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Non-carcinogenic and carcinogenic health risk assessment of selected metals in soil around a natural water reservoir, Pakistan

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ABSTRACT

Contaminants in surface soil can directly pose significant human health risks through oral ingestion, dermal contact and particle inhalation, especially for children. Both non-cancer and cancer risks associated with selected metal levels (Cd, Cr, Cu, Fe, Mn, Pb and Zn) were evaluated in surface soil around Mangla Lake during summer and winter. The results based on average pseudo-total metal concentrations followed the decreasing order: Fe (4038 mg/kg) > Mn (394 mg/kg) > Zn (40 mg/kg) > Pb (17 mg/kg) > Cr (21 mg/kg) > Cu (15 mg/kg) > Cd (1.3 mg/kg) during summer and Fe (3673 mg/kg) > Mn (407 mg/kg) > Zn (30 mg/kg) > Cr (26 mg/kg) > Pb (26 mg/kg) > Cu (14 mg/kg) > Cd (1.8 mg/kg) during winter. Present metal levels in the soil were also compared with other studies and guideline values which showed significant increase in the metal concentrations in this study. The metal levels also showed considerable spatial variations around the lake. The correlation study and multivariate principal component analysis revealed significant anthropogenic contributions of the metals in soils. Aqua-regia extractable (pseudo-total) contents were used as the reference to establish the percentage of bioavailability. After considering the bioavailability (Cd > Pb > Cr > Zn > Cu > Fe > Mn during both seasons), the non-cancer and cancer risks posed by Cd, Pb and Cr was relatively higher than rest of the metals, though the overall hazard index (HI) and cancer risk levels were within the safe limits (1.0 and 1.0*E*-06, respectively). The overall cancer risk to the adults based on pseudo-total metal concentrations exceeded the target value (1.0*E*-06), mainly contributed by Cr. A method considering bioavailability is suggested to produce a more realistic estimation for human health risks of trace metals contamination in soil.

1. Introduction

Soil is of prime significance in environmental research because it is the site of many types of interactions between minerals, air, water and the living organisms. It generally reacts more slowly to outside influence than do water and air, as it is able to bind substances or incorporate them into soil complexes. However, a side effect of this function is that it binds not only the nutrients but also the pollutants (Luo et al., 2007a; Qishlaqi et al., 2009). Surface soil contaminated with toxic trace metals can pose significant human health risks due to oral ingestion (Luo et al., 2011; Okorie et al., 2011), inhalation of particles and fugitive particulates (Laidlaw and Filippelli, 2008; Schmidt, 2010), and dermal contact (Siciliano et al., 2009), especially in the residential/park areas (Ljung et al., 2007; Luo et al., 2012a,b). The health risk of trace metals in soil depends on the fraction that is available for absorption that means only a fraction of the total soil metal content may be available to human beings (Luo et al., 2011, 2012a,b). The soil pollution was typically assessed by total/pseudo-total concentrations compared with corresponding soil guideline values (Morton-Bermea et al., 2009) that may overestimate the actual health risk (Elless et al., 2007; Peijnenburg et al., 2007). A realistic evaluation of actual health risks associated with trace metals in soil requires evaluation of bioavailable metal contents.

Recently, the bioavailable contents of trace metals in soils have become an important consideration for many researchers (An and Kampbell, 2003; McLaughlin et al., 2000; Nolan et al., 2003). The 'bioavailable fraction' is the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by (micro)organisms or plants, from either the direct surrounding of the organism or the plant, or by ingestion of food (Peijnenburg and Jager, 2003). Several methods have been anticipated to simulate and quantify metal reactivity as well as the physicochemical and biologically available pools of the metals in soil (Nolan et al., 2003). One of the most popular methods for estimating metal bioavailability is chemical extraction by means of various mild to strong extracting agents, resulting in operationally defined specific metal fractions (Meers et al., 2007). The commonly used empirical extractants include weak extractants (water,

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salt solutions), reductive extractants, weak acids, strong complexing agents (chelating agents), combined salt–acid extractants and diluted strong acids (Peijnenburg et al., 2007). The assumption in these chemical extraction approaches is that the extracted metal fractions are mobile and/or could possibly be detrimental to soil biota (Luo et al., 2012b). Many researchers investigated the human health risk assessment only through oral ingestion of trace metals in soil (Guney et al., 2010; Hu et al., 2011). However, it is necessary to estimate the human health risks of trace metals in soil through multi-pathways (ingestion, inhalation and dermal) considering bioavailability adjustments.

The main objectives of this study were; (1) to measure the concentrations of selected metals (Cd, Cr, Cu, Fe, Mn, Pb and Zn) in the soils around Mangla Lake, Pakistan; (2) to determine the spatial variations in the metal levels around the Lake; (3) to assess the bioavailability of the metals in the soil samples; (4) to identify the major pollution sources of the metals; and (5) then to evaluate the non-carcinogenic and carcinogenic human health risks based on pseudo-total and bioavailable concentrations of the metals in soils through multi-pathway exposures for children and adults. Plausible seasonal variations in the metal distribution and their risk assessment would also be investigated. It is anticipated that the study would provide baseline data that could evolve a health related pollution abatement program and could motivate some futuristic studies on the trends of trace metal distribution, their risk assessment, transportation and enrichment around the major water reservoirs.

2. Materials and methods

2.1. Site description and soil sampling

Composite surface soil samples were collected during summer (May) and winter (December) 2011 from the surrounding residential areas (urban/periurban) and parks/picnic points around Mangla Lake, Pakistan (Fig. 1) which is the twelfth largest lake in the world. The lake is situated in Mirpur district of Azad Jammu and Kashmir and constructed across the Jhelum River during 1961–1967. The total population in the surrounding areas of the lake is approximately 0.5 million. Besides providing 1500 MW hydroelectric energy, the lake is the major water reservoir and provides irrigation water to the agricultural land in the plans of Punjab, which provide the food requirements for more than three million people. In addition, the lake water is also supplied to the surrounding areas as drinking water. The climate around Mangla Lake is sub-tropical with hot/rainy summer and cold/dry winter. The rainy season extends from July to September. The temperature ranges from 45 °C in summer to -2 °C in winter and average rainfall in the area is about 1300 mm/year (AJK at Glance, 2013; Pakistan Bureau of Statistics, 2010). The lake is a major source of irrigation/drinking water; hence any contamination around the lake would severely affect the water quality and the contaminants may enter into the food-chain, thus causing detrimental effects to the consumers. Since 1967, the adjoining area around the lake has undergone significant agricultural, urbanization and industrial development and consequently much water and sediments pollution has occurred due to these anthropogenic activities as highlighted by Saleem et al. (2013, 2014) and other investigations (Butt et al., 2011; Water Quality Monitoring in AJK, 2004). Thus, the present study was conducted to investigate the metals pollution in soils of major surrounding areas (more human influenced areas) around the lake, geogenic and anthropogenic sources and their health risk towards the local population.

A total of 180 composite surface (1–15 cm top layer) soil samples were collected from ten major sampling sites (as shown in Fig. 1) with the help of a plastic scoop in each season in pre-cleaned zip-locked polythene bags. Each composite soil sample was composed of five to ten sub-samples within an area of 10–15 m^2 from same locations during both seasons and coordinates of each sampling site are described in Table S1 (Supplementary material). The samples were collected during summer (before the rainy season) and winter (after the rainy season) in order to assess the build-up and/or leaching of the pollutants from soils and to evaluate the effects of anthropogenic activities on the relative distribution of the metals in soils. The soil samples were oven dried, grounded, homogenized, sieved through a 2 mm plastic sieve to remove stones, gravels, coarse particles and then stored in zip-locked polythene bags before analysis (Iqbal and Shah, 2011; Radojevic and Bashkin, 1999).

2.2. Soil characterization and chemical analysis

Soil pH was determined using a soil to deionized water suspension of 1:2.5 (w/v). Electrical conductivity (EC) and total dissolved solids (TDS) were measured separately in the suspension. To measure the pseudo-total metal contents, 1–2 g dried soil sample was digested in a microwave system (MARS, CEM®) using a freshly prepared acid mixture of 9 mL HNO_3 and 3 mL HCl (USEPA, 2007). For each digestion, a reagents blank was also prepared with the same amount of acids without soil sample. The digested sample was then filtered through the fine filter paper (0.45 μm, pore size) and made up to 50 mL with deionized water and stored at 4 °C. To determine the bioavailable contents of trace metals, a selective single step extraction procedure, using 0.1 M $Ca(NO_3)_2$, was performed at room temperature (An and Kampbell, 2003). An aliquot of 5.0 g of the soil sample was added to 50 mL of 0.1 M $Ca(NO_3)_2$ solution and the extraction was performed in pre-cleaned glass vessel by shaking on an auto-shaker at 240 vibrations per minute for 16 h. A reagent blank was also prepared with the same amount of 0.1 M $Ca(NO_3)_2$ solution without soil sample. Three replicate extractions were performed for each soil sample. The final extracts were separated from the solid residue through filtration using a fine filter paper (0.45 μm, pore size) to analyze the mobile/bioavailable contents of the metals (An and Kampbell, 2003; Radojevic and Bashkin, 1999; Rodrigues et al., 2010). Since no standard method is available to assess the bioavailability of the metals in soil and there are various limitations of each method. The method used in the present study is considered as one of the best method showing the bioavailability of metals but sometime it may underestimate the actual risk.

Selected metals (Cd, Cr, Cu, Fe, Mn, Pb and Zn) in $Ca(NO_3)_2$ and acid extracts of the soil samples were analyzed using flame atomic absorption spectrophotometer (Shimadzu AA-670, Japan) under optimum analytical conditions as shown in Table S2 (Supplementary material). Calibration line method was used for the quantification of metals and freshly prepared working standards were used for the calibration with each batch. The samples were appropriately diluted whenever required (Iqbal and Shah, 2011; Radojevic and Bashkin, 1999; Shah et al., 2012). The quality of the analytical data was assured by using standard reference material (SRM 2711), analysis of reagent blanks and analysis of replicates. Generally, the contribution of the blank was <5 percent of the measured metal levels in the samples. The percentage recoveries of the metals in the standard reference material samples ranged from 96 to 103 percent (Table S2). Working standards of the metals were prepared from stock solution of 1000 mg/L by successive dilutions. All the measurements were made in triplicate. Some of the soil samples were also analyzed at an independent laboratory for cross comparison and a maximum of ± 2.5 percent difference was observed in the two results.

The percentage of bioavailable concentrations (*BAC* percent) of each metal was calculated as the percentage of the fraction bioavailable in $Ca(NO_3)_2$-extract ($C_{bioavailable}$, mg/kg) relative to the pseudo-total concentration ($C_{pseudo-total}$, mg/kg) of the metal in acid-extract using the following equation:

$$BAC\ \text{percent} = \left(\frac{C_{bioavailable}}{C_{pseudo-total}}\right) \times 100 \qquad (1)$$

2.3. Human exposure and health risk model

Risk assessment is a multi-step procedure including data collection and evaluation, exposure assessment, toxicity evaluation and risk characterization (De Miguel et al., 2007; Rovira et al., 2011; USDOE, 2011; USEPA, 1989, 2004). In the present study, Cd, Cr, Cu, Fe, Mn, Pb and Zn were selected as potential hazardous agents with regard to human health. These elements have toxicological health effects on human and some are carcinogenic (Cd, Cr and Pb induce both non-cancer and cancer risks) (USEPA, 2002, 2011a,b; USDOE, 2011; WHO, 2011) (Supplementary file).

Humans' exposure to trace metals in surface soil can occur through three main routes (De Miguel et al., 2007): (a) direct oral ingestion of substrate particles (Chronic Daily Intake via ingestion, CDI_{ing}); (b) inhalation of suspended particulates emitted from soil through mouth and nose (Chronic Daily Intake via inhalation, CDI_{inh}); and (c) dermal absorption of trace metals in particles adhered to exposed skin (Chronic Daily Intake via dermal absorption, CDI_{derm}). Both cancer and non-cancer risks related to these exposure pathways were considered. In the step of exposure assessment, a specific approach characteristic for humans' exposure to surface soil in residential areas was applied, taking care of the non-cancer hazard exposure for children. The cancer risk was computed for the lifetime exposure, estimated as the incremental probability of an individual developing cancer over a lifetime as a result of total exposure to the potential carcinogen. The dose received (chronic daily intake, CDI) via three exposure pathways considered was computed using Eqs. (2)–(9) adapted from USEPA (1989, 1997, 2001) and USDOE (2011). The values for input parameters and toxicological characteristics of the metals used for health risk assessment are described in Supplementary file.

Non-carcinogenic (nc) hazard

$$CDI_{ing-nc} = \left(\frac{C \times IngR \times EF \times ED}{BW \times AT_{nc}}\right) \times 10^{-6} \qquad (2)$$