論文の内容の要旨
Abstract of Dissertation

論文題目　**Characterization of organic ligands in urban wastewaters and analysis of heavy metal speciation in water environment**

（都市排水中の有機配位子の特性評価と水環境における重金属類の化学形態分析）

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（本文）**(Abstract)**

Trace metals are essential for aquatic organisms however they are toxic at elevated concentrations. Metal speciation or their geochemical behavior plays a fundamental role in their toxicity as metals strongly complexed to organic ligands or absorbed to particles may not readily bioavailable. Water quality guidelines for trace metals in natural waters have historically ignored this important concept and have been traditionally expressed either as dissolved or total metal concentrations. However, development of such regulations and models requires a better understanding of the speciation of metals or metal complexation characteristics in urban wastewaters such as wastewater treatment plant (WWTP) effluents, combine sewer overflow (CSO) and surface runoff. Although the metal speciation or complexation in natural waters has been investigated, the metal binding characteristics of dissolved organic matter (DOM) in different urban wastewaters has not well understood. Therefore it is important to understand binding properties of different type of DOM, which play an important role in the speciation pattern of metals and hence their ecological behavior. The overall aim of the work presented in this study was to gain a better understanding of the behavior of trace metals in urban waters and characterize DOM complexation in different wastewaters. Combination of physical, chemical and electrochemical technique was used to better characterize the nature of DOM responsible for complexing heavy metals in urban wastewaters.

Total Zn concentration was observed as 27 ~ 48 μg/L in the secondary effluent of three WWTP. Total Cu concentration was detected as 4 ~ 18 μg/L while that of Ni was 2~ 5 μg/L. Cadmium was detected only in one WWTP and average concentration was 5.8 μg/L. The metal speciation study showed that, in conventional WWTP effluents, labile Zn was 4.8~16 μg/L, labile Cu was 0.6~3.3 μg/L and labile Ni was 0.6~3.7μg/L with respect to Empore chelating disk. Cadmium and lead presented at very trace level and < 0.11 μg/L and < 0.05 μg/L (under the detection limits) respectively. The results indicate more than 55% of total Zn, Cu and Ni were either strongly complexed by organic ligand or bound by particles in effluents

from WWTP. The ultrafiltration was effectively used to separate trace metal as well as DOC according to their molecular weight to analyze labile and complexed form of Zn, Cu, Ni and Cd. Size fractionated experiments reveal that the distribution of the heavy metals between the different size-fractions in effluents from WWTPs showed large variations. The labile Cu were chiefly (47~75%) distributed in smallest fraction (< 500Da) while the labile Zn, on the other hand, were predominantly found in the colloidal fractions (37~ 49 % was in 500Da~1kDa fraction).

Metal titration study by square wave anodic stripping voltammetry was performed to determine conditional stability constant (K') and binding site concentration [L_T] in unfractionated DOM samples as well as fractionated DOM samples of WWTP's effluents. The conditional stability constant (log K') with DOM in WWTP effluent varies in the order of Cu >Zn >Cd in three WWTP effluents, while binding site concentrations decreased in the order Zn>Cu>Cd. The strong class of Zn complexing ligands (L_1) in effluents from WWTP predominately appeared to be in colloidal fractions (>500Da), where 35% of these ligands were in 500Da~1kDa and 32 % in 1~10kDa. Strong Cu binding sites (L_1) resided predominately (46%) in largest colloidal fraction (10kDa-0.5μm), while remaining strong Cu binding ligands were equally distribute in medium (1~10kDa) and small (500Da~1kDa) colloidal fraction. The Zn and Cu competition study indicates that, the strong type (L_1) ligands are unique to a particular metal; that is, other metals at similar concentrations show no real competitive ability. The Ca/Mg exchange experiments showed at the elevated concentration level of Ca/Mg (> 100mg/L) there is a competition of Ca/Mg for organic binding sites, leading to Zn/Cu displacement and increase the labile metal pool.

Metal complexation of effluent from conventional activated sludge treatment process was compared with advanced treated wastewater effluent by sand filtration and ozonation. Although the sand filtration preceded by coagulation does not do significant changes in Zn, Cu or Cd complexation in treated effluents, ozonation caused decline of 0.1~0.2 log unit in conditional stability constant of Cu and Zn and also a decrease of 12~16% in Zn binding sites while 16~33% of decrease also observed in Cu binding sites of ozonated effluent, compare with that of secondary effluent. Cadmium showed no significant effect by either sand filtration (preceded by coagulant addition) or ozonatation. Metal complexation parameters of DOM in CSO also determined and compared with DOM of WWTP influents and road runoff, since the CSO is basically including untreated influent as well as runoff. According to the metal binding site existed in different DOM type, it was observed that stability constant of DOM follow the order of, influent > CSO ≥ effluent > road runoff for all the Zn, Cu and Cd. Two kinds of binding sites were detected in DOM from influent, CSO and effluent while only one type ligand was detected in road runoff. Comparison of metal complexation parameters with DOM in wastewater effluent, CSO and road runoff with natural river water and reference humic and fulvic acid (Suwanee River) shows Zn binds more strongly to urban wastewaters (WWTP's effluent and CSO) than DOM river water or humic/fulvic acid (Suwanee River). Simple simulation results for a mixture of river water DOM and DOM from urban wastewaters showed DOM from WWTP effluent and CSO form thermodynamically strong complexes with Zn, dramatically reducing labile Zn concentration. It was observed that there is no such an influence when the DOM from road runoff mixed with river water DOM. The number of sampling to represents wet weather pollution in this study was limited and therefore it is recommended to conduct more sampling related to surface runoff, roof runoff and road runoff considering the seasonal variation, land use pattern variation to understand the impact of these non point sources on metal speciation in urban water environment. It is also recommended to further study on naturally occurring processes, such as biodegradation and photodegradation, which might significantly modify the properties of DOM and hence effect to the metal speciation.