

論文の内容の要旨

Abstract of Dissertation

論文題目 Comparative assessment of potential mobility of heavy metals in soakaway sediment of infiltration facilities and soil using sequential extraction and isotopic dilution techniques

(逐次抽出法と同位体希釈法による浸透ます堆積物及び土壌中の重金属移動性の比較評価)

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**(本文) (Abstract)**

In the present era of high population growth, rapid urbanization and climate change, uncertainty of natural phenomenon and land use pattern are rapidly increasing. Particularly rainfall frequency and its amount became too unpredictable to regulate stormwater runoff or wet weather flow. Further, urbanization is a global phenomenon that includes various point and diffuse non-point pollution sources, which can impart various toxic contaminants into the environment. Particularly, diffuse non-point pollution sources are difficult to identify, categorize, control and prevent due to their dynamic nature. Road dust is one of such non-point pollution source of heavy metal which is toxic, prevalent and persistent in the urban environment. On the other hand, urban areas require artificial infiltration facilities (AIF) to enhance groundwater recharge and to regulate storm water runoff and wet weather flow. However, AIF systems such as soakaways, provide a sink which traps the road dust coming with urban runoff. Prolonged accumulation of road dust in soakaway sediment is likely to cause groundwater contamination.

Although the information of total metal content in the solid phase of contaminated soil/sediment is useful to estimate its overall contamination potential, the magnitude and intensity of contaminant mobilization to groundwater does not necessarily depend directly on total metal content. Precise assessment of heavy metal fate and its toxicity must take into account of the partitioning of heavy metal. It is a known fact that trace metals are distributed among several different soil components with varying degree of

strength and ways. This strength and ways of association with different component enable trace metal to behave as highly labile species, easy to get exchanged with ambient environment, through to increasingly non-labile (fixed) forms. However, under certain condition, these fixed forms of metal also can turn into the labile pool. In response to this accepted fact, researchers from worldwide conducted various research to find the most accurate technique to quantify the labile pool of heavy metal.

One of the most widely used technique for speciation is selective sequential dissolution (SSD) that relies on the solubility of individual solid-phase components by selective reagents where each reagent in SSD targets one major solid phase. However, in no case a reagent can remove all of a targeted solid-phase without attacking other components. In addition, metal redistribution and re-adsorption may occur during a given step. While, isotope dilution technique (IDT) is highly accurate with a 0.2% of possible error of estimation of isotopic ratio against 5% of error in estimation of elemental concentration. IDT is one of the most accurate methods available to quantify exchangeable metal concentration (E-value) which is based on the assumption that stable isotopic tracers added to the soil solution will exchange with the potentially mobile forms of the elements present in the solid phase. There are limited studies available in literature that had used both techniques for the mobile metal pool assessment.

Moreover, there is no scale present to measure the heavy metal retention properties of soil and sediments. Henceforth, the present research aims at precise understanding of the heavy metal sorption properties of soil/sediment using an integrated analytical approach for column leaching experiment. In addition, the compliance between SSD technique proposed by the Community Bureau of Reference (BCR) and isotopic dilution techniques for the determination of mobile pool of heavy metal contained in soakaway sediment, road dust, and soil samples were also examined. Study also has an objective to observe the influence of soil properties on the metal sorption capacity and its variation with ageing.

More specifically, the objective of this study includes (i) Understanding the metal partitioning and their relative affinity for different fractions of soil and sediments with the comparison among different metals. ii) Tracing the source of metal contamination using isotopic fingerprinting. iii) Probing the reactivity, fate and mobility of heavy metal using the sorption coefficient ( $K_d$ ) and isotopically exchangeable metal concentration (E) in soakaway sediments of AIF. iv) Understanding the factors that

affect heavy metal retention by soil and sediments. v) Tracing the ageing effect on the metal sorption, and vi) Development of heavy metal retention index (HMRI).

Four sediments samples were collected in July and November 2007, from different infiltration facilities (constructed in the early 1980's) at Nerima ward, Tokyo. All four soakaway sediments were different on the basis of their locations viz besides the park, near residence with and without receiving some portion of domestic water use, and near parking area. Two soil samples representing the surface (depth<1.0m) soil and bottom soil (depth >1.0m) were also collected besides. Apart from this highway road-dust samples were also collected. The samples were processed and preserved in refrigerator till analysis. Initially, samples were characterised by determining the parameters like pH, moisture content, organic content (i.e. ignition loss) and cation exchange capacity (CEC) using standard methods. For speciation analysis, the 'BCR (three steps) sequential extraction method' was applied in order to sequentially extract metals in the order of decreasing mobility. The three fractions represent the exchangeable and carbonate bound lead, the Fe/Mn oxide bound lead and organic bound lead, respectively. The remaining amount, termed as 'residual fraction' which is supposed to be associated with silicate fractions. The total lead content and their isotopic ratios were measured separately with ICP-MS.

Isotopic data were used in this study to first distinguish the partitioning of anthropogenic and natural lead in different fractions, obtained by BCR sequential extraction, and then to anticipate their mixing process in the soakaway sediment of AIF. In general, total contamination level of a particular metal in different samples followed similar order of road dust > soakaway sediment >> soil, except that of Pb which showed higher value for soakaway sediment. Trend showed that heavy metal contamination threat to groundwater from road dust and soakaway sediment is much higher than that of soil. The results obtained through BCR fractionation showed that irrespective of total metal burden, the exchangeable fractions of all metals were found maximum in soakaway sediment except Cd. This is due to changing oxidation-reduction condition due to wet and dry periods in soakaway sediment. In general, residual fractions shares highest percentage of total metal among different fractions. This observation is valid for each sample and metal with only exception in case of Cu in Soakaway sediment, which is found to be associated with oxidisable fractions more.

Investigation of the difference in Pb content, partitioning and its isotope signature among four sediment samples considering their sampling locations showed that the lowest  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios were mostly observed in exchangeable fractions of soil and sediment samples, while residual fractions mostly showed the highest  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios than those of other fractions. In general, both ratios were higher in the soil than those of sediments. Among soil samples, residual fraction of bottom soil exhibited higher ratios than surface soil indicating higher contribution of natural lead with depth. The plot of  $^{206}\text{Pb}/^{207}\text{Pb}$  versus  $^{208}\text{Pb}/^{207}\text{Pb}$  showed two well demarcated cluster formations by soil and sediments samples that describe the partitioning between anthropogenic and natural lead; and some points falling in between soil and sediment samples pertinently illustrated the mixing processes between these two different pools of lead.

It was found that only exchangeable fraction measured through BCR is not a good criterion for the estimation of mobile metal pools. It is also pointed out that metal extracted by chemical reagents not only underestimates the exchangeable portion but also overestimates the potential mobile pool of heavy metal as evident from the comparison of percentage of E-value and potential mobile pool. Although there is a difference in quantification of mobile pool between the two techniques, mobility potential ranking of heavy metal can be evaluated by BCR. Nevertheless, sequential extraction shares a common goal with IDT to determine the reactive pool of metal. Moreover, combination of isotope dilution analysis with selective dissolution method can give more insight into mobile pool of heavy metals. The information obtained in the study is a vital contribution for obtaining international standardized agreement between both techniques.

Column leaching experiments were conducted using surface soil, underlying soil and soakaway sediment to first understand the potential mobility of heavy metals and then to distinguish the difference of mobility characteristics of these contaminant among different samples. Artificial road runoff (ARR), prepared in the laboratory using highway road dust and pure water ( $L/S=25$ ), was used as leaching solution to mimic actual condition of urban runoff received by artificial infiltration facilities (AIF). Continuous leaching was carried out by feeding ARR with flow rate of 0.12 ml/minute to simulate 10mm/hr of infiltration. Leachates were collected at the regular interval of 24hrs (daily basis) and analysed for pH, DOC (dissolved organic carbon), major ions and heavy metals. Experiments were carried out in batches for 30 days under continuous

flow conditions as well as for 20 days under intermittent flow condition. An extra batch of columns operated under continuous flow condition was installed to compare with the intermittent flow. This is because the amount of eluent passed to column under intermittent flow condition for 20 days is equivalent to the amount that was passed in continuous flow mode for 10 days. At the end of experiment each column samples were divided into two i.e. upper half and lower half and then analyzed for several parameters to evaluate the change during experiment. The E-value increases with time which was the highest for Pb and least for Cu, some exception for specific sample did exist. The most important thing observe was higher isotopically exchangeability for Cu and Zn after 20 days of intermittent leaching than that of after 30 days.

The strong retention of Pb to the solid system may be one of the reasons of not having much difference between two flow conditions. The important change in chemical partitioning before and after leaching was seen as the increase of exchangeable fraction and decrease of percentage contribution of residual fraction with the time of leaching. The easy transport of mobile pool associated with solid system but due to higher dynamic attachment of free and labile metal complexes of feed water on solid system likely is the reason behind change in metal speciation. A general finding was the change in reducible fraction which was the most significant for Pb while oxidisable fraction change exhibited highest change for Cu. The fraction of Zn bound to organic matter changed insignificantly except the initial stages of experiments of the column packed with soakaway sediment. Pb showed the highest retention than that of Cu and Zn. Further, the concentration of stable complexes in the collected leachates seems to be quite stable throughout the experiments especially in the case of soil samples. Therefore, the increase and decrease of metal retention is due to the variation in the retention of free and labile complexes of metals. It can thus be concluded that it is labile fraction which is scanned by the solid materials for retention. Henceforth, high labile concentration in ARR is a subject of more concern from the pollution point of view through infiltration facilities.

The hierarchical levels of normalized factors established for heavy metal retention index (HMRI) was designed to estimate heavy metal retention capacity. Three different index are proposed based on six physicochemical parameters (classical HMRI), three special parameters for each Cu (specific HMRI) and nine combined parameters (integrated HMRI). All three HMRI is validated with actual results obtained for column leaching

experiment. Integrated HMRI not only decreases the extra sensitivity of specific parameters but also decreases the roughness of physicochemical parameters.

Results obtained in this study effectively predict the risk associated with the release of retained heavy metal and nitrate with changing environmental conditions in AIF. The information obtained in the study can be utilised in better management of non-point pollutants accumulated in infiltration facilities in urban area.