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

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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

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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

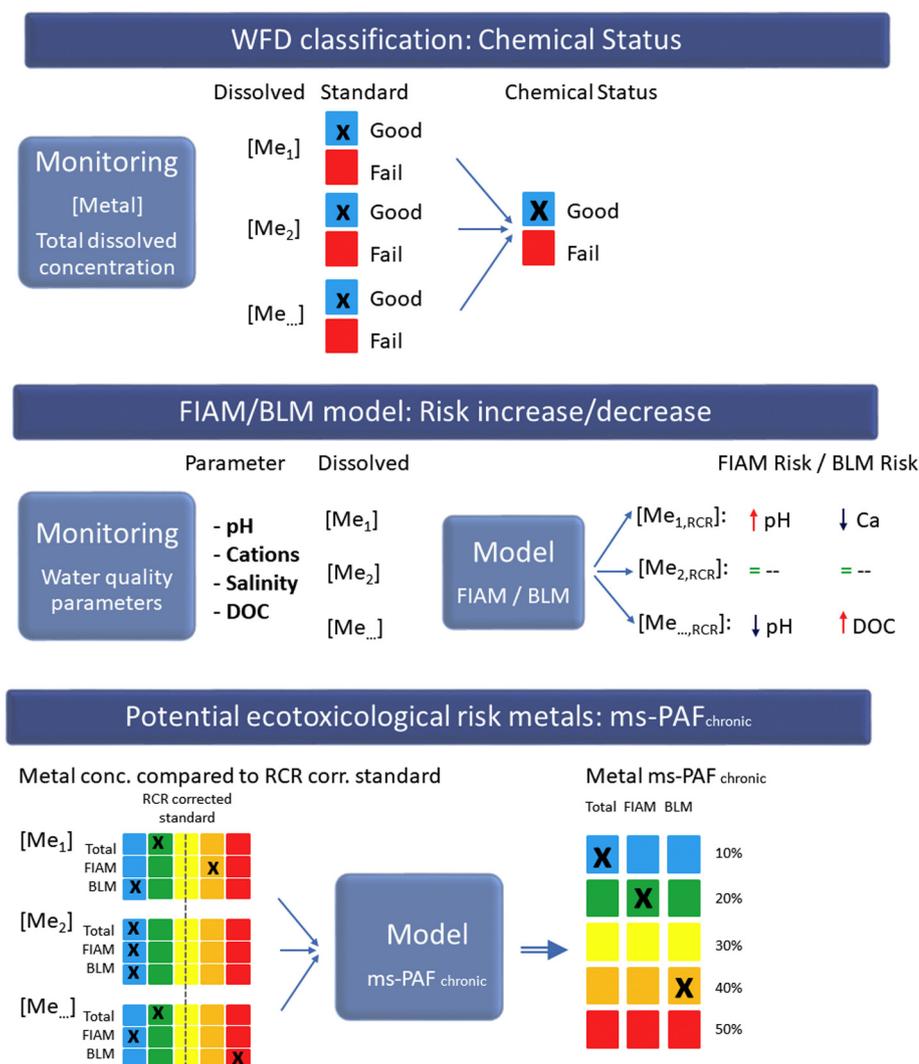


Fig. 1. Overview of three steps to translate monitoring data on the dissolved metal concentrations and local water quality towards a ms-PAF based ecotoxicological risk characterization for metals using either the dissolved metal concentration, a FIAM model corrected RCR_{FIAM} or a BLM corrected RCR_{BLM} . Step 1 shows the WFD classification of the chemical status based on dissolved metal concentrations. Step 2 uses the local water quality in combination with either the FIAM or the BLM model to indicate if there is an increase or decrease in the location specific metal risks based on local water quality parameters, indicated by an upward (higher risk) or downward (lower risk) arrow. In Step 3 the ms-PAF is calculated for all three methods, scoring the potential ecotoxicological impact on a scale of 0% to 50% potential mortality. In this example the dissolved metal based ms-PAF is 10%, not taking into account the local water quality parameters. The FIAM based ms-PAF is 20%, caused by a higher RCR_{FIAM} for metal 1. The RCR_{FIAM} for metal 1 is increased due to a locally lower PH as compared to standard water (see step 2). The BLM based ms-PAF is 40% due to an increased RCR_{BLM} for metal 3. This increase is caused by a deviation of the DOC concentration (lower) as compared to standard water (see step 2).

HCO_3^-) when entering the Netherlands (Gaillardet et al., 1999). The degassing of CO_2 increases the pH and decreases the alkalinity. There is also a mixing of two different sources of water, from the River IJssel and Lake Zwartee Meer. Therefore Lake Ketelmeer shows a spatially varied macro chemical water quality (pH, alkalinity, DOC). The position of Lake Ketelmeer in relation to the water quality sample locations is presented in Fig. 2.

Seven water quality samples were taken in 1999 and analyzed by OMEGAM, a Dutch accredited testing laboratory. The samples were filtered on a $0.45\ \mu m$ filter to remove suspended matter, and acidified with 0.1 M nitric acid for conservation. The water sample depth was 1 m below the surface water level. The original water temperature of the samples is no longer available. Storage of the water samples was at lower than $10\ ^\circ C$ at the day of sampling (ice packs), and transported to the lab on a daily base (lab storage at $4\ ^\circ C$). Detection on the ICP-MS was within 72 h according to (NEN-EN-ISO 17294-2, 2004).

2.2. The AA-QS and the original water quality test conditions

The AA-QS concentrations for Cd, Cu, Ni, Pb and Zn were taken from the Fraunhofer Institute fact sheets for fresh surface water in Europe (Lepper, 2002; Lepper, 2004). For Cd, Cu and Zn the water hardness is taken into consideration (Meyer, 1999; Technical Advisory Group on the Water Framework Directive, UK, 2008). For the current analysis the AA-QS for water hardness class 4 is chosen, based on the average water hardness in The Netherlands. For the Cr no AA-QS was

available, therefore the Dutch surface water standard (Commissie Integraal Waterbeheer, 2000) was used. The WFD AA-QS water quality standards for surface water are presented in Table 1.

By dividing the measured dissolved concentration (presented in Table 2) by the AA-QS an “uncorrected” Risk Characterization Ratio ($RCR_{dissolved}$) can be calculated for reference purposes (Eq. (1)).

$$RCR_{dissolved} = \text{Dissolved}/AA - QS \tag{1}$$

Dissolved: metal concentration in water after filtration ($\mu g/l$)

AA - QS: annual average quality standard ($\mu g/l$)

2.3. FIAM model CHARON

The FIAM model CHARON (De Rooij, 1991) is used to calculate the free metal ion concentration. CHARON stands for the Chemistry Applied to the Research Of Natural systems. CHARON is an extended and modified version of the chemical equilibrium model CHEMEQ developed by the Rand Corporation (Shapley and Cutler, 1970) and is currently developed and maintained by Deltares. The metals Cd, Cu, Ni, Cr and Zn are selected for the CHARON model.

One of the parameters needed to carry out the FIAM calculation is the alkalinity. The alkalinity is not measured in Lake Ketelmeer. Since the pH gradient in the lake is caused by CO_2 degassing (and therefore the HCO_3^- concentration), the measured pH change can be used to calculate the change in carbonate and bicarbonate concentration (Eq.

Table 2

Location of seven monitoring stations for Lake Ketelmeer plus two monitoring stations on the lake boundaries. Year average results for the water quality and total dissolved metals (after filtration) in 1999.

Location	x	y	pH	Alkalinity ^a meq/l	DOC mg/l	Salinity ^b meq/l	Dissolved concentrations after filtration (0,45 µm), 1999 (Omegam)					
							Cd µg/L	Cr µg/L	Cu µg/L	Ni µg/L	Pb µg/L	Zn µg/L
Monitoring stations lake												
Ketelmeer K2	182.16	511.30	8.5	2.0	3.8	–	< 0.1	< 1	5.0	2.0	< 5	15
Ketelmeer K3	180.10	510.90	8.3	2.3	3.7	–	< 0.1	< 1	4.5	2.0	< 5	9
Ketelmeer Oost 2	180.80	513.44	8.2	2.5	6.1	–	< 0.1	< 1	5.0	2.5	< 5	20
Ketelmeer Oost 3	182.44	513.42	8.6	1.8	3.8	–	< 0.1	< 1	4.0	2.0	< 5	13
Ketelmeer Oost 6	183.33	512.98	8.2	2.5	3.5	–	< 0.1	< 1	3.5	2.0	< 5	7
Ketelmeer Oost 8	181.20	513.10	7.9	3.0	3.3	–	< 0.1	3.0	7.0	2.5	< 5	21
Ketelmeer Ljm BRT	181.20	512.60	7.8	3.1	3.0	–	< 0.1	< 1	6.0	< 1	< 5	7
Monitoring stations boundaries												
Kampen	190.99	508.06	8.0	2.8	3.6	0.3	0.07	1.6	3.5	2.0	2.5	15.4
(East boundary)												
Ketelmeer West 1	172.26	513.68	8.3	2.3	4.6	0.3	0.06	1.7	3.2	2.0	1.8	12.7
(West boundary)												

^a Alkalinity calculated based on the pH and the CO₂/HCO₃⁻ equilibrium.

^b No data for salinity, average Rhine data is taken.

The RCR_{BLM} is calculated by dividing the predicted environmental concentration (PEC), which is based on the measured dissolved metal concentration and the local water quality, by the water quality specific predicted no effect concentration (PNEC).

$$RCR_{BLM} = PEC/PNEC \quad (6)$$

PEC: Predicted Environmental Concentration (µg/l)

PNEC: Predicted No Effect Concentration (µg/l)

If the RCR_{FIAM} is > 1, the site specific free metal ion concentration is higher than the FIAM corrected AA-QS under standard water quality conditions (DSW). The site exceeds the risk associated with the AA-QS. If the RCR_{BLM} is > 1, the site specific predicted environmental metal concentration is above the predicted no effect concentration. The site might negatively impact organisms (ECHA, 2016).

In addition to the dissolved concentration for the metals Cu, Ni, Pb and Zn the PNEC-pro model requires input for DOC, pH, Ca, Mg and Na. The DOC, pH and alkalinity are given in Section 3, Results, Table 2. The calculation of the Ca, Mg and Na concentration based on the alkalinity is explained above. The BLM model results for the PEC and the RCR_{BLM} are given in Table S.1 (supportive information).

The RCR calculation based on the dissolved concentration, the FIAM model and the BLM model is summarized in Fig. 3.

2.6. Ms-PAF model OMEGA

The concept of calculating the Potentially Affected Fraction (PAF) is based on the observed median lethal concentration [LC₅₀] or no-observed-effect concentration [NOEC] for individual toxic components and individual species. The potential toxic risk for multiple substances is then calculated using the distribution of the LC₅₀ or NOEC values (Posthuma et al., 2002) following the methodologies as proposed by (De Zwart and Posthuma, 2005):

- (i) Response Addition (RA), or
- (ii) Concentration Addition (CA).

The numerical model 'Optimal Modeling for Ecotoxicological Assessment' (OMEGA) incorporates these methodologies to calculate the ecotoxicological risk for multiple contaminants (Hendriks and Van de Guchte, 1997). The model used the ecotoxicological data for approximately 200 substances (Bruijn de et al., 1998). The data is derived by establishing dose effect relations for a toxicant under standard water

conditions defined by DSW (Aldenberg et al., 2001).

The dissolved metal concentration is used as input. Based on the method of correction the input concentration is calculated by Eqs. (7)–(9).

$$\text{Metal}_{(\text{dissolved})} = RCR_{\text{dissolved}} * AA - QS (= \text{Metal}_{(\text{dissolved})}) (\mu\text{g/l}) \quad (7)$$

$$\text{Metal}_{(\text{FIAM})} = RCR_{\text{FIAM}} * AA - QS (\mu\text{g/l}) \quad (8)$$

$$\text{Metal}_{(\text{PNEC})} = RCR_{\text{BLM}} * AA - QS (\mu\text{g/l}) \quad (9)$$

2.7. Spatial distribution of metals in lake Ketelmeer

For the nine sample locations (see Table 2) a triangulation interpolation between data points is used with linear interpolation between the data points (Surfer, version 11.3.862). The choice for triangulation above Kriging interpolation is to limit the data interpolation to the area between the system boundaries. The resulting spatial pattern is plotted on a Google map, using the Dutch coordinate system (RD-coordinates).

2.8. Combined use of the models

The monitoring data (Table 2) and AA-QS standards (Table 1) contain the information needed to calculate the FIAM free metal ion concentration based on the local water quality. The monitoring data can also be used for the BLM model to calculate the Predicted Environmental Concentration and Predicted No Effect Concentration. Therefore the RCR_{FIAM} and RCR_{BLM} can be calculated and the correlation between (i) the dissolved concentration and RCR_{FIAM} corrected concentration, (ii) the dissolved concentration and the RCR_{BLM} corrected concentration and (iii) the RCR_{FIAM} corrected concentration and RCR_{BLM} corrected concentration can be studied.

The ms-PAF calculation is based on dissolved concentrations, without taking into account local water quality parameters. By using the RCR_{FIAM} corrected concentration, the ms-PAF_{FIAM} calculation becomes dependent on local water quality parameters.

3. Results

3.1. Site specific metal concentration and local water quality parameters

Table 2 summarizes the coordinates of the sampling location (Dutch RD), the measured dissolved metals concentration and the water quality

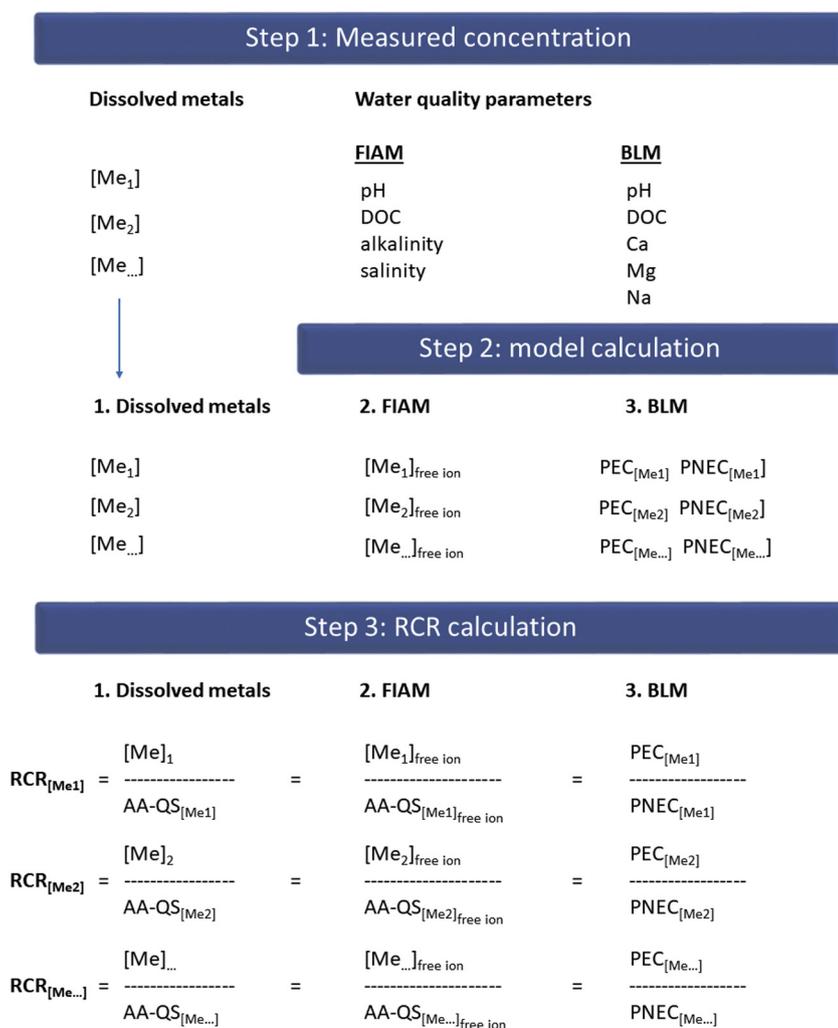


Fig. 3. Summary of steps leading to the calculation of the RCR_{dissolved}, RCR_{FIAM} and RCR_{BLM}. Step 1 contains the monitoring data needed for the calculation, both the dissolved metal concentrations and the local water quality parameters. In step 2 the FIAM and BLM model calculations are carried out, yielding the free ion metal concentrations (FIAM) and PEC/PNEC metal concentrations (BLM) based on the local water quality parameters. In step 3 the RCR for each metal is calculated, according to each method. Both the dissolved metals and the FIAM method require the AA-QS metal concentration. The FIAM model calculates the AA-QS free metal ion concentration for standard water as the reference concentration. The BLM model corrects both the measured metal concentrations and the no-effect metal concentrations for the local water quality parameters.

parameters pH, alkalinity, dissolved organic carbon (DOC) and salinity. The eastern boundary (inflow) is represented by the location “Kampen”. The western boundary (outflow) is represented by “Ketelmeer West 1”. 70% of the reporting standard is used for analysis if the measured value is below the reporting standard.

Some of the metals are below the reporting level for the locations within the lake (Cd, Pb, Cr for most locations). Only Cr exceeds the AA-QS standard on one location (Ketelmeer Oost 8). This relatively good (below AA-QS) water quality for metals is in line with findings in other studies. With the exception of location Ketelmeer Oost 8, the lake is classified as a WFD water body with good chemical quality.

The FIAM model results for the free metal ion concentrations and the RCR_{FIAM} are given in Table S.1 (Supportive information). A parameter analysis, using only one of the four local water quality parameters, shows that the pH is the main parameter to determine if the free metal ion concentration is lower or higher than for reference conditions (DSW). The middle-north part of the lake has a relatively low pH, resulting in a higher free metal ion concentration.

The BLM model results for the PEC and the RCR_{BLM} are given in Table S.1 (Supportive information). A parameter analyses for the BLM model reveals that DOC is the main parameter determining an increase in the bioavailable metal concentration at low DOC concentrations. For Ni, a DOC concentration of < 4 mg/l leads to non-valid results for the BLM model. The north-eastern part of the lake has the lowest DOC concentrations, and therefore the highest bioavailable metal concentrations. Also hard water (as defined by the Ca²⁺ concentration, with values of 80–90 mg/l) often results in non-valid results for the BLM

model for Cu.

3.2. Comparison between the measured dissolved metal concentration, the FIAM free ion metal concentration and the PNEC Pro calculated metal concentration at risk

For each of the locations in the lake a RCR_{dissolved}, RCR_{FIAM} and RCR_{BLM} is calculated for the metals Cu, Ni, Zn and Pb. The RCR's indicate how far below or above the dissolved metal concentration is, compared to a critical concentration (the AA-QS for RCR_{dissolved}, the AA-QS_{FIAM} for RCR_{dissolved} and the PNEC for RCR_{BLM}). Each of the RCR's take water quality parameters into account in a different way. Fig. 4 plots the correlation between the three different combinations of RCR's for each of the nine locations to see if there are similarities or differences in the increase or decrease of the RCR.

Fig. 4 shows that trends between RCR factors, based on the measured dissolved metal concentrations and water quality parameters, as calculated by the different RCR methods (see Eqs. (1), (5) and (6)) often do not correlate (R² < 0.75; < 50% of standard deviation explained). The correlation between the RCR_{dissolved} and RCR_{PNEC} (BLM) for Cu and Ni is even negative. This is due to the lack of model results for the BLM model due to out of boundary conditions for four (Ni) to five (Cu) locations. This also explains the lack of correlation between the RCR_{FIAM} and RCR_{PNEC} for Cu and Ni. When focusing on the correction between the RCR_{dissolved} and RCR_{FIAM}, it stands out that for Cu, Zn and Pb, the RCR_{FIAM} is higher than the RCR_{dissolved}. For most locations within the lake the local water quality increases the free metal ion concentration

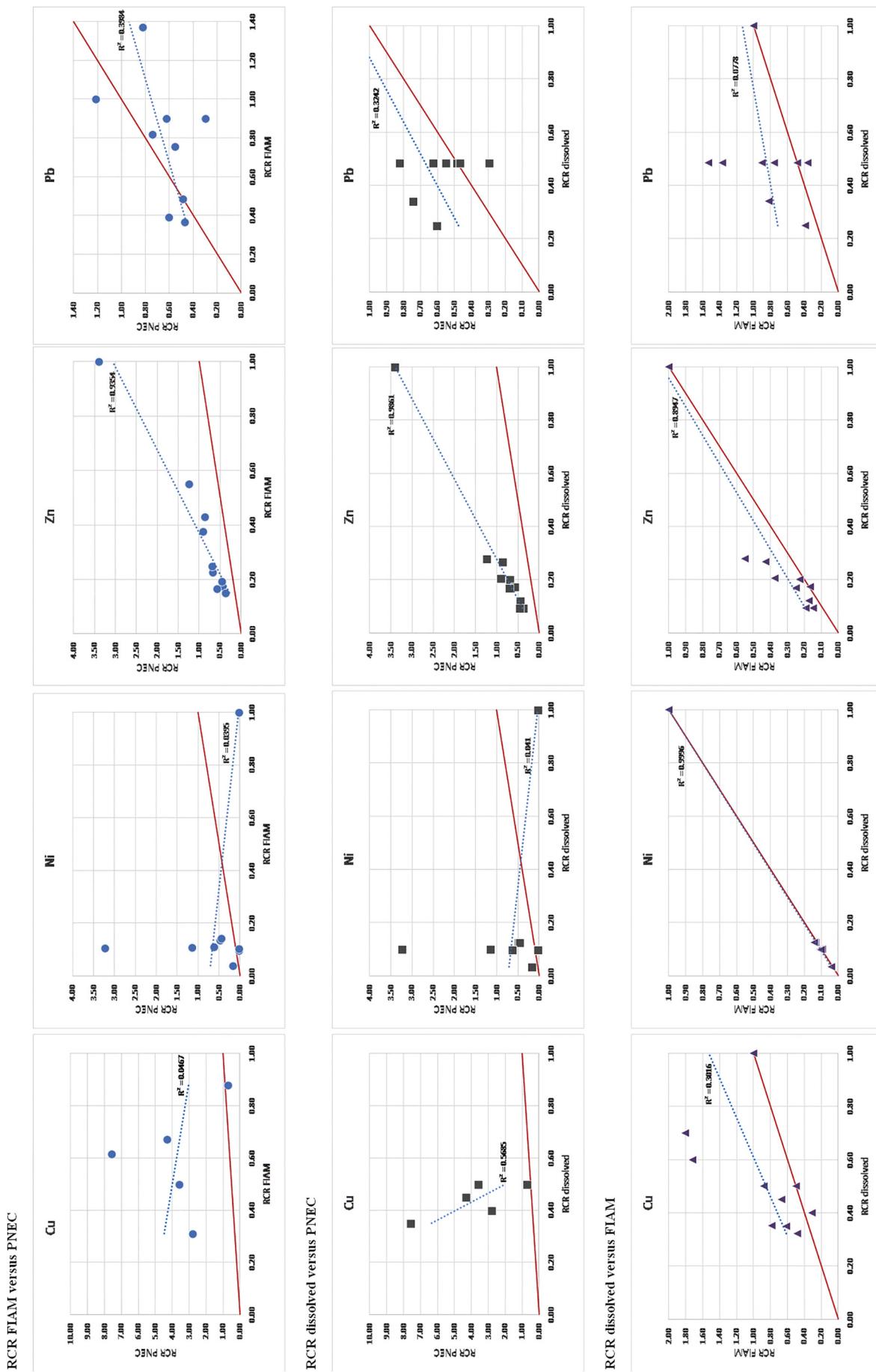


Fig. 4. Comparison of RCR factors for the measured dissolved concentration and the PNEC (BLM) calculated concentration. The dots are the calculated RCRs (dissolved, FIAM and PNEC) for each location, the dotted line the linear best fit (with R^2) and the red line gives the 1:1 correlation between two RCR factors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

as compared to standard water.

3.3. Ms-PAF

The results of the ms-PAF analysis for each location in the lake are given in Table S.2 (Supportive information). The ms-PAF results indicate how many of the organisms are at risk of experiencing an observable toxicological impact due to the presence of a mixture of metals. The calculations have been carried out for the dissolved metal, the FIAM corrected dissolved concentration and the BLM based corrected dissolved concentration (see Eqs. (7)–(9)). The BLM model, PNEC Pro, only has BLM's for four of the six metals. Two of the nine sample locations also had conditions which were out of the calibration range for the BLM model for Cu and Ni. Therefore the PNEC model tends to under predict the ms-PAF.

A possible cross validation of the relation between the calculated chronic ms-PAF and the real metal exposure in the field is the use of bioaccumulation in sediment bioassays. This has been tried in the Netherlands (Besten et al., 1995) and has resulted in a second-tier risk assessment called TRIAD (Chapman, 1996). TRIAD has three pillars consisting of chemical, toxicological and ecological measurements. Correlation between the water quality, the sediment quality, the impact on bioassays and the amount of bioaccumulation was often difficult to prove (Swartjes, 1999; Lahr et al., 2003). Improvements were made by including soil and sediment conditions, and comparing these with ms-PAF model results (Veltman et al., 2007; Veltman et al., 2008). A whole-sediment toxicity bioassay as applied for marine sediments (Forrester et al., 2003; Schipper et al., 2010) also correlates bioaccumulation with sediment concentrations, expressing this correlation with biota-sediment accumulation factors (BSAFs) (Botwe et al., 2017). Unfortunately, the bioassays for Lake Ketelmeer for this period (1999) are based on acute toxicity bioassays and a limited set of chronic exposure in vivo bioassays (on *Daphnia magna* and *Chironomus riparius*) under non-reference test conditions (Lahr et al., 2003). The Ketelmeer bioassays with positive results (exceeding the Maximum Tolerated Effect (MTE)) have elevated PAH and PCB sediment concentrations, not elevated metal concentrations. Validation of the calculated ms-PAF with field observed bioassay MTE values for metals is therefore not possible.

3.4. Spatial distribution of metals in Lake Ketelmeer

The impact of using the dissolved metal concentration, the FIAM corrected free ion concentration or the BLM based PNEC pro correction on the ms-PAF can be illustrated when looking at spatial pattern of areas with a high ms-PAF versus areas with a low ms-PAF. Figs. 5–7 give the spatial distribution for lake Ketelmeer of the calculated chronic exposure ms-PAF. Fig. 5 is based on the measured dissolved metal concentrations. Fig. 6 uses the RCR_{FIAM} corrected metal concentrations and Fig. 7 the RCR_{BLM} corrected metal concentrations. In case of the RCR_{FIAM} and RCR_{BLM} corrected metal concentration, the input for the ms-PAF model is based on the calculated bioavailable fraction in natural water compared to the bioavailable fraction at the AA-QS concentration in DSW, as is explained by Eqs. (7)–(9). By applying the RCR_{FIAM} / RCR_{BLM} correction factor to the dissolved metal concentration in the ms-PAF model, the ecotoxicological risk prediction has become depended on water quality parameters like pH, alkalinity, salinity and DOC. This is normally not the case when the ms-PAF is calculated.

The chronic ms-PAF based on the sum of the dissolved metal concentration is low for the whole lake (11%). The FIAM based ms-PAF shows an increase of up to 27% in the middle north part of the lake, related to a locally lower pH (7.8 versus 8.0 to 8.5 for the rest of the lake). The PNEC (BLM) based ms-PAF has a maximum of 45% in the north-eastern part, related to a locally low DOC concentration.

4. Discussion

While water quality standards worldwide are mainly based on dissolved metal concentrations, guidelines have been written on how to incorporate metal speciation and bioavailability for protecting aquatic ecosystems (Scott et al., 2001). For some metals, like Cd, this has led to different standards for different types of water (EPA, 2001; Lepper, 2004). A broader adaptation of water quality influencing the bioavailable metal fraction and hence the water quality standard has been hampered by the perceived complexity of FIAM modeling. While simpler multiple regression models have been developed (van Hattum et al., 1996; Hendriks and van de Guchte, 1997), these models were not adapted by policy makers. In the last ten years BLM models are slowly being adapted within the EU for second tier risk assessment of monitoring data (Rüdel et al., 2015). BLM models are currently available for four metals, although the validated range of water quality parameters variation does not yet cover all natural water bodies (Verschoor et al., 2012). In this paper we illustrated that the outcome of these more complex models can be simplified by calculating a site-specific Risk Characterization Ratio (RCR_{FIAM}/RCR_{BLM}). These RCR's take into account the measured metal concentration and the local water quality, and compare the outcome with a water quality standard like the AA-QS (used in this paper).

There are some specific trends in the calculated RCR's. The RCR based on the dissolved metal concentration (the standard method for comparison with the AA-QS) is low in all parts of the lake, leading to the conclusion that the lake meets the WFD chemical status “good”, or ‘not at risk’. The use of the FIAM model results in an exceedance of the RCR_{FIAM} for Cu (1.8) and Pb (1.5) in the north middle part of the lake, an area with a relative low pH (7.9, versus 8.0–8.5 for the rest of the lake). Local acidification might lead to an “at risk” status for Cu and Pb for this part of the lake. The BLM model shows the highest RCR values (RCR_{BLM} 7.5 for Cu, RCR_{BLM} 3.2 for Ni) in the north-eastern corner of the lake. This is due to the low DOC concentration in that part of the lake.

The RCR's for each of the three methods can also be used to calculate the potential ecotoxicological risk, as expressed by the ms-PAF (see Table S.2, Supportive information). The ms-PAF expresses the potential impact of the combined (multi-substances) concentration of contaminants on organisms (Potentially Affected Fraction, as compared to no impact NOEC levels). Using the FIAM/BLM based RCR's results in the inclusion of the impact of local water quality parameters (like pH, alkalinity, salinity and DOC) on the ecotoxicological risk assessment. This is normally not a part of the ms-PAF risk assessment. The chronic ms-PAF shows the same trend as the RCR's based on the different calculation methods. The chronic ms-PAF is low (11%) based on the total dissolved metal concentration, which is in line with the WFD chemical status classification (“good”). With the FIAM calculated free metal ion concentration, the chronic ms-PAF increases to 27% in the north middle part of the lake due to the lower pH in that part of the lake. Locations with a lower pH (< 8.0) correspond with locations with a high RCR_{FIAM} (> 1) for Cu and Pb, resulting in a more than twice as high chronic ms-PAF for these locations. This strong pH dependency based on the RCR_{FIAM} is not unexpected. The relation with pH and the metal bioavailability and toxicity to fish has been shown to exist for low alkalinity lakes (Spry, 1991). The relatively large impact of a locally twice as high chronic ms-PAF based on a relative small shift in pH (pH 7.8 versus an average pH of 8.2) in an alkaline lake is not expected (Adhikari and Ayyappan, 2006). The BLM calculated bioavailable concentration yields the highest chronic ms-PAF value (45%), in the north-eastern part of the lake. This corresponds with local low DOC concentrations (3.0–3.5 mg/l). The simplified BLM model PNEC Pro is calibrated on a dataset by (Verschoor et al., 2012). This dataset shows DOC as the most discriminating parameter (followed by pH and Ca^{2+}). Most data in the dataset used by (Verschoor et al., 2012) has a DOC concentration of > 5.0 mg/l. This might explain why low DOC concentrations often

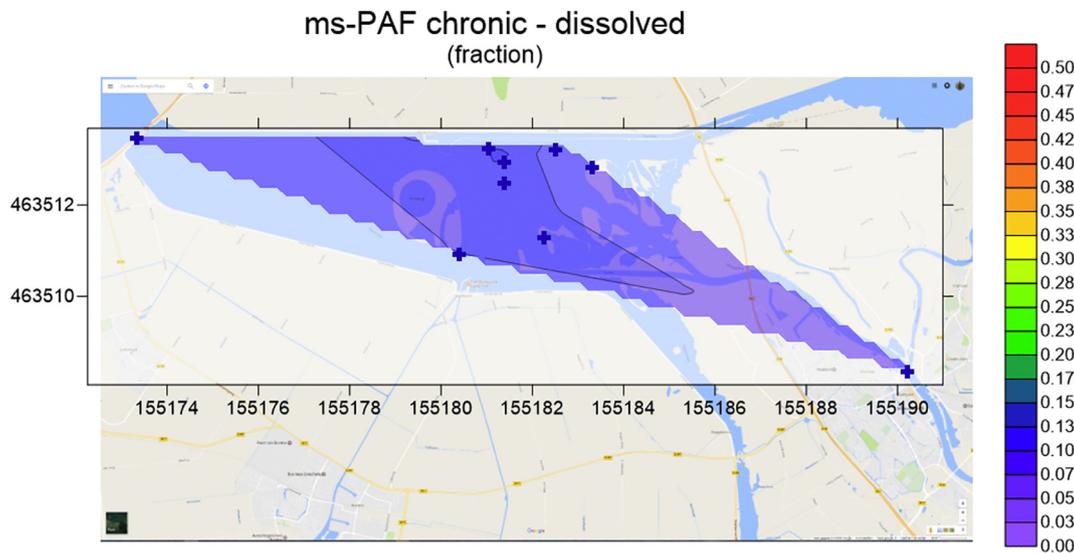


Fig. 5. Chronic ms-PAF distribution across the lake based on dissolved metal concentrations. Measurement locations shown as crosses. The ms-PAF is expressed as a fraction (0.0–1.0).

non valid model results. It is recommended to include more datasets based on extensive BLM modeling with low (1.0–5.0 mg/l) DOC concentrations.

While trends between the RCR_{FIAM} and RCR_{BLM} are inconclusive (partly due to out of boundary conditions for the BLM model), it is recommended to look closer at potential ecotoxicological impacts in the north middle to north east part of the lake and monitor the development in pH and DOC concentration in the lake. It is unfortunate that the available bioassays around the same timeframe of the water quality measurements were inconclusive with regard to acute or chronic toxicity. Based on the proceedings in the development of whole sediment bioassays (Botwe et al., 2017) it is recommended to repeat the lake survey, including these bioassays.

5. Conclusion

Understanding the relation between contaminant concentrations (like metals) and the local water quality of a water body with regard to the potential ecotoxicity of the contaminants is important to define

effective measures to improve the ecological health and therefore the ecological status of the water body (Rebecca, 2006). In the WFD the chemical status of a surface water body is defined by the concentration of individual contaminants in surface water compared to a standard like the AA-QS. To include the impact of multiple contaminants on the WFD classification, a modification based on the calculation of the ms-PAF has been proposed (Wijdeveld and Schipper, 2017). In this paper this approach is taken a step further by including the impact of general water quality parameters (pH, alkalinity, salinity and DOC) on the relative toxicity of metals. To do this in a comprehensive way for water managers and policy makers, the concept of Risk Characterization Ratio's (RCR) for dissolved metals is introduced. The calculation of these RCR's can be based on a more fundamental understanding on what causes the increase or decrease of the ecotoxicity of metals, while still maintaining the link with the accepted and well know standards like the AA-QS for surface water. In this study both a FIAM and BLM model were used to calculate the impact of local water quality parameters (pH, DOC, salinity and alkalinity) on the RCR. After the calculation of the RCR's, the concept of a water quality dependant ecotoxicity could also be applied

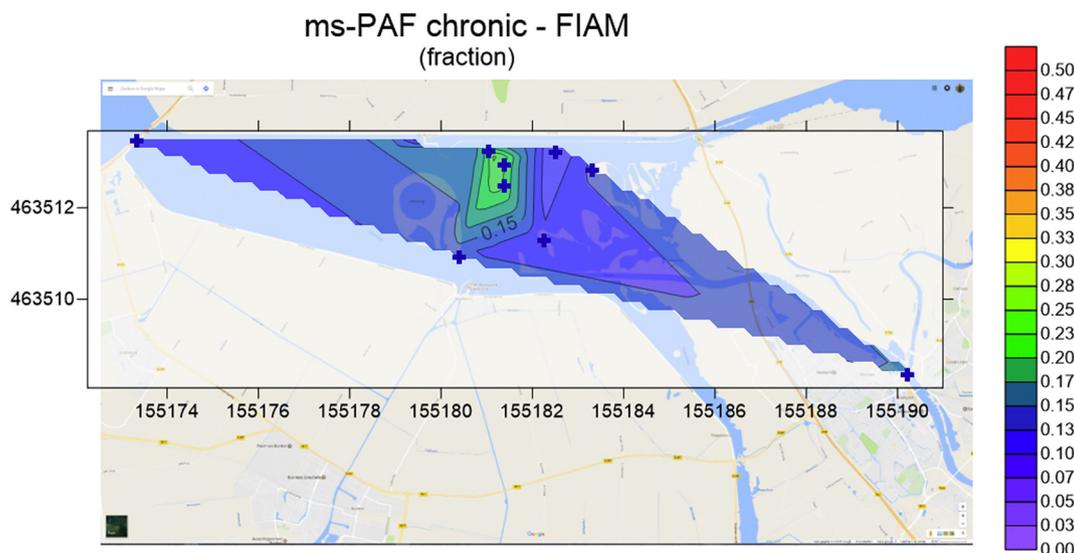


Fig. 6. Chronic ms-PAF distribution across the lake based on the RCR_{FIAM} corrected metal concentrations. The measured dissolved metal concentrations are corrected based on the local water quality, using the RCR_{FIAM} correction factor. Measurement locations shown as crosses. The $ms-PAF_{FIAM}$ is expressed as a fraction (0.0–1.0).

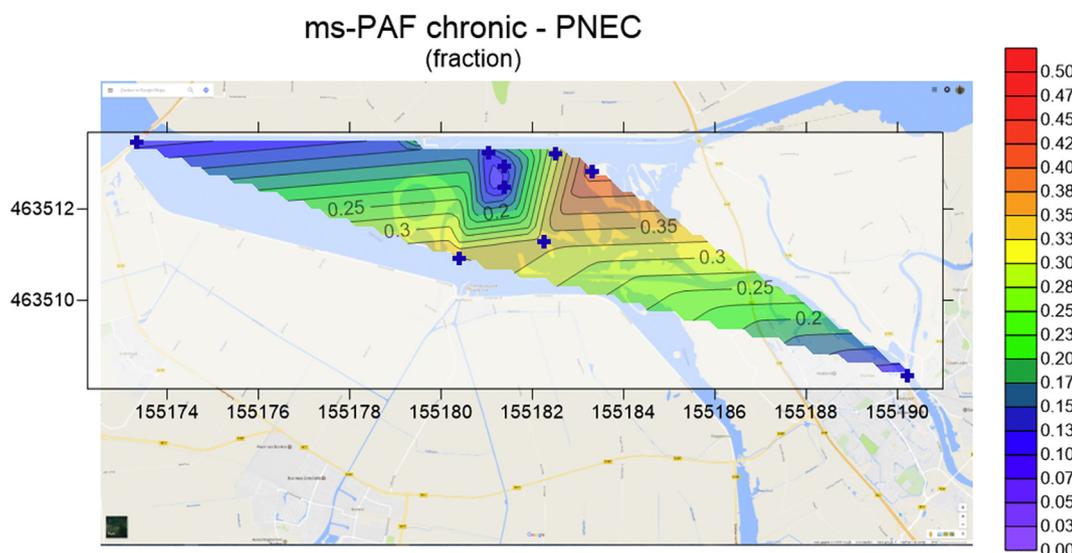


Fig. 7. Chronic ms-PAF distribution across the lake based on RCR_{BLM} corrected metal concentrations. The measured dissolved metal concentrations are corrected based on the local water quality, using the RCR_{BLM} correction factor. Measurement locations shown as crosses. The $ms-PAF_{BLM}$ is expressed as a fraction (0.0–1.0).

to the ms-PAF model.

An application for a Dutch lake illustrates the usefulness of these RCR's. Calculating the free metal ion concentration with the FIAM model, the north middle part of the lake is highlighted as potentially at risk due to a local lower pH (and hence a RCR_{FIAM} for Cu and Pb > 1). The calculation of the BLM based bioavailable metal fraction shows an area of high risk in the north eastern part of the lake, due to RCR_{BLM} of > 1 for Cu and Ni. This is due to the local low DOC concentration. The calculated RCR factors were also used for the calculation of the local chronic ms-PAF. Plotting the spatial distribution of the chronic ms-PAF based on the total dissolved metal, the free metal ion and the BLM bioavailable concentration directly highlights areas with an increased ecotoxicological risk, and links these areas to local differences in water quality parameters such as pH or DOC concentrations. This makes it easier to target these areas and to act appropriately. Since the local water quality plays such an import role in the RCR of the metal, it is advised to systematically measure all majors cat- and anions in the water (and include other general water quality parameters like DOC, COD and BOD).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <https://doi.org/10.1016/j.catena.2018.03.024>. These data include the Google map of the most important areas described in this article.

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