



Variation in the availability of metals in surface water, an evaluation based on the dissolved, the freely dissolved and Biotic Ligand Model bioavailable concentration

A.J. Wijdeveld^{a,*}, C.A. Schipper^a, T.J. Heimovaara^b

^a Deltares, P.O. Box 177, 2600 MH Delft, The Netherlands

^b Technical University of Delft, Faculty of Civil Engineering and Geosciences, P.O. Box 5048, 2600 GA Delft, The Netherlands

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ABSTRACT

In this study the spatial distribution of dissolved metals in surface water is studied at nine locations in Lake Ketelmeer (the Netherlands). The measured dissolved metal concentrations are combined with the local water quality parameters for salinity, pH, alkalinity and DOC to calculate a FIAM Free Ion Activity Model (FIAM) and the Biotic Ligand Model (BLM) based bioavailable metal concentration. The BLM model is used for Cu, Ni, Pb and Zn and the FIAM model for Cd, Cr, Cu, Ni, Pb and Zn.

To be able to compare the dissolved metal concentration with the FIAM or BLM based bioavailable metal concentration, an accepted reference standard can be used which is also corrected for the bioavailable concentration. Here the Water Framework Directive (WFD) Annual Average Quality Standard (AA-QS) is used, corrected for the FIAM and BLM based bioavailable metal concentration under reference conditions. This yielded a site specific Risk Characterization Ratio (RCR_{FIAM}/RCR_{BLM}).

The FIAM model shows an exceedance of the site specific AA-QS for Cu (RCR_{FIAM} of 1.8) and Pb (RCR_{FIAM} of 1.5) in the northern middle part of the lake. This is due to a lower pH in this part of the lake. The BLM model was inconclusive with regard to spatial trends for Cu and Ni due to out of boundary conditions for the model. For locations where the BLM model was within the model boundary conditions, the RCR_{BLM} could be as high as 7.5 for Cu and 3.2 for Ni. The main water quality parameter causing the high RCR_{BLM} was the low DOC concentration.

To establish if the locally increased RCR for Cu and Pb (FIAM) or Cu and Ni (BLM) poses an ecotoxicological risk to organisms the multi substances Potentially Affected Fraction (ms-PAF) model is used. The FIAM based ms-PAF indicates that the northern middle part of the lake has the highest chronic metal exposure risk, with an ms-PAF of 27%. The BLM based ms-PAF has a maximum of 45%, but lacks a spatial trend due to the missing BLM corrected Cu and Ni concentrations for some locations.

1. Introduction

The overall purpose of this study is the combined use of measured dissolved metal concentrations and local water quality dependant bioavailable metal concentration to improve the potential ecotoxicological risk evaluation.

In 2008 the European Commission set environmental water quality standards for 33 priority substances and 8 other substances in water as part of the WFD (European Communities (2000a); European Communities (2000b)). The list of priority substances was updated in 2011 with 15 additional priority substances (COM/2011/0876, 2011). Water quality standards for metals in surface water, like the Annual

Average Quality Standard (AA-QS), are based on the total dissolved metal concentration. The dissolved concentration is defined by the metal concentration in water passing through a 0.45 μm filter.

In reality metals interact with other dissolved components in the water, resulting in metal-ligand formation. Only a fraction of the total dissolved metal concentration is available as free metal ion. The division of the dissolved metal concentration into metal ligands and the free metal ion is called speciation. The ecotoxicity of metals depends on the speciation of the metal (Long and Angino, 1977; Scott et al., 2001; van Hattum et al., 1996). The metal-ligand formation in natural water bodies is impacted by water quality parameters like pH, salinity, dissolved organic carbon (DOC) and alkalinity. The bioavailable metal

* Corresponding author.

E-mail addresses: Arjan.wijdeveld@deltares.nl (A.J. Wijdeveld), Cor.schipper@deltares.nl (C.A. Schipper), T.J.Heimovaara@tudelft.nl (T.J. Heimovaara).

concentration is impacted by this metal ligand formation (Long and Angino, 1977; Scott et al., 2001; van Hattum et al., 1996). Many metal ligands are not taken up by organisms, and therefore are less bioavailable (Brown and Markich, 2000). The Free Ion Activity Model (FIAM) calculates the metal-ligand formation and free metal ion concentration, taking into account the natural water quality (Stumm and Morgan, 1970; Campbell, 1995a; Stumm and Morgan, 1996; Parker and Pedler, 1996). In the FIAM model it is assumed that the free metal ion activity better describes the observed toxicological effect on organisms (Weng et al., 2001). Although the use of FIAM models has been criticized (Campbell, 1995b) and improved upon (Brown and Markich, 2000), the conceptual approach to study the behavior of the free metal ion and metal-ligands for exposure of biota to metals is the basis for the development of more advanced models to describe the toxicity of metals (Rüdel et al., 2015).

The next step in understanding the ecotoxicity of metals is to consider the interaction of the metal with the organism by the formation of a biotic ligand. The biotic ligand is a biological receptor that is used as the target site at which metals bind for uptake by organisms. These types of numerical models are called BLM models (Verschoor and Vink, 2010), and are conceptually more complex and require up to 10 input parameters to quantify all interactions (Bootsma and Vink, 2016). At the moment, BLM models have been derived for Cu, Ni, Zn and Pb (Verschoor et al., 2012; Scientific Committee on Health and Environmental Risks, Risk Assessment Report on Zn (2007), Ni (2009) and Cu (2009)). BLMs are recognized as useful and robust methods to determine site-specific risks. They are accepted as second tier risk assessment of monitoring data (Rüdel et al., 2015).

In this study all three methods (the measured total dissolved metal concentration, the FIAM calculated free ion concentration and the BLM bioavailable metal concentration) are compared, taking into account the dissolved metal concentration and the local water quality parameters in a lake. To compare the results for each method a reference point is needed to define an unacceptable metal concentration. For the dissolved concentration, the reference point is the AA-QS, for the FIAM model the AA-QS corrected for the local water quality and for the BLM model the Predicted No Effect Concentration (PNEC) is used. Both the FIAM and BLM models calculate a Risk Characterization Ratio (RCR) for each metal at each location in the lake.

To be able to define if the RCR based in either the FIAM or BLM increases or decreases, the reference risk condition should not only reflect the concentration (AA-QS), but also the reference water quality conditions for this risk concentration. Most of the AA-QS standards within the WFD are based on ecotoxicological dose-effect response curves (Wijdeveld, 2007). These ecotoxicological tests are carried out under standardized conditions, including water quality parameters like pH, alkalinity, salinity and DOC. Water quality parameters for standard water are defined by Dutch Standard Water (DSW) (Janssen, 2004). The FIAM model calculates the free metal ion concentration in standard water based on the AA-QS metal concentration, which gives the reference risk concentration for the FIAM model. The RCR_{FIAM} is calculated by using the measured dissolved metal concentration and the local water quality parameters to calculate the location specific free metal ion concentration and divide this by the free metal ion concentration for AA-QS in standard water. The RCR_{BLM} divides the PNEC calculated exposure levels for the measured dissolved metal concentration by the predicted no-effect concentrations based on the local water quality (Muñoz et al., 2009).

Both the RCR_{BLM} and RCR_{FIAM} indicate if the metal exposure is higher or lower compared to reference standard water conditions. Each metal concentration for each calculation method can now be compared by expressing the deviation from the reference point as the Risk Characterization Ratio ($RCR_{dissolved}$, RCR_{FIAM} and RCR_{BLM}). This approach has been adopted by the European Union System for the Evaluation of Substances (EUSES) (Vermeire et al., 1997).

Ecotoxicological risk assessments are carried out by establishing the

concentration-effect relation for individual chemical components like metals and individual test species under reference water quality conditions (Posthuma et al., 2002). The PAF calculations are based on the observed median lethal concentration [LC50] or no-observed-effect concentration [NOEC] for individual toxic components and individual species. The water quality test conditions for the LC50 and NOEC are carried out in standard water (DSW). Individual (metal) risks can be added to a multi-substance Potentially Affected Fraction (ms-PAF) by either (i) Response Addition (RA) or (ii) Concentration Addition (CA), depending on the mode of action (De Zwart and Posthuma, 2005). The ms-PAF does not take into account the variation in the bioavailable fraction based on local water quality parameters. By applying the RCR_{FIAM} correction factor to the measured metal concentration, the ms-PAF can be corrected for the local water quality.

An alternative approach to study the direct relation between contaminant concentrations and the impact of local water quality conditions would be the use of mortality percentages in bioassays (Lahr et al., 2003). However the bioassays for this site, Lake Ketelmeer, were carried out in sediment and not in surface water. Sediment toxicity is based on historical pollution, and does not have to be representative of the current surface water quality, and hence is not directly related to the WFD 'good chemical status' objective. (Botwe et al., 2017) used sediment bioaccumulation bioassays, correlating bioaccumulation to different sediment metal fractions (the exchangeable (carbonate-bound), reducible (iron/manganese oxide-bound), oxidable (organic/sulphide-bound) and residual/refractory (silicate/mineral-bound) phase). These sediment phases are partly impacted by local water quality conditions. For the current Lake Ketelmeer site, the required sediment metal fraction data is missing. Therefore, this study will not investigate sediment based bioassays.

The water quality based metal risk evaluation based on the FIAM or BLM corrected (RCR) concentrations can be summarized by the flow chart in Fig. 1. This flow chart summarizes the overall goal of this study, how to assist water managers to assess the impact of local water quality conditions on the potential ecotoxicity of the water body so that the measures they take to improve the surface water quality and meet the WFD objective 'good chemical status' are effective. For this purpose, the first step in Fig. 1 is to calculate the WFD chemical status based on the individual metal concentrations. In the next step, the local water quality parameters (pH, Ca and DOC) are used to calculate if the location specific risk according to either the FIAM or BLM model is higher or lower than for standard water. In the last step of Fig. 1 the potential ecotoxicity (expressed by the ms-PAF) is illustrated for all three scenario's. This results in (in this specific case) a higher location specific potential ecotoxicity for the FIAM and BLM based ms-PAF. This means that for this water body the local water quality has to be taken into account.

2. Material and methods

The WFD chemical status of a water body is derived from the individual metal concentrations compared to the AA-QS. By using the FIAM / BLM model, the RCR corrected concentrations are calculated based on the local water quality, and the main parameters increasing or decreasing the risk are determined. The RCR corrected concentrations can then be used in the ecotoxicological ms-PAF risk model. This results in a ms-PAF for metals based on the total dissolved, the FIAM free ion and BLM bioavailable metal.

2.1. General description of the sample location

Lake Ketelmeer is a Dutch lake at the end of the river IJssel (a branch of the River Rhine), and flows into Lake IJsselmeer. The choice for Lake Ketelmeer is due to the presence of a strong pH gradient. The pH shifts from 7.5 to 8.5 from east to west. This is caused by the River Rhine, which is oversaturated with regard to dissolved CO₂ (mainly as

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