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Speciation of Heavy Metal in Ero Dam Sediment, Ikun-Ekiti, Nigeria

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Abstract

Heavy metal speciation trends in the sediment of Ero dam, Ikun-Ekiti, Ekiti State, Nigeria were studied using three-step BCR (European Community Bureau of Reference) sequential extraction techniques, namely exchangeable, reducible, oxidizable fraction and total metals. The elements studied are Cr, Ni, Cu, Pb, Zn and Cd. A higher fractions of metals studied were found in the bound form with residual. The results showed that: BCR1; Cr>Zn>Ni>Cd>Cu>Pb. BCR2; Zn>Cr>Ni> Cd>Pb>Cu. BCR3; Zn>Cu>Ni>Pb>Cr>Cd. The highest value of 80% (Zn) from BCR3 and lowest value of 0.87% Pb from BCR1. The result shows that Zn and Cr could easily be released in the water body.

Keywords: Speciation, Sediment, Dam, Heavy Metals, Extract ants.

Introduction

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 [1-2].

According to literature prolonged contact between aquatic organisms and [4, 5], heavy metal in our natural environment has soluble metals in these environments [3, 4]. As a receiver, a great attention worldwide by environmental, consequence, the present heavy metals can be biological and chemical scientists as well as public; due accumulated by aquatic organisms includes fish through to their unique characteristics such as biological water, food and sediments.

The occurrences of metals in stream sediment can be a times adduced to geo-genic or anthropogenic activities of man in such an environment. Many industrial processes concentrate copper, cadmium, lead and zinc. These metals like gathering end up in the earth [6]. A large number of trace metals are transported to the oceans from natural sources. However, these natural sources are supplemented by releases from anthropogenic process which, from some metals, can exceed natural in-puts [7].

It is necessary to identify and quantify the forms in which a metal is present in sediments to gain a more precise understanding of the potential and actual impacts of elevated concentrations and to evaluate processes of downstream transport, deposition and release under changing environmental conditions [8].

Materials and Methods

Collection of sample sediment Sampling and Preparation

A total of 25 surface sediment samples were collected from five sampling location from Ero dam (latitude $7^0$35 N, longitude $5^0$31 E) Ikun-Ekiti, Ekiti State. Sediment samples were kept in cleaned plastic bags and dried in the laboratory. The sediment samples were then prepared in 63 ìm size for extraction purpose.

Preparation of sample

The sediments were spread over a polyethylene sheet and air-dried at room temperature for one week. The residual moisture was removed by heating at 105±50 C for 3 h. Samples were ground to a fine powder using mortal and pestle and sieved through a <1 µm sieve [10]. The Heavy Metals present in different geochemical fractions of the soil was determined by the sequential extraction scheme as described below [11].

1. ***Exchangeable/ Acid soluble fraction*****:** A 20-ml of Acetic acid solutions (0.11mol.L-1) was be added into a centrifuge tubes (soil: solution ratio is 1:40) and shaken for 16 hours on the end-over-end shaker at room temperature (22 ± 5 °C). No delay should occur between the addition of the extract solution and the beginning of the shaking. The extractant was be separated from the solid residue by centrifugation for 15 minutes at 3000 rpm, and the supernatant liquid (BCR1). Will be decanted into a polyethylene container and stored in a refrigerator at 4 °C until analysis. The residues will be washed with 20-Ml deionized water, shaken for 15 minutes on an end-over-end shaker and centrifuged for 15 minutes at 3000 rpm. After decanting the supernatant, the residues are ready for the next step.

2. ***Reducible fraction:*** To the residues from Step 1, 20-mL of hydroxylamine hydrochloride (0.1 mol.L-1) at pH 1.5 will be added (soil: solution ratio is 1:40) and then shaken for 16 hours on the end-over-end shaker at room temperature (22 ± 5 °C). No delay should occur between the addition of the extractant solution and the beginning of the shaking. The extract will be separated from the solid phase by centrifugation and decantation as described for step 1.

   The residues will then be washed with 20-mL deionized water, shaken for 15 minutes on the end-over-end shaker and centrifuged for 15 minutes at 3000 rpm. The supernatant is will be decanted and stored at 4 °C until analysis (BCR2).

3. ***Oxidizable fraction:*** To the residues from Step 2, 8.8 mol.L-1 of hydrogen peroxide will be added at a soil solution ratio of 1:10 and, then shaken for 1 hour at room temperature (22 ± 5 °C) by end-over-end shaker The solution will be heated up to 85 °C for 1 hour. The extraction is repeated by using the same procedure. Then, the sample will be shaked for 16 hours at 350 rpm at room temperature (22 ± 5 °C). The extract will be separated from the solid phase by centrifugation and decantation as described for BCR1. The supernatant will be decanted and stored at 4 °C (BCR3). The residue was digested with aqua regia method by using microwave assisted digestion.

4. ***Aqua regia:*** For the last residue from BCR3 and total concentration in the soil, samples will be directly digested by using the microwave assisted digestion procedure according to the Standard method (US-EPA 3052, 1996) in order to determine the total metal contents.

Dried soil 0.5 g in PTFE vessels 14.5-mL of aqua regia solution will be added (followed by microwave digestion application note manual). Aqua regia solution will be prepared by mixing acid with concentrated Hydrochloric acid and concentrated Nitric acid at a ratio 3:1. This procedure will be performed by high pressure and temperature. The recommended temperature will be obtained in two steps: in the beginning is a raising temperature, the temperature increases from room temperature to 200°C within 10 minutes; and the holding temperature means the temperature holds at 200°C throughout digestion for 20 minutes. Then, samples will be cooled down and filtered by using whatman No.41 filter paper. The volume will be adjusted to 50 mL with deionized water in volumetric flask. To validate the method, the accuracy of the total digestion procedures for determining metals in the extracts will be compared to the results of the Certified Reference Material, CRM 025-050 (RTC).

Results and discussions

Table 1.Fraction of elements in sediment following the sequential exctraction procedure

Metal	Exchangeable	Reducible	Oxidizable	Total Metal
Cr	5.48	5.00	0.33	6.19
Ni	1.11	2.00	1.55	33.7
Zn	4.39	13.2	19.2	44.8
Pb	<0.10	0.19	0.61	18.5
Cd	0.29	0.46	0.24	2.15
Cu	0.14	0.13	1.93	4.05

The element contents determined in the four fractions (average of 5 different locations) following the Sequential extraction procedure are shown in Table 1.

BCR 1 (Exchangeable fraction): For exchangeable step can occur in natural as similar as rain in environment. Other researches widely accepted that the exchangeable metal in sediments is more mobile, highly toxic and the most bioavailable fraction[9;15;16].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 bio-available Cu and Cd ranges between 1 and 3 % are very low in the sediments while Ni is below 10%. In all samples, 48 % of Cr and 38 % of Zn are in bio-available form.

BCR 2 (Reducible fraction): Logically, Fe and Mn occur mainly in the oxide fraction. In the soil Fe (80 %) and Mn (20%) are main contributors. Zinc and Chromium bond to oxides occur in the proportions, around 63 % and 24 % respectively. The fraction of Ni, Pb, Cd and Cu associated with oxides is very less in the sediment.

BCR 3 (**Oxidizable fraction):** High amounts of Zn (up to 80 %). The weight of all other elements in this fraction is relatively low.

Residual Fraction:-The proportion of Zn (above 40 %) in the residual form of is much higher than the other elements. The order of element follows Zn>Ni>Pb>Cr>Cu>Cd.

In summary, Cr, and Pb are present mainly in the exchangeable and reducible fraction, while the main fraction for Ni, Zn & Pb is the residual.

Conclusion

The elements studied are Cr, Ni, Cu, Pb, Zn and Cd. A higher fractions of metals studied were found in the bound form with residual. Also, Zn shows higher percentage of exctraction when compared with other elements The result shows that Zn and Cr could easily be released in the water body.

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