Original Article

DETERMINATION OF TOTAL HEAVY METAL BY SEQUENTIAL EXTRACTION FROM SOIL

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Abstract

Understanding the chemical speciation of metals in solution is necessary for evaluating their toxicity and mobility in soils. Sequential extraction of metals from soil, based on the Tessier's procedure, was used to evaluate soil contamination in the Bhilai Industrial area. The contents of Al, As, Cd, Cu, Fe, Mn, Pb, Zn in the five fractions (exchangeable, bound to carbonates, bound to iron and manganese oxide, bound to organic matter and residual) were determined by ICP-AES and HG-ICP-AES. A higher fraction of metals i.e. As, Cu, Mn and Pb were found in the bound form with oxide and sulfide of Fe. A major fraction of all metals were found to be present in the carbonate forms in increasing order: As $\approx$ Cr < Ni $\approx$ Mn < Hg < Pb < Fe < Cu < Zn in the soil. The contents of Cu in the exchangeable fraction exceeded the normal values for sensitive soil.

Keywords: sequential extraction procedure, metal partitioning in soil, heavy metals, soil contamination.

1. Introduction

At present, it is widely recognized that the distribution, mobility and bioavailability of heavy metals and radionuclide in the environment depends not only on their total concentration butalso on the association form in the solid phase to which they are bound. The behavior of heavy metals in plant-soil environments is dependent on the chemical speciation and the relative distribution of chemical forms of metals in soil solutions. Some variations of the chemical or physical conditions in the environment can accelerate to some extent the release of toxic metals into it, thus causing contamination. These, in turn, will influence the availability and mobility of these metals in soils [1]. The accumulation of heavy metals in environmental samples represents a potential risk to human health due to the transfer of these elements to aquatic media, their uptake by plants and their subsequent introduction into the food chain. The toxicity, bioavailability and mobility of metals are related to their

species [2-3]. The use of sequential extraction procedures for environmental studies provides an important tool for the determination of the different chemical forms or ways of binding between trace metals and soil components [4]. Chemical extraction is employed to assess operationally defined metal fractions, which can be related to chemical species, as well as to potentially mobile, bioavailable or ecotoxic phases of a sample. It is generally accepted that the ecological effects of metals (e.g., their bioavailability, ecotoxicology and risk of groundwater contamination) are related to such mobile fractions rather than to the total concentration [5-6]. Sequential extraction experiments have been shown to provide a convenient means to determine the metals associated with the principal accumulative phases in sedimentary deposits. Chemical fractionation schemes for partitioning trace metals in soils and sediments have been used extensively since the 70s and are based on three to six fractions [4,7-11], many of them being slightly modified Tessier's schemes [8]. The objective of this study was

to investigate the partitioning of Al, As, Cu, Fe, Mn, Pb, Zn in soil collected from Industrial area of Bhilai City. Determinations were carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES) or hydride-generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES).

2. Materials and Methods

2.1 Collection of sample

All contaminated soil samples (0 to 15 cm) used in this study were collected from different locations of Bhilai Industrial area (latitude: 21°12'36"N, longitude: 81°22' 47" E) near Raipur, capital of Chhattisgarh state, central India).

2.2 Preparation of sample

Samples were taken from 0 to 15 cm depth, using a small shovel, after manual removal of leaves, roots and stones. Soils were sieved through a 2 mm sieve in order to eliminate stones and other materials extraneous to soil, and then stored in polyethylene bags for transport to the laboratory. The sieved soils were spread over a polyethylene sheet and air-dried at room temperature for one week. The residual moisture was removed by heating at 105 ± 5^0 C for 3 h. Samples were ground to a fine powder in a tungsten-carbide swing mill for 3 min and sieved through a <1 µm sieve. The HMs present in different geochemical fractions of the soil was determined by the sequential extraction scheme [8].

2.3 Chemical and reagents

The AR grade (E. Merck, Germany) chemicals were used for digestion of the soil and plant samples. The ICP multi-element (23 elements) standard (E. Merck, Germany) was used for preparation of the calibration curve.

2.4 Chemical analysis

An instrument: inductively coupled plasma- atomic emission spectrometry (ICP-AES) Ultima-2 from Jobin Yvon, France equipped with parallel flow nebulizer and cyclonic spray chamber was used for the monitoring of the heavy metals (i.e. Cr, Mn, Fe, Ni, Cu, Zn, and Pb). Atomic Absorption Spectrophotometer (AAS) GBC 932 Australia equipped with Hydride Generator (HG-3000) was used for the determination of the total arsenic and mercury using sodium borohydride for reduction. The standard addition method was used for the quality control and data validation of the method.

3. Summary of the sequential extraction procedure (SEP)

According to the Tessier′s procedure, the SEP operationally groups heavy metals into the following five fractions:

F.1. Soluble and exchangeable

The soluble and exchangeable metals from soil were extracted with 20 mL of a 1.0 M $MgCl_2$ solution adjusted to a pH of 7.0 by mechanical shaking for 1 h at 20 °C.

F.2. Bound to carbonates

The carbonates in the residue from the previous step were extracted with 20 mL of a 1.0 M NaAc solution adjusted to a pH of 5.0 with HAc by continuously shaking for 4 h at room temperature.

F.3. Bound to iron and manganese oxides

Metals bound to iron and manganese oxides were extracted from the residue of the second extraction by shaking with 50 mL of a 0.04 M $NH_2OH.HCl$/25 % HAc solution. The

extraction was performed at 96±3 °C for 5.5 h.

F.4. Bound to organic matter

Metals bound to organic matter were extracted by pouring 7.5 mL of a 0.02 M HNO_3 solution and 12.5 mL of a 30 % H_2O_2 solution adjusted to a pH of 2.0 onto the residue from F3, then providing continuous agitation for 2 h at the temperature of 85°C. An additional volume of 7.5 mL of the 30 % H_2O_2 solution adjusted to a pH of 2.0 is then added, while maintaining continuous agitation and a temperature of 85°C for another 3 h. This solution was then cooled to room temperature. An aliquot of 12.5 mL of a 3.2 M NH_4Ac/ 20 % HNO_3 solution was added and shaken for 30 min.

F.5. Bound to the soil matrix (residual fraction)

The residue from F4 was quantitatively transferred into a digestion vessel and metals were dissolved in aqua regia using 7 mL of 10 M HCl and 2.3 mL of 15.8 M HNO_3. The temperature of the reaction mixture was slowly risen until reflux conditions and maintained for 2 h. Three parallel extractions were carried out, in each case using 2.5g soil. All solid/liquid separations were performed by centrifuging, at 5000 rpm for 15 min. The supernatant was removed and analyzed for metals. The residue was washed with 20 mL of de-ionized water. After centrifugation for 15 min the supernatant was discarded. All dilutions were made to 50 mL with 2 % (v/v) HNO_3. For each fraction a blank was subjected to the same procedure.

4. Results and discussions

The element contents determined in the five fractions (average of 3 parallel samples) following the SEP are shown in Table 1, while the distribution among the fractions is presented in Figure 1. The data show a preferential distribution of elements among fractions.
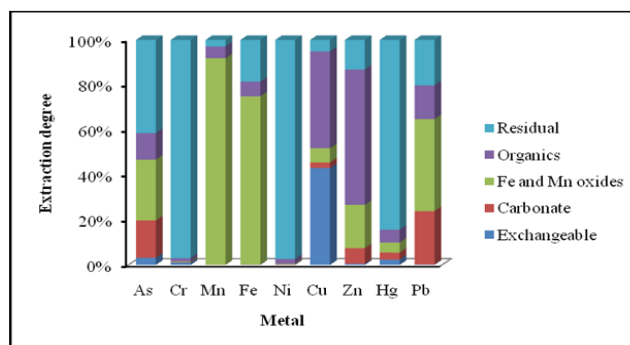

Figure 1: Partitioning of metals in soil

1. **Bioavailable Species:-**The exchangeable and bond to carbonates species, corresponding to the first two fractions, are generally called "bio-available", as they exhibit a mobility relative to the environment and are potentially available for plants. Results show that the amounts of As, Mn, Ni, Hg and Pb, in bio-available form are very low, namely below 1 % in soil .The bio-available As, Cr and Mn ranges between 1 and 5 % in the soil, is exclusively bound to carbonates. In both samples, 30 % of Cd and 20 % of Pb are in bio-available form. Pb (40%) is mainly mainly bound to carbonates while relatively

Table 1 Fractions of elements in soil following the sequential extraction procedure (m=3)

Metal	Exchangeable	Carbonates	Fe/Mn oxides	Organic	Residual
Concentration (mg kg^{-1})					
As	<0.10	0.52	0.85	0.37	1.3
Cr	9.25	1.78	2.45	12.6	828
Mn	<0.10	1.34	2133	121	68
Fe	5.43	17.5	8738	762	2165
Ni	<0.11	0.18	0.32	2.4	110
Cu	204	11.7	30.1	204	24
Zn	0.14	1.9	5.29	16.5	3.61
Hg	<0.12	0.16	0.23	0.29	4.3
Pb	0.14	21.8	37.5	13.8	18.5

high proportions of Fe (32%) and Cu (21 %) are bio-available as exchangeable species.

2. **Species bound to Fe-Mn oxides:-** Logically, Fe and Mn occur mainly in the oxide fraction. In the soil Fe (80 %) and Mn (20%) are main contributors. Copper and Lead bond to oxides occur in the same proportions, around 39 % and 49 % respectively. The fraction of As, Cr, Ni, Zn and Hg associated with oxides is very less in the soil especially in the case of Hg.

3. **Species bound to organic matter:-** High amounts of Cu (up to 68 %) and also Ni, and Hg are bound to the organic matter.

4. **Species in residual fraction:-**The proportion of Fe (above 68 %) in the residual form of is much higher than the other elements. The order of element follows Fe>Cr>Ni> Mn>Cu. The weight of As and Zn in this fraction is relatively low.

In summary, Cu, Fe, Mn, and Pb are present mainly in the oxides fraction, Cu is bound to organic matter, while the main fraction for As & Cr is the residual. For all elements, an increase of the fraction bound to Fe/Mn oxides occurs with an increase of Fe and Mn content in soil.

5. Conclusions

This study has shown that soil composition and physicochemical characteristics strongly influence metal partitioning in soil. Elements are mainly bound to Fe/Mn oxides and are present in the exchangeable fraction in only small amounts, except for Cu and to a slight extent Cr and Ni. The amount in this oxide fraction increases with the increase of Fe and Mn contents in soil. The organic matter has an important influence on the mobility of several species. Thus, elements like Cu, Ni and Hg can be retained on organic matter. Metals immobilized on the organic matter in soil become less mobile and less bio-available which results in a decrease of the exchangeable fraction. A significant proportion of elements are present in residual formecosystem. Consequently, a periodical evaluation of the soil status is necessary in the area.

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