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Evaluation of Heavy Metal Bioavailability in Natural River Waters Using DGT and Chemical Equilibrium Model

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薄膜拡散勾配(DGT)法と化学平衡モデルを用いた河川水中重金属の生物利用性の評価、○韓　書平[1]、内藤　航[2]、益永　茂樹[1]
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1. Introduction

Heavy metals exist in natural waters as both inorganic and organic forms. It is known that the bioavailability and toxicity of metals to aquatic organisms depends on their chemical speciation[1].Hence, determination of metal speciation, especially bioavailable fraction of metals can provide valuable information for assessing and managing heavy metal risks to aquatic organisms.

Diffusive Gradients in Thin-films (DGT) is a useful technique for determining bioavailable fractions of metals in aquatic systems. In this study, we used DGT technique to determine-labile metal speciation in wide ranges of Japanese surface waters and compared the DGT measurements with the model prediction estimated by WHAM VI.

2. Study area and methods

In this study, Onda River and Tsurumi Riverin Kanagawa-ken as typical municipal river; Kosaka River and Shimonai River in Akita-ken; Hazama River in Miyagi-ken as typical rivers impacted by mining were selected as sampling areas. Ni, Cu, Zn, and Pb were metals of interest. Water quality parameters, such as pH, DO, conductivity and temperature were measured by Horiba Multi-Parameter Water Quality Meter in situ. Water samples were taken in plastic jars. Then particulate fraction was removed by syringe filter (ADVANTEC) with 0.45μm pore size, and both of filtered (dissolved) and unfiltered samples were acidified to pH=1 by HNO_3. After treatment according to the EPA METHOD 3005A, metal concentrations were determined by ICP-MS (Agilent 7700X). Additionally, raw river water samples were brought back to our laboratory and DGT units were immersed in 1 liter of the samples for 24 hours on a rotary shaker with a speed of 100 rpm a 20°C constant temperature oven. DGT units were obtained from DGT Research Ltd. Then DGT-labile metals were dissolved from the units by HNO_3 (1M) and were determined by ICP-MS[2]. Major cations and anions in the filtered samples were analyzed by ion analyzer (DKK-TOA, IA-300) within one week. DOC was analyzed by TOC-VCSH (Shimadzu).

Calculations of chemical speciation were performed using WHAM VI. Input water chemistry parameters included pH, temperature, majors ions (Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}), and trace metals (Ni, Cu, Zn, and Pb) as dissolved concentrations. The concentration of fulvic acid was assumed to be twice the DOC concentration in every site and as the main binding substances in river water. For other parameters, the default values were used.

3. Results and Discussion

DGT-labile concentrations and calculated results for Ni, Cu, and Zn in study areas were summarized in Fig.1 and Table 1. The fraction of DGT-labile in total Ni, Cu, and Zn concentrations were 36.9-63.1%, 10.8-19.3% and 51.2-63.5%, respectively. Concentrations of DGT-Pb were lower than detection limit at most sites. As for sites adjacent to abandoned mines, the proportion of $[Me]_{DGT}$ in total Ni, Cu, Zn, and Pb were 36.0-87.5%, 7.2-24.4%, 60.4-90.7%, and 0-19.0%, respectively. In general, bioavailable fractions of Ni, Zn, Cu and Pb in urban river were lower those in rivers adjacent to abandoned mines.

As for Zn, a good agreement between WHAM model estimation ($[Zn]_{WHAM}$) and $[Zn]_{DGT}$ was observed.$[Ni]_{WHAM}$ was a little higher than $[Ni]_{DGT}$.WHAM model underestimated bioavailable concentration of Cu at most sites where DOC concentration was lower than 3.5 mg/L, probably because Cu existed as low molecular weight fulvic-Cu complexes (ratio>90%), and these complexes can diffuse into DGT units. Pb might have existed mostly as particulate-bound speciation since dissolved Pb concentrations were low at most sites.

Table 1. Fractions of dissolved or DGT-labile metal against total or dissolved metal concentration (%)

Sampling sites	Cu			Zn		
River (ID)	$C_{Dissolved}/C_{Total}$	C_{DGT}/C_{Total}	$C_{DGT}/C_{Dissolved}$	$C_{Dissolved}/C_{Total}$	C_{DGT}/C_{Total}	$C_{DGT}/C_{Dissolved}$
Onda R. (O-1)	61.8	17.2	27.8	78.2	51.2	65.5
Tsurumi R. 1 (T-1)	79.9	19.3	24.2	93.4	55.4	59.3
Tsurumi R. 2 (T-2)	63.7	14.6	22.9	86.1	57.6	66.9
Tsurumi R. 3 (T-3)	88.6	10.8	12.2	90.2	63.5	70.5
Hazama R.1 (H-1)	95.9	19.4	20.2	91.0	74.0	81.3
Hazama R.2 (H-2)	56.6	24.4	43.1	98.9	82.2	83.1
Hazama R.3 (H-3)	69.6	22.5	32.3	87.8	75.4	85.8

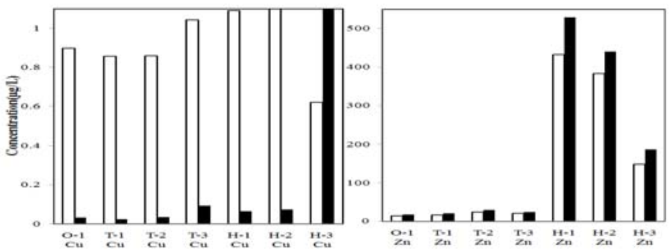

Fig. 1. Comparison of DGT-labile concentration and WHAM model calculation (Blank bars: DGT-labile; Black bars: WHAM)

4. Conclusions

Bioavailable metal concentrations were higher in rivers adjacent to abandoned mines those in urban river, especially for Ni, Cu and Zn. Model estimation was indicated to overestimate $[Me]_{WHAM}$ for Ni. The best agreement was observed between $[Zn]_{WHAM}$ and $[Zn]_{DGT}$. $[Cu]_{DGT}$ were higher than $[Cu]_{WHAM}$ at most sites where DOC was low and Cu mainly existed as low molecular weight fulvic complexes. Pb existed as particulate-bound speciation at most sites.

References

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