



# Desk top study to evaluate options outside BLM thresholds (low pH and low calcium issues)

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

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# Executive summary

The assessment of compliance of surface waters with environmental quality standards (EQSs) for metals has to deal with a number of issues that do not apply to other substances. For example, it is known that a proportion of a given metal dissolved in water is of limited bioavailability. This non-available fraction does not exert any adverse environmental effects. In order to account for this, bioavailability models known as biotic ligand models (BLM) have been developed. Whilst these can be applied to the majority of water types that might be encountered, there are some water types in the UK for which they have not been calibrated. To this end, the Environment Agency has commissioned a report to address BLM boundary condition issues that affect compliance assessment for copper and zinc in waters of low pH and low calcium concentration.

The Environment Agency has created a simplified version of the BLM to allow reporting of bioavailable metal as part of its routine monitoring programme within a tiered assessment approach to metal compliance. The simplified versions are known as bioavailability assessment tools. The input parameters required to determine bioavailable copper and zinc levels using these tools are dissolved organic carbon (DOC), pH and calcium. The BLM allow for unbounded inputs for DOC but only provide acceptable outputs in the range pH 6 to 9 for zinc and pH 5.5 to 8.5 for copper. Below the lower pH range, the default output is 100 per cent bioavailability for the metal. In terms of compliance reporting, this raises the possibility of step changes in water body compliance in response to a small change in pH from inside to outside the pH boundary conditions. In the case of zinc, outputs relating to calcium (Ca) concentrations less than 7 mg/l also default to a bioavailability of 100 per cent and to the lower predicted no effect concentration (PNEC) applicable to soft waters. This situation raises unacceptable difficulties for compliance reporting without necessarily reflecting the true nature of the bioavailability of the metal. This project seeks to provide the Environment Agency with a method to assess metal bioavailability in low pH waters.

Extrapolation of the estimated bioavailability of copper and zinc for waters of pH outside the current BLM boundary conditions can be made on the basis of a titration of the notional complexation capacity against increasing hydrogen ion concentration. The method proposed here incorporates this principle into a simple calculation tool. Testing of the approach on a small number of real waters provides evidence of its practicality and lack of serious bias. It is recommended that the Environment Agency adopt the proposed approach until further information makes it possible to extend the operation of the BLM to lower pH values or to refine the extrapolation described here.

Extension of the operation of the zinc BLM to calcium concentrations outside its operating range is more problematic. The simple expedient of setting the calcium level at the lowest that will result in a BLM output runs some risk of underestimating bioavailability. This has to be judged against the more obvious risk of overestimating bioavailability by using the BLM in its present form. It is recommended that where calcium concentrations are lower the lower BLM limit, this value might be used as a substitute, but that the results should be regarded as tentative within the tiered compliance assessment. It might be that for zinc a more careful appraisal of background concentrations, rather than issues of bioavailability, should be prioritised in the tiered assessment.

The method recommended here is proposed on the basis of the need for a practicable approach to the problems of BLM boundary conditions. A more sound technical justification for these proposals will require further investigation. Given the effort already expended in developing the various BLM, the scope and costs of such investigations are unlikely to be trivial. It is therefore recommended that the method presented in this report should be adopted in the short to medium term to help implement quality standards for metals.

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# 1 Introduction

The Water Framework Directive (WFD) allows for the bioavailability of metals in water to be taken into account when compliance is assessed against environmental quality standards (EQSs). Implementation of the proposed WFD EQS for copper (Cu) and zinc (Zn) without adequate consideration of bioavailability will lead to incorrect assessment of the risk to ecosystems from these metals.

The chosen approach to address bioavailability issues has been to use biotic ligand models (BLMs) that have been developed over the past 25 years. These BLMs are based on an assessment of the chemical forms and their respective bioavailabilities and toxicities to different types of aquatic life. The technical justification for using a BLM is founded primarily on the evidence provided by the extensive series of ecotoxicity tests carried out over recent years. BLMs that cover bioavailability and chronic toxicity have been developed for copper and zinc (and a number of other metals). However, these were developed primarily for use within a risk assessment framework and as such are relatively complicated compared with what might be required for routine compliance assessment. Given these limitations, the Environment Agency together with partners from the metals industry has addressed practical issues in a previous work package (Peters *et al.* 2009a and b). Key outputs from this earlier work are 'user friendly' bioavailability assessment tools that are more compatible with regulatory monitoring and assessment regimes.

These tools operate through the use of more restricted input parameters compared with the full BLM. Inputs are limited to the variables that exert principal control over bioavailability - pH and concentrations of dissolved organic carbon (DOC) and calcium (Ca). Most models, including BLMs, are subject to what are known as "boundary conditions". These are limits to the range of input values that can be accepted. In the case of BLMs boundary conditions can arise for two reasons:

- BLM were intended to reflect physicochemical characteristics of waters corresponding to those prevailing over most of Europe rather than aiming to cover all possible water types. Hence data for waters of (say) pH outside the accepted usual range were not considered.
- Ecotoxicological tests upon which the BLM have been justified cannot be conducted under more extreme conditions that nevertheless might be found in some types of waters. For instance, the laboratory test organisms used in ecotoxicological testing might not tolerate a pH value of 5.5, despite this being the pH of a variety of real waters in, for example, moorland habitats.

The fact that BLMs are not calibrated for waters of low pH or low calcium concentration such as those found in the west of England, in Wales and in Scotland means that an alternative solution to assessing metal bioavailability is needed for these water types. This short project was initiated to find a pragmatic method of extending bioavailability models to such waters. The intention was that the project should focus on an approach that took account of the technical issues, but was simple and practicable enough to be used on a routine basis in compliance assessment. This method might represent an interim solution that allows the implementation of BLM to take place before more detailed and technically verifiable approaches can be developed.

## 2. Objectives and methodology

This project's overall objective was to review the Cu and Zn bioavailability assessment tools and examine the options and implications of allowing these tools to operate outside the stated boundary conditions.

Specifically, the work aimed to:

- Explore different options for allowing current bioavailability models to operate outside the model boundaries and associated uncertainties and compatibility with WFD protection goals.
- Examine the operation of the bioavailability assessment tools being embedded into the Environment Agency National Laboratory Service to allow routine reporting.
- Outline proposals and make recommendations on how they might be incorporated into and affect the ease of use of these bioavailability assessment tools.
- Examine the applicability of any proposals by conducting limited trials on real waters.

Outputs from previous and current projects (supplied by the Environment Agency) relevant to the above were also considered.



# 3. Review of the bioavailability assessment tools

The WFD requires the derivation of EQS for specific pollutants set at a national scale. In the case of metals, including copper and zinc, EQS levels derived from ecotoxicological testing are of the same order as many of the concentrations found in surface waters. This is especially true where lack of robust test data prompts the use of assessment factors which drive down the proposed EQS to concentrations close to ambient levels. This raises the issue of potentially widespread non-compliance with EQS where, in the great majority of cases, no adverse environmental effects are observed. Two strategies have been considered to address this regulatory anomaly. The first is to acknowledge that for metals as naturally occurring substances, there are background concentrations that pose minimal ecological risk; the second is to recognise that a proportion of metal present in the environment is in forms that are not bioavailable and hence should not be considered as part of any assessment of compliance. BLM form part of this second strategy in which issues of bioavailability are taken into account.

The WFD makes explicit provision for the assessment of the bioavailability of metals such as copper and zinc. BLMs provide a site-specific prediction of bioavailable metal based on a number of input parameters associated with ambient water quality. The development of BLMs has been under way for the last 25 years (Pagenkopf 1983, Paquin *et al.* 2002). The current models have attained a high level of sophistication that attempts to relate conceptual models of chemical speciation and measurements of different chemical species to the results of aquatic toxicity tests both for individual metals (Cd, Cu, Pb, and Zn) and mixtures of metals.

The Environment Agency recently established a simplified version of the BLMs (Peters *et al.* 2009a and 2009b) to allow reporting of bioavailable metal as part of its routine monitoring programme, within a tiered assessment approach to metal compliance. Within these simplified versions the input parameters required to estimate bioavailable copper and zinc levels are restricted to pH and concentrations of dissolved organic carbon (DOC) and calcium. The BLMs allow for unbounded inputs for DOC but only provide acceptable outputs in the range pH 6 to 9 for zinc and pH 5.5 to 8.5 for copper. Below the lower pH range the default output is 100 per cent bioavailability for the metal. In terms of compliance reporting, these cut-off limits raise the possibility of step changes in water body compliance in response to a small change in pH from inside to outside the pH boundary conditions. In the case of zinc, calcium concentrations below 7 mg/l also lead the model to default to a bioavailability of 100 per cent and the lower predicted no effect concentration (PNEC) applicable to soft waters (see Chapter 4). This situation raises unacceptable difficulties for compliance reporting and does not reflect the true nature of the bioavailability of the metal.

## 3.1 Specific boundary condition issues

The bioavailability assessment tool (version V was used here) calculates a number of related and relatively interchangeable measures of bioavailability including predicted no effect concentration (PNEC) in the water concerned and the bioavailable fraction BioF (the fraction between zero and one of the total deemed to be bioavailable). In this report we will concentrate on the BioF value as the key parameter of interest. The notes below summarise the observations relating to boundary values that were made in

the course of preparing for this work. As noted above these observations relate to using Version V of the bioavailability assessment tool.

**Copper** lower pH boundary condition of pH 5; below this value no results for PNEC or BioF are calculated for copper.

**Copper** some results calculated but red “sensitive” conditions indicated for pH in the range 5.0 - 6.0. Where sensitive issues are identified, the BioF is set to one.

[This reporting of sensitive conditions seems to be erratically related to calcium levels and does not appear to be consistent across the range of possible DOC values. In addition, if calcium concentration is varied from 60 mg/l to zero, sensitive conditions are indicated for all DOC values below 8 mg/l and above 10 mg/l. For DOC of between 9 and 10 mg/l, PNEC and BioF values are calculated for low calcium concentration. These issues are ignored for the purposes of this report.]

**Zinc** lower pH boundary condition of pH 6.0; below this value BioF is set to one.

**Zinc** lower boundary condition for calcium concentration is 7 mg/l; below this, the BioF is set to one and the default PNEC reverts to the soft water PNEC in the zinc risk assessment report of 3.1 µg/l. Where this PNEC is applied, bioavailability is not taken into account (though background value might be). This effectively makes consideration of DOC concentration irrelevant.

These boundary conditions lead to limitations for the classification and reporting of sites that are of low pH, but not covered by the UK standards for acid conditions (conditions of low acid neutralising capacity) in surface waters, particularly for rivers in Scotland. As noted earlier, the bioavailability assessment tool currently ‘caps’ the calculation for conditions outside the validation boundaries by assuming 100 per cent bioavailability. This means that a change in the reported pH value of one could (by transferring the water to a point outside the boundary condition) lead to a large change in estimated bioavailability from somewhat lower than 100 per cent (BioF <1) to 100 per cent (BioF = 1). For example, a water of pH 6.0 and DOC and calcium concentrations of 10 mg/l would have a zinc BioF of 0.5 (50 per cent bioavailable). If the same water were assessed on another occasion and the pH was reported as 5.9, the bioavailability would be assigned as 100 per cent. Such a small change in reported pH might arise because of a real small change or as a result of small measurement error.

This kind of step change is highly undesirable from the point of view of regulation and compliance assessment since it leads to unwarranted instability in the classification of compliance. A water could remain essentially of the same quality and be classed as oscillating in and out of compliance, leading to predictably confusing consequences with respect to the perceived need for remedial measures. This administrative drawback would be reason enough to address boundary conditions, but added to it is the fact that such changes in perceived compliance do not reflect true environmental risk posed by the metal under consideration. Hence there is a need to establish a strategy to deal with boundary conditions so that BLM can be used for waters of low pH and low calcium concentration.

## 4. Proposals for dealing with boundary conditions

Unless some alternative approaches are devised, copper and zinc concentrations of waters outside the relevant pH BLM boundary values could be categorised as 100 per cent bioavailable, whereas waters of slightly higher pH would be assessed as containing a proportion of metal that is not bioavailable. For the lower pH waters there is therefore the potential of overestimating the risk posed by metals.

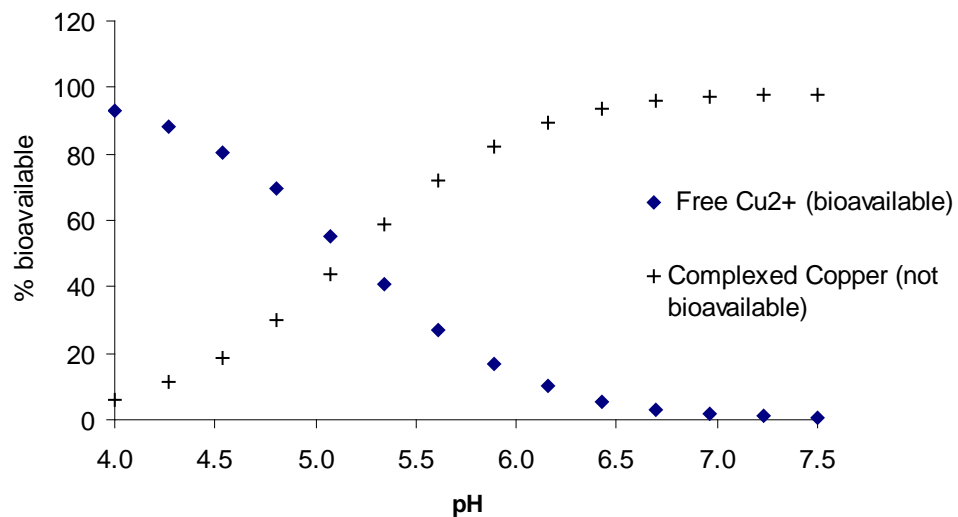
Knowledge of the behaviour of metals in water makes it clear that as the water pH decreases, the point will be reached when all dissolved metal is in a form that must be considered bioavailable. The principal cause of non-bioavailability is complexation by naturally occurring dissolved organic matter. As pH reduces hydrogen ion concentration increases, where the ions displace metal at complexation sites on the dissolved organic matter, leaving the metal essentially as a free (bioavailable) ion in solution. Recognition of this fact makes it possible to establish the limits within which a solution of boundary issue needs to be sought. The following strategy is proposed.

- To decide on a lower pH value for which metal should be considered to be 100 per cent bioavailable. On the basis of experience in the determination of metal complexation in different waters (see Dixon and Gardner 1998, Gardner *et al.* 2000) it is proposed that a pH of 4.0 should be adopted. This value is probably relatively conservative since many waters of pH around this level also contain enough dissolved organic matter to maintain a low (or in some cases not so low) level of complexation. Nevertheless some waters are not so high in organic matter, so pH 4.0 is judged to be as low a value for which it can be confidently claimed that complexation might be present in the majority of waters. Furthermore, the value of pH 4.0 is proposed on the basis that modelling of percentage bioavailability using the well established chemical speciation model, MINEQL, indicates that for plausible values of DOC and of the stability of metal-DOC complexation, the capacity of dissolved organic matter (DOM) to associate with metal appears to run out at pH 4.0 (Figure 4-1). Setting this lower boundary of complexation establishes a range of pH values between an upper level represented by the relevant BLM boundary condition and this lower limit of pH 4.0. This is the range over which it is necessary to devise a transition of percentage bioavailability. This transition will need to be from the percentage bioavailability, for any given water composition, indicated by the BLM at some point in its pH range of operation and 100 per cent bioavailability at pH 4.0, see Figure 4-2.
- To propose a method for a graduated transition of bioavailability across the defined pH range. Two such methods are obvious suggestions:
  - a linear model – to draw a straight line between the percentage bioavailability values represented in Figure 4-2 for pH 5.5 or 6.0 to 100 per cent at pH 4.0;
  - a titration model – to mimic the speciation model with a reverse S-curved, titration-like transition.

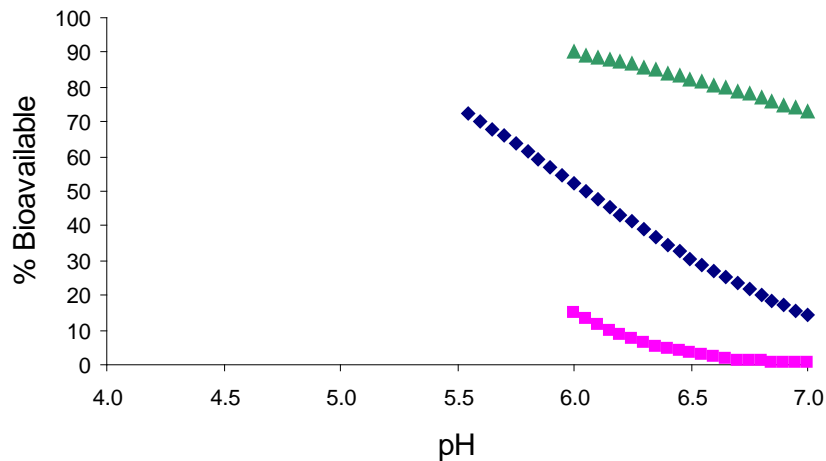
The linear model has the advantage of simplicity, with respect to both concept and calculation, but the disadvantage that it does not follow the known form by which complexation and bioavailability changes with pH. The respective advantages and disadvantages of the titration model are the reverse of those of the linear model.

Given that the titration model is a truer representation of the form (if not necessarily the actual unknown values) of the behaviour of metal bioavailability with decreasing pH it was decided to pursue this approach.

At this point it is worth stating the potential limitations of the approach. Firstly, a few waters (those with very low concentrations of DOC) might reach the point of 100 per cent metal bioavailability at a pH greater than 4.0. However, because of their low DOC levels, these waters will be close to 100 per cent metal bioavailability at pH 5 - 6 so the transition to pH 4.0 will not involve a great change (or a large error) in estimated bioavailability. Secondly, the true transition might not follow exactly the modelled one. This is likely for waters where the type of DOC varies – different types of DOC will have different responses to reduced pH. This is one of the compromises of the approach but it is difficult to see how it can be addressed without a great deal more knowledge about the nature of DOC than we have at present. All that might be said is that there will be a transition from lower to higher bioavailability and the proposed approach takes into account what is currently understood about the nature of this change.



**Figure 4-1 Transition of metal complexation over the pH range 4.0 to 7.5 modelled using a chemical speciation model – in this case for copper**



**Figure 4-2 The gap between estimated bioavailability at BLM boundary conditions for various waters and bioavailability at pH 4 (the different coloured lines indicate different waters)**

Figure 4.3 shows the curve of free copper ion fitted with a Weibull curve (the Weibull “reliability function”<sup>1</sup> or reversed Weibull cumulative distribution function - cdf). The Weibull curve was chosen here because:

- It is relatively simple to calculate compared with other options such as power curves;
- It fits the reverse S-shaped form that is required to mimic the titration curve without having to resort to large changes in the nature of the function. This feature of coping with all the required curves within the same mathematical framework gives the approach a degree of unity that a more *ad hoc* approach would lack.
- It is not subject to unpredictable behaviour outside the range of values over which it was developed (unlike power curves).

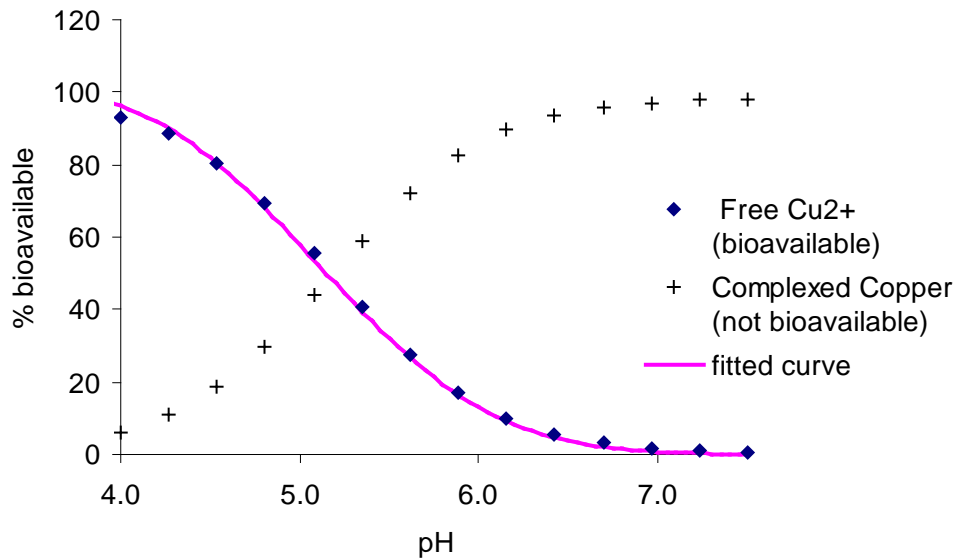
The Weibull reliability function is of the form:

$$f(x) = e^{-(x/\alpha)^\beta}$$

The function is defined by two principal parameters – the shape parameter  $\beta$  (which as the name implies determines the overall shape) and the scale parameter  $\alpha$  which determines the horizontal compression of the shape. The shape parameter used to fit the titration curve of Figure 4-3 was 2.7.

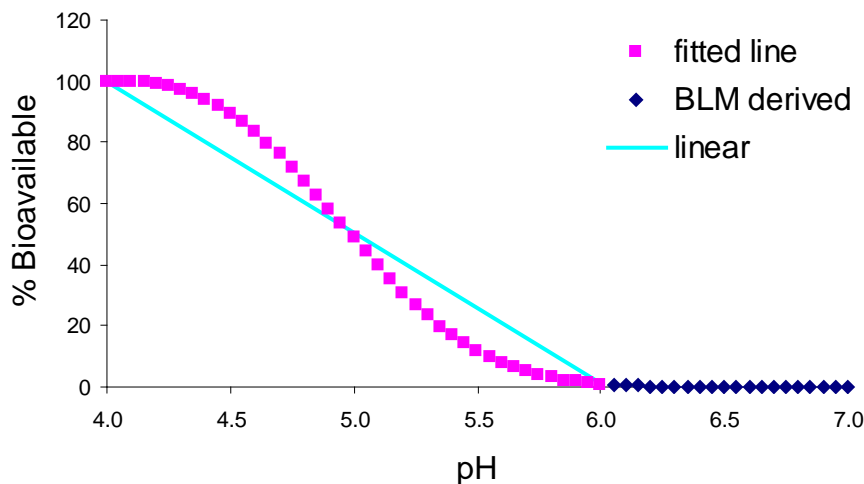
It is then possible to vary scale parameter in order that the curve at pH 6 corresponds to any chosen level of bioavailability corresponding to a water type of interest. In this way the curve generated forms a smooth link between percentage bioavailability at the boundary condition and 100 per cent bioavailability at pH 4.0.

<sup>1</sup> [http://www.weibull.com/AccelTestWeb/weibull\\_distribution.htm](http://www.weibull.com/AccelTestWeb/weibull_distribution.htm)

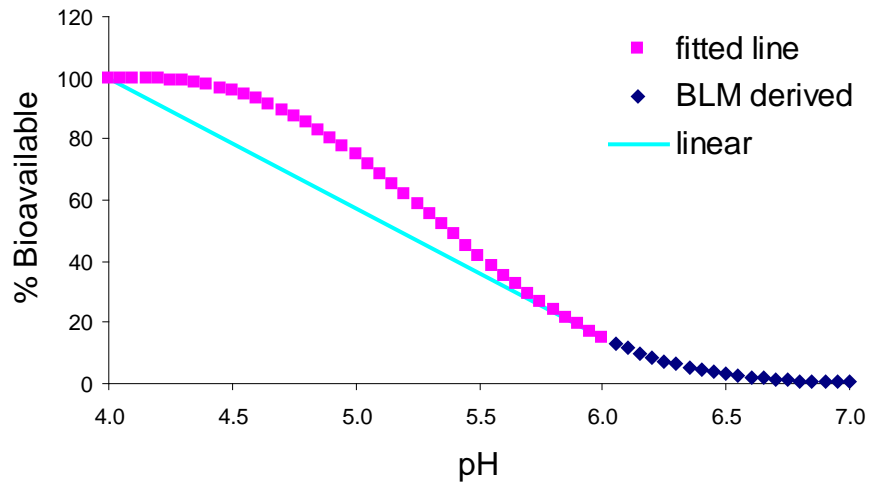


**Figure 4-3 Speciation titration curve (blue diamonds) and the fitted Weibull function**

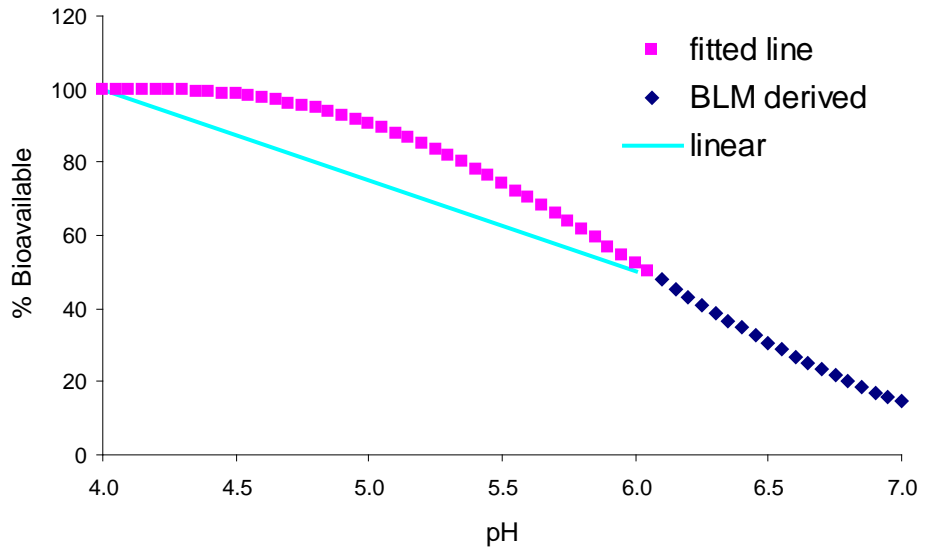
Figure 4-4 (a to d) illustrates this for waters whose bioavailability at pH 6 varies from one to 90 per cent. Also shown in Figure 4-4 is a comparison between the titration-type transition with a linear model where use of a linear model leads mainly to an underestimation of bioavailability. This can be by as much as 20 per cent for waters of moderate complexing capacity at pH 4.8 (Figure 4.4(c)). Where complexing capacity is high, negative or positive bias in estimation of bioavailability is possible - at pH 4.7 there is a negative bias of up to around 15 per cent, at pH 5.5 there is a positive bias of up to approximately 15 per cent (Figure 4,4(a)).



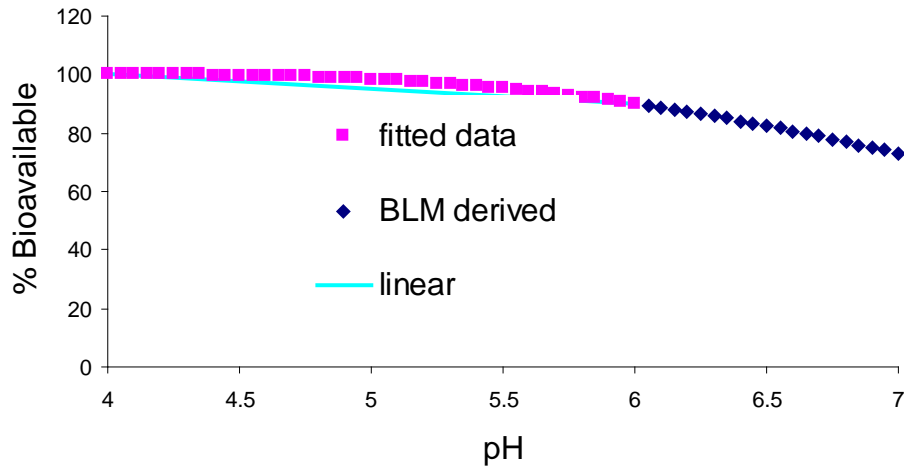
a) Percentage bioavailability at pH 6 = one percent



b) Percentage bioavailability at pH 6 = 15 percent



c) Percentage bioavailability at pH 6 = 50 percent



d) Percentage bioavailability at pH 6 = 90 percent

**Figure 4-4 (a-d) Transitions of different percentage bioavailability values at pH to 100 percent at pH 4**

## 4.1 Proposed method where boundary issues relate to pH

The following procedure is recommended to estimate bioavailability at pH values outside the BLM boundary conditions (note that the BLM notation of BioF equal to one corresponds to a percentage bioavailability of 100):

- If the measured sample pH is below four, 100 per cent bioavailability should be assumed, that is, in BLM terms a BioF of one.
- For reported pH between 4.0 and 6.0, if BLM fails to report a BioF value other than one owing to pH constraints or “sensitive conditions”, the water pH should be set to pH 6.0 and the BLM should be run again. This provides a BLM-derived BioF.
- Use the “BLM boundary pH calculation tool” provided to convert the Biof at pH 6.0 into a BioF at the measured pH value.

The calculation tool is an algorithm created to output the BioF value at any chosen pH, given an input of the BioF value at pH 6 and the measured pH (below 6). It works by using the Weibull distribution as described above, using an estimated scale coefficient based on the BioF value at pH 6.0. The option for undertaking the calculations performed by the tool should be built into the Environment Agency’s regime for reporting metal data, possibly as part of the bioavailability assessment tool.

## 4.2 Proposed method for zinc where issues arise from low calcium

In the case of zinc in waters of calcium concentration below 7 mg/l, the BLM increases the perceived risk in two ways at the same time, firstly by failing to account for reduced bioavailability because of complexation by DOC (by reporting a BioF of one) and



secondly by applying the lower PNEC value of 3.1 µg/l. This is likely to lead to overestimation of the risks posed by zinc in soft waters.

On the basis of existing data, the obvious suggestion would be to avoid this issue by inputting a value of 7 mg/l to the BLM whenever the measured calcium concentration is below this level. The BLM could then provide an estimate of bioavailability less than one.

Versions of the desktop BLM more recent than that available for this study are capable of operating down to calcium concentrations of 5 mg/l. Given that that work carried out concurrently with this study (see Chapter 6, below) has indicated that there may be no need for a separate, lower soft water PNEC, this might make it possible for a lower default value of 5 mg/l to be used.

Section 5 below tests the operation of the above proposals for some real waters.

# 5. Trials using real waters

## 5.1 Extrapolation of bioavailability to lower values of pH

Data for some examples of real waters of likely interest were obtained from the UK acid waters monitoring programme<sup>2</sup>. This is a long-term study conducted on behalf of the Department for Environment, Food and Rural Affairs (Defra) of waters that might be vulnerable to and therefore indicative of long-term changes in the pressures leading to surface water acidification. Data for this comparison (Appendix A) for seven streams (two in Wales, three in England and one in each of Northern Ireland and Scotland) were obtained from site summaries relating to the year 2006-2007. The relevant inputs of annual average values were used in the BLM. For all samples, the BLM was able to calculate BioF values for copper at the measured pH value – corresponding to bioavailability of between six and 60 per cent, but owing to the low concentrations of calcium no outputs were available for zinc.

For both metals the pH values were then set at six (as described in the protocol above) and the model was run again. For zinc only, the calcium level was set at 10 mg/l to provide the starting values for the interpolation of bioavailability for pH values between six and four. A value of 10 mg/l was used to avoid the quirks of functionality mentioned in Section 3.1 above. The model was run again for both metals for input pH of 6.2, 6.4 and 6.6 to provide an indication of bioavailability outputs for higher pH values – see Table 5-1.

**Table 5-1 BLM derived percentage bioavailability for zinc at different pH values (calcium concentration set at 10 mg/l)**

pH	Zinc % bioavailability			
	6.0	6.2	6.4	6.6
<b>Beaghs Burn</b>	36	34	31	29
<b>Old lodge stream</b>	56	53	50	47
<b>Afon Gwy</b>	88	87	86	85
<b>Afon Hafren</b>	86	85	84	82
<b>R. Etherow</b>	40	38	35	32
<b>Dargall Lane</b>	96	96	96	97
<b>Narrator Brook</b>	91	91	90	90

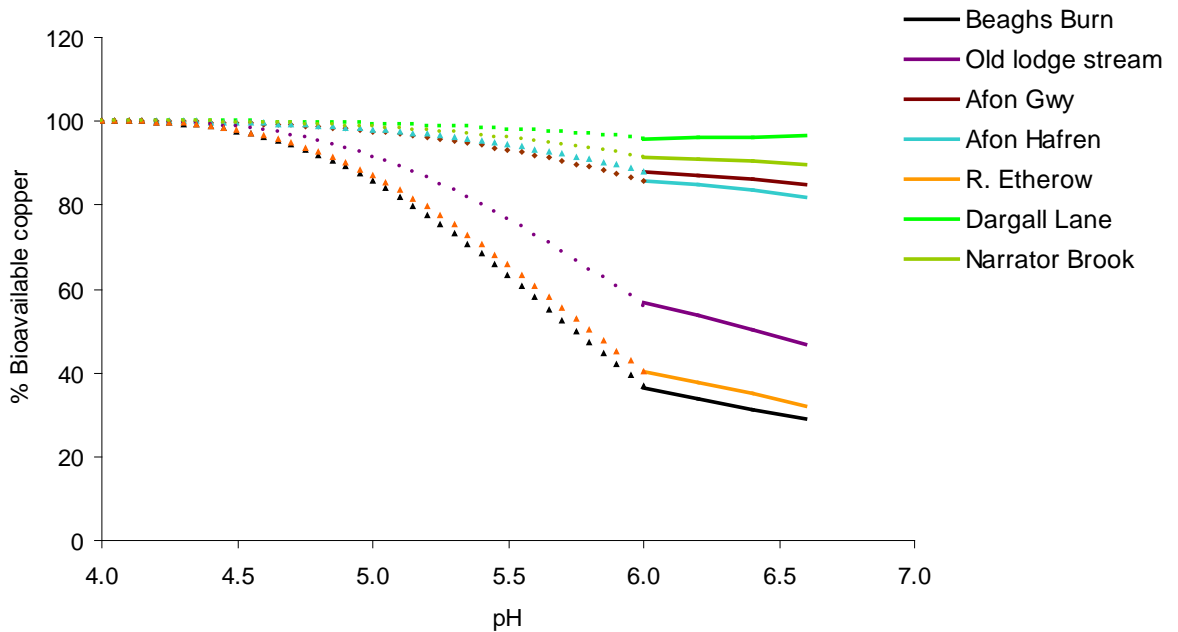
The same procedure was adopted for copper except that the pH range was extended down until the natural pH was reached, see Table 5-2.

<sup>2</sup> <http://www.ukawmn.ucl.ac.uk/map.htm>

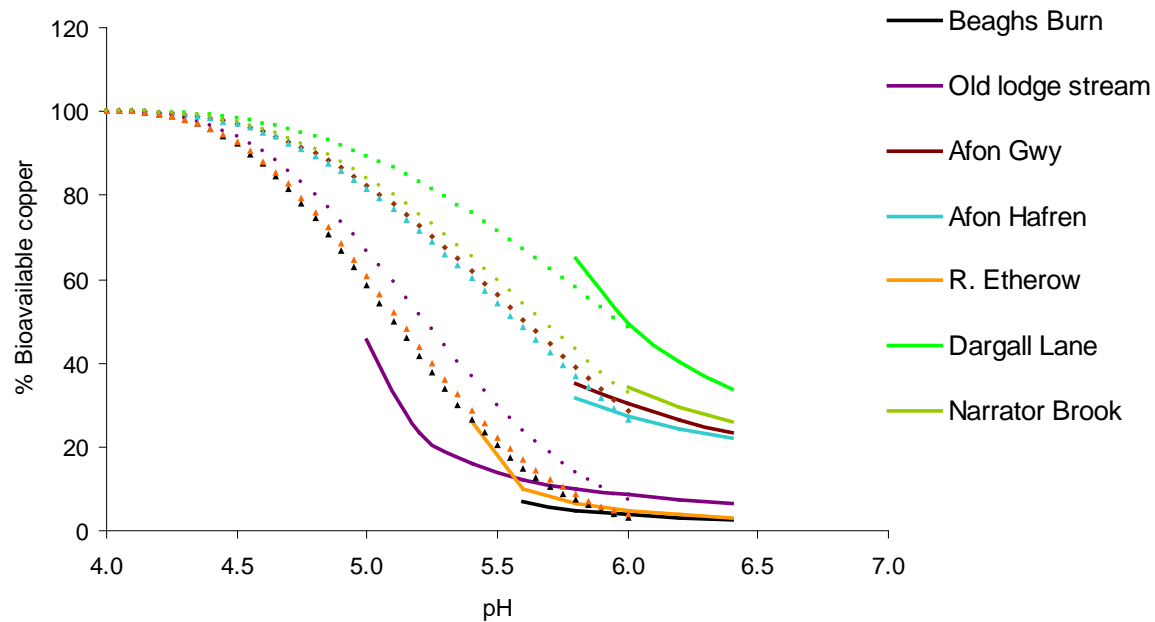
**Table 5-2 BLM derived percentage bioavailability values for copper (measured calcium levels)**

pH	Copper % bioavailability							
	5.0	5.2	5.4	5.6	5.8	6.0	6.2	6.4
<b>Beaghs Burn</b>				7	5	4	3	3
<b>Old lodge stream</b>	46	23	16	12	10	8	7	7
<b>Afon Gwy</b>					35	30	26	24
<b>Afon Hafren</b>					32	27	24	22
<b>R. Etherow</b>			26	10	6	5	4	3
<b>Dargall Lane</b>					65	50	40	34
<b>Narrator Brook</b>						34	30	26

Figure 5.1 shows the extrapolation of percentage bioavailability for the different metal bioavailability values at pH 6. The illustration of extrapolation for zinc is without special interest. All the percentage bioavailability values at pH 6 were relatively high, thus minimising the difficulty of extrapolating upwards to 100 percent at pH 4. For copper, the illustration is relatively encouraging insofar as the extrapolations follow the trends established by the BLM. For the latter metal, the BLM predictions were not extended to pH values below the natural pH value.



**Figure 5-1 a) Extrapolation of percentage bioavailability for zinc**

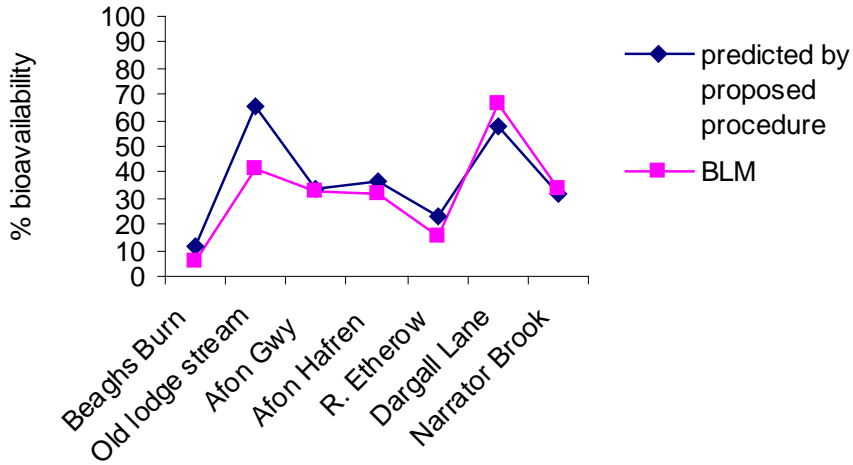


**Figure 5-1 b) Extrapolation of percentage bioavailability for copper – including BLM predictions down to natural pH values**

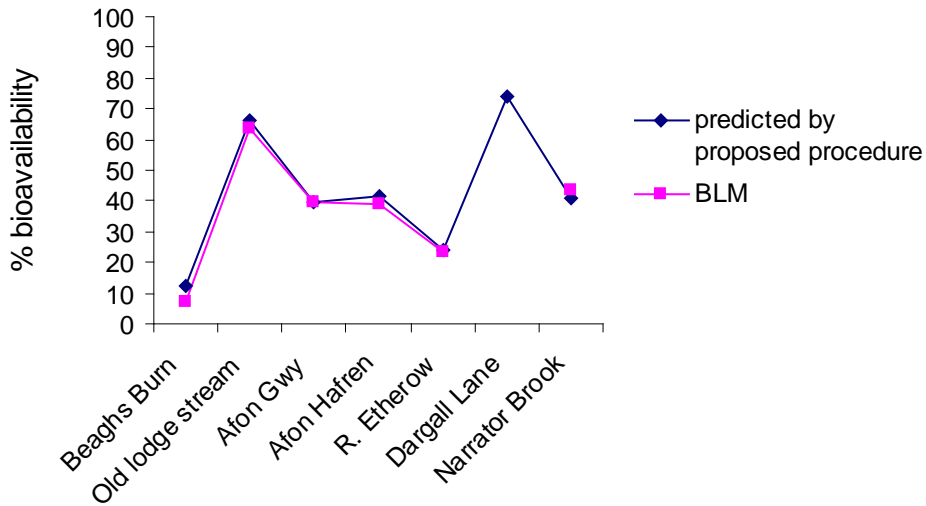
The calculator tool was then applied to compare the percentage bioavailability that could be predicted by the BLM and by the extrapolation tool. This was for copper only. Figure 5-2 illustrates the comparison between the BLM outputs expressed and the predictions by extrapolation, for these specific waters. The comparison is quite a good one, with the bioavailability for only one sample (Old Lodge) being different by a substantial amount by extrapolation – and this was an overprediction and hence precautionary.

If the calcium concentration of all samples is set at the same value – the value used here was 10 mg/l as required to process zinc data – agreement between predicted percentage bioavailability produced by the pH extrapolation and that predicted by the BLM is much closer – see Figure 5-3.

It is unclear exactly why this might be the case, because two factors are operating at the same time. Firstly, resetting the calcium levels changes the percentage bioavailability estimates by the BLM at pH 6.0, hence changing the starting point of the pH-related extrapolation. These changes are small for most samples except one (Dargall Lane). At the same time the change in calcium concentration alters the output of the BLM at the natural pH. This makes it difficult to identify the factors that affect the comparison. However, it appears that if the complicating effect of interaction between calcium and pH is removed, the description of the change in bioavailability with pH is handled similarly by the BLM and by the proposed extrapolation method.



**Figure 5-2 Comparison of percentage copper bioavailability outputs of BLM and those predicted by the proposed method on the basis of bioavailability at pH 6**



**Figure 5-3 Comparison of percentage bioavailability of copper predicted by the BLM and that produced by the extrapolation from pH 6 using a default calcium concentration of 10 mg/l**

## 5.2 Calcium issues for zinc

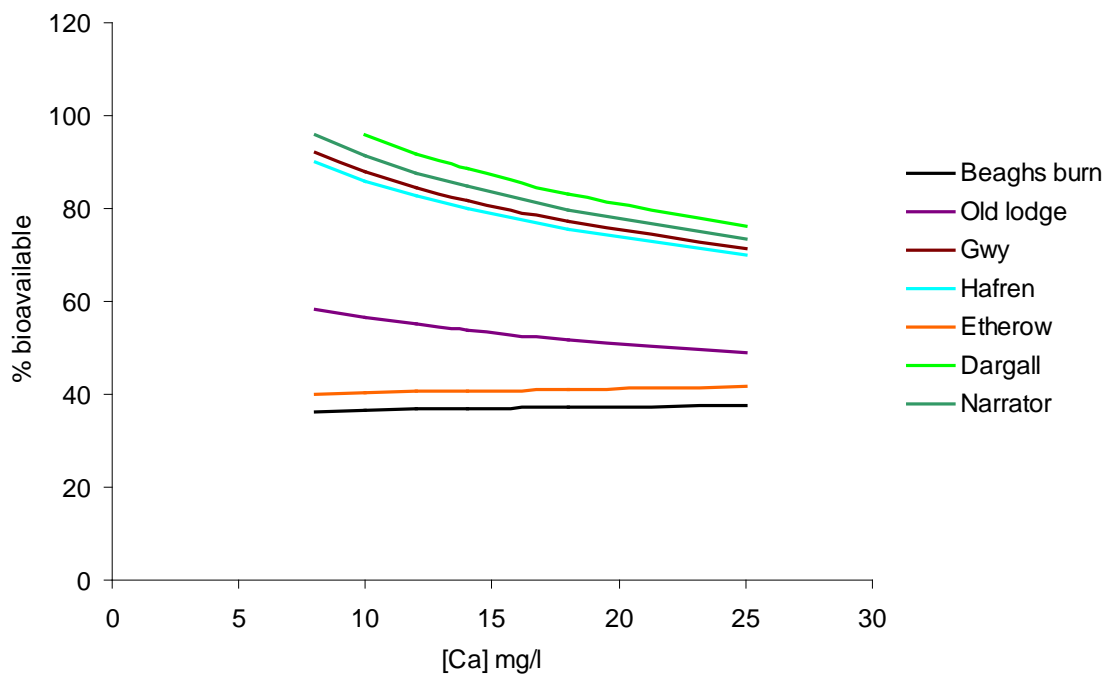
Consideration of the BLM reference data set shows that the main influence of calcium on bioavailability at low calcium concentrations is weak. Figure 5.4 shows BLM outputs for the test waters considered above for a range of calcium concentrations from 25 mg/l down to the point at which the BLM stops giving an output.

Three tentative conclusions may be drawn. For waters of high DOC (Beaghs Burn and River Etherow), there is a trend for bioavailability to be relatively low and to slightly decrease as calcium concentration falls. In this case, use of a default calcium concentration of 10 mg/l would seem to be overprotective.

For waters of low DOC, the tendency is for bioavailability to increase with decreasing calcium concentration – though this increase is generally from a starting point of high (above 80 per cent) bioavailability. Here, use of a default calcium concentration higher than the truth might underestimate bioavailability, but given the high initial value this would not be by more than 10 to 15 percent.

Finally, the example of the Old Lodge Stream (moderate DOC level and low pH) shows intermediate behaviour – bioavailability is relatively low but shows a rising trend. In this last case the imposition of a calcium concentration of, say, 10 mg/l to allow the BLM to provide an output runs the risk of greater underestimation of bioavailability – because of the low starting point there is more scope for such an underestimation.

Unlike the case of decreasing pH, there is no reason to assume that as calcium concentration falls to zero bioavailability will rise to 100 per cent. Extrapolation of the effect of decreasing calcium concentrations outside the range for which the BLM is validated is therefore less certain than the same process for pH, for which sound theoretical models exist.



**Figure 5-4 Bioavailability versus calcium concentration for zinc – BLM outputs**

## 6. Comments on the recently published review of zinc BLM

The Environment Agency commissioned a review of BLM use in soft waters concurrently with this report. The final draft review, *Evaluation of the use of bioavailability corrections for zinc under low pH and low Ca conditions*, has recently been published. This has a bearing on the overall conclusions of our report. The work described in the review is a technical evaluation of the use of BLM for zinc beyond current boundary conditions. It is an assessment of aspects of bioavailability and toxicity of zinc for waters of pH below six and calcium concentrations below 7 mg/l.

The aims and scope of the review are therefore different from those of this report which focuses on the practicality of dealing with the boundary conditions inherent in the current BLM.

The BLM review makes the following conclusions and recommendations.

1. “At pH values much lower than 5.5, Zn binding to DOC will generally be relatively low, but between pH 5.5 and 6.0 a reduction in Zn bioavailability due to DOC binding could be important.” This is consistent with the approach proposed in this report, though here it is emphasised that the decrease in complexation by DOC from higher to lower pH is likely to be a smooth titration function. The authors of the review recognise this, but choose to set pH 5 as a value below which complexation should be considered as unimportant, though not necessarily zero. Figure 4.3 of the review is essentially the same portrayal of complexation across the pH range of interest as that presented in Figure 4-3 and subsequent figures in this report.
2. Setting the calcium concentration at the lower boundary value when it is in fact lower is recommended as the approach to deal with low calcium concentrations. The review reports the result of calculations of speciation that indicate the error in estimated BioF introduced by this option is not likely to exceed 25 percent. This is in accord with the more pragmatic estimation made here. The review notes that the use of an assessment factor of two serves to ensure this potential error does not lead to underprotection of aquatic life.
3. The review concludes that there is no firm evidence to support the need for a reduced PNEC for waters outside the boundary conditions – though lack of evidence for a different PNEC is not necessarily the same as evidence against having one.
4. Issues regarding the relative effect of zinc on different forms of life are discussed. The authors of the review correctly note the difficulty of working with field data, where the ecological parameters are in any case uncertain, but are made more so by confounding factors resulting from the possible effects of other environmental stresses and acclimation.

Overall, the conclusions of the review agree with and provide further technical support for the approach proposed here.

## 7. Conclusions and recommendations

Extrapolation of the estimated bioavailability of copper and zinc for waters of pH outside current BLM boundary conditions can be made on the basis of titration of the notional complexation capacity against increasing hydrogen ion concentration. The proposed method incorporates this principle into a simple calculation tool that can supplement the planned process of reporting and assessment. Testing of the approach on a small number of real waters provides evidence of its practicality and lack of serious bias. It is recommended that the Environment Agency should adopt the proposed approach until further information makes it possible to extend the operation of the BLM to lower pH values or to refine the extrapolation method described here.

Extension of the operation of the BLM for zinc to calcium concentrations outside its operating range may be a little more problematic. The simple expedient of setting the calcium level at the lowest that will result in a BLM output runs some risk of underestimating bioavailability. This has to be judged against the more obvious risk of overestimation of bioavailability by using the BLM in its present form. It is recommended that where calcium concentrations are lower than the lower BLM boundary concentration, this value might be used as a substitute, but that the results should be regarded as tentative within the tiered compliance assessment. (Note that issues of functionality in the BLM for low calcium concentrations also need to be examined). It might be that for zinc a more careful appraisal of background concentrations, rather than issues of bioavailability, should be prioritised in the tiered assessment.

The method recommended here is proposed on the basis of the need for a practicable approach to the problems of BLM boundary conditions. A more sound technical justification for these proposals will require further investigation. Given the effort already expended in developing the various BLM, the scope and costs of such investigations are unlikely to be trivial. It is therefore recommended that these solutions should be adopted in the short to medium term to help implement quality standards for metals.



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## APPENDIX A

### UK AWMN Monitoring data

	pH	ANC mgCaCO <sub>3</sub> /l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Sol.Al ug/l	Sollab.Al ug/l	Cl mg/l	SO <sub>4</sub> mg/l	XSO <sub>4</sub> mg/l	NO <sub>3</sub> mg/l	Si mg/l	DOC mg/l	Alkalinity mg/l CaCO <sub>3</sub>
Beaghs Burn	5.68	6.7	1.7	1.068	5.474	0.312	40.5	8.64	9.7625	2.256	0.864	0.1488	6.272	17.304	2.8546
Old lodge stream	5.02	1.5	2.82	1.524	12.006	1.092	138.78	68.85	25.844	7.296	3.6288	0.53196	6.752	9.552	-0.2667
Afon Gwy	5.89	0.8	0.98	0.696	3.266	0.11466	96.39	63.18	5.751	3.096	2.256	0.744	1.568	2.46	0.5975
Afon Hafren	5.79	0.3275	0.8	0.78	3.933	0.1404	135	102.6	6.958	3.408	2.448	0.806	2.56	2.76	0.2765
R. Etherow	5.49	3.45	2.62	1.5	5.221	0.585	129.6	34.29	8.4845	8.544	7.344	2.232	9.6	14.784	0.3141
Dargall Lane	5.79	1.4	0.88	0.588	3.381	0.30186	35.1	40.5	7.455	3.936	2.88	0.6634	2.272	1.404	1.3091
Narrator Brook	6.01	0.85	0.596	0.804	5.313	0.819	99.9	60.21	9.585	3.6	2.256	0.42966	5.76	1.98	0.739

Desk top study to evaluate options outside BLM thresholds (low pH and low calcium issues)



