (Western Wales) | (1) Siliceous (570) | 45 | * | 77 | 24 |
| | (2) Calcareous | 22 | * | 46 | 7.0 |
| | (4) Peat (18) | 65 | * | 79 | 49 |
| Mining-MBRC: RBD06 | All (14) | 93 | * | 245 | 35 |
| (Dee) | (1) Siliceous (10) | 100 | * | 290 | 35 |
| | (2) Calcareous | 17 | * | 176 | 70 |
| Mining-MBRC: RBD07 (North west) | All (2) | 290 | * | 408 | 162 |
| Mining-MBRC: RBD09 | All (44) | 2.8 | 9.9 | 65 | 29 |
| (Humber) | (1) Siliceous (22) | 8.4 | 12 | 65 | 40 |
| | (2) Calcareous | <1 | 5.7 | 39 | 20 |
| | (4) Peat (4) | 3.9 | 8.9 | 128 | 457 |

Sample numbers are shown in brackets after the typology information in Column 2.

**Table 5.3b: Mining-MBRC data (median values) by river basin district for the trace elements (all concentrations in µg/l)**

| | WFD typology | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|---|
| r-MBRC | All (10,000) | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| Mining-MBRC | All (150) | 0.83 | <0.1 | 1.3 | 2.1 | 0.13 | 5.4 |
| Mining-MBRC: RBD03 (South west) | All (70) Siliceous | 1.2 | <0.1 | 0.81 | 1.5 | 1.5 | 3.3 |
| Mining-MBRC: RBD05 (Western Wales) | All (33) Siliceous | 0.29 | 0.16 | 1.5 | 1.4 | 1.4 | 11 |
| Mining-MBRC: RBD09 | All (45) | 0.57 | 0.10 | 1.8 | 4.2 | 4.2 | 5.8 |
| (Humber) | (1) Siliceous (22) | 0.50 | <0.1 | 1.8 | 4.0 | 0.58 | 4.4 |
| | (2) Calcareous (18) | 0.80 | 0.11 | 1.6 | 4.2 | 0.38 | 6.4 |
| | (4) Peat (4) | 1.0 | 0.15 | 3.0 | 19 | 0.97 | 42 |

Sample numbers are shown in brackets after the typology information in Column 2.

Care should be taken when interpreting values in these tables, partly because they have been generated without consideration of which metals are linked to mining activities in specific regions. For example, while lead and zinc are known to have been mined in the Trent (Peak District) region (part of RBD09), assuming chromium has not, the chromium mining-MBRC value should not be too different to the default. In many cases, the mining that has taken place has been very localised, and may therefore only be differentiated at the sub-catchment scale. Equally, stream water geochemistry should be taken into account, to consider whether geochemical conditions are likely to mobilise sufficient metal from the ore-body into the water column to have an impact on the MBRC value. This is the case for aluminium and iron, which have lower concentrations in calcareous stream waters than other typologies. Another example is copper, which is also known to have been mined in the Humber region (RBD09), but which only has substantially higher background levels than the default in peat typologies. The final consideration when applying this, or any other mining-MBRC based on background sampling of low-order streams, is that these data are not related to sampling of adit or spoil-heap drainage directly, but reflect streams in which such waters may be a (diffuse) component of existing drainage. Therefore, concentrations of the expected pollutants are likely to be much lower than would be found in sampling of point-sources in mine-drainage studies. A combination of the diffuse nature of mine-water contribution, and the non-specific allocation of samples to mining districts and the robust nature of using median concentrations is the likely cause of the moderate arsenic and copper concentrations in the stream waters of the south of the Tamar (RBD03) catchment, where the maximum reported arsenic concentration is 34 µg/l.

Mining-MBRC values could prove useful when examining the underlying reasons for compliance failure in regions where mining activities have taken place, possibly as part of a site-specific assessment, but they should be used in context and interpreted with care. Further work could potentially provide more useful information, given the mining history of the UK and the likelihood of mining-related failures to meet WFD standards. Evaluating mining-MBRCs at the catchment or sub-catchment scale is likely to yield the most reliable results, because of the propensity for mining to take place in fairly localised regions, the influence of which can be ‘averaged out’ at larger scales. However, this is likely to be complicated by the probability of low sample numbers at smaller scales of consideration.

## 5.2 Analysis of data by selected catchments

To further explore the possibility of deriving local variables, analysis of samples by catchment was undertaken. Samples were selected by visual inspection of data locations and topographical maps. National coverage of catchment polygons was not available for this project, but could be used in future to categorise samples more rapidly and completely. This section offers some examples of how this could be undertaken.

The following tables (Tables 5.4 to 5.6) show some large variations in data between sub-catchments within a larger catchment system, and within a RBD. These figures could be used in a hierarchical derivation of local MBRCs.

### 5.2.1 The Tamar catchment

Data for the Tamar catchment was subdivided into 10 sub-catchments, as shown in Figure 5.1 and Table 5.4. These sub-catchments all had good coverage of samples, with a minimum of 27 samples within each area.

With the exception of iron and manganese, overall Tamar catchment background concentrations were lower than r-MBRC default values, although some sub-catchment MBRCs were higher than default r-MBRCs (and overall Tamar catchment MBRCs). This shows the value of using increasingly localised scales, both to establish more accurate background concentrations, and to identify likely exceedances of standards.

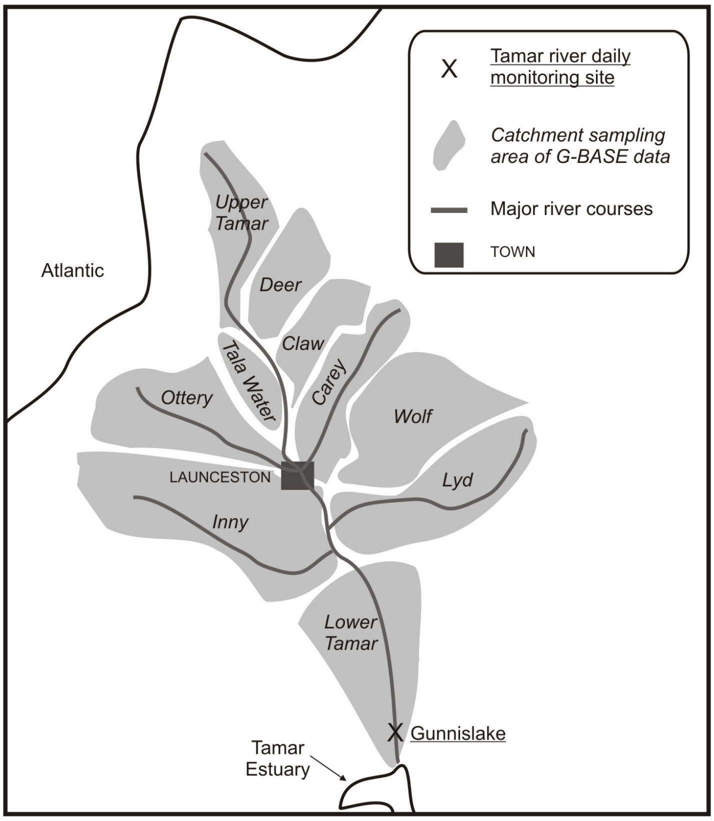


**Figure 5.1: Location of sample points in Tamar sub-catchments**
The Gunnislake sampling point of the River Tamar is shown for reference to Table 5.7.

### Table 5.4a: RBD03, Tamar catchment and sub-catchment minor element data (median values unless otherwise indicated; all concentrations in µg/l)

| Catchment label (sample numbers) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|
| Proposed standard | 25 | 16 | 7 |
| r-MBRC default | 7.4 | 59 | 22 |
| r-MBRC for RBD03 | 7.9 | 260 | 41 |
| Tamar | 7.9<br>23* | 260<br>930* | 41<br>160* |
| Carey (48) | 7.4 | 359 | 47 |
| Claw (27) | 7.7 | 454 | 43 |
| Deer (37) | 7.8 | 362 | 64 |
| Inny (54) | 8.1 | 52 | 12 |
| Lower Tamar (12) | 6.3 | 26 | 12 |
| Lyd (48) | 6.5 | 45 | 12 |
| Ottery (49) | 8.2 | 329 | 57 |
| Tala Water (31) | 9.0 | 665 | 63 |
| Upper Tamar (37) | 9.7 | 240 | 58 |
| Wolf (64) | 8.4 | 301 | 32 |

The location of the sub-catchment labels is summarised in Figure 5.1.
* 90th percentile of the catchment data

### Table 5.4b: RBD03, Tamar catchment and sub-catchment trace element data (median values unless otherwise indicated; all concentrations in µg/l)

| Catchment label (sample numbers) | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| Proposed standard | 0.5 | Cr(III) 4.7<br>Cr(VI) 3.4 | 8.2 | 4.9 - 35.6 | 6 | 7.8 |
| r-MBRC default | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| r-MBRC for RBD03 | 0.64 | <0.1 | 1.0 | 3.0 | 0.08 | 1.9 |
| Tamar | 0.64<br>2.3* | <0.1<br>0.22* | 1.0<br>1.9* | 3.0<br>5.8* | 0.08<br>0.23* | 1.9<br>7.0* |
| Carey (50) | 0.56 | <0.1 | 1.1 | 4.3 | 0.10 | 2.1 |
| Claw (27) | 0.58 | <0.1 | 1.3 | 4.0 | 0.10 | 1.7 |
| Deer (37) | 0.55 | <0.1 | 1.2 | 2.6 | 0.09 | 1.7 |
| Inny (54) | 1.3 | <0.1 | 0.84 | 1.3 | 0.05 | 2.0 |
| Lower Tamar (12) | 2.3 | <0.1 | 1.0 | 0.84 | <0.05 | <1.5 |
| Lyd (48) | 0.90 | <0.1 | 0.81 | 1.1 | <0.05 | <1.0 |
| Ottery (49) | 0.68 | <0.1 | 1.1 | 4.2 | 0.08 | 2.9 |
| Tala Water (31) | 0.68 | <0.1 | 1.3 | 4.9 | 0.13 | 2.5 |
| Upper Tamar (37) | 0.50 | <0.1 | 0.92 | 2.2 | 0.10 | 1.6 |
| Wolf (64) | 0.48 | <0.1 | 1.1 | 4.3 | 0.07 | 1.9 |

The location of the sub-catchment labels is summarised in Figure 5.1.
* 90th percentile of the catchment data

Variations can be seen between metals generally of higher concentration in the more upland area in the north of the catchment, for example in the Claw, Deer, Tala Water and Ottery sub-catchments, and those more associated with the mineralised region in the southern part of the catchment, for example in the Lower Tamar sub-catchment.

Iron, manganese and nickel tend to have higher background concentrations in the north, whilst arsenic and zinc appear to have higher concentrations in the south. Concentrations of iron and manganese in the south are the only sub-catchments with median concentrations below default r-MBRCs. The remaining sub-catchment concentrations for iron and manganese are closer to the Tamar MBRC, showing the scale of variation and the usefulness of a hierarchical approach to setting MBRCs. Whilst median concentrations of chromium are below the detection limit throughout the catchment, the basic intrusive rocks in the centre appear to be associated with isolated higher levels (see Section 7).

In terms of consistency of metal concentrations across catchments, for example, although aluminium and chromium have sub-catchment concentrations below the default r-MBRC, they are fairly consistent across the catchment, and thus also with the Tamar value.  This shows that for these metals, it would be reasonable to apply the catchment (Tamar) default rather than a sub-catchment MBRC. In contrast, metals such as arsenic and zinc tend to have more widely varying concentrations, suggesting that increasingly localised MBRC values would be more reliable for these metals.

If this trend applies to other catchments, it could provide valuable information on the most appropriate scale of MBRC to apply for different metals.  Where data exist to support this approach, it may provide evidence for the use of a specific MBRC, or a measure of the confidence in which a particular scale of MBRC value could be effectively applied.

### 5.2.2 The Witham catchment

Concentrations of minor and trace elements in the Witham catchment of Lincolnshire are shown in Tables 5.5a and 5.5b, whilst sample locations are shown in Figure 5.2. Table 5.5 also includes default r-MBRCs and overall RBD10 median concentrations.

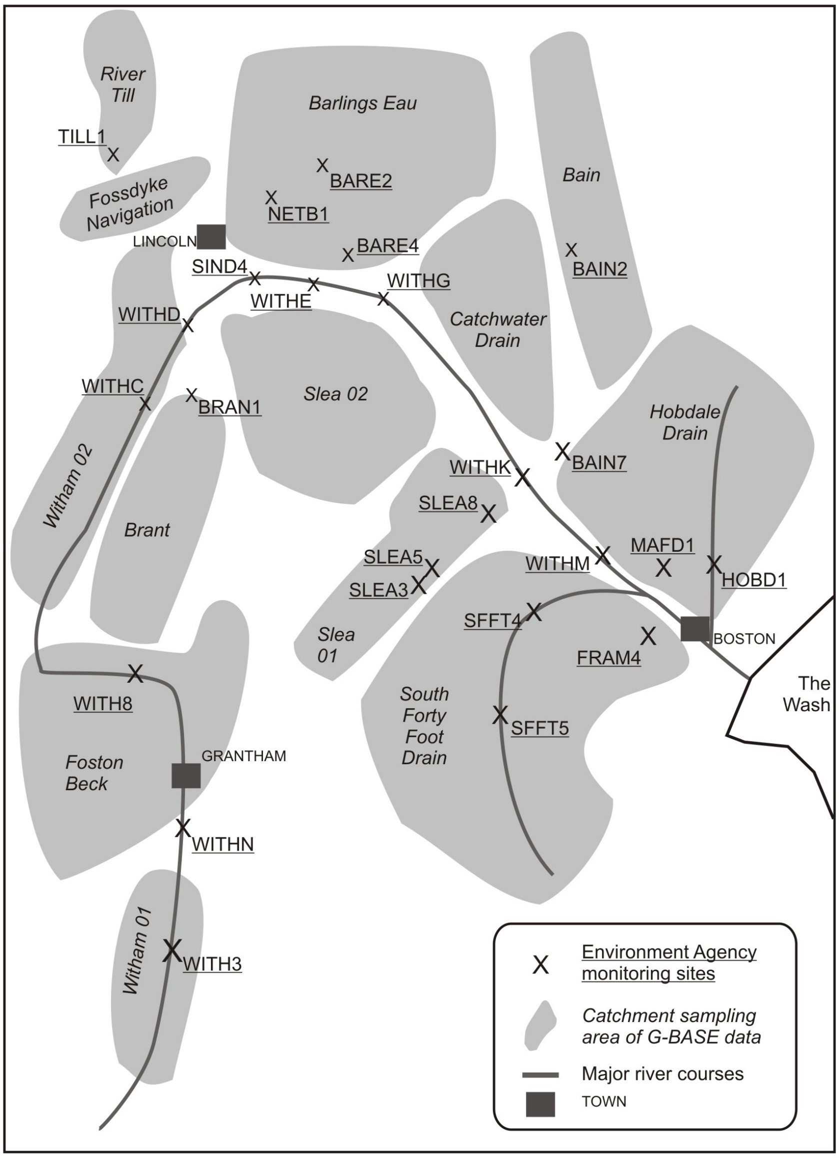


**Figure 5.2: Location of sample points in Witham sub-catchments**
EA monitoring site names correspond to Table 5.8

**Table 5.5a: RBD10, Witham catchment and sub-catchment minor element MBRCs (median values unless otherwise indicated, all concentrations in µg/l)**

| Catchment label (sample numbers) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|
| Proposed standard | 25 | 16 | 7 |
| r-MBRC default | 7.4 | 59 | 22 |
| RBD10 (all data) | 4.5 | 38 | 19 |
| Witham (all data) | 9.7<br>*36** | 47<br>*210** | 18<br>*450** |
| Bain (45) | 9.7 | 33 | 13 |
| Barlings Eau (99) | 11 | 49 | 13 |
| Brant (22) | 11 | 56 | 57 |
| Catchwater Drain (30) | 10 | 43 | 7 |
| Fossdyke Navigation (5) | 15 | 88 | 447 |
| Foston Beck (28) | 7.6 | 45 | 21 |
| Hobhole Drain (36) | 8.8 | 38 | 21 |

| Catchment label (sample numbers) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|
| River Till (30) | 14 | 50 | 30 |
| Slea 01 (18) | 13 | 21 | 14 |
| Slea 02 (31) | 19 | 44 | 8 |
| South Forty Foot Drain (110) | 7.1 | 58 | 33 |
| Witham 01 (19) | 5.2 | 28 | 8 |
| Witham 02 (18) | 12 | 92 | 294 |

The location of the sub-catchment labels is summarised in Figure 5.2.
* 90th percentile of the catchment data

**Table 5.5b: RBD10, Witham catchment and sub-catchment trace element MBRCs (median values unless otherwise indicated, all concentrations in µg/l)**

| Catchment label (sample numbers) | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| Proposed standard | 0.5 | Cr(III) 4.7<br>Cr(VI) 3.4 | 8.2 | 4.9 -35.6 | 6 | 7.8 |
| r-MBRC default | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| RBD10 (all data) | 1.5 | <0.1 | 1.3 | 3.8 | 0.06 | 2.1 |
| Witham (all data) | 2.0 | 0.10 | 1.8 | 5.1 | 0.11 | 5.7 |
| | *5.6** | *0.42** | *4.3** | *9.7** | *0.41** | *23** |
| Bain (45) | 2.5 | <0.1 | 0.9 | 3.7 | 0.12 | 3.8 |
| Barlings Eau (99) | 1.9 | 0.10 | 1.6 | 5.1 | 0.11 | 4.6 |
| Brant (22) | 2.6 | 0.10 | 2.6 | 5.7 | 0.24 | 12 |
| Catchwater D. (30) | 1.9 | 0.13 | 1.6 | 6.0 | 0.08 | 5.8 |
| Fossdyke Nav. (5) | 1.1 | <0.1 | 1.2 | 6.8 | 0.07 | 6.0 |
| Foston Beck (28) | 2.0 | 0.14 | 2.0 | 4.7 | 0.08 | 3.7 |
| Hobhole Drain (36) | 3.7 | 0.16 | 1.8 | 4.8 | 0.15 | 11 |
| River Till (30) | 2.8 | <0.1 | 2.0 | 4.7 | 0.14 | 5.1 |
| Slea 01 (18) | 1.2 | 0.16 | 2.0 | 5.0 | 0.15 | 7.2 |
| Slea 02 (31) | 1.1 | 0.16 | 1.8 | 5.1 | 0.19 | 12 |
| South F.F.D. (110) | 1.9 | <0.1 | 2.1 | 5.2 | 0.08 | 4.3 |
| Witham 01 (19) | 1.0 | 0.11 | 1.6 | 5.7 | 0.05 | 1.6 |
| Witham 02 (18) | 1.4 | <0.1 | 2.1 | 7.6 | 0.26 | 19 |

The location of the sub-catchment labels is summarised in Figure 5.2.
* 90th percentile of the catchment data

RBD10 median concentrations of minor elements are below those of the overall r-MBRC, whilst trace elements are close to or below the r-MBRC. Again, metal concentrations in individual sub-catchments show substantial variations compared with higher scale MBRCs. This lowland catchment is predominantly of calcareous typology, with some peat samples in the South Forty Foot Drain sub-catchment. Relatively large variations occur between different sub-catchments, with a general trend of increasing arsenic concentrations towards the coast, and a lesser trend in the copper data suggesting a predictable trend in likely failures. Nickel concentrations are higher in the west of the catchments identified.

Aluminium and chromium concentrations appear to be reasonably consistent across sub-catchments, while zinc concentrations in particular show a much wider variation.

### 5.2.3 The Waveney catchment.

The rivers Waveney and Yare of Norfolk/Suffolk have each been subdivided into three smaller catchments, with the locations of sub-catchment sample points shown in Figure 5.3. Metal concentrations for each of the sub-catchments, along with default MBRCs, are given in Tables 5.6a and 5.6b.

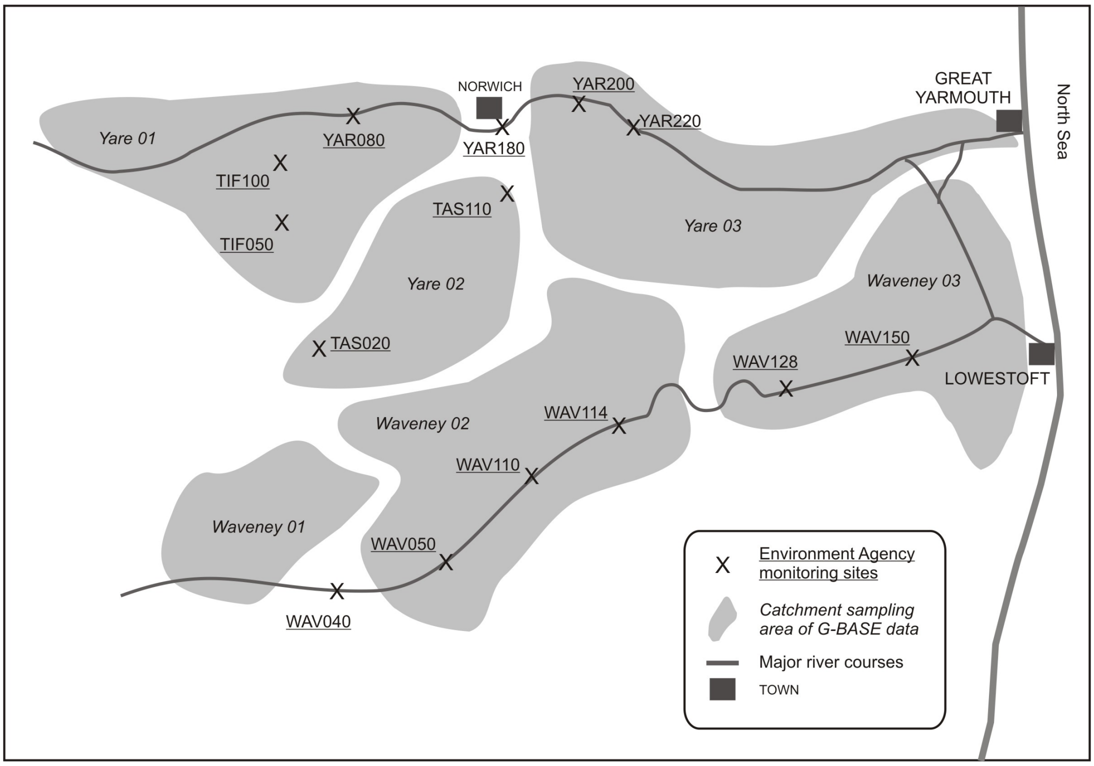


Figure 5.3: Location of sample points in Waveney sub-catchments

**Table 5.6a: RBD10, Waveney catchment and sub-catchment minor element data (median values unless otherwise indicated, all concentrations in µg/l)**

| Catchment label (sample numbers) | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|
| Proposed standard | 25 | 16 | 7 |
| r-MBRC default | 7.4 | 59 | 22 |
| RBD10 (all data) | 4.5 | 38 | 19 |
| Waveney (all data) | 3.2<br>*13** | 61<br>*440** | 58<br>*810** |
| Waveney 01 (21) | 4.7 | 67 | 43 |
| Waveney 02 (46) | 4.0 | 59 | 69 |
| Waveney 03 (34) | 2.8 | 191 | 201 |
| Yare 01 (43) | 1.7 | 39 | 25 |
| Yare 02 (30) | 2.3 | 44 | 32 |
| Yare 03 (47) | 4.2 | 82 | 70 |

The location of the catchment labels is summarised in Figure 5.3.
* 90th percentile values

**Table 5.6b: RBD10, Waveney catchment and sub-catchment trace element data (median values unless otherwise indicated, all concentrations in µg/l)**

| Catchment label (sample numbers) | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| Proposed standard | 0.5 | Cr(III) 4.7<br>Cr(VI) 3.4 | 8.2 | 4.9 -35.6 | 6 | 7.8 |
| r-MBRC default | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| RBD10 (all data) | 1.5 | <0.1 | 1.3 | 3.8 | 0.06 | 2.1 |
| Waveney (all data) | 2.3<br>*6.6** | 0.11<br>*0.60** | 1.4<br>*5.2** | 3.4<br>*4.9** | <0.05<br>*0.20** | 2.4<br>*11** |
| Waveney 01 (21) | 3.9 | 0.11 | 3.1 | 4.0 | 0.11 | 3.9 |
| Waveney 02 (46) | 3.1 | 0.16 | 2.8 | 3.4 | 0.072 | 3.2 |
| Waveney 03 (34) | 1.9 | 0.17 | 0.7 | 2.6 | <0.05 | 2.0 |
| Yare 01 (43) | 1.8 | <0.1 | 1.0 | 3.4 | <0.05 | 1.5 |
| Yare 02 (30) | 1.8 | <0.1 | 0.7 | 2.5 | <0.05 | <1.5 |
| Yare 03 (47) | 2.3 | 0.27 | 1.4 | 3.6 | <0.05 | 2.9 |

The location of the catchment labels is summarised in Figure 5.3.
* 90th percentile values

These lowland catchments within RBD10 are of calcareous typology, although more detailed geological mapping by the British Geological Survey reveals a locally complex assemblage of Quaternary sediments of varying composition. Whilst much of the minor element data are close to the default r-MBRC, 'Waveney 03' has very high iron and manganese concentrations. Chromium and lead appear to have reasonably similar concentrations across sub-catchments, while other trace elements tend to show more variation, with no readily identifiable trends.

This again indicates that while default MBRC values could be used in the 'added risk' approach, there are still likely to be isolated failures in compliance resulting from natural variations in metal concentrations. In many cases, evaluation of the sub-catchment MBRC could prove valuable in identifying non-anthropogenic excesses.

## 5.3 Comparison of stream data with larger rivers

Low order stream water geochemical data have been used throughout this report, because such streams are generally free from intensive anthropogenic activity. These therefore meet the requirements of the WFD to establish background concentrations for natural waters. However, it raises the question of whether MBRC values derived in this way are still relevant to higher order rivers. These larger systems will integrate hydrochemistry from a more extensive area of catchment, so might be expected to have background concentrations closer to 'default' values. However, higher order rivers are generally avoided in the G-BASE programme as they tend to be sites of transport, settlement and industrial activity. Thus, they are more likely to be associated with conditions not indicative of 'background'.

Environment Agency records were used to explore this issue along with G-BASE data for the River Tamar. Unfortunately, some detection limits quoted in the Environment Agency data were high compared to the natural abundance of a metal or proposed standard, which would hinder the establishment of background concentrations.

Systematic differences were found in the data following data analysis, as discussed below. If larger rivers are likely to be the source of compliance problems, more work may be needed and would benefit from using digital catchment areas to categorise sample sites. Environment Agency river data are likely to be available for the north and south of England, where G-BASE data are not.

Environment Agency data for the Tamar (Devon/Cornwall), Witham (Lincolnshire) and Waveney (Norfolk/Suffolk) rivers, along with BGS G-BASE data for the River Tamar, are compared in Tables 5.7 to 5.9.

**Table 5.7a: RBD03, Tamar river minor element data, from BGS records (median values; all concentrations in µg/l)**

| Catchment label | Aluminium (ICP-MS) | Iron | Manganese |
|---|---|---|---|
| Proposed standard | 25 | 16 | 7 |
| r-MBRC | 16 | 59 | 22 |
| r-MBRC for RBD03 | 7.9 | 260 | 41 |
| Tamar (all data)^ | 7.8 | 217 | 37 |
| Gunnislake, River Tamar | 11 | 134 | 19 |

The location of the Gunnislake sample site is shown on Figure 5.1.

^ These represent all sites sampled within RBD03 (Figure 2.4), including sites identified as being within the mining-MBRC subset, which are excluded from RBD03 r-MBRC.

**Table 5.7b: RBD03, Tamar river trace element data, from BGS records (median values, all concentrations in µg/l)**

| Catchment label | Arsenic | Chromium | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|
| Proposed standard | 0.5 | Cr(III) 4.7<br>Cr(VI) 3.4 | 8.2 | 4.9 - 35.6 | 6 | 7.8 |
| r-MBRC | 1.3 | 0.12 | 1.6 | 3.6 | 0.10 | 3.4 |
| r-MBRC for RBD03 | 0.64 | <0.1 | 1.0 | 3.0 | 0.08 | 1.9 |
| Tamar (all data)^ | 0.67 | <0.1 | 1.0 | 2.8 | 0.072 | 2.0 |
| Gunnislake, River Tamar | 4.2 | <0.1 | 4.4 | 2.5 | 0.060 | 5.5 |

The location of the Gunnislake sample site is shown on Figure 5.1.

^ These represent all sites sampled within RBD03 (Figure 2.4), including sites identified as being within the mining-MBRC subset, which are excluded from RBD03 r-MBRC.

BGS data for the Tamar represent low order stream samples, and so relate closely to data presented earlier for RBD03. Concentrations in the river at Gunnislake (in the south of the catchment, shown on Figure 5.1) are higher for aluminium, arsenic, copper and zinc than the median for the Tamar. This reflects the dominance of metalliferous ore-bodies in the southern part of the catchment, where mining activities have taken place. At this location, metal concentrations are presumably not sufficiently diluted by flows from further upstream to reduce them to the level of the overall catchment value.

Data availability is restricted for the Witham (Table 5.8) and Waveney (Table 5.9). From this relatively incomplete dataset few conclusions can be drawn, except for copper. Copper concentrations in both tables are higher in some of the larger river samples than in the low order stream data. This does not necessarily imply that the ‘default’ MBRC is too low; rather, it is more likely to represent an additional anthropogenic impact. Default MBRCs are still likely to offer a reasonable measure of background concentration, but we recommend the use of more localised MBRCs where necessary.

**Table 5.8: RBD10, Witham catchment main river course data, from Environment Agency records (median values; all concentrations in µg/l)**

| Site | Iron | Manganese | Arsenic | Chromium | Copper | Lead | Nickel | Zinc |
|---|---|---|---|---|---|---|---|---|
| Proposed standard | 16 | 7 | 0.5 | Cr(III) 4.7<br>Cr(VI) 3.4 | 8.2 | 6 | 4.9 - 35.6 | 7.8 |
| Witham (all data)* | 45 | 15 | 1.9 | <0.1 | 1.7 | 0.12 | 5.2 | 5.8 |
| BAIN2 | | | | | 1.4 | | | |
| BAIN7 | | | | | 1.7 | | <5 | |
| BARE2 | <30 | | | | | | | |
| BARE4 | | | | | 2.4 | | | |
| BRAN1 | | | | | 2.9 | | | |
| FRAM4 | | | | <0.5 | 8.8 | <2 | <5 | |
| HOBD1 | | | | <0.5 | 3.5 | | <5 | |
| MAFD1 | | | | | 2.3 | | | |
| NETB1 | | | | <0.5 | 2.2 | <2 | <5 | |
| SFFT4 | | | | | 2.7 | | | |
| SFFT5 | | | | | 2.8 | | | |
| SIND4 | 74 | | | <0.5 | 3.1 | <2 | <5 | |
| SLEA3 | | | | | 1.3 | | | |
| SLEA5 | 80 | | | <0.5 | 4.4 | <2 | <5 | |
| SLEA8 | | | | | 3.4 | | | |
| STEP3 | | | | <0.5 | 1.8 | <2 | <5 | |
| TILL1 | | | | | 2.8 | | | |
| WITH3 | | | | | 2 | | | |
| WITH8 | 63 | | | <0.5 | 2.3 | <2 | <5 | |
| WITHC | | | | | 2.4 | | | |
| WITHD | 64 | | | <0.5 | 2.5 | <2 | 5.9 | |
| WITHE | | | | | 3.6 | | | 6 |
| WITHG | | | | | | | | 5.9 |
| WITHK | | | | | 3.7 | | | |
| WITHM | <30 | 49 | <1 | <0.5 | 2.8 | <2 | <5 | <5 |
| WITHN | 35 | | | | | | | |

* BGS data

**Table 5.9: RBD10 Waveney catchment main river course data, from Environment Agency records (median values; all concentrations in µg/l)**

| Catchment | Site | Iron | Chromium | Copper | Lead | Nickel |
|---|---|---|---|---|---|---|
| Proposed standard | | 16 | Cr(III) 4.7<br>Cr(VI) 3.4 | 8.2 | 6 | 4.9 -35.6 |
| Waveney (all data)* | | 73 | 0.14 | 2.2 | 0.06 | 3.2 |
| Yare | TAS020 | | | 2.1 | | |
| Yare | TAS110 | | | 2.4 | | |
| Yare | TIF050 | 71 | | | | |
| Yare | TIF100 | | | 3.9 | | |
| Waveney | WAV040 | 92 | | 3.1 | | |
| Waveney | WAV050 | | | 2.5 | | |
| Waveney | WAV110 | | | 7 | <2 | <5 |
| Waveney | WAV114 | | | 2.6 | | |
| Waveney | WAV128 | 83 | | | | |
| Waveney | WAV150 | | <0.5 | 2.4 | <2 | |
| Yare | YAR080 | | | 2.1 | | |
| Yare | YAR180 | | | 2.6 | | |
| Yare | YAR200 | | | 1.8 | | |
| Yare | YAR220 | | | 2.4 | | |

* BGS data

# 6 Assessment of MBRC application across the UK

## 6.1 Comparison of MBRC values with Northern Ireland data

The r-MBRC values presented so far were generated from BGS G-BASE data for England and Wales. However, similar geochemical baseline survey work was recently undertaken in Northern Ireland and towards the end of this project, the complete dataset from Northern Ireland became available. These data were incorporated into this study as part of a validation exercise, but have not been discussed further as the main focus of the project is on England and Wales as the administrative region of the Environment Agency.

The Northern Ireland data, that are currently being published (Geological Survey of Northern Ireland, *in prep.*) includes maps, summary statistics and a preliminary description of the distribution of metals in stream waters. The dataset includes ICP-MS analysis for the whole country (along with other routine analyses).

The overall median of the Northern Ireland dataset, as well as medians classified by WFD geological typology, were used to identify any systematic differences with r-MBRCs developed for England and Wales.

Northern Ireland has a substantially different geological environment to that of areas sampled in England and Wales, including granites, basalts, meta-sediments and extensive areas of mineralised terrain. However, these lithologies are still classified under the four standard WFD typologies, allowing direct comparison of these classes despite the underlying geological differences. This exercise was used to establish how comparable typology-specific MBRCs were for these different datasets, to see whether typology-specific MBRCs could be more widely applied to data poor catchments across the UK.

### 6.1.1 Comparison of 'default' MBRCs for Northern Ireland and England and Wales

The dataset medians for both regions − England and Wales (E&W) and Northern Ireland (NI) − are shown in Table 6.1. Two medians are shown for arsenic and chromium east and west of Northern Ireland, because these were sampled at different times and were subject to different detection limits. However, detection limits for chromium are beneath both proposed standards, so exceedances are reported as one value for each chromium species. The percentage exceedances are comparable to the data for England and Wales given in Table 4.3. The data have not been 'cleaned' here by removing mining activity samples in Northern Ireland (as was done in Section 4.1.1), because insufficient work has been done to date to delineate such areas.

**Table 6.1: Dataset median and percentage failure of proposed standards of the Northern Ireland dataset**

| Metal | | Northern Ireland | | England & Wales | |
|---|---|---|---|---|---|
| | Standard µg/l | NI-MBRC (median) µg/l | NI-MBRC > proposed standard (% of samples) | r-MBRC (median) µg/l | r-MBRC > proposed standard (% of samples) |
| **Minor elements** | | | | | |
| Aluminium (ICP-MS) | 25 | 19 | 41 | 7.4 | 18 |
| Aluminium (ICP-AES) | 25 | n/a | n/a | 16 | 37 |
| Iron | 16 | 220 | 96 | 59 | 84 |
| Manganese | 7 | 48 | 88 | 22 | 76 |
| **Trace elements** | | | | | |
| Arsenic | 0.5 | East: 0.59<br>West: 0.95 | 54<br>82 | 1.3 | 87 |
| Chromium | Cr(III) 4.7<br>Cr(VI) 3.4 | East: 0.34<br>West: <0.4 | Cr(III): <1<br>Cr(VI) 1 | 0.12 | Cr(III): <1<br>Cr(VI) <1 |
| Copper | 8.2 | 1.2 | 2 | 1.6 | 4 |
| Nickel | 4.9* | 1.7 | 8 | 3.6 | 28 |
| Nickel | 35.6* | 1.7 | <1 | 3.6 | <1 |
| Lead | 6 | 0.08 | <1 | 0.10 | 1 |
| Zinc | 7.8 | 2.4 | 19 | 3.4 | 28 |

All aluminium analyses by ICP-MS in Northern Ireland. The detection limit of Cr analyses was higher (0.4 µg/l) for the western part of Northern Ireland. Arsenic data are reported separately due to differences in the detection limit between samples analysed from the east and west.
* A range of possible standards exist for Ni; here, the lowest and highest values are used for comparative purposes.

The median concentration of iron in Northern Ireland is much higher than that of England and Wales, with a concomitant increase in the proportion of samples which would fail the proposed standard of 16 µg/l. A similar situation exists for manganese. Aluminium is close to the data for Wales (by ICP-AES), which would seem reasonable given the greater similarity in composition of the bedrock and topography, compared to the low-lying region of eastern England. A similar process is likely to be responsible for higher iron and manganese concentrations.

The trace elements, whilst showing considerable variation within the dataset (Geological Survey of Northern Ireland, *in prep*), have default MBRCs generally close to or lower than England and Wales values (with the exception of chromium). One of the largest differences occurs for nickel, where the NI default MBRC is below the 10th percentile of the E&W r-MBRC data (Table 4.1b). Arsenic would have a substantial number of failures for proposed standards in the west of NI, though there were fewer exceedances in the east. The zinc median is lower than in England and Wales, but still gives a failure rate of 19 per cent.

Overall, a similar situation exists in Northern Ireland to that in England and Wales, where standards for iron, manganese and arsenic are likely to lead to substantial failure in compliance; aluminium and zinc are of secondary concern, while copper and chromium are of least concern. Nickel is probably of ‘medium’ concern for England and Wales, but of less concern in Northern Ireland.

For minor elements (aluminium, iron and manganese), the NI-MBRC is higher than the E&W r-MBRC, so use of the E&W r-MBRC would be slightly more protective in Northern Ireland. That is, there would be comparatively more exceedances if the median concentrations of each dataset were used independently to establish the background. In this situation, iron would likely prove to be the most problematic metal, as the difference between the two MBRC values is substantial, but applying the E&W r-MBRC to Northern Ireland could be considered over-protective.

For trace elements, with the exception of chromium, the E&W r-MBRC is slightly higher than the equivalent NI value, so would be slightly less protective if applied to Northern Ireland. However, the E&W r-MBRC would still be sufficiently protective to identify samples which should be more closely scrutinised.

### 6.1.2 Comparison of WFD typology-specific MBRCs for Northern Ireland and England and Wales

The Northern Ireland data categorised by WFD typology is given in Table 6.2, along with equivalent r-MBRC data for England and Wales (also presented in Table 4.2). The calcareous typology dominates Northern Ireland (3,300 samples), compared to the siliceous (1,850 samples) and peat typologies (750 samples). However, peat samples are all formed on the uplands, dominated by the Sperrin Mountains and North East Antrim, so no distinction between upland and lowland peat ($WFD_p$) is made here.

**Table 6.2a: Summary of the minor element NI-MBRCs and r-MBRCs by WFD geological typologies (all concentrations in µg/l)**

| WFD category | Aluminium | Iron | Manganese |
|---|---|---|---|
| European* | 18 | 67 | 16 |
| Proposed standard | 25 | 16 | 7 |
| NI-MBRC | 19 | 220 | 48 |
| r-MBRC | 7.4 | 59 | 22 |
| NI-MBRC: WFD Siliceous | 16 | 190 | 61 |
| r-MBRC: WFD Siliceous | 18 | 120 | 25 |
| NI-MBRC: WFD Calcareous | 17 | 180 | 39 |
| r-MBRC: WFD Calcareous | 6.3 | 41 | 19 |
| NI-MBRC: WFD Salt | n/a | n/a | n/a |
| r-MBRC: WFD Salt | n/a | 140 | 66 |
| NI-MBRC: WFD Peat | 82 | 800 | 76 |
| r-MBRC: WFD Peat | 12 | 120 | 81 |

* (Salminen *et al.*, 2005).
All aluminium data by ICP-MS analysis.
r-MBRC relates to England and Wales data only.

Aluminium concentrations are generally higher in Northern Ireland, particularly over peat and calcareous lithologies. Iron concentrations show a similar pattern, whilst manganese concentrations are higher in Northern Ireland over the calcareous and siliceous lithologies. These suggest that the use of the r-MBRC for Northern Ireland would have led to a higher failure rate, creating more work to meet compliance.

Trace element data show that, if r-MBRC values were extrapolated to Northern Ireland, background concentrations of copper, lead and especially nickel and zinc would be overestimated. Whilst arsenic concentrations are generally lower in the Northern Ireland dataset, applying the E&W r-MBRC would lead to a background over siliceous lithologies half of what it actually is. Chromium concentrations, where measurable, are higher in Northern Ireland, but are still close to detection limits.

The results show that extrapolation of MBRC values to a different geological environment should be treated with caution. Further data collection should be a priority for areas with a large geological and geographical contrast to areas where data are already available. A further problem would be predicting where these variations are likely to occur, although priorities based on geological and geochemical understanding could be developed.

**Table 6.2b: Summary of the trace element NI-MBRCs and r-MBRCs by WFD geological typologies (all concentrations in µg/l)**

| WFD category | Arsenic east | Arsenic west | Chromium east | Chromium west | Copper | Nickel | Lead | Zinc |
|---|---|---|---|---|---|---|---|---|
| European* | 0.63 | | 0.38 | | 0.88 | 1.9 | 0.093 | 2.7 |
| Proposed standard | 0.5 | | Cr(III) 4.7<br>Cr(VI) 3.4 | | 8.2 | 4.9 - 35.6 | 6 | 7.8 |
| NI-MBRC | 0.59 | 0.95 | 0.34 | <0.4 | 1.2 | 1.7 | 0.08 | 2.4 |
| r-MBRC | 1.3 | | 0.12 | | 1.6 | 3.6 | 0.10 | 3.4 |
| NI-MBRC: WFD Siliceous | 1.2 | 0.98 | <0.2 | <0.4 | 1.3 | 1.6 | 0.09 | 2.6 |
| r-MBRC: WFD Siliceous | 0.61 | | 0.14 | | 1.6 | 2.9 | 0.16 | 5.1 |
| NI-MBRC: WFD Calcareous | 0.31 | 0.92 | 0.49 | <0.4 | 1.1 | 1.9 | 0.06 | 2.0 |
| r-MBRC: WFD Calcareous | 1.5 | | 0.11 | | 1.6 | 3.7 | 0.09 | 2.8 |
| NI-MBRC: WFD Salt | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
| r-MBRC: WFD Salt | n/a | | n/a | | n/a | n/a | n/a | n/a |
| NI-MBRC: WFD Peat | 0.51 | 1.0 | 0.39 | 0.44 | 1.1 | 1.3 | 0.25 | 4.7 |
| r-MBRC: WFD Peat | 1.6 | | 0.15 | | 1.6 | 5.5 | 0.13 | 7.4 |

* (Salminen *et al.*, 2005).
r-MBRC relates to England and Wales data only.

It is clear that the use of a single value, whether as a proposed standard or via the ‘added risk’ approach of standard plus background reference concentration, offers only a coarse evaluation of the risk posed to an ecosystem. These standards could easily give rise to failures in compliance as a result of high natural metal concentrations in stream waters. In the UK, the use of ‘added risk’ would undoubtedly reduce the number of failures, but we would further recommend the development of a hierarchical approach to compliance which encompasses more specific location- or typology-based MBRCs.

## 6.2 Assessment of data status throughout the UK

Problems could be anticipated in applying generic MBRC values to areas of the UK where there is currently no data. Unfortunately, no regional geochemical baseline stream water data exist for the nine metals of interest in most of Scotland or the north of England. The limited data suite available is equivalent to that of Wales (ICP-AES only) and is found only over the Shetlands. There are also no plans to resample areas of Wales and the west of England for which only ICP-AES data exist. Figure 2.4 illustrates the area yet to be sampled by the G-BASE project in the south of England. It is anticipated that this sampling will be completed by 2015, although schedules are subject to annual funding revisions. As previously described, Northern Ireland has a complete dataset.

Given the dearth of samples for much of England and Wales, the next section attempts to highlight areas of similar geological characteristics to those with the highest concentrations. This is not a definitive or quantitative guide to minor or trace element concentrations, nor does it highlight areas of higher concentrations which have yet to be sampled, as experience has shown that the G-BASE dataset frequently turns up such areas which were not previously measured or anticipated. Further data acquisition is still recommended, but our approach is intended to help bridge a knowledge gap until such data are available.

# 7 MBRCs and 'Added Risk'

Use of metal background reference concentrations within the 'added risk' approach is anticipated to vary depending on the metal under consideration, the value of the MBRC in comparison with the proposed standard, and the best available data. The options include the use of a single MBRC value (or in some cases a recommendation that the added risk approach itself is not required, and therefore neither is an MBRC), a range of values, a preferred option (such as a local value) in specific locations, or site specific geological assessment.

This section synthesises the findings of this report, to develop an approach to the use of 'added risk' with appropriate selection of MBRCs. Detailed local analysis of the priority metals identified within this study (iron, manganese and arsenic) is provided, in order to more clearly demonstrate how the background data may be used.

## 7.1 Recommendations on the Use of 'Added Risk'

Comparison of the MBRC values derived in Table 4.2a, Table 4.2b, based on WFD typology, and those in Table 5.1a and Table 5.2b which give the MBRC based on river basin district, with the relevant standard, suggest recommendations for use of the added risk approach that can be made for the metals under consideration. These are summarised as:

Chromium and Lead – added risk approach is not required

Copper – use of added risk with a **single** MBRC value (Cu MBRC = 1.6 µg/l)

Aluminium, arsenic, iron, manganese, nickel and zinc – use of added risk with **derived** MBRC.

**Chromium** and **lead** background concentrations are consistently sufficiently low, spatially and typologically, in comparison with the proposed standards, that the added risk approach is not considered necessary. This is substantiated by chromium and lead being in our lowest category of concern in causing failures of the proposed standards (less than five percent failure).

For **copper** the MBRC values derived in this report do not vary substantially either spatially, or typologically (as a proxy for geology). In addition to this, copper also falls into our lowest risk category in terms of probable failures of the proposed standard (less than five percent failure). For these reasons we recommend that the added risk approach should be used for copper, but can be implemented with a single value for the MBRC (the default r-MBRC value, 1.6 µg/l).

For the remaining metals under consideration; aluminium, arsenic, iron, manganese, nickel and zinc, we would recommend implementation of the added risk approach using a specific MBRC value, which has been derived to be most relevant to the location being assessed. This is based on the variation, both spatially and typologically, of the MBRC values for these metals determined by this study. In this case, however, it may be justified to further divide these metals into two sets, based on their risk categorisation of causing probable failures. **Aluminium**, **nickel** and **zinc** are, in our assessment, of medium concern in causing probable failures, so a decision could be made on this basis to justify for example a single MBRC value (default r-MBRC), or for example, use of a river basin district derived MBRC in all cases (except where none is available, and then to return to the default r-MBRC value) for assessment of compliance within the added risk approach. For nickel, there is generally less spatial and typological variation of the MBRC values, which suggests selection of a single value for the MBRC would be appropriate, but that in this case the final decision may also rest on the standard implemented, whether this will be a range, or the other conditions (such as hardness) that may be applied. Clearly, if the final standard implemented for nickel is 20 µg/l instead of for example 7.8 µg/l, this will change the relevance of the variation seen in the derived MBRC values in comparison with the standard. In comparison, **arsenic**, **iron** and **manganese** have been classified as of most concern in terms of probable failures of the proposed standards (more than 75 percent failures). This, along with generally more variation in MBRCs spatially and typologically, suggest that these factors should be taken into account in deriving an MBRC value to use in the added risk approach on a case by case basis. In order to do this we have devised a hierarchical approach to the selection of relevant MBRC values, which is given in Section 7.2 and Figure 7.1.

It should be noted though, that the development of MBRC values for use in the added risk approach is meant to prevent unnecessary failures of the standard due to natural (low anthropogenic impact) concentration of the metal in question. But, it will inevitably not prevent all such failures, simply as a result of the confidence in the statistical measures taken, and site to site variations. Thus it is important to note that subsequent failures should trigger more detailed site specific assessment, but not necessarily to exclude natural conditions as a cause of the failure.

## 7.2 Selection of MBRCs

The findings of this report suggest that the MBRC values most likely to represent prevalent metal background concentrations at a given site are the most localised, for example at a catchment or sub-catchment scale. This would account for localised variations in metal concentrations in the underlying geology, as well as variations based on other superimposed influences such as organic carbon or pH. The relevance of derived MBRC values examined in this report is likely to be in the order:

MBRC (catchment) ↑
MBRC (RBD – typology) $\approx$ MBRC (RBD)
MBRC (typology)
Default MBRC (all data)

MBRC expected to be increasingly close to 'local reality'.

However, it must be noted that this is generalisation for the metal studied, and would not necessarily hold true in every individual situation. Equally, in deriving an MBRC value to use in the added risk approach, some statistical consideration should be given to the number of samples used to derive the value and the confidence thereby in the statistical measures of the population used, and the potential effects of outliers. So, for example, in using data from spatially restricted areas, the 90th percentile is likely to be a more accurate descriptor of the upper limit of the background concentration than the 50th percentile (median value), but at low sample numbers any outliers will have a greater effect in skewing the values of the higher percentile data.

Figure 7.1 shows the hierarchical selection steps for determining an appropriate MBRC value within the application of the added risk approach. This stepwise approach makes use of the most appropriate data available to derive an MBRC value, which is ultimately discounted in the comparison of the monitored value against the standard.

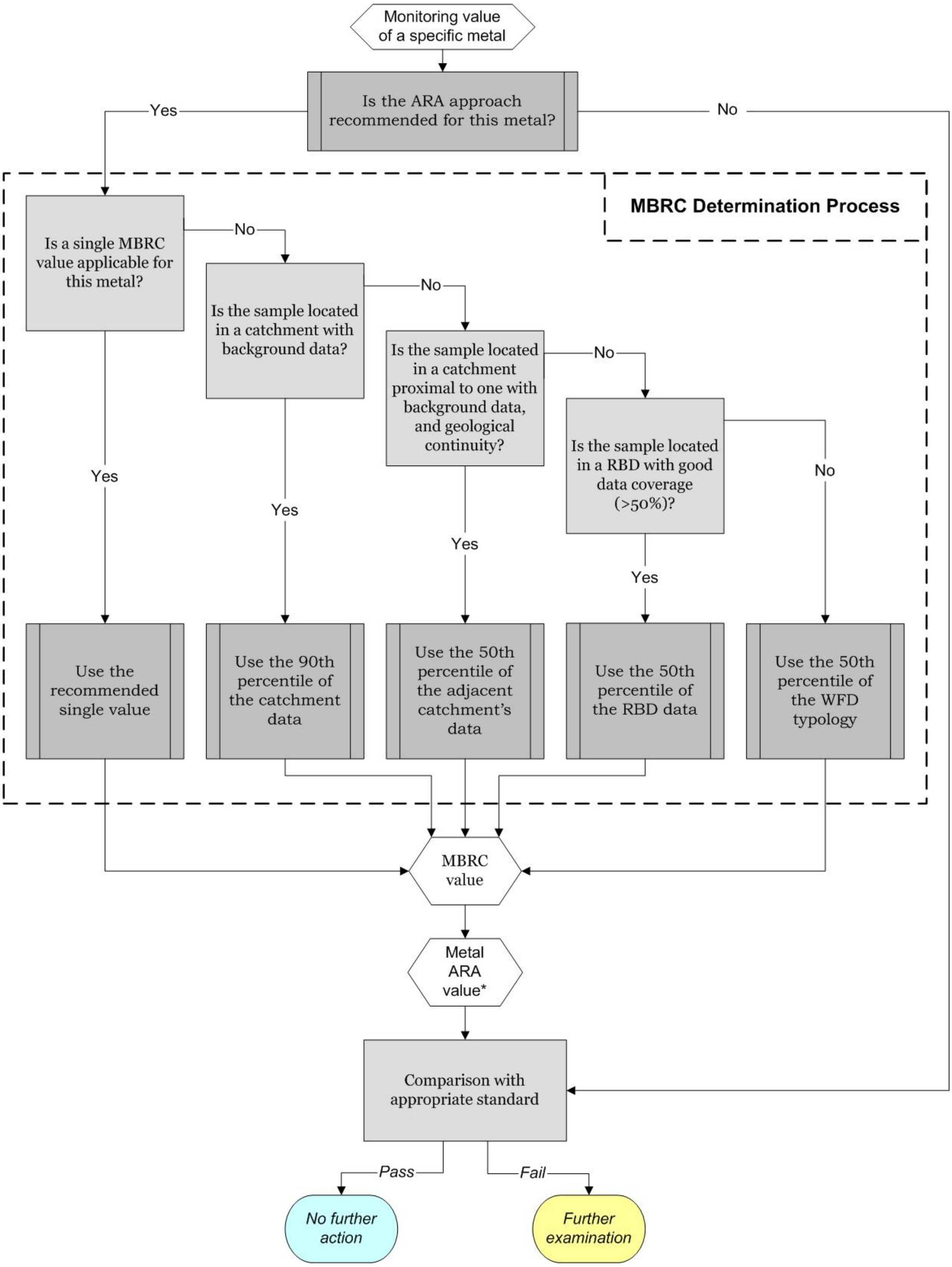


Figure 7.1: Flow-chart for the selection and application of MBRC values in the Added-Risk Approach.

This process enables a systematic approach to the selection of an appropriate MBRC value that is applicable to the whole of England and Wales, recognising that background metal concentration data is not yet available uniformly across the regions. It also uses different percentile values of the data, to reflect the reduced confidence that can be placed in data that is from a location and geological environment less similar to that from which the monitoring sample is taken. This prevents the added risk approach being under-protective when applied in this way.

In this report, catchment scale MBRC values are only available for the Tamar, Witham, and Waveney catchments in section 5 (Tables 5.4a, 5.4b, 5.5a, 5.4b, 5.6a, and 5.6b). This is because we did not have access to the existing digital catchment shapefile for the purposes of this project. With such access it would be possible to resolve catchment scale data for all catchments where the data exists in a similar way to that for the Tamar, Witham and Waveney. River Basin District scale MBRC values are given in Table 5.1a and 5.1b (resolved also for WFD typology where possible, should this be required, in Tables 5.2a and 5.2b), and default WFD typology MBRCs are given in Table 4.2a and 4.2b. With access to the correct digital shapefiles to speed resolution of data points, it would also be possible to resolve the data to a sub-catchment scale if required.

The maps given in Appendix 1 could be used to support a decision on the spatial proximity and geological continuity of samples from an area adjacent to one with data, for iron, manganese and arsenic. In keeping with the reporting throughout this study, these are produced as the median for each PM250/50 category (as well as the interquartile range). These maps provide the best possible information in the absence of digital catchment data within this project, as they include geological data and grid coordinates by which to locate samples. The median value (50th percentile) is used rather than the 90th percentile, to reflect the reduced confidence that should be attached to this extrapolation, and ensure the assessment is sufficiently protective towards the aquatic ecosystem. It should be noted that geologically contiguous data could lie in separate river basin districts. For example some of the catchments in RBD01 which are just south of the watershed with RBD04 or RBD10 will share a geological parent material, which could be used to follow this pathway through the decision process, rather than having to use the final action box ('Use the 50th percentile of the WFD typology'), which would otherwise be required.

Table 7.1 gives the percentage data coverage for the river basin districts in England and Wales, supporting the decision to use an RBD scale MBRC where there is good data coverage (greater than, or approximately equal to 50 percent in the scheme) in comparison with the default WFD typology MBRC. Further sampling is planned within the BGS G-BASE project for RBDs 01, 02, 03, 04 and RBD 10 which will increase the data coverage of these districts and allow robust MBRCs at the RBD scale to be derived for all nine metals of interest.

**Table 7.1 The percentage data coverage for the River Basin Districts of England and Wales**

| River Basin District | MBRC data status: Percentage Coverage | |
|---|---|---|
| | Al, Fe, Mn | As, Cr, Cu, Ni, Pb, Zn |
| RBD 01* | 6 | 5 |
| RBD 02* | 0 | 0 |
| RBD 03* | 6 | 6 |
| RBD 04* | 84 | 11 |
| RBD 05 | 100 | 17 |
| RBD 06 | 100 | 0 |
| RBD 07 | 48 | 3 |
| RBD 08 | 0 | 0 |
| RBD 09 | 73 | 68 |
| RBD 10* | 97 | 97 |
| Scottish Border | 0 | 0 |

* These are RBDs in which G-BASE sampling is scheduled to be completed before implementation of the WFD River Basin Planning second cycle (2015), and which is planned to include data on all 9 metals of interest here.

## 7.3 Further Assessment

Although the schematic in Figure 7.1 is designed to aid selection of the most appropriate MBRC for a particular location, as has been noted previously, this does not necessarily mean that any failures of the proposed standard are automatically the result of anthropogenic impacts, and should simply trigger a more specific assessment. This could include, for example a more detailed assessment of the influence of underlying geology or other factors.

Conductivity, pH and dissolved organic carbon have a reasonable influence on geochemical variations in these metals. These parameters are shown in Figures 7.2 to 7.4 largely to help explain any failures in meeting standards in the north of England, where there are areas where there are no BGS unimpacted metal stream water data (RBDs 07, 08, 09 and Scottish Border).

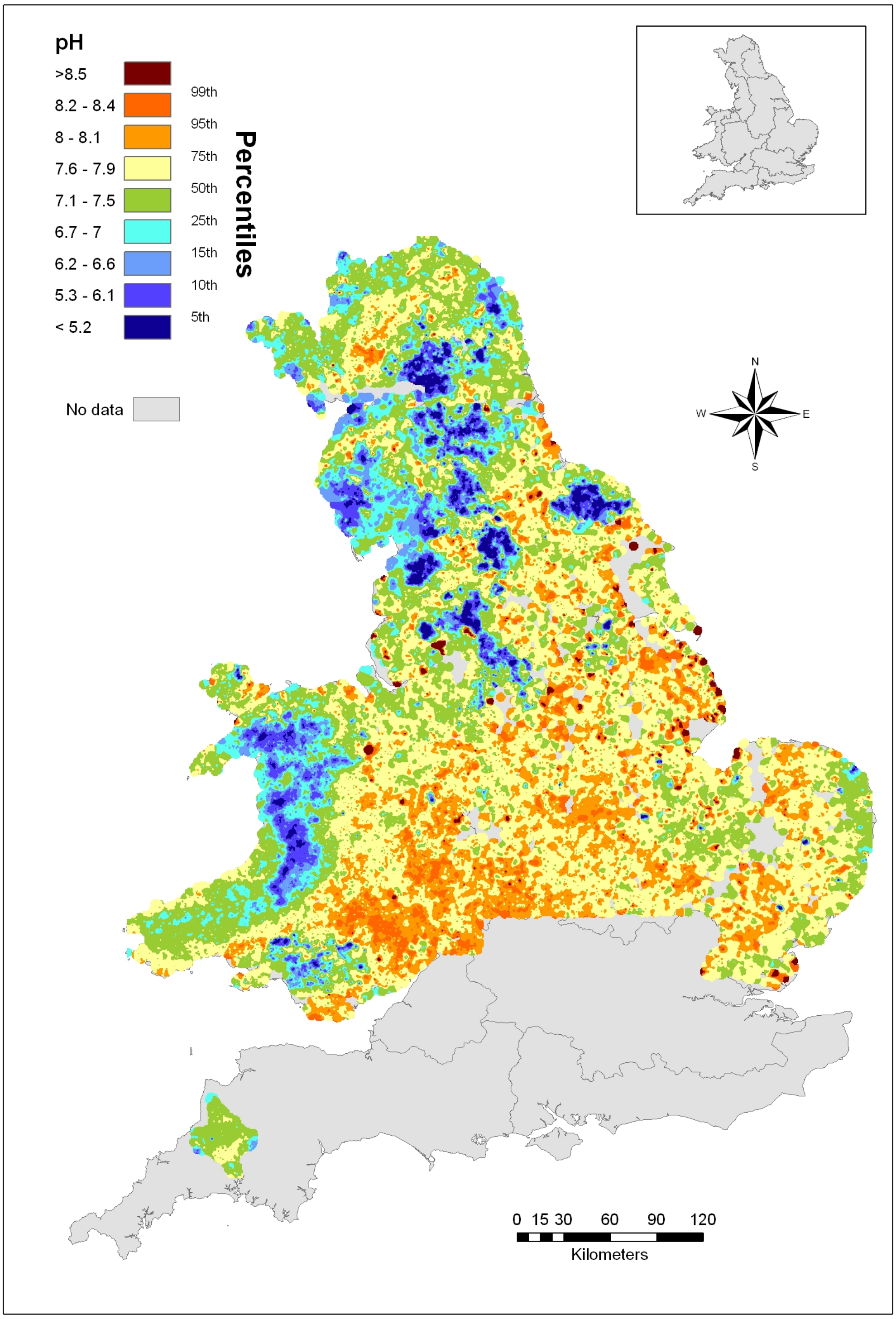


**Figure 7.2: pH in stream waters of England and Wales**

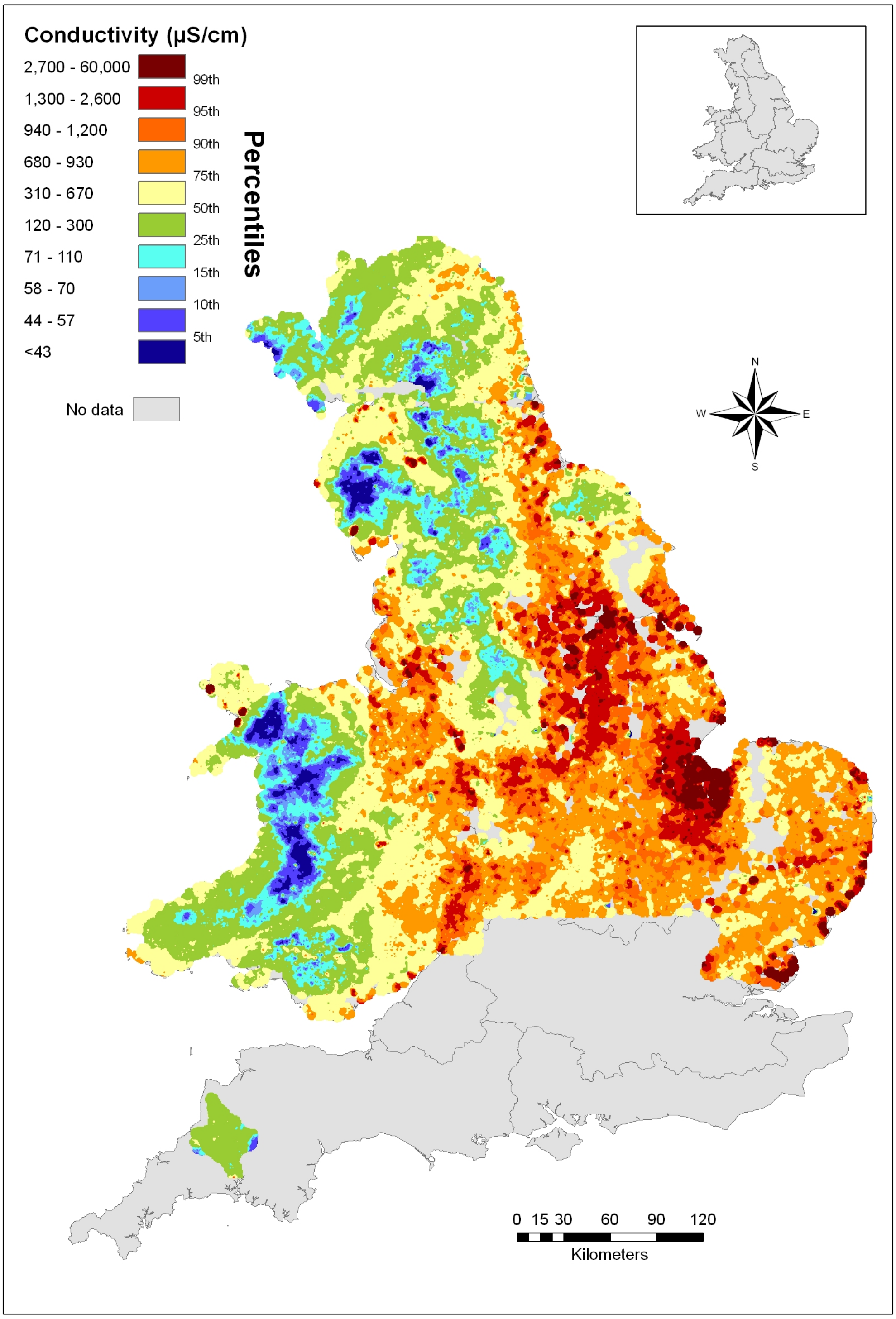


Figure 7.3: Conductivity of stream waters in England and Wales

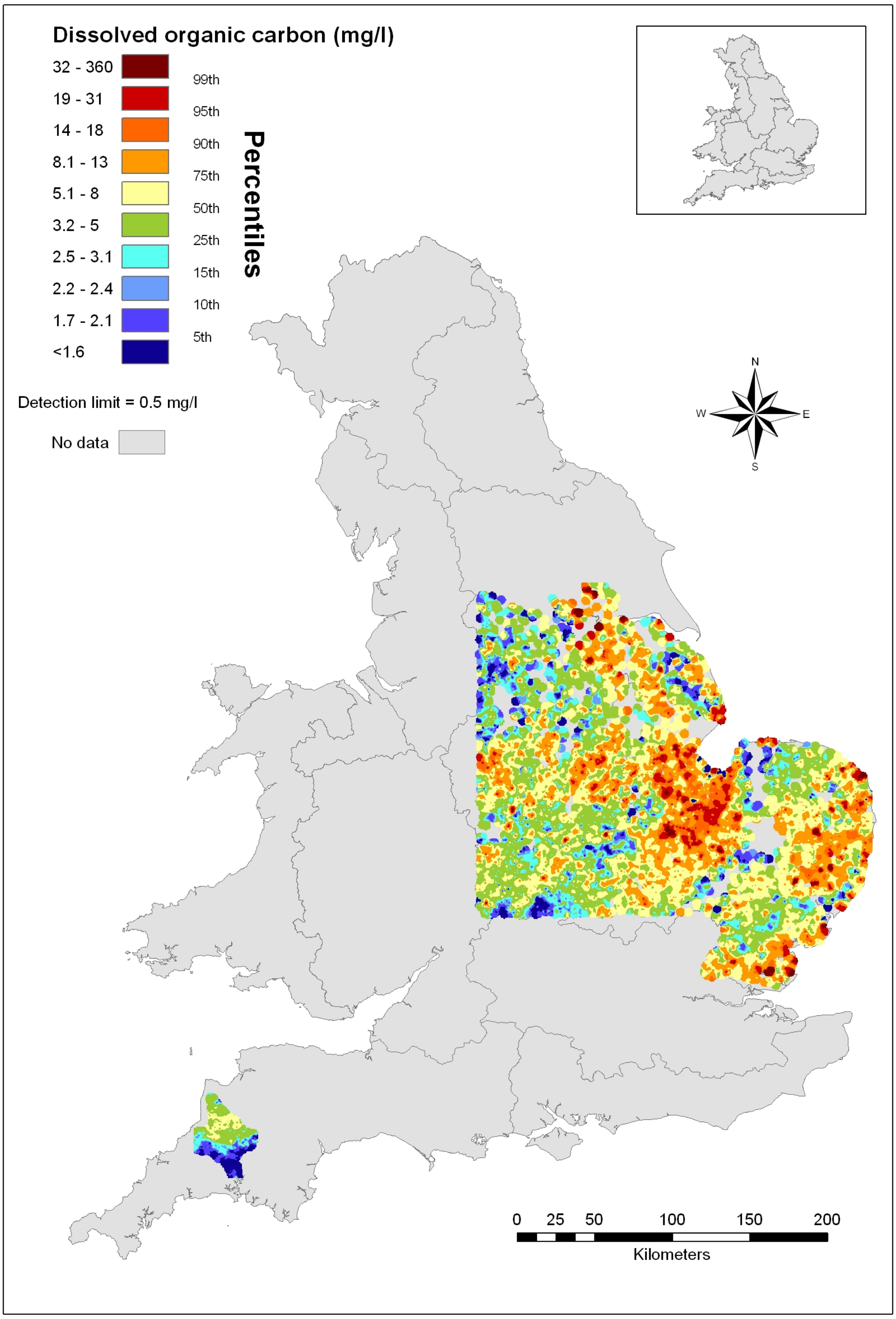


**Figure 7.4: Dissolved organic carbon concentrations in stream waters of England and Wales**

### 7.3.1 Geological Assessment for Iron, Manganese and Arsenic

For the three priority metals identified here as being of most concern in terms of potential failures of the proposed standards, the ANOVA analysis showed the ‘PM 250/50’ classification to be the most significant influencing variable for iron and arsenic, and only narrowly outscored by organic carbon for manganese (Table 3.1). However, use of the ‘PM 250/50’ classification in examining influences on manganese concentrations is still relevant and pragmatic as dissolved organic carbon data are only available for approximately half of the manganese trace metal dataset, whilst PM250/50 categories are available for the whole of England and Wales. More detailed geological characterisation can therefore be used to highlight cases where samples may fail a compliance assessment due to the nature of the underlying geology, even where the added risk approach (discounting the derived MBRC) has been applied.

Generalised maps of arsenic, iron and manganese levels in each RBD, along with more detailed information on the geological environments with higher metal concentrations in associated tables, are given in Appendix 1. These are shown with BGS standard codes for geological formations, with a look-up table provided in Appendix 2. Only ‘PM 250/50’ categories which include 10 or more samples are used in this analysis, to ensure a robustness of approach.

In these maps, geological units with a median exceeding the ‘added risk’ value defined in Table 4.3 are coloured pale pink. ‘PM 250/50’ categories which exceed the value for each metal in stream water differ, and thus are presented separately for the metals considered. Sample site data are also shown, and are coded as to whether they fall above the ‘added risk’ value (coded red) or below it (coded blue). This is designed to show areas where local geology may be influencing the background concentration. For example, where a red-coded sample falls on a pink-coloured formation, failure to meet the standard is considered likely, due to a respectively higher concentration of the metal of interest in the underlying geological formation. These maps also show the extent of sampling in a RBD, because all sample locations are given. However, discrepancies can arise, for example where a ‘PM 250/50’ category covers a wide area but with insufficient detail to discriminate between different environments. In this case, local geological knowledge is extremely valuable.

Data are presented in order of river basin district number where analytical data is available. This is followed by a brief discussion of probable influences in areas of England and Wales that do not have stream water metal data. Because the ‘added risk’ value encapsulates the proposed standard as well as overall dataset MBRC median, these outputs are only applicable for the standards as they are currently defined. However, the data given for formations in the tables in Appendix 1 include the interquartile range as well as the median and sample numbers for each formation.

One key finding in areas affected by glacial deposits (till = diamicton) is that digital mapping does not sufficiently discriminate between these sediments at the regional scale to adequately explain geochemical variations. This problem could be minimised if catchment-specific data were collected. For example, the extensive till cover in RBD10 (Anglian) shows variable concentrations for several metals. The significance of the till is marked in these areas, and the absence of till deposits in the south of England could diminish the confidence with which extrapolation from RBD10 could be undertaken.

### 7.3.2 Summary of data availability and extrapolation (As, Fe, Mn)

It is already apparent that the lack of specific stream water metals data in some areas may cause problems in setting localised MBRCs, and require the more generalised data options in Figure 7.1 to be used. However, for some areas it may be possible to make broad generalisations about the likely overall concentrations of metals based on similar geology elsewhere, although there is a high level of uncertainty associated with this type of extrapolation, and it should not be taken as a substitute for real data. The following sections summarise, for each river basin district, the geological characteristics that may be useful in identifying areas where we might expect high concentrations of metals, or where extrapolations from other areas could be made. The information relates only to the three priority metals identified, namely arsenic, iron, and manganese.

### *River Basin District 1 (Thames)*

The data for this RBD is extremely restricted, with only 200 data points generated over three areas: close to Banbury, Epping and a small area of Gloucestershire (ICP-AES data only). This RBD is scheduled for complete sampling in the future, with which it should be possible to generate summary data as good as that available for RBD10.

Areas which have geological and topographical continuity with RBD04 and RBD10 could be used as a guide to areas where samples may exceed the ‘added risk’ value. Such extrapolations could be made with greater confidence where there is good continuity than it can in areas that are different to those where data is available. Environments in this region include low-lying coastal areas, which in East Anglia and along the Lincolnshire coast are associated with high concentrations of all three metals. Other areas of concern could include some of the mudstones (such as the Oxford Clay) which are found throughout the area and are contiguous with RBD10. There are also systematic differences in the region below that sampled so far, which include the absence of till over much of the region. This could alter the background compositions seen over lithologies further north, either by the absence of trace elements, or by no longer ‘masking’ formations with high natural abundances.

### *River Basin District 2 (South East)*

No data for this RBD were available for this project. Sampling is scheduled, from which it should be possible to generate summary data as good as that available for RBD10. It is likely that sampling for RBD01 will be complete before that for RBD02, and could therefore be used to extrapolate from. However, the geology of the region around London suggests that it should be possible to use information from RBD01 and RBD10 to aid interpretation of samples which exceed the proposed standard. If these fall over a geological environment recognised in areas to the north to be associated with high concentrations, this will indicate that background data should be acquired in this region.

Such environments include low-lying coastal sediments which are found in this RBD. Further north, in RBD10, these are often associated with higher concentrations of the three metals. There is an absence of till over this RBD, which may affect the composition of waters compared to the same solid geological formations found in RBD10, which makes it more difficult to predict concentrations. Any stream water environment that is less oxidising is more likely to have high iron and manganese concentrations, whilst any formations with low levels of carbonate minerals may have higher aluminium concentrations (indirectly controlled by a lower stream water pH).

### *River Basin District 3 (South West)*

The data available for this RBD is restricted to the Tamar catchment. Formations in the Tamar catchment extend beyond its boundaries and where geological conditions are similar, the Tamar data may be used as a reasonable first approximation to the likely background concentrations across these formations. However, a large number of samples from the catchment are excluded from the r-MBRC dataset, because of the presence of mineralisation and mining. Local variations, such as impeded drainage, changes in stream water pH or ore-forming minerals could change local backgrounds. The extensive mining activities in Devon and Cornwall should be carefully considered when undertaking such an extrapolation.

Low-lying coastal regions have been found in other areas (such as RBD07 and RBD10) to incur widespread failures to meet proposed standards for the three metals, so where present in this RBD, any failures in compliance may need to be checked for high local background concentrations arising from this source. An outcrop of the Mercia Mudstone in this RBD has also been found in other regions (such as RBD05 and RBD10) to have high levels of dissolved trace elements. Another source of elevated concentrations in stream waters is noted where there are minor intrusions of basic igneous rocks, which appear to give higher concentrations of chromium in stream waters, and may affect other elements.

The rest of this RBD is scheduled to be sampled; the data generated should be of the same analytical quality as that available for the Tamar catchment, allowing more accurate background concentrations to be calculated for catchments in the RBD.

### *River Basin District 4 (Severn)*

Data are already available for iron and manganese over much of this RBD, with the only exception being to the east of the Severn Estuary. This region is scheduled for sampling to collect a suite of data, from which local backgrounds may be calculated. ICP-MS data are only available in the area east of Redditch, with no plans to resample previous regions for ICP-MS analysis of stream waters. Areas which fall into the same geological categories as those which exceed the ‘added risk’ are indicated on the maps, outside the present areas of sampling. The other type of geological environment associated with high concentrations of trace elements is that of low-lying coastal areas, such as those found around the Severn Estuary. Samples collected here which exceed the standard should be tested further for naturally high background concentrations.

### *River Basin District 5 (Western Wales)*

Data are already available for iron and manganese over the whole of this RBD. ICP-MS data are only available in the Pembrokeshire area, with no plans to resample the sites with ICP-AES data for ICP-MS analysis.

### *River Basin District 6 (Dee)*

Samples have been collected over the whole of this region, with analysis only being available by ICP-AES. The low sample density over the north reflects a low density of stream networks in the area and a densely populated area around the Wirral. There are no plans to resample the stream network to acquire samples for ICP-MS analysis. This RBD is small, and thus its maps (Appendix 1) are at a smaller scale than others included.

### *River Basin District 7 (North West)*

The data available for this RBD is restricted to the southern half of the area. Geological categories with concentrations exceeding the ‘added risk’ value are also indicated over the unsampled area. This information and that from any extrapolation of data from RBD09 may help identify local backgrounds which will lead to failure in compliance. However, where substantial differences in geological or topographical environment occur, it may be necessary to characterise the background further. As indicated for other areas without data, any local effects caused by mining or impeded drainage (giving rise to more poorly oxidising waters), or arising from low-lying coastal areas, may indicate regions where establishing background concentrations should be prioritised.

There are no current plans to resample the drainage sites of this RBD (which has been entirely sampled for stream sediments).

### *River Basin District 8 (North East)*

No samples have been collected for full stream water analysis in this area (although the area has been completely sampled for stream sediments). There are no plans to resample sites to acquire stream water data. The conductivity and pH data which is available are included in Figures 7.2 and 7.3. Combined with geological information, this should help explain possible failures in compliance. However, this extrapolation will be most difficult over formations for which there are no data in regions further south. Indications of general formations and geographical environments with widespread failures are made in summaries of other RBDs and data tables; such information could help to prioritise the acquisition of more information or explain failures, though it is unlikely to adequately explain all variations in minor and trace element data.

### *River Basin District 9 (Humber)*

The data available for this RBD is restricted to the southern half of the area. Formations with concentrations exceeding the ‘added risk’ value are also indicated over unsampled areas. This information and that from any possible extrapolation of data from RBD09 may help to identify local backgrounds which will lead to failure in compliance. However, where substantial differences in geological or topographical environment occur, it may be necessary to characterise the background further. As indicated for other areas without data, any local effects caused by mining or impeded drainage (giving rise to more poorly oxidising waters), or arising from low-lying coastal areas, may indicate regions where establishing background concentrations should be prioritised.

There are no current plans to resample the drainage sites of this RBD (which has been entirely sampled for stream sediments). Stream water pH and conductivity data are included in Figures 7.2 and 7.3.

### *River Basin District 10 (Anglian)*

This RBD has data coverage for all but a very small proportion of the area along the southern margin, north of London, with all metal data being measured by the best available analytical technique. This should enable straightforward assessment of any failures of the standards.

# 8 Conclusions and recommendations

The nine metals of interest studied in this work can be classified into three levels of priority according to the magnitude of probable compliance failure of the standard if the background concentration of the metals is not taken into account (i.e. using the total risk approach).

- Highest (more than 75 per cent failure) for iron, arsenic, manganese;
- Intermediate (more than 20 per cent failure) for aluminium, zinc and nickel (depending on the standard used);
- Lowest (less than five per cent failure) for copper, chromium and lead.

Lack of consideration of background concentrations, particularly for the highest priority metals, could therefore lead to substantial problems in complying with proposed WFD standards.

The range of natural background concentrations of the nine metals examined here firmly point to the 'added risk' approach being the preferred option for all the metals studied, with the exception of chromium and lead, for which background concentrations are sufficiently low in comparison with the standard, that it is not required.

Our recommendations for the use of the added risk approach can be summarised as:

Chromium and Lead – added risk approach is not required

Copper – use of added risk with a single MBRC value (Cu MBRC = 1.6 μg/l)

Aluminium, arsenic, iron, manganese, nickel and zinc – use of added risk with derived MBRC

This study shows that setting MBRCs at an increasingly local scale is advisable, whilst a generic UK MBRC would be preferable to one generated from the FOREGs data (European-scale), for example.

MBRC values that represent the background concentrations at a given site can be derived in a hierarchical manner for required metals (aluminium, arsenic, iron, manganese, nickel and zinc), by considering spatial, WFD typological and geological influences, as described in Section 7. At the higher tiers of derivation, the MBRCs derived are likely to be increasingly representative of the background concentration at a given site, but this may be hampered in certain locations by availability of data. In these cases lower tiers of derivation, for example simple look up tables of generic 'default' river basin district or WFD typology based values for the MBRCs are still available, and are anticipated remain 'fit for purpose' in terms of their use in the added risk approach. For metals in this group that are of lower priority in terms of the level of anticipated failures of the standard (aluminium, nickel and zinc), it is likely that the use of 'default' MBRCs would be sufficient for most purposes, reducing the requirement for the derivation of a specific MBRC at each compliance assessment point. However, it must be recognised, that the 'priority' assessments given may change if the value of the proposed standards also change, since these have yet to be finalised.

Although some very broad assumptions about metal background concentrations can be made in the absence of real data, based on observed geological features, obviously far greater confidence is placed in the values derived for areas where data is available. This is reflected in the recommended decision process (Figure 7.1), and is also evident in the comparison of data from England and Wales with that from Northern Ireland.

It is currently difficult to assess background metal concentrations in larger river systems, because such systems in the UK tend to be affected by anthropogenic activities. Preliminary analysis of selected catchments where both background concentration data and larger river data were available indicated a greater probability of reaches failing the proposed standard in the larger river. However, this could very easily be due to anthropogenic impact, and could therefore be taken as indicating that the use of the 'added risk' approach would still ensure appropriate discrimination in this respect.

For the WFD River Basin Planning (RBP)1 cycle, it is likely that for several of the metals considered here the current EQSs will be used in compliance assessment, although it would be possible to make use of the generic approaches described in this report. Although the finalised values of the standards implemented will be critical in establishing whether the added risk approach is valid for any given metal, for RBP2 it is recommended that an approach based on that shown in this report is implemented.

Any substantial changes in the proposed standards should be examined for their consequence on an added risk regulatory regime. Appendix 3 briefly examines very recently released changed proposed standard concentrations for copper, nickel and lead, and demonstrates that these would have very little effect on the conclusions drawn from the main body of this report.

This report makes the following recommendations for further work:

- Use digital catchment mapping to attribute existing geochemical data to specific catchments, to enable generation of catchment scale MBRCs where suitable data is available. This will improve provision of data required for the decision process given in Figure 7.1, including medians to use in adjacent catchments and would also improve the maps provided in Appendix 1. The required shapefiles were not available for this work because of a licensing issue related to the collaborative nature of the project, but this could be solved simply by directly contracting the work instead.
- Although outside the remit of the Environment Agency, examination of data in Northern Ireland where the recently released background data covers the whole country could also provide useful information for areas of Scotland with similar geological environments (which are not reflected in the data available in England and Wales).
- Similar work for stream sediments could be considered depending on the requirement to implement WFD standards for sediment. Stream sediment background data is available for all of the UK, except those areas of southern England identified as 'planned for future sampling' in Figure 2.4.
- Undertake 'data mining' exercises with additional sources of data in an attempt to provide additional information for areas that are currently data poor.

- Refine the mining-MBRC dataset by using information on the chemical composition of mineralisation, and sampling at abandoned mine sites, in specific orefields to produce a set of mining-related MBRCs.

# Appendix 1: Detailed geological analysis of river basin districts

The following text, maps, and tables provide further geological information that could be used to look at underlying causes for compliance failure. Further explanation of the methods applied and outputs generated is given in Section 7.2.

## River Basin District 1 (Thames)

### Iron

The median concentration of these very restricted data (26 µg/l) is below that of the overall dataset median (Table 5.1a), whilst no distinction of WFD typology can be made as all samples fall into the ‘calcareous’ category. Of the 26 ‘PM 250/50’ categories with samples (only nine with 10 or more samples), none has a median concentration above 75 µg/l. Figure A1.1a shows the location of samples which exceed the ‘added risk’ value. Extrapolation from formations in RBDs 04 and 10 may help to provide more background information.

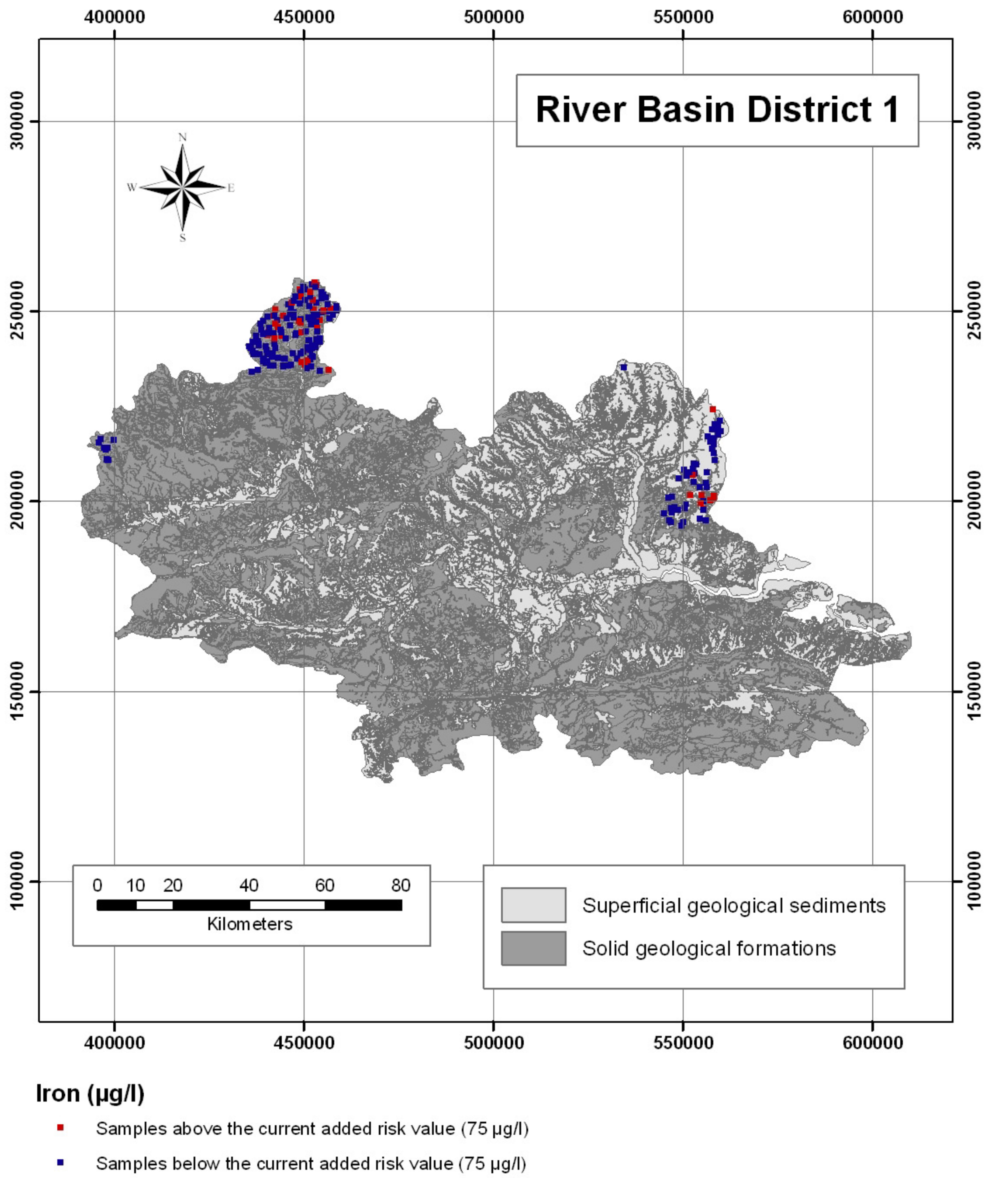


**Figure A1.1a: Comparison of iron stream water data and 'PM 250/50' categories in RBD01 exceeding the 'added risk' value.**

## Manganese

The median concentration of these very restricted data (11 µg/l) is below that of the overall dataset median (Table 5.1a), whilst no distinction of WFD typology can be made as all samples fall into the 'calcareous' category. Of the 26 'PM 250/50' categories with samples (only nine with 10 or more samples), only one has a median concentration above 29 µg/l (Table A1.1). Its location is shown in Figure A.1.1b. Some samples exceed the 'added risk' value in the Banbury area, assessment of which may be aided by comparison with the same formations in RBD04.

**Table A1.1: Manganese summary statistics for 'PM 250/50' categories in RBD01 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| LC-ARG\H-CLSI | 22 | 17 | 45 | 180 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

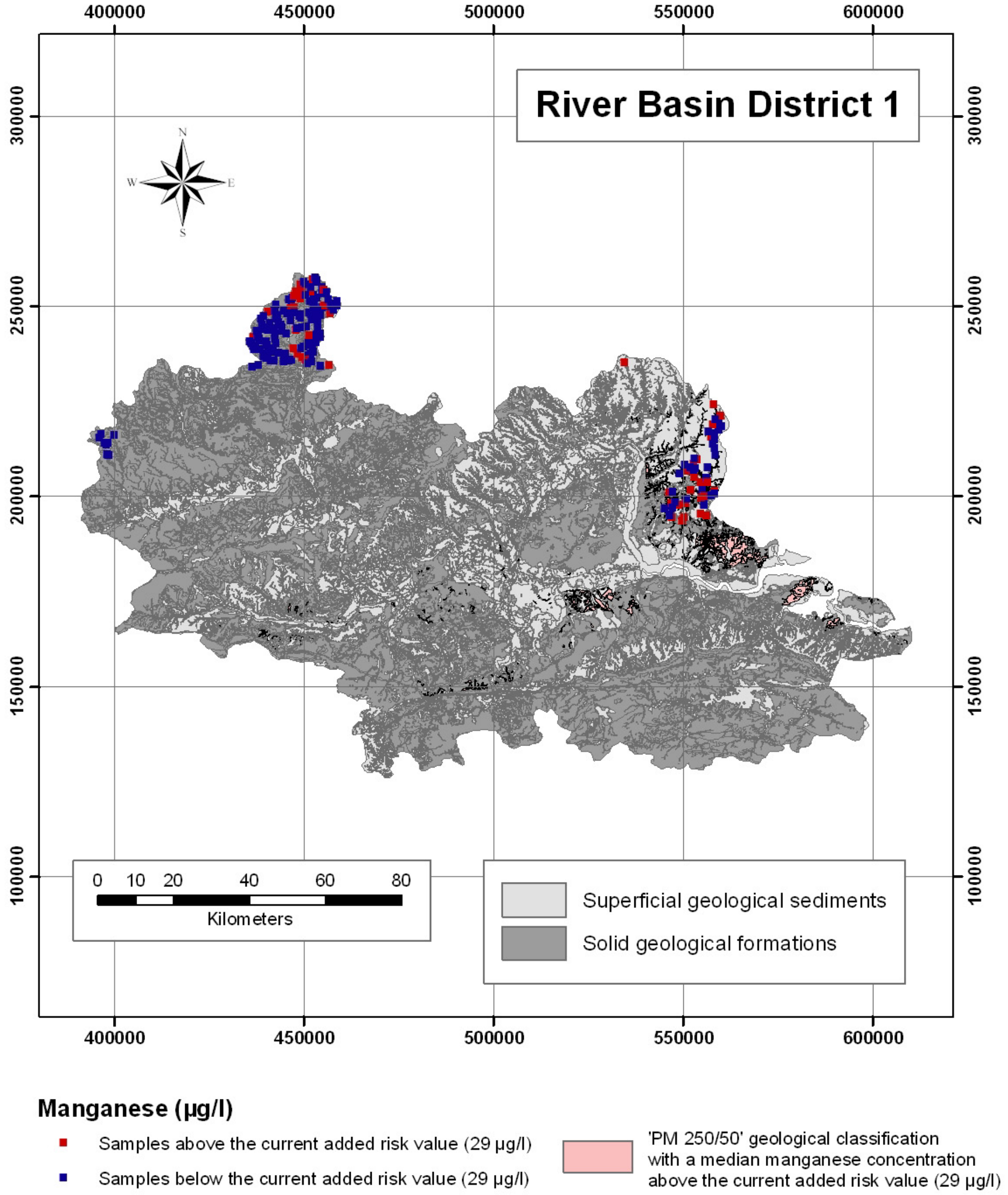


**Figure A1.1b: Comparison of manganese stream water data and 'PM 250/50' categories in RBD01 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Arsenic

The median concentration of these very restricted data (0.98 µg/l) is below that of the overall dataset median (Table 5.1a), whilst no distinction of WFD typology can be made as all samples fall into the 'calcareous' category. Of the 22 'PM 250/50' categories with samples (only nine with more than 10 samples), only the London Clay and associated drift have median concentrations above 1.8 µg/l (Table A1.2).

For locations of individual samples with a concentration greater than 1.8 µg/l (Figure A1.1c), several are in the Banbury area, often associated with the Charmouth Mudstone formation. This suggests that with more sampling and extrapolation from RBD04 where the formation also occurs and more data are available, these could be explained.

**Table A1.2: Arsenic summary statistics for 'PM 250/50' categories in RBD01 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| LC-ARG\DMTN | 12 | 0.87 | 1.9 | 3.3 |
| LC-ARG\H-CLSI | 22 | 1.5 | 2.1 | 3.5 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

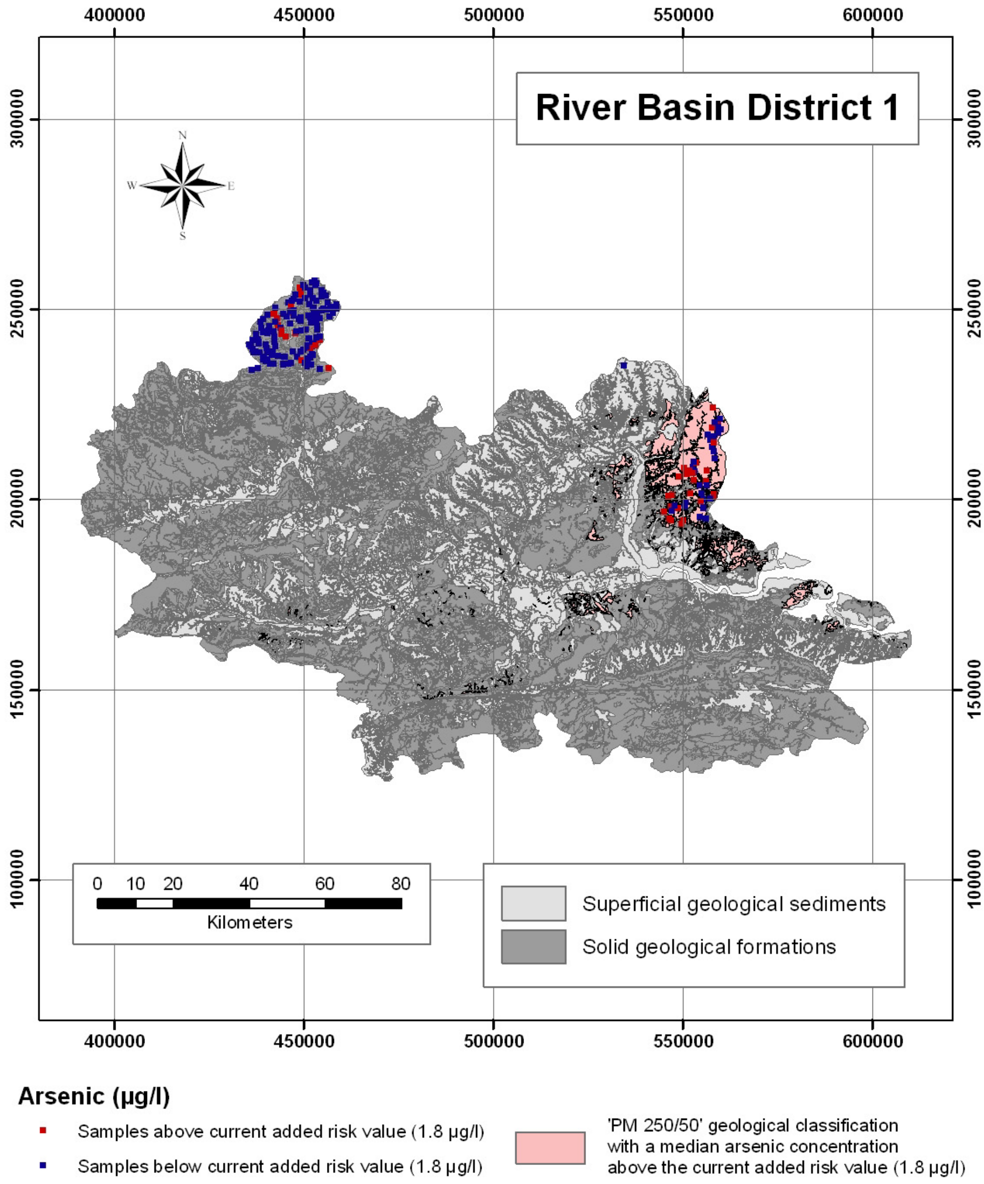


**Figure A1.1c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD01 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

# River Basin District 3 (South West)

## Iron

The iron concentrations in this region are much higher (with a median of 260 µg/l) than that of the whole dataset as shown in Table 5.1a, with most samples in the 'siliceous' typology (Table 5.2a). These high concentrations indicate that more than 43 per cent of samples will fail the 'added risk' concentration of 75 µg/l in this RBD, which is the percentage shown in Table 4.2. This implies an increased workload, even after the application of tier 2 assessments.

Formations associated with iron concentrations exceeding the 'added risk' value are shown in Table A1.3 and their locations in Figure A1.2a. For all formations, even the 25th percentile exceeds the 'added risk' value, and they represent more than 90 per cent of the sample site data in the r-MBRC dataset for this area. This shows that almost all sites would fail the proposed standard and the 'added risk' value in this area.

**Table A1.3: Iron summary statistics for 'PM 250/50' categories in RBD03 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| BFBF-SDAR\ | 32 | 122 | 225 | 375 |
| BFBF-SDAR\CLSI | 25 | 213 | 337 | 446 |
| CKF-ARSD\ | 88 | 122 | 281 | 547 |
| CKF-ARSD\CLSI | 152 | 243 | 403 | 709 |
| CKF-ARSD\SAGR | 26 | 164 | 281 | 400 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

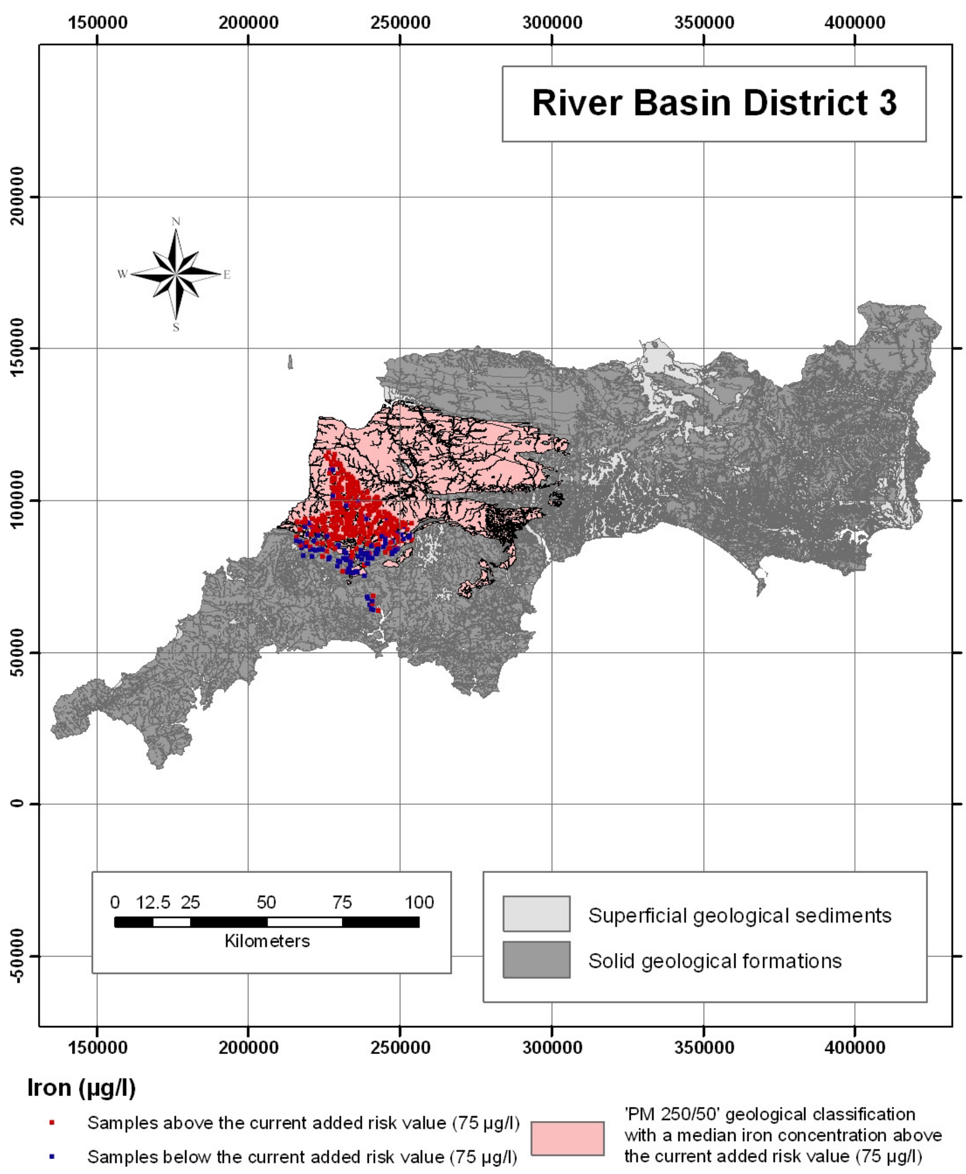


**Figure A1.2a: Comparison of iron stream water data and 'PM 250/50' categories in RBD03 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Manganese

The manganese concentrations in this region are higher (with a median of 41 µg/l) than that of the whole dataset as shown in Table 5.1a, with most samples in the 'siliceous' typology. These higher concentrations indicate that more than 43 per cent of samples will fail the 'added risk' concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2. Geological categories of 'PM 250/50' classification which have median concentrations exceeding the 'added risk' value are given in Table A1.4, and their location in Figure A1.2b. These data show that more than 90 per cent of r-MBRC samples in this RBD will fail the ‘added risk’ value, suggesting that the need for a tier 2 assessment could be widespread. Geological categories associated with failures of the ‘added risk’ value extend greatly beyond the boundaries where samples are already collected. These may indicate a further widespread compliance problem, but they are not the only areas of RBD03 where this may happen.

**Table A1.4: Manganese summary statistics for ‘PM 250/50’ categories in RBD03 exceeding the ‘added risk’ value (all concentrations in µg/l)**

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| BFBF-SDAR\ | 32 | 22 | 80 | 186 |
| BFBF-SDAR\CLSI | 25 | 41 | 59 | 95 |
| CKF-ARSD\CLSI | 152 | 27 | 45 | 83 |
| CKF-ARSD\ | 88 | 19 | 41 | 88 |
| CKF-ARSD\SAGR | 26 | 17 | 34 | 89 |
| UDCS-ARG\CLSI | 19 | 14 | 32 | 57 |

* The look-up tables for all the 1:250,000 solid formations (information before the ‘\’ in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the ‘\’ field, this indicates that there are no drift sediments mapped in that location.

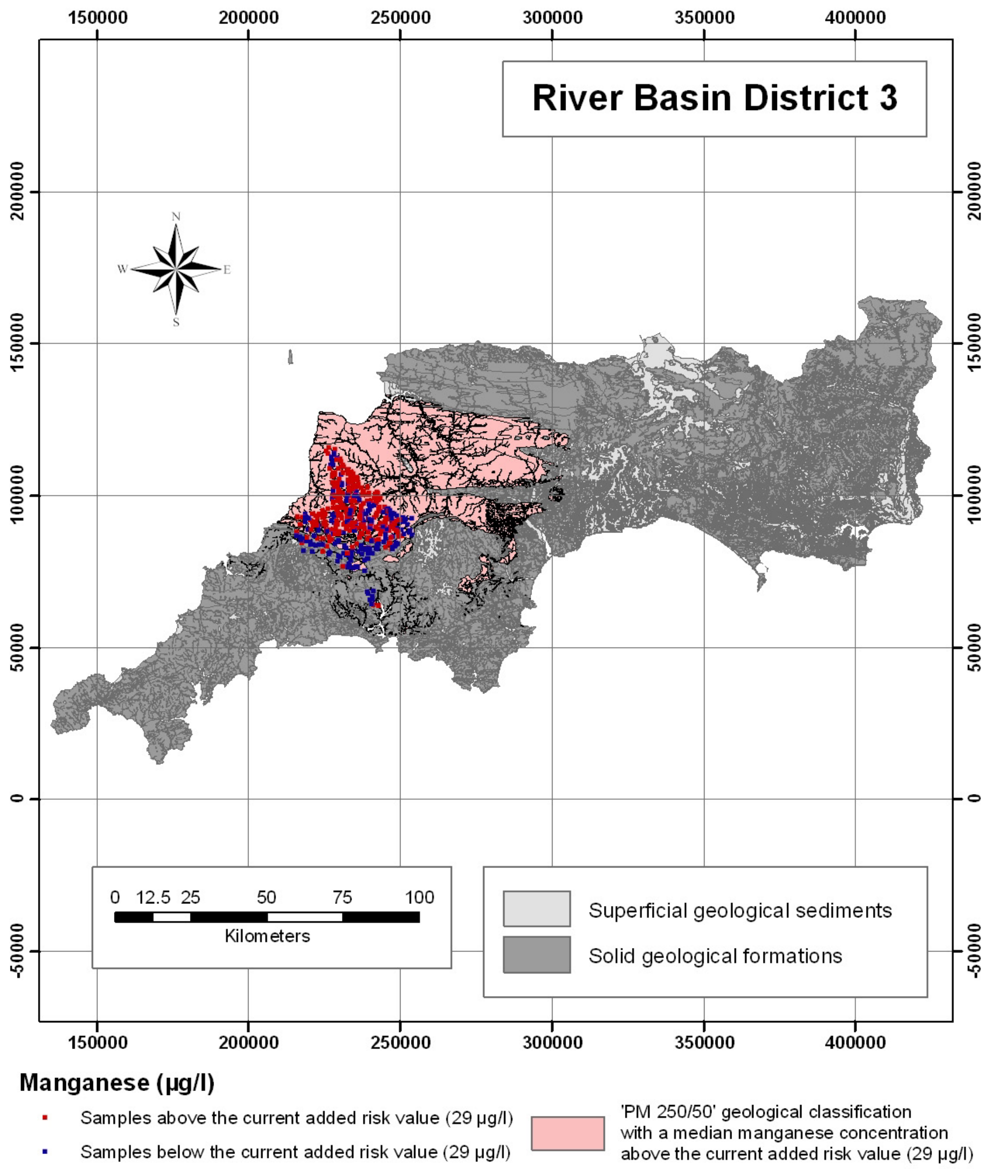


**Figure A1.2b: Comparison of manganese stream water data and 'PM 250/50' categories in RBD03 exceeding the 'added risk' value**

Note: Extension of the pink colouration over areas of unsampled 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Arsenic

The arsenic concentrations in this region are lower (with a median of 0.98 µg/l) than that of the whole dataset as shown in Table 5.1b, with most samples in the siliceous typology. These lower r-MBRCs indicate that fewer than 37 per cent of samples will fail the 'added risk' concentration of 1.8 µg/l, which is the percentage shown in Table 4.2. This figure might change if samples from areas of mineralisation and mining are included, because of arsenic mining in this area.

No geological categories with 10 or more samples have a median concentration above 1.8 µg/l, even in the mining district in the south. However, lavas in the catchment have very high concentrations (median of 6 µg/l) over the west of the catchment. Should monitoring samples in this formation fail, further work may be necessary to assess whether this is an indirect effect of mineralisation or whether it is due to the dispersed lithologies (Figure A1.2c).

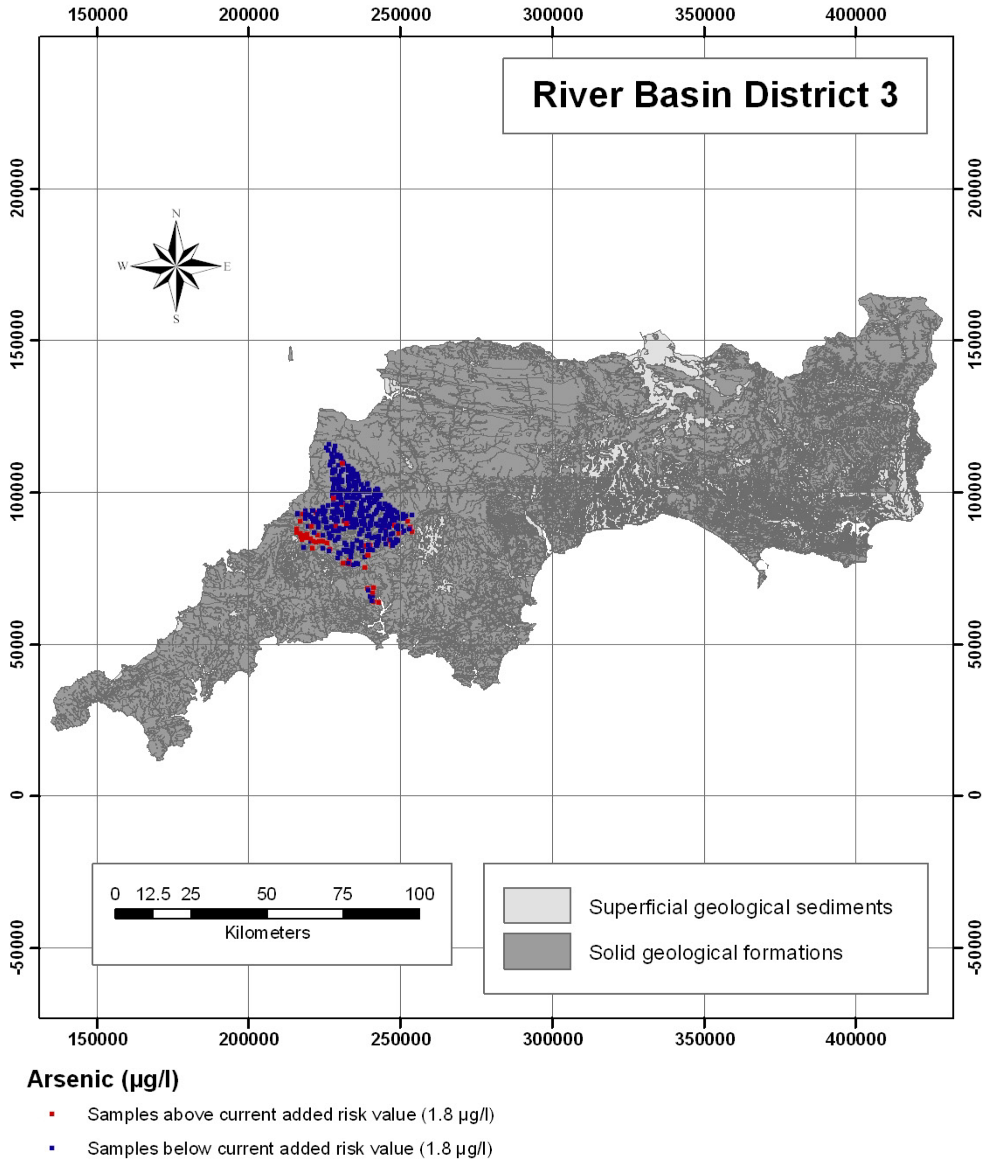


**Figure A1.2c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD03 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

# River Basin District 4 (Severn)

## Iron

The iron concentrations in this region (with a median of 260 µg/l) are close to that of the whole dataset as shown in Table 5.1a, with higher concentrations over all WFD typologies except ‘calcareous’ (which accounts for the majority of samples) (Table 5.2a). Approximately 43 per cent of samples will fail the ‘added risk’ concentration of 75 µg/l in this RBD, which is the overall percentage shown in Table 4.2.

Formations associated with iron concentrations exceeding the ‘added risk’ value are shown in Table A1.5 and their locations in Figure A1.3a. The number of geological categories in Table A1.5 reflects the size of this RBD and its geological diversity.

**Table A1.5: Iron summary statistics for ‘PM 250/50’ categories in RBD04 exceeding the ‘added risk’ value (all concentrations in µg/l)**

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| ASHL-ARSD\ | 41 | 80 | 179 | 304 |
| ASHL-ARSD\DMTN | 47 | 59 | 160 | 307 |
| BHWW-SDST\ | 44 | 21 | 47 | 72 |
| BHWW-SDST\CLSI | 56 | 30 | 54 | 79 |
| BHWW-SDST\DMTN | 20 | 33 | 45 | 206 |
| BHWW-SDST\SAGR | 16 | 17 | 43 | 64 |
| BLI-ARLM\CLSI | 17 | 44 | 65 | 294 |
| BLI-LMST\CLSI | 12 | 27 | 46 | 62 |
| BRI-SDST\ | 18 | 18 | 44 | 104 |
| BRI-SDST\CLSI | 60 | 30 | 49 | 74 |
| BRI-SDST\DMTN | 27 | 45 | 65 | 303 |
| BRI-SDST\SAGR | 14 | 46 | 76 | 190 |
| CARA-ARG\ | 67 | 39 | 89 | 207 |
| CARA-ARG\CLSI | 38 | 102 | 210 | 318 |
| CARA-ARG\DMTN | 100 | 74 | 140 | 230 |
| CARA-ARG\SAGR | 19 | 76 | 129 | 303 |
| CARA-ARG\UNKN | 14 | 18 | 165 | 369 |
| CHAM-ARG\ | 267 | 21 | 35 | 56 |
| CHAM-ARG\CLSI | 152 | 25 | 40 | 74 |
| CHAM-ARG\DMTN | 14 | 43 | 166 | 701 |
| CHAM-ARG\H-CLSI | 23 | 27 | 48 | 63 |
| CHAM-ARG\SAGR | 25 | 20 | 44 | 86 |
| CM-ARSD\ | 41 | 40 | 99 | 264 |
| CM-ARSD\DMTN | 12 | 40 | 70 | 850 |
| CMR-ARG\ | 34 | 51 | 139 | 453 |
| CMR-ARG\DMTN | 14 | 99 | 187 | 577 |
| CWY-ARSD\ | 35 | 61 | 188 | 437 |
| CWY-ARSD\DMTN | 67 | 146 | 275 | 525 |
| CWY-SDST\ | 12 | 83 | 162 | 296 |
| CWY-SDST\DMTN | 23 | 164 | 202 | 431 |
| DYS-ARG\ | 30 | 16 | 37 | 62 |
| ETM-ARSD\ | 30 | 26 | 44 | 117 |
| HA-ARSD\ | 39 | 25 | 46 | 186 |
| HA-ARSD\CLSI | 12 | 49 | 56 | 110 |
| HA-ARSD\DMTN | 17 | 112 | 161 | 275 |
| HA-ARSD\SAGR | 19 | 54 | 85 | 162 |
| KDCP-CONG\ | 12 | 21 | 42 | 53 |

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| KDCP-CONG\CLSI | 24 | 32 | 52 | 85 |
| LDVY-ARG\ | 161 | 57 | 122 | 328 |
| LDVY-ARG\CLSI | 36 | 92 | 174 | 270 |
| LDVY-ARG\DMTN | 178 | 86 | 175 | 396 |
| LDVY-ARG\SAGR | 12 | 63 | 113 | 171 |
| LLDA-ARSD\ | 15 | 30 | 52 | 229 |
| LLDA-ARSD\DMTN | 33 | 77 | 181 | 393 |
| LLVN-SDST\DMTN | 13 | 133 | 201 | 512 |
| LORS-SDAR\ | 14 | 29 | 51 | 122 |
| LPEM-SDAR\DMTN | 16 | 7 | 39 | 122 |
| LPEM-SDST\ | 24 | 4 | 52 | 172 |
| LPEM-SDST\DMTN | 21 | 22 | 86 | 214 |
| LUDL-ARG\CLSI | 32 | 20 | 45 | 114 |
| LUDL-ARG\DMTN | 77 | 14 | 36 | 72 |
| LUDL-ARSD\ | 58 | 17 | 34 | 93 |
| LUDL-ARSD\CLSI | 17 | 22 | 36 | 105 |
| LUDL-ARSD\DMTN | 48 | 20 | 62 | 103 |
| LUDL-ARSD\H-CLSI | 12 | 14 | 42 | 65 |
| LUW-ARG\ | 77 | 41 | 89 | 202 |
| LUW-ARG\CLSI | 23 | 21 | 145 | 236 |
| LUW-ARG\DMTN | 69 | 40 | 71 | 119 |
| LUW-ARG\SAGR | 13 | 44 | 60 | 159 |
| MCM-ARG\ | 10 | 14 | 42 | 79 |
| MCM-ARG\DMTN | 19 | 26 | 55 | 158 |
| MMG-ARG\ | 180 | 17 | 39 | 81 |
| MMG-ARG\CLSI | 276 | 21 | 38 | 84 |
| MMG-ARG\DMTN | 22 | 22 | 40 | 92 |
| MMG-ARG\PEAT | 11 | 60 | 115 | 274 |
| MMG-ARG\SAGR | 42 | 26 | 36 | 54 |
| NGF-ARSD\ | 43 | 78 | 122 | 238 |
| NGF-ARSD\DMTN | 27 | 77 | 97 | 251 |
| PEG-SDST\ | 126 | 224 | 502 | 1240 |
| PEG-SDST\DMTN | 45 | 296 | 606 | 914 |
| PEG-SDST\H-CLSI | 11 | 143 | 268 | 1515 |
| PNG-LMAR\ | 10 | 25 | 29 | 48 |
| RG-ARG\DMTN | 11 | 23 | 43 | 104 |
| RG-ARSD\ | 306 | 19 | 40 | 79 |
| RG-ARSD\CLSI | 222 | 23 | 42 | 74 |
| RG-ARSD\DMTN | 139 | 28 | 52 | 117 |
| RG-ARSD\H-CLSI | 55 | 15 | 40 | 69 |
| RG-ARSD\SAGR | 23 | 18 | 42 | 94 |
| RLS-LMST\ | 11 | 59 | 94 | 127 |
| SAL-ARSD\ | 49 | 29 | 43 | 68 |
| SAL-ARSD\CLSI | 25 | 38 | 54 | 96 |
| SAL-ARSD\DMTN | 13 | 33 | 65 | 108 |
| SMG-ARSD\CLSI | 68 | 28 | 49 | 130 |
| SMG-ARSD\H-CLSI | 44 | 11 | 29 | 53 |
| UPEM-SDST\DMTN | 19 | 22 | 59 | 104 |
| WEN-ARG\ | 43 | 45 | 103 | 344 |
| WEN-ARG\CLSI | 35 | 36 | 76 | 232 |
| WEN-ARG\DMTN | 87 | 61 | 119 | 278 |
| WEN-ARG\SAGR | 13 | 37 | 71 | 98 |
| WESH-ARG\ | 16 | 22 | 50 | 104 |
| WESH-ARG\CLSI | 24 | 58 | 102 | 146 |
| WESH-ARG\DMTN | 13 | 29 | 120 | 405 |
| YST-ARSD\ | 11 | 14 | 39 | 74 |
| YW-SDAR\DMTN | 15 | 37 | 105 | 162 |

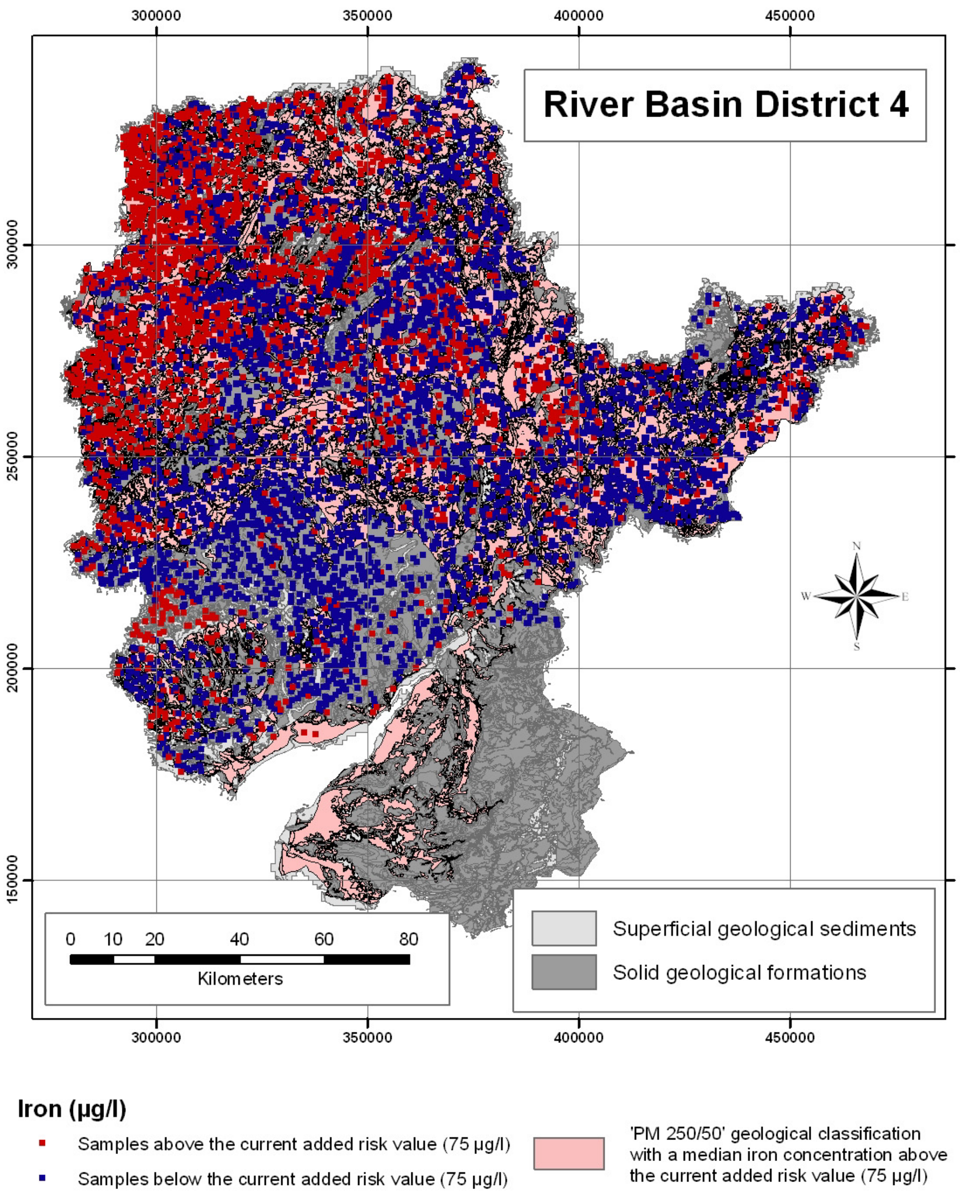


**Figure A1.3a: Comparison of iron stream water data and 'PM 250/50' categories in RBD04 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Manganese

The manganese concentrations in this region (with a median of 18 µg/l) are close to that of the whole dataset as shown in Table 5.1a, with higher concentrations over the 'salt' and 'peat' WFD typologies (Table 5.2a). These data indicate that approximately 43 per cent of samples will fail the 'added risk' concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2.

Formations associated with manganese concentrations exceeding the 'added risk' value are shown in Table A1.6 and their locations in Figure A1.3b. As with iron, there are a relatively large number of these classes in Table A1.6, due to the large size of the catchment. The highest concentrations are generally associated with upland areas forming the western edge of the RBD watershed. Pink shaded areas perform a reasonable job of anticipating where ‘added risk’ failures are likely to occur.

**Table A1.6: Manganese summary statistics for ‘PM 250/50’ categories in RBD04 exceeding the ‘added risk’ value (all concentrations in µg/l)**

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| BHWW-SDST\DMTN | 20 | 6 | 41 | 88 |
| BLI-ARLM\CLSI | 17 | 16 | 79 | 460 |
| BRI-SDST\DMTN | 27 | 11 | 31 | 135 |
| BRI-SDST\SAGR | 14 | 16 | 48 | 94 |
| CARA-ARG\SAGR | 19 | 33 | 49 | 126 |
| CARA-ARG\UNKN | 14 | 14 | 39 | 78 |
| CHAM-ARG\DMTN | 14 | 20 | 92 | 546 |
| CM-ARSD\ | 41 | 18 | 54 | 125 |
| CMR-ARG\DMTN | 14 | 20 | 49 | 110 |
| CWY-ARSD\ | 35 | 46 | 98 | 138 |
| CWY-ARSD\DMTN | 67 | 56 | 114 | 222 |
| CWY-SDST\ | 12 | 38 | 63 | 109 |
| CWY-SDST\DMTN | 23 | 11 | 54 | 135 |
| ETM-ARSD\ | 30 | 16 | 57 | 119 |
| HA-ARSD\ | 39 | 20 | 34 | 95 |
| HA-ARSD\CLSI | 12 | 16 | 34 | 53 |
| HA-ARSD\DMTN | 17 | 41 | 90 | 249 |
| HA-ARSD\SAGR | 19 | 16 | 30 | 83 |
| LDVY-ARG\ | 161 | 11 | 37 | 106 |
| LDVY-ARG\DMTN | 178 | 14 | 35 | 79 |
| LLVN-SDST\DMTN | 13 | 11 | 39 | 56 |
| LPEM-SDAR\DMTN | 16 | 5 | 35 | 94 |
| LPEM-SDST\DMTN | 21 | 6 | 43 | 67 |
| MCM-ARG\ | 10 | 2 | 35 | 113 |
| MMG-ARG\DMTN | 22 | 13 | 39 | 87 |
| MMG-ARG\PEAT | 11 | 17 | 135 | 417 |
| PEG-SDST\ | 126 | 24 | 102 | 203 |
| PEG-SDST\DMTN | 45 | 29 | 73 | 163 |
| PEG-SDST\H-CLSI | 11 | 20 | 67 | 340 |
| RLS-LMST\ | 11 | 10 | 30 | 49 |
| SAL-ARSD\ | 49 | 15 | 34 | 55 |
| SAL-ARSD\DMTN | 13 | 23 | 68 | 231 |
| UPEM-SDST\DMTN | 19 | 8 | 32 | 52 |
| WESH-ARG\DMTN | 13 | 21 | 48 | 62 |

* The look-up tables for all the 1:250,000 solid formations (information before the ‘\’ in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the ‘\’ field, this indicates that there are no drift sediments mapped in that location.

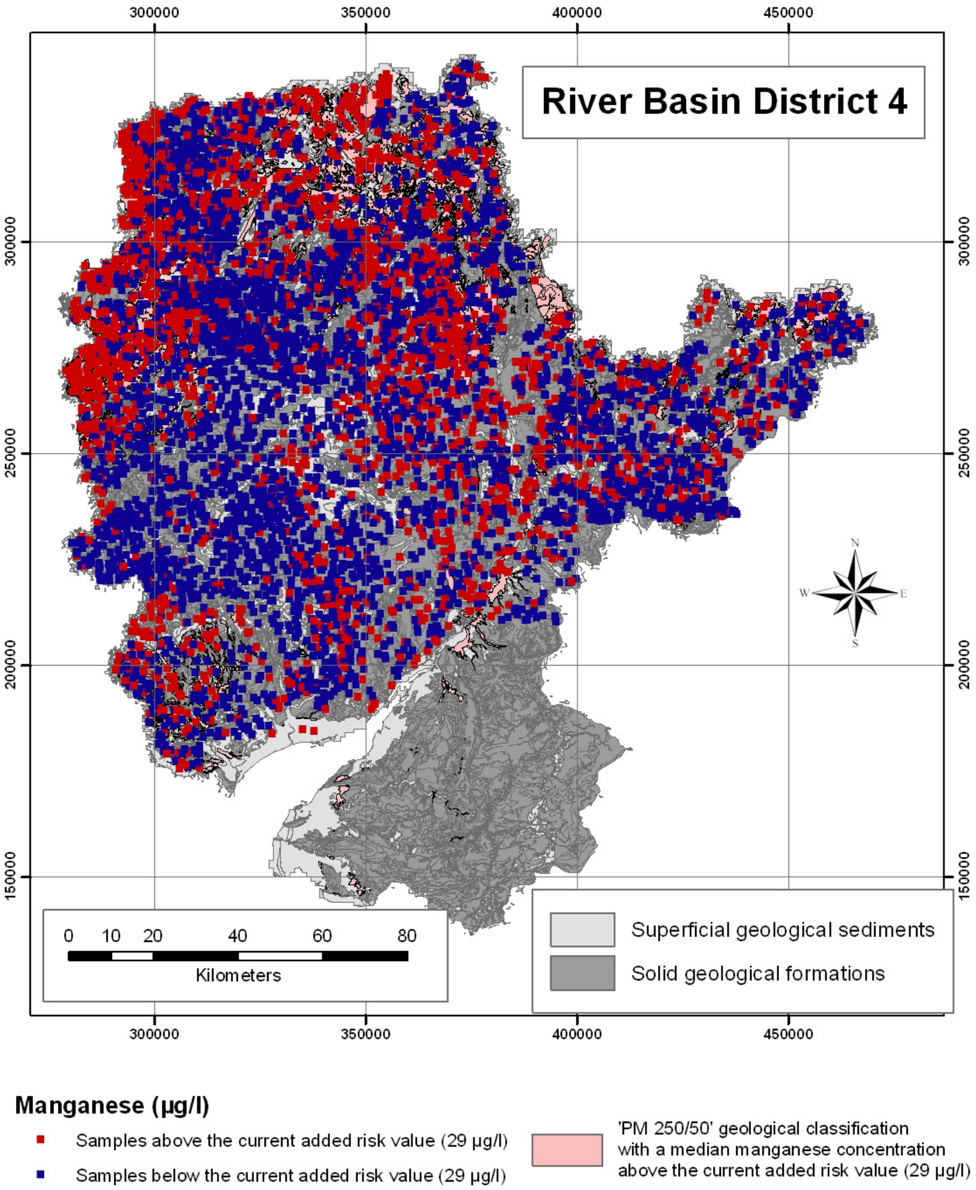


**Figure A1.3b: Comparison of manganese stream water data and 'PM 250/50' categories in RBD04 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Arsenic

The overall arsenic concentration (with a median of 1.4 µg/l) is close to that of the whole dataset as shown in Table 5.1b, with most samples in the calcareous typology. These higher concentrations indicate that approximately 37 per cent of samples will fail the 'added risk' concentration of 1.8 µg/l, which is the overall percentage shown in Table 4.2.

The Mercia Mudstone group forms the basis of all three 'PM 250/50' categories exceeding the 'added risk' value in Table A1.7 and Figure A1.3c. The extension of this geological formation to the Severn Estuary (with a small outcrop in the north east of the area) is highlighted in Figure A1.3c, and samples from this area which fail the standard, should be examined further for high natural background concentrations. The dearth of samples from the western area creates a problem, and there is limited data for Pembrokeshire , which may relate to some of these formations. However, there may be no alternative but to either collect background samples over the main formations, or address the reasons for failure.

**Table A1.7: Arsenic summary statistics for 'PM 250/50' categories in RBD04 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| MMG-ARG\SAGR | 32 | 2.7 | 5.8 | 11.1 |
| MMG-ARG\CLSI | 118 | 1.9 | 4.4 | 8.5 |
| MMG-ARG\ | 86 | 1.7 | 3.3 | 6.2 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

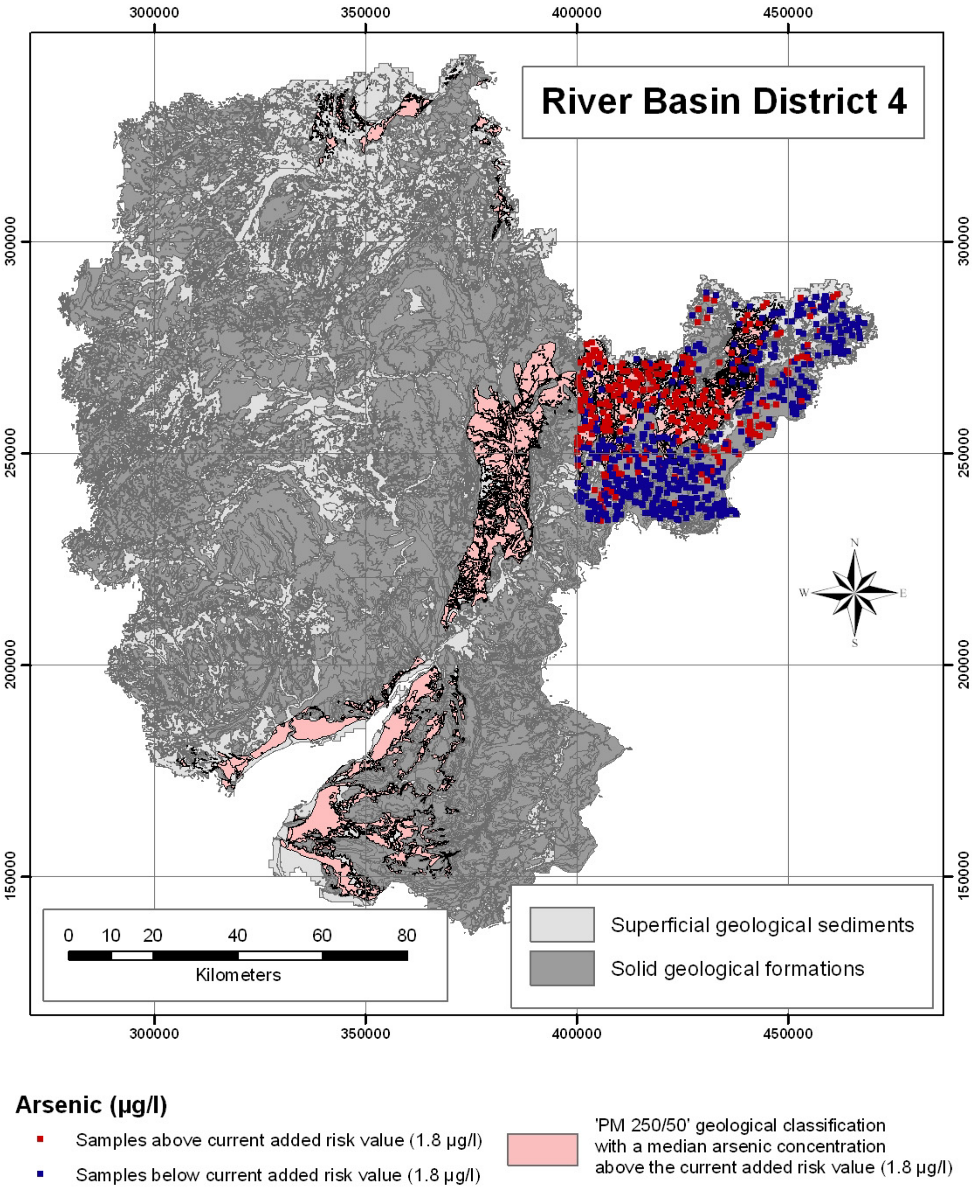


**Figure A1.3c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD04 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

# River Basin District 5 (Western Wales)

## Iron

The iron concentrations in this region are higher (with a median of 100 µg/l) than that of the whole dataset as shown in Table 5.1a, with higher concentrations in ‘peat’ typology (median of 169 µg/l), which are all upland peat samples ($WFD_p$) (Table 5.2a). These high concentrations indicate that more than 43 per cent of samples will fail the ‘added risk’ concentration of 75 µg/l in this RBD, which is the overall percentage shown in Table 4.2. The ‘PM 250/50’ categories which have a median exceeding the ‘added risk’ value are shown in Figure A1.4a and Table A1.8. The large number of categories reflects the high overall median concentration and geological diversity of the region.

**Table A1.8: Iron summary statistics for ‘PM 250/50’ categories in RBD05 exceeding the ‘added risk’ value (all concentrations in µg/l)**

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| AGF-SDAR\ | 34 | 56 | 128 | 299 |
| AGF-SDAR\CLSI | 13 | 197 | 225 | 296 |
| AGF-SDAR\DMTN | 59 | 63 | 141 | 383 |
| BFMB-ARG\ | 52 | 43 | 119 | 217 |
| BFMB-ARG\CLSI | 15 | 60 | 92 | 170 |
| BFMB-ARG\DMTN | 12 | 157 | 211 | 343 |
| BFMB-ARG\SUPD | 18 | 45 | 138 | 278 |
| CWY-ARSD\ | 27 | 146 | 339 | 553 |
| CWY-ARSD\DMTN | 29 | 104 | 207 | 402 |
| CWY-SDST\DMTN | 16 | 221 | 411 | 782 |
| DBF-ARSD\DMTN | 10 | 65 | 130 | 275 |
| DYN-ARG\DMTN | 18 | 50 | 77 | 180 |
| GMCB-ARG\ | 14 | 167 | 321 | 476 |
| GWNM-MELG\DMTN | 15 | 99 | 137 | 365 |
| LCM-ARSD\ | 17 | 40 | 217 | 344 |
| LCM-ARSD\DMTN | 33 | 60 | 193 | 275 |
| LDVY-ARG\CLSI | 31 | 44 | 120 | 273 |
| LDVY-ARG\DMTN | 253 | 73 | 128 | 276 |
| LDVY-ARG\SAGR | 51 | 49 | 107 | 176 |
| LLDA-ARSD\CLSI | 58 | 50 | 87 | 145 |
| LLDA-ARSD\DMTN | 123 | 47 | 94 | 204 |
| LLDA-ARSD\H-SAGR | 16 | 47 | 85 | 150 |
| LLDA-ARSD\SAGR | 35 | 63 | 110 | 187 |
| LMC-ARG\ | 33 | 196 | 297 | 517 |
| LMC-ARG\CLSI | 10 | 193 | 238 | 742 |
| LPEM-SDAR\ | 16 | 24 | 98 | 210 |
| LPEM-SDAR\DMTN | 22 | 89 | 177 | 307 |
| LPEM-SDST\DMTN | 48 | 66 | 136 | 205 |
| LUDL-ARG\DMTN | 10 | 33 | 105 | 219 |
| LUDL-ARSD\ | 15 | 86 | 244 | 387 |
| LUDL-ARSD\DMTN | 63 | 30 | 88 | 189 |
| MCM-ARG\ | 32 | 29 | 137 | 277 |
| MCM-ARG\DMTN | 39 | 85 | 121 | 300 |
| MG-ARG\DMTN | 20 | 74 | 133 | 206 |
| MG-ARSD\ | 19 | 256 | 344 | 587 |
| MG-ARSD\DMTN | 12 | 77 | 178 | 616 |

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| MG-SDST\ | 11 | 194 | 487 | 621 |
| MWG-ARG\ | 38 | 50 | 103 | 265 |
| MWG-ARG\DMTN | 42 | 72 | 202 | 404 |
| MWG-ARG\PEAT | 11 | 77 | 432 | 1055 |
| MYSH-ARG\ | 16 | 202 | 349 | 655 |
| NGW-SCHI\DMTN | 15 | 45 | 126 | 413 |
| NNH-SCHI\CLSI | 11 | 67 | 104 | 198 |
| NNH-SCHI\DMTN | 18 | 100 | 132 | 259 |
| N-SCHI\CLSI | 15 | 155 | 290 | 398 |
| N-SCHI\DMTN | 25 | 83 | 135 | 299 |
| NYG-ARG\ | 20 | 225 | 570 | 897 |
| OGW-ARG\CLSI | 41 | 48 | 131 | 242 |
| OGW-ARG\DMTN | 179 | 35 | 95 | 184 |
| OGW-ARG\PEAT | 41 | 42 | 143 | 522 |
| OGW-ARG\SAGR | 30 | 75 | 182 | 411 |
| OGW-LATU\DMTN | 30 | 52 | 99 | 224 |
| OGW-SDST\DMTN | 29 | 26 | 84 | 184 |
| OGW-TULA\ | 10 | 90 | 278 | 1,189 |
| OGW-TULA\DMTN | 12 | 110 | 150 | 380 |
| PEG-SDST\ | 24 | 239 | 431 | 770 |
| PEG-SDST\DMTN | 14 | 133 | 530 | 949 |
| PLQC-SDST\DMTN | 11 | 101 | 167 | 305 |
| SLR-ARSD\ | 33 | 139 | 201 | 406 |
| TESH-ARG\ | 40 | 40 | 89 | 132 |
| TESH-ARG\CLSI | 26 | 87 | 168 | 311 |
| TESH-ARG\DMTN | 14 | 84 | 168 | 380 |
| TESH-ARG\H-CLSI | 19 | 41 | 99 | 145 |
| UIIN-BAFI\ | 15 | 72 | 137 | 239 |
| UIIN-BAFI\PEAT | 10 | 56 | 103 | 913 |
| UPEM-ARSD\DMTN | 12 | 78 | 127 | 305 |
| UPEM-SDST\ | 17 | 41 | 106 | 220 |

* The look-up tables for all the 1:250,000 solid formations (information before the ‘\’ in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the ‘\’ field, this indicates that there are no drift sediments mapped in that location.

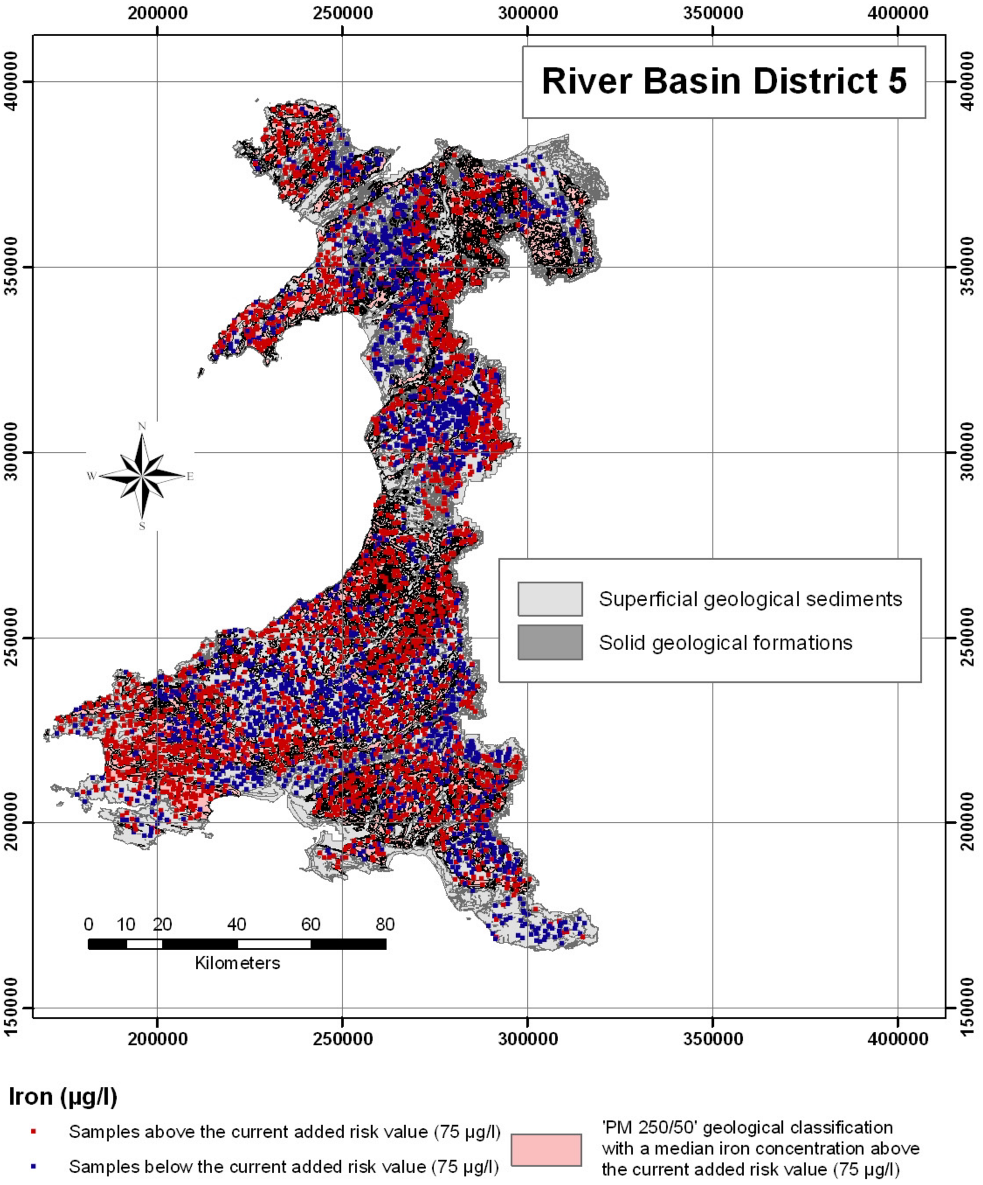


**Figure A1.4a: Comparison of iron stream water data and 'PM 250/50' categories in RBD05 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Manganese

The manganese concentrations in this region (with a median of 19 µg/l) are close to that of the whole dataset as shown in Table 5.1a, although a disparity occurs in the 'peat' typology (median of 67 µg/l). These higher concentrations indicate that approximately 43 per cent of samples will fail the 'added risk' concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2. The data which fail are reasonably well described by the geological categories listed below.

### Table A1.9: Manganese summary statistics for ‘PM 250/50’ categories in RBD05 exceeding the ‘added risk’ value (all concentrations in µg/l)

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| BFMB-ARG\DMTN | 12 | 16 | 34 | 147 |
| CWY-ARSD\ | 27 | 69 | 139 | 281 |
| CWY-ARSD\DMTN | 29 | 71 | 104 | 208 |
| CWY-SDST\DMTN | 16 | 37 | 68 | 142 |
| LMC-ARG\CLSI | 10 | 14 | 31 | 122 |
| LPEM-SDAR\DMTN | 22 | 11 | 31 | 66 |
| LPEM-SDST\ | 85 | 10 | 35 | 120 |
| LPEM-SDST\DMTN | 48 | 26 | 55 | 102 |
| MCM-ARG\ | 32 | 12 | 45 | 78 |
| MCM-ARG\DMTN | 39 | 17 | 38 | 113 |
| MG-ARG\DMTN | 20 | 8 | 33 | 68 |
| MWG-ARG\DMTN | 42 | 12 | 39 | 96 |
| MWG-ARG\PEAT | 11 | 37 | 83 | 285 |
| NGW-SCHI\DMTN | 15 | 23 | 38 | 322 |
| NNH-SCHI\CLSI | 11 | 7 | 53 | 146 |
| NNH-SCHI\DMTN | 18 | 5 | 57 | 225 |
| N-SCHI\CLSI | 15 | 31 | 74 | 114 |
| N-SCHI\DMTN | 25 | 36 | 87 | 220 |
| NYG-ARG\ | 20 | 10 | 37 | 109 |
| OGW-ARG\ | 116 | 7 | 28 | 81 |
| OGW-ARG\CLSI | 41 | 12 | 29 | 96 |
| OGW-ARG\DMTN | 179 | 8 | 31 | 101 |
| OGW-ARG\H-CLSI | 15 | 9 | 30 | 83 |
| OGW-ARG\PEAT | 41 | 25 | 100 | 184 |
| OGW-ARG\SAGR | 30 | 19 | 31 | 115 |
| OGW-SDST\ | 28 | 9 | 38 | 123 |
| OGW-TULA\ | 10 | 16 | 39 | 158 |
| PEG-SDST\ | 24 | 28 | 84 | 144 |
| PEG-SDST\DMTN | 14 | 27 | 62 | 134 |
| RN-SDST\DMTN | 10 | 10 | 36 | 100 |
| TESH-ARG\DMTN | 14 | 16 | 42 | 53 |
| UIIN-BAFI\PEAT | 10 | 6 | 82 | 298 |
| UPEM-SDST\ | 17 | 14 | 75 | 96 |

* The look-up tables for all the 1:250,000 solid formations (information before the ‘\’ in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the ‘\’ field, this indicates that there are no drift sediments mapped in that location.

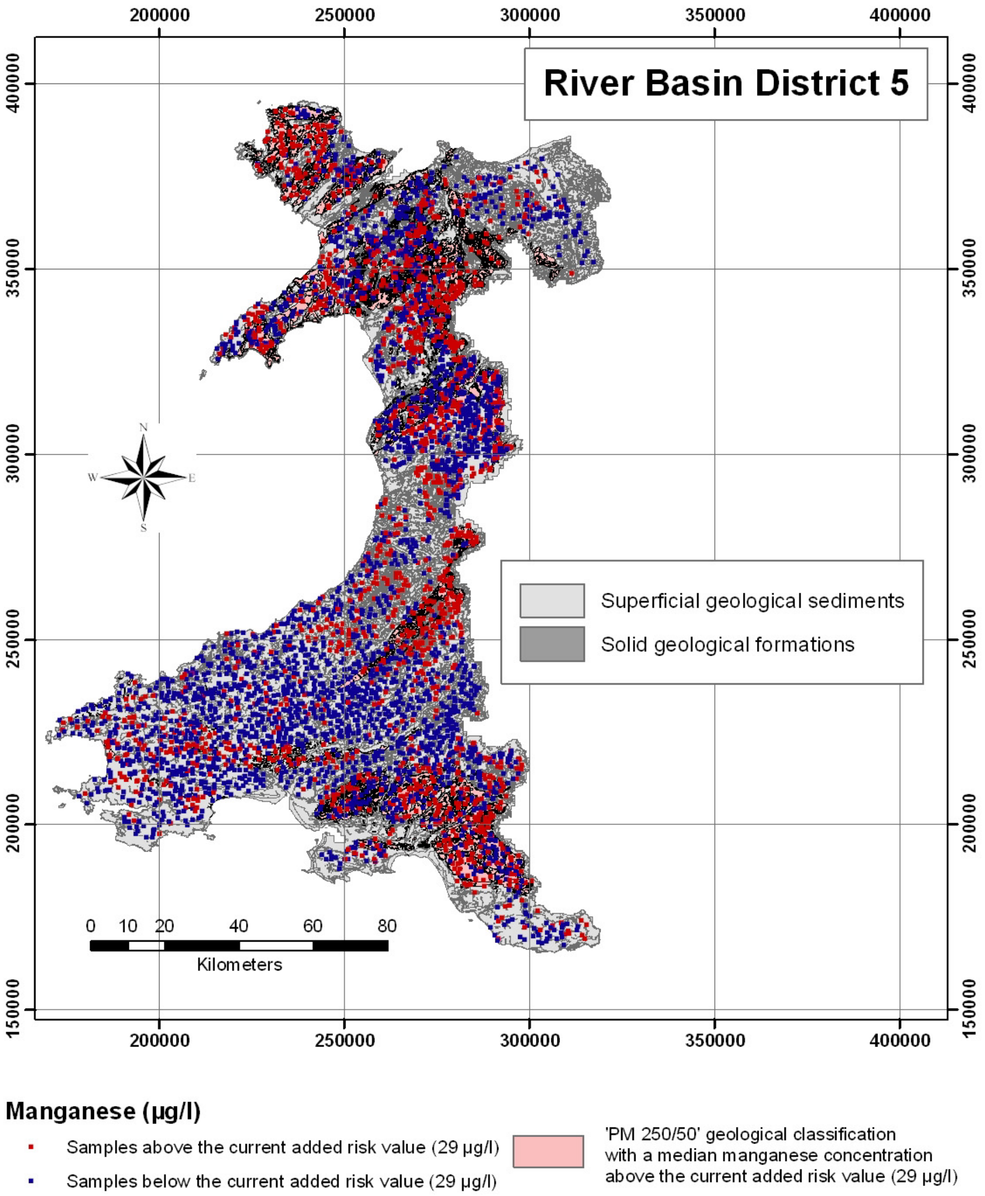


**Figure A1.4b: Comparison of manganese stream water data and 'PM 250/50' categories in RBD05 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the added risk value.

## Arsenic

The median concentration of these very restricted data (0.57 µg/l) is below that of the dataset median (Table 5.1b), which is also true of the two WFD typologies over which samples occur (Table 5.2b). This is reflected in the fact that no 'PM 250/50' categories have medians which exceed the 'added risk' value (Figure A1.4c), and only a small number of samples exceed this value. There is insufficient data in related formations to indicate their background concentrations; a systematic investigation may be necessary to investigates whether failures are a result of background concentrations.

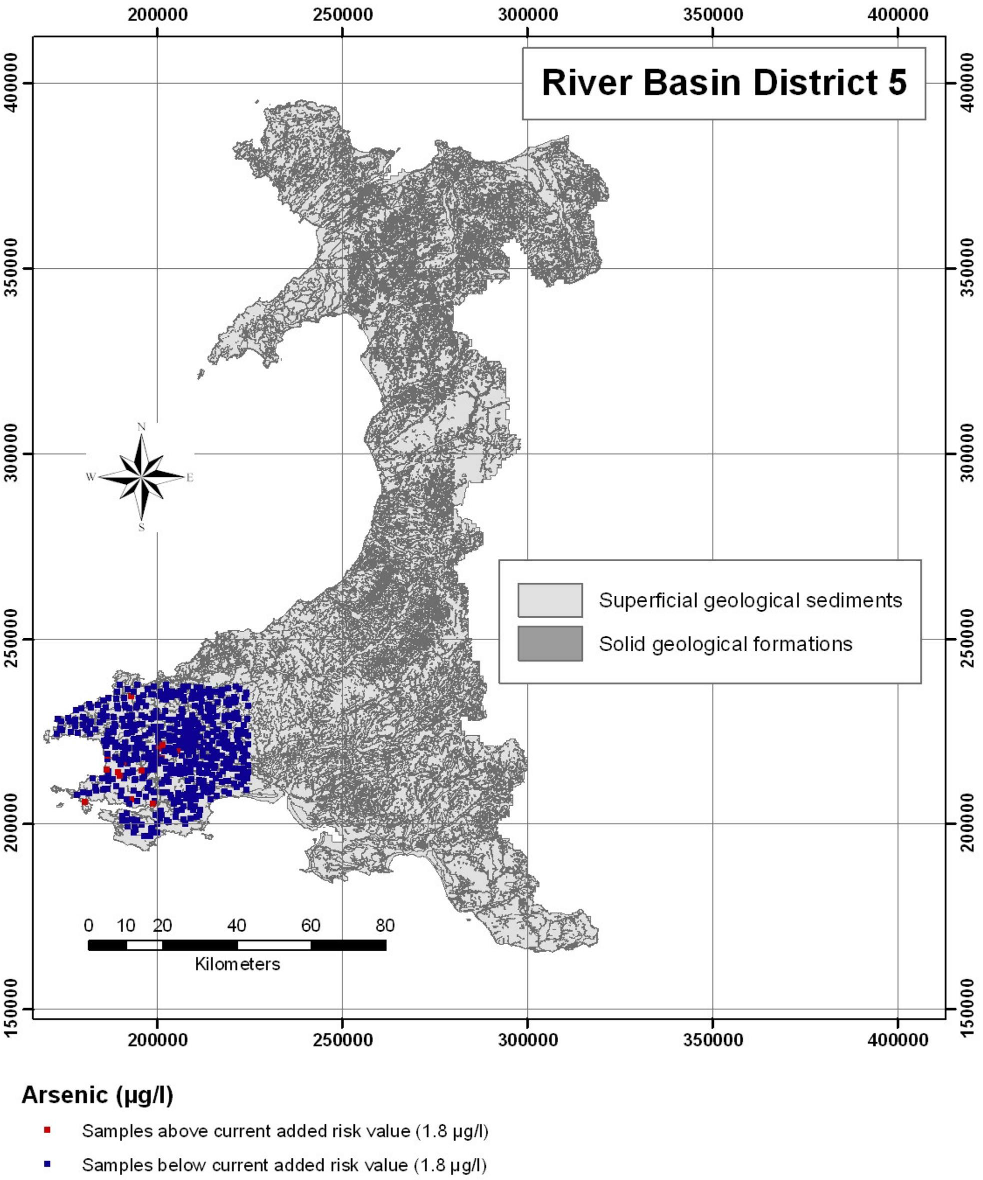


**Figure A1.4c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD05 exceeding the 'added risk' value**

# River Basin District 6 (Dee)

## Iron

The iron concentrations in this region are higher (with a median of 150 µg/l) than that of the whole dataset as shown in Table 5.1a, with higher concentrations over the 'salt' typology (median of 188 µg/l), and much lower concentrations over the calcareous typology (Table 5.2a). The high concentrations indicate that more than 43 per cent of samples will fail the ‘added risk’ concentration of 75 µg/l in this RBD, which is the overall percentage shown in Table 4.2. The ‘PM 250/50’ categories which have a median concentration exceeding the ‘added risk’ value are shown in Figure A1.5a and Table A1.10. These classes show some similarities to those in adjacent RBDs, and geological categories are reasonably good at accounting for sites exceeding the ‘added risk’ value. Exceptions are found in areas with very low sample numbers.

**Table A1.10: Iron summary statistics for ‘PM 250/50’ categories in RBD06 exceeding the ‘added risk’ value (all concentrations in µg/l**

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| ASHL-ARG\DMTN | 19 | 57 | 286 | 494 |
| ASHL-ARSD\ | 14 | 61 | 206 | 502 |
| ASHL-ARSD\DMTN | 21 | 36 | 108 | 301 |
| CARA-ARG\ | 34 | 50 | 82 | 163 |
| CARA-ARG\DMTN | 26 | 52 | 113 | 244 |
| MMG-ARG\DMTN | 18 | 142 | 185 | 1,309 |
| MMG-ARG\SAGR | 11 | 70 | 200 | 1,730 |
| OGW-ARG\ | 41 | 44 | 97 | 204 |
| OGW-ARG\DMTN | 102 | 86 | 170 | 303 |
| OGW-TUFF\ | 17 | 32 | 171 | 259 |
| OGW-TUFF\DMTN | 22 | 118 | 256 | 492 |
| OGW-TUFF\PEAT | 12 | 77 | 532 | 820 |
| PEG-SDST\DMTN | 22 | 115 | 201 | 503 |
| SAL-ARSD\DMTN | 14 | 77 | 125 | 226 |

* The look-up tables for all the 1:250,000 solid formations (information before the ‘\’ in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the ‘\’ field, this indicates that there are no drift sediments mapped in that location.

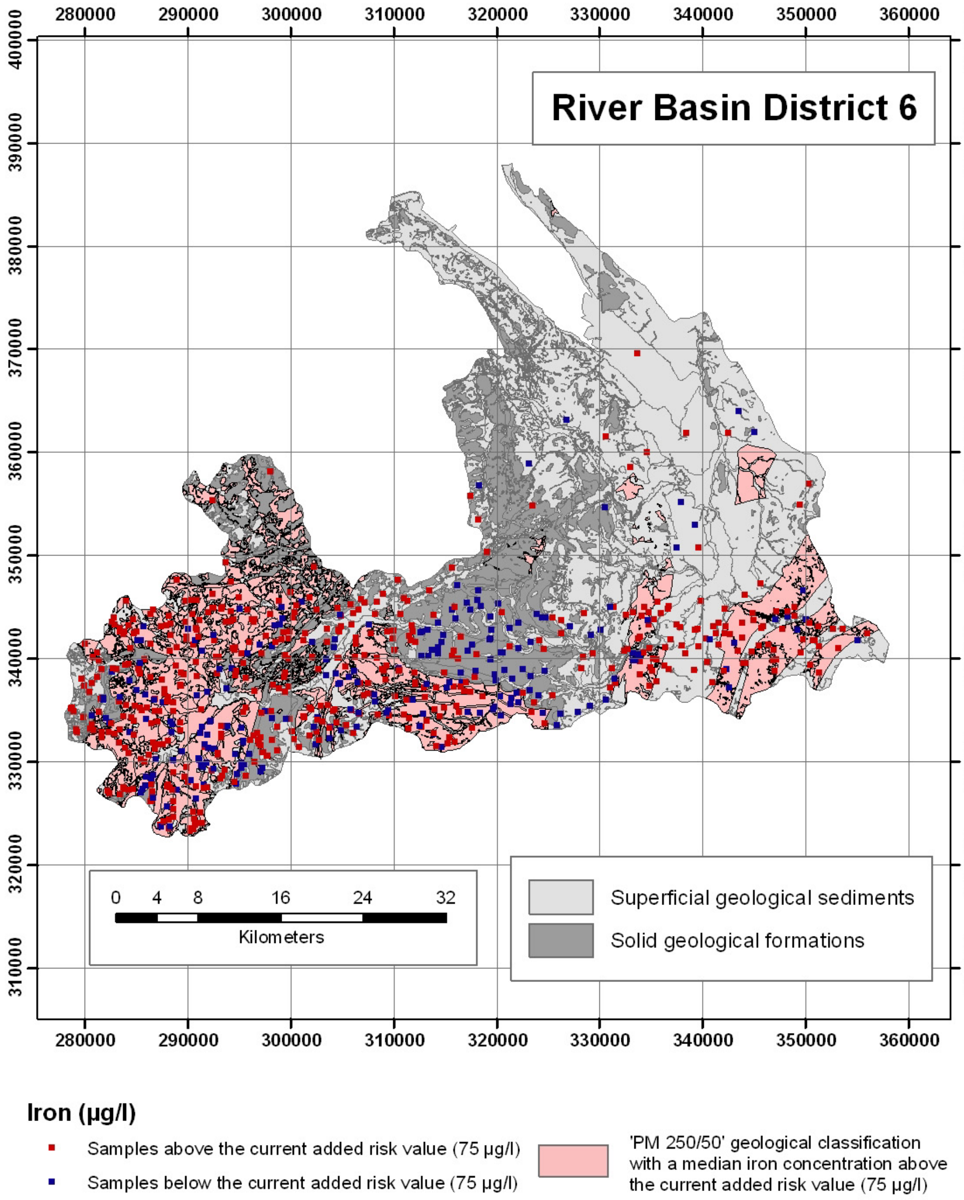


**Figure A1.5a: Comparison of iron stream water data and 'PM 250/50' categories in RBD06 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Manganese

The manganese concentrations in this region are higher (with a median of 37 µg/l) than that of the whole dataset as shown in Table 5.1a, although a disparity occurs in the 'salt' typology (median of 67 µg/l). These higher concentrations indicate that more than 43 per cent of samples will fail the 'added risk' concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2. The 'PM 250/50' categories with a median exceeding the 'added risk' value are shown in Figure A1.5b and Table A1.11. These classes show some similarities to those in adjacent RBDs, and over this RBD for iron. Geological categories are reasonably good at accounting for sites exceeding the 'added risk' value. Exceptions tend to be found in areas with low sample numbers.

**Table A1.11: Manganese summary statistics for 'PM 250/50' categories in RBD06 exceeding the 'added risk' value (all concentrations in μg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| ASHL-ARG\DMTN | 19 | 8 | 40 | 382 |
| CARA-ARG\DMTN | 26 | 17 | 43 | 78 |
| MMG-ARG\DMTN | 18 | 56 | 86 | 916 |
| MMG-ARG\SAGR | 11 | 38 | 44 | 175 |
| OGW-ARG\DMTN | 102 | 13 | 37 | 77 |
| OGW-TUFF\DMTN | 22 | 35 | 72 | 244 |
| OGW-TUFF\PEAT | 12 | 38 | 102 | 315 |
| PEG-SDST\DMTN | 22 | 34 | 59 | 102 |
| SAL-ARSD\DMTN | 14 | 30 | 49 | 109 |
| SSG-SDST\DMTN | 10 | 18 | 43 | 78 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

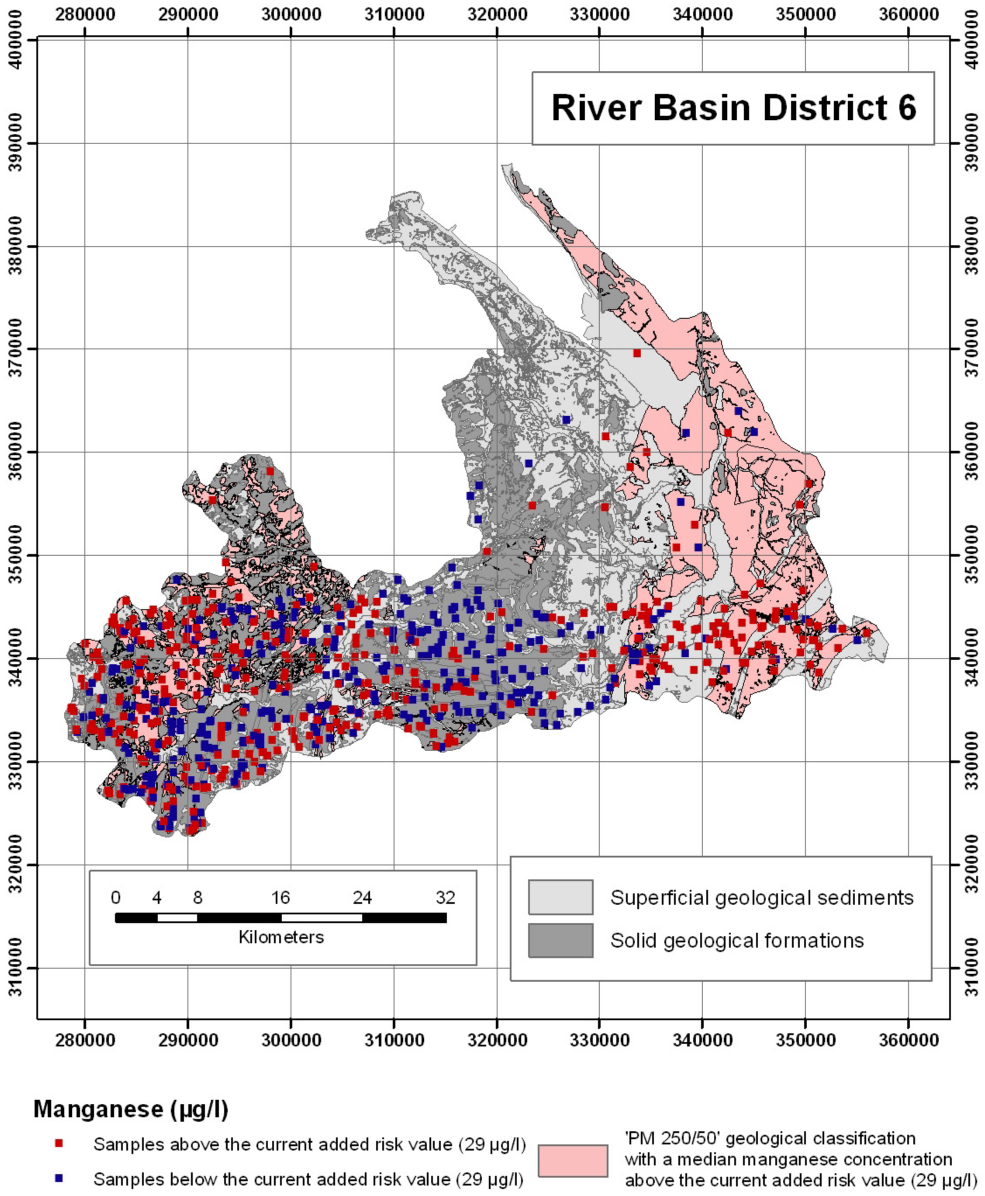


**Figure A1.5b: Comparison of manganese stream water data and 'PM 250/50' categories in RBD06 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Arsenic

There are no data for arsenic in this area. Low-lying coastal areas and the Mercia Mudstone group are associated with high arsenic stream water concentrations in other RBDs; thus, failures in these environments in this RBD should be investigated to see if the same cause is attributable. It is difficult to make predictions for formations further west and south, as there are no comparable ICP-MS data for those areas in RBDs 04 and 05.

# River Basin District 7 (North west)

## Iron

The iron concentrations in this region are higher (with a median of 150 µg/l) than that of the whole dataset as shown in Table 5.1a, with higher concentrations over 'peat' typology (median of 343 µg/l), (Table 5.2a). These high concentrations indicate that more than 43 per cent of samples will fail the 'added risk' concentration of 75 µg/l in this RBD, which is the overall percentage shown in Table 4.2. The 'PM 250/50' categories which have a median exceeding the 'added risk' value are shown in Figure A1.6a and Table A1.12. This dataset shares similarities with other areas, which may aid the extrapolation of data to other regions.

**Table A1.12: Iron summary statistics for 'PM 250/50' categories in RBD07 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| CHAM-ARG\DMTN | 11 | 40 | 89 | 591 |
| MG-ARG\ | 31 | 33 | 106 | 416 |
| MG-ARG\DMTN | 11 | 128 | 166 | 238 |
| MG-SDST\ | 74 | 35 | 116 | 408 |
| MG-SDST\PEAT | 15 | 135 | 322 | 580 |
| MMG-ARG\CLSI | 21 | 52 | 117 | 195 |
| MMG-ARG\DMTN | 20 | 97 | 173 | 350 |
| MMG-ARG\SAGR | 17 | 57 | 140 | 229 |
| SSG-SDST\DMTN | 17 | 82 | 187 | 351 |
| WHT-HALI\CLSI | 12 | 61 | 87 | 197 |
| WHT-HALI\DMTN | 10 | 39 | 151 | 369 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

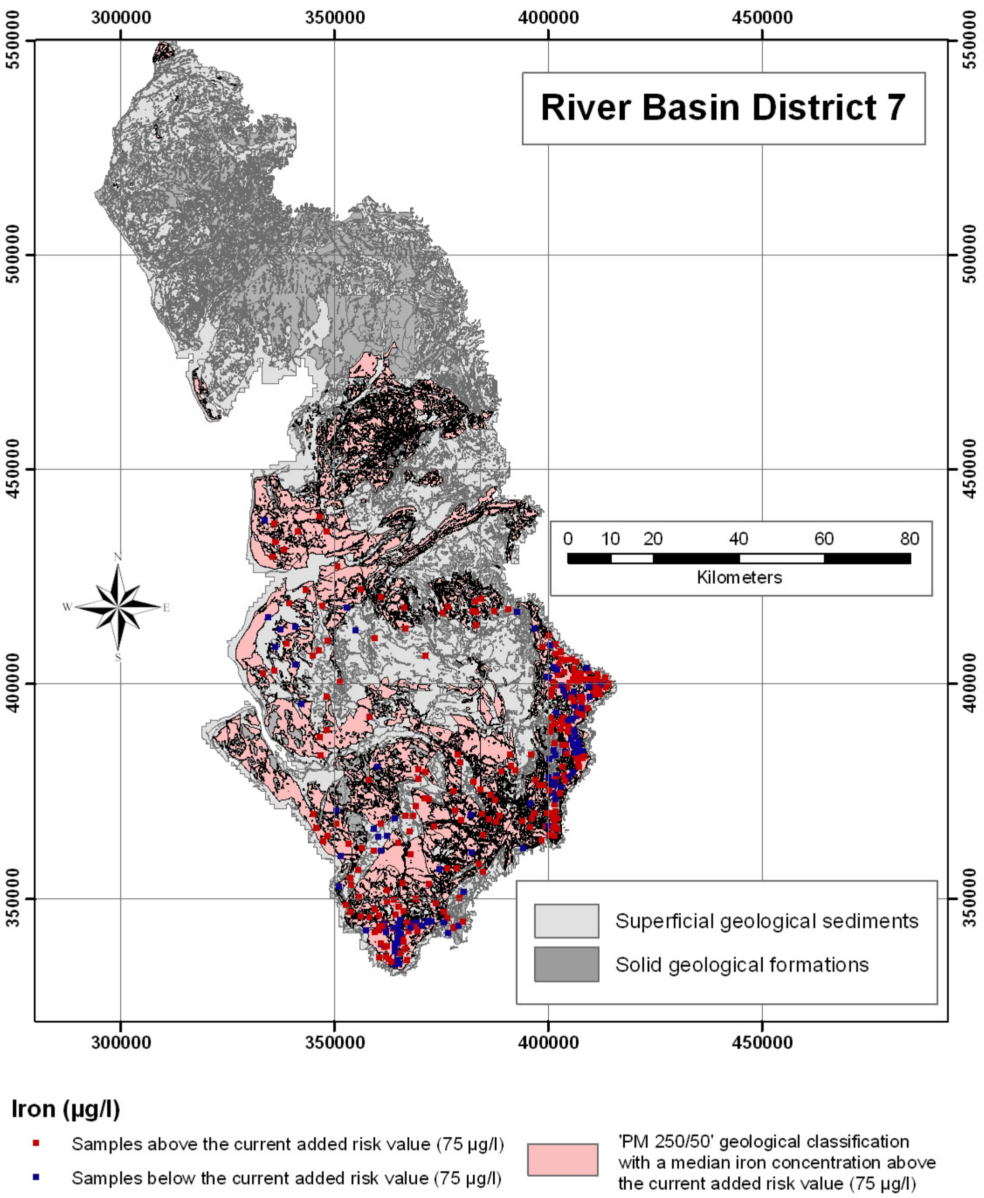


**Figure A1.6a: Comparison of iron stream water data and ‘PM 250/50’ categories in RBD07 exceeding the ‘added risk’ value**
Note: Extension of the pink colouration over unsampled areas of ‘PM 250/50’ categories indicates areas which may also have a higher background concentration than the ‘added risk’ value. This does not preclude other unsampled regions exceeding the ‘added risk’ value.

## Manganese

The manganese concentrations in this region are higher (with a median of 71 µg/l) than that of the whole dataset as shown in Table 5.1a, although a disparity occurs in the ‘peat’ WFD typology (median of 129 µg/l). These higher concentrations indicate that more than 43 per cent of samples will fail the ‘added risk’ concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2. The ‘PM 250/50’ categories which have a median exceeding the ‘added risk’ value are shown in Figure

A1.6b and Table A1.13. This dataset shares similarities with other areas, which may aid the extrapolation of data to other regions.

**Table A1.13: Manganese summary statistics for 'PM 250/50' categories in RBD07 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| CHAM-ARG\DMTN | 11 | 49 | 109 | 578 |
| MG-ARG\ | 31 | 10 | 35 | 122 |
| MG-ARG\DMTN | 11 | 37 | 48 | 89 |
| MG-SDST\ | 74 | 10 | 57 | 142 |
| MG-SDST\PEAT | 15 | 26 | 163 | 236 |
| MMG-ARG\CLSI | 21 | 15 | 101 | 142 |
| MMG-ARG\DMTN | 20 | 51 | 99 | 195 |
| MMG-ARG\SAGR | 17 | 20 | 51 | 140 |
| SSG-SDST\DMTN | 17 | 31 | 52 | 89 |
| WHT-HALI\CLSI | 12 | 34 | 50 | 211 |
| WHT-HALI\DMTN | 10 | 19 | 109 | 559 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

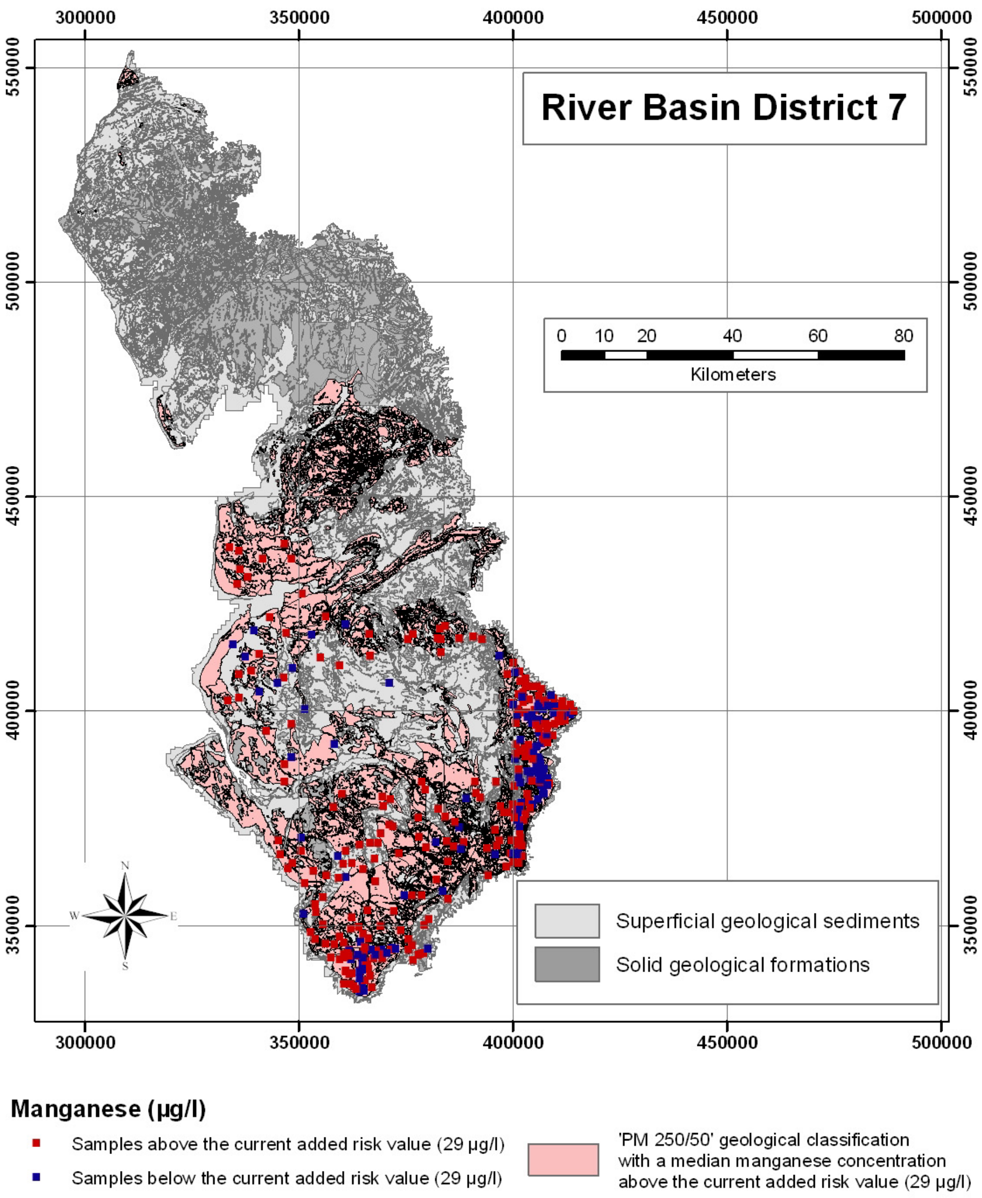


**Figure A1.6b: Comparison of manganese stream water data and ‘PM 250/50’ categories in RBD07 exceeding the ‘added risk’ value**

Note: Extension of the pink colouration over unsampled areas of ‘PM 250/50’ categories indicates areas which may also have a higher background concentration than the ‘added risk’ value. This does not preclude other unsampled regions exceeding the ‘added risk’ value.

## Arsenic

The data for arsenic in this area are very restricted (Figure A1.6c), with all summary statistics in Tables 5.1b and 5.2b showing concentrations below the overall dataset median and the ‘added risk’ value (1.8 µg/l). Few individual samples exceed this value, and no ‘PM 250/50’ categories do so.

Low-lying coastal areas and the Mercia Mudstone group are associated with high arsenic stream water concentrations in other areas; failures in these environments in this RBD should be investigated to see if the same cause is attributable. Some extrapolation may be possible from data in RBD09 (to the east), although this will be problematic for formations which do not occur in that area.

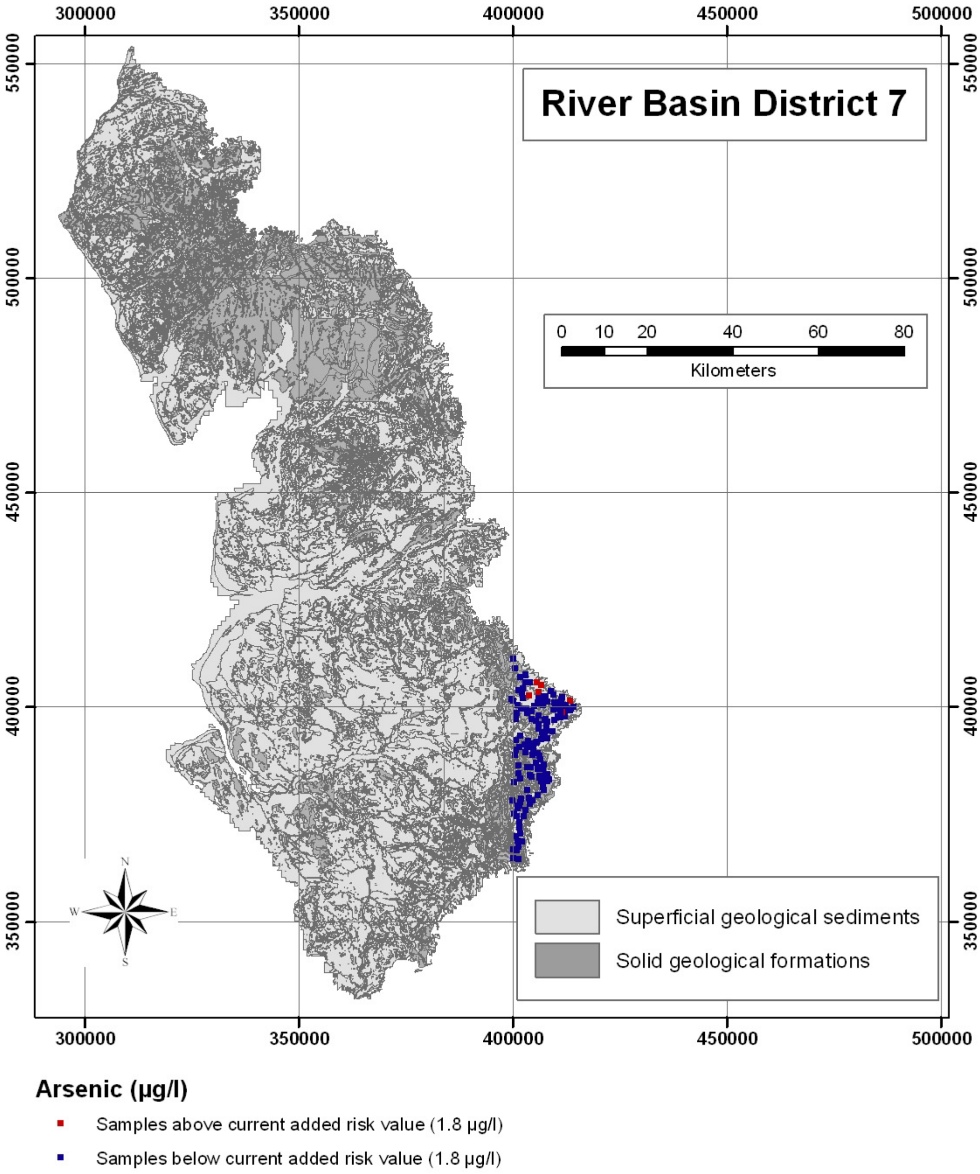


**Figure A1.6c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD07 exceeding the 'added risk' value**

# River Basin District 9 (Humber)

## Iron

The iron concentrations in this region (with a median of 51 µg/l) are close to that of the whole dataset as shown in Table 5.1a, with higher concentrations over the 'peat' typology (median of 394 µg/l). These data indicate that more than 43 per cent of samples will fail the 'added risk' concentration of 75 µg/l in this RBD, which is the overall percentage shown in Table 4.2. This suggests an increased workload, applying tier 2 assessments. The ‘PM 250/50’ categories which have a median exceeding the ‘added risk’ value are shown in Figure A1.7a and Table A1.14. Regions with a median exceeding the ‘added risk’ value reasonably explain the individual sample point data. The northerly extension of the Mercia Mudstone group may give rise to further samples which would fail the ‘added risk’ value, as could geological bodies along the coastal strip. Some lithologies in the region of the North York moors are associated with higher trace element concentrations further south, for which data from RBD10 may assist.

**Table A1.14: Iron summary statistics for ‘PM 250/50’ categories in RBD09 exceeding the ‘added risk’ value (all concentrations in µg/l)**

| ‘PM 250\50’ category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| LCM-ARG\CLSI | 29 | 64 | 117 | 272 |
| LI-ARG\SAGR | 18 | 37 | 94 | 126 |
| MG-ARG\ | 173 | 53 | 165 | 405 |
| MG-ARG\CLSI | 56 | 81 | 181 | 307 |
| MG-ARG\DMTN | 58 | 86 | 199 | 480 |
| MG-ARG\H-CLSI | 33 | 66 | 135 | 356 |
| MG-SDST\ | 205 | 30 | 136 | 516 |
| MG-SDST\CLSI | 14 | 40 | 92 | 158 |
| MG-SDST\DMTN | 31 | 40 | 170 | 520 |
| MG-SDST\H-CLSI | 10 | 13 | 106 | 233 |
| MG-SDST\PEAT | 14 | 413 | 772 | 2,198 |
| SSG-SDAR\PEAT | 15 | 50 | 110 | 260 |

* The look-up tables for all the 1:250,000 solid formations (information before the ‘\’ in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the ‘\’ field, this indicates that there are no drift sediments mapped in that location.

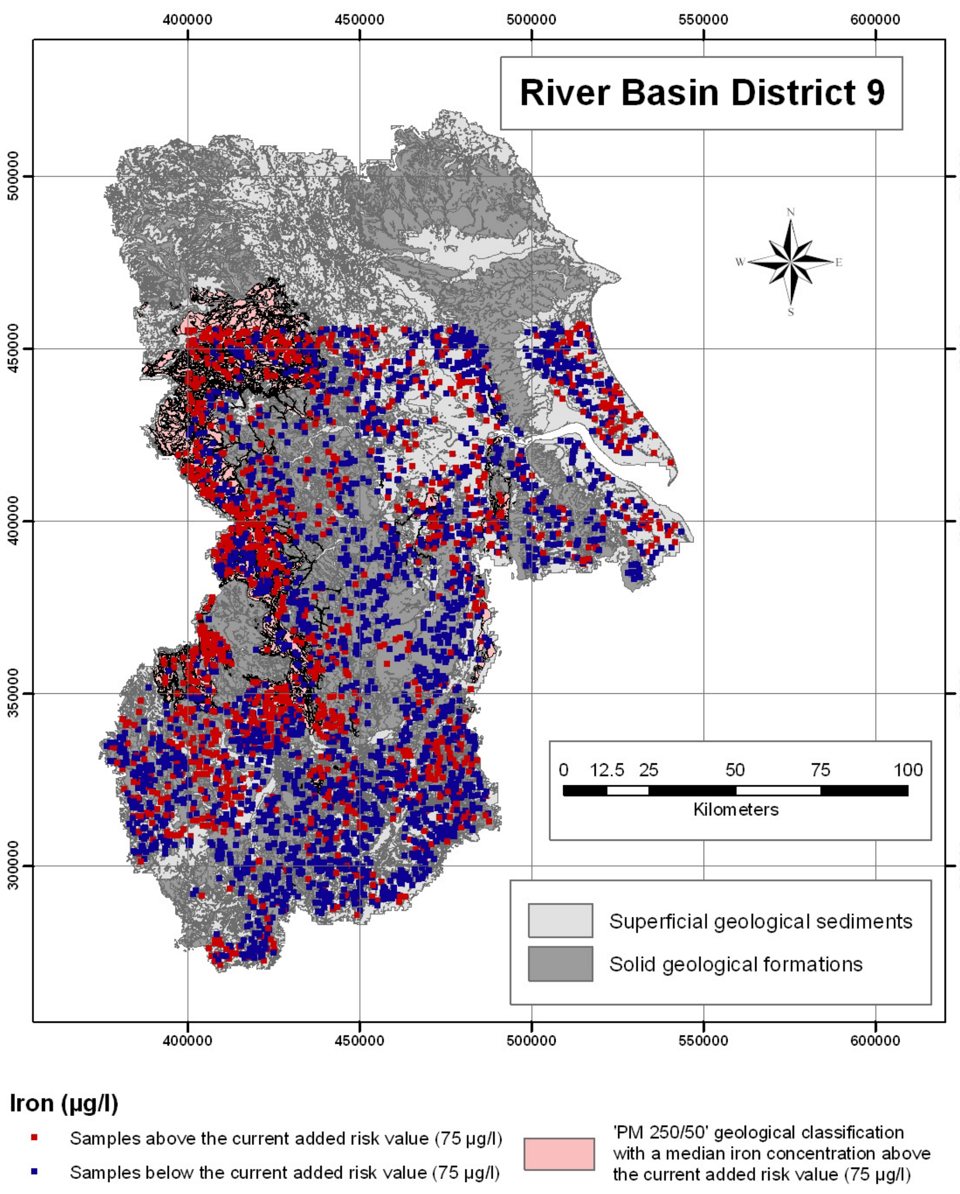


**Figure A1.7a: Comparison of iron stream water data and 'PM 250/50' categories in RBD09 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Manganese

The manganese concentrations in this region are higher (with a median of 34 µg/l) than that of the whole dataset as shown in Table 5.1a, although a disparity occurs in the 'peat' WFD typology (median of 123 µg/l). These higher concentrations indicate that more than 43 per cent of samples will fail the 'added risk' concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2.

The 'PM 250/50' categories which have a median exceeding the 'added risk' value are shown in Figure A1.7b and Table A1.15. Regions with a median exceeding the 'added risk' value reasonably explain the individual sample point data. The northerly extension of the Mercia Mudstone group may give rise to further samples which would fail the 'added risk' value, as could geological bodies along the coastal strip. Some lithologies in the region of the North York moors are associated with higher trace element concentrations further south, for which data from RBD10 may assist.

**Table A1.15: Manganese summary statistics for 'PM 250/50' categories in RBD09 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| AMC-ARG\CLSI | 20 | 29 | 148 | 476 |
| BLI-LMST\CLSI | 12 | 49 | 144 | 286 |
| CHAM-ARG\H-CLSI | 28 | 14 | 131 | 256 |
| CK-CHLK\CLSI | 174 | 33 | 118 | 537 |
| CK-CHLK\DMTN | 94 | 58 | 115 | 212 |
| CM-ARG\ | 16 | 41 | 113 | 276 |
| DYS-ARG\ | 10 | 30 | 103 | 371 |
| KC-ARG\SAGR | 15 | 53 | 91 | 175 |
| KDCP-CONG\CLSI | 10 | 41 | 85 | 225 |
| LCM-ARG\ | 140 | 22 | 74 | 206 |
| LCM-ARG\CLSI | 29 | 14 | 74 | 456 |
| LCM-SDST\ | 53 | 30 | 70 | 90 |
| LI-ARG\SAGR | 18 | 24 | 68 | 149 |
| MCM-ARG\ | 69 | 20 | 66 | 289 |
| MCM-ARG\CLSI | 23 | 14 | 62 | 125 |
| MCM-SDST\ | 16 | 12 | 62 | 346 |
| MG-ARG\ | 173 | 19 | 61 | 139 |
| MG-ARG\CLSI | 56 | 11 | 56 | 333 |
| MG-ARG\DMTN | 58 | 24 | 55 | 135 |
| MG-ARG\H-CLSI | 33 | 10 | 49 | 205 |
| MG-SDST\ | 205 | 14 | 44 | 88 |
| MG-SDST\CLSI | 14 | 11 | 43 | 72 |
| MG-SDST\DMTN | 31 | 13 | 42 | 309 |
| MG-SDST\H-CLSI | 10 | 14 | 40 | 160 |
| MG-SDST\PEAT | 14 | 6 | 39 | 222 |
| MMG-ARG\PEAT | 24 | 6 | 38 | 47 |
| MMG-ARG\SAGR | 121 | 4 | 37 | 332 |
| SSG-SDAR\PEAT | 15 | 13 | 36 | 275 |
| SSG-SDAR\SAGR | 10 | 17 | 36 | 141 |
| SSG-SDST\CLSI | 149 | 10 | 36 | 630 |
| SSG-SDST\DMTN | 13 | 8 | 35 | 159 |
| SSG-SDST\SAGR | 22 | 7 | 35 | 174 |
| UCM-ARG\ | 26 | 12 | 31 | 122 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

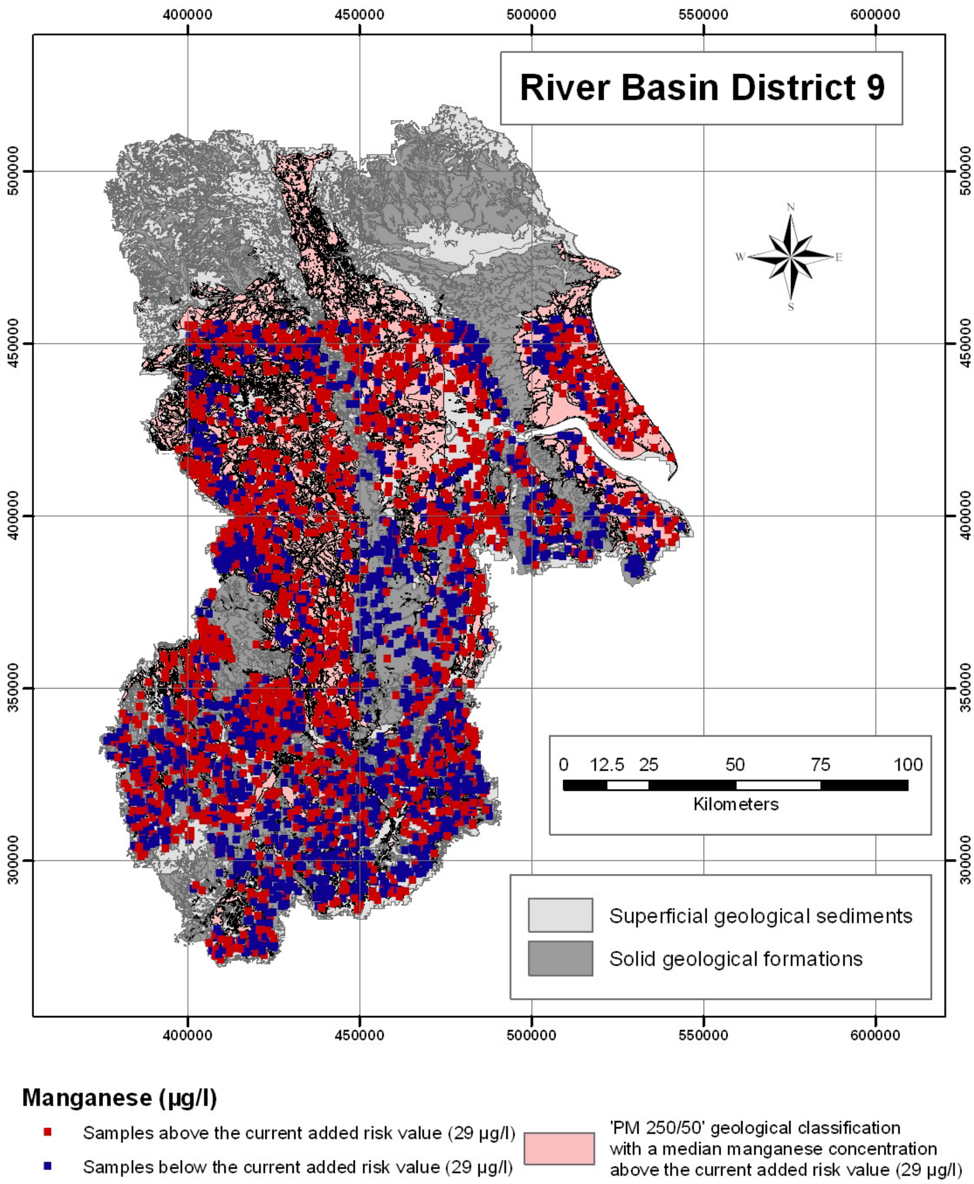


**Figure A1.7b: Comparison of manganese stream water data and ‘PM 250/50’ categories in RBD09 exceeding the ‘added risk’ value**
Note: Extension of the pink colouration over unsampled areas of ‘PM 250/50’ categories indicates areas which may also have a higher background concentration than the ‘added risk’ value. This does not preclude other unsampled regions exceeding the ‘added risk’ value.

## Arsenic

The arsenic concentrations in this region are greater than that of the whole dataset (with a median of 1.5 µg/l) as shown in Table 5.1b, with the greatest disparity in the ‘lowland peat’ $WFD_p$ typology (median of 2.7 µg/l). These higher concentrations indicate that more than 37 per cent of samples will fail the ‘added risk’ concentration of 1.8 µg/l, which is the overall percentage shown in Table 4.2. Thus, there will be more work in tier 2 assessments, as well as tier 2 failures expected for this RBD. Figure A1.7c shows an area without ICP-MS data in the south west (south of Stoke-on-Trent), because this was sampled before ICP-MS analysis was introduced. The distribution of 'PM 250/50' categories in Table A1.16 shows in Figure A1.7c that individual sample points are generally well described. Regions with no data could undergo preliminary assessment using extrapolation from other areas of this RBD and RBD10 with the same formations.

**Table A1.16: Arsenic summary statistics for 'PM 250/50' categories in RBD09 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| AMC-ARG\CLSI | 20 | 1.8 | 3.2 | 9.7 |
| BLI-LMST\CLSI | 12 | 1.8 | 2.2 | 4.3 |
| CHAM-ARG\CLSI | 114 | 1.6 | 2.1 | 2.9 |
| CHAM-ARG\DMTN | 31 | 1.4 | 1.8 | 3.1 |
| CHAM-ARG\H-CLSI | 28 | 1.5 | 2.1 | 3.1 |
| CK-CHLK\CLSI | 173 | 1.3 | 3.0 | 6.6 |
| CK-CHLK\DMTN | 94 | 1.8 | 4.0 | 7.1 |
| MCM-ARG\CLSI | 23 | 0.82 | 1.8 | 2.7 |
| MMG-ARG\ | 234 | 1.3 | 2.2 | 3.4 |
| MMG-ARG\CLSI | 563 | 1.4 | 2.1 | 3.7 |
| MMG-ARG\H-CLSI | 45 | 1.7 | 2.4 | 4.2 |
| MMG-ARG\PEAT | 23 | 1.2 | 2.1 | 3.7 |
| MMG-ARG\SAGR | 104 | 1.1 | 2.0 | 3.7 |
| OXKL-ARG\CLSI | 23 | 0.91 | 1.8 | 3.8 |
| SSG-SDAR\CLSI | 71 | 1.3 | 1.9 | 2.6 |
| SSG-SDAR\PEAT | 15 | 1.6 | 2.7 | 4.8 |
| SSG-SDAR\SAGR | 10 | 1.9 | 4.6 | 6.2 |
| SSG-SDST\CLSI | 145 | 1.4 | 2.9 | 5.9 |
| SSG-SDST\SAGR | 20 | 1.2 | 2.3 | 4.4 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

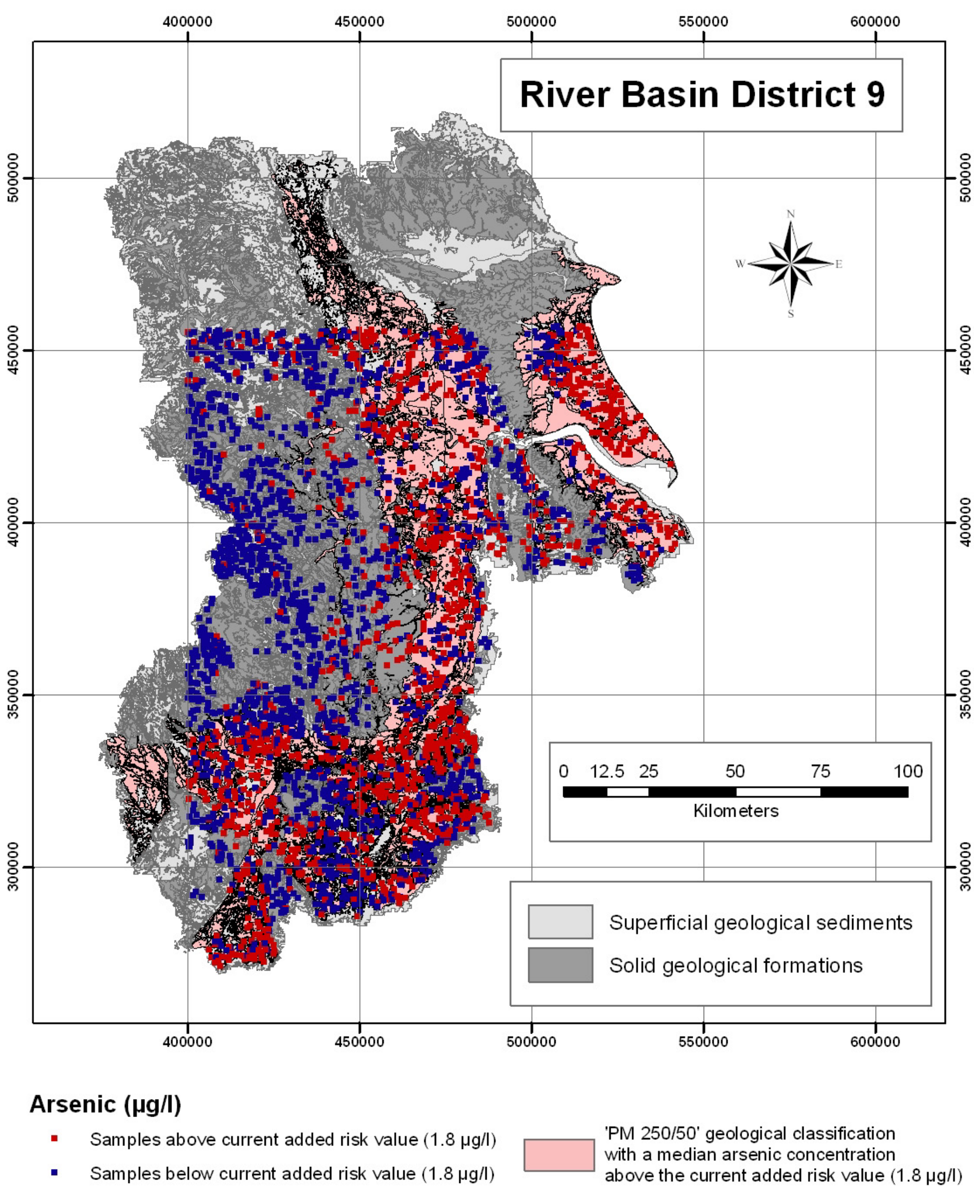


**Figure A1.7c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD09 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## River Basin District 10 (Anglian)

### Iron

The iron concentrations in this region are lower (with a median of 38 µg/l) than that of the whole dataset as shown in Table 5.1a, although a disparity occurs in the 'peat' WFD typology (median of 72 µg/l). These lower concentrations indicate that less than

43 per cent of samples will fail the 'added risk' concentration of 75 µg/l in this RBD, which is the overall percentage shown in Table 4.2.

The location of classes listed in Table A1.17 is shown in Figure A1.8a compared with actual sample locations which have more than 75 µg/l iron. Areas which are poorly described by this statistical summary are located in a non-systematic geographical context, but appear to be associated with localised areas in catchments. These data could be used to add local knowledge in the event of failure at the tier 2 stage.

**Table A1.17: Iron summary statistics for 'PM 250/50' categories in RBD10 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| ACWW-ARG\CLSI | 146 | 52 | 120 | 221 |
| GLT-ARG\PEAT | 36 | 42 | 97 | 140 |
| LGS-SDST\PEAT | 12 | 53 | 73 | 149 |
| NCRC-SDST\PEAT | 69 | 38 | 85 | 249 |
| OXKL-ARG\PEAT | 59 | 39 | 83 | 179 |
| SARR-SDST\CLSI | 13 | 21 | 149 | 2180 |
| SYS-SDST\CLSI | 11 | 42 | 87 | 177 |
| WWB-ARG\CLSI | 28 | 46 | 82 | 174 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

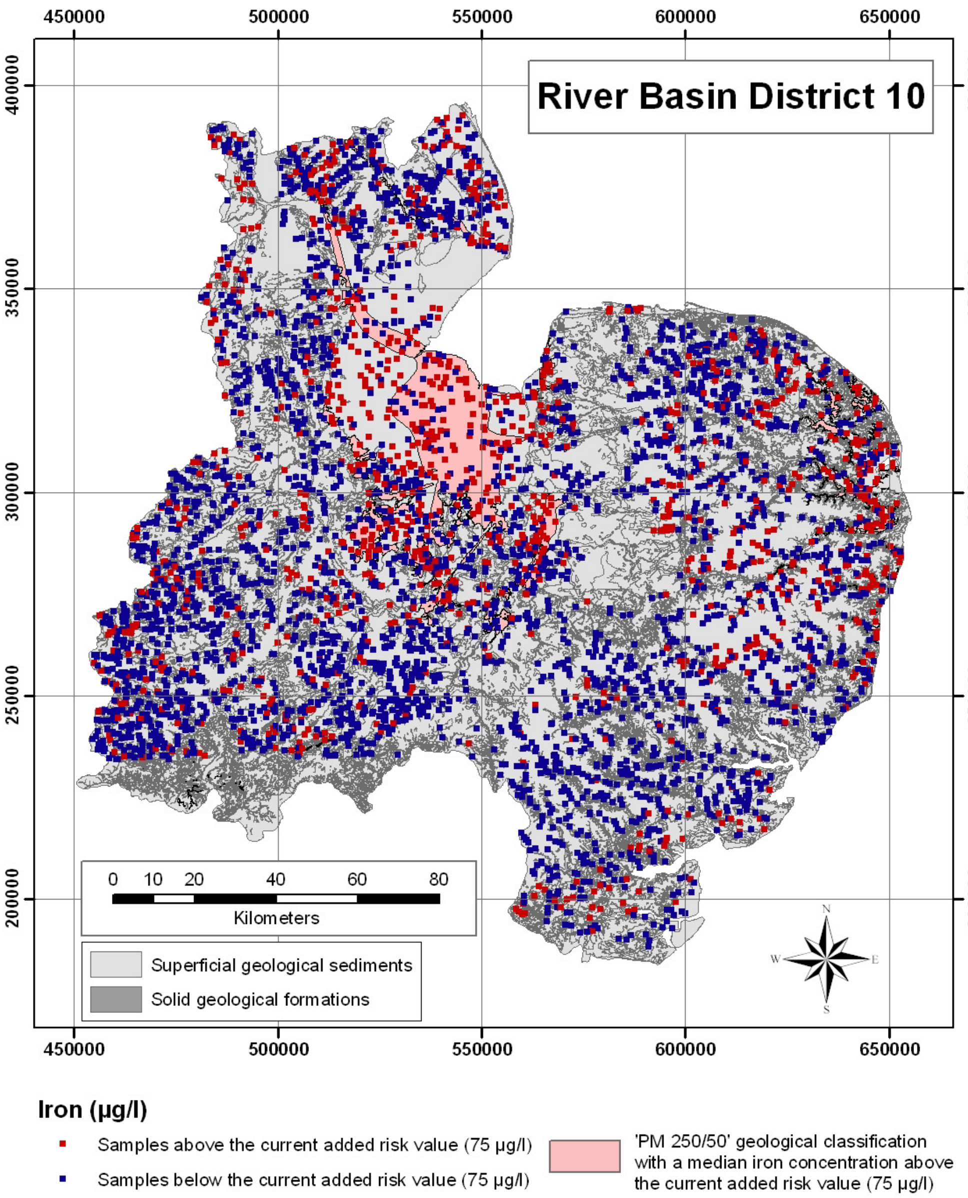


**Figure A1.8a: Comparison of iron stream water data and 'PM 250/50' categories in RBD10 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

## Manganese

The manganese concentrations in this region (with a median of 19 µg/l) are close to that of the whole dataset as shown in Table 5.1a, although a disparity occurs in the 'peat' WFD typology (median of 52 µg/l). These lower concentrations indicate that close to 43 per cent of samples will fail the 'added risk' concentration of 29 µg/l in this RBD, which is the overall percentage shown in Table 4.2.

The location of classes listed in Table A1.18 is shown in Figure A1.8b, compared with actual sample locations which have more than 29 µg/l manganese. Areas which are poorly described by this statistical summary are located in the south east of the RBD, a low-lying area of Essex, and over the till of the East Norfolk/Suffolk border. These areas are also inadequately described for arsenic (below).

**Table A1.18: Manganese summary statistics for 'PM 250/50' categories in RBD10 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| ACWW-ARG\CLSI | 146 | 70 | 180 | 516 |
| ACWW-ARG\DMTN | 15 | 11 | 30 | 198 |
| ACWW-ARG\PEAT | 43 | 27 | 58 | 346 |
| CK-CHLK\CLSI | 62 | 7 | 35 | 108 |
| CK-CHLK\DMTN | 19 | 7 | 51 | 442 |
| GLT-ARG\PEAT | 36 | 19 | 37 | 114 |
| KC-ARG\CLSI | 82 | 12 | 44 | 480 |
| LGS-SDST\CLSI | 16 | 9 | 29 | 126 |
| LGS-SDST\PEAT | 12 | 27 | 72 | 114 |
| LI-ARG\ | 26 | 15 | 50 | 219 |
| LI-ARG\CLSI | 29 | 5 | 39 | 138 |
| LI-ARG\SAGR | 19 | 21 | 52 | 822 |
| NCRC-SDST\ | 29 | 13 | 40 | 107 |
| NCRC-SDST\CLSI | 249 | 20 | 66 | 201 |
| NCRC-SDST\PEAT | 69 | 79 | 175 | 302 |
| NCRC-SDST\SAGR | 34 | 6 | 38 | 205 |
| OXKL-ARG\ | 118 | 12 | 30 | 69 |
| OXKL-ARG\CLSI | 258 | 10 | 38 | 168 |
| OXKL-ARG\PEAT | 59 | 28 | 120 | 384 |
| SARR-SDST\CLSI | 13 | 9 | 173 | 1197 |
| SYS-SDST\CLSI | 11 | 20 | 34 | 189 |
| UCK-CHLK\PEAT | 25 | 19 | 43 | 207 |
| WWB-ARG\CLSI | 28 | 13 | 90 | 264 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

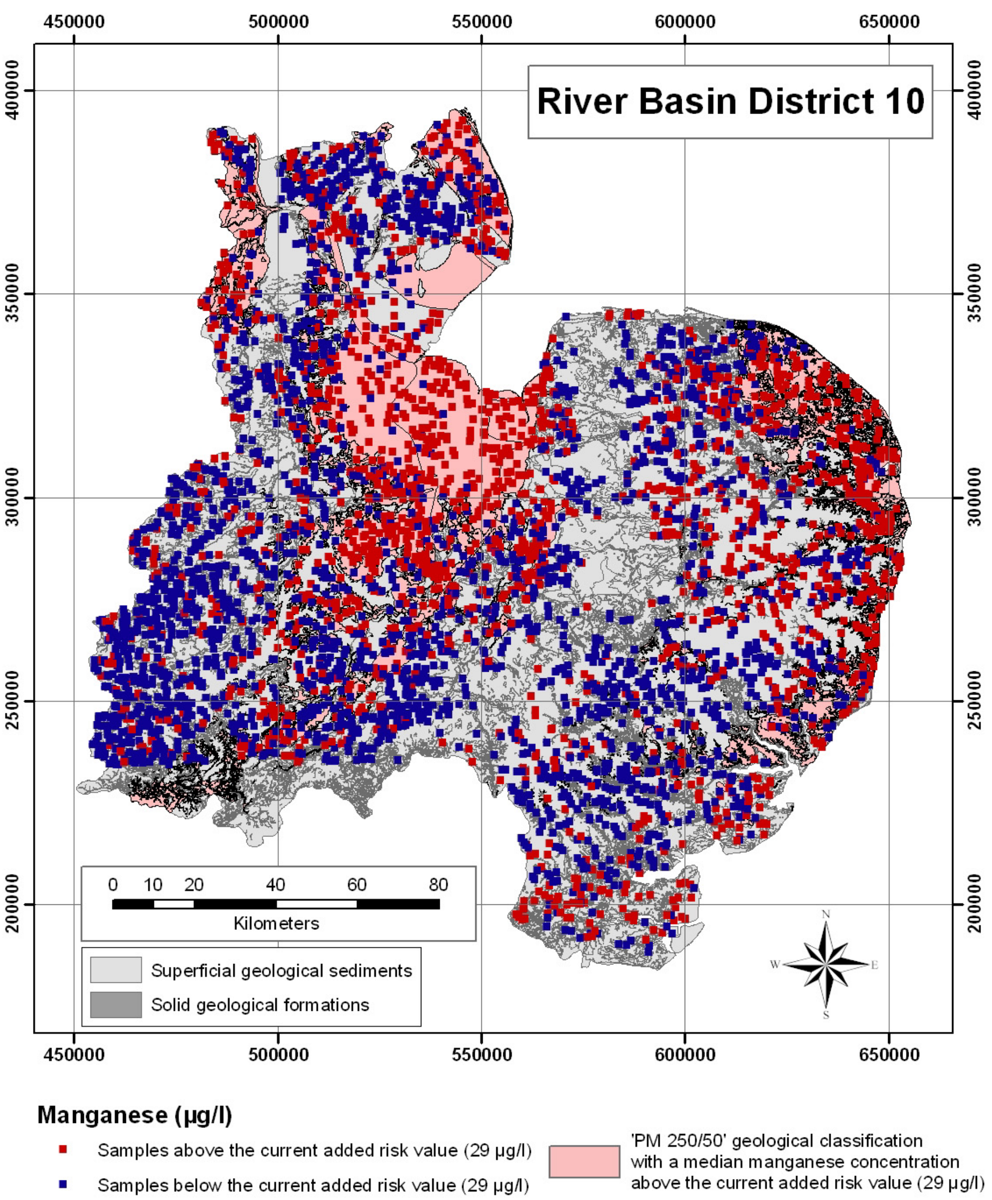


**Figure A1.8b: Comparison of manganese stream water data and 'PM 250/50' categories in RBD10 exceeding the 'added risk' value**

Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the added risk value.

## Arsenic

The arsenic concentrations in this region are greater than that of the whole dataset (with a median of 1.5 µg/l) as shown in Table 5.1b, with the greatest disparity occurring in the 'peat' WFD typology (median of 1.9 µg/l). These higher concentrations indicate that more than 37 per cent of samples will fail the 'added risk' concentration of 1.8 µg/l, which is the overall percentage shown in Table 4.2. Thus, there will be more work in tier 2 assessments as well as tier 2 failures expected for this RBD.

The map shows that many of the samples which exceed the standard are within areas included in the categories listed in Table A1.19. The most significant areas which do not appear to be adequately explained are the low-lying regions of Essex in the south east, and the till over the upper areas of the catchment draining to the east coast over the Norfolk/Suffolk border.

**Table A1.19: Arsenic summary statistics for 'PM 250/50' categories in RBD10 exceeding the 'added risk' value (all concentrations in µg/l)**

| 'PM 250\50' category* | Number of samples | 25th percentile | Median | 75th percentile |
|---|---|---|---|---|
| ACWW-ARG\ | 19 | 0.96 | 1.8 | 3.1 |
| ACWW-ARG\CLSI | 146 | 4.0 | 7.3 | 13 |
| ACWW-ARG\PEAT | 43 | 1.6 | 2.3 | 3.4 |
| AMC-ARG\CLSI | 56 | 1.9 | 3.6 | 5.2 |
| AMC-ARG\DMTN | 14 | 1.1 | 1.9 | 3.8 |
| CK-CHLK\CLSI | 62 | 1.9 | 3.4 | 5.4 |
| CK-CHLK\DMTN | 19 | 1.6 | 3.4 | 8.2 |
| KC-ARG\ | 47 | 1.1 | 1.8 | 2.6 |
| KC-ARG\CLSI | 82 | 1.7 | 3.1 | 11 |
| KC-ARG\DMTN | 22 | 1.0 | 2.5 | 3.6 |
| KC-ARG\PEAT | 43 | 1.3 | 2.0 | 2.4 |
| KC-ARG\SAGR | 28 | 1.5 | 2.3 | 4.1 |
| LC-ARG\DMTN | 18 | 1.4 | 1.9 | 3.2 |
| LI-ARG\ | 26 | 1.8 | 2.4 | 4.4 |
| LI-ARG\CLSI | 29 | 1.4 | 2.6 | 3.9 |
| LI-ARG\SAGR | 19 | 1.1 | 1.8 | 2.6 |
| LOCR-ARG\CLSI | 26 | 2.2 | 3.8 | 12 |
| NCRC-SDST\CLSI | 249 | 1.1 | 1.9 | 3.2 |
| NCRC-SDST\DMTN | 78 | 1.4 | 2.2 | 4.2 |
| NCRC-SDST\SAGR | 34 | 1.1 | 1.9 | 3.0 |
| OXKL-ARG\CLSI | 258 | 1.6 | 2.6 | 3.9 |
| SYS-SDST\CLSI | 11 | 1.7 | 3.0 | 4.1 |
| UCK-CHLK\PEAT | 25 | 1.0 | 1.9 | 3.2 |
| WWB-ARG\CLSI | 28 | 2.0 | 4.0 | 6.8 |

* The look-up tables for all the 1:250,000 solid formations (information before the '\' in each case) are found in Appendix 2. The information for all the 1:50,000 lithologies are found in Appendix 2; where there is no text after the '\' field, this indicates that there are no drift sediments mapped in that location.

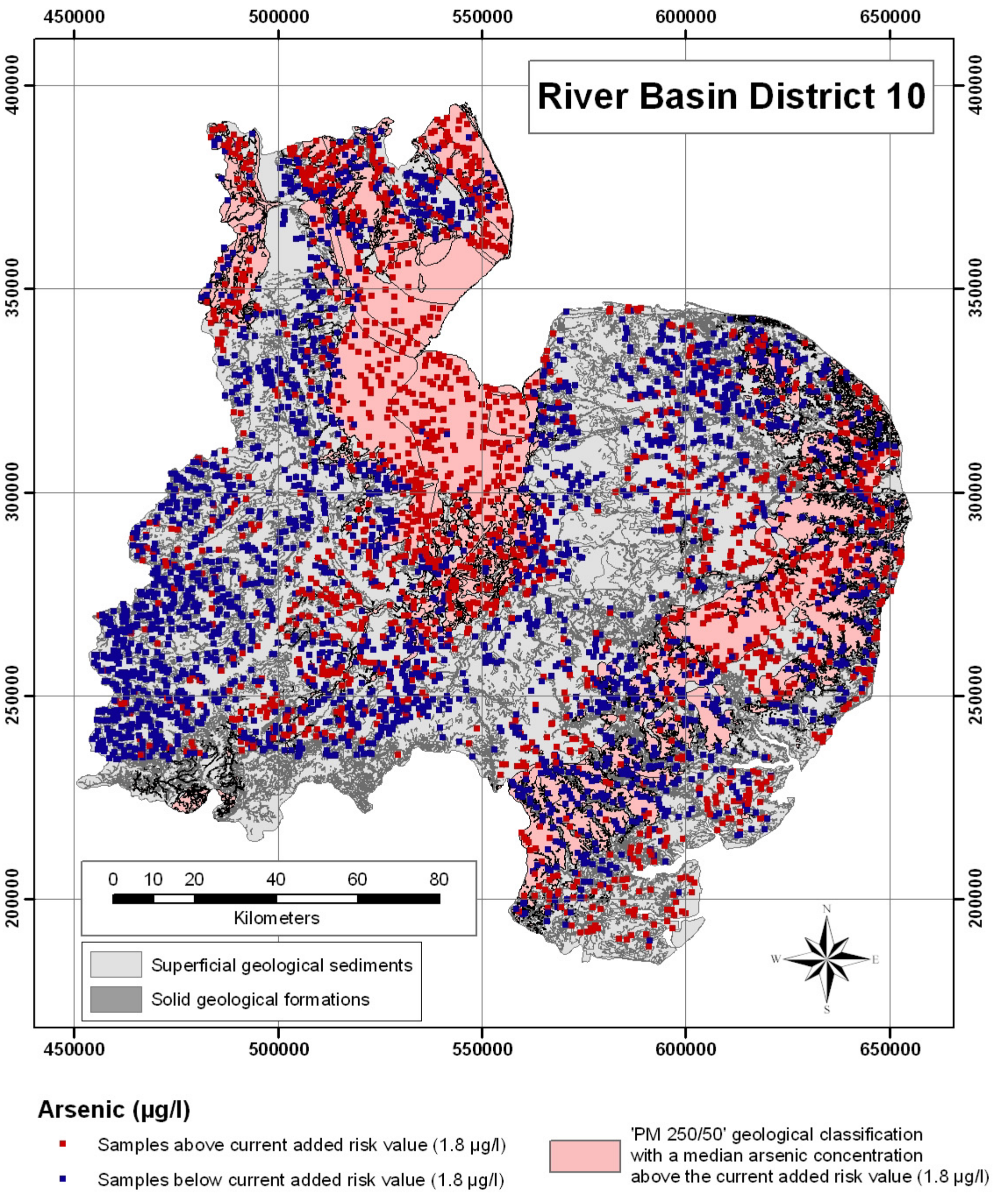


**Figure A1.8c: Comparison of arsenic stream water data and 'PM 250/50' categories in RBD10 exceeding the 'added risk' value**
Note: Extension of the pink colouration over unsampled areas of 'PM 250/50' categories indicates areas which may also have a higher background concentration than the 'added risk' value. This does not preclude other unsampled regions exceeding the 'added risk' value.

# Appendix 2: Geological classes used in Appendix 1 tables

These tables provide the look-up for the full names for the codes provided in Appendix 1. They are structured such that ‘PM250/50’ category is comprised of:

**lex-rock/drift**, which equates to:

**‘Table A2.1’-‘Table A2.2’/’Table A2.3’**.

Thus in Table A1.1, the PM250/50 class identified is “**LC-ARG\H-CLSI**” which translates as 1:250,000 mapping ‘**London Clay Formation – argillaceous**’ overlain by 1:50,000 mapping of drift (superficial) deposits of ‘**clay-silt**’.

Note that not all of the country has drift deposits mapped as overlying the solid formations, so there will not be a drift category for every ‘PM250/50’ code.

**Table A2.1 Lithology name (‘lex’) codes for the 1:250,000 solid geological classes.**

| Lex code | Description |
|---|---|
| ACWW | AMPTHILL CLAY FORMATION AND WEST WALTON FORMATION (UNDIFFERENTIATED) [OBSOLETE CODE: USE WWAC] |
| AGF | ABERYSTWYTH GRITS GROUP |
| AMC | AMPTHILL CLAY FORMATION |
| ASHL | ASHGILL ROCKS (UNDIFFERENTIATED) |
| BFBF | BUDE FORMATION AND BIDEFORD FORMATION (UNDIFFERENTIATED) |
| BFMB | DIDYMOGRAPTUS BIFIDUS BEDS AND DIDYMOGRAPTUS MURCHISONI BEDS (UNDIFFERENTIATED) |
| BHWW | BROMSGROVE SANDSTONE FORMATION, HELSBY SANDSTONE FORMATION, WILDMOOR SANDSTONE FORMATION AND WILMSLOW SANDSTONE FORMATION (UNDIFFERENTIATED) |
| BLI | BLUE LIAS FORMATION |
| BRI | BRIDGNORTH SANDSTONE FORMATION |
| CARA | CARADOC ROCKS (UNDIFFERENTIATED) |
| CHAM | CHARMOUTH MUDSTONE FORMATION |
| CK | CHALK GROUP |
| CKF | CRACKINGTON FORMATION |
| CM | COAL MEASURES GROUP [OBSOLETE EXCEPT IN NORTHERN IRELAND: USE PCM, SWCM, CMSC] |
| CMR | CWMERE FORMATION |
| CWY | CWMYSTWYTH GRITS GROUP |
| DBF | DEVIL'S BRIDGE FORMATION |
| DYN | DOL-CYN-AFON FORMATION |
| DYS | DYRHAM FORMATION |
| ETM | ETRURIA FORMATION |
| GLT | GAULT FORMATION |
| GMCB | GASWORKS MUDSTONE AND CARTLETT BEDS (UNDIFFERENTIATED) |
| GWNM | GWNA MELANGE FORMATION [OBSOLETE NAME AND CODE: SEE NGW] |
| HA | HALESOWEN FORMATION |
| KC | KIMMERIDGE CLAY FORMATION |
| KDCP | KIDDERMINSTER FORMATION AND CHESTER PEBBLE BEDS FORMATION (UNDIFFERENTIATED) |
| LC | LONDON CLAY FORMATION |

| Lex code | Description |
|---|---|
| LCM | LOWER COAL MEASURES FORMATION [OBSOLETE NAME AND CODE: USE PLCM, SWLCM, LCMS] |
| LDVY | LLANDOVERY ROCKS (UNDIFFERENTIATED) |
| LGS | LOWER GREENSAND GROUP |
| LI | LIAS GROUP |
| LLDA | LLANVIRN TO ASHGILL ROCKS (UNDIFFERENTIATED) |
| LLVN | LLANVIRN ROCKS (UNDIFFERENTIATED) |
| LMC | LOWER COAL MEASURES FORMATION AND MIDDLE COAL MEASURES FORMATION (UNDIFFERENTIATED) [OBSOLETE NAME AND CODE: USE PLCM, SWLCM, LCMS] |
| LOCR | LOWER CRETACEOUS ROCKS (UNDIFFERENTIATED) |
| LORS | LOWER OLD RED SANDSTONE |
| LPEM | LOWER PENNANT MEASURES [OBSOLETE NAME AND CODE: SEE PES AND MEMBERS THEREIN] |
| LUDL | LUDLOW ROCKS (UNDIFFERENTIATED) |
| LUW | WENLOCK ROCKS AND LUDLOW ROCKS (UNDIFFERENTIATED) |
| MCM | MIDDLE COAL MEASURES FORMATION [OBSOLETE NAME AND CODE: USE PMCM, MCMS, SWMCM] |
| MG | MILLSTONE GRIT GROUP [SEE ALSO MIGR] |
| MMG | MERCIA MUDSTONE GROUP |
| MWG | MAWDDACH GROUP |
| MYSH | MYDRIM SHALES FORMATION |
| N | MONIAN SUPERGROUP |
| NCRC | NORWICH CRAG FORMATION AND RED CRAG FORMATION (UNDIFFERENTIATED) |
| NGF | NANTGLYN FLAGS FORMATION |
| NGW | GWNA GROUP |
| NNH | NEW HARBOUR GROUP |
| NYG | NANT-YSGOLLON MUDSTONE FORMATION |
| OGW | OGWEN GROUP |
| OXKL | KELLAWAYS FORMATION AND OXFORD CLAY FORMATION (UNDIFFERENTIATED) [OBSOLETE CODE: USE KLOX] |
| PEG | PENSTROWED GRITS FORMATION |
| PLQC | PLATEAU BEDS AND QUARTZ CONGLOMERATE GROUP (UNDIFFERENTIATED) |
| PNG | PENARTH GROUP |
| RG | RAGLAN MUDSTONE FORMATION |
| RLS | RUGBY LIMESTONE MEMBER |
| RN | RHINOG FORMATION |
| SAL | SALOP FORMATION |
| SARR | SANDRINGHAM SAND FORMATION, ROXHAM MEMBER AND RUNCTON MEMBER (UNDIFFERENTIATED) |
| SLR | SLADE AND REDHILL FORMATION |
| SMG | ST MAUGHANS FORMATION |
| SSG | SHERWOOD SANDSTONE GROUP |
| SYS | SPILSBY SANDSTONE FORMATION |
| TESH | TETRAGRAPTUS SHALES FORMATION |
| UCK | UPPER CHALK FORMATION |
| UCM | UPPER COAL MEASURES FORMATION [OBSOLETE NAME AND CODE: USE PUCM, UCMS] |
| UDCS | UPPER DEVONIAN ROCKS AND LOWER CARBONIFEROUS ROCKS (UNDIFFERENTIATED) |
| UIIN | UNNAMED IGNEOUS INTRUSION OF UNKNOWN AGE |
| UPEM | UPPER PENNANT MEASURES [OBSOLETE NAME AND CODE: SEE PES AND MEMBERS THEREIN] |
| WEN | WENLOCK ROCKS (UNDIFFERENTIATED) |
| WESH | WENLOCK SHALE FORMATION [OBSOLETE NAME AND CODE: USE CBRD] |
| WHT | WILKESLEY HALITE FORMATION |

| Lex code | Description |
|---|---|
| WWB | WEST WALTON FORMATION |
| YST | STRETTON GROUP |
| YW | WENTNOR GROUP |

**Table A2.2 Rock code for 1:250,000 geological mapping**

| Rock_250,000 | RCS_D |
|---|---|
| ARG | SILICICLASTIC ARGILLACEOUS-ROCK |
| ARLM | SILICICLASTIC ARGILLACEOUS-ROCK and LIMESTONE |
| ARSD | SILICICLASTIC ARGILLACEOUS-ROCK and SANDSTONE (UNDIFFERENTIATED) |
| BAFI | MAFITE |
| CHLK | CHALK |
| CONG | CONGLOMERATE |
| HALI | HALITE |
| LATU | LAVA (UNDIFFERENTIATED) and TUFF |
| LMAR | LIMESTONE and SILICICLASTIC ARGILLACEOUS-ROCK |
| LMST | LIMESTONE |
| MELG | MELANGE (OBSOLETE NAME AND CODE - SUITE OF ROCK TYPES) |
| SCHI | SCHIST |
| SDAR | SANDSTONE (UNDIFFERENTIATED) and SILICICLASTIC ARGILLACEOUS-ROCK |
| SDST | SANDSTONE (UNDIFFERENTIATED) |
| TUFF | TUFF |
| TULA | TUFF and LAVA (UNDIFFERENTIATED) |

**Table A2.3 Drift sediment 1:50,000 names**

| Rock code | Rock name |
|---|---|
| CLSI | Clay-silt |
| DMTN | Diamicton = till |
| H-CLSI | Head (clay silt) |
| H-SAGR | Head (sand and gravel) |
| PEAT | Peat |
| SAGR | Sand and gravel |
| SUPD | Undifferentiated |

# Appendix 3: Updates for possible alternative standards

## (June – September 2007)

Alternative standards for copper, nickel and lead have been proposed since the completion of the main phase of work on this project, although these are also not confirmed as the standards at the time of closedown of this project. See Box 1 at the end of this appendix for further details.

For completeness and ease of reference the background data are given below for the alternative standards for copper, nickel and lead, exactly as presented in Table 4.2 and Figures 3.2, 3.3, 3.4 in the main body of the report.

It can be seen that the implications of the alternative standards compared with the previous proposed standards (cross-referencing to the available background data) have not changed from those described in the main body of the report for any scenario other than the proposed lowest standard for nickel (4.9 µg/l). Even in this latter case, the percentage exceedance represents a worst case scenario until the conditions of application are established and applied.

**Table A3.1 Comparison of r-MBRC data with the more recently proposed standards, and the proposed standard plus background.**

Data for new (alternative) standards in **bold**.

| | Element | Standard | r-MBRC (median) | Standard + r-MBRC | Samples > standard | Samples > (standard + r-MBRC) |
|---|---|---|---|---|---|---|
| | | µg/l | µg/l | µg/l | % | % |
| Table 1.1 | Copper | 8.2 | 1.6 | 9.8 | 4 | 3 |
| **NEW** | **Copper (low)*** | **7.9** | **1.6** | **9.5** | **4** | **3** |
| **NEW** | **Copper (high)*** | **27.2** | **1.6** | **28.2** | **<1** | **<1** |
| Table 1.1 | Nickel (low)* | 4.9 | 3.6 | 8.5 | 28 | 9 |
| Table 1.1 | Nickel (high)* | 35.6 | 3.6 | 39 | <1 | <1 |
| **NEW** | **Nickel** | **20** | **3.6** | **23.6** | **1** | **1** |
| Table 1.1 | Lead | 6 | 0.10 | 6.1 | 1 | 1 |
| **NEW** | **Lead** | **7.2** | **0.1** | **7.3** | **<1** | **<1** |

* A range of possible standards exist, which will depend on stream conditions which are not yet available to assess.

None of these metals (Cu, Ni, Pb) are judged by the findings of this report to be of highest concern in terms of potential compliance failures of the proposed standards as a result of natural background concentrations. The data presented in table A3.1 indicates that relatively small changes in the value of the standard are unlikely to make much difference in terms of potential failures. Conversely, the application of the added risk approach using MBRCs developed in this study will be most important for the metals at highest risk of failing the standard – that is, for arsenic, iron and manganese.

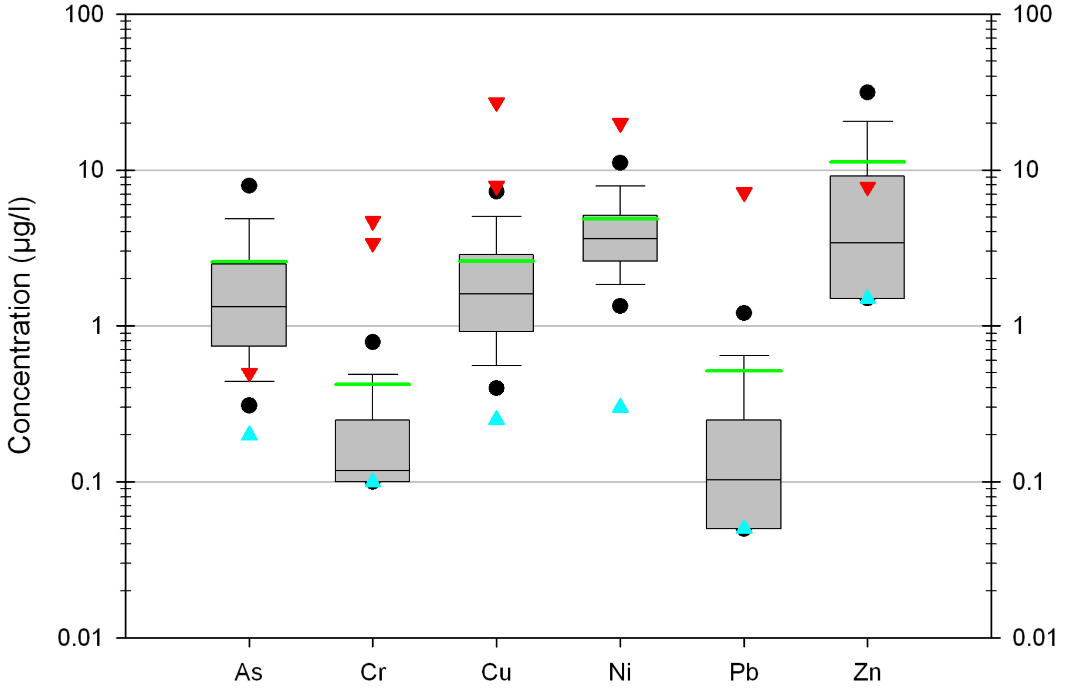
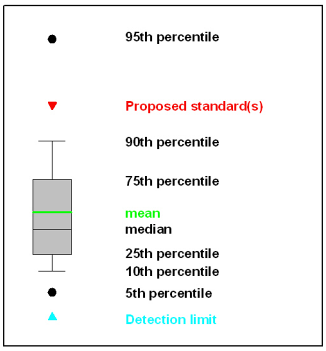


**Figure A3.1: Boxplot summaries of the stream water data for trace elements.**
An update of Figure 3.2b to include the ‘new’ proposed standards shown in Table A3.1.



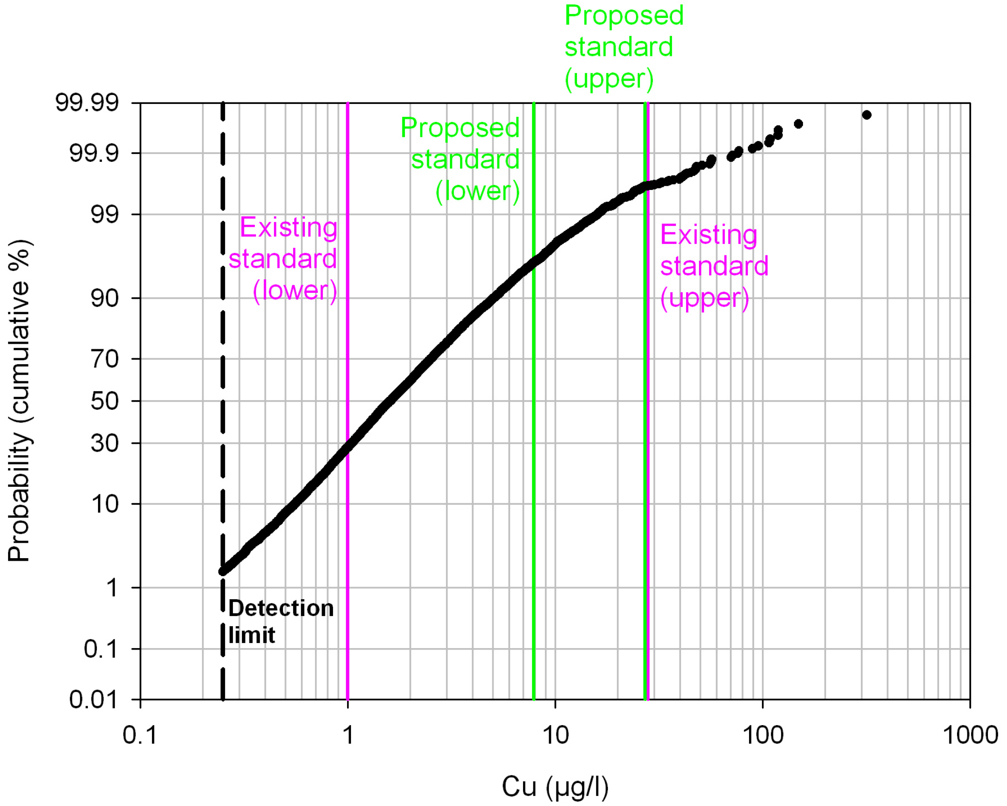


**Figure A3.2a: Probability plot of copper in stream waters**
An update of Figure 3.3f, showing the 'new' proposed standards shown in Table A3.1.

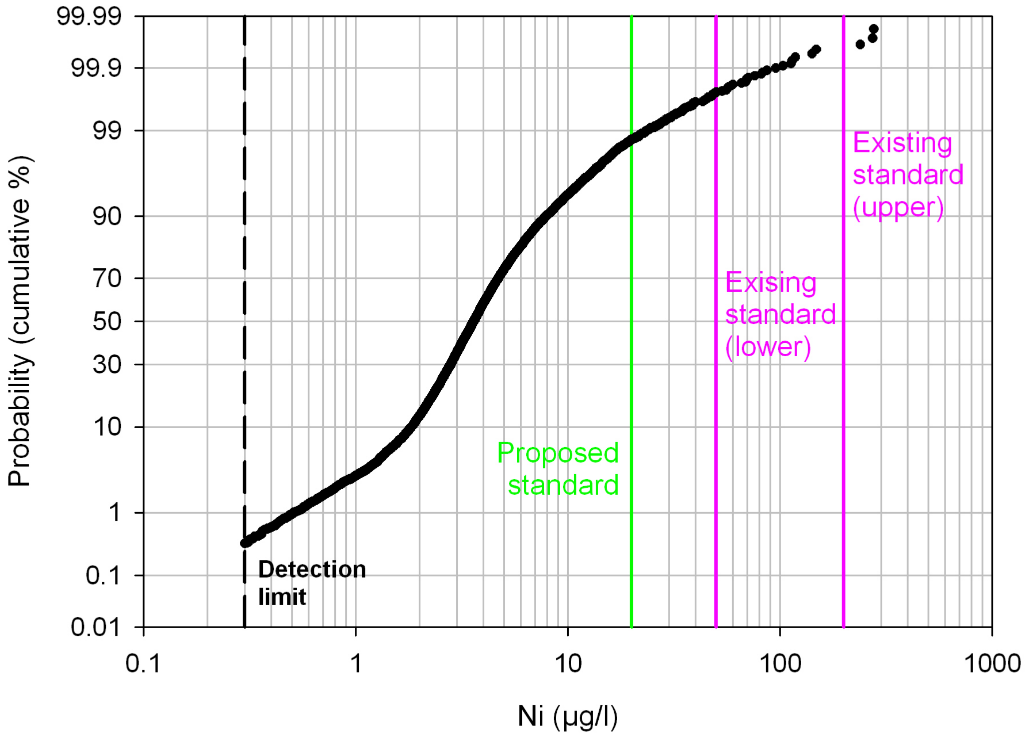


**Figure A3.2b: Probability plot of nickel in stream waters**
An update of Figure 3.3g, showing the 'new' proposed standards shown in Table A3.1.

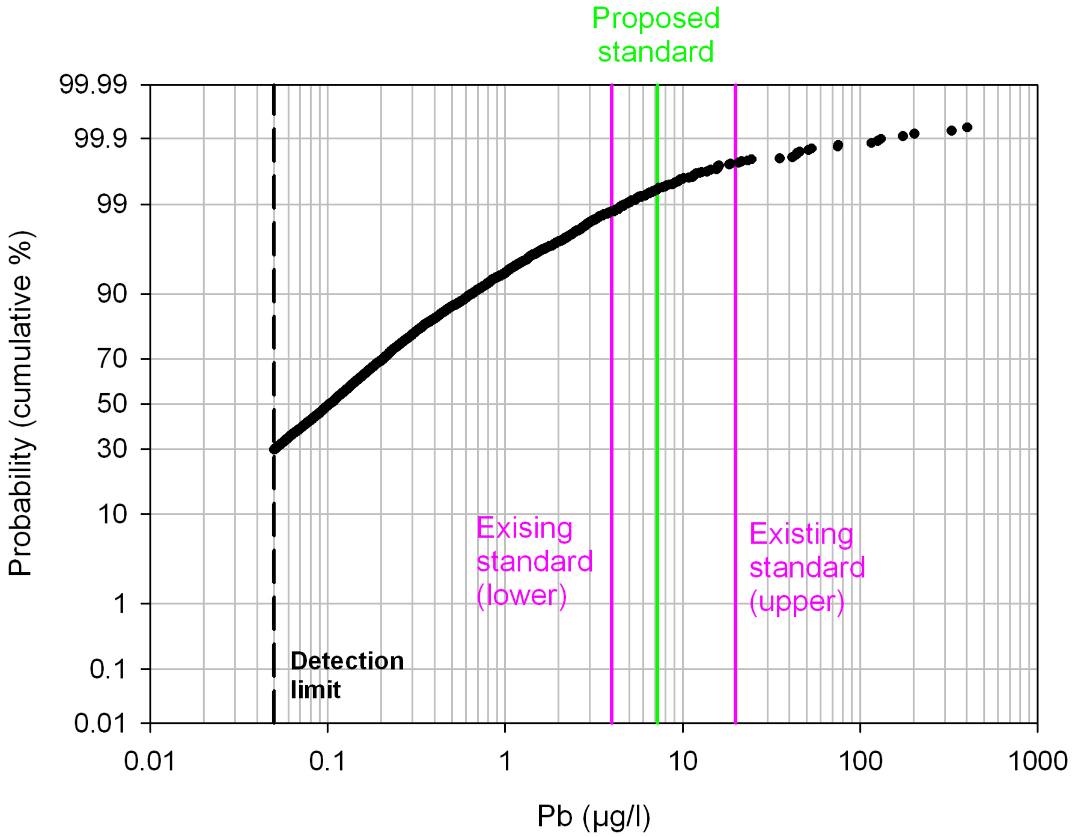


**Figure A3.2c: Probability plot of lead in stream waters**
An update of Figure 3.3h, showing the 'new' proposed standards shown in Table A3.1.

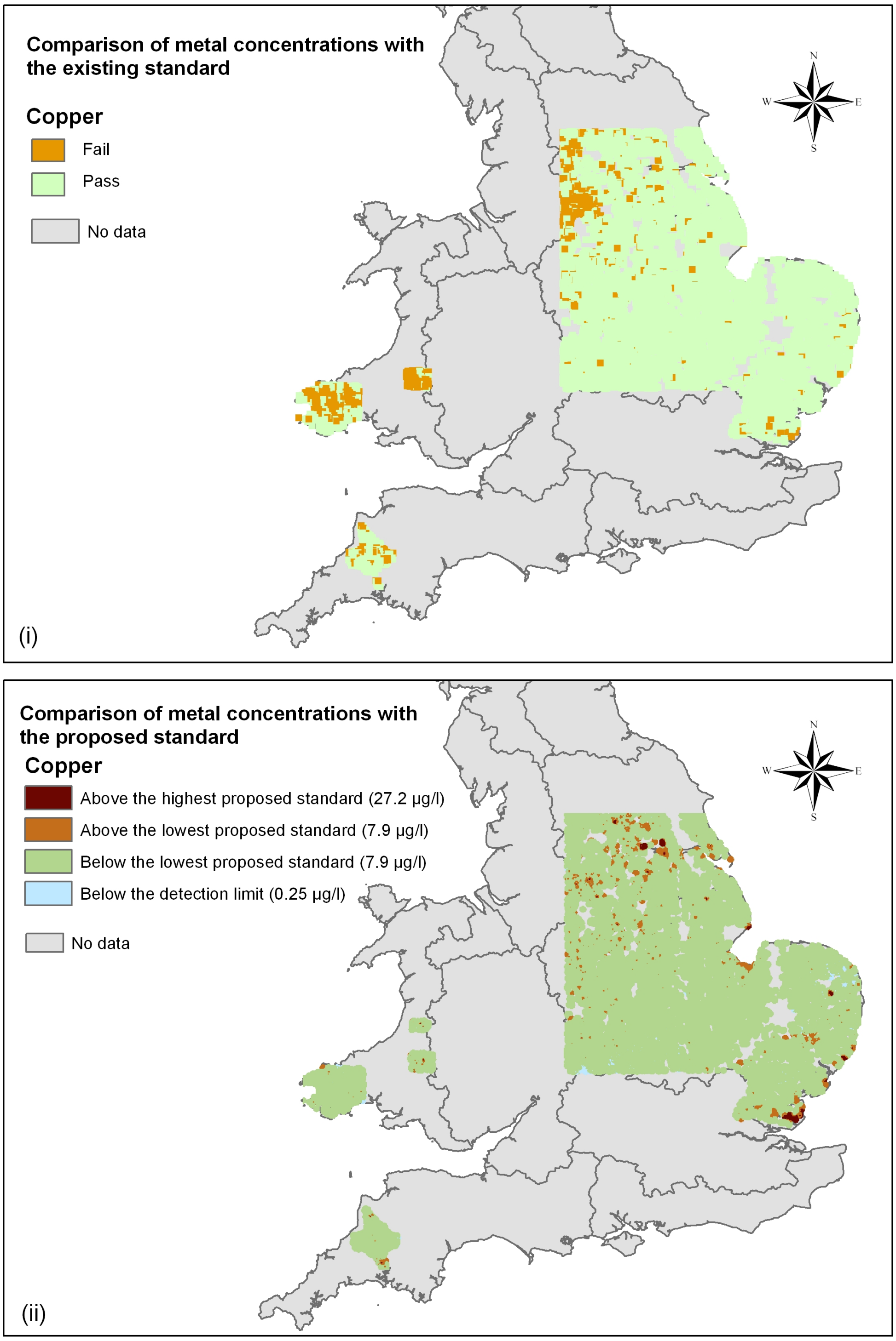


**Figure A3.3a: Comparison of copper concentrations with (i) existing standards, and (ii) proposed standards**
An update of Figure 3.4f, showing the ‘new’ proposed standards shown in Table A3.1.

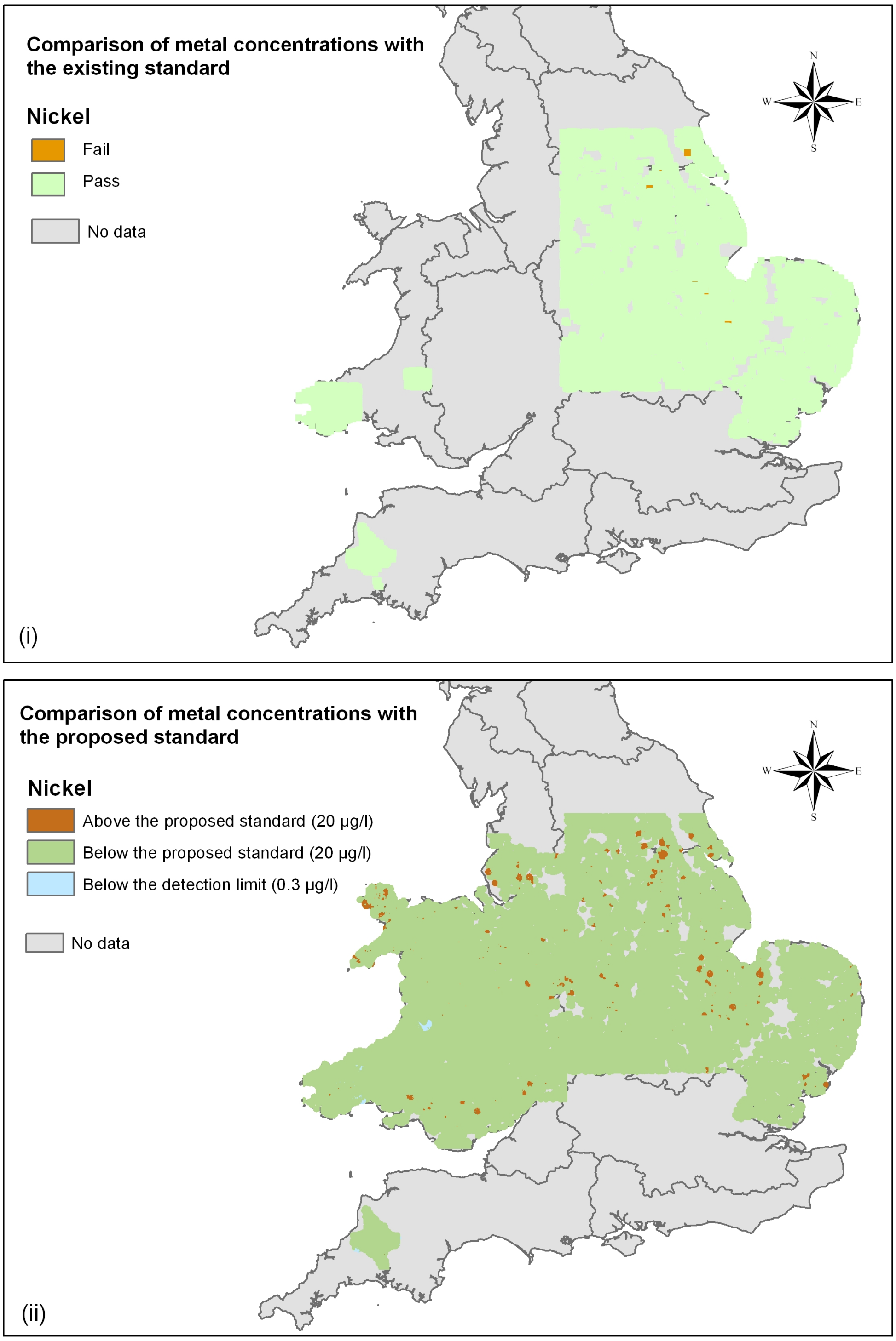


**Figure A3.3b: Comparison of nickel concentrations with (i) existing standards, and (ii) proposed standards**
An update of Figure 3.4g, showing the 'new' proposed standards shown in Table A3.1. Note that the ICP-AES data has been included here, because the detection limit concentration is below that of the proposed standard, providing useful information even where the data is below detection limit (i.e. it does not exceed the standard).

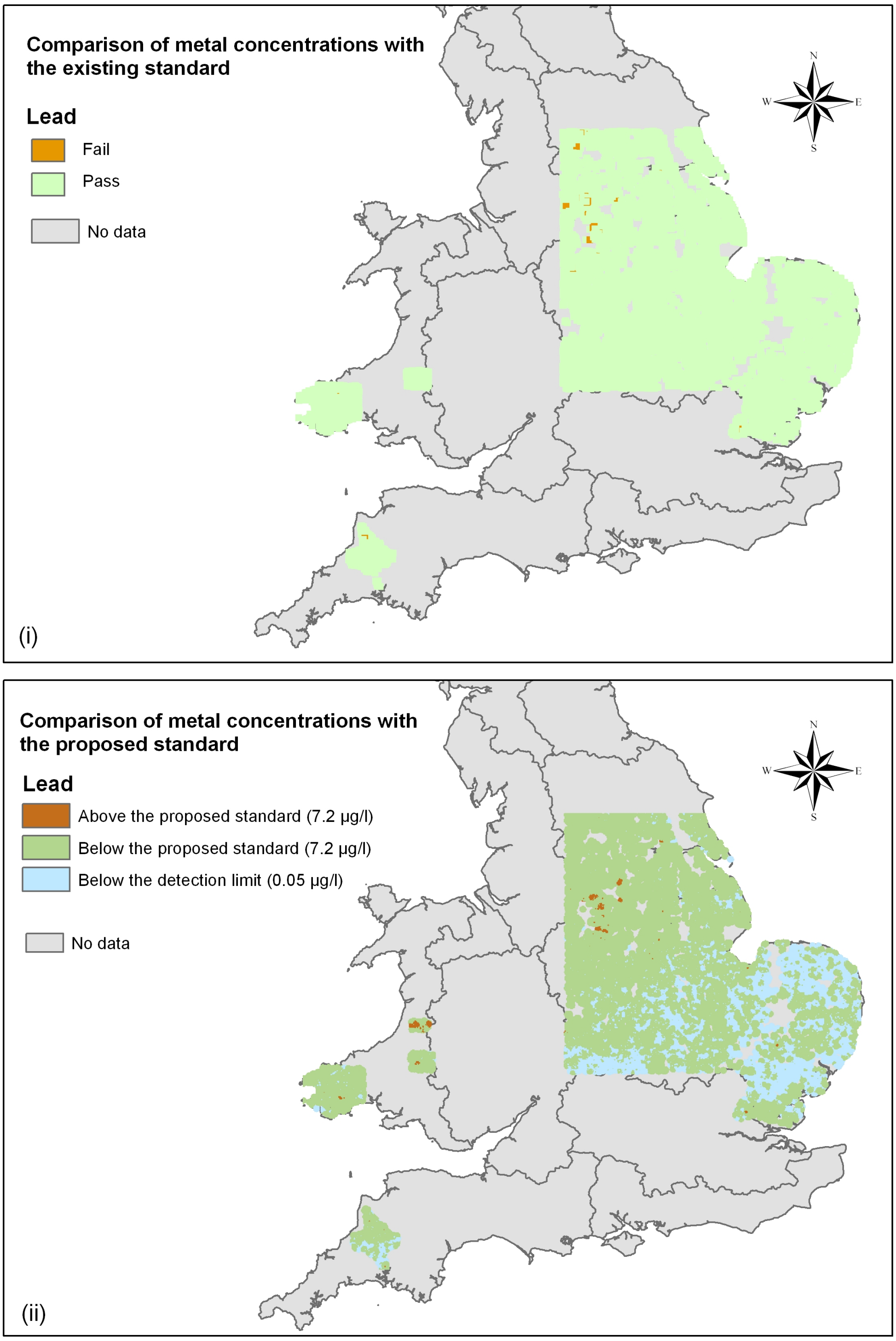


**Figure A3.3c: Comparison of lead concentrations with (i) existing standards, and (ii) proposed standards**
An update of Figure 3.4g, showing the ‘new’ proposed standards shown in Table A3.1.

**Box 1. Environmental Quality Standards.**

During the development of this report some of the Environmental Quality Standards values provided to the authors were amended.

Several of these were due to a change of policy at a European level where D.G. Environment amended the standards proposed for Nickel and Lead that form part of the Proposed WFD Article 16 Daughter Directive.
The EQS for Nickel and Lead that are now contained in the Agreed version of the text have been set as interim values pending the satisfactory conclusion of the Risk Assessment Reports (RARs) under EU Existing Substances Regulations (793/93). In both cases this revised text has only set an AA-EQS that will be used in both fresh and other waters. A short term (MAC) standard has not been identified. The values are provided in Annex I Part A of the Daughter Directive. It is not clear how these interim values were calculated but we suspect that they may have used the FOREGS Atlas data taking a high percentile value.

The RAR for Ni is now close to completion and we believe that a safety factor of 2 will be applied in setting the Predicted No-Effects Concentration (PNEC) for water. If this is confirmed we are likely to see the final standard being more stringent than the current interim value.
The voluntary RAR for Lead is also due to be further considered by EU TCNES IV 2007 (December)but the outcome for this study is not yet clear.

**Irrespective of the above, the authors of this project (SC050063) have been advised their report should still consider the potential consequences for a TGD based standard as it is clear that the interim standards will not be maintained indefinitely. Indeed for Nickel agreement on a safety factor of 2 means that the final standard may revert to a value close to that originally proposed.**

In addition to the above a number of draft EQ Standards proposed for Specific Pollutants under Annex VIII have been amended in the version that was subject to Stakeholder review earlier this summer. This affects the substances that are set out in Table 1 Part B including the metals and metalloids namely arsenic, copper, iron and zinc. For each of these substances it has been decided that a robust EQS cannot yet be set using the EU Technical Guidance Document. It was therefore decided to adopt the existing standards set under 76/464/EEC as interim values. Clearly several of these (Cu and Zn) are still subject to the EU Risk Assessment process and any values may be revised further upon finalisation of the RARs.

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Rio House
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Tel: 0870 8506506
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