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Using biotic ligand models to help
implement environmental quality
standards for metals under the Water
Framework Directive

Science Report – SC080021/SR7b



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Author(s):

Adam Peters, Graham Merrington, and Bruce Brown

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Research Contractor:

wca environment Ltd, Brunel House, Volunteer Way,
Faringdon, Oxfordshire SN7 7YR
Tel: 01367 244311

Environment Agency's Project Manager:

Bruce Brown/Lindsey Sturdy, Chemicals Science,
Science Department

Collaborator(s):

Katrien Delbeke, European Copper Institute
Frank van Assche, International Zinc Association –
Europe
Chris Schlekot, Nickel Producers Environmental
Research Association

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Steve Killeen

Head of Science

Executive summary

The Water Framework Directive (WFD, EC 2000) requires EU Member States to ensure that all inland and coastal waters achieve 'good' water quality status by 2015. This goal will be realised through a range of measures, including the use of environmental quality standards (EQSs) for a number of individual chemicals.

The most-polluting chemicals have been identified under Annex X of the WFD as priority substances or priority hazardous substances, for which standards will be set at an EU level. The metals cadmium, nickel, lead and mercury are included in this annex. In addition to these priority substances and priority hazardous substances, Annex VIII of the WFD also requires Member States to identify other pollutants that are discharged to water in 'significant quantities'. These pollutants are referred to as Annex VIII substances, and the WFD requires Member States to develop their own standards for these substances. In the UK, and most likely in many other Member States, the list of Annex VIII substances includes copper (Cu) and zinc (Zn).

By accounting for bioavailability in assessing metal compliance against an EQS, it is possible to provide the most environmentally and ecologically relevant metric of metal risk. This consideration of bioavailability removes, or at least reduces, many of the confounding issues related to the assessment of metal compliance, such as ambient background concentrations, forms of differing toxicity and the alteration of those forms in response to water quality. Biotic ligand models (BLMs) enable chemical and biological interactions to be taken into account; a BLM relates, through water chemistry, the toxicity of the metal to a dissolved concentration, which can then be used in compliance assessment. Unlike many other speciation-based approaches, the BLMs have been rigorously tested in the laboratory and field, and routinely predict ecological effects to many aquatic taxa across a wide range of water chemistries to within a factor of two, an acceptable level of variability within routine ecotoxicity testing.

This collaborative project has developed and tested a simple, user-friendly version of the copper BLM with the purpose of providing a rapid screening tool to fit into Environment Agency monitoring and assessment systems. This model is *not* intended to replace the existing BLM, but to deliver a method requiring quick, low resource input, high data throughput and rapid interpretation of monitoring data. This project effectively transforms BLMs from the preserve of researchers into practical and accessible tools for regulators and stakeholders.

Several hydrometric area and waterbody based scenarios are used to examine the implications of using the potential EQSs and BLMs when compared with existing standards. Default input parameters have also been used in these scenarios and their performance relative to the use of matched data is assessed.

Consideration has been given to the use of water column ambient metal background concentrations within a compliance regime. The use of metal background concentrations and the BLMs within a simple tiered approach is also assessed, and a 'road map' is provided for embedding these approaches and tools within a regulatory framework.

The adoption of the BLMs would represent a 'step change' in working practice for the Environment Agency, and while many of the technical and practical challenges associated with their use have been addressed in this project, there remain some key decisions to be made. These decisions are generally aimed at policy makers, with science providing a number of options for consideration. Policy makers should consider the following points:

- i. The added risk approach was originally adopted for performing generic, large scale risk assessments, but may not necessarily be appropriate for application to EQSs. A more suitable approach for the initial tiers of an assessment may be to include a small contribution from the ambient background concentration in the generic predicted no-effect concentration (PNEC), for example the 5th percentile of dissolved metal concentrations taken from monitoring from the hydrometric area.
- ii. There is a widely held view, amongst regulators and the regulated, that the new EQSs developed using WFD methodology are overly precautionary and shrouded in uncertainty. However, the most significant scientific evidence for Cu and Zn does not necessarily support this view. The production of ecotoxicity data for Zn for a range of aquatic species (beyond fish) since the current national standards were set has resulted in lower, but *less* uncertain and, therefore, *less* precautionary PNECs to be established. Furthermore, the development of Cu and Zn BLMs has enabled bioavailability modification to be taken into account in compliance assessment in a scientifically robust manner. An account of bioavailability offers considerably greater ecological relevance than the hardness-based corrections that are currently applied. Nevertheless, an assessment factor of 2 was applied to the HC₅ (hazardous concentration for 5 per cent of the ecosystem) taken from the Zn ecotoxicity dataset to derive a PNEC for generic risk assessment purposes. It is appropriate to consider whether or not the PNEC derived through the risk assessment process is directly applicable as an EQS. Algae were considered to be the most sensitive species to Zn, although a recent UK study found benthic macroinvertebrates to be more sensitive than diatoms to the effects of minewaters. It is appropriate to consider a validation of the PNEC values against available field data.
- iii. Having considered the above issues, it will be possible to establish suitable proposals for generic PNECs for both Cu and Zn. A detailed assessment of compliance against standards for both Cu and Zn – set on the basis of these bioavailability-based systems, but considering a variety of possible options – will be required before it is possible to establish the most appropriate option. This assessment would also include a comparison with the current situation of Cu and Zn compliance with existing EQSs. Such an assessment should provide information for policy makers to assess the potential impacts of such changes appropriately. This exercise will also provide a view as to which stages of the process should be considered as compliance assessment, and which stages as programmes of measures under the WFD.

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1 Introduction

1.1 Report structure

This report identifies practical solutions to three key issues that currently prevent the implementation of the speciation-based models needed to assess compliance with copper (Cu) and zinc (Zn) environmental quality standards (EQSs) in the UK. These issues are:

- the need for simple speciation-based models that are compatible with Environment Agency systems and processes and which can facilitate the rapid throughput of monitoring data;
- the practical need to reduce the number of required input parameters into speciation-based models, potentially through the use of default values;
- the fitting of any physico-chemical boundary conditions of speciation-based models to water conditions encountered in the UK.

In this introductory section of the report, we briefly describe how the issues above were identified. We also outline the characteristics of biotic ligand models (BLMs) and how the use of such speciation-based tools in a regulatory framework offers benefits to the regulator and the regulated.

In Section 2, we describe the development of a user-friendly Cu predicted no-effect concentration (PNEC) estimator tool, based on the existing multiple-input Cu BLM and Environment Agency water quality data. Independent peer review of this model is included and a response to this review is provided in this section.

In Section 3, we describe the suitability of the Cu and Zn BLMs, in terms of their physico-chemical boundary conditions, to UK freshwaters and outline the limitations and uncertainties of the BLMs' predictions under certain water conditions.

Section 4 provides examples of the effect of using the BLMs for selected hydrometric areas in England and Wales. The scenarios outlined in this section have been developed using Environment Agency data and demonstrate the impact of using default values for certain physico-chemical parameters. Outputs from these scenarios are compared with the existing hardness-based EQSs for both Cu and Zn.

Section 5 considers some of the outstanding implementation issues for the use of the BLMs in compliance assessment. These issues include the use of single EQS values for Cu and Zn, the consideration and derivation of ambient background concentrations of Cu and Zn, and the development of short-term EQSs for Cu and Zn.

In Section 6, we provide a 'road map' to outline the process for embedding the BLMs into routine regulatory procedures. We indicate how a pilot scheme may work within current Environment Agency systems. An example of a waterbody-based default look-up table is also given in this section.

Finally, in Section 7, we provide our conclusions on the use of the BLMs and recommendations on the use of speciation-based methods to assess EQS compliance for metals under the Water Framework Directive.

1.2 What is a biotic ligand model and why use it?

The Water Framework Directive (WFD, EC 2000) requires EU Member States to ensure that all inland and coastal waters achieve 'good' water quality status by 2015. This objective will be facilitated through a range of measures, including the use of EQSs for a number of individual chemicals.

The most-polluting chemicals have been identified under Annex X of the WFD as priority substances or priority hazardous substances, for which standards will be set at an EU level. The metals cadmium (Cd), nickel (Ni), lead (Pb) and mercury (Hg) are included in this annex. In addition to these priority substances and priority hazardous substances, Annex VIII of the WFD also requires Member States to identify other pollutants that are discharged to water in 'significant quantities'. These pollutants are referred to as Annex VIII substances, and the WFD requires Member States to develop their own standards for these substances. In the UK, and most likely in many other Member States, the list of Annex VIII substances includes Cu and Zn.

The methodology used to derive EQSs under the WFD was developed by Lepper (2005) and is largely based on the EU Technical Guidance Document (EC 2003). This latter document was originally developed for the assessment of risks associated with chemicals produced in high volumes, and primarily organic chemicals. The suitability of this methodology for the derivation of EQSs and the difficulties that it presents for regulators and the regulated community have been outlined elsewhere (Crane and Babut 2007). Nevertheless, the methodology is a departure from the process previously used in the UK for setting EQSs under earlier directives (Zabel and Cole 1999); the new approach generally addresses uncertainty and biological differences in a more precautionary way. Thus, the new methodology, coupled with the use of more-recent ecotoxicological data (the EQSs for both Cu and Zn date back to the mid-1980s), routinely results in proposed EQSs under the WFD that are significantly lower than those currently used in the UK.

Regulators face additional issues when setting and implementing water quality standards for metals. When assessing compliance, difficulties can arise because of variation in background concentrations, the existence of different chemical species and changes in this speciation according to local physico-chemical conditions. Annex I, part B, of the WFD Daughter Directive on priority substances (EC 2008) suggests that Member States may account for both natural backgrounds and/or physico-chemical conditions of the water that may affect (bio)availability when assessing monitoring results against a metal EQS. The most-relevant metrics with which to assess environmental risk should account for metal bioavailability and, thereby, resolve many of the implementation difficulties mentioned previously.

There are several speciation-based tools, such as BLMs, that account for (bio)availability in freshwaters. Through the use of site-specific physico-chemical data, these models estimate the fraction of the measured metal in the water sample that is biologically relevant and, therefore, able to exert toxic effects.

There are a variety of other analytical approaches for assessing metal toxicity (e.g. Unsworth *et al.* 2006), but they generally have a limited ability to take account of competitive effects at the 'biotic ligand'. They are, at present, not able to account fully for bioavailability in the same way as the BLM approaches. In addition, the available analytical techniques tend to be highly specialised and are not generally suitable for routine regulatory use.

Biotic ligand models have received a great deal of attention over the last 10 years, partly because of work undertaken by metals industry groups responding to requirements under the Existing Substances Regulations (793/93/EEC). These developments have led to a significant advance in understanding how water chemistry

can have mitigating effects on metal ecotoxicity in the laboratory and also, importantly, under field conditions.

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 naturally occurring cations, together with complexation by abiotic ligands, for binding with a biotic ligand – the site of toxic action. These relationships are shown in the schematic in Figure 1.1 with the free metal ion represented by Me^{2+} , the naturally occurring cations by Na^+ , H^+ , Mg^{2+} and Ca^{2+} and the abiotic ligands by POC, DOC, CO_3^{2-} , etc.; the site of toxic action is represented by the fish gill. Extensive technical reviews of the development of the BLM have been published (e.g. Paquin *et al.* 2002).

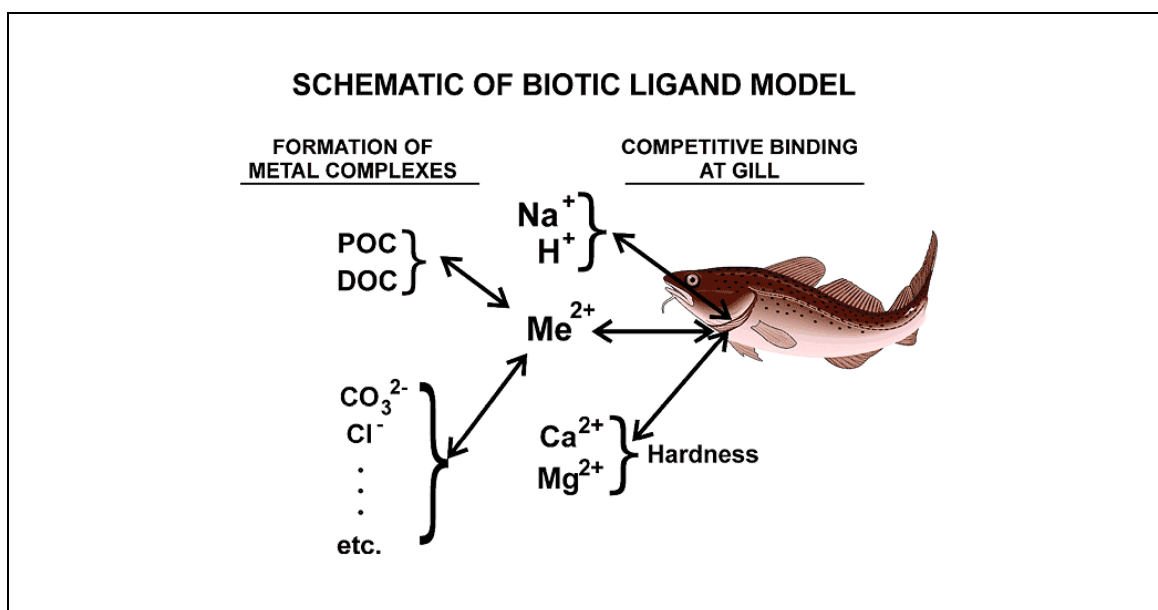


Figure 1.1 Simplified schematic of the biotic ligand model; Me^{2+} is the free metal ion, POC and DOC are particulate and dissolved organic carbon, respectively (source: <http://www.hydroqual.com>)

By accounting for (bio)availability in assessments of metal EQS compliance, it is possible to provide the most environmentally relevant metric of metal risk and remove, or at least reduce, many of the confounding issues related to assessing metal compliance, such as ambient background concentrations, forms of differing toxicity and the alteration of those forms in response to water quality.

Biotic ligand models allow chemical and biological interactions to be taken into account and relate, through water chemistry, metal toxicity to a dissolved concentration, which can then be used in compliance assessment. Unlike many other speciation-based approaches, the BLMs have been rigorously tested in the laboratory and field; they routinely predict ecological effects to many aquatic taxa across a wide range of water chemistries to within a factor of two. This variability is acceptable for routine ecotoxicity testing (The Netherlands 2004, ECI 2007, Denmark 2007).

1.3 Using biotic ligand models in a regulatory framework

The use of BLMs in a compliance-based regulatory framework is an area which has received substantial attention (Santore *et al.* 2001, Niyogi and Wood 2004, Vijver and de Koning 2007). The US Environmental Protection Agency (US EPA 2007) has recently adopted the acute Cu BLM to revise its acute criterion for freshwater because the model can account for Cu speciation reactions and interactions with organisms under a wide range of water quality conditions.

There are also significant potential economic and environmental benefits associated with BLMs as they can be used to rank and prioritise site investigations and subsequent WFD programmes of measures. Risk areas identified through the use of crude 'total' or 'dissolved' metal metrics can be verified through the use of BLMs. A recent study has demonstrated the propensity for overprediction of metals risk using existing total dissolved metal metrics (Zwolsman and De Schamphelaere 2007).

The Environment Agency has trialled the use of BLMs within a tiered regulatory framework (Environment Agency 2008c). This work demonstrated that BLMs offer a reliable and practical approach for assessing metal bioavailability, and suggested that they could be incorporated into a tiered assessment of compliance without putting the ecological status of surface waters at risk. Nevertheless, there are some significant practical issues associated with the use of the current generation of chronic BLMs for Cu and Zn. Finding solutions to these issues is the key objective of this project.

Both the Cu and Zn BLMs are supported by Microsoft Windows based platforms, and the Zn BLM also runs directly in Excel (The Netherlands 2004). However, compared with existing methods of compliance assessment for metals, BLMs are 'input hungry' (up to 13 input parameters are required) and relatively cumbersome to use when high sample throughput is required (in England and Wales more than 200,000 metal samples are assessed per year). The outputs for the Cu BLM are in the form of Microsoft Notepad, which is not readily transposed into the other Microsoft packages that are likely to be used in the collation and interpretation of monitoring data.

There is a major need for versions of the BLMs that are compatible with Environment Agency systems and processes. These versions should facilitate the rapid throughput of monitoring data and require limited user knowledge or skill, yet deliver appropriate outputs at the appropriate point in the compliance assessment process.

All the BLMs rely on the input of values for dissolved organic carbon (DOC), but in countries like the UK DOC is not routinely monitored. A methodology for deriving default DOC values has been developed in a collaborative project between the Environment Agency and industry (Environment Agency 2008d). The output from this project provides precautionary, but practical, spatially referenced DOC default values.

Even with the use of DOC defaults, there is a further need to reduce the number of input parameters for the models, especially for the Cu BLM, before they can be routinely used by regulators. An analysis of the sensitivity of model outputs to the use of default input parameters (such as calcium (Ca) concentrations) in comparison with using matched data is also required. The use of the BLMs would represent a step change in the Environment Agency's approach to Cu and Zn EQS compliance assessment, therefore the analyses should also be developed into local scenarios to facilitate communication with staff in Environment Agency regions and areas.

The operating conditions of the BLMs, in terms of water physico-chemistries, are partly determined by the requirements of EU Technical Guidance Document (EC 2003) to fit with the 10–90th percentile conditions of aquatic environments encountered across the whole EU. Laboratory conditions of experimentation used to validate these models will

also have been set to fit with these conditions. It is therefore necessary to assess the physico-chemical boundary conditions of the BLMs in relation to water conditions encountered in the UK.

Finally, there is a requirement to assess the influence of the assessment factor of 2 that was used to derive the PNEC for Zn when monitoring compliance of selected UK data (The Netherlands 2004). As the Zn PNEC is also an 'added' value (i.e. the background Zn concentration from the waterbody must also be added), an assessment of the methods to derive background concentrations is also necessary.

A number of different terms are used to describe the limit values that are used in environmental quality criteria. A toxicity reference value, which is typically set to protect 95 per cent of the entire ecosystem, is derived from a species sensitivity distribution (SSD) where sufficient data are available. This is referred to as the HC₅ (the hazardous concentration for 5 per cent of the ecosystem) and is usually derived directly from ecotoxicity data. This HC₅ is then converted into a PNEC through the application of an assessment factor, which is intended to take into account any remaining uncertainties, such as greater species diversity in real ecosystems. Assessment factors used to derive a PNEC from an HC₅ are between 1 and 5 (EC 2003). The resulting PNEC may then be proposed for adoption as an EQS, but it is not until the proposal has been formally adopted by Government that it becomes an EQS.

The work described in this report is intended to help the transition of BLMs from being the preserve of researchers into practical and widely used tools for regulators and other stakeholders. If adopted, the use of BLMs will have a significant bearing on the future management of metals and their risk assessment under the WFD.

2 Development of a user-friendly copper biotic ligand model

2.1 Introduction

The Cu BLM can calculate the PNEC for Cu as a function of local water quality conditions. The PNEC calculated by the BLM varies with the speciation of Cu and interactions between Cu and other competing ions at the site of biotic uptake (the biotic ligand). The most important parameter in determining the Cu PNEC for a given set of conditions is the concentration of DOC, which plays an important role in Cu speciation. The solution pH is also an important variable because this can affect both the extent of Cu binding to DOC and the competitive interactions at the biotic ligand. Other major water quality parameters, such as Ca, sodium (Na) and alkalinity concentrations, can also have an effect on the calculated PNEC, but are less important than pH and DOC conditions.

This chapter describes our approach in developing and testing a simplified screening version of the Cu BLM (the so-called Cu PNEC Estimator) and its subsequent review. This screening tool allows large numbers of samples to be processed quickly and efficiently using only a few input parameters.

Alkalinity is not used as an input parameter for the Cu PNEC Estimator. Therefore, the effect of certain assumptions regarding alkalinity input data on the results of Cu BLM calculations, and the implications for the simplified BLM are considered in detail.

2.2 Alkalinity input data

Calculations performed with the Cu BLM can be sensitive to alkalinity input concentrations.

Alkalinity data used in the development of the Cu PNEC Estimator varied only with pH; the alkalinity concentrations were calculated according to two sets of conditions:

- i. Alkalinity concentrations calculated on the basis of pH alone (Scenario 1)
This results in very low alkalinity concentrations over much of the relevant range of pH, with rapidly increasing concentrations above pH 8 and very high concentrations at extreme pH values.
- ii. Alkalinity calculated on the basis of an assumed constant concentration of dissolved inorganic carbon of approximately 2 mM (Scenario 2)
The maximum possible alkalinity is limited to a value that is considered to be reasonable for many surface waters and results in a more consistent increase in alkalinity concentrations over the normal range of pH for surface waters. At lower pH values, the remaining dissolved inorganic carbon is assumed to be present as dissolved carbon dioxide (CO₂).

The alkalinity concentrations (expressed as mg·l⁻¹ CaCO₃) as a function of pH are shown for both scenarios in Figure 2.1.

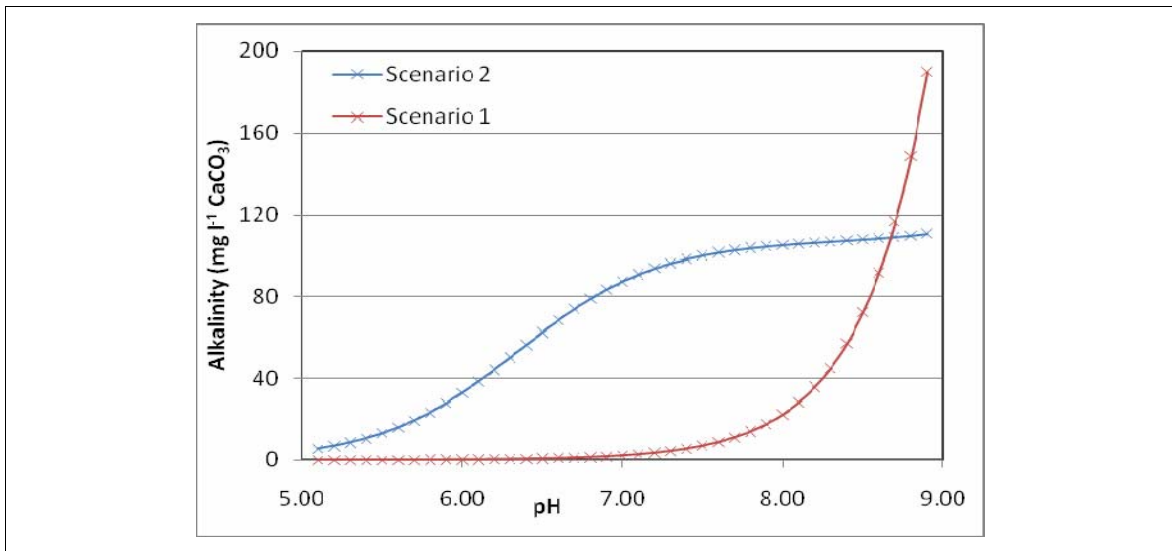


Figure 2.1 Alkalinity concentrations for two BLM calculation scenarios

The effect of these two different alkalinity scenarios on the outcome of the Cu BLM calculations was assessed using both scenarios to determine alkalinity inputs for a set of matched pH, DOC and Ca data. The results of these calculations are compared in Figure 2.2., revealing that Scenario 2 results in PNEC values that are consistently about 60 per cent of those calculated using alkalinity inputs from Scenario 1.

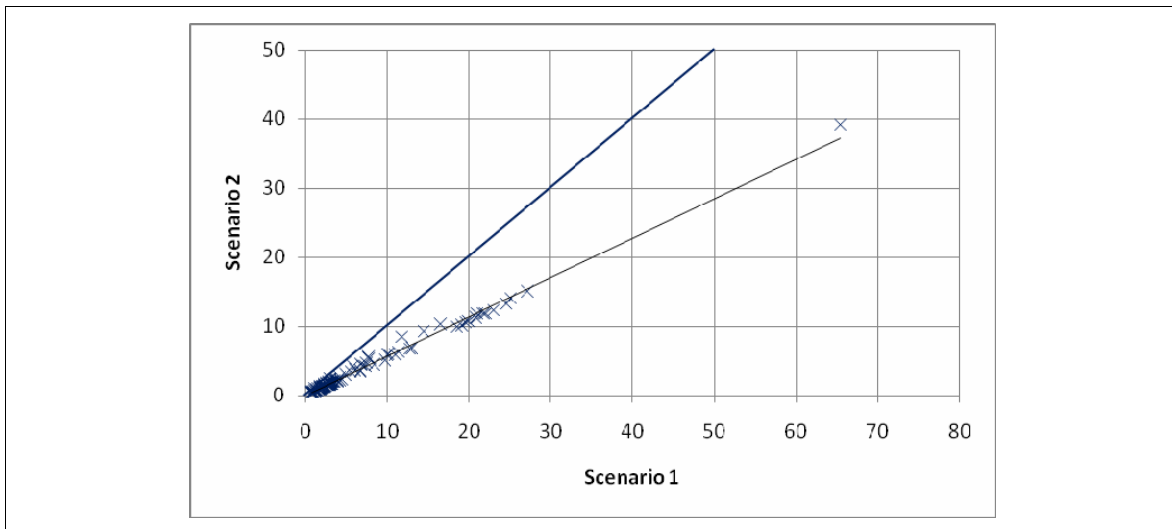


Figure 2.2 Effect of different alkalinity input data on Cu BLM PNEC predictions; the blue line shows a 1:1 relationship and the black line is a linear regression on the data

As the use of different alkalinity input data had a significant influence on the PNEC calculated by the Cu BLM, all data points used in the testing dataset for the Cu PNEC Estimator were matched measured data for pH, DOC, Ca and alkalinity (with other input variables set to default values).

Initially, models were developed using both of the alkalinity input scenarios and tested against a small set of matched monitoring data. The alkalinity inputs from Scenario 2

provided consistently better predictions of those PNECs derived using matched pH, DOC, Ca and alkalinity data.

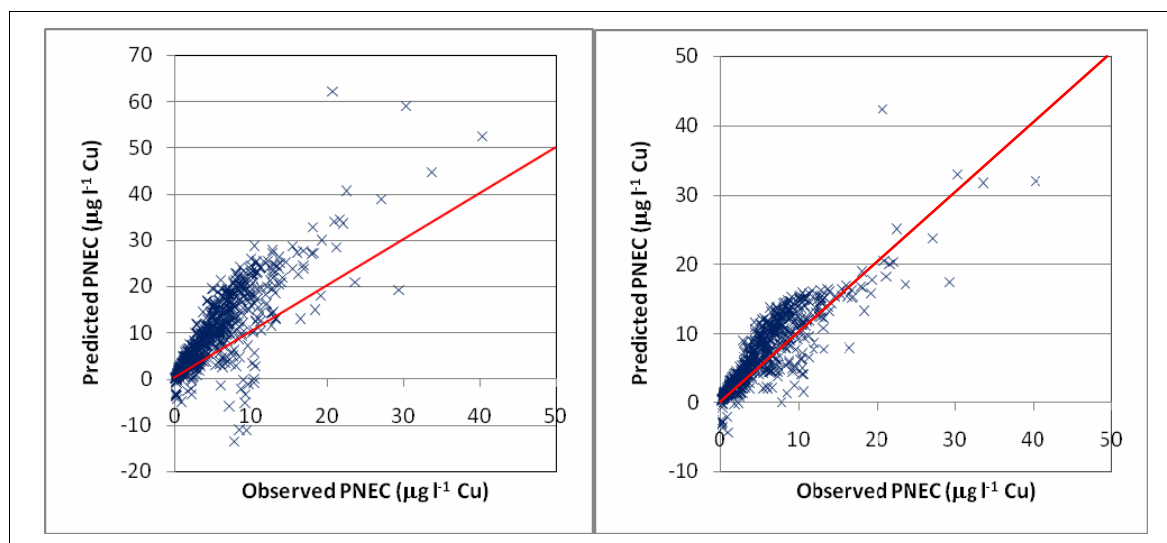


Figure 2.3 Comparison of observed and predicted PNECs using different alkalinity input data (Scenario 1 (left), Scenario 2 (right)); the red line represents a 1:1 relationship between the observed and predicted PNECs

The model developed using alkalinity inputs from Scenario 1 (Figure 2.3, left) is able to predict the PNEC values calculated using the Cu BLM with a root mean square error of $6.5 \mu\text{g}\cdot\text{l}^{-1}$; the relative error in the PNEC estimation is 189 per cent. Ninety five per cent of the predicted PNECs are, therefore, expected to be within $13 \mu\text{g}\cdot\text{l}^{-1}$ of the true PNEC value. The average error in the PNEC predictions is approximately $4 \mu\text{g}\cdot\text{l}^{-1}$ higher than the true PNEC value and the average relative error is 88 per cent. It can be clearly seen from Figure 2.3 (left) that this model has a tendency to overestimate the PNEC (or underestimate potential Cu toxicity).

The model developed using alkalinity inputs from Scenario 2 (Figure 2.3, right) is able to predict the PNEC values calculated using the Cu BLM with a root mean square error of $2.8 \mu\text{g}\cdot\text{l}^{-1}$; the relative error in the PNEC estimation is 135 per cent. Ninety five per cent of the predicted PNECs are, therefore, expected to be within $5.6 \mu\text{g}\cdot\text{l}^{-1}$ of the true PNEC value. The average error in the PNEC predictions is approximately $1.2 \mu\text{g}\cdot\text{l}^{-1}$ higher than the true PNEC value and the average relative error is 35 per cent. It can be seen from Figure 2.3 (right) that the Scenario 2 model is able to provide significantly improved predictions of the true PNEC.

In the environment, alkalinity is typically observed to co-vary with Ca concentrations (or hardness), rather than solely as a function of pH (although pH and hardness concentrations do also tend to co-vary). The relationships between pH and alkalinity, and Ca and alkalinity, for the dataset used for the testing of the Cu PNEC estimations are shown in Figure 2.4 and 2.5, respectively.

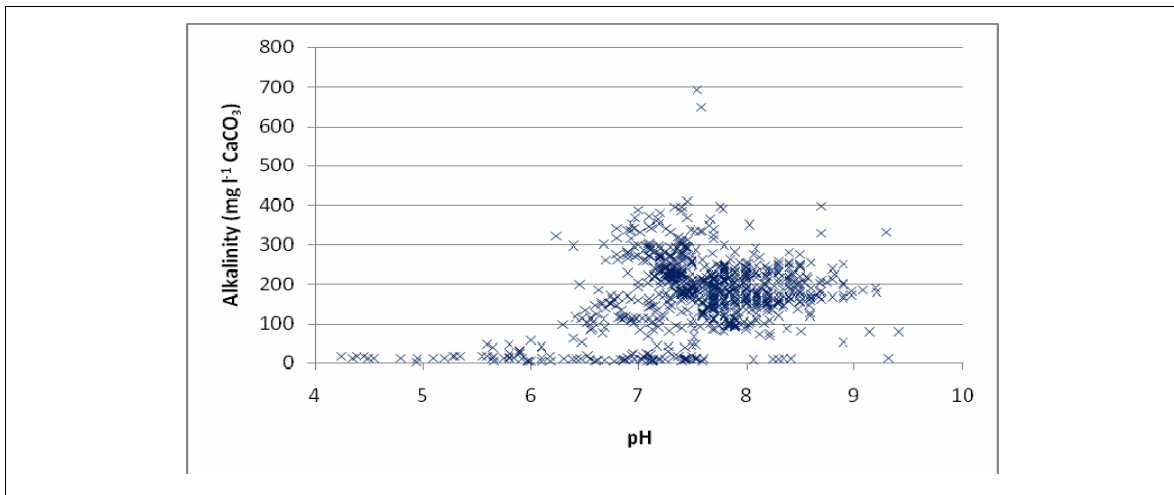


Figure 2.4 pH and alkalinity data for a representative selection of monitoring data

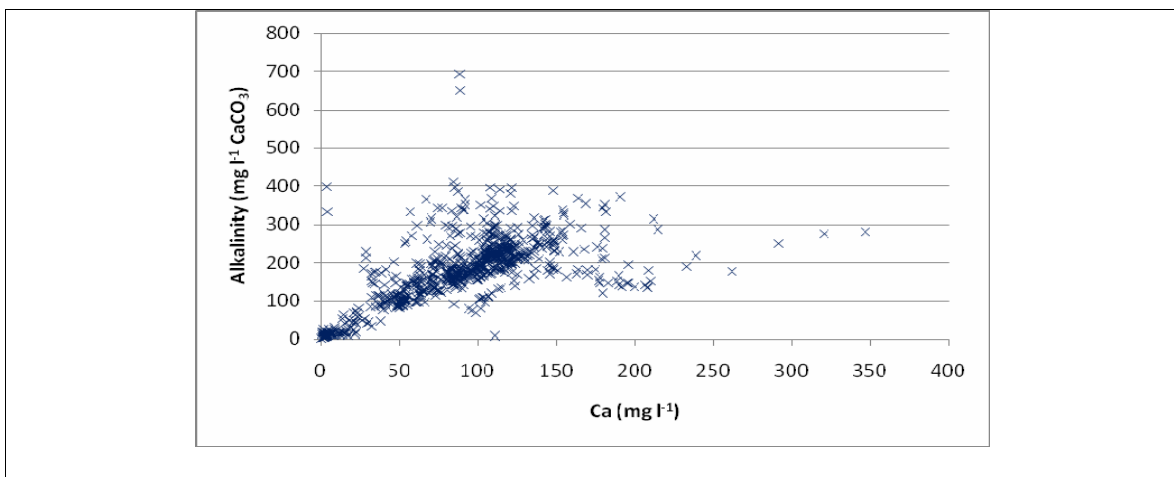


Figure 2.5 Ca and alkalinity data for a representative selection of monitoring data

There is a much stronger relationship between Ca and alkalinity than there is between pH and alkalinity when field data are considered. We, therefore, recommend that measured alkalinity data should be used when using the Cu BLM for calculating PNECs, although in cases where the data are unavailable it may be possible to estimate a reasonable alkalinity input concentration from the relationship between Ca and alkalinity. Such estimations of alkalinity should use locally relevant data where possible.

2.3 Copper biotic ligand model calculations

Predictions of the Cu HC₅ were made using the Cu BLM to calculate the HC₅(50) for different sets of pH conditions and DOC and Ca concentrations. The HC₅(50) calculated by the Cu BLM is taken as the PNEC for those water conditions since agreement was reached by the Technical Committee for New and Existing Substances that no further assessment factor was required to extrapolate from the HC₅(50) to the PNEC (ECI 2007).

Input files used in the development of the selected model took alkalinity values that had been calculated from pH, assuming equilibrium with atmospheric CO₂ and a constant dissolved inorganic carbon concentration (Scenario 2, see Section 2.2). This assumption about the alkalinity concentrations initially provided the best fit to data using measured alkalinity inputs. The input files also used a fixed ratio of magnesium (Mg) to Ca concentrations (Mg = 0.3 × Ca) throughout. The BLM calculations covered the pH range 5.00 to 8.95, DOC concentrations between 0.1 and 30 mg·l⁻¹ and Ca concentrations between 3 and 300 mg·l⁻¹. Other inputs remained fixed at the default values given in Table 2.1. The Cu BLM output data for two fixed Ca concentrations (10 and 100 mg·l⁻¹) are summarised in Figure 2.6.

Table 2.1 Default values for fixed parameters used in the BLM calculations

Parameter	Temp (°C)	Cu (µg·l ⁻¹)	% HA	Na (mg·l ⁻¹)	K (mg·l ⁻¹)	SO ₄ (mg·l ⁻¹)	Cl (mg·l ⁻¹)	S (mg·l ⁻¹)
Default	10	5	0.01	3	1	12	6	0.001

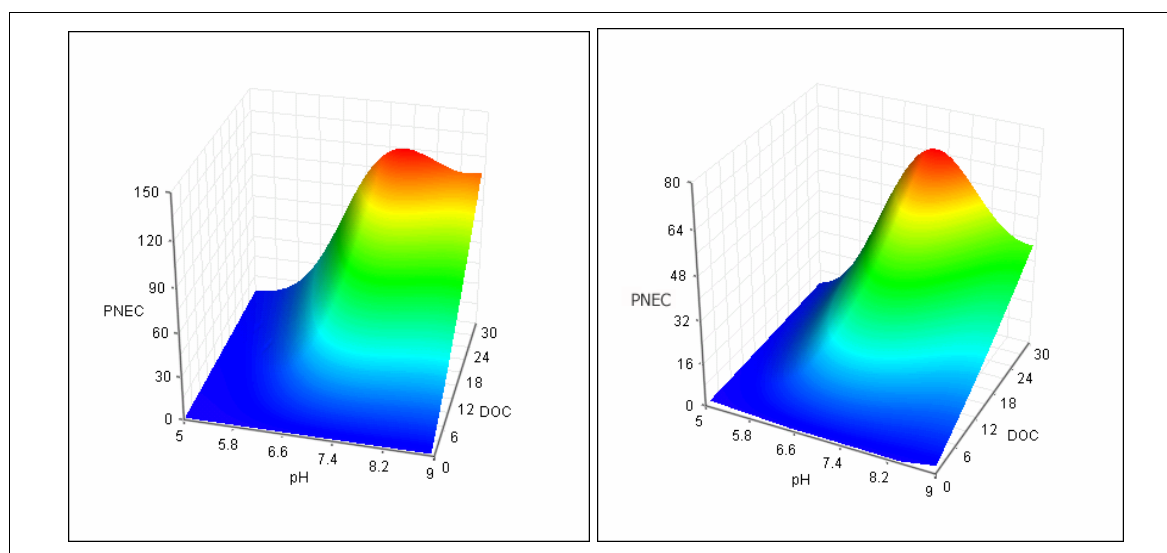


Figure 2.6 Variation of PNEC as a function of pH and DOC concentration at 10 mg·l⁻¹ Ca (left) and at 100 mg·l⁻¹ Ca (right)

2.4 Cu PNEC Estimator development

The relationships between the Cu HC₅, i.e. PNEC, and the combination of pH, DOC and Ca conditions were fitted according to the general expression below, where *a* to *g* are fitted constants:

$$\text{PNEC} = a + (b \cdot \text{pH}^c) + (d \cdot \text{DOC}^e) + (f \cdot \text{Ca}^g)$$

The constants were optimised by minimising the root mean square error between the estimate and the Cu BLM prediction. This approach is sensitive to the magnitude, but not to the direction of any errors. A total of 8400 PNEC calculations using the Cu BLM were used to ‘train’ the Cu PNEC Estimator. Alternative general expressions relating the HC₅ to the pH, DOC and Ca conditions were found not to provide improved fits to the training dataset.

We used different models for different ranges of conditions to improve the quality and reliability of the PNEC estimates. This approach achieved considerable improvements, particularly under sensitive conditions. The models cover different ranges of pH and DOC concentrations. Two pH ranges are used: <7 and ≥ 7 , and four ranges of DOC concentrations are used: ≤ 1 , $1-3$, $>3-10$ and $>10 \text{ mg}\cdot\text{l}^{-1}$.

2.5 Cu PNEC Estimator testing

A dataset of representative monitoring data from each of the Environment Agency Regions in England and Wales was prepared. Each data point used matched data for pH, DOC, Ca and alkalinity. Approximately 80 data points were selected from each region. Given the large numbers of sites with very low DOC concentrations, an additional 160 data points with higher DOC concentrations ($>1.5 \text{ mg}\cdot\text{l}^{-1}$) were also included. The full testing dataset contained 786 entries. The ranges (and averages) of the various parameters covered by the testing dataset are shown in Table 2.2 and the combinations of pH, DOC and Ca in the test dataset are shown in Figure 2.7.

Table 2.2 Ranges of abiotic conditions covered by the testing dataset

Parameter	pH	DOC ($\text{mg}\cdot\text{l}^{-1}$)	Ca ($\text{mg}\cdot\text{l}^{-1}$)	Alkalinity ($\text{mg}\cdot\text{l}^{-1} \text{ CaCO}_3$)	PNEC ($\mu\text{g}\cdot\text{l}^{-1}$)
Minimum	4.25	0.2	0.5	1	0.1
Maximum	9.41	18.6	374	692	40.2
Average	7.53	4.0	90	177	4.8

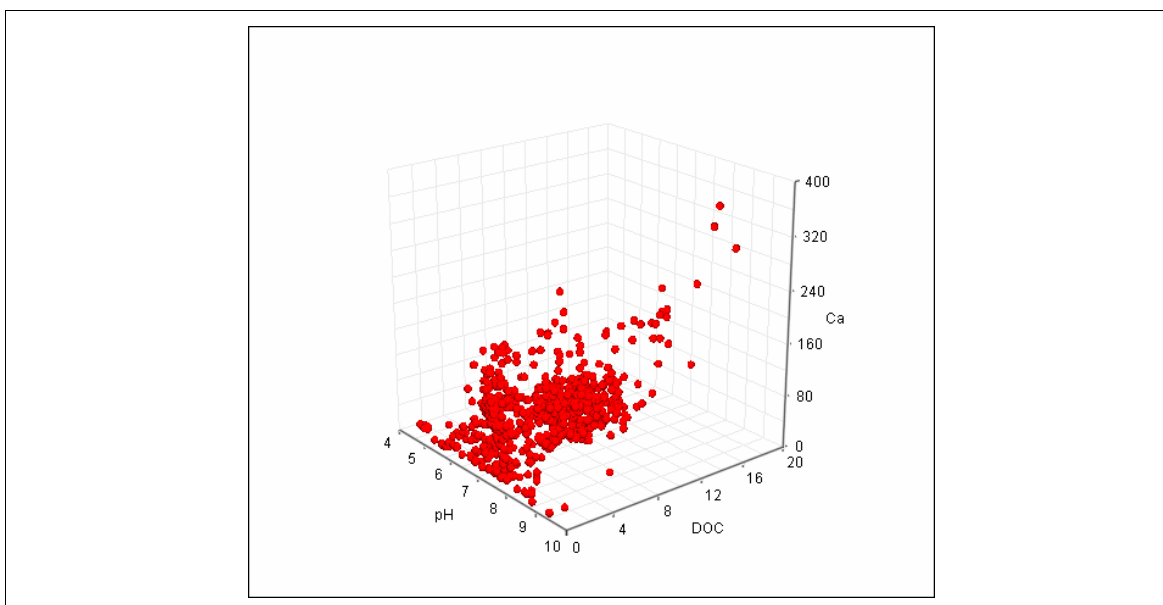


Figure 2.7 Combinations of pH, DOC and Ca in the testing dataset

A comparison of the outputs from the Cu PNEC Estimator and the Cu BLM are shown in Figure 2.8 and 2.9. These figures demonstrate the reasonable performance of the Cu PNEC Estimator. Values above the solid red line suggest underprotection, but the majority of values fall within a factor of two of the value predicted from the Cu BLM.

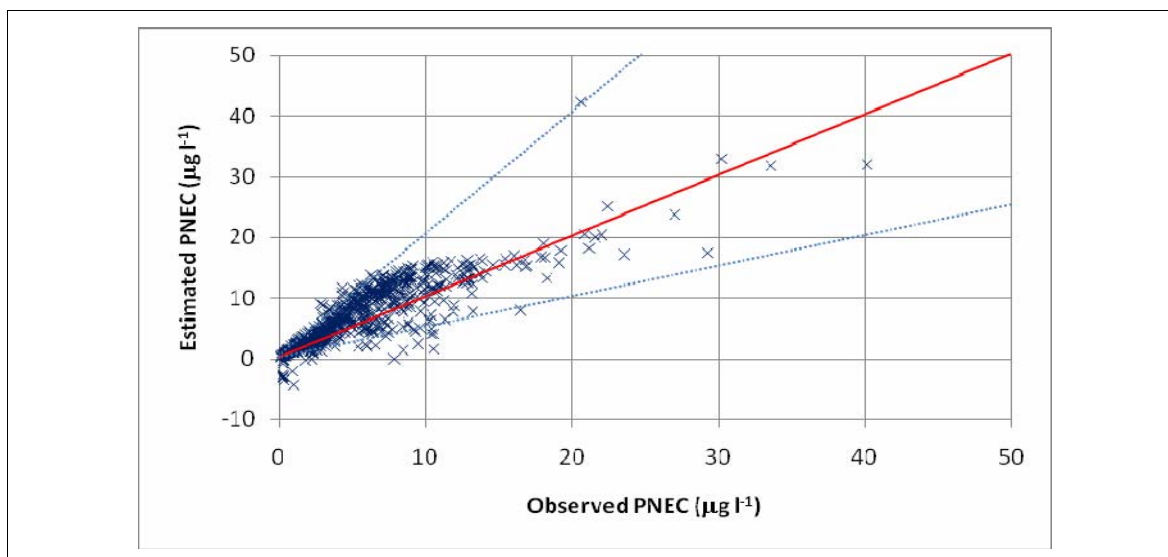


Figure 2.8 Test dataset predictions; the red line represents a 1:1 relationship between observations and predictions, data within the blue dashed lines are within a factor of 2 of the true result

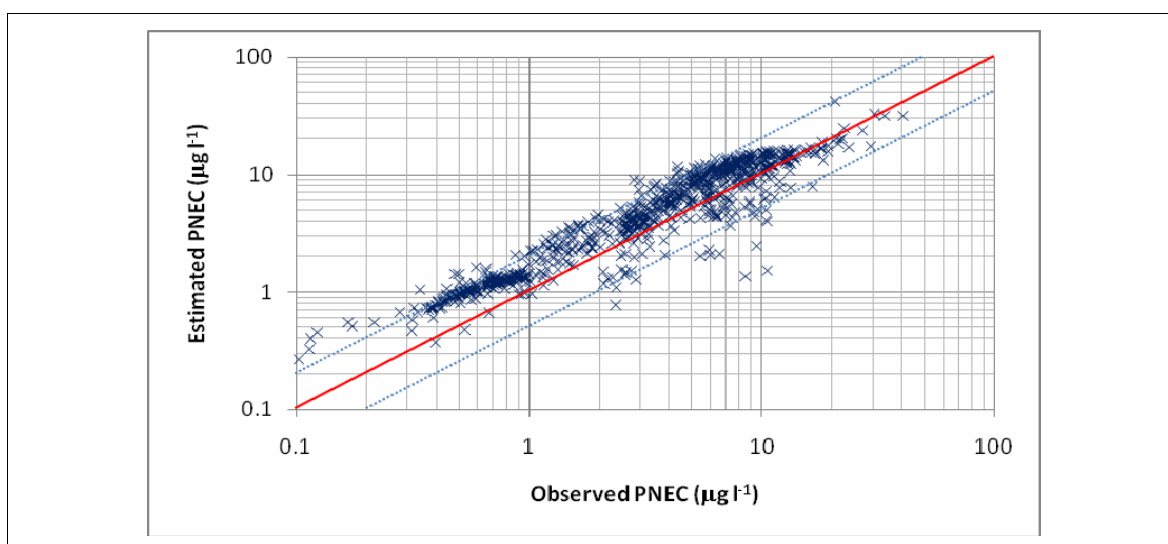


Figure 2.9 Test dataset predictions (log-log scale, results with negative predictions not shown); the red line represents a 1:1 relationship between observations and predictions, data within the blue dashed lines are within a factor of 2 of the true result

The Cu PNEC Estimator is able to predict the PNEC values calculated using the Cu BLM with a root mean square error of $2.8 \mu\text{g}\cdot\text{l}^{-1}$ for the test dataset; the relative error in the PNEC estimation is 135 per cent. Twenty eight per cent of the estimated PNECs are within $0.5 \mu\text{g}\cdot\text{l}^{-1}$ of the true value, 45 per cent are within $1 \mu\text{g}\cdot\text{l}^{-1}$ and 73 per cent are within $3 \mu\text{g}\cdot\text{l}^{-1}$. Eighty seven per cent of the PNEC estimates are within a factor of 2 of the true PNEC value. The frequency distribution of errors in the PNEC estimation is shown in Figure 2.10. The majority of estimates are close to the true PNEC calculated by the Cu BLM. Although there are a small number of relatively large errors, these occur at higher PNEC values ($>10 \mu\text{g}\cdot\text{l}^{-1}$). Similarly, some estimates have large relative errors, although these occur at low PNEC values (typically $<1 \mu\text{g}\cdot\text{l}^{-1}$).

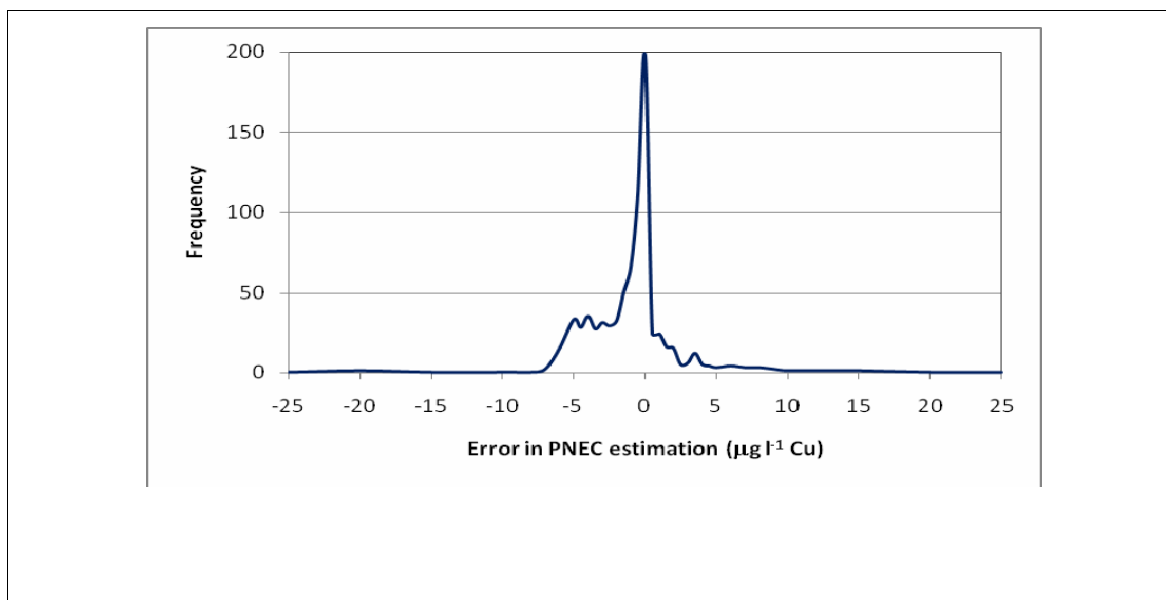


Figure 2.10 Frequency distribution of absolute errors in the PNEC estimation; negative errors indicate underprotective estimates

2.6 Issues arising from a critical review of the Cu PNEC Estimator

The draft version of the Cu PNEC Estimator was independently reviewed by Dr Karel De Schampelaere (University of Ghent, Belgium). The review is included in Annex 1. The reviewer highlighted a number of issues, and the following sections focus on the specific recommendations that were made (see also Annex 1, 'Conclusions and recommendations', point 3).

2.6.1 Use a relationship between alkalinity and calcium to estimate alkalinity

Copper BLM calculations were performed with combinations of high and low Ca and alkalinity concentrations over a range of pH values to assess the influence of potentially mismatched Ca and alkalinity inputs. The inputs may be considered to be mismatched where one is at a high concentration and the other at a low concentration. This is based on the general covariance of alkalinity and Ca concentrations in surface freshwaters that was observed in the test dataset for the Cu PNEC Estimator (see Section 2.2). The results of the Cu BLM calculations are shown in Figure 2.11, along with Cu PNEC Estimator calculations, for a DOC concentration of $1 \text{ mg}\cdot\text{l}^{-1}$; the same situation is also seen at higher DOC concentrations.

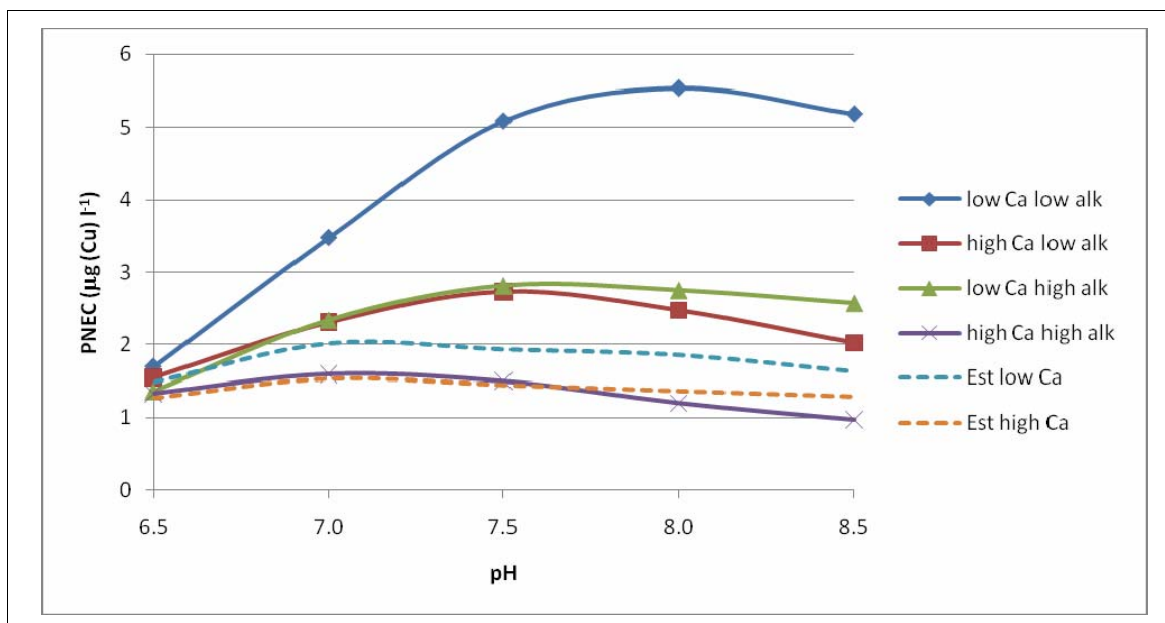


Figure 2.11 Influence of Ca and alkalinity input data on the Cu PNEC over a range of pH values using a DOC concentration of $1 \text{ mg}\cdot\text{l}^{-1}$; Est indicates Cu PNEC Estimator calculations

These calculations indicate that the Cu PNEC Estimator is able to provide reasonable estimates of the Cu PNEC for situations where either the Ca concentration or the alkalinity are relatively high, but tends to overestimate toxicity under low Ca and alkalinity conditions, such as may be found in soft waters, where pH values are above 7.

2.6.2 Use an equation that better represents the true functional relationships between pH, dissolved organic carbon, calcium and the predicted no-effect concentration. Alternatively, it could be considered to split up the input parameter space into more subspaces

This possibility has been tested by taking a subset of the test dataset with pH values between 7.0 and 8.5. A suite of 12 models was developed from the training dataset to cover the following pH ranges: $7.0 \leq \text{pH} < 7.5$, $7.5 \leq \text{pH} < 8.0$ and $8.0 \leq \text{pH} < 8.5$. Within each pH range, models were divided between the following DOC concentrations, $\text{DOC} \leq 1$, $1 < \text{DOC} \leq 3$, $3 < \text{DOC} \leq 10$ and $\text{DOC} > 10 \text{ mg}\cdot\text{l}^{-1}$. These 12 models cover a range of conditions included within four models used by the Cu PNEC Estimator. By dividing the subspace into three separate regions of pH it should be possible for predictions to match better the true pH effect on the PNEC.

A subset of 610 data points from the testing dataset were used to identify whether or not the increased number of models could improve the estimates of the test dataset PNEC values. The outputs from the revised suite of models and the Cu PNEC Estimator are shown in Figure 2.12. The root mean square error for PNEC estimations using the Cu PNEC Estimator was $2.74 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ (rsd $\pm 64\%$ of the true PNEC value). Using the suite of 12 models, PNEC values were estimated with a root mean square error of $2.78 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ (rsd $\pm 68\%$ of the true PNEC value). These findings appear to indicate that increasing the number of models may have a limited impact on the predictive capabilities of the Cu PNEC Estimator.

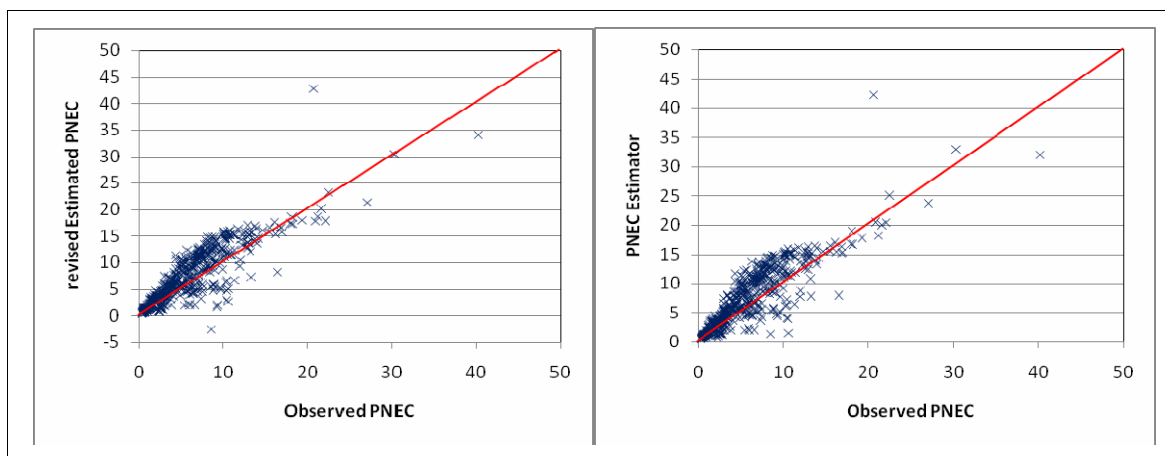


Figure 2.12 Observed and predicted PNECs using the suite of 12 models (left) and the Cu PNEC Estimator (right)

The use of look-up tables, with interpolation between values, could provide more-accurate PNEC estimations, although this approach would require a considerable investment in reprogramming the Cu PNEC Estimator.

The use of an alternative generic equation that relates the input variables (pH, DOC and Ca) to the PNEC may be able to improve estimates of the Cu PNEC, or enable the entire pH range to be covered by a single model (as indicated by Figure D of De Schampheleere’s comments, see Annex 1), although this possibility has not yet been assessed in detail.

2.6.3 Include sodium as a variable in the Cu PNEC Estimator

Copper BLM calculations were performed in which all major ions (Mg, Na, K, Cl, SO₄ and alkalinity) co-varied with Ca. The conversion factors to estimate the concentrations of these other ions from the Ca concentration were derived from a set of 256 matched data points for Ca, Mg, Na, K, Cl, SO₄ and alkalinity from 10 Scottish rivers. The ratio of the concentration of each ion to the concentration of Ca was calculated for each data point, and the mean ratio was used to estimate the BLM inputs for each ion. The ratios used are given in Table 2.3. Copper BLM predictions were performed for several pH values over a range of Ca concentrations (and consequently for a range of concentrations of the other major ions). The results are shown in Figure 2.13, along with Cu PNEC Estimator calculations, for a DOC concentration of 1 mg·l⁻¹; the same situation is also seen at higher DOC concentrations.

Table 2.3 Ratios used to estimate major ion concentrations from Ca

Ion	Na	K	Mg	Cl	SO ₄	Alkalinity
Ratio	0.77	0.12	0.26	1.28	0.68	2.59

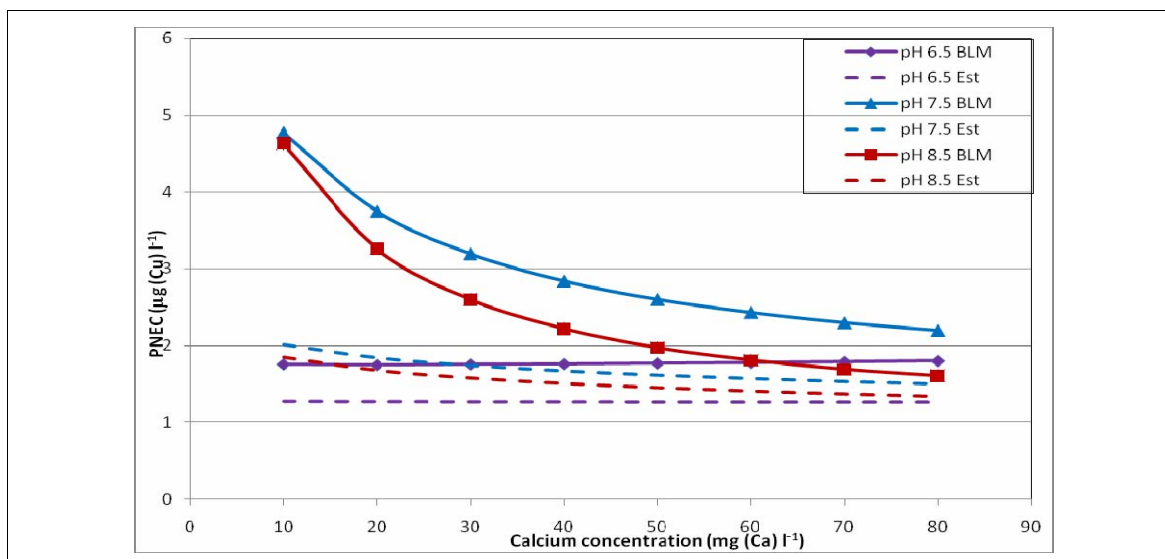


Figure 2.13 Variation in the Cu PNEC over a range of ionic strength conditions at pH 6.5, 7.5 and 8.5 and a DOC concentration of $1 \text{ mg}\cdot\text{l}^{-1}$; BLM indicates Cu BLM calculations, Est indicates Cu PNEC Estimator calculations

These calculations show that at low concentrations of Ca and other major ions, the Cu PNEC Estimator provides overestimations of the toxicity of Cu. These findings are consistent with those shown in Figure 2.11. The Cu PNEC Estimator calculations are at least two times more conservative than the Cu BLM calculations at Ca concentrations of $20 \text{ mg}\cdot\text{l}^{-1}$ and below (at $\text{pH} > 6.5$).

2.6.4 Take account of the copper biotic ligand model validation boundaries

We briefly assessed this suggestion by examining whether models trained only within the boundaries of the BLM validation could improve the estimation of PNEC values within that validation range. Data from the test dataset with $\text{pH} \geq 7.0$ and with DOC concentrations between 1.6 and $23 \text{ mg}\cdot\text{l}^{-1}$ were used. Three models were developed from the training dataset to cover the range of pH between 7.0 and 8.5 for the following DOC ranges: $1.5 \leq \text{DOC} < 3$, $3 \leq \text{DOC} < 10$ and $10 \leq \text{DOC} < 23 \text{ mg}\cdot\text{l}^{-1}$. These three models were then used to estimate PNEC values for the 406 members of the test dataset that were within the relevant ranges of pH and DOC.

The Cu PNEC Estimator provided estimates with a root mean square error of $3.35 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ (rsd $\pm 59\%$), and the three alternative models provided estimates with a root mean square error of $3.69 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ (rsd $\pm 61\%$). These initial findings do not suggest that the predictive ability of the Cu PNEC Estimator would be significantly improved by restricting the ranges of the operating models to the validation ranges of the Cu BLM. However, we proposed that, as a minimum, an alert should be included in the Cu PNEC Estimator for any cases where predictions are for pH values < 5.5 or > 8.5 .

2.7 Modifications to the draft Cu PNEC Estimator

Our investigations following the peer review of the Cu PNEC Estimator revealed that the estimator had a tendency toward overprotection relative to Cu BLM calculations for waters with low Ca concentrations and neutral to high pH. We thought this conservative

output could be due to the method used to estimate alkalinity input data, which was originally estimated from the solution pH. It was noted that in the test dataset, which used measured alkalinity data, there was a relationship between the Ca and alkalinity concentrations in the waters (Figure 2.14).

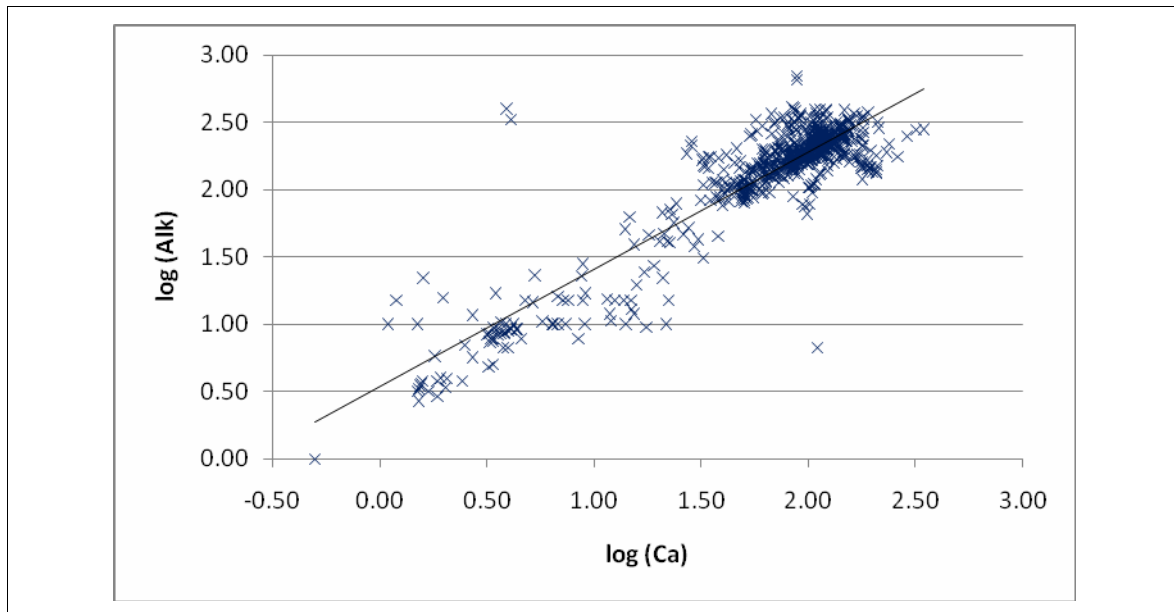


Figure 2.14 Relationship between log [Ca (mg·l⁻¹)] and log [alkalinity (mg·l⁻¹ CaCO₃)]

Alkalinity concentrations can be estimated from Ca concentrations according to the regression shown in Figure 2.14. This relationship was used to estimate alkalinity concentrations for low Ca and neutral to high pH conditions.

$$\log_{10}[\text{Alk}] = 0.8704 \cdot \log_{10}[\text{Ca}] + 0.5383 \quad (r^2 = 0.82)$$

Three alternative generic models were considered:

Original model **PNEC = a + (b · pH^c) + (d · DOC^e) + (f · Ca^g)**

Linear model **PNEC = a + (b · pH^c) + (d + DOC · e) + (f · Ca^g)**

Polynomial model **PNEC = (a + b · DOC) · pH⁴) + (c + d · DOC) · pH³) +
(e + f · DOC) · pH²) + (g + h · DOC) · pH) + (i · Ca^j) + k**

The revised original model used the same expression as the original Cu PNEC Estimator, but used the training dataset with revised calculations for low Ca and neutral to high pH conditions. The revised linear model used an alternative expression to give

a more linear response to DOC increases compared with the original Cu PNEC Estimator, and used the training dataset with revised calculations for low Ca and neutral to high pH conditions. The revised polynomial model used a more complex fourth order polynomial expression for pH in which the constants were related to the DOC concentration; it also used the training dataset with revised calculations for low Ca and neutral to high pH conditions. Table 2.4 summarises the performance of the revised models against the testing dataset.

Table 2.4 Performance of model revisions compared with the original Cu PNEC Estimator, assessed in terms of the root mean square error for the model application range

pH range	DOC range (mg·l ⁻¹)	Original Estimator	Revised original	Revised linear	Revised polynomial
4.3 to 9.4	0.2 to 18.6	2.80	5.96	3.70	9.54
<7	DOC <1	0.34	0.22	0.16	0.22
<7	1 ≤ DOC < 3	1.53	1.37	1.39	31.12
<7	3 ≤ DOC < 10	4.06	4.39	4.29	7.18
<7	10 ≤ DOC < 50	3.38	5.90	3.86	15.55
≥7	DOC <1	0.77	0.61	0.53	0.47
≥7	1 ≤ DOC < 3	1.93	1.93	1.90	2.43
≥7	3 ≤ DOC < 10	3.25	4.28	4.00	3.62
≥7	10 ≤ DOC < 50	6.39	26.78	11.60	13.03

Notes: ¹ The first row shows the performance of the suite of models against the full dataset, the rest of the table shows the performance of the individual submodels. Revised models use an alternative method for calculating the alkalinity input for pH ≥6.4 and Ca <80 mg·l⁻¹.

Given that the main issue identified was the method for estimating the alkalinity concentrations used in the training dataset, testing against the testing dataset should provide a better performance of the revised models for low Ca and neutral to high pH conditions because the testing data set used measured data for alkalinity inputs. The revised polynomial model provided the worst overall fit to the observed data (Figure 2.17). The calculations were compromised by a single data point with an extremely low Ca concentration that resulted in a very large error in the pH <7, 1 to 3 mg·l⁻¹ DOC range. This model also tended not to perform as well as the other models in the high DOC range. The complex polynomial model was expected to provide a more realistic variation in the PNEC as a function of pH, but in reality failed to provide a better overall prediction.

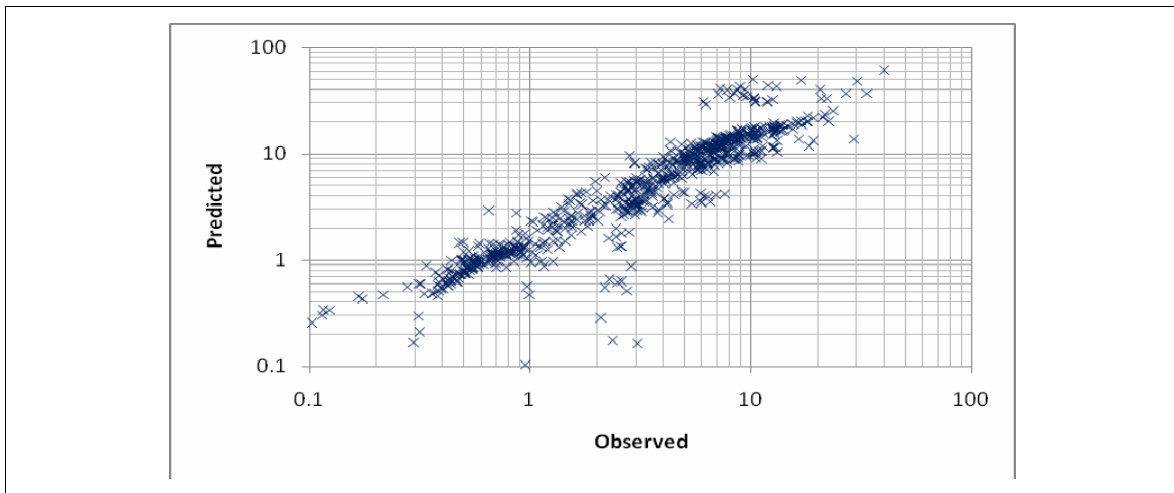


Figure 2.15 Performance of the revised original PNEC Estimator

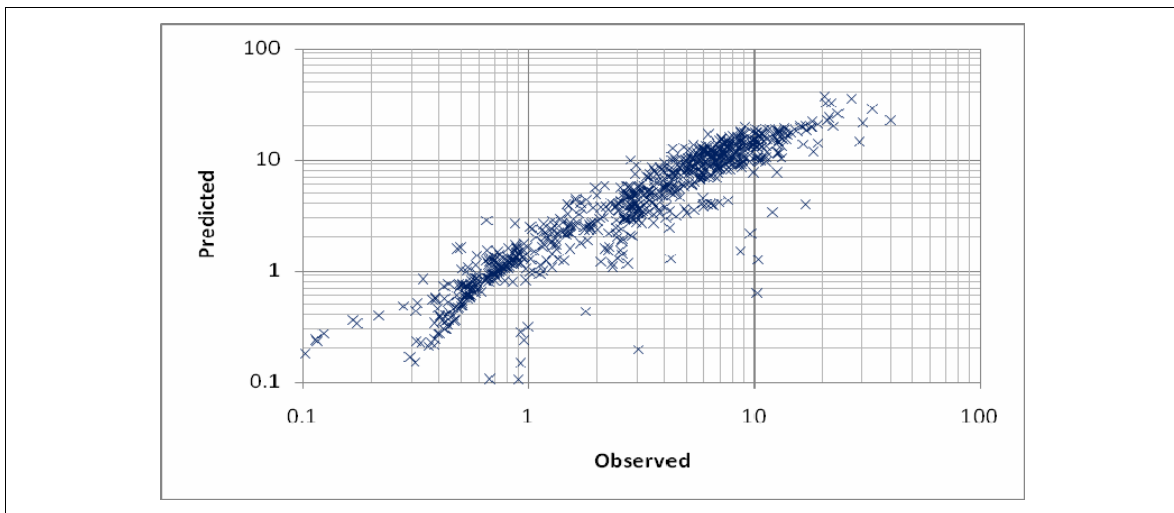


Figure 2.16 Performance of the revised linear PNEC Estimator

The revised original model used the same general expression as the original Cu PNEC Estimator and simply reflects differences in the original and revised training data sets (Figure 2.15). The performance of the revised original model was slightly reduced compared with the original model, possibly because the revised version is trained over a slightly larger range of DOC concentrations, and the effect of Ca in the revised training data set is more pronounced. Lower Ca concentrations result in higher PNEC values, and this effect is more pronounced with the revised training data.

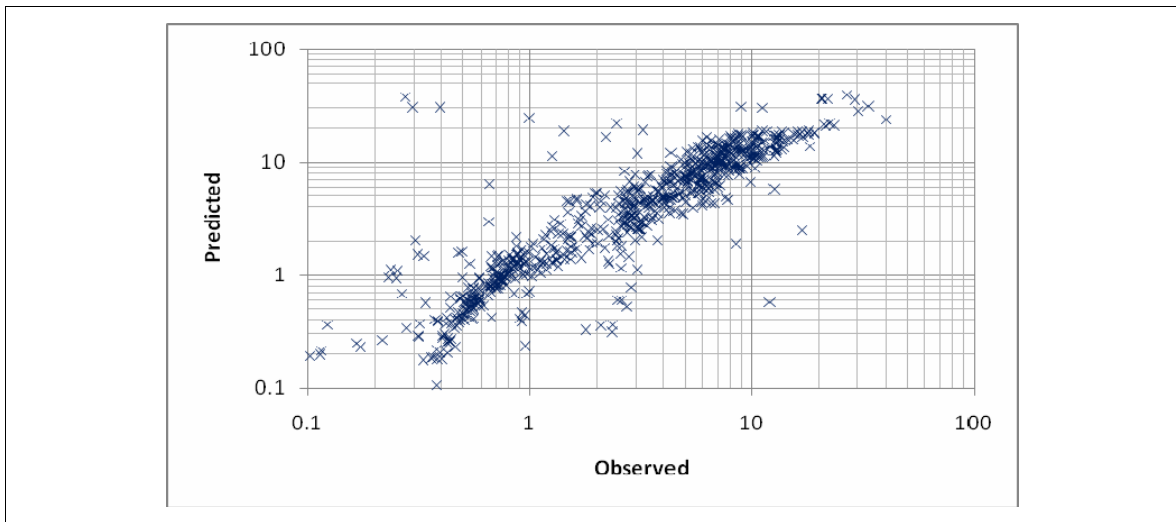


Figure 2.17 Performance of the revised polynomial PNEC Estimator

The revised linear model performed comparably to the original Cu PNEC Estimator, with a slight reduction in its performance in the high pH and high DOC concentration range (Figure 2.16). This model is expected to provide a more realistic response to variations in the DOC concentrations which should be linear for a given set of pH and Ca conditions. Figure 2.18 shows that the output of the original Cu PNEC Estimator is not entirely linear, although it is relatively close. Figure 2.19 shows a comparable output for the revised linear model. The revised linear model suffers from essentially the same problem as the original Cu PNEC Estimator: both contain a number of models developed over different ranges of DOC concentrations and continuity between different DOC ranges (i.e. between different submodels) is poor.

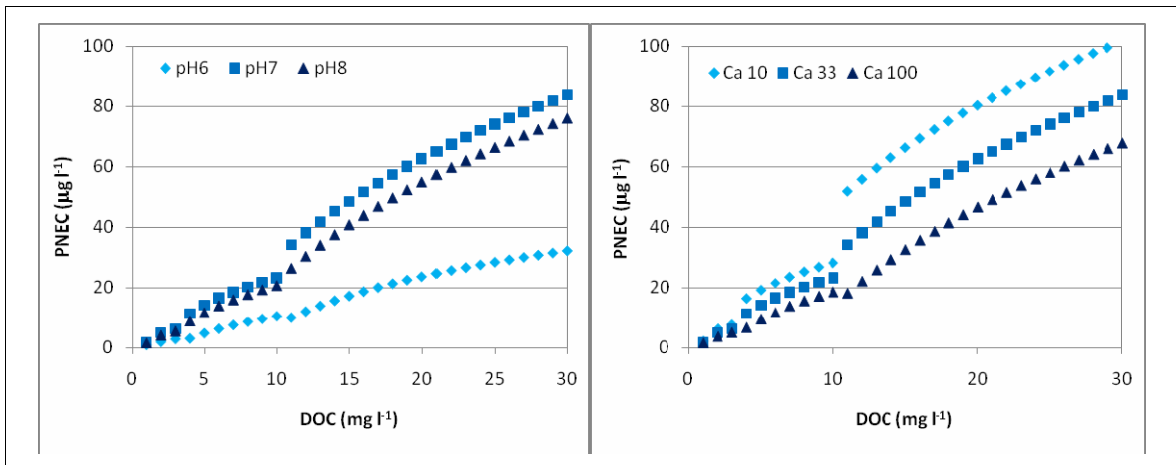


Figure 2.18 Variation in the predicted PNEC with increasing DOC concentrations for three pH values at 33 mg·l⁻¹ Ca (left) and for three Ca concentrations at pH 7 (right) with the original Cu PNEC Estimator

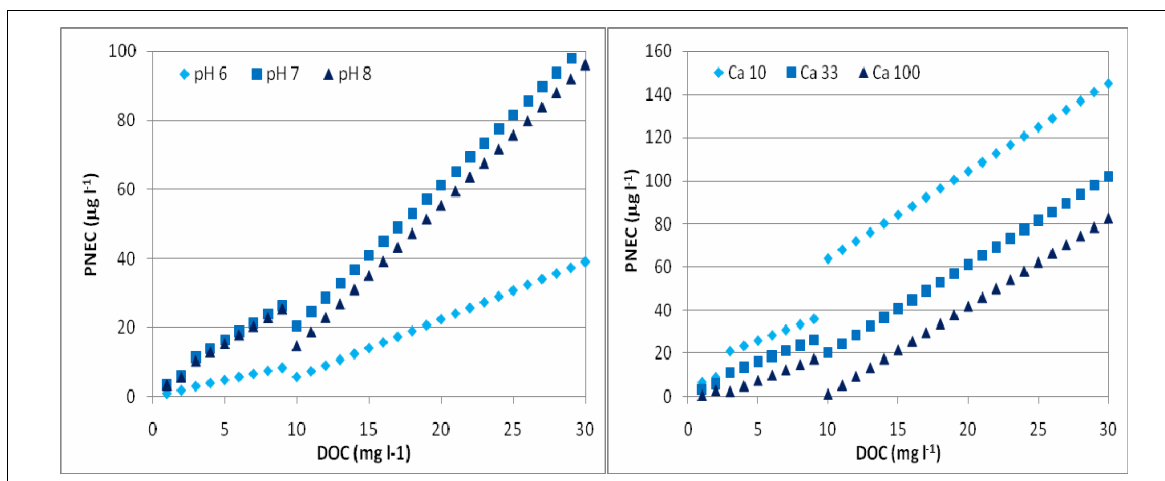


Figure 2.19 Variation in the predicted PNEC with increasing DOC concentrations for three pH values at $33 \text{ mg}\cdot\text{l}^{-1}$ Ca (left) and for three Ca concentrations at pH 7 (right) with the revised linear model

The separate submodels were fitted over the different ranges of DOC concentrations to reduce a tendency to predict negative PNECs at low concentrations. A model fitted over a wide range of DOC concentrations may also have a large root mean square error relative to the PNECs at low DOC concentrations. Consequently, the models may be particularly uncertain under relatively sensitive conditions (i.e. low DOC concentrations). Splitting the DOC concentrations into several ranges can solve this problem; it results in poor continuity between different submodels, but offers much greater certainty under relatively sensitive conditions.

On the basis of our results from testing against the test dataset of 786 data points of matched measured data for pH, DOC, Ca and alkalinity, we recommend using the original Cu PNEC Estimator. It is possible that the testing dataset has not allowed a sufficiently rigorous assessment of the various models, although the testing dataset is considered to reflect the range of conditions typically observed in England and Wales.

2.8 Summary

Testing of the Cu PNEC Estimator against the testing dataset specifically developed for this project does not provide a complete test of the ability of the estimator to predict Cu PNECs under real environmental conditions. This limitation in the testing is largely due to a lack of Na data in the master dataset from which the test dataset was compiled; in the absence of measured Na concentrations, a low default value of $3 \text{ mg}\cdot\text{l}^{-1}$ was applied in all cases.

The testing dataset used measured alkalinity input data, so should provide an adequate test of the effect of alkalinity on the PNEC. An alternative approach could be undertaken which assumes that the concentrations of all of the major ions (Mg, Na, K, SO_4 , Cl and alkalinity) co-vary with the Ca concentration (or that $\log [\text{major ion}]$ is linearly related to $\log [\text{Ca}]$). This assumption should then allow more-accurate BLM calculations to be made because of an improved description of the water quality.

This latter approach (assuming that major ion concentrations co-vary with the Ca concentration) was followed to assess the differences between the Cu PNEC Estimator and the Cu BLM on a subset of data for the River Thames (Figure 2.20). The results suggest that the Cu PNEC Estimator consistently overestimates chronic Cu toxicity, i.e.

underestimates the resulting PNEC. This conservative output is thought to be caused principally by the estimator's failure to take account of the protective effect of Na.

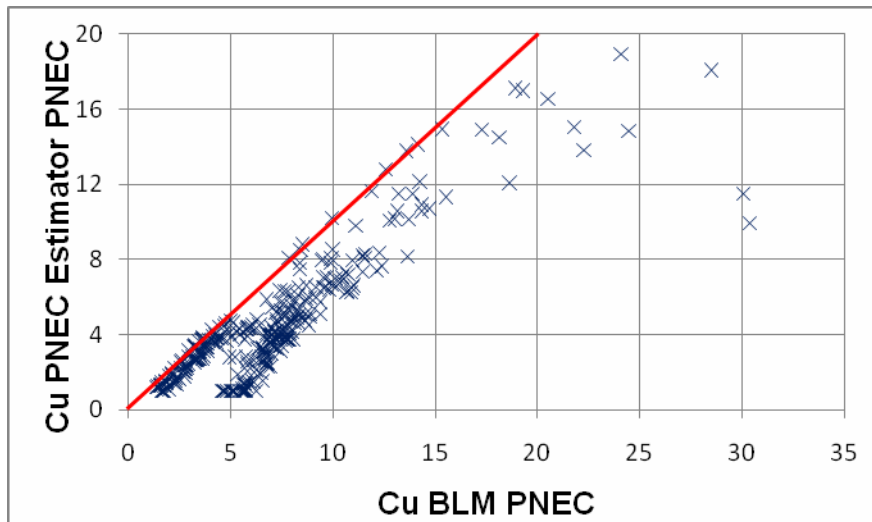


Figure 2.20 Comparison of the performance of the Cu PNEC Estimator against the Cu BLM assuming covariance of major ion concentrations (all concentrations in $\mu\text{g (Cu)}\cdot\text{l}^{-1}$ (dissolved)) for a subset of data for the River Thames

The conservatism observed in the Cu PNEC Estimator means that it is unlikely that the tool will estimate a PNEC that is significantly higher than the true PNEC. In a tiered assessment approach, this conservatism is important because sites which pass when assessed against the Cu PNEC Estimator will not be considered again. Only sites where the dissolved Cu concentration is higher than the PNEC derived by the Cu PNEC Estimator will receive further attention.

Data from ECI suggest that the Cu PNEC Estimator may provide PNEC estimates that are even more conservative than those in Figure 2.20 for data from the River Thames. The PNEC predictions using data from several European regions were found to be consistently underestimated by the Cu PNEC Estimator by a median factor of 1.5 times (10th percentile 0.9 times and 90th percentile 2.8 times). The results of the calculations are shown in Figure 2.21.

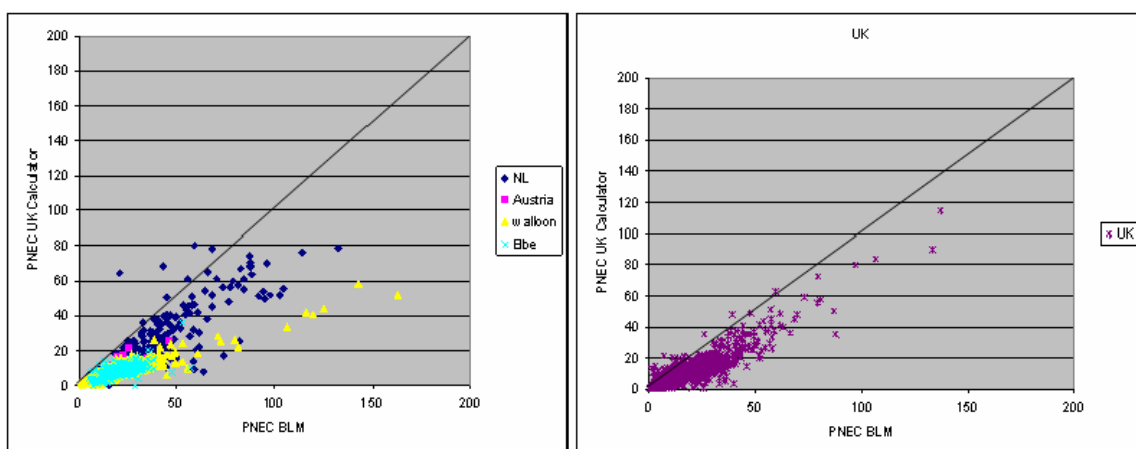


Figure 2.21 Review of Cu PNEC Estimator performance by ECI for selected European waters (left, NL = the Netherlands) and the UK (right)

Given that the principal difference between the predicted and true PNECs is probably due to the protective effect of Na on chronic Cu toxicity, we took into account the Na concentrations found in these different European conditions and investigated their relationships with Ca concentrations in more detail.

Generic relationships between Ca and Na concentrations were established for data from four regions and rivers (Walloon, Elbe, UK and Sweden) as a linear regression that could be used to estimate an Na concentration from a Ca concentration. These relationships are shown in Figure 2.22 for the three regions and one river. It is apparent from this plot that Na concentrations are more typically lower in the UK than in many other parts of Europe, and are also likely to be lower relative to Ca concentrations. This relationship suggests that PNECs calculated using the Cu PNEC Estimator will be slightly more accurate (slightly less conservative) for UK water chemistries than for other European water chemistries with higher Na concentrations.

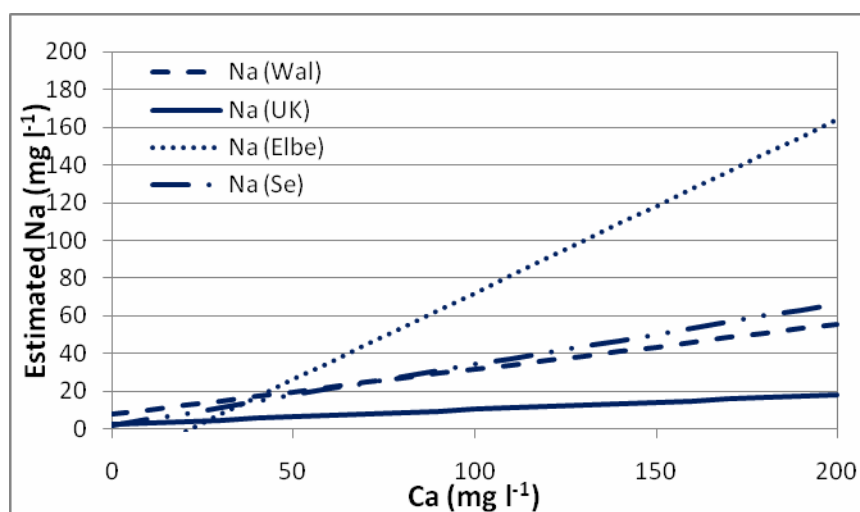


Figure 2.22 Estimation of Na concentrations from Ca concentrations for four European regions, based on linear regression from monitoring data (Wal = Walloon, Se = Sweden)

The assessment provided by ECI indicates that for slightly more than 10 per cent of the locations considered, the Cu PNEC Estimator predicted a higher PNEC than the Cu BLM. These calculations are false negatives, i.e. they may 'pass' using the estimator but not when assessed using the Cu BLM (this would only be the case if the risk characterisation ratio (RCR), i.e. environmental concentration/PNEC, was close to 1). This relatively low frequency of false negatives may be considered acceptable within a compliance assessment because the dissolved Cu concentration would need to be very close to the PNEC for the assessment to be concluded incorrectly.

Refining the Cu PNEC Estimator to provide an average or typical result that is closer to the true PNEC value will inevitably result in a higher frequency of false negatives because of the remaining uncertainties in the Cu PNEC Estimator. A higher frequency of false negatives would not be acceptable within a risk-based tiered compliance assessment approach when further tiers of assessment still remain.

To conclude, we have developed a simple screening tool to mimic the HC₅(50) predictions given by the Cu BLM. This simple tool has been developed for and validated, as far as possible, against water conditions in England and Wales.

The Cu PNEC Estimator is not intended to replace the Cu BLM, which will still provide the most-robust site-specific PNEC predictions. However, over 200,000 water samples

are processed for metal analysis every year in England and Wales and it is not possible to run the Cu BLM for all these samples in a cost-effective manner. As a simple screening tool, the Cu PNEC Estimator provides reasonable, but consistently conservative PNEC predictions, with the facility for a large throughput of samples.

The use of the estimator in combination with waterbody-based DOC defaults will further increase the degree of overprotection which is inherent in the current Cu PNEC Estimator, although we expect the implications of this on the ability of the Cu PNEC Estimator to function as a useful prioritisation tool are relatively limited.

3 Applicability of biotic ligand models to UK surface water conditions

3.1 Introduction

The BLMs for Cu and Zn, which have been developed as part of the Existing Substances Regulations (ESR, 793/93/EEC) 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 limits of the validation between the different BLMs, principally because of differences in the conditions of the field collected test waters that were used and 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.

3.2 Copper biotic ligand model

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

3.2.1 Validation range

The Cu BLM is considered to be validated in the pH range 5.5 to 8.5, between 10 and 300 mg·l⁻¹ Ca and between DOC concentrations of 1.6 and 23 mg·l⁻¹ (ECI 2007).

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 restriction 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.

3.2.2 Calcium concentrations

Calcium concentrations have less influence on the overall result of the PNEC than either pH or DOC. They tend to make little difference to the PNEC at low DOC concentrations and under low pH conditions, but cause a significant reduction in the PNEC when both the pH and DOC concentration are high (although the PNECs are still somewhat higher than under either low pH or low DOC conditions). The most-sensitive conditions, i.e. those conditions that relate the lowest PNEC, occur at low Ca concentrations, particularly when the pH is low, although the greatest effect of Ca concentrations is seen at high pH, when the PNEC can be lowered significantly by increased Ca concentrations (Figure 3.1).

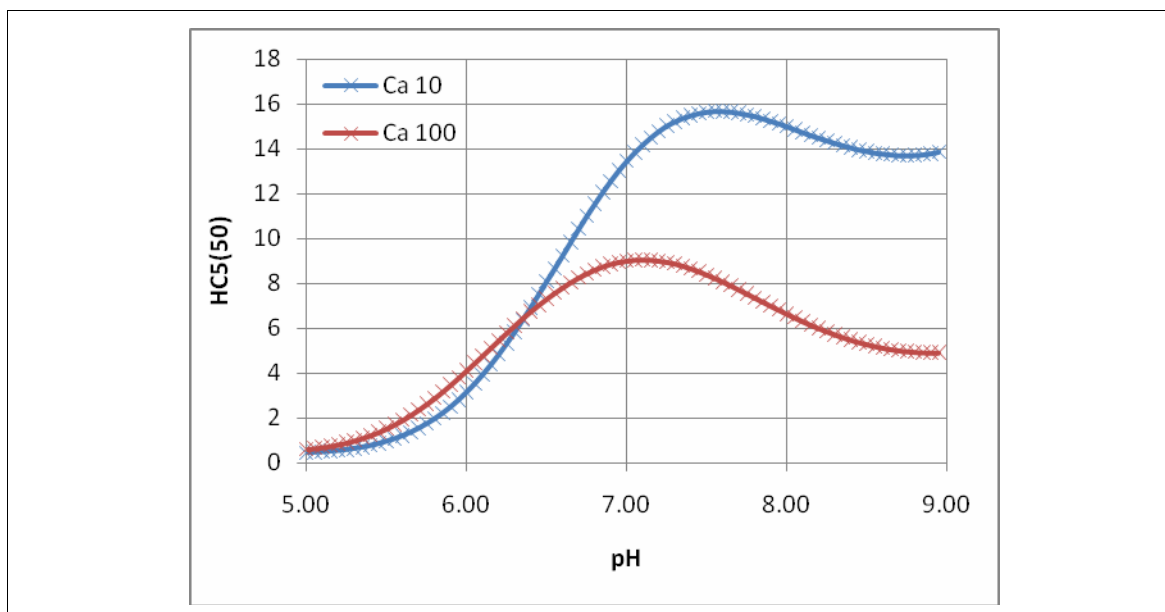


Figure 3.1 HC₅(50) values for Cu at a constant DOC concentration of 5 mg·l⁻¹ and at two Ca concentrations (10 and 100 mg·l⁻¹)

There are a limited number of ecotoxicity tests that have been performed under conditions of either extremely low or high hardness (or Ca) concentrations (Table 3.1). Both algae and invertebrates have been tested at low Ca concentrations, and algae have been tested at high Ca concentrations. These tests cover the range of hardness concentrations between ca. 8 and 486 mg·l⁻¹ as CaCO₃, approximately equivalent to 2.5 to 150 mg·l⁻¹ Ca.

Table 3.1 Cu toxicity data relevant to extremes of Ca concentrations

Species	Hardness (mg·l ⁻¹ CaCO ₃)	DOC (mg·l ⁻¹)	NOEC (µg·l ⁻¹)	Reference ¹
<i>Pseudokirchneriella subcapitata</i>	7.9 and 10	12 and 2.7	94.7 and 52.9	Heijerick <i>et al.</i> 2002
<i>Hyalella azteca</i>	<10	1	30	Deaver and Rodgers 1996
<i>Chlorella vulgaris</i>	388, 389 and 486	5 to 15.8	55.6 to 172.9	De Schamphelaere <i>et al.</i> 2006

Notes: ¹ Reference details from Cu voluntary risk assessment report (ECI 2007).

3.2.3 pH conditions

The pH conditions can have a significant influence on the Cu PNEC, although the effects of pH are relatively slight at low DOC concentrations and are greatest at high DOC concentrations (Figure 3.2).

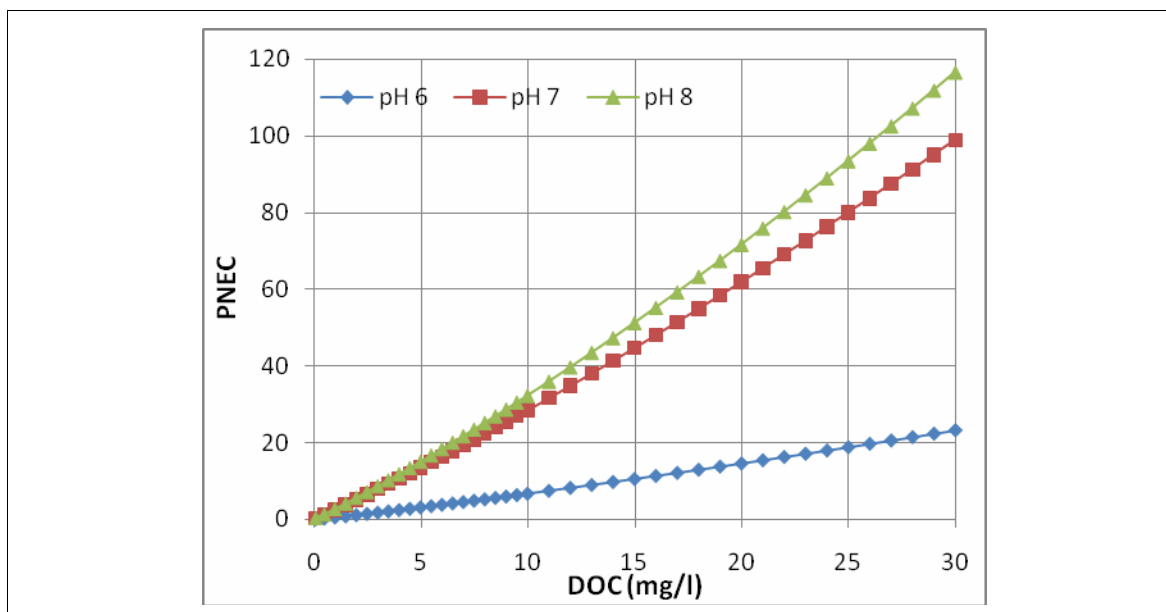


Figure 3.2 Variation in Cu PNEC as a function of DOC concentration for three different pH values (6, 7 and 8)

Ecotoxicity data that have been collected under the extremes of pH conditions include algal tests at low pH and tests on invertebrates at high pH (Table 3.2). These tests cover the range between pH 5.5 and pH 9.

Table 3.2 Cu toxicity data relevant to extremes of pH

Species	pH	DOC ($\text{mg}\cdot\text{l}^{-1}$)	NOEC ($\mu\text{g}\cdot\text{l}^{-1}$)	Reference ¹
<i>Chlorella vulgaris</i>	5.5	10.3	404.1	De Schampelaere <i>et al.</i> 2006
<i>Ceriodaphnia dubia</i>	9	2 and 2.9	20 and 10	Belanger and Cherry 1990
<i>Daphnia pulex</i>	8.5 to 8.7	0.1 to 0.475	4 to 40	Winner 1985

Notes: ¹ Reference details from Cu voluntary risk assessment report (ECI 2007).

3.2.4 Dissolved organic carbon concentrations

Dissolved organic carbon concentrations affect the concentration of bioavailable Cu and modify the bioavailability of Cu to a much greater extent than either pH or Ca concentrations, although at low pH the effect of increased DOC concentrations is very limited. The most-sensitive conditions are always at low DOC concentrations.

Changes in DOC concentrations result in changes in the PNEC value that are approximately linear at a given pH, at least over the range of concentrations of interest in UK freshwaters. At pH 7, a $1 \text{ mg}\cdot\text{l}^{-1}$ increase in the DOC concentration will increase the PNEC by approximately $3 \mu\text{g}\cdot\text{l}^{-1}$ (dissolved Cu).

Table 3.3 Cu toxicity data relevant to low DOC concentrations

Species	DOC (mg·l ⁻¹)	pH	NOEC (µg·l ⁻¹)	Reference ¹
<i>Chlamydomonas reinhardtii</i>	0.5	6.6	22	Schafer <i>et al.</i> 1994
<i>Lemna minor</i>	0.5	6.5	30	Teissier <i>et al.</i> 1998
<i>Ceriodaphnia dubia</i>	0.5	7.6	10 to 20	Cerda and Olive 1993
<i>Ceriodaphnia dubia</i>	0.5	6.3 to 7.6	4	Jop <i>et al.</i> 1995
<i>Daphnia pulex</i>	0.1 to 0.475	8.5 to 8.7	4 to 40	Winner 1985
<i>Chironomus riparius</i>	0.5	6.8	16.9	Taylor <i>et al.</i> 1991
<i>Paratanytarsus parthenogeneticus</i>	0.5	6.9	40	Hatakeyama and Yasuno 1981
<i>Onchorynchus mykiss</i>	0.2	7.5	2.2	Marr <i>et al.</i> 1996

Notes: ¹ Reference details from Cu voluntary risk assessment report (ECI 2007).

In all cases, tests performed at low DOC concentrations resulted in low NOECs, highlighting the importance of DOC as a modifier of Cu bioavailability. The relatively large number of tests performed at low DOC concentrations covers primary producers, invertebrates and fish, and these tests have been undertaken in the pH range 6.5 to 8.7 (Table 3.3). It is not relevant to consider tests undertaken at very high DOC concentrations, where Cu toxicity would likely be low.

3.2.5 Validation of BLM predictions under extreme bioavailability conditions

Results are available from several chronic ecotoxicity tests conducted under extreme bioavailability conditions, although they have generally not been conducted on particularly sensitive species. For example, De Schampelaere *et al.* (2006) conducted tests on *Chlorella vulgaris* at a low pH of 5.5 (see Table 3.2). Under the conditions of the test (pH 5.5, DOC 10.3 mg·l⁻¹, Ca 98 mg·l⁻¹), the test species is predicted to be the 25th most sensitive species out of a total of 27 species in the BLM database (i.e. the 3rd least sensitive species). A similar situation is observed for many of the other tests that have been performed under relatively extreme conditions.

Ceriodaphnia dubia was tested by Belanger and Cherry (1990) under high pH conditions (pH 9.0, DOC 2.9 mg·l⁻¹, Ca 39 mg·l⁻¹). Under these conditions, the test species is expected to be the 7th most sensitive species out of the 27 species included in the BLM database, and the rotifer *Brachionus calyciflorus* is predicted to be the most sensitive species, although it has only been tested under relatively insensitive conditions. Tests on *B. calyciflorus* have been performed at pH values of 6.0 and 7.8 and at DOC concentrations of greater than 4 mg·l⁻¹. At the higher pH, *B. calyciflorus* is predicted by the BLM to be the most sensitive species, but under the lower pH conditions, the fish *Oncorhynchus kisutch* (Coho salmon) is predicted to be the most sensitive species (particularly when Ca concentrations are low).

At low Ca concentrations (10 mg·l⁻¹), *O. kisutch* is predicted to be the most sensitive species below pH 6.50, and *B. calyciflorus* is predicted to be the most sensitive species at higher pH values. At higher Ca concentrations (100 mg·l⁻¹), the switch between *O.*

kisutch and *B. calyciflorus* as the most sensitive species is predicted to occur at the lower pH of 5.75.

The effect of alkalinity on the PNEC is similar to that of Ca, i.e. increasing alkalinity results in a decrease in the PNEC. Alkalinity and Ca concentrations in the field are commonly found to co-vary. However, this effect has not been well reproduced by the Cu PNEC Estimator because alkalinity is estimated from pH (see Section 2.6.1). We will give further consideration to this effect before we finalise the Cu PNEC Estimator for use by the Environment Agency.

Sodium generally has a protective effect against Cu toxicity to aquatic life, and increasing concentrations of Na result in increasing PNEC values. Sodium concentrations may, in many cases, co-vary with Ca concentrations and illustrative calculations suggest that when the concentrations of both of these ions vary together, the net result is still a reduction in the PNEC with increasing Ca concentration (see Figure 2.13).

There does not appear to be any robust scientific justification at present to question the PNEC values calculated by the Cu BLM under relatively extreme bioavailability conditions, because in general the most sensitive species have not been tested under such conditions. It should be remembered, however, that each individual species that is represented in the BLM toxicity database will exist only within a particular range of environmental conditions. For example, many crustaceans depend on available Ca for the formation of their exoskeletons and typically would not be present in waters of very low hardness or Ca concentrations.

In general, rotifers are relatively tolerant of pH, with peak occurrences between pH 4.5 and 8.5 (Berzins and Pejer 1987). However, the fecundity of *B. calyciflorus* is greatly reduced outside the pH range 6 to 8, although the closely related species *B. urceolaris* does show appreciable reproduction at pH 5 (Yin and Niu 2007).

Under the sensitive conditions of low pH (5.5), low Ca concentrations ($10 \text{ mg}\cdot\text{l}^{-1}$) and low DOC concentrations ($1 \text{ mg}\cdot\text{l}^{-1}$), those species that the BLM predicts to be the most sensitive are generally fish species (7 of the 10 most sensitive species and all of the 5 most sensitive species). Under these conditions, the PNEC is $0.2 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ Cu. However, the available test data for fish have all been collected at rather higher pH values and it is not clear whether or not these species would tolerate the low pH conditions under which they are predicted to be the most sensitive species to Cu.

Bossuyt *et al.* (2004) compared the acute response of field-collected cladocerans with copper and zinc and found that the sensitivity of the different communities differed by a factor of less than 2. They also found no significant difference in the sensitivity of field-collected cladocerans and literature data normalised to a single hardness value.

3.3 Zinc biotic ligand model

A different approach has been taken to implement bioavailability corrections for Zn within the ESR risk assessment (The Netherlands 2004). In this case, BLMs for chronic toxicity to representative species from three trophic levels (i.e. algae, *Daphnia* and fish) were developed, and these models were used to determine a bioavailability factor (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. An assessment

factor of 2 was applied to the HC₅ to derive the PNEC within the ESR risk assessment (The Netherlands 2004).

A separate PNEC was derived for very soft waters (waters with a hardness of less than 25 mg·l⁻¹ CaCO₃) in which a water effect ratio (WER) of 1:2.5 was applied to the generic PNEC. This value is 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 µg·l⁻¹ dissolved Zn.

3.3.1 Validation range

In the validation studies, 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 concentrations ranged between 4.8 and 27.4 mg·l⁻¹, pH ranged between 5.2 and 8.4, and hardness ranged between 2.5 and 238 mg·l⁻¹ as CaCO₃.

3.3.2 Calcium concentrations

Calcium concentrations have the effect of increasing NOEC values for all three BLM species. The BLM development studies showed that the modifying effect of hardness was a factor of 10 for rainbow trout, a factor of 3 to 4 for *D. magna*, and a factor of 2 for algae. Higher Ca concentrations can reduce toxicity through increased competition at the biotic ligand.

The Zn BLM performs calculations using Ca concentrations in the range between 5 and 150 mg·l⁻¹. For screening purposes, Ca concentrations higher than 150 mg·l⁻¹ are set to this maximum value to allow a calculation to be performed. This will result in conservative predictions of the PNEC because of the generally protective effect of Ca on Zn toxicity. It is possible that this may result in some degree of underprotection under high pH conditions, although the magnitude of the error is likely to be relatively small. Changes in Zn bioavailability as a function of pH are shown for different Ca concentrations as BioF values (Figure 3.3) and as PNEC values (Figure 3.4). Low BioF values, indicating low bioavailability, result in higher PNEC values.

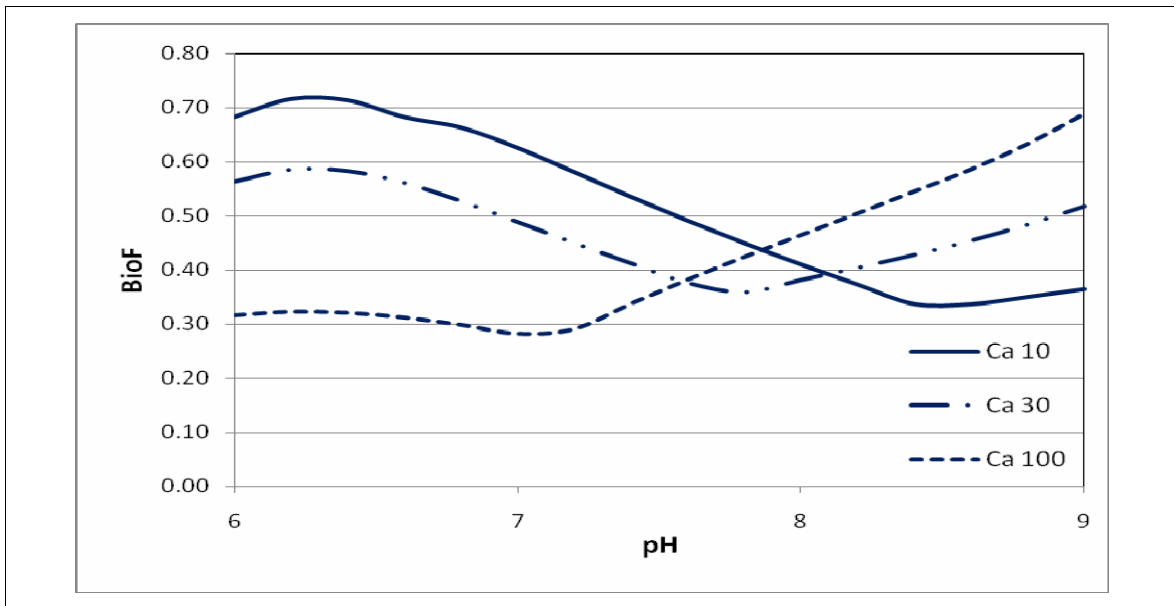


Figure 3.3 BioF values for Zn at a constant DOC concentration of 5 mg·l⁻¹ and at three Ca concentrations (10, 30 and 100 mg·l⁻¹); high BioF values indicate high Zn bioavailability and would result in low corrected PNEC values

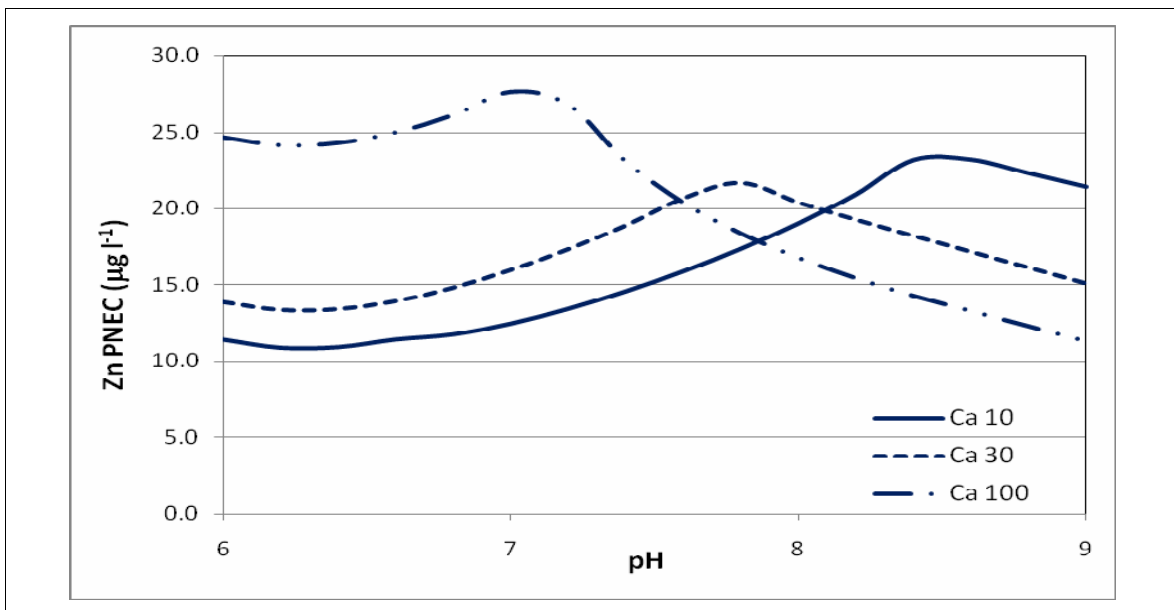


Figure 3.4 Variation in the Zn PNEC at a constant DOC concentration of 5 mg·l⁻¹ and at three Ca concentrations (10, 30 and 100 mg·l⁻¹)

Analysis of the Zn BLM has shown that the DOC concentration accounts for most of the variation in BioF values for Zn, and variation in Ca concentrations accounts for less than 15 per cent of the variation in the BioF value (Environment Agency 2008d). It is clear from Figure 3.5 that under the sensitive conditions of low DOC concentrations (1 mg·l⁻¹) and high pH (pH >8), increases in the Ca concentration do not significantly alter the bioavailability of Zn.

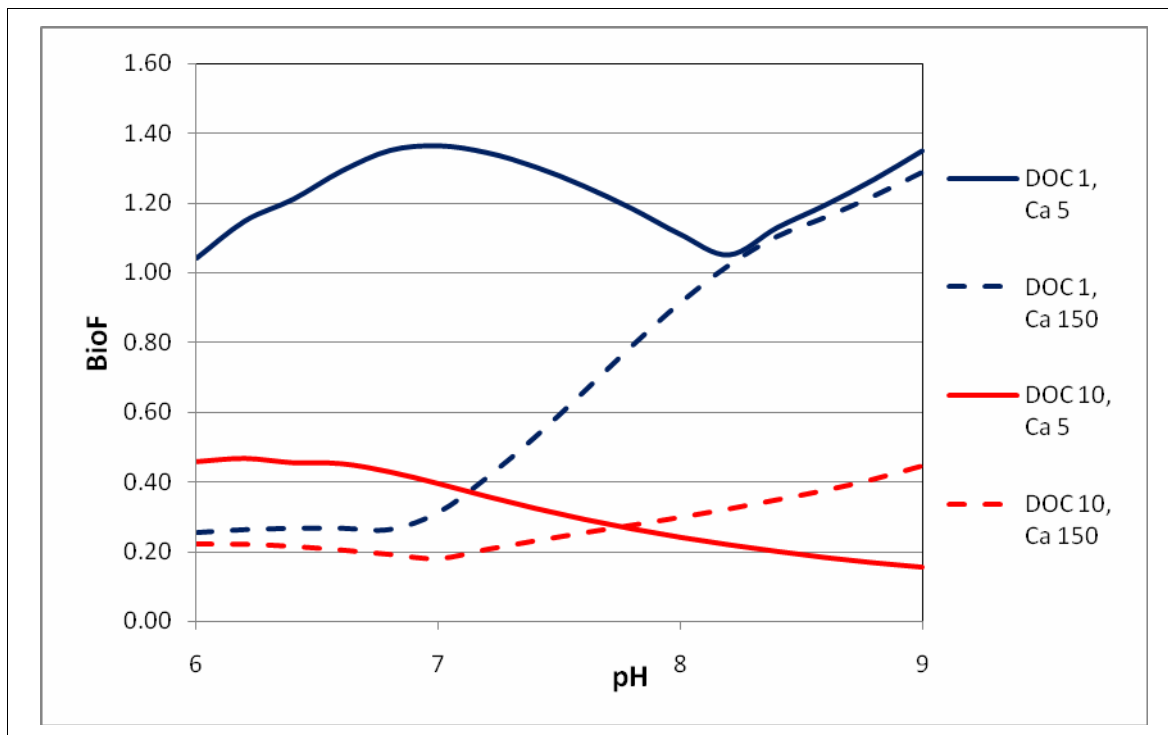


Figure 3.5 Zn bioavailability as a function of pH at different Ca and DOC concentrations

It is unlikely that calculations in which high Ca concentrations are set to the limit value of $150 \text{ mg}\cdot\text{l}^{-1}$ will result in underprotection under sensitive conditions (i.e. when DOC concentrations and PNECs are low), although some degree of underprotection is possible under less-sensitive conditions (i.e. where pH, DOC and Ca concentrations are all high).

Limiting the lower Ca concentration to $5 \text{ mg}\cdot\text{l}^{-1}$ may not provide a conservative estimate of the PNEC, although in cases where the Ca concentration is below this value, the soft water PNEC for Zn should be applied. The soft water PNEC is derived by applying a WER to the generic PNEC, and a value of 2.5 for the WER was proposed in the ESR risk assessment (The Netherlands 2004).

3.3.3 pH conditions

The effect of pH on Zn toxicity is complicated by the fact that it affects both the binding of Zn to DOC and also the binding of Zn at the biotic ligand. Under low pH conditions, a lower proportion of the metal is bound to DOC, but there is also increased competition (from protons) for binding at the biotic ligand. Under high pH conditions, the reverse situation is seen: metal binding to DOC is more extensive, but there is less proton competition at the biotic ligand.

Changes in bioavailability as a function of the DOC concentration at three different pH values are shown in Figure 3.5 and Figure 3.6 as the BioF value and the PNEC respectively.

The change in bioavailability with increasing DOC concentrations depends on the solution pH because at high pH there is a greater increase in the PNEC for a given increase in the DOC concentration (Figure 3.6).

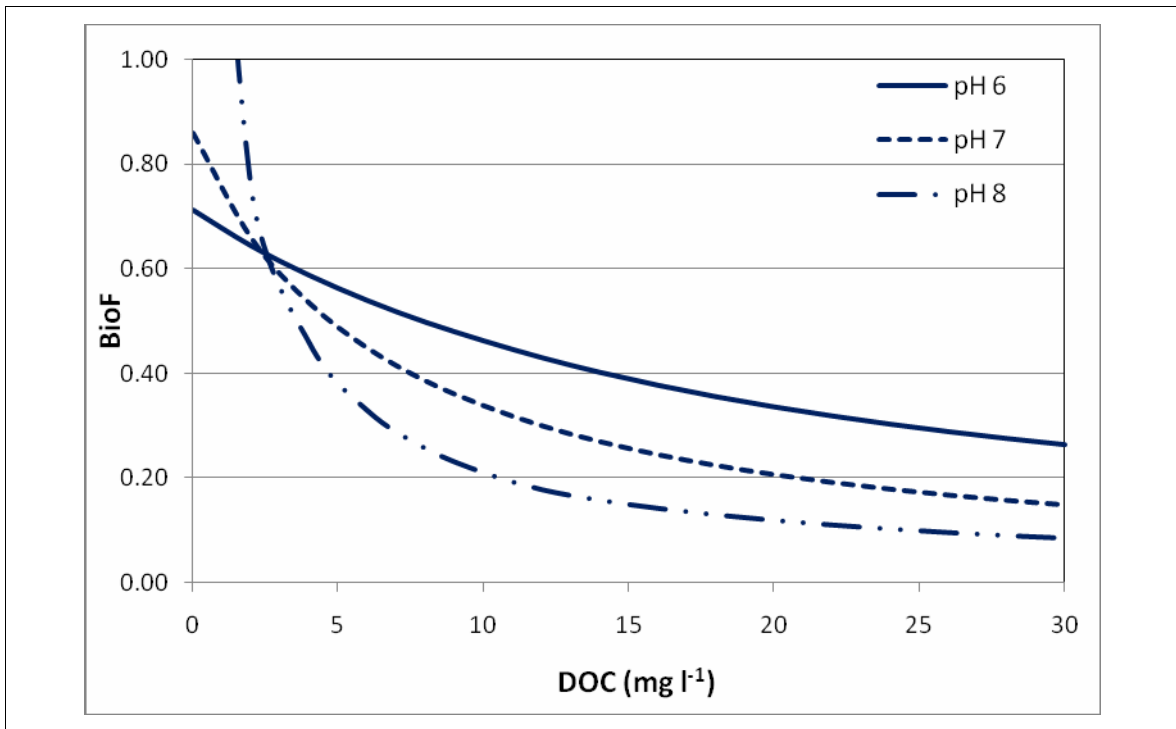


Figure 3.6 Variation in Zn BioF as a function of DOC concentration for three different pH values (6, 7 and 8)

Low DOC concentrations result in higher bioavailability of Zn, and this is particularly true at high pH values.

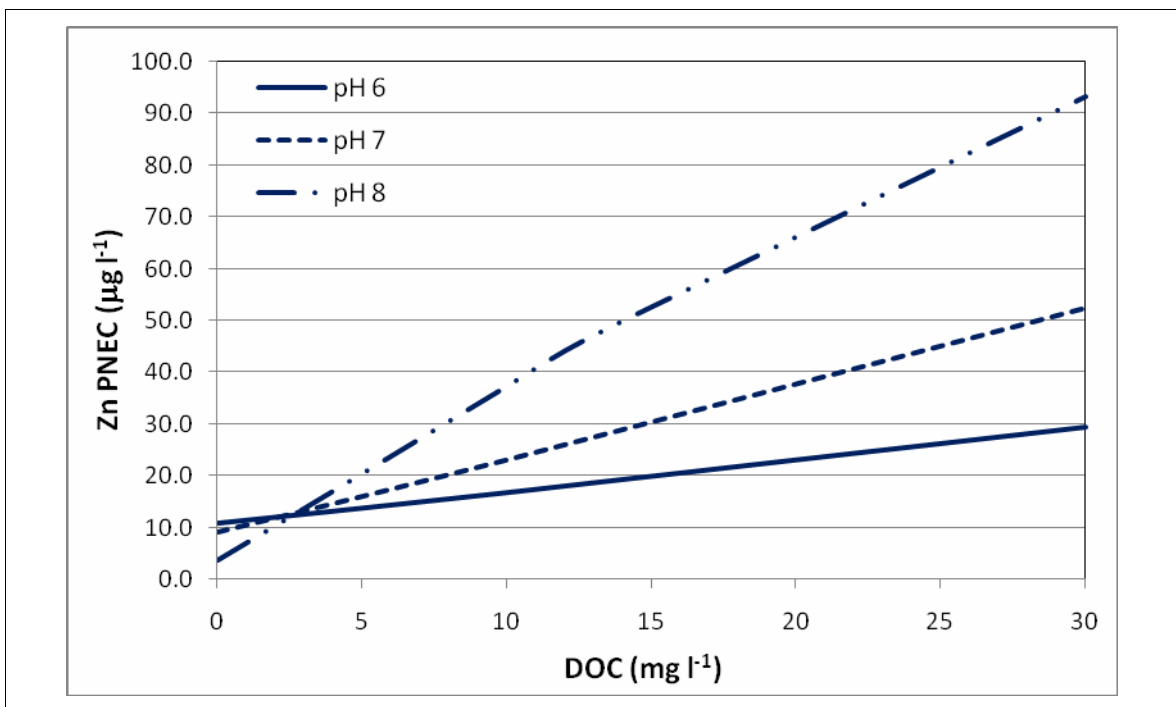


Figure 3.7 Variation in Zn PNEC as a function of DOC concentration for three different pH values (6, 7 and 8)

3.3.4 Dissolved organic carbon concentrations

As is seen for the Cu BLM, the effect of increasing DOC concentrations on the Zn PNEC is approximately linear (for a given set of pH and Ca conditions), and the slope of the relationship depends on the pH (see Figure 3.6). Higher pH values have higher slopes because of increased Zn binding to DOC.

The variation in slope at a given pH value when compared with the case for Cu (Figure 3.2) results from the different binding affinities of the metals. At pH 7, a $1 \text{ mg}\cdot\text{l}^{-1}$ increase in the DOC concentration will increase the PNEC by approximately $2.3 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ (dissolved Zn).

3.3.5 Conditions resulting in BioF values greater than 1

Under some conditions, the Zn BLM calculates BioF values that are greater than 1, indicating that bioavailability under these conditions may be greater than under the conditions for which the generic PNEC has been set. These conditions tend to occur when the DOC and Ca concentrations are low and the pH is high. Where low Ca concentrations ($<5 \text{ mg}\cdot\text{l}^{-1}$) are encountered, the soft water PNEC for Zn should be applied.

3.4 WHAM development and validation

The availability of comprehensive models of metal speciation in natural waters was a prerequisite for developing BLMs. WHAM is the most prominent of these models (Tipping 1994, 1998) and is used in the BLMs, although not all of the BLMs use the same version of WHAM. WHAM is based on conventional chemical reactions and the parameter values are consistent with the known chemical properties of the metal cations. Assumptions have to be made about the nature of dissolved organic matter when the models are applied to natural freshwaters. Several studies have found that WHAM is able to provide good predictions of measured free metal ion concentrations (Tipping 2002, Bryan *et al.* 2002, Zhang 2004), although in some cases there are discrepancies between measurements and model predictions (e.g. Meylan *et al.* 2004). Field validation of WHAM is also limited by available analytical techniques and the differences between these techniques (e.g. Unsworth *et al.* 2006).

The use of WHAM as a subcomponent of the BLMs is considered to have been validated through the validation of the BLMs themselves. The BLMs are able to describe adequately the variation in ecotoxicity between different waters for tested species; it is, therefore, implicit that the chemical speciation components of the BLMs are able to provide an acceptable description of the binding of metals by DOC.

3.5 Range of application of the screening biotic ligand models

The screening BLMs proposed for both Cu and Zn are not considered to require limits to the DOC conditions under which they are applicable. The effect of DOC on metal bioavailability is purely chemical, reducing concentrations of metal ions which can compete for binding at the biotic ligand. The effects of both pH and Ca are more physiological; they can both affect the concentration of metal which may be bound to the biotic ligand. There may, therefore, be a greater need to consider limiting the range

of conditions over which the screening BLMs can operate with respect to these abiotic parameters.

Changes in Ca concentrations tend to have a relatively limited effect on the PNEC, compared with that from changes in DOC concentrations, for both the Cu and Zn BLMs. Furthermore, given the large range of Ca concentrations that are found in UK surface waters, limiting the range of Ca concentrations over which the screening BLMs can be used may result in significant numbers of locations where bioavailability corrections cannot be applied.

The BLMs used for screening purposes are, therefore, limited only to the range of pH conditions over which they can be applied. For the Zn BLM, predictions can be made between pH 6 and 9, and for the Cu BLM, predictions outside the pH range 5.5 to 8.5 will be highlighted with a warning remark.

4 Generic scenarios for selected hydrometric areas

4.1 Background

When deriving default input parameters for screening BLMs, their ability to retain reasonable predictive accuracy is a key consideration. If modelled outputs deviate from the outputs of matched data then the modelled output should tend to overprotect rather than underprotect.

Several generic scenarios for EU conditions have been used in the EU risk assessments for Cu, Ni and Zn. In this project, we have examined several of these scenarios specifically for conditions found in the UK, including conditions within each Environment Agency regulatory region or WFD river basin district, for possible default use. These scenarios provide an excellent communication tool to the regions and water quality teams in the Environment Agency for whom the BLM represents a radical change in their way of working. However, it should be stressed that the derivation and use of default values for water parameters, and the underlying assumptions that accompany this process, are not unique to the use of the BLMs (US EPA 2007). The current use of hardness-based EQSs for metals also relies upon defaults for hardness; the sensitivity of these defaults against matched hardness data is unknown.

Example scenarios are given below for hydrometric areas representing a range of physico-chemical conditions in England and Wales. These scenarios are in the form of graphs of estimated PNECs for:

- matched data – i.e. the matched DOC, Ca and pH data;
- default DOC – matched pH and Ca data, but with a waterbody default DOC value set at the 25th percentile of that in the waterbody;
- default Ca – matched pH and DOC data, but with a waterbody default Ca value set at the 25th percentile of that in the waterbody for Zn and the 75th percentile for Cu;
- default DOC and Ca – matched pH data, but waterbody defaults for both DOC and Ca.

The derivation of default values for DOC are briefly discussed further in Section 6.2.1. A comparison with the current hardness-banded Cu and Zn EQSs is made with each scenario¹ to provide an indication of how the implementation of BLMs might affect compliance assessment.

4.2 Midlands Region

Figure 4.1 shows that the 50th percentile PNEC in the Midlands Region is $9.2 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved). The average Ca concentration is $68 \text{ mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $226 \text{ mg}\cdot\text{l}^{-1} \text{ CaCO}_3$). The current national Dangerous

¹ Hardness values for each scenario are calculated using a factor of 0.3 to account for both Mg and Ca concentrations contributing to total hardness (where $[\text{Mg}]$ is typically $0.3 \times [\text{Ca}]$ and $[\text{Ca}]$ is $0.4 \times [\text{CaCO}_4]$).

Substances Directive (DSD) EQS (DoE 1989) for Cu at this water hardness is $10 \mu\text{g (Cu)}\cdot\text{l}^{-1}$ (dissolved). A revised EQS for Cu was proposed in 1993 which would have resulted in an EQS of $8 \mu\text{g (Cu)}\cdot\text{l}^{-1}$ (dissolved).

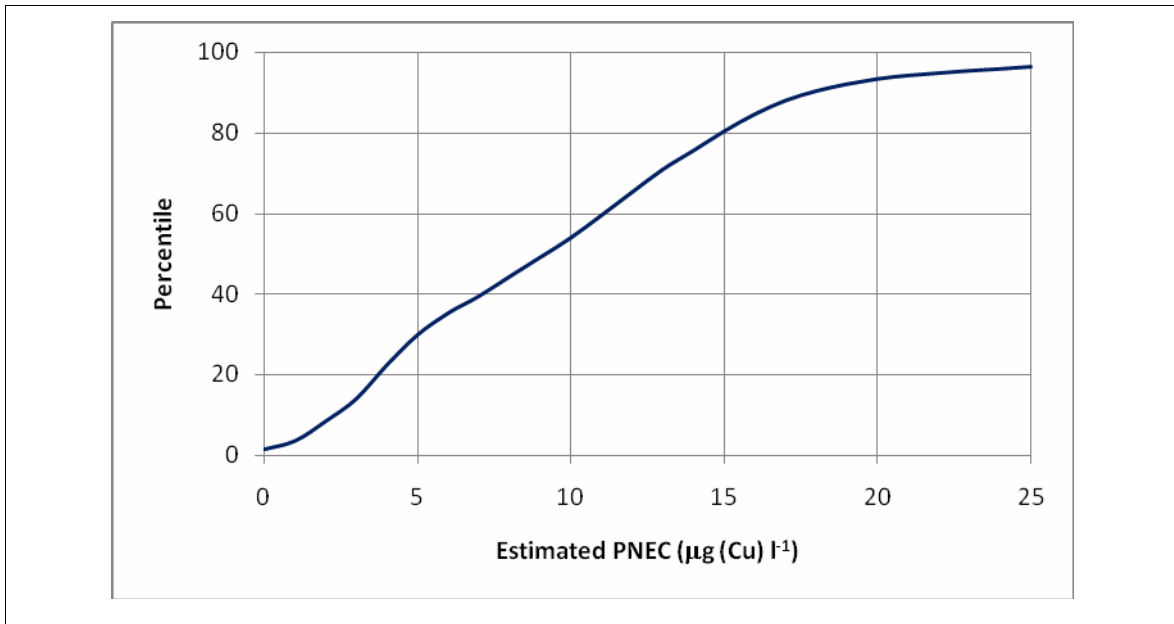


Figure 4.1 Cumulative frequency distribution of estimated PNECs for Cu in the Midlands Region

The scenarios for Cu for the two hydrometric areas in the Midlands Region (Severn and Trent) are given in Figure 4.2 and Figure 4.3.

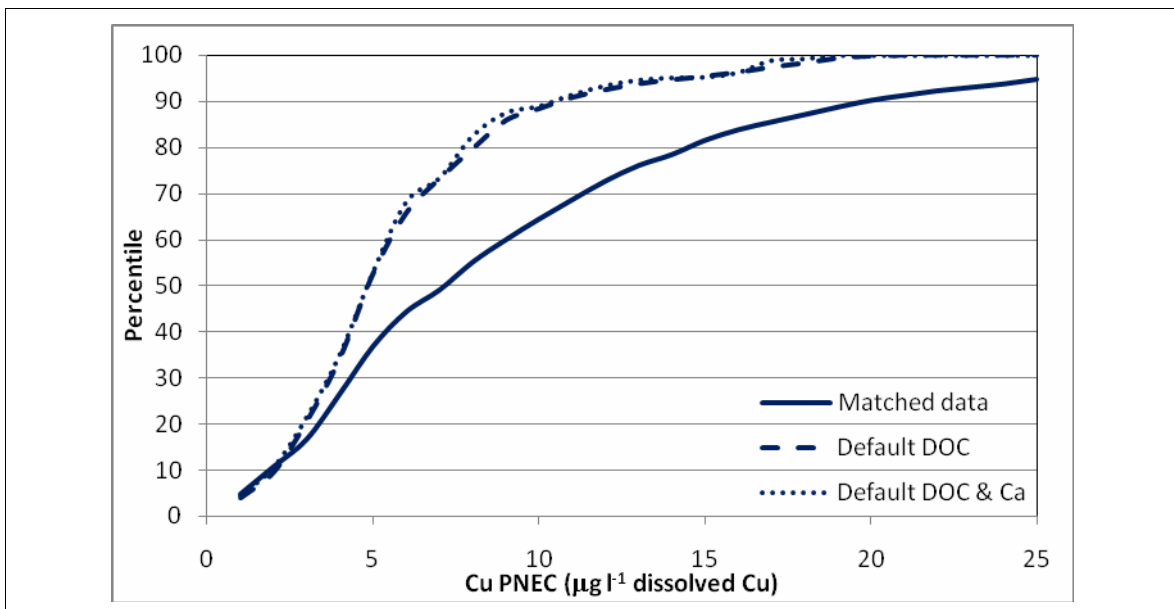


Figure 4.2 Comparison of cumulative frequency distributions for the River Severn of estimated PNECs for Cu using matched data, default DOC values and both default DOC and Ca values with PNEC estimates $<1 \mu\text{g}\cdot\text{l}^{-1}$ not shown (3097 data points)

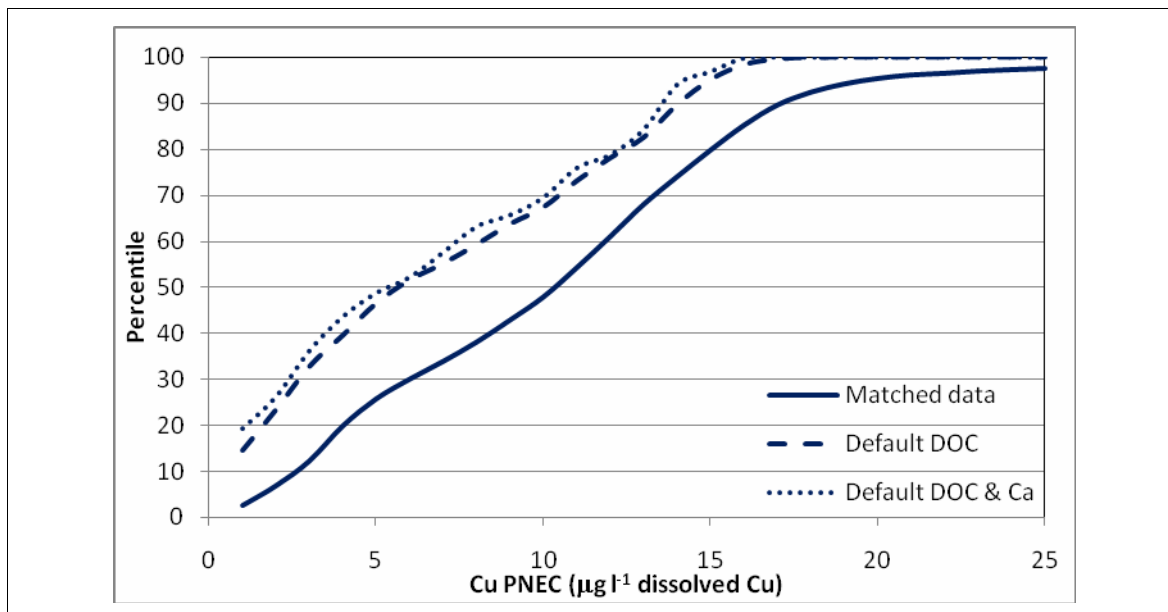


Figure 4.3 Comparison of cumulative frequency distributions for the River Trent of estimated PNECs for Cu using matched data, default DOC values and both default DOC and Ca values with PNEC estimates <math><1 \mu\text{g}\cdot\text{l}^{-1}</math> not shown (5413 data points)

The 50th percentile PNEC for the Trent hydrometric area is approximately $10 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Cu) where matched data are used, falling to approximately $6 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.3). The average Ca concentration for these data is $88 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $292 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Cu at this water hardness is $28 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for salmonid waters and $28 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for non-salmonid waters. A revised EQS for Cu has been proposed, which would have resulted in an EQS of $12 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved).

It is clear from the graphs above that once a default value has been applied to the DOC concentration, there is little change when a default Ca value is also applied. The scenarios for Zn for the River Trent are shown in Figure 4.4.

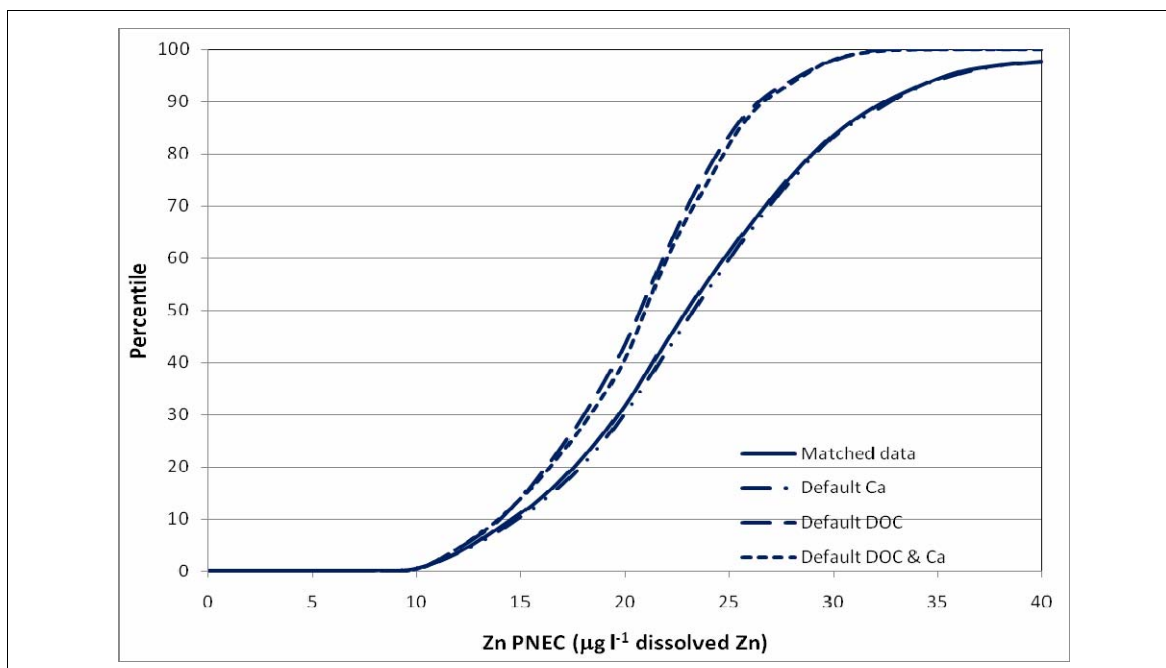


Figure 4.4 Comparison of cumulative frequency distributions for the River Trent of estimated PNECs for Zn using matched data, default Ca values, default DOC values and both default DOC and Ca values (2860 data points)

The 50th percentile PNEC for the Trent hydrometric area is approximately $23 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Zn) where matched data are used, falling to approximately $21 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied. The average Ca concentration for these data is $88 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $292 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Zn at this water hardness is $125 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for salmonid waters and $500 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for non-salmonid waters. A revised EQS for Zn has been proposed, which would have resulted in an EQS of $50 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (dissolved).

4.3 South West Region

The scenarios for Cu and Zn for the Dart hydrometric area are given in Figures 4.5 and 4.6, respectively.

The 50th percentile PNEC for the Dart hydrometric area is approximately $4.3 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Cu) where matched data are used, falling to approximately $3.3 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.5). The average Ca concentration for these data is $36 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $120 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Cu at this water hardness is $10 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for salmonid waters and $10 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for non-salmonid waters. A revised EQS for Cu has been proposed, which would have resulted in an EQS of $3 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved).

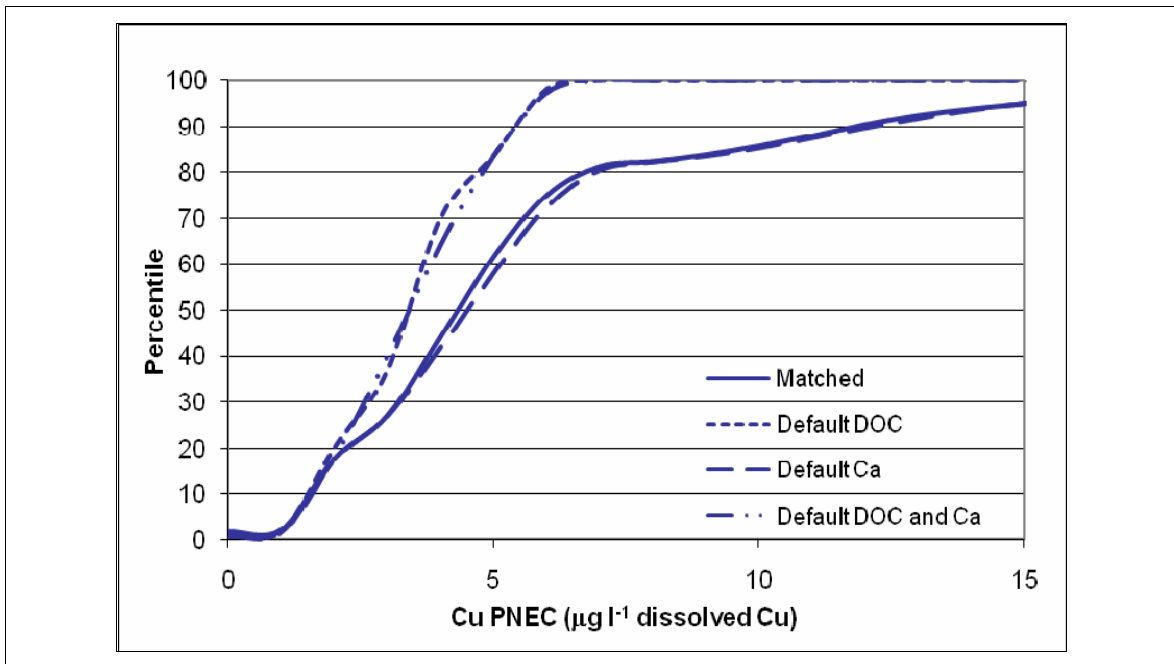


Figure 4.5 Comparison of cumulative frequency distributions for the River Dart of estimated PNECs for Cu using matched data, default Ca values, default DOC values and both default DOC and Ca values (1713 data points)

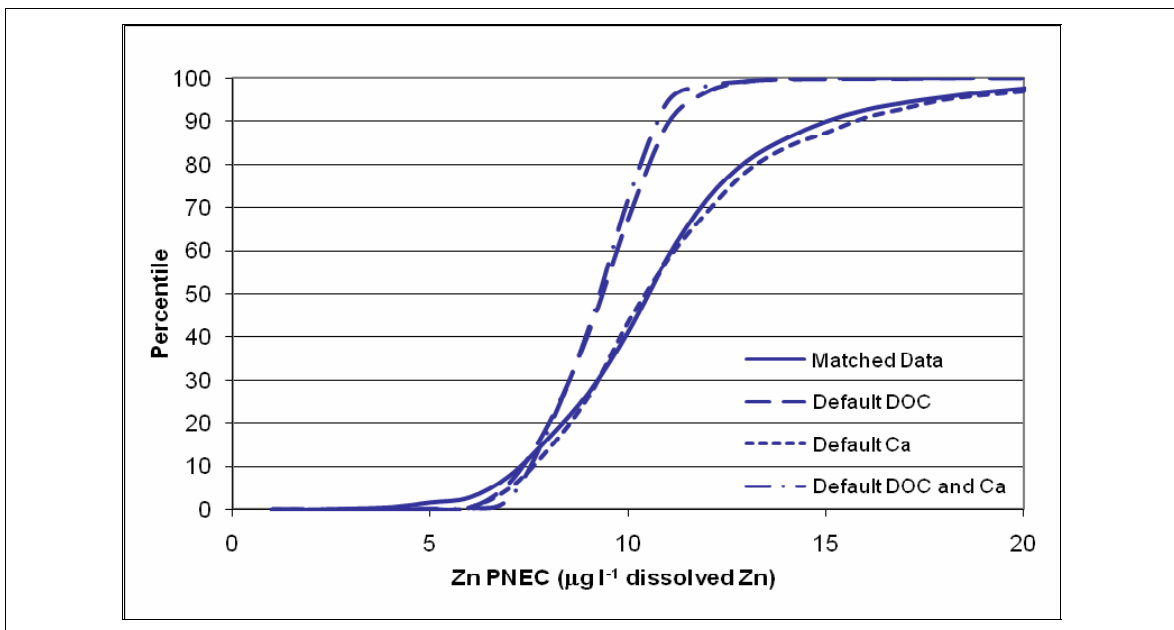


Figure 4.6 Comparison of cumulative frequency distributions for the River Dart of estimated PNECs for Zn using matched data, default Ca values, default DOC values and both default DOC and Ca values (1713 data points)

The 50th percentile PNEC for the Dart hydrometric area is approximately $10 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Zn) where matched data are used, falling to approximately $9 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.6). The average Ca concentration for these data is $36 \text{ mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $120 \text{ mg}\cdot\text{l}^{-1} \text{ CaCO}_3$). The current national DSD EQS (DoE 1989) for Zn at this water hardness is $75 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for salmonid waters and $250 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for non-salmonid waters. A

revised EQS for Zn has been proposed, which would have resulted in an EQS of $15 \mu\text{g (Zn)}\cdot\text{l}^{-1}$ (dissolved).

4.4 Anglian Region

The scenarios for Cu and Zn for the Great Ouse hydrometric area are given in Figures 4.7 and 4.8, respectively.

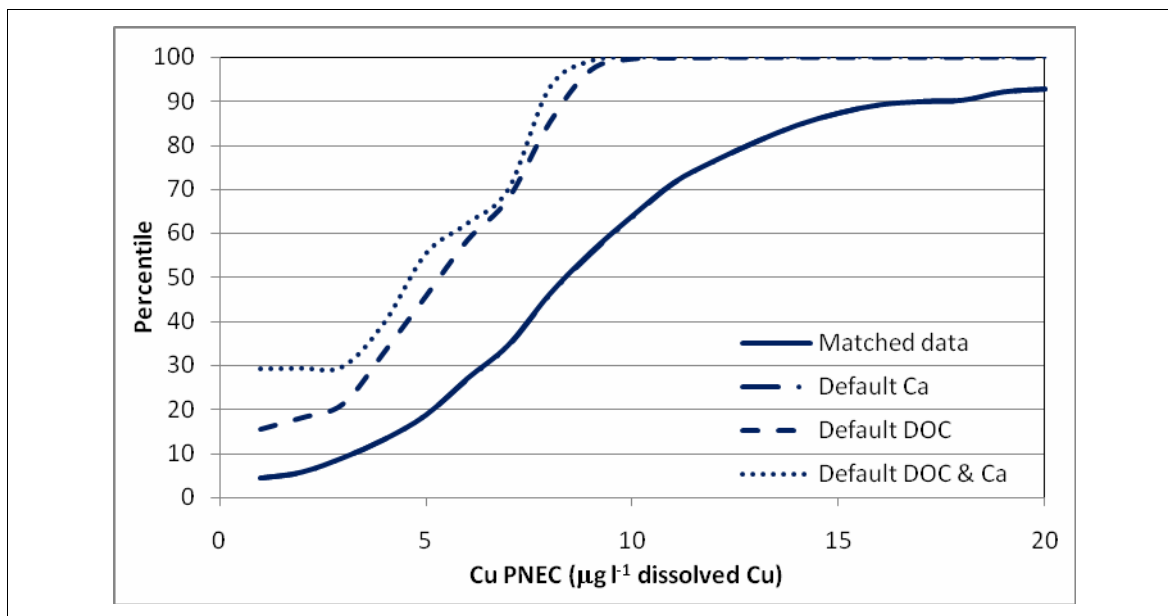


Figure 4.7 Comparison of cumulative frequency distributions for the Great Ouse of estimated PNECs for Cu using matched data, default Ca values, default DOC values and both default DOC and Ca values (877 data points)

The 50th percentile PNEC for the Great Ouse hydrometric area is approximately $8 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Cu) where matched data are used, falling to approximately $5 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.7). The average Ca concentration for these data is $156 \text{ mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $520 \text{ mg}\cdot\text{l}^{-1} \text{ CaCO}_3$). The current national DSD EQS (DoE 1989) for Cu at this water hardness is $28 \mu\text{g (Cu)}\cdot\text{l}^{-1}$ (dissolved) for salmonid waters and $28 \mu\text{g (Cu)}\cdot\text{l}^{-1}$ (dissolved) for non-salmonid waters. A revised EQS for Cu has been proposed, which would have resulted in an EQS of $12 \mu\text{g (Cu)}\cdot\text{l}^{-1}$ (dissolved).

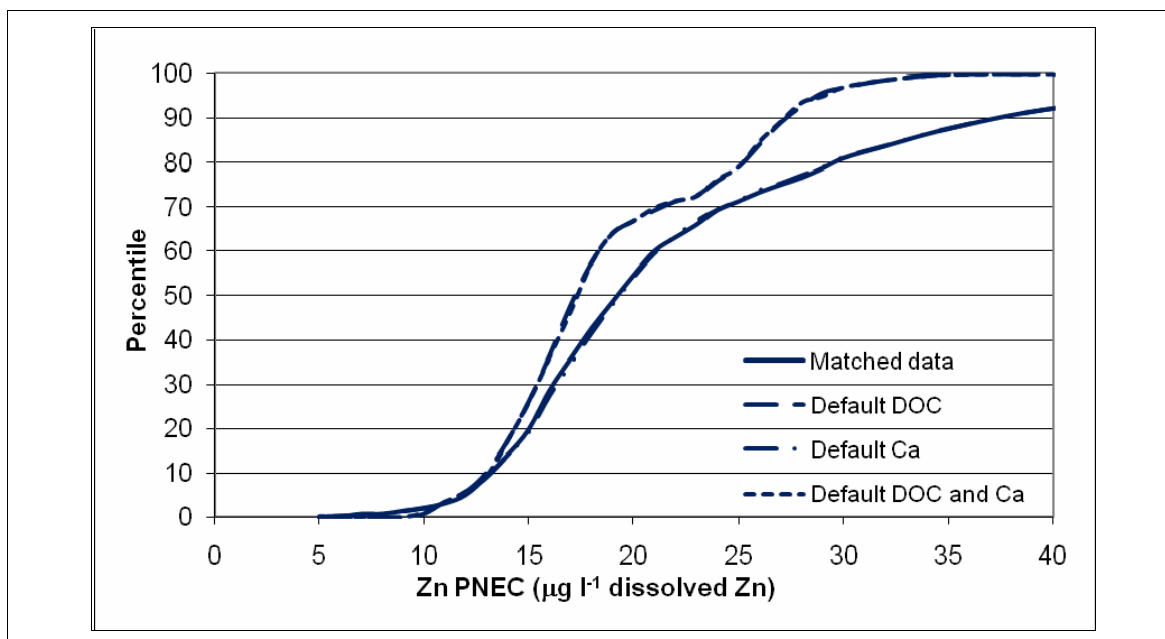


Figure 4.8 Comparison of cumulative frequency distributions for the Great Ouse of estimated PNECs for Zn using matched data, default Ca values, default DOC values and both default DOC and Ca values (877 data points)

The 50th percentile PNEC for the Great Ouse hydrometric area is approximately $19 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Zn) where matched data are used, falling to approximately $17 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.8). The average Ca concentration for these data is $156 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $520 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Zn at this water hardness is $125 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for salmonid waters and $500 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for non-salmonid waters. A revised EQS for Zn has been proposed, which would have resulted in an EQS of $50 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (dissolved).

4.5 Welsh Region

The scenarios for Cu and Zn for the Dovey hydrometric area are given in Figures 4.9 and 4.10, respectively.

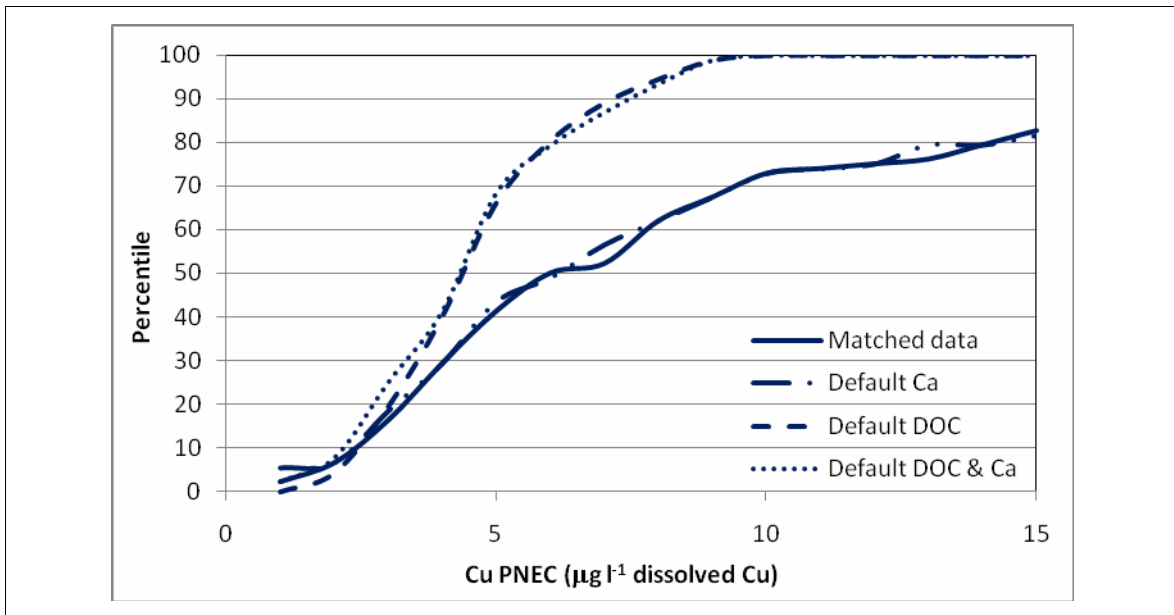


Figure 4.9 Comparison of cumulative frequency distributions for the River Dovey of estimated PNECs for Cu using matched data, default Ca values, default DOC values and both default DOC and Ca values (92 data points)

The 50th percentile PNEC for this hydrometric area is approximately $6 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Cu) where matched data are used, falling to approximately $4 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.9). The average Ca concentration for these data is less than $3 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $10 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Cu at this water hardness is $1 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for salmonid waters and $1 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for non-salmonid waters. A revised EQS for Cu has been proposed, which would have resulted in an EQS of $0.5 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved).

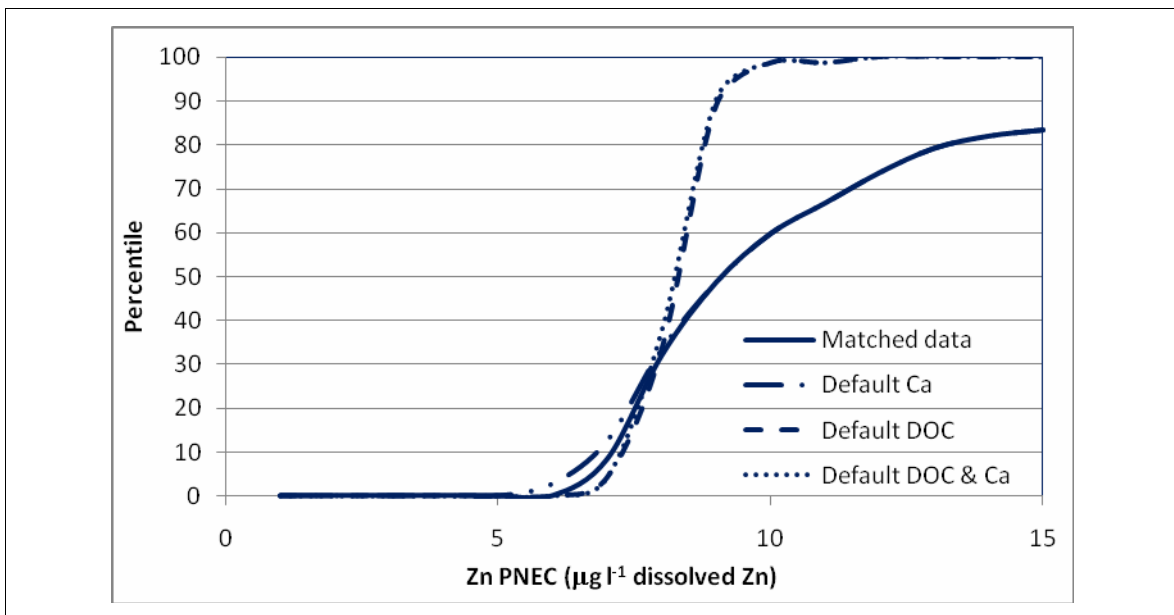


Figure 4.10 Comparison of cumulative frequency distributions for the River Dovey of estimated PNECs for Zn using matched data, default Ca values, default DOC values and both default DOC and Ca values (92 data points)

The 50th percentile PNEC for this hydrometric area is approximately $9 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Zn) where matched data are used, falling to approximately $8 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.10). The average Ca concentration for these data is less than $3 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $10 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Zn at this water hardness is $8 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for salmonid waters and $75 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for non-salmonid waters. A revised EQS for Zn has been proposed, which would have resulted in an EQS of $8 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (dissolved).

4.6 Thames Region

The scenarios for Cu and Zn for the Thames hydrometric area are given in Figures 4.11 and 4.12, respectively.

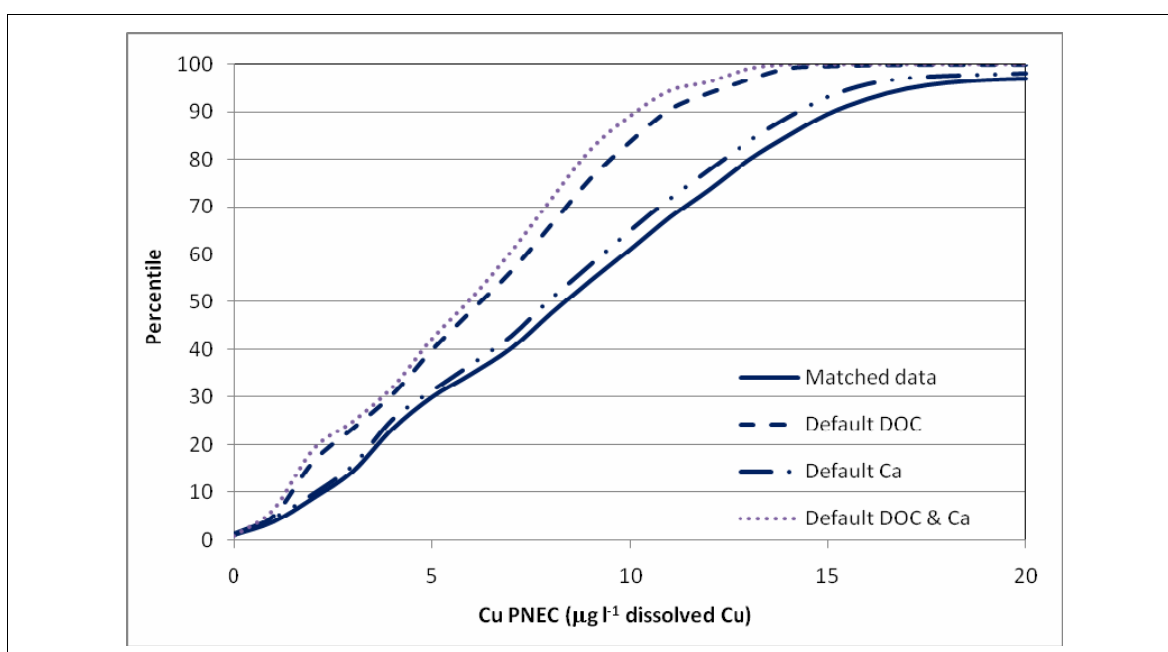


Figure 4.11 Comparison of cumulative frequency distributions for the River Thames of estimated PNECs for Cu using matched data, default Ca values, default DOC values and both default DOC and Ca values (3995 data points)

The 50th percentile PNEC for this hydrometric area is approximately $8 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Cu) where matched data are used, falling to approximately $6 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.11). The average Ca concentration for these data is $105 \text{mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $350 \text{mg}\cdot\text{l}^{-1} \text{CaCO}_3$). The current national DSD EQS (DoE 1989) for Cu at this water hardness is $28 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for salmonid waters and $28 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved) for non-salmonid waters. A revised EQS for Cu has been proposed, which would have resulted in an EQS of $12 \mu\text{g}(\text{Cu})\cdot\text{l}^{-1}$ (dissolved).

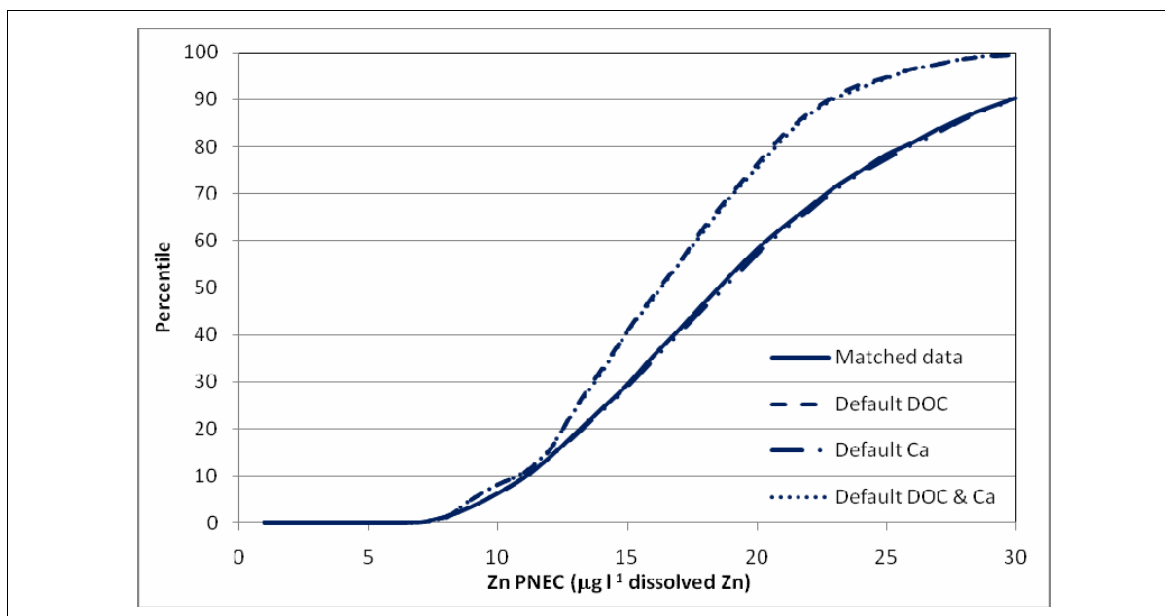


Figure 4.12 Comparison of cumulative frequency distributions for the River Thames of estimated PNECs for Zn using matched data, default Ca values, default DOC values and both default DOC and Ca values (3995 data points)

The 50th percentile PNEC for this hydrometric area is approximately $18 \mu\text{g}\cdot\text{l}^{-1}$ (as dissolved Zn) where matched data are used, falling to approximately $16 \mu\text{g}\cdot\text{l}^{-1}$ where default DOC values are applied (Figure 4.12). The average Ca concentration for these data is $<105 \text{ mg}\cdot\text{l}^{-1}$ (approximating to a hardness equivalent of about $350 \text{ mg}\cdot\text{l}^{-1} \text{ CaCO}_3$). The current national DSD EQS (DoE 1989) for Zn at this water hardness is $125 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for salmonid waters and $500 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (total) for non-salmonid waters. A revised EQS for Zn has been proposed, which would have resulted in an EQS of $50 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$ (dissolved).

Calculations were also performed using the Cu BLM for a subset of 230 data points from the Thames hydrometric area for scenarios using both measured and default DOC concentrations. The results of these calculations are shown in Figure 4.13. The BLM calculations used measured alkalinity data and estimated concentrations of other major ions from Ca concentrations (according to the relationships shown in Section 2.6.3). Using an estimated Na concentration, rather than a low default value, for the Cu BLM calculations should result in more-accurate PNEC values and make the Cu PNEC Estimator calculations more conservative relative to the Cu BLM predictions.

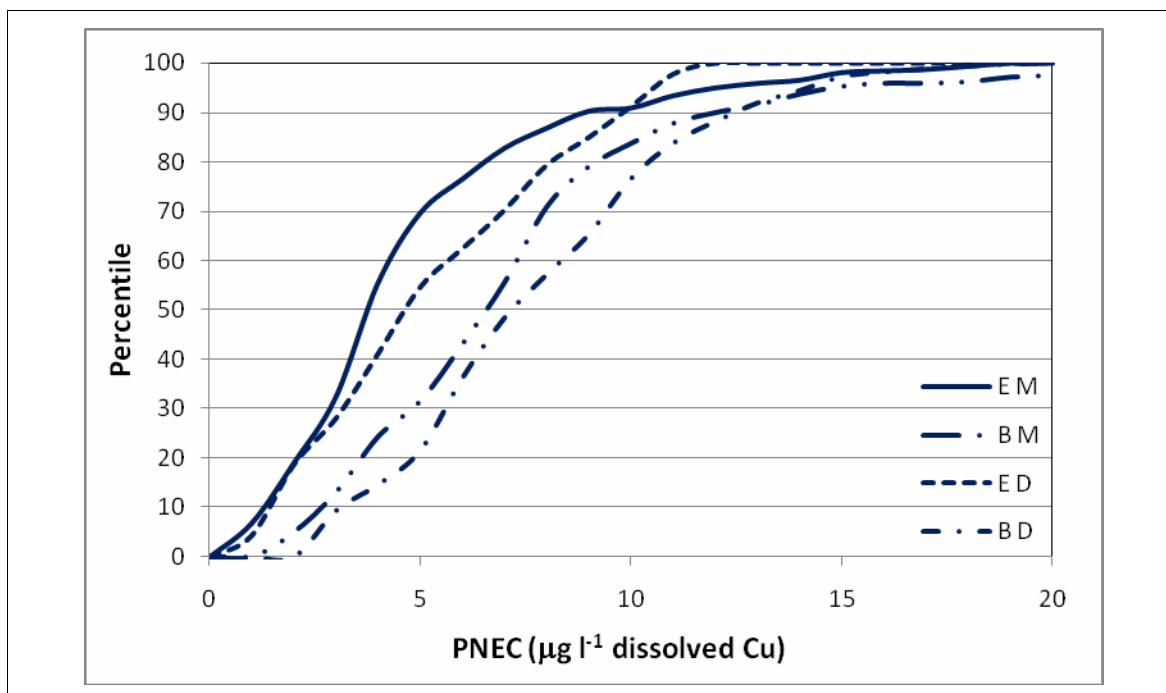


Figure 4.13 Comparison of cumulative frequency distributions for the River Thames of estimated PNECs and PNECs calculated with the Cu BLM using matched data and default DOC values; E and B indicate Cu PNEC Estimator and Cu BLM calculations, respectively, and M and D indicate measured or default DOC concentrations, respectively (230 data points)

The Cu PNEC Estimator results in conservative estimates of the PNEC compared with those values from the Cu BLM (Figure 4.14 and Table 4.1). The Cu PNEC Estimator typically results in PNECs that are around 2 to 3 $\mu\text{g}\cdot\text{l}^{-1}$ (dissolved Cu) lower than the true PNEC values, although they are much more conservative in a very small number of cases (Figure 4.14). This situation differs from the findings regarding the testing of the Cu PNEC Estimator, where it was found to slightly overestimate true PNEC values. This difference is most likely due to the Na concentrations used: in the case above, Na concentrations were assumed to vary with Ca concentrations, whereas for the development and testing of the Cu PNEC Estimator, a low Na concentration was assumed for all conditions. This treatment of Na in the development of the Cu PNEC Estimator appears to result in generally conservative estimates of the true PNEC value.

Table 4.1 Cu PNECs for the Thames hydrometric area calculated by the Cu PNEC Estimator and the Cu BLM using measured and default DOC data¹

DOC input	Cu PNEC Estimator		Cu BLM	
	Measured	Default	Measured	Default
10th Percentile	1.29	1.57	2.75	3.33
25th Percentile	2.56	2.83	4.13	5.29
50th Percentile	3.82	4.48	6.67	7.09

Notes: ¹ All PNEC values are expressed as $\mu\text{g}\cdot\text{l}^{-1}$ dissolved Cu.

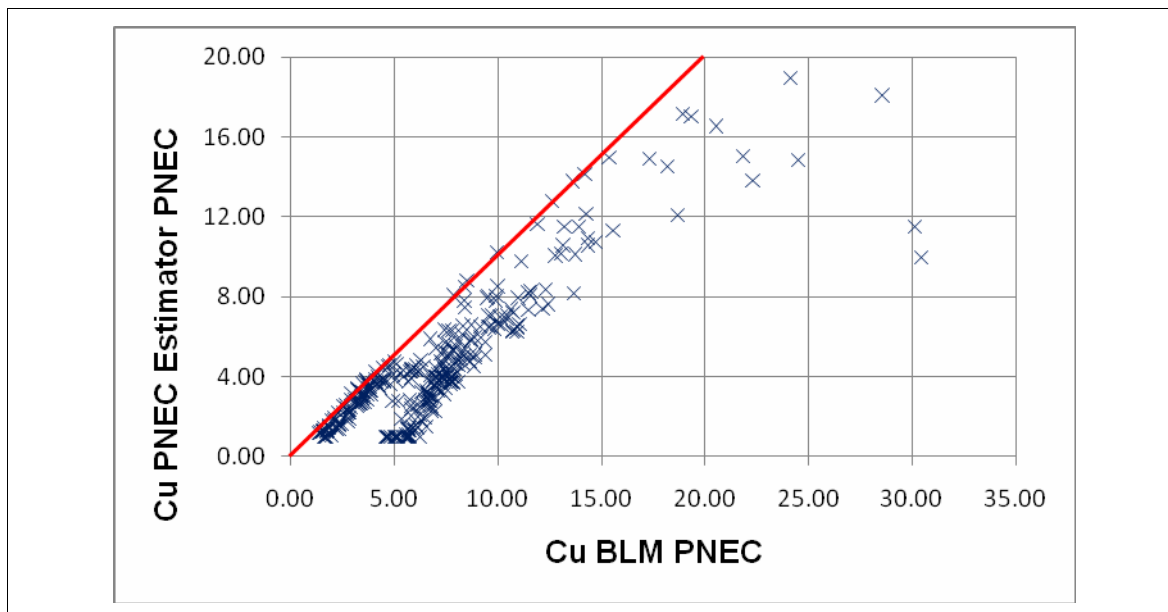


Figure 4.14 Comparison of Cu PNEC Estimator and Cu BLM calculations for the data shown in Figure 4.13

Figure 4.13 also shows that the distributions of calculations performed using measured DOC data have resulted in lower PNEC values than those generated using the default DOC values (set at the 25th percentile for the waterbody). This situation is in contrast to other examples shown in this section. We reduced the number of data points used in the calculations by including only freshwater samples taken for particular purposes. This was necessary because performing Cu BLM calculations for all of the data points (3995) would have been impractical, especially if the calculations also needed to be repeated using default DOC data. Selecting only samples collected for particular purposes may have introduced some bias into the data used. The sampling points from which data were used may not provide the best reflection of the typical DOC concentrations for the waterbody because, in many cases, the measured DOC concentrations were lower than the default DOC concentrations.

4.7 Comparison of zinc standards expressed as different forms (total or dissolved)

It is difficult to compare the different EQS values for dissolved and total Zn. However, assuming the standard environmental conditions employed in the EU Technical Guidance Document (EC 2003) and a typical partition coefficient, approximately 35 to 40 per cent of total zinc would likely be present in the dissolved phase.

Assuming these conditions are appropriate for the River Trent, the EQS for salmonid waters of $125 \mu\text{g}\cdot\text{l}^{-1}$ total Zn is approximately equivalent to 40 to $50 \mu\text{g}\cdot\text{l}^{-1}$ dissolved Zn, comparable with the revised EQS of $50 \mu\text{g}\cdot\text{l}^{-1}$ dissolved Zn that was proposed. The partitioning of Zn between the dissolved and particulate phases is determined by a variety of factors, such as the quality and quantity of suspended matter and the local water chemistry conditions, including pH, DOC and concentrations of suspended solids.

4.8 Derivation of generic predicted no-effect concentrations for individual hydrometric areas

Generic PNECs can be established for individual hydrometric areas based on information about the range of bioavailability conditions, or PNECs, which can be expected for the area. Precisely how such a generic PNEC should be set depends on the purpose for which the PNEC will be used. A PNEC that is to be used as the first tier in a tiered risk assessment should be set at, or close to, the highest bioavailability conditions that may be expected. This approach would take a low percentile of the distributions shown earlier in this section and significant failures would be expected. A PNEC that is used to describe the typical conditions within a hydrometric area may be set as the 50th percentile, although it may not necessarily be protective over the entire range of conditions which are experienced.

Generic PNECs that are to be applied as a first tier screen within a tiered assessment process might reasonably be based on the 5th or 10th percentile of the distribution of PNECs. In the case of Cu, this is likely to be in the range 1 to 3 $\mu\text{g}\cdot\text{l}^{-1}$ dissolved Cu, and for Zn the range might be closer to 5 to 15 $\mu\text{g}\cdot\text{l}^{-1}$ dissolved Zn (using the generic PNEC from the ESR risk assessment). Generic PNECs that are set on this basis are likely to generate regular failures because they represent relatively extreme conditions of bioavailability; however, they would provide a relatively high level of protection where they are met. A conservative generic PNEC is considered to be a practical option where tools are available that allow corrections for bioavailability to be considered, as is the case for Cu and Zn.

There may be cases where generic PNECs set on a hydrometric area basis are advantageous, although environmental regulators may prefer to use a single screening level standard (set on a countrywide basis), which can be corrected for bioavailability. If this is the case, then a generic bioavailability correction (BioF) for each hydrometric area may be more useful than a PNEC. Generic BioF values could either be based upon typical sets of conditions (which would result in a typical bioavailability), or on the typical resulting bioavailability (regardless of the conditions). The latter approach has been taken in this case because there are a variety of different combinations of conditions that can result in a similar PNEC.

5 Final compliance package

5.1 Introduction

The key objectives of the project have been met and discussed in the previous sections; however, there remain a number of outstanding generic implementation issues that require resolution. These issues are not specifically related to the use of the BLMs, but are concerned more broadly with the implementation of metal EQSs. These include the use of single EQSs for Cu and Zn rather than the derivation of site-specific values (cf. US EPA 2007), the derivation and use of background concentrations of Cu and Zn, the framework of compliance in which speciation and background considerations may be used and the development of short-term EQSs for Cu and Zn.

The solutions to these many challenges are likely to be found through a combination of scientific assessment and policy decisions. There are unlikely to be definitive answers to some of these issues and, therefore, multiple criteria organisational considerations will have a great bearing on the decisions that are taken. This section describes some of the scientific thinking behind these issues and provides some options for technical resolution. It does not consider the broader organisational or policy-related debate, which is beyond the scope of this project.

5.2 Generic predicted no-effect concentration or environmental quality standard values

There are two possible methods by which monitoring data can be assessed for compliance against an environmental benchmark. These two methods are:

- i. Use of a single generic PNEC (or EQS) against which compliance will be assessed.
This PNEC relates to conditions of high bioavailability (i.e. worst case conditions in reference to environmental risk) and is effectively expressed as a concentration of bioavailable metal. Monitoring data for dissolved metals are corrected for bioavailability by multiplying by a bioavailability factor (BioF), obtained from the BLM, to convert them into a bioavailable metal concentration. The bioavailable concentration from field data is then compared with the generic EQS.
- ii. PNEC values are derived on a site-specific basis and are expressed as a dissolved metal concentration.
The site-specific PNEC is then compared directly to the monitored dissolved metal concentration.

The first method, in which a generic PNEC or EQS is applied, may be more readily integrated into a tiered approach for compliance assessment. Traditionally, the use of single generic (or hardness-banded) EQSs has been the methodology followed in the UK for metals. However, in the example above, the generic PNEC may be applied as a screening level assessment to all sites; those sites at which measured concentrations do not exceed this PNEC will not require assessment for bioavailability. Those sites where dissolved metal concentrations do exceed the generic PNEC are further assessed in terms of their metal bioavailability, i.e. the BioF is calculated.

If such an approach is used, it will be important that the generic PNEC is low enough to ensure that false negatives do not occur at an unacceptably high rate, i.e. that sites where metal bioavailability is high are identified as potential issues when their metal levels are also elevated. For example, the use of the generic scenarios presented in the Cu voluntary risk assessment report (ECI 2007) may not be sufficiently protective over the complete range of conditions found in England and Wales, although they would be protective in most cases.

The second method for compliance assessment represents a significantly more streamlined process with fewer steps and does not rely on the derivation of a generic PNEC or EQS that must be useable under all physico-chemical conditions. However, it marks a significant departure from the current system of compliance assessment; using as many EQSs as there are waterbodies, rather than a single limit value, may be viewed by some as complex and unmanageable. This approach has been adopted by the US EPA (2007) in assessing acute Cu exposures. Furthermore, the approach can be streamlined through the use of 'look-up' tables, which are tools widely used by regulators.

There are difficulties in defining the conditions under which bioavailability is maximised because of a number of confounding factors. For example, there are differences in organism responses to metal toxicity under different water quality conditions. Invertebrates may be most sensitive at low pH conditions, but algae more sensitive at high pH, so the bioavailability of metal to invertebrates may be different to that for algae, i.e. bioavailability can be organism specific.

Furthermore, because the generic PNEC accounts for toxicity under extreme water conditions, it may behave as a 'funnel' not a 'filter', i.e. all sites end up requiring bioavailability assessment. For example, in the Cu voluntary risk assessment report (ECI 2007), when the ecotoxicity database was normalised to one specific set of water conditions using the BLM, an average reduction across all species in Cu toxicity of 10–80 per cent was noted. This suggests that by setting the generic EQS at the bioavailability of water quality extremes, the majority of waterbodies will fail the first screen, which would make it useless. However, the ability to automatically provide a bioavailability correction factor from a limited set of supporting parameters means that this need not represent a significant problem.

The Cu BLM recalculates the entire SSD to determine a PNEC under specific bioavailability conditions at the site of interest. A generic PNEC or EQS, set at the 5th or 10th percentile of the calculated PNECs for all the hydrometric areas, may provide a first tier screen, although the usefulness of such a screen may be limited because of the number of sites which require further investigation. The majority of the calculations of PNEC values for selected hydrometric areas were performed with the Cu PNEC Estimator tool rather than the Cu BLM. The use of the Estimator appears to result in slightly lower PNEC values than the Cu BLM, which could further exacerbate this problem. A first tier screening EQS of $1 \mu\text{g}\cdot\text{l}^{-1}$ would be consistent with the current national EQS for Cu, and we propose that this value be considered as a generic EQS for Cu.

The situation for Zn is different to that for Cu as a generic PNEC has been derived in the Zn risk assessment report (The Netherlands 2004) and this has been applied in the calculations throughout this report ($7.8 \mu\text{g}(\text{Zn})\cdot\text{l}^{-1}$, see Section 3.3). It should be noted, however, that a PNEC derived for generic risk assessment purposes may not necessarily be directly applicable as an EQS. The effect on the characterisation of Zn risks of using an assessment factor of 2 on the HC_5 to derive the PNEC is discussed further in Section 5.3.3.

5.3 Background concentrations

5.3.1 Introduction

The derivation and use of background concentrations of metals in assessing EQS compliance are not new challenges, yet the fact that they remain challenges indicates mixed progress in meeting them. The difficulties of establishing background concentrations of metals in any media include:

- Definition – what is a background concentration of a metal?
- Derivation and measurement – once a definition has been agreed, do datasets exist that enable a background concentration in the media to be determined?
- How do metal background concentrations vary across waterbodies and do they meet the ecological and environmental requirements of the definition?
- Framework for use – how will the metal background concentration be used (Section 5.6)?

With regard to definition, it is clear that the usual, or ambient, concentration of a metal in freshwaters consists of a natural geochemical fraction and an anthropogenic fraction (ISO 2004). The anthropogenic fraction refers to moderate diffuse inputs into the waterbody and not inputs from local point sources that generally result in appreciably elevated concentrations. Therefore, as there are very few regions in Europe that could claim to be unaffected by low level anthropogenic metal inputs, the term ‘natural’ background is redundant and therefore perhaps ‘ambient’ background would be a more appropriate term. The ambient background concentration of a metal would, therefore, be the concentration of metal measured in a waterbody subject to low anthropogenic pressure.

Different ecoregions can be identified across the UK in terms of the physico-chemical characteristics of the waters, the boundaries of the environmental compartments and their representative species. Such ecoregions have also been termed ‘metalloregions’ and can be differentiated on the basis of the natural background concentration of the metal under consideration and the presence of well-defined abiotic factors that influence metal bioavailability (ICMM 2007). The metalloregion approach recognises that background concentrations of a metal in a given ecoregion can differ from one ecosystem to another, resulting in different sensitivities to the toxic effects of metals because of acclimation or adaptation. This approach further suggests that instead of using ‘generic’ species sensitivity distributions to derive PNECs or EQSs, it is preferable to use ‘endemic’ test organisms to characterise the sensitivity of the ecosystem as they represent the natural environment under investigation. However, while this approach is probably technically correct, it will likely be of limited practical relevance for most metals because of the paucity of knowledge on the geographical distribution of metal background concentrations in many ecological systems.

In the Netherlands, background concentrations of metals are widely used in the derivation and use of environmental risk limits. The methodology to determine the background is to use the geometric mean values (90th percentiles are used for groundwaters) of measured monitoring data from pristine areas, although this is an area of active discussion (Fraters *et al.* 2001). Nevertheless, it is acknowledged that the final choice of methodology for the derivation of backgrounds is a policy and not a scientific decision (van Vlaardingen *et al.* 2005). Corrections for background concentrations should be applied to the measured exposure data to render them comparable to the $PNEC_{add}$. It is also possible, in principle, to correct the $PNEC_{add}$ to be

directly comparable with the measured environmental concentration, through the addition of a background correction. Whilst the two approaches result in slightly differing RCRs, the conclusions of the characterisations are likely to be the same.

When a background concentration is applied, the PNEC is defined as:

$$\text{PNEC}_{\text{site}} = \text{PNEC}_{\text{generic}} + \text{Concentration}_{\text{background}}$$

This implies that the background concentration may be applied either to the effects side of the assessment ($\text{PNEC}_{\text{generic}} + \text{Concentration}_{\text{background}}$) or to the exposure side of the assessment ($\text{PNEC}_{\text{site}} - \text{Concentration}_{\text{background}}$) by rearranging the equation. This is appropriate where all of the parameters are expressed in the same terms, such as a dissolved metal concentration. If all of the parameters are expressed in different forms then corrections may need to be applied, or assumptions made about the bioavailability of the background concentration.

Where the $\text{PNEC}_{\text{generic}}$ is effectively expressed as a bioavailable concentration of the metal (i.e. under conditions of maximum bioavailability) and the $\text{PNEC}_{\text{site}}$ is expressed as a dissolved metal concentration (for comparison against a measured dissolved metal concentration), then a bioavailability correction is required for a background concentration that is expressed as a dissolved concentration (e.g. if it is derived from dissolved metal monitoring data).

This implies that a background concentration expressed as dissolved metal can be subtracted from a measured dissolved concentration before assessment against the $\text{PNEC}_{\text{generic}}$, but that a background concentration which is expressed as a dissolved concentration should be corrected for bioavailability before being added to the $\text{PNEC}_{\text{generic}}$ (which is expressed as a bioavailable concentration).

Alternatively, it has sometimes been assumed that background concentrations are entirely unavailable (Crommentuijn et al. 1997), although there is no scientific justification for making this assumption, particularly where the background concentrations are derived from dissolved metal monitoring data.

5.3.2 Methods for the determination of background concentrations

Efforts to describe background concentrations over large spatial scales have largely failed because of the variability in background concentrations and difficulties in defining what the background concentration should actually represent. However, if we were to take the definition of the ambient background concentration (ABC) of a metal as that concentration measured in a waterbody with relatively low (or possibly relatively recent) anthropogenic pressure or pristine conditions, then a number of datasets are available in the UK that could facilitate the derivation of ABCs.

In a recent collaborative project with the British Geological Survey (BGS), the Environment Agency (2008a) reviewed the feasibility of developing ABCs for metals across England and Wales using the G-Base Atlas. This atlas is based on measured metal concentrations from one-off samples taken from stream waters at relatively unimpacted sites. The feasibility study also used these measurements to derive median background reference concentrations for four broad geological typologies (carboniferous, siliceous, peat and salt). For many metals, the parent materials explained very little of the variability in ABCs (at best 38 per cent). Furthermore, the data coverage of G-Base is very limited and has only partial coverage of England and Wales. However, it was clear from the project that the spatial scale at which the ABCs needed to be derived to ensure compliance with an EQS depended on a number of

factors including the metal under consideration. Unsurprisingly, the more localised and site specific the scale of derivation, the more relevant the ABC.

Other data resources do exist in which samples of stream waters have been taken from relatively pristine waters or primary streams, including the FOREGS database (<http://www.gsf.fi/publ/foregsatlas>). Unlike G-Base, this data set has national coverage, but suffers from low sample intensity ($n \approx 80$ for the UK) and therefore gives only limited spatial discrimination. A recent analysis of pressures on RIVPACS reference sites (Davy-Bowker *et al.* 2007) considered Cu and Zn concentrations at these unimpacted sites and reported the ranges of dissolved Cu and Zn concentrations for the different GB TWINSPAN end groups. This information may also be useful in defining appropriate ABCs for use in compliance assessment.

The ABC may also be adequately described by a low percentile of the ambient local monitoring data or the reporting limit, or limit of detection of the analytical method. Alternatively, the ABC may be set on the basis of an 'average' or typical concentration taken from a dataset that includes only monitoring at locations which have not been directly impacted by local emissions of the substance of interest. Indeed, according to the ISO (2004) definition for soils, the 'usual background value' of a substance in soils can be set at a chosen value taken from the frequency distribution of usual concentrations. Such approaches could be applied to a large number of datasets, although the methodology using a typical concentration assumes that any significant emissions will result in higher concentrations and therefore only have a limited effect on the background concentration derived. The second approach was taken for the Environment Agency BGS Report (Environment Agency 2008a), although data coverage was not complete for England and Wales because of the specialist nature of the dataset.

Both of these approaches have been assessed using Environment Agency data ($n = 482$) for dissolved Zn from the Mersey hydrometric area. As the data were taken from an older Environment Agency dataset, it had a significant proportion of 'less than' values. In order to estimate the background concentration as a low percentile of a distribution, it was necessary to extrapolate information about the frequency distribution of the data (Figure 5.1). This results in a relationship between the dissolved Zn concentration and the percentile of the data distribution:

$$\text{Percentile} = 57.61 \times (\log_{10} (\text{dissolved Zn, } \mu\text{g}\cdot\text{l}^{-1})) - 22.37$$

Values for the 5th and 10th percentiles can then be derived accordingly as 3.0 and 3.7 $\mu\text{g}\cdot\text{l}^{-1}$ dissolved Zn. Clearly, the value of a particular percentile of the dataset will depend, to some extent at least, on the overall size of the dataset. The second approach, in which the ABC is set to the reporting limit or limit of detection of the analytical method would, in this case, give a value 5 $\mu\text{g}\cdot\text{l}^{-1}$. This last method is the least sophisticated and scientifically robust of the methods considered so far.

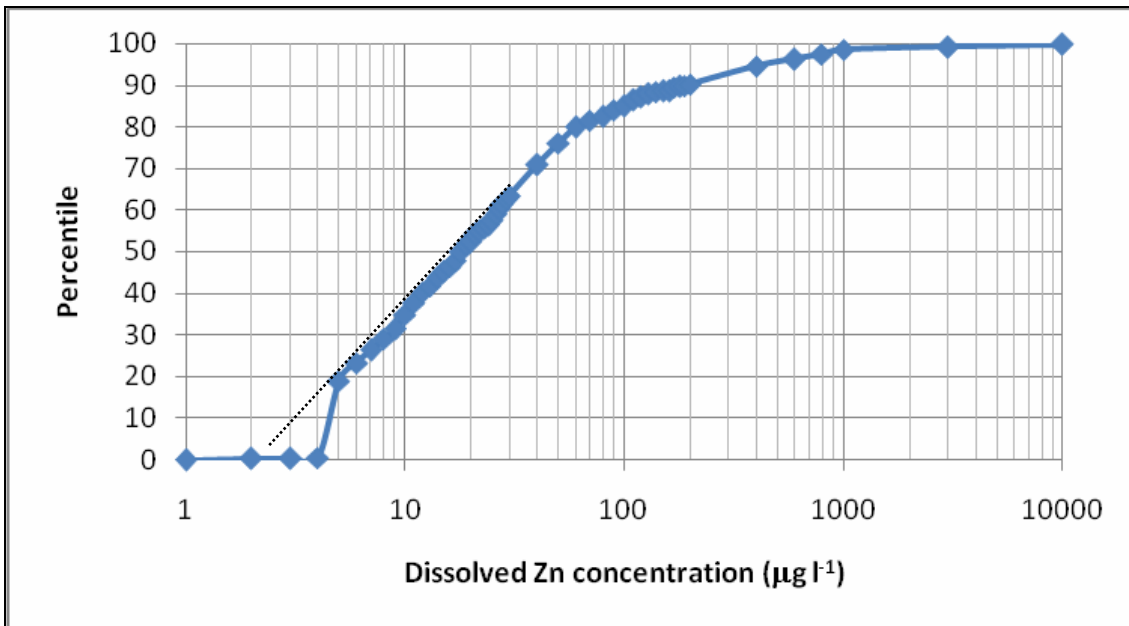


Figure 5.1 Frequency distribution of Zn monitoring data for the Mersey hydrometric area (dotted line shows possible extrapolation from the linear section of the plot to derive the 5th and 10th percentiles of the data distribution)

A comparison of the ABCs derived for Cu and Zn from several data sources for the Tamar hydrometric area are shown in Table 5.1. The river basin default for an ABC is derived on a significantly greater scale than that for the hydrometric area. In England and Wales, there are 11 river basin districts and 59 hydrometric areas, including the Tamar.

Table 5.1 A comparison of ambient background concentrations ($\mu\text{g}\cdot\text{l}^{-1}$) for the Tamar hydrometric area in south-west England

Metal	FOREGS	BGS G-Base (median)	Environment Agency monitoring data ¹
Cu			
River basin district default	1.45–1.97	1.6	1.8
Hydrometric area specific	<1.97	1.0	0.5
Zn			
South West Region default	2.68–4.00	3.4	3.2
Hydrometric area specific	<2.86	2.0	2.5

Notes: ¹ Set at the 10th percentile.

It is imperative that once an ABC has been derived, the ecological and environmental relevance of this value for the area in which it is to be used must also be considered. The Environment Agency collects a significant amount of biological data at monitoring sites across England and Wales, and studies have used this information to assess the effectiveness of potential EQSs (Crane *et al.* 2007). Such an assessment should also be made to ensure that there are no detrimental biological effects from using specific ABCs.

Should it be necessary for the generic PNEC to include background concentrations, particularly in the early tiers of a tiered approach, then we would recommend that a low percentile of ambient monitoring data (covering an appropriate geographical scale, such as on a hydrometric area basis) be added to the generic PNEC. This approach would allow sites with low background concentrations to be screened out of further assessment relatively early in the process, yet would still potentially allow a more-detailed assessment of local background concentrations at later stages in the overall assessment process. This approach permits more-detailed local assessments of background concentrations to be considered within programmes of measures, rather than as a part of the classification process.

Initially, there may be relatively little coherent information available for the detailed assessment of background concentrations. A relatively precautionary approach in the initial stages of an assessment may trigger localised data gathering in areas where issues arise. Consequently, the new data could allow generic background concentrations to be revised for the relevant locations, enabling an improved assessment at earlier tiers for future classification.

5.3.3 Influence of assessment factor and background concentrations on zinc risk characterisation

Whether or not an ABC is accounted for in assessing compliance against an EQS can have an appreciable difference on overall compliance with the EQS. The rate of compliance does, however, depend upon the relative magnitude of both the background concentration and the PNEC. In cases where the ABC is very small relative to the EQS there will be little effect on compliance, but in cases where the ABC is comparable in magnitude to the EQS, the importance of taking background concentrations into account is much greater.

The risk assessment of Zn used an approach to account for backgrounds termed 'added risk' (The Netherlands 2004). This approach allowed modelled environmental concentrations to be used and provided a means of separating current emissions from historic issues. As mentioned previously, historic inputs cannot be distinguished from recent inputs when using environmental monitoring data. The Zn PNEC was also derived as a $PNEC_{add}$, i.e. it was corrected for the background Zn concentration in the test systems.

The relevance of using such approaches towards environmental monitoring data, as would be required if the $PNEC_{add}$ were to be used as an EQS, can certainly be questioned. There is relatively little information available about the acclimation and adaptation of organisms to Zn, and in particular on the potential consequences for ecosystems. Nevertheless, it has also been recognised that the use of the added risk approach may simply be a pragmatic risk management option when applied to monitoring data (Crommentuijn *et al.* 1997).

Some illustrative calculations are shown in Figure 5.2 for the River Mersey; RCRs have been calculated for 483 matched monitoring data points, assuming different scenarios for both the PNEC and the background concentration. When an assessment factor of 2

is used in deriving the PNEC, the importance of background concentrations is much greater compared with the situation when an assessment factor of 1 is applied. This effect occurs because the background concentration is almost 40 per cent of the PNEC value with the lower PNEC, whereas with the higher PNEC (derived using the lower assessment factor) the background concentration accounts for only around 20 per cent of the PNEC value.

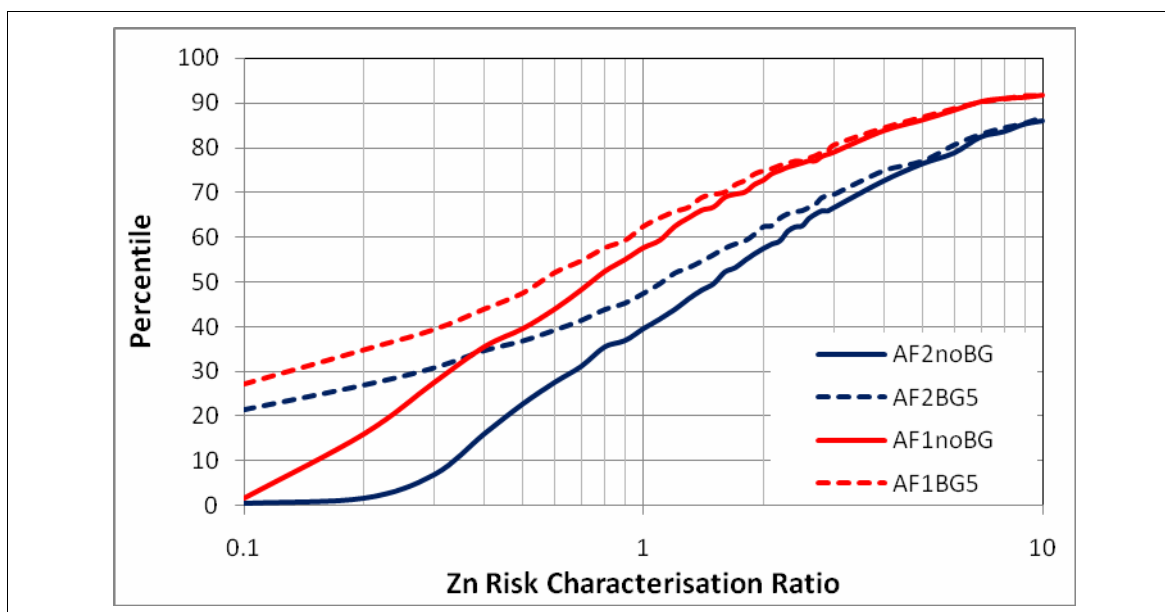


Figure 5.2 Risk characterisation ratios for Zn in the River Mersey showing the effect of different assessment factors and background concentrations; AF is the assessment factor: either 2 (as applied in the ESR RAR) or 1, BG is the background concentration: either 0 (no BG) or the 5th percentile of monitoring data for the hydrometric area (estimated to be $\sim 3 \mu\text{g}\cdot\text{l}^{-1}$)

It can also be clearly seen from this example that the size of the assessment factor applied to the HC_5 in deriving the PNEC has a significant effect on overall compliance. An assessment factor of 2 was applied in the risk assessment because of the possibility that an assessment factor of 1 may not be adequately protective of some primary producers, such as algae. A recent study of streams affected by mining (Environment Agency 2008b) concluded that diatoms were less sensitive than macroinvertebrates to the effects of metals. The principal contaminant at many of the contaminated streams included in this study was Zn, suggesting that the application of the additional assessment factor to ensure protection of primary producers may not be necessary. An assessment of ecological and chemical monitoring data from England and Wales (Crane *et al.* 2007) also concluded that the risk assessment PNEC for Zn may be unnecessarily stringent, although this study only considered impacts on macroinvertebrates and did not consider potential effects on primary producers.

5.4 Screening level bioavailability corrections

Bioavailability corrections for dissolved metal concentrations can be calculated from associated monitoring data on the pH, DOC and Ca conditions relevant to the location. Such calculations would be undertaken with simplified screening models that are able to provide the relevant bioavailability correction for the sample or location. It is possible

that these screening level corrections may be incorporated into laboratory information management systems to report a BioF value calculated from the supporting parameters. This approach is comparable to the identification of appropriate hardness bandings for different waterbodies under the current national EQS.

5.4.1 Default values for bioavailability correction parameters

Default values for DOC and Ca concentrations have been derived on a waterbody basis for cases where eight or more matched monitoring data points were available (matched data for pH, DOC and Ca). Waterbodies for which fewer than eight matched data were available have default values derived on a hydrometric area basis (Environment Agency 2008d). It was considered that a minimum of eight monitoring data points were required to derive sufficiently robust default values. Whilst a larger number of samples will give a better estimate of the true 25th percentile, a requirement for more than eight matched data points would have significantly reduced the number of waterbodies for which default values could be calculated.

5.5 Refined bioavailability corrections

The screening level BLMs provide a good indication of whether or not bioavailability is likely to be high or low, but their output may not provide a sufficiently reliable basis for expensive management decisions. The screening BLMs are good for identifying locations where bioavailability is likely to be high, and are therefore a useful tool in prioritising large numbers of sites. Full BLM calculations are, however, recommended to confirm the screening BLM estimates before a true EQS failure can be confirmed at a specific site.

It is recommended that the full Cu BLM is used with measured data for pH, DOC, Ca, Na and alkalinity to assess fully the risks from Cu exposure. Consideration should also be given to using measured (or locally estimated) data for the other BLM parameters for increased accuracy, although their influence on the final PNEC may be small.

It may be necessary to consider how much the Environment Agency wishes to be certain that an EQS has been exceeded at a site for it to require remedial action. A minimum quantity of data may be required. For example, data from 12 monthly samples may need to be processed using refined bioavailability corrections to assess properly the site's compliance against the standard. This level of monitoring represents a relatively high tier of the assessment, i.e. sites where a refined assessment of bioavailability is necessary have already been identified as potentially at risk, so a higher degree of confidence is likely to be required in the assessment (Crane *et al.* 2008). A rather lower degree of confidence is acceptable for the screening BLMs because the consequence of failure is to progress to a more-refined assessment of bioavailability. Approaches such as these may need to be taken because it is important that costly action is not imposed solely because inadequate monitoring has been undertaken, although the issue of statistical certainty may be less important in cases where the EQS is exceeded by a considerable margin.

5.6 Tiered approaches to compliance assessment

The use of a tiered approach in the assessment of risk is not new (DETR 2000). Generally, lower tiers are coarse with conservative screens that require limited detailed input and technical skill for the interpretation of outputs. Failure at a lower tier results in

progression to higher tiers that require increased information and effort commensurate with the levels of potential risk. A tiered approach to compliance assessment has been proposed previously as a method for accounting for metal bioavailability (Environment Agency 2008c). Figure 5.3 builds on this previous project and shows a modified tiered approach that could be used for all metals, accounts for speciation and backgrounds and incorporates the use of screening BLMs, such as the Cu PNEC Estimator, and the full BLMs.

Tier 1

The first tier in the scheme simply considers a face value comparison between the monitored data and a generic PNEC or EQS. The ability of this tier to function as a filter (i.e. a genuine screen that removes sites from further consideration), rather than a funnel (i.e. all or nearly all sites 'fail' this tier) will determine its value. For metals such as Cu and Zn, for which simplified user-friendly BLMs are available and may be readily embedded into Environment Agency systems, this tier may be bypassed to reach Tier 2. This tier may also include a small background contribution defined from regional or national monitoring data.

Tier 2

This tier will make use of the user-friendly screening BLMs embedded in monitoring and assessment systems. Samples failing this screen will progress to Tier 3 and the use of the full BLM.

Tier 3

The use of the full BLM represents a refinement of Tier 2 and will inevitably be used for a reduced number of sites and localised assessment.

Tier 4

This tier uses specific localised ABCs where there are indications that any generic ABC correction applied at earlier tiers would have been inappropriate. The use of specific local ABCs for metals for which speciation-based approaches, such as BLMs, exist is expected to be limited because of the exclusion of locations requiring attention by earlier tiers of the assessment. Water quality situations that lie outside the boundary conditions of the models may represent an exception. At present, the relative uncertainty associated with the derivation and use of ABCs is significantly greater than that from the use of the BLMs, and ABCs should, therefore, preferably be considered after the use of the speciation-based models, although this situation may change as more information becomes available over time.

Tier 5

At this tier the failure has been clearly determined and consideration of a programme of measures to ameliorate the situation, within the appropriate cost/benefit framework, may be undertaken. The advantage of using the speciation-based models at an earlier tier for those metals for which they are available is that a number of causal factors may be identified which provide focus for the programme of measures.

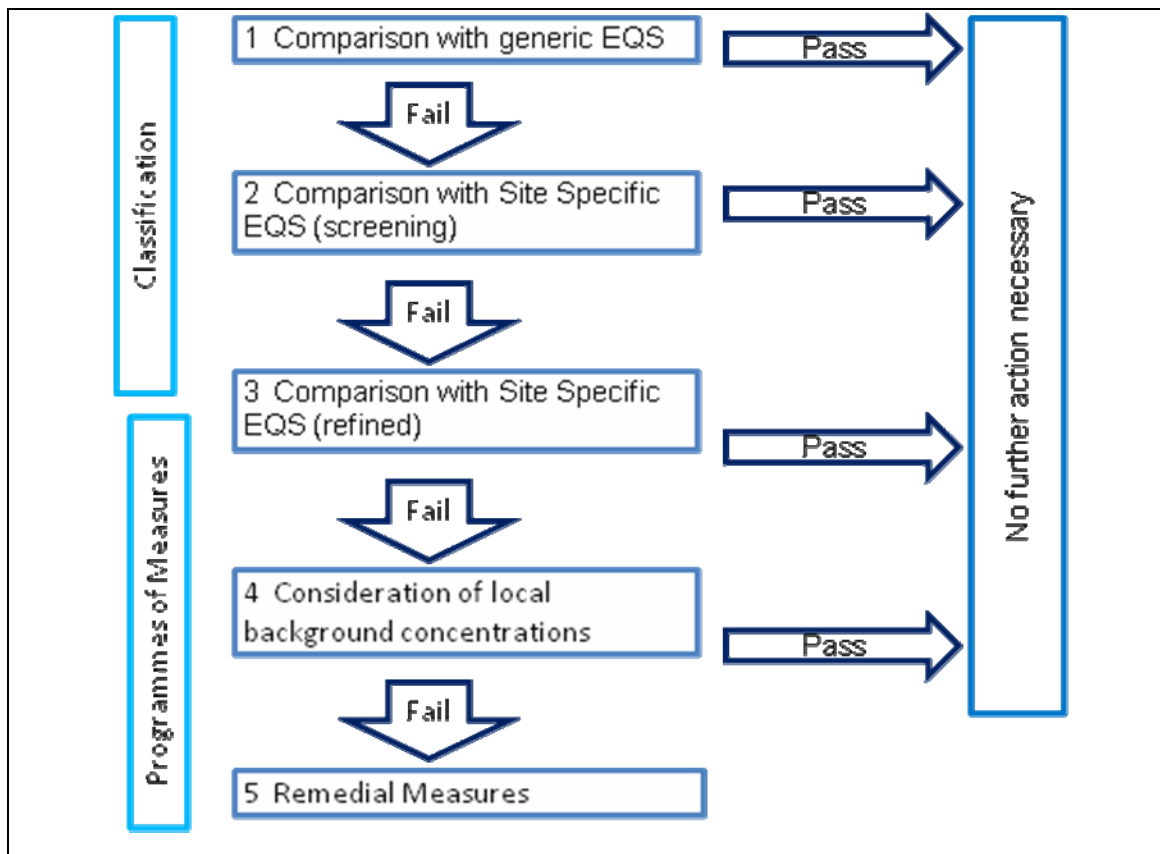


Figure 5.3 Flow diagram of the stages of a tiered compliance assessment

5.7 Short-term standards

An acute Cu BLM is used by the US EPA in the derivation of their water quality criteria (WQC) for Cu. The use of such a model to identify maximum allowable concentrations (MACs) of Cu in waterbodies may be appropriate where long-term standards are also to be based on the BLM. There is no acute Zn BLM available at the present time.

Differences in the responses of organisms to acute and chronic exposures to metals may differ. Cromentuijn *et al.* (1997) concluded that the relationship between water hardness and the chronic toxicity of metals appears to be much less consistent than that between hardness and acute toxicity. It is possible, therefore, that the protective effect of hardness (or Ca concentrations) may be greater under acute conditions. This may result in changes to the ordination of species within the SSD. If this is the case, then approaches that are based on extrapolation from chronic effects to acute effects (or vice versa) through the use of an acute/chronic ratio (ACR) might produce questionable results.

5.8 Approaches where bioavailability corrections cannot be made

In some cases, the water chemistry conditions will be such that the BLMs cannot be applied reliably to determine the bioavailability conditions of the waterbody in question. In these cases, there are a limited number of approaches that can be taken; these involve applying the following as the EQS:

- the generic PNEC;
- the generic PNEC + background concentration;
- the soft water PNEC for Zn (only where Ca concentrations $<5\text{-mg l}^{-1}$).

5.9 Summary

The final compliance package for metal standards should include not only a practical means of determining the relevant bioavailability conditions for a given sampling location, but also consideration of several other issues, namely:

- generic EQS values;
- ambient background concentrations;
- short-term (acute) standards.

UK regulators have expressed a strong preference for a single EQS value that can be modified to suit local conditions through the use of a bioavailability correction factor (BioF). This approach is in contrast to the current EQS system for both Cu and Zn, where distinct standards are applied to waters of different hardness, or a standard can be interpolated from a relationship between the EQS and water hardness. The most important requirement appears to be a relatively simplistic system that can be implemented efficiently and cost effectively.

A possible alternative may be the use of look-up tables for PNEC values under particular combinations of conditions. An example of such a look-up table for Cu is included in Annex 2, although there are potentially significant problems with using such tables arising from the need to interpolate between different PNEC values. An automated implementation of the Cu PNEC Estimator is believed to be a rather more practical approach towards the assessment of bioavailability for UK environmental regulators.

A tiered approach to compliance assessment is recommended so that the Environment Agency can prioritise its available resources towards the greatest potential environmental risks. It may not be necessary for all of the stages shown in Figure 5.3 to be conducted in all cases.

6 Embedding the biotic ligand models in regulatory organisations

6.1 Introduction

The previous sections in this report clearly demonstrate that BLMs could be used as part of an implementation package for EQSs for metals under the WFD. However, despite their utility, practical challenges still exist associated with embedding the BLMs within a large regulatory organisation, for which the use of such tools would represent a step-change in working practice. Furthermore, there is a need to demonstrate the compatibility of the approaches outlined in the previous section with current regulatory reporting frameworks.

The successful roll out of any approach within the Environment Agency must minimise, as far as possible, any additional burden placed on staff. Where an additional burden is unavoidable, there should be a clear regulatory and business advantage to its introduction. In the case of implementing bioavailability-based standards for metals, the regulatory advantage is that this approach is far more scientifically robust and ecologically relevant for assessing potential environmental deterioration owing to metals. It is more proportionate and calibrated than current approaches and will lead to fewer cases of both overprotection (with associated compliance costs for dischargers) and underprotection (with associated environmental costs). Furthermore, by implementing a screening level tier that can automatically report information on metal bioavailability, any additional burden that is placed on Environment Agency staff will be minimised. The criteria for success in the embedding of the proposed approach into regulatory practice are whether:

- the approach delivers the same or greater levels of metals EQS compliance;
- there is a similar or lower level of resources (including time) and costs to the business compared with current systems;
- a more ecologically relevant, and scientifically robust, compliance assessment is the result;
- Environment Agency staff and external stakeholders recognise its ease of interpretation and understanding;
- the approach is accepted by both regulators and the regulated.

The implementation of any new policy is unlikely to be represented by a clearly delineated change or handover. It is more likely that iterative, adaptive management from policy to implementation will take place.

The trialling or 'road testing' of the tiered approach should preferably be undertaken in several pilot catchments (e.g. the Ribble) and be run entirely by the same operational regulatory staff who routinely carry out these activities, with both existing and proposed approaches run in parallel for comparison. This would enable the criteria determining success, as outlined above, to be assessed.

This section of the report outlines a 'road map' describing how this embedding might take place. While specific examples of Environment Agency systems are mentioned, many of these systems and modes of operation are generic and can be applied to other systems of monitoring and assessment.

6.2 Possible methods of working

6.2.1 The use of default parameters

The lack of routine monitoring data for several important physico-chemical input parameters for the BLMs, especially DOC, would hamper their broad-scale use. This potential limitation has been recognised and is being addressed by an existing collaborative project between the Environment Agency and industry (Environment Agency 2008d). One of this project's aims is to derive and assess the suitability of waterbody-based default values for DOC across England and Wales. This has been undertaken and the use of default DOC values, set at the 25th percentile of the waterbody or hydrometric area DOC distribution, has been demonstrated to deliver a reasonable, if precautionary, screen for Cu and Zn risk.

How these default values for DOC and Ca (calculated in a similar way, see Section 4) are presented and used will have significant bearing on the simplicity and ease with which the BLMs can be used. Figure 6.1 is a screen shot of these default data in an Excel spreadsheet. In addition to these default values, the waterbody codes and the eastings and northings of the location of the waterbody are given. These additional data should dovetail with the current Environment Agency data management system (WIMS).

1	Region	HA	SMTP USER REF	SMPT EASTING	SMPT NORTHING	Waterbody ID Code	DOC 25 th	Ca 25 th (Zn)	Ca 50 th generic	Ca 75 th (Cu)	Source
121	South West	Exe				Hydrometric Default	1.4	17	32	50.7	
122			70523081	301500	92200	GB108045008730	3.55	77	79	88	WB
123			70523095	302100	90700	GB108045008730	3.55	77	79	88	WB
124			70220159	326225	95420	GB108045008870	2.71	57	65	72.4	WB
125			70220609	324530	96260	GB108045008880	2.3	28	31.5	35.5	WB
126			70220616	324630	96480	GB108045008880	2.3	28	31.5	35.5	WB
127			70220660	321340	100450	GB108045008880	2.3	28	31.5	35.5	WB
128			70220666	321309	100641	GB108045008880	2.3	28	31.5	35.5	WB
129			70540110	292546	91506	GB108045009040	2.17	26	26	32	WB
130			70591666	284280	101490	GB108045009090	1.78	30.5	57.5	62.5	WB
131			70591679	284280	101480	GB108045009090	1.78	30.5	57.5	62.5	WB
132			70532976	307175	106085	GB108045009110	2.15	47	50	59	WB
133			70532979	307220	106080	GB108045009110	2.15	47	50	59	WB
134			70420116	308730	88570	GB108045009170	2.55	40	45	47.8	WB
135			70423210	314330	100570	GB108045009190	3.2	30.9	32.9	35.12	WB
136			70422020	308380	97900	GB108045009200	2.68	17.75	19	27.25	WB
137			70422024	308370	97980	GB108045009200	2.68	17.75	19	27.25	WB
138			70230688	329370	108220	GB108045014830	2	19	20	23	WB
139			70230694	329530	108470	GB108045014830	2	19	20	23	WB
140			70533633	305600	108400	GB108045014880	1.64	64	71	73	WB
141			70533637	305963	108339	GB108045014880	1.64	64	71	73	WB
142			70534620	314640	111880	GB108045014920	2.64	14	14	14	WB
143			70534624	314590	111770	GB108045014920	2.64	14	14	14	WB
144			70533990	312170	107950	GB108045014940	2.03	7	8	9	WB
145			70533993	312106	107825	GB108045014940	2.03	7	8	9	WB
146			70531044	295780	100810	GB108045014970	2.15	56	60.5	63.75	WB
147			70531047	295750	100850	GB108045014970	2.15	56	60.5	63.75	WB
148			70557055	289800	120190	GB108045015040	2.11	9	10	10.5	WB
149			70557059	289565	120317	GB108045015040	2.11	9	10	10.5	WB
150			70540224	293608	101640	GB108045015050	1.74	14.8	16.5	20	WB
151			70550180	294867	115284	GB108045015050	1.74	14.8	16.5	20	WB
152			70550274	292988	121759	GB108045015050	1.74	14.8	16.5	20	WB

Figure 6.1 A screen shot of the database of default parameters

6.2.2 Integration into current analytical systems

The Environment Agency laboratories use automated data management systems to schedule analytical requirements and capture the completed sample measurements. Automated control of sampling, analysis and reporting is common practice in large routine laboratories, although the degree of automation and the specific software packages and data flow arrangements (e.g. archiving of final results) vary.

The laboratory information management system (LIMS) used in the Environment Agency's National Laboratory Service (NLS) is compatible with offline packages, such as Excel, and this permits screening level BLMs to be integrated into the LIMS. This integration will allow routine reporting of a bioavailability correction factor (BioF) for specific metals, a bioavailable metal concentration, a site-specific PNEC or other numeric or coded outputs.

The Environment Agency also undertakes analysis for other environmental chemical parameters on samples at the same laboratory facility, so site-specific measurements for DOC, alkalinity, etc., could be used if available. The final screening BLM outputs could then be transferred, along with all other analytical results and any metadata, to the central database (WIMS), which holds all sample measurements, site details, etc. WIMS holds all such data from around 1981. A schematic of the monitoring and assessment process is shown in Figure 6.2. The screening BLM would fit into box 3 of the schematic and a consideration of background concentrations and use of the full BLMs in box 4, as required by the tiered approach described above in Section 5.6.

Under normal practice, the Environment Agency derives the final value for calculated parameters, such as un-ionised ammonia, from the component determinands once the sample data leaves the laboratory and prior to final transfer to WIMS within a software environment called MIDAS. However, we were advised at an early stage of this project that the software changes required to accommodate BLMs in MIDAS would probably be prohibitively costly. Therefore, the option of embedding BLMs within the laboratory data systems was viewed as the best option.

The screening BLMs could also possibly be used after final transfer of the appropriate raw sample data to WIMS by using batches of monitoring data retrieved from the archive either centrally or at local river basin level. However, at a Environment Agency workshop on implementing BLMs, stakeholders expressed a preference for the routine reporting of screening BLM outputs via laboratories, but with access to the full BLMs at a local level to investigate potential EQS compliance failures.

To successfully embed BLMs within the Environment Agency's NLS, the following practical issues and associated organisation decisions will need to be resolved:

- i. Because of the high sample numbers, the screening BLMs will need to be incorporated into the NLS LIMS such that they enable automated routine reporting of outputs with minimal manual intervention.
- ii. Ideally, the linkage of the screening BLMs into the NLS LIMS should be able to pick up and use site-specific supporting parameters where they exist and defer to the look-up table of default values when they are absent.
- iii. Agreement is needed on which screening BLM outputs to report and store on WIMS. It is recommended that as a minimum, the BioF value should be reported.

The full Cu BLM will still need to be used to assess sites that do not successfully pass the screening at earlier tiers of the assessment (i.e. using the Cu PNEC Estimator). However, the resources required to run the Cu BLM could be minimised by establishing relationships between the input parameters required by the Cu BLM and the input

parameters used for the Cu PNEC Estimator. Relationships of this type should ideally be established on relevant spatial scales, such as on a hydrometric area basis.

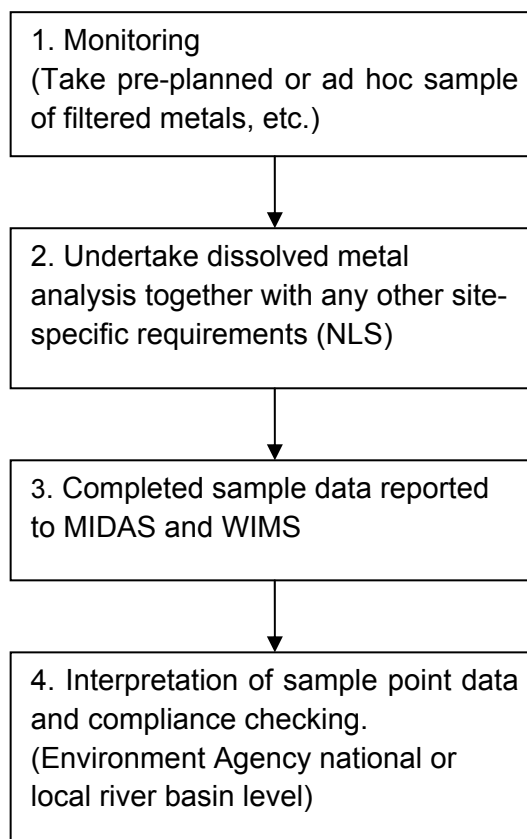


Figure 6.2 Schematic of the monitoring and assessment process

6.2.3 Road testing

The routine consideration of bioavailability within a compliance regime for metals represents a considerable change to existing practice for regulators. This change, together with the practical difficulties that may be encountered whilst embedding BLMs into the laboratories, means that it may be prudent to trial the use of BLMs for routine reporting on a limited scale within the Environment Agency. This road testing of the screening BLM approach may be undertaken at a catchment level or at a regional level. The majority of fresh surface waters sampled for the WFD in England and Wales are analysed at the NLS Starcross laboratory and so this may be the best option for initial road testing.

There is likely to be a desire within the Environment Agency to use the full BLMs widely for investigating the ecological relevance of failures against the existing hardness-based metal EQSs for both Cu and Zn. There will, therefore, be a need for training and support for local teams using BLMs to investigate and prioritise action on waterbodies affected by pressures from metals.

7 Conclusions and recommendations

7.1 Conclusions

A simplified, user-friendly Cu BLM has been developed which will provide estimates of the Cu PNEC over a wide range of surface water conditions to within an acceptable degree of accuracy. Assessments of this Cu PNEC Estimator tool suggest that it is likely to provide a slightly conservative estimate of the PNEC in many cases, compared with the use of the full Cu BLM with more extensive input data. This tool will enable a greater number of sites and samples to be assessed more efficiently than through the use of the Cu BLM because of the simplified model's limited number of input parameters, ease of use and potential for integration into automated systems.

The performance of this tool, in terms of accuracy and precision of prediction, has been assessed and peer reviewed, and it was found to provide reasonable predictions of Cu toxicity within the range of conditions found within England and Wales, although some aspects of the model have been identified for potential improvement. This user-friendly version of the BLM is not intended to replace the full Cu BLM, which should be used when site-specific assessments are required, and when potential risks have been identified and more extensive monitoring datasets are available.

The BLMs for both Cu and Zn are not limited to the DOC conditions under which they are applicable. The effect of DOC on metal bioavailability is a purely chemical one which reduces the concentration of metal ions that compete for binding at the biotic ligand. The screening BLM (Cu PNEC Estimator) is, however, limited to providing predictions of bioavailability where DOC concentrations are less than $30 \text{ mg}\cdot\text{l}^{-1}$. As DOC concentrations above this limit are relatively rare, this limitation is not likely to have a significant effect on the number of samples that can be processed using the Cu PNEC Estimator.

The effects of both pH and Ca are more physiological; they can both affect the concentration of metal which may be bound to the biotic ligand. There may, therefore, be a greater need to consider limiting the range of conditions over which the BLMs can operate with respect to these abiotic parameters.

Changes in Ca concentrations tend to have a relatively limited effect on the PNEC compared with changes in DOC concentrations for both the Cu and Zn BLMs. Furthermore, given the large ranges of Ca concentrations that are found in UK surface waters, limiting the range of Ca concentrations over which the BLMs may be applied may result in significant numbers of locations where bioavailability corrections cannot be applied.

The BLMs used for screening purposes are, therefore, limited only to the range of pH conditions over which they can be applied. For the Zn BLM, predictions can be made between pH 6 and 9, and for the Cu BLM, predictions can be made within the pH range 5.5–8.5.

Generic PNECs can be established for individual hydrometric areas based on information about the range of bioavailability conditions, or PNECs, which can be expected for the area. Precisely how such a generic PNEC should be set depends on the purpose for which the PNEC will be used. A PNEC that is to be used as the first tier in a tiered risk assessment should be set at, or close to, the highest bioavailability

conditions that may be expected. This would be a low percentile of the distributions and significant failures may be expected. A PNEC that is used to describe the typical conditions within a hydrometric area may be set as the 50th percentile, although it would not necessarily be protective over the entire range of conditions which are experienced.

Generic PNECs that are to be applied as a first tier screen within a tiered assessment process might reasonably be based on the 5th or 10th percentile of the distribution of PNECs. In the case of Cu, this is likely to be in the range 1 to 3 $\mu\text{g}\cdot\text{l}^{-1}$ dissolved Cu, and for Zn the range might be closer to 5 to 15 $\mu\text{g}\cdot\text{l}^{-1}$ dissolved Zn. There may be cases where generic PNECs set on a hydrometric area basis are advantageous, although environmental regulators may prefer to use a single screening level standard (set on a countrywide basis), which can be corrected for bioavailability. If this is the case, then a generic bioavailability correction (BioF) for each hydrometric area may be more useful than a PNEC.

The final compliance package for metal standards should include not only a practical means of determining the relevant bioavailability conditions for a given sampling location, but also consideration of several other issues, such as the generic EQS value, ambient background concentrations and short-term (i.e. acute) standards.

UK regulators have expressed a strong preference for a single EQS value that can be modified to suit local conditions through the use of a bioavailability correction factor (BioF). This approach is in contrast to the current EQS system for both Cu and Zn, where distinct standards are applied to waters of different hardness, or a standard can be interpolated from a relationship between the EQS and water hardness. It is clear that any system that is to be successfully implemented will need to be relatively simplistic and not place an excessive additional burden on either the regulators or the regulated.

A tiered approach to compliance assessment is recommended so that the Environment Agency can prioritise its available resources most effectively towards the greatest potential environmental risks, although it may not be necessary for all of the stages in the tiered assessment (see Figure 5.3) to be conducted in all cases.

The derivation of ambient background concentrations for UK freshwaters remains a significant scientific and policy challenge.

The Cu PNEC Estimator does not take account of the protective effect of Na on chronic Cu toxicity, which can affect the resulting PNEC by a factor of between 1 and 3. Assuming a low and constant Na concentration in the development of the Cu PNEC Estimator has, therefore, resulted in estimates that are typically conservative, by a factor of between 1 and 3, and this is believed to be principally because of the protective effect of Na on chronic Cu toxicity. There is an average overestimation of toxicity (underestimation of the PNEC) by a factor of 1.5, with a relatively low associated frequency of false negatives. The Cu PNEC Estimator in its current form is believed to be appropriate for use in a tiered compliance assessment, where it will enable sites requiring more-detailed consideration to be identified efficiently.

It will be necessary to undertake a thorough compliance assessment to properly understand the implications of the conservatism of the Cu PNEC Estimator in terms of its ability to identify locations where more-detailed consideration is required.

An example using a limited dataset for Scotland has been assessed against the first two tiers of the proposed tiered approach (Table 7.1). The dataset consisted of 621 matched data points for pH, DOC, Ca and dissolved Cu, and Cu PNEC Estimator calculations could be performed for 513 of these data points. Sixty six of the 513 data points had dissolved Cu concentrations in excess of 1 $\mu\text{g}\cdot\text{l}^{-1}$ (87 per cent of samples removed at this tier) and of these, 2 had dissolved Cu concentrations in excess of the

PNEC calculated by the Cu PNEC Estimator. Thus, from the starting set of 513 samples, only 2 (~0.4 per cent) still require assessing at Tier 3 of the tiered assessment. The situation shown here may not be typical of that in England and Wales.

A different situation is seen for a selection of 2860 samples from the River Trent (Table 7.1). Only 1 of the samples was below the first tier assessment concentration of $1 \mu\text{g}\cdot\text{l}^{-1}$ (dissolved Cu), although 92 per cent of samples assessed at Tier 2 (using the Cu PNEC Estimator) passed and were screened out from further assessment. This left a total of 236 samples, approximately 8 per cent of the starting dataset, requiring assessment at Tier 3.

Table 7.1 Application of the tiered approach to limited datasets from Scotland and the River Trent¹

Scotland dataset	Tier 1	Tier 2	Tier 3
Samples assessed	513	66	2
Percentage assessed (%)	100	13	0.4
Percentage removed (%)	87	97	??

Trent dataset	Tier 1	Tier 2	Tier 3
Samples assessed	2860	2859	236
Percentage assessed (%)	100	99.97	8
Percentage removed (%)	0.03	92	??

Notes: ¹ Percentage assessed: percentage of the total number at the start requiring assessment at this level; percentage removed: percentage of the number assessed in this tier removed from progressing to the next tier.

We also assessed the effect of using default DOC concentrations on the compliance assessment of the River Trent data, focusing on the increase in conservatism caused by the use of default DOC concentrations. The same set of 2860 data points were used and the first tier was not applied. The BioF values were not calculated by the Cu PNEC Estimator for 27 samples using default DOC concentrations and for 31 samples using measured DOC concentrations (the BioF was not calculated for these 4 additional samples because their measured DOC concentrations were $>30 \text{ mg}\cdot\text{l}^{-1}$). The following results were obtained:

RCR values >1 for 380 samples using default DOC concentrations, 13.4 per cent (86.6 per cent screened out).

RCR values >1 for 229 samples using measured DOC concentrations, 8.1 per cent (91.9 per cent screened out).

This preliminary analysis indicates that the Cu PNEC Estimator is able to prioritise samples for more-detailed consideration effectively when using either default or measured DOC concentrations, although the proportion of samples screened out from further assessment is slightly higher when measured DOC data are applied. The relevance of this partial compliance assessment to the general situation regarding potential EQS passes or failures across the whole of the UK is unclear and warrants

further consideration, although it would appear that the tools to assess this effectively are now available.

We anticipate that it would take a reasonably experienced user between 1 and 5 days to process 200 samples (or sites) with the Cu BLM, depending upon the availability of additional data (amongst other factors). It may be possible to reduce this effort using simple relationships relating major ion concentrations that are required by the Cu BLM to other parameters, such as Ca. If suitable relationships between major ion concentrations, such as Na and alkalinity, can be adequately estimated from Ca concentrations on a local (e.g. hydrometric area) basis, then the information requirements for performing calculations using the Cu BLM would be no greater than those required for the Cu PNEC Estimator.

It may also be possible to reduce further the number of samples requiring additional consideration by assigning failures to samples with RCRs of greater than a certain limit value. The ECI review of the Cu PNEC Estimator indicates that more than 90 per cent of Cu PNEC Estimator predictions are within a factor of 3 of the true PNEC value. It may, therefore, be possible to assign failures to samples with RCRs of greater than 3 (samples with RCRs of between 1 and 3 cannot be classified confidently because of the uncertainties in the Cu PNEC Estimator outputs). A total of 23 of the 236 samples that required assessment using the Cu BLM from the River Trent compliance assessment (approximately 10 per cent) could be screened out in this way.

7.2 Recommendations

Generic PNECs must be set such that they protect the most sensitive environments, if they are to be applied at all as an initial screening tool. Given the likelihood that this initial tier will identify risks at very large numbers of sites, we recommend that the Environment Agency aims to implement the screening BLMs for both Cu and Zn within their automated systems. This automation will provide an initial bioavailability correction for monitoring data calculated on the basis of locally derived supporting parameters. The output of the Cu PNEC Estimator should be included as an additional determinand in WIMS, expressed as a bioavailability correction.

The Cu BLM will need to be used for compliance assessment at prioritised sites and will inevitably require an appreciable resource, although this is minimised significantly through the initial use of the Cu PNEC Estimator. Further developments to improve the predictive ability of this early, and potentially automated, stage in the assessment process may help to remove the requirement to undertake Cu BLM calculations for priority sites. There are significant advantages in the initial use of the estimator in terms of resource inputs for regulators, hence further consideration of this issue is warranted.

There are considered to be two principal sources of error in the Cu PNEC Estimator. The first of these is its inability to describe correctly the changes in the true PNEC value as a function of the input parameters. This results in errors that are distributed about the true value and are unconservative in approximately half of the calculations. The other source of error stems from the absence within the model of any consideration of the protective effect of Na on chronic Cu toxicity; the estimator assumes a constant low Na concentration at all times. Consequently, the Cu PNEC Estimator is always more conservative than the Cu BLM (where adequate input data for the calculations are available).

Successful revisions of the Cu PNEC Estimator would need to reduce both these perceived sources of error, i.e. improve both the variability and the tendency towards conservatism. Other requirements, such as an ability for the estimator to be operated automatically within a LIMS and to work from only a limited set of input parameters,

would still need to be met. An alternative revised model, which is both more precise and more accurate, may be able to replace both the Cu PNEC Estimator screening stage and assessment using the Cu BLM if its predictive powers are adequate. The Environment Agency may wish to consider such a replacement as a future update to the present system.

The required supporting parameters may be determined analytically, ideally from the same sample from which a metal concentration is measured; alternatively, default values may be used when appropriate analytical information is lacking. Default values for DOC and Ca should be derived on a waterbody basis wherever possible, although in cases where currently available monitoring data are inadequate, a default set on the basis of the hydrometric area may be applied. Defaults that are set on a hydrometric area basis should be viewed as provisional. However, within the proposed tiered approach, sites that are identified as potentially being at risk will require more-detailed monitoring data to be collected in order to make a more accurate assessment of compliance with the EQS.

The database of default supporting parameters should be reviewed and revised periodically to update it with newly available monitoring data and to correct any problems that may arise from its use. The most appropriate review period is likely to be comparable with the duration of river basin planning cycles (approximately seven years), although initially an earlier review may be warranted. The default value database does not currently include default values for pH as it is assumed that this will usually be monitored routinely, although in principle default values for pH could also be included.

Where local environmental conditions are consistently outside the validation ranges of the BLMs there are currently few options for assessing compliance. Compliance may simply be limited to an assessment against the generic PNEC, which is likely to be set at a relatively conservative level. Undertaking ecological and chemical monitoring at some of these sites may allow them to be assessed for any potential ecological impacts, although it will be important that the biological metrics selected for monitoring are likely to be sensitive to the effects of the metal in question.

The ability of the BLMs to predict the most-sensitive species from the SSD under a given set of conditions may also raise the possibility of using targeted ecotoxicity testing to assess compliance under some conditions. However, this approach may find relatively limited application because of the ranges of conditions that most test species are able to tolerate. The rotifer *Brachionus calyciflorus* is predicted to be the most sensitive species to Cu under most conditions, although successful testing with this species is unlikely to be possible in waters of very low pH, for example.

We therefore recommend that further study is undertaken where the local environmental conditions are identified to be consistently outside the BLM boundaries, with a view to considering whether these boundaries should be adjusted, or alternative approaches taken.

There are a number of decision points that must be addressed to finalise the implementation of speciation-based models into a regulatory framework. These points are generally aimed at policy makers, with science providing a number of options for consideration. Brief outlines of some of the key considerations are given below and all should be prefaced with the need to establish whether or not the implementation of bioavailability is consistent with the UK policies of 'no deterioration'.

Policy makers should consider the following points:

- i. The added risk approach was adopted for performing generic, large-scale risk assessments, but may not necessarily be appropriate for application to Environmental Quality Standards. A more suitable approach for the initial

tiers of an assessment may be to include a small contribution from the ambient background concentration in the generic PNEC, e.g. the 5th percentile of dissolved metal monitoring data from the hydrometric area. However, the selection and use of such a value as part of an EQS would not be based on science.

- ii. There is a widely held view, amongst regulators and the regulated, that the new EQSs developed using WFD methodology are overly precautionary and shrouded in uncertainty. However, the significant scientific evidence does not necessarily support this view. The production of ecotoxicity data for Zn for a range of aquatic species (beyond fish) since the current national standards were set, has resulted in lower, but less uncertain and therefore less precautionary, PNECs to be established. Furthermore, the development of Cu and Zn BLMs has enabled bioavailability modification to be taken into account in compliance assessment in a scientifically robust manner. An account of bioavailability offers considerably greater ecological relevance than the hardness-based corrections that are currently applied. Nevertheless, an assessment factor of 2 was applied to the HC₅ of the Zn ecotoxicity dataset to derive a PNEC for generic risk assessment purposes. It is appropriate to consider whether or not the PNEC derived through the risk assessment process is directly applicable as an EQS. Algae were considered to be the most-sensitive species to Zn, although a recent UK study (Environment Agency 2008b) found benthic macroinvertebrates to be more sensitive than diatoms to the effects of minewaters. It is appropriate to consider a validation of the PNEC values against available field data.
- iii. Having considered the above issues, it will be possible to establish suitable proposals of generic PNECs for both Cu and Zn. A detailed assessment of compliance against standards for both Cu and Zn set on the basis of these bioavailability-based systems, but considering a variety of possible options, will be required before it is possible to establish the most appropriate 'option'. This assessment would also include a comparison with the current situation of Cu and Zn compliance with the existing EQSs. Such an assessment should be able to provide information for policy makers to assess the potential impacts of such changes appropriately. This exercise will also provide a view as to which stages of the process should be considered as compliance assessment, and which stages as programmes of measures under the WFD.

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List of abbreviations

BLM	biotic ligand model
BioF	bioavailability factor
Ca	calcium
Cl	chloride
Cu	copper
DOC	dissolved organic carbon
DSD	dangerous substances directive
EQS	environmental quality standard
ESR	Existing Substances Regulations
HA	humic acid
HC ₅	hazardous concentration for 5 per cent of the ecosystem
K	potassium
LIMS	laboratory information management system
MAC	maximum allowable concentration
Mg	magnesium
MIDAS	Management Information and Data Archive System
NLS	National Laboratory Service
Na	sodium
Ni	nickel
PNEC	predicted no-effect concentration
RAR	risk assessment reports
RIVPACS	River Invertebrate Prediction and Classification System
S	sulphur
SO ₄	sulphate
SSD	species sensitivity distribution
TWINSpan	Two Way Indicator Species Analysis
WER	water effect ratio
WFD	Water Framework Directive
WIMS	Water Information Management System (Environment Agency central database)
WQC	water quality criteria
Zn	zinc

Annex 1 Critical review of the Cu PNEC Estimator

Karel De Schampheleere - Ghent University, Belgium
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Personal interpretation/summary of the work done

The Cu PNEC Estimator is intended to approximate PNEC values calculated with the Cu BLM software, which was developed by the International Copper Association for the EU risk assessment. Therefore a set of simplified equations have been developed.

The equations have been developed from 'observed PNECs' for a training data set, consisting of waters with various combinations of pH, Ca and DOC. The 'observed PNECs' are those calculated with the BLM software. pH was varied between 5 and 9, DOC between 0.1 and 30 mg/L, and Ca between 3 and 300 mg/L. Mg was considered as a covariate of Ca (with $Mg = 0.3 \times Ca$ - note: it is not clear if this conversion is on a molar basis or on a mg/L basis, if it is a molar ratio than it is reasonable, otherwise it is not). During the model training, alkalinity was assumed to be related to pH (following a relation shown in Figure 1 (scenario 2)). All other parameters were kept 'at their defaults'. The model equations derived were of the following form:

$$PNEC = a + (b \cdot pH^c) + (d \cdot DOC^e) = (f \cdot Ca^g)$$

Where a to g are fitted constants. To improve quality, different equations (different a to g) were fitted for different ranges of pH and DOC.

Following model development, the model was tested using a set of natural waters. 'Observed' PNECs were calculated with the BLM software using as input pH, Ca, DOC (as for the training), but now a measured value for alkalinity was used as an input (i.e. it was not estimated from Ca here). These observations were compared with 'predictions' from the PNEC Estimator. The majority of the predictions was within factor of 2, 73 per cent of the predictions were within 3 $\mu\text{g/L}$ of the 'observed PNEC'. The PNEC Estimator shows some bias towards underprotection, i.e. predicted PNECs higher than observed PNECs (Figure 8, 9) and this is more obvious at very low PNEC values ($<1\mu\text{g/L}$). There are also a few predicted PNEC values <0 .

In depth analysis and critical review

I recognize the effort put into the development of this PNEC Estimator. It is truly a difficult task to convert a very complex and very non-linear system as the Cu BLM software to a set of quite simple equations, which also seem to work reasonably well for most test waters (Figure 8 and 9).

Nevertheless, I do have some suggestions that could possibly further improve the PNEC Estimator. I also have some questions with regard to some of the choices that have been made during the development and validation phase.

To my opinion there seems to be room for improvement since the PNEC Estimator exhibits some bias (under protection). Indeed, Figure 9 shows that the majority of the data-points are above the 1:1 reference line. The first possible explanation I can give for this, is the difference in the way alkalinity is treated in the training phase vs. the testing/validation phase. In the training phase, alkalinity was a function of pH (scenario 2 in Figure 1), while in the natural waters testing set this relation is not very clear. I am illustrating this point in Figure A below. In the upper panel, one can clearly see that the pH-alkalinity relation used in the PNEC Estimator (blue diamonds) is not found back in the testing dataset (red diamonds). On the contrary, the relation between Ca and alkalinity found in the natural waters is much clearer (linear on log-log scale, lower panel of Figure A). This does not surprise me, as I observed a similar trend in the GEMS-database (a large harmonized monitoring database of European rivers and lakes). Here too a very clear relationship between Ca and alkalinity was observed, and a less strong one with pH. **I believe relating alkalinity to Ca (and not to pH) in the test set would probably lead to a more realistic PNEC Estimator.** Actually, the authors of this report themselves mentioned that a reasonable alkalinity input could be obtained from such a relationship when using the Cu BLM software. A minor note in this context is that the relation between alkalinity and pH in scenario 2 is mechanistically a bit doubtful. It is calculated from an open system assuming a constant inorganic carbon concentration. Based on my experience with field waters, the latter assumption is not realistic.

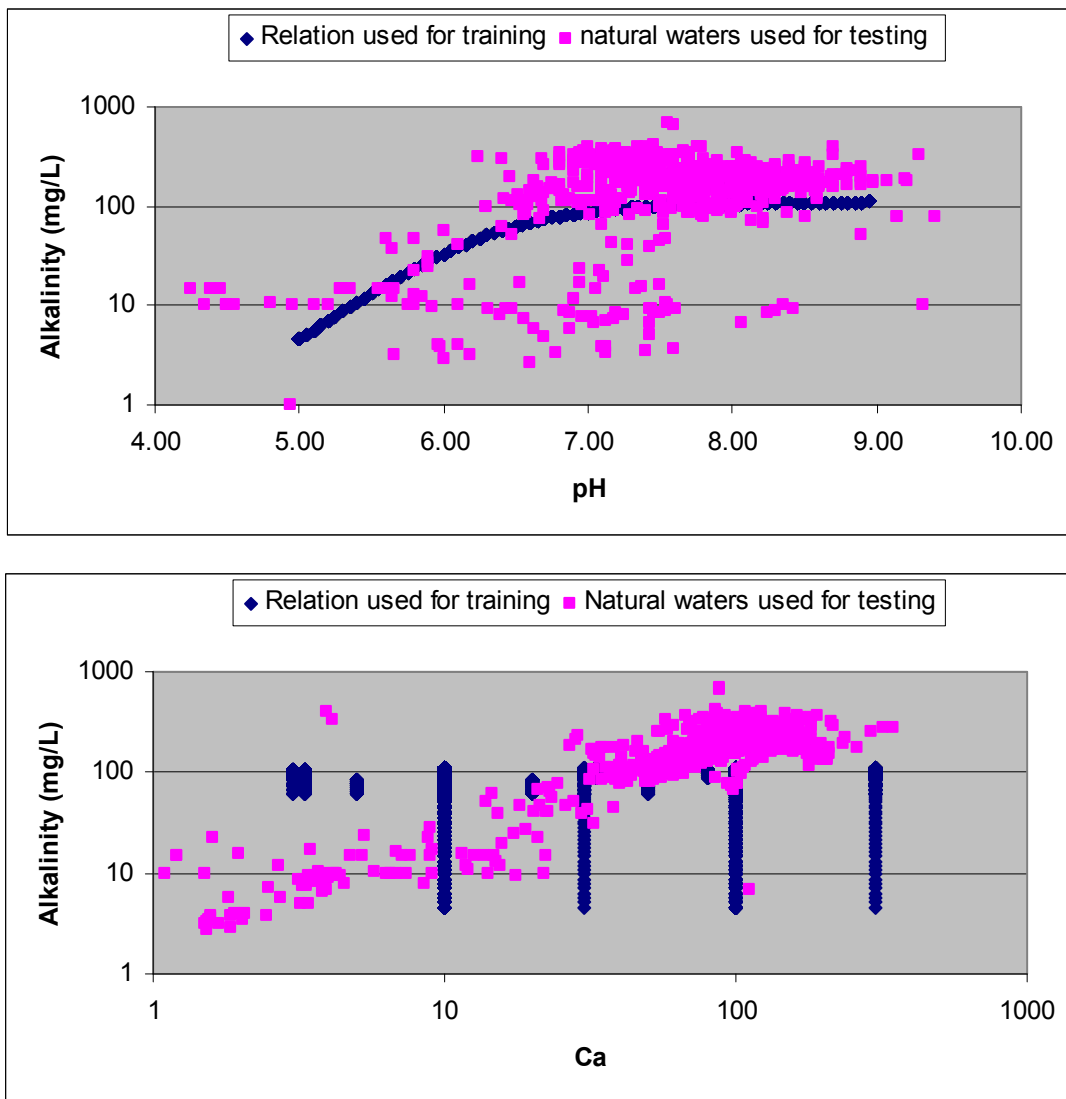


Figure A Relation between Ca, pH and alkalinity in training and testing set

A second possible explanation for the bias in the predictions could be that **the model shows some bias in predicting the training set from which it was developed**. I have explored this by plotting the residuals (observed - predicted PNEC) against the observed PNEC (Figure B). I did this for different ranges of conditions of pH and DOC (the same ranges as those for which different equations were derived). It can be noted that, whatever the range of pH and DOC considered, the distribution of residuals is not random and that there is a bias toward errors >0 at both low and high observed PNEC, and errors <0 at intermediate observed PNEC. (Figure B). **To my opinion this suggests that the functional form of the equation is not able to capture the combined effects of Ca, pH and DOC entirely correctly.**

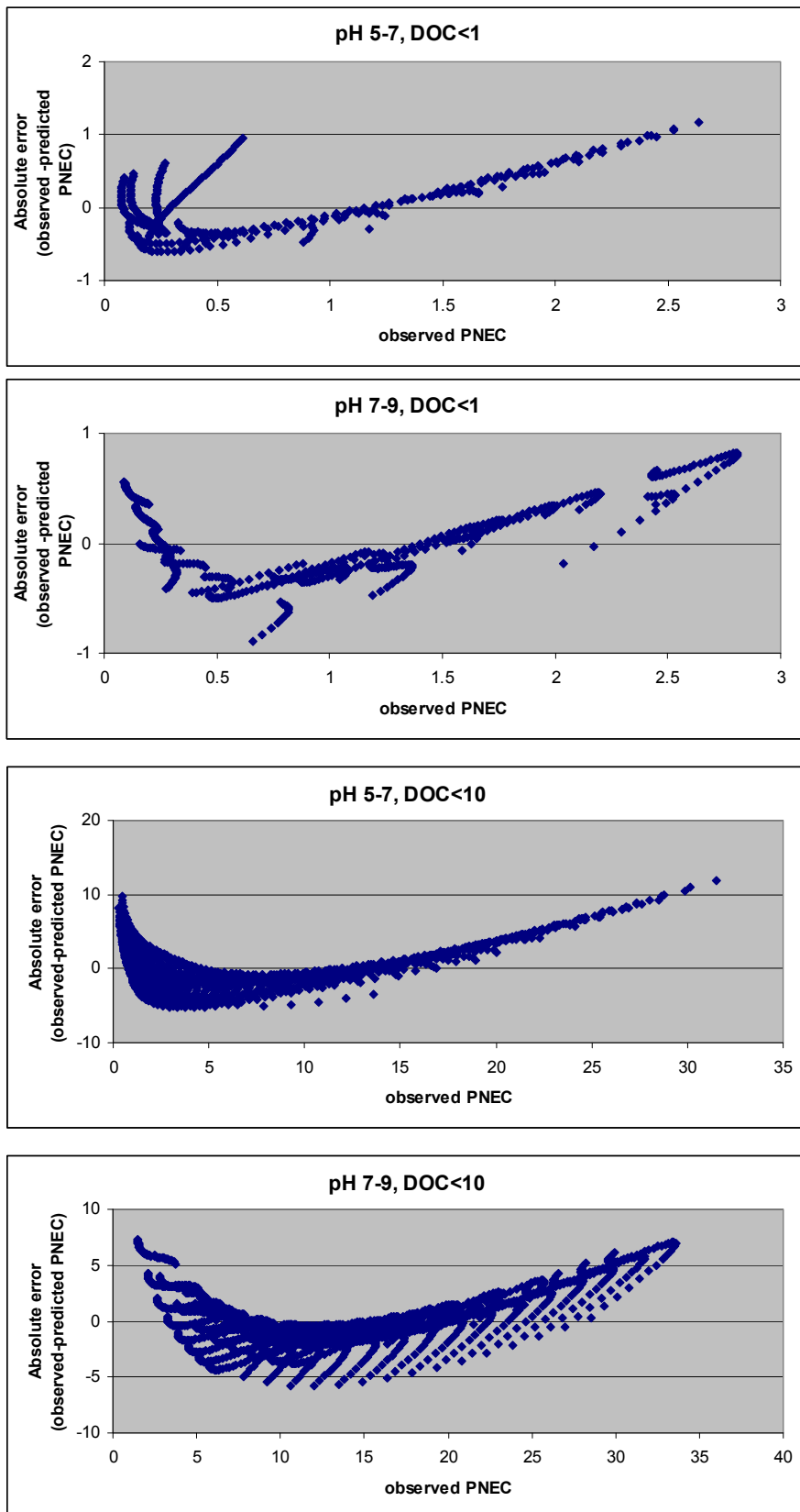


Figure B Absolute error (residuals) of PNEC estimator predictions for the training set

So what is it then that the mode structure does not capture? Recall that the generic model equation of the PNEC Estimator is a sum of an intercept and three power terms:

$$\text{PNEC} = a + (b \cdot \text{pH}^c) + (d \cdot \text{DOC}^e) = (f \cdot \text{Ca}^g)$$

However, I have noted in Figure 6, that the effect of DOC on observed PNECs (calculated with BLM) is linear and that the effect of pH is bell-shaped (with maximum PNECs at near neutral pH). **These observed functional forms are likely not to be captured entirely correctly by the power terms.** I am illustrating this point by means of an example where I have plotted observed PNECs (for DOC<1) as well as predicted PNECs against pH (Figure C). The plots clearly show that the functional form of PNEC vs. pH is not the same for observations and predictions.

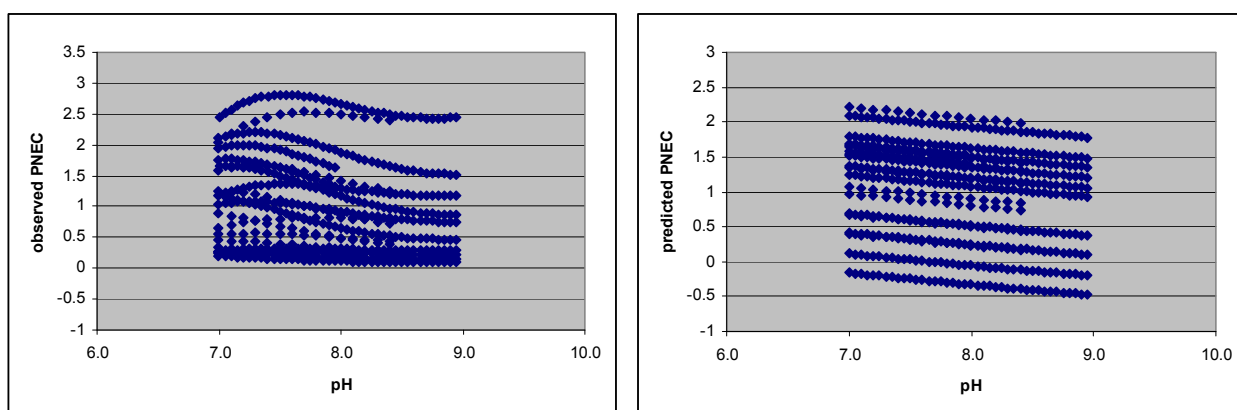


Figure C Observed (left) and predicted (right) as a function of pH at DOC<1.

It would be more correct to have a simple linear effect of DOC (i.e. $e = 1$) and a curvilinear effect of pH (possibly 4th order polynomial, see Figure D). The linearity of the DOC effect is also in line with mechanistic speciation considerations. I do, however, agree that splitting up the pH-DOC input space into several subspaces, with different equations for the different subspaces, could be a reasonable alternative. Although it is to be commended that this splitting up is already the case in the current model, perhaps it has to be split up in even more subspaces to increase the accuracy. Another possibility, which I have not been able to look at, is the inclusion of interaction terms (e.g. higher DOC effect at higher pH, more effect of Ca at higher DOC). The key issue, however, is - and I have experienced this myself when developing the Zn BLM tool - that **it is very hard to grasp the complexity of the BLM with simple algebraic equations.** That's why **an algorithm in which the PNEC value is simply interpolated from values extracted from tables containing the PNEC as a function of pH, DOC, and Ca could be a valuable alternative.** I found that such an approach resulted in much higher comparability between observed and predicted PNECs for Zn.

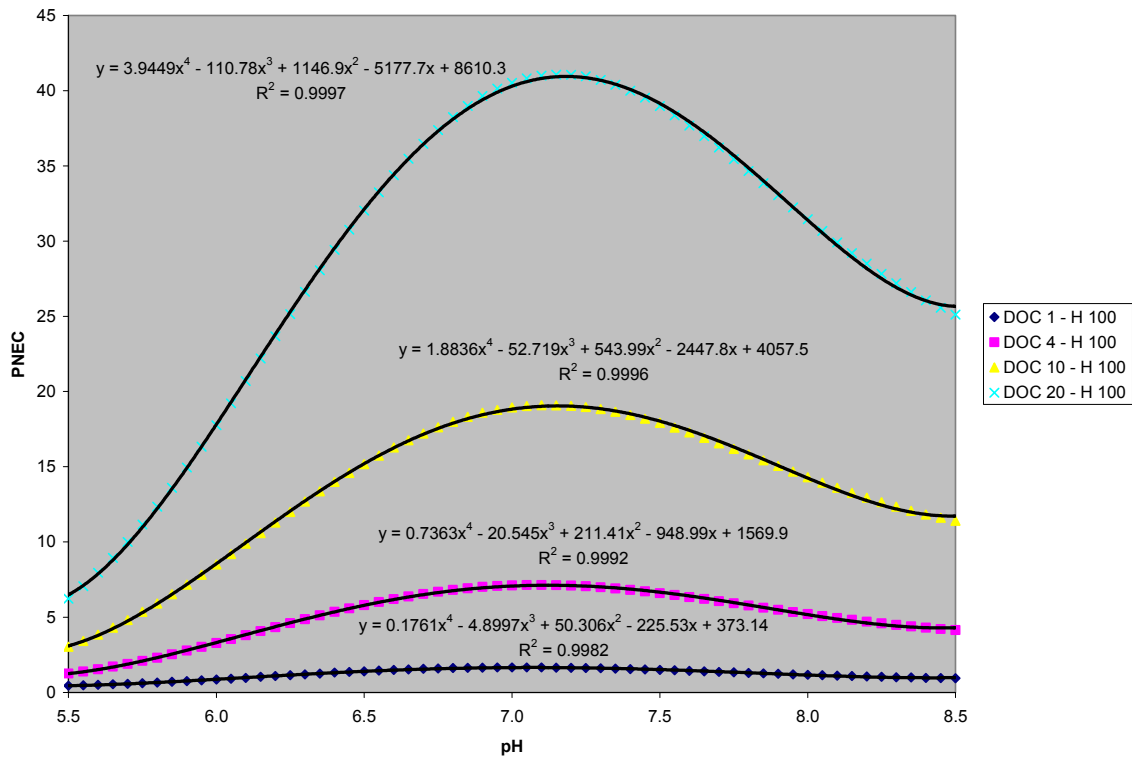


Figure D Effect of pH on observed PNEC at Ca=100mg/L and different DOC

A third important comment I want to make is perhaps not really related to the comparability of the Cu BLM software with the PNEC Estimator. However, it may be important for assessing the risks of Cu in general. Although it is obvious that pH and DOC should be included as input variables of the PNEC estimator, **it is less clear why Ca (with Mg as the covariate) was chosen as the third input variable, while another important variable (i.e. Na) was ignored.** Na can easily reach concentrations of near 100 mg/L (about 5 mmol/L) and at such a concentration, Na competition is likely going to be an important competitor with Cu. Ca, on the contrary, can only influence the PNEC by competing with Cu for DOC sites. I realize both parameters may affect the PNEC, but it should be considered to include both variables in the PNEC estimator, as well as in using the BLM software. **If it is not possible to include 4 variables, it should be considered to use a correlation between Ca and Na** (which is also very nice in most cases I have seen). It also strikes me a bit that the **default Na concentration used in *all* calculations is on the (very) low side**, i.e. 3 mg/L. This is a typical value for very soft waters, but not at all for lowland rivers for example. This could normally result in PNEC calculations (done with both the Cu BLM software and the PNEC Estimator) which are well below the 'true value'.

Finally, I would like to comment on one particular 'issue for consideration by the project board'. **I do strongly recommend that the calculation of the PNEC estimates should be restricted to within the validation range of the BLM.** There could be some flexibility

regarding DOC (since the effect of DOC is merely a speciation effect), but not with regard to pH or Ca (it is uncertain how organisms 'behave' outside the validation range. Please do note, however, that the Cu BLM does not have a Ca boundary (like Zn BLM) but rather a hardness boundary (which varies between 10 and 500 mg CaCO₃/L). If the model is only going to be used within the boundaries, than these boundaries should be converted appropriately to Ca (using the same Mg:Ca ratio of 0.3). The Ca range would then be about 3 to 155 mg/L. Anyhow, whether or not it is decided to use the BLM outside the boundaries, **I recommend that separate model equations be used for waters inside and waters outside the BLM boundaries. In practice this could be achieved by using the BLM boundaries as boundaries for the input parameters subspaces**, e.g. instead of the subspace [pH 5-7, DOC<3], which has been used now, the subspace could be defined as [pH 5.5-7, DOC 1.6-3]. An example of a subspace outside the model boundaries could be [pH<5.5, DOC<1.6]. I believe this practice could also increase the accuracy of the PNEC Estimator for waters within the model boundaries. Indeed, the current model equations have been developed for a range of test waters, several of which have water chemistry outside the BLM validation range. Hence, uncertain BLM calculations may have also affected the PNEC Estimator equations inside the BLM boundaries.

Conclusions and recommendations

1. Converting the complexity of the BLM into simple algebra is not easy. However, the current PNEC Estimator should be considered a reasonable first effort as it approximates most observed PNECs within 2-fold.
2. Nevertheless, there is some bias in the predictions, which suggests that the model can be further improved.
3. I specifically recommend the following for improving the PNEC Estimator (and PNEC predictions with Cu BLM in general):
 - a. use a relationship between alkalinity and Ca to estimate alkalinity (instead of the pH-alkalinity relationship);
 - b. try to use an equation that represents more correctly the true functional relationships between the input (pH, DOC, Ca) and the output (PNECs). Alternatively, it could be considered to split up the input parameter space into more subspaces. A second alternative is to use an interpolation approach (similar as in the Zn BLM tool);
 - c. include Na as a variable in the PNEC Estimator as well as in the Cu BLM calculations (either using measured values of Na, or via a correlation with Ca);
 - d. take into account the BLM validation boundaries in the development of the PNEC Estimator.

Annex 2 Look-up tables for Cu PNEC

Hardness 10 mg·l⁻¹ (CaCO₃)

Hardness	DOC concentration (mg·l ⁻¹)						
10	pH	1	3	5	10	15	20
pH (pH units)	6.6	1.8	5.8	10.0	21.5	34.1	47.8
	6.8	2.3	7.4	12.8	27.4	43.4	60.8
	7.0	4.0	12.7	21.8	45.8	71.8	99.6
	7.2	5.0	15.7	26.8	56.2	87.7	121.2
	7.4	5.8	18.3	31.3	65.4	101.9	140.6
	7.6	6.5	20.4	34.8	72.6	112.8	155.5
	7.8	6.9	21.7	37.1	77.2	119.9	165.1
	8.0	7.1	22.4	38.1	79.4	123.3	169.8
	8.2	7.1	22.4	38.2	79.7	123.7	170.4
8.4	7.0	22.1	37.7	78.6	122.1	168.4	

Hardness 30 mg·l⁻¹ (CaCO₃)

Hardness	DOC concentration (mg·l ⁻¹)						
30	pH	1	3	5	10	15	20
pH (pH units)	6.6	1.7	5.4	9.3	19.5	30.5	42.1
	6.8	2.1	6.7	11.5	24.4	38.2	52.7
	7.0	3.2	10.1	17.3	36.3	56.3	77.3
	7.2	3.8	12.0	20.6	43.0	66.9	91.8
	7.4	4.3	13.6	23.2	48.7	75.5	103.7
	7.6	4.6	14.6	25.0	52.3	81.3	111.7
	7.8	4.7	15.1	25.8	54.0	83.9	115.3
	8.0	4.7	15.0	25.7	53.9	83.8	115.2
	8.2	4.6	14.6	25.2	52.8	82.1	112.9
8.4	4.4	14.2	24.4	51.3	79.8	109.8	

Hardness 100 mg·l⁻¹ (CaCO₃)

Hardness	DOC concentration (mg·l ⁻¹)						
100	pH	1	3	5	10	15	20
pH (pH units)	6.6	1.7	5.2	8.9	18.7	29.1	39.9
	6.8	2.0	6.4	10.9	22.9	35.7	49.0
	7.0	2.3	7.3	12.6	26.4	41.2	56.7
	7.2	2.5	8.0	13.8	29.2	45.5	62.8
	7.4	2.6	8.4	14.5	30.7	48.1	66.5
	7.6	2.6	8.5	14.7	31.2	48.8	67.6
	7.8	2.6	8.3	14.4	30.6	48.0	66.5
	8.0	2.4	7.9	13.7	29.3	46.0	63.9
	8.2	2.3	7.5	13.0	27.7	43.6	60.5
8.4	2.2	7.1	12.3	26.2	41.3	57.3	

Hardness 300 mg·l⁻¹ (CaCO₃)

Hardness	DOC concentration (mg·l ⁻¹)						
300	pH	1	3	5	10	15	20
pH (pH units)	6.6	1.5	4.6	7.8	16.3	25.1	34.4
	6.8	1.6	5.0	8.6	18.0	27.9	38.2
	7.0	1.7	5.2	9.0	18.9	29.5	40.5
	7.2	1.6	5.2	9.0	19.0	29.8	41.0
	7.4	1.6	5.0	8.7	18.4	28.9	40.0
	7.6	1.4	4.6	8.1	17.3	27.2	37.7
	7.8	1.3	4.2	7.4	15.8	24.9	34.7
	8.0	1.2	3.8	6.7	14.3	22.6	31.5
	8.2	1.1	3.4	6.0	12.9	20.5	28.5
8.4	1.0	3.1	5.5	11.8	18.7	26.1	

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Tel: 0870 8506506
Email: enquiries@environment-agency.gov.uk
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