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Application of diffusive gradient in thin films (DGT) and a chemical equilibrium model for assessing bioavailability levels of trace metals in effluent-affected rivers

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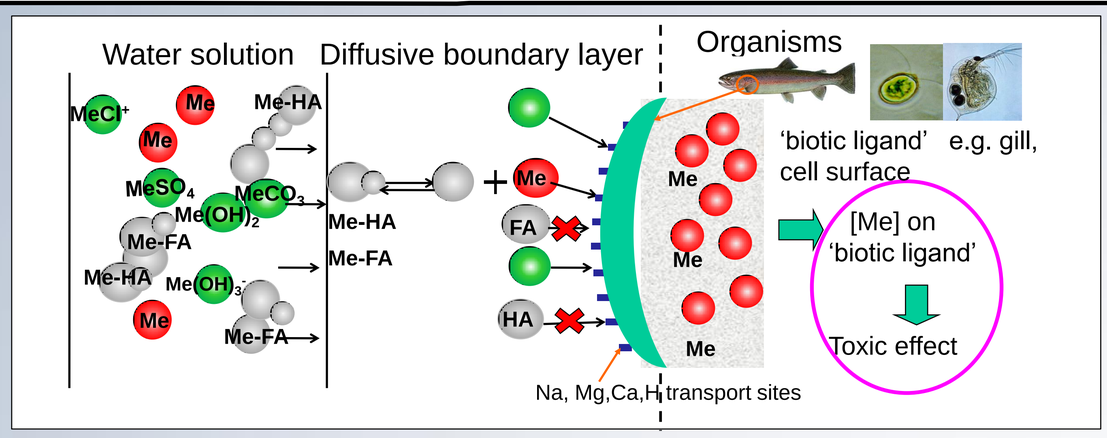
BACKGROUND

Free ions and easily dissociable humic-metal complexes are more likely to represent a bioavailable fraction than the total metal, and bioavailability speciation of metals easily go cross a biological membrane and induce toxicity to aquatic organisms.

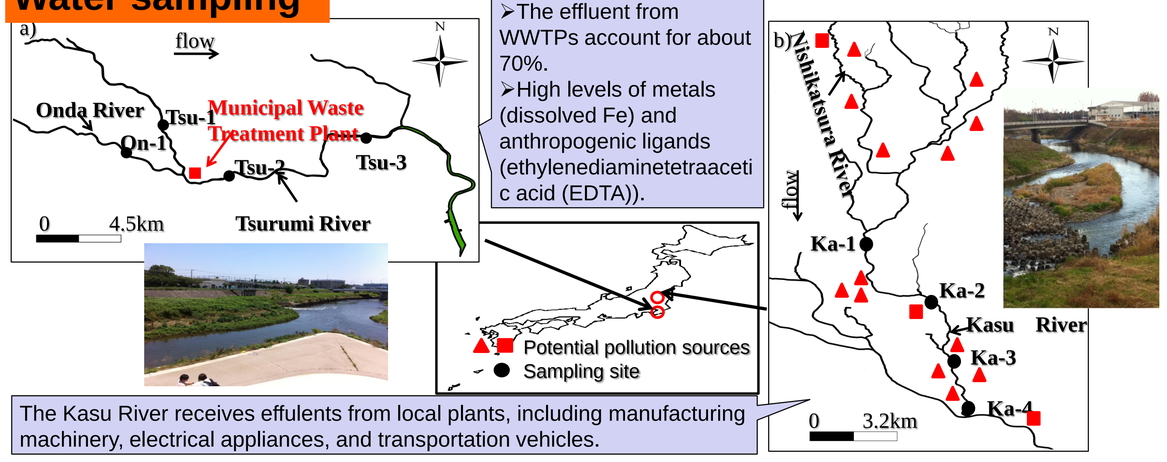


PURPOSE

(i) Using DGT method and model prediction to determine more accurate concentrations of bioavailability in effluent-affected rivers,
(ii) Considering anthropogenic contaminants, to identify important speciation of metals(metal-EDTA complexes),
(iii) To assess the water quality with respect to biological effect based on the results of bioavailability concentrations.

MATERIALS AND METHODS

Water sampling



➢The effluent from WWTPs account for about 70%.
➢High levels of metals (dissolved Fe) and anthropogenic ligands (ethylenediaminetetraaceti c acid (EDTA)).

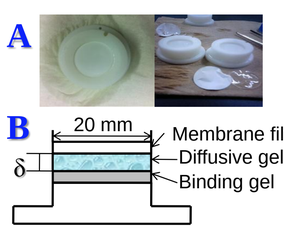
The Kasu River receives effluents from local plants, including manufacturing machinery, electrical appliances, and transportation vehicles.

Water pretreatment and measurement

DGT-labile concentrations

$$C_{labile} = \frac{C_{elu}(V_{gel} + V_{acid})\Delta g}{f_e D t A}$$

t : 24 h ;
C_{elu} : the concentration of metal in nitric acid;
V_{gel} : the volume of the resin gel (0.15 ml);
V_{acid} : the volume of the nitric acid (2 mL);
f_e : the elution efficiency (fe = 0.8);
D : the diffusion coefficient;
A : the area of diffusion gel layer (A=3.14 cm ^{2});
Δg : the thickness of the diffusive gel (0.94 mm).



Raw water samples

Filtration (ADVANTEC membrane , 0.45μm)
HNO_3 +HCl
Unfiltration
DGT deployment for 24 h
HNO_3(1M)
Measurement of ions: Major cations (Na^+, Mg^{2+}, K^+, Ca^{2+}) Major anions (Cl^-, NO_3^-,PO_4^{3-}, SO_4^{2-}) ion analyzer (DKK-TOA, IA-300)
DOC measurement by TOC-VCSH (Shimadzu)
Acid digestion for 2-3 h
Dissolve binding gel
Determination of metals (ICP/MS, Agilent 7700X)

Model calculation

Water chemistry input

EDTA (0.1 mg/L for the Onda river and 0.065 mg/L for the Tsurumi river)
Fulvic acids and humic acids
Major cations (Na^+, Mg^{2+}, K^+, Ca^{2+}) Major anions (Cl^-, NO_3^-,PO_4^{3-}, SO_4^{2-})
Temperature pH
Dissolved Ni, Cu, Zn , Pb, Al and Fe(Ⅲ)

Modified database (Tipping et al, 2011; Keizer and Van Riemsdijk, 1994) → **Calculation by WHAM 7.0**

Free metal ions | Dissociated humic complexes | Inorganic-metal

$$C_{dynmax} = C_{free} + C_{inorg} + \frac{C_{FA}D_{FA}}{D_{inorg}} + \frac{C_{HA}D_{HA}}{D_{inorg}}$$

Compare → DGT-labile

CONCLUSIONS

• At most sites downstream of a WWTP, bioavailable concentrations of metals increased. As for the rivers affected by industry effluent, bioavailable metals were higher than that in rivers affected by the WWTP effluent. This may be due to the higher ratios of metal/DOC in the rivers impacted by metal industry effluent than that of the rivers impacted by the WWTP.
• For urban rivers affected by WWTPs, dissolved iron increased the bioavailable concentrations, because more free ions of Cu and Pb released from their binding sites with humic substances.
• Adding EDTA into the urban rivers, the fraction of complexes with humic substances for Cu and Pb largely decreased, and the binding fraction with EDTA significantly increased, following the sequence of Ni>Pb>Cu>Zn. And bioavailable concentrations predicted considering EDTA decreased in urban rivers, because large fraction of metals bound with EDTA.

RESULTS AND DISCUSSION

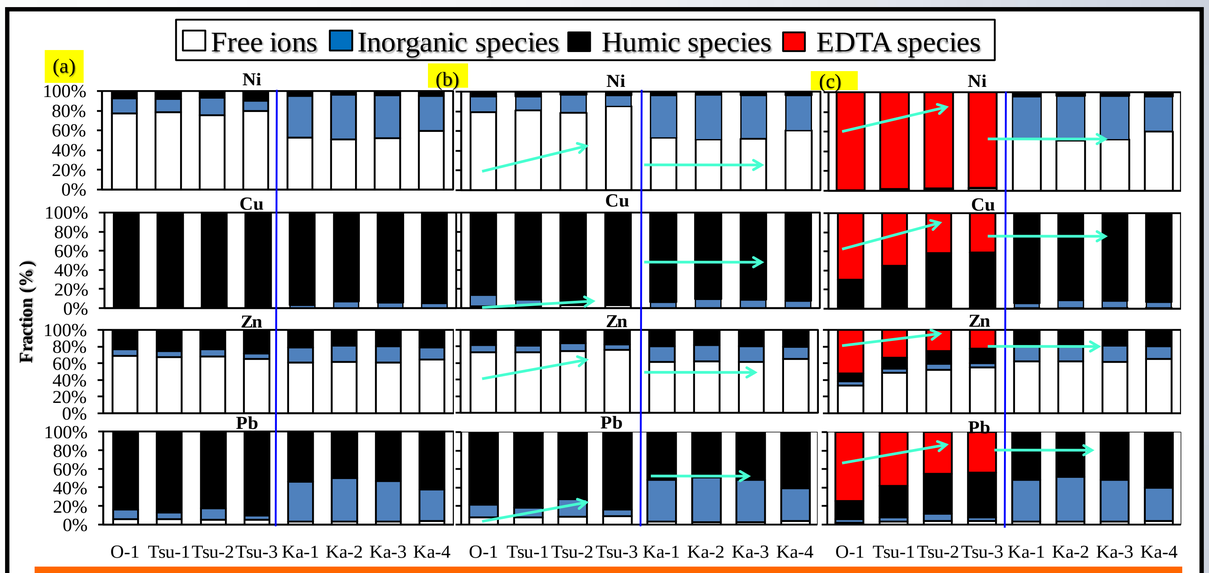


Fig.1.The fractions of free ions, inorganic metal species, humic metal species, and EDTA species calculated by WHAM 7.0. (a) Dissolved iron (III) and EDTA was assumed to be not present in the WHAM 7.0. b) Only dissolved iron(III) was assumed that free ions are in equilibrium with their hydroxides and free ions compete with other metals for binding to HS. c) Both dissolved iron(III) and EDTA were assumed to be in the WHAM 7.0.

➢With dissolved iron (III) in urban rivers(Fig.1 (b)) , because of the competitive binding of iron with humic substances, free Cu and free Pb significantly increased by 37.7-154% and 0-19.2%(Fig.1(a)), respectively.
➢From the results of (Fig.1 (c)), EDTA has considerable binding with trace metals in urban rivers, and fractions of EDTA complexes for Ni, Cu, Zn, and Pb were 97.1-99.2% 40.9-69.6%, 22.5-52.7%, and 43.5-75.3%, respectively. Moreover, complexes of humic substances with Cu and Pb largely decreased. Considering EDTA in the WHAM 7.0, free ions and complexes of metals with humic substances were predicted accurately.

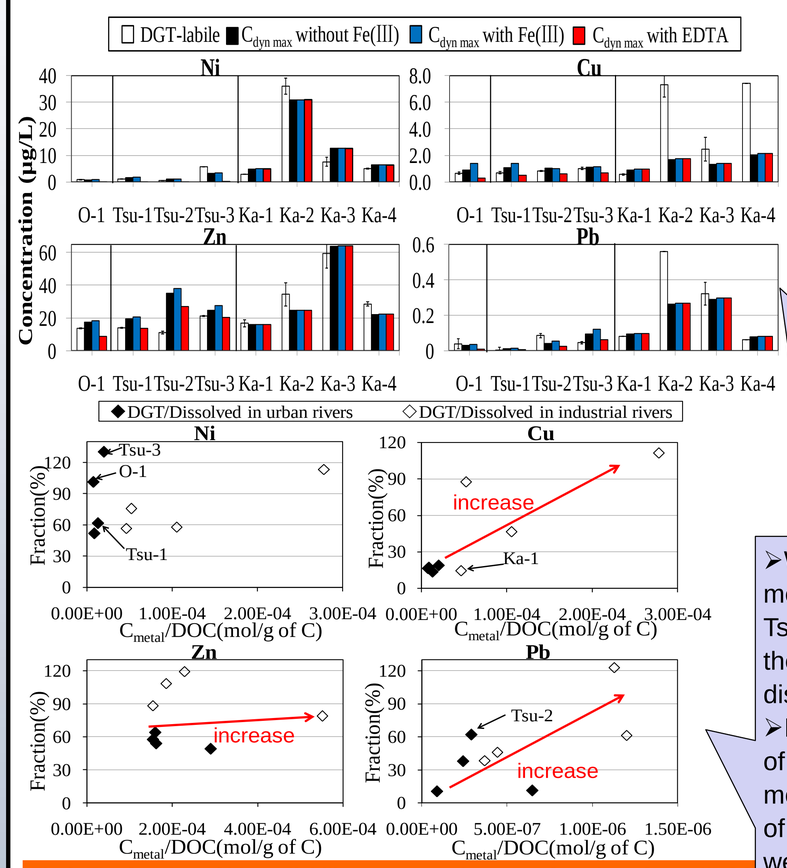


Fig.3. The fraction of bioavailability concentrations as a function of metal/DOC

➢Considering the dissolved iron(III) in urban rivers, predicted bioavailable concentrations for Cu and Pb increased (0-9.2% for Pb and 0-41.4% for Cu). Whereas for the rivers impacted by industry effluent, the predicted bioavailable concentrations had no differences.
➢Considering EDTA, for urban rivers, bioavailable concentrations for Ni, Cu, Zn and Pb were 97.2-99.1%, 37.1-79.0%, 26.4-52.7%, and 49.1-73.2% lower than those results predicted without of EDTA.

➢When the mole ratio of metal/DOC increased from the Tsurumi River to the Kasu River, the fractions of DGT-labile in dissolved concentrations increased.
➢In the Kasu River, the complexes of humic-metal likely dissociated more quickly during the deployment of DGT and higher metal species were measured by DGT.

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