

# **Investigation of Heavy Metal Bioavailability in Japanese and Chinese River Waters**

In order to develop efficient and effective assessment and management schemes of risk posed by heavy metals to aquatic biota, bioavailable concentrations of heavy metals (Ni, Cu, Zn, and Pb) were studied for wide ranges of surface water bodies with different water chemistry both in Japan and China using the technique of diffusive gradients in thin-films (DGT). The bioavailable fractions of heavy metals in dissolved forms tended to be higher in Japanese rivers impacted by mine drainages and in Chinese rivers strongly affected by metal industries. As for the effect of dissolved organic carbon (DOC) on heavy metal speciation and bioavailability, inverse relationships between bioavailable fractions and DOC were observed for Cu and Pb as large portion of those metals were present as organic complexes. On the other hand, bioavailable fractions of Ni and Zn varied little among water bodies probably because they mainly present as free ionic or inorganic species regardless of DOC. The variation of binding sites affinities of humic substances accessible to metal were calculated from the plots of  $[Me]_{DGT}$  versus the ratio of bound metal to DOC, the result provided little evidence of strong affinities of binding sites accessible to Cu and inert Cu species, and there was clear evidence of strong affinities of binding sites accessible to Pb and inert Pb species, while Ni and Zn bound to weak binding sites and showed high labile species in sampling rivers.

## 1 Question 1:

### Comparison of Heavy Metal Bioavailability in Japanese and Chinese River Waters



### Investigation of Heavy Metal Bioavailability in Japanese and Chinese River Waters

## Question 2:

(Yellow highlighted sentence is difficult to understand and I do not know how I should correct. What is heterogeneity? How do I know evidence of strong or weak binding sites?)

### Answer:

Log of the DGT measure concentration of metals plotted against [Me] dissolved/DOC. (regression line 1) It is still difficult to realize this. Please show me in figure style.

Log of the DGT measured concentration of metals plotted against [Me]organic/DOC. (regression line 2)

| Rivers          | Metals | Slope 1 | Slope 2 | $\Gamma$ 1 | $\Gamma$ 2 |
|-----------------|--------|---------|---------|------------|------------|
| Chinese rivers  | Ni     | 1.58    | 1.13    | 0.63       | 0.88       |
|                 | Cu     | 0.62    | 0.64    | 1.62       | 1.57       |
|                 | Cu 2   | 1.65    | 1.65    | 0.60       | 0.61       |
|                 | Zn     | 0.98    | 1.35    | 1.02       | 0.74       |
|                 | Pb     | 1.47    | 1.68    | 0.68       | 0.60       |
| Japanese rivers | Ni     | 0.90    | 0.75    | 1.11       | 1.33       |
|                 | Cu     | 0.59    | 0.71    | 1.69       | 1.41       |
|                 | Cu 2   | 1.11    | 0.61    | 0.90       | 1.65       |
|                 | Zn     | 0.84    | 1.05    | 1.19       | 0.95       |
|                 | Pb     | 1.21    | 1.06    | 0.83       | 0.95       |

As a representative constituent of natural organic matter, FA and HA can be regarded as a heterogeneous ligand with a distribution of binding sites. The occupancy of the sites and therefore the effective binding strength depends on the metal to ligand ratio. The heterogeneity can be described by a heterogeneity parameter,  $\Gamma$ , which provides a measure of the variation in the affinities of binding sites that can be available to a metal.

The slope of this plot effectively provides  $1/\Gamma$ .

For a true kinetically limited situation, a value of  $\Gamma$  approaching 1 indicates a homogeneous ligand.

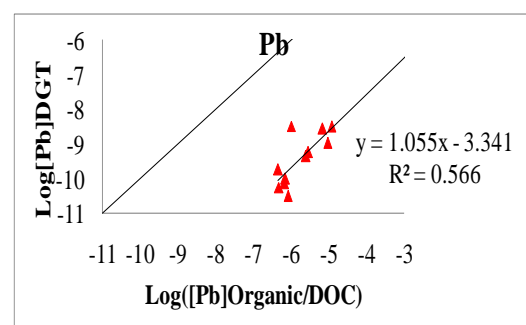
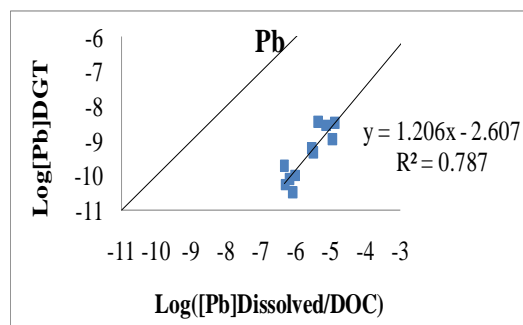
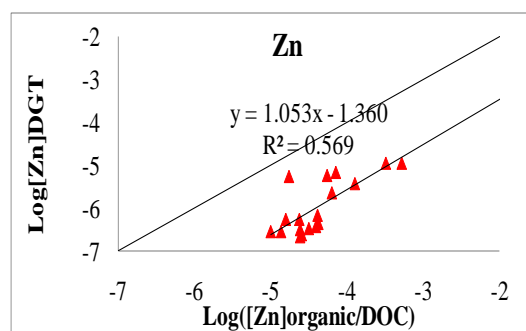
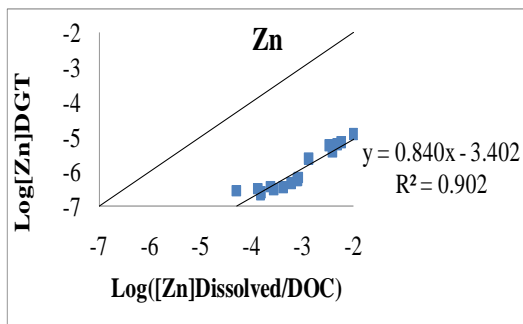
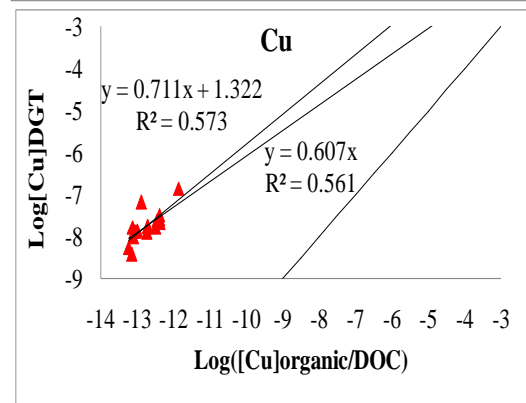
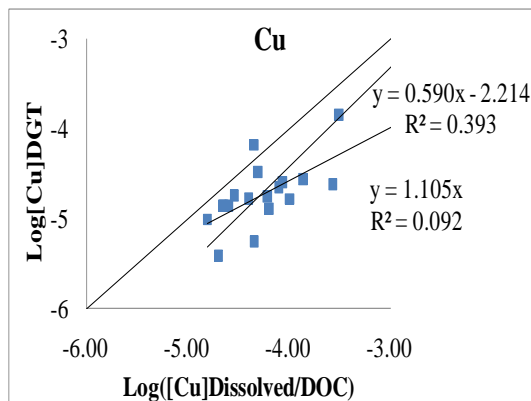
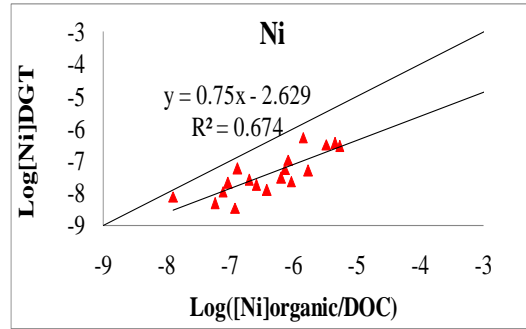
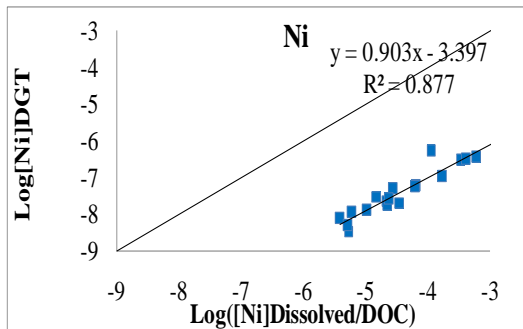
1) Progressively lower values indicate increasing heterogeneity, with 0.5 or less being typical of established heterogeneous binding, as for Cu and Pb, if there is large fraction of strong organic ligands to metal, the value of  $\Gamma$  is near to  $\leq 0.5$ .

2) as for Ni, Cd and Zn, they present in natural waters as inorganic and free ions with lower fraction of strong organic ligands bound to metal or weak ligands bound to metal, the value of  $\Gamma$  is usually higher, usually near to 1 or larger 1.

➤ Typical values of  $\Gamma$  reported for metal binding by isolated humic substances are 0.3–0.5 for CuII, 0.6–0.8 for PbII, 0.8–1.0 for CdII, and 0.6 for NiII, showing that

CuII complexes are very heterogeneous whereas the CdII ones are close to homogeneous ( $\Gamma = 1$ ).

1) Japanese rivers



## 2) Chinese rivers

