

The importance of dissolved organic carbon in the assessment of environmental quality standard compliance for copper and zinc

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



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Executive summary

The regulation of metals in the aquatic environment through the use of environmental quality standards (EQSs) presents a challenge to environmental regulators. Bioavailability corrections through the use of biotic ligand models (BLMs) allow an accurate assessment to be made of potential metal toxicity, but the implementation of such corrections requires additional data, which may not be available. This report sets out a methodology for the estimation and validation of waterbody and hydrometric area specific dissolved organic carbon (DOC) concentrations, one of the most-important parameters required to run the BLMs, for use in assessing compliance against EQSs within a tiered assessment approach.

The BLMs for both copper (Cu) and zinc (Zn) indicate that the most-sensitive conditions for exposure to these metals occur when DOC concentrations are low, and particularly if this occurs in combination with relatively extreme pH conditions (i.e. pH <6 for Cu). These extreme pH conditions are also close to the validation boundaries of the models.

The generic predicted no-effect concentration (PNEC) values provided in the Cu Existing Substances Regulations (ESR) voluntary risk assessment report are calculated for conditions that may be considered representative of several different areas or regions within Europe. Considering the range of bioavailability conditions across Europe, a generic reasonable worst case PNEC, protective to 90 per cent of the EU surface waters, was determined. Because the UK surface waters include water chemistry conditions that cover relatively wide ranges for all of the important BLM input parameters, it is necessary to consider the suitability of such a generic PNEC for a local compliance assessment. An indicative initial assessment, using only information on pH and DOC concentrations, suggests that there may be some assessment sites where the conditions are such that a generic PNEC, of approximately $8 \mu\text{g}\cdot\text{l}^{-1}$, may not be sufficiently protective for use as a first tier screen within a tiered compliance assessment.

Because the generic PNEC for Zn was set for conditions of high bioavailability, the generic PNEC from the ESR Zn risk assessment report should provide an adequately protective first tier screening value, although any areas requiring application of the PNEC for soft waters would require screening based on their calcium (Ca) concentrations.

We therefore propose that the initial tier of assessment is undertaken against a PNEC value that can be considered sufficiently protective, even under conditions of very high bioavailability. If such an approach is taken, then the need for DOC monitoring data (and other supporting parameters) will be deferred to the next tier of the assessment process. Applying the generic PNEC at this tier does not remove the requirement for DOC monitoring data, but introduces an additional tier of assessment at the beginning of the process where DOC information is needed.

Supporting information on the pH, DOC, and Ca conditions at compliance assessment sites will be required to assess any sites that fail the initial screening tier. The DOC concentrations are particularly important in defining the bioavailability of Cu and Zn and of other metals not specifically addressed in this study, such as nickel. As DOC is currently not a routinely analysed parameter, default values may need to be derived where possible to minimise any additional monitoring requirements for compliance assessment. The DOC concentrations can vary considerably in some waterbodies and be relatively consistent in others. The variability of the DOC concentrations will not always be an issue for compliance assessment because the overall conclusion of the

assessment depends not only on the DOC concentration, but also on the pH and Ca conditions (to a more-limited extent) and the metal exposure concentration.

The findings of this study suggest that it is not practical to undertake bioavailability-based compliance assessments on large spatial scales, such as for a whole hydrometric area, using generalised information about the key physico-chemical properties of the areas of interest. Wherever possible, default values for BLM input parameters (such as the 25th percentile DOC concentration) should be derived and applied on a local scale, and we suggest that the scale of individual waterbodies is probably the most-appropriate basis for deriving default values at present.

Where the compliance assessment is undertaken as part of a tiered assessment approach, information about DOC concentrations will only be required in cases where potential risks have already been identified for a metal in an earlier tier. In cases where metal exposure is low or close to background levels, there may not be any requirement to consider bioavailability. In cases where default DOC concentrations need to be applied, then provided they are used in a relatively precautionary way they will highlight any potential need for further consideration through the identification of possible risks at assessment sites.

The outputs from the approach for deriving default DOC values for use with BLMs were tested by undertaking field monitoring at a number of sites for which default DOC values had been derived, to enable a comparison to be made with recent measured data. The default DOC concentrations derived on an individual waterbody basis provide a good estimate of the DOC concentrations from monitoring in the majority of cases. In some cases, the average measured DOC concentrations are significantly higher than the default concentrations. In cases such as these, the default concentrations will provide a low estimate of the site-specific PNEC or bioavailability factor. Within a tiered compliance assessment approach, this may result in more-detailed consideration of the local conditions, including DOC concentrations, if potential risks are identified.

The hydrometric area based default values tend to perform less well than waterbody-based default values, but are still protective in the majority of situations. Individual waterbodies that are typified by low DOC concentrations always tend to perform badly when hydrometric area based defaults are applied because the default DOC concentrations may be appreciably higher than the actual DOC concentrations. In cases such as these, an adequately protective assessment cannot be assured from the use of a hydrometric area based default value. Hydrometric area based default DOC concentrations would be applied in any cases where there is little or no information available about local DOC concentrations prior to undertaking an assessment. It is unlikely, therefore, that it will be possible to identify waterbodies that might potentially be at risk when a hydrometric area based default DOC concentration must be applied.

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1 Introduction

1.1 Report structure

Under the Water Framework Directive, ‘good status’ is based, in part, upon compliance with environmental quality standards (EQSs). Setting and implementing EQSs for metals under the Water Framework Directive presents a unique set of problems. When assessing compliance, difficulties arise as a result of variation in natural background concentrations, the existence of several chemical species (some more toxic than others), and the alteration of this speciation in response to local physico-chemical conditions, especially dissolved organic carbon (DOC). The use of biotic ligand models (BLMs) is the most-successful and most-robust method for resolving these difficulties (Van Genderen et al. 2008, Natale et al. 2007). By gathering site-specific physico-chemical data, these models allow us to determine the fraction of measured metal in the water sample that is biologically relevant and, therefore, able to exert toxic effects.

The scope of our study was limited to copper (Cu) and zinc (Zn), although the results are considered to be applicable to a number of other metals for which DOC has an effect on bioavailability. Several published BLMs rely significantly upon the input of DOC values, e.g. those for Cu, nickel (Ni), and Zn. However, the Environment Agency does not routinely monitor DOC across England and Wales. In this project, we develop and test a methodology for the derivation of default DOC values from spatially referenced Environment Agency monitoring data. Specifically, the key aims of the work are to:

- Determine the water conditions under which DOC has the greatest influence upon Cu and Zn toxicity,¹ as predicted by the respective BLMs.
- Establish an evidence-based methodology for the derivation of DOC default values from monitoring data for use with BLMs which could negate the need for routine DOC monitoring.
- Assess the suitability of these default values for use within a ‘metals’ EQS compliance framework by comparing EQS predictions based on estimated abiotic parameters with those based on measured abiotic parameters from a targeted monitoring trial.

In this introductory section, we outline how and why EQSs have changed under the Water Framework Directive. We specifically discuss the implications of these changes for metals and how a number of the regulatory challenges presented may be met by accounting for speciation and (bio)availability. The importance of DOC in the speciation of metals in freshwaters is discussed before broadly outlining the function of BLMs.

Section 2 uses the BLMs to review the abiotic water conditions under which Cu and Zn bioavailability are greatest and also under what DOC conditions change in bioavailability is most significant. Specifically, this section focuses upon the sensitivity of the BLM outputs to changing DOC inputs. We also provisionally assess the suitability of the generic, reasonable worst case predicted no-effect concentration (PNEC) from the Cu voluntary risk assessment report (VRAR) to freshwater physico-chemical conditions in England and Wales.

¹ Although BLMs have been published for a number of metals, including Cu, Ni, and Zn, a rapid throughput BLM tool is currently only available for Cu and Zn. Rapid throughput BLM tools were required for the current analyses, and therefore the scope of the study was limited to Cu and Zn. The conclusions regarding the use of default versus measured DOC values will be applicable to other metals that are influenced by DOC, such as Ni.

In Section 3, we describe a methodology for establishing where in England and Wales DOC default values could be used or where monitoring may be required. We then use this methodology to derive spatially referenced default DOC values, from Environment Agency monitoring datasets, to be used as BLM inputs. Through the use of the BLMs, we compare Cu and Zn compliance using default DOC inputs compared with measured data.

Section 4 takes the outputs from the previous section and, through a targeted monitoring exercise undertaken over nine months, assesses the utility of the default DOC values. The results from this exercise are also discussed in the context of the implications of using waterbody-specific DOC default values for Cu and Zn compliance assessment.

Finally, in Section 5, we provide conclusions on the importance of DOC in the assessment of compliance against EQSs for metals under the Water Framework Directive and outline a methodology for how the defaults *should* be used. Gaps in data or knowledge are identified and a number of recommendations are made.

Annex 1 at the end of the report gives waterbody-specific default values for DOC and calcium (Ca).

1.2 Environmental quality standards for metals and the Water Framework Directive

Historically, freshwater monitoring in England and Wales has been driven by the need to meet national and European regulatory requirements. For metals (and other chemicals), these requirements have often led to the derivation of EQSs, i.e. numerical limits (typically expressed as concentrations or doses of chemicals) in the environment below which unacceptable effects are not expected to occur. For metals such as Cu and Zn, EQSs have been derived to assess freshwater compliance under the Dangerous Substances Directive (76/464/EEC and Daughter Directives) and Freshwater Fish Directive (78/659/EEC). To account for speciation-based changes in potential aquatic ecotoxicity (International Council on Mining and Metals (ICMM) 2007), the EQSs for Cu and Zn were hardness banded, e.g. Freshwater Fish Directive standards for Zn (Table 1.1).

Table 1.1 Hardness-banded zinc environmental quality standards from the Freshwater Fish Directive (78/659/EEC)

Hardness (mg CaCO ₃ ·l ⁻¹)	Total zinc (mg·l ⁻¹) ¹	
	Salmonid	Cyprinid
≤10	0.03	0.3
>10 and ≤50	0.2	0.7
>50 and ≤100	0.3	1.0
>100	0.5	2.0

Notes: ¹ Standard is dependent on the average yearly hardness.

The values suggest that increasing water hardness effectively reduces toxicity, although relatively recent evidence suggests that such a simplistic relationship is not a robust way to assess risks from metals in the environment (Dutch National Institute for Public Health and the Environment (RIVM) 2004). Figure 1.1 shows ecotoxicity data for Zn, with black triangles and clear squares representing individual toxicity test results for a number of aquatic species, across a wide range of water hardness values that reflect the 10th to the 90th percentile of hardness conditions in EU surface waters. It is clear that the protective effect of increasing hardness is equivocal.

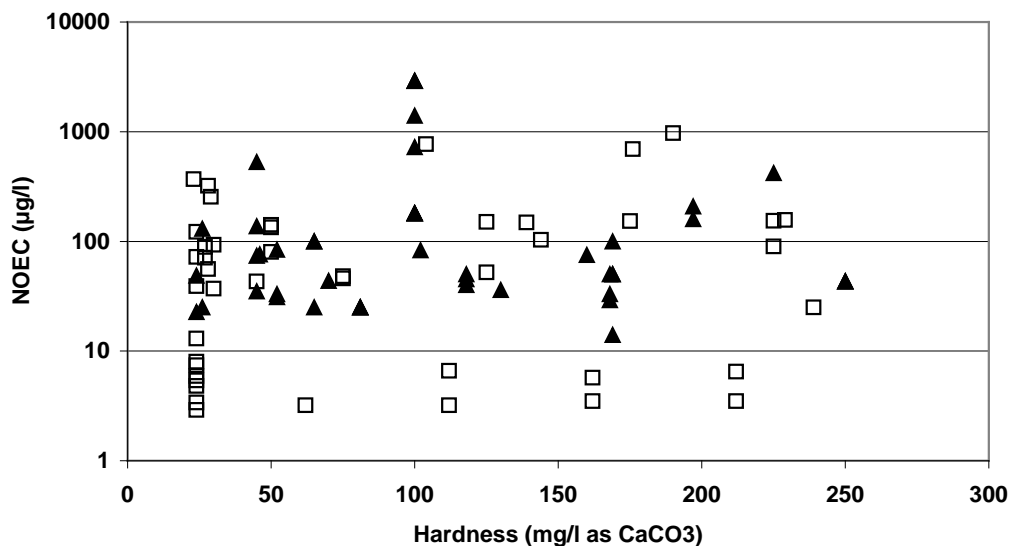


Figure 1.1 Effect of hardness on zinc toxicity in freshwaters (RIVM 2004)

The Water Framework Directive came into force at the end of 2000 (European Commission (EC) 2000). The key objectives of the directive are to prevent deterioration of the status of all surface water and groundwater bodies, and to protect, enhance, and restore all bodies of surface water and groundwater with the aim of achieving good status by the end of 2015. To achieve these objectives, EQSs have been derived for several polluting substances which supersede many of the standards from earlier legislation (such as the Dangerous Substances Directive). For some substances, EQSs have been set by the EC to apply across the whole of the EU; for others, it is the responsibility of Member States both to select these and derive their corresponding EQSs. In the UK, Cu and Zn fall into this latter category and are termed 'specific pollutants'.

For many substances, including Cu and Zn, the UK Technical Advisory Group for the Water Framework Directive has agreed to use outputs from risk assessments produced under the Existing Substances Regulations (ESR) (793/93/EEC). The aquatic PNECs for Cu and Zn in these assessments can be considered as simplified EQSs. The assessments incorporate a highly developed understanding of metal behaviour and fate, and accurately predict potential aquatic risks from Cu and Zn (European Copper Institute (ECI) 2008, RIVM 2004). Biotic ligand models for Cu and Zn were used in the assessments and have been made available for use in this project.

1.3 The importance of dissolved organic carbon in relation to metal toxicity in freshwaters

In freshwaters, metals exist in different forms or species, in part dependent upon the intrinsic physico-chemical characteristics of the freshwater itself. Importantly, these different metal species have different ecotoxicological potencies, which are largely unrelated to the quantity of total or dissolved metal in the water column. Therefore, accounting for the form or species of a metal in a waterbody is key in determining its potential ecological effects.

The mitigating effect of DOC on the aquatic toxicity of metals has been demonstrated in laboratory trials since the early 1970s (Zitko et al. 1973, Sunda and Guillard 1976, Giesy et al. 1983). These early trials also showed that it was often the 'free metal' ion that had the strongest relationship with observed toxicity and that increasing DOC

concentrations reduced the free ion activity (Paquin et al., 2002 and references therein).

Dissolved organic compounds, such as humic and fulvic acids, contain a wide diversity of functional groups that are able to form complexes with dissolved metal ions. This complex formation effectively renders the metal ions chemically unavailable to organisms, with a consequent reduction in metal bioavailability. The metal binding sites are generally considered to be composed of carboxylic acid and phenolic functional groups and exhibit a wide range of metal binding affinities. Trace metal ions, such as Cu^{2+} and Zn^{2+} , compete with other cations (e.g. Ca^{2+} , Mg^{2+} , and H^+) for occupancy of the binding sites on the fulvic acid molecule. The actual concentrations of truly dissolved metal ions, therefore, depend on the pH, DOC concentration, and concentrations of other major cations in the solution. These interactions between the metals and organic ligands can be modelled relatively reliably for a variety of different metal ions (Tipping and Hurley 1992, Tipping 1994 and 1998, Benedetti et al. 1995, Kinniburgh et al. 1996).

The BLMs take account of these interactions and also of the competitive interactions between different cations at the site of biological uptake (the biotic ligand) to predict the toxicity of dissolved metals to freshwater organisms. Examples of the influence of changing water physico-chemistry on metal bioavailability are given in Figure 1.2. The graphs show how Cu toxicity (and hence bioavailability) varies with pH and DOC. It is clear that Cu toxicity is greatest at high pH and low DOC concentrations for algae, but also at low pH and low DOC concentrations for cladocerans. High DOC concentrations (e.g. 50th percentiles) in the test waters always result in reduced metal availability and reduced toxicity when compared with low DOC concentrations (e.g. 5th percentiles).

Accounting for the chemically available metal fraction in a water column through an understanding of the local water conditions establishes an environmentally relevant metric when assessing potential risk from metals. Furthermore, if this is coupled with knowledge of the resulting interactions at the site of toxic action, such as a fish gill, it enables an estimate of the bioavailable metal concentration in the water to be calculated. This is the general principle of BLMs.

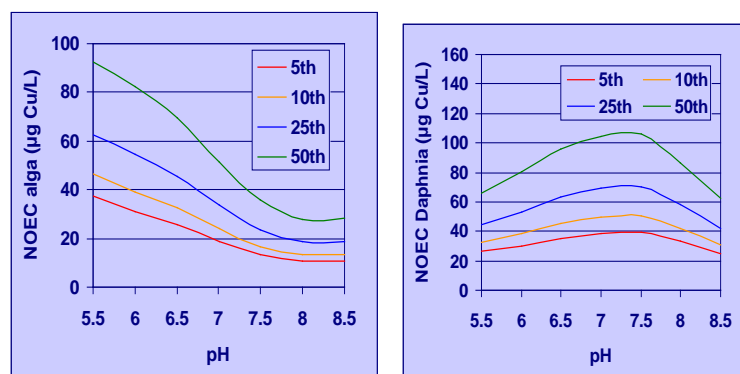


Figure 1.2 Differences in pH sensitivity between algae and invertebrates for different percentiles of dissolved organic carbon concentrations in EU surface waters (cited in ECI 2008)

1.4 The use of biotic ligand models

The underlying theory of the BLM is not new (Pagenkopf 1983); through the use of chemical equilibrium modelling, the BLM addresses the competition between the free metal ion and other cations for complexation with a biotic ligand, which is assumed to be the site of toxic action. This is typically the gill structures of fish and invertebrates

and algal cell surfaces. The relationships between the various solution components are shown in Figure 1.3, with the free metal ion represented by Me^{2+} , the competing cations by Na^+ , H^+ , Mg^{2+} , and Ca^{2+} , and the abiotic ligands by POC (particulate organic carbon), DOC, and CO_3^{2-} . The site of toxic action is represented by the fish gill. Extensive technical reviews of the development of the BLM have been published previously (e.g. Paquin et al. 2002).

Regulatory interest in these models has increased significantly over the last decade (Santore et al. 2001, Niyogi and Wood 2004, US Environmental Protection Agency (EPA) 2007, Vijver and de Koning 2007). The Environment Agency has also more-recently published a report examining the use of BLMs to implement EQSs for metals under the Water Framework Directive (Environment Agency 2009). The report specifically addresses some of the practical issues that surround the use of BLMs within routine assessment and compliance frameworks for Cu and Zn in freshwaters. All of the regulatory bodies responsible for monitoring freshwaters in the UK have adopted the BLMs, with the Environment Agency automating their use within laboratory systems.

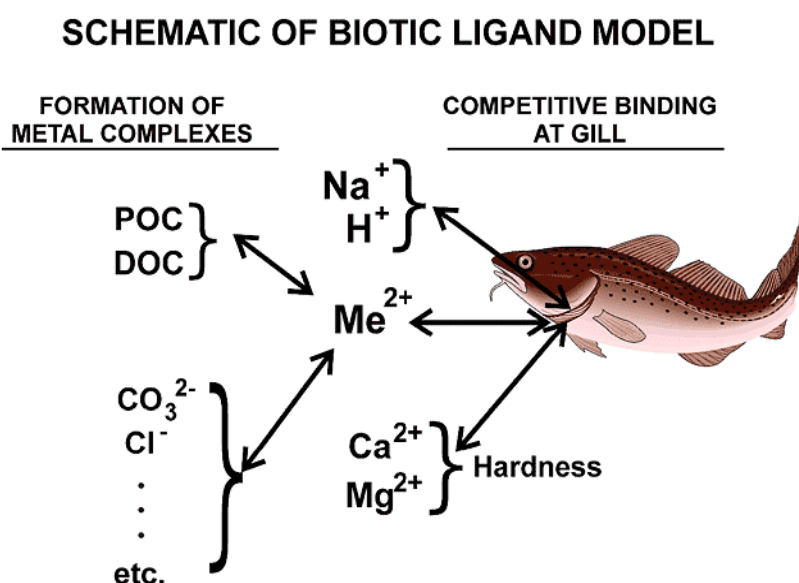


Figure 1.3 Simplified schematic of the biotic ligand model (Me^{2+} is the free metal ion, POC and DOC are particulate and dissolved organic carbon, respectively) (source: <http://www.hydroqual.com>)

The models for Cu and Zn differ in their structure and outputs. For Cu, the BLM uses detailed site chemistry (some 13 input parameters) to recalculate the entire Cu ecotoxicity database and redraws a species sensitivity distribution (SSD) from the data to determine an HC_5 (a concentration that is hazardous to 5 per cent of the ecosystem) for the specific site chemistry under consideration. The outputs from the model are robust in predicting Cu toxicity to aquatic organisms in the laboratory and the field (ECI 2008). The importance of the relationship between the ecotoxicity of Cu, as predicted by the Cu BLM, and DOC is shown in Figure 1.4 for the River Ouse catchment in the north east of England.

The Zn BLM is supported by Microsoft Excel and uses only pH, DOC, and Ca/hardness inputs. It defines a bioavailability correction (bioavailability factor, BioF) that can be applied to measured Zn concentrations. Importantly, the generic Zn PNEC to which the product of the Zn concentration from the monitoring data and the corresponding BioF is to be compared is an 'added' value, i.e. it requires consideration of the background Zn concentration from the waterbody (RIVM 2004).

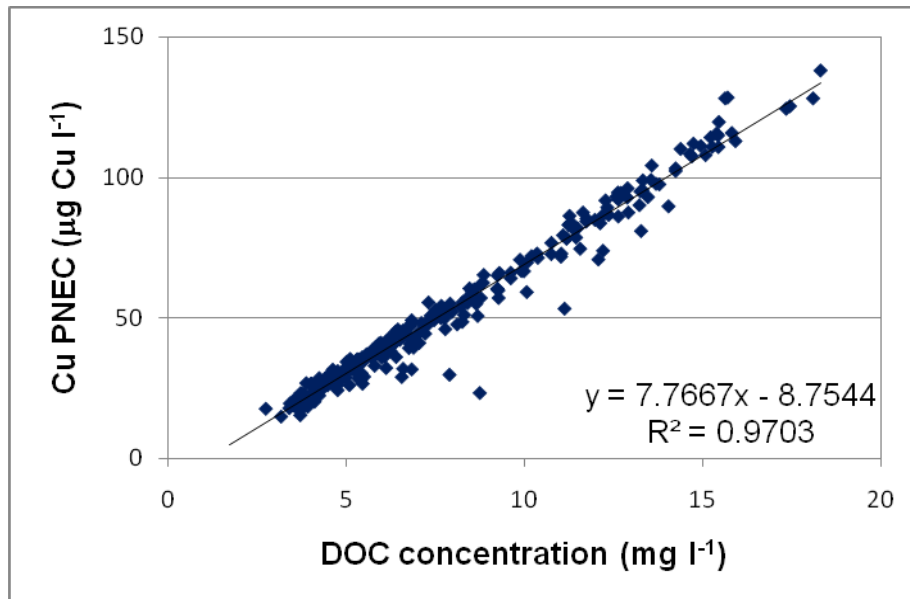


Figure 1.4 Relationship between copper predicted no-effect concentrations and dissolved organic carbon concentrations within a single UK catchment

The use of the BLMs requires significantly more supporting information in the assessment of metal compliance than that required for previous EQS values for Cu and Zn (e.g. Table 1.1). A screening Cu PNEC Estimator, based on the full Cu BLM, has been developed by the Environment Agency (2009) which effectively reduces the number of input parameters to the same number as those required for the Zn BLM: pH and DOC concentrations in addition to information about hardness (or Ca concentrations). This enables large numbers of calculations to be made efficiently, although with a reduction in precision and accuracy when compared with the full Cu BLM.

The work described in this report will facilitate the routine regulatory use of BLMs for the assessment of Cu and Zn compliance in England and Wales. Furthermore, the outputs will also facilitate future metals management and risk assessment under the Water Framework Directive for regulators and stakeholders.

2 Sensitivity analysis of the biotic ligand models for copper and zinc

A sensitivity analysis of the BLMs provides the opportunity to identify clearly the abiotic water conditions under which Cu and Zn bioavailability are greatest and also under what conditions *change* in bioavailability is most significant. Therefore, the focus of this section is on establishing the physico-chemical water conditions that are likely to pose a potential risk at a hypothetical Cu concentration. Consideration will also be given to whether there is likely to be sufficient DOC present in a waterbody to reduce Cu toxicity. Having identified those conditions under which establishing DOC concentrations will be most important for each metal, we develop a series of options from which it will be possible to assess the need for routinely measured DOC values (Section 3).

The BLMs for Cu and Zn which have been developed as part of the ESR risk assessments were validated to cover the range of conditions between the 10th and 90th percentiles of available EU monitoring data for the key abiotic parameters (i.e. pH, DOC, and Ca). There are some differences in the validation limits for the two BLMs, principally because of differences in the conditions of the field-collected test waters that were used and in the species tested. It is important that the BLMs can be applied to the majority of UK monitoring locations, which include both very soft, acid waters and also very hard waters.

Both BLMs have been widely peer reviewed and validated against laboratory and field data (RIVM 2004, ECI 2008).

2.1 The copper biotic ligand model

The Cu BLM is considered to be validated in the pH range 5.5–8.5, between 10 and 500 mg CaCO₃·l⁻¹ (equivalent to Ca concentrations of between approximately 3 and 150 mg·l⁻¹), and between DOC concentrations of 1.6 and 23 mg·l⁻¹ (ECI 2008). The validation range for the DOC concentrations represents the range of DOC concentrations in the waters used for validation testing, but it is proposed that there should be no restrictions on the range of DOC concentrations to which the BLM is applicable because the effect of DOC is linearly related to the PNEC for a given set of pH and Ca conditions.

The Cu BLM will calculate PNEC values for conditions that are outside its validation range, although the results need to be considered with caution in these circumstances. The version of the Cu BLM available for this sensitivity analysis (Version 0.0.0.17) does not provide a warning for conditions that are outside the validation range, although this is expected to be included in a future update.

2.1.1 Initial sensitivity analysis for the copper biotic ligand model

From the work of Vijver and de Koning (2007) and the Environment Agency (2007), it is clear that the key input parameters for the Cu BLM are pH, DOC, and Ca (given below in terms of hardness). These three key input parameters were tested in the assessment of the sensitivity of the Cu BLM to DOC inputs. The ranges were fitted to

the operating range of the model as given above, but at the lower end of the model for DOC ($1.6\text{--}12\text{ mg}\cdot\text{l}^{-1}$). This range of DOC values was chosen to capture the most-probable range of conditions found in UK waters which is expected to be in the range of $1\text{--}15\text{ mg}\cdot\text{l}^{-1}$ (Tipping et al. 1997), but likely would be lower in lowland catchments. The other parameter inputs to the model are temperature ($15\text{ }^{\circ}\text{C}$), humic acid percentage (0.01 per cent), magnesium (Mg) ($2.0\text{ mg}\cdot\text{l}^{-1}$), sodium (Na) ($5.3\text{ mg}\cdot\text{l}^{-1}$), potassium (K) ($1.1\text{ mg}\cdot\text{l}^{-1}$), sulphate (SO_4) ($6.60\text{ mg}\cdot\text{l}^{-1}$), chloride (Cl) ($5.6\text{ mg}\cdot\text{l}^{-1}$), sulphide (S) ($0.01\text{ mg}\cdot\text{l}^{-1}$), and alkalinity ($0.01\text{ mg}\cdot\text{l}^{-1}$). The inputs for these parameters were kept as the default values for the EU's reasonable worst case conditions (given above in parentheses). In all likelihood, the temperature value is probably too high for average UK conditions, but it is unlikely to make a significant difference to the outputs (Environment Agency 2007). The default Na and alkalinity concentrations are also lower than typical UK conditions.

The dissolved Cu concentration used for the model runs was $8\text{ }\mu\text{g}\cdot\text{l}^{-1}$, a value which was chosen as it is close to the PNEC initially derived by the UK as a potential Annex VIII EQS, based on the draft VRAR available at the time, and because it is close to the more-recent VRAR generic, reasonable worst case PNEC of $7.8\text{ }\mu\text{g}\cdot\text{l}^{-1}$ (ECI 2008; see also Section 2.1.2).

The model output is a PNEC based on the 50 per cent lower confidence limit of the HC_5 for the site conditions used as inputs. This PNEC is then used to divide the predicted environmental concentration (PEC) of Cu ($8\text{ }\mu\text{g}\cdot\text{l}^{-1}$ in all cases) to give an indication of the potential risk at the site, assuming a copper exposure concentration of $8\text{ }\mu\text{g}\cdot\text{l}^{-1}$. The change in PEC/PNEC ratios (also known as risk characterisation ratios) with water conditions is plotted in Figure 2.1 for a hardness of $36\text{ mg CaCO}_3\cdot\text{l}^{-1}$ for the range of input parameters. Only one plot is shown, although hardness values from $36\text{--}408\text{ mg CaCO}_3\cdot\text{l}^{-1}$ were run, with the lines showing very similar patterns to those in Figure 2.1. For higher hardness concentrations than that in Figure 2.1, the PEC/PNEC ratios under the same conditions of pH and DOC are all higher.

Table 2.1 reinforces the conclusion from Figure 2.1 that hardness is not as significant in determining change in the risk characterisation ratios relative to pH or DOC. The mean values and standard deviations of the risk characterisation ratios given for the complete hardness ranges at the bottom of Table 2.1 also show the limited difference at the same values of pH and DOC.

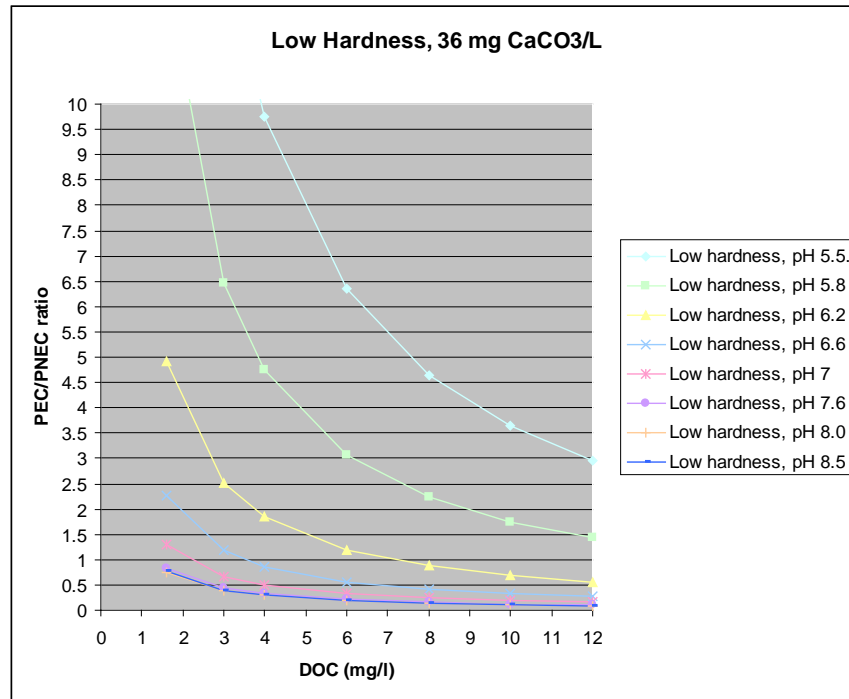


Figure 2.1 The influence of dissolved organic carbon and pH on the PEC/PNEC ratio of copper under low hardness (36mg CaCO₃·l⁻¹) conditions

Table 2.1 PEC/PNEC ratios, as a measure of risk, given for a range of water chemistry conditions

	Water conditions					
	DOC of 1.6 mg·l ⁻¹			DOC of 12 mg·l ⁻¹		
	pH 5.5	pH 7.0	pH 8.5	pH 5.5	pH 7.0	pH 8.5
Hardness						
36 mg CaCO ₃ ·l ⁻¹	24.24	1.29	0.76	2.95	0.16	0.09
408 mg CaCO ₃ ·l ⁻¹	13.3	2.01	1.78	2.20	0.24	0.21
Without accounting for hardness						
Mean	18.32	1.77	1.22	2.64	0.20	0.16
Range	13.3–	1.29–	0.75–	2.20–	0.16–	0.09–
	24.2	2.01	1.67	3.03	0.24	0.21
Standard deviation	4.28	0.27	0.35	0.33	0.03	0.05

Relative reductions in PEC/PNEC ratios with increasing DOC concentrations are shown for three pH values in Table 2.2. The greatest changes in the ratio are observed across all pH values for increases in DOC from 1.6 to 6 mg·l⁻¹. The consistency of changes in the risk characterisation ratios is noticeable across all pH ranges and hardness, with the exception of those changes at low pH and low hardness where DOC increases from 8–12 mg·l⁻¹ make relatively little difference.

Table 2.2 Factor reductions in PEC/PNEC ratios per mg·l⁻¹ of dissolved organic carbon with dissolved organic carbon increases from 1.6–12 mg·l⁻¹ at the same hardness and pH

DOC ranges (mg·l ⁻¹) at given pH values	Hardness (mg CaCO ₃ ·l ⁻¹)					
	36	83	158	257	307	408
pH 5.5						
1.6–3.0	1.83	1.75	1.70	1.66	1.66	1.62
3.0–6.0	2.08	2.71	1.97	1.90	1.89	1.88
6.0–8.0	1.37	1.36	1.34	1.34	1.33	1.32
8.0–10.0	0.58	1.27	1.27	–	1.25	1.25
10.0–12.0	0.40	1.22	1.21	–	1.21	1.21
pH 7.0						
1.6–3.0	1.92	1.92	1.92	1.92	1.92	1.92
3.0–6.0	2.06	2.06	2.05	2.06	2.06	2.06
6.0–8.0	1.35	1.35	1.35	1.35	1.35	1.35
8.0–10.0	1.27	1.26	1.26	1.26	1.26	1.26
10.0–12.0	1.21	1.21	1.21	1.21	1.21	1.21
pH 8.5						
1.6–3.0	1.92	1.93	1.94	1.94	1.94	1.95
3.0–6.0	2.05	2.05	2.06	2.06	2.06	2.07
6.0–8.0	1.35	1.35	1.35	1.35	1.35	1.35
8.0–10.0	1.26	1.26	1.26	1.26	1.26	1.26
10.0–12.0	1.21	1.21	1.21	1.21	1.21	–

The factor reductions shown in Table 2.2 expressed as percentage reductions in bioavailability per 1 mg·l⁻¹ increase in DOC unsurprisingly show a similar pattern of consistency across the pH and hardness bands. The greatest reductions (≈ 25–40 per cent) are seen when DOC increases from 1.6–6 mg·l⁻¹, with relatively smaller decreases in availability per unit increase in DOC above 6 mg·l⁻¹ of between 10–17 per cent. These differences are directly related to the number of available binding sites on the DOC, since at a constant pH value and DOC concentration, the number of binding sites available to Cu will be approximately constant (although much higher Cu concentrations may increase the number of available sites slightly). The factor increase in site density between DOC values of 1.6 and 6 mg·l⁻¹ is about twice that for between 6 and 12 mg·l⁻¹.

Nevertheless, it is the water conditions that cross the ranges where the PEC/PNEC ratio is around 1 or bounding the EQS (i.e. no basis for relaxing Cu EQS value) that are the most relevant. Furthermore, it is also critical to determine the circumstances under which DOC increases cause the PEC/PNEC ratio to fall from above 1 to below 1. In general, PEC/PNEC ratios of greater than 1 occur for the following circumstances:

- Across the hardness range used for this assessment and across all DOC values (1–12 mg·l⁻¹) at pH 5.9 and below.
- Above pH 5.9, for combinations of the highest hardness and lowest DOC concentrations.
- At pH 7 and above and for the complete hardness range, for the lowest values of DOC (1.6 mg·l⁻¹).

In general, conditions of low pH and low DOC concentrations tend to result in low PNEC values. A pictorial representation of the conditions of DOC and pH under which risk characterisation ratios are above and below 1 for a Cu PEC of 8 µg·l⁻¹ is shown in Figure 2.2 (Section 2.1.2). The transition from one side of the potential ‘risk boundary’ to the other should be an area which receives considerable focus when using Environment Agency data from the field.

In conclusion, from this initial assessment of the Cu BLM, it would appear that there is limited merit in monitoring DOC in waters with pH of greater than 7, and for which robust predictions support the view that DOC concentrations are unlikely to fall below 5–6 mg·l⁻¹. However, if predictions are not robust and variability is significant then monitoring may be needed.

This simplified 'risk boundary' has been used to provide a provisional assessment of whether sites for which both pH and DOC monitoring data are available would be expected to contain sufficient DOC to place them under the conditions of limited risk shown in Figure 2.2 (see Section 3).

2.1.2 Assessment of a generic PNEC for copper

A reasonable worst case BLM-normalised PNEC of 7.8 µg·l⁻¹ has been agreed under the ESR Cu VRAR (ECI 2008). This EU-wide reference PNEC is based on a range of typical EU scenarios as well as monitoring data across Europe and is aimed at a 90 per cent protection level for European surface waters. The BLM-normalised PNEC is close to the derived non-normalised PNEC (6.1 µg·l⁻¹).

The advantage of applying a generic PNEC, which has been assessed as appropriate to the reasonable worst case conditions, is that it is possible to screen measured dissolved metal concentrations against such a value as an initial tier. Only those sites that fail an assessment against the generic PNEC need to be assessed using the BLM. A generic PNEC can only be applied in this way if sites that are assessed against it fall within the range of conditions that it represents.

To assess the range of conditions for which the generic Cu PNEC could be considered as sufficiently protective, an initial investigation was done whereby different combinations of pH and DOC that can result in a Cu PNEC of 7.8 µg·l⁻¹ were considered. This was approximated by taking Cu BLM calculations with PNEC values between 7.5 and 8.0 µg·l⁻¹ and plotting them on a chart to show their pH and DOC conditions. This is shown in Figure 2.2. Combinations of pH and DOC that lie above the red curve would be protected by a generic PNEC of approximately 7.8 µg·l⁻¹, whereas those that lie below the red curve would not be protected if assessed against the generic PNEC.

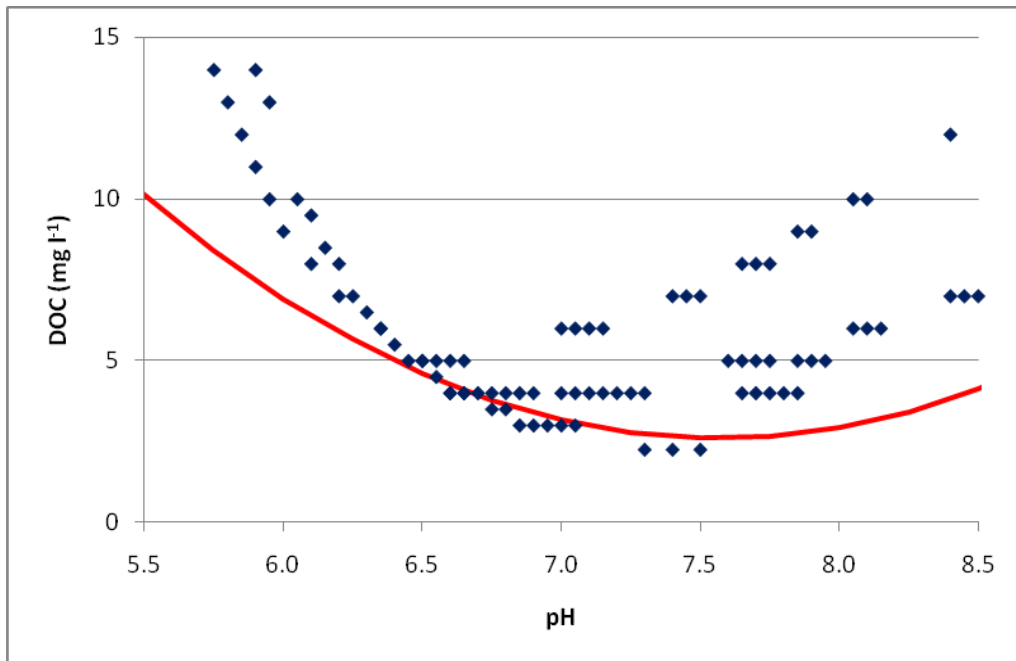


Figure 2.2 Identification of conditions where a generic predicted no-effect concentration may not be sufficiently protective (data shown are the pH and DOC combinations of Cu BLM calculations which result in a PNEC of between 7.5 and 8.0 $\mu\text{g}\cdot\text{l}^{-1}$; the red polynomial curve approximates the relationship between pH and DOC at a constant Cu PNEC of 8 $\mu\text{g}\cdot\text{l}^{-1}$)

From this plot, it would seem likely that the combination of some physico-chemical conditions encountered in UK freshwaters will result in the generic Cu PNEC given in the Cu VRAR being unprotective. Specifically, these conditions are often related to relatively low levels of DOC. Figure 2.3 shows an estimate, based on DOC and pH values for 20,943 samples from UK monitoring data, of the conditions under which the current generic PNEC may not be sufficiently protective.

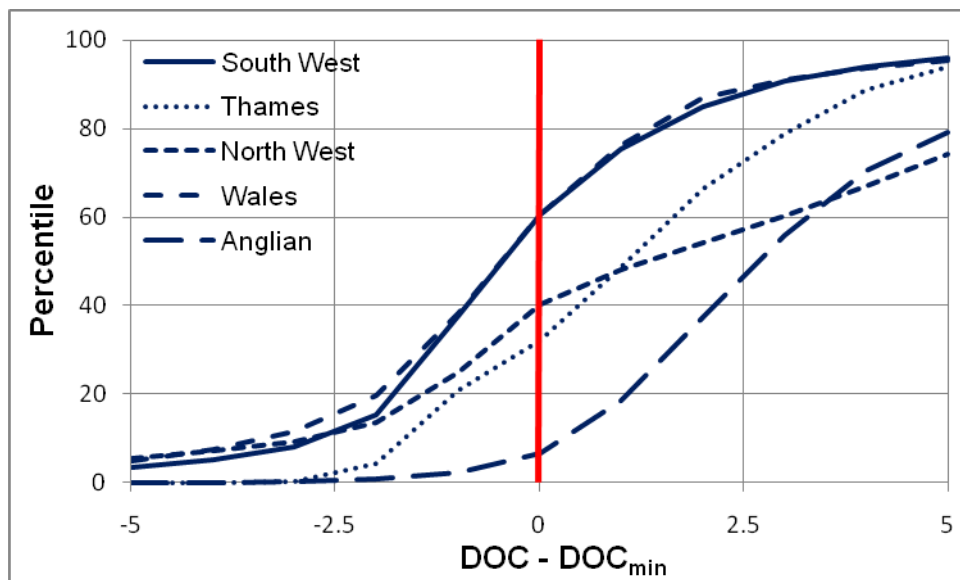


Figure 2.3 Identification of the occurrence of conditions where a generic predicted no-effect concentration of 7.8 $\mu\text{g}\cdot\text{l}^{-1}$ may not be sufficiently protective

The preliminary indications are that whilst in some regions PNEC values are typically expected to be greater than $8 \mu\text{g}\cdot\text{l}^{-1}$ (e.g. Anglian Region), in other regions conditions may be such that PNEC values would be less than $8 \mu\text{g}\cdot\text{l}^{-1}$ for a significant proportion of sites (e.g. South West and Wales Regions).

Using the full BLM, it is therefore important to carry out further work to refine the generic PNEC to be used as an initial screening EQS in the UK. The assessment above is based on individual samples only, and because the Cu PNEC is effectively expressed as an annual average concentration, future assessments should be based on annual average data. The use of individual samples is likely to include extremes of both pH and DOC which are not relevant to the average situation at the site in question.

2.2 The zinc biotic ligand model

A different approach to that used for Cu was taken to implement bioavailability corrections for Zn within the ESR risk assessment report (RAR) (RIVM 2004). This approach was to develop BLMs for chronic toxicity to representative species from three trophic levels (i.e. algae, *Daphnia*, and fish), and to use these models to determine a BioF for each species. The BioF values are calculated as the ratio between the reference PNEC for the species and the site-specific PNEC for the species, where the reference PNEC relates to conditions of high bioavailability. The highest BioF value (that relating to the smallest correction for bioavailability) is then used to correct a generic PNEC for Zn. The generic PNEC is derived from the HC_5 of an SSD, which consists of tests performed under conditions of high bioavailability, and therefore represents zinc toxicity under the most-sensitive conditions. An assessment factor of 2 was applied to the HC_5 to derive the PNEC within the RAR (RIVM 2004).

The Zn BLM makes a correction for bioavailability, but does not fully describe the effect of bioavailability on aquatic ecosystems because it does not recalculate the effects SSD following the bioavailability correction. The bioavailability correction applied (BioF_{max}) is equivalent to the response of the organism that is least affected by changes in bioavailability under the conditions in question. This results in an important methodological difference between the Cu BLM and the Zn BLM, although the implications of this on any resulting risk characterisation are unclear.

A separate PNEC was derived for very soft waters (waters with a hardness of less than $25 \text{ mg CaCO}_3\cdot\text{l}^{-1}$) in which a water effect ratio (WER) of 2.5 was applied to the generic PNEC. This was based on toxicity studies on species that are different to those for which the BLMs were developed. These species were selected for the tests because of their ability to survive and reproduce under low water hardness conditions.

Calculations in this report have been performed using the generic PNEC applied in the risk assessment, which is $7.8 \mu\text{g}\cdot\text{l}^{-1}$ dissolved Zn without a background correction.

In the validation studies for the BLM, field waters from several sites in Europe were tested and the chronic toxicity of zinc was measured in these waters with the same three organisms for which the BLMs were developed. In the test waters, the DOC concentration ranged from 4.8 to $27.4 \text{ mg}\cdot\text{l}^{-1}$, pH ranged from 5.2 to 8.4, and hardness ranged from 2.5 to $238 \text{ mg CaCO}_3\cdot\text{l}^{-1}$.

2.2.1 Initial sensitivity analysis for the zinc biotic ligand model

A different approach has been taken for the sensitivity analysis of the Zn BLM compared to that for Cu because the Zn BLM (V.4) is Excel-based and consequently more straightforward to use. Monte Carlo simulation (10,000 trials per simulation) was

used to examine the sensitivity of the model, with input parameters for pH varying between 6–9, Ca between 5–150 mg·l⁻¹, and DOC from 1.6 to 12 mg·l⁻¹. All distributions were entered as uniform distributions, so each value was equally likely to be selected during simulation. Calcium and pH were entered with an assumed correlation of 0.6.

Figure 2.4 shows that if there truly is an equal probability of surface waters with pH, DOC, and Ca values falling within the specified ranges, then about half the time the most-likely BioF_{max} (the maximum bioavailable fraction calculated by the BLM) will be around 50–55 per cent. An unexpected finding is that some combinations of parameters that are within the specified model ranges can lead to BioF_{max} values greater than 100 per cent (this turns out to be the case if DOC is very low). Such values indicate conditions under which a PNEC of less than 7.8 µg·l⁻¹ may be appropriate.

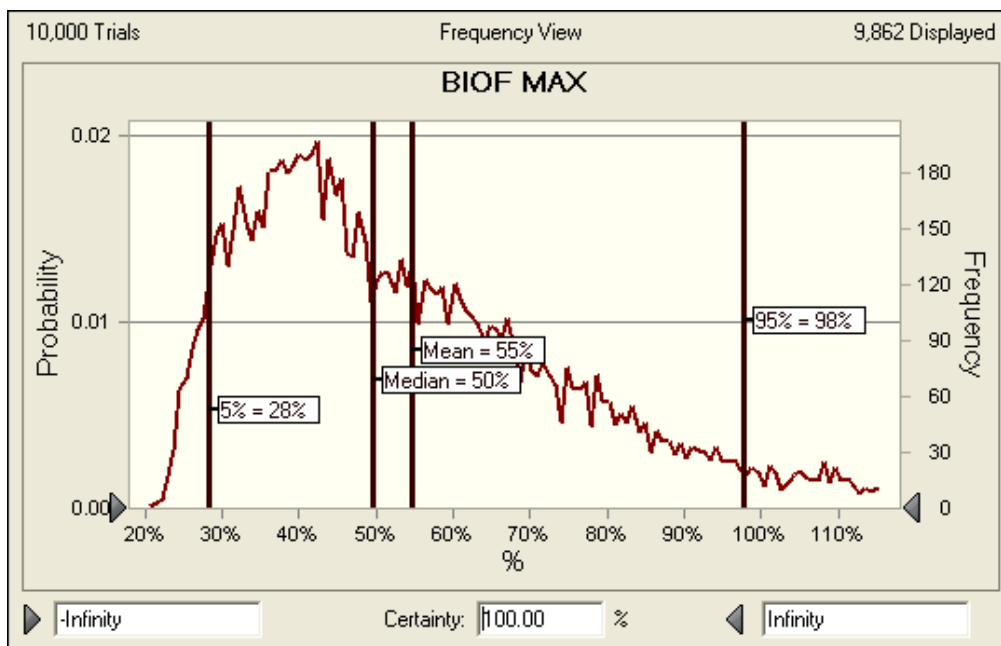


Figure 2.4 Forecast chart for BioF_{max} from the zinc biotic ligand model

The outputs from the sensitivity analysis from the Monte Carlo simulation are shown in Figure 2.5. From this, it is clear that the major contribution to model variability is due to variability in DOC (84.3 per cent), with pH (2.4 per cent) and Ca (13.4 per cent) contributing relatively little to variability in the BioF_{max}. The minus sign in front of all of these values means that the relationship is negative (i.e. higher DOC, pH, and Ca are all related to lower BioF_{max} values), and the asterisks by pH and Ca remind us that these parameters have been entered as correlated variables.

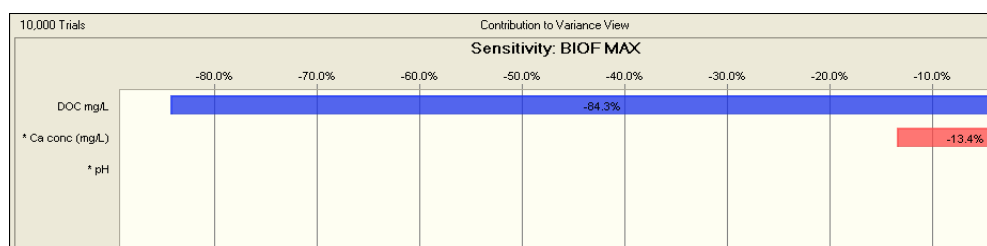


Figure 2.5 Sensitivity chart of input parameters for zinc BLM

Scenario analysis shows that values of $BioF_{max}$ between 90 and 100 per cent (i.e. where there is no basis for relaxing the Zn EQS value) occurred across the range of pH and Ca values allowed within the model, but only at DOC concentrations below $5.9 \text{ mg}\cdot\text{l}^{-1}$ (mean = 3.3, standard deviation = 1.1). This again shows that pH and Ca are not as important as DOC, at least when the parameters all vary uniformly across the range allowed by the Zn BLM. This may not be the case if the statistical distribution or correlation structure of values differs substantially in real systems.

Values of $BioF_{max}$ as high as 3.46 have been observed for some of the Zn BLM calculations performed, and $BioF$ values greater than 1 have been calculated for waters with pH values in the range 6.4–9, hardness concentrations between 15 and $239 \text{ mg CaCO}_3\cdot\text{l}^{-1}$, Ca concentrations between 5.9 and $127 \text{ mg}\cdot\text{l}^{-1}$, and DOC concentrations between 0.2 and $3.2 \text{ mg}\cdot\text{l}^{-1}$. A small proportion of these calculations apply to waters for which the soft water PNEC should be applied (10 of 175 calculations). It would appear that low DOC concentrations, low Ca (or hardness) concentrations, and high pH values can all result in $BioF_{max}$ values in excess of 1, and that combinations of high pH, low DOC, and low hardness can result in very high values of $BioF_{max}$ (Figure 2.6).

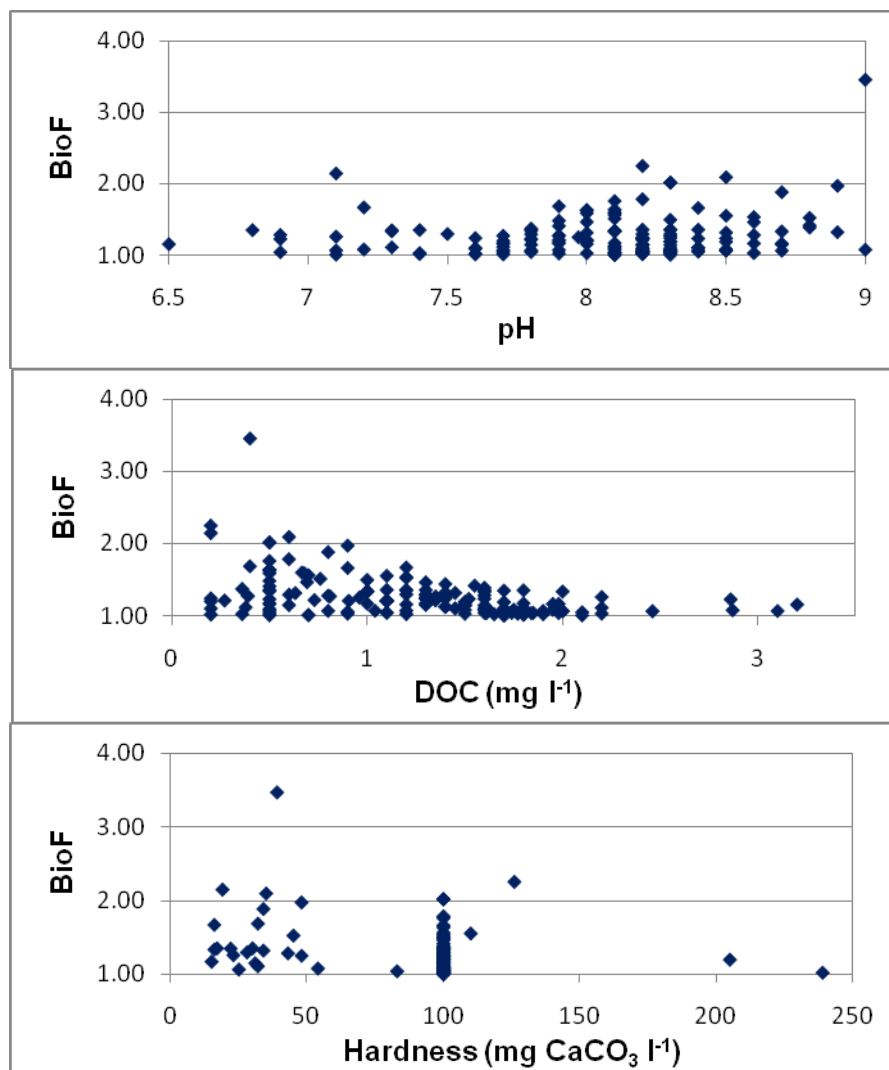


Figure 2.6 Water chemistry conditions under which $BioF_{max}$ values of greater than 1 may occur with the zinc biotic ligand model

Following this initial sensitivity analysis of both models, the next step is to assess how waters in England and Wales from the field match with the model ranges, and determine the potential risk conditions of waters in regard to maximum Cu and Zn bioavailability. There are clearly some combinations of conditions that can result in $BioF_{max}$ values that are greater than 1 being calculated by the Zn BLM. It is not clear, however, whether or not these represent errors in the predictions being made by the BLM or genuine increases in bioavailability. The Zn BLM is parameterised for DOC concentrations down to $1 \text{ mg}\cdot\text{l}^{-1}$, but makes extrapolations at lower values. The majority of instances where $BioF$ values of greater than 1 occur are at DOC concentrations of less than $1 \text{ mg}\cdot\text{l}^{-1}$. The soft water PNEC that has been derived for Zn is, however, lower than the generic PNEC, suggesting that there are conditions under which ecosystems are more sensitive to Zn.

The calculation of $BioF_{max}$ values that are greater than 1 for some combinations of water quality conditions suggests that screening sites against the generic PNEC may not necessarily be protective in all cases. However, the frequency of occurrence of these high $BioF_{max}$ values is low, so in practice they may not represent a significant issue.

2.3 Summary

The BLMs for both Cu and Zn indicate that the most-sensitive conditions for exposure to these metals occur when the DOC concentrations are low, and particularly if this occurs in combination with relatively extreme pH conditions (i.e. $\text{pH} < 6$ or > 8.5 for Cu). These extreme pH conditions are also close to the validation boundaries of the models.

The generic PNEC values provided in the ESR Cu VRAR are calculated for conditions that may be considered to be protective of 90 per cent of EU surface waters (ECI 2008). Because UK surface waters comprise water chemistry conditions that cover relatively wide ranges for all of the important BLM input parameters, it is necessary to consider the suitability of such a generic PNEC for a local compliance assessment. An initial investigation suggests that there are likely to be significant numbers of assessment samples (> 25 per cent in some regions) where the conditions are such that a generic PNEC of approximately $8 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ may not be sufficiently protective for use as a first tier screen within a tiered compliance assessment.

Because the generic PNEC for Zn was set for conditions of high bioavailability, the generic PNEC from the ESR RAR should provide an adequately protective first tier screening value.

Supporting information on the pH, DOC, and Ca conditions at compliance assessment sites will be required to assess any sites that fail the initial screening tier. Monitoring data for Na and alkalinity may also be helpful in assessing Cu bioavailability if available. The DOC concentrations are particularly important in defining the bioavailability of both Cu and Zn. As DOC is currently not routinely analysed, default values may need to be derived, where possible, to minimise any additional monitoring requirements for compliance assessment.

3 Derivation of default dissolved organic carbon concentrations for England and Wales

The water chemistry conditions under which DOC is of greatest importance in reducing Cu and Zn (bio)availability have been highlighted in the previous section. The importance of DOC in reducing Cu and Zn (bio)availability is unquestionable, yet there is little chance that routine DOC monitoring will be undertaken at all Water Framework Directive monitoring sites in the UK. This phase of the project was targeted at establishing where in England and Wales default DOC values could be used and where there was a need to undertake DOC monitoring. The specific aims were to:

- Establish a transparent and justifiable process by which default DOC values could be selected for spatially referenced points in England and Wales.
- Determine the variability of DOC in freshwaters in England and Wales, if possible.
- Develop and run a process whereby spatially referenced points that required DOC monitoring in England and Wales could be identified and then validated against field data (Section 4).

3.1 The monitoring data

The datasets used for this part of the project were obtained from the Environment Agency's National Data Unit, which searched all Environment Agency records from 1990–2007 for information on surface waterbodies for which there were DOC and matched Cu, Ni, and Zn data. The Environment Agency data cover England and Wales and are split into eight regions. These regions are historically the administrative sectors into which the Environment Agency was partitioned and have limited, if any, relevance to the spatial delineation under the Water Framework Directive. The regions have, however, relatively recently been divided into hydrometric areas through which the Water Framework Directive will be administered, although some hydrometric areas do straddle more than one region. The hydrometric area is a unit that fits on a scale between a river basin district (of which there are 11 in England and Wales) and a waterbody (of which there are many hundreds and possibly thousands). Figures 3.1 and 3.2 show the distribution of river basin districts and hydrometric areas in the UK, respectively.

There are 59 hydrometric areas in England and Wales, and data for all but one (Anglesey) have been used in this project. The size and availability of data for each hydrometric area is enormously variable, as is the number of waterbodies in each. Data were only retrieved for the largest (or most-important) waterbodies in each hydrometric area. Therefore, it is possible that some smaller waterbodies may not be represented in this dataset. No data for lakes or reservoirs have been considered in the project, primarily because of the paucity of this type of data held by the Environment Agency.

Historically, the regions of the Environment Agency have never had a strategic long-term programme for the monitoring of DOC in freshwaters. Many of the records

retrieved for each of the regions were highly variable, and both temporally and spatially stochastic, highlighting the disparate range of priorities that have historically driven the need to monitor DOC, rather than the requirements of national or international obligations.

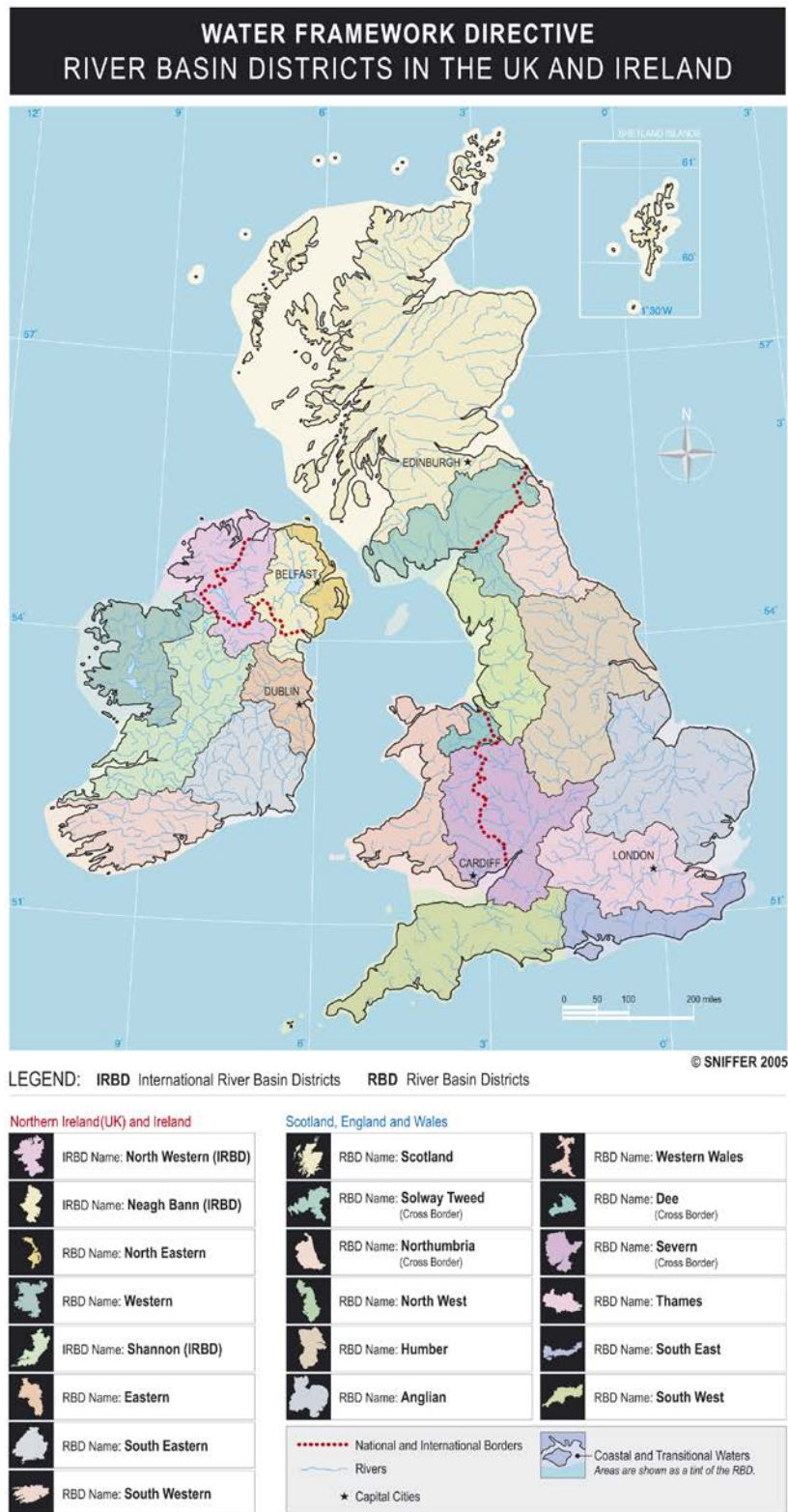


Figure 3.1 Map of the river basin districts in the UK and Ireland



Figure 3.2 Map of the hydrometric areas in the UK

3.2 The process of default dissolved organic carbon value selection

The process undertaken to select default DOC values needs to be transparent and justifiable to the project sponsors and to a wider regulator and regulated community. The underlying reason for the selection of default DOC values for use with the BLMs for the assessment of metal compliance is to reduce the need for wide-scale regular DOC monitoring in England and Wales.

The process is described below and is tiered, with effort involved in each tier increasing as the number of hydrometric areas and waterbodies decreases. Risk characterisation ratios (RCRs) are used throughout the process and are calculated by dividing a PEC (or in many cases a measured environmental concentration) by the PNEC for either Cu or Zn. The PNECs were calculated using the BLMs for Cu and Zn referred to in Section 2 of this report.

The following sections describe each of the tiers and provide examples of the outputs. The process is primarily based on pragmatism and follows general risk assessment paradigms. Although all Environment Agency regions were taken through the tiered process, only a selected few are shown here for the sake of brevity and clarity.

3.2.1 Tier 1:- The 'worst case' scenario

Initially, it was thought that it may be possible to set default DOC values relating to regions or at least hydrometric areas, i.e. across relatively large geographical scales. Therefore, it was decided to assess the potential for the use of DOC defaults under the 'worst case' bioavailability conditions against worst case metal concentrations. The 10th and 90th percentiles of those conditions were selected for each hydrometric area to assess whether the 10th percentile hydrometric area based DOC default value could provide a practical and precautionary input to the BLMs. This approach would be in line with a precautionary 'generic' screening assessment undertaken using the EU Technical Guidance Document (EC 2003). The use of the various percentiles of all of the reported data for a hydrometric area does not suffer from the problem of requiring all of the parameters to have been reported for a single sample, as some of the later tiers do, and therefore a larger proportion of the whole dataset can be used.

The worst case conditions for Cu were selected based on the knowledge gained from the sensitivity analysis undertaken in Section 2.1, in which low DOC, low pH, and low Ca gave maximum bioavailability. Other reasonable worst case inputs to the BLM were kept the same as in Section 2.1 (i.e. humic acid percentage 0.01 per cent, Mg 2.0 mg·l⁻¹, Na 5.3 mg·l⁻¹, K 1.1 mg·l⁻¹, SO₄ 6.60 mg·l⁻¹, Cl 5.6 mg·l⁻¹, S 0.01 mg·l⁻¹, and alkalinity 0.01 mg·l⁻¹), apart from temperature, which was changed to 10 °C. It is important to note that these water chemistry conditions may not necessarily occur together in the water column, but represent a potential worst case in respect of metal availability.

For Zn, there are two sets of conditions that may potentially represent the worst case depending upon the pH conditions. Therefore, both low (10th percentile) and high (90th percentile) pH conditions were selected from each hydrometric area. Once the conditions had been established for each hydrometric area, the BLMs were run with these input parameters. It is important to note that these water chemistry conditions may not necessarily occur together in the water column, but represent a potential worst case in respect of metal availability.

Examples of this process are given in Tables 3.1 and 3.2 for two hydrometric areas. There were 4,370 samples for the Thames hydrometric area and 497 samples for the

Lee hydrometric area for 2003–2007. It is clear from Table 3.2 that under the conditions used as inputs to the BLMs the hydrometric areas give an RCR of greater than 1 for both metals, indicating a potential risk.

Table 3.1 The ‘worst case’ conditions for two selected hydrometric areas in England and Wales

Hydrometric area	pH		DOC (mg·l ⁻¹)	Ca (mg·l ⁻¹)	Cu (µg·l ⁻¹)	Zn (µg·l ⁻¹)
	10th %ile	90th %ile	10th %ile	10th %ile	90th %ile	90th %ile
Thames	7.10	8.18	0.42	68.8	4.6	27.8
Lee	7.13	8.26	0.39	86.6	4.8	48.75

Table 3.2 The potential risks represented by copper and zinc in two selected hydrometric areas when ‘worst case’ conditions are chosen using a 10th percentile dissolved organic carbon default value

Hydrometric area	Cu PNEC ¹	Zn BioF ²		RCR		
	10th %ile (µg·l ⁻¹)	Low pH	High pH	Cu	Zn (at low pH)	Zn (at high pH)
Thames	1.27	0.66	1.72	3.62	2.35	6.13
Lee	1.14	0.56	1.71	4.21	3.50	10.69

Notes: ¹ Calculated using the Cu BLM.
² Calculated using the Zn BLM.

This first tier was run for all the hydrometric areas in the dataset and, as shown in the examples in Tables 3.1 and 3.2, few hydrometric areas were identified as not having potential risks (all areas were considered to be potentially at risk for Zn at high pH). This tier did not significantly reduce the number of hydrometric areas or waterbodies for which DOC monitoring is required. A re-examination of the dataset and the historical context in which much of it was collected suggested that the ‘worst case’ conditions may not have been reasonable. The reasons for this include the following:

- Reporting requirement values for Cu and Zn are often recorded in the dataset instead of measured values. For example, if a value of 4 µg·l⁻¹ is measured, but there is only a requirement under a specific directive to report values of over 5 µg·l⁻¹, a value of <5 µg·l⁻¹ will be reported. This is due to the monitoring data being collected to fulfil reporting requirements for a number of national and EU directives, not as a means to be able to assess potential metal risks using BLMs. This effectively elevates the exposure concentrations in the waterbodies.
- Pollution incident data have been included in the dataset which gives ‘one off’ relatively high metal concentrations and low pH values.
- There is a historical bias in some regions to metal monitoring at sites where there is a high likelihood that metals may be found. This effectively skews the dataset to potentially contaminated sites.

3.2.2 Tier 2: The reasonable ‘worst case’ scenario

The Tier 1 screening was not considered to provide a reliable estimate of the potential risks from Cu and Zn because of unrealistic combinations of physico-chemical water conditions. There was a need to reduce the levels of uncertainty and increase realism within the assessment, and to ensure that hydrometric areas were prioritised effectively in order to select those for which DOC monitoring was required. Therefore, 25th and

75th percentile conditions were used for the inputs into the risk characterisation calculations.

Tables 3.3 and 3.4 give examples of this approach for a number of regions, hydrometric areas, and waterbodies in England and Wales. The Midlands Region is characterised by circumneutral pH values, low to moderate DOC concentrations, and low to moderate Ca concentrations. The South West Region is characterised by low pH, low DOC concentrations, and low Ca concentrations. The North West Region is characterised by low to moderate pH, low to moderate DOC concentrations, and low to moderate Ca concentrations. The Anglian Region is characterised by high pH, high DOC concentrations, and high Ca concentrations. Therefore, these regions represent a range of bioavailability conditions that may be considered as broadly typical of UK conditions.

Table 3.3 The water chemistry conditions selected to represent reasonable ‘worst case’ conditions in selected hydrometric areas

Region	Hydrometric area	pH		DOC	Ca	Cu	Zn
		25th %ile	75th %ile	(mg·l ⁻¹) 25th %ile	(mg·l ⁻¹) 25th %ile	(µg·l ⁻¹) 75th %ile	(µg·l ⁻¹) 75th %ile
Midlands	Severn	6.8	7.6	1.7	2.87	6.90	52.8
Midlands	Trent	7.6	8.0	3.7	71.6	8.39	81.0
South West	Dart	7.13	7.8	0.78	16.4	1.6	19
South West	Tamar	6.9	7.4	1.6	7.6	–	22
North West	Lyne Esk	7.3	7.8	1.2	57.1	1.7	8.4
North West	Mersey	7.0	7.6	1.1	36.5	5.1	46.3
Anglian	Welland	8	8.4	3.8	120	3	5
Anglian	Great Ouse	7.6	8.3	3.6	117	4.5	24.8

Table 3.4 The potential risks represented by copper and zinc in selected hydrometric areas when ‘worst case’ conditions are chosen using a 25th percentile dissolved organic carbon default value¹

Region	Hydrometric area	Cu	ZnBioF		RCR		
		PNEC	Low pH	high pH	Cu	Zn (at low pH)	Zn (at high pH)
		25th %ile (µg·l ⁻¹)					
Midlands	Severn	5.67	SW	SW	1.21	SW	SW
Midlands	Trent	15.31	0.51	0.62	0.55	5.3	6.4
South West	Dart	3.18	1.33	1.20	0.50	3.2	2.9
South West	Tamar	5.68	1.46	1.35	ND	4.1	3.8
North West	Lyne Esk	4.5	0.67	0.99	0.38	0.72	1.06
North West	Mersey	3.6	0.92	0.88	1.42	5.48	5.20
Anglian	Welland	12.7	0.63	0.75	0.24	0.4	0.5
Anglian	Great Ouse	12.7	0.52	0.74	0.35	1.6	2.4

Notes: ¹ SW = soft water, the ZnBLM will not function under these conditions; ND = no dissolved Cu data.

Tier 2 of this assessment, assessing hydrometric areas for potential risks from Cu and Zn based on their 25th or 75th percentile conditions of pH, DOC, Ca, Cu, and Zn, provided a limited degree of screening by removing hydrometric areas that were not expected to be potentially at risk from the metals (e.g. some of the hydrometric areas in the Anglian Region). This screen highlights the limited suitability of using default DOC values based on data for the whole hydrometric area. It is possible that some of the waterbodies in hydrometric areas that have been screened out during this stage may still be at risk from either Cu or Zn (risks from Zn seem rather more likely than risks

from Cu), even though the hydrometric area overall is not considered to be at risk. This is one of the potential limitations of this probabilistic approach.

For Tier 3, it was necessary to refine further the spatial scales over which the assessment is based to individual waterbodies and to address whether the potential risks associated with Cu or Zn are likely to be real risks.

3.2.3 Tier 3: Actual versus predicted risks

For hydrometric areas where a potential risk was identified from Tier 2, an additional assessment needs to be undertaken. This more-detailed assessment derives a default DOC concentration for all of the waterbodies within a hydrometric area. For sites that have eight or more matched data points (i.e. data for pH, DOC, Ca, and Cu or Zn), the default DOC concentration is set as the 25th percentile of the DOC concentrations for that individual waterbody. The 25th percentile DOC concentration for the hydrometric area is applied as a default value to those sites that have reported fewer than eight data points (cf. Table 3.3).

Bioavailability conditions, bioavailable metal concentrations, and RCRs were calculated for each set of matched data (pH, DOC, Ca, and either Cu or Zn) using both the measured and the default DOC concentrations. The calculations performed using the measured data can be considered to provide a reasonable representation of the true bioavailability and risk conditions. The calculated RCR values were then compared with one another by plotting them on a graph (Figure 3.3) to identify occasions when the default DOC value was not protective.

For Zn, the Zn BLM was used for all the calculations along with the generic PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$.

For Cu, an approximate value of the PNEC was estimated using an equation with inputs for pH, DOC, and Ca which was fitted to output data from the Cu BLM (Environment Agency, 2009). The root mean squared error in the estimation was 4.63 from a training dataset of 280 Cu BLM calculations. Using this procedure increases the error in the calculations, but does allow relatively large volumes of data to be processed more quickly than performing the Cu BLM calculations. Because this is essentially a screening procedure, it is considered acceptable, although relatively few hydrometric areas were identified for further consideration after the second tier as a result of potential Cu risks.

Data points that were not protected by the bioavailability conditions arising from the default DOC concentration assigned to the waterbody are identified from the plots as those points that fall below the 1:1 line. Figure 3.3 shows example plots of the RCR values calculated based on measured DOC data against those calculated from default

DOC values for three hydrometric areas from England and Wales. Default DOC concentrations for the River Ouse appear to be less protective than those for the River Ribble; this is indicated by the greater number of data points lying below the 1:1 line with RCR values of greater than 1.

Tier 3 has identified hydrometric areas that contain waterbodies where typical DOC concentrations are lower than the hydrometric area 25th percentile, or where they are extremely variable. Data for such waterbodies fall below the 1:1 relationship line and require more-detailed consideration in the next tier. However, a number of hydrometric areas, including many from the Anglian and North East Regions are suitable candidates for the use of a default DOC value set at either the hydrometric area or local waterbody 25th percentile. The Dart hydrometric area (South West Region) is a good example of such conditions.

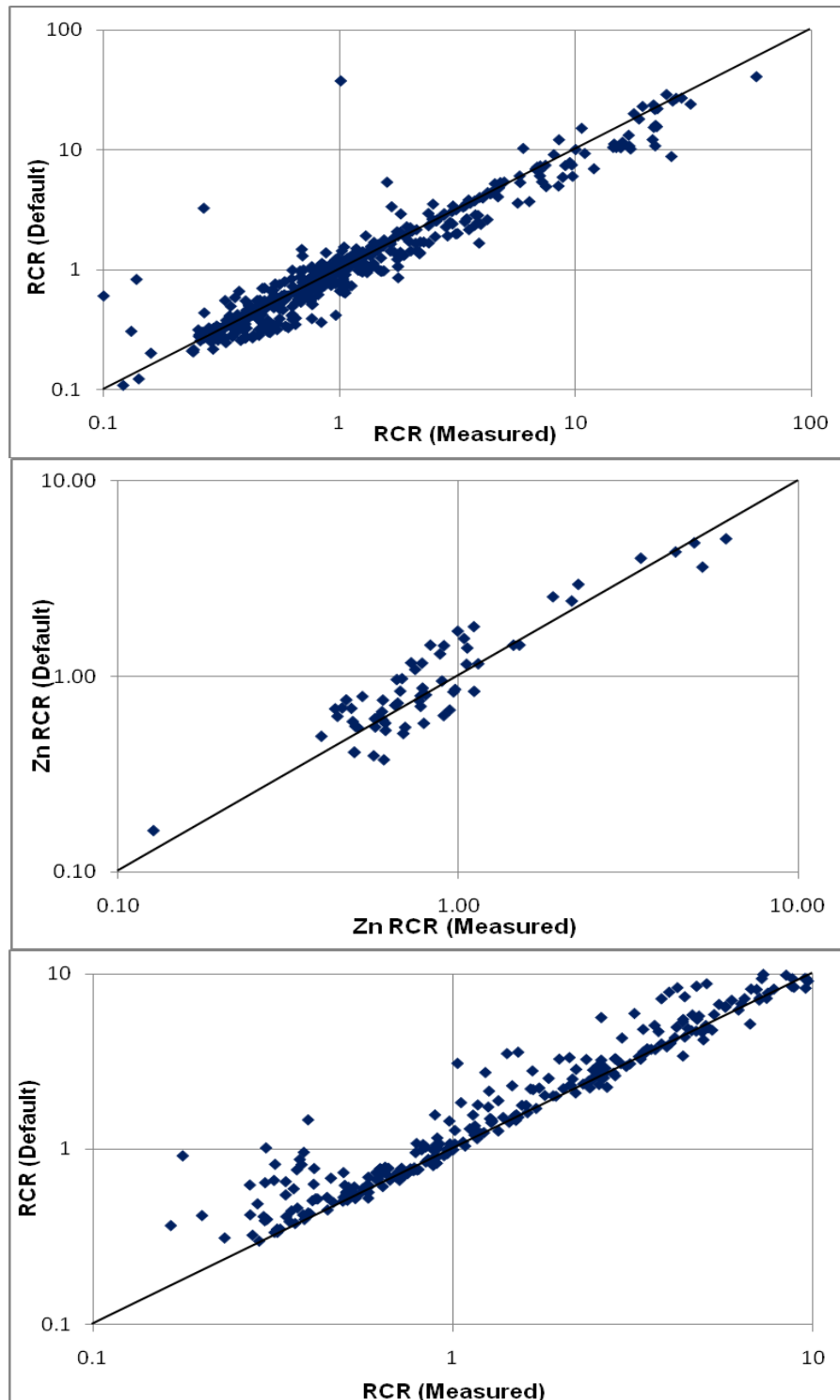


Figure 3.3 Comparison of risk characterisation ratio values for zinc calculated using measured or default dissolved organic carbon concentrations for three hydrometric areas in England and Wales (X axes show RCR values using measured data and the Y axes show those from using default DOC concentrations; the hydrometric areas are Great Ouse (top), Mersey (middle), and Ribble (bottom))

3.2.4 Tier 4: Actual versus predicted risks and bioavailability correction

The fourth tier of this process focuses on those hydrometric areas for which there were sites that fell below the 1:1 line on the plots in Tier 3. The points that represent the greatest risk, in terms of providing adequate protection through the use of default DOC concentrations, are those for which the RCR calculated from the matched DOC data is greater than 1, but the predicted value is less than 1. However, there is also an upper limit to the RCR values that can be modified by bioavailability, therefore bounding the area under the 1:1 line when prioritising potential sites for which DOC monitoring may be required. This upper limit can be crudely defined as the greatest ratio of RCR values with and without taking bioavailability (i.e. using the BLMs) into account. For example, there is likely to be an upper metal concentration (PEC) for which use of the BLMs will not give an RCR below 1. This maximum bioavailability factor for the hydrometric area was calculated as the RCR value at conditions of high bioavailability ($7.8 \mu\text{g}\cdot\text{l}^{-1}$, the generic PNEC for Zn or $8 \mu\text{g}\cdot\text{l}^{-1}$ for Cu) divided by the RCR value taking bioavailability into account (the 'true' RCR value with matched DOC data). The maximum value for this bioavailability factor for the hydrometric area represents an estimate of the maximum reduction in bioavailability that could occur in a waterbody within that hydrometric area. This can be considered as the maximum reduction possible for an RCR value, and thus is the maximum RCR value that could be reduced to 1 as a result of bioavailability correction. Figure 3.4 gives a hypothetical example of the delineation of this area.

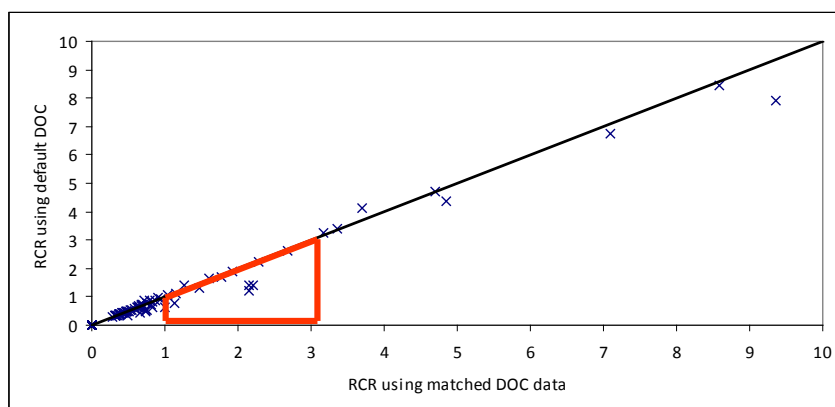


Figure 3.4 Example of the critical area of the graph for measured dissolved organic carbon concentrations, where the default dissolved organic carbon concentration is not protective and the risk characterisation ratio value is within a potentially correctable range

Those data points with positive differences between the RCR values using measured and default DOC values (matched – default) and having 'true' RCR values of between 1 and the maximum bioavailability factor for the hydrometric area were considered as candidates for further DOC monitoring. Because the default DOC concentrations are set at the 25th percentile for each waterbody (or for the hydrometric area if sufficient waterbody information is not available), all waterbodies may be expected to have some data which have positive differences between the 'true' and default RCR values, but may not fall into the delineated area. Additionally, the Environment Agency is expected to base water quality classifications upon annual average data, i.e. 12 monthly and not simply 'one off' samples. Waterbodies that only occurred once within this subset were, therefore, discarded (these are unlikely to affect compliance with an EQS). Those for which there was more than one occurrence are proposed for further consideration.

All the hydrometric areas that contained data points with positive differences between the RCR values using measured and default DOC values were run through the process

outlined above for this tier, though only a few examples are given here. For the Thames hydrometric area for Zn, the maximum factor difference between the RCR with the default PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ and the RCR with application of bioavailability correction is 4.06. Of the 1,764 data points for which both BioF_{max} and the bioavailable Zn concentration can be calculated, 398 fall in the 'underprotective' area. However, of these, 116 have bioavailability-corrected RCR values of between 1 and 4.06. These are from 44 different waterbodies, although 18 of these waterbodies only occur once within the relevant area. This leaves 26 waterbodies with potential risks because of Zn which may not be adequately protected by the use of a default DOC concentration.

A further example of this process for Zn is given for the Tamar hydrometric area in the South West Region, an area of significant historical mining activity. For this hydrometric area, the maximum factor difference between the RCR with the default PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ and the RCR with application of bioavailability correction is 5.02. Of the 1,987 data points for which both BioF_{max} and the bioavailable Zn concentration can be calculated, 421 fall in the underprotective area. Of these, 144 fall into the underprotective area with bioavailability-corrected RCR values of between 1 and 5.02. These data are from 37 different waterbodies, although 10 of these waterbodies only occur once within the relevant area. This leaves 27 waterbodies with potential risks because of Zn which may not be adequately protected by the use of a default DOC concentration.

The Great Ouse hydrometric area has a maximum factor difference of 61.0 (although the 95th percentile is 2.9) between the RCR with the default PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ and the RCR with application of bioavailability correction. In all, 242 of 505 data points for which both BioF_{max} and the bioavailable Zn concentration can be calculated fall in the underprotective area. A total of 114 of these have bioavailability-corrected RCR values of between 1 and 61.0. These data are from 36 different waterbodies, although 7 of these only occur once within the relevant area. This leaves 29 waterbodies with potential risks because of Zn which may not be adequately protected by the use of a default DOC concentration.

Finally, for the Mersey hydrometric area, the maximum factor difference is 6.97 between the RCR with a default PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ and the RCR with the application of bioavailability correction. Of the 417 data points for which both BioF_{max} and the bioavailable Zn concentration can be calculated, 116 fall in the underprotective area. Of these, 54 have bioavailability-corrected RCR values of between 1 and 6.97. These data are from 30 different waterbodies, although 13 of these waterbodies only occur once within the relevant area. This leaves 17 waterbodies with potential risks because of Zn which may not be adequately protected by the use of a default DOC concentration.

This tier has identified a list of waterbodies within each hydrometric area where the bioavailability correction is likely to be important in properly assessing risks from Cu and Zn, although these lists require further refinement for the number of sampling sites to be manageable. Furthermore, this tier has also screened out waterbodies for which bioavailability correction will likely not result in compliance with an EQS.

3.2.5 Tier 5: Final selection of monitoring sites

The fifth tier of this process finalises the list of potential waterbodies where monitoring of DOC should be undertaken by considering two questions:

- How underprotective is the highlighted default RCR prediction from those waterbodies identified in Tier 4?
- How often are unprotected data points highlighted for the waterbody, in light of the fact that compliance with an EQS is to be considered on an annual average basis (EC 2000)?

The fourth tier of data screening identified monitoring data for which the default RCR was not protective of the true conditions. Data for which the default RCR value is >95 per cent of the 'true' RCR value may be considered to be acceptable for limited numbers of individual samples.

In addition, the Environment Agency will assess compliance with EQSs as an annual average, commonly from 12 monthly samples per year. A single failing sample will not, therefore, necessarily indicate a failure for the year. Data were screened to assess whether more than 25 per cent of all calculable samples for the waterbody were identified within the fourth tier data subset.

Therefore, the first stage of this screening tier is to remove any waterbodies from the list where the default RCR values for all of the identified data are within 5 per cent of the 'true' RCR value. Since the 25th percentile of the DOC concentrations, either for the waterbody or for the hydrometric area, was used as the default value, a proportion (25 per cent) of the default data would not normally be expected to be protective of the true situation.

The second stage is to determine the frequency at which samples are identified from all of the calculable data for an individual waterbody. Cases were considered not to require further consideration when the number of identified examples (both underprotective and within the maximum bioavailability correction range) was less than 25 per cent of the total number of samples. Therefore, if there are year-on-year data (i.e. 12 monthly samples), the requirement is that if three or more of the relevant underprotective samples occur in a year, the waterbody is recommended for DOC sampling.

This procedure identifies candidate waterbodies for which there are some, but relatively few, monitoring data available (less than eight matched data points) *and* where the available DOC monitoring data suggest typical concentrations that are below the 25th percentile for the hydrometric area and where the anticipated risks from Zn fall into a potentially correctable range.

There are 123 waterbodies in the Thames hydrometric area. Of these, 26 are considered candidates for possible DOC monitoring. However, 7 of these waterbodies have predicted RCR values using the default DOC concentrations which fall within 5 per cent of the 1:1 line, and 14 represent less than 25 per cent of the samples taken for that waterbody (risks on an annual average basis are unlikely when the RCR is >1 for only 25 per cent of the time). This leaves only five waterbodies in the Thames hydrometric area as candidates for the requirement of DOC sampling (Table 3.5).

Five of the waterbodies identified in Tier 4 for the Mersey hydrometric area have all of their identified underprotective default data within 5 per cent of the true RCR values, i.e. they lie very close to the 1:1 relationship line. These five waterbodies are not, therefore, subject to further consideration. The percentage of identified relevant underprotective default data, as a proportion of the total number of matched data points, is less than 25 per cent for a further six waterbodies. Because of the low frequency of occurrence of such samples, these waterbodies were also not subject to further consideration. From a total of 54 waterbodies identified within the Mersey hydrometric area, 6 have been identified as candidates for DOC monitoring (Table 3.5).

Table 3.5 Examples of candidate waterbodies for dissolved organic carbon monitoring in the Thames and Mersey hydrometric areas

Waterbody code	Waterbody name	Hydrometric area
GB106039029860	Chess	Thames
GB106039023000	Colne Brook	Thames

Waterbody code	Waterbody name	Hydrometric area
GB106039023140	Kennet	Thames
GB106039023530	Salt Hill Stream	Thames
GB106039023760	Thames	Thames
GB112069060680	Netherley Brook	Mersey
GB112069060870	Todd Brook	Mersey
GB112069060960	Goyt	Mersey
GB112069061010	Mersey	Mersey
GB112069061050	Etherow	Mersey
GB112069064570	Eagley Brook	Mersey

The outcome of the final tier is a list of waterbodies from hydrometric areas across England and Wales for which:

- There are either few data available or the DOC concentrations can be extremely variable.
- It is likely that the RCRs lie within a range where the conclusion about EQS failure may be altered.
- It is likely that such conditions will exist for at least 25 per cent of the sampling occasions.

This process has successfully resulted in a justifiable reduction in the total number of waterbodies for which DOC monitoring would be required within England and Wales. The data given above for the Thames and Mersey hydrometric areas are shown as examples and do not represent the complete prioritisation. However, there were numerous waterbodies that were either not included in the datasets or only occurred once (in terms of matched data). Those waterbodies with only one matched data point were not considered to be sufficiently well represented to allow application of a default DOC concentration. There was also a large range of temporal variability in samples with matched data from different waterbodies (some waterbodies had multiple samples on the same day).

It has not been possible to assess DOC variability because of large intra-hydrometric area variability in many cases. The third tier screened out those hydrometric areas where the variation in DOC concentrations between different waterbodies within the hydrometric area was such that poorly represented waterbodies could be adequately protected by use of the hydrometric area 25th percentile DOC concentration. This would be the case if, for example, all of the poorly represented waterbodies (less than eight matched data points) had typical DOC concentrations in excess of the 25th percentile DOC concentration for the hydrometric area.

There were many missing data. For many of the hydrometric areas in Wales, only one or two waterbodies had any reported Ca measurements with matched data for pH, DOC, and Zn. There have also been occasions where matched data are available for all of the required parameters (i.e. pH, DOC, Ca, and Zn for the Zn BLM), but the bioavailability-corrected RCR values have not been calculable because of one or more of the input parameters being out of the validation range of the BLM. This appears to have occurred principally as a result of the measured Ca concentrations being either above or below the model's boundaries. In the Anglian Region, many waterbodies had Ca concentrations that were above the $150 \text{ mg}\cdot\text{l}^{-1}$ upper limit, whereas in the North West Region, many waterbodies had Ca concentrations that were below the $5 \text{ mg}\cdot\text{l}^{-1}$ lower limit. On a limited number of occasions, when one or more of the input parameters for the Zn BLM has been close to the validation boundaries (either low or high pH, low DOC, and low Ca) the BLM has calculated a BioF_{max} value in excess of 100 per cent. Such errors are clearly more common in waterbodies or hydrometric areas where the typical conditions are close to these limits.

The various screening stages undertaken demonstrate that if default DOC concentrations are to be applied for the compliance assessment of EQSs for Cu and Zn, they will need to be set on an individual waterbody basis. This is due to the large degree of variability that is possible between different waterbodies within a single hydrometric area, and to the fact that the variability of DOC concentrations cannot be predicted from any of the other routinely reported parameters. Annex 1 gives all of the calculable hydrometric area and waterbody default values for Ca and DOC in England and Wales.

3.3 Summary

It is clear from this assessment that it is not a practical option to undertake bioavailability-based compliance assessments on large spatial scales, such as for a whole hydrometric area, using generalised information about the key physico-chemical properties of the areas of interest. Wherever possible, default values for BLM input parameters should be derived and applied on a local scale, and we suggest that the scale of individual waterbodies is probably the most-appropriate basis for deriving default values at present.

Dissolved organic carbon concentrations can vary considerably in some waterbodies and be relatively stable in others. The variability of the DOC concentrations will not always be an issue for compliance assessment because the overall conclusion of the assessment depends not only on the DOC concentration, but also the pH and Ca conditions and the metal exposure concentration.

Where the compliance assessment is undertaken as part of a tiered assessment approach, information about DOC concentrations will only be required in cases where potential risks have already been identified for a metal in an earlier tier. In cases where metal exposure is low or close to background levels, there is unlikely to be any requirement to consider bioavailability. In cases where default DOC concentrations need to be applied, provided that they are used in a relatively precautionary way, they will highlight any need for further consideration through the identification of potential risks at assessment sites.

4 Testing the default dissolved organic carbon concentrations

Several waterbodies were identified from the previous section for which the hydrometric area and waterbody default DOC values may not be sufficiently protective when undertaking bioavailability corrections for Cu and Zn using the BLMs. It was imperative that conclusions drawn from the tiered screening of sites and selection of DOC defaults was validated through a pilot field monitoring programme. Sites were selected for this 'road testing' of the default DOC values to represent a range of DOC conditions, i.e. some which fitted with the DOC default and some which did not (a positive and a negative bias). However, it should be stressed that we were only able to assess waterbodies which already *had* DOC monitoring in freshwaters.

Collection of data started in January 2008 and continued for nine months until September 2008. In addition to DOC, a number of other relevant parameters were also included, such as pH, alkalinity, Ca, Na, and trace metals. This monitoring was undertaken to gain some insight into the variability of DOC conditions within a limited selection of waterbodies and hydrometric areas. Waterbodies from the following hydrometric areas were included in the survey: Mersey (North West), Great Ouse (Anglian), Severn (Midlands), and Dart (South West).

4.1 Dissolved organic carbon monitoring results

A summary of the DOC concentrations from the 2008 monitoring survey are shown in Table 4.1 as summary statistics for each individual site. The 25th percentiles of the monitoring data are also shown in comparison with the default values on both a waterbody and a hydrometric area basis in Table 4.2. The default values were calculated as the 25th percentiles of available historic monitoring data for the relevant waterbody or hydrometric area (see Section 3.2).

Table 4.1 Summary statistics of the 2008 dissolved organic carbon monitoring data

Region	Site (waterbody name)	25th %ile (mg·l ⁻¹)	50th %ile (mg·l ⁻¹)	Mean (mg·l ⁻¹)	Standard deviation (mg·l ⁻¹)	Geomean (mg·l ⁻¹)
Anglian	GRAFHAM WATER RESERVOIR AT VALVE TOWER	4.61	4.72	4.78	0.27	4.78
Anglian	HUNDRED FOOT RIVER EARITH RD.BR.	4.38	4.55	4.62	0.46	4.60
Anglian	MIDDLE LEVEL MD MULLICOURT PRIORY SLUICE	16.40	17.50	17.17	1.36	17.12
Anglian	R.OUSE CLAPHAM INTAKE	4.04	4.48	5.13	1.82	4.90
Anglian	R.OUSE OFFORD INTAKE	4.71	4.89	5.12	0.85	5.07
Anglian	R.OUSE WQMS FOXCOTE INTAKE	2.80	3.01	3.79	1.68	3.53
Anglian	R.WISSEY A10 RD.BR.HILGAY	3.94	4.22	4.42	0.94	4.35
Midlands	AFON BANWY AT NEW	3.96	5.75	6.93	4.12	5.95

Region	Site (waterbody name)	25th %ile (mg·l ⁻¹)	50th %ile (mg·l ⁻¹)	Mean (mg·l ⁻¹)	Standard deviation (mg·l ⁻¹)	Geomean (mg·l ⁻¹)
Midlands	BRIDGE AFON LWYD - AT STAYLITTLE ROAD	2.30	3.92	4.00	2.11	3.51
Midlands	DRAYCOTE BROOK RESERVOIR VALVE TOWER-SWAD	5.68	5.76	5.77	0.14	5.77
Midlands	SMESTOW BROOK AT PRESSWOOD	5.56	5.59	5.61	0.21	5.60
Midlands	SOWE RIVER STONELEIGH	5.43	5.64	5.64	0.48	5.62
North West	RIVER ALT ABOVE ALTMOUTH PUMPING STATION	9.40	10.14	10.96	3.24	10.57
North West	RIVER IRWELL AT FOOT BRIDGE AT SALFORD UNIVERSITY	4.63	4.86	5.53	1.31	5.40
North West	RIVER MERSEY ABOVE HOWLEY WEIR	5.42	5.79	6.08	0.81	6.03
North West	RIVER MERSEY AT FLIXTON ROAD BRIDGE	4.13	4.98	5.13	1.48	4.97
North West	ROSTHERNE MERE NEAR OUTLET	6.96	7.07	7.28	0.61	7.26
South West	HARBOURNE RIVER ABOVE HATCHLANDS FISH FARM BLUE POST TOTNES	0.78	0.79	1.66	1.52	1.28
South West	RIVER AVON AT HATCH	1.12	1.58	1.81	0.94	1.64
South West	RIVER DART AT TOTNES WEIR	1.62	2.18	2.71	2.39	2.22
South West	RIVER ERME AT SEQUER'S BRIDGE	1.52	1.76	2.00	0.87	1.86
South West	RIVER TEIGN AT RUSHFORD SAMPLING DISCONTINUED - SEE URN WSTW6046B	2.66	2.66	3.36	1.55	3.15
South West	SLAPTON STREAM ABOVE VALLEY SPRINGS TROUT FARM KINGSBRIDGE	0.86	0.93	0.93	0.20	0.92
South West	THE GARA AT TORCROSS	2.39	2.81	2.98	0.94	2.86

Table 4.2 Comparison of the 2008 dissolved organic carbon monitoring data with the default values

Region	Site	2008 25th %ile (mg·l ⁻¹)	Waterbody default 25th %ile (mg·l ⁻¹) ¹	Hydrometric area default 25th %ile (mg·l ⁻¹)
Anglian	GRAFHAM WATER RESERVOIR AT VALVE TOWER	4.61	4.8	6.0
Anglian	HUNDRED FOOT RIVER EARITH RD.BR.	4.38	5.6	6.0
Anglian	MIDDLE LEVEL MD MULLICOURT PRIORY SLUICE	16.40	11.2	6.0
Anglian	R.OUSE CLAPHAM INTAKE	4.04	NA	6.0
Anglian	R.OUSE OFFORD INTAKE	4.71	NA	6.0
Anglian	R.OUSE WQMS FOXCOTE INTAKE	2.80	NA	6.0
Anglian	R.WISSEY A10 RD.BR.HILGAY	3.94	NA	6.0
Midlands	AFON BANWY AT NEW BRIDGE	3.96	3.0	2.3
Midlands	AFON LWYD - AT STAYLITTLE ROAD	2.30	1.6	2.3
Midlands	DRAYCOTE BROOK RESERVOIR VALVE TOWER-SWAD	5.68	6.7	2.3
Midlands	SMESTOW BROOK AT PRESSWOOD	5.56	NA	2.3
Midlands	SOWE RIVER STONELEIGH	5.43	5.4	2.3
North West	RIVER ALT ABOVE ALTMOUTH PUMPING STATION	9.40	10.3	6.4
North West	RIVER IRWELL AT FOOT BRIDGE AT SALFORD UNIVERSITY	4.63	6.2	6.4
North West	RIVER MERSEY ABOVE HOWLEY WEIR	5.42	6.9	6.4
North West	RIVER MERSEY AT FLIXTON ROAD BRIDGE	4.13	5.8	6.4
North West	ROSTHERNE MERE NEAR OUTLET	6.96	7.9	6.4
South West	HARBOURNE RIVER ABOVE HATCHLANDS FISH FARM BLUE POST TOTNES	0.78	0.7	1.3
South West	RIVER AVON AT HATCH	1.12	1.2	1.3
South West	RIVER DART AT TOTNES WEIR	1.62	1.5	1.3
South West	RIVER ERME AT SEQUER'S BRIDGE	1.52	1.3	1.3
South West	RIVER TEIGN AT RUSHFORD	2.66	2.0	1.3
South West	SAMPLING DISCONTINUED - SEE URN WSTW6046B			
South West	SLAPTON STREAM ABOVE VALLEY SPRINGS TROUT FARM KINGSBRIDGE	0.86	0.9	1.3
South West	THE GARA AT TORCROSS	2.39	2.0	1.3

Notes: ¹ NA = not applicable.

4.2 Performance of waterbody-based dissolved organic carbon default values

The DOC results from the monitoring programme are shown in Figure 4.1, along with the default DOC concentrations on both a waterbody and a hydrometric area basis. In general, the waterbody-based default DOC concentrations appear to provide a reasonable estimate of the DOC concentrations that might be expected for a particular waterbody, although there are some cases where the default concentrations are towards the higher end of the range of observed DOC concentrations from the monitoring.

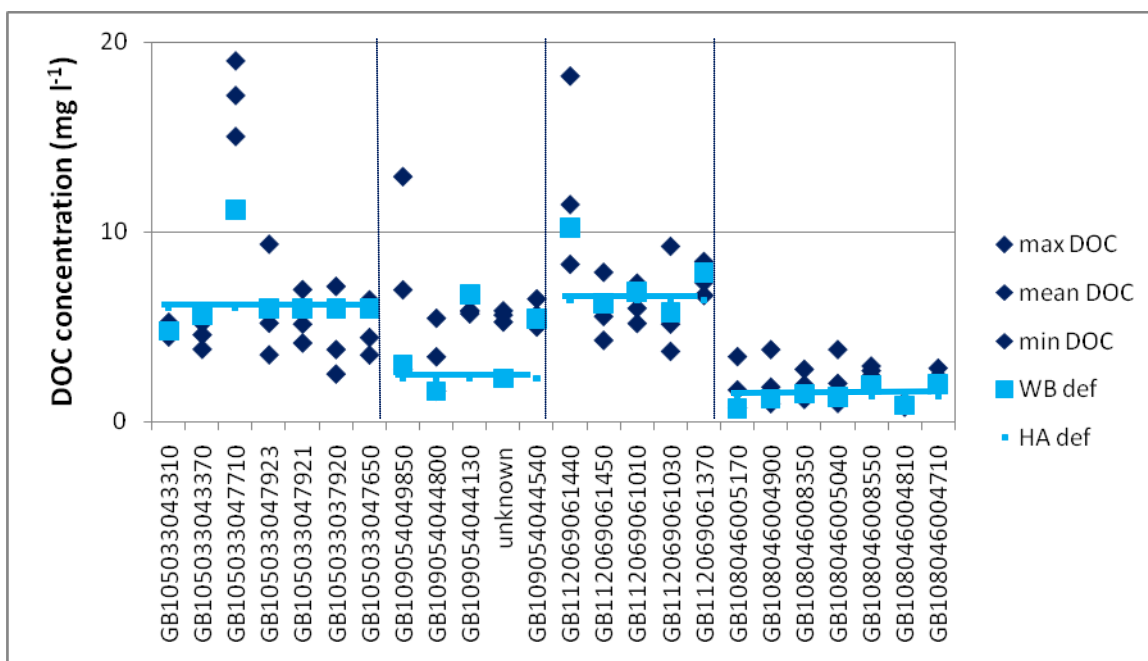


Figure 4.1 Comparison of measured and default dissolved organic carbon concentrations (dark blue diamonds indicate the minimum, mean, and maximum measured concentrations from the 2008 monitoring data, large pale blue squares indicate waterbody default concentrations, and small pale blue squares indicate hydrometric area default concentrations)

Figure 4.2 compares the concentrations from the monitoring data, expressed as either 25th percentiles or means, against the default DOC concentrations. It appears that default values derived on a hydrometric area basis are less likely to ensure protection than waterbody-specific default values, but could also result in a considerable degree of overprotection. The default DOC concentrations are rarely higher than the mean measured concentrations from the 2008 monitoring survey, and when they are the degree of underprotection appears to be very small.

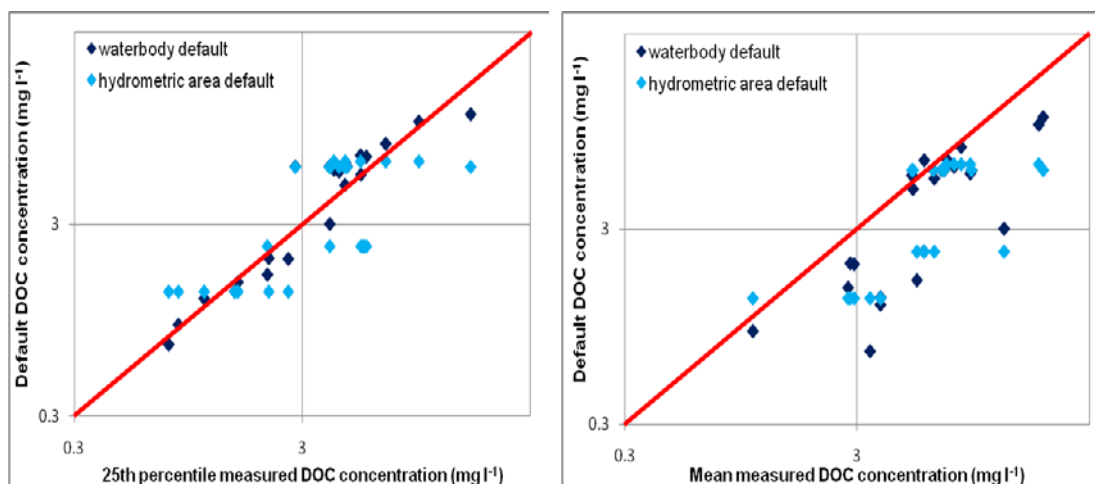


Figure 4.2 Comparison of the 25th percentiles (left) and means (right) of dissolved organic carbon concentrations from the 2008 monitoring data against waterbody and hydrometric area default values for all sites

The default DOC concentrations derived on an individual waterbody basis provide a good estimate of the DOC concentrations from monitoring in the majority of cases. In some cases, the average measured DOC concentrations are significantly higher than the default concentrations. In cases such as these, the default concentrations will provide a low estimate of the site-specific PNEC or BioF. Within a tiered compliance assessment approach, this may result in more-detailed consideration of the local conditions, including DOC concentrations, if potential risks are identified.

4.3 Performance of hydrometric area based dissolved organic carbon default values

Of the seven waterbodies sampled in the Anglian Region, there were no waterbody-specific default values available for four of the sites. In these cases, the hydrometric area default concentrations were used. One of the waterbodies sampled in the Midlands Region could not be identified by its waterbody identification code, therefore the hydrometric area defaults were also used for this site (see Table 4.2).

The hydrometric area based default values tend to perform less well than waterbody-based default values, but are still protective in the majority of situations. Hydrometric area based default DOC values were the same or lower than the corresponding waterbody-based values in 11 out of 19 waterbodies for which both types of default values were available. Individual waterbodies that are typified by low DOC concentrations always tend to perform badly when hydrometric area based defaults are applied because the default DOC concentrations (derived from the entire hydrometric area) may be appreciably higher than the actual DOC concentrations within a particular waterbody. Eight of the 24 waterbodies considered in the testing of the default DOC concentrations had waterbody-specific DOC default values that were lower than the corresponding hydrometric area based values, although half of these sites had waterbody-based DOC default values that were within 10 per cent of the hydrometric area derived ones.

An adequately protective assessment cannot be assured from the use of a hydrometric area based default value. Hydrometric area based default DOC concentrations would be applied in cases where there is little or no information available about local DOC conditions prior to undertaking an assessment. It is unlikely, therefore, that it will be

possible to identify waterbodies that might potentially be at risk when a hydrometric area based default DOC concentration must be applied.

4.4 Effect of using default values on predicted no-effect concentrations for copper and zinc

The DOC monitoring data and related default DOC values are required for the calculation of site-specific PNEC values and BioFs, using BLMs and related approaches, within a tiered compliance assessment framework (Environment Agency 2009). It is, therefore, useful to consider the influence of applying default DOC and Ca concentrations in the calculation of site-specific PNEC values and BioFs.

The PNEC values were calculated using either measured or default input data within the Zn BLM and Cu PNEC Estimator (Environment Agency 2009). The Cu PNEC values reported here will tend to underestimate the true PNEC because of the method of calculation used. Default DOC concentrations were derived as the 25th percentile of monitoring data for the waterbodies (or hydrometric areas) and default Ca concentrations were derived as the 50th percentile of monitoring data (see Section 3).

Table 4.3 shows averages of the PNEC values calculated using the 2008 monitoring data for sites with 10 or more samples analysed during the course of the monitoring programme. There were three waterbodies with the appropriate data, all in the North West Region (Mersey hydrometric area). The mean, median, and geometric mean PNEC values for both Cu and Zn were similar at all three sites. Mean PNEC values, calculated from the monitoring data, were therefore used to summarise the typical PNEC conditions for each waterbody over the monitoring period. The calculation of the PNEC is based on measured pH data in all cases.

Table 4.3 Summary statistics of the calculated predicted no-effect concentration values for copper and zinc at sites with 10 or more samples

Waterbody ID	Metal	Mean	Median	Geometric mean
GB112069061440	Cu	20.8	17.7	19.2
GB112069061440	Zn	37.9	33.9	37.3
GB112069061450	Cu	13.5	11.7	13.2
GB112069061450	Zn	21.3	20.6	21.2
GB112069061030	Cu	13.6	13.0	13.2
GB112069061030	Zn	18.9	18.0	18.7

The mean Cu PNEC values for each waterbody, calculated using the measured data, are compared with the mean PNEC values calculated based on both waterbody and hydrometric area default values (Figure 4.3). Points that lie below the red line, which represents a 1:1 relationship between the PNECs calculated using measured data and those based on default data, indicate that the default DOC concentrations are likely to be protective. In the majority of cases, the PNEC values calculated using the default values are close to those that would be calculated from measured data, although they can tend to be overprotective. In some instances, the PNECs based on default values are slightly underprotective relative to the measured data. There are no cases where the PNEC values based on default DOC concentrations are underprotective by more than a factor of 2, although there are a few occurrences (eight for Cu and three for Zn, see also Figures 4.4–4.6) where they are overprotective by more than a factor of 2.

The mean Zn PNEC values for each waterbody, calculated using the measured data, are compared with the mean PNEC values calculated using both waterbody and hydrometric area default values in Figure 4.4. The figure indicates that, in the majority of cases, the PNEC values calculated using the default values are protective, although in some instances they are slightly under-protective relative to the measured data.

Instances of overprotection are more dramatic, i.e. the difference is greater, than those of underprotection.

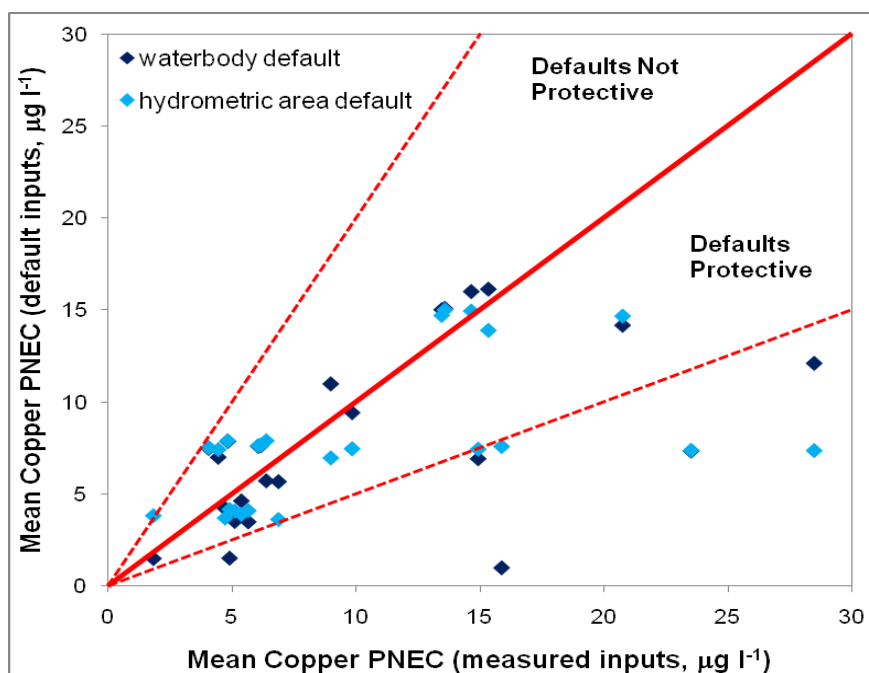


Figure 4.3 Comparison of mean copper predicted no-effect concentration values calculated using measured input data or default dissolved organic carbon and calcium concentrations (defaults have been applied on both a waterbody and a hydrometric area basis; dashed lines indicate a factor of 2 from the true result)

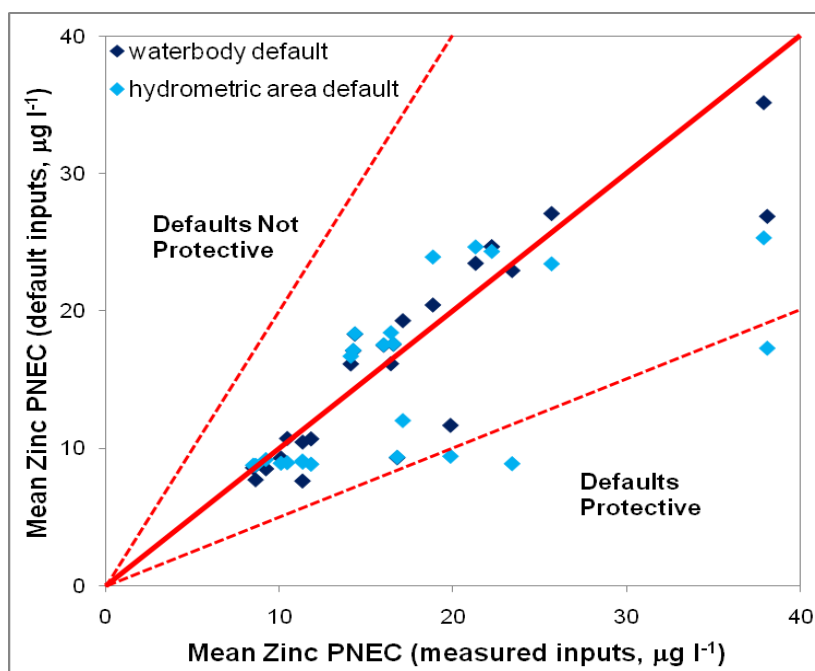


Figure 4.4 Comparison of mean zinc predicted no-effect concentration values calculated using measured input data or default dissolved organic carbon and calcium concentrations (defaults have been applied on both a waterbody and a hydrometric area basis; dashed lines indicate a factor of 2 from the true result)

An overview of the above results for each site is given in Figures 4.5 and 4.6 for copper and zinc, respectively. For both metals, each area that was studied is considered in more detail in the following sections.

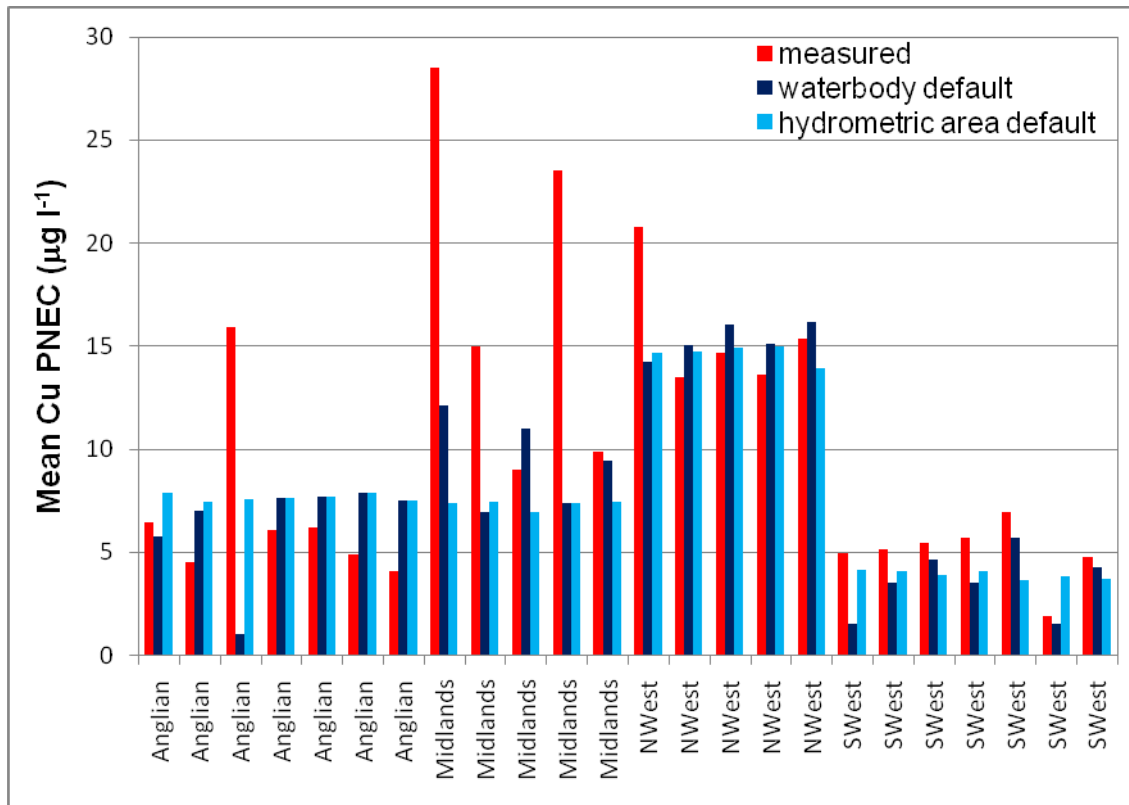


Figure 4.5 Comparison of calculated copper predicted no-effect concentration values using measured data, waterbody defaults, or hydrometric area defaults

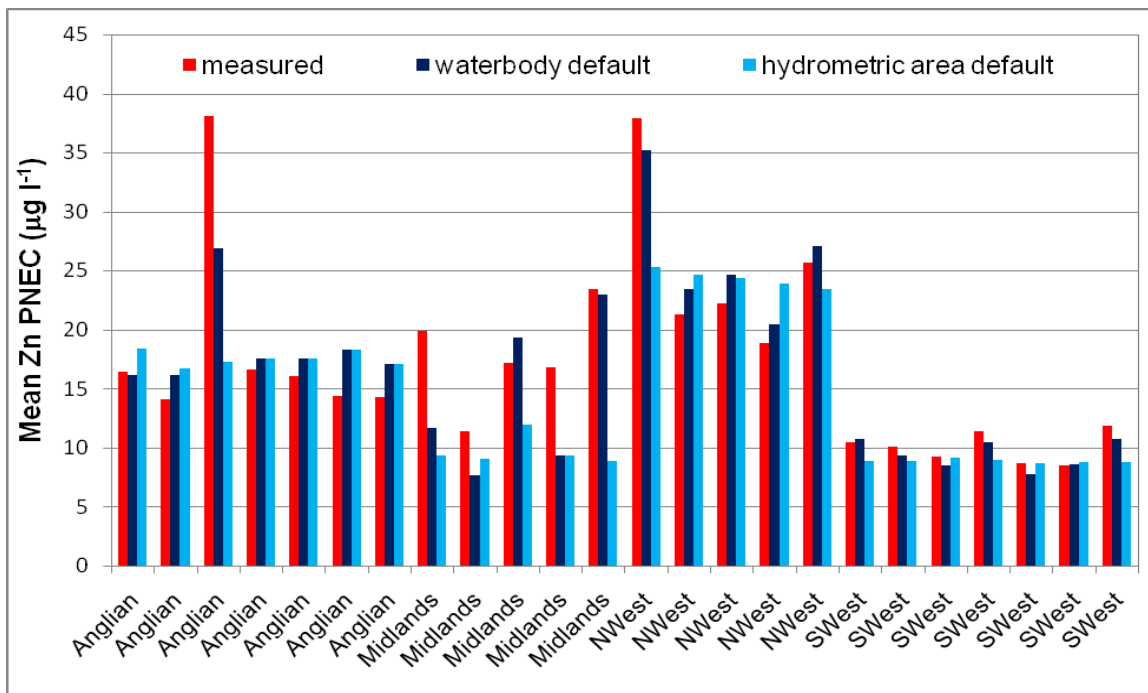


Figure 4.6 Comparison of calculated zinc predicted no-effect concentration values using measured data, waterbody defaults, or hydrometric area defaults

4.4.1 Anglian Region

Waterbody-specific default values were only available for three of the seven sites sampled in the selected hydrometric area (Great Ouse) for this region. In two of these cases, the default-derived PNEC values were similar to, or lower than, the measured PNEC values for both metals. The use of hydrometric area default DOC and Ca concentrations in the calculation of site-specific PNEC values for Cu and Zn has resulted in PNEC values that are slightly higher than those calculated on the basis of the measured data at all but one site (Figures 4.7 and 4.8). This indicates that the default values for this region may require further investigation.

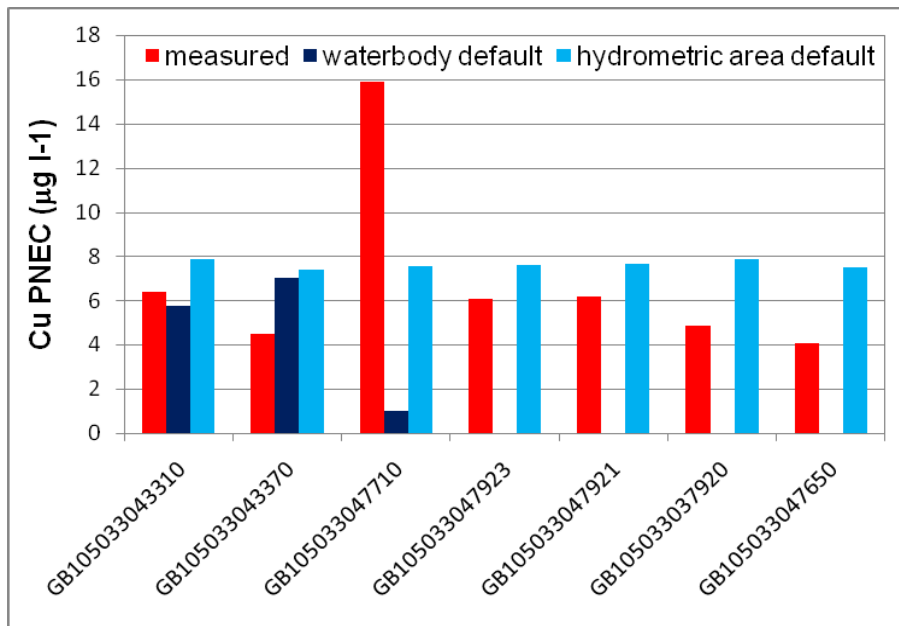


Figure 4.7 Anglian copper predicted no-effect concentrations

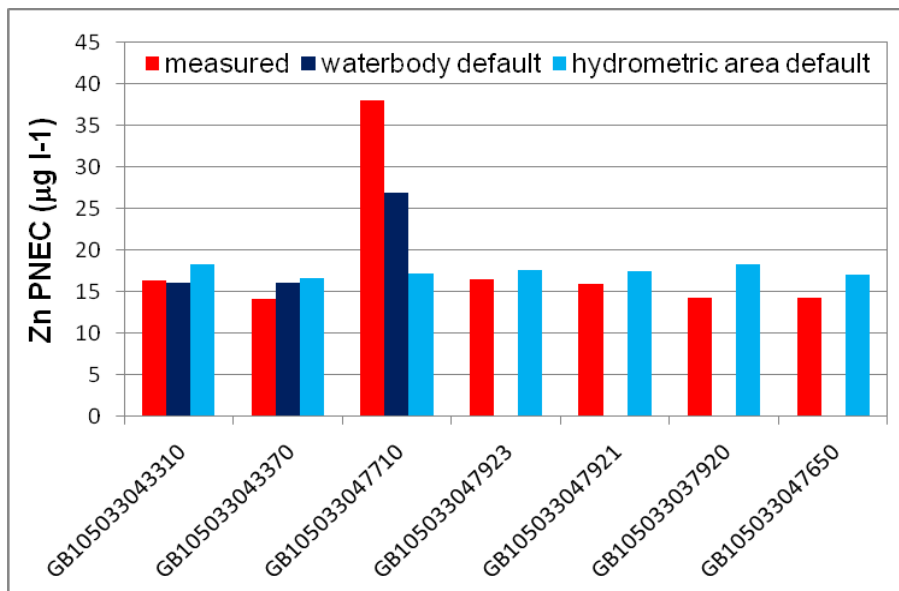


Figure 4.8 Anglian zinc predicted no-effect concentrations

4.4.2 Midlands Region

Waterbody-specific default values were available for four of the five waterbodies sampled in the selected hydrometric area (Severn) for this region. In three of these cases, the PNEC values calculated for both metals using waterbody-specific default concentrations were lower than those calculated using measured data. Often the default concentrations resulted in PNEC values that were a lot lower than those calculated using measured data. One waterbody had an average measured PNEC that was slightly lower than that calculated using the waterbody-specific default values.

The PNEC values calculated using the hydrometric area defaults were lower than those calculated using the measured data at all of the sites for both metals (Figures 4.9 and 4.10).

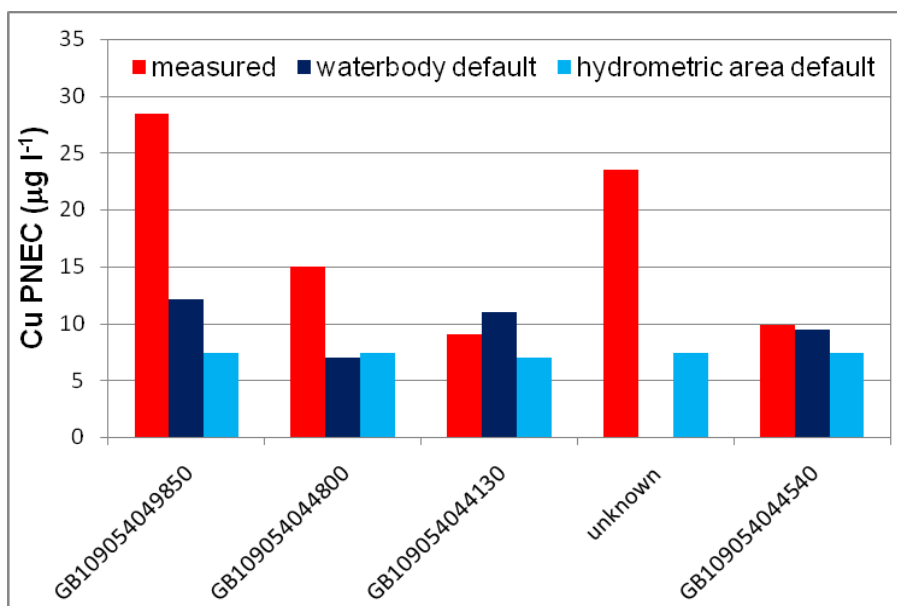


Figure 4.9 Midlands copper predicted no-effect concentrations

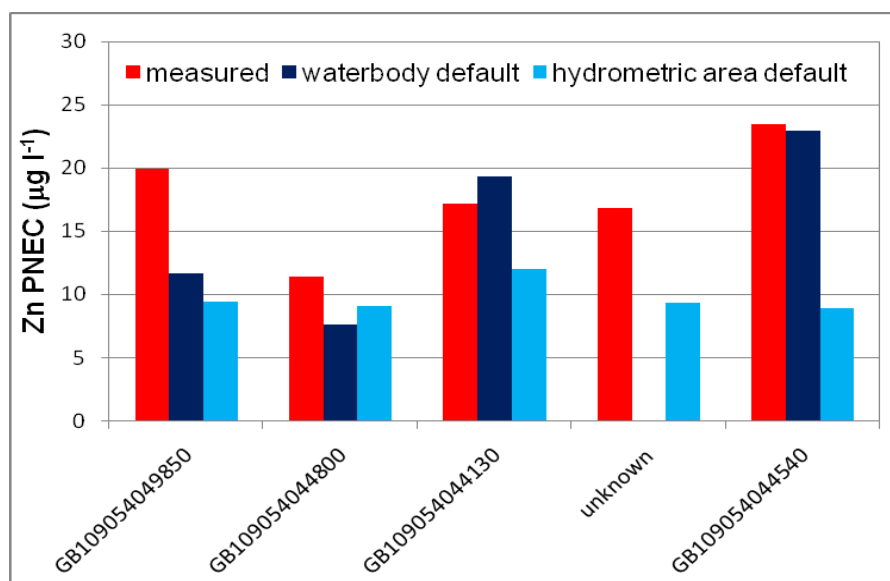


Figure 4.10 Midlands zinc predicted no-effect concentrations

4.4.3 North West Region

Waterbody-specific default values were available for all of the sites monitored in the selected hydrometric area (Mersey) for the North West Region. Average PNEC values calculated for both copper and zinc based on the waterbody-specific default values were, in four out of five cases, slightly higher than those calculated using the measured data, although the differences were relatively small. This suggests that there may be uncertainty in the waterbody-specific default values for this region. Average PNEC values calculated using hydrometric area based default values were also higher than those calculated using measured data for three of the five waterbodies (Figures 4.11 and 4.12).

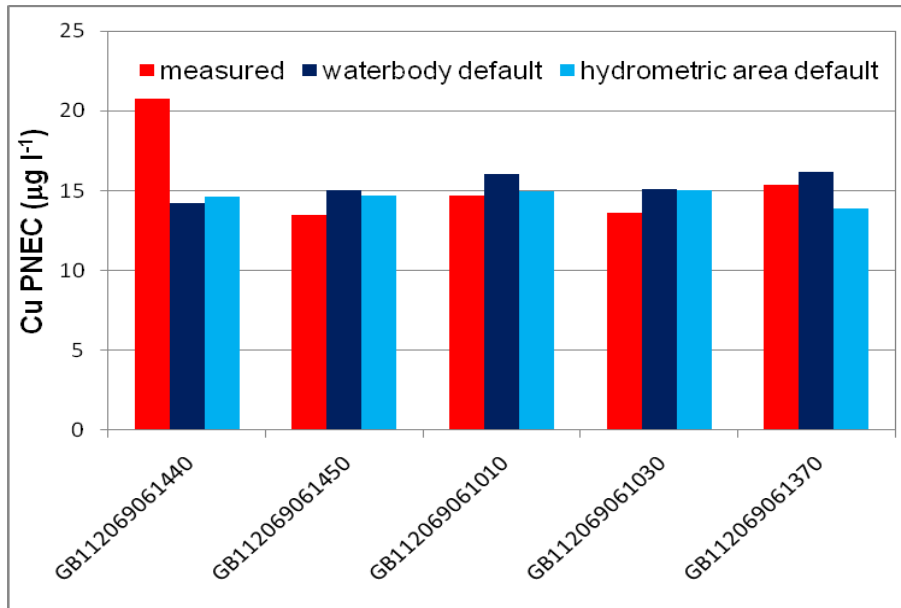


Figure 4.11 North West copper predicted no-effect concentrations

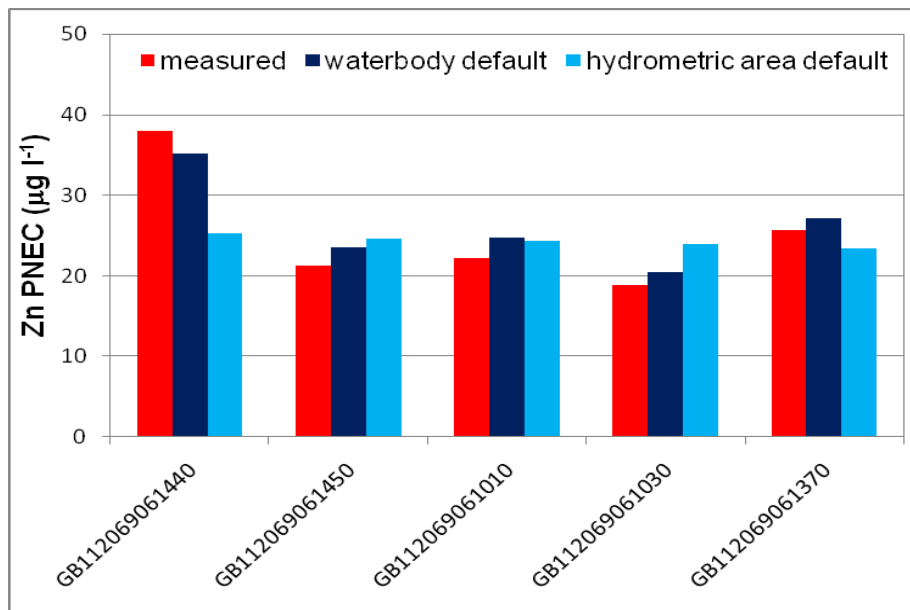


Figure 4.12 North West zinc predicted no-effect concentrations

4.4.4 South West Region

The waterbody-specific default values for the South West Region, represented by the Dart hydrometric area, performed very well. The average PNEC values calculated using the default concentrations were lower than, or similar to, those calculated using the measured data for all of the waterbodies. The hydrometric area based default values also performed well in the majority of cases, although one of the sampled sites was typified by DOC concentrations somewhat lower than the general situation for this hydrometric area. In this case, the hydrometric area default provided an average Cu PNEC approximately twice that calculated using measured data, although the difference did not have a significant effect on the corresponding Zn PNEC (Figures 4.13 and 4.14).

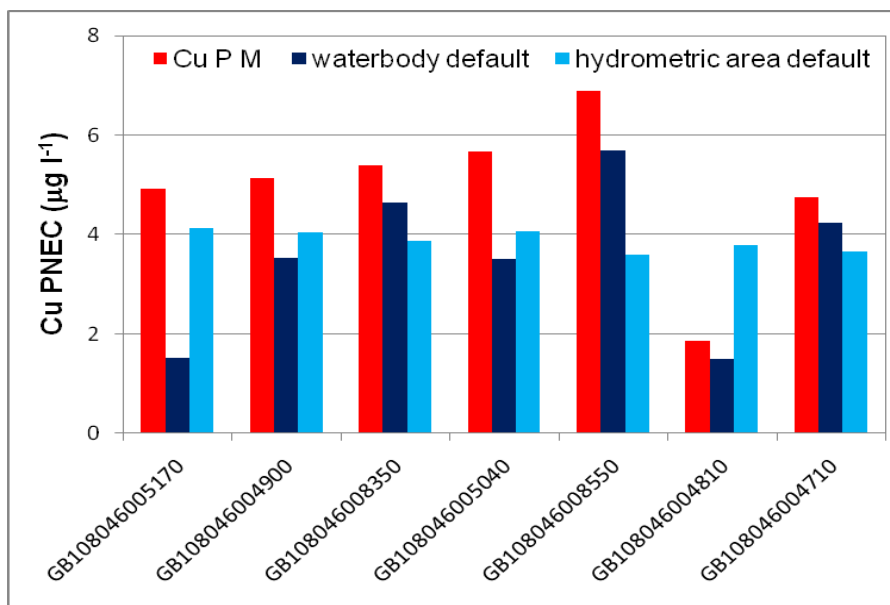


Figure 4.13 South West copper predicted no-effect concentrations

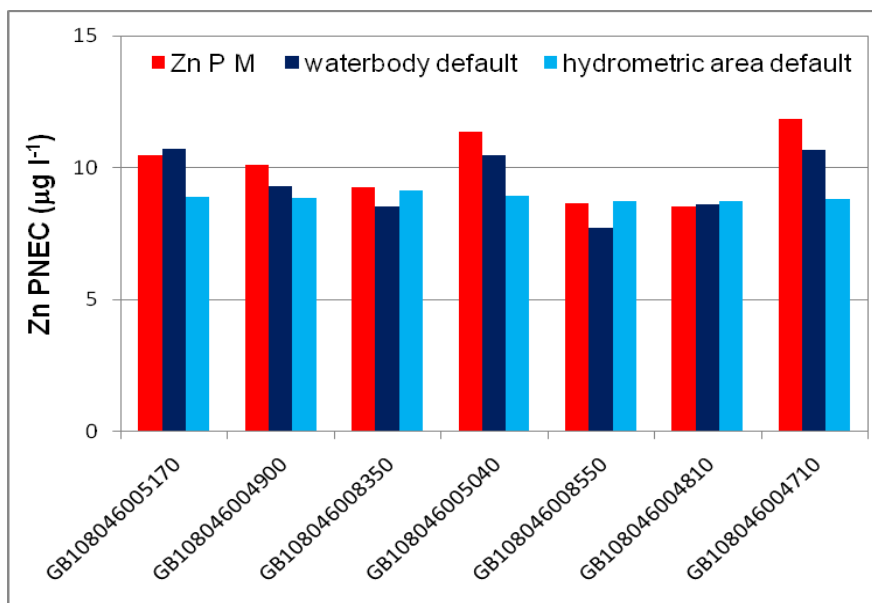


Figure 4.14 South West zinc predicted no-effect concentrations

4.5 Effect of using default values on risk characterisation ratios for copper and zinc

As noted in the previous section, the DOC monitoring data and related default DOC values are required for the calculation of site-specific PNEC values and BioFs, using BLMs and related approaches, within a tiered compliance assessment framework (Environment Agency 2009). The purpose of the compliance assessment is essentially to undertake a risk characterisation for each waterbody, or group of waterbodies, considered. It is, therefore, useful to consider the influence of applying default DOC and Ca concentrations in the calculation of RCRs, within the context of a tiered compliance assessment.

The RCR values were calculated as the measured metal concentration divided by the site-specific PNEC value. Alternatively, the BioF can be applied to the measured dissolved metal concentration to convert it into a 'bioavailable' value, which is then compared with a reference PNEC representing conditions of high bioavailability. The RCR value provides an indication of the level of risk, with values of less than 1 being considered as not at risk, and values of greater than 1 being considered as potentially at risk. Within a tiered compliance assessment framework, the identification of a potential risk may result in progression to a further tier or it may indicate a failure of the quality standard.

Table 4.4 shows averages of the RCR values calculated based on the 2008 monitoring data for those sites with 10 or more samples analysed during the course of the monitoring programme. Mean, median, and geometric mean RCR values for both Cu and Zn were similar at all three sites. Mean RCR values, calculated from the monitoring data, were therefore used to summarise the typical risk for each waterbody over the monitoring period.

Table 4.4 Summary statistics of the calculated risk characterisation ratios for copper and zinc at sites with 10 or more samples

Waterbody ID	Metal	Mean	Median	Geometric mean
GB112069061440	Cu	0.47	0.46	0.43
GB112069061440	Zn	1.24	0.97	1.04
GB112069061450	Cu	0.35	0.35	0.35
GB112069061450	Zn	0.49	0.50	0.47
GB112069061030	Cu	0.26	0.26	0.26
GB112069061030	Zn	0.68	0.63	0.63

The mean RCRs for all sites from the 2008 monitoring programme are shown in Figures 4.15 and 4.16 for Cu and Zn, respectively. The figures show how the RCR values calculated using measured data compare with those calculated using both the waterbody-specific and hydrometric area based default values. Data points that lie above the red line indicate that the default concentrations result in RCR values that are greater than those resulting from measured data.

Whilst the RCR values calculated from waterbody-specific defaults tend to lie close to the 1:1 line, the hydrometric area based RCR values tend to be more variable for both Cu and Zn.

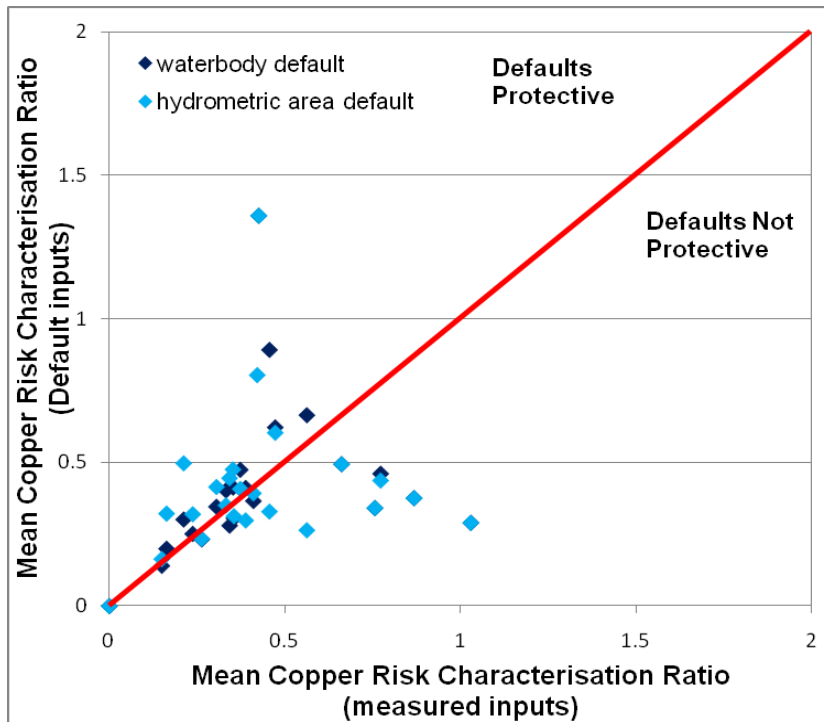


Figure 4.15 Comparison of mean copper risk characterisation ratio values calculated using measured input data or default dissolved organic carbon and calcium concentrations (defaults have been applied on both a waterbody and a hydrometric area basis)

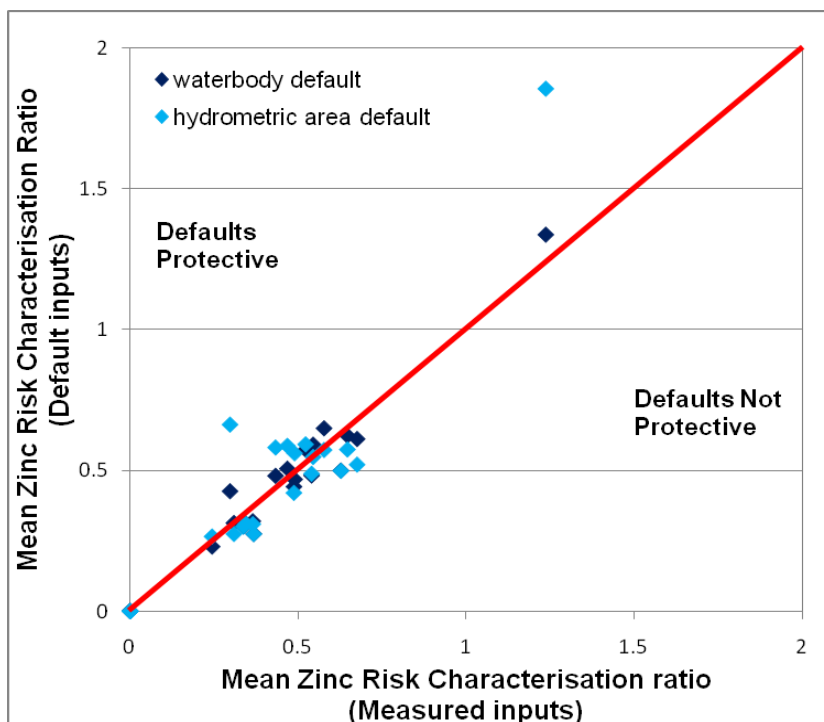


Figure 4.16 Comparison of mean zinc risk characterisation ratio values calculated using measured input data or default dissolved organic carbon and calcium concentrations (defaults have been applied on both a waterbody and a hydrometric area basis)

For Cu, there were three waterbodies included in the 2008 monitoring programme where the use of default values (either waterbody specific or hydrometric area based) resulted in a different conclusion to that which would have been drawn from the use of measured data (i.e. risk indicated on the basis of one set of data, but not on the basis of the other) (Figure 4.17). In two of these cases, the use of default values indicated a potential risk where the measured data did not, and in one case the measured data indicated a potential risk, but the default data did not. Assessments using waterbody-based default values were overprotective by more than a factor of 2 for two sites, and underprotective by more than a factor of 2 for three sites. Assessments using hydrometric area based default values were overprotective by more than a factor of 2 for two sites, and underprotective by more than a factor of 2 for two sites.

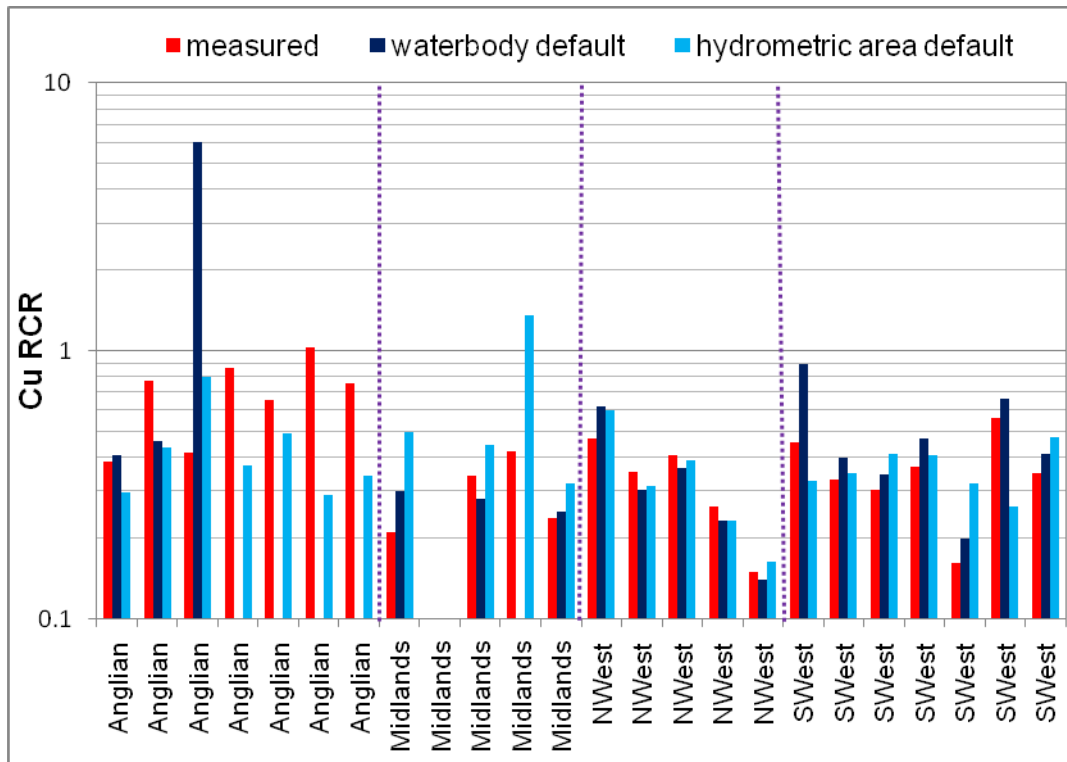


Figure 4.17 Comparison of mean copper risk characterisation ratio values calculated using measured input data or default dissolved organic carbon and calcium concentrations (defaults have been applied on both a waterbody and a hydrometric area basis)

In the case of Zn, there were no instances where the monitoring data resulted in a conclusion that differed from that which would have been drawn using the default values applied on either a waterbody-specific or a hydrometric area basis (Figure 4.18). Assessments using hydrometric area based default values were overprotective by more than a factor of 2 for a single site, and were not underprotective by more than a factor of 2 for any sites.

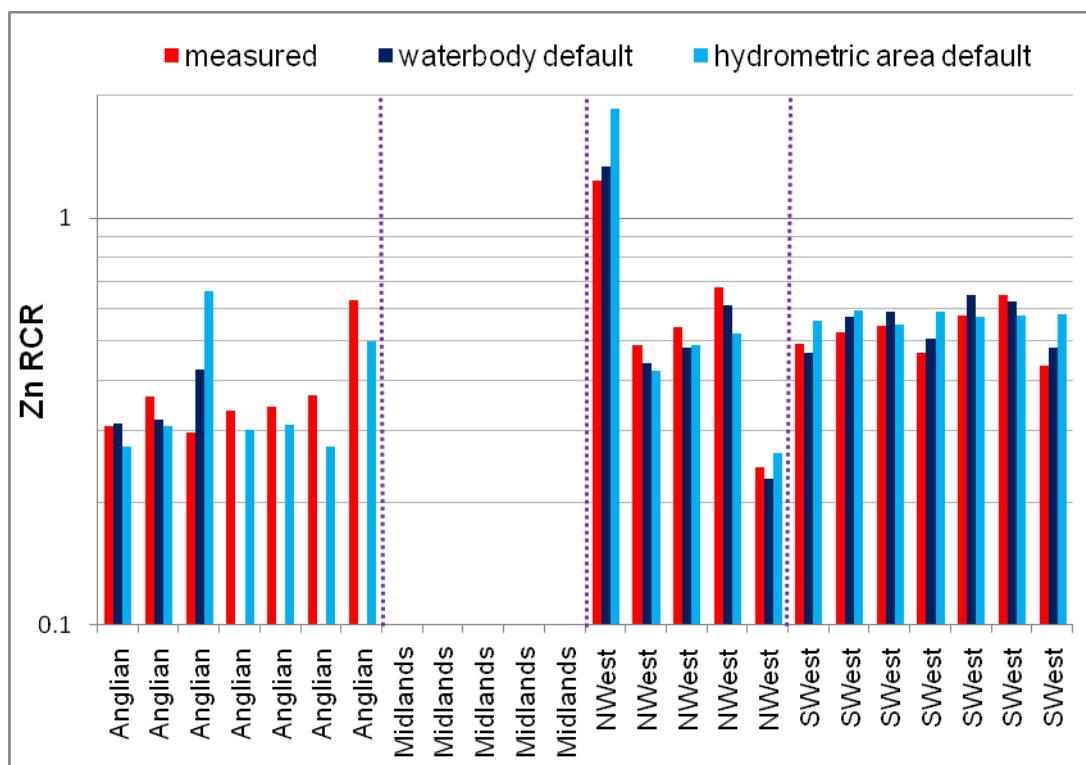


Figure 4.18 Comparison of mean zinc risk characterisation ratio values calculated using measured input data or default dissolved organic carbon and calcium concentrations (defaults have been applied on both a waterbody and a hydrometric area basis)

The alternative to using either default DOC concentrations or including routine DOC monitoring at a large number of compliance assessment sites is to undertake the compliance assessment against a generic PNEC. For Cu, a reasonable worst case PNEC for UK conditions of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ has been proposed (ECI 2008) based on data for the River Otter. A generic PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ has also been proposed for Zn (RIVM 2004). The 2008 monitoring data was screened against the two generic PNEC values, and the RCRs were compared with those obtained using the BLM-based approaches.

For Zn, data which failed the generic PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ showed RCRs of between 0.2 and 3.8 when assessed using the BLM. Data that failed the BLM-based site-specific PNEC values all had generic RCRs of greater than 1. In the case of Cu, data that failed the generic PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ all had site-specific RCRs of less than 1, when calculated using the Cu PNEC Estimator (Environment Agency 2009). All of the sites for which the site-specific bioavailability-based RCR was above 1 (i.e., risk indicated), using the Cu PNEC Estimator, had RCRs based on the generic PNEC of less than 1 (i.e. risk not indicated). All of these sites, however, had RCR values of less than 1 when calculated using the Cu BLM (i.e. risk not indicated).

To more accurately assess the validity of the generic PNEC for Cu, the data from the field sampling programme was used to calculate Cu PNEC values using the Cu BLM. The RCR values calculated using both the Cu PNEC Estimator and the Cu BLM were compared with RCR values calculated using the generic PNEC value for Cu ($7.8 \mu\text{g}\cdot\text{l}^{-1}$). These data are shown in Figure 4.19 as the ratio of the bioavailability-corrected PNEC to the generic PNEC for both the Cu PNEC Estimator and the Cu BLM. Values of greater than 1 indicate that the generic PNEC is not sufficiently protective under the local conditions, and values less than 1 indicate that the generic PNEC is adequately protective for such conditions. This analysis suggests that for 40 per cent of the sites included in the field monitoring programme, the generic PNEC for Cu is not sufficiently

protective for the local conditions when the Cu BLM is used. The Cu PNEC Estimator indicates that approximately 50 per cent of sites may not be protected, although this model is known to provide conservative estimates of Cu toxicity (Environment Agency 2009).

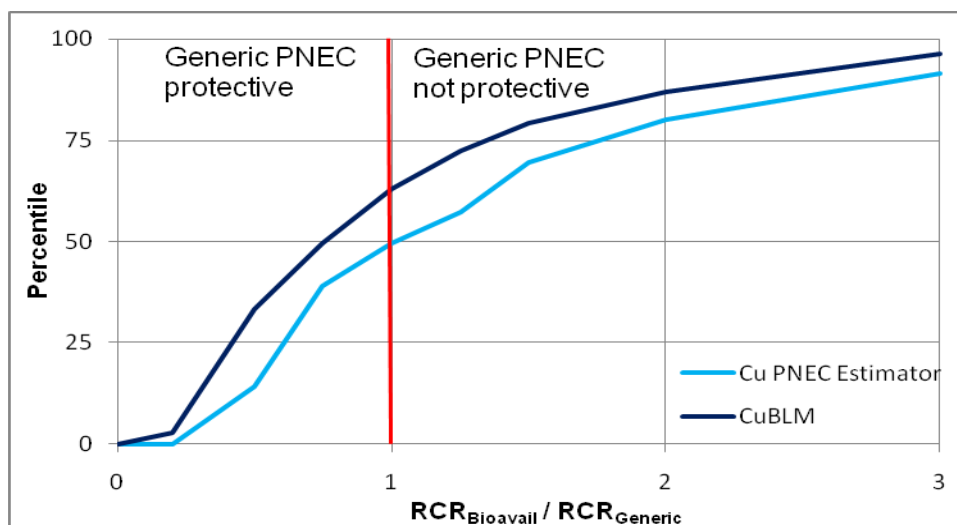


Figure 4.19 Ratio of bioavailability-corrected risk characterisation ratio values to generic ones using both the copper BLM and the copper PNEC Estimator

4.5.1 Summary of findings

Average Cu PNEC values of less than $8 \mu\text{g}\cdot\text{l}^{-1}$ were common in the South West and Anglian Regions, but less so in the North West and Midlands Regions. This suggests that applying the generic Cu PNEC of $7.8 \mu\text{g}\cdot\text{l}^{-1}$ from the Cu VRAR (ECI 2008) may not provide a sufficiently conservative screen as a first tier within a tiered compliance assessment.

The reliability of the waterbody-specific default values appears to depend largely upon the quantity of data available from which the default values can be derived. Waterbody-specific default values for the South West Region performed very well, but those from other regions, which tended to have less data available, performed rather less well.

The default DOC concentrations derived on an individual waterbody basis provide a good estimate of the DOC concentrations from monitoring in the majority of cases. In some cases, the average measured DOC concentrations are significantly higher than the default concentrations. In such cases, the default concentrations will provide a low estimate of the site-specific PNEC or BioF. Within a tiered compliance assessment approach this may result in more-detailed consideration of the local conditions, including DOC concentrations, if potential risks are identified.

The hydrometric area based default values tend to perform less well than waterbody-based default values, but are still protective in the majority of situations. Individual waterbodies that are typified by low DOC concentrations always tend to perform badly when hydrometric area based defaults are applied because the default DOC concentrations may be appreciably higher than the actual DOC concentrations. In cases such as these, an adequately protective assessment cannot be assured from the use of a hydrometric area based default value. Hydrometric area based default DOC concentrations would be applied in any cases where there is little or no information available about local DOC concentrations prior to undertaking an assessment. It is unlikely, therefore, that it will be possible to identify waterbodies that might potentially be at risk when a hydrometric area based default DOC concentration must be applied.

5 Conclusions and recommendations

5.1 Conclusions

The BLMs for both Cu and Zn indicate that the most-sensitive conditions for exposure to these metals occur when the DOC concentrations are low, and particularly if this occurs in combination with relatively extreme pH conditions (i.e. pH <6 or >8.5 for Cu). These extreme pH conditions are also close to the validation boundaries of the models.

The results of this analysis will, in general, be applicable to other metals with bioavailabilities that are influenced by DOC, e.g. Ni.

The generic PNEC values provided in the ESR Cu VRAR (ECI 2008) are calculated for conditions which may be considered representative of several different areas or regions within Europe for the purpose of a generic risk assessment. Because UK surface waters include water chemistry conditions that cover relatively wide ranges for all of the important BLM input parameters, it is necessary to consider the suitability of such a generic PNEC for a local compliance assessment. An initial assessment suggests that there are likely to be some assessment samples where the conditions are such that a generic PNEC of approximately $8 \mu\text{g}\cdot\text{l}^{-1}$ may not be sufficiently protective for use as a first tier screen within a tiered compliance assessment. A more comprehensive assessment, based on annual average data is considered to be appropriate to address this issue more thoroughly.

We therefore propose that the initial tier of assessment is undertaken against a PNEC value which can be considered as sufficiently protective, even under conditions of very high bioavailability. If such an approach is taken, then the need for DOC monitoring data (and other supporting parameters) will be deferred to the next tier of the assessment process. Applying the generic PNEC at this tier does not remove the requirement for DOC monitoring data, but introduces an additional tier of assessment at the beginning of the process where DOC information is needed.

Because the generic PNEC for Zn was set for conditions of high bioavailability, the generic PNEC from the ESR RAR should provide an adequately protective first tier screening value, provided that sites for which the soft water PNEC should be applied are considered separately.

Supporting information on the pH, DOC and Ca conditions at compliance assessment sites will be required to assess any sites which fail the initial screening tier. The DOC concentrations are particularly important in defining the bioavailability of both Cu and Zn. As DOC is currently not a routinely analysed parameter, default values may need to be derived where possible to minimise any additional monitoring requirements for compliance assessment. Default values for Ca input concentrations for BLM calculations have also been established. Default values could probably also be established for pH, with a limited further reduction in the reliability of the calculated PNEC values if DOC input values are already based on default values.

DOC concentrations can vary considerably in some waterbodies and be relatively stable in others. The variability of the DOC concentrations will not always be an issue for compliance assessment because the overall conclusion of the assessment depends not only on the DOC concentration, but also the pH and Ca conditions and the metal exposure concentration.

An alternative approach for assessing metal bioavailability when there is a lack of data for supporting parameters has been proposed by Van Genderen and Klaine (2008). Their approach uses information about watercourses to derive models which are able to predict acute Cu toxicity. The models are fitted to toxicity test data collected for the river basins included in the study. This approach does, however, require that some toxicity testing is undertaken, and to validate such an approach for chronic toxicity, a considerable amount of testing would be required. The models developed include properties such as stream order and downstream distance from urbanisation to predict potential copper LC₅₀ values for fathead minnows. A further limitation of this approach is that it is of most relevance to the species used for the testing, and may be of less relevance to locally sensitive species.

Where the compliance assessment is undertaken as part of a tiered assessment approach, information about DOC concentrations will only be required in cases where potential risks have already been identified for a metal in an earlier tier. In cases where metal exposure is low or close to background levels, there is unlikely to be any requirement to consider bioavailability. In cases where default DOC concentrations need to be applied then, provided they are used in a relatively precautionary way, they will highlight the need for further consideration through the identification of potential risks at assessment sites.

The findings of this study suggest that it is not practical to undertake bioavailability-based compliance assessments on large spatial scales, such as for a whole hydrometric area, using generalised information about the key physico-chemical properties of the areas of interest. Wherever possible, default values for BLM input parameters should be derived and applied on a local scale, and we suggest that the scale of individual waterbodies is probably the most-appropriate basis for deriving default values at present.

The default DOC concentrations derived on an individual waterbody basis provide a good estimate of the DOC concentrations from monitoring in the majority of cases. In some cases the average measured DOC concentrations are significantly higher than the default concentrations. In cases such as these, the default concentrations will provide a low estimate of the site-specific PNEC or BioF. Within a tiered compliance assessment approach this may result in more detailed consideration of the local conditions, including DOC concentrations, if potential risks are identified.

The hydrometric area based default values tend to perform less well than waterbody-based default values, but are still protective in the majority of situations. Individual waterbodies that are typified by low DOC concentrations always tend to perform badly when hydrometric area based defaults are applied because the hydrometric area default DOC concentrations may be appreciably higher than the actual DOC concentrations in the waterbody. In cases such as these, an adequately protective assessment cannot be assured from the use of a hydrometric area based default value. Hydrometric area based default DOC concentrations would be applied in any cases where there is little or no information available about local DOC concentrations prior to undertaking an assessment. It is unlikely, therefore, that it will be possible, at present, to identify waterbodies that might potentially be at risk when a hydrometric area based default DOC concentration must be applied.

5.2 Recommendations

Default values for BLM input parameters can be derived on a waterbody-specific basis for both DOC and Ca. Default values should preferably be applied on a waterbody-specific basis.

Where waterbody-specific information is not available then hydrometric area based defaults may be suitable for use in BLM calculations, although they may not necessarily be sufficiently conservative to ensure protection in all cases.

The database of default values for DOC and Ca should be updated periodically so that additional monitoring data that are collected can also be included in the derivation of default parameters, and waterbody coverage increased. This is likely to provide additional information for those sites where the greatest potential risks are identified.

Further consideration of a generic PNEC for Cu may be required to ensure that sites which are sensitive to Cu can be adequately identified at the first tier of a tiered assessment. This should be based on average conditions at individual compliance assessment sites, rather than on the basis of individual samples, because the Cu PNEC is expressed as an annual average concentration.

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List of abbreviations

BLM	biotic ligand model
BioF	bioavailability factor
BioF _{max}	maximum bioavailability factor
Ca	calcium
CaCO ₃	calcium carbonate
Cl	chloride
Cu	copper
DOC	dissolved organic carbon
EC	European Commission
ECI	European Copper Institute
EPA	Environmental Protection Agency
EQS	environmental quality standard
ESR	Existing Substances Regulations
HA	hydrometric area
HC ₅	hazardous concentration for 5 per cent of the ecosystem
ICMM	International Council on Mining and Metals
K	potassium
Me ⁺	free metal ion
Mg	magnesium
Na	sodium
Ni	nickel
OH ⁻	hydroxide
PEC	predicted environmental concentration
PNEC	predicted no-effect concentration
POC	particulate organic carbon
RAR	risk assessment report
RCR	risk characterisation ratio
RIVM	Dutch National Institute for Public Health and the Environment
S	sulphide
SO ₄	sulphate
SSD	species sensitivity distribution
VRAR	voluntary risk assessment report

WB	waterbody
WER	water effect ratio
Zn	zinc

Annex 1 Database of default biotic ligand model input parameters for England and Wales

Table A.1 Default biotic ligand model input parameters for England and Wales

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
Southern					
Southern	Arun, Ouse Cuckmere	Hydrometric Default	3.89	39	HA
Southern	Arun, Ouse Cuckmere	GB107041012330	4.56	38.85	WB
Southern	Arun, Ouse Cuckmere	GB107041012460	3.3	30	WB
Southern	Arun, Ouse Cuckmere	GB107041012640	3.89	39	HA
Southern	Arun, Ouse Cuckmere	GB107041012710	3.89	39	HA
Southern	Arun, Ouse Cuckmere	GB107041012730	4.11	38	WB
Southern	Arun, Ouse Cuckmere	GB107041012880	4.47	110.5	WB
Southern	Arun, Ouse Cuckmere	GB107041017950	5.53	44	WB
Southern	Arun, Ouse Cuckmere	GB107041018000	4.04	28.55	WB
Southern	Arun, Ouse Cuckmere	GB207041013070	4.19	38.4	WB
Southern	Arun, Ouse Cuckmere	GB207041013350	2.99	61	WB
Southern	Medway, Stour	Hydrometric Default	3.18	50	HA
Southern	Medway, Stour	GB106040018070	4.63	32	WB
Southern	Medway, Stour	GB106040018160	5.5	58.1	WB
Southern	Medway, Stour	GB106040018180	4.69	45.55	WB
Southern	Medway, Stour	GB106040018260	4.12	31	WB
Southern	Medway, Stour	GB106040018440	4.24	63	WB
Southern	Medway, Stour	GB106040018500	4.56	35	WB
Southern	Medway, Stour	GB106040024150	2.55	106	WB
Southern	Medway, Stour	GB106040024222	3.28	93	WB
Southern	Medway, Stour	GB107040013550	3	29	WB
Southern	Medway, Stour	GB107040013590	3.45	35.1	WB
Southern	Medway, Stour	GB107040013640	4.17	42.45	WB
Southern	Medway, Stour	GB206040018670	4.12	64	WB
Southern	Medway, Stour	GB207040019830	3.52	108	WB
Southern	Test	Hydrometric Default	1.23	108	HA
Southern	Test	GB107042016460	2.23	110	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
Southern	Test	GB107042016790	2.91	80.05	WB
Southern	Test	GB107042016840	2.33	105	WB
Southern	Test	GB107042022580	2.2	110	WB
Southern	Test	GB107042022750	2.13	112	WB
Southern	Isle of Wight	Hydrometric Default	3.85	61.45	HA
Southern	Isle of Wight	GB107101005970	3.74	61.4	WB
North West					
North West	Derwent	Hydrometric Default	1.36	5.07	HA
North West	Derwent	GB102075073420	1.36	5.07	HA
North West	Derwent	GB112075070350	0.7	2.24	WB
North West	Derwent	GB112075070360	2.01	5.35	WB
North West	Derwent	GB112075070430	2.11	2.51	WB
North West	Derwent	GB112075073560	2.22	5.45	WB
North West	Douglas	Hydrometric Default	9.1	56.75	HA
North West	Douglas	GB112070064820	9.99	56.75	WB
North West	Duddon	Hydrometric Default	0.93	1.86	HA
North West	Duddon	GB112074070010	0.92	1.88	WB
North West	Eden	Hydrometric Default	2.51	12.4	HA
North West	Eden	GB102076070980	3.1	62.55	WB
North West	Eden	GB102076071020	1.61	6.16	WB
North West	Eden	GB102076074040	2.51	12.4	HA
North West	Eden	GB102076074100	2.5	3.13	WB
North West	Leven, Kent	Hydrometric Default	1.7	6.91	HA
North West	Leven, Kent	GB112073071110	1.04	4.33	WB
North West	Leven, Kent	GB112073071140	1.32	4.06	WB
North West	Leven, Kent	GB112073071190	1.6	5.62	WB
North West	Leven, Kent	GB112073071400	2.82	10.55	WB
North West	Leven, Kent	GB112073071420	1.9	7.45	WB
North West	Lune	Hydrometric Default	3.96	35.7	HA
North West	Lune	GB112072065980	2.49	34.45	WB
North West	Lune	GB112072066250	4.76	36.65	WB
North West	Lune	GB112072071820	3.96	35.7	HA
North West	Lyne	Hydrometric Default	4.5	35.3	HA
North West	Lyne	GB102077074170	9.43	39.45	WB
North West	Lyne	GB102077074190	3.2	29.9	WB
North West	Mersey	Hydrometric Default	6.41	46.8	HA
North West	Mersey	GB112069061010	6.85	44.23	WB
North West	Mersey	GB112069061030	5.77	32.9	WB
North West	Mersey	GB112069061110	6.41	46.8	HA
North West	Mersey	GB112069061370	7.87	51.4	WB
North West	Mersey	GB112069061440	10.26	81.05	WB
North West	Mersey	GB112069061450	6.24	39.6	WB
North West	Ribble	Hydrometric Default	4.85	51.9	HA
North West	Ribble	GB112071065490	5.84	47.9	WB
North West	Ribble	GB112071065500	4.77	50.35	WB
North West	Ribble	GB112071065610	3.19	59.3	WB
North West	Weaver	Hydrometric Default	8.13	805.5	HA
North West	Weaver	GB112068060500	8.13	1170	WB
North East					
North East	Coquet, Wansbeck, Blyth	Hydrometric Default	4.9	36.9	HA

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
North East	Coquet, Wansbeck, Blyth	GB103022076720	4.59	35	WB
North East	Coquet, Wansbeck, Blyth	GB103022077060	5.91	64.9	WB
North East	Hull	Hydrometric Default	1.73	94.8	HA
North East	Hull	GB104026067000	1.97	94.85	WB
North East	Hull	GB104026067080	1.73	94.8	HA
North East	Ouse, Humber Estuary	Hydrometric Default	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027057410	4.72	40.6	WB
North East	Ouse, Humber Estuary	GB104027057450	7.09	57.2	WB
North East	Ouse, Humber Estuary	GB104027057510	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027057570	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027057720	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027057770	5.25	68.7	WB
North East	Ouse, Humber Estuary	GB104027062640	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027062650	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027062720	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027062750	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027063020	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027063170	6.06	75.9	WB
North East	Ouse, Humber Estuary	GB104027063180	7.45	84.75	WB
North East	Ouse, Humber Estuary	GB104027063220	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027063260	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027063310	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027064160	4.95	65.65	HA
North East	Ouse, Humber Estuary	GB104027064240	6.48	63.3	WB
North East	Ouse, Humber Estuary	GB104027064251	5.11	54.2	WB
North East	Ouse, Humber Estuary	GB104027068311	3.11	94	WB
North East	Ouse, Humber Estuary	GB104027068312	4.95	65.65	HA
North East	Ouse, Humber	GB104027068480	4.95	65.65	HA

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
North East	Estuary Ouse, Humber	GB104027069590	4.4	65.3	WB
North East	Estuary Ouse, Humber	GB204027069580	4.25	18.1	WB
North East	Tees	Hydrometric Default	6.14	22.1	HA
North East	Tees	GB103025072190	6.7	23.05	WB
North East	Tees	GB103025072590	6.14	22.1	HA
North East	Tees	GB103025075930	6.14	22.1	HA
North East	Tees	GB103025076080	6.14	22.1	HA
North East	Tees	GB203025072570	6.14	22.1	HA
North East	Trent	Hydrometric Default	No data	112.5	HA
North East	Trent	GB104028058480	5.92	112.5	WB
North East	Tweed	Hydrometric Default	3.28	25.9	HA
North East	Tweed	GB102021073080	3	25.9	WB
North East	Tyne	Hydrometric Default	5.7	17.9	HA
North East	Tyne	GB103023074790	4.21	63.1	WB
North East	Tyne	GB103023075340	7.28	10.7	WB
North East	Tyne	GB103023075710	3.52	37.05	WB
North East	Tyne	GB103023075800	9.31	20.9	WB
North East	Wear	Hydrometric Default	5.65	54.9	HA
North East	Wear	GB103024077470	5.65	54.9	HA
North East	Wear	GB103024077520	5.48	11	WB
North East	Wear	GB103024077620	4.55	69.9	WB
South West					
South West	Exe	Hydrometric Default	1.4	32	HA
South West	Exe	GB108045008730	3.55	79	WB
South West	Exe	GB108045008870	2.71	65	WB
South West	Exe	GB108045008880	2.3	31.5	WB
South West	Exe	GB108045009040	2.17	26	WB
South West	Exe	GB108045009090	1.78	57.5	WB
South West	Exe	GB108045009110	2.15	50	WB
South West	Exe	GB108045009170	2.55	45	WB
South West	Exe	GB108045009190	3.2	32.9	WB
South West	Exe	GB108045009200	2.68	19	WB
South West	Exe	GB108045014830	2	20	WB
South West	Exe	GB108045014880	1.64	71	WB
South West	Exe	GB108045014920	2.64	14	WB
South West	Exe	GB108045014940	2.03	8	WB
South West	Exe	GB108045014970	2.15	60.5	WB
South West	Exe	GB108045015040	2.11	10	WB
South West	Exe	GB108045015050	1.74	16.5	WB
South West	Exe	GB108045015070	1.17	50	WB
South West	Exe	GB108045015090	1.27	11	WB
South West	Exe	GB108045015130	1.21	95	WB
South West	Exe	GB108045020900	1.6	11.65	WB
South West	Camel	Hydrometric Default	1.8	19	HA
South West	Camel	GB108049000030	1.37	12.15	WB
South West	Camel	GB108049000040	1.37	16.55	WB
South West	Camel	GB108049000050	1.7	12	WB
South West	Camel	GB108049000070	2.77	16.45	WB
South West	Camel	GB108049000110	1.8	19	HA

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
South West	Camel	GB108049000120	2.9	36.5	WB
South West	Camel	GB108049000190	2	13.2	WB
South West	Camel	GB108049000210	1.75	20.35	WB
South West	Camel	GB108049000220	2.6	31	WB
South West	Camel	GB108049000230	2.92	22.9	WB
South West	Camel	GB108049000300	5.6	32.75	WB
South West	Camel	GB108049000350	4.3	10.7	WB
South West	Camel	GB108049000380	1.4	16.3	WB
South West	Camel	GB108049000410	1.75	27	WB
South West	Camel	GB108049000450	2.02	23.85	WB
South West	Camel	GB108049000500	1.42	4.6	WB
South West	Camel	GB108049000520	1.3	23.2	WB
South West	Camel	GB108049000530	4.87	11	WB
South West	Camel	GB108049000560	1.75	13.2	WB
South West	Camel	GB108049000570	1.07	38.3	WB
South West	Camel	GB108049000600	1.2	33.3	WB
South West	Camel	GB108049000620	0.8	19.05	WB
South West	Camel	GB108049000630	1.15	22.8	WB
South West	Camel	GB108049000650	1.25	37.2	WB
South West	Camel	GB108049000670	1.45	20.6	WB
South West	Camel	GB108049000690	1.7	22.4	WB
South West	Camel	GB108049000700	2.45	25.9	WB
South West	Camel	GB108049000710	2	38.4	WB
South West	Camel	GB108049000720	1.8	19	HA
South West	Camel	GB108049006890	4.35	74.7	WB
South West	Camel	GB108049006910	2.6	37.7	WB
South West	Camel	GB108049006980	2.07	10.3	WB
South West	Camel	GB108049007010	2.32	33.05	WB
South West	Camel	GB108049007030	2.2	2.8	WB
South West	Camel	GB108049007040	3.75	1.6	WB
South West	Camel	GB108049007050	1.5	30.1	WB
South West	Camel	GB108049007060	2	12.6	WB
South West	Camel	GB108049007170	1.42	16	WB
South West	Camel	GB108049007220	2.87	16.4	WB
South West	Camel	GB108049007230	4	28.5	WB
South West	Camel	GB108049007240	3.8	17.6	WB
South West	Camel	GB108049007250	4.15	17.5	WB
South West	Camel	GB108049007270	4.35	22.5	WB
South West	Camel	GB108049007280	4.1	30.4	WB
South West	Camel	GB108049013730	3.07	31.2	WB
South West	Camel	GB108049013760	2.55	23.3	WB
South West	Camel	GB108049013800	2	14.6	WB
South West	Dart	Hydrometric Default	1.33	15	HA
South West	Dart	GB108046004710	2	32	WB
South West	Dart	GB108046004810	0.9	49	WB
South West	Dart	GB108046004900	1.23	19	WB
South West	Dart	GB108046005040	1.34	26	WB
South West	Dart	GB108046005170	0.71	35	WB
South West	Dart	GB108046008350	1.5	10.1	WB
South West	Dart	GB108046008430	2.21	12.3	WB
South West	Dart	GB108046008460	1.2	109	WB
South West	Dart	GB108046008480	1.83	66	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
South West	Dart	GB108046008550	1.98	5.58	WB
South West	Fal	Hydrometric Default	1.87	14	HA
South West	Fal	GB108048001140	3.1	11.5	WB
South West	Fal	GB108048001150	2.47	17.2	WB
South West	Fal	GB108048001160	1.1	19.65	WB
South West	Fal	GB108048001170	2.4	11.9	WB
South West	Fal	GB108048001230	1	31.3	WB
South West	Fal	GB108048001250	1.8	20.65	WB
South West	Fal	GB108048001270	2.6	11.3	WB
South West	Fal	GB108048001280	2.4	22.7	WB
South West	Fal	GB108048001330	1.32	14	WB
South West	Fal	GB108048001340	1.1	35.8	WB
South West	Fal	GB108048001350	2.5	10.8	WB
South West	Fal	GB108048001380	1.5	30.05	WB
South West	Fal	GB108048001390	2.7	7.25	WB
South West	Fal	GB108048001400	1.25	16.5	WB
South West	Fal	GB108048001410	2.4	5.7	WB
South West	Fal	GB108048001420	2.07	6.5	WB
South West	Fal	GB108048001440	1.3	25.3	WB
South West	Fal	GB108048001450	1.3	7.8	WB
South West	Fal	GB108048001550	4.3	33.5	WB
South West	Fal	GB108048001640	5.95	16.1	WB
South West	Fal	GB108048001650	4.875	41.15	WB
South West	Fal	GB108048001670	3.15	30.1	WB
South West	Fal	GB108048001680	2.6	26.5	WB
South West	Fal	GB108048001710	4.5	60.8	WB
South West	Fal	GB108048001730	2.9	28	WB
South West	Fal	GB108048001750	2.67	27.8	WB
South West	Fal	GB108048001820	1.7	17.4	WB
South West	Fal	GB108048001830	3.8	14.8	WB
South West	Fal	GB108048001840	2.85	22.6	WB
South West	Fal	GB108048001850	1.57	28.55	WB
South West	Fal	GB108048001860	2.5	13.2	WB
South West	Fal	GB108048001870	3.42	13.8	WB
South West	Fal	GB108048001880	4.75	16.55	WB
South West	Fal	GB108048001980	1.42	34.7	WB
South West	Fal	GB108048002000	1.4	20.9	WB
South West	Fal	GB108048002050	3.85	21	WB
South West	Fal	GB108048002060	0.8	16.5	WB
South West	Fal	GB108048002070	2.35	16.1	WB
South West	Fal	GB108048002080	2.12	16.5	WB
South West	Fal	GB108048002090	3.05	14.3	WB
South West	Fal	GB108048002100	2.3	12.3	WB
South West	Fal	GB108048002110	2.3	21.05	WB
South West	Fal	GB108048002140	2.1	41	WB
South West	Fal	GB108048002210	2.1	45.7	WB
South West	Fal	GB108048002220	2	27.65	WB
South West	Fal	GB108048002250	2.5	19.95	WB
South West	Fal	GB108048002280	1.7	11.2	WB
South West	Fal	GB108048002290	2.92	12.25	WB
South West	Fal	GB108048002300	4.4	12.3	WB
South West	Fal	GB108048002310	2.8	8.3	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
South West	Fal	GB108048002320	0.9	20.5	WB
South West	Fal	GB108048002330	2.7	19.5	WB
South West	Fal	GB108048002340	2.1	19.8	WB
South West	Fal	GB108048002350	2.4	14.1	WB
South West	Fal	GB108048002380	2.9	16.9	WB
South West	Fal	GB108048002390	2.4	18.25	WB
South West	Fal	GB108048002400	2.35	11.4	WB
South West	Fal	GB108048002410	3.3	30.3	WB
South West	Fal	GB108048002420	2.37	21.15	WB
South West	Fal	GB108048002460	1	16.15	WB
South West	Fal	GB108048002470	3.4	38.6	WB
South West	Fal	GB108048002500	3.1	28.15	WB
South West	Fal	GB108048002510	2.8	17.45	WB
South West	Fal	GB108048007630	1.75	4.3	WB
South West	Fal	GB108048007640	4.23	3.8	WB
South West	Fal	GB108048007650	2	4.2	WB
South West	Avon	Hydrometric Default	2.215	96.6	HA
South West	Avon	GB108043011040	0.44	93.15	WB
South West	Avon	GB108043015840	0.44	99.2	WB
South West	Piddle	Hydrometric Default	1.54	97.8	HA
South West	Piddle	GB108044009690	0.44	97.2	WB
South West	Piddle	GB108044009760	1.99	19	WB
South West	Piddle	GB108044010080	1.72	98.8	WB
South West	Torridge	Hydrometric Default	1.1	15	HA
South West	Torridge	GB108050008180	3.02	11.4	WB
South West	Torridge	GB108050008210	3.8	11.5	WB
South West	Torridge	GB108050008250	2.09	14.3	WB
South West	Torridge	GB108050014270	2.34	11.3	WB
South West	Torridge	GB108050014350	2.46	17	WB
South West	Torridge	GB108050014380	1.68	14	WB
South West	Torridge	GB108050014530	2.07	15	WB
South West	Torridge	GB108050014620	1.29	26	WB
South West	Torridge	GB108050014660	2.77	13	WB
South West	Torridge	GB108050019920	0.86	15	WB
South West	Torridge	GB108050019940	1.16	11.5	WB
South West	Torridge	GB108050019970	1.1	15	HA
South West	Torridge	GB108050019990	1.14	17	WB
South West	Torridge	GB108050020040	1.29	17	WB
South West	Frome	Hydrometric Default	2.31	113	HA
South West	Frome	GB109053021840	2.69	98.4	WB
South West	Frome	GB109053022290	2.31	113	WB
South West	Frome	GB109053027370	3.23	114	WB
South West	Frome	GB109053027650	0.44	119	WB
South West	E & W Lyns	Hydrometric Default	1.6	7	HA
South West	Tamar	Hydrometric Default	1.7	13	HA
South West	Tamar	GB108047003640	1.2	8.8	WB
South West	Tamar	GB108047003640	1.2	8.8	WB
South West	Tamar	GB108047003640	1.2	8.8	WB
South West	Tamar	GB108047003640	1.2	8.8	WB
South West	Tamar	GB108047003640	1.2	8.8	WB
South West	Tamar	GB108047003650	1.65	0.9	WB
South West	Tamar	GB108047003650	1.65	0.9	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
South West	Tamar	GB108047003650	1.65	0.9	WB
South West	Tamar	GB108047003650	1.65	0.9	WB
South West	Tamar	GB108047003650	1.65	0.9	WB
South West	Tamar	GB108047003660	1.55	1.7	WB
South West	Tamar	GB108047003660	1.55	1.7	WB
South West	Tamar	GB108047003660	1.55	1.7	WB
South West	Tamar	GB108047003660	1.55	1.7	WB
South West	Tamar	GB108047003660	1.55	1.7	WB
South West	Tamar	GB108047003660	1.55	1.7	WB
South West	Tamar	GB108047003750	1.7	13	HA
South West	Tamar	GB108047003880	1.7	23	WB
South West	Tamar	GB108047003890	1.2	23.8	WB
South West	Tamar	GB108047003890	1.2	23.8	WB
South West	Tamar	GB108047003890	1.2	23.8	WB
South West	Tamar	GB108047003890	1.2	23.8	WB
South West	Tamar	GB108047003890	1.2	23.8	WB
South West	Tamar	GB108047003930	2.05	50.04	WB
South West	Tamar	GB108047003960	2	58.75	WB
South West	Tamar	GB108047004000	1.85	58.8	WB
South West	Tamar	GB108047004010	1.5	11.7	WB
South West	Tamar	GB108047004020	1.75	3.85	WB
South West	Tamar	GB108047004040	1.4	5.9	WB
South West	Tamar	GB108047004050	1.22	2.85	WB
South West	Tamar	GB108047007660	4.87	17.75	WB
South West	Tamar	GB108047007670	1.5	11.2	WB
South West	Tamar	GB108047007680	1.8	2.3	WB
South West	Tamar	GB108047007690	1.45	8.7	WB
South West	Tamar	GB108047007700	1.4	5.5	WB
South West	Tamar	GB108047007710	1.4	15.85	WB
South West	Tamar	GB108047007720	1.5	14.3	WB
South West	Tamar	GB108047007730	1.7	13	HA
South West	Tamar	GB108047007740	3.47	17.9	WB
South West	Tamar	GB108047007750	1.32	6.25	WB
South West	Tamar	GB108047007760	2.2	19	WB
South West	Tamar	GB108047007770	1.6	15.7	WB
South West	Tamar	GB108047007780	2.57	15.5	WB
South West	Tamar	GB108047007790	2.1	14	WB
South West	Tamar	GB108047007800	3.9	18.9	WB
South West	Tamar	GB108047007810	2.1	15.05	WB
South West	Tamar	GB108047007820	2.4	14.65	WB
South West	Tamar	GB108047007830	3.7	16.5	WB
South West	Tamar	GB108047007840	1.5	9.45	WB
South West	Tamar	GB108047007850	1.2	21.4	WB
South West	Tamar	GB108047007860	1.1	18.3	WB
South West	Tamar	GB108047007870	1.1	2.5	WB
South West	Tamar	GB108047007890	1.7	17	WB
South West	Tamar	GB108047007910	3.3	17.4	WB
South West	Tamar	GB108047007920	2.2	29.9	WB
South West	Tamar	GB108047007930	2.3	15.6	WB
South West	Tamar	GB108047007940	3.75	17.5	WB
South West	Tamar	GB108047007950	1.1	2.65	WB
South West	Tamar	GB108047007960	1.9	16.1	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
South West	Tamar	GB108047007970	4.07	16.4	WB
South West	Tamar	GB108047007980	2.85	16.3	WB
South West	Tamar	GB108047007980	2.85	16.3	WB
South West	Tamar	GB108047007990	3.95	13.7	WB
South West	Tamar	GB108047008000	3.8	18.9	WB
South West	Tamar	GB108047008010	3.2	13.1	WB
South West	Tamar	GB108047008020	3.65	10.9	WB
South West	Tamar	GB108047008030	4.7	17.3	WB
South West	Tamar	GB108047008040	4.37	12.85	WB
South West	Tamar	GB108047008050	4.62	17.35	WB
South West	Tamar	GB108047008060	4.87	14.55	WB
South West	Tamar	GB108047008070	4.85	20.75	WB
South West	Tamar	GB108047013880	4.27	18.95	WB
South West	Tamar	GB108047013890	4.62	16.35	WB
South West	Tamar	GB108047013900	3.6	14.6	WB
South West	Tamar	GB108047013910	3.4	16.3	WB
South West	Tamar	GB108047013920	4.2	13.1	WB
South West	Tone	Hydrometric Default	4.46	102	HA
South West	Tone	GB108052015470	3.88	107	WB
South West	Tone	GB108052015480	2.59	86.2	WB
South West	Tone	GB108052021260	5.82	117	WB
Wales					
Wales	Cleddau	Hydrometric Default	2.24	12.7	HA
Wales	Cleddau	GB110061025050	2.24	12.7	HA
Wales	Cleddau	GB110061030670	1.71	11.5	WB
Wales	Cleddau	GB110061031340	2.365	14.7	WB
Wales	Clwyd	Hydrometric Default	2.66	28.5	HA
Wales	Clwyd	GB110066059860	2.66	28.5	HA
Wales	Clwyd	GB110066059960	2.06	58.1	WB
Wales	Clwyd	GB110066060020	2.8	22.9	WB
Wales	Clwyd	GB110066060030	2.66	28.5	HA
Wales	Dee	Hydrometric Default	3.59	9.6	HA
Wales	Dee	GB111067051760	8.33	1.39	WB
Wales	Dee	GB111067051970	3.74	3.2	WB
Wales	Dee	GB111067052020	3.18	11.05	WB
Wales	Dee	GB111067052110	2.44	93.2	WB
Wales	Dee	GB111067052170	2.72	95	WB
Wales	Dee	GB111067052240	3.11	3.92	WB
Wales	Dee	GB111067057080	2.39	19.55	WB
Wales	Dovey	Hydrometric Default	1.6	2.56	HA
Wales	Dovey	GB110064048390	1.32	4.21	WB
Wales	Dovey	GB110064048440	0.6	2.71	WB
Wales	Dovey	GB110064048710	1.82	2.35	WB
Wales	Dovey	GB110064048730	2.99	1.92	WB
Wales	Dovey	GB110064048800	1.5	2.69	WB
Wales	Dovey	GB110064054620	2.42	1.9	WB
Wales	Glaslyn	Hydrometric Default	1.55	3.72	HA
Wales	Glaslyn	GB110065053600	1.06	3.93	WB
Wales	Glaslyn	GB110065053660	1.38	2.89	WB
Wales	Glaslyn	GB110065053660	1.38	2.89	WB
Wales	Glaslyn	GB110065053860	1.14	3.59	WB
Wales	Glaslyn	GB110065053940	1.55	3.72	HA

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
Wales	Glaslyn	GB110065054010	1.04	3.72	WB
Wales	Glaslyn	GB110065054190	1.06	4.26	WB
Wales	Glaslyn	GB110065058520	1.06	5.15	WB
Wales	Glaslyn	GB110065058590	1.55	3.72	HA
Wales	Loughor	Hydrometric Default	1.92	29.45	HA
Wales	Loughor	GB110059032180	1.48	28	WB
Wales	Loughor	GB110059032310	1.4	36.1	WB
Wales	Rheidol	Hydrometric Default	1.74	5.71	HA
Wales	Rheidol	GB110063041570	1.92	5.08	WB
Wales	Rheidol	GB110063041710	1.63	6.46	WB
Wales	Taff	Hydrometric Default	1.96	40.45	HA
Wales	Taff	GB109057027260	2.9	53.45	WB
Wales	Taff	GB109057027270	1.42	34.5	WB
Wales	Taff	GB109057027280	0.91	46.3	WB
Wales	Tawe	Hydrometric Default	1.74	30.3	HA
Wales	Tawe	GB110058026140	1.64	51.7	WB
Wales	Tawe	GB110058026280	1.53	29.4	WB
Wales	Tawe	GB110058032430	1.74	30.3	HA
Wales	Tawe	GB210058026470	3.6	66.9	WB
Wales	Teifi	Hydrometric Default	2.99	1.14	HA
Wales	Teifi	GB110062039170	2.29	10.8	WB
Wales	Teifi	GB110062043540	3.38	0.98	WB
Wales	Tywi	Hydrometric Default	1.7	12.2	HA
Wales	Tywi	GB110060029290	1.68	12.1	WB
Wales	Tywi	GB110060029590	1.42	11.9	WB
Wales	Tywi	GB110060036280	1.36	13.4	WB
Wales	Usk	Hydrometric Default	1.4	40.2	HA
Wales	Usk	GB109056026870	1.15	48.6	WB
Wales	Usk	GB109056026910	1.18	44.4	WB
Wales	Usk	GB109056032890	1.41	39.15	WB
Wales	Usk	GB109056032900	1.4	40.2	HA
Wales	Usk	GB109056032910	1.4	40.2	HA
Wales	Usk	GB109056040083	1.24	46	WB
Wales	Wye	Hydrometric Default	2.49	42	HA
Wales	Wye	GB109055037111	2.08	44.1	WB
Wales	Wye	GB109055037112	1.67	39.5	WB
Wales	Wye	GB109055037113	2.49	42	HA
Wales	Wye	GB109055042260	1.59	1.99	WB
Midlands					
Midlands	Severn	Hydrometric Default	2.3	3.47	HA
Midlands	Severn	GB109054044130	6.74	85.4	WB
Midlands	Severn	GB109054044380	6.57	192.5	WB
Midlands	Severn	GB109054044510	2.78	62.2	WB
Midlands	Severn	GB109054044540	5.44	97.8	WB
Midlands	Severn	GB109054044580	2.1	4.09	WB
Midlands	Severn	GB109054044760	1.7	2.33	WB
Midlands	Severn	GB109054044790	1.05	2.76	WB
Midlands	Severn	GB109054044790	1.05	2.76	WB
Midlands	Severn	GB109054044800	1.64	1.87	WB
Midlands	Severn	GB109054044830	3.04	129.5	WB
Midlands	Severn	GB109054049141	3.6	109	WB
Midlands	Severn	GB109054049142	2.92	24.7	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
Midlands	Severn	GB109054049142	2.92	24.7	WB
Midlands	Severn	GB109054049144	3.56	36.2	WB
Midlands	Severn	GB109054049300	4.7	15.4	WB
Midlands	Severn	GB109054049310	5.3	13.2	WB
Midlands	Severn	GB109054049600	3.51	5.52	WB
Midlands	Severn	GB109054049680	3.7	138	WB
Midlands	Severn	GB109054049720	2.85	7.47	WB
Midlands	Severn	GB109054049740	3.2	2.64	WB
Midlands	Severn	GB109054049800	2.3	16	HA
Midlands	Severn	GB109054049810	2.6	1.61	WB
Midlands	Severn	GB109054049850	3.01	8.11	WB
Midlands	Severn	GB109054049880	2.78	3.67	WB
Midlands	Severn	GB109054049890	2.54	1.65	WB
Midlands	Severn	GB109054049950	2.2	13.05	WB
Midlands	Severn	GB109054049970	2.6	1.7	WB
Midlands	Severn	GB109054049990	2.65	1.74	WB
Midlands	Severn	GB109054050090	3.4	118	WB
Midlands	Severn	GB109054050170	3.35	66.3	WB
Midlands	Severn	GB109054055000	2.3	16	WB
Midlands	Trent	Hydrometric Default	4.2	96	HA
Midlands	Trent	GB104028042410	3.61	111	WB
Midlands	Trent	GB104028042460	3.75	113	WB
Midlands	Trent	GB104028042480	3.1	121	WB
Midlands	Trent	GB104028042570	6.28	65	WB
Midlands	Trent	GB104028046530	3.8	109	WB
Midlands	Trent	GB104028046680	4.2	96	HA
Midlands	Trent	GB104028046740	6.67	81.9	WB
Midlands	Trent	GB104028046840	3.4	117	WB
Midlands	Trent	GB104028046990	4.2	96	HA
Midlands	Trent	GB104028047050	8.35	78.4	WB
Midlands	Trent	GB104028047180	6.82	93.8	WB
Midlands	Trent	GB104028047190	5.6	115	WB
Midlands	Trent	GB104028047210	7.4	125	WB
Midlands	Trent	GB104028047220	5.29	108	WB
Midlands	Trent	GB104028047290	5.68	107	WB
Midlands	Trent	GB104028047300	5.68	108	WB
Midlands	Trent	GB104028047370	3.44	92.9	WB
Midlands	Trent	GB104028047420	6.44	92.6	WB
Midlands	Trent	GB104028052300	3.19	77.8	WB
Midlands	Trent	GB104028052310	2.65	65.2	WB
Midlands	Trent	GB104028052320	8.03	81.8	WB
Midlands	Trent	GB104028052330	7.04	66.9	WB
Midlands	Trent	GB104028052340	4.2	96	HA
Midlands	Trent	GB104028052350	4.42	108	WB
Midlands	Trent	GB104028052360	4.2	96	HA
Midlands	Trent	GB104028052380	4.2	96	HA
Midlands	Trent	GB104028052390	2.34	63.9	WB
Midlands	Trent	GB104028052420	3.83	109	WB
Midlands	Trent	GB104028052450	4.13	71.3	WB
Midlands	Trent	GB104028052650	5.86	41.7	WB
Midlands	Trent	GB104028052670	1.51	89.9	WB
Midlands	Trent	GB104028052770	5.43	30.55	WB

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
Midlands	Trent	GB104028052850	4.2	96	HA
Midlands	Trent	GB104028052900	4.2	96	HA
Midlands	Trent	GB104028053110	6.3	96.55	WB
Midlands	Trent	GB104028053240	3.3	67.4	WB
Midlands	Trent	GB104028053270	3.8	95.25	WB
Midlands	Trent	GB104028057780	4.63	51.1	WB
Midlands	Trent	GB104028057880	4.92	73.8	WB
Midlands	Trent	GB104028058460	0.7	95.2	WB
Midlands	Trent	GB104028064340	4.2	96	HA
Midlands	Witham	Hydrometric Default	5.77	116.5	HA
Midlands	Witham	GB105030062420	5.77	116.5	WB
Anglian	Ancholme	Hydrometric Default	6.23	168	HA
Anglian	Ancholme	GB104029067520	6.2	168.5	WB
Anglian	Ancholme	GB104029067580	6.23	168	HA
Anglian	Blackwater, Chelmer	Hydrometric Default	5.29	125	HA
Anglian	Blackwater, Chelmer	GB105037028630	4.59	108	WB
Anglian	Blackwater, Chelmer	GB105037033530	5.62	128	WB
Anglian	Blackwater, Chelmer	GB105037041160	4.92	139	WB
Anglian	Blackwater, Chelmer	GB105037041330	5.17	115	WB
Anglian	Blackwater, Chelmer	GB106037028200	12	111	WB
Anglian	Bure, Waveney	Hydrometric Default	4	135	HA
Anglian	Bure, Waveney	GB105034050930	3.64	125	WB
Anglian	Bure, Waveney	GB105034051360	10.4	195	WB
Anglian	Bure, Waveney	GB105034055880	4.1	133	WB
Anglian	Bure, Waveney	GB205034051340	7.82	74.8	WB
Anglian	Great Ouse	Hydrometric Default	5.99	144	HA
Anglian	Great Ouse	GB105033038050	5.56	106.5	WB
Anglian	Great Ouse	GB105033043310	4.8	122	WB
Anglian	Great Ouse	GB105033043370	5.64	131	WB
Anglian	Great Ouse	GB105033047710	11.2	249	WB
Anglian	Great Ouse	GB105033047790	5.99	144	HA
Anglian	Great Ouse	GB105033047922	5.99	144	HA
Anglian	Great Ouse	GB205033047930	5.78	143	WB
Anglian	Nene	Hydrometric Default	5.47	130	HA
Anglian	Nene	GB105032050381	5.5	130	WB
Anglian	Nene	GB105032050382	5.34	130	WB
Anglian	Stour	Hydrometric Default	5.3	135	HA
Anglian	Stour	GB105036040880	5.3	135	HA
Anglian	Stour	GB105036040940	5.3	135	WB
Anglian	Stour	GB105036041000	5.3	135	HA
Anglian	Stour	GB205036041090	5.3	135	HA
Anglian	Welland	Hydrometric Default	4.54	129	HA
Anglian	Welland	GB105031050580	4.68	127	WB
Anglian	Welland	GB105031050680	4.45	129	WB
Anglian	Witham	Hydrometric Default	3.01	134	HA

Region	Hydrometric area	Waterbody ID code	DOC 25th %ile (mg·l ⁻¹)	Ca 50th %ile generic (mg·l ⁻¹)	Source
Anglian	Witham	GB105030051590	1.7	132	WB
Anglian	Witham	GB105030062420	6.07	142	WB
Thames	Blackwater, Chelmer	Hydrometric Default	6.44	114	HA
Thames	Blackwater, Chelmer	GB106037028100	7.28	104	WB
Thames	Blackwater, Chelmer	GB106037028130	8.42	104.5	WB
Thames	Blackwater, Chelmer	GB106037028180	5.73	123	WB
Thames	Lee	Hydrometric Default	2.6	123.5	HA
Thames	Lee	GB106038033240	1.88	127	WB
Thames	Lee	GB106038033390	3.13	125	WB
Thames	Lee	GB106038077850	3.65	120	WB
Thames	Lee	GB106038077850	3.65	120	WB
Thames	Thames	Hydrometric Default	2.77	112	HA
Thames	Thames	GB106039017190	2.77	112	HA
Thames	Thames	GB106039017320	3.86	83.4	WB
Thames	Thames	GB106039017340	2.77	112	HA
Thames	Thames	GB106039017390	2.77	112	HA
Thames	Thames	GB106039017420	1.19	115	WB
Thames	Thames	GB106039017430	2.77	112	HA
Thames	Thames	GB106039017440	6.62	93.8	WB
Thames	Thames	GB106039017630	3.34	65.75	WB
Thames	Thames	GB106039022850	5.68	172.5	WB
Thames	Thames	GB106039023000	3.33	116.5	WB
Thames	Thames	GB106039023030	3.93	103	WB
Thames	Thames	GB106039023090	3.45	116	WB
Thames	Thames	GB106039023120	1.01	113	WB
Thames	Thames	GB106039023140	1.06	113	WB
Thames	Thames	GB106039023160	3.5	95.4	WB
Thames	Thames	GB106039023171	2.77	112	HA
Thames	Thames	GB106039023172	2.77	112	HA
Thames	Thames	GB106039023220	0.88	112	WB
Thames	Thames	GB106039023231	2.68	113	WB
Thames	Thames	GB106039023232	4.1	78.9	WB
Thames	Thames	GB106039023270	3.92	105	WB
Thames	Thames	GB106039023330	5.59	124.5	WB
Thames	Thames	GB106039023460	3.86	106	WB
Thames	Thames	GB106039023510	5.28	118	WB
Thames	Thames	GB106039023590	4.94	105.5	WB
Thames	Thames	GB106039029800	3.49	118	WB
Thames	Thames	GB106039029850	3.71	120.5	WB
Thames	Thames	GB106039030240	4.2	124	WB
Thames	Thames	GB106039030331	2.62	117	WB
Thames	Thames	GB106039030332	3.16	117	WB
Thames	Thames	GB106039030440	1.7	105	WB
Thames	Thames	GB206039023940	3.91	106	WB

Notes: Further details, such as SMPT User Reference codes and coordinates of sampling locations, are included in the electronic version of the database.