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Heavy metals in agricultural soils and crops and their health risks in Swat District, northern Pakistan

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ABSTRACT

This study assessed the concentrations of heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) in agricultural soils and crops (fruits, grains and vegetable) and their possible human health risk in Swat District, northern Pakistan. Cd concentration was found higher than the limit (0.05 mg/kg) set by world health organization in 95% fruit and 100% vegetable samples. Moreover, the concentrations of Cr, Cu, Mn, Ni and Zn in the soils were shown significant correlations with those in the crops. The metal transfer factor (MTF) was found highest for Cd followed by Cr > Ni > Zn > Cu > Mn, while the health risk assessment revealed that there was no health risk for most of the heavy metals except Cd, which showed a high level of health risk index (HRI $\geqslant$ 10E-1) that would pose a potential health risk to the consumers.

1. Introduction

Generally, both natural (weathering, erosion of parent rocks, atmospheric deposition and volcanic activities, etc.) and anthropogenic (sewage irrigation, addition of manures, fertilizers and pesticides, etc.) activities are responsible sources of soil and crops contamination with heavy metals (HMs) (Khan et al., 2008; Shah et al., 2010; Sekomo et al., 2011). Hazardous HMs such as cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn) contamination of agricultural soils and crops (fruits, grains and vegetable) is a detrimental environmental problem due to their non-biodegradable and persistent nature (Radwan and Salama, 2006; Khan et al., 2010; Muhammad et al., 2011). Soil usually acts as both a sink and a source of a variety of pollution such as water pollution, and therefore exerts significant effects on living organisms including all available plants (Khan et al., 2010). The chemical properties of soils depend primarily on the type of weathered rocks of the concerned area. Particularly, the mafic and ultramafic rocks usually contain high concentrations of HMs, which contaminate the agricultural soil as well as growing crops nearby (Kafayatullah et al., 2001; Shah et al., 2010).

Agricultural crops especially fruits, grains and vegetables form an important part of our diet and act as a buffering agent during digestion process. Crops may contain a range of both essential and toxic metals (Jan et al., 2010; Yang et al., 2011). Metals like Cr, Cd, Mn and Ni can be very toxic and their high accumulation inside living bodies over time can cause serious harmful diseases (Khan et al., 2010; Sun et al., 2010). The ingestion of Cd contaminated food can cause both chronic and acute health effects such as bone fracture, kidney dysfunction, hypertension and even cancer (Nordberg et al., 2002; Turkdogan et al., 2003). Similarly, Cr contamination can cause abnormal thyroid artery, polycythaemia, over production of red blood cells (RBCs) and right coronary artery problems. High dose of Mn and Cu can cause mental diseases such as Alzheimer's and Manganism (Dieter et al., 2005). Ni ingestion can cause severe health problems, including fatal cardiac arrest, skin rashes, fatigue, headache, heart problems, dizziness and respi-

Abbreviations: AAS, atomic absorption spectrophotometer; ANOVA, analysis of variance; BDL, below detection limits; CA, cluster analysis; CAS, Chinese Academy of Sciences; Cd, cadmium; Cr, chromium; CRL, Centralized Resource Laboratory; Cu, copper; DIM, average daily intake of metals; FAO, Food and Agriculture Organization; GIS, Geographic Information System; H_2SO_4, Sulfuric acid; $HClO_4$, Perchloric acid; HM, heavy metals; HNO_3, Nitric acid; HRI, health risk index; Mn, manganese; MTF, metal transfer factor; Ni, nickel; RBCs, red blood cells; RfD, reference dose; SEPA, State Environmental Protection Administration China; SPSS, Statistical Package for the Social Sciences; SRMs, standard reference materials; TWAS, Academy of Sciences for the Developing World; USEPA, United States Environmental Protection Agency; WDM, wet digestion method; WHO, World Health Organization; Zn, zinc.

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ratory illness (Muhammad et al., 2011). Sufficient amount of Zn is very important for normal body functions and its deficiency can cause anorexia, diarrhoea, dermatitis and depression, immune dysfunction and poor wound healing, nevertheless, its toxicity can causes a sideroblastic anemia (Muhammad et al., 2011).

Therefore, the World Health Organization (WHO), United States Environmental Protection Agency (USEPA), and other regulatory bodies of various countries have established the maximum health-based guideline values for HM concentrations in agricultural soils and crops. However, to be able to minimize HMs contaminations in soils and crops, a better understanding about HMs accumulation and appropriate agriculture practices will also be required (Khan et al., 2010). However, HM contamination in agricultural soils and crops has not been investigated in Swat District of northern Pakistan. Therefore, we present in this paper a detail study about the HM concentrations in agricultural soils and crops originated from various natural and anthropogenic sources such as geological weathering of mafic and ultramafic rocks, atmospheric deposition, mining, sewage irrigation, addition of manure, use of pesticides and fertilizers. Assessment of possible health risk to consumers through ingestion of HM contaminated fruits, grains and vegetable was also the aim of this study.

2. Materials and methods

2.1. Study area

Swat District is an administrative district located in Khyber Pakhtunkhwa, northern Pakistan (Fig. 1). Geographically, it lies between 34–36° North Latitude and 71–73° East Longitude, with a total area of 5337 km^2 and a population of 1.25 million (Qasim et al., 2011). The northern part of Swat District has a Mediterranean climate while its southern part has a sub-tropical climate. Its average annual temperature and annual rainfall are 19 °C and 966 mm, respectively. Swat valley consists of sky rocketing mountains, lush green forests, meadows as well as clear ponds, lakes, streams and rivers. The exposed rocks in the region are composed of mafic and ultramafic rocks such as serpentinite, green schist, talc-carbonate schist and met basalts (Shah et al., 2010; Arif et al., 2011), while the soil of the region is mainly sandy loam type with a maximum land slop 22% and depth 0–45 cm (Nafees et al., 2008). Agriculture is the main occupation and source of income for majority of the local people. Particularly, the agricultural land, which can be broadly divided into irrigated and rain fed land, is very limited within the mountainous area. The Swat River and its upstream and downstream tributaries are the main sources of agricultural irrigation. Wheat and maize are the two primary crops grown in winter and summer seasons, respectively, while apples, onions, persimmons, potatoes, tomatoes, and rice. are also mostly grown in different parts of the study area.

2.2. Sampling and pre-treatment

2.2.1. Agricultural soil sampling

The soil samples (n = 25) were collected from a depth of 0–25 cm with a stainless steel auger from five locations of the study area as shown in Fig. 1. Each soil sample was prepared by first randomly collecting several sub-samples around each sampling site, followed by thoroughly mixing of the sub-samples to from a composite sample of 1 kg using quartile method. The sample was sealed in a clean polyethylene bag and brought to the laboratory. After drying, the soil samples were mechanically grounded and passed through a sieve up to 2 mm and stored properly for further analysis.

2.2.2. Agricultural crops sampling

Locally grown agricultural crops, including fruit (n = 30), grain (n = 20) and vegetable (n = 35) (Table 1), were harvested from the same locations where the soil samples were collected. The fresh crop samples were collected in clean polyethylene bags and transported to the laboratory. The collected samples were washed with double distilled water to remove the air borne pollutants, then the edible parts of the samples were air dried for a day followed by subsequent oven drying at 70–80 °C for 24 h to remove the moisture. Further, the dried samples were grounded using an electronic grinder and stored properly in the paper bags at room temperature for further analysis.

2.3. Extraction

2.3.1. Agricultural soil extraction

The collected soil samples were extracted using wet digestion method (WDM). Briefly, 0.5 g dried powdered soil sample was put into a 50 mL conical flask and then 15 mL of aqua-regia (HNO_3, H_2SO_4 and $HClO_4$) in the ratio of 5:1:1 was added. They were kept overnight and then gently heated on the hot plate at 80 °C until a transparent extract was obtained. The digested extracts were filtered into clean volumetric flasks and diluted up to 100 mL volume using highly purified de-ionized water and kept at room temperature for further analysis.

2.3.2. Agricultural crops extraction

Agricultural crop samples (2.0 g) were mixed in conical flasks with 15 mL Perchloric acid ($HClO_4$) and Nitric acid (HNO_3) solution in the ratio of 1:4. After overnight cold digestion, they were heated on the hot plate at different temperatures until a transparent solution was obtained. After cooling the digested samples were filtered through Watt man filter paper No. 42 and diluted up to 100 mL volume using highly purified de-ionized water and kept at room temperature for further analysis.

2.4. Analytical procedure

Analytical grade chemicals with a high spectroscopic purity 99.9% (Merck Darmstadt, Germany) were used for sample preparation and analyses. Standard solutions of all six elements were prepared by diluting their corresponding 1000 mg/L certified standard solutions (Fluka Kamica, Busch Switzerland). The concentrations of selected heavy metals (Cd, Cr, Cu, Mn, Ni, and Zn) in the soils and crops extracts were analyzed using atomic absorption spectrophotometer (Perkin Elmer AAS-700). The blank reagents and standard reference materials (SRMs) of selected metals were used to verify the accuracy and precision of digestion, while in view of data quality assurance, each sample batch was analyzed in a triplicate under standard opt-ionizing conditions within the confidence limit of 95%. The instrumental conditions and detection limits for selected HMs were given in Table 2. All analyses were performed in the Centralized Resource Laboratory (CRL), University of Peshawar, Pakistan.

2.5. Data analysis

2.5.1. Metal transfer factor

Soil to plant metal transfer factor (MTF) was calculated as the ratio of metal concentration in plants to metal concentration in soils. The required MTF was calculated by using the following Eq. (1) (Khan et al., 2010).

$$\mathrm{MTF} = C_{\mathrm{plant}}/C_{\mathrm{soil}} \quad (1)$$

where C_{plant} and $C_{\mathrm{soil,}}$ represent the HM concentrations in the extracts of plants/crops and soils on dry weight basis, respectively.

2.5.2. Daily intake of metals

The average daily intake of metals (DIM) was calculated by using the following Eq. (2) (Khan et al., 2008, 2010; Jan et al., 2010).

$$\mathrm{DIM} = C_{\mathrm{metal}} \times C_{\mathrm{factor}} \times D_{\mathrm{food\ intake}}/\mathrm{BW}_{\mathrm{average\ weight}} \quad (2)$$

In which C_{metal}, C_{factor}, $D_{\mathrm{food\ intake}}$ and $\mathrm{BW}_{\mathrm{average\ weight,}}$ represent the HM concentrations in plants/crops (mg/kg), conversion factor, average daily intake of food (crops) and body weights, respectively. The conversion factor (0.085) was used to convert fresh crops into dry weight (Jan et al., 2010). The average daily intakes of food (crops) for adult and child were considered to be 0.345 and 0.232 kg/person-day, respectively (Khan et al., 2008, 2010), while the average adult and child body weights were considered as 73 kg and 32.7 kg, respectively (Jan et al., 2010).

2.5.3. Health risk index

To estimate the chronic health risk, health risk index (HRI) through food (crops) consumption was calculated by using the following Eq. (3) (Khan et al., 2008; Jan et al., 2010).

$$\mathrm{HRI} = \mathrm{DIM}/\mathrm{RfD} \quad (3)$$

Here, HRI, DIM and RfD, represent the human health risk index, daily intake of metal and reference dose of metal, respectively. The reference dose (RfD) values for Cd, Cr, Cu, Mn, Ni and Zn are 5.0E−04, 1.5, 3.7E−02, 1.4E−01, 2.0E−02 and 3.0E−01 mg/kg-day, respectively (USEPA, 2005; Shah et al., 2012). The exposed population is assumed to be safe when HRI < 1.

2.6. Statistical analysis

The data were statistically analyzed using Statistical Package for the Social Sciences (SPSS), version 17 and Microsoft Excel, 2010 computer packages. The measurements were expressed in term of mean and standard deviation. Moreover, one-way analysis of variance (ANOVA), inter-metal correlation and cluster analysis