Development and use of the zinc bioavailability assessment tool *(Draft)*

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

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Executive summary

A chronic Biotic Ligand Model (BLM) has been developed for zinc by the International Zinc Association through delivery of the Zinc Risk Assessment under the Existing Substance Regulations (793/93/EEC). It can be used to account for zinc bioavailability in freshwaters and can be used to assess potential risks to aquatic ecosystems. Although relatively simple compared to BLMs that have been developed for other metals, eg copper, discussion with UK Regulators indicated that it would still require considerable resource and skill to interpret the results. To facilitate the wider use of the zinc BLM therefore it is necessary to develop a simplified version of the ZnBLM

This project has developed a simplified version of the existing model in order to allow for automated inclusion of a Zn bioavailability consideration into the monitoring and assessment frameworks of UK Regulators. The simplified model runs in Microsoft Excel and requires data input for site-specific dissolved organic carbon, pH and calcium. The tool uses a series of algorithms and constants which can be readily automated into current regulatory data management systems. The performance of this model against the existing version is reviewed and discussed. Guidance on the use of the zinc tool and interpretation of the outputs from the tool, including screen shots, is also given. Equivalent tools have been developed for copper and manganese.

Independent peer review of the Zn bioavailability assessment tool, its performance in relation to the ZnBLM and its intended purpose was provided by Bill Stubblefield of Parametric. This review is given in full in an Annex.

Acknowledgements

The project team thanks the following individuals for their assistance in completing this project: Tim Doran at the Environment Agency's Data Unit, Alan Mugglestone and Nick Pryke of the National Laboratory Service, Ashley Roberts of the Scottish Environment Protection Agency, David McMullan of the Department of Environment Northern Ireland and Dena Grabinar of Alchymy.

Peer review of the zinc bioavailability assessment tool was provided by Dr Bill Stubblefield of Parametrix, USA.

Contents

1 Aims and objectives

The aim of this project is to produce a simple system which will allow Zn bioavailability to be estimated, within acceptable limits of accuracy, and which can be readily integrated with automated Laboratory Information Management Systems. Specifically, the system should:

- Be Microsoft™ Excel-based, mimic the outputs of the current ZnBLM (version 4), and be constructed in a similar manner to the system recently produced for Cu for the Environment Agency (2009a),
- Use a series of algorithms and constants which can be readily automated into current regulatory data management systems.

This report presents the background to the need for such a system, describes the methodology used to produce the system, and identifies the next steps that need to be taken. An independent peer review of the first draft of the report, provided by Dr Bill Stubblefield of Parametrix, Oregon, USA, is included as an Annex. All of the comments made by this independent review were addressed in the production of the zinc bioavailability assessment tool.

2 Background

The Water Framework Directive (WFD, EC 2000) requires EU Member States to ensure that all inland and coastal waters achieve 'good' water quality status by 2015. One of the measures to be used to deliver this requirement are environmental quality standards (EQS). Traditionally, the methods of derivation for EQS have been led to production of single value limits. However, for metals this can lead to inappropriate and unimplementable EQS because of:

- Variations in ambient background concentrations of metals in freshwaters waters due to underlying geology or historical industrial activity,
- The existence of different chemical species in the water column, and
- Changes in this speciation according to local physico-chemical conditions.

Yet, Annex I, part B, of the WFD Daughter Directive on priority substances (EC 2008) suggests that Member States may account for both natural backgrounds and/or physico-chemical conditions of the water that may affect (bio) availability when assessing monitoring results against a metal EQS. The most-relevant and technically robust metrics with which to assess aquatic metal risk should account for metal bioavailability.

Zinc bioavailability in the freshwater environment can be calculated using the Zn Biotic Ligand Model (ZnBLM). This model was developed by the International Zinc Association for use in the Existing Substances Regulations (793/93/EEC) risk assessment of zinc and zinc compounds (The Netherlands, 2004). The model calculates bioavailability correction factors for three trophic levels (fish: *Oncorhynchus mykiss*; invertebrates: *Daphnia magna*; and algae: *Pseudokirchneriella subcapitata*) from information about the physicochemical conditions of the water in question (De Schamphelaere et al. 2005). The lowest of these correction factors is then applied to the dissolved Zn concentration to estimate a bioavailable concentration, which can be compared to the generic Predicted No Effect Concentration (PNEC).

The ZnBLM uses input data for pH, dissolved organic carbon (DOC) and calcium (Ca) or hardness to predict bioavailability factors for each of the three trophic levels, and the highest bioavailability factor (least effect of bioavailability) is applied in correcting the exposure concentrations. The application of a bioavailability correction in this way is considered to be a relatively conservative means of applying a bioavailability correction. This is because it applies the correction, which is applicable to the trophic level which is least affected by bioavailability, regardless of the relative sensitivity of that species or trophic level under the particular conditions. The concentrations of competing cations, such as Na and Mg, are estimated from the Ca concentration according to relationships established for European surface waters.

Discussion with UK environmental regulators has indicated that it is unlikely to be possible to implement the ZnBLM in its current form because of the need to extrapolate between different look-up tables (in the model) to derive the site-specific PNEC value for the many thousands of sites routinely sampled in the UK. It is therefore necessary to produce a simpler model that mimics the original ZnBLM, in a format that can be incorporated into regulatory analytical and monitoring systems. The drive to account for Zn bioavailability in an automated way within current the regulatory frameworks of monitoring and assessment would have several benefits, including:

- Low additional resource requirement, for what is effectively a step-change in the assessment of Zn compliance in freshwater systems,

- Limited changes to current internal structures and procedures
- Delivery of a complete functioning solution to the assessment of Zn bioavailability, the ease, simplicity and scientific benefit of which would be readily demonstrable.

2.1 What is a bioavailability assessment tool?

Bioavailability can mean a number of different things depending on the area of science, but for this purpose bioavailability is a combination of the physicochemical factors governing metal behaviour and the biological receptor - its specific pathophysiological characteristics such as route of entry, and duration and frequency of exposure. Effectively, this means that a measure of bioavailability will reflect what the organism in the water column actually "experiences". This is important as it has long been established that measures of total metal in waters have limited relevance to potential environmental risk (Campbell 1995, Niyogi and Wood 2004).

One way to account for bioavailability is through the use of BLMs. Unlike many other speciation-based approaches, BLMs have been rigorously tested in the laboratory and field; they routinely predict ecological effects to many aquatic taxa across a wide range of water chemistries to within a factor of two. Recent European guidance recommends that where bioavailability models exist, they should be used in setting and assessing EQS for metals under the WFD (European Commission 2010). However, there are some major drawbacks in implementing BLMs in a routine regulatory context. Specifically, the model complexity, runtime per sample, input data requirements, and the level of operator skill needed to interpret the outputs mean that few regulatory organisations have adopted BLMs. This is equally the case for the chronic MnBLM.

It is against this backdrop that bioavailability assessment tools, initially for copper and zinc, were developed (Environment Agency 2009a, UKTAG 2012a and 2009b). These tools maximise the use of our current understanding of metal fate and behaviour (in this case zinc) in freshwaters, but are practical regulatory tools with few data inputs. They provide a simple straight forward method to account for metal bioavailability in freshwaters. Generally, the bioavailability assessment tools overestimate chronic toxicity (i.e. underestimate the resulting EQS, but are typically within a factor of two) compared to the full BLMs (Environment Agency 2010).

2.2 When should the bioavailability assessment tool be used?

The bioavailability assessment tool can be used in an early tier within a tiered EQS compliance framework (Figure 1.1) or to assess site-specific issues for dischargers. The use of the tool in a tiered approach is consistent with classic risk assessment paradigms in that analyses in early tiers are precautionary, but simple to perform with large numbers of sites. As progress is made through the tiers the site numbers are reduced and the levels of precaution and uncertainty decrease. A description of the activity within each tier shown in Figure 1.1 is given below. The bioavailability assessment tool would be used in Tier 2.

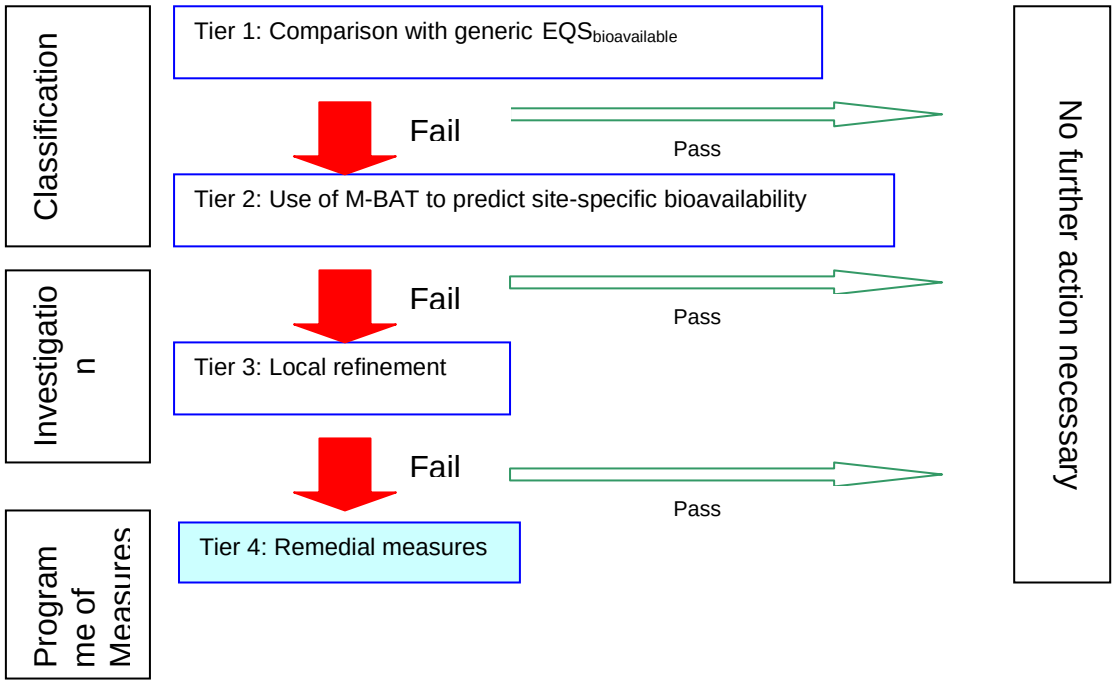

Figure 1.1 Stages of a tiered EQS compliance assessment under the Water Framework Directive

The first tier in the scheme compares the annual average concentration from monitoring data with the generic 100 percent "bioavailable" zinc EQS (10.9 µg l^{-1}). Although the EQS is expressed as a "bioavailable" concentration, it is compared to measurements of dissolved metal. This means that the assessment is conservative and false negatives are minimised. Supporting parameters (such as pH, DOC and Ca) are not required to run the analysis in this tier. Sites, or samples, failing at this tier progress to the second tier, in which information on additional supporting parameters (pH, DOC and Ca) are required as inputs to the bioavailability assessment tool. The generic $EQS_{bioavailable}$ can be precautionary as its use is part of a tiered risk-based framework, so "failure" at this tier leads to further analysis but not to more expensive regulatory action.

Tier 2 makes use of the zinc bioavailability assessment tool. Samples failing this screen progress to Tier 3.

Tier 3 includes the use of a potential range of tools to help refine the assessment of bioavailability, such as the use of the 'full' BLMs or further sampling and analysis, particularly where default values may have been used for the input parameters, and the consideration of background concentrations. Only when these factors have been accounted for can we safely assume the EQS has been breached.

At Tier 4, the failure of a site to achieve good chemical status has been clearly determined. Consideration of a programme of measures to mitigate the situation, within a cost/benefit framework, may be required. The advantage of using the bioavailability-based approach at an earlier tier is that causal factors may be identified which help to focus the programme of measures.

3 Development of a bioavailability assessment tool for zinc

The methodology undertaken for the development of the model is described below. This methodology follows a similar format to that described for the copper bioavailability assessment tool (Environment Agency 2009a), with an initial run of calculations using the original model followed by the development of algorithms from these data to mimic the outputs closely. Refinement of these algorithms was then undertaken before testing against a UK and then selected European datasets.

3.1 Inputs for the bioavailability assessment tool

A complete set of ZnBLM (V4) calculations incorporating the full validated range of pH, Ca and DOC conditions were made for a total of 6081 different combinations of pH, DOC and Ca conditions. The pH ranged from 6 to 9 (in increments of 0.2), DOC from 0.1 to 30 mg L^{-1} (in increments of between 0.2 and 2) and Ca from 5 to 150 mg L^{-1} (in increments of between 5 and 10). The $BioF_{max}$ output from the ZnBLM was used to calculate Zn PNEC values by application to the generic PNEC for Zn, according to Equation (1)

$$PNEC_{Bioavail.} = PNEC_{Generic} / BioF_{max} \quad (1)$$

3.2 Development of the model

We developed algorithms from the data generated from the original model to describe the influence of water quality conditions on the $BioF_{max}$ value calculated by the ZnBLM. The input parameters used for the development of the simplified model were the same input parameters used by the ZnBLM (pH, DOC, and Ca). Analysis of the ZnBLM has indicated that DOC accounts for approximately 84% of the variation in $BioF_{max}$ values, with Ca accounting for approximately 13% of the remaining variation (Environment Agency 2009b). Initial trials, and the experiences of other researchers (STOWA 2007), indicated that a quadratic relationship allowed the best description of pH on Zn bioavailability. Consideration of the parameter to be predicted suggested that improved predictions could be obtained by estimating the value of the PNEC itself, rather than the $BioF_{max}$ or $\log_{10}$(PNEC).

The proposed zinc bioavailability assessment tool uses 8 models, covering different ranges of input parameters, with the general expression shown in Equation (2):

$$PNEC = A.\mathbf{DOC} + B / (C.\mathbf{pH}^2 - D.\mathbf{pH} + E) + (F.\mathbf{Ca}^G) + H \quad (2)$$

Where *A*, *B*, *C*, *D*, *E*, *F*, *G* and *H* are constants.

Optimisation of the constants was performed by minimising the root mean squared error (RMSE) between the estimate and the ZnBLM prediction for each physico-chemical data range. These comparisons used a reference PNEC of 7.8 μg l^{-1} to calculate the PNEC on a dissolved concentration basis. It should be noted that this is not the lowest PNEC calculated within the operating range of the ZnBLM. The results

of PNEC estimations using a single model over the complete range of conditions are shown in Figure 3.1.

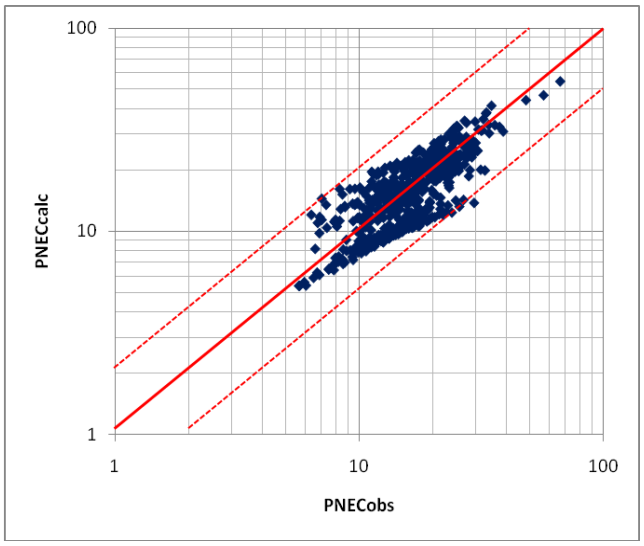

Figure 3.1 Zn PNEC estimation using a single model for all data. The solid red line indicates a 1:1 relationship and the two dotted red lines indicate a factor of 2 difference from the true result

3.3 UK test data set

In order to improve estimates of the PNEC the generic model applied in Figure 3.1 was split into 8 sub-models to cover different ranges of water quality conditions. The ranges of conditions covered by each of the individual sub-models are provided in Table 3.1.

Table 3.1 Ranges of water quality conditions covered by each of the individual sub-models of the zinc bioavailability assessment tool

Model	Model Boundaries		
	pH	DOC	Ca
1	< 8	< 10	< 30
2	< 8	≥ 10	< 30
3	≥ 8	< 10	< 30
4	≥ 8	≥ 10	< 30
5	< 8	< 10	≥ 30
6	< 8	≥ 10	≥ 30
7	≥ 8	< 10	≥ 30
8	≥ 8	≥ 10	≥ 30

The suite of models was tested against a set of 632 matched monitoring data, for pH, DOC and Ca, from a representative selection of UK areas. These data ranged in pH from 6 to 9, DOC from 0.2 to 19 mg L^{-1} and Ca from 5.01 to 149 mg L^{-1}. The results of the ZnBLM were then compared to the results of the PNEC estimation (Figure 3.2 and 3.3). The RMSE value for this test dataset is 2.3 µg l^{-1}, indicating that 95% of the

estimates fall within 4.6 µg l^{-1} of the true result. All estimates are within a factor of 2 of the true result.

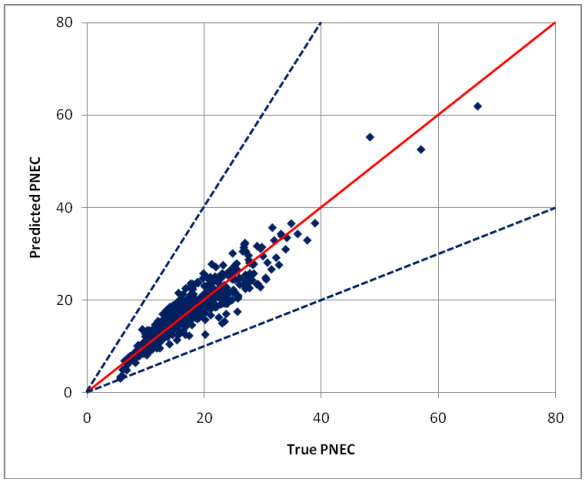

Figure 3.2 Comparison of PNECs generated by the original ZnBLM (True) as compared to the zinc bioavailability assessment tool (Predicted). The 1:1 line is shown in red. Dark blue dashed lines indicate predictions within a factor of 2 of the true result

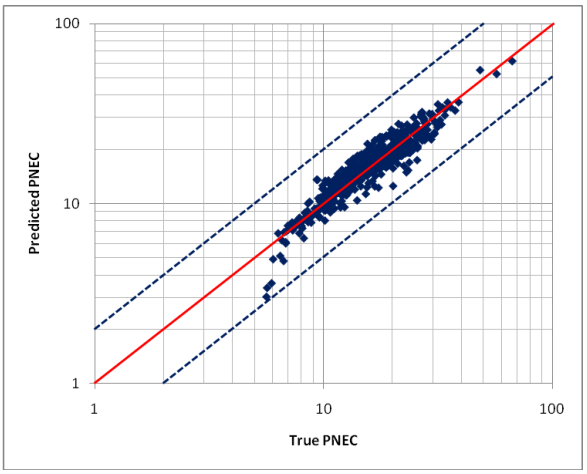

Figure 3.3 Comparison of PNECs generated by the original ZnBLM (True) as compared to the zinc bioavailability assessment tool (Predicted). The 1:1 line is shown in red. Dark blue dashed lines indicate predictions within a factor of 2 of the true result

3.4 Performance of the model

The errors in the estimates of the PNEC shown in Figures 3.2 and 3.3 are generally equally distributed about the 1:1 line, i.e. they can be either over-protective or under-protective. There is an apparent deviation towards conservative PNEC estimates at low PNEC values, although this affects only a very small proportion of the test dataset. This is considered to be due to the fitting procedure, which serves to reduce larger errors in the estimated PNEC value more than smaller errors. A view was taken that it was unlikely that under-protective PNECs estimations would be acceptable to the Environment Agency if the estimator is used in a tiered compliance framework. Such an approach has been proposed for the compliance assessment of Cu (Environment

Agency 2009a), although the greater effect of bioavailability, and larger resulting range of PNEC values for Cu means that the accuracy of the copper bioavailability assessment tool is lower than that for zinc.

Revisions were therefore made to the estimates in order to prevent the calculation of estimated PNEC values which are *higher* than the true value. This occurs at the expense of overall accuracy (Figure 3.6), but results in estimates which are unlikely to be under-protective. Two different corrections have been undertaken and the results of these are shown in Figures 3.4 and 3.5, respectively. These two corrections reduce the value of the estimated PNEC so that estimated PNEC values are rarely higher than the true value. The first correction (Figure 3.4) affects higher values more than lower values, and the second correction (Figure 3.5) has a greater effect on low PNEC values, resulting in less over-protection at low PNEC values.

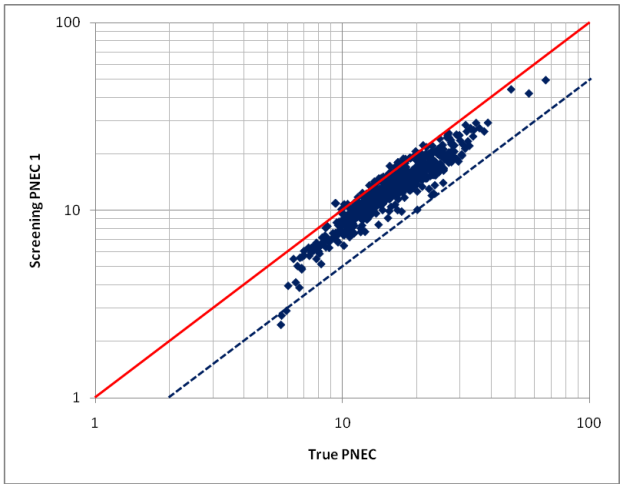

Figure 3.4 Correction 1 applied to the zinc bioavailability assessment tool (Screening PNEC 1). The 1:1 line is shown in red. Dark blue dashed lines indicate predictions within a factor of 2 of the true result

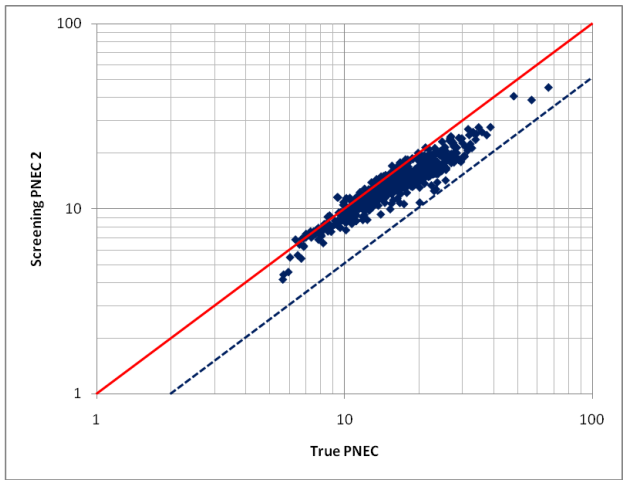

Figure 3.5 Correction 2 applied to the zinc bioavailability assessment tool (Screening PNEC 2). The 1:1 line is shown in red. Dark blue dashed lines indicate predictions within a factor of 2 of the true result

Screening PNEC 1 (Figure 3.4) results in slightly fewer under-protective estimates, although there is a tendency towards over-protective estimates at low PNEC values. Screening PNEC 2 (Figure 3.5) results in less over-protective estimates at low PNEC values, but also results in a slightly higher degree of overall under-protection.

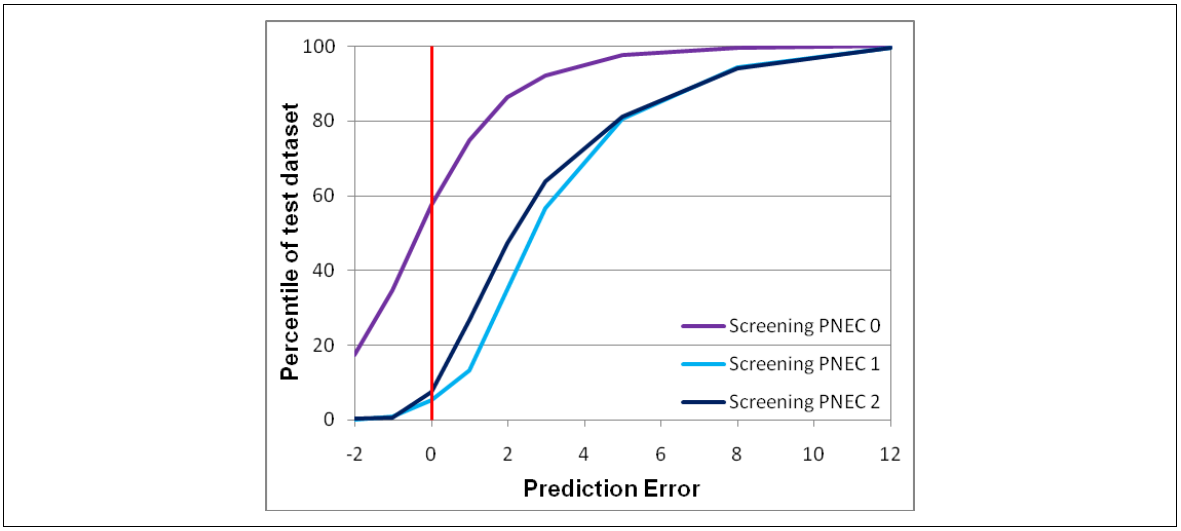

Figure 3.6 Cumulative frequency distributions of errors in PNEC estimators, where PNEC 0 is the results from the bioavailability assessment tool without correction and PNECs 1 and 2 are the estimator with either correction 1 or 2 applied. Negative prediction errors indicate under-protective estimates and positive prediction errors indicate over-protective estimates

Screening PNEC 1 provides estimates which are protective for approximately 95% of these test data, whereas Screening PNEC 2 provides estimates which are protective for approximately 92% of these test data. Screening PNEC 1 was therefore used along with the uncorrected version (Screening PNEC 0) in tests against other European datasets (Table 3.3).

3.5 European test dataset

The models were also tested against selected data (n = 977) from four other European locations (Sweden, Austria, Elbe, and Walloon; Figures 3.7 and 3.8). Summary information about the ranges of the relevant physicochemical conditions in each of these four Regions is shown in Table 3.2. These Regions represent a variety of different types of conditions, such as low pH and Ca (Sweden), and low DOC (Austria).

Table 3.2 Ranges of relevant physicochemical conditions in the four selected European Regions

Parameter	Statistic	Sweden	Elbe	Austria	Walloon
pH	Minimum	5.65	7.0	6.9	5.8
	Mean	6.78	7.94	8.0	7.8
	Maximum	8.27	9.1	8.5	8.5
DOC	Minimum	1.3	2	0.5	1.1
	Mean	7.3	5.1	2	3.2
	Maximum	20	7.6	9.3	8.1
Ca	Minimum	0.6	38	5	9
	Mean	5.6	86	45	65

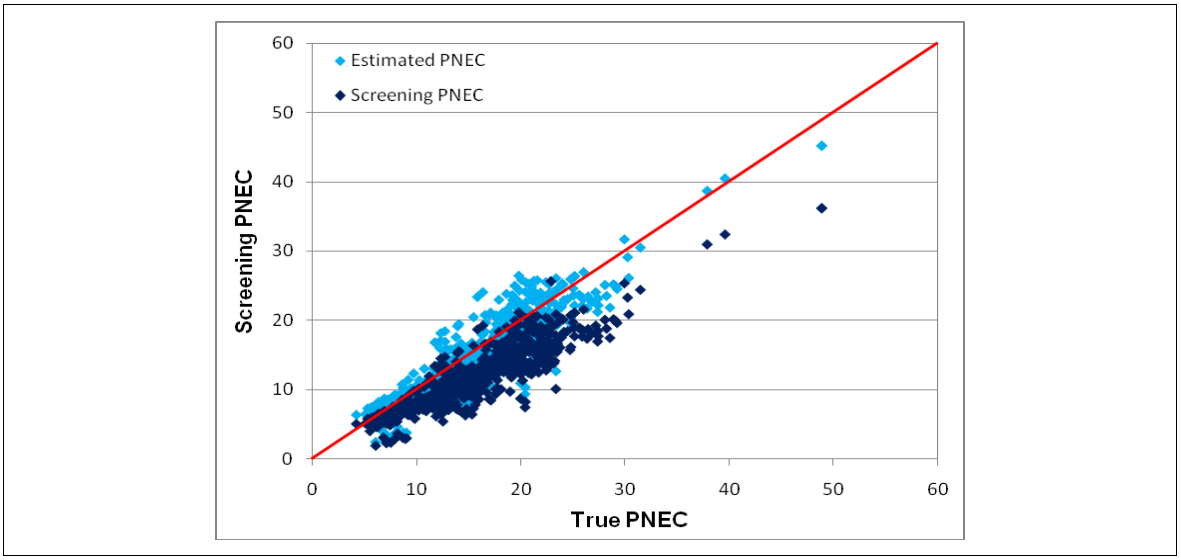

Figure 3.7 Comparison of Zn PNEC predictions by the two models. Estimated PNEC is the original model, and Screening PNEC is the model corrected to avoid under-protective predictions

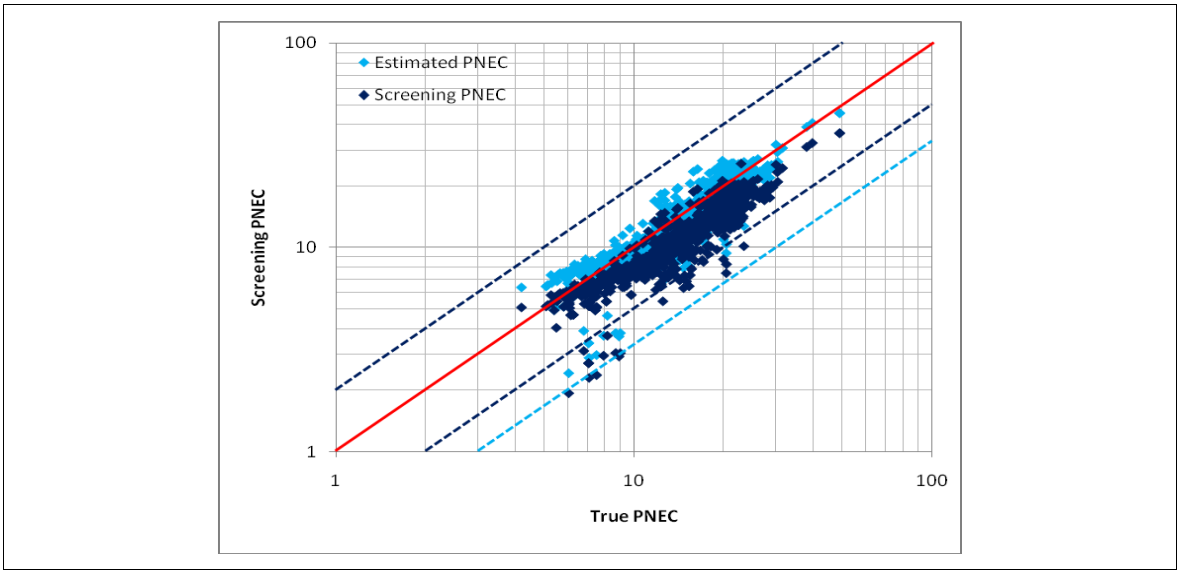

Figure 3.8 Comparison of Zn PNEC predictions by the two models. Estimated PNEC is the original model, and Screening PNEC is the model corrected to avoid under-protective predictions. Dark blue dashed lines indicate predictions within a factor of 2 of the true result and pale blue dashed lines indicate predictions within a factor of 3 of the true result

True PNEC values were calculated using the modified original ZnBLM which enables calculations to be performed when Ca concentrations are beyond the validation boundary conditions of the BLM. This assessment has not taken account of the fact that, according to the Zn risk assessment (The Netherlands 2004), a "soft waters PNEC" should be applied when Ca concentrations are less than approximately 5 mg l^{-1}. Table 3.3 clearly shows that whilst the corrected PNEC ($PNEC_{screen}$) provides a conservative prediction, with greater absolute errors, when compared with the uncorrected method ($PNEC_{est}$), the mean PNEC values are within 25% of the mean true PNEC value for the selected European data.

Table 3.3 The performance of the zinc bioavailability assessment tool using both corrections when compared to the original ZnBLM

Region	RMSE (μg l^{-1})		Mean PNEC (μg l^{-1})		
	$PNEC_{est}$	$PNEC_{screen}$	True PNEC	$PNEC_{est}$ [1]	$PNEC_{screen}$ [2]
Sweden	1.4	3.9	15.0	14.4	11.5
Austria	1.8	2.9	9.7	9.6	7.7
Elbe	2.8	5.1	18.9	18.0	14.4
Walloon	2.9	4.4	14.3	13.3	10.8

Notes: [1]uncorrected Zn PNEC estimate

[2]Zn PNEC estimate corrected to avoid under-protection (Screening PNEC 1)

The overall goodness of fit for each individual sub-model (expressed as the root mean squared error, RMSE) when applied to the training dataset and both of the testing datasets is shown in Table 3.4. The testing datasets also include the number of samples that each individual sub-model was applied to (n).

Table 3.4 The performance of the individual submodels of the zinc bioavailability assessment tool when compared to the original ZnBLM, for both the training and EU testing datasets.

Model boundaries			Training	UK Test		EU Test	
pH	DOC	Ca	RMSE	RMSE	n	RMSE	n
< 8	< 10	< 30	0.8	1.4	90	3.9	298
< 8	≥ 10	< 30	2.0	1.9	19	4.6	47
≥ 8	< 10	< 30	2.0	1.0	9	1.4	22
≥ 8	≥ 10	< 30	6.9	6.0	2	na	0
< 8	< 10	≥ 30	3.2	2.7	364	5.3	266
< 8	≥ 10	≥ 30	5.3	3.2	6	12.6	2
≥ 8	< 10	≥ 30	2.1	1.4	139	3.1	342
≥ 8	≥ 10	≥ 30	3.2	2.5	2	na	0

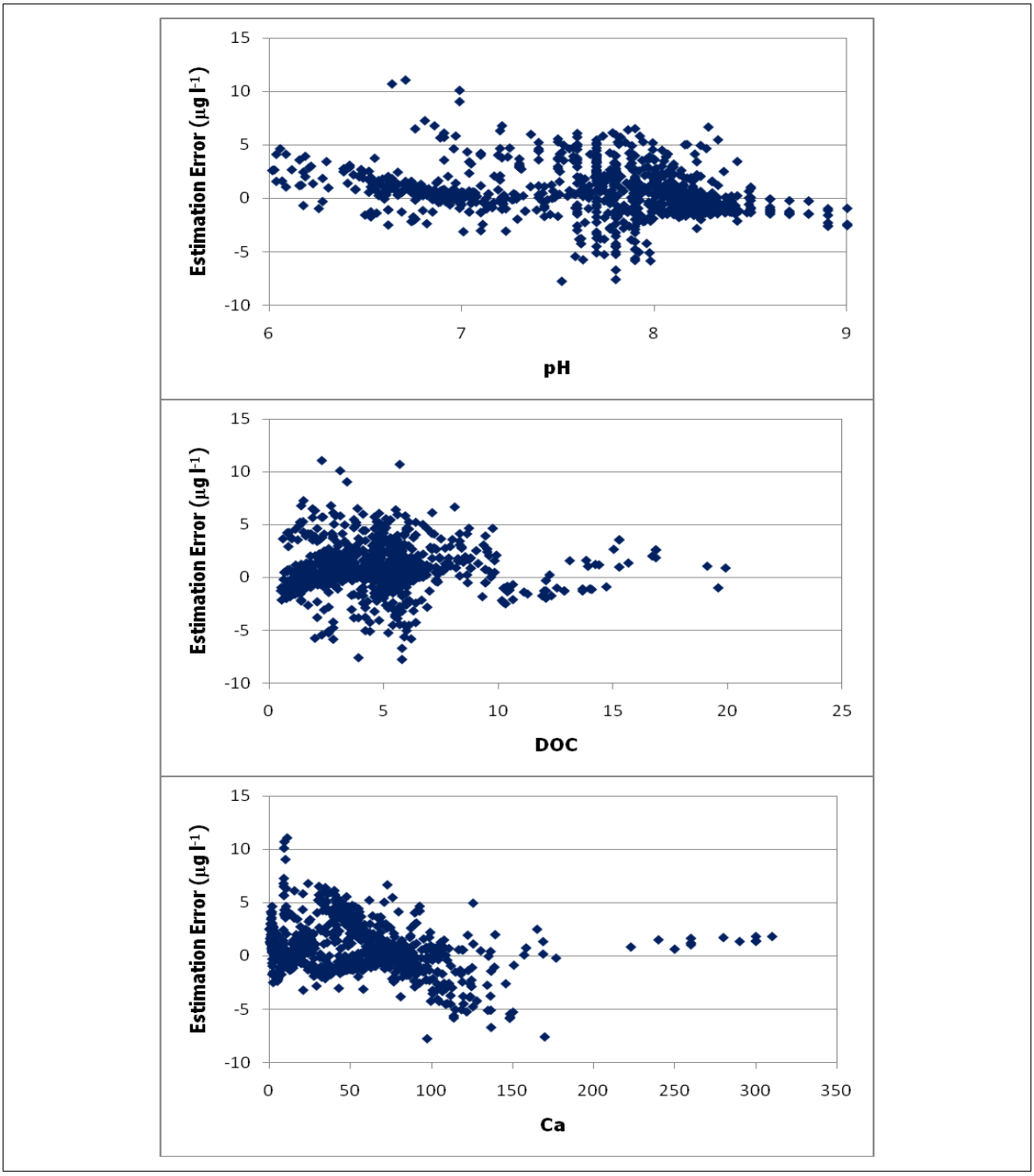

Figure 3.9 Residual errors in Zn PNEC estimation for European test dataset (n = 977) as a function of pH, DOC and Ca

Plots of the residual errors in the PNEC predictions (Figure 9) do not appear to show any consistent bias as a function of the input parameters.

4 Using the bioavailability assessment tool

This section describes how to use the zinc bioavailability assessment tool to assess the potential aquatic risks of zinc. The data input requirements are outlined along with what to do to get started. The bioavailability assessment tool will operate in versions of Excel™ from 2003 onwards.

4.1 Data inputs

The bioavailability assessment tool accounts for zinc bioavailability for specific locations through the use of local water chemistry data, specifically pH, DOC (mg l^{-1}) and Ca (mg l^{-1}). These estimates can be based on a single sampling occasion or, in accordance with the requirements of the WFD, from monitoring data from 12 monthly sampling occasions over a period of one calendar year.

A hazard assessment can be performed if no measured zinc data are available; the tool will give an indication of the relative sensitivity of waters to potential zinc exposure. However, if a risk or EQS compliance assessment for zinc is to be undertaken, dissolved zinc monitoring data are required. For a compliance assessment, the annual average of the measured metal data needs to be calculated and entered into the bioavailability assessment tool.

Columns are also available in the tool for sample ID, location, water body code and date (Figure 3.2), although none of these need to be entered for the tool to work.

4.2 What if some data are absent?

The bioavailability assessment tool requires data inputs for pH, DOC and Ca. Without these, the tool will not run (and you will be prompted for an input). Dissolved organic carbon is a determinand that is not routinely monitored in freshwaters in England and Wales or many other European Member States. However, in the past some DOC data was collected across most Environment Agency regions. These historical data allow estimation of DOC default values for many waterbodies and most hydrometric areas in England and Wales that can potentially be used in the absence of measured DOC data (Environment Agency 2009b). Importantly, as mentioned in Section 1, only sites that progress through Tier 1 will require the collation of additional data, such as DOC.

4.3 Getting started

The bioavailability assessment tool runs in Excel™ and upon opening it, it is imperative to ensure that the macros are enabled, otherwise the tool will not work. The first page that you should see is shown in Figure 3.1, once the macros have been enabled.

The following are step-by-step instructions on how to run the tool. These are the same instructions that are given on the front page of the tool.

1. Click the Start button on the Introduction Page. This will open the PNEC Calculator Sheet (Figure 3.2).

2. This sheet contains an empty table (if it isn't empty, click the Clear Data button to empty it).

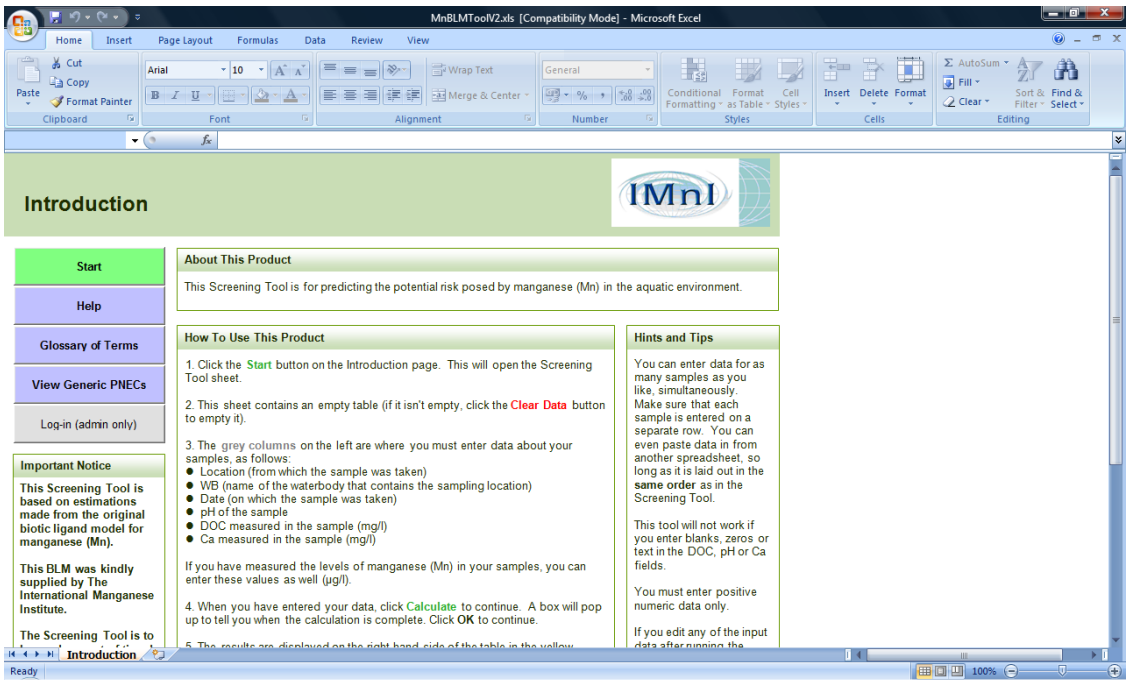

Figure 4.1 Screenshot of Introduction Page

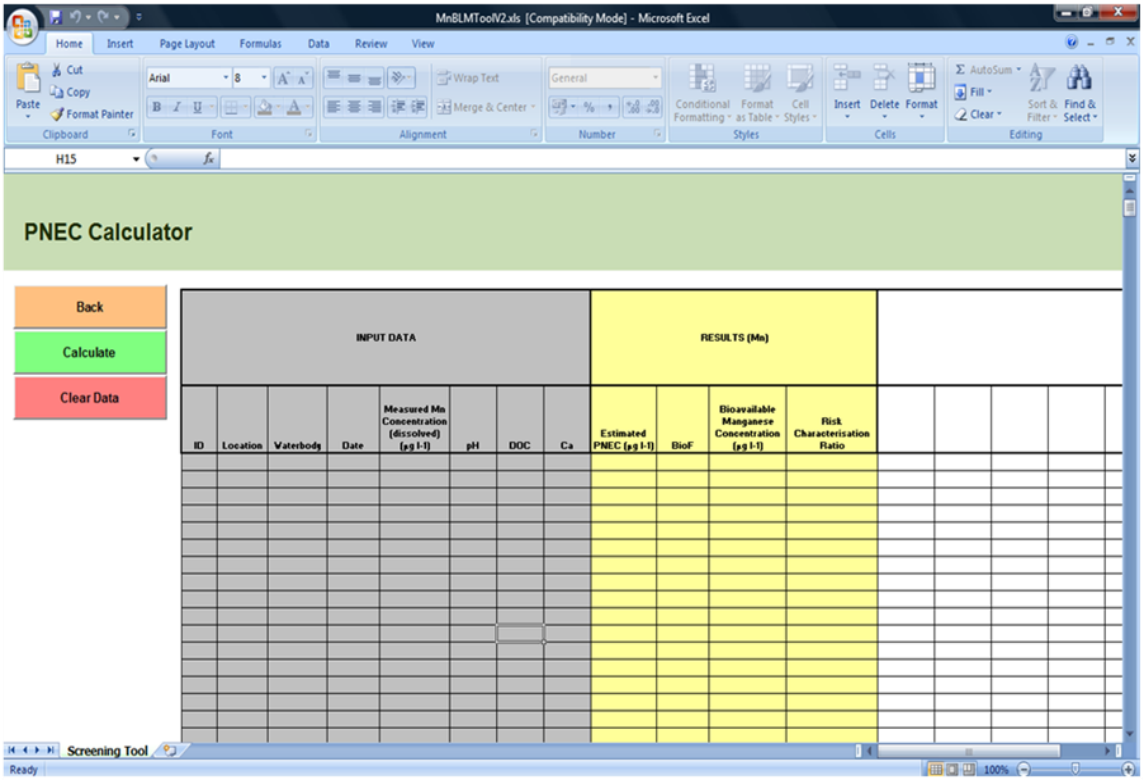

Figure 4.2 Screenshot of PNEC Calculator Page

3. The grey columns on the left (Figure 3.2) are where you must enter data about your samples, as follows:

- Location (from which the sample was taken)
- WB (name of the waterbody that contains the sampling location)
- Date (on which the sample was taken)
- pH of the sample (this should be an annual average) (required)
- DOC measured in the sample (this should be an annual median or a default value in mg l^{-1}) (required)
- Ca measured in the sample (this should be an annual average mg l^{-1}) (required).

4. If you have measured the levels of dissolved zinc in your samples, you can enter these values as well (µg l^{-1}). These data are not necessary to run the tool and you can undertake a hazard assessment without the measured metal data.

5. When you have entered your data, click Calculate to continue. A box will pop up to tell you when the calculation is complete. Click OK to continue.

6. The results are displayed in the green columns on the right-hand side of the table.

7. In all cases, the following results are shown:

- Estimated PNEC for each site (µg l^{-1})
- BioF (calculated using the reference $EQS_{bioavailable}$ for zinc).

8. Where you have entered data about the measured concentrations of zinc, the following results are also shown:

- Bioavailable concentration (µg l^{-1})
- Risk characterisation ratio for each site.

9. Some results are highlighted. Hover your cursor over the highlighted cells, and a comment will appear. This will explain why the result has been flagged. It will be for one or both of the following reasons.

- The inputted values of the abiotic water parameters result in a higher level of zinc bioavailability than the $EQS_{bioavailable}$. In this case, the estimated PNEC shown has been set as equal to the $EQS_{bioavailable}$. This indicates sensitive conditions at the sampling point in question. These cells are shown with a white background and red text.
- The allowable range for Ca is 1 mg l^{-1}. Where input data for calcium is below 1mg/l the result will be highlighted with the cell in the spreadsheet being shown as a white background and red text. Hovering over the cell gives the reason for the flag. This is also the case where calcium is above 200mg/l.

You can enter data for as many samples as you like, simultaneously. Make sure that each sample is entered on a separate row. You can even paste data in from another spreadsheet, so long as it is laid out in the same order as in the bioavailability assessment tool.

This tool will not work if you enter blanks, zeros or text in the DOC, pH or Ca fields.

You must enter positive numeric data only. If you edit any of the input data after running the programme, the results will not adjust automatically. You will have to click

Calculate again, even if you have only changed one row. If you want to re-run the spreadsheet with a completely new set of input data, as if from the beginning, click Clear Data and start again.

4.4 What do the outputs mean?

The bioavailability assessment tool will account for zinc bioavailability for specific locations through the use of local water chemistry data, specifically pH, DOC (mg l^{-1}) and Ca (mg l^{-1}). If only data for pH, DOC and Ca are entered into the tool, the results will appear under the column headers 'Estimated PNEC' and 'BioF'. If total dissolved metal concentrations are added, in addition to the abiotic parameters, bioavailable metal and risk characterisation will also be calculated. How these outputs are calculated and what they mean is discussed below.

4.4.1 Estimated PNEC and BioF

The estimated PNEC is calculated from the relationships shown in Section 2.2 that were developed on the basis of the BLM outputs. The PNEC can be considered as a site-specific EQS, and is useful in ranking sites in terms of their sensitivity to zinc toxicity.

The BioF is calculated by dividing the generic $EQS_{bioavailable}$ by the estimated PNEC. This step involves only one generic EQS for the UK, but allows account to be taken of bioavailability at individual sites. The BioF is then used in the next stage of calculations, if total dissolved metal data have been added in the columns to the left. Values of BioF should always be below one in this tool.

4.4.2 Bioavailable metal concentration and risk characterisation ratio

If measured dissolved zinc data have been added to the sheet in the left hand column, there is an opportunity to assess potential risks at individual sites and undertake an EQS compliance assessment. The bioavailable zinc concentration and risk characterisation ratio will be calculated, the former by multiplying the measured data by the BioF and the latter by dividing the measured metal concentration by the site-specific PNEC.

The bioavailable zinc concentration gives an estimate of the amount of zinc in the sample that is biologically active and of ecological relevance. The risk characterisation ratio, or risk quotient, provides an indication of whether the site being assessed has passed or failed the zinc EQS and by what extent. The risk characterisation ratio is a commonly used metric in bioavailability assessment risk assessments, and a value equal to, or above, unity indicates a potential risk. It is information in this final column that can be used to determine which sites progress to Tier 3, as shown in Figure 1.1, and which sites exit the compliance process and require no further action.

5 Conclusions

One of the practical difficulties preventing the use of approaches that account for metal bioavailability is the complexity of the processes that need to be followed. Chronic BLMs for several metals have been in existence for nearly 10 years, yet none have been incorporated into routine regulatory risk assessment. The development of simplified tools to increase the use of BLMs is a practical way forward.

In this project, a simplified version of the chronic ZnBLM was developed. The bioavailability assessment tool mimics the ZnBLM, but runs in Microsoft Excel™ and requires data for site-specific dissolved organic carbon, pH and calcium. The tool uses a series of algorithms and constants which can be readily automated into current regulatory data management systems.

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Annex

Peer review of simplified ZnBLM undertaken by Dr W. Stubblefield, Parametrix, USA.

Stubblefield review comments: ***The development of a simplified ZnBLM for automated use in UK regulatory data management systems***

The stated goal for this project is to produce a simple system which can be used to estimate zinc bioavailability in natural water samples taking into consideration appropriate physical-chemical properties. Ideally, this capability should be able to be incorporated into existing regulatory data management systems. The approach described is consistent with the current state-of-the-science regarding estimation of zinc bioavailability in natural waters and should achieve the stated project goal. Although good agreement was achieved between observed and predicted PNEC values (within a factor of two), significant efforts were devoted to the development of "correction approaches" that could be used to eliminate any instances of under-protective PNEC estimations. Given the conservatism inherent to the process of PNEC derivation, it is conceivable that these efforts to ensure adequate protection may lead to zinc standards that are unnecessarily strict in some instances.

Specific comments to the report are as follows:

Section 2: Additional background information is needed regarding the "original" zinc BLM. Reference should be provided to the source for the original model and a brief description of the parameters that were found to be important for the model. It is also important to discuss what organisms are included in the BLM, i.e., algae, ceriodaphnia, fathead minnows, etc.

Section 3: No information is provided regarding the source of the data that are used for the development of the "simplified model." This should be provided.

Section 3.1: …DOC from 0.1-30 mg/L… ("-" needed)

Section 3.2: Some discussion is needed regarding why the three modeled parameters (i.e., DOC, pH, calcium) were included and what the relative contribution to zinc toxicity can be attributed to each.

Section 3.5: The paragraph preceding Figure 4 indicates that two different corrections were used in revising the original model, however, no description of what these corrections were is provided. Some discussion of what the corrections were should be included.

Figure 3: Some discussion should be included to address why the predicted PNECs tail-off compared with the true PNECs for those data points on the lower end of the curve.

Section 3.6: This section states "…that it was unlikely that under-protective PNEC estimations were acceptable for the environment agency if the estimator was to be used in a tiered compliance framework." Some additional explanation for the statement would be beneficial.

Figure 6: This figure (or associated text) needs to provide some discussion of the difference between Screening PNEC 1 and Screening PNEC 2. It would also be helpful to label the area below zero as "under-protective" and the area above zero as "over-protective."

Paragraph preceding Section 3.7: Some explanation should be provided for why Correction 2 was eliminated from further consideration.

Section 3.7: Additional information should be provided for why the four European locations, i.e., Sweden, Austria, Elbe and Walloon were chosen and how they differ among each other.

Figure 8: As was the comment on Figure 3, some discussion of why the screening and true PNECs differed at the lower end of the curve. The

Table 2: The caption for this table indicates that both corrections were used for the PNEC estimator, however, the paragraph immediately preceding Section 3.7 suggests that Correction 2 had been abandoned and was not used. This difference needs to be clarified.

Paragraph following Table 2: This section refers to Table 2 and discusses values for PNECcalc 2 and PNECcalc1, however, neither of these values is actually contained in Table 2. This paragraph should be revised to reflect the actual content of Table 2 or vice versa. In the first sentence the term “outwith” should probably be revised; perhaps “exceed” would be better.

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