
Heavy metals speciation in sediment accumulated within an infiltration facility and evaluation of metal retention properties of underlying soil

Spéciation des métaux lourds dans les sédiments accumulés dans un ouvrage d'infiltration et évaluation de la capacité du sol en à piéger les métaux

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RESUME

L'analyse de spéciation des métaux lourds a été effectuée sur des échantillons de sédiments prélevés dans des puits filtrants appartenant à un ouvrage d'infiltration d'eau pluviale à Tokyo ainsi que sur un carottage de sol recueilli près de ce même ouvrage. On a retrouvé une quantité importante de métaux dans la fraction meuble des échantillons de sédiment, ce qui présente un risque de diffusion dans le sol environnant avec modifications du contexte environnemental. L'analyse détaillée des caractéristiques du sol montre une hétérogénéité importante du sol en profondeur et une capacité d'adsorption réduite des métaux lourds, soulevant la question du risque de pollution à long terme du sous-sol.

ABSTRACT

Heavy metal speciation analysis was carried out on sediment samples accumulated in soakaways in a stormwater infiltration facility in Tokyo, Japan and on a soil core sample collected near the facility. A significant amount of metals was present in potential mobile fractions in the sediment samples, posing threat of release to underlying soil with changing environmental conditions. Detail analyses on soil characteristics indicated significant heterogeneity with depth and reduced adsorption capacity for heavy metals in case of underlying soil; raising concern over the long term pollution retention potential of underlying soil.

KEYWORDS

Heavy metals, infiltration, sediment, soil, speciation.

1 INTRODUCTION

Infiltration facilities have been in use for several decades in the developed countries. Secondary benefits include recharge of groundwater and reduction of non-point pollutant loads from urban surfaces to surface waters. Heavy metals are ubiquitous toxic substances in urban runoff and are often observed at elevated concentrations in road runoff (USEPA 1983; Barret et al., 1998). The most common heavy metals found in urban runoff are chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb) and cadmium (Cd). They are distributed to the urban road surface mostly through traffic activities (Ball et al., 1991). Heavy metals in runoff are mostly associated with particulate matters and accumulated within infiltration facilities through trapping and adsorption to soakaways sediments (Sansalone et al., 1996). However, concern for pollution of subsoil and groundwater from stormwater infiltration exists (Mikkelsen et al., 1997) and there have been few reported incidences of groundwater pollution from infiltration (Pitt et al., 1999).

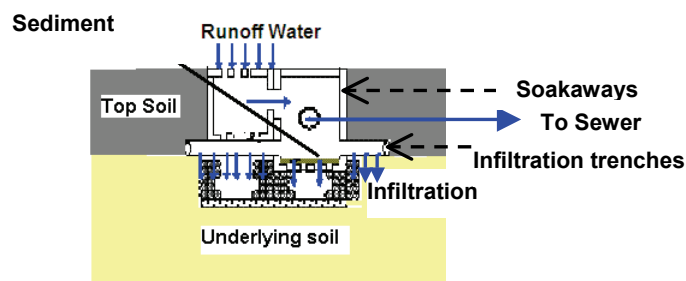


Figure 1: Schematic view of infiltration facility in Tokyo (Nerima ward)

In Tokyo, infiltration facilities were constructed in the early 1980's over approximately 1400 hectares area at Nerima ward by Tokyo Metropolitan Sewerage Bureau as part of the 'Experimental Sewer System' (Fujita, 1984). The primary aim was to reduce runoff discharge to combined sewer system, and thus control urban flooding. The infiltration system consisted of soakaways, trenches, infiltration LU-curb, etc (Figure 1). Even though the infiltration performance of the facilities was evaluated as satisfactory after two decades of operation (Furumai et al. 2005), possible heavy metals pollution through infiltration of runoff water needs to be assessed.

A field survey on soakaways showed differences in accumulated sediment depth. A total of 61 sediment samples were analyzed for heavy metal content which confirmed significant accumulation of heavy metals in the soakaways sediments (Aryal et al., 2006a). These accumulated metals can be mobilized through weakening of bonds (Charlesworth and Lees, 1999) due to aging, long dry periods, formation of organic chelates and complexation (Becker and Peiffer, 1997), and through mobilization of colloids, etc. Vertical profiles of heavy metals in some sediment core samples showed the bottom layers having lower content than the upper layers, indicating possible desorption/release of heavy metals from the anoxic bottom layers (Aryal et al., 2006b). Once the metals are released to the soil system, the fate of the metals are dictated by the soil properties (e.g., pH, organic matter, cation exchange capacity, etc.), the character of the leachate and speciation (Pitt et al., 1999). The study on the content and speciation of accumulated heavy metals within the facility, detail soil characterization and understanding of heavy metals adsorptive behaviour in the underlying soil is essential to ensure sustainability of such facilities. The present study focuses on depth-wise soil characterization, metal speciation in soil and soakaways sediment samples and assessment of soil adsorptive capacity.

2 MATERIALS AND METHODS

2.1 Sampling of soil and sediment

The study area for the study was the infiltration facilities at Nerima ward, Tokyo.

Sediment samples were collected from three soakaways in which significant sediment accumulation (>8cm) was observed. The samples were air dried, sieved (2.0mm nylon sieve), homogenized and kept in refrigerator in plastic bottles before analysis.

A soil core sample (5 m depth) was collected from a park in the study area at a horizontal distance of approximately five meter from the nearest soakaways. Though the release point of infiltrated water to subsoil is approximately at a depth greater than one meter from surface (Figure 1), significant differences in colour and texture observed between the a upper one meter soil (dark brown) and the soil below one meter depth (light brown, typical 'Kanto loam') advocated for analysing the near surface (<1.0m) soil together with underlying soil at greater depth (>1.0m). The soil core was divided in 10cm segments, air dried, sieved (2.0mm nylon sieve), homogenized and stored for further analysis. A total of 25 sliced 10cm-segments out of 50 were analyzed for pH, organic content (i.e. ignition loss), humic content, cation exchange capacity (CEC) and heavy metal content.

2.2 Adsorption test

Heavy metal adsorption test was carried out at room temperature on air dried soil samples with multi-element metal solution of 2mg/L concentration. The metal solution was prepared from 'Wako W-V 113-13781' and pH was adjusted to 2.0. The L/S ratio was 20 and the contact time was 6 hours under 150rpm horizontal shaking. Metal speciation analysis was carried out before and after the adsorption test to know the distribution.

2.3 Analyses

The pH was measured following EPA method 9045D. Ignition loss was measured by heating dry soil (oven dried at 110°C for 24 hours) at 600°C for 1 hour and observing the weight loss. The cation exchange capacity measured was 'effective CEC' (CEC_e) as per ISSS method with BaCl₂. The humic substances extraction and fractionation were carried out according to IHSS method with NaOH solution. The functional groups in humic substances were qualitatively analysed with FT-IR.

For total metal content, sediment and soil samples were digested in a microwave (model MCS-9700) as per EPA method 3051a with the digestion time increased to 10 minutes from the original 4.5 minutes mentioned in the method. The digestion procedure was calibrated with certified reference material 'NIST 1649a (Urban dust)'.

For speciation analysis, the 'BCR (three step) sequential extraction method for metals' was applied to both the sediments and the soil samples. The BCR sequential extraction method is an operational extraction scheme that sequentially extracts metals in the order of decreasing mobility (Hlavay et al., 2004.). The potential mobile fractions determined in the scheme are listed as 1) Acid Exchangeable, 2) Reducible and 3) Oxidisable. The three fractions usually represent the exchangeable and carbonate bound metals, the Fe/Mn oxide bound metals and organic bound metals, respectively. The remaining amount, termed the 'residual metal content' is calculated by subtracting the three fractions from the total content.

Liquid-solid separation was carried out by centrifugation followed by filtration (0.2 µm) of the supernatant. The metals in the extracts were all measured with ICP-MS (Model 'HP 4500'). The samples were measured in triplicate except for humic content analysis which was done in duplicate. The coefficient of variation was lower than 10% in all cases, except for Cd determination.

3 RESULTS AND DISCUSSION

3.1 Vertical profile of soil properties

The near surface soil (0~1.0m depth) had higher pH, %ignition loss, CEC_e and humic content than lower layer (1.0~5.0m depth) 'Kanto loam' soil (Figure 2.). The difference in humic content is large even though the difference in ignition loss is comparatively less. The difference in CEC_e is very significant. The humic content (extracted by NaOH) in soil is much lower compared to ignition loss value indicating most of the humic matter in inert insoluble humin phase for both type of soil.

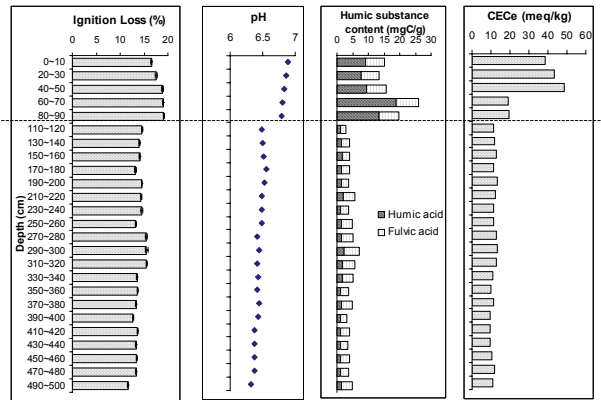


Figure 2. Vertical profile of %ignition loss, pH, humic content and cation exchange capacity in soil
*The dotted line separates the surface soil (0~1.0m) from the deeper soil (1~5m) segments.

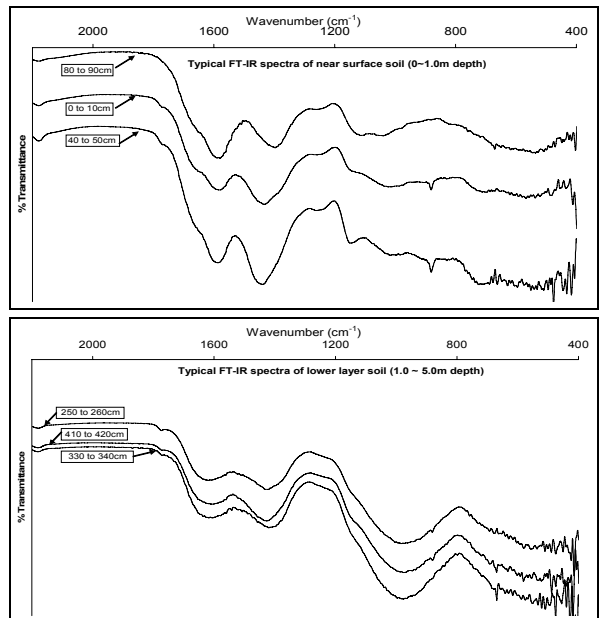


Figure 3. Typical FT-IR spectra of humic substances in near surface (0 ~ 1.0m depth) soil and lower layer (1.0 ~ 5.0m depth) soil.

The organic matter usually plays an important role in heavy metal retention in soil (Pitt et al., 1999). The soil humic substances in lower layer soil were dominated by fulvic acids (mobile at low pH) while in near surface soil humic acids (relatively immobile) were dominant (Figure 2). 'Fourier Transform Infrared (FT-IR)' spectra obtained for extracted humic substance from soil core segments showed significant difference between the near surface soil and lower layer soil (Figure 3). In the lower layer soil the occurrence of broad deep peaks in the fingerprint region of the spectra around $800\text{-}1000\text{cm}^{-1}$ can be attributed to alkenes and other low molecular weight compounds. The aromatic $\text{C}=\text{C}$ bond peaks (double peaks around $1400\text{-}1600\text{cm}^{-1}$) tend to attenuate at greater depth indicating a decrease in the aromaticity which is an indication of lower humic acid content. These results indicate less potential of the organic matter for heavy metal retention at greater depth. The CEC_e is contributed by organic matter and clay minerals in soil. The lower CEC_e in soil at greater depth may be due to less contribution from organic matter.

3.2 Heavy metal contents

The heavy metal content profiles (Figure 4) show an overall decreasing trend with depth. The heavy metal content in the surface soil was higher than the lower layer (1.0~5.0m) soil, especially for lead, nickel and cadmium.

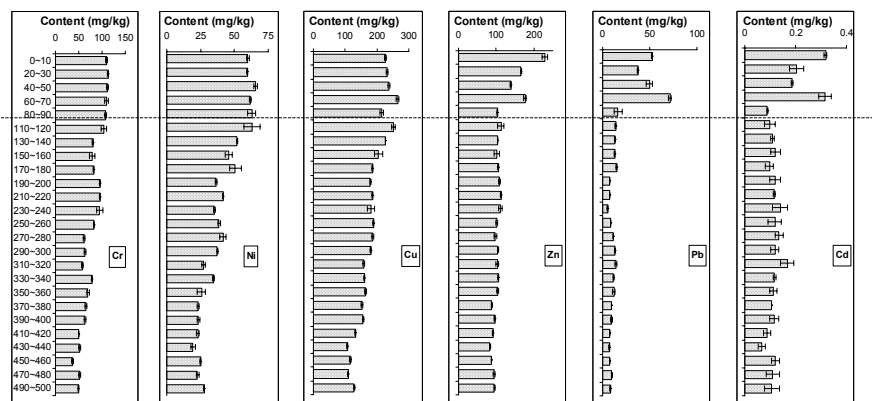


Figure 4. Vertical profile of heavy metal content (mg/kg-dry wt.) in soil [error bar=SD, n=3].
*The dotted line separates the near surface soil (0~1.0m) from the lower layer soil (1.0~5.0m).

Sample Type	Range of metal content (mg/kg-dry wt.)					
	Cr	Ni	Cu	Zn	Pb	Cd
Sediment	86 – 111	56 – 140	184 – 338	1161 – 1551	205 – 253	1.5 – 3.0
Near surface soil	108 – 113	60 – 66	215 – 265	103 – 228	16.5 – 71.3	0.09 – 0.32
Lower layer soil	37 – 104	19 – 63	107 – 252	83 – 113	5.2 – 14.7	0.07 – 0.17

Table 1 Heavy metal content range in sediment, near surface (0~1.0m depth) soil and lower layer (1.0 ~ 5.0m depth) soil

The metal content of the sediment samples are much elevated compared to the surface soil heavy metal content, especially for Zn, Pb and Cd which are almost 5 to 10 times as high as the content in the soil. The Zn and Cu content in the sediments are comparable to Durand et al (2004) while the Cd and Pb content are lower than the values observed in that study. Durand et al. (2004) reported higher Ni and Cr content for road runoff receiving basin sediments but lower content for basin sediments in the residential area.

3.3 Speciation of heavy metals in soil and sediments

In order to investigate the difference in the potential of release of adsorbed metals between soil and the sediments, speciation of heavy metals were performed on 10 sliced segments from soil core (5 from <1.0m depth + 5 from >1.0m depth) and three soakaways sediment samples, following the BCR three step sequential extraction method. Typical plot of metal speciation in one 10cm segment from near surface soil, one segment from lower layer soil and in soakaways sediment samples (designated as 'Sed-A', 'Sed-B' and 'Sed-C') is shown in Figure 5.

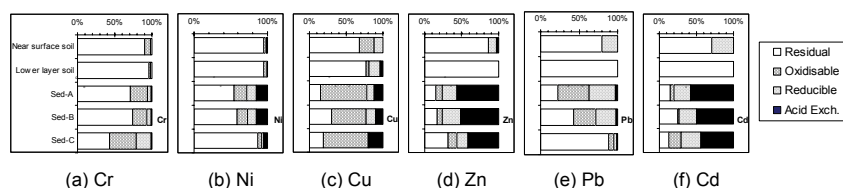


Figure 5. Heavy metal speciation (expressed in percentage of total content) in one near surface soil segment (40-50cm), one lower layer soil segment (170-180cm) and in soakaways sediments.

In the soil, insignificant amount of metals was present in exchangeable fraction and the residual fraction was the major fraction. In case of lower layer soil, virtually no mobile fraction was observed (Figure 5).

The acid exchangeable fraction in the sediment would be most sensitive for heavy metal desorption/release to the underlying soil. In the sediments acid exchangeable fraction is the major fraction for Zn and Cd while it is a significant portion for Cu and Ni indicating possible release under low pH condition (Figure 5). Though Cr content in surface soil and sediment are almost comparable and range of Cu content overlaps (Table 1), the speciation is much different (Figure 5). The sediments accumulated in the facility consist of mostly nearby road dust and wash-off from nearby surface soil. The road dusts are generated through crushing and grinding of road surface as well as erosion and wash-off from nearby surface soil. The large difference in content and speciation between near surface soil and sediments can be attributed to pollution from anthropogenic activities (e.g., traffic activities) and the processes occurring within the soakaways.

The acid exchangeable fraction and reducible fraction for Zn and Cd in sediments are comparable to the distribution observed by Durand et al. (2004) and Charlesworth & Lees (1999). Very little oxidisable (i.e., organic bound) fraction was observed which is lower than the values observed in the above mentioned studies. This is in direct contrast to the result of Akcay et al. (2003) for river sediments, where oxidisable fraction is the dominant fraction. For Cu, the dominant fraction was oxidisable fraction and the percentage is comparable to Charlesworth & Lees (1999), Durand et al. (2003) and Akcay et al. (2003). Changes in the organic matter with aging and long dry period resulting in oxidation of organic matter are the likely environmental scenarios for mobilization of Cu in soakaways sediments. For both Pb and Cr, the residual fraction is the dominant fraction, while significant amount exists in the oxidisable and reducible fractions. This is also different from observed speciation in soil. The distribution of Pb is in contrast to what have been observed by Charlesworth & Lees (1999) for soakaways sediments but in agreement with Durand et al (2004) for the first two sediment samples. The heavy metal speciation in soakaways sediments differed significantly from one another, especially in case of Pb and Cr (Figure 5). This difference may be due to the difference existing at source (e.g., road dust composition, speciation, etc.) and/or different environmental conditions existing within the soakaways. The mobility order for the metals in sediments in terms of percentage in acid exchangeable fraction can be given as $Zn > Cd > Cu > Ni > Pb > Cr$.

3.4 Evaluating adsorption potential of soil

The significant difference in heavy metal speciation between soil and soakways sediments and possibility of metals in significant amount reaching the subsoil, made it necessary to investigate the metal retention characteristics of the soil. In order to investigate the retention capacity of heavy metal by the underlying soil, air dried subsamples from two sliced samples (40~50cm and 170~180cm) were subject to adsorption test with multi-element metal solution (2mg/L strength, L/S=20) adjusted to pH 2.0. The pH=2.0 was employed to simulate adverse situation in which low pH leachate from the facility reach the subsoil. The final pH, after 6 hours of contact time, was 2.54 and 2.10, respectively. The three step BCR sequential extraction test was carried out on the residue to recover the adsorbed metals and observe the change in the speciation after adsorption.

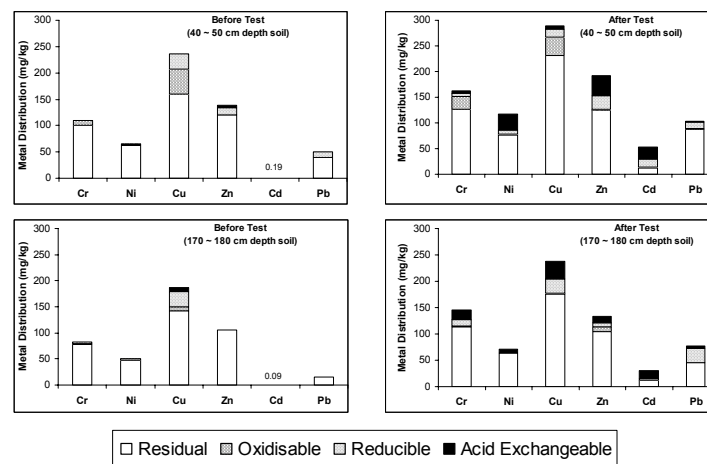


Figure 6. The distribution of heavy metals in different fractions in the soil core samples before (at left) and after (at right) batch adsorption test.

Even at such low pH soil samples showed some adsorptive capacity in the adsorption test. The soil sample at greater depth (170~180cm) showed less metal adsorption potential compared to near surface (40~50cm) sample, particularly for Zn Cd and Ni.

In case of Zn, Cd and Ni, most of the adsorbed metal moved to the acid exchangeable fraction for both soil samples. Major portion of adsorbed Cr moved to oxidisable fraction in near surface soil segment. Significant amount of metals moved to the residual fraction. Apart from Cr in near surface soil, there was little adsorption of heavy metal in the oxidisable fraction (i.e. complexed with organic matter). On the contrary desorption from oxidisable and reducible fractions were observed in case of Cu. The organic matter in soil seems to have less stable bond with the metals than expected and is particularly selective for metals. It is evident that the desorbed portion were re-adsorbed to the residual portion (i.e. clay minerals) resulting in higher increment in that fraction. The batch adsorption provides long contact time which might be the reason that re-adsorption could take place. However, in the natural environmental condition with infiltrating water, re-adsorption by the clay matter is not expected to be this much since the adsorption to these sites are often less rapid compared to organic/carbonate sites. In general, metal adsorbed to organic sites in soil is regarded as less mobile than metal bound to carbonate or Fe/MnO sites. Hence, little adsorption to oxidisable fraction, indicating little adsorptive potential of organic matter for metals, is a concern for long term metal retention capacity of soil.

4 CONCLUSION

The sediment samples in soakaways had 5 to 10 times Zn, Cd and Pb content compared to that in surface soil. A significant amount of heavy metals in sediments was present in acid exchangeable fraction posing threat for immediate release to underlying soil at low pH, especially for Zn and Cd. Considerable amount of Cu, Pb and Cr in sediments are bound to organic matter which, though considered less mobile, may mobilize through oxidation of organic matter induced by long dry periods, microbiological activities, etc. Significant difference in soil characteristics was observed with depth indicating difference in metal retention capacity at different layers. From adsorption test results, surface soil seemed to have greater metal adsorption capacity than underlying 'Kanto loam' soil under low pH condition.

Further insight into mechanisms of leaching of metals from infiltration facilities through desorption tests, and enhanced understanding of heavy metals selectivity and competition for adsorptive sites in soil through competitive adsorption tests are necessary in order to make a proper assessment of pollution.

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