UKTAG River & Lake Assessment Method

Specific Pollutants (Metals)

Metal Bioavailability Assessment Tool (M-BAT)

by

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

Publisher: **Water Framework Directive – United Kingdom Advisory Group (WFD-UKTAG)**
c/o SEPA
Strathallan House
Castle Business Park
Stirling
FK9 4TZ
Scotland
www.wfduk.org

July 2014

ISBN: 978-1-906934-57-6

Health and safety statement

WARNING. Working in or around water is inherently dangerous; persons using this standard should be familiar with normal laboratory and field practice. This published monitoring system does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and to ensure compliance with any national regulatory guidelines.

It is also the responsibility of the user if seeking to practise the method outlined here, to gain appropriate permissions for access to water courses and their biological sampling.

Corrigendum

1.1 Background – why is bioavailability important?

The Water Framework Directive (WFD) (2000/60/EC) requires European Union Member States to ensure that all inland and coastal waters achieve ‘good’ water quality status by 2015. One of the measures used to deliver this requirement are Environmental Quality Standards (EQS). An EQS is the concentration of a chemical in the environment ~~**above**~~ **below** which there is not expected to be an adverse effect on the specific endpoint being considered, e.g. the protection of aquatic life. A water body cannot achieve good status if the EQS for any WFD Priority/Priority Hazardous Substance or Specific Pollutant, is exceeded.

UKTAG Guide to the Metal Bioavailability Assessment Tool (M-BAT)

Water Framework Directive: River and Lake

Purpose of document: To provide guidance on the use of the metal bioavailability assessment tool (M-BAT) for practitioners involved in monitoring, assessment and classification using the new $EQS_{bioavailable}$ that have been developed for a number of metals under the Water Framework Directive (WFD).

Note: this document does not fully describe all aspects of the M-BAT development and application; for this please refer to the full technical reports as outlined in Section 4.

1. Introduction

1.1 Background – why is bioavailability important?

The Water Framework Directive (WFD) (2000/60/EC) requires European Union Member States to ensure that all inland and coastal waters achieve 'good' water quality status by 2015. One of the measures used to deliver this requirement are Environmental Quality Standards (EQS). An EQS is the concentration of a chemical in the environment above which there is not expected to be an adverse effect on the specific endpoint being considered, e.g. the protection of aquatic life. A water body cannot achieve good status if the EQS for any WFD Priority/Priority Hazardous Substance or Specific Pollutant, is exceeded.

EQSs for the protection of aquatic life have been derived for a number of metals under previous legislation, i.e. the Dangerous Substance Directive (76/464/EEC). Several of these EQSs were expressed as hardness bandings to reflect the indications that toxicity to aquatic life was influenced by water hardness. Scientific knowledge and understanding on the impact of metals has since developed and shows that the toxicity of metals is dependent on a range of water quality parameters in addition to water hardness, principally pH and dissolved organic carbon (DOC). These parameters influence the amount of metal that is actually bioavailable. This is the fraction of the metal which is responsible for toxic effects in flora and fauna. This is important as it supports the long established consideration that measures of total metal in waters have limited relevance to potential environmental risk (Campbell 1995; Niyogi and Wood 2004).

The bioavailability of a metal depends on a number of physico-chemical factors which govern both metal behaviour and the interactions of the toxic forms of the metals with a biological receptor. This is diagrammatically represented in Figure 1. For example, as shown in Figure 1 if the metal ions (Me^{2+}) bind to other ions, such as carbonate ions (CO_3^{2-}) or DOC then it reduces the ability of the ions to bind to the organism and have an impact. In addition other ions such as sodium (Na^+) and hardness (Ca^{2+}) can compete with the metal ions in binding to the organisms and prevent the metal binding.

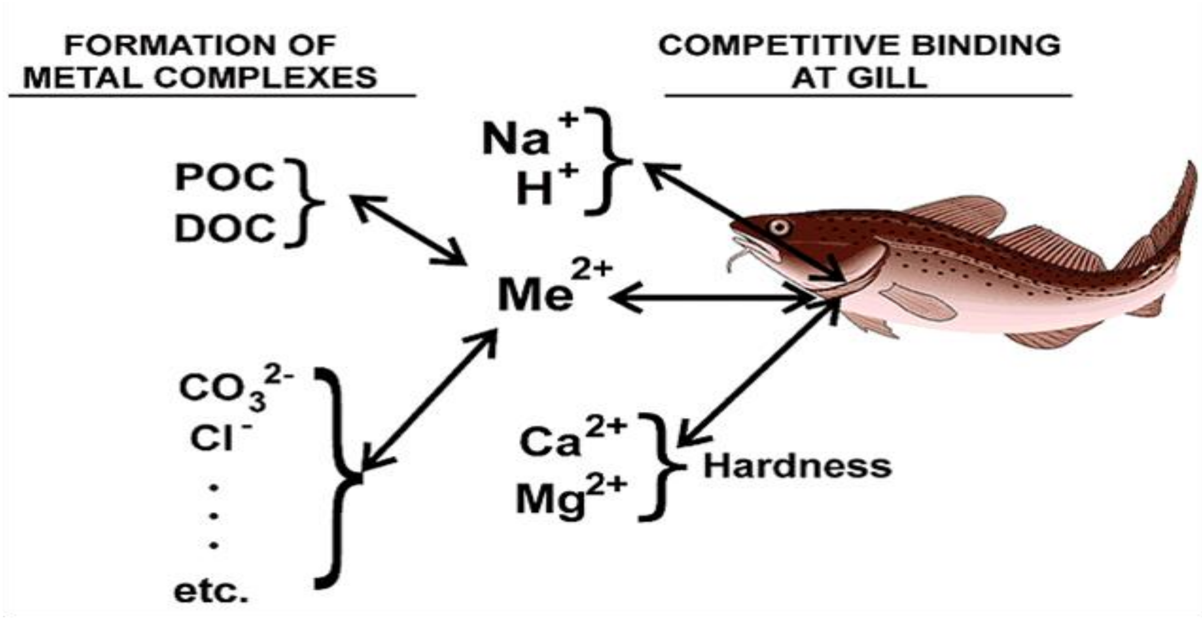

Figure 1: Factors affecting the bioavailability of metals in water

This increased understanding of the impact of certain metals on the aquatic environment has enabled EQSs to be derived for a number of metals based on their bioavailable concentration. They are derived to reflect concentrations of concern in conditions of high bioavailability and are referred to as $EQS_{bioavailable}$. The WFD Daughter Directive on priority substances (2008/105/EC) (Annex 1, Part B3) states that Member States may take account of the effect of hardness, pH or other water quality parameters that affect the bioavailability of metals. The new freshwater EQSs developed for copper, zinc and manganese, which are UK Specific Pollutants have been derived as bioavailable EQSs and take into account consideration of pH, DOC and calcium. The revised EQS for nickel (an EU priority substance under WFD) is also expressed as a bioavailable concentration.

1.2 How do we determine bioavailable concentrations in the environment?

It is very difficult to measure the bioavailable concentration of a metal directly. We therefore have to rely on models to predict the bioavailable concentration from dissolved concentrations.

After many years of research, such models are now available for several metals including copper, zinc, manganese and nickel. They are known as Biotic Ligand Models (BLMs). A BLM is a predictive tool that can take account of water quality parameters such as pH, and calcium to determine the amount of bioavailable metal present.

However, the complexity of the models, the runtime per sample, input data requirements and level of operator skill needed to interpret the model outputs mean that few regulatory organisations have adopted the full BLMs. The UK is no different. However the value of adopting a bioavailability-based approach is recognised and so the UK has developed simplified metal bioavailability assessment models for each of the available metal BLMs. These have been combined into a single tool, the Metal Bioavailability Assessment Tool (M-BAT) (See Section 1.3).

1.3 Metal Bioavailability Assessment Tool (M-BAT)

The M-BAT is a simplified version of the BLMs for copper, zinc, manganese and nickel. The key output of the M-BAT is an estimate of the bioavailable concentration of a metal under the conditions found at a site, which can then be compared with the $EQS_{bioavailable}$ to assess compliance.

M-BAT operates in MS Excel and is therefore more compatible with the IT systems available to the regulatory Agencies than the full BLMs. It is also simpler to use as, for example, it requires far fewer data inputs compared to the 'full' BLMs. The main parameters which influence bioavailability are pH, calcium and DOC and therefore the tool is based on these parameters. This avoids the need for inclusion of the wide range of parameters required for some of the full BLMs. Comparison between the simplified models and the 'full' BLMs have been made during their development. This analysis shows that the outputs of MBAT are close to those achieved with the 'full' BLMs but are slightly precautionary relative to the full BLM.

Further information on the development of the bioavailability assessment tools is provided in the key reports outlined in Section 4.

1.4 The metals included in M-BAT

The M-BAT covers all the metals for which a bioavailable EQS has been derived. These are the UK Specific Pollutants zinc, copper and manganese, and the EU Priority Substance nickel.

1.5 Application of M-BAT

M-BAT is applicable to all UK freshwaters. The outputs from M-BAT can be used in one of two ways:-

- To assess compliance with an $EQS_{bioavailable}$ and undertake classification
- To estimate the 'vulnerability' of a location to metal inputs – taking into account the relevant water quality parameters at the site, i.e. pH, DOC and calcium.

2. Using the M-BAT

This section describes how to use the M-BAT to assess the potential risk of copper, zinc, manganese and nickel in the freshwater environment.

The M-BAT operates in versions of MS Excel from 2003 onwards. Upon opening M-BAT it is imperative to ensure that macros are enabled, otherwise the tool will not work.

Step-by-step instructions for running the tool are given on the front page of the tool.

2.1 Data inputs

a) pH, DOC and Ca

The M-BAT determines the bioavailability of certain metals at specific locations through the use of local water chemistry data, specifically pH, DOC (mg L^{-1}) and Ca (mg L^{-1}). These are mandatory inputs for the tool to run. Without these parameters the tool will not run and a prompt will appear requesting an input.

The input values for each of the three parameters can be either an individual sample result or a summary value derived from sampling results for a relevant time period, eg a calendar year or a 3 year time period under WFD. For both pH and calcium where a summary value is used the average is recommended but for DOC the median value is recommended.

b) Dissolved metal

The dissolved metal concentration which is included in the tool can be added as an individual sample result or as a summary value, e.g. the average of available data for the time period being considered, e.g. three year period for WFD compliance.

c) Other

Sample ID, location, water body and date on which the sample was taken can also be entered into the tool, although these are not mandatory for the calculation to run.

2.2 What if data for some of the fields are absent?

The M-BAT requires data inputs for pH, DOC and Ca. Ideally monitoring for copper, zinc, manganese and nickel will be accompanied by monitoring for pH, DOC and calcium.

There may be situations however where the data is not available. In addition, when using historical data, information on all three parameters may not available. This is particularly the case for DOC as to date it has not been routinely monitored in freshwaters in the UK or many other European Member States. Where associated data is not available then relevant data for the site, eg previous monitoring data or data from similar sites, can be used to give an indication of levels and enable the tool to run.

2.3 Outputs from the M-BAT

As noted in Section 1.5 outputs from MBAT can be used in one of two ways:

a. to assess compliance with a bioavailable EQS and undertake classification
b. to estimate the ‘vulnerability’ of a location to metal inputs.

(a) EQS compliance assessment

If dissolved metal concentrations are available along with pH, Ca and DOC data the associated bioavailable metal concentration will be calculated. This is required for EQS compliance and classification purposes. The bioavailable metal concentration gives an estimate of the amount of metal in the sample that is biologically active and of ecological relevance and is used to assess compliance with the $EQS_{bioavailable}$.

It is calculated by multiplying the measured dissolved concentration by the BioF which is also an output of M-BAT.

In addition the risk characterisation ratio (RCR) is calculated. The RCR is a commonly used metric in screening risk assessments and provides an indication of whether the site being assessed has passed or failed the EQS and by what extent. The RCR is calculated by comparing the bioavailable concentration determined with the $EQS_{bioavailable}$. Where the RCR is greater than 1 this indicates the bioavailable concentration is above the EQS and therefore at risk.

A further output is the $PNEC_{dissolved.}$ The site specific PNECdissolved can be considered a site specific EQS (expressed as dissolved concentration) and is discussed further below.

(b) Site vulnerability to metals

If only data for pH, DOC and Ca are entered into the M-BAT (i.e. without data for dissolved metal concentrations) the output will be a site-specific $PNEC_{dissolved}$. The site-specific $PNEC_{dissolved}$ can be considered as a site-specific EQS (expressed as dissolved metal), and is useful in ranking sites in terms of their sensitivity to metal toxicity.

2.4 Operating boundaries of M-BAT

Each of the BLMs have been developed and validated for particular ranges of pH, Ca and DOC. This has been reflected in the simplified models which have been developed and make up M-BAT. The operating ranges for pH, Ca and DOC for each of the components of M-BAT, i.e. copper, zinc, manganese and nickel are shown in Table 1.

If any of the input parameters fall outside the validated ranges the relevant boundary value, ie either the upper or lower value is used as a substitute. For example if the pH input value is below the lower boundary for a metal the lower boundary value is used as a substitute. Where this is done a flag appears in the tool with a comment box which explains what has been done. In most circumstances this use of a substituted value will not lead to a risk of higher bioavailability, but in other instances this may be unclear and the comment indicates further advice should be obtained. Further advice can be obtained via the contact page on the UKTAG website.

Table 1: Operating ranges of the models within MBAT

	pH	Calcium (mg/l)	DOC (mg/l)
Copper	6 – 8.5	3.1 - 93	Upper value of 15mg/l
Zinc	6 - 8	3 - 160	Upper value of 20mg/l
Manganese	5.5 – 8.5	1 - 200	Upper value of 20mg/l
Nickel	6.5 – 8.7	2 - 88	Upper value of 20mg/l

3. Background concentrations

3.1 General advice

Metals occur naturally in the aquatic environment due to weathering of surface geology. Natural background concentrations are therefore determined by local geology. The general definition of natural background level is the concentration that is present owing to natural and geological processes only, i.e. the background level with no anthropogenic contribution. However in reality truly pristine areas are rare within Europe and inevitably any estimate of natural background concentration will include a contribution from anthropogenic sources because of inputs from historical anthropogenic activity, e.g. mining. This anthropogenic input is hard to quantify and distinguish from naturally occurring levels and therefore in reality any assessment of a background concentration will be an ‘ambient background concentration’ (ABC).

The EU have stated in the EQS Directive (2008/105/EEC), Annex 1, Part B3 that Member States can take into account background concentrations for metals when assessing monitoring results against the EQS.

For most metals, the local background concentration would be accounted for only if there is a failure of the EQS. During an investigation of an EQS failure consideration should be given to the potential influence of ambient background concentrations at the particular site being studied. Suitable ABCs cannot be specified here because this will be a very local assessment. It should therefore use information from e.g. headwaters or neighbouring sites to estimate a local ABC. This ABC would be subtracted from the measurements of dissolved metal concentration to ‘refine’ the assessment of risk.

3.2 Zinc

The situation for zinc however is slightly different as consideration of background concentration is an explicit part of the zinc EQS and therefore needs to be taken into account as part of the initial compliance assessment. Zinc is found widely in the environment and at relatively high levels compared to other metals. For this reason the EQS was derived taking into consideration the background concentration to avoid setting regulatory standards below the background level. For this reason, a local background concentration should be subtracted from the monitoring data before the bioavailability estimate is performed using MBAT. A national background concentration has been assigned in Scotland and Northern Ireland. For England and Wales specific values have been derived for individual hydrometric areas in addition to a national value for use in those areas where an area specific value has not been able to be derived. Appendix A sets out recommended background concentrations for zinc.

4. Key Documents

The following key documents are hosted on the WFD UK Technical Advisory Group (WFD-UKTAG) website www.wfduk.org.

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 of England and Wales, Bristol, UK.

Merrington G, Wilson I, Peters A. 2014. The development and use of the nickel bioavailability tool.

WFD-UKTAG. 2012. Development and use of the copper bioavailability tool (draft).

WFD-UKTAG. 2012. Development and use of the manganese bioavailability tool (draft).

WFD-UKTAG. 2013. Development and use of the zinc bioavailability tool (draft).

WFD-UKTAG. 2014a. Metals Bioavailability Assessment Tool (MS Excel)

WFD-UKTAG. 2014b. Estimation of ambient background concentrations for metals in freshwater.

5. Glossary

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. It is calculated by dividing the Generic or Reference EQS by the calculated site-specific EQS.
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, i.e. pH, calcium concentrations, hardness, dissolved organic carbon, etc.
MBAT or BAT	Metal Bioavailability Assessment Tool or Bioavailability Tool. Effectively this 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.
DOC	Dissolved organic carbon. The input to the screening 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[1].
EQS	Environmental Quality Standard. A term used for long-term water quality standard in Europe, using the annual average concentration of a substance.
PNEC	Predicted No Effect Concentration. This concentration is derived from the ecotoxicological data and site-specific water quality data using the BLM.

[1] Environment Agency. 2010. The importance of dissolved organic carbon in the assessment of environmental quality standard compliance for copper and zinc. Draft final report SC080021/SR7a. Environment Agency, Bristol, UK.

6. References

Campbell PGC. 1995. Interactions between trace metals and aquatic organisms: a critique of the free-ion activity model. In: Tessier A, Turner DR. Editors. Metals speciation and bioavailability in aquatic systems. Chichester, UK. John Wiley and Sons, pp 45-102.

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. 2010. The importance of dissolved organic carbon in the assessment of environmental quality standard compliance for copper and zinc. Draft final report SC080021/SR7a. Environment Agency, Bristol, UK.

European Commission. 2000. Directive 2000/60/EC of the European Parliament and the Council of 23rd October 2000 establishing a framework for Community action in the field of water policy. European Communities Official Journal L327, 22.12.2000, 1-72.

European Commission. 2008. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC.

Merrington G, Wilson I, Peters A. 2014. The development and use of the nickel bioavailability tool.

Niyogi S, Wood CM. 2004. Biotic ligand model, a flexible tool for developing site-specific water quality guidelines for metal. Environ Sci Technol 38:6177-6192.

WFD-UKTAG. 2012. Development and use of the copper bioavailability tool (draft).

WFD-UKTAG. 2012. Development and use of the manganese bioavailability tool (draft).

WFD-UKTAG. 2013. Development and use of the zinc bioavailability tool (draft).

WFD-UKTAG. 2014a. Metal Bioavailability Assessment Tool

WFD-UKTAG. 2014b. Estimation of ambient background concentrations for metals in freshwater.

Appendix A: Recommended Ambient Background Concentrations for zinc in freshwaters

The zinc EQS is an ‘added risk’ EQS that requires background to be accounted for as part of the assessment of compliance with the EQS. This approach was taken for zinc due to the fact it is found widely in the environment and at relatively high levels. This approach helps avoid the setting of regulatory standards which are below ambient background concentrations. For zinc background concentrations need to be subtracted from the measured dissolved concentration of zinc prior to analysing the data using the M-BAT. (NB: the approach used in Scotland is slightly different as the background concentration has been incorporated into the EQS and therefore does not need to be considered separately).

UKTAG have adopted a method for estimating Ambient Background Concentrations (ABCs) for zinc based on a low (5^{th}) percentile of monitoring data (UKTAG 2014b). ABCs have been derived by assessing a dataset of around 150000 data points and using a low percentile to ensure significant anthropogenic influences are excluded. Where there are sufficient data, ABCs have been defined for a catchment or group of catchments. Where there are insufficient data or data are subject to uncertainty because many of the measured values are reported as ‘less than’ concentrations a default value based on pooled data has been used. This approach was also used where minimal differences between catchments were identified from the dataset.

This approach does not distinguish between anthropogenic and natural (e.g. geological) sources of zinc because this is not possible, but provides the best practical estimate of ABCs that can be used in assessing compliance with the new zinc EQSs.

In Scotland and NI, a default ABC of 1ug/l is adopted for freshwaters. In England and Wales, an ABC specific to a freshwater hydrometric area (HA) is used. ABCs in different hydrometric areas (HAs) can differ from one another, reflecting variations in geology, past and present land use, and industrial pressures. Where it has not been possible to determine a hydrometric area specific value due to lack of sufficient data, a default of 1.4ug/l dissolved zinc can be applied. This was derived based on the pooled data from England and Wales. Values for the ABC are outlined in Table 1.

As more monitoring data are gathered the ABCs will be refined and where relevant, further HA-specific ABCs may be proposed.

Table 1: Ambient Background Concentrations (ABCs) for dissolved zinc to be used in conjunction with the EQS for zinc

Area/Region	ABC (ug/l)
Freshwaters in England and Wales	
Tyne	4.8
Tees	4.1
Ouse, Humber	2.9
Nene	4.0
Great Ouse	3.1
River Stour	3.0
Blackwater/Chelmer	3.6
Lee	3.3
Thames	2.0
Test	2.0
Avon/Hants	3.1
Exe	1.4

Area/Region	ABC (ug/l)
Dart	1.7
Clywd/Conwy	2.0
Dee	2.9
Eden	1.2
Anglesey	3.0
Tamar	2.9
Fal	5.8
Camel	7.1
Tone/Parrett	3.3
Frome, Bristol Avon	2.3
Wye	2.0
Usk	2.2
Taff	2.8
Neath	2.8
Loughar	3.9
Tywi	2.0
Teifi	2.5
Rheidol/Ystwyth	4.1
Dovey	3.2
Glaslyn	2.6
All other freshwaters not listed	1.4
Freshwaters in Scotland and Northern Ireland	
For all freshwaters	1.0