論文の内容の要旨

# ABSTRACT OF DISSERTATION

論文題目 Competitive adsorption dynamics and speciation of heavy metals in soil system below rainwater infiltration facilities

(雨水浸透施設下の土壌層における重金属の存在形態と競合的吸着挙動に関する研究)

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（本文）(Abstract)

Artificial Infiltration facilities were introduced to urban areas with the aim of reducing urban flooding from stormwater runoff. In Japan the “Tokyo Metropolitan Sewage Works” constructed infiltration facilities that constitute of infiltration soakaways and trenches at Nerima Ward in Tokyo during early 1980’s as part of ‘Experimental Sewer System’ (ESS).

Among the micropollutants in runoff that are directed to subsoil below infiltration facilities heavy metals are the most problematic due to their persistent (non-biodegradable) nature and relatively easy change in speciation with changing environment. Significant accumulation of heavy metals was observed within infiltration facilities in Nerima by recent studies. This poses threat of migration downward and contamination of subsoil and groundwater. The major volume of dissolved metals in runoff is also reaching the soil system below the facilities. The retention behaviour of the heavy metals reaching the subsoil is essential for assessing its fate and devise better management technologies.

The fate of the heavy metals in soil system depends on metals sorption dynamics in the soil system which is dependent on soil characteristics, environmental conditions, heavy metals preference for certain chemical binding sites and the nature of competition among heavy metals, etc. The binding sites for heavy metals in soil are limited, hence competition is becomes intense as it becomes increasingly occupied. The competition and environmental factors (e.g., soil character, chemical forms, etc.) influence the speciation of metals.

This study aimed at clarifying the processes dictating the sorption behaviour of heavy metals below infiltration facilities with special notion given to competition among metals and speciation. Speciation of heavy metals determines the fate of the metals under a variety of environmental scenarios, and hence was exclusively covered throughout this study. Speciation analysis of metals bound in soil and sediments had been carried out in this study following ‘BCR (Community Bureau of Reference) sequential extraction method’.

The analysis of the soil characteristics at site is essential to predict changes in metal retention characteristics with depth which is crucial in case infiltration of runoff water. A soil core of approximately 5 metre depth was collected from nearby the infiltration facilities at Nerima. There was two distinct layer of soil existing at the site. The first one metre sample was of dark brown colour organic soil while from one metre below the soil type was typical of loam soil in the

‘Kanto’ area, i.e., ‘Kanto loam’ soil. The significant apparent difference prompted inclusion of the surface organic rich soil together with the kanto loam soil for analysis.

The soil core was analyzed for generating vertical profile of soil properties and to observe the soil background heavy metal speciation patterns. The soil properties like pH, cation exchange capacity (CEC), organic content, humic matter content as well as fractional distribution of humic acid and fulvic acid, and humic matter functional group analyses were performed on the soil core along with metal content and metal speciation analyses. From analyses of soil core segments differences in soil chemical and mineralogical characteristics were observed with depth.

The two layers, surface soil and underlying soil, differed significantly in their properties. The kanto loam soil had lower pH, cation exchange capacity and organic content than the surface soil. The difference in cation exchange capacity and soil humic substance was very significant. A decreasing trend was observed for humic substance and also oxide contents in the underlying soil that indicated lesser adsorption potential for underlying soil at greater depth. The lower functional groups presence in the underlying soil indicated possibility of greater competition in underlying soil compared to surface soil. Preliminary adsorption experiments indicated lesser adsorption capacity for the underlying soil.

Analysis of composite or bulk soil samples from the site representing surface soil and underlying Kanto loam soil analysis was in line with the observations form soil core analyses. Surface soil samples from different locations outside the Kanto area were compared with the surface soil and underlying (i.e. below the infiltration facility at Nerima, Tokyo) ‘Kanto loam’ soil from the study site. The properties of the soil were much different from surface soil and underlying soil at site. The redundant nature of the observed properties for the soils stressed for the development of an integrated index for evaluating the metal retention characteristics of different soils.

The adsorption dynamics of heavy metals in subsoil is of concern for its speciation and fate. Even though the surface soil is not expected to receive runoff water at the current setup, the significant variation in character of the surface soil and underlying soil led to the use of both soil types for analyzing competitive adsorption dynamics in soil. This was useful for making a comparative evaluation of the metal adsorption dynamics in the soils with regard to the difference in soil character.

The adsorption dynamics were evaluated with single metal and combination of two metal scenarios that helped to clarify the one to one interaction between the heavy metals in soil during adsorption. The differences in interaction in different soil types (i.e., surface soil and underlying soil) were analyzed in a batch system. The speciation in soil after the adsorption test, i.e., the distribution of the adsorbed metals within soil, were analysed with sequential extraction method, namely BCR sequential extraction scheme. The analyses involved adsorption isotherm analyses, comparing the adsorptivity and site selectivity of metals revealed through distribution to put more light on the adsorption phenomenon and eventually the fate of the adsorbed metals.

The competition effect on adsorption of heavy metals in general was found less pronounced in surface soil when compared to the underlying sub soil below infiltration facilities. It concurred with the observations from the preliminary experiments with soil core sample.

It was found that the competition affect the adsorption a heavy metal differently. Zinc (Zn), nickel (Ni) and cadmium (Cd) were observed to be more affected by competition, either among themselves or by more competitive heavy metals (e.g., Cr, Cu and Pb). Chromium (Cr) and lead (Pb) seemed to be very little affected by competition. The effect of competition was also very specific for the metals, for example Zn was most affected by Cu, while Ni was most affected by presence of Zn.

The interaction of heavy metal produced different change to the binding sites in surface soil and underlying soil in different ways. In some cases improvement of adsorption for a metal was observed for surface soil in presence of another metal cation. In case of underlying soil the effect was always negative.

In the underlying soil ('kanto loam soil') the distribution of Cu, Pb and Cr were more to the mobile exchangeable or carbonate bound phases in contrast to the surface soil where organic and oxides sites seem to be selective of Cr, Cu and Pb. The more mobile metals, Zn, Cd and Ni, preferred the exchange sites. The organic binding sites in underlying soil seemed less capable of retaining metals as a whole and the surface soil organics showed little preference for the metals Zn, Cd and Ni. This is in contrast to numerous literatures that predict and hypothesize role of organic matter in the removal of Zn and Ni.

The selectivity of the organic matter to heavy metals seemed to be specific to the type of organic matter in that soil and no general conclusion can be made on that. It was also observed that the more competitive metals prefer the organic binding sites at low metal load. But as the metal load increases and the binding sites become occupied more of these metals move to the more mobile fractions (i.e., acid exchangeable fraction). The more mobile metals (Zn, Cd and Ni) are limited to the exchange sites for adsorption. Thus the presence of other more competitive heavy metals dictated the speciation of the mobile metals.

The effect of infiltration of runoff water on change in soil character and speciation of heavy metals were investigated. The effect of flow condition on the extent and the mode of such change were assessed since it has influence on the metal retention and fate of heavy metals resulting from changes in soil character. Post analysis of a laboratory soil column simulating impact of infiltration of runoff water was performed.

It was found that infiltration of runoff water introduced significant changes to underlying soil character and metal speciation. Two different flow conditions were evaluated, continuous flow and intermittent flow conditions (i.e., having dry periods in between). It was observed that the changes to soil character, especially soil organic matter were more significant under intermittent flow condition. It seemed that dry weather before a wet weather even has the potential to enhance mobility of metals by introducing changes in soil organic matter and other binding sites.

The leaching behaviour of soakaways sediment bound heavy metals was of importance as they constitute a significant metal load to underlying soil. The soakaways sediment samples at Shakuji area in Nerima, Tokyo had high accumulation of heavy metals. The heavy metals speciation patterns indicated potential for release. The sediments potential to leach heavy metals under different environmental scenario (e.g., acid rain situation, anoxic condition and leaching through organic chelating agents were evaluated in this study. The action of organic chelates appeared to have the greatest influence on initiating heavy metals migration from soakaways sediments to soil system below followed by acid rain condition. The leaching in anoxic environment was significant only for Zn and Cu.

The speciation analyses revealed significant changes due to organic chelating agent and at low ORP condition. The chelating action affected the heavy metals having strong complex with organic matter or soil oxides (e.g., Pb, Cu) as well as for known mobile metals like Zn and Cd. Migration of metals from sediment organic fraction revealed the vulnerability of the organic matter to organic chelates as well as anaerobic microbial activities. Zn was found the most mobile among the heavy metals. While in the soil system Cu seemed to be less mobile, sediment leaching experiments indicated potential for Cu migration to soil as organic labile complexed form.

The experiments conducted in this study provided better understanding of the competitive adsorption dynamics and the speciation of different heavy metals in soil system below rainwater infiltration facilities by clarifying the by clarifying the site selectivity of the metals and the role of soil properties in dictating the speciation. It also gave insight on the expected changes in speciation resulting from long term infiltration of runoff water and the effects of weather conditions on the speciation and long term fate of incoming metals, the vulnerability of the sediment bound heavy metals to different environmental stress. These are expected to aid in better management of the facilities.