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Risk assessment of total and bioavailable potentially toxic elements (PTEs) in urban soils of Baghdad–Iraq

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HIGHLIGHTS

- Levels of As in Baghdad soil are elevated (36 mg/kg).
- As bioaccessibility is lower than the MDL in both macrophage & gastric surrogates.
- 56–68% of Mn, V, and Zn are bioaccessible in gastric surrogate (GS).
- Co, Cu & Pb-levels in GS are significantly higher than in the macrophage surrogate.
- Risk assessment based-total PTEs overestimates the risk of the bioavailable PTEs.

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ABSTRACT

The solubility of soil-associated potentially toxic elements (PTEs) in surrogate biological fluids provides valuable information about their potential health hazard. This work addresses the concentrations and bioaccessibility of nine PTEs (As, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn) in thirty eight agricultural land and playground soils collected from a semi-arid urban area of Baghdad–Iraq. Two surrogate biological fluids (SBFs), macrophage vacuole (MS) and gastric (GS) solutions, were used to extract the metals to simulate the biological availability of the PTEs via inhalation and ingestion exposure routes. ICP/AES was used to quantify PTEs in both strong acid digests (for total concentration), and in the SBF extracts. Soil contamination factors showed that some sites exhibited elevated levels of As (36 ± 10 mg/kg), however, these levels of As are not likely to have significant human health impacts whether the particulate arsenic is ingested or/and inhaled. Soil-geochemical variables (including: pH, EC, $CO_3^{=}$, soil organic carbon (SOC)) and major elements (e.g. Al, Ca, and Fe) were used to interpret the lability of PTEs in the soils. Hazardous index (HI) based non-cancer risk of inhalation and ingestion of PTEs was estimated to be 2-fold higher for that based on total element concentrations compared with that for bioavailable fractions for both children and adults. A similar conclusion was reached for the estimated cancer risk (which was lower than the threshold level of concern for children and adults). A sensitivity analysis showed that there is a 97% chance for children and 90% for adults to have hazardous indices of the total PTEs >1 (the acceptable value); the corresponding metrics for the bioavailable fraction of the elements were 39% for children, and 3% for adults; these results were sensitive to the concentrations of "airborne" soil particles.

Abbreviations: ADI, average daily intake; CF, contamination factor; CM, correlation matrix; CR, cancer risk; EC, electric conductivity; EF, enrichment factor; EPA, Environmental Protection Agency; FB, fortified blank; GIS, geographic information system; GPS, Geographic Positioning System; GS, gastric solution; HEPA, high efficiency particulate air; HI, hazardous index; HQ, hazardous quotient; IAEA, Iraqi Atomic Energy Agency; ICP/AES, Inductively Coupled Plasma/Atomic Emission Spectroscopy; MCS, Monte Carlo simulation; MDL, method detection limit; MRL, minimal risk level; MS, macrophage solution; PCA, principal component analysis; PTEs, potentially toxic elements; RB, reagent blank; SBF, surrogate biological fluid; SM, supplementary materials; SOC, soil organic carbon; SRM, Standard Reference Material; TA, thermal analysis.

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1. Introduction

Urban soils may have elevated levels of potentially toxic elements (PTEs) from both point and diffuse sources of pollution (Wong et al., 2006). Anthropogenic sources of toxic elements in urban environment include local industrial emissions (such as power plants, coal combustion, metallurgical industries, and chemical plants); traffic emission (e.g. vehicle exhaust particles); domestic emissions; pavement surface; constructions; and atmospheric deposition (Chrastny et al., 2012; Davis et al., 2009; Luo et al., 2011; Schauer et al., 2006; Sharma et al., 2009). The residence time of these toxic metals in soils is long and represents a continuing risk for both the urban ecological system and human health (Sun et al., 2010). The toxicity of soil-trace elements is highly dependent on their solubility and bioaccessibility (Smith, 2009), and there is a significant body of literature on identifying various pools/species of metals in soils. (Barsby et al., 2012; Basta and Gradwohl, 2000; Hamel et al., 1998; Karadaş and Kara, 2011; Pelfrêne et al., 2012; Pouschat and Zagury, 2006).

Soil disturbance that may be induced by construction activities such as excavation of soil, movement of vehicles and construction equipment over soil, or children playing in yards or playgrounds, has recently been given more attention by the US Environmental Protection Agency (EPA) (Moya et al., 2011). Accidental ingestion of contaminated soils by hand to mouth habits (especially for children) is a significant concern in certain urban environments. However, few studies have examined the impact of inhaled disturbed soil (Drysdale et al., 2012), and performed a risk assessment of the inhaled or/and ingested potentially toxic elements. In particular, the health risk from the fraction of PTEs that result from the dissolution of the disturbed contaminated soil is poorly understood. Typically, risk modelers/managers have used total concentrations of PTEs to evaluate the potential toxic effects of elements in soils, taking into consideration the screening levels that are published by US EPA (Man et al., 2010; Zheng et al., 2010); though this might not be accurate enough for risk assessment or it may overestimate the actual risk, since the metals in soils can exist in a variety of chemical and physical forms and not all the forms of a given metal are available/mobile to the same extent in biological fluids. Metal speciation and solubility is also dependent on land use type and soil texture (Gramss et al., 2004; Juhasz et al., 2009; Pelfrêne et al., 2013; Yu et al., 2012). Several studies have looked at the bioaccessibility of soil-PTEs in gastric fluid (Barsby et al., 2012; Karadaş and Kara, 2011; Pelfrêne et al., 2012; Pouschat and Zagury, 2006), and other studies have used surrogate macrophage vacuole fluid to assess the potential toxicity of the inhaled particles (Biswas et al., 2009; Li et al., 2003). However, the inhalation of re-suspended soil and the subsequent impact of the soluble soil-PTEs in the lung fluid, have received limited study, thus further study is needed.

Risk analysis is extremely important in toxicology and public health studies. However, risk assessment based on total PTE concentrations might overestimate the risk induced by PTE exposure. In this study, the bioaccessibility of PTEs in soils was evaluated by performing chemical extractions using two surrogate biological fluids (SBFs) (macrophage vacuole (MS) and gastric (GS) solutions). Then the risk of PTEs was estimated based upon both total concentration and the bioavailable fractions of PTEs in the SBFs.

Baghdad–Iraq, an urban semi-arid area (Wilderson, 1991; Sly, 2009), is the largest city in Iraq with a population of about 7,216,000 (Britannica, 1978; Cohen, 2004), and is the second largest city in the Middle East after Cairo–Egypt. Baghdad has suffered serious contamination due to continuous armed conflicts, and the chaotic situation which led to the looting and sabotaging of facilities such as the chemical and munition factories. The chemicals/munitions affected not just water and air, but also land. The natural vegetation cover in many areas has been lost to leave bare sites behind due to the contamination of soils with high levels of organic and inorganic compounds including toxic metals. Poorly vegetated soils facilitate wind erosion of metal contaminated soil particles, which has threatened to usher in a public health tragedy for the people in Iraq (Programme, U.N.E., 2005; UNEPA, 2003).

Thirty eight samples were collected within Baghdad borders, 27 of which were agricultural, and 11 were playground soils. Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES) was used to quantify the total concentrations of elements in the soils after strong acid digestion, and in the SBF extractable fractions. Geochemical properties of the soils (including: acidity (pH), electric conductivity (EC), carbonate ($CO_3^{=}$), and soil organic carbon (SOC)) along with several major elements (e.g. Al, Ca, and Fe) were measured to interpret the variation of the bioaccessible elements in both SBFs. Multivariate analysis (principal component analysis (PCA) and correlation matrix (CM)) was applied to reduce the complexity of the data and to establish relationships among PTEs, major elements, and the geochemical properties of the soil. To consider the impact and the sensitivity of the variables used for risk assessment of elements, a Monte Carlo simulation was applied. Results from this study will add valuable information with regard to risk assessment of PTEs in the airborne soil particles. Risk estimated based upon the actual bioavailable PTEs avoids overestimating the risk induced by the total PTEs exposure.

2. Materials and methods

2.1. Sites selection

Baghdad, the capital and the largest city in Iraq, located between 33.3191°N and 44.3920°E, was chosen as a study area. Baghdad area is located in the middle of Iraq and has two rivers flowing within its borders: Tigris and Diyala, where most agricultural activities are concentrated (between upper and lower Mesopotamia). Baghdad area, where the alluvial plain begins, is characterized by a wide variation in land use; the soil in this part of the country has been formed by alluvial material deposited by the Tigris and Diyala rivers, these soils are strongly calcareous having about 20% lime; they are reddish or pinkish tinge (Buringh, 1960). They likely contain gypsum because the catchment area of the Tigris has gypsum crusts and deposits. These can be subdivided into river levee soils and river basin soils. The former are usually loamy whereas the latter are clayey. These are the most important soils in the lower Mesopotamian plain. The levee soils are well drained being one to three meters higher than the basin soils and having loamy texture (Buringh, 1960). In the last few years, more than 50% of Baghdad areas turned desert; the permanent pasture became subject to erosion because of the reduced vegetation cover. Additionally, much of the cropland lost its inherent productivity due to poor agricultural practices and over exploitation. The direct loss of agricultural land is most acute around urban centers, where established agricultural land is being lost to alternative uses, including urbanization, industrialization, and transport infrastructure (Omer, 2011). Baghdad is an industrial city; many industries [including power plants, chemical industries, waste water treatment plants, Iraqi Atomic Energy Agency (IAEA), and one of the largest oil refineries in Iraq (Al-Doura Refinery)] are established within the borders of Baghdad city (see supplementary materials, Figure SM1).

Thirty eight near-surface (5–10 cm) soil samples were collected within Baghdad borders in summer 2011; twenty seven of which were agricultural lands, and eleven were playground soils. Soil samples were distributed within the borders of Baghdad to cover the whole city; however, some areas (especially the western side) were hard to reach due to security situation. The specific 38 (playgrounds and agricultural lands) sites that have been chosen in this study are close to the residential areas where industries are established, in an attempt to study the impact of the industrial activities on the agricultural sites and the playgrounds where people are in contact with and children always play. Soil samples were taken after removing the plant residues using plastic scoop; a clean hand person (using gloves) placed the soil in a Ziploc