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

by
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Executive summary

The International Manganese Institute has developed a chronic biotic ligand model (BLM) which can account for manganese (Mn) bioavailability in freshwaters and can be used to assess potential risks to aquatic ecosystems. However, the model is relatively complicated to use and requires considerable resources and skill to interpret the outputs.

To facilitate the wider use of this tool, this project sought to develop a simplified version of the Mn BLM, creating a manganese bioavailability assessment tool for use by regulators and those responsible for managing the water environment.

The bioavailability assessment tool mimics the Mn BLM, but runs in Microsoft Excel™ and requires data on site-specific dissolved organic carbon, pH and calcium levels. The tool uses a series of algorithms and constants which can be readily automated within current regulatory data management systems. The performance of this model against the original version is reviewed and discussed in this report. Guidance on the use of the Mn bioavailability assessment tool and interpretation of its outputs, along with screenshots, is given in this report. Equivalent tools have been developed for copper and zinc.

Finally, an environmental quality standard (EQS) compliance assessment is provided for matched monitoring data from samples and sites in England and Wales using the bioavailability assessment tool to account for Mn bioavailability. In addition as data was available for Sweden and Austria as part of the European risk assessment work this data was also used to enable further assessment to be undertaken. The results of this assessment show that, at worst, only two percent of the 6,000 sites or samples exceed the Mn EQS of 123 $\mu g l^{-1}$ after considering bioavailability, compared with up to 10 percent exceedance when bioavailability is not considered.

Contents

1 Introduction

This report describes an approach to account for manganese (Mn) bioavailability in freshwaters that meets the requirements of the EU Water Framework Directive (WFD) and can be used in routine regulatory systems. The project builds on a chronic biotic ligand model (BLM) developed by the International Manganese Institute to account for manganese (Mn) bioavailability in freshwaters, aiming to create a simplified version of the MnBLM. Where the term manganese or Mn is used in this report, it refers to the Mn^{2+}(aqueous) ion. Specifically, this report:

- describes the development of a bioavailability assessment tool for Mn in freshwaters;
- explains how the bioavailability assessment tool can be used, including in regulatory frameworks;
- using freshwater monitoring data from England and Wales, Sweden and Austria, tests the tool by assessing compliance against proposed environmental quality standards (EQS) for Mn.

This introductory section gives the background to the development and purpose of the tool.

Section 2 describes in more detail the construction and testing of the tool.

Section 3 gives instructions on how to use the bioavailability assessment tool, its data requirements, inputting data, and the interpretation of its outputs.

The results of the EQS compliance assessment for Mn for England and Wales, Austria, and Sweden are given in Section 4. A background to the compliance process in the UK is provided along with a discussion of where and how ambient background concentrations should be used.

1.1 Background

The original MnBLM created by the International Manganese Institute was developed and validated using aquatic toxicity testing (Peters *et al.*2010a). In summary, chronic ecotoxicity tests were performed with fish, invertebrates and algae to assess the effect of water quality parameters on manganese ecotoxicity, in the form of the Mn^{2+} ion. The aim of this testing was to develop a model to predict the chronic ecotoxicity of Mn to aquatic organisms in freshwaters as a function of water physico-chemistry.

The model is able to predict Mn^{2+} ecotoxicity to test organisms to within a factor of two in most cases. At relatively low freshwater pH values, invertebrates are the most sensitive taxa, while at relatively high pH algae are the most sensitive. The point at which algae become more sensitive than invertebrates depends on the calcium (Ca) concentration, and occurs at higher pH when Ca concentrations are low. The sensitivity of invertebrates decreases with increasing Ca, whereas the sensitivity of algae decreases with decreasing pH. Dissolved organic carbon (DOC) concentrations have very little effect on the toxicity of manganese to aquatic organisms. Fish and invertebrates are more sensitive to manganese at low pH, especially if water hardness is low. Under high pH conditions algae are the most sensitive, regardless of water hardness conditions. There are no conditions under which fish would be expected to be the most sensitive trophic level (Peters *et al.*2010a).

The drawback to using the MnBLM is the considerable technical skill required to use it and interpret its outputs. As a result such complex models are unlikely to be widely used in routine regulatory practices. However, it is possible to develop a simplified version of the MnBLM. The next section describes the development of a simplified model with widespread applicability in the assessment of potential aquatic metal risks.

1.2 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 Mn) 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. Detailed descriptions of the bioavailability assessment tools for Cu and Zn are provided in previous Environment Agency reports (UKTAG 2012a, 2009b). 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).

1.3 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.

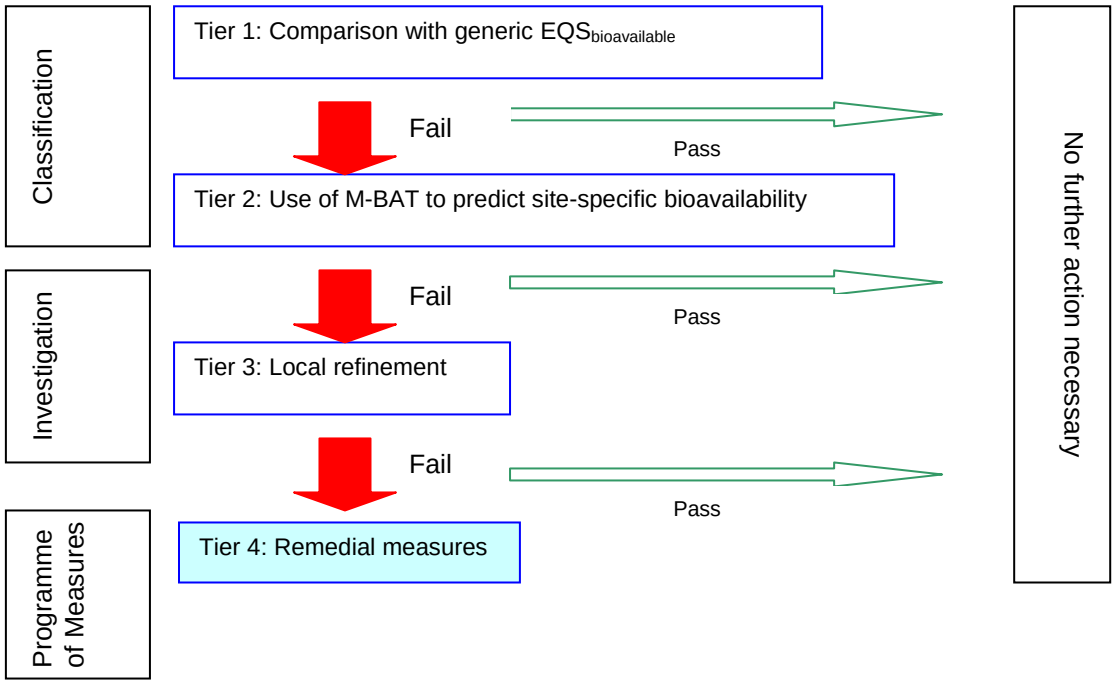

Figure 1.1 Stages of a tiered EQS compliance assessment under the Water Framework Directive

The first tier in the scheme compares the annual average concentration from monitoring data with the generic 100 percent "bioavailable" Mn EQS (123 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 Mn 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.

2 Development of a bioavailability assessment tool for manganese

The MnBLM is a relatively complicated model, with several stages of calculations. These stages are:

- Calculation of the chemical speciation of manganese and other relevant solution components under the conditions of interest.
- Calculation of manganese activity at the relevant effect level (e.g. EC_{10}).
- Calculation of the concentration of dissolved manganese at the effect level.

To simplify the process of assessing potential risks posed by Mn on a site-specific basis, a simplified bioavailability assessment tool was developed which relates the water quality conditions, expressed as the pH, DOC and Ca concentrations, directly to an ecologically acceptable manganese concentration under those conditions.

The bioavailability assessment tool for manganese bioavailability in freshwaters was developed from an extensive dataset of MnBLM calculations covering a wide range of water quality conditions. The dataset consisted of 3,600 calculations covering a pH range between 5.5 and 8.5, Ca concentrations between 1 and 200 mg l^{-1}, and DOC concentrations between 0.5 and 32 mg l^{-1}. For each discrete set of conditions, the EC_{10}(concentration that would have an effect on 10 percent of the population) for dissolved Mn was calculated for the four endpoints covered by the MnBLM (fish growth, invertebrate reproduction, algal growth, and algal biomass).

2.1 Use of the MnBLM

The MnBLM was used to calculate EC_{10} values for dissolved Mn (in mg l^{-1}) for the four endpoints covered by the model (fish growth, invertebrate reproduction, algal growth, and algal biomass). The input values for pH, DOC and Ca were set for the various conditions covered by the dataset, and the concentrations of other major ions required to perform the chemical speciation calculations (Mg, Na, K, Cl, SO_4, and alkalinity) were calculated based on relationships with Ca concentrations established from European surface waters (Peters *et al*. 2010b).

The MnBLM was used to calculate the free ion activity of manganese at the EC_{10} for each endpoint, based on the predicted chemical speciation for each set of water quality conditions. The corresponding dissolved manganese concentration at the EC_{10} was then calculated for each of the endpoints. These procedures resulted in a dissolved manganese concentration for each set of water quality conditions and each ecotoxicological endpoint.

2.2 Development of algorithms

The algorithms were developed separately for the two most sensitive endpoints, which are the EC_{10} for invertebrates, and the EC_{10} for algal biomass. The invertebrate endpoint is always more sensitive than the fish endpoint, and the algal biomass

endpoint is always more sensitive than the algal growth endpoint. Fish and invertebrates have a very similar (although not identical) response to manganese toxicity, and both of the algal endpoints are predicted using the same model. It is therefore only necessary for these two critical endpoints to be calculated (i.e. the EC_{10} for invertebrates, and the EC_{10} for algal biomass).

Simple equations which were able to relate the Mn EC_{10} to the water quality conditions (pH, DOC, Ca) were derived and constants were used to provide the best fit of predicted results to the MnBLM calculated results. The training data for each required endpoint were split into several different ranges of Ca concentrations, and the values for the constants in the equations were fitted separately for each Ca band. Equation 1 shows the general relationship used to estimate the site-specific EC_{10} for invertebrate reproduction, and Equation 2 shows the general relationship used to derive the EC_{10} for algal biomass.

The EC_{10} for invertebrate reproduction is estimated as:

$$EC_{10} = ((a*DOC)+b)/((c*(pH^2))-(d*pH)+e)+(f*(Ca^g))+h) \quad \text{Equation 1}$$

The EC_{10} for algal biomass is estimated as:

$$EC_{10} = (10^{((a*pH)+b)}) \quad \text{Equation 2}$$

Where a, b, c, d, e, f, g, and h are fitted constants.

2.3 Constructing the bioavailability assessment tool

The algorithms to predict EC_{10} values for algal biomass and invertebrate reproduction needed to be combined to provide a single output which was the estimated site-specific predicted no-effect concentration (PNEC) for manganese. A site-specific EC_{10} was therefore calculated for each of the two endpoints. These results were then compared to the reference EC_{10} for each endpoint to derive a BioF value for each endpoint (Equation 3). The reference EC_{10} for each endpoint was set as the EC_{10} under conditions which maximise bioavailability to that organism. Invertebrates (and fish) are most sensitive at low Ca concentrations, whereas algae are most sensitive at high pH. This situation is relatively common in metal toxicity and results in different taxa being the most sensitive under different water quality conditions.

$$\text{BioF} = \text{reference } EC_{10} / \text{site-specific } EC_{10} \quad \text{Equation 3}$$

The reference EC_{10} for invertebrate reproduction is 0.426 mg l^{-1} and relates to low pH and low Ca conditions such as a soft, acid water. The reference EC_{10} for algal biomass is 0.31 mg l^{-1} and relates to high pH conditions such as a hard, alkaline water.

A BioF value was then derived for each of the endpoints predicted by the model, as the reference EC_{10} divided by the site-specific EC_{10}. The maximum possible BioF value is one, which represents high manganese bioavailability for each of the endpoints.

To calculate the site-specific manganese PNEC, the highest of the two calculated BioF values ($BioF_{max}$) was selected and used to calculate the site-specific manganese PNEC from the generic PNEC for manganese (Equation 4). The generic PNEC was derived from the HC_5 (hazardous concentration for five percent of the species) of the species sensitivity distribution of ecotoxicity data plus an assessment factor. This is the subject of a separate report (UKTAG 2012b); the resulting PNEC value was 123 µg l^{-1}.

$$\text{Site-specific PNEC} = \text{generic PNEC}/BioF_{max} \quad \text{Equation 4}$$

2.4 Testing the bioavailability assessment tool

The manganese bioavailability assessment tool was tested by comparing the estimated site-specific PNEC against the site-specific PNEC calculated using the full MnBLM for 916 surface waters from across England and Wales. The results are shown in Figure 2.1 as the MnBLM calculated PNEC plotted against the bioavailability assessment tool calculated PNEC. The tool tends to overestimate manganese toxicity under almost all circumstances, which means that where no risk is identified by the tool there will be no risk from manganese toxicity. In some cases where a marginal risk is identified there may be no actual risk.

Nearly all of the 916 predictions used to validate the tool overestimate manganese toxicity: 63 percent of the predictions are within a factor of two of the true result, 86 percent are within a factor of 2.5, and 97 percent are within a factor of three. Only 1.2 percent of the predictions overestimate the PNEC (are less stringent), whereas 73 percent underestimate the PNEC by more than 0.1 mg l^{-1}, 5.8 percent underestimate the PNEC by more than 0.5 mg l^{-1}, and 1.1 percent by more than 1 mg l^{-1}.

The Mn bioavailability assessment tool therefore provides a precautionary estimate of the sensitivity of freshwaters to manganese toxicity, and in cases where the risk characterisation ratio is less than two, this may be further refined through the use of full MnBLM speciation calculations.

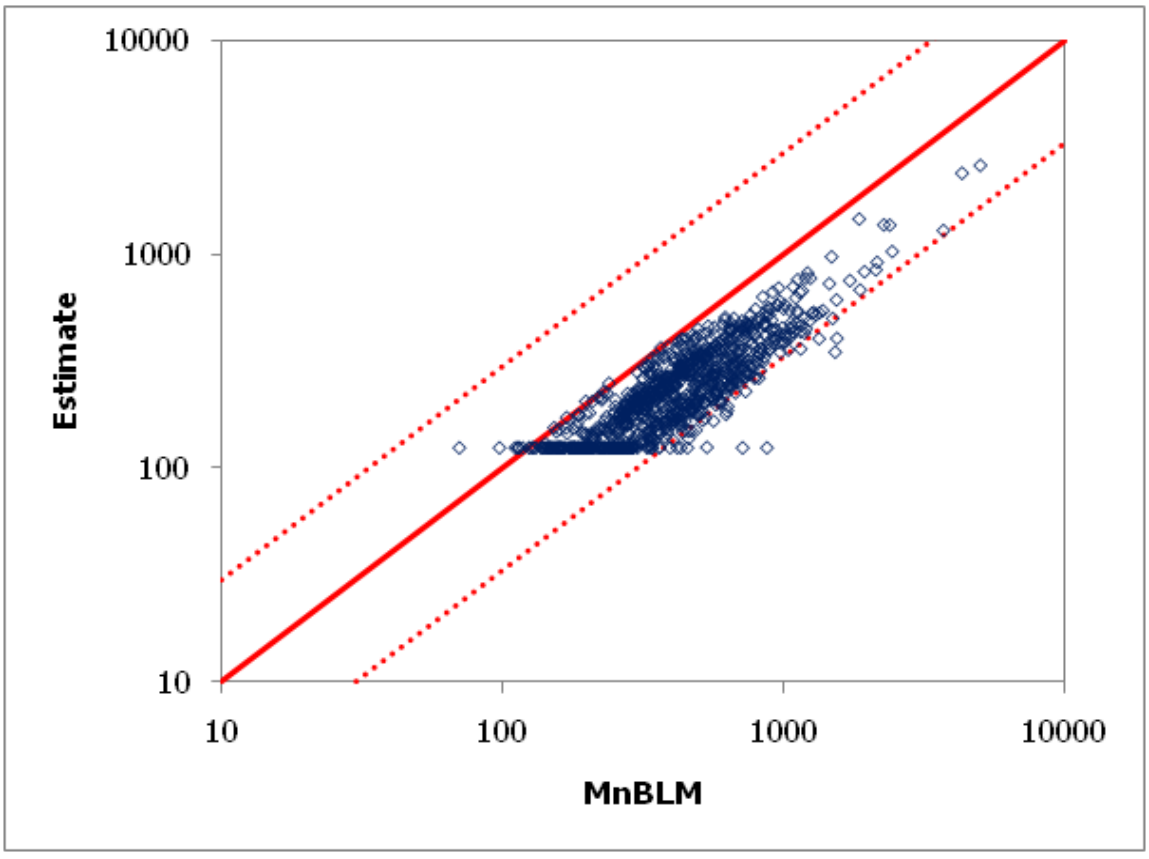

Figure 2.1 Manganese PNEC calculated using MnBLM (x-axis) and manganese bioavailability assessment tool (y-axis). All values in µg l^{-1} dissolved manganese.

3 Using the bioavailability assessment tool

This section describes how to use the Mn bioavailability assessment tool to assess the potential aquatic risks of Mn. 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.

3.1 Data inputs

The bioavailability assessment tool accounts for Mn 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 Mn data are available; the tool will give an indication of the relative sensitivity of waters to potential Mn exposure. However, if a risk or EQS compliance assessment for Mn is to be undertaken, dissolved Mn 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.

3.2 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.

3.3 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).

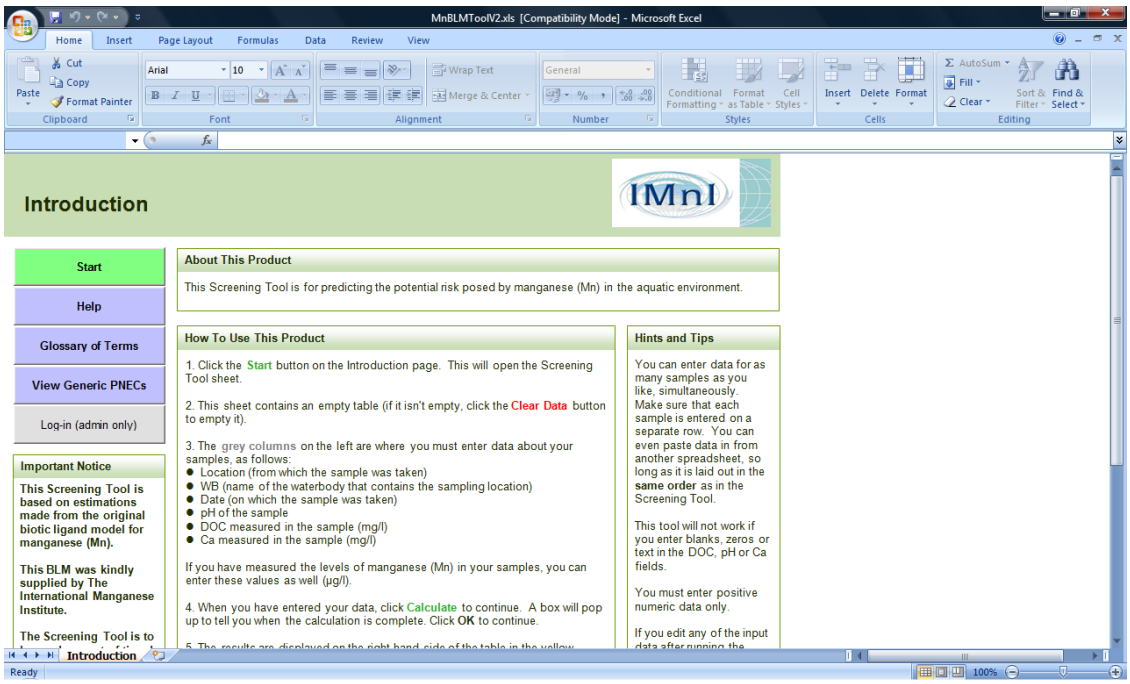

Figure 3.1 Screenshot of Introduction Page

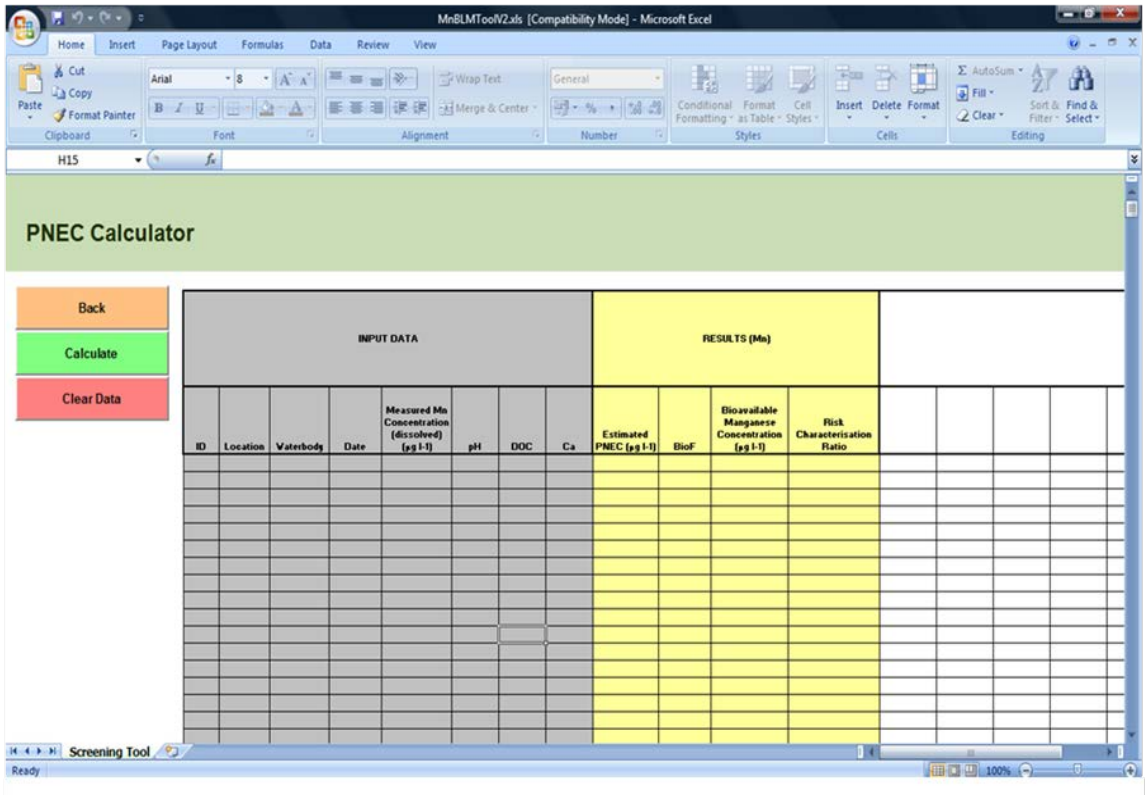

Figure 3.2 Screenshot of PNEC Calculator Page

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 Mn 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 Mn of 123 µg l^{-1}).

8. Where you have entered data about the measured concentrations of Mn, 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 Mn 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.

3.4 What do the outputs mean?

The bioavailability assessment tool will account for Mn 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.

3.4.1 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 manganese toxicity.

The BioF is calculated by dividing the generic $EQS_{bioavailable}$ (123 µg Mn l^{-1}) 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.

3.4.2 Bioavailable metal concentration and risk characterisation ratio

If measured dissolved Mn 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 Mn 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 Mn concentration gives an estimate of the amount of Mn 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 Mn 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.

4 Compliance assessment

This section of the report provides an indicative assessment of potential compliance in England and in Wales, Austria and Sweden against a proposed EQS regime for Mn in freshwaters. In addition as data was available for Austria and Sweden as part of the European risk assessment work this data was also used to enable further assessment.

4.1 Datasets

Any EQS regime needs to reflect the real risk to the environment and the protection being sought in order to avoid unnecessary costs to society or possible environmental impacts. However, an EQS regime also needs to be as simple as possible to minimise regulatory burdens. The need to strike this balance between precision and practicality is helped by taking account of metal bioavailability.

Monitoring data from England and Wales, Austria, and Sweden were used in this exercise. For data from England and Wales we derived average pH, calcium and dissolved manganese concentrations, and median DOC concentrations for those sites where matched data existed for the years 2000 to 2010. We then used the Mn bioavailability assessment tool to assess compliance against the proposed EQS of 123 µg Mn l^{-1} (UKTAG 2012b). The way these data were treated is in accordance with the European guidance (European Commission 2009).

The Swedish dataset was for freshwaters from 2000-2008. These data were used in an indicative face-value compliance assessment, where annual averages had not yet been calculated. This led to a more precautionary approach as data extremes were still present in the dataset. The median DOC for these data was 8.4 mg l^{-1}. The data were from EIONET (http://www.eionet.europa.eu).

The Austrian monitoring data used in this exercise was from 2000-2004 for river sites. The dissolved Mn data and measured DOC were matched for each site. Median DOC for the Austrian dataset was relatively low at 1.3 mg l^{-1}. These data, like the Swedish dataset, were used in a face-value compliance assessment, where annual averages had not yet been calculated. The values recorded as “at or below the limit of quantitation” were treated according to the WFD guidance (European Commission 2010). These data were taken from the website of the Umweltbundesamt, Austria (http://wisa.lebensministerium.at).

4.2 Compliance results

The results for Mn monitoring data from England and Wales, Sweden and Austrian when passed through the first two tiers of the approach shown in Figure 1.1 are given in Table 4.1. The maximum site-specific Mn PNEC for the English and Welsh dataset was 2,625 µg l^{-1} (pH 6.31, DOC 2.0 mg l^{-1} and Ca 85 mg l^{-1}). Just four sites passed through to Tier 2 after consideration of bioavailability.

For Austrian waters, 123 samples passed through Tier 1 and into Tier 2, but this was reduced to just 37 samples after the use of the bioavailability assessment tool. The maximum sample-specific Mn PNEC for the Austrian dataset was 851 µg l^{-1} (pH 7.5, DOC 4 mg l^{-1} and Ca 85 mg l^{-1}).

Finally, for the Swedish dataset, 323 samples passed through Tier 1 to Tier 2 (i.e. the samples had a dissolved Mn concentration greater than 123 µg l^{-1}), but only 13 of these

samples remained after accounting for bioavailability with the bioavailability assessment tool. The maximum site-specific Mn PNEC for the Swedish dataset was 1,584 µg l^{-1} (pH 6.72, DOC 16 mg l^{-1} and Ca 39 mg l^{-1}).

Table 4.1 Indicative EQS compliance assessment for Mn using bioavailability assessment tool for matched site monitoring data from England and Wales, Austria, and Sweden

Country	Number of samples	Number of sites passing to Tier 2	Percentage of sites passing to Tier 2	Number of sites passing to Tier 3	Percentage of sites passing to Tier 3
England and Wales*	196	19	9.7	4	2.0
Austria	3,297	123	3.7	37	1.1
Sweden	3,928	323	8.2	13	0.3

*These data are representative of annual averages according to the WFD guidance (EC 2009).

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 MnBLM was developed. The bioavailability assessment tool mimics the MnBLM, 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.

The bioavailability assessment tool tends to overpredict Mn toxicity; only 1.2 percent of the predictions underpredict toxicity. Used within a tiered risk-based approach, this level of precaution is acceptable. Recent EU guidance (European Commission 2010) has endorsed the use of bioavailability assessment tools in this way for compliance and risk assessment.

An EQS compliance assessment for matched monitoring data from samples and sites in England and Wales, Sweden, and Austria used the bioavailability assessment tool to account for Mn bioavailability. The results of this assessment show that, at worst, only two percent of the 6,000 sites or samples considered exceed the Mn EQS of 123 µg l^{-1} after considering bioavailability.

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Glossary

AA	Annual average.
BioF	Bioavailability factor. The BioF is based on a comparison between the expected bioavailability at the reference site and that relating to site-specific conditions. Through the use of a BioF, differences in bioavailability are accounted for by adjustments to the monitoring data but the EQS remains the same. It is calculated by dividing the generic or reference $EC_{10}$by the calculated site-specific EC_{10}.
BLM	Biotic ligand model. This is a predictive tool that can account for variations in metal toxicity and calculates a site-specific PNEC using information on the chemistry of local water sources, that is, pH, calcium concentrations, hardness, dissolved organic carbon.
DOC	Dissolved organic carbon. The input to the bioavailability assessment tool for DOC should be site-specific median concentrations from at least eight sampling occasions. Default waterbody values of DOC are available for some waterbodies from the Environment Agency.
EQS	Environmental quality standard.
Extended BioF	Bioavailability factor derived from an extension of the BLM which covers extreme conditions (low pH and low hardness).
Generic EQS	Generic predicted no effect concentration, sometimes also termed the reference or generic EQS. This is representative of conditions of high bioavailability and is expressed as “bioavailable” metal concentration.
PEC	Predicted environmental concentration. These are usually replaced in the bioavailability assessment tool with measured environmental concentrations of dissolved manganese in the waters of interest.
PNEC	Predicted no effect concentration. This concentration is derived from ecotoxicological data and site-specific water quality data using BLM.
RCR	Risk characterisation ratio, also sometimes called the risk quotient. This is calculated by dividing the PEC by the PNEC. Values equal to or greater than one present a potential risk.
Bioavailability assessment tool	The bioavailability assessment tool is a simplified version of the BLM. It performs the same calculations as the BLM, but is run in MS Excel, requires fewer data inputs, and gives outputs that are precautionary relative to the full BLM but that are readily interpretable in the context of basic risk management and EQS compliance assessment.