Assessing bioavailable metals in effluent-affected rivers: Effect of iron and chelating agents on the distribution of metal speciation

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Abstract: To assess bioavailability levels and indentify important speciation for trace metals (Ni, Cu, Zn, and Pb), the rivers affected by a waste water treatment plant (WWTP) was studied. Biologically available concentrations were measured by the diffusive gradients in thin films (DGT) method, and DGT results were compared with those predicted by WHAM 7.0. At most sites downstream of the WWTP, bioavailable metals increased. Due to the competitive binding of iron with humic substances, free ions for Cu and Pb increased. High level of ethylenediaminetetraacetic acid (EDTA) was in sampling rivers, EDTA had considerable binding capacity with metals, the fractions of EDTA complexes with metals followed the sequence of Ni > Pb > Cu > Zn, this likely attributed to the result that, measured bioavailable concentrations by DGT were lower than predicted results.

Introduction

The toxicity of dissolved metals is related with chemical speciation (Allen and Hansen, 1996). Chemical speciation of metals is affected by chemical parameters in waters. Humic substances (HS) play an important role in the binding of metals with organics (Tipping, et al., 2011). In addition, anthropogenic ligands, ethylenediaminetetraacetic acid (EDTA), has considerable binding capacity with metals, so neglecting the presence of EDTA in chemical models leads to overestimation of free metal ions in waters (Vega and Weng, 2013). Also competitive binding of free iron(III) with HS, free Cu and free Pb are expected to be released substantially from humic complexes based on chemical models (Tipping et al., 2002).

Inflow of municipal wastewater increases the levels of pollutants (anthropogenic ligands and dissolved metals) in the aquatic environment. In previous studies, metal speciation has been evaluated in the rivers affected by waste water treatment plants (WWTPs) (Han, et al., 2013). However, the knowledge of real metal speciation (e. g. metal complexes with EDTA, humic acids and fulvic acids) is limited. The aims of this study are (i) to determine accurate metal speciation in effluent-affected rivers, and (ii) to estimate the effect of chelating agents on the distribution and bioavailability of metal species.

Material and Methods

Study area
Water samples were collected from Tsurumi River and its tributary, Onda River. The rivers are typical urban rivers (**Figure 1**). The effluents from local WWTPs account for about 70% of its stream water (Ministry of Land, Infrastructure, Transport and Tourism, 2012).

Determination of total, dissolved, and labile metal concentrations

The samples were acid digested according to EPA method 3005A for total and dissolved metal measurement (U.S. Environmental Protection Agency, 1992). Concentrations of DGT-labile metals were determined using diffusive gradients in thin films (DGT) units (www.dgtresearch.com) in the laboratory, the details of the measurements were described in the previous study (Han et al., 2013). Finally, concentrations of metals were determined by inductively-coupled plasma-mass spectrometry (ICP-MS) (Agilent 7700x).

Metal speciation was predicted by WHAM 7.0 (Tipping, et al., 2011). The dynamic concentrations were calculated according to the same procedures described in the previous studies (Han et al., 2013; Balistrieri and Blank, 2008).
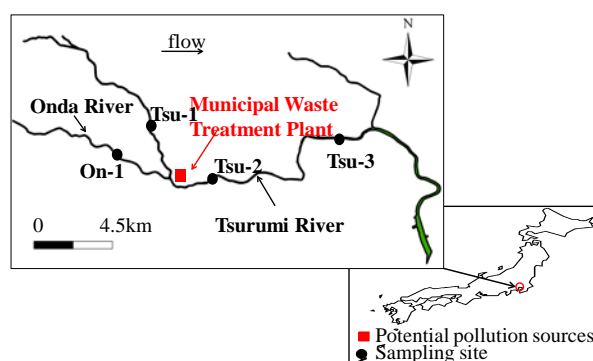

Figure 1 The location of sampling sites and municipal wastewater treatment plant in the rivers studied

Results and Conclusions

Effect of dissolved iron(III) on predicted dynamic concentrations

Dissolved iron is widespread in the sampling rivers, probably because of iron(III) addition in WWTPs and other human activities **(Table 1).** The iron species have considerable effect on metal speciation. The comparisons between DGT-labile concentrations and calculated concentrations with and without considering iron(III) are shown in **Figure 2**. In Onda and Tsurumi rivers, range of DGT-labile Ni, Cu, Zu, and Pb were 0.61–5.76, 0.67–1.02, 11.17–17.22, and 0–0.09 µg/L, respectively. Without consideration of dissolved iron(III) in WHAM 7.0, dynamic Ni Cu, Zu, and Pb concentrations ([Me]max dynamic) were 0.87–3.33, 0.89–1.15, 17.46–35.19, and 0.01–0.10 µg/L, respectively. Assuming that free iron(III) was in equilibrium with its hydroxide and reacted with HS, dynamic concentrations for Ni and Zn were similar to

Table 1 Water parameters for sampling sites during December 2011 and February 2012 (n≥3)

| Items | Rivers | | | | Items | Rivers | | | |
| | Onda | Tsurumi | | | | Onda | Tsurumi | | |
	O-1	Tsu-1	Tsu-2	Tsu-3		O-1	Tsu-1	Tsu-2	Tsu-3
Temp. (°C)	14.3	13.5	14.5	15.0	DOC (mg/L)	2.05	2.43	2.28	3.01
pH	7.34	7.27	7.40	7.14	EDTA (mg/L)	0.1 [b]	0.065 [b]	0.065 [b]	0.065 [b]
K^+(mg/L)	10.5	9.79	10.1	8.81	Dissolved Ni (µg/L)	0.92	1.85	1.17	3.59
Na^+(mg/L)	21.8	20.5	24.3	30.5	Dissolved Cu (µg/L)	4.25	5.17	4.84	5.44
Mg^{2+}(mg/L)	5.06	5.56	5.63	6.97	Dissolved Zn (µg/L)	21.4	24.4	43.1	31.8
Ca^{2+}(mg/L)	32.8	33.3	32.8	31.5	Dissolved Pb (µg/L)	0.10	0.05	0.14	0.41
PO_4^{3-}(mg/L)	N.D. [a]	0.02	N.D. [a]	0.02	Dissolved Fe (µg/L)	875	853	871	848
Cl^-(mg/L)	26.8	22.5	27.4	33.3	Dissolved Al (µg/L)	19.1	23.5	26.6	31.1
NO_3^-(mg/L)	26.3	17.3	25.7	27.7	Log $K_{SO, Fe(OH)_3}$ [c]	0.12	0.17	0.11	0.08
SO_4^{2-}(mg/L)	41.7	41.6	42.4	45.3	Log $K_{SO, Fe(OH)_3}$ [c]	-36.42	-36.47	-36.41	-36.38

[a] N.D.; Not detected.   [b] Concentration of EDTA was from monitoring data of the Onda River and the Tsurumi River (Ministry of the Environment, Japan, 2005).
[c] The solubility of iron(III) hydroxide was recalculated based on Liu and Millero (1999).

those without iron(III) consideration, whereas dynamic concentrations for Cu and Pb increased by 0–41.4% and 0–9.2%, respectively (excluding Cu at Tsu-2). These results can be explained when we assume that there was the competitive binding of free iron(III) with HS and free Cu would be released from the binding sites of HS.
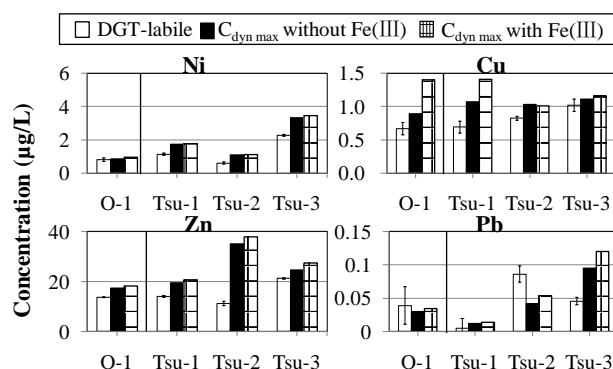

Figure 2 DGT-labile concentrations and max dynamic metal concentrations predicted by WHAM 7.0. Concentrations of humic substances (HS) were assumed to be 1.2 times the DOC concentration, and they consisted of a mixture of 90% fulvic acid and 10% humic acid. By ignoring the formation of colloidal iron and colloidal aluminium oxides, max dynamic concentrations were predicted with and without considering dissolved iron. When dissolved iron(III) was assumed to be present in WHAM 7.0, and free ions was assumed to be in equilibrium with iron hydroxide and free iron competes with other metals for binding to HS, the solubility of iron(III) hydroxide was derived by the empirical equation of Liu & Millero (1999).

Metal speciation

From **Figure 2,** measured DGT-labile concentrations were lower than calculated concentrations at most sites. Similarly, in the previous studies, DGT-labile concentrations were lower than predicted concentrations (Han et al, 2013). In our sampling rivers, besides metal complexes with humics, other metal complexes with organic ligands, such as EDTA, were likely to be present. These metal complexes must have contributed to DGT-labile concentrations which were lower than model predicted concentrations. EDTA was indicated to have had considerable binding with dissolved metals when observed EDTA concentrations (100 and 65 µg/L for Onda and Tsurumi rivers, respectively) were used in model calculation **(Figure 3)**. The fractions of dissolved EDTA bound Ni, Cu, Zn and Pb were 97.1–99.2%, 40.9–69.6%, 22.5–52.7%, and 43.5–75.3%, respectively. Hence, chemical parameters, such as EDTA and iron concentrations, have strong influence on the metal speciation in effluent-affected rivers and influence the bioavailable metal concentrations. Furthermore, overestimation of humic complexes with Cu and Pb, and overestimation of Ni and Zn free ions can occur when the presence of EDTA is ignored.

Conclusions

Using DGT measurement and model prediction, bioavailable metal levels and metal speciation in effluent-affected rivers was discussed. Consideration of competitive binding of iron(III) with HS did not affect the dynamic concentrations of Ni and Zn, whereas it increased the dynamic concentrations of Cu and Pb due to the increase of free Cu and Pb ions. Urban rivers are enriched with iron as they are often impacted by WWTP effluents which received $FeCl_3$ during wastewater and sludge treatment. Therefore, metal toxicity to aquatic organisms should be more highlighted in urban rivers. Based on model prediction by WHAM 7.0, EDTA had considerable binding with metals, and the metal complexes with HS decreased largely for Cu and Pb. The fractions of metal complexes with EDTA followed the sequence of Ni > Pb > Cu > Zn.

Formation of metal-EDTA complexes may be one of the causes of lower DGT-labile concentrations than model predicted concentrations. For effluent-affected rivers, ignoring the presence of EDTA will lead to overestimation of metal complexes with HS for Cu and Pb, and overestimation of free ion for Ni and Zn. These results are useful for assessing metal speciation and bioavailability levels in rivers impacted by WWTP.
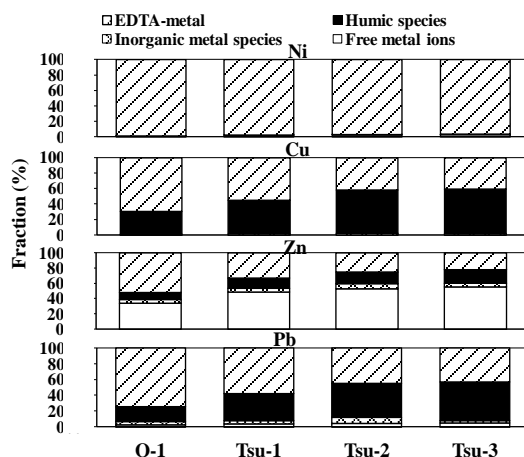

Figure 3 The fractions of free ions, inorganic metal species, humic-metal species, and EDTA-metal species calculated by WHAM 7.0.

Concentrations of humic substances were assumed as 1.2 times of DOC concentrations, and they consisted of a mixture of 90% fulvic acid and 10% humic acid. Free ions for aluminium and iron(III) were assumed to be in equilibrium with their hydroxides and free ions compete with other metals for binding to HS. The solubility for aluminium hydroxide was log $K_{SO} = 8.5$ (Tipping et al., 2002), and the solubility for iron(III) hydroxide was derived by the empirical equation of Liu & Millero (1999). The concentration of EDTA was 100 μ/L for Onda River and 65 µg/L for Tsurumi River (Ministry of the Environment, Japan, 2005).

Acknowledgements

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