DELIVERING A PRACTICAL METHODOLOGY TO ACCOUNT FOR METAL BIOAVAILABILITY IN THE WATER FRAMEWORK DIRECTIVE – CASE STUDIES

Graham Merrington[1], Peter Simpson[1], Chris Schlekat[2], Katrien Delbeke[3], Frank Van Assche[4], Frederik Verdonck[5], Patrick Van Sprang[5]

[1]wca environment, Brunel House, Volunteer Way, Faringdon, UK [2]Nickel Producers Environmental Research Association (NiPERA), 2525 Meridian Parkway, Suite 240, Durham, NC 27713 USA
[3]European Copper Alliance, Tervurenlaan 168, B-1150 Brussels, Belgium [4]International Zinc Association, Avenue de Tervuren 168, B-1150 Brussels, Belgium [5]ARCHE, (Assessing Risks of Chemicals), Stapelplein 70 box 104, 9000 Gent, Belgium

INTRODUCTION

Accounting for the bioavailability of metals in routine water monitoring represents a step-change in the way regulators assess the potential risks of metals in the aquatic environment. Guidance on how bioavailability may be incorporated into compliance assessments, classification and local risk assessment are included in the recent EU Technical Guidance for deriving Environmental Quality Standards (EQS) under the European Water Framework Directive (WFD). The guidance supports the use of a tiered compliance assessment regime for metals (Figure 1) that incorporates bioavailability and recommends using Biotic Ligand Models (BLMs).

The bio-met project has developed an online resource (www.bio-met.net) that includes a user friendly software tool (User-friendly BLM) for calculating the bioavailability of copper, nickel and zinc and assessing EQS compliance in European freshwaters.

However, a reasonable question remains before widespread adoption of this new approach: "How will the pattern of EQS exceedances differ from conventional assessments when bioavailability is taken into account?"

This poster gives three examples of EQS compliance for copper, nickel and zinc when bioavailability is accounted for. For two examples, how this compliance changes from existing standards to accounting for bioavailability is also shown. The examples are from Sweden, France and Austria.

THE TIERED APPROACH AND PROCESSING DATA

To determine compliance with an EQS regulators will usually monitor the metal concentration at a site over a period of at least a year.

1. The mean dissolved metal concentration is compared to the generic $EQS_{bioavailable}$. Some European Member States will also assess the "confidence off failure" as this stage using guidance given in ISO/WD 5667-20. If the EQS is exceeded the assessment passes to tier 2
2. pH, dissolved calcium and dissolved organic carbon data are used in the user-friendly BLM to account for site-specific bioavailability. The outputs of these calculations include a local bioavailable metal concentration (which can be compared to the $EQS_{bioavailable}$), a local $EQS_{dissolved}$ (which can be compared to local dissolved concentrations of metals) and also a local risk characterisation ratio. As per stage 1, some Member States in Europe will assess the "confidence in failure". If the EQS is exceeded the assessment passes to tier 3
3. Tier 3 allows for local issues, including ambient background concentrations.

The input data for the examples below are available freely available from European Environment Agency website or directly from the Member State Regulator. The $EQS_{bioavailable}$ for the metals are 1 µg Cu l^{-1}, 10.9 µg Zn l^{-1} and 4 µg Ni l^{-1}. The first two are proposed Annex VIII EQS in the UK. The $EQS_{bioavailable}$ for nickel is proposed at EU level, but is not finalised.

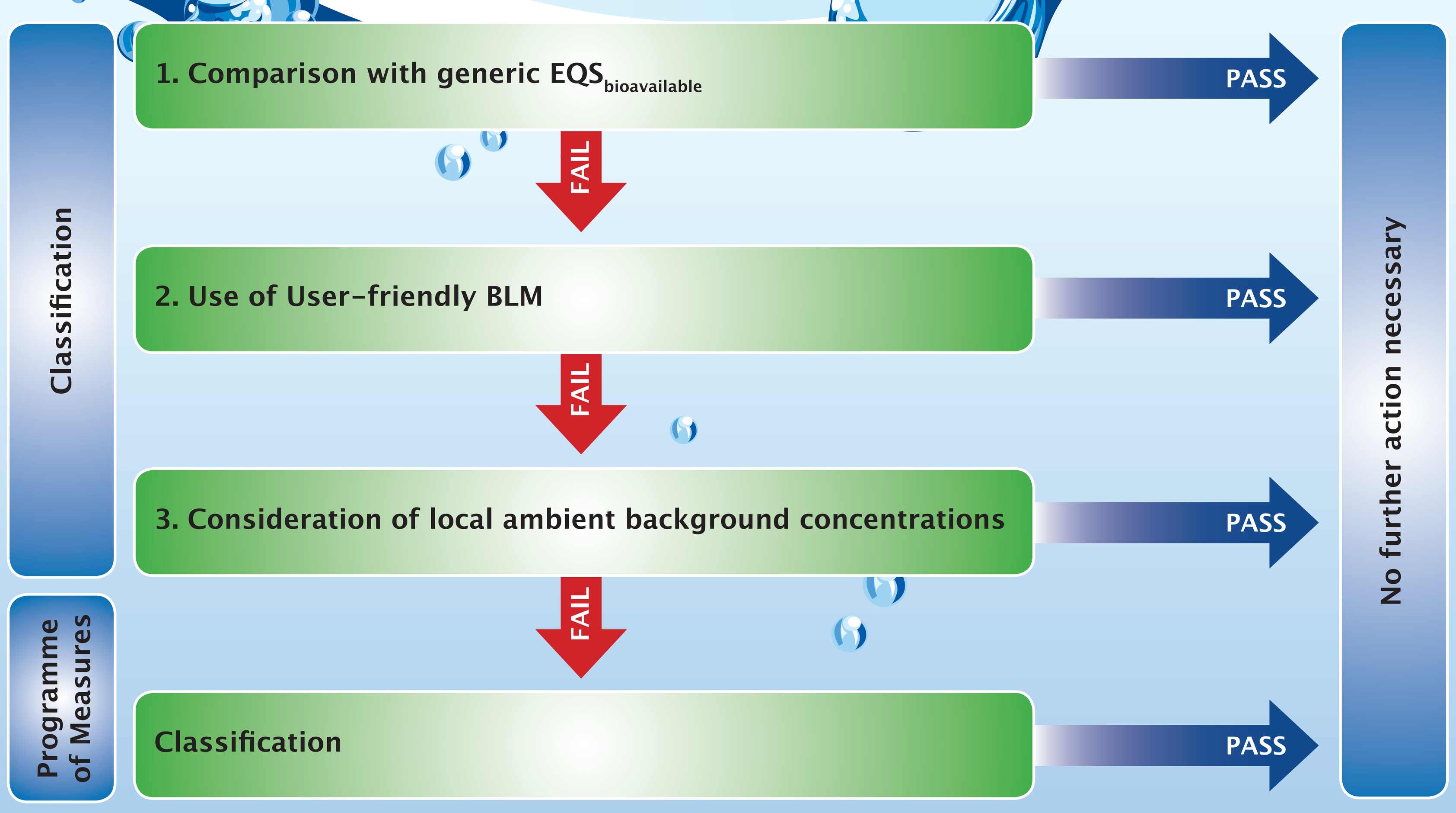
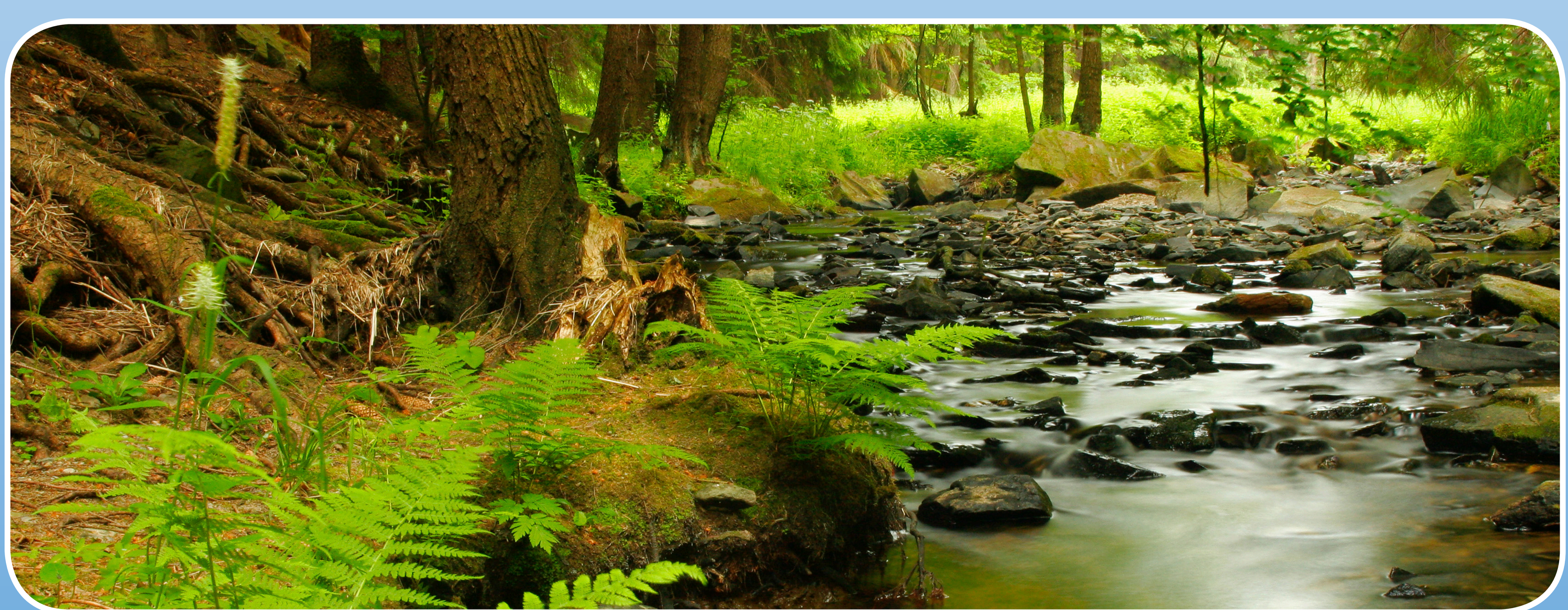


Figure 1. A tiered approach to account for metal bioavailability in regulatory compliance assessment.



SWEDISH MONITORING DATA

Table 1 shows the compliance assessment results for a series of Swedish rivers and lakes. These data were made directly available from KEMI and cover the period 2000-2008. These data are not annual averages at sites, but represent a 'face value' assessment with samples, which tends to be more precautionary than a full compliance assessment.

For copper and zinc an additional comparison is made between EQS failure using the existing EQS (for zinc this is hardness-based) with the one that fully accounts for bioavailability. These data show that the EQS failure rates after accounting for bioavailability are lower than when bioavailability is not considered. The existing zinc EQS in Sweden is an 'added' value, although no ambient background has been included here. The waters in this dataset have a mean pH of 6.5, but a median dissolved organic carbon of 8.4 mg l^{-1}. This means these waters are relatively insensitive to exposures of copper, nickel and zinc which is supported by the low levels of EQS failure observed after bioavailability is accounted for.

			Outputs from User-friendly BLM		
Metal	Number of samples	Mean (and range) of dissolved metal, µg L^{-1}	Mean (and range) of local $EQS^{dissolved}$ µg L^{-1}	Number of Exceedances (%)	Number of Exceedances (%) with Existing EQS*
Copper	3942	1.55 (0.14-64)	34 (2.3-167)	0.2	4
Nickel	3928	0.89 (0.03-6.4)	9.0 (2.7-29)	1	-
Zinc	3942	4.64 (0.2-180)	32 (10.9-132)	0.8	38

Table 1. Monitoring data from Sweden used to account for bioavailability.

*The EQS for Cu in Sweden (4 µg L^{-1}) is calculated using the BLM, but not implemented with it. Naturvårdsverket 2008. Förslag till gränsvärden för särskilda förorenande ämnen. Stöd till Vattenmyndigheterna vid statusklassificering och fastställande av miljökvalitetsnormer. Swedish Environmental Protection Agency. Report 5799. In Swedish.

FRENCH MONITORING DATA

Table 2 shows the compliance assessment results for monitoring data from Northern France for the year 2007 obtained from the European Environment Agency's website. There are relatively few sites, but each site has been sampled between 8 and 12 times over the period. The number of metals monitored at each site varies with fewer sites recording dissolved copper and zinc. The waters in this dataset have median dissolved organic carbon of 3.6 mg l^{-1} and pH (mean = 7.9), the mean calcium concentrations for these sites is 74 mg L^{-1}. The Table clearly shows the relatively high exceedances for zinc and especially Cu using existing hardness based standards, as compared to accounting for bioavailability. The levels of nickel exceedance are also relatively low when bioavailability is considered.

			Outputs from User-friendly BLM		
Metal	Number of samples	Mean (and range) of dissolved metal, µg L^{-1}	Mean (and range) of local $EQS^{dissolved}$ µg L^{-1}	Number of Exceedances (%)	Number of Exceedances (%) with Existing EQS*
Copper	142	2.85 (0.7-13)	11 (2.6-52)	1	88
Nickel	316	2.16 (0.5-35)	6.87 (4.0-22)	2	-
Zinc	142	14 (0.5-140)	23 (13-72)	14	58

Table 2. Monitoring data from French used to account for bioavailability.

*Hardness-based, for Good Status.
http://sierm.eaurmc.fr/eaux-superficielles/fichiers-telechargeables/grilles-seq-eau-v2.pdf

AUSTRIAN MONITORING DATA

Table 3 shows the compliance assessment results for Austrian monitoring data for 2006, obtained from the SWAD database. There are about 150 sites, but each site had been sampled multiple times over the year. At each site, pH, DOC, total water hardness, alkalinity and the total and dissolved fraction of copper, nickel and zinc was measured. The waters in this dataset have a high pH (mean = 8.0). Average DOC is 2.5 mgl^{-1} and total hardness averages 10.7 °dH.

Overall, there are relatively few EQS failures for copper, nickel and zinc. For copper and zinc, an additional comparison is made between EQS failure using the existing EQS with the one that fully accounts for bioavailability. These data show that the EQS failure rates after accounting for bioavailability are equal (for Cu) and higher (for Zn) than when bioavailability is not considered. Also, the location of the exceedances changes when considering DOC and pH in addition to hardness (results not shown here).

			Outputs from User-friendly BLM		
Metal	Number of samples	Mean (and range) of dissolved metal, µg L^{-1}	Mean (and range) of local $EQS^{dissolved}$ µg L^{-1}	Number of Exceedances (%)	Number of Exceedances (%) with Existing EQS
Copper	1206	1.04 (0.1-5.3)	7 (1-155)	0.7	0.6
Nickel	1206	0.93 (0.02-9.6)	5 (2-42)	0.4	-
Zinc	1206	3.08 (0.8-95.16)	20 (11-97)	2.1	0.6

Table 3. Monitoring data from Austria used to account for bioavailability.

CONCLUSIONS

- Data are available to undertake bioavailability assessments, even at a screening level.
- There are relatively few EQS failures for copper, nickel and zinc, aside from nickel in Poland, although it is not clear as to whether the metals are dissolved or total.
- Bio-availability based EQS give robust and realistic assessments of potential metal risks.
- The number of EQS exceedances may change little, or decrease compared to existing generic or hardness based standards, but it is likely that the location of exceedances will change when accounting for bioavailability.