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Tracing source and distribution of heavy metals in road dust, soil and soakaway sediment through speciation and isotopic fingerprinting

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ABSTRACT

Soakaway sediment trapped in urban infiltration facilities exhibits high heavy metal content that makes it an important diffuse pollution source of groundwater contamination. In this study, heavy metal (Cu, Zn, Cd and Pb) content, speciation and stable isotopic variation of Pb in soakaway sediments were coupled and compared with soils (surface and underlying), and road dusts (residential and highway) to trace their contamination characteristics, mobility and source. Soakaway sediment and residential road dust were found to exhibit higher metallic content of anthropogenic origin with high mobility. Isotopic ratios in exchangeable fraction showed the least ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios. Although there were significant differences in total metal content and speciation between two road dust samples, their isotopic signatures exhibited close resemblance and aligned with anthropogenic markers such as paint, petrol and aerosols. Heterogeneity of isotopic signature in different fractions of soakaway sediments seems to have originated from the mixing of multiple sources of heavy metals. Study concludes that mobility, source and contamination characteristics of metals in soakaway sediment were different from urban soil and road dust samples due to their complex environment and regular metal supply by road runoff.

1. Introduction

In the present era of high population growth, rapid urbanization and climate change, rainfall intensity has become too unpredictable to adequately regulate stormwater runoff or wet weather flow. Considering the gradual increase of impervious zones due to concrete structures like road, building, pavements etc. and limited drainage efficiency of mega-cities during heavy rain, artificial infiltration facilities (AIF) are going to be an integral part of infrastructure development in the urban areas, especially in developing countries; to enhance groundwater recharge and regulate stormwater runoff (Furumai, 2008; Harrison and Wilson, 1985; Kumar et al., 2010; Mikkelsen et al., 1996). A schematic diagram of AIF has been provided in Supplementary 1. Further, road dust is widely recognized as the major non-point source of heavy metal which is difficult to categorize and manage due to their dynamic nature. AIF provides a sink which trap the road dust and soil coming with stormwater runoff, which is likely to cause groundwater contamination (Kumar et al., 2013). Significant accumulation of heavy metals has been reported in trapped sediments (known as soakaway sediment) of AIF (Aryal et al., 2006; Hossain et al., 2007; Murakami et al., 2009). The long term accumulation of heavy metal in AIF must be regarded as a “Chemical Time Bomb” waiting to be set off by the appropriate time and climatic/environmental triggers (Bacon et al., 2006; Kumar et al., 2013).

Once heavy metal contaminates fresh water resources, it is likely to get into the food chain. Due to the toxic and bio-accumulative nature of heavy metal, it is going to affect human health adversely, especially young kids exposed to contaminated soil of playgrounds. On the other hand, it was estimated that by 2008 more than half of the world's population will start living in towns and cities, whereas by 2030 this number will swell to almost 5 billion, with urban growth concentrated mainly in Africa and Asia (UNDESA Population Division, 2005). This is why mega-cities have captured much public attention. Therefore, it is imperative to understand the distribution of heavy metal content, speciation, mobility and to trace their source in the soakaway sediment of urban infiltration facilities for the aspects of groundwater pollution and sustainable management of diffuse pollution source. In this study four metals (Cu, Zn, Cd and Pb) have been monitored and assessed keeping in the mind of the availability of their stable isotopes like ^{63}Cu/^{65}Cu, ^{66}Zn/^{67}Zn, ^{111}Cd/^{114}Cd and ^{207}Pb/^{208}Pb, as well as the toxicity. As a matter of fact, while Cd and Pb are highly toxic to all organisms even in low concentration, Cu and Zn being the essential elements for life, are moderately/slightly toxic.

Although the information of total metal content in the solid phase of contaminated soil/sediment is useful to estimate its overall contamination potential, the mobility of heavy metal does not necessarily depend directly on total metal content, but on their partitioning among different solid phases of a particular sample (Bacon et al., 2006; Cuong and

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Obbard, 2006; Teutsch et al., 2001; Ure, 1996). In particular, highly mobile species that are superficially bound to the solid system (i.e. carbonates) become more important when assessing groundwater vulnerability through heavy metal leaching. In addition, non-mobile (fixed) forms of heavy metals can also turn into the mobile pool under certain conditions. Various studies have been conducted to assess the mobile pool of heavy metals and its potential contamination threat for soil, pond and marine sediments (Bacon et al., 2006; Durand et al., 2004; Shi et al., 2008, 2010; Tessier et al., 1979; Ure, 1996), literature focusing specifically on soakaway sediment is not common though.

Further, sequential extractions do not provide any information about the origin and mixing processes of metal which can be achieved through isotope fingerprinting. Stable isotope ratios of lead (Pb) are probably the most frequently used ratios for this purpose, which can easily identify the natural or anthropogenic contribution of metals in different environmental samples, distinguishing between sources, tracing elements along their route from source to burial, and assessing the effect of remedial actions taken to reduce emissions from a specific polluter (Cloquet et al., 2006; Dawson et al., 2010; Emmanuel and Erel, 2002; Hamilton and Clifton, 1979; Ip et al., 2007; Labonne et al., 1998; Marcantonio et al., 2002; Monna et al., 1997; Roy and Negrel, 2001; Vilomet et al., 2003). This is because Pb isotope abundances are not affected to any measurable extent by physical or chemical processes in terrestrial environment (Helland et al., 2002), while significant differences can be easily noticed in the historical records of anthropogenic Pb isotope variations to trace the changing sources of pollutant Pb through time. Therefore, the coupled application of sequential extraction and isotope ratio offer an additional index to assess the behaviour of metal and their varying abilities to bind with the different soil components (Bacon et al., 2006). Kumar et al. (2009) attempted to understand the partitioning processes of mobile lead through coupling of both techniques, yet a comprehensive study tracing mobility, source and contamination characteristics of different heavy metals in soakaway sediment including soils of different depths, road dusts of different origins and anthropogenic markers like paint, aerosols is lacking.

In the light of above discussion, we decided to monitor the soakaway sediment depositions in four artificial infiltration facilities with varying vicinity. The aims of the current study were threefold, namely to: 1. Compare heavy metal content of soakaway sediment with that of soil samples of different depths and road dust of different origins i.e. residential and highway, to ascertain the differences/similarity of each entity, with a key focus on discrimination between impacted and non-impacted sites and samples; 2. Investigate the application of coupling of heavy metal speciation and isotopic fingerprinting to gain better understanding of local anthropogenic Pb contributions (through isotope ratios) to soakaway sediments; and 3. Gather further information regarding the possible sources and types of anthropogenic Pb contamination in the region. In this aim, we investigated Pb elemental and isotopic compositions of urban soil, road dust, aerosols and yellow paints. To better constrain the possible sources of these metals, we also compared our results with the literature values of various anthropogenic markers.

2. Material and methods

2.1. Sample collection

The experiment was carried out by using soil, soakaway sediment and highway road dust samples collected in Tokyo. Soil samples representing surface soil (mixture of upper 20 cm) and underlying soil (depth > 1.0 m) were collected which represents the surface black andosol soil layer and typical 'Kanto loam' soil, respectively. Four soakaway sediment samples were collected using a plastic pipe from different AIF (constructed in the early 1980's) at Nerima City (latitude 35° 73′ and longitude 139° 65′), Tokyo in July, 2007 which were located beside the park, near a parking area and near the residences (Supplement 2). AIF located near the residences were of two types one which was found receiving runoff only after rain (like another two AIF near park and parking area), while another used to receive some portion of domestic water use, more likely gardening water respectively. Highway road dust was collected in September 2008, with the help of highway maintenance technicians using a sweeper vehicle, while residential road dust was collected using a vacuum cleaner (Hitachi CV-100S6) from road surface. All the samples were then air-dried overnight at room temperature, homogenized and sieved through 2 mm nylon sieve and preserved in acid washed plastic containers at 4 °C till analysis.

In this study, one sample each of yellow paint and aerosol was also collected. Yellow paint, used for marking the division of lanes on the road, was collected by scraping. Aerosol sample was collected beside the University of Tokyo, Hongo campus (latitude 35° 71′ and longitude 139° 76′) in July 2008; using three suction pumps equipped with timer and filter and placed beside the road crossing for 24 h. Each pump timer was set for 8 h which was connected in sequence so that when one pump switched off another starts. The sampling height was about 1 m and the sampler had an uncertainty of ±2.0%. The glass fibre filters were carefully desiccated prior and after sampling to ascertain correct measurements. The yellow paint and filter paper thus obtained were digested using microwave with HNO_3 (9 mL) and HCl (1 mL) (EPA 3051a) and analysed for isotope ratios. Sequential extraction was not feasible for both aerosol and paint samples due to limited amount of samples.

2.2. Sample characterization

Hygroscopic water content (HWC) was measured by weight loss at 105 °C for 1 h (Topp, 1993). Ignition loss was measured as an estimate for organic matter content which was determined by measuring weight loss after keeping sample at 600 °C for 1 h (Kirel, 1993). The effective cation exchange capacity (CEC) was measured using extraction with 0.1 M $BaCl_2$. Soil pH was measured by suspending soil in water with liquid/solid ratio of 1:5. Iron oxide and hydrous oxide contents, collectively referred as Fe-oxide here, were calculated from the concentrations of Fe released during the oxide dissolution step and percentages of silicate mass fraction were calculated from the residual mass (Topp, 1993). It is a known fact that Al and Mn concentrations released during oxide dissolution stages are always significantly lower than Fe concentrations (Emmanuel and Erel, 2002); therefore, no attempt was made to estimate the abundance of these oxides. Selected chemical and physical properties of experimental samples are shown in Table 1 with error terms, obtained by analysing triplicate of each sample.

2.3. Total metal digestion, sequential extraction and isotopic analyses

Total metal content of different samples was determined after *aqua-regia* digestion using microwave (Multiwave 3000, Anton Paar). A good recovery (between 90 and 105%) was obtained with certified reference material (CRM-8704, Buffalo River Sediment). For speciation analysis, heavy metals (Cu, Zn, Cd and Pb) contained in these samples were fractionated according to a modified BCR (Community Bureau of Reference), three-step sequential extraction procedure (Rauret et al., 1999). In this study BCR is preferred over Tessier method as the previous takes 51 h for the extraction of four phases with respect to 17 h in Tessier providing better extraction efficiency. Another advantage with the BCR is more effective extraction of oxidisable fraction due to two phase peroxide (H_2O_2) treatment with complete evaporation of the reagent. Further, Tessier differentiate loosely bound metals into two phases i.e. exchangeable fraction extracted using $MgCl_2$ and carbonate bound metals extracted using sodium acetate. From the point of metal leaching process from the soakaway both fractions are vulnerable enough to leach down easily. The first three fractions were exchangeable, reducible, and oxidisable which are associated with carbonates,