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Tiered approach to the assessment of metal compliance in surface waters

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Executive summary

The aquatic environment is sensitive to damage from a wide range of chemicals. Environmental quality standards (EQSs) are one of the instruments used by the Environment Agency to protect and improve water quality. Derived from toxicological data, the EQS values set limits for chemicals and elements in water bodies.

The Environment Agency is considering options for implementing future metals' EQSs under the Water Framework Directive (2000/60/EC). This project has found that a tiered assessment system offers a viable option for considering metal compliance.

Zinc and copper have been used to investigate the approach, using predicted no-effect concentrations (PNEC) from EU risk assessment reports (RAR) as the potential basis for EQS values.

The tiered approach has three levels; site-specific assessments of water quality only move up to the next level when observed metal concentrations exceed the value of the preceding tier. The tiers progressively take account of the background concentrations of metals and their bioavailability:

Tier 1: compares observed concentrations with the PNEC, akin to a provisional EQS for copper, but which represent a very conservative value for zinc. The copper PNEC includes a nominal background concentration for test conditions, but not ambient environment conditions, and a minimal correction for bioavailability. The zinc PNEC does not factor in either background concentrations or bioavailability.

Tier 2: compares observed concentrations with the PNEC plus an accepted aquatic background concentration of the metal to reflect regional or local situations.

Tier 3: compares observed concentrations with a predicted 'bioavailable' PNEC derived from biotic ligand models (BLMs).

For zinc, a high proportion of data were shown to 'fail' Tier 1 assessment (over 50 per cent of the total, based on Environment Agency 1995 data for the whole of England and Wales). This level of non-compliance was significantly greater than the number of data failing under the current EQS regime (11 per cent), which takes account of the bioavailability of zinc in surface waters by banding the EQS according to water hardness. The much higher failure rate for the PNEC is partly because this value is based on the 'added risk' approach used in the EU RAR for zinc. This calculated $PNEC_{add}$ should be used in conjunction with a background concentration in order to derive a maximum permissible concentration.

The three-tier approach was applied to a second dataset (12 sites with up to 10 years of monitoring data). By making allowances for background concentrations and bioavailability, non-compliant data dropped from 52 to 24 per cent at Tier 3, slightly below the failure rate of the same dataset to the current EQS regime (31 per cent). The Tier 3 application of the BLM-derived PNEC was found to be effective at predicting good ecological quality for water in rivers not expected to be impacted by polluting diffuse or point sources of zinc.

The tiered assessment process accurately predicted non-compliance at sites significantly impacted by diffuse and point sources derived from urban populations. It also flagged non-compliance in rivers with high concentrations of zinc stemming from underlying geology, but observed biological quality in these latter rivers was assessed as fair or better. Either indigenous organisms adapt to high metal background concentrations, or the existing indicators of ecological quality are poor indicators for metal pollution. The Environment Agency should work to identify potentially better biological indicators of metal pollution.

For copper, non-compliance was observed more locally: approximately 6 per cent of samples were non-compliant at the first tier of assessment. This proportion of 'failures' is significantly lower than non-compliance under the current EQS regime (around 20 per cent failure) because the PNEC (8.2 µg/l) is significantly higher than the existing EQS for the softest waters (1 µg/l).

As for zinc, the use of BLMs to predict bioavailable copper concentrations at Tier 3 filtered out sites where adverse environmental impacts were not expected. Sites heavily influenced by mineralogy or pollution would be expected to fail an assessment even taking account of background concentrations or bioavailability. Indeed, localised areas of extremely high copper concentrations meant that non-compliance was observed even after applying all tiers of the assessment.

In cases where water quality parameters fall outside the copper BLM validation ranges (i.e. low pH, DOC, or hardness), the BLM (Tier 3) assessment should be run even if the water body 'passes' at Tier 1 or Tier 2. The PNEC value was not necessarily designed to be protective at extremely low values of pH, DOC, or hardness.

The choice of background concentrations is critical to the overall assessment of compliance, and is the subject of other Environment Agency research. For the purpose of this assessment, median values given in a draft report done in collaboration with the British Geological Survey have been used in most cases, with mean concentrations used for illustration purposes. Reported data is, however, limited and biased towards the east of England and the Midlands. The selected background concentrations may, therefore, lead to an underestimate of concentrations based on local mineralogy.

Depending on the confidence in the background concentration data and assuming the relevant input data for the BLM are available, it was shown to be possible to promote the BLM assessment from Tier 3 to Tier 2 for compliance assessment. The use of the BLM at the Tier 2 stage of assessment helps to narrow down the number of sites for which a closer examination of background concentrations would be necessary.

Additional analysis of the tiered approach to surface water compliance is recommended once definitive background data are agreed. Further studies will allow a full financial appraisal of the benefits of adopting this procedure compared with alternative systems. The BLMs were shown to be a reliable and practical approach to assess metal bioavailability, suggesting that they could be incorporated into a tiered assessment of compliance without putting ecological status at risk. Furthermore, the tiered approach may also be incorporated into the derivation of consents for effluent discharges to surface waters.

Acknowledgements

Contents

1   Introduction

1.1   Background

The aquatic environment is sensitive to damage from a wide range of chemicals. The Environment Agency therefore uses a variety of standards and targets to protect and improve the quality of the UK's water resources. In particular, environmental quality standards (EQS), derived from toxicological data, are values used to assess and limit the levels of chemicals in the aquatic environment so that water bodies are protected from deterioration. The EQSs are used, for example, to calculate discharge consents of effluents to surface waters. They also help the Environment Agency to check national progress in protecting water quality and to identify where urgent action may be necessary. Indeed, EQSs may drive considerable investment in water quality programmes and the development of new techniques and technologies to achieve quality targets.

1.2   Derivation of quality standards

Environmental quality standards are key to protecting the environment, controlling risks to domestic, industrial and agricultural water supplies, and ensuring that people can enjoy water-based leisure activities in safety. Given their unequivocal importance, due consideration should be given to their calculation, interpretation and implementation. How, for example, is the toxicologically derived limit value that forms the basis of the EQS calculated? What is the technical feasibility of assessing compliance to an EQS, and are there any cost/benefit implications?

Environmental quality standards are derived by assessing toxicity data for a range of organisms from a number of trophic levels within the aquatic system (typically fish, algae, and invertebrates). The most reliable and sensitive (i.e. lowest) value for a reported no observed effect concentration (NOEC) is then identified. Ideally, the NOECs are from chronic tests that include sub-lethal endpoints.

A so-called assessment factor is then applied to the NOEC to create a predicted no-effect concentration (PNEC). The assessment factor accounts for uncertainty in the data: results for reported species may not include the most-sensitive species present in the actual environment. The assessment factor varies depending on the amount of data available, but usually varies between a factor of 10 and 1000 (EU Technical Guidance Document 2002). A PNEC may also be derived using the EU Technical Guidance Document (TGD) probabilistic approach (species sensitivity distribution (SSD) approach) providing that the minimum quantity of reliable, long-term toxicity data is available. Depending on the available information, an assessment factor of 1 to 5 is generally applied to the 5th percentile of the SSD to derive the PNEC.

For synthetic organic compounds, the PNEC can be used as an EQS value designed to protect the vast majority of organisms present in surface waters. For risk assessment purposes (EU TGD 2002), the PNEC is then compared with the predicted environmental concentration (PEC). If the PEC/PNEC ratio (often described as the risk characterisation ratio (RCR)) exceeds one then an adverse impact may be occurring in the environment.

For this project, it is assumed that the calculation of the toxicologically derived limit value is robust and the value widely accepted; the focus of this report is on the implementation of the EQS, specifically how compliance with the EQS is assessed.

1.3 Consideration of background concentrations

Many metals (e.g. copper, zinc, chromium) occur naturally in the environment. Even without the existence of humans and their industrial activity, significant concentrations of metals would occur in water owing to the underlying natural geology. Yet some metals are also essential to life: they participate in key enzymatic and metabolic processes. Aquatic organisms thus possess biological mechanisms to regulate their metal accumulation, absorbing the required quantity for metabolic functions and excreting the excess. In many cases where high concentrations of metals occur naturally, indigenous species have adapted to tolerate the elevated background concentrations.

For metals, the simple translation of a PNEC based on laboratory-derived toxicity data into an EQS value could, therefore, lead to a gross overestimate of the potential toxicity of metals in the aquatic environment. Laboratory toxicity experiments are generally carried out in waters with very low background concentrations of metals, into which additions of metals are made to determine the toxicity thresholds. Metal concentrations in the test and culture water are normally minimised to ease data interpretation, whereas elevated metal concentrations may occur naturally, especially in metalliferous regions. Metal speciation and ambient background metal concentrations ought to be taken into account when deriving EQSs. Existing legislation allows for these factors to some extent: under the EU Dangerous Substances Directive, metal PNECs have been classified into 'hardness bands' to translate laboratory-derived PNECs into working EQS values which may be used for regulatory compliance assessment.

To accommodate natural variations in metal concentrations, the 'added risk' approach has been developed and used within the EU TGD methodology (EU TGD 2002). This takes the laboratory-derived PNEC and allows the addition of a background concentration in order to derive an EQS. Therefore the PNEC, described as the $PNEC_{add}$, is the value at which toxic effects may occur ignoring contributions from background concentrations and applies only to the 'added' contribution over and above the background level. Although the added risk approach appears to be highly pragmatic, it leads to lengthy debates about what is an appropriate background concentration.

To keep calculations and comparisons simple and consistent, the use of a single background concentration value is preferred. The most conservative choice for a background concentration would be the observed concentrations in 'pristine' environments not influenced by human activity. However, in countries such as the UK, the presence of mineral-rich geology means that even in pristine areas, elevated metal concentrations are reported. This wide natural variation in metal concentrations makes it difficult to agree on a single background concentration value, even before the debate over whether a mean, median, or percentile concentration is most appropriate.

Furthermore, there are few rivers in the UK, even in upland areas, that are unaffected by human activity. Metals enter the water from agriculture, atmospheric deposition, industrial discharges, and road runoff. Logically, it would therefore seem appropriate to apply local background concentrations to PNEC values in order to derive local EQS values for metals. However, in many cases, there are insufficient data on local metal concentrations to derive these site-specific values and a workable methodology has yet to be agreed at either a Member State or EU level. In addition, the link between metal concentrations and ecological quality has yet to be fully elucidated; it is not currently possible to accurately conclude just how elevated metal concentrations can become before biodiversity and ecological quality are adversely affected.

Ongoing monitoring studies of background concentrations of metals in UK waters (EA 2006) will provide more data to feed into this debate.

1.4 Metal bioavailability

The influence of metal speciation on bioavailability and subsequent metal toxicity is considerable. The bioavailability of metals such as zinc and copper are controlled by ambient water quality, including pH, calcium concentration, alkalinity, and the presence of dissolved organic ligands (estimated by dissolved organic carbon measurements). As a consequence, the monitoring of total metal concentrations in water is a blunt and inaccurate metric by which to regulate discharges of these metals and implement environmental protection. Even dissolved measurements can lead to a significant overestimate of metal toxicity owing to interactions of the toxic free metal ion with other dissolved phase substances (e.g. major ions and organic metal-complexing agents).

Recent developments in the understanding of the mechanisms that affect metal bioavailability and toxicity in water has led to the development of biotic ligand models (BLM) for copper and zinc (e.g. Heijerick *et al.* 2002, De Schamphelaere *et al.* 2005). These models enable the prediction of the ecotoxicologically relevant metal concentration on a site-specific basis based on a combination of the physico-chemical properties of the water column and known ecotoxicological data.

1.4.1 Copper biotic ligand model

The copper BLM (Cu-BLM) has been developed over a number of years as an instrument to predict the toxic fraction of copper present in natural waters over a range of environmental conditions (typically pH 6–9). The concept of the Cu-BLM was established around 20 years ago (Pagenkopf 1983, Campbell 1995). It relies essentially on a curve-fitting exercise to match observed toxicity from approximately 150 ecotoxicity tests to measurable water quality parameters. The model predicts the free ion (Cu^{2+}) concentration from parameters that include pH, alkalinity, temperature, calcium, other major cations and anions, and most importantly dissolved organic carbon (DOC) as a measure of complexing ligands. The speciation model within the BLM is based on the established Windermere Humic Acid Model (WHAM V) which amends copper ion concentrations based on observed DOC concentrations.

However, DOC measurements are actually a rather poor predictor of copper complexation (Gardner and Comber 2003). Organic molecules with complexing properties (i.e. organic ligands) may be derived from synthetic chemicals (e.g. ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA)), natural biological exudates (e.g. proteins, phospholipids), and sewage-derived organics as well as fulvic and humic acids. Consequently, a factor has to be applied to measured DOC values, based on empirical observations, to correct for humic acid content (assumed to be 50 per cent). This adjustment brings predicted Cu^{2+} concentrations in line with observed values (Dwane and Tipping 1998).

Although the measurement of DOC has been shown to be a poor predictor of copper complexation capacity in surface waters, the Cu-BLM can provide predictions of copper speciation (and hence toxicity) largely within a factor of two of test data (De Schamphelaere and Janssen 2004). More detail regarding the Cu-BLM may be found in the copper EU Risk Assessment Report (EU RAR 2006). Santore (2006) further reviewed the information on variability in natural organic matter (NOM) quality in surface waters and the implications on copper speciation and bioavailability modelling. Santore concluded that a wide range of WHAM and BLM field validations demonstrated

that the variability in outputs attributable to NOM quality is comparable in magnitude to the 'noise' inherent to laboratory ecotoxicity testing.

The current form of the Cu-BLM generates predictions based on three steps:

1. The BLM predicts bioavailability of dissolved copper based on observed chronic toxicity threshold values (NOEC or 10th percentile effect concentrations (EC10)) amended for the specified water quality conditions.

2. These individual effects observations are combined to generate species mean NOECs (SM-NOECs) for each aquatic species' endpoint, defined as the geometric mean of individual NOECs for each species' endpoint (e.g. mortality, growth, reproduction). Where multiple toxicity endpoints have been measured for a species, the most-sensitive species mean endpoint is used as the SM-NOEC.

3. Finally, a PNEC is derived as the 50 per cent lower confidence limit of the 5th percentile value of the SM-NOECs, using a log-normal distribution.

Although the model requires a number of input parameters (calcium, sodium, potassium, magnesium, alkalinity, pH, DOC, sulphate, chloride, sulphide, temperature, and percentage humic acid content of DOC), several of the major ions have little impact on freshwater predictions, as demonstrated later in Section 3.2.1.

Organisms exposed to elevated metal concentrations, including copper, can adapt and tolerate significant changes with time. As a consequence, in the aquatic environment organisms can often be observed in metal-rich waters where they would not necessarily be expected. Illustrations of metal tolerance are provided in subsequent chapters. The ability to adapt to elevated metal concentrations can serve to complicate laboratory toxicity experiments depending on the previous exposure regime of the test organisms. Versions of the Cu-BLM have been produced that allow for an assumed background concentration of 0.5 µg/l, being the median copper concentration in the test media used in the ecotoxicity database, as well as a version that accounts for all known background concentrations for ecotoxicity. Although this should provide more accurate laboratory predictions, background concentrations for copper in laboratory test media should normally be very low (hence, the use of only 0.5 µg/l as a correction concentration). In the environment (see Section 3), observed copper concentrations can range in the 10s and 100s of µg/l, so it is justified to apply an additional background concentration (as advocated in the tiered approach to compliance assessment) to take account of local situations.

The physico-chemical ranges for parameters covered by the Cu-BLM are provided in Table 1.1. From the validation data, the copper RAR concludes that the validity ranges for the Cu-BLM are pH 6.0 to 8.7 (but as low as pH 5.6 if invertebrates are driving the species sensitivity distribution), hardness of 10 to 500 mg/l $CaCO_3$, and DOC of 0.5 to 20 mg/l. The Cu-BLM tends to be over-protective at low DOC concentrations. Based on these parameters, the dataset used to assess the Tier 3 approach contained DOC and pH values falling between these values; only one site had hardness below the lower range (around 7.5 mg/l $CaCO_3$).

A revised copper RAR was made available at the beginning of 2007. The final report is expected by mid/end 2007.

Table 1.1 Physico-chemical ranges for the Cu-BLM development and validation

Endpoint	Species	pH	Hardness (mg/l CaCO$_3$)	DOC (mg/l)
Developed and validated				
Chronic	*P. subcapitata*	6.0–8.7	10–500	1–20
Chronic	*D. magna*	5.6–8.5	10–500	1–20
Chronic	*O. mykiss*	6.0–8.0	30–360	0.5–1.3
Chronic	*P. promelas*	6.6–8.6	12–212	1–5
Cross-species validations and spot-checks				
Chronic	*Bracchionus*	6.0–7.8	100	5–15
Chronic	*Chlorella*	5.5–8.7	24–250	1.5–15.8
Chronic	*Chlamydomonas*	6.6–8.1	26–503	0.5–9.8
Acute	Field *Cladoceran*	6.8–8.3	-	1.6–37.7
Acute	Field *Cladoceran*	4.1–5.5[1]	-	3.5–5.7
Acute	*Lampsilis siliquoidea*	8.0–8.7	45–300	1–16

Notes: [1] The pH falls outside the BLM boundaries of the *D. magna* model. Within this lower pH range, the cladoceran observed NOEC values were always higher than the BLM predicted NOEC values.

1.4.2 Zinc biotic ligand model

The zinc BLM (Zn-BLM) is a Microsoft Excel based model. It predicts the modifying effects of pH, DOC, and calcium (or hardness) on chronic zinc toxicity to algae, *Daphnia*, and fish (De Schamphelaere *et al*. 2005); the effects of other major ions are accounted for by correlating these parameters with calcium. The model predicts site-specific NOECs for each of the three species based on the input water parameters for that site which are between defined ranges (pH 6–9, DOC 1–20 mg/l, and Ca 5–150 mg/l or, in the absence of Ca data, hardness 15–428 mg/l CaCO$_3$). Under most circumstances, the NOECs suggest that algae are the most-sensitive species.

The data can be further manipulated by comparison of each predicted NOEC (NOEC$_x$) with that based on 'worst case' reference conditions (NOEC$_{ref}$) where the zinc present is fully bioavailable (reference conditions: DOC of 1.8 mg/l for all; for algae, pH 8.4 and Ca of 88 mg/l or hardness ca. 250 mg/l CaCO$_3$; for *Daphnia* and fish, pH 6.6 and Ca of 8.8 mg/l or hardness ca. 25 mg/l CaCO$_3$). By dividing the reference NOEC$_{ref}$ by the predicted NOEC$_x$, an estimate of the fraction of bioavailable zinc present in the water is generated for each species. Consequently, this may result in values for fish and *Daphnia* greater than those for algae in waters with low pH and low calcium. The most conservative, i.e. the highest, value of the three 'bioavailability factors' (BioF) calculated, is taken for further use. Using this value, a 'bioavailable zinc concentration' can be generated for the observed or predicted environment concentration (PEC), namely by removing the 'background concentration' of zinc and multiplying the resulting concentration by the BioF. Finally, the PEC/PNEC ratio can be calculated by dividing the amended bioavailable PEC by the PNEC$_{add}$ of 7.8 µg/l generated from the zinc EU Risk Assessment Report (EU RAR 2006). This process can be summarised as:

1. The BioFs are derived for each of the three BLM species as follows:

$$BioF_{water,X} = \frac{NOEC_{ref}}{NOEC_x}$$

2. The highest of the $BioF_{water,X}$ values for the three species is selected to ensure that the most conservative approach is taken, i.e. to allow the smallest correction for bioavailability.

3. The zinc background concentration ($Cb_{dissolved}$) is subtracted from the zinc concentration measured through monitoring:

$$PEC_{add} = PEC_{dissolved} - Cb_{dissolved}$$

4. The bioavailable concentration of the added zinc concentration in the water at the site or region X can be calculated from:

$$PEC_{add,bioavailable} = PEC_{add} \times BioF_{water,X}$$

5. Subsequently, the RCR is calculated:

$$RCR = PEC_{add,bioavailable}/PNEC_{add}$$

This process obviously relies on several assumptions including those regarding the reference conditions and the background concentrations.

As described in Section 1.3, the use of an 'added risk' approach requires the availability of robust background concentrations for metals in the aquatic environment. In the zinc RAR, the above methodology was applied to more generic local and regional scenarios, where a range of background concentrations (3 to 12 µg/l) were used to assess the impact of bioavailability on the PEC/PNEC ratio. In most cases, the lowest predicted $NOEC_x$ generated by the BLM is associated with algae (effectively at pH 6.4 or higher). Under certain circumstances, however, the ratio of $NOEC_{ref}/NOEC_X$ may give a greater bioavailable fraction for *Daphnia* and fish, even though the absolute value of the $NOEC_X$ is lower for algae (i.e. at very low hardness values).

The above methodology is useful when carrying out generic chemical risk assessments, where a precautionary approach is being adopted. However, absolute PNEC values (rather than relative values) are more appropriate for site-specific comparisons with observed dissolved zinc concentrations. In such cases, the predicted $NOEC_X$ (essentially a PNEC based on site-specific physico-chemical parameters) for the most-sensitive species associated with the ambient water quality would be used, without the need to generate a ratio with generic worse-case situations. Consequently, for the purpose of this project, the most precautionary $NOEC_X$ value (in all cases the NOEC for algae for the datasets used in this project), rather than a relative value, was used in comparisons with observed dissolved zinc concentrations. This $NOEC_X$ value is referred to in this report as the 'PNEC-BLM$_{algae}$'

This second approach for the zinc assessment was more consistent with the copper assessment methodology as it meant that PNECs for the most-sensitive species were derived in both cases. However, for thoroughness, a comparison was carried out using

both zinc assessment methodologies. Results showed that at the Tier 3 level, comparison of observed concentrations with the PNEC-BLM$_{algae}$ was only marginally less conservative (i.e. resulted in fewer 'failures' where observed concentrations were greater than the PNECs) than if the RAR-derived approach was used.

The zinc RAR has been finalised by the Rapporteur and sent to the European Chemicals Bureau for final review by the European Committee of Health and Environmental Risks.

1.5 Options for a tiered approach to the assessment of regulatory compliance

The key issues of metal background concentrations and bioavailability are not being widely considered currently in standards setting regimes in Europe. Recent projections using surface water data from England and Wales (n >1000) show water quality failures, i.e. concentrations above the potential PNEC, could be greater than 50 per cent in the case of zinc. However, there is little evidence to suggest that surface waters in England and Wales are significantly degraded by metal pollution. On the contrary, the tightening of consents for discharges to the aquatic environment and the decline of the UK's manufacturing industry have reduced zinc inputs to surface waters over time. This situation, therefore, suggests that the standard-setting procedure (including the issue of implementation) has not been followed correctly and/or that the standards do not adequately take account of metal background concentrations or speciation, i.e. actual risks are lower. This project focuses on these areas of uncertainty.

The Environment Agency is considering options for implementing metal EQSs under the Water Framework Directive. It is looking to provide a practical methodology by which reported environmental concentrations may be assessed using an approach that progressively becomes more site-specific. The proposed tiered approach filters data through three tiers of assessment in order to methodically evaluate compliance with the EQS:

Tier 1: observed concentrations are compared with the PNEC/EQS without any corrections.

Tier 2: observed concentrations are compared with the PNEC/EQS plus an accepted background concentration of the metal.

Tier 3: observed concentrations are compared with a site-specific standard that accounts for the local bioavailability of the metal, based on in situ water chemistry.

Figure 1.1 provides a schematic representation of the proposed methodology.

To fully examine this tiered approach, an assessment of the performance of the models proposed for use at Tier 3 is also necessary to ensure their accuracy, reliability, and usability. This analysis has therefore been incorporated into the objectives of this project.

Tier 1

Face value comparison
of
PEC with PNEC

$PEC > PNEC_{add}$ or $PNEC_{total}$ — **No** → Pass

Yes

Tier 2

Compare $PNEC_{add}$ with background concentration (local)

$PEC\ (- bkg) > PNEC_{add}$ — **No** → Pass

Yes

Tier 3

Analysis of bioavailability using BLMs

$PEC \times BIOF > PNEC_{bioav}$ — **No** → Pass

Yes

Fail
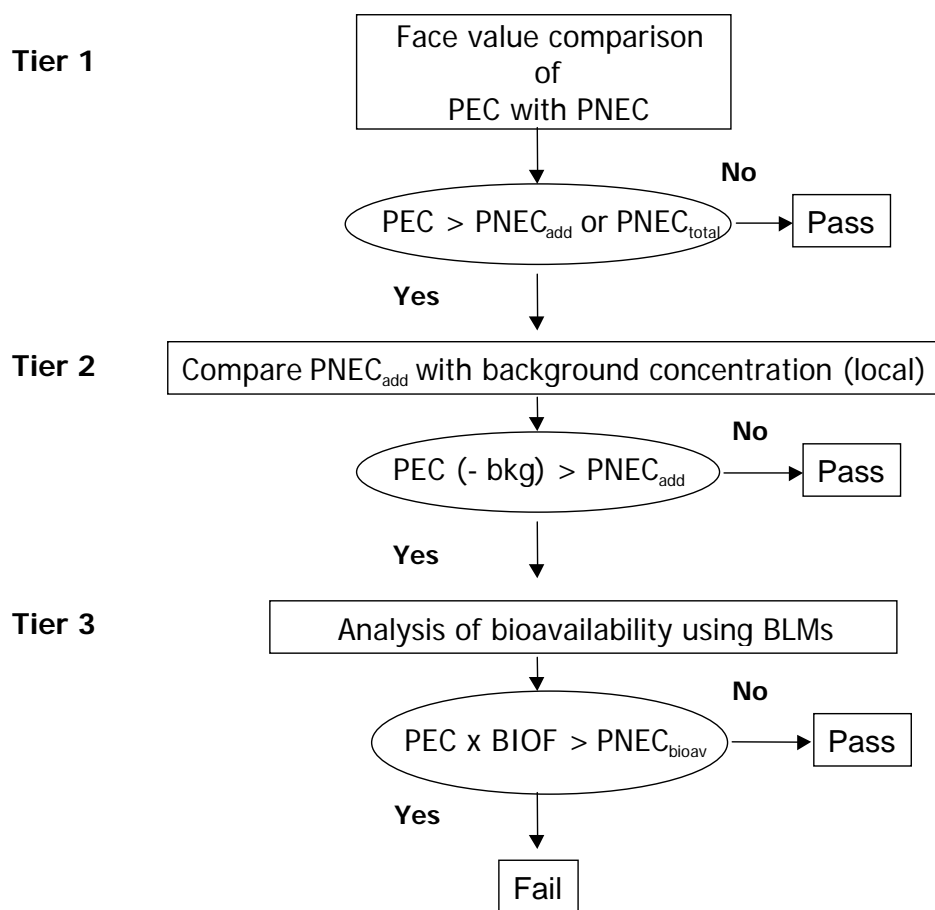
Figure 1.1 Proposed tiered assessment

1.6   Copper and zinc specific issues

Both copper and zinc are essential elements, with widely varying concentrations in UK waters due to natural geology as well as anthropogenic inputs from diffuse and point sources. Historically, industrial discharges and mining contributed significantly to surface water concentrations of these elements. Within the last five decades, the reduction in the UK's manufacturing industry and closure of the majority of the mines mean that the UK is left with only the legacy of these polluting discharges (e.g. mine drainage water, runoff from contaminated land) concentrated in localised areas. There are, however, numerous lower-level point and diffuse sources of these metals to the aquatic environment as they are found in a wide range of common products including plumbing materials, pharmaceuticals, biocides, anodes, batteries, personal care products, electrical goods, and electronics.

Both metals are currently regulated as List 2 chemicals under the Dangerous Substances Directive. The EQSs for copper and zinc are set according to the hardness of the water body. For zinc, the type of fishery present in the water (salmonid or cyprinid) also affects the EQS. Lower EQSs are set for soft waters, inherently reflecting the increased bioavailability of metals in soft, lower pH waters.

The RARs for copper and zinc use EU TGD methodology to derive PNEC values using two different approaches:

The copper RAR uses a total risk approach where the PNEC incorporates a 'reasonable worst case' water quality and applies a bioavailability correction using the

BLM to derive a total dissolved PNEC value of 8.2 µg/l of copper. This derived value may be considered to be equivalent to an EQS as it takes some account of background concentrations and bioavailability, albeit very conservative. The decision not to use the 'added risk' approach was largely driven by uncertainties and observed variations in background concentrations, as described above (Sections 1.3 and 1.4.1). The PNEC does, however, include background concentrations of copper present in test and culture media, assumed to be around 0.5 µg/l of dissolved copper. A small 'background' concentration has been allowed for in two alternative versions of the BLM: (i) in which a constant value of 0.5 µg/l has been subtracted from observed toxicity effect concentrations, and (ii) in which the actual measured test media background copper concentration has been subtracted. This correction for laboratory background concentrations is relatively small and would not account for localised elevated copper concentrations observed in the aquatic environment. The copper RAR, therefore, suggests that a Tier 2 application of the risk assessment is applied to localised areas with elevated observed copper concentrations. In addition, the normalisation of the PNEC to the bioavailability of copper only takes a 'reasonable worst case' scenario of low pH, DOC, and hardness. Hence, the copper PNEC is a very conservative figure (as required by the RAR processes), offering a first tier screening concentration, which if exceeded, would lead to more detailed assessment of site-specific bioavailability and background concentrations.

The zinc RAR uses the 'added risk' approach to derive a $PNEC_{add}$ of 7.8 µg/l dissolved zinc for waters with hardness greater than 24 mg/l $CaCO_3$. For soft waters (hardness <24 mg/l $CaCO_3$), a $PNEC_{add}$ of 3.1 µg/l dissolved zinc was derived taking account of increased metal toxicity in very soft waters. In all cases, the $PNEC_{add}$ needs to be compared with environmental levels where the 'natural' background has been subtracted so that 'additional toxicity' is compared with 'additional environmental inputs' to ensure like for like comparison. For the purpose of the RAR, a lower limit of 3 µg/l and upper limit of 12 µg/l zinc were used (12 µg/l being a geometric mean value) based on European monitoring data. The application of a bioavailability factor (derived using the Zn-BLM) is proposed in a tiered approach where initial PEC/PNEC ratios exceed 1. The zinc $PNEC_{add}$ may be considered a more conservative value compared with the copper PNEC as no account is taken for background concentrations and bioavailability effects. A greater degree of 'failure' may, therefore, be expected for zinc at the Tier 1 stage before background and bioavailability are factored in.

In both cases, the progression through the tiers proposed in Figure 1.1 represents an increasingly site-specific assessment of water quality, particularly if local background concentrations are applied, leading to site-specific bioavailability calculations. Although a bioavailability factor has already been applied to the copper PNEC, site-specific data may not reflect the reasonable worst case used to derive the value, and therefore offers more relevance on a local scale. For zinc, Tier 3 is the first use of a bioavailability correction.

This project was jointly funded by the Environment Agency and the metals industry (International Copper Association represented by the European Copper Institute, and the International Lead Zinc Research Organisation). It is a practical attempt to test the tiered approach using the PNECs cited in the corresponding RARs for copper and zinc (Tier 1), combined with potential background concentrations (Tier 2), and the use of BLMs to predict site-specific metal bioavailability (Tier 3) (see Figure 1.1).

1.7　Objectives

The objectives of this project were to develop an approach for the regulation of metals by assessing compliance in ways that take account of background concentrations and speciation/bioavailability. Further, the project assesses the extent of water bodies failing to meet potential metal standards when backgrounds and speciation are not considered. Specifically, this project is a practical trial of a tiered approach to the assessment of compliance and will:

- compare potential standards against measured concentrations from Environment Agency data sources, particularly after accounting for background concentrations and bioavailability, through the use of BLMs;

- determine the sensitivity of the BLM predictions for each metal to the inclusion or exclusion of driving data (such as some key anions or estimates of DOC);

- assess the value of the tiered approach by comparing historical EQS failure data and paired biological data to determine prevalence of Type I errors (false positives);

- assess the likely number of sites in England and Wales for which the tiered approach would be needed and for which metals;

- assess the financial and time-related cost of derogation or exception, against the cost of performing the refinements to PECs or setting site-specific EQSs as well as risk reduction measures;

- provide a critique of the potential use of the tiered approach and formulate recommendations and target areas for any further work.

2   Methodology

2.1   Datasets

This assessment focused on copper and zinc – metals for which reliable BLMs were available in combination with readily available aquatic monitoring data. Four sources of data were made available for use within this project:

- Environment Agency monitoring data (WIMS physico-chemical data and biological General Quality Assessment (GQA) monitoring data);

- Scottish Environmental Protection Agency (SEPA) monitoring data for 20 sites covering many years;

- Centre for Environmental Hydrology (CEH) data generated in 2005 and 2006 for a limited number of sites in the north west of England as part of a metal speciation project undertaken for the Environment Agency, including some matched biological data;

- background concentrations derived as a part of a recent draft report (EA 2006).

The SEPA and CEH data were of limited use due to the lack of matched comprehensive biological monitoring data with which to compare BLM outputs. The results of this study, therefore, principally rely on the Environment Agency dataset.

Two Environment Agency datasets were used in this assessment:

- a full 1995 dataset of chemical and biological parameters (but with limited DOC data);

- Environment Agency data for selected sites from 1995 to 2006 that included DOC data and biological monitoring information.

The full 1995 dataset including chemical and biological monitoring data was used to assess compliance at the Tier 1 and Tier 2 levels. However, the lack of DOC data meant there was insufficient information available to run the BLMs as part of the Tier 3 assessment.

Data for DOC were limited because it is not routinely determined in chemical monitoring programmes, and therefore a full dataset was not available for the UK. Hence, a limited number of identified sites were manually searched to select suitable site data. The initial, large dataset covering sites across the UK in the last 10 years was reduced considerably when limited to sites reporting data for dissolved metal, hardness/calcium, pH, and DOC.

A list of candidate sites was drawn up based on the following criteria:

- zinc or copper concentrations were predominantly (although not exclusively) greater than the PNECs;

- other metal concentrations were generally low;

- other possible polluting substances were low (e.g. ammonia, BOD);

- there was a maximum geographical spread;

- where available, sites on large rivers were selected.

ANNEX A provides tables for the selected sites based on available 1995 monitoring data and ANNEX B gives a summary of the data available for the selected sites covering 1995 to 2006 used for assessing the tiered approach. The limited availability of DOC data affected the information that could be obtained for the requested sites. The sites, years, and number of data points that were analysed further are also presented.

For zinc, DOC data for 15 rivers were available, amounting to over 1000 data points. However, only 10 sites had data for more than one year with at least 12 data points per year. Nevertheless, a reasonable spread of zinc and copper concentrations associated with the DOC data was obtained (see ANNEX A). This dataset provided sufficient information with which to undertake a thorough assessment of the tiered approach.

2.2 Tiered assessment

2.2.1 Tier 1

The Tier 1 assessment compares reported data for dissolved copper and zinc with the PNEC/EQS values for these metals (Table 2.1), without considering potential background concentrations and bioavailability.

The PNECs are taken from the draft RARs for zinc and copper. The zinc value is actually a $PNEC_{add}$; the 'added risk' approach (EU TGD 2002) would be applied by adding this value to background (regional or local) concentrations to derive the EQS. Consequently, comparing observed concentrations of zinc from monitoring programmes at sites where elevated zinc background concentrations may occur will lead to an overstatement of possible environmental impact from Tier 1 assessments.

For copper, the PNEC from the RAR corresponds more closely to an EQS, as it does incorporate a background concentration and is normalised for bioavailability. However, the value can be considered extremely conservative as the background values correspond to background concentrations in laboratory tests, not environment conditions. Additionally, the bioavailability normalisation was based on a 'reasonable worst case' scenario.

The reasonable worst case scenario is outlined in the copper RAR (pH 6.6 and 8.1, DOC of 2.6 mg/l, and hardness of 37 mg/l $CaCO_3$). Comments received back from consultation may lead to minor amendments to the PNEC in the final report (see Table 2.1). Environment Agency data suggest that for England and Wales, the 10th and 90th percentiles for pH, DOC, and hardness are 7.2–8.2, 1.0–6.2 mg/l, and 33–351 mg/l $CaCO_3$, respectively; these values lie within the corresponding ranges used for the copper RAR. It therefore appears that the PNEC should be protective for most English and Welsh rivers, with the exception of some very soft, low DOC rivers, or those with high natural background concentrations of copper.

Table 2.1   Values used at Tier 1 of the assessment

Element	PNEC (µg/l)	Current EQS (µg/l)[3]		Comments
Copper	8.2[1]	Hardness		Long-term PNEC
		0–50 mg/l $CaCO_3$	1	for freshwater
		50–100 mg/l $CaCO_3$	6	
		100–250 mg/l $CaCO_3$	10	
		>250 mg/l $CaCO_3$	28	
Zinc	7.8[2]	Hardness		Long-term
		0–50 mg/l $CaCO_3$	8	$PNEC_{add}$ for
		50–100 mg/l $CaCO_3$	50	freshwater
		100–250 mg/l $CaCO_3$	75	
		>250 mg/l $CaCO_3$	125	

Notes: [1] The PNEC (8.2 µg/l) is based on the copper RAR (EU RAR Feb 2006). A revised report was made available at the beginning of 2007 and a final report is expected mid/end 2007. The revised RAR will include additional ecotoxicity endpoints, already included in the BLM software used for the calculations in this report. The revised RAR will result in a somewhat lower reasonable worst case PNEC (6.4 µg/l) and will include PNECs for a range of EU scenarios, agreed upon under the nickel risk assessment. The PNEC values for these EU scenarios range between 7.9 and 22 µg/l.
[2] A $PNEC_{add}$ value to be added to the background to derive a maximum permissible concentration. The value is taken from the zinc RAR currently with the European Committee of Health and Environmental Risks for final review and is not a finalised agreed value until this process is complete.
[3] Zinc EQS based on the more stringent values for salmonid than for cyprinid fish.

2.2.2   Tier 2

Where observed dissolved concentrations of copper or zinc exceed the PNEC values, the next tier of assessment takes account of background concentrations of the metals. This is the level of metal to which indigenous organisms would be expected to have 'acclimatised'; indeed this concentration would be responsible, in part, for the diversity of the organisms found there.

For zinc, the addition of a background to the $PNEC_{add}$ value from the zinc RAR provides a more 'true' EQS. For copper, as stated in Section 1.6, the PNEC derived in the corresponding RAR already incorporates a measure of background concentration associated with the laboratory toxicity tests. The addition of a further background concentration could be seen as a relaxation in the quality standard; however, it could also represent an improvement in the accuracy for localised conditions.

The value of metal background concentrations has been the subject of intense debate, not least because it can have a profound impact on any assessment of metal compliance. The Environment Agency has commissioned a project with the British Geological Survey to determine English and Welsh background concentrations for selected metals, including copper and zinc. The current data are not comprehensive, but cover a large proportion of the east of England, the Midlands, and a few localised areas of the south west of England and Wales. Currently, only interim conclusions are available and so for illustrative purposes the median value has been used in this report (i.e. Cu = 1.6 µg/l and Zn = 3.4 µg/l, Table 2.2; EA 2006).

Data provided in the copper RAR (EU RAR 2006) cite European background concentrations ranging from 0.2 to 5.0 µg/l, suggesting the value selected for this

assessment may be an underestimate of actual values, particularly in areas influenced by underlying mineralogy.

The zinc RAR (EU RAR 2006) reports EU background concentrations ranging between 2.5 and 12 µg/l for total zinc, with the upper limit being a geometric mean of monitoring data used in the zinc RAR. Less data is available for dissolved zinc, but values of 1 to 35 µg/l have been reported, depending on the source. A median value of 3.4 µg/l dissolved zinc for the UK may, therefore, be considered a reasonable estimate, outside of localised areas of zinc mineralogy.

Table 2.2   Values used at Tier 2 of the assessment

Element	Concentration		
	PNEC (µg/l)	Background concentration (µg/l)[1]	Tier 2 assessment value
Copper	8.2	1.6 (2.6)	9.8
Zinc	7.8	3.4 (11.1)	11.2

Notes: [1] Median values are used to derive the Tier 2 assessment value. Figures in parenthesis are average background concentrations (EA 2006).

2.2.3   Tier 3

When observed dissolved metal concentrations exceed the Tier 2 (PNEC plus background) concentration, the final tier of assessment takes account of the bioavailable fraction of metal present in the sample, based on its water chemistry. The bioavailable metal fraction (assumed to be the toxic fraction) is calculated using the BLMs described in Sections 1.4.1 and 1.4.2.

There is already an allowance for bioavailability incorporated into the copper PNEC. However, the normalisation for bioavailability is based on a 'reasonable worst case' scenario, and is, therefore, highly precautionary, as required under the risk assessment process. For the purpose of a tiered approach to metal compliance, the majority of waters will not be represented by this worst case situation of low pH, low DOC, and low hardness. By applying more realistic, site-specific water quality data, a more accurate estimate of the bioavailable fraction of copper may be calculated.

All of the necessary data was supplied by the Environment Agency to run the Zn-BLM, which required only DOC, calcium, and pH to predict NOEC values (essentially PNECs) and the percentage of bioavailable zinc. The BLMs (particularly the Cu-BLM) are sensitive to DOC concentrations (see Section 2.3.1), so predictions were only made where actual DOC values were available. For calcium and pH values, a good degree of consistency was observed for any given annual dataset. If these values were absent for any site or date (which was for less than 2 per cent of all data) an annual mean value was used in order to run the Zn-BLM. This approach was also used for the Cu-BLM parameters that had little impact on the predicted PNECs (magnesium, potassium, sodium, chloride, temperature, percentage humic acid, sulphide).

For the Cu-BLM, four test results out of the approximately 150 ecotoxicity datasets have been queried (flagged in the BLM). For the purpose of testing the model in subsequent chapters, these data points were omitted, although tests by the model developers have demonstrated that these data have little impact on final predictions. In addition, copper BLMs were made available which take account of background copper concentrations in the individual laboratory tests (typically <1 µg/l). Two options were made available later in the project: the first was to remove reported background concentrations in test waters, the second to subtract a fixed 0.5 µg/l copper background. The latter approach leads to a uniform lowering of the PNEC by the set

factor, whereas the variable changes in the former model can lead to varying differences in the predictions. As this project was designed to test the implementation of a tiered assessment methodology from a theoretical viewpoint, it was decided that all the tests should use the initial Cu-BLM supplied by the European Copper Institute.

As described in Section 1.4.2, the Zn-BLM generates predicted NOEC values for fish, algae, and *Daphnia* and a percentage value for bioavailable zinc, based on the most-conservative NOEC value relative to the reference conditions. The zinc RAR process for calculating bioavailable zinc concentrations amends observed (or predicted) dissolved zinc concentrations by multiplying them by the bioavailable fraction after removing a background concentration. This predicted bioavailable fraction of zinc is then compared with the $PNEC_{add}$ (7.8 µg/l). This process obviously relies on several assumptions including those regarding the reference conditions and the background concentrations.

To provide a comparison with the Cu-BLM assessment (wherein PNECs are derived and compared with observed concentrations), observed zinc concentrations were generally compared to the Zn-BLM predicted NOEC outputs for the most-sensitive species (algae exclusively, and therefore referred to as the '$PNEC$-BLM_{algae}' in this report). However, for comparative purposes, the zinc RAR methodology (shown to be slightly more conservative in most cases) was applied to the monitoring data provided by the Environment Agency and the differences in outputs discussed (see Section 3).

2.3   Biotic ligand model performance testing

2.3.1   Sensitivity to input parameters

One of the objectives of this project was to investigate the sensitivity of the BLMs to changes in key input parameters. This work aimed to assess:

- the validity of using default values in the absence of measured data (thereby potentially reducing the required dataset, particularly for the Cu-BLM);

- the relative importance of parameters in controlling the bioavailability predictions.

To achieve these objectives a series of scenarios were run for both BLMs, where average concentrations for input parameters were calculated for the Environment Agency's 1995 dataset and used as baseline input data. For each parameter, the model then was run using the maximum and minimum observed concentrations to assess the impact on the output values.

For the Cu-BLM, an additional set of scenarios were undertaken where DOC, pH, and calcium concentrations were set at their maxima and minima, rather than at average conditions, and the same exercise repeated. These extra scenarios were necessary because the Cu-BLM has a large number of input variables, several of which appear to have little impact on the calculated PNEC. The scenarios were geared to confirm the relative (in)sensitivity of different parameters and to check how extreme values of the key parameters (DOC, calcium, and pH) would affect the PNEC and, therefore, the potential EQS.

2.3.2   Biotic ligand model data aggregation

The practical implementation of the Tier 3 assessment using the BLMs must also be considered. The usability of the models is critical to their incorporation into the regulatory compliance process. Most compliance monitoring involves the assessment of water quality over a period of 12 months. Running the BLMs (particularly the Cu-BLM) requires a certain amount of data manipulation and computing time. This project also considered the impact of deriving PNECs based on i) inputs of data from each site and date (a relatively laborious process) and taking a mean of all PNEC values to derive an 'annual average', or ii) calculating mean annual values of the input parameters and running the models once with these data.

2.4   Surrogates for dissolved organic carbon values

The sensitivity of the BLMs to DOC concentrations meant that the use of average or default values would lead to considerable errors in bioavailability predictions (particularly for the Cu-BLM). The DOC data in the Environment Agency's datasets is also severely restricted, which could hamper speciation predictions using the BLMs. The importance of DOC as an environmental variable is now established, however, so it is expected that it will become more widely available in the future. For this retrospective analysis, nevertheless, an alternative way of estimating DOC would be valuable.

There are well-established relationships between DOC and colour measurements. As colour is relatively easy to measure in filtered samples, if an accurate correlation was established, then colour could be a useful surrogate for DOC. Colour is reported by the Environment Agency as absorbance at 420 nm, although other wavelengths (as well as fluorescence) may be used to provide more selective analysis.

Several of the 30 sites (for zinc) from the Environment Agency's datasets had values for both colour and DOC. Correlations between these two measures were compared to assess the potential for using colour as a surrogate for DOC.

2.5   Comparison of tiered assessment data with biological monitoring data

The Environment Agency uses biological indices to determine the ecological status of a watercourse. Two commonly used systems are the Biological Monitoring Working Party (BMWP) system and the related average score per taxon (ASPT). The BMWP system was developed in the 1970s and provides scores for around 80 different groups of invertebrates based on their perceived tolerance to organic pollution. The higher the BMWP score assigned, the less pollution tolerant the group.

A weakness with the BMWP system is its dependence on the sampling effort; the more vigorous the sampling, the greater the potential for collecting a larger range of organisms. The ASPT is used to overcome this limitation: it is calculated by dividing the BMWP score by the number of groups present.

As different types of watercourse can support different ranges of animals, the River Invertebrate Prediction and Classification System (RIVPACS) was developed to predict the taxon richness and expected ASPT at different types of sites, if those sites were unpolluted. The expected values for a particular site are its 'reference state'. The ratio of the observed/expected values can be used to judge the true biological condition of the site.

The ASPT ratios (also referred to as an Ecological Quality Index, EQI) are used in the biological General Quality Assessment (GQA) by the Environment Agency to grade watercourses from very good to bad. Table 2.3 provides the grades according to the EQI for ASPT.

Table 2.3   Biological grades under the GQA system

Grade	EQI for ASPT	Environmental quality
A	1.00	Very Good
B	0.90	Good
C	0.77	Fairly Good
D	0.65	Fair
E	0.50	Poor
F	<0.50	Bad

The GQA methodology was developed to assess impacts from pollution derived from organic load, ammonia, and low dissolved oxygen. Although it was not developed to measure potential metal pollution, it has produced the only cohesive dataset to attempt to match observed ecological quality in a river system with measured metals concentrations and predictions of bioavailability. The matched biological and chemical data were, therefore, analysed in detail in this project to investigate whether the tiered approach to metal compliance in surface waters could predict good ecological quality in the water column.

Biological monitoring data was limited for the sites where Tier 3 (BLM) data was also available. In some cases, data were limited to a single year, on the basis of the raw data supplied (from 1996 to 2003). Data gaps were substituted with mean values according to the following hierarchy:

1. Where multiple years' data were available means for individual years were applied.

2. For datasets with only two pre-2000 and two post-2000 datasets, mean pre- and post-2000 BMWP scores, etc., were applied to the appropriate years.

3. Where a single year's BMWP data were available, the mean of the spring and autumn data were applied to all data.

3 Results and discussion

3.1 Tiered assessment

Two sets of data have been used to evaluate a tiered approach to the assessment metal compliance in surface waters:

- A 'complete' set of data from the Environment Agency's WIMS database for 1995. This set provides an overview of the number of possible failures at each tier across England and Wales. The absence of DOC values for this dataset, meant that these data could only be assessed at the Tier 1 and 2 levels. If DOC data had been available to enable assessment at Tier 3, 19 out of 7230 data points would have been below the lower end of the BLMs' defined ranges for pH (pH 6.0) and 15 above the upper end (pH 9.0) (see Sections 1.4.1 and 1.4.2). For hardness, 159 out of around 4000 measurements were less than 15 mg/l $CaCO_3$, the low end of the range for the Zn-BLM (83 for the Cu-BLM compared with the corresponding value of 10 mg/l $CaCO_3$); 166 data points were greater than 428 mg/l $CaCO_3$ at the high end of the range (75 for the corresponding Cu-BLM value of 500 mg/l $CaCO_3$). Approximately 8 per cent of data for the Zn-BLM and 4 per cent for the Cu-BLM were outside of the defined ranges for the BLM parameters, demonstrating the diversity of waters encountered in the UK.

- A selected (limited) number of data from individual sampling points on a variety of rivers where input parameters, in particular DOC data, were available to run the zinc and copper BLMs. Sites were selected to provide a range of copper and zinc concentrations, with a bias towards PNEC + background 'failures' (i.e. Tier 2 failures). For the Zn-BLM Tier 3 assessment, all of the selected sites had water quality parameters that fell within the validated ranges for DOC, calcium, and pH. This was also the case for the Cu-BLM, with the exception of calcium in the River Twrch which measured around 3 mg/l, just below the validated lower limit of 4 mg/l.

3.1.1 Tiers 1 and 2 assessment using the Environment Agency 1995 dataset

Table 3.1 summarises the number of 'failures' at Tiers 1 and 2 for copper and zinc. The data show a stark contrast between the two metals.

For copper, a relatively low proportion of data points exceed the PNEC value (Tier 1), but most of these 'failures' also exceed the PNEC + background concentration (Tier 2), thus requiring the application of the Cu-BLM (Tier 3). A large proportion of the elevated copper concentrations are associated with copper mineralogy in the south west of England, in particular Cornwall. This suggests copper to be a localised issue, rather than a country-wide problem.

Comparison at the Tier 2 level using a background concentration based on the median or mean reported concentration (EA 2006) makes only a 1 per cent difference in the overall percentage failure rate for copper. The degree of compliance using the copper PNEC is more favourable than that with the existing EQS, which has a failure rate of around 20 per cent. This apparently poor compliance is caused because a low EQS

value of 1 µg/l is used for the softest waters (0–50 mg/l CaCO$_3$), leading to compliance 'failures' in soft waters of the UK. It is, therefore, possible that the copper PNEC, which utilises a 'reasonable worst case' scenario based on European waters, may not be sufficiently protective for certain localised UK waters lying outside of the 10th/90th percentiles used in the copper RAR.

The situation for zinc appears to be a much more widespread issue, largely due to the ubiquitous presence of zinc in the environment. A far higher proportion of data points exceed the Tier 1 PNEC value. As previously discussed, this result is unsurprising given that the Tier 1 assessment for zinc is very conservative compared with that for copper. For zinc, the observed concentrations (which include background concentrations) are being compared with a PNEC$_{add}$ that does not include background concentrations and, therefore, exceedances at Tier 1 would be expected. The copper PNEC also allows a small degree of normalisation for bioavailability.

However, even when background zinc concentrations (based on median background concentrations) are factored into comparisons at the Tier 2 level, the number of 'failures' is reduced only by a small margin; 60 per cent of samples remain non-compliant and, therefore, requiring Tier 3 assessment. Assessment against a mean background concentration reduces the number of 'failures' to 40 per cent of the total reported data, which still represents a substantial proportion of sites in England and Wales. The zinc PNEC is effectively equivalent to the existing EQS for the softest (most vulnerable) waters supporting salmonid fish (8 µg/l). Significantly fewer 'failures' occur when measured concentrations are compared with the existing EQS regime (which extends to 125 µg/l for waters of high hardness). The RAR PNEC is fixed for waters of all hardness values.

Table 3.1 Summary of the number of samples 'failing' at each tier of assessment for the 1995 dataset

Assessment		Number of data points[1]	
Description	**Value**	**Zinc**	**Copper**
Reported metal concentrations	–	469	2952
'Failure' of existing EQS	>EQS (8–125 µg/l Zn; 1–28 µg/l Cu)	52 (11%)	593 (20%)
'Failure' at Tier 1	>PNEC (7.8 µg/l Zn; 8.2 µg/l Cu)	340 (72%)	169 (5.7%)
'Failure' at Tier 2	>PNEC + BG$_{med}$ (11.2 µg/l Zn; 9.8 µg/l Cu)	283 (60%)	124 (4.2%)
'Failure' at Tier 2	>PNEC + BG$_{mean}$ (18.9 µg/l Zn; 10.8 µg/l Cu)	188 (40%)	93 (3.1%)

Notes: [1] The 1995 dataset comprised a total of 7230 data points; percentages in parentheses are percentage 'failures'.

3.1.2 Tiers 1, 2, and 3 assessment using selected Environment Agency datasets from 1995 to 2006

The datasets for copper and zinc covering 1995 to 2006 were selected to enable testing of the whole tiered approach by including outputs from the BLMs. Full datasets for individual river sites are provided in ANNEX B and ANNEX C.

For zinc (Table 3.2), the lowland urbanised rivers such as the Anker, Tame, Trent, and Severn 'fail' at Tiers 1 and 2 for the majority of the data points, thus requiring

assessment at Tier 3. The same is the case for samples taken from metalliferous areas, such as the upper Tyne valley and, to a degree, the River Lynher, where applying a 'generalised' background concentration has no effect on the rate of metal compliance (Figure 3.1).

For more rural rivers (e.g. Blackwater, Nene, Otter, and Axe), compliance with the zinc PNEC$_{add}$ at Tier 1 is almost 100 per cent without the need to apply any further data manipulation which reflects low background zinc conditions (Table 3.2 and Figure 3.1). Rivers such as the Tavy and Ouse lie between these two situations, so the application of a background concentration at Tier 2 has a significant impact on the number of non-compliances. Water quality data for the rivers assessed in Table 3.2 are provided in ANNEX B.

At Tier 3, assessment of the observed zinc concentrations using either of the two methodologies described in Section 2.2.3 showed little difference between them as approaches for considering bioavailability, and therefore levels of compliance. Comparison with the PNEC-BLM$_{algae}$ based on reported water quality was only marginally less conservative than considering observed concentrations using the methodology in the zinc RAR (where the most conservative ratio of NOECs for fish, *Daphnia*, and algae to reference conditions is used to predict the percentage of bioavailable zinc present).

Application of the Zn-BLM has a significant impact on the number of 'failures' at Tier 3. Rivers known to receive high levels of urban and diffuse inputs still exceed the PNEC-BLM (whether expressed as the PNEC-BLM$_{algae}$, or by considering 'bioavailable zinc' using the RAR procedure). These rivers include the Tame and the Trent, where metal pollution may be expected. Similarly, samples from sites influenced by underlying mineralogy still lead to exceedances at the Tier 3 level (e.g. Tyne and Lynher).

For other rivers that are little affected by urban or minewater drainage (e.g. Anker, Severn, Nene, and Tavy), the vast majority of 'failures' at Tier 2 are eliminated using the Tier 3 assessment, as would be expected for waters of high ecological quality (see Section 3.4 and no obvious sources of zinc pollution.

Table 3.2   Data for zinc for selected sites summarised for each tier

River	Year	Total data points	Tier 1 >PNEC (7.8 µg/l)	Tier 2 >PNEC+BG (11.2 µg/l)	Tier 3 >PNEC-BLM$_{algae}$ +BG	>PNEC-BLM+BG (Zn-RAR)
Tame[1]	1995	40	40	40	39	40
Anker[2]	1995	17	16	11	0	0
Severn[3]	1995	25	25	25	0	1
	1996	12	12	12	0	0
	1997	12	12	12	1	1
	1998	5	5	5	0	0
Trent[1]	1995	10	10	10	5	9
	1996	11	11	11	10	10
	1997	13	13	13	11	11
	1998	10	10	10	4	9
	1999	12	12	12	5	9
Blackwater[2]	1995	3	0	0	0	0
	1996	3	1	0	0	0
	1997	3	1	0	0	0
	1998	4	0	0	0	0
	1999	4	1	0	0	0
	2000	4	0	0	0	0
	2001	4	1	1	1	1
	2002	4	0	0	0	0
	2003	11	1	0	0	0
	2004	13	1	0	0	0
	2005	12	1	0	0	0
Nene[2]	1995	3	1	1	0	0
	1996	4	3	3	0	0
	1997	4	4	3	0	1
	1998	4	2	1	0	0
	1999	4	1	1	0	0
	2000	4	2	1	0	0
	2001	4	1	0	0	0
	2002	4	4	2	0	1
	2003	12	4	2	0	0
	2004	12	1	0	0	0
	2005	12	3	0	0	0
Tyne[3]	2003	12	12	12	6	7
	2004	12	12	12	11	11
	2005	12	12	12	12	12
Ouse[3]	2003	12	7	5	0	0
	2004	12	6	2	0	0
	2005	7	5	2	0	0
Otter[3]	1995	24	6	5	3	4
	1996	26	5	2	1	1
	1997	15	4	3	0	0
	1998	12	5	0	0	0
	1999	12	0	0	0	0
	2000	13	0	0	0	0
	2001	3	1	0	0	0
	2002	12	1	0	0	0
	2003	10	0	0	0	0
	2004	12	0	0	0	0
	2005	12	0	0	0	0

River	Year	Total data points	Tier 1 >PNEC (7.8 µg/l)	Tier 2 >PNEC+BG (11.2 µg/l)	Tier 3 >PNEC-BLM$_{algae}$ +BG	>PNEC-BLM+BG (Zn-RAR)
Lynher[4]	1995	26	26	26	24	26
	1996	26	26	26	25	26
	1997	16	16	16	13	16
	1998	12	12	12	11	12
	1999	12	12	12	9	12
	2000	12	11	11	9	11
	2001	9	9	9	7	9
	2002	12	12	12	6	12
	2003	12	12	12	10	12
	2004	12	12	12	9	12
	2005	12	12	11	9	11
Axe[1]	1995	30	5	2	0	1
	1996	29	4	4	1	3
	1997	15	1	1	0	1
	1998	15	6	1	0	1
	1999	13	0	0	0	0
	2000	12	0	0	0	0
	2001	7	0	0	0	0
	2002	11	0	0	0	0
	2003	12	0	0	0	0
	2004	14	0	0	0	0
	2005	12	0	0	0	0
Tavy[4]	1995	26	20	5	1	4
	1996	26	19	5	0	4
	1997	16	14	4	1	3
	1998	12	10	5	1	4
	1999	12	3	0	0	0
	2000	12	6	1	0	0
	2001	8	5	0	0	0
	2002	12	6	2	0	0
	2003	12	4	1	0	0
	2004	12	2	0	0	0
	2005	12	4	2	0	1
Total		**1008**	**544**	**423**	**245**	**309**

Notes: [1] Ca 50–100 mg/l; pH >7.5; DOC >3 mg/l.
[2] Ca >100 mg/l; pH >7.5; DOC >3 mg/l.
[3] Ca <50 mg/l; pH >7.5; DOC >3 mg/l.
[4] Ca <50 mg/l; pH >7.5; DOC <3 mg/l.
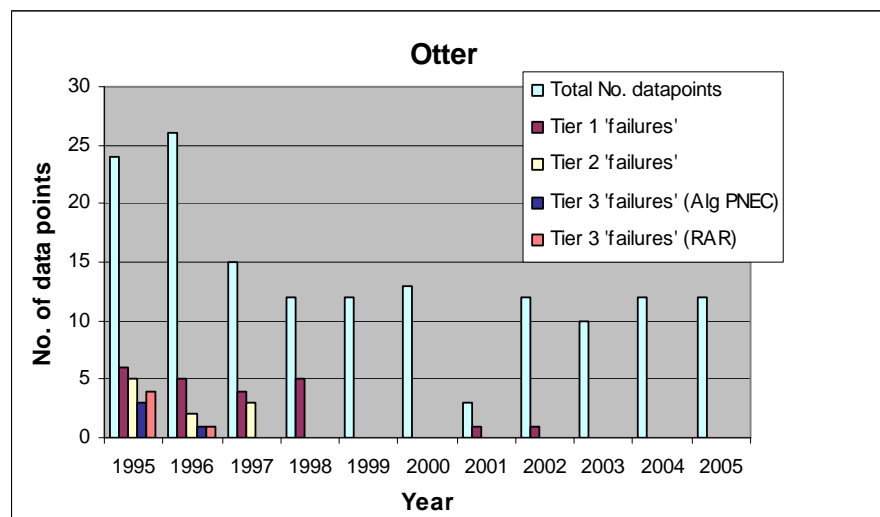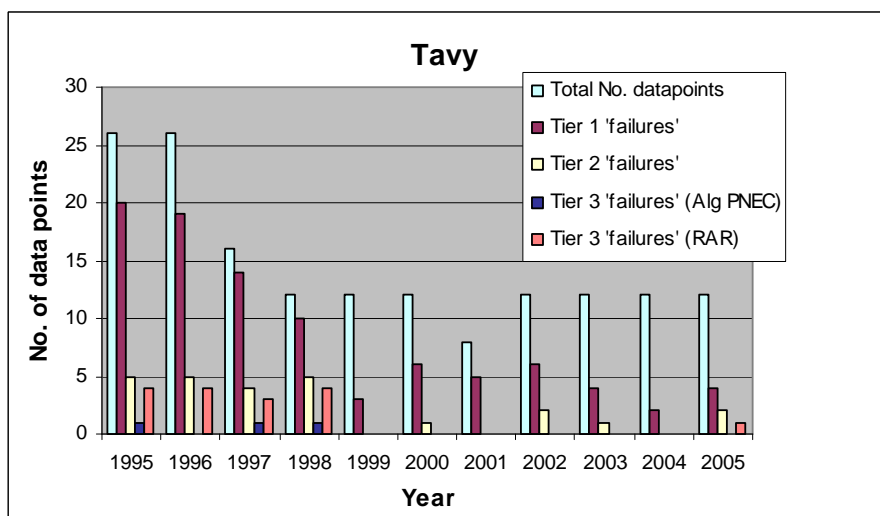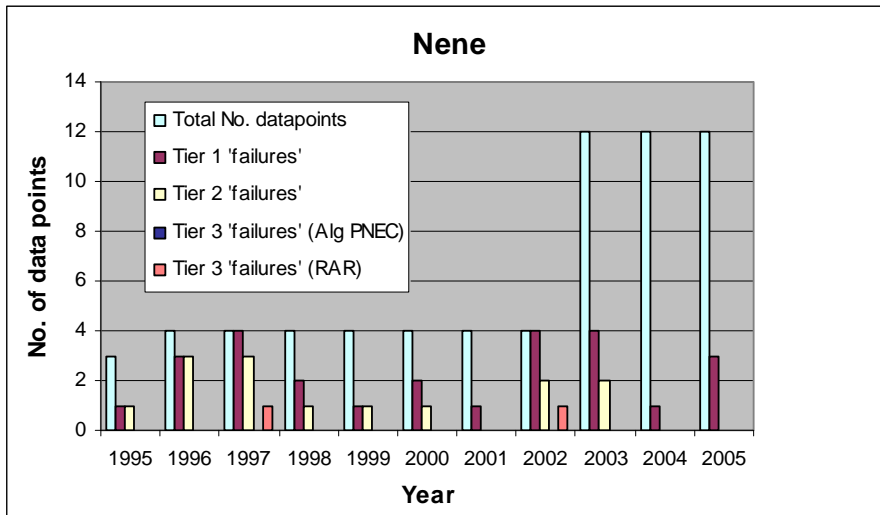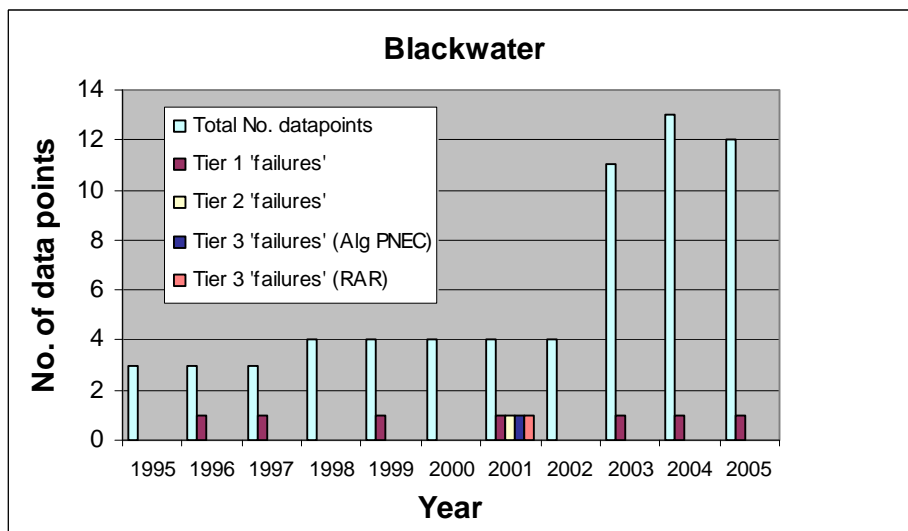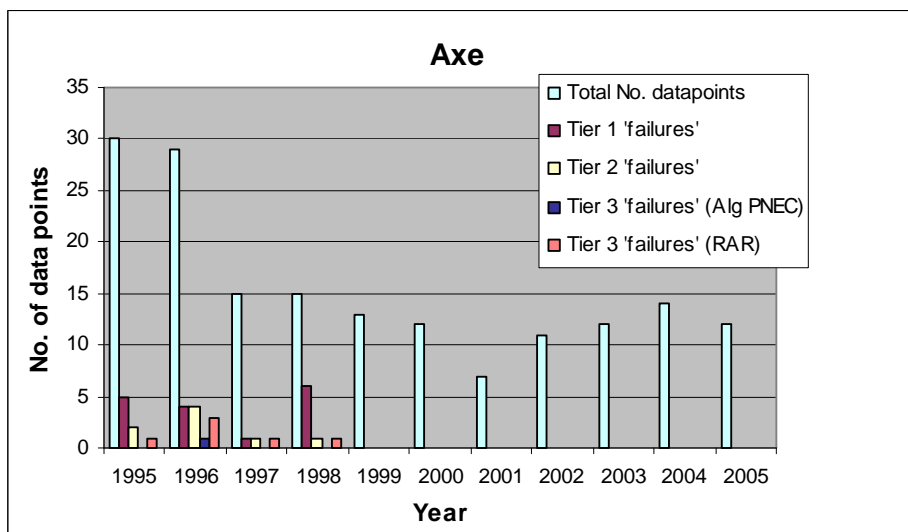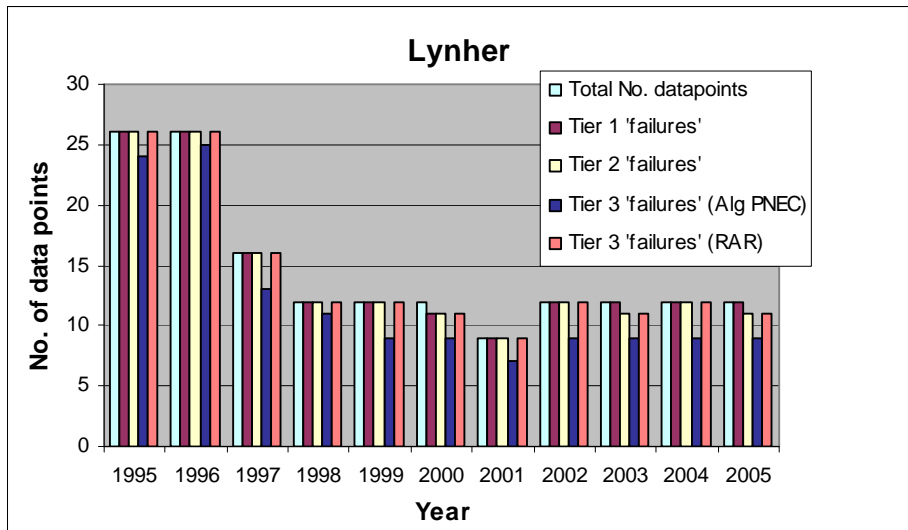
Nene

Tavy

Otter

Figure 3.1 Number of samples 'failing' for each tier of the assessment for zinc in the rivers Nene, Otter, Tavy, Lynher, Axe, and Blackwater

For copper, the situation was more polarised with most of the sites showing either compliance at the Tier 1 or Tier 2 level (e.g. Nene and Twrch) or failure at the Tier 3 level for sites impacted by mine water drainage (e.g. Carnon sites and Hicks Stream) (Table 3.3 and Figure 3.2). The BLM adjustment only reduced the number of 'failures' for sites such as The Cut (above Thames) and the River Lynher.

For waters with low pH and DOC concentrations, the BLM-adjusted PNEC was at or lower than the RAR-derived PNEC. This result is unsurprising as the latter is based on a 'reasonable worst case' for Europe, but the localised conditions found in certain parts of the UK fall outside the selected parameters.

This situation is important: if the ambient water quality lies outside the 'reasonable worst case' used to generate the RAR PNEC, then it is possible that a water body could 'pass' at the Tier 1 or 2 assessment, but <u>fail</u> at the Tier 3 assessment, due to low pH, DOC, and calcium levels in the water. Using the tiered assessment at face value, the BLM would not have to be run as the water body 'passes' at the earlier tiers.

This discrepancy may be overcome by specifying that the Tier 3 BLM assessment is automatically run for any site which lies outside of the conditions used to generate the PNEC, i.e. pH <6.0, DOC <0.5 mg/l, or hardness <10 mg/l. Indeed, there may be scope to use the Cu-BLM to identify potentially sensitive sites with respect to copper pollution.

Full datasets for water quality parameters, PNECs, and the ratios of observed copper concentrations to PNEC values for each tier of assessment are provided for each river in ANNEX B and ANNEX C.

Table 3.3 Data for copper for selected sites summarised for each tier

River	Year	Total data points	Tier 1 >PNEC (8.2 µg/l)	Tier 2 >PNEC+BG (9.8 µg/l)	Tier 3 >PNEC-BLM+BG
The Cut (above Thames)[2]	1995	11	4	3	0
	1996	11	10	10	1
	1997	10	10	8	0
	1998	11	2	0	0
	1999	11	4	1	1
	2000	14	3	2	1
	2001	12	3	0	0
	2002	12	1	1	0
	2003	12	0	0	0
	2004	12	0	0	0
	2005	12	1	0	0
	2006	8	0	0	0
Twrch[5]	1995	1	0	0	0
	1997	3	0	0	0
	1998	11	0	0	0
	1999	5	0	0	0
	2000	4	0	0	0
	2001	2	0	0	0
	2002	12	0	0	0
	2003	2	0	0	0
	2005	6	0	0	0
	2006	7	0	0	0

River	Year	Total data points	Tier 1 >PNEC (8.2 µg/l)	Tier 2 >PNEC+BG (9.8 µg/l)	Tier 3 >PNEC-BLM+BG
Nene[2]	1995	3	1	0	0
	1996	4	0	0	0
	1997	4	0	0	0
	1998	4	0	0	0
	1999	4	0	0	0
	2000	4	0	0	0
	2001	4	0	0	0
	2002	4	0	0	0
	2003	12	0	0	0
	2004	12	0	0	0
	2005	12	0	0	0
	2006	9	0	0	0
Lynher[4]	1995	26	3	3	1
	1996	26	8	3	3
	1997	16	6	4	0
	1998	12	2	2	0
	1999	12	3	2	0
	2000	12	1	0	0
	2001	9	1	0	0
	2002	12	1	0	0
	2003	12	4	3	3
	2004	12	2	0	0
	2005	12	3	2	1
	2006	6	3	2	0
Hicks Stream[5]	1995	44	44	44	44
	1996	37	37	37	37
Carnon at Twelveheads[5]	1995	45	45	45	45
	1996	36	36	36	36
Carnon at Devoran[6]	1995	15	15	15	15
	1996	14	14	14	14
	1997	8	8	8	8
	1998	11	11	11	11
	1999	12	12	12	12
	2000	12	12	12	12
	2001	11	11	11	11
	2002	12	12	12	12
	2003	12	12	12	12
	2004	12	12	12	12
	2005	13	13	13	13
	2006	8	8	8	8
Total		**734**	**378**	**348**	**313**

Notes: [1] Ca 50–100 mg/l; pH >7.5; DOC >3 mg/l.
   [2] Ca >100 mg/l; pH >7.5; DOC >3 mg/l.
   [3] Ca <50 mg/l; pH >7.5; DOC >3 mg/l.
   [4] Ca <50 mg/l; pH >.5; DOC <3 mg/l.
   [5] Ca <50 mg/l; pH <7.5; DOC <3 mg/l.
   [6] Ca 50–100 mg/l; pH <7.5; DOC <3 mg/l.
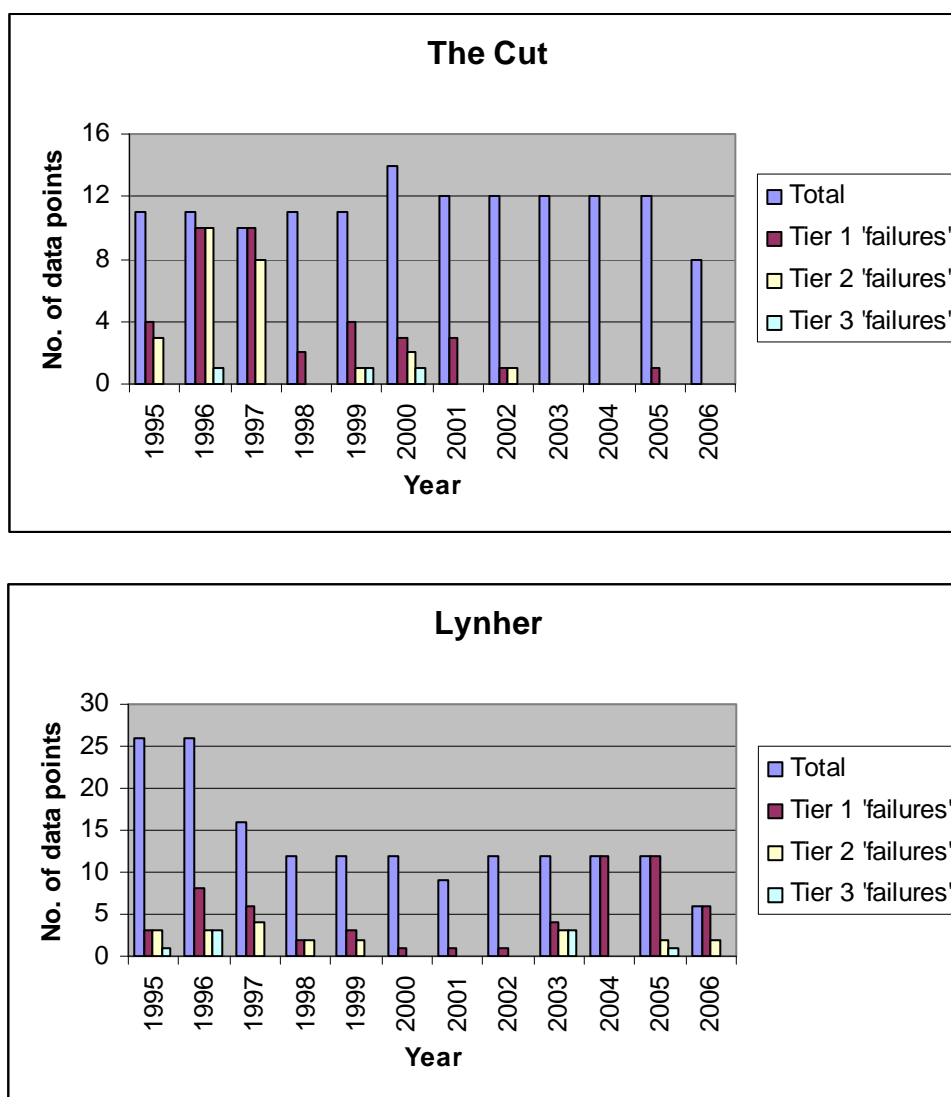
Figure 3.2 Number of samples 'failing' for each tier of the assessment for copper in The Cut (above Thames) and Lynher

Overall, the improvement in compliance at each tier of assessment can be seen in Table 3.4. For copper, owing to the bias in the data towards contaminated sites, the reduction in non-compliance between tiers of assessment was not dramatic, and not dissimilar to comparisons with the current EQS regime, which takes account of hardness. The tiered approach was further confounded by the fact that for several of the selected rivers, pH and DOC were lower than the 'reasonable worst case' situation used to derive the copper PNEC; therefore, not resulting in significant reductions in the number of non-compliances.

For zinc, significant improvements were demonstrated between each tier, as sites thought to be unaffected by, or free from, zinc pollution were 'filtered' out, leaving only those affected by mine water drainage or underlying zinc mineralogy. These water bodies would be expected to fail as they are impacted by significant anthropogenic inputs. The number of data points 'failing' at Tier 3 is similar to the number that fail under the current EQS regime, which implicitly applies a metal bioavailability factor by taking account of water hardness. This agreement lends weight to the output of the BLMs.

There is even an argument that suggests BLM assessments should be incorporated before adjustments for background concentrations. The application of background

concentrations to laboratory-derived toxicity values remains uncertain, and questionable if the results are used to produce standards for assessing environmental quality. Moreover, the BLMs offer a rapid and validated measure of bioavailability. The final column in Table 3.4 shows the effect of applying the BLM to sites which 'fail' at Tier 1. The number of 'failures' is similar whether background concentrations are added before or after applying the BLM. The assessment process appears to be relatively insensitive to background concentration adjustments; the use of the BLM at Tier 2 speeds up the process of refining sites for which more accurate background data is required.

Table 3.4   Summary of all selected site data for the Tier 1, 2, and 3 assessment for copper and zinc

Metal	Total number of data points	>Existing EQS	Tier 1	Tier 2	Tier 3	
			>PNEC	>PNEC+BG[1]	>PNEC-BLM+BG[1]	>PNEC-BLM
Copper	734	373	378	348 (8)	313 (10)	316
Zinc	1008	316	544	423 (22)	245 (42)	243

Notes: [1] Figures in parenthesis represent percentage reduction between tiers of assessment.

Given the improvements in the rate of compliance following the Tier 3 assessment, the performance of the BLMs has been assessed in more detail in Section 3.2.

3.2   Biotic ligand model performance data

3.2.1   Sensitivity analysis

Zinc biotic ligand model

The only input parameters required to predict no observed effect concentrations (NOECs) for zinc are pH, DOC, and calcium (or hardness in the absence of calcium data). Consequently, a relatively simple matrix of variables was used to generate NOECs (Table 3.5). The minimum, mean, and maximum pH and hardness values acceptable for use within the Zn-BLM were inputted. For DOC, the minimum and maximum values were again used, along with a more typical value of 7 mg/l for UK water conditions, rather than an 'average' of 10.5 mg/l. In each case, the mean values were held for two parameters and the extremes inputted for the third (Figure 3.3). Whilst only three values for each parameter may not constitute a significant relationship, the exercise was useful in determining the relative importance of each parameter in influencing the BLM results.

Algae appear to be the most-sensitive organisms, exhibiting the lowest NOECs under all of the modelled scenarios (Figure 3.3). Of the three variables, pH caused the most significant variation in NOEC between the extreme values for algae (a 7.8-fold change) and fish (a 3.6-fold change). For *Daphnia*, however, pH was the least sensitive variable (a 1.6-fold change), compared with DOC (a 3.1-fold change). For fish and algae, DOC and hardness exhibited typically a two- to threefold variation between extremes. The NOEC for algae was shown to decrease with increasing pH, compared with the

opposite trend for fish and *Daphnia*. Although this behaviour is not fully explained, it is thought that unlike *Daphnia* and fish, non-specific adsorption of zinc onto binding sites occurs for algae, meaning that there is no limit to the absorption capacity (De Schamphelaere *et al.* 2005).

None of the parameters exhibited perfect linear responses to changes in other variables; laboratory-based ecotoxicity experiments do not show linear responses with changes in these parameters (Heijerick *et al.* 2002).

The maximum BioF for zinc was calculated from the highest of the ratios of reference NOECs to the predicted NOECs for each of the three BLM species, as described in Section 1.4.2. Dissolved organic carbon was found to be the main factor controlling levels of bioavailable zinc with a relative change of a factor of 5.1 between extreme values compared with 1.3 and 1.4 for pH and hardness, respectively (Table 3.5).

Table 3.5   Input data used for the Zn-BLM sensitivity analysis

pH	DOC (mg/l)	Hardness (mg/l CaCO₃)	NOEC (µg/l Zn)			Maximum BioF (%)
			Algae	Daphnia	Fish	
6.0	7.0	200	185.0	211.4	332.2	37.1
7.5	7.0	200	41.6	317.5	411.7	28.4
9.0	7.0	200	23.7	337.2	1209.0	49.8
Ratio of extremes for pH			**7.8**	**1.6**	**3.6**	**1.3**
7.5	1.0	200	17.5	191.4	266.8	67.6
7.5	7.0	200	41.6	317.5	411.7	28.4
7.5	20.0	200	34.3	595.4	727.9	13.2
Ratio of extremes for DOC			**2.0**	**3.1**	**2.7**	**5.1**
7.5	7.0	15	67.9	224.9	213.5	41.5
7.5	7.0	200	41.6	317.5	411.7	28.4
7.5	7.0	428	39.3	486.4	694.3	30.1
Ratio of extremes for hardness			**1.7**	**2.2**	**3.3**	**1.4**
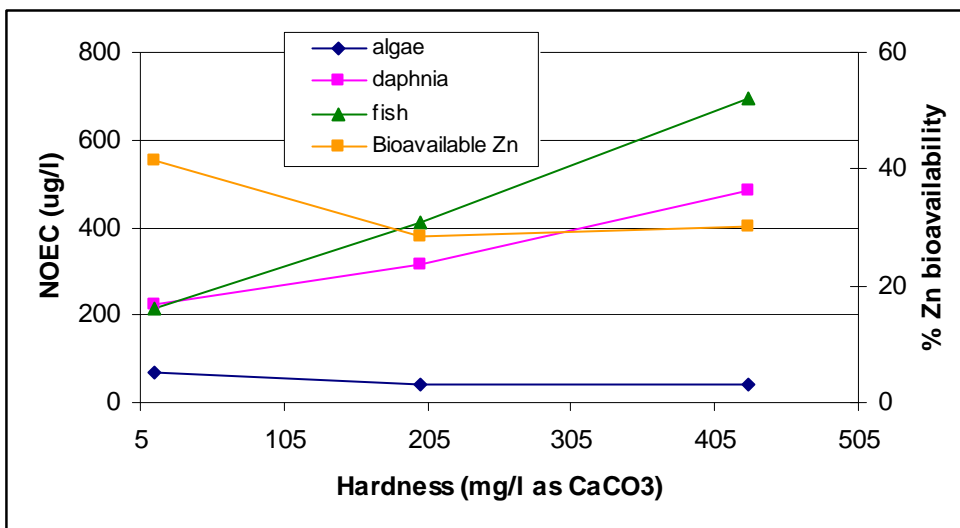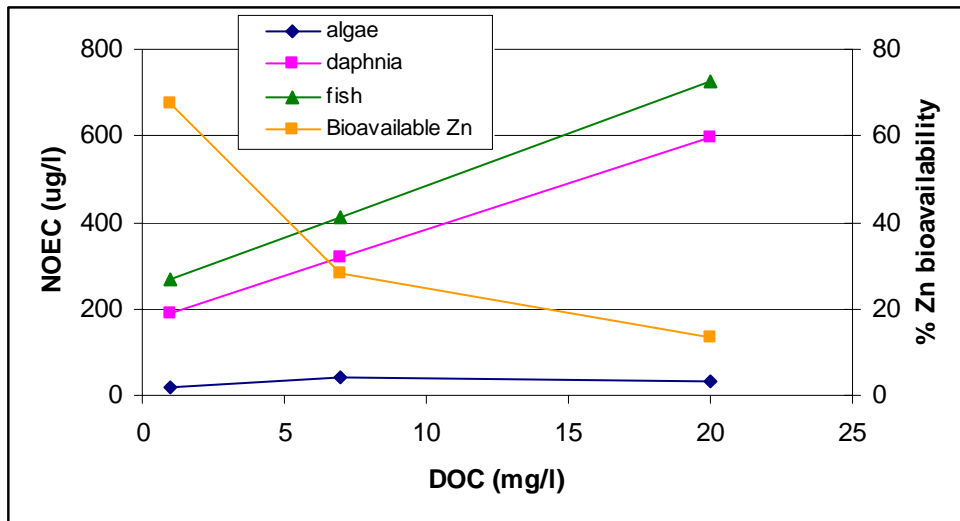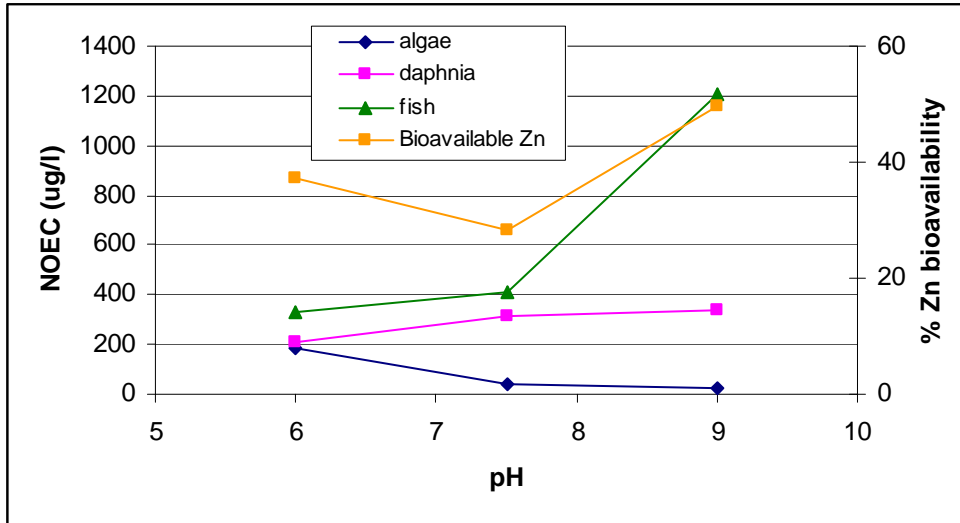
Figure 3.3 BLM-derived NOECs plotted for varying pH, DOC, and hardness

The data presented in Figure 3.3 and Table 3.5 show that all three parameters vary significantly across the range of waters potentially encountered in the UK; although some scenarios, such as a combination of pH 6.0 and hardness of 200 mg/l CaCO$_3$, are likely to be outside of those considered 'natural' and are not realistic. Nevertheless, the relative importance of all three parameters suggests that default values should be avoided.

Hardness and pH are routinely measured parameters and, therefore, should provide no issues for use within the Zn-BLM. However, DOC is not currently determined on a routine basis and, therefore, may be unavailable for sites of interest. A default DOC value of 7 mg/l could generate NOEC predictions (for algae) that are up to 2.4 times larger or smaller than values generated from actual DOC data. It is, therefore, import to obtain accurate DOC data to run the Zn-BLM.

In many cases, the measure of absorbance at a defined wavelength (typically 420 nm) may be used as a surrogate for DOC. Absorbance measurements on filtered samples are rapid and cheap compared to DOC analysis. The potential for using surrogates for DOC are explored in Section 3.3.

Copper biotic ligand model

Assessing the sensitivity of the Cu-BLM is a more complex exercise owing to the larger number of input variables:

- calcium
- magnesium
- sodium
- potassium
- sulphate
- sulphide
- chloride
- pH
- alkalinity
- percentage humic acid
- DOC
- temperature.

The following matrix was used to assess sensitivity (Table 3.6). All data for minima, mean, and maxima were drawn from the full Environment Agency 1995 dataset. Values for percentage humic acid (HA) were varied between 10 and 90 per cent as 0 and 100 per cent were not allowed by the model. For each scenario, a PNEC based on the 50 per cent lower confidence limit of the HC5 (5th percentile) was calculated and plotted against the changing variables (Figure 3.4).

Table 3.6   Input data used for Cu-BLM sensitivity analysis

	Temperature (°C)	pH	HA (%)	DOC (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SO$_4$ (mg/l)	Cl (mg/l)	Alkalinity (mg/l CaCO$_3$)	S (mg/l)
Mean values	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
Temperature$_{min}$	0	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
Temperature$_{max}$	25	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
pH$_{min}$	11	5.8	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
pH$_{max}$	11	9.4	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
DOC$_{min}$	11	7.9	50.0	0.2	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
DOC$_{max}$	11	7.9	50.0	54.8	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
Ca$_{min}$	11	7.9	50.0	5.0	3.0	8.7	25.0	5.0	61.9	63.2	121.9	0.022
Ca$_{max}$	11	7.9	50.0	5.0	169.0	8.7	25.0	5.0	61.9	63.2	121.9	0.022
Mg$_{min}$	11	7.9	50.0	5.0	56.7	0.1	25.0	5.0	61.9	63.2	121.9	0.022
Mg$_{max}$	11	7.9	50.0	5.0	56.7	33.8	25.0	5.0	61.9	63.2	121.9	0.022
Na$_{min}$	11	7.9	50.0	5.0	56.7	8.7	4.4	5.0	61.9	63.2	121.9	0.022
Na$_{max}$	11	7.9	50.0	5.0	56.7	8.7	140.0	5.0	61.9	63.2	121.9	0.022
K$_{min}$	11	7.9	50.0	5.0	56.7	8.7	25.0	0.54	61.9	63.2	121.9	0.022
K$_{max}$	11	7.9	50.0	5.0	56.7	8.7	25.0	16.5	61.9	63.2	121.9	0.022
SO$_{4min}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	1.0	63.2	121.9	0.022
SO$_{4max}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	423.0	63.2	121.9	0.022
Cl$_{min}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	7.7	121.9	0.022
Cl$_{max}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	1110	121.9	0.022
Alkalinity$_{min}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	10.0	0.022
Alkalinity$_{max}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	356.0	0.022
S$_{min}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.015
S$_{max}$	11	7.9	50.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.106
HA$_{min}$	11	7.9	10.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
HA$_{max}$	11	7.9	90.0	5.0	56.7	8.7	25.0	5.0	61.9	63.2	121.9	0.022
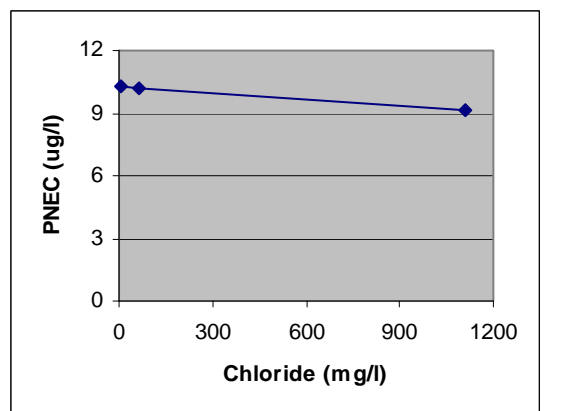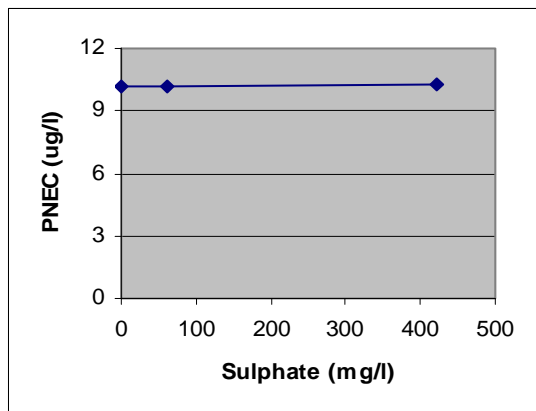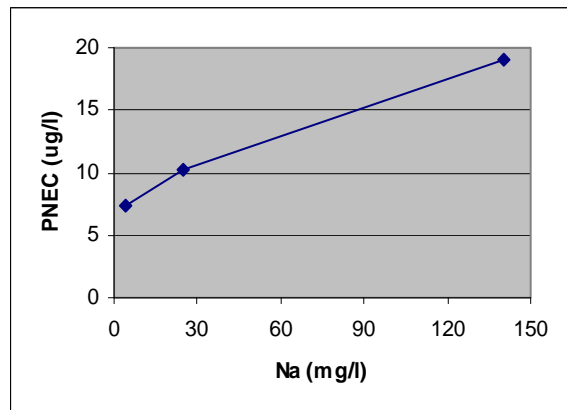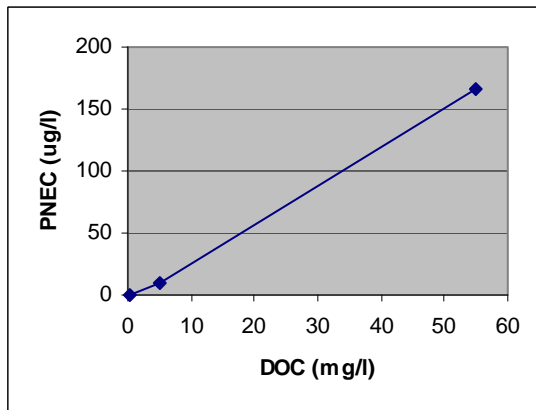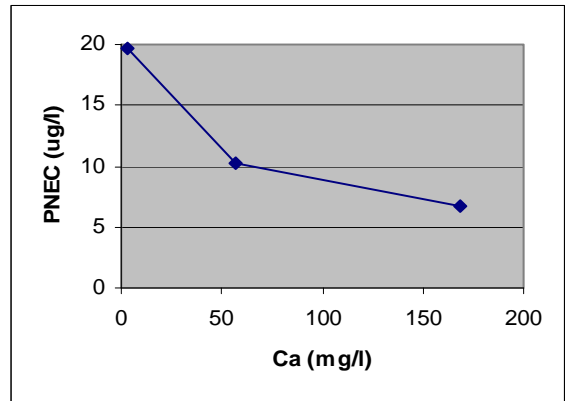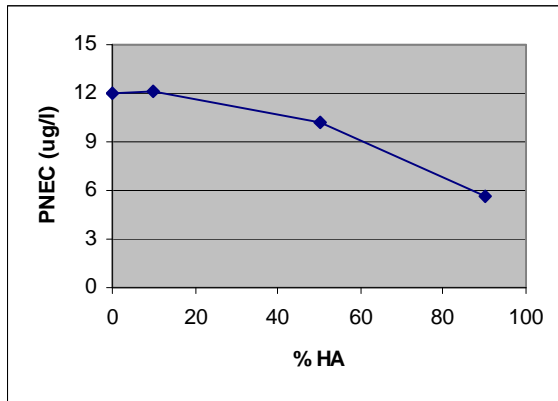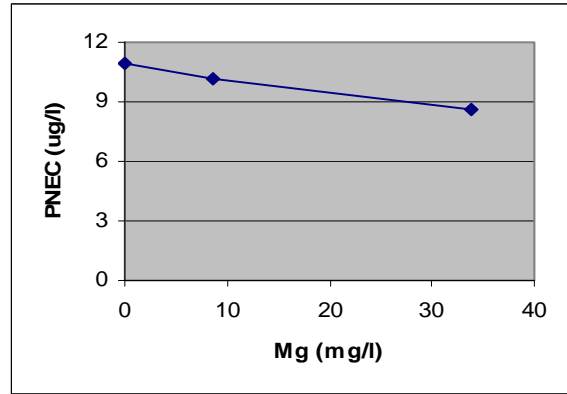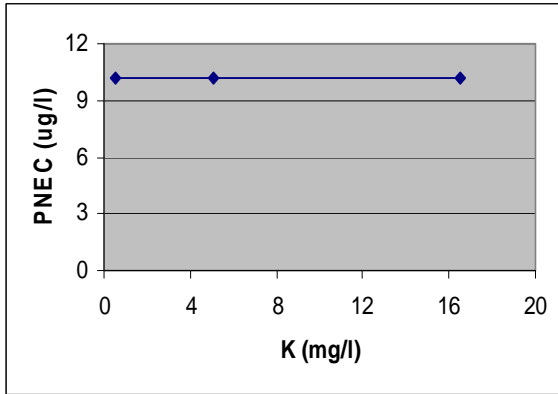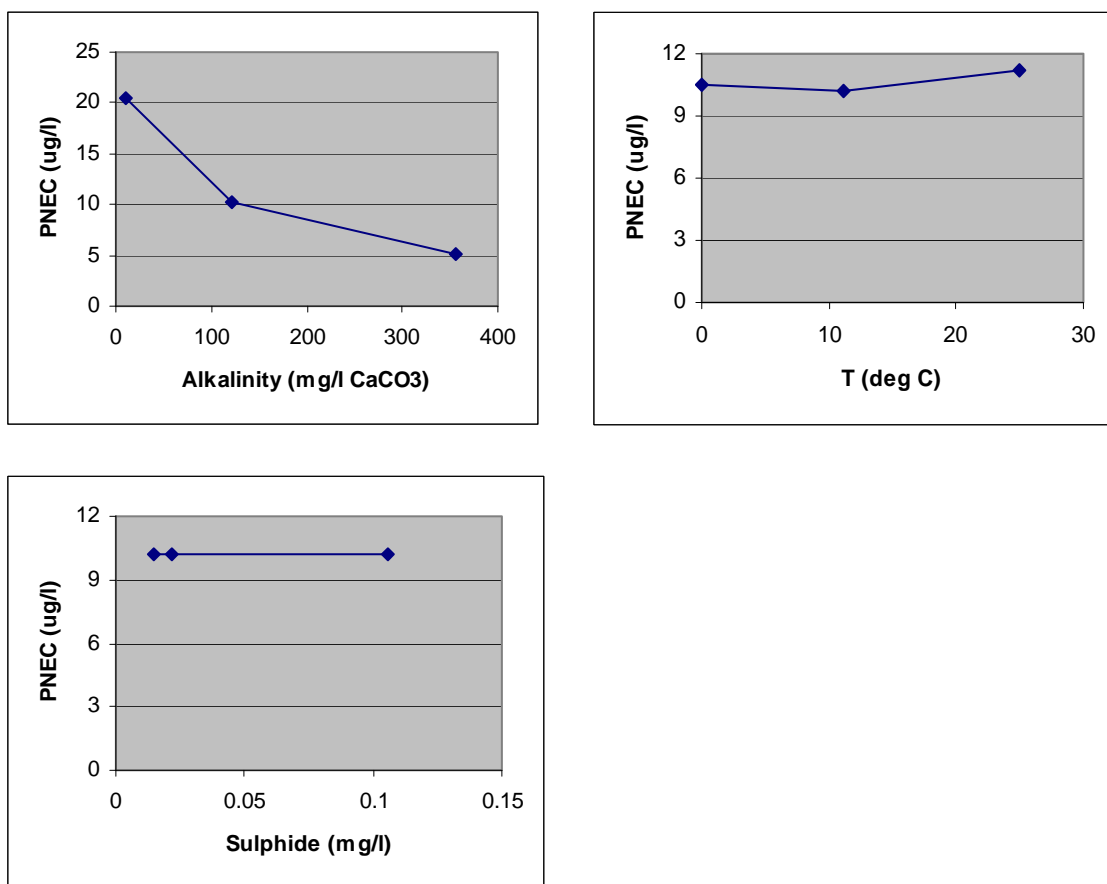
Figure 3.4 Sensitivity analysis for Cu-BLM

The data provided in Figure 3.4 show that for some parameters the calculated PNEC is almost independent of their value, namely:

- sulphide
- sulphate
- chloride
- potassium
- temperature.

The PNEC based on extreme values for magnesium also only varied by a factor of 1.3 between maximum and minimum values, so can also be considered as effectively constant.

As expected, DOC concentration is critical to the PNEC predictions because of strong complexation of copper with organic ligands (Dixon *et al.* 2000). The calculated factor of 360 between extremes of DOC concentrations is almost two orders of magnitude higher than any of the other parameters. This result shows that it is essential to have high quality DOC data for the Cu-BLM. Calcium, pH, sodium, and alkalinity all vary by approximately a factor of three, similar to the Zn-BLM, with HA content varying by a factor of two. The copper PNEC derived from the copper RAR used a 'reasonable worst case' HA content of 0.01 per cent, compared with the default value of 50 per cent used for the Tier 3 assessment in this study. The data in Figure 3.4 show that HA content is not a particularly sensitive parameter: the extremely low value only leads to a

predicted PNEC greater by a factor of 1.2 compared with that derived using the default value which would not affect the conclusions regarding compliance across the different tiers of assessment.

To confirm the relative insensitivity of these variables – and to check for possible impacts on PNECs at extreme values of the key parameters (DOC, Ca, and pH) rather than at average conditions – an additional set of scenarios were undertaken where DOC, pH, and Ca were set at their maxima and minima, and the same exercise repeated (Table 3.7).

Table 3.7   Summary of PNEC$_{max}$/PNEC$_{min}$ ratios for each variable at extreme values of key parameters[1]

	PNEC$_{max}$/ PNEC$_{min}$ ratio under average conditions	DOC = 1 mg/l	DOC = 20 mg/l	Ca = 3 mg/l	Ca = 169 mg/l	pH 9.4	pH 5.8
Temperature	1.1	1.1	1.1	1.1	1.0	4.3	1.1
DOC	360.2	-	-	28.0	25.9	26.1	19.4
Calcium	2.9	2.8	3.1	-	-	2.8	1.1
pH	2.9	2.3	3.1	5.1	2.9	-	-
Magnesium	1.3	1.3	1.3	2.5	1.3	1.4	1.1
Sodium	2.6	2.5	2.5	2.5	2.6	2.0	2.2
Potassium	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphate	1.0	1.0	1.0	1.1	1.0	1.1	1.2
Chloride	1.1	1.1	1.2	1.2	1.1	1.0	1.2
Alkalinity	4.0	3.6	3.6	4.2	2.0	2.4	1.2
Sulphide	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HA	2.2	1.9	2.0	1.1	2.1	4.7	1.0

Notes: [1] Shaded cells represent parameters will little impact on Cu PNEC-BLM calculation

Results based on the more extreme ranges of the three key parameters show that default values for potassium, sulphate, sulphide, and chloride can be used with a high degree of confidence. At very low calcium and high magnesium concentrations, the ratio of PNECs is 2.5, which may be considered significant, but this scenario in the natural environment is unrealistic. A default value for magnesium could, therefore, also be considered appropriate. Similarly, for temperature variations, only one particular scenario (pH 9.4) produced a ratio of the extreme values over 1.1. The unlikelihood of encountering these conditions in the environment suggests the temperature of 15°C used in the Cu-RAR would be an acceptable default value.

The other parameters (Ca, Na, alkalinity, HA, pH, and DOC) are important variables for which field data should be sought. In the case of HA content, a default value of 50 per cent is used owing to the difficulty in determining the humic acid content of a sample. Extensive research has been undertaken by CEH to validate the WHAM models used as part of the Cu-BLM that require the HA content to be inputted. These percentage HA values are, therefore, fairly well established, and have some degree of authenticity as default values. However, at high pH, significant errors may occur in the predictions of the copper PNEC. At extreme water quality conditions (e.g. low pH, low Ca, low DOC), changing the percentage HA from the default of 50 to 0.01 per cent, as used in the PNEC value derived in the copper RAR, only had a minimal impact as observed under more 'average' conditions.

3.2.2　Data aggregation

Predicted annual values for PNECs using BLM outputs may be calculated in two ways: Individual, date-specific data can be input to calculate predicted PNECs; these are then averaged to give a final PNEC prediction for a site. Alternatively, it is possible to take an annual mean of the input data first and then run the BLM using these means to produce a single PNEC prediction. Table 3.8 shows that the two approaches produce similar PNEC predictions using the Zn-BLM. The differences between the two methodologies are generally less than 5 per cent; PNECs derived using the mean of individual calculations are generally higher than those using annualised input values. Only where the DOC data varies significantly during the year (particularly where the number of data points for the year was low – as is the case for the Otter and the Axe in 2001) do more significant variations occur.

For copper, a similar variation occurs between the two methodologies (Table 3.9). Where input data are reasonably consistent throughout the year (see ANNEX B), the PNECs derived by the two methods are within 5 per cent of each other. As the Cu-BLM is more sensitive to changes in DOC, if values for this input parameter vary over the course of the year, then larger variations between the two PNEC predictions are observed. Under these circumstances, PNECs are invariably higher where individual, date-specific PNECs were averaged compared to PNECs calculated using annualised input values. This difference reflects the bias caused by individual high results for PNECs derived from high individual DOC values throughout the year, which are masked when a mean DOC concentration is calculated.

The validity of individual high reported values may be questioned; they may result from sampling errors, contamination, or analytical inaccuracies. The findings presented above suggest that it is acceptable to use annualised input values when considering a large amount of data (on an annual basis). This form of aggregation should save a considerable amount of data manipulation and computing time.

Table 3.8　PNEC data derived from the Zn-BLM$_{algae}$

River	Year	PNEC-BLM$_{algae}$ (µg/l Zn)		Number of samples	Difference (%)
		Mean from individual predictions	Derived from annual mean of input variables		
Nene	1995	27.9	27.8	23	0.3
	1996	27.7	27.6	24	0.4
	1997	25.7	25.3	24	1.4
	1998	24.9	24.7	26	0.8
	1999	25.1	24.6	16	1.8
	2000	25.5	25.2	12	1.2
	2001	23.4	23	12	1.6
	2002	23.4	22.9	12	2.2
	2003	26.9	25.6	12	4.9
	2004	25.5	24.9	12	2.2
	2005	24.0	23.9	12	0.5
Blackwater	1995	25.0	24.7	26	1.2
	1996	23.3	23.6	23	-1.3
	1997	22.8	22.7	21	0.4
	1998	24.7	24.3	24	1.6
	1999	25.3	24.9	16	1.6
	2000	28.8	28	11	2.8
	2001	23.4	22.8	10	2.6
	2002	22.3	21.9	12	1.8

River	Year	PNEC-BLM$_{algae}$ (µg/l Zn)		Number of samples	Difference (%)
		Mean from individual predictions	Derived from annual mean of input variables		
	2003	26.2	25.6	11	2.3
	2004	22.8	22.5	13	1.3
	2005	21.9	21.1	12	3.5
Tame	1995	36.66	36.4	40	0.7
Anker	1995	36.8	37.7	17	-2.5
Severn	1995	27.1	26.5	25	2.1
	1996	25.1	24.5	12	2.2
	1997	37.7	40.4	12	-7.3
	1998	26.8	26.2	6	2.3
Trent	1995	42.8	42.6	10	0.4
	1996	43.0	42.8	11	0.5
	1997	37.6	37.7	13	-0.3
	1998	41.4	41.2	11	0.4
	1999	35.9	36.5	12	-1.7
Tavy	1995	23.7	21.9	26	7.7
	1996	23.3	21.7	26	6.9
	1997	23.6	22.7	16	4.0
	1998	20.9	20.2	12	3.7
	1999	21.2	20.3	12	4.2
	2000	23.4	22.8	12	2.5
	2001	25.9	24.5	8	5.3
	2002	29.1	27.5	12	5.6
	2003	34.0	32.3	12	5.1
	2004	29.6	28.2	12	4.6
	2005	31.6	30.6	12	3.0
Lynher	1995	21.2	20.9	26	1.6
	1996	18.5	18	26	2.5
	1997	22.5	22.1	16	1.8
	1998	18.9	18.8	12	0.8
	1999	21.6	21.5	12	0.5
	2000	19.0	18.7	12	1.8
	2001	25.8	25.1	9	2.6
	2002	24.7	24.1	12	2.6
	2003	26.6	26	12	2.3
	2004	22.9	22.4	12	2.4
	2005	24.4	23.3	12	4.4
Ouse	2003	36.4	35.1	12	3.5
	2004	40.7	39.5	12	2.9
	2005	36.2	34.3	10	5.4
Tyne	2003	49.3	44.1	12	10.5
	2004	52.1	56.0	12	-7.5
	2005	43.3	41.1	12	5.1
Axe	1995	23.8	22.5	26	5.3
	1996	21.8	20.9	26	4.1
	1997	24.6	23.5	14	4.4
	1998	25.6	24.2	12	5.5
	1999	30.8	29.7	12	3.4
	2000	34.2	29.7	12	13.1
	2001	31.3	25.0	7	20.0
	2002	35.8	33.7	11	5.8

River	Year	PNEC-BLM$_{algae}$ (µg/l Zn)		Number of samples	Difference (%)
		Mean from individual predictions	Derived from annual mean of input variables		
	2003	29.7	27.6	12	7.0
	2004	28.2	26.8	14	4.8
	2005	29.0	26.4	12	9.0
Otter	1995	25.0	23.9	24	4.5
	1996	21.6	20.3	26	6.2
	1997	28.2	27	15	4.4
	1998	36.6	35.3	12	3.6
	1999	20.0	19.5	12	2.6
	2000	28.8	27.2	13	5.7
	2001	54.9	36.4	3	33.7
	2002	34.9	31.9	12	8.7
	2003	21.8	21.1	10	3.4
	2004	25.3	24.7	12	2.2
	2005	28.8	26.6	12	7.6

Table 3.9   PNEC data derived from the Cu-BLM

River	Year	PNEC (µg/l Cu)		Number of samples	Difference (%)
		Mean from individual predictions	Derived from annual mean of input variables		
Lynher	1995	10.6	11.5	26	-8.4
	1996	8.2	8.7	26	-6.6
	1997	11.7	11.7	16	-0.3
	1998	8.7	8.7	12	0.3
	1999	11.8	11.7	12	0.9
	2000	9.9	9.5	12	3.6
	2001	10.2	10.5	9	-3.3
	2002	9.5	9.9	12	-4.0
	2003	9.0	9.1	12	-1.6
	2004	9.4	9.6	12	-1.9
	2005	10.5	10.8	12	-3.1
	2006	8.3	8.5	6	-2.0
Hicks Stream	1995	13.9	11.7	44	16.2
	1996	10.3	10.3	37	-0.4
Carnon at Twelveheads	1995	4.2	4.2	45	-1.5
	1996	5.0	5.1	36	-2.2
Carnon at Devoran	1995	1.9	1.6	15	16.3
	1996	2.5	2.4	14	3.2
	1997	1.7	1.6	8	3.0
	1998	2.4	2.1	11	11.5
	1999	2.9	2.4	12	17.0
	2000	1.8	1.6	12	10.3
	2001	2.1	1.9	11	9.9
	2002	1.8	1.5	12	15.5
	2003	1.7	1.5	12	10.2

River	Year	PNEC (µg/l Cu)		Number of samples	Difference (%)
		Mean from individual predictions	Derived from annual mean of input variables		
	2004	1.9	1.8	12	5.9
	2005	1.9	1.7	13	9.3
	2006	1.8	1.6	8	9.2
The Cut (above Thames)	1995	17.0	15.8	11	7.1
	1996	20.8	20.1	11	3.4
	1997	16.3	15.6	10	4.4
	1998	17.1	16.5	11	3.3
	1999	14.4	14.1	11	1.9
	2000	16.3	16.1	14	1.3
	2001	13.6	13.9	12	-2.3
	2002	18.4	17.1	12	7.2
	2003	13.1	13.3	12	-1.4
	2004	13.5	13.9	12	-2.8
	2005	12.8	13.0	12	-1.4
	2006	11.8	11.3	8	4.2
Nene	1995	47.1	31.2	3	33.7
	1996	16.9	13.4	4	20.7
	1997	10.6	9.6	4	9.2
	1998	8.0	7.4	4	7.2
	1999	8.5	7.5	4	11.2
	2000	9.7	9.0	4	7.0
	2001	6.6	6.5	4	1.1
	2002	7.7	6.9	4	10.1
	2003	9.7	8.3	12	14.4
	2004	7.6	7.3	12	4.2
	2005	7.7	7.6	12	1.5
	2006	9.8	9.6	9	1.9
Twrch	1995	2.4	2.4	1	0.0
	1997	19.2	21.5	3	-11.8
	1998	15.7	15.6	11	0.8
	1999	14.2	13.9	5	1.8
	2000	19.3	17.9	4	7.2
	2001	10.7	10.4	2	2.8
	2002	18.8	19.0	12	-0.9
	2003	5.9	6.1	2	-4.3
	2005	19.0	19.2	6	-0.9
	2006	10.4	11.2	7	-8.1

3.3 Surrogates for dissolved organic carbon

The importance of measured values for DOC has been demonstrated in Section 3.2. However, the lack of reported DOC data may hamper speciation predictions using the BLMs. The importance of DOC as an environmental variable is now established, and it is expected that monitoring data will become more widely available in the future. However, for the retrospective analysis of monitoring data, an alternative way of estimating DOC would be useful.

There are well-established relationships between DOC and colour measurements. Colour is relatively easy to measure in filtered samples (typically the absorbance at 420 nm) and could be a useful surrogate if an accurate relationship with DOC is established.

From the data supplied by the Environment Agency for the 30 sites for zinc, a number of sites had data for both colour and DOC (Table 3.10).

Table 3.10 Correlation between colour and DOC

River	Number of data points	Correlation R^2 [1]	Slope (absorbance units per mg/l DOC)
Trent	45	0.0125	0.55
Axe	155	0.9299	4.59
Lynher	154	0.9294	5.20
Otter	145	0.9237	4.88
Tavy	155	0.8937	7.56

Notes: [1] R^2 is the correlation coefficient based on the relationship between colour and DOC.

Good correlation exists for four out of the five river sites, but data for the River Trent site showed no discernible correlation. This finding is possibly due to the Trent being the only river in the suite to receive a significant amount of urban drainage, including road runoff, wastewater treatment works effluent, and industrial discharges. These inputs would probably contain a number of organic substances contributing to the measured DOC, compared with more rural rivers where sources of DOC could be more limited. Industrial and anthropogenic organic chemicals are likely to exhibit different patterns of UV/vis absorption and this may explain the lack of an observed relationship.

For the other four datasets, the slopes were of the same order of magnitude, although they did vary between 4.6 and 7.6, suggesting a significant degree of site specificity.

Overall, the data suggests that the use of colour as a surrogate for DOC is limited for the following reasons:

- Historic colour data is limited to a similar degree to that for DOC.

- For maximum confidence in predictions, site-specific relationships would need to be developed, therefore requiring DOC data to be collected anyway.

- If sufficient confidence could be established for the relationship between colour and DOC, then the option for using colour for long-term monitoring may be possible on a site-by-site basis.

- For rivers impacted by urban drainage (a large proportion of the Environment Agency's monitoring network) correlation between DOC and colour may not exist.

3.4 Comparison of the tiered approach with observed biological monitoring data

There needs to be confidence that any 'relaxation' of quality standards using a tiered approach to the assessment of compliance will not lead to a degradation of ecological quality. Data derived from BLMs reflect observations made mostly in the laboratory under carefully controlled conditions. Behaviour of organisms in the environment can differ significantly. As a consequence, comparison of the tiered approach with available biological monitoring data was a key objective of this project.

In the UK, the ecological 'health' of a river is determined with periodic benthic sampling surveys (see Section 2.5). These surveys determine the presence and abundance of organisms (predominantly invertebrates) associated with different water quality in order to classify river reaches based on BMWP scores, number of taxa, and ASPT ratios.

These parameters tend to be more responsive to pollution from ammonia, elevated biological oxygen demand (BOD), and oxygen depletion, rather than metal pollution. As a consequence, a direct comparison between these biological indicators and metal levels cannot necessarily be drawn, particularly as the Zn-BLM predicts toxicity to algae as the most sensitive species, rather than invertebrates. However, elevated metal concentrations would probably have some degree of impact on these types of biological communities. Metals partition into the solid phase, so high concentrations of metals measured in the water column during routine sampling would imply higher concentrations accumulating in nearby sediments. High levels of metals in sediments would affect the benthic invertebrates measured as part of a biological sampling process. Furthermore, dissolved zinc levels greater than approximately 100 µg/l (for which there are numerous sites, see Section 3.4.1) are predicted to affect *Daphnia*, water-column-dwelling invertebrates often treated as surrogates for the types of organisms sampled during biological monitoring programmes. In short, although GQA data may not provide a direct measure of potential metal toxicity, some inferences may be made.

3.4.1 Comparison of biological monitoring data with the Environment Agency 1995 dataset

The ASPT ratios were calculated for all of the 1995 biological data supplied by the Environment Agency and compared with the dissolved zinc concentrations in order to understand how zinc may have been influencing the ecological quality of the sample sites.

The first graph in Figure 3.5 illustrates the ASPT ratio compared with the dissolved zinc concentration for all the 1995 data points (approximately 470 in total). The lower limit of the zinc concentrations was the limit of detection (5 µg/l). The data is spread across the environmental quality bands, but there appears to be a general downward trend in zinc concentrations with increasing ecological quality. However, regression analysis does not show this relationship to be significant (R^2 = 0.0077).

Given that the BMWP and, hence, the ASPT ratio is based on perceived tolerance to organic pollution, in order to assess whether or not there is any relationship between environmental quality and zinc concentration, confounding factors such as high

ammonia, high BOD, and high concentrations of other heavy metals need to be removed. The results of removing these factors are presented in the second graph of Figure 3.5. It is, however, appreciated that there may be other factors influencing the ecological quality at a site, particularly as a full dataset for metal concentrations was not available for each site.

All dissolved zinc data

High Ammonia (>1.3 mg/l), BOD (>6mg/l) and metals (>EQS) removed
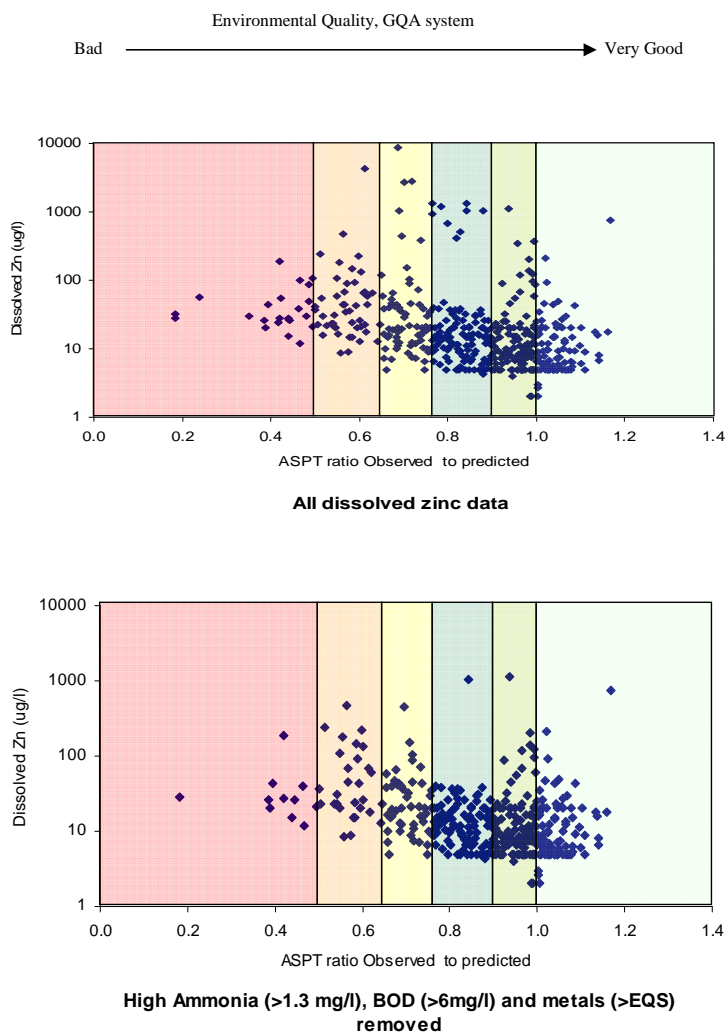
Figure 3.5 Dissolved zinc versus ASPT ratios

There are still a number of sites where the dissolved concentration of zinc is in the hundreds or thousands of micrograms per litre and yet the ASPT ratio indicates that the environmental quality is very good. This suggests that the level of dissolved zinc does not always correlate with the environmental quality, a finding that lends weight to the importance of the bioavailable fraction.

Table 3.11 provides the details on the number of data points that were removed when each of the confounding factors were taken out. Removing high ammonia, BOD, and metals (other than zinc) removed 79 data points from 469. However, on face value, dissolved zinc concentrations on 210 occasions would still exceed the Tier 2 value (PNEC+BG) and, therefore, would be considered compliance 'failures'. This amounts to 54 per cent of all data and covers all of England and Wales. This data shows the ubiquitous nature of zinc in the aquatic environment as well as the scale of the problem

that the Environment Agency will have to address upon implementation of a proposed EQS for zinc.

Table 3.11 Data points with confounding factors removed for the 1995 zinc data

	All dissolved zinc		Removing ammonia >1.3 mg/l		Removing ammonia >1.3 mg/l; BOD >6 mg/l		Removing ammonia >1.3 mg/l; BOD >6 mg/l; metals >EQS	
	Number	%	Number	%	Number	%	Number	%
Data points	469		437		430		390	
Data points >PNEC (7.8 µg/l)	340	72	309	71	302	70	264	68
Data points >PNEC+BG (11.2 µg/l)	283	60	252	58	246	57	210	54
GQA – poor or bad quality	71		47		44		40	
GQA – fair or better	398		390		386		350	
Data points removed			32		7		40	
Cumulative data points removed			32		39		79	

A similar exercise was carried out with the copper and ecological data provided by the Environment Agency for 1995 (Figure 3.6). Again, although there is a suggestion that elevated copper concentrations are associated with poorer quality waters, there were no significant statistical correlations. However, the overall number of samples where dissolved copper concentrations exceeded the Tier 2 value (PNEC+BG) amounted to less than five per cent of the total observations.

It has already been stated that the 'total risk' approach used to derive a PNEC value in the copper RAR does make a small correction for background and bioavailability based on a 'reasonable worst case' scenario. However, these data reflect the localised issues associated with copper in England and Wales, being predominantly limited to the south west of England, and potentially North Wales. Removing confounding parameters such as elevated ammonia, BOD, and other metal concentrations greater than their EQS (accounting for hardness-related values) failed to make a significant impact on the overall situation (Table 3.12). Again, many 'failures' at Tier 2 for copper were associated with water bodies considered of 'fair' quality or better.
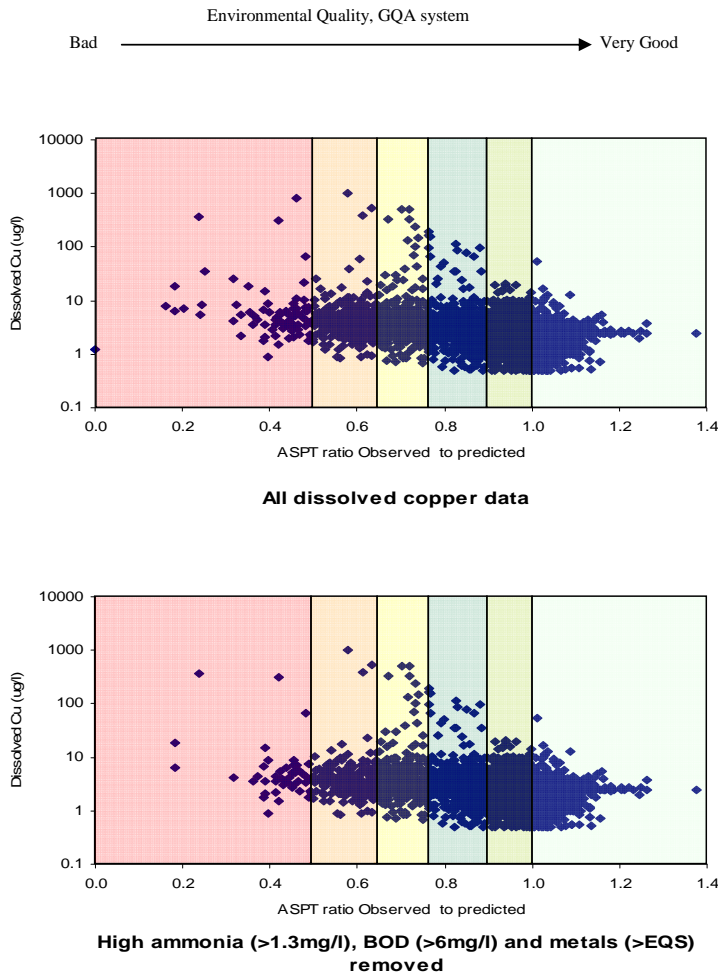
Figure 3.6 Dissolved copper versus ASPT ratios

Table 3.12 Data points with confounding factors removed for the 1995 copper data

	All dissolved copper		Removing ammonia >1.3 mg/l		Removing ammonia >1.3 mg/l; BOD >6 mg/l		Removing ammonia >1.3 mg/l; BOD >6 mg/l; metals >EQS	
	Number	%	Number	%	Number	%	Number	%
Data points	2952	-	2859	-	2829	-	2818	-
Data points >PNEC (8.2 µg/l)	169	6	146	5	141	5	137	5
Data points >PNEC+BG (9.8 µg/l)	124	4	108	4	102	4	101	4
GQA – poor or bad quality	339		274		253		251	
GQA – fair or better	2613		2585		2576		2567	
Data points removed			93		30		11	
Cumulative data points removed			93		123		134	

3.4.2 Comparison of biological monitoring data with Tier 3, BLM-derived data

For the selected sites for copper and zinc, Tier 3 BLM outputs for environmental concentration (EC)/PNEC ratios were compared with biological indices to determine if compliance at Tier 3 would lead to a degraded biological status.

Figure 3.7 provides a plot of the EC/PNEC-BLM ratio versus ASPT scores (observed/predicted) for the selected sites for copper. The data show that, in general, EC/PNEC-BLM ratios of less than one are associated with waters of higher ecological quality; however, quite surprisingly, waters where the ratio is in excess of 1000 are still classified 'fair', possibly suggesting the insensitivity of ASPT scores to metal toxicity. Plotting the EC/PNEC-BLM ratio versus BMWP scores (observed/predicted) shows a much more polarised situation (Figure 3.8), as does plotting the EC/PNEC-BLM ratio versus the number of taxa (observed/predicted) (Figure 3.9).
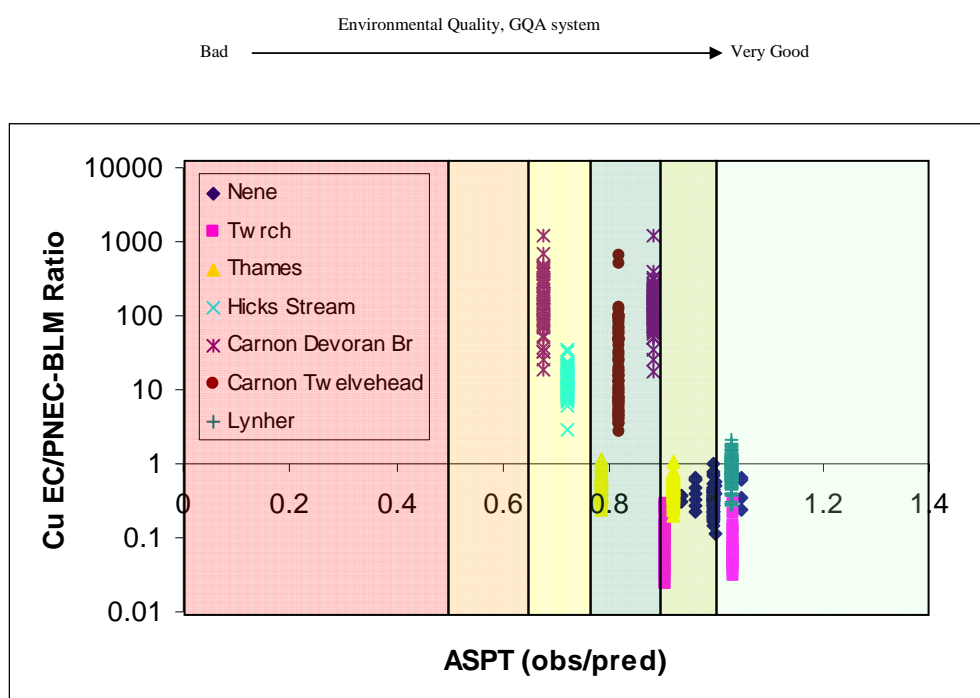
Figure 3.7 Plot of the Cu EC/PNEC-BLM ratio versus ASPT scores (observed/predicted)
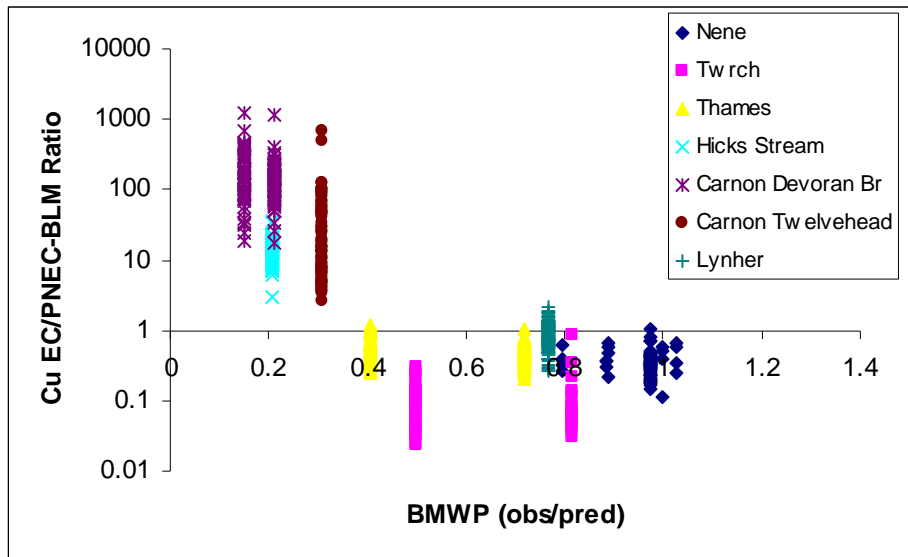
Figure 3.8 Plot of the Cu EC/PNEC-BLM ratio versus BMWP scores (observed/predicted)
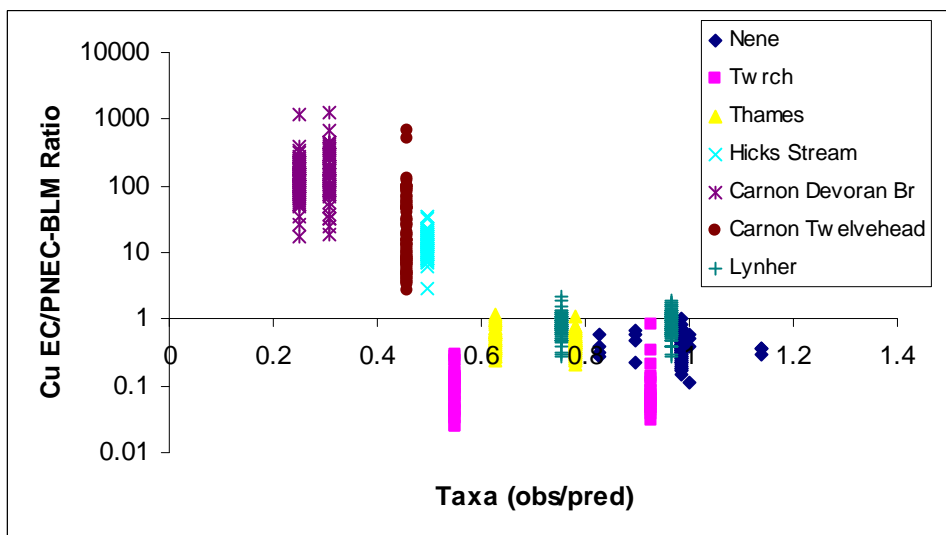
Figure 3.9 Plot of the Cu EC/PNEC-BLM ratio versus number of taxa (observed/predicted)

The data in the figures above suggest that where the EC/PNEC-BLM score is greater than one, adverse effects on water quality should be observed. However, based on ASPT observed-to-predicted scores, ecological quality is still considered 'fair'. This may be an indication of acclimatisation of the indigenous organism population to elevated trace metal concentrations with time – a well-established fact at many other locations. Two- to threefold decreases in acute copper toxicity have been reported elsewhere for *Daphnia magna* (Bossuyt *et al.* 2000) and fish (Taylor *et al.* 2000). The fact that all of the elevated copper EC/PNEC ratios are for sites located in Cornwall further supports this hypothesis. If acclimatisation is a widespread phenomenon, then the rather low background concentrations derived for samples taken in the Midlands and north of England and reported in the Environment Agency interim report on background

concentrations (EA 2006) would be a significant underestimate of the values that should be applied to more metalliferous regions. Regional background values for some metals may be more appropriate.

Zinc data show a similar, but not identical situation (Figure 3.10–Figure 3.12). There are, in general, more rivers that show EC/PNEC-BLM$_{algae}$ ratios greater than one, with no obvious trend towards 'poorer' quality water at higher ratios. However, certain trends are observable and may be explained. The situation with the Lynher and Tavy in the South West is typical of that for copper. These rivers have a ratio in excess of one, but the water quality is classified as very good, presumably for the same reasons, i.e. organism adaptation. The South Tyne site exhibits a similar trend to the sites in the south west of England, with EC/PNEC-BLM$_{algae}$ ratios exceeding one, but the water being classified as very good. The South Tyne was historically an area mined for lead, and zinc is generally associated with lead ores, so a degree of organism adaptation appears to have occurred here as well. There are reported data that support the assumption of adaptation in indigenous organisms for *Daphnia magna* (Muyssen and Janssen 2000, Muyssen and Janssen 2001a), *Raphidocelis subcapitata* and *Chlorella vulgaris* (Muyssen and Janssen 2001b).

The site from the River Ouse exhibits an EC/PNEC-BLM$_{algae}$ ratio of less than one, but is classified as having poor quality water. This is probably a result of other pollutants present in this industrialised river that also carry a high suspended sediment loading.
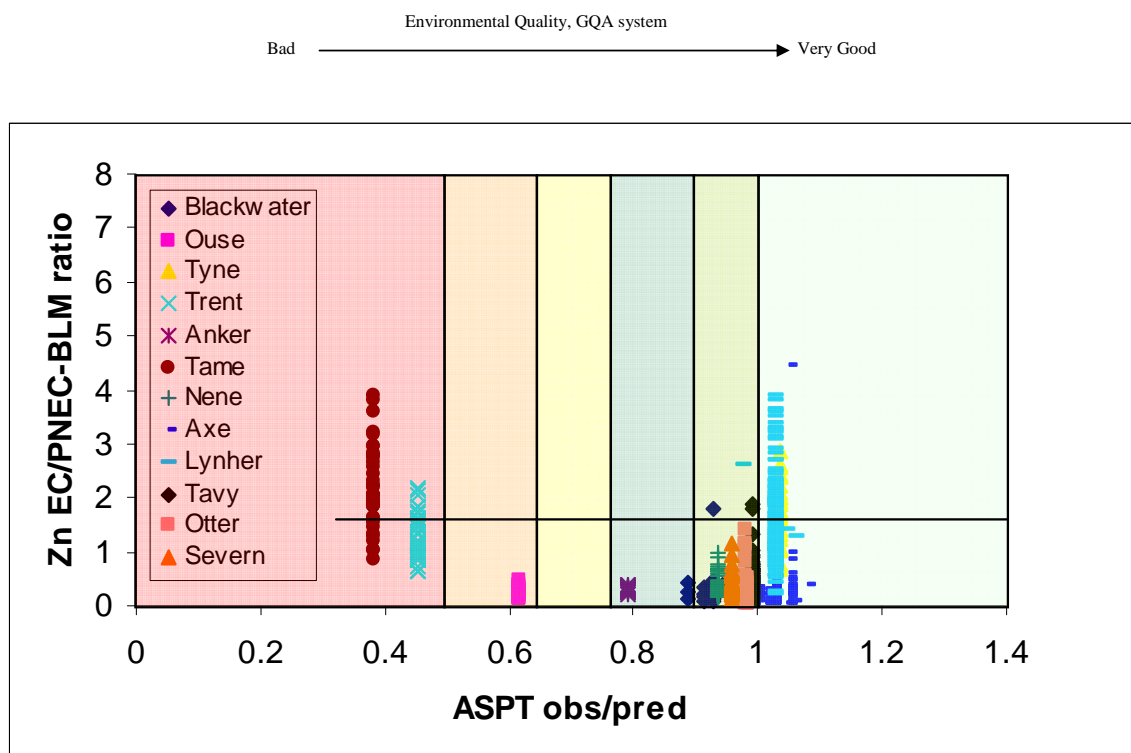
Figure 3.10 Plot of the Zn EC/PNEC-BLM$_{algae}$ ratio versus ASPT scores (observed/predicted)
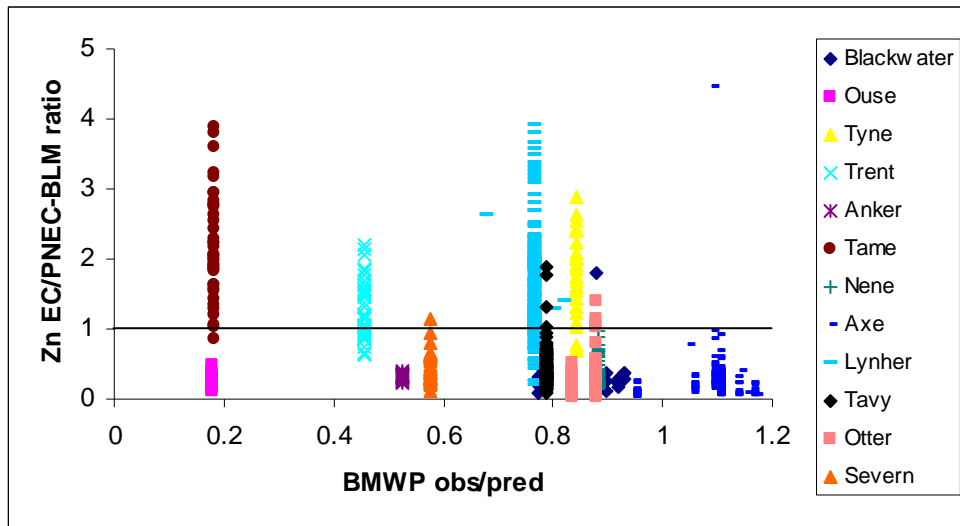
**Figure 3.11 Plot of the Zn EC/PNEC-BLM$_{algae}$ ratio versus BMWP scores
(observed/predicted)**
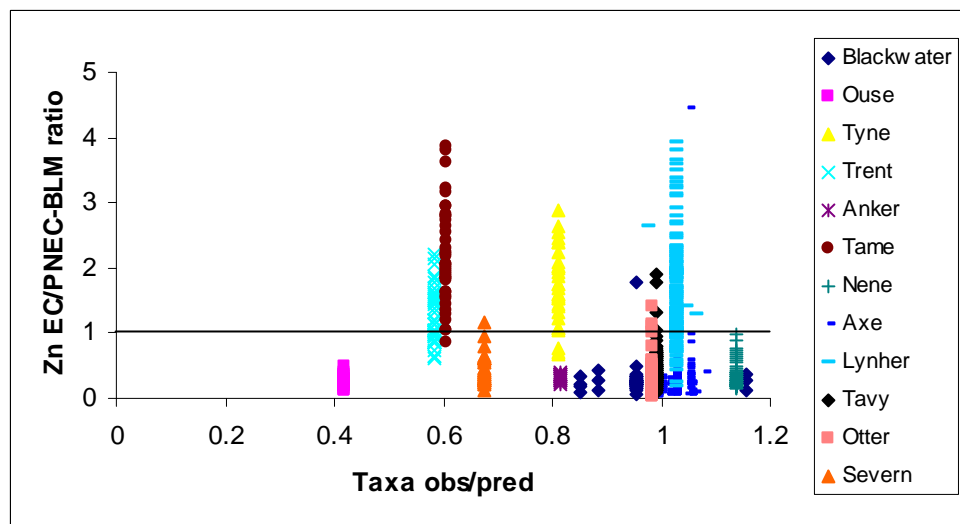
**Figure 3.12 Plot of the Zn EC/PNEC-BLM$_{algae}$ ratio versus number of taxa
(observed/predicted)**

The Tame and Trent are classified as having bad ecological quality and also exhibit
zinc EC/PNEC-BLM$_{algae}$ ratios greater than one. These data can demonstrate one of
two scenarios: either the BLM accurately predicts that zinc concentrations are causing
a negative impact on the rivers, or that other sources of pollution are present (other
than high BOD, high ammonia, or other metals). Like the Ouse, the Trent and Tame
(the Tame being a tributary of the Trent) drain urban industrialised catchments subject
to point and diffuse sources of nutrients, metals, pesticides, and industrial chemicals.
Consequently, it is not possible to accurately identify the source of the poor water
quality.

Figure 3.11 and Figure 3.12 for EC/PNEC-BLM$_{algae}$ ratios plotted against BMWP scores
(observed/predicted) and number of taxa (observed/predicted), respectively, show a
similar pattern, with high biological indices ratios for water with EC/PNEC-BLM$_{algae}$

ratios lower than one (with the exception of metalliferous areas), and lower biological indices ratios for urban rivers.

The data shown above for the tiered approach to metal compliance in surface waters versus ecological quality shows that moving from Tier 2 (EC/PNEC+BG) to Tier 3 (EC/PNEC-BLM$_{algae}$) reduces the number of non-compliances significantly, without appearing to lead to a negative impact on the ecological quality of the water body. For example, for the rivers Nene, Blackwater, Severn, and Tavy, where 'failure' at Tier 2 leads to a 'pass' at Tier 3, all measures of ecological quality support the assumption that the sites are not significantly impacted. This is encouraging in terms of reducing the number of 'non-compliances' for sites where pollution from zinc would be unexpected. A similar pattern could not be shown for copper because of the low PNEC-BLM values generated for several of the sites.

For consistency with the approach used for the copper assessment, the majority of Tier 3 assessments for zinc in this study have used 'raw' BLM-PNEC$_{algae}$ predictions to compare with observed dissolved zinc concentrations. The methodology proposed in the zinc RAR generates PEC/PNEC ratios by calculating the bioavailable fraction of zinc and comparing it with the RAR-derived PNEC (Section 1.4.2). Calculations following this methodology produce the same pattern of data, but do generate higher ratios (Figure 3.13) because bioavailable zinc concentrations are higher (produced using the ratio of NOEC$_{ref}$ to NOEC$_X$). Consequently, at low pH and DOC values, NOECs for fish and *Daphnia* are closer to their corresponding reference values (even though the absolute NOEC values for algae are actually much lower than those for fish or daphnia).
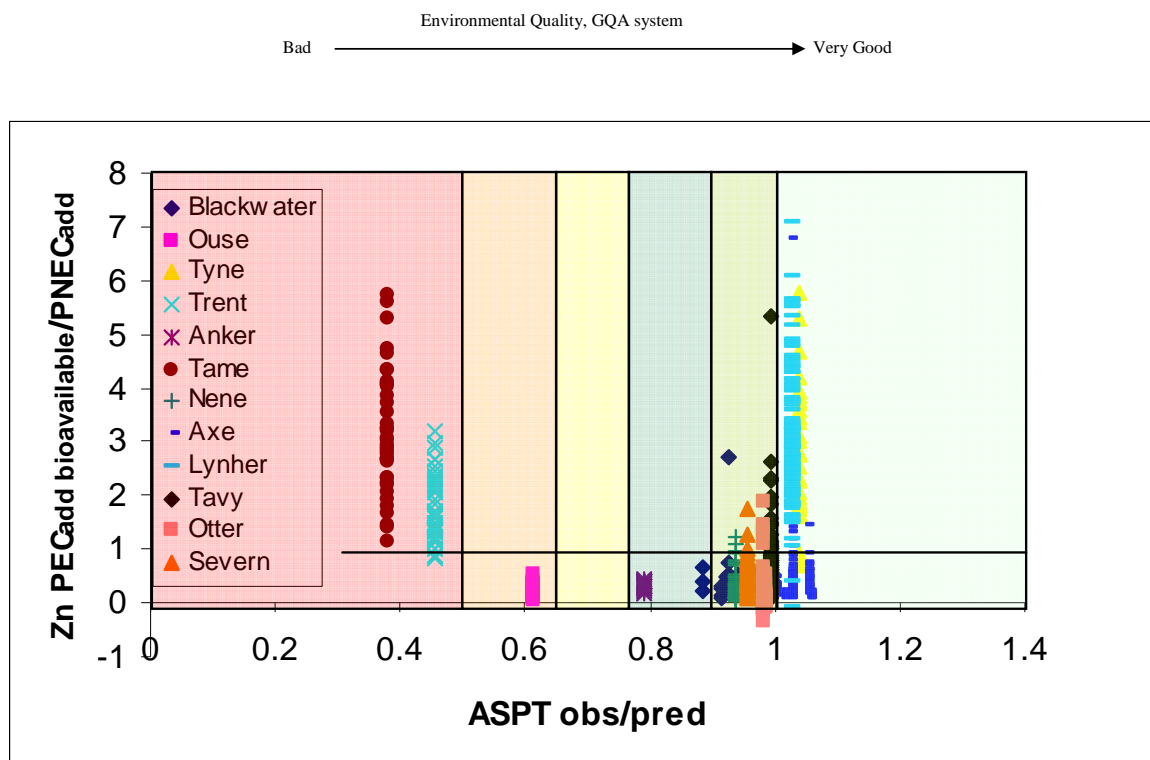
Figure 3.13 Plot of the zinc RAR PEC$_{add,bioavailable}$/PNEC$_{add}$ ratio versus ASPT scores (observed/predicted)

With this approach, there is a relative increase in the PEC/PNEC ratio for several of the waters: by a factor of around 1.5 for the Tame, Trent, Lynher and Tyne; therefore, increasing the number of exceedances. Furthermore, some additional 'failures' now occur for the Otter and Severn, particularly where dissolved zinc concentrations are relatively low (Otter) or there are sporadic high concentrations of dissolved zinc (Severn). The zinc RAR approach is potentially more consistent: it compares predicted bioavailable zinc with a PNEC that should also reflect bioavailability. Simply comparing observed zinc concentrations with the BLM-PNEC$_{algae}$ means that background concentrations are incorporated into the observed concentration.

However, until a definitive background concentration can be agreed, decisions regarding which scheme to use are rather academic. The fact that some reported zinc concentrations are less than the median background concentration (EA 2006) certainly makes definitive assessments difficult.

3.5   Implications for compliance monitoring

Data provided in this chapter for copper and zinc show contrasting issues associated with compliance monitoring and ecological quality. Copper appears to be a localised issue, associated with the south west of England where mineralogy dominates the observed concentrations; for this reason, it may be assumed that areas of similar geology, but not included in this assessment (e.g. Anglesey) may also exhibit the same issues. Non-compliance for these limited sites is observed at all three tiers of assessment, and the ratio of concentrations to expected effects are, in some cases, several orders of magnitude higher.

Whether such high concentrations of copper actually adversely impact the indigenous biology of the catchment is not easily determined, not least because the biological indices used to assess ecological quality are not necessarily sensitive to metal pollution. It appears that in some areas where copper levels are 'naturally' high, some form of adaptation of local biological communities may have occurred, resulting in some biological indices suggesting at least 'fair' water quality. Acclimatisation has been observed in laboratory tests and field situations. Therefore, although these sites fail to meet the required status with respect to purely chemical measures of water quality (at any tier of assessment), further assessment of the potential for assigning localised background concentrations for these specific regions is needed, along with better indicators of biological status with respect to metal pollution, before definitive conclusions can be drawn regarding impacts.

Compared with the existing statutory EQS system (1 to 28 µg/l, depending on hardness), these soft water sites dominated by copper mineralogy are already failing the numeric quality standard. A switch to a revised standard that sits roughly in the middle of the current classification system (and is set based on a 'reasonable worst case' with respect to the bioavailability of copper) is, therefore, unlikely to have a significant impact on the current number of non-compliances for copper.

The tiered assessment method does allow waters that are thought free from copper pollution (a limited quantity) to be classified as compliant. This assessment is supported by biological monitoring data (based on the qualifications provided above regarding metal pollution and GQA data), whether based on ASPT or BMWP scores or the number of taxa present. This in situ biological monitoring data provides reassurance that implementing a tiered assessment regime for compliance purposes is not a 'license to pollute' surface waters, leading to degradation in ecological quality.

For zinc, a much different picture emerges from the data assessment. The RAR-derived PNEC$_{add}$ of 7.8 µg/l is right at the lowest end of the current UK zinc EQS range

(8 to 125 µg/l, depending on hardness). As a consequence, waters currently considered as compliant, would be deemed as 'failing' without the addition of a relevant background concentration. Such a high degree of non-compliance (72 per cent of the 1995 Environment Agency dataset, see Table 3.1) suggests widespread zinc pollution of UK surface waters, which is not reflected in biological field monitoring data. The data demonstrate the importance of applying a relevant background concentration to the $PNEC_{add}$ value. For copper, water bodies exhibited copper concentrations several orders of magnitude higher than the standards calculated at all three tiers of assessment, but for zinc, the ratio for non-compliant sites is typically less than 10.

Applying the Tier 3 assessment leads to significantly higher zinc PNEC-BLM values that significantly reduce the number of non-compliances. This process leaves mostly rivers known to be influenced by underlying mineralogy as 'failing'. As for copper, however, even where observed concentrations exceed PNEC values, the observed biological quality does not necessarily support concern for environmental impacts. Indeed, waters can often be classified as fair or better. This may reflect the fact that current ecological monitoring data is not sensitive to the effects of metal pollution, or more likely, that adaptation to ambient metal concentrations has occurred. There is no evidence to suggest that using all three tiers of the assessment for zinc would lead to degraded ecological status within rivers, based on existing biological monitoring data, accepting the proviso that it may not be the best indicator of metal pollution.

The full implication of compliance assessment can only be determined after definitive background concentrations are established, as the 'added risk' approach to standard setting for metals requires the $PNEC_{add}$ to be added to a background concentration. This is particularly important for zinc where the PNEC is derived solely as an addition. For copper, the situation is slightly different as the RAR-derived PNEC includes a small correction for background concentrations in the laboratory test waters from which the toxicity data are derived, although this alone does not allow for localised impacts of mineralogy experienced in the UK.

The financial and time-related cost of derogation or exception cannot be weighed against the cost of performing refinements to PNECs or setting site-specific EQS. However, this project has established that all of the data required for undertaking all three tiers of assessment are currently available, although DOC is decidedly 'patchy'. The cost of determining DOC on a more regular basis (at around £10 per sample) is likely to be in the tens of thousands rather than millions of pounds. The incorporation of the Tier 3 models into annual compliance assessment would be negligible. Compared to the costs associated with designing and implementing programmes of measures to reduce environmental discharges of zinc and copper – with the associated potential for appeals and court action – site-specific assessment of metal compliance may provide good value for money.

This project suggests that the use of a tiered assessment need not be restricted to the assessment of surface water. There is scope for its application in the assessment of discharges to surface waters, and wastewater treatment works effluent in particular. Previous studies have shown organic ligands present in sewage effluent can complex copper to a significant degree, and that the complexation is retained and stable after dilution into receiving water (Van Veen *et al*. 2002). The use of a tiered approach to consent-setting for metals may, therefore, lead to the provision of adequate environmental protection without the necessity of installing costly tertiary treatment on wastewater treatment works receiving essentially domestic sewage which is a possibility under current policy.

4   Conclusions

The following conclusions can be drawn from this assessment of a tiered approach to metal compliance in surface waters:

1. Sufficient data was obtained from the Environment Agency to assess the proposed tiered approach using i) a combination of individual year data (1995) for Tier 1 and 2, and ii) a range of data (1995 to 2006) for a selected number of sites for which DOC data and biological monitoring data were also available (approximately 1000 data points for copper and zinc) for Tier 1, 2, and 3 assessments.

2. For zinc, over 70 per cent of reported data for 1995 exceeded the Tier 1 assessment where observed concentrations are compared with the RAR-derived $PNEC_{add}$ of 7.8 µg/l. This rate of non-compliance is significantly greater than the rate when the same data is compared with the current EQS regime (11 per cent 'failure'). After assessing the data at Tier 2 where the background is added to the $PNEC_{add}$ (as per the EU TGD 'added risk' approach), the number of non-compliances dropped to 60 per cent of the total dataset. This outcome reflects both the ubiquitous nature of zinc in the aquatic environment, with inputs from diffuse and point sources, and the fact that the PNEC may be too conservative. It also suggests that without taking account of zinc speciation (at Tier 3), there is the potential for a large proportion of English and Welsh water bodies to be considered polluted by zinc which appears to be an unlikely scenario based on field biological monitoring data.

3. For copper, an evaluation of the 1995 data against the RAR-derived PNEC suggested non-compliance to be much more of a localised issue associated with mineralogical conditions. Only 4 per cent of 1995 data (almost 3000 reported data points) were shown to be non-compliant at the Tier 2 level; many of these were associated with mining areas in Devon and Cornwall. This outcome showed an improved situation compared with the current EQS regime, where the lowest EQS (to protect salmonid fisheries) is only 1 µg/l.

4. The Tier 3 assessment significantly reduced the number of 'failures' for zinc to approximately 24 per cent, slightly less than those determined by comparison with the current EQS system, which also takes account of metal bioavailability by banding the EQS according to water hardness. The proposed approach also had the effect of eliminating non-compliances for rivers considered to be largely untouched by urban or mine water drainage and, therefore, unlikely to be impacted by zinc pollution. This assumption was supported by available biological monitoring data.

5. Applying the Tier 3 approach to the copper data also reduced the number of non-compliances for rivers not associated with copper pollution. For mineralogical areas, concentrations of copper were sufficiently elevated to mean that the water was non-compliant even at the Tier 3 level. However, the biological indices suggested these waters were of fair or better quality, which may indicate that some form of adaptation has occurred at these sites, or that current biological monitoring data are not accurate measures of metal pollution.

6. If a water body exhibits water quality parameters that lie outside of the Cu-BLM validation range (i.e. low pH, DOC, or hardness), then even though it may pass the Tier 1 or 2 assessments, the Tier 3 BLM assessment should also be run because the PNEC for copper may not be sufficiently protective under these situations.

7. The tiered approach could be used in a flexible way given the uncertainties associated with background concentrations. The potential for using the BLM at a

Tier 2 level was demonstrated, reducing the number of 'failures' to a more manageable number for which background considerations could then be applied.

8. The Tier 3 BLM for zinc is a Microsoft Excel spreadsheet that predicts the bioavailable fraction of the metal based on identified key parameters. The Zn-BLM is sensitive to DOC concentrations and this input value cannot easily be substituted for a default value without seriously compromising predictions.

9. The BLM for copper requires more input values than its zinc counterpart, but several parameters (sulphate, sulphide, chloride, potassium, temperature, and magnesium) have an insignificant impact on the BLM outputs, even at extreme values potentially encountered in UK waters. The Cu-BLM is more complex, applying a species sensitivity distribution to generate a PNEC. The model, therefore, takes a significantly longer time to run, particularly if more than 10 datasets are run in one go. The greater number of toxicity data contributing to the derivation of the PNEC should ensure a more accurate prediction.

10. The Cu-BLM is extremely sensitive to DOC concentration, which is to be expected based on the known chemical speciation of copper in natural waters. There is no substitute for using high quality DOC data in the model. The lack of large DOC datasets for UK waters will, therefore, hamper its use on historical data. For waters with low DOC and low pH, the Cu-BLM tends to predict a lower PNEC than the RAR-derived PNEC (8.2 µg/l), thus the number of EQS 'failures' are not significantly reduced when the Tier 3 Cu-BLM derived PNEC is compared with observed copper concentrations.

11. For the purpose of assessing regulatory compliance, the use of annual averages for the input parameters (rather than calculating individual BLM standards for each specific date and then taking an average of the calculated BLM standards) was deemed acceptable. This aggregation method significantly reduces staff time and the computing power required when assessing compliance for metals at sites on a year-to-year basis.

12. At Tier 3, comparison of zinc EC/PNEC-BLM$_{algae}$ ratios with biological monitoring data (such as BMWP and ASPT scores, and number of taxa data) showed that, in general, EC/PNEC-BLM ratios of less than one (i.e. observed concentrations were less than predicted no-effect levels) were associated with better quality water. Thus, supporting the use of the model.

13. The EU Zn RAR methodology for generating PNECs (which takes a more conservative estimate of zinc bioavailability rather than taking the PNEC for the most sensitive species, i.e. algae) leads to a more conservative PNEC being predicted under certain water quality conditions. This can lead to a greater proportion of data points 'failing' compliance even in waters deemed of better than fair ecological quality. This outcome suggests that the RAR approach is a very conservative estimate of zinc bioavailability (as required by the EU risk assessment process), which can be over-protective under localised conditions.

14. For certain sites (those in the south west of England for copper and zinc, and the Tyne for zinc), non-compliance at all tiers of assessment were observed, but the water was still classified as of at least fair quality, based on ASPT and BMWP scores, and the number of taxa present. This may be due to i) the adaptation of organisms to high metal backgrounds, in which case the use of a global (and quite conservative) background value for copper and zinc may not be applicable in metalliferous areas; or ii) the possibility that these biological indices are a poor measure of metal pollution. For the copper assessment, the ASPT scores may also have been 'artificially' elevated owing to the presence of a low number of high scoring taxa. This may bias the assessment of ecological quality, when in fact, the

observed versus predicted BMWP scores and number of taxa are significantly decreased.

15. The uncertainty over setting appropriate background concentrations for copper and zinc means that definitive assessments of the impact of their use at Tier 2 cannot be fully evaluated at this stage. It is particularly relevant in the case of zinc, as the PNEC is expressed as an addition over and above the background concentration (compared with a total dissolved value for copper). Consequently, the value used for the zinc background can have an impact on compliance assessment, depending on the methodology used.

5   Recommendations

Based on the data provided, a number of recommendations can be made to improve and strengthen the conclusions provided in Section 4:

1. The implementation of a speciation-based assessment should be considered by the Regulators as an effective way of regulating metals in surface waters. If necessary, a flexible approach to the order of the tiers in the tiered assessment may be considered, provided it is recognised that if the ambient water quality parameters fall outside of the validation range for the Cu-BLM, then the BLM will need to be run, as the potential standard will not necessarily be protective under such conditions.

2. As well as assessing surface water compliance, the tiered assessment may also be incorporated into the consent-setting procedure for discharges of effluents to surface waters, thus providing a more accurate assessment of impact, and potentially minimising the need for costly (and potentially unnecessary) treatment and appeals.

3. The impact of the tiered approach should be considered in more detail when definitive background concentrations for metals are available. A similar exercise should be undertaken with a comprehensive dataset to allow a more accurate determination of the degree of compliance at each stage of the tiered assessment process. This would then allow the financial implications of implementing the tiered assessment versus derogation and exemptions to be completed.

4. Regional background concentrations for metals should be considered, particularly for areas dominated by certain types of mineralogy (i.e. Cornwall, and possibly North Wales for copper and the north east of England for zinc).

5. The implementation of a speciation-based assessment requires confidence that the 'relaxed' standards generated by the models will not adversely impact resident biological communities present in the water. Comparison with biological monitoring data as part of this project suggests that minor exceedances under Tier 1 and Tier 2 assessments, leading to passes at Tier 3 were associated with rivers of good ecological quality, not obviously subject to metal pollution. However, BMWP GQA monitoring was designed to be an indicator of general river pollution, not necessarily metal pollution. It has been suggested that the presence of stonefly, mayfly, and caddisfly larvae may be a better indicator of metal pollution; the correlation between metal concentrations and the presence of these species should be studied in more detail.

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List of abbreviations

ASPT	average score per taxon
BG	background
BioF	bioavailability factor
BLM	biotic ligand model
BMWP	Biological Monitoring Working Party
CEH	Centre for Environmental Hydrology
DO	dissolved oxygen
DOC	dissolved organic carbon
EC	environmental concentration
EDTA	ethylenediaminetetraacetic acid
EU	European Union
NOEC	no observed effect concentration
NOM	natural organic matter
NTA	nitrilotriacetic acid
PEC	predicted environmental concentration
PNEC	predicted no-effect concentration
$PNEC_{add}$	predicted no-effect concentration to be added to background
RAR	risk assessment report
SEPA	Scottish Environmental Protection Agency
TGD	Technical Guidance Document
UK	United Kingdom

ANNEX A   Summary of selected sites and data available for tiered assessment (1995 only)

Table A.1   Summary of selected sites for zinc (using 1995 data only)

Site Name	DO % Sat	pH	mg/l						Dissolved concentration (µg/l)					
			BOD	SS	Ammonia	Alkalinity	Ca	Mg	Cd	Cr	Cu	Ni	Pb	Zn
TREGILLOWE	82.9	7.04	0.78	----	0.07	79.33	36.3	19.8	----	----	16.67	----	----	1313
MINSTERLEY BROOK	96.7	7.91	1.59	19.2	0.06	----	----	----	----	----	----	----	6.67	761
EREWASH	83.9	7.8	4.38	10	0.69	----	----	----	----	----	----	----	1.91	226
SOUTH TYNE	102.0	7.38	1.4	4.5	0.05	63.33	25.3	3.9	----	1.03	1.55	3.77	5.1	126
DERWENT	97.0	7.99	1.1	2.6	0.05	77.58	25.7	6.1	----	1	1.02	1.19	3.84	97
SOUTH TYNE	106.0	7.54	1.8	4.33	0.05	67.33	28.6	4.5	0.22	1.07	1.42	2.12	4.7	93
NENE	100.4	8.23	2.64	5.83	0.09	216.67	132	13.6	0.1	1	8.4	10	0.5	68
TAME	112.5	8.07	4.25	8.07	0.73	----	----	----	----	----	----	----	0.87	60
TRENT	93.3	7.92	3.08	13.56	0.39	----	----	----	----	----	----	----	0.94	47
WEAR	98.0	7.51	1.3	15.8	0.02	50.33	23.6	2.8	0.11	----	1.09	----	7.23	46
SOUTH TYNE	98.0	7.53	1.5	7	0.02	33.33	15.5	1.3	----	1.84	1.87	1.07	8.22	44
AIRE	68.5	7.35	5.52	7.33	0.89	117.67	60.7	15.7	0.1	7.24	7.1	10.43	1.98	39
TRENT	92.6	8.03	2.11	17.15	0.2	----	112.8	26.3	----	----	----	----	2.19	31
LYNHER	96.4	7.54	1.33	3.55	0.06	27.67	11.8	4.1	0.23	1	8.17	5	2	30
NIDD	98.6	7.46	1.96	3.67	0.16	37.33	19.3	5.8	0.11	1	1.43	1.61	2.54	26
TORRIDGE	103.1	8.32	2.29	----	0.05	39.33	12.7	5.2	0.2	1	2.5	5	2	21
SWALE	99.2	7.93	1.93	3	0.1	183	78.9	13.3	0.12	1	2.08	1	2.11	20
OUSE	86.9	7.7	2.29	12.13	0.5	145.6	63.4	11.3	0.1	1.02	1.76	1.07	2.04	20
THAMES	96.5	7.87	1.65	----	0.24	189.67	91.7	5.5	----	2	5.27	5	1.13	16
MANIFOLD	94.3	7.57	1.07	15.67	0.02	----	----	----	----	----	----	----	0.55	13

| Site Name | DO % Sat | pH | mg/l | | | | | | Dissolved concentration (µg/l) | | | | | |
			BOD	SS	Ammonia	Alkalinity	Ca	Mg	Cd	Cr	Cu	Ni	Pb	Zn
ANKER	89.9	8.04	2.52	14.44	0.22	----	----	----	----	----	----	----	0.7	12
DOVE	105.8	8.05	1.55	8.25	0.04	----	----	----	----	----	----	----	0.75	12
SEVERN	100.5	7.87	1.76	4.09	0.08	----	30.9	7.4	----	----	----	----	0.56	10
TAVY	99.0	7.51	1.42	3.61	0.02	20.29	8.8	2.3	0.5	1	4.14	5	2	9
STOUR	89.7	7.93	2.75	60.67	0.18	----	81.0	4.0	0.5	1.67	4.33	5.33	2	8
BLACKWATER	104.1	8.16	1.55	6.13	0.09	239.33	130.0	8.5	0.1	1	2.8	5	0.5	8
AXE	104.5	8.09	1.82	32.21	0.08	108.43	51.9	5.4	0.5	1.14	2.93	5	2	5.43
OTTER	105.8	8.1	1.83	39.97	0.05	87.5	36.8	10.8	0.5	1.17	2.83	5	2	5.83
STOUR	91.8	8.35	2.71	12.93	0.15	198	105.5	4.6	0.5	1.5	2.75	5	2	6.5

Table A.2 Summary of selected sites for copper (using 1995 data only)

Site Name	DO % Sat	pH	BOD	TSS	Ammonia	Alkalinity	Ca	Mg	Cd	Cr	Cu	Ni	Pb	Zn
					mg/l				Dissolved concentration (µg/l)					
CARNON	89.72	5.97	1	11.9	0.65	48.6	145.25	9.9	3.85	5	329.5	60	10.5	
DAFEN	93.8	7.15	3.05	----	0.61	53	----	----	----	----	236.4	----	82.6	----
HICK'S MILL STREAM	96.13	6.9	1.45	18.93	0.18	22.8	16	5	1.27	----	115	5	2	507
SEATON	95.25	7.45	1.05	----	0.26	23	13	4.25	----	----	80	----	----	----
REDRUTH STREAM	98.58	7.57	1	----	0.23	18.3	16.67	7.03	----	1	66.7	20	2	----
CARNON	95.51	6.98	----	3.28	0.23	17.7	17.44	7.21	0.94	----	50.6	13.85	2	689
COLNE	92.18	8	4.5	----	0.07	253	----	----	----	1	35.7	5	4.6	39
HANCOCKS WATER	78.53	7.88	7.8	----	1.71	271	101.67	9.9	----	----	25	----	----	----
ALT	83.99	7.5	6	23.5	6.32	133	62.95	14.5	----	----	21.5	----	----	----
FRAYS RIVER	88.09	7.9	3.3	----	0.15	247	----	----	----	----	19.6	----	----	----
ROTHER	82.08	7.45	5.95	7.63	3.66	156	76.15	16.2	----	----	17.5	----	----	----
MARLEY GAP BK	94.64	8.07	5.33	----	0.66	204	----	----	0.1	1	16.9	5	1.53	21
ASHRIDGE STREAM	57.58	7.57	4.87	----	0.86	216	----	----	----	----	15.8	----	----	----
TWRCH	107.7	6.67	1.15	----	0.04	9.32	----	----	0.2	----	13.1	----	2	----
DITTON BROOK	60.7	7.47	7.42	45.83	1.6	127	69.47	15.07	0.12	1.3	12.5	6.35	0.65	21.8
LEIGHTON BROOK	64.39	7.57	5.83	31	2.38	174	77.6	20.83	----	----	10.6	----	----	----
IVEL	107	8.25	2.25	----	0.06	240	----	----	0.1	2.3	10.3	13	0.77	14.3
LOX YEO	86.85	7.98	3.28	----	0.44	201	77	20.7	----	----	9.3	----	----	----
ELY	86.66	8.07	1.57	----	0.25	134	----	----	0.2	----	9.2	----	2	----
NORTH MILLS BROOK	67.17	7.8	3.3	15	0.21	232	113	6.8	----	----	9	----	----	----
THE CUT (ABOVE THAMES)	86.46	7.83	2.65	----	0.11	230	109.25	6.9	----	3.3	8.5	5.5	1.1	32.8
NIDD	88.33	7.44	1.8	4.67	0.25	101	43.77	13.03	----	----	8.4	----	----	----
NENE	100.35	8.23	2.44	5.83	0.1	217	132	13.67	0.1	1	8.4	10	0.5	68

Site Name	DO % Sat	pH	mg/l						Dissolved concentration (µg/l)					
			BOD	TSS	Ammonia	Alkalinity	Ca	Mg	Cd	Cr	Cu	Ni	Pb	Zn
LYNHER	96.42	7.54	1.5	3.55	0.1	27.7	11.83	4.08	0.23	1	8.2	5	2	30
AIRE	76.13	7.5	4.43	9.67	0.28	116	52.08	14.55	0.1	7.4	8.1	8.81	1.18	23.3
MAWDDACH	102.1	6.82	0.77	----	0.03	12	----	----	0.2	----	7.23	----	2	----
BLACKWATER	85.17	7.74	2.02	----	0.57	150	----	----	----	----	7.1	----	----	----
GANNEL	94.76	7.53	1.05	----	0.5	36.5	18	8.9	----	----	7	----	----	----
AIRE	70.54	7.42	4.9	24	0.75	----	----	----	0.11	3.5	6.24	5.69	1.04	28

Table A.3 Summary of available data for the identified zinc sites which include DOC data

River	Number of data points that include DOC data										
	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Anker	17	-	-	-	-	-	-	-	-	-	-
Axe	30	29	15	15	13	12	7	11	12	14	12
Blackwater	26	23	21	24	16	11	10	12	11	13	12
Dove	11	-	-	-	-	-	-	-	-	-	-
Lynher	26	26	16	12	12	12	9	12	12	12	12
Manifold	10	-	-	-	-	-	-	-	-	-	-
Minsterley Bridge	3	-	-	-	-	-	-	-	-	-	-
Nene	23	24	24	26	16	12	12	12	12	12	12
Otter	24	26	15	12	12	13	3	12	10	12	12
Ouse	-	-	-	-	-	-	-	-	12	12	10
Severn	25	12	12	6	-	-	-	-	-	-	-
Tame	40	-	-	-	-	-	-	-	-	-	-
Tavy	26	26	16	12	12	12	8	12	12	12	12
Trent	10	11	13	11	12	-	-	-	-	-	-
Tyne	-	-	-	-	-	-	-	-	12	12	12

Table A.4 Summary of available data for the identified copper sites which include DOC data

River	Number of points that include DOC data											
	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Nene	3	4	4	4	4	4	4	4	12	12	12	9
Twrch	1	-	3	11	5	4	2	12	2	-	6	7
The Cut (above Thames)	11	11	10	11	11	14	12	12	12	12	12	8
Lynher	26	26	16	12	12	12	9	12	12	12	12	6
Hicks Stream	44	37	-	-	-	-	-	-	-	-	-	-
Carnon at Devoran	15	14	8	11	12	12	11	12	12	12	13	8
Carnon at Twelveheads	45	36	-	-	-	-	-	-	-	-	-	-

ANNEX B Summary of annual data (1995–2006) used for the tiered assessment

Table B.1 Summary of chemical data for the identified zinc sites[1]

| | | | Mean annual concentrations | | |
| | | | DOC | | Dissolved Zn |
River	Year	Ca (mg/l)	(mg/l)	pH	(µg/l)
Nene	1995	128	6.8	8.3	9.8
	1996	130	7.1	8.4	14.3
	1997	128	6.2	8.3	13.3
	1998	137	6.2	8.4	8.8
	1999	118	5.7	8.3	8.8
	2000	124	6.0	8.3	8.3
	2001	127	5.2	8.2	6.8
	2002	119	5.0	8.2	10.6
	2003	124	5.0	8.0	7.5
	2004	128	5.0	8.0	5.5
	2005	128	4.7	8.0	7.2
Blackwater	1995	133	5.9	8.3	5.7
	1996	133	6.0	8.4	6.0
	1997	138	5.5	8.4	7.0
	1998	141	5.9	8.3	5.8
	1999	144	5.9	8.2	5.5
	2000	149	7.0	8.2	4.3
	2001	142	4.5	8.1	11.4
	2002	131	4.4	8.3	7.3
	2003	138	4.3	7.8	6.3
	2004	138	4.3	8.1	6.0
	2005	139	4.1	8.1	5.6
Tame	1995	95	7.9	7.9	80.0
Anker	1995	105	8.5	8.1	11.7
Severn	1995	33	3.9	7.8	12.4
	1996	32	3.5	7.8	8.5
	1997	29	6.2	7.7	14.4
	1998	33	3.7	7.8	13.6
Trent	1995	90	9.5	7.9	45.6
	1996	90	8.7	7.7	60.7
	1997	95	7.8	7.8	56.7
	1998	86	8.3	7.8	43.4
	1999	90	7.7	7.9	33.0
Tavy	1995	9	1.9	7.6	9.9
	1996	9	1.9	7.6	9.9
	1997	9	2.1	7.6	13.6
	1998	10	1.8	7.6	11.5
	1999	9	1.8	7.6	6.9
	2000	8	2.1	7.7	7.9
	2001	9	1.9	7.4	8.1
	2002	8	2.3	7.4	8.7
	2003	9	2.5	7.3	7.1

River	Year	Ca (mg/l)	DOC (mg/l)	pH	Dissolved Zn (µg/l)
			Mean annual concentrations		
	2004	9	2.2	7.3	7.3
	2005	9	2.9	7.5	8.6
Lynher	1995	12	1.9	7.6	36.3
	1996	13	1.5	7.6	38.1
	1997	12	2.0	7.6	34.9
	1998	13	1.5	7.6	26.7
	1999	13	2.0	7.6	25.4
	2000	12	1.6	7.6	24.8
	2001	13	1.8	7.3	31.0
	2002	13	1.8	7.4	27.1
	2003	12	1.7	7.2	31.6
	2004	13	1.6	7.4	29.1
	2005	13	1.9	7.4	26.0
Ouse	2003	64	6.7	7.9	9.2
	2004	61	7.5	7.8	8.7
	2005	63	6.5	7.9	9.5
Tyne at Warden Bridge	2003	37	7.6	7.8	73.0
	2004	24	9.3	8.0	83.4
	2005	35	7.1	7.9	84.9
Axe	1995	62.9	4.2	8.1	6.5
	1996	63.6	3.8	8.1	10.5
	1997	65.5	4.4	8.1	6.8
	1998	64.6	4.5	8.1	7.4
	1999	63.1	5.8	8.0	2.8
	2000	58.3	5.6	8.0	2.5
	2001	63.7	5.7	8.0	3.2
	2002	61.6	6.2	7.8	2.8
	2003	64.6	4.7	7.8	4.8
	2004	64.9	4.6	7.8	5.0
	2005	66.2	4.9	8.0	5.0
Otter	1995	46.3	4.3	8.2	9.7
	1996	43.7	3.5	8.2	6.5
	1997	44.2	4.8	8.1	8.6
	1998	41.3	6.1	7.9	7.1
	1999	47.8	3.4	8.2	3.1
	2000	47.9	4.7	8.0	4.4
	2001	39.6	4.7	7.4	5.1
	2002	42.8	5.3	7.9	3.9
	2003	47.6	3.2	8.0	4.7
	2004	46.1	4.1	8.0	5.0
	2005	54.0	4.8	8.0	5.0

Notes: [1] For which there were greater than 12 data points.

Table B.2 Summary of chemical data for the identified copper sites

River	Year	pH	Dis-solv-ed Cu (µg/l)	Mean annual concentration (mg/l)							
				DOC	Ca	Mg	Na	K	SO$_4$	Cl	Alka-linity
Nene	1995	8.3	4.6	17.9	132.5	12.1	65.0	11.3	183.0	86.5	204.3
	1996	8.4	5.0	7.1	132.5	12.2	83.8	12.6	197.0	115.5	195.5
	1997	8.3	4.9	5.8	129.0	11.6	79.0	12.9	173.0	104.0	202.0
	1998	8.4	3.0	6.1	146.5	11.6	54.8	9.8	155.3	77.3	223.5
	1999	8.3	3.6	5.5	121.5	11.3	47.5	8.4	136.8	70.8	200.5
	2000	8.3	3.3	6.1	119.5	10.1	47.8	8.6	124.3	70.8	190.5
	2001	8.1	3.3	5.0	122.5	9.4	36.5	7.3	118.1	52.2	204.8
	2002	8.3	2.9	5.1	116.5	9.6	41.6	8.5	121.5	58.5	191.0
	2003	8.0	2.8	5.0	124.3	11.0	61.5	11.3	146.8	81.0	202.8
	2004	8.0	2.5	5.0	128.0	10.8	45.2	8.5	126.3	65.2	204.0
	2005	8.0	2.3	4.7	128.0	10.8	60.5	10.3	135.8	81.9	204.0
	2006	8.0	2.6	5.4	128.0	10.8	70.4	11.1	141.9	97.9	204.0
Twrch	1995	6.4	1.0	1.4	3.5	1.0	3.1	0.3	63.0	7.1	6.2
	1997	7.0	1.2	3.7	3.3	1.0	3.1	0.3	63.0	6.5	7.4
	1998	7.0	1.0	2.7	3.1	0.9	3.1	0.3	63.0	6.5	7.4
	1999	6.8	1.0	3.1	2.7	0.8	3.1	0.3	63.0	6.5	7.4
	2000	6.9	1.1	3.4	2.7	0.8	3.1	0.3	63.0	6.5	7.4
	2001	6.6	1.0	3.2	2.3	0.7	3.1	0.3	63.0	6.5	7.4
	2002	7.1	1.1	3.0	3.7	1.0	3.1	0.3	63.0	6.5	7.4
	2003	6.8	1.0	1.5	3.8	1.0	3.1	0.3	63.0	6.5	6.6
	2005	7.0	1.2	3.3	3.2	0.9	3.1	0.3	63.0	6.5	7.2
	2006	6.8	1.0	2.6	3.2	0.9	3.1	0.3	63.0	6.5	8.2
The Cut (above Thames)	1995	7.8	8.6	8.6	134.0	10.1	73.6	13.6	93.3	101.4	244.6
	1996	7.8	11.4	9.3	109.1	8.5	77.5	13.0	90.6	105.7	219.5
	1997	8.0	10.8	8.0	115.3	7.8	90.6	14.2	98.0	122.4	235.8
	1998	7.7	7.0	7.8	106.7	8.6	71.2	11.6	87.7	104.4	228.9
	1999	7.8	7.4	7.4	112.2	8.1	66.0	11.1	89.9	93.5	231.1
	2000	7.7	7.1	7.9	101.9	8.1	50.3	9.2	73.4	66.7	199.1
	2001	7.6	7.4	6.3	112.1	8.3	68.3	10.9	79.3	92.8	214.8
	2002	7.7	6.6	7.5	98.6	8.5	56.9	10.8	74.6	76.3	178.2
	2003	7.7	5.9	5.7	112.9	7.3	84.1	13.9	84.9	105.4	205.5
	2004	7.6	6.1	6.1	111.0	8.4	74.6	12.9	84.2	101.9	216.0
	2005	7.7	6.4	5.7	111.0	8.4	85.7	13.1	94.1	113.4	216.0
	2006	7.9	5.6	5.6	111.0	8.4	81.5	12.6	93.1	103.9	216.0
Carnon at Devoran	1995	6.1	424.1	1.3	106.6	9.3	36.9	6.1	268.5	71.6	26.8
	1996	6.3	288.6	1.5	100.0	10.1	36.8	6.1	238.9	73.0	27.9
	1997	6.3	274.4	1.0	71.9	9.6	30.4	4.8	185.6	57.3	12.4
	1998	6.5	241.4	1.0	84.8	10.1	31.9	4.7	218.0	63.4	15.7
	1999	6.5	260.5	1.1	79.5	8.4	32.6	4.6	198.6	62.8	15.2
	2000	6.3	264.9	1.0	72.6	8.1	31.4	4.5	188.3	63.8	12.8
	2001	6.4	296.2	1.0	90.2	9.3	38.2	5.1	201.4	78.5	15.0
	2002	6.3	229.8	0.9	79.5	8.8	38.9	5.0	187.5	84.0	17.8
	2003	6.2	233.5	0.9	70.6	9.0	36.9	5.0	170.2	78.3	18.3
	2004	6.4	193.5	0.9	64.4	8.6	36.2	4.7	153.2	76.2	19.5

River	Year	pH	Dis-solv-ed Cu (μg/l)	Mean annual concentration (mg/l)							
				DOC	Ca	Mg	Na	K	SO₄	Cl	Alka-linity
	2005	6.3	156.5	1.0	69.8	8.7	40.7	5.0	167.5	87.5	20.0
	2006	6.4	162.5	0.8	67.3	8.7	40.0	4.9	157.8	86.9	20.0
Carnon at Twelve-heads	1995	6.9	137.8	1.0	17.9	7.1	19.3	3.1	42.3	32.9	17.1
	1996	7.1	76.1	1.0	17.5	6.9	19.0	3.1	37.8	33.1	21.4
Lynher	1995	7.6	7.6	1.9	12.3	3.9	14.5	2.4	11.7	20.1	24.7
	1996	7.6	7.6	1.5	12.8	3.8	11.2	2.2	11.7	19.4	25.8
	1997	7.6	7.7	1.9	12.4	3.8	11.3	2.3	11.1	19.7	21.9
	1998	7.6	7.2	1.5	12.9	3.9	10.2	2.1	11.2	18.7	22.3
	1999	7.6	7.0	2.0	12.9	3.9	10.6	2.4	12.0	18.3	22.3
	2000	7.6	7.0	1.6	12.3	3.6	9.9	2.0	10.8	17.3	23.9
	2001	7.3	6.9	1.8	12.6	4.1	12.2	2.5	12.6	18.2	25.2
	2002	7.4	6.8	1.8	12.5	3.7	10.5	2.2	11.5	18.0	27.9
	2003	7.2	7.9	1.7	12.3	3.8	11.5	2.4	12.1	19.7	28.3
	2004	7.4	7.0	1.6	12.6	3.8	11.5	2.3	11.3	19.2	24.7
	2005	7.4	7.2	1.9	13.2	3.8	11.6	2.3	11.4	19.4	24.7
	2006	7.7	8.1	1.5	13.0	3.9	10.9	2.2	10.5	19.2	24.7
Hicks Stream	1995	7.5	136.7	2.0	17.7	5.6	19.9	4.7	30.5	30.5	20.9
	1996	7.2	142.2	1.8	16.1	5.1	19.3	4.5	30.0	29.1	19.9

Notes: Ca = calcium; K = potassium; Na = sodium, Cu = copper; DOC = dissolved organic carbon; SO₄ = sulphate; S = sulphide; Cl = chloride; Mg = magnesium.

ANNEX C Environmental concentration/PNEC ratios for zinc and copper for selected sites on an annual basis for each tier of assessment

Table C.1   EC/PNEC data for annual average zinc data

| River | Year | Concentration (µg/l Zn) | | | | Tier 1 | Tier 2 | Tier 3 |
		Zn (observed)	PNEC	PNEC+ BG	PNEC -BLM	EC/PNEC ratio	EC/PNEC +BG ratio	EC/PNEC- BLM ratio
Nene	1995	9.8	7.8	11.2	27.9	1.3	0.9	0.4
	1996	14.3	7.8	11.2	27.7	1.8	1.3	0.5
	1997	13.3	7.8	11.2	25.7	1.7	1.2	0.5
	1998	8.8	7.8	11.2	24.9	1.1	0.8	0.4
	1999	8.8	7.8	11.2	25.1	1.1	0.8	0.3
	2000	8.3	7.8	11.2	25.5	1.1	0.7	0.3
	2001	6.8	7.8	11.2	23.4	0.9	0.6	0.3
	2002	10.6	7.8	11.2	23.4	1.4	0.9	0.5
	2003	7.5	7.8	11.2	26.9	1.0	0.7	0.3
	2004	5.5	7.8	11.2	25.5	0.7	0.5	0.2
	2005	7.2	7.8	11.2	24.0	0.9	0.6	0.3
Blackwater	1995	5.7	7.8	11.2	25.0	0.7	0.5	0.2
	1996	6.0	7.8	11.2	23.3	0.8	0.5	0.3
	1997	7.0	7.8	11.2	22.8	0.9	0.6	0.3
	1998	5.8	7.8	11.2	24.7	0.7	0.5	0.2
	1999	5.5	7.8	11.2	25.3	0.7	0.5	0.2
	2000	4.3	7.8	11.2	28.8	0.5	0.4	0.1
	2001	11.4	7.8	11.2	23.4	1.5	1.0	0.5
	2002	7.3	7.8	11.2	22.3	0.9	0.6	0.3
	2003	6.3	7.8	11.2	26.2	0.8	0.6	0.2
	2004	6.0	7.8	11.2	22.8	0.8	0.5	0.3
	2005	5.6	7.8	11.2	21.9	0.7	0.5	0.3
Tame	1995	80.0	7.8	11.2	36.7	10.3	7.1	2.2
Anker	1995	11.7	7.8	11.2	36.8	1.5	1.0	0.3
Severn	1995	12.4	7.8	11.2	27.1	1.6	1.1	0.5
	1996	8.5	7.8	11.2	25.1	1.1	0.8	0.3
	1997	14.4	7.8	11.2	37.7	1.8	1.3	0.4
	1998	13.6	7.8	11.2	26.8	1.7	1.2	0.5
Trent	1995	45.6	7.8	11.2	42.8	5.8	4.1	1.1
	1996	60.7	7.8	11.2	43.0	7.8	5.4	1.4
	1997	56.7	7.8	11.2	37.6	7.3	5.1	1.5
	1998	43.4	7.8	11.2	41.4	5.6	3.9	1.0
	1999	33.0	7.8	11.2	35.9	4.2	2.9	0.9
Tavy	1995	9.9	7.8	11.2	23.7	1.3	0.9	0.4
	1996	9.9	7.8	11.2	23.3	1.3	0.9	0.4
	1997	13.6	7.8	11.2	23.7	1.7	1.2	0.6

River	Year	Concentration (µg/l Zn)				Tier 1	Tier 2	Tier 3
		Zn (observed)	PNEC	PNEC+ BG	PNEC -BLM	EC/PNEC ratio	EC/PNEC +BG ratio	EC/PNEC- BLM ratio
	1998	11.5	7.8	11.2	21.0	1.5	1.0	0.5
	1999	6.9	7.8	11.2	21.2	0.9	0.6	0.3
	2000	7.9	7.8	11.2	23.4	1.0	0.7	0.3
	2001	8.1	7.8	11.2	25.9	1.0	0.7	0.3
	2002	8.7	7.8	11.2	29.1	1.1	0.8	0.3
	2003	7.1	7.8	11.2	34.0	0.9	0.6	0.2
	2004	7.3	7.8	11.2	29.6	0.9	0.7	0.2
	2005	8.6	7.8	11.2	31.6	1.1	0.8	0.3
Lynher	1995	36.3	7.8	11.2	21.2	4.7	3.2	1.7
	1996	38.1	7.8	11.2	18.5	4.9	3.4	2.1
	1997	34.9	7.8	11.2	22.5	4.5	3.1	1.5
	1998	26.7	7.8	11.2	19.0	3.4	2.4	1.4
	1999	25.4	7.8	11.2	21.6	3.3	2.3	1.2
	2000	24.8	7.8	11.2	19.0	3.2	2.2	1.3
	2001	31.0	7.8	11.2	25.8	4.0	2.8	1.2
	2002	27.1	7.8	11.2	24.7	3.5	2.4	1.1
	2003	31.6	7.8	11.2	26.6	4.0	2.8	1.2
	2004	29.1	7.8	11.2	23.0	3.7	2.6	1.3
	2005	26.0	7.8	11.2	24.4	3.3	2.3	1.1
Ouse	2003	9.2	7.8	11.2	36.4	1.2	0.8	0.3
	2004	8.7	7.8	11.2	40.7	1.1	0.8	0.2
	2005	9.5	7.8	11.2	36.2	1.2	0.9	0.3
Tyne	2003	73.0	7.8	11.2	49.3	9.4	6.5	1.5
	2004	83.4	7.8	11.2	52.1	10.7	7.4	1.6
	2005	84.9	7.8	11.2	43.3	10.9	7.6	2.0
Axe	1995	6.5	7.8	11.2	23.8	0.8	0.6	0.3
	1996	10.5	7.8	11.2	21.8	1.3	0.9	0.5
	1997	6.9	7.8	11.2	24.6	0.9	0.6	0.3
	1998	7.4	7.8	11.2	25.6	1.0	0.7	0.3
	1999	2.8	7.8	11.2	30.8	0.4	0.3	0.1
	2000	2.5	7.8	11.2	34.2	0.3	0.2	0.1
	2001	3.3	7.8	11.2	31.3	0.4	0.3	0.1
	2002	2.9	7.8	11.2	35.8	0.4	0.3	0.1
	2003	4.8	7.8	11.2	29.7	0.6	0.4	0.2
	2004	5.0	7.8	11.2	28.2	0.6	0.4	0.2
	2005	5.0	7.8	11.2	29.0	0.6	0.4	0.2
Otter	1995	9.7	7.8	11.2	25.0	1.2	0.9	0.4
	1996	6.5	7.8	11.2	21.6	0.8	0.6	0.3
	1997	8.6	7.8	11.2	28.2	1.1	0.8	0.3
	1998	7.1	7.8	11.2	36.6	0.9	0.6	0.2
	1999	3.1	7.8	11.2	20.0	0.4	0.3	0.2
	2000	4.4	7.8	11.2	28.8	0.6	0.4	0.2
	2001	5.1	7.8	11.2	54.9	0.6	0.5	0.1
	2002	3.9	7.8	11.2	34.9	0.5	0.3	0.1
	2003	4.7	7.8	11.2	21.8	0.6	0.4	0.2
	2004	5.0	7.8	11.2	25.3	0.6	0.4	0.2
	2005	5.0	7.8	11.2	28.8	0.6	0.4	0.2
EC/PNEC ratio >1						**49**	**29**	**19**

Notes: Shaded cells highlight observed concentrations exceeding PNEC.

Table C.2 EC/PNEC data for annual average copper data

River	Year	Concentration (µg/l Cu)				Tier 1 EC/PNEC ratio	Tier 2 EC/PNEC +BG ratio	Tier 3 EC/PNEC-BLM ratio
		Cu (observed)	PNEC	PNEC +BG	PNEC -BLM			
Lynher	1995	7.6	8.2	9.8	10.6	0.9	0.8	0.9
	1996	7.6	8.2	9.8	8.2	0.9	0.8	1.1
	1997	7.7	8.2	9.8	11.7	0.9	0.8	0.9
	1998	7.2	8.2	9.8	8.7	0.9	0.7	1.0
	1999	7.0	8.2	9.8	11.8	0.9	0.7	0.7
	2000	7.0	8.2	9.8	9.9	0.9	0.7	0.9
	2001	6.9	8.2	9.8	10.2	0.8	0.7	0.8
	2002	6.8	8.2	9.8	9.5	0.8	0.7	0.8
	2003	7.9	8.2	9.8	9.0	1.0	0.8	1.0
	2004	7.0	8.2	9.8	9.4	0.9	0.7	0.8
	2005	7.2	8.2	9.8	10.5	0.9	0.7	0.9
	2006	8.1	8.2	9.8	8.3	1.0	0.8	1.0
Hicks Stream	1995	136.7	8.2	9.8	13.9	16.7	14.0	13.6
	1996	142.4	8.2	9.8	10.3	17.4	14.5	15.4
Carnon at Twelveheads	1995	137.8	8.2	9.8	4.2	16.8	14.1	69.1
	1996	76.1	8.2	9.8	5.0	9.3	7.8	22.3
Carnon at Devoran	1995	424.1	8.2	9.8	1.9	51.7	43.3	328.6
	1996	288.6	8.2	9.8	2.5	35.2	29.4	167.2
	1997	274.4	8.2	9.8	1.7	33.5	28.0	185.0
	1998	241.4	8.2	9.8	2.4	29.4	24.6	141.1
	1999	260.5	8.2	9.8	2.9	31.8	26.6	153.0
	2000	264.9	8.2	9.8	1.8	32.3	27.0	193.6
	2001	296.2	8.2	9.8	2.1	36.1	30.2	163.1
	2002	229.8	8.2	9.8	1.8	28.0	23.4	156.7
	2003	233.5	8.2	9.8	1.7	28.5	23.8	232.4
	2004	193.5	8.2	9.8	1.9	23.6	19.7	117.6
	2005	156.5	8.2	9.8	1.9	19.1	16.0	96.6
	2006	162.5	8.2	9.8	1.8	19.8	16.6	98.4
The Cut (above Thames)	1995	8.6	8.2	9.8	17.0	1.0	0.9	0.5
	1996	11.4	8.2	9.8	20.8	1.4	1.2	0.6
	1997	10.8	8.2	9.8	16.3	1.3	1.1	0.7
	1998	7.0	8.2	9.8	17.1	0.9	0.7	0.4
	1999	7.4	8.2	9.8	14.4	0.9	0.8	0.6
	2000	7.1	8.2	9.8	16.3	0.9	0.7	0.5
	2001	7.4	8.2	9.8	13.6	0.9	0.8	0.6
	2002	6.6	8.2	9.8	18.4	0.8	0.7	0.4
	2003	5.9	8.2	9.8	13.1	0.7	0.6	0.5
	2004	6.1	8.2	9.8	13.5	0.7	0.6	0.5
	2005	6.4	8.2	9.8	12.8	0.8	0.6	0.5
	2006	5.6	8.2	9.8	11.8	0.7	0.6	0.5
Nene	1995	4.6	8.2	9.8	47.1	0.6	0.5	0.3
	1996	5.0	8.2	9.8	16.9	0.6	0.5	0.4
	1997	4.9	8.2	9.8	10.6	0.6	0.5	0.5
	1998	3.0	8.2	9.8	8.0	0.4	0.3	0.4

River	Year	Concentration (µg/l Cu)				Tier 1 EC/PNEC ratio	Tier 2 EC/PNEC +BG ratio	Tier 3 EC/PNEC-BLM ratio
		Cu (observed)	PNEC	PNEC +BG	PNEC -BLM			
	1999	3.6	8.2	9.8	8.5	0.4	0.4	0.5
	2000	3.3	8.2	9.8	9.7	0.4	0.3	0.4
	2001	3.3	8.2	9.8	6.6	0.4	0.3	0.5
	2002	2.9	8.2	9.8	7.7	0.4	0.3	0.4
	2003	2.8	8.2	9.8	9.7	0.3	0.3	0.4
	2004	2.5	8.2	9.8	7.6	0.3	0.3	0.3
	2005	2.3	8.2	9.8	7.7	0.3	0.2	0.3
	2006	2.6	8.2	9.8	9.8	0.3	0.3	0.3
Twrch	1995	2.0	8.2	9.8	2.4	0.2	0.2	0.8
	1997	1.2	8.2	9.8	19.2	0.1	0.1	0.1
	1998	1.0	8.2	9.8	15.7	0.1	0.1	0.1
	1999	1.0	8.2	9.8	14.2	0.1	0.1	0.1
	2000	1.1	8.2	9.8	19.3	0.1	0.1	0.1
	2001	1.0	8.2	9.8	10.7	0.1	0.1	0.1
	2002	1.1	8.2	9.8	18.8	0.1	0.1	0.1
	2003	1.0	8.2	9.8	5.9	0.1	0.1	0.2
	2005	1.2	8.2	9.8	19.0	0.1	0.1	0.1
	2006	1.0	8.2	9.8	10.4	0.1	0.1	0.1
EC/PNEC ratio >1						**21**	**18**	**20**

Notes: Shaded cells highlight observed concentrations exceeding PNEC.

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