Chemosphere 154 (2016) 249–257

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Fractionation of trace elements in agricultural soils using ultrasound assisted sequential extraction prior to inductively coupled plasma mass spectrometric determination

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HIGHLIGHTS

- We assessed the total, speciation and environmental risk of trace metals in soils.
- Fractionation of trace elements was carried out by sequential extraction method.
- Critical contaminated metals that need a special attention have been identified.
- Trace metal contamination in soils were achieved by using CF, I_{geo}, and EF.
- Cadmium enrichment and degree of contamination were higher in soils.

ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form
17 March 2016
Accepted 25 March 2016

Handling Editor: Martine Leermakers

Keywords:
Trace elements speciation
Sequential extraction
Enrichment factor
Individual contamination factors
Risk assessment code
Index of geo-accumulation

ABSTRACT

The main objectives of this study were to determine the concentration of fourteen trace elements and to investigate their distribution as well as a contamination levels in selected agricultural soils. An ultrasonic assisted sequential extraction procedure derived from three-step BCR method was used for fractionation of trace elements. The total concentration of trace elements in soil samples was obtained by total digestion method in soil samples with aqua regia. The results of the extractable fractions revealed that most of the target trace elements can be transferred to the human being through the food chain, thus leading to serious human health. Enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), risk assessment code (RAC) and individual contamination factors (ICF) were used to assess the environmental impacts of trace metals in soil samples. The EF revealed that Cd was enriched by 3.1–7.2 (except in Soil 1). The I_{geo} results showed that the soils in the study area was moderately contaminated with Fe, and heavily to extremely polluted with Cd. The soil samples from the unplanted field was found to have highest contamination factor for Cd and lowest for Pb. Soil 3 showed a high risk for Tl and Cd with RAC values of greater than or equal to 50%. In addition, Fe, Ni, Cu, V, As, Mo (except Soil 2), Sb and Pb posed low environmental risk. The modified BCR sequential extraction method provided more information about mobility and environmental implication of studied trace elements in the study area.

1. Introduction

Environmental pollution by trace metals is a global problem due to their non-biodegradable properties. In addition, trace elements in the environment are of high ecological importance since they tend to bioaccumulate and enter the food chain (Ghrefat and Yusuf, 2006). Furthermore, elements such as Hg, Tl, Sb, Cd, Pb and Te have toxic effects on living organisms, when they exceed maximum allowable or even at ultra-trace levels (Ghrefat and Yusuf, 2006). The occurrence of trace elements in the environment is mainly due to anthropogenic activities, such as industrial emissions, mining or smelting, agricultural activities and traffic operations (Rosende et al., 2014). Trace elements in aforementioned sources may be released and accumulated in soil by various processes such as leaching, weathering, combustion and biological reaction, among others (Li et al., 2016). Therefore, there is a need to conduct a study on the environmental implications of trace metals in areas where extensive traffic operation or agricultural activities takes place.

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http://dx.doi.org/10.1016/j.chemosphere.2016.03.123
0045-6535/

In the past decades, more attention has been focusing on the speciation analysis of trace elements rather than the total metal content. This is the toxicity, bioavailability, mobility and other properties of each element depend on the chemical association of the different components of the sample (Akan et al., 2010; Castillo et al., 2011). Therefore, fractionation of trace in solid matrices using sequential extraction procedures together with total metal content has been carried out in order to identify the chemical species in which trace metals are present in different environmental matrices (Ma et al., 2016; Castillo et al., 2011; Okoro et al., 2012; Al-Hwaiti et al., 2015). Among other extraction protocols (Tessier et al., 1979; Campbell and Shiller, 1988), Community Bureau of Reference (BCR) sequential extraction procedure is one of the most widely used method (Kazi et al., 2005; Nemati et al., 2011; Sungur et al., 2014). However, the main disadvantage of conventional BCR sequential extraction technique is that it is tedious and time-consuming because it requires long shaking time about 16 h for steps 1 and 2 as well as separation of the extracted solution (filtration) at each step. Therefore, there is a need for development of fast and improved sequential extraction procedures.

In view of the above, the fractionation of trace metals from environmental matrices requires simple, fast and inexpensive techniques such as ultrasonic based systems. The latter has been employed for sample preparation strategies (Safarifard and Morsali, 2012). The use of ultrasound force has been considered to accelerate sequential extraction techniques. This is because the cavitational impact made by ultrasound waves can separate the molecule size and uncover another surface, thus resulting in a strongly bended solution (Prasad et al., 2010). In addition, when a solid sample is treated by ultrasound, particles distribution occurs and this lead to an increase in the surface area available for the reaction. During this process, the molecule fracture thus expanding the force of the extractant to dissolve (extract) the analyte of interest (Prasad et al., 2010; Safarifard, and Morsali, 2012). The application of ultrasonic techniques for extraction of trace metals from different matrices has been demonstrated to be rapid and effective (Samaras et al., 2011; Jiang et al., 2012; Davidson and Delevoye, 2001; Kazi et al., 2006; Rusnák et al., 2010; Safarifard and Morsali, 2012; De La Calle et al., 2013).

The objectives of this study were firstly to determine the concentration of various trace metals (Cr, V, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Tl and Pb) in agricultural soils collected from collected one of the farmsteads situated near Glen agricultural College (Bloemfontein, Free State province, South Africa). Secondly, to investigate the speciation (bioavailability and potential mobility) and contamination level of trace metals in different chemical fractions in soil samples using a modified BCR sequential extraction procedure. The ultrasonic assisted procedure was employed to enhance the fractionation of different metal species in soil samples. The concentrations of trace in different fractions and in digested soils were quantified by inductively coupled plasma-mass spectrometry (ICP-MS). Certified reference material BCR 701 and BCR 143R were used to validate the fractionation and total digestion protocols.

2. Experimental

2.1. Reagents and material

Ultrapure water produced by Millipore Direct-Q 3UV-R water purification system (Merck) was used throughout the study and all chemical were of analytical grade unless otherwise stated. Ammonium acetate was made from glacial acetic acid (Merck, Darmstadt, Germany) and ammonium hydroxide (Sigma Aldrich, St. Loius, MO, USA). Ultrapure nitric acid (69%), hydrogen peroxide (30%), oxalic acid and hydrochloric acid (ultrapure) were purchased from Sigma Aldrich (St. Loius, MO, USA). A Spectrascan multi-element standard solution at a concentration of 100 mg L^{-1} (Teknolab, Norway) was used to prepare working standard solutions for quantification of analyte in the sample solutions. Certified reference materials BCR 143R and BCR 701 (Sigma Aldrich, St. Loius, MO, USA) that have certified/indicative aqua regia soluble and for extractable metal contents in the three steps of the sequential extraction procedure, respectively, were used to validate the results obtained in this study. All plasticware used in this study were previously treated for a week in 5% ultrapure nitric acid and rinsed with deionized water and then with ultrapure water.

2.2. Instrumentation

The metal concentrations of trace elements in the soil samples were determined using an Agilent 7900 ICP-MS (Agilent Technologies Inc., Tokyo, Japan) with Ultra High Matrix Introduction (UHMI) option and He cell gas option. The operating parameters for the each element were set as recommended by the manufacturer Branson 5800 ultrasonic bath (Danbury, CT, USA) was used for the ultrasonic extractions with parameters time 0–90 min, temperature 0–70 °C. Centrifugation was carried out to separate the supernatant from the agricultural soil samples by, Eppendorf centrifuge 5702 (Eppendorf Ag, Hamburg Germany). An OHAUS starter 2100 pH meter (Pine Brook, NJ, USA) was used for pH adjustments of the reagents and to measure the pH of samples. Then, aqua-regia digestion was performed using digestion block (Digi-Block Digester ED36S, Labtech, Wilmington, MA). For determination of total organic matter (TOM), soil samples were dried in an oven at 105 °C to constant weight. The soil samples were then put in a muffle furnace for TOM determination by measuring their loss upon ignition at 550 °C for 6 h (Okedeyi et al., 2014). The conductivity of the soil samples was determined using the Mettler Toledo SevenGo Pro-SG7 probe meter with a 1:2 ratio of sediment and ultrapure water.

2.3. Sample collection and preparation

2.3.1. Description of study area

Farmsteads located around Glen Agricultural College area are situated approximately 28 km North of Bloemfontein (Free State province, South Africa). The area lies along the Modder River which supplies the farmsteads with irrigation water. Further from the main river channels, most of the land use is primarily for small- and medium-scale livestock farming. In addition, due its clay-loamy soil nature, this area is also extensively used for commercial growing of crops such as tomato, cabbage, maize and potatoes. Therefore, due to natural and anthropogenic activities such run-offs from the regional road (R30), railways, residential area effluents and wastewater tailings, among others occurring on the higher ends of the study area, the quality of the agricultural soil and crops produced may be negatively impacted. In addition, traffic and agricultural activities are likely to introduce significant quantities of trace metal constituents are generated from tire wear, brake linings leakage of oil and lubricants as well as, application of metal containing fertilizers pesticides and herbicides.

2.3.2. Sample collection and preparation

Agricultural soil samples from different fields (tomato field coded Soil 1, cabbage field coded Soil 2, and unplanted field coded soil 3) were collected from one of the farmsteads situated near Glen agricultural College with the geographic coordinates (28°56′09.0″S 26°19′25.2″E) respectively. It should be noted that in each sampling point three replicates of the same were collected. Preventive