WORKSHOP ON METAL BIOAVAILABILITY UNDER THE WATER FRAMEWORK DIRECTIVE: POLICY, SCIENCE AND IMPLEMENTATION OF REGULATORY TOOLS

DRAFT WORKSHOP REPORT

June 2011

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EXECUTIVE SUMMARY

The recent and positive SCHER Opinion[1] on the use and implementation of approaches to account for the bioavailability of metals in freshwaters, means that steps now need to be taken to prepare regulatory agencies to implement these approaches. Currently only a few Member States (MS) account for metal bioavailability in setting Environmental Quality Standards (EQS), permitting, or compliance assessment. These MS have often based their activity on Biotic Ligand Models, but several policy, technical, and practical questions remain in relation to the use of these tools within regulatory frameworks.

This one-day workshop, the first of its kind, provided experts from MS regulatory agencies with an opportunity to review the current state of knowledge on implementing bioavailability-based approaches for metals under the Water Framework Directive. Through the day, practical demonstrations and lessons from those MS that have trialled this approach were given and Member States posed questions and sought clarifications. Most importantly, all participants were provided with a User-friendly Biotic Ligand Model and charged with assessing the practicality of the methods using their own data and national approaches.

The conclusions from the workshop were that bioavailability needs to be accounted for in a regulatory context as it provides the most accurate, scientifically robust assessment of potential risks for metals such as copper, nickel, manganese and zinc. The approach can also be used to identify and prioritise sites, and for classification and communication purposes the method allows for only one $EQS_{bioavailable}$.

There is a requirement to improve monitoring coverage in freshwaters, especially for dissolved organic carbon and calcium, but also for dissolved metals. In addition to this support, there remains a need for sound practical advice for laboratories performing low level metal analyses.

There has been a great deal of progress in the development of the biotic ligand models in the last decade. Simplified and user-friendly models allow for implementation of approaches, but it must be made clear what the basis of these models is and how they relate to the full biotic ligand models. There are several approaches to the treatment of monitoring data that fall outside the validated ranges of the models and there is a need for best practice support to provide the context in which these decisions can be made.

Those Member States that have trialled the approach (France, The Netherlands and UK) suggest that there is generally a significant reduction in the exceedances of copper EQS, when compared with existing (often hardness-based) EQS. For zinc there are some declines in exceedances, but they tend to be less dramatic than for copper. However, what is important is that the location of exceedances changes when account is taken of bioavailability when compared with existing EQS based on alternative metrics. For example, in the UK many softwaters in Wales would have been described as the most sensitive waters for metal

[1] http://ec.europa.eu/health/scientific_committees/environmental_risks/docs/scher_o_127.pdf

exposures as based on hardness EQS. In fact these waters often have relatively high dissolved organic carbon and therefore the metals present limited risk. However, the calcareous streams of southern England, where water is relatively hard, would not have been identified as potentially at risk. Yet these waters have very low DOC and high pH and are in fact very sensitive to metal additions.

Compliance and classification approaches are straightforward to undertake using this new approach. Permitting is often based on total loads and BAT and the use of bioavailabilty for this remains challenging.

Member States are encouraged to trial the approach using their own data in their own systems. It is possible to automate the tools within laboratory systems. An additional discussion may be held prior to Working Group E in October 2011.

This report is a record of a meeting held on the 21st of June 2011.

CONTENTS

GLOSSARY

AA	Annual average.
BioF	The 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 (bio)availability are accounted for by adjustments to the monitoring data, but the EQS remains the same. BioF is calculated by dividing the Generic or Reference $EQS_{bioavailable}$ by the calculated site-specific dissolved EQS.
BLM	Biotic Ligand Model. This is a predictive tool that can account for variation in metal toxicity and calculates a site-specific PNEC using information on the chemistry of local water sources, i.e. pH, dissolved organic carbon, etc.
DOC	Dissolved organic carbon. The input to the screening tool for DOC should be site-specific median concentrations from at least eight sampling occasions. This is because metal EQS are expressed as AA concentrations, and the short-term EQS or Maximum Allowable Concentrations are not relevant here.
Generic EQS	Generic EQS or reference 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 User-friendly BLM tool with measured and monitored environmental concentrations of dissolved metals.
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 1 present a potential risk.
User-friendly BLM Tool	The User-friendly tool mimics the BLM outputs in a precautionary way. It requires relatively few inputs and can readily be used in a compliance assessment framework.

1 INTRODUCTION

This document presents the outcomes of a workshop held on the 21st of June 2011 at a Commission venue attended by 58 delegates representing 18 European administrations. The Environmental Quality Standard (EQS) Directive (2008/105/EC) suggests that when Member States are assessing monitoring results against an EQS account can be taken of:

- natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value; and
- hardness, pH or other water quality parameters that affect the bioavailability of metals.

This workshop was specifically aimed at exploring regulatory experiences in relation to these bullet points and providing an open and transparent forum in which the advantages and remaining challenges of taking a bioavailability-based approach for metals could be presented.

1.1 Aims and Objectives of the workshop

The aim of this workshop was to bring together representatives from Member State competent authorities with responsibility for the policy context, technical appraisal, and monitoring and assessment of metal EQS. The workshop opening acknowledged that different personnel from different backgrounds and with different information needs are required to implement a bioavailability-based approach that is compliant with the needs of the Water Framework Directive.

The key aim of the workshop was to provide an opportunity for MS representatives to share their experiences of implementing bioavailability-based approaches for metals. The workshop provided opportunity for open discussion on the steps that need to be taken to meet the needs of the Directive and to deliver a practical and transparent methodology to account for bioavailability.

The objectives and topics of the workshop are aimed at providing clarity on how bioavailability may be implemented and to provide an outline for the writing of practical guidance. The participants' tasks were to evaluate the information given, identify any reasonable concerns and suggest practical ways to overcome any outstanding issues. There remain challenges with the approach and these are openly identified in this report.

1.2 Workshop and Report Structure.

The one-day workshop was structured so that, in the morning, presentations outlining the key areas of the policy, technical and implementation issues were provided (Appendix 1). These presentations were followed by questions.

In the afternoon, the participants were allocated to one of three breakout groups - policy, technical or implementation. These groups were chaired and the initial breakout questions were provided at the start of the day, although any questions could be posed and discussed. At the start of each of the breakout sessions a demonstration of the User-friendly BLM tool was provided. The tool was provided to each participant on a memory stick.

One of the breakout group members made notes of the discussions, questions and agreements on a flip chart, which was then used as an aide memoire at a plenary session at the end of the afternoon, before a final summing up. The agenda for the day is provided in Appendix 3.

This report provides a summary of the day's discussion with all of the morning's presentations given in Appendix 1. A sheet of Frequently Asked Questions (Appendix 2), developed and circulated before the Workshop, has been developed further to include questions asked in the morning session and those questions received by email.

In addition, Section 2 provides an outline of the demonstration of the User-friendly BLM. Section 3 gives the summaries of the breakout groups, and flags key areas of agreement and highlights concerns and topics requiring greater input to ensure consistency and understanding. Meeting conclusions are given in Section 5 and Recommendations and next steps are provided in Section 6.

2 HOW CAN THE BIOAVAILABILITY APPROACH BE USED?

The term "bioavailability" used in this report, as outlined in the Policy Presentation at the Workshop (Appendix 1), can be considered to be:

…….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 is the exposure that the organisms experience in the water column.

The technical foundations and key scientific concepts behind the development of the biotic ligand models are given in the technical presentation in Appendix 1. It has long been established that measurements of total metal in waters have limited relevance to potential environmental risk (Campbell 1995; Niyogi and Wood 2004). In addition to the poor predictive capability of total metal measurements, it has also been demonstrated that existing "hardness-based" EQS are also poor for assessing copper (Cu), nickel (Ni) and zinc (Zn) aquatic toxicity (ECI 2007; The Netherlands 2008).

There are currently chronic biotic ligand models and user-friendly tools for Cu, Ni, Mn and Zn. The Excel™ model provided to participants at the workshop (Biomet Tool_Spreadsheet_Workshop_170611) is based upon the chronic biotic ligand models for Cu, Ni and Zn. The development of the user-friendly tools is also discussed in the technical presentation (Appendix 1) and is also described in regulatory reports[2].

It should be stressed that the use of biotic ligand models may not be the *only* approach through which account can be taken of mitigating effects of water physico-chemical conditions on chronic metal exposures. Indeed, for cadmium a hardness correction is available and the new draft WFD EQS proposal for Pb[3] provides a mechanism for DOC correction. This latter approach is also currently used in The Netherlands for several metals (Appendix 1, Policy Presentation).

A demonstration of the Excel-based User-friendly BLM for Cu, Ni and Zn was given to each of the breakout groups at the workshop. The sections below give an outline of how the tool runs, the required inputs, the outputs and the interpretation of these data using the same example dataset as discussed at the meeting.

2.1 Using the User-friendly BLM.

The User-friendly BLMs have been developed in order to facilitate regulatory use. The models on which these user-friendly versions are based are complex, have relatively long run times per sample, require a great deal of input data (<14 individual input parameters), and have a

[2] http://publications.environment-agency.gov.uk/PDF/SCHO0209BPJI-E-E.pdf
[3] http://ec.europa.eu/health/scientific_committees/environmental_risks/docs/scher_o_136.pdf

requirement for a high level of operator skill to interpret the outputs. The User-friendly BLM has been developed to provide a fit-for-purpose tool to allow regulatory compliance assessment, classification and site prioritisation that can run in Excel™ or, if required, be automated into laboratory information systems (as is currently done by the Environment Agency of England and Wales).

In order to make the model run from a memory stick, double click on the icon and the screen shown in Figure 2.1 will appear. It is imperative if the model is to function that the content is enabled – this will require clicking on the 'Options' box circled in the figure and enabling the macros.

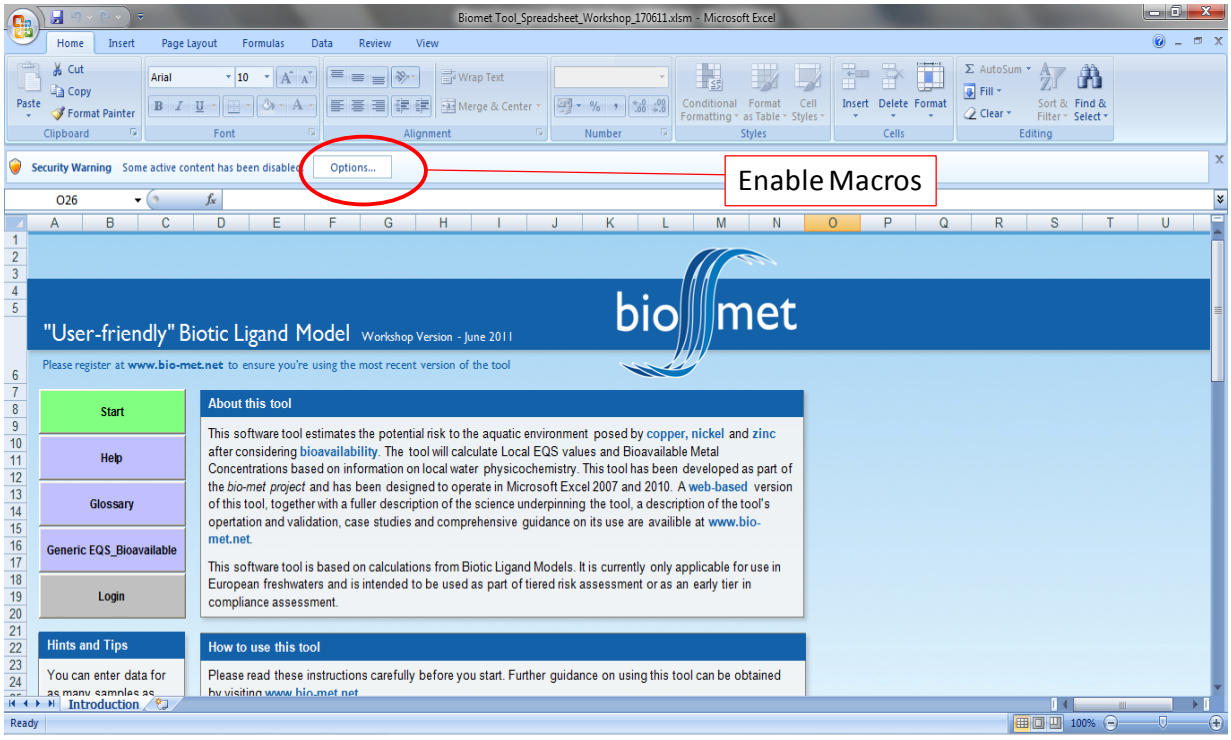


Figure 2.1 The first screen of the User-friendly BLM

The front page of the tool provides a description of the tool, and instruction on how to use it. In the left hand bar there are several buttons that could be helpful, including a glossary of terms and a list of the generic EQS used in the tool. These EQS are $EQS_{bioavailable}$, and are derived under physico-chemical conditions of very high bioavailability. For Ni the current value in the tool is 2 µg l^{-1}, but this has yet to be finalised at the Commission level. The values for Cu (1 µg l^{-1}) and Zn (10.9 µg l^{-1}) are those proposed by the UK as Specific Pollutants.

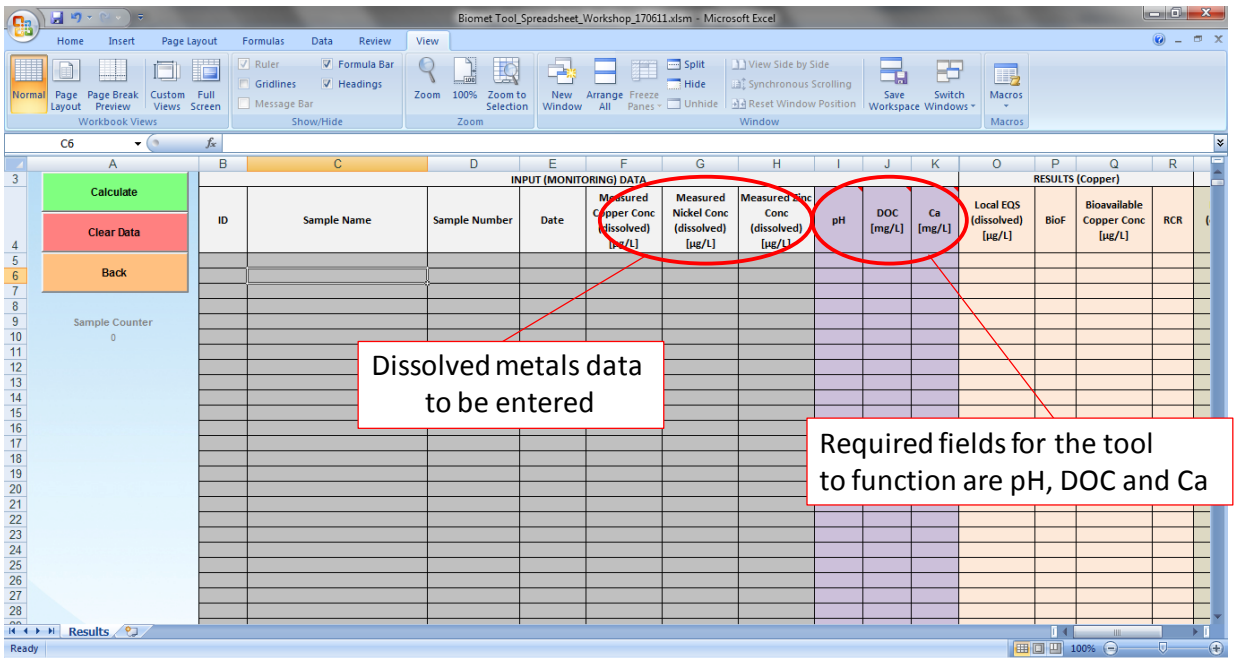


Figure 2.2 Required fields to run the tool

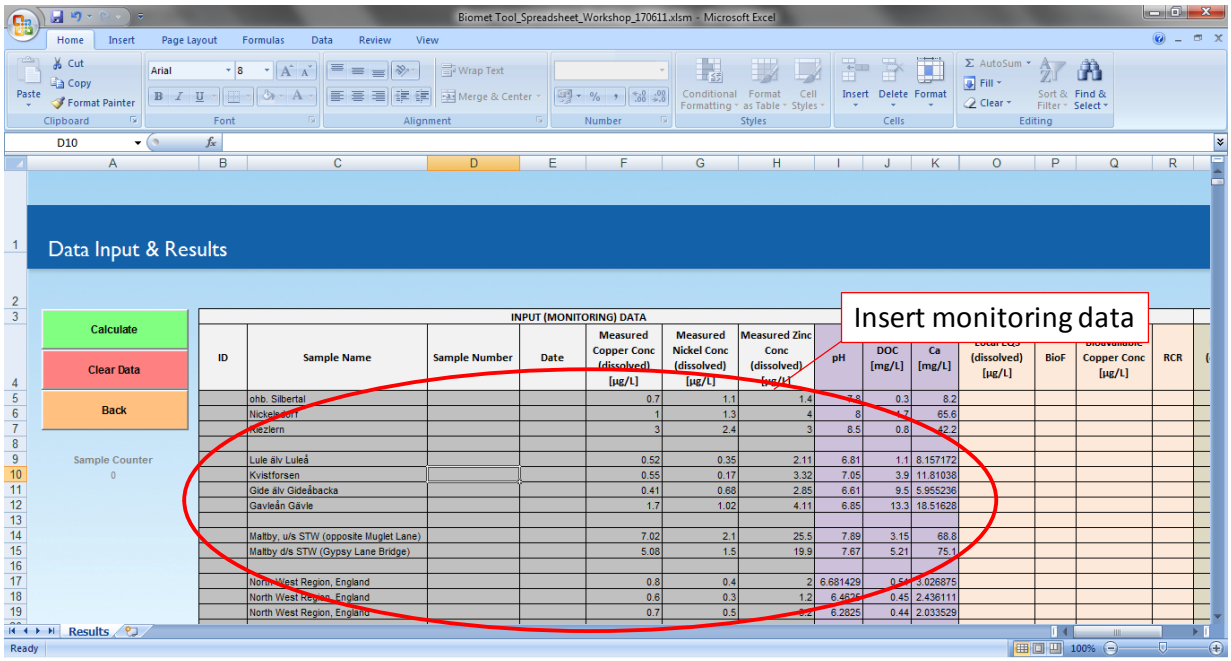


Figure 2.3 Data entered into the tool prior to pressing the 'calculate' button

On clicking the 'Start' button the user is taken to the screen in Figure 2.2. The required fields to run the model are circled in the figure: matched waterbody or site annual average pH, dissolved Ca and annual median dissolved organic carbon (Section 3.3). If just these data are entered

without the dissolved metal concentrations, the User-friendly BLM will effectively perform a hazard assessment. Such an assessment can be used to identify sites or waterbodies that would be sensitive to specific metal exposures.

Figure 2.3 shows the tool when the required data fields are filled, and the dissolved metal concentrations. The data shown as examples in the Figure are from sites in Austria, Sweden and the UK.

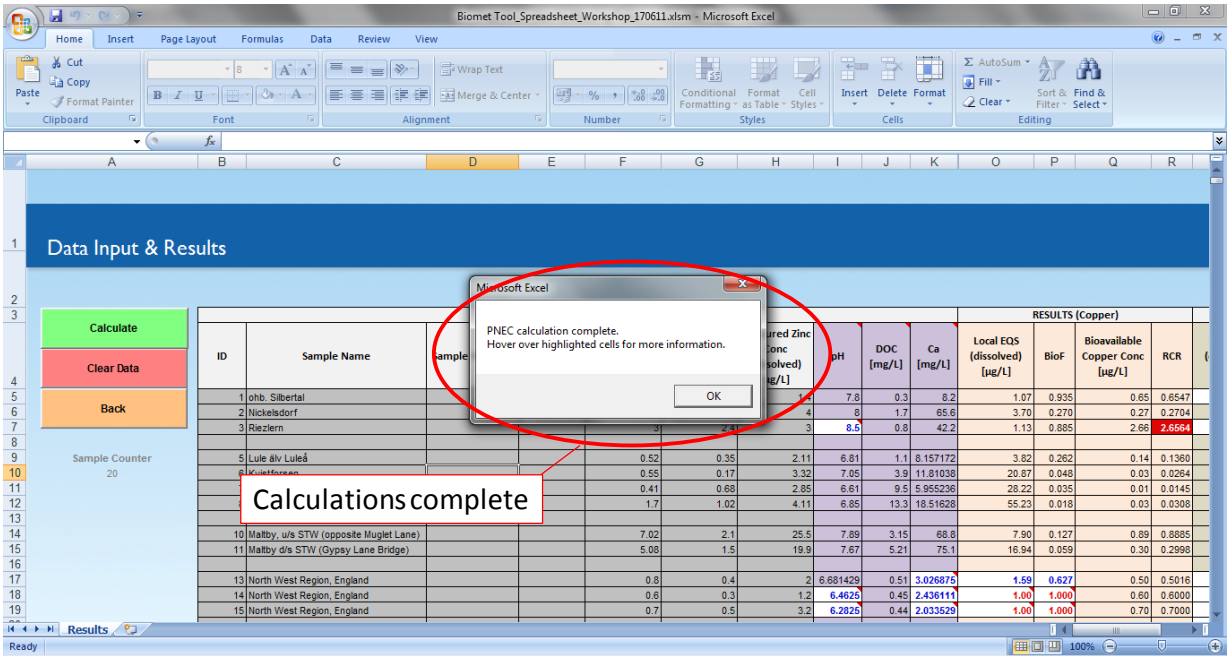


Figure 2.4 The screen seen once the calculations are complete

Once the 'calculate' button has been pressed the tool begins to populate the fields to the right of the required fields, one row at a time. When the calculations are complete the message shown in Figure 2.4 shows.

2.2 What do the outputs from the User-friendly tool mean?

Once the calculations are complete some of the required fields have white cell backgrounds and are marked in blue text. There are comments boxes (or flags) in the top right corner of these cells. Figure 2.5 shows the screen that will be seen once the calculations have been completed. The flags are shown by hovering over the red triangle with the cursor, as seen in Figure 2.5. The flag is identifying that the data entered for pH is above the validated range from the full biotic ligand models for Zn and Ni, but not Cu. The calculations have been performed by keeping the pH values within the validated range, and the flag states that the results for these metals, for this row of data, should be treated with caution.

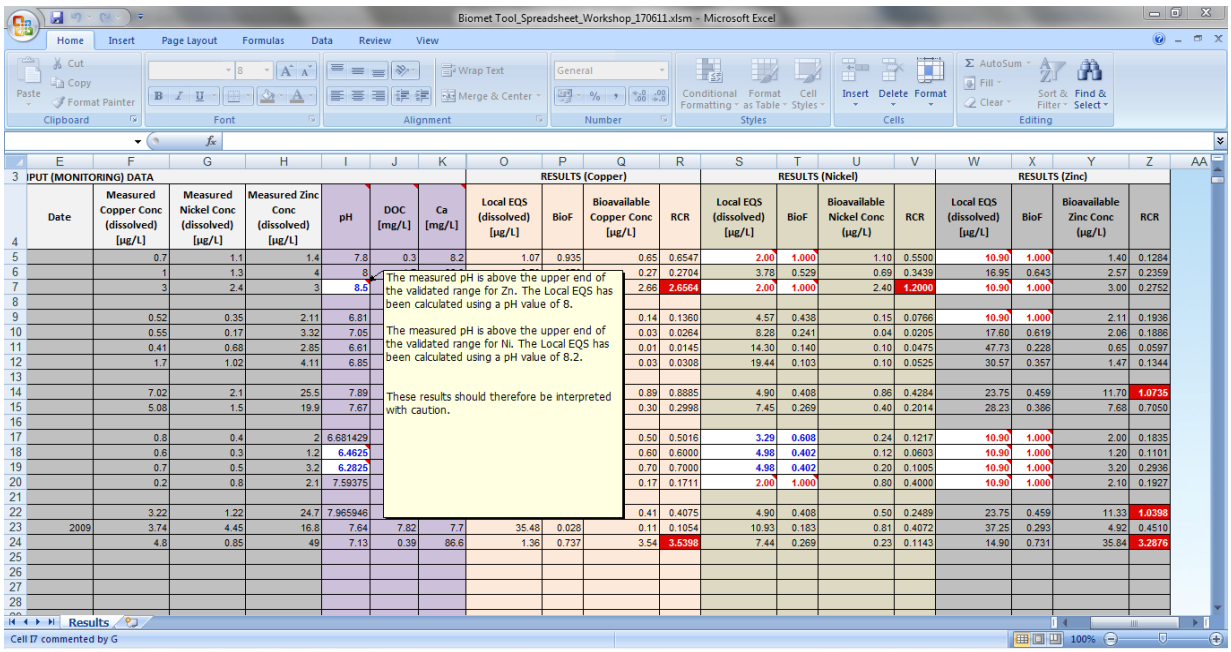


Figure 2.5 The screen seen once the calculations are complete

Data in the other required fields marked with blue text are also flagged, and outside the validated range of the full biotic ligand model for the metals noted in the flags. The columns to the right of the required fields for all the metals are headed individually:

Local EQS (dissolved) (µg l^{-1}) – this is the calculated dissolved concentration of metal that is equivalent the $EQS_{bioavailabe}$ at the local water conditions at the site. Where this value is in red text with flag this represents sensitive conditions and high bioavailability. Where this value is in blue text it is calculated from data that is outside the validated range of the BLM for that specific metal.

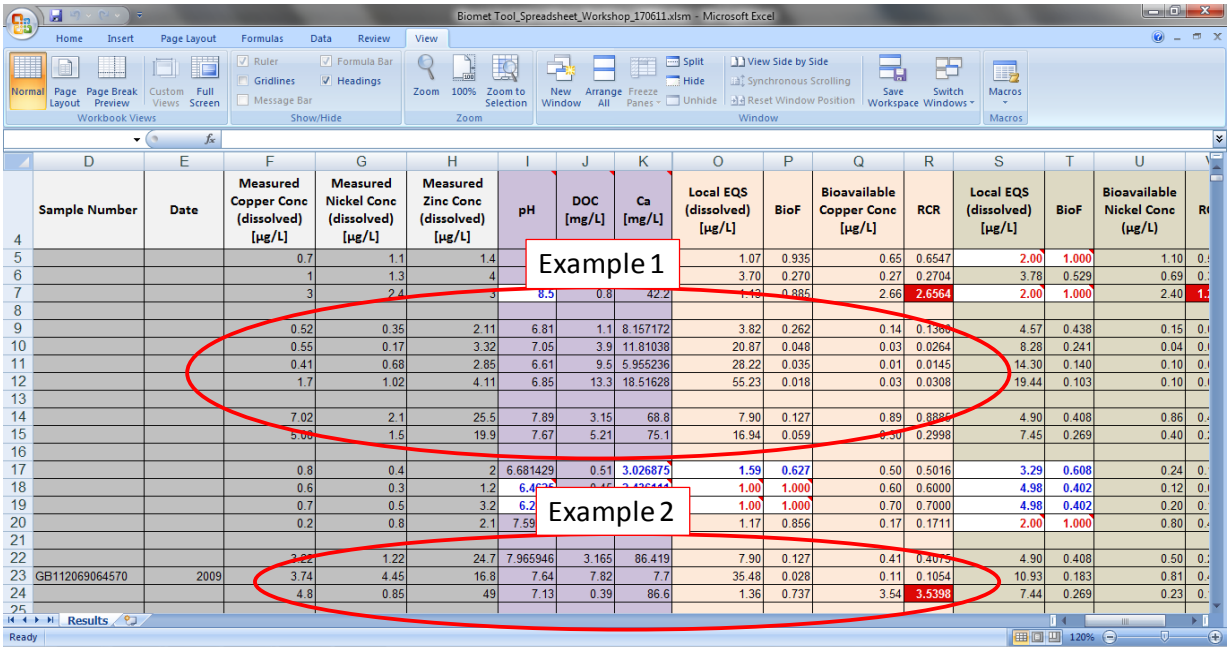
BioF - is the ratio of the generic $EQS_{bioavailable}$ divided by the local EQS. This value is always 1 or less. When the value is 1, it is marked in red text and effectively means the metal in the specific water conditions at this site is 100% bioavailable and the site is relatively sensitive.

Bioavailable metal concentration (µg l^{-1}) – this is the concentration of metal that is bioavailable at the site or waterbody. This value is calculated by multiplying the dissolved metal concentration for the site by the BioF.

RCR - is the risk characterisation ratio for the site or waterbody under consideration. A value of 1 or greater identifies a potential risk. Under these circumstances the cell is red and the text white. These last two columns are not available when no dissolved metal data are available.

Figure 2.6 shows the results for some of the data for Cu (a magnified version of part of Figure 2.5). Copper has been chosen simply out of convenience as it is easy to see, being closest to

the required fields. Two examples are given, illustrating two important points that are developed further in the breakout groups and have been noted by those Member States that have trialled the bioavailability-based approaches.



	D	E	F	G	H	I	J	K	O	P	Q	R	S	T	U
4	Sample Number	Date	Measured Copper Conc (dissolved) [µg/L]	Measured Nickel Conc (dissolved) [µg/L]	Measured Zinc Conc (dissolved) [µg/L]	pH	DOC [mg/L]	Ca [mg/L]	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Copper Conc [µg/L]	RCR	Local EQS (dissolved) [µg/L]	BioF	Bioavailable Nickel Conc (µg/L)
5			0.7	1.1	1.4				1.07	0.935	0.65	0.6547	2.00	1.000	1.10
6			1	1.3	4				3.70	0.270	0.27	0.2704	3.78	0.529	0.69
7			3	2.4	3	8.5	0.8	42.2	1.13	0.885	2.66	2.6564	2.00	1.000	2.40
8															
9			0.52	0.35	2.11	6.81	1.1	8.157172	3.82	0.262	0.14	0.1366	4.57	0.438	0.15
10			0.55	0.17	3.32	7.05	3.9	11.81038	20.87	0.048	0.03	0.0264	8.28	0.241	0.04
11			0.41	0.68	2.85	6.61	9.5	5.955236	28.22	0.035	0.01	0.0145	14.30	0.140	0.10
12			1.7	1.02	4.11	6.85	13.3	18.51628	55.23	0.018	0.03	0.0308	19.44	0.103	0.10
13															
14			7.02	2.1	25.5	7.89	3.15	68.8	7.90	0.127	0.89	0.8886	4.90	0.408	0.86
15			5.06	1.5	19.9	7.67	5.21	75.1	16.94	0.059	0.30	0.2998	7.45	0.269	0.40
16															
17			0.8	0.4	2	6.681429	0.51	3.026875	1.59	0.627	0.50	0.5016	3.29	0.608	0.24
18			0.6	0.3	1.2	6.4			1.00	1.000	0.60	0.6000	4.98	0.402	0.12
19			0.7	0.5	3.2	6.2			1.00	1.000	0.70	0.7000	4.98	0.402	0.20
20			0.2	0.8	2.1	7.59			1.17	0.856	0.17	0.1711	2.00	1.000	0.80
21															
22			3.22	1.22	24.7	7.965946	3.165	86.419	7.90	0.127	0.41	0.4075	4.90	0.408	0.50
23	GB112069064570	2009	3.74	4.45	16.8	7.64	7.82	7.7	35.48	0.028	0.11	0.1054	10.93	0.183	0.81
24			4.8	0.85	49	7.13	0.39	86.6	1.36	0.737	3.54	3.5398	7.44	0.269	0.23
25															

Figure 2.6 The results for Cu for two examples from the dataset run at the Workshop

Example 1 illustrates the effect upon Cu bioavailability of increasing DOC. The sites in rows 9 through 12 have similar pH and Ca concentrations, but DOC increases from 1.1 mg l^{-1} to 13.3 mg l^{-1}. The Cu exposures (i.e. the measured dissolved Cu concentrations) at these sites are relatively low, but the change in bioavailability conditions due to the DOC can be noted from the change in BioF. Effectively, the bioavailability is >20% available when the DOC is at its lowest, but decreases to less than 2% when DOC reaches a maximum.

Example 2, specifically rows 23 and 24, shows how accounting for bioavailability and not just hardness can change the picture of compliance. The data in row 23 under existing hardness-based standards would have been identified as softwater and would have the lowest EQS for Cu applied - a value of 1 µg l^{-1} in the UK. This site would therefore have exceeded the Cu EQS and been identified as non-compliant. However, when bioavailability is taken into account this site clearly presents no risk and is not an exceedance. The data presented in row 24 is the opposite, in that the waters are relatively hard and would, under the hardness-based EQS, have attracted an EQS of 28 µg l^{-1} and therefore not been identified as presenting a potential risk for Cu. However, when bioavailability is taken into account it is clear that at this site there is a potential risk from Cu. The change in the compliance picture when accounting for bioavailability, both in terms of scale and location of exceedances, is readily illustrated with these two examples.

2.3 The Hardness Conversion Tool

A Hardness Conversion Tool has also been developed because the User Friendly BLM uses input data for Ca, rather than for hardness. In cases where hardness data are available the tool can be used to calculate the equivalent concentration of Ca at the water hardness. This calculation takes into account the fact that both Ca and Mg contribute to hardness, and that it is only the Ca component that is used for the BLM input. A contribution from Mg is calculated assuming that the ratio between Ca and Mg concentrations is as identified by Peters et al. (2011)[4].

The tool will convert input water hardness data, expressed in a variety of units, into an equivalent Ca concentration, in units of mg l^{-1}. This data can then be used as input data for the User-friendly BLM. Basic background information on the tool and its use is provided on the introduction sheet (Figure 2.7).

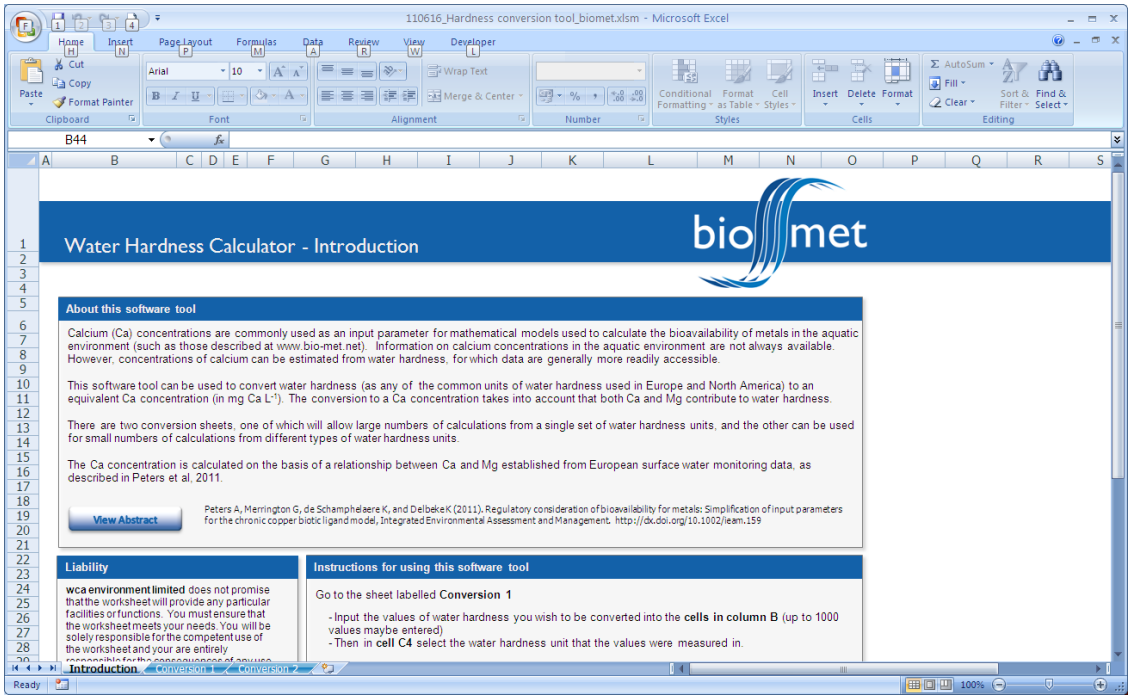


Figure 2.7 Introductory sheet of the Hardness Conversion Tool

Hardness data, expressed as mg l^{-1} of $CaCO_3$, CaO, or Ca, as degrees of hardness (English, French, German, and USA), or as moles per litre can be converted into an equivalent Ca concentration (in mg l^{-1}). Large numbers of samples which are all expressed in the same hardness units can be processed on the first conversion sheet (Figure 2.8), and the second

[4] Peters A, Merrington G, Delbeke K, de Schamphelaere K. 2011. Regulatory consideration of bioavailability for metals: Simplification of input parameters for the chronic copper Biotic Ligand Model. Integrated Environmental Assessment and Management 7:437-444.

conversion sheet can be used for small numbers of samples which are expressed in different hardness units.

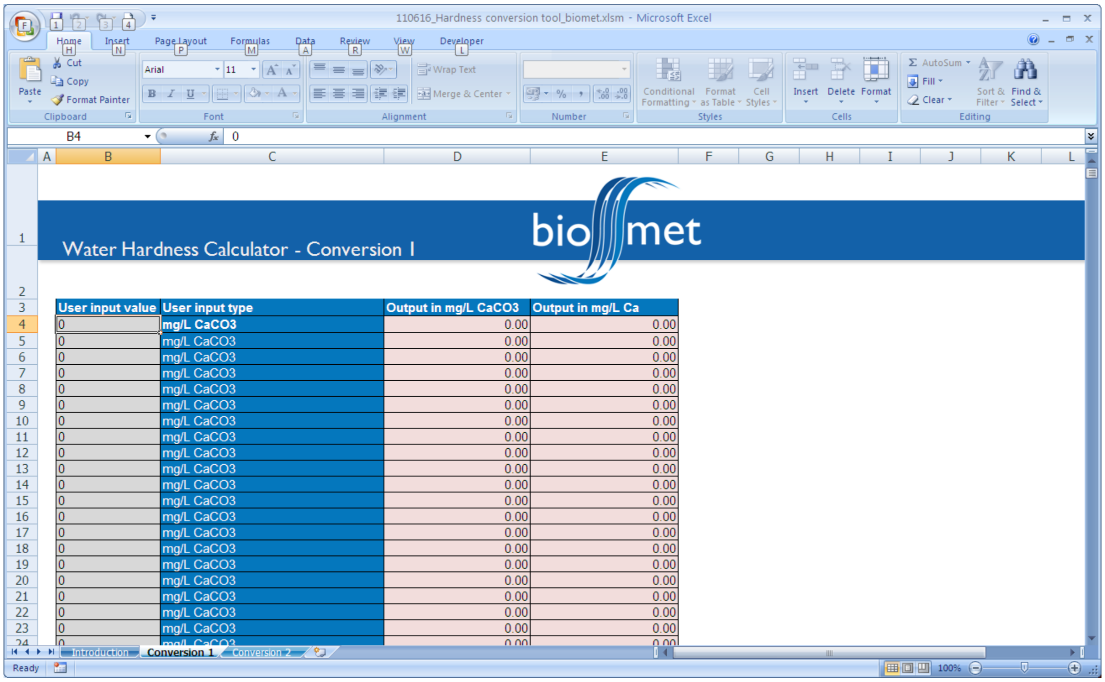
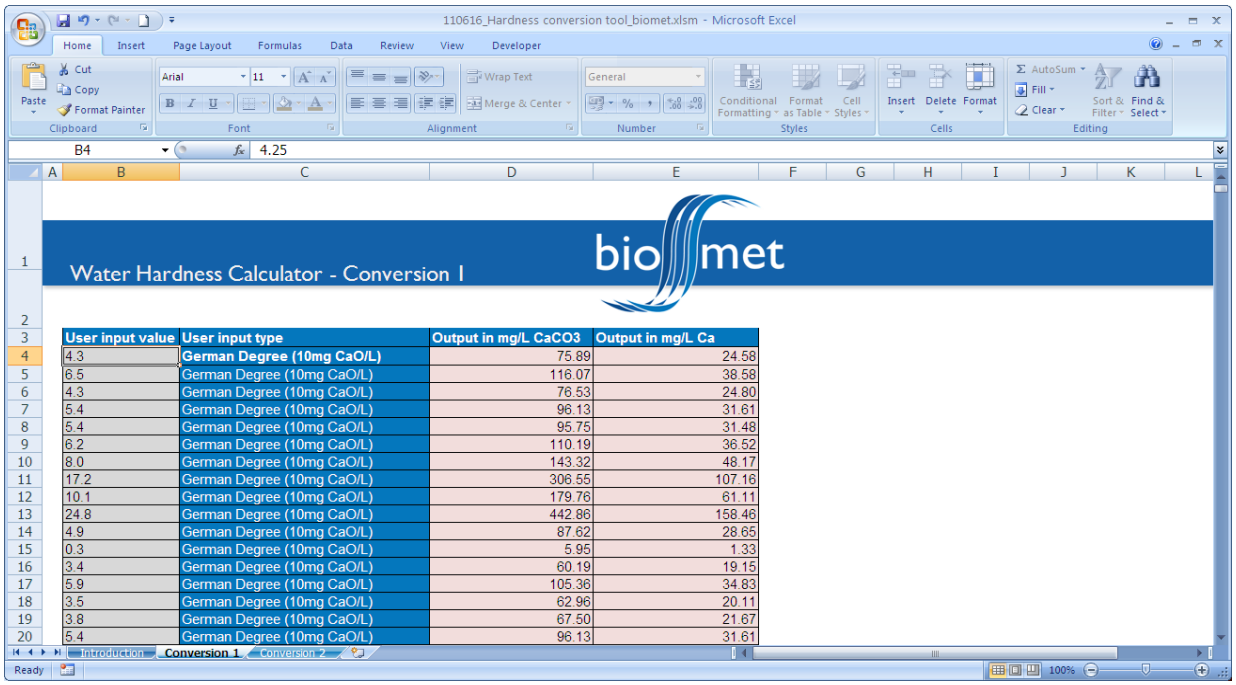


Figure 2.8 Conversion sheet of the Hardness Calculator Tool

Data is pasted into the column (User Input Data), and the correct unit used for the input hardness data is selected from the drop down list in cell C4 (below Use Input Type).



User input value	User input type	Output in mg/L CaCO3	Output in mg/L Ca
4.3	German Degree (10mg CaO/L)	75.89	24.58
6.5	German Degree (10mg CaO/L)	116.07	38.58
4.3	German Degree (10mg CaO/L)	76.53	24.80
5.4	German Degree (10mg CaO/L)	96.13	31.61
5.4	German Degree (10mg CaO/L)	95.75	31.48
6.2	German Degree (10mg CaO/L)	110.19	36.52
8.0	German Degree (10mg CaO/L)	143.32	48.17
17.2	German Degree (10mg CaO/L)	306.55	107.16
10.1	German Degree (10mg CaO/L)	179.76	61.11
24.8	German Degree (10mg CaO/L)	442.86	158.46
4.9	German Degree (10mg CaO/L)	87.62	28.65
0.3	German Degree (10mg CaO/L)	5.95	1.33
3.4	German Degree (10mg CaO/L)	60.19	19.15
5.9	German Degree (10mg CaO/L)	105.36	34.83
3.5	German Degree (10mg CaO/L)	62.96	20.11
3.8	German Degree (10mg CaO/L)	67.50	21.67
5.4	German Degree (10mg CaO/L)	96.13	31.61

Figure 2.9 Introductory sheet of the Hardness Conversion Tool

The tool converts the input data (expressed as hardness in German Degrees in the Figure 2.9) to mg l^{-1} $CaCO_3$, and also into an equivalent Ca concentration. This equivalent Ca concentration takes account of the fact that both Ca and Mg contribute to hardness.

2.4 DOC input data

Input data for DOC is required for BLM calculations to be performed. DOC is a particularly important factor in the bioavailability modification of metals in freshwaters. Information on measured DOC concentrations in the watercourses is always preferable, but in some cases where no information is already available on DOC concentrations for a specific site other approaches can be taken to provide an indication of bioavailability and better inform whether or not any action needs to be taken, e.g. to measure DOC concentrations.

DOC information for other sampling locations within the same waterbody, or surrounding waterbodies, may be able to provide an indication of the local concentrations. In these cases it is recommended to take a relatively low percentile, e.g. the 25th percentile[5], of the monitoring data in order to ensure that the resulting value is unlikely to be under protective.

DOC concentrations can also be estimated from UV absorbance data and dissolved iron concentrations. These methods are less accurate, but may allow screening level assessment to

[5] Merrington G, Peters A, Brown B, Delbeke K, van Assche F, Sturdy L, Waeterschoot H, Batty J. 2008. The use of biotic ligand models in regulation: the development of simplified screening models and default water parameters. Paper presented at SETAC World Congress, Sydney, August 3-7th.

be undertaken in cases where this information is available to inform the development of monitoring programmes for DOC data, by highlighting areas where it is of the greatest importance. Equations 1 and 2 relate dissolved iron concentrations to DOC concentrations from the data shown in Figure 2.10.

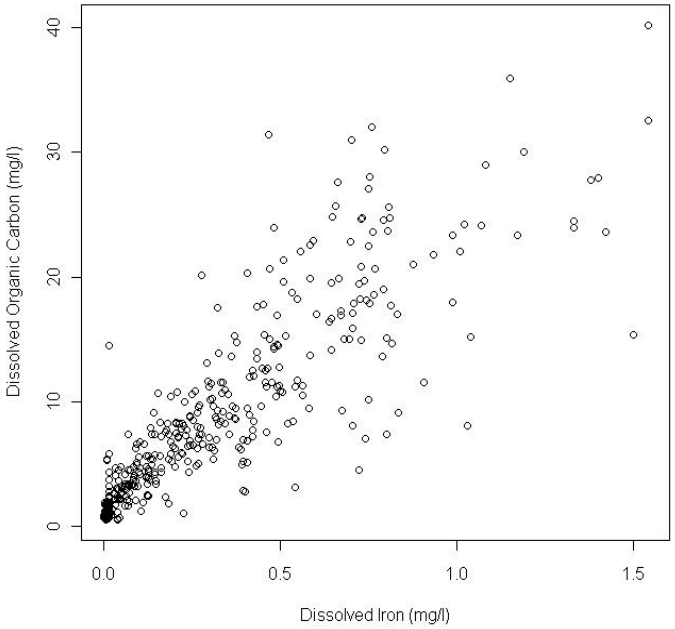


Figure 2.10 Relationship between dissolved iron and dissolved organic carbon (from 407 samples from England, Scotland and Wales).

$DOC\ (mg\ l^{-1}) = 20.79\ .\ Fe\ (dissolved,\ mg\ l^{-1}) + 2.32$ $r^2 = 0.738$ Eq. 1

$\log_{10}(DOC,\ mg\ l^{-1}) = 0.56\ .\ \log_{10}(Fe,\ dissolved,mg\ l^{-1}) + 1.24$ $r^2 = 0.781$ Eq. 2

2.5 Summarising input data for calculations

The Generic $EQS_{Bioavailable}$ is expressed as an annual average concentration. It is possible to calculate bioavailability for each sample and calculate the annual average of the bioavailable metal concentration, or alternatively it is possible to summarise the input data to calculate an average bioavailability factor. The two approaches result in very similar results where the same input information is used.

The calculation of bioavailability for each sampling occasion is often considered to be preferable, but may only be possible where all of the required parameters are analysed for the same samples. If samples for metals and the supporting parameters are taken at different times then calculation in this way may not be appropriate.

Averaging of input parameters may be chosen for several reasons. In some cases samples may only be taken 4 times per year for some supporting parameters, and averaging data from

multiple years may provide a better indication of the "average" conditions. A missing result for a single determinand may prevent calculation of the bioavailability for a given sample, but is less important overall when taken as part of an average. This approach may therefore be more tolerant of minor problems in the sampling and analysis procedure which may result in the occasional loss of data.

Where average values are used for the input parameters it is appropriate to consider how the data are summarised to provide the average values. The number of samples used and time period over which they were taken need to be defined, as well as the location, or locations, which are used. In addition, whist an arithmetic mean may be used for dissolved metal concentrations this may tend to overestimate the "average" situation if the exposure follows a log-normal distribution. The arithmetic mean is usually appropriate for pH (which is already log transformed), and Ca concentrations which are often relatively consistent over time for a given location. It is recommended that median (50^{th} percentile) DOC concentrations are used rather than artithmetic means because this will better represent the "average" concentration if the distribution of concentrations is log-normal, whereas an arithmetic mean may result in overestimation of the average DOC concentration.

2.6 Dealing with sites which lie outside the boundary conditions of the BLMs

This subsection provides some considerations on how to deal with sites where the water chemistry conditions are outside the applicability range of the BLMs. An important factor in this issue is whether or not elevated exposures occur at the sites, because bioavailability normalisation is only likely to be required where dissolved metal concentrations are at, or above, the Generic $EQS_{Bioavailable}$. Only in these cases is the question of the applicability of the BLM likely to be important.

No boundaries are set for DOC concentrations because this only affects the exposure of the organisms to available metals, but boundaries are set for both pH and Ca, which both affect uptake and binding at the biotic ligand, and are physiologically important for aquatic organisms. The boundaries which commonly cause surface waters to be outwith the applicability range of the BLMs are hard waters (high Ca concentrations), where the Ca concentration may exceed the BLM application range, and soft waters where the Ca concentration is below the applicability range of the BLM. Low pH may also cause waters to be outwith the applicable range of the BLMs, and in some instances both low pH and low Ca may be encountered in the same waters.

Hard waters, where the Ca concentration exceeds the BLM application range, especially for the Ni BLM, can be treated relatively easily. The upper limit to the applicable range of Ca concentrations exists because there is a limit to the protective effect from Ca as a competitor for binding sites on the "Biotic Ligand", and increases in Ca concentrations do not result in further reductions in metal bioavailability. This situation can be adequately handled by limiting

the input data to the maximum allowable Ca concentration, and BLM predictions performed by doing so should continue to be reliable.

In contrast, the boundaries established for soft, acid waters occur because the majority of test organisms used for BLM development are unable to survive and reproduce adequately under the relatively extreme conditions. These water quality conditions may support different species than those found in harder water, higher pH environments. Protons (H^+) and Ca ions may both compete with metals for binding sites at the biotic ligand. As pH decreases the competition from protons will increase (resulting in lower metal bioavailability), whereas as hardness decreases the competition from Ca will decrease (resulting in higher metal bioavailability). The relative importance of competition from protons and Ca for each individual metal may affect organism responses under these conditions. A reduction in pH may also result in a decrease in metal binding to DOC, due to increased competition from protons, resulting in increased metal bioavailability. Changes in pH can also result in changes to the inorganic speciation of a metal, and the fraction which exists as bioavailable species (e.g. Cu^{2+}), although significant changes in speciation around the lower pH limit for the BLMs are unlikely for Cu, Ni, and Zn.

Several options for treating conditions which are outwith the applicability range of the BLMs were discussed in the breakout group on technical issues, and five possible approaches suggested.

1. Consider 100% bioavailability of the metal (i.e. apply the Generic $EQS_{Bioavailable}$)
2. Assume model predictions still apply outside boundary conditions
3. Extrapolation (e.g.consider complexation of metal by DOC only)
4. Bioassays (including ecotox tests, WER, and ecological community monitoring)
5. Use specific local EQS

The first option applies the Generic $EQS_{Bioavailable}$ outside the applicable conditions, and can effectively result in a step change to the standard where the boundary conditions are exceeded. The second option applies the BLMs and assumes that no boundary conditions apply and that the models can be extrapolated beyond their validated range. This approach cannot be applied with the User Friendly BLM used at the workshop as the input values are capped at the validated range, although it can be applied using the full models. This results in increasing predicted sensitivity with decreasing Ca concentrations, and an order of magnitude reduction in Ca concentrations (e.g. from 5 to 0.5 mg l^{-1}) will result in an order of magnitude increase in the predicted sensitivity. BLM development experiments suggest that there may be an intrinsic sensitivity at "infinite dilution", which is not consistent with these predictions. Under high hardness conditions the BLMs may underestimate the bioavailability by assuming an increased competitive effect from Ca, which would also not be observed. Use of the full BLM models

outside of the boundary conditions that they have been validated for must therefore be undertaken with considerable caution.

Extrapolation beyond the applicable range of the BLM to take account of chemical availability, i.e. accounting for DOC complexation of the metal, outside of the application range of the BLMs may represent a pragmatic solution in some cases. The low pH and Ca concentrations may have physiological implications for interactions at the biotic ligand, but have very predictable effects on metal complexation by DOC, which typically the most important factor in bioavailability modification. As the degree of metal complexation by DOC can be predicted this could be taken into account in establishing the localised BIOF, or localised EQS. An extension of the user-friendly BLM based on this approach has been proposed for use in the UK.

Bioassays provide a means of validating any predictions or assumptions that are made about the protection of aquatic ecosystems in relatively extreme environments. Water Effect Ratios, which compare the results of toxicity tests in locally collected water and standardised water have been used in the US. These tests use a Water Effects Ratio to correct the EQS under standard conditions to the local EQS. Such tests would need to use test species which are appropriate to the water chemistry conditions of the local surface waters. Ecological monitoring will be performed under the WFD and may provide a means to ensure that any deterioration in ecological quality can be identified, where there is uncertainty in the adequacy of an EQS for relatively extreme environmental conditions. The use of additional biological monitoring may be valuable in supporting the application of the standards under potentially sensitive conditions.

An example of a specific EQS would be the $PNEC_{softwater}$ for Zn which was derived for the Existing Substances Regulations Risk Assessment Report on Zinc and Zinc compounds[6], although other approaches to developing specific localised standards may be more appropriate.

[6] http://ecb.jrc.ec.europa.eu/risk-assessment/REPORT/zincmetalreport072.pdf

3 REPORTS FROM BREAKOUT GROUPS

Breakout groups were used at the workshop in order to further develop and discuss issues under the three main subject areas of policy, technical and implementation in relation to the adoption of bioavailability-based approaches. The participants in each group were initially randomly allocated to a particular group, to ensure an even split of people within groups, but all participants were given an opportunity to change groups prior the beginning of the afternoon session. Each breakout group was assigned a separate room, and following the demonstration of the tool, as outlined in the previous section, each of the groups discussed key topics about the approach.

The following subsections provide an outline of the discussions in each group, the group participants, and a short list of breakout questions that were used to start the discussion. These questions were not viewed as exhaustive, as can be seen from many of the issues raised. The chairs for each of the groups are underlined in the participant list.

3.1 Policy issues related to implementation of bioavailability-based approaches for metals

Group participants:

Sandrine Andres, John Batty, Flemming Ingerslev, Jeroen Vanhooren, Zdenka Kelnarova, Caroline Latour, Enn Liive, Gerrit Niebeek, Mark Owen, Alfred Rauchbüchl, Jorge Rodríquez Romero, Reet Talkop, Joanne Vassallo, Friederike Vietoris, Caroline Whalley, Araceli Zorrilla Quinzá

The following questions were provided to start the discussions:

- Policy context: why use bioavailability to assess metals compliance? Classification and permitting issues.
- How can the method/approach be included in national legislation?
- Communication of messages – the changing compliance picture?
- Managing bioavailability across river basin districts and cross-boundary and border issues.
- Does the approach relax the environmental standards? Does it allow more metal to be discharged?
- Lessons from other regulators: case studies from France and the UK.
- What about accumulation in sediments (especially if standards become less stringent)?
- Will areas currently identified as sensitive still be priorities (and vice versa)?

For compliance and classification under the WFD there was interest in considering whether the bioavailability-based approach actually relaxed environmental standards. What were the experiences of other regulators? It was certainly true that from UK and Dutch experience, using a bioavailability approach meant that a different failure profile was seen for sites (in

relation to where, and how many) compared to approaches where the EQS are based on hardness. However, it was stressed that accounting for bioavailability was not a means of making problems and exceedances disappear, but it was possible to more clearly and justifiably identify sites where there may be a problem or a need for investigation. For the UK there are likely to be many more failures for metals than there is budget to provide programmes of measures, so accounting for bioavailability will enable identification of sites where resources can be utilised most efficiently.

Are there point and diffuse discharges of metals which will be problematic to deal with accounting for bioavailability? For point sources, there is a need to account for the use of Best Available Technology (BAT) to tackle local discharge issues, which will of course depend on the metal and the type of catchment. For point source emissions bioavailability should not be used to relax permits. For diffuse sources this is potentially more difficult, especially in urbanised catchments where there are potentially multiple sources of diffuse metal inputs.

In The Netherlands, bioavailability is only likely to be considered where there are specific issues with metals, as indicated by the exceedance of an EQS. This is in keeping with the use of a tiered approach to ensure resource and effort is commensurate with the magnitude of potential risks.

Regulatory organisations in France have used the user-friendly tools from the Environment Agency of England and Wales, to investigate the impact of considering bioavailability on compliance for metals. The dataset used was not ideal, but it was clear that for some metals, especially Cu, reduction in exceedances was noted, but not for all sites. Another feature of the work was that for some stations there was considerable variability in bioavailability (Appendix 2 FAQs). For larger river basins there is perhaps less variability in the input parameters and exposures, whereas smaller waterbodies are sometimes more susceptible to rapid changes in external influences, such as rainfall. Despite the variability, the metric of compliance is the annual average and this variability should not prevent a bioavailability-based approach from being used.

Some additional policy context was added in relation to the marked variability in Member State standards for specific pollutants (especially Zn) where the use of a bioavailability approach can help to greatly reduce the range of variability in EQS.

For permitting it is not entirely clear how the approach may be used. There is a possibility that bioavailability can be used to check compliance with EQS in a waterbody. But generally, effluent measures are undertaken using 'total' metals, with a specific focus upon loads. As stated earlier, it was strongly suggested that there is no desire to relax loads in effluent, but to use bioavailability to measure potential effect in the environment. Bioavailability should be used to check if a waterbody is at risk and prioritise those locations where additional measures are needed.

However, it was suggested that it may be valuable, in terms of the amount of information that is available to regulators, to measure both total and dissolved metals in effluents. For sewage treatment works (and other industries) permits that have been set based on hardness-banded EQS, such as for Cu, are probably overly stringent. The user-friendly tools give greater accuracy in terms of potential risks. However, emissions, discharges and losses should be decreased using BAT, if this approach is not enough to meet the EQS additional measures – beyond BAT will need to be taken.

Nevertheless, the current best-fit and potentially easiest way to account for bioavailability under the WFD is through standard-setting, compliance and permitting. Issues around input parameter variability were again discussed and are addressed specifically in the FAQs document in Appendix 2.

This breakout group agreed that it would be useful to broaden Member States' experience of using the tools by trialling them with their own datasets. This would provide local context and confidence in the approaches. It was suggested that perhaps an additional meeting could be scheduled prior to WG E to report back on findings and experiences. These experiences could be fed into the operation and construction of the tools ensuring they are fit for regulatory purpose.

In order to include the BLM approach in national legislation the EQS Directive, including part B, Annex I is transposed into national legislation. The methods to take bioavailability into account are elaborated in policy documents (an approach favoured by The Netherlands). For the UK there is an option in transposition of EQS Dir. (i.e. Pt B of Annex 1 of EQS Dir, is a footnote) and this is similar to the approach to be taken in France.

A key point in this group was in relation to the communication of messages to people beyond the regulatory community about the likely changes in compliance. This has also been discussed at Strategic Co-ordination Group (SCG) but in relation to the persistent organic chemicals where, despite the implementation of measures, there continue to be recorded incidences of exceedance.

This type of communication is likely to be gradual. For some Member States using bioavailability, the approach is being phased in and is only being used for those sites that have been identified as having potential risks. There was a strong recommendation that the FAQs (Appendix 2) are transposed into a 'plain English' version to ensure greater understanding across stakeholder groups.

In order to use the bioavailability approach across river basin districts (and cross boundaries) it was felt that considerable cooperation with all neighbouring countries would be required, especially on the input parameters for the tool (DOC, pH and Ca) that need to be measured.

Sediment bioavailability was mentioned in this group, and bioavailability approaches are being developed for sediments, although they are less well developed than for freshwaters. The

accumulation of metals in sediments is potentially an issue. For many Member States sediment and biota monitoring is conducted in marine waters. Generally, the water column is monitored in fresh waters unless there is a known sediment problem. Additional monitoring of sediments can be performed to identify any trends, but bioavailability is not likely to be considered.

There was concern that total metal load should not increase in waters, but it is likely that areas currently identified as priorities using non-bioavailability-based methods, may no longer be considered as priorities. In the UK this has been the case where previously considered priority sites in soft water areas are not identified as potentially at risk, because these waters often have relatively high DOC (implementation presentation, Appendix 1). The converse is also true where hard waters, often with low DOC, are actually the priority areas when using BLMs, but would not have been identified under the hardness-based EQS regime. MS may need to consider these findings irrespective of whether they choose to adopt these tools.

3.2 Technical and scientific considerations on the regulatory use of bioavailability

Group participants:

Wolfgang Ahlf, Christiane Heiss, Sabina Hoppe, Martien Janssen, Willie Peijnenburg, Olivier Perceval, Adam Peters, Chris Schlekat, Jos P.M. Vink, Katrien Delbeke.

The following questions were provided to start the discussions:

- How were the User-Friendly BLMs constructed? How robust is the underpinning?
- How were the BLMs and User-Friendly BLMs validated?
- What about additional routes of exposure to metals, such as diet-mediated effects?
- Are there other methods to account effectively for bioavailability, apart from BLMs?
- Availability corrections? Hardness, DOC?
- Tiered Approaches.
- Lessons from other regulators: case studies from France and the UK.
- How do new proposed standards compare to the current standards for the same metals?

An outline of how the User-friendly model was developed was given in the technical presentation (Appendix 1), but it is clear that there is a requirement for more information, such as a detailed description of the match between the simple model and full model. Such comparisons between the models must also include information on the range of water chemistry properties of the waters included in the datasets which are used for the assessment, in order to ensure that they are adequately validated over the entire range of water chemistries which the User Friendly BLM will be used for. Detailed information on the models from which they user Friendly models are derived is also required, including the applicable range of water chemistry conditions, the details of the ecotoxicity datasets used, the BLM parameters, and the method of calculation (e.g. within the Hydroqual BLM framework, or another framework).

In addition to the descriptions of accuracy, there needs to be some additional documentation giving the full computation picture that sits behind both the 'look up table' and 'algorithm' versions of the User-friendly BLMs. This can probably be done through the Bio-met.net site[7]. This needs to describe the methods behind the development of the tools in sufficient detail for users to understand how they have been constructed.

Guidance on how to use the User-friendly tool, and the boundaries within which the models are applicable (applicability domain), should be explicitly indicated. The tool clearly flags input data and results that are calculated outside the validated boundary conditions (Section 3.3). Treatment of data outside the validated boundaries will probably need to be undertaken on a case by case basis whilst further experience with the standards is acquired in these systems.

A suggestion was put forward for performing a pilot trial with a whole range of monitoring data from all Member States. This ties in with the suggestion from the policy breakout group, whereby Member States take the tools away and trial them with their own data and compliance regimes. This exercise would provide valuable information on the proportion of sites whose water chemistry conditions lie outside the applicability range of the BLMs, and the regions in which these conditions tend to be located. This should also provide feedback on problems encountered with the application of the tools such as bugs in the programme, and also difficulties encountered in applying the bioavailability approach.

A query was made as to the need to validate the User-friendly BLM models, at least initially, against characterization of biological quality elements. There is need to thoroughly identify metals for which diet-borne exposure could contribute significantly to the overall toxicity. For these metals BLMs are not likely to be useful tools. Although the group agreed that for those metals listed as PS under the WFD (and Cu and Zn), direct ecotoxicity toward pelagic species is the most critical QS. Standards for secondary poisoning were not considered to be critical for these metals, and the result of mesocosm studies suggest that the standards are likely to be protective of the lower trophic levels of the ecosystems. Whilst metal exposure via food can result in effects it is not clear whether such conditions could occur at water exposure levels which comply with the Generic $EQS_{Bioavailable}$.

The tiered approach was recommended for use as a way of incorporating bioavailability. This is because it offers a system by which the amount of effort and resource expended is appropriate to the potential risk to the environment. Monitoring for dissolved metals and assessing compliance initially against the $EQS_{Bioavailable}$ allows sites with low exposures to be removed from the requirement to monitor for the supporting parameters required for bioavailability correction. It is likely that the steps may differ between Member States depending on local issues and needs (for example the consideration of ambient backgrounds, before or after bioavailability).

There is a need to measure dissolved metal and other parameters in some samples, and they should preferably all be analysed for at the same time. This remove issues in relation to

[7] http://bio-met.net/

temporal variability, but at what critical moment should we monitor those physico-chemical parameters which affect metal bioavailability? For example, in The Netherlands physicochemical parameters are measured only four times a years (as in France). One way of dealing with that problem, is to monitor these parameters concurrently with trace metals. There is limited information available about the effect of variation in bioavailability over time and its potential importance in terms of EQS compliance. A study from The Netherlands[8] indicates that the variability in dissolved metal exposure concentrations is likely to result in the majority of the variability in the Risk Characterisation Ratios. The effect of variability in the physicochemical parameters which control metal bioavailability is, therefore, unlikely to pose a more serious problem for metals for which BLMs are used than for other chemical standards which are not normalised for bioavailability.

There are additional policy areas for consideration. In the UK, for instance, the Environment Agency wish to use the BLMs for water qualification, and it has developed an extension of the BLM to cope with low values of dissolved Ca and pH. This is a practical policy decision, which alleviates the problem that there could be a step change in the standard when a small change to the chemistry of the water causes it to be outside the validated applicability range of the BLM. In Sweden there may be a requirement to develop a suitable regulatory approach for soft waters in the mining areas in the north. Sites with low exposures (e.g. <1 $\mu g\ l^{-1}$ dissolved Cu, <2 $\mu g\ l^{-1}$ dissolved Ni, or <10 $\mu g\ l^{-1}$ dissolved Zn) do not require BLM calculations to be performed under a tiered approach. In order to deal with situations to outside the boundaries there are several alternatives (implementation presentation, Appendix 1):

- Consider 100% availability of the metal (i.e. apply the Generic $EQS_{Bioavailable}$)
- Assume model predictions still apply outside boundary conditions
- Extrapolation (e.g.consider complexation of metal by DOC only)
- Bioassays (including ecotox tests, WER, and ecological community monitoring)
- Use specific EQS

Soft, acid waters are often considered to be environments which are particularly sensitive to contamination by trace metals. These systems may also often have relatively high levels of DOC, which protects against metal toxicity, but this is not always the case and where DOC concentrations are low the waters will be very sensitive to many metals.

It was recommended that, if there are compliance issues for soft, acid waters, gathering additional evidence would be valuable. This information should include measurements (or predictions) of "available" metal concentrations, and information on organism responses, from individual species tests or ecological community monitoring. Ecological monitoring performed

[8] Verschoor A, Vink J, Snoo G, Vijver M. 2011 Spatial and temporal variation in watertype-specific no-effect concentrations of Cu, Ni, and Zn. Environ Sci Technol. 45:6049:6056

under the WFD may be useful for this, although it was noted that the interpretation of such data is currently difficult. It would be valuable to review how these situations are handled periodically to share experiences between different regulatory regimes.

3.3 Practical implementation of bioavailability-based approaches

Group participants:

Bruce Brown, Darragh Cunningham, Madalina David, Maria C Diaz Muñiz, Carola Hermoso Arnao, Christian A Jensen, Markus Lehmann, Maria Linderoth, Maria D Ron-Vaz, Karine Tack, Dorien Ten Hulscher, Frank Van Assche, Davide A.L. Vignati, Ligita Vircava, Paul Whitehouse.

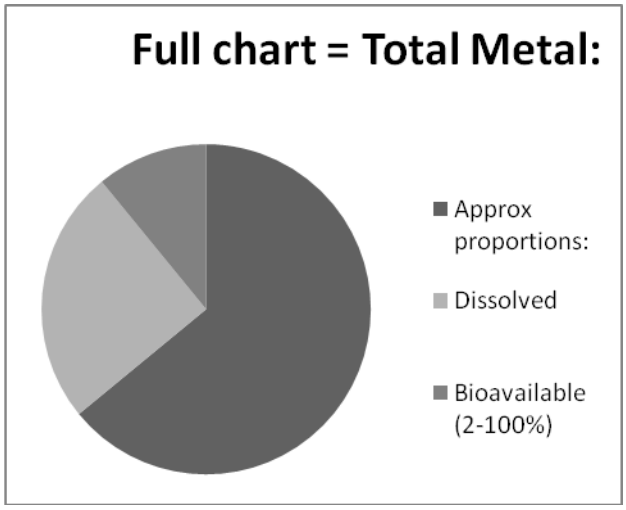
The following questions were provided to start the discussions:

- Data requirements and monitoring needs to implement a bioavailability–based approach (e.g. how many supporting parameters are required?)
- Analytical requirements – what sensitivity is required?
- Applying the bioavailability correction to monitoring data or Quality Standard (options 2 and 3 in the WFD technical guidance, respectively)
- What if data for some parameters are unavailable? Use of defaults and surrogate measures.
- Over what scales do the measurements need to be made?
- Do measurements of dissolved metal and supporting parameters need to be concurrent, and what frequency of monitoring will be required?
- Could natural/ambient backgrounds be included?
- Practical compliance monitoring, classification and site/issue prioritization.
- Permitting and setting discharge limits.
- What about the boundary conditions? Dealing with waters outside the validated ranges. What ranges do current EQSs have?

There is a need to explain (as identified by other groups) the basis of the tool, its provenance and history, and document what specifically lies behind the User-friendly tool. In addition to outlining the tool's pedigree, a clear set of instructions of how to use the tool and interpret the outputs would be very useful.

Is there a case for retaining the option to use the "full" BLM? Some Member States may choose to use the User-friendly tool and others to use "full" BLM. However, the outputs of the two tools

are very similar and there is no significant difference.. The User-friendly tool gives predictions very similar to full BLMs and both tools have pedigree, so by using the user-friendly tool one is not making a significant compromise compared to the full BLM.



This diagram was used to illustrate the *hypothetical* differences in the relative proportions of metals in each of the total, dissolved and bioavailable pools in the water column. The $EQS_{bioavailable}$ looks very low compared to existing standards so there may be some communication issues to broader stakeholder groups (as identified by the policy breakout group).

Is there a need for some form of standardisation of how the tool is used and instruction on the inputs needed? For example:

- documentation
- minimum criteria (again there was a clear call for concise documentary instruction - a user manual?)
- links to tools to be used for each metal

There is a need for version control of a standalone tool, but by the end of the summer (2011) the tool will be released online and this ensure consistency of outputs. To use the tool online the user will be prompted to leave an email address and any changes in versions will be communicated to the user. The online version will also mean that those users with earlier versions of Microsoft Excel can still perform the calculations.

Member State experiences of accounting for bioavailability have been very similar, in that for Cu there are generally large scale reductions in exceedances, whereas for Zn the fall in

exceedances have been less dramatic. The French experience on the Somme River was given at a recent SETAC event and is included in Appendix 1 of this report[9].

There is currently limited experience of using bioavailability approaches for permitting.

There was concern expressed in relation to the potential variability in the BioF within waterbodies. It was felt that this was likely due to variability in DOC. It is important to understand for which waterbodies this variability exists, as it is these that will require more intensive monitoring of input parameters (FAQs, Appendix 2). Default DOC values can be used if the DOC has been shown to have low variability. But if measured annual data (12 samples per year) are available, then it is best to use an annual median rather than an average due to the skewed distribution of DOC. If possible, it is best to have matched measured DOC and dissolved metal at each site. Seasonal variability is only really an issue when we have to rely on defaults, but it is not a problem when coincident dissolved metals, DOC, pH and Ca data are collected.

The sampling regime to fulfil a bioavailability-based approach for metals is no different to any other substance. The key data requirements are:

- $[M^+]$ – dissolved metal, at an appropriate limit of detection
- DOC
- pH
- hardness (Section 3.4) or Ca

In terms of analytical requirements, there was considerable discussion in relation to the needs of the QA/QC Directive which requires that the limit of detection should be no worse than 10% of the $EQS_{bioavailable}$. So, for DOC which is a key supporting parameter, the limit of detection would need to be around 0.5 mg l^{-1} and for Cu, as used in the user-friendly tool, 0.1 µg l^{-1}. These detection limits are not challenging with modern laboratory instrumentation.

In addition, aspects of sample preparation can have a dramatic effect upon analytical accuracy and precision (e.g. filtration). It was recognised that filtering samples for dissolved metals is a potential source of contamination which needs to be minimised by adopting best practices. There is perhaps an opportunity to share best practice amongst Member State analytical laboratories, which will ensure learning is shared and previous mistakes are not repeated. There is a need for some Member States to shift from total to dissolved metal monitoring, but some Member States have little or no experience in this regard.

For permit discharges for a site the local water conditions need to be considered. However, note needs to be taken of whether the waterbody flows into a more vulnerable zone – the

[9] EQS for a metal : Is it possible to determine a lonely legal value? Interest of the Biotic Ligand Model (BLM)? GEOFFROY L., TACK K., ANDRES S.; SETAC 2010, 23-27 may 2010, Seville, Espagne.

permit needs to be stringent enough and should be set to the most vulnerable conditions in catchment. Sewage treatment (STP) discharges introduce a great deal of DOC and so effectively this may mitigate metal ecotoxicity. So when permitting for discharges it is probably appropriate to set the permit on the upstream DOC concentration. Concern was raised in relation to the effect of advanced treatments at STP to remove trace levels of organics, in order to meet permit conditions. It is possible that both the amount and characteristics of the related DOC may change with unintended consequences for metals bioavailability.

What are the time frames over which metal speciation changes in relation to different influents? This question was addressed during the plenary session presentations where the scientific advice offered is that the timescales for speciation reactions to occur are relatively quick and should not be an issue.

BLMs are currently only applicable for freshwaters and there was much discussion about transitional water bodies such as estuaries. Saltwater intrusion limits scope and applicability of the BLMs, and there is a need to be explicit as to the salinity limit for the tools.

There was agreement that background concentrations of metals have most relevance in local assessments of risk, and at a local scale. However, it is difficult to discriminate between 'ambient' and 'natural' backgrounds. Perhaps this can only be done in headwater streams that are free from anthropogenic input, and only present the geogenic conditions.

Finally, a discussion was held as to whether it was appropriate to have multiple or one EQS. For classification and communication it was agreed that one EQS was better, but for vulnerability and hazard mapping then site-specific dissolved EQS were helpful.

4 CONCLUSIONS

From the discussions in the breakout groups, and the comments and interactions after the presentations, the following conclusions were drawn:

- Bioavailability needs to be taken into account in the regulatory context of the WFD. The reason for this is that it clearly reflects the latest science and understanding
- The risk of not accounting for bioavailability is being both over-protective (i.e. taking measures where they are not needed because they have been wrongly identified as an issue), and under-protective (i.e. not taking measures where they are needed, but hadn't been identified) (Section 2.2, Example 2)
- Using bioavailability approaches can help improve identification of real problems in sensitive waters, and in prioritising sites or performing investigations
- The biotic ligand models are relatively complex because, in part, these models reflect complex realities. Yet retaining some of the existing 'old' approaches that are not representing the current science is not an option due to the potential for drawing spurious conclusions from their use
- Simplified models and tiered approaches seem to be promising tools to implement bioavailability correction in practice[10]
- For classification and communication purposes, a single EQS seems more practical. However, site-specific EQS can have a role in vulnerability and hazard assessments

In relation to monitoring and assessment, the following conclusions were agreed:

- There is a need to extend more widely the monitoring of dissolved concentrations of metals in the aquatic environment
- Total concentrations may still be needed for other purposes (e.g. estimation of loads in permitting), but dissolved concentrations are needed for compliance checking of chemical status
- Analytical issues need careful attention (filtering, etc) due to the requirement to ensure that the limits of detection are 10% of the $EQS_{bioavailable}$

[10] ENVIRONMENT AGENCY. 2009. Using biotic ligand models to help implement environmental quality standards for metals under the Water Framework Directive. Science Report SC080021/SR7b, Environment Agency, Bristol, UK.
ENVIRONMENT AGENCY. 2011. Lockdown and embedding of the Cu/Zn screening tools and finalisation of the implementation of their EQSs for the Water Framework Directive. Environment Agency, Bristol, UK. (in press)

- There is a need to monitor *at least* the most important parameters that influence bioavailability: Ca, DOC and pH. We recommend that these are monitored at the same time as dissolved metal

- Additional costs for DOC would seem to be in the range of 20-50 € per sample

- In some circumstances it might be possible to use default values for Ca, DOC and pH. However, this will only be when sufficiently developed datasets are available to ensure the variability in the waterbody is well known

The user-friendly models were presented to the participants on memory sticks and these will be trialled by Member States. The conclusions drawn in relation to the models from the meeting were:

- It was agreed that very significant progress has been made in past decade in relation to the usability of the models

- Simple models are needed to be implemented in tiered approaches, and these models need to match the full models as far as possible

- There is a need to properly document the approach that lies behind the construction of the User-friendly tool, and how it relates to the full models

- When waters are outside the boundary conditions of the model, we recommended a case by case approach, based on clear documentation of the possibilities and implications

- Is there a requirement for EU validation/endorsement of models and tools, now they are being used outside the original setting in which they were agreed (TCNES for the Existing Substance Regulations), and for models which have been developed de novo under REACH (Mn and Zn)?

The use of tiered approaches was discussed in relation to its value in facilitating the adoption of bioavailability-based approaches. The main conclusions were:

- One of the main advantages of any tiered approach is that it is simple. In addition, there can be flexibility in implementation steps of tiered approaches (for example when accounting for ambient background concentrations)

- Any tiered approach needs to be based on simplified models that are protective enough so that we have high confidence we do not overlook problems, for example elimination of type II errors

- The use of default values for Ca, DOC, pH in tiered approach is possible if they are protective enough to account for variability, and this decision needs to be based on a thorough knowledge of variability at waterbody level

- Clear documentation when using the tiered approach and tools on decision making is important, to enable someone to repeat the steps taken and come to the same conclusions

For those Member States that have trialled and implemented the models the following broad conclusions can be drawn:

- For copper, using the bioavailability-based approaches there is quite a substantial reduction in the number of EQS exceedances

- For zinc, there is some reduction in the number of EQS exceedances, but the reduction is less dramatic than for Cu

- The location of the exceedances changes when accounting for bioavailability

- There is a need to ensure 'Best Practice' is promoted in sampling and analytical work

In terms of permitting, several key conclusions were drawn:

- Bioavailability models are readily implementable in order to assess compliance with chemical standards in waterbodies that are inside the calibration intervals of the models

- Permits should really be based on BAT

- The efficiency of waste water treatment usually involves measuring total concentrations, hence permits should keep total concentrations. However, it may be sensible to also include dissolved concentrations as this can then be related back to the compliance checking

- A question was raised as to whether permits for sewage treatment discharges should be based on upstream DOC values

5 RECOMMENDATIONS AND NEXT STEPS

The following recommendations were agreed at the workshop:

- A pilot exercise should be undertaken to allow Member States to test the User-friendly tool with their own data – this can be carried out now
- A further discussion session prior to next WGE meeting in October should be organised to discuss the findings of the pilot exercise and the broader adoption of this approach

6 ACKNOWLEDGMENTS

We would like to thank participants for their support in making this a successful and productive meeting, and for the excellent thought-provoking contributions. We would also like to thank the International Zinc Association, International Copper Association and the Nickel Institute for the provision of the chronic biotic ligand models on which the User-friendly tool is based.

Finally, we would like to acknowledge the support of the DG Environment in taking this work forward.

APPENDIX 1. Presentations

Policy Presentation – Gerrit Niebeek and John Batty

Adobe Acrobat Document

Technical Presentation – Adam Peters and Olivier Perceval

Adobe Acrobat Document

Implementation Presentation – Bruce Brown and Mario Carere

Adobe Acrobat Document

French Experience of using BLMs – Karine Tack

Adobe Acrobat Document

APPENDIX 2. Frequently asked Questions

THE IMPLEMENTATION OF BIOAVAILABILITY-BASED APPROACHES FOR METALS – Date of last entry 24/6/2011.

Number	Question	Answer
	Complexity	
1	The BLMs are too complicated to implement and interpret in a regulatory framework	Simplified BLM tools have been developed and are simple Excel spreadsheets that can either be used on any PC or alternatively the underpinning calculations can be embedded into laboratories or the regulatory compliance checking process.
2	The BLMs would require dedicated staff to run them and understand them	If used as stand alone tools, many samples can be run through the Simplified BLM tools in a batch process that just requires data entry of the monitoring results. Simplified BLM tools can also be integrated into laboratory systems for automated production of outputs. The outputs are readily interpretable, including a simple risk characterization ratio.
3	The calculation of backgrounds is much easier to do	The use of natural background concentrations is not a replacement for bioavailability consideration. The calculation of backgrounds has much scientific and technical pedigree than accounting for bioavailability using BLMs and so bioavailability should be given a greater influence than backgrounds when checking compliance, permitting etc. Backgrounds can be considered in the tiered approach following account being taken of bioavailability.
	Expense and resources	
4	The BLMs or User-friendly BLM tools would be expensive to run and require more trained staff	In addition to being technically robust, the user-friendly BLM tools are freely available and simple to use, so minimal training is required to use them. In many cases, the help pages should provide sufficient information for users. In some cases it is possible for the estimation of bioavailability corrections to be automated within laboratory information management systems, thus reducing the need for resources.
5	The BLMs or user-friendly BLM tools require too many additional inputs that we do not measure	The user-friendly tools require a maximum of 4 inputs. These are the dissolved metal concentration, pH, calcium and dissolved organic carbon (DOC). Data for pH and calcium are usually more readily available than DOC. If site specific monitoring data for the key parameters are not available, default values based on historic data may be used. The full BLMs do require more inputs but these can be estimated from calcium using a freely available Excel calculation (from a peer-reviewed journal article) if there are no monitoring data.
6	We have no DOC data. Therefore we cannot implement the method.	DOC has an important influence on bioavailability so it is preferable to use actual monitoring data. However, in the absence of DOC monitoring data it is possible to use precautionary default values based on read across from similar catchment types or to estimate DOC concentrations from other data that is available such as UV absorbance or dissolved iron (Peters 2011,).
	Scientific Rigor	
7	The science on 'bioavailability' is not well developed	The science underpinning the understanding of bioavailability and BLMs is well studied. More than 500 papers have been published in the scientific literature on BLMs since 2000. SCHER Opinions over the last 4 years have supported the use of bioavailability-based approaches in ESR metals risk assessments and recent EQS guidance documents. It is also notable that REACH guidance recognizes the use of BLMs in establishing Generic Exposure Scenarios for metals.
8	Where is the technical evidence to support this approach	There are a number of technical reviews of BLMs within the literature and the evidence is also presented and reviewed in the relevant ESR metals risk assessments. One key piece of evidence is that the predictions of toxicity from BLMs match what is observed in the field remarkably well and usually within a factor of 2.
9	These models don't cover all aquatic species, what about the species for which there are no BLMs?	Studies on different species have shown that the models used are broadly applicable between different species (the binding constants for both toxic metals and competing ions show remarkable consistency between different

		species) the BLMs are therefore applied to additional species by defining the sensitivity to the toxic metal (which is expressed as the fractional occupancy of the biotic ligand at the threshold level, e.g. EC10.)
10	Some studies suggest that metal toxicity can be underestimated when applying BLMs to fresh waters with elevated levels of Al, and Fe.	Limits have been set for Al and Fe concentrations when running the Cu BLM, levels in excess of 300 mg l^{-1} would be considered to be outside the boundaries due to possible competition for DOC binding from these metals.
11	According to De Laender et al., (2005) & De Schamphelaere, (2003) toxicity for both Cu and Zn can be underestimated when applying BLMs on fresh waters with elevated levels of humic substances, Al, Fe and low pH. As these conditions are common here in Sweden what is the solution used in this model to prevent this?	It is not clear which specific papers are referred to here, although it is customary when performing BLM calculations for the purpose of EQS compliance assessment to assume that only 50% of the DOC is actually active. This is to ensure that DOC which may be inactive with respect to metal binding does not result in unprotective estimates. This approach was agreed under ESR some years ago. Was such an approach taken in the papers refer to?
12	Which geochemical model is used to calculate the chemical speciation in this version of chronic BLM?	The speciation codes are the same as those used in WHAM (Tipping 1994 Computers and Geosciences 20:973)
13	What about the influence of other metals present in the waters? Most important in Scandinavia Al & Fe?	Truly dissolved Fe and Al can compete for binding sites on DOC, although due to their tendency to precipitate any effects may be limited. The conservative assumption that only 50% of DOC is "active" is likely to result in the concentration of available binding sites being overestimated (rather than underestimated) even where there are appreciable levels of these metals in true solution. Boundary conditions for Al & Fe have been set in the chronic CuBLM, and competition for DOC binding sites from Fe and Al is taken into account in the Ni BLM.
14	These models are based on species that are not representative for our waters. Do we need to develop BLMs specifically for our waterbodies?	Studies show that the models are capable of predicting toxicity to species that are endemic to specific regions, e.g., Scandinavia (Deleebeeck et al 2007 Comparison of nickel toxicity to cladocerans in soft versus hard surface waters Aquatic Toxicology 84:223.).
15	Not all DOC is created equal. We have special DOC in our waterbodies that is not considered in the BLM development.	Studies show that the models are capable of predicting metal toxicity in wide ranges of natural waters that exhibit ranges of DOC types.
16	Are the chronic and acute BLMs interchangeable?	We would strongly recommend that considerable caution is exercised when trying to make comparisons between different BLMs, even when they are for the same potentially toxic metal. This is especially important in the case of comparisons between acute and chronic BLMs, and particularly so in the case of copper due to the fact that whilst there is a protective effect of calcium on acute copper toxicity there is only a very limited protective effect of calcium on chronic copper toxicity. In addition to Cu^{2+}, $CuOH^{+}$ and $CuCO_3$ are also included as potentially toxic copper species in the chronic copper BLM, which is a further difference between the acute and chronic models.
17	According to Van Genderen et al. (2005) and Sciera (2004) using the acute copper BLM on waters with lower hardness then 50mg $CaCO_3$ may underestimate the toxicity of copper, in this case to larval fathead minnow. Is this addressed in the current version of the chronic BLM?	Calcium has only a very limited competitive effect on chronic copper toxicity, as can be readily observed by performing calculations in which Ca is varied but all other conditions remain constant with the chronic Cu BLM.
18	Hard waters are often outside the applicable range for the BLMs	The protective effect of Ca which is observed in some BLMs does not increase indefinitely with increasing Ca concentrations. There is typically a limit above which no further protective effect is observed. In these cases limiting the input value for Ca prevents overestimation of the protective effect (under estimation of bioavailability), predictions are still likely to be reasonably accurate at higher Ca concentrations although caution should still be exercised in using the results.
19	Some studies have shown that BLMs may be unreliable in soft waters	Boundary conditions are set for the BLMs for both pH and Ca concentrations. These boundaries exist because of the ability of the test organisms upon which the models were developed to survive in waters with these extreme chemistries. Considerable care must be exercised if the BLMs are applied to water chemistries which are outside these boundaries (e.g. very soft, low pH waters).

20	What about multi-metal issues? Won't the metal binding capacity of the DOC all be used up by other metals in some cases?	Metals which bind to DOC more strongly than the metal of interest may reduce the capacity of the DOC to bind metal. The complexation capacity for Cu is expected to be approximately >100 $\mu g\ l^{-1}$ at a DOC concentration of 1 mg l^{-1}. Thus other competing metals are unlikely to significantly reduce the complexation of the metal of interest where the competing metals are present at acceptable levels. In some cases competition from some ions (e.g. Fe) may be taken into account by the models (NiBLM).
21	The underpinning requirement of the BLMs is that the system is at equilibrium condition…but this never happens in nature!	Many natural systems exist in, or close to, a steady state pseudo-equilibrium, and in the vast majority of cases the assumption that the waterbody is close to equilibrium will be appropriate for bioavailability calculations.
22	Is it only the free metal ion that is toxic? What about other metal species?	Whilst the free metal ion is the principal toxic metal species some models also include other inorganic metal complexes, such as hydroxides and carbonates, as toxic species where the free metal ion underestimates toxicity at high pH. These issues are taken into account, where relevant, by the models.
Practical implementation and coverage		
23	What metals have BLMs and user-friendly tools?	There are BLMs and user-friendly tools for Cu, Ni, Mn and Zn. Under development are BLMs for Pb, Co, Al, Fe and Ag. The BLM concept would not be appropriate for metals which tend to form organometallic compounds, such as Hg, because of the importance of volatility of the organic forms and the key exposure route being an organic Hg form.
24	The Excel tool is not the BLM.	The results of the Excel-based user friendly model have been validated against the full BLMs.
25	The Excel tool shows predictions that are mostly below the 1:1 line when plotted against the full-BLMs	The predictions are all within a factor of 2. For some metals, such as Cu, the exclusion of some parameters (especially Na) that may have a protective effect means that the predictions are overprotective. However, within a tiered risk based framework this is acceptable.
26	It is not possible to do a compliance assessment using these methods.	Indicative compliance assessments using BLMs have been undertaken in a number of countries including the UK. If a generic bioavailability based EQS is in place then compliance assessments using BLMs need not be any more complex than any other calculated parameter.
27	It is not possible to do permitting and account for bioavailability.	Permitting can be based on the existing regimes in place with permits expressed as dissolved metal. The use of BLMs allows the permit to be more precisely defined so that it better reflects local sensitivity of the water conditions to the metal. The use of BLMs affects only the acceptable level of metal in the receiving water; other aspects of permitting are not affected.
28	The allowable range of pH/DOC/Ca does not cover the waters I am interested in.	The applicable range of water chemistry conditions which the BLMs can be applied to is limited by the ability of standard test species to survive and reproduce under extreme conditions of pH and Ca. Typically low pH (,6) and low Ca concentrations (<5 mg l^{-1}) cannot be tolerated by standard test species (such as *Daphnia magna*), although the limited available testing on soft water species does not suggest that they are likely to be more sensitive than other sensitive species which have been tested. Furthermore, studies show that the models are able to predict toxicity to organisms from soft waters.
29	Is it possible to extrapolate beyond the boundaries of the models?	It is possible to extrapolate the working range of the BLMs below the current low pH boundary. This has been done in the UK using a speciation based approach and drawing a curve of metal availability according to titration with DOC. This approach is empirical and is, in part, a policy and practical solution. The lowest pH selected is at a point where water not at good status due anyway because of its pH.
30	The upper Ca range on the model for Ni is only 88 mg L^{-1} we have waters that have much greater Ca. What is the implication of having a high Ca exceedance?	At Ca concentrations above this there are limited additional protective effects. So, while Ca concentrations may be higher in the waters the positive influence of ecotoxicity mitigation is limited. Other boundaries, low Ca, high/low pH are less easy to resolve. But, boundary concentrations are also set to reflect where organisms can live and where test organisms can survive.
31	How do I summarize the input data for the tool for the calculation of annual average	The ideal situation would be to have matched dissolved metal data and Ca, DOC and pH for every site for every sampling occasion. However, the

	compliance?	difference between doing this and using annual average pH and Ca and an annual median for DOC is very limited. A median DOC value should be used as DOC may be more variable in waters and using the median is a more appropriate statistic. It is probably possible in most cases to not need to measure values every time, for example hardness or Ca. But, for DOC it is difficult to tell immediately and generally needs a few years of monitoring to get default concentration for a waterbody, although some waterbodies this would not be appropriate. For very variable aquatic systems matched data should always be used in assessing annual average compliance.
32	Temporal variation in the bioavailability conditions makes the results unreliable and difficult to interpret	The available evidence tends to suggest that the variability in risk characterisation ratios for BLM metals is due more to variation in the exposure concentrations than it is to variation in the bioavailability, and temporal variation is of similar importance to other standards.
33	Permitting is normally down using total metals loads, how does this work with the BLMs and user-friendly tools?	Permits are typically influenced by an EQS in the receiving water (amongst other issues), replacing the EQS with a site specific one which is calculated using the BLM need not necessarily affect other issues associated with permitting.
34	How can account be taken of different inputs down through a catchment and the effect upon bioavailability?	The bioavailability issues can be assessed for the most sensitive part of the catchment using BLMs and the maximum tolerable dissolved metal calculated. Existing models such as SIMCAT etc. can be used to estimate the influence of different inputs to the dissolved metal loadings. This is similar to the issue of changing hardness values down a catchment for hardness banded EQSs. BLMs can also be used to calculate the sensitivity of the contributing flows in a catchment to metals so that any localized areas at risk can be identified.
35	Can the BLMs be used in marine waters?	The BLMs have been developed and validated using synthetic and natural freshwaters. Whilst the BLM principles may also apply to marine waters the BLMs currently available should not be used for marine systems due to the differences in the conditions in marine and fresh waters.

REFERENCES

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Tipping E. Corbishley HT. Koprivnjak JF. Lapworth DJ. Miller MP. Vincent CD. Hamilton-Taylor J. 2009. Quantification of natural DOM from UV Absorption at Two Wavelengths. Environmental Chemistry. Rapid Communication. October.

APPENDIX 3. Meeting Agenda from 21st of June 2011.

9.00	Workshop overview, goals and introductions (Jorge Rodriguez Romero)
9.20	Welcome, information and logistics (John Batty)
9.30	*Implementing a bioavailability-based approach for assessing potential metal risks in the Netherlands* – (Gerrit Niebeek)
10.15	*Scientific underpinning of the bioavailability approach* – common questions and answers (Adam Peters)
11.00	Coffee
11.20	*Implementation in monitoring and assessment frameworks* – common questions and answers (Bruce Brown)
12.20	General discussion (chaired by Jorge Rodriguez Romero)
12.35	Breakout session organisation (Graham Merrington)
12.45	Lunch
13.45	Breakout session
15.00	Coffee
16.15	Plenary: Workgroup summaries and discussion (chaired by John Batty)
17.00	Summing up and next steps (Jorge Rodriguez Romero)
17.15	End