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HEAVY METALS IN JAMAICA. Part 3[1]: THE DISTRIBUTION OF CADMIUM IN JAMAICAN SOILS

Gerald C. LALOR, Robin RATTRAY, Peter SIMPSON and Mitko VUTCHKOV

International Centre for Environmental and Nuclear Sciences, University of the West Indies, Mona, Kingston, Jamaica

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ABSTRACT

The distribution of cadmium in soils across Jamaica is reported. The island-wide average is 20 mg kg^{-1} and concentrations as high as 409 mg kg^{-1} have been observed in some of the *Terra rossa* soils overlying Tertiary Limestones in central Jamaica and in a smaller region in a residential district near to a disused mine. In certain areas the enrichment is up to three orders of magnitude with respect to bedrock. The cadmium and zinc concentrations are highly correlated. Despite the high concentrations of cadmium found in certain localities, no cases of cadmium poisoning have been recognized in Jamaica, probably because the neutral and slightly alkaline soils and the underlying limestone help to fix the cadmium and thus maintain low concentrations in the underground and surface waters. However, changes in land use or other conditions may increase the risk.

RESUMEN

Este artículo trata de la distribución del cadmio en los suelos de Jamaica. El promedio en toda la Isla es 20 mg kg^{-1} y se han observado concentraciones hasta de 409 mg kg^{-1} en algunos suelos *Terra rossa* que yacen sobre piedra caliza terciaria en el área central de Jamaica y en una región de menor dimensión en un distrito residencial cerca de una mina abandonada. En ciertas áreas el enriquecimiento es hasta tres veces mayor con respecto al del lecho de roca. La correlación entre las concentraciones de cadmio y de zinc es muy elevada. A pesar de las altas concentraciones de cadmio halladas en ciertas localidades, no se ha reconocido ningún caso de envenenamiento por este metal, probablemente debido a que los suelos neutros y levemente alcalinos y la piedra caliza debajo ayudan a fijar el cadmio, manteniendo una concentración baja en las aguas subterráneas y superficiales. Sin embargo, los cambios en el uso del suelo u otras condiciones, podrían aumentar el riesgo.

INTRODUCTION

The average concentration of Cd in the earth's crust is 0.2 mg kg^{-1}, which ranks it 64th in elemental abundance. It is widely distributed in shales, igneous rocks, coal, sandstones, limestones, lake and oceanic sediments, and soils (Waldron 1980).

Cadmium goes into solution readily on weathering and tends to accumulate in surface soils due to the adsorptive capacity of the humus content of surface horizons and inputs from atmospheric deposition, fertilizers, and cycling through plants. It occurs in nature in the +2 valence state, as uncomplexed Cd^{2+}, in various chloride, hydroxide and carbonate species, and in organic chelates. It is most mobile in acidic soils within the pH range 4.5 - 5.5 and is less so in alkaline soils.

Cadmium is widely used in industry and, because it is so similar to zinc in chemistry and geochemistry, it is also frequently found in a wide variety of zinc-containing consumer goods. These and several other sources *e.g.* phosphate fertilizer, fodder phosphate, sewage sludge, and leachate from landfill sites add to the soil burden. The combustion of coal, oil, paper and urban organic trash add Cd to the atmosphere (Kabata-Pendias and Pendias 1984, Alloway 1990); and smoking can increase cadmium intake significantly (Frieberg *et al.* 1971).

Cadmium accumulates from the soil in plants and from water in aquatic animals. Cadmium has no proven essential metabolic function although a few animal studies suggest that very small quantities may be needed (Schwartz and Spallholz 1978). There appears to be no homeostatic mechanism for cadmium in the

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human body, and its retention time there is of the order of several decades. It accumulates in the intestine, liver, and kidney and is toxic to virtually all systems (ATSDR-Cadmium 1988).

Cadmium is highly persistent in the environment and the burden is increasing due to anthropogenic activities. This has lead to concern about the accumulation of cadmium in man (OECD 1995). The Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives suggested a provisional tolerable weekly intake of 7 µg cadmium daily per kg of body weight (WHO 1972) which they agreed to maintain at its meeting in 1993. Several governments have set maximum allowable limits on cadmium intakes.

MATERIALS AND METHODS

Site selection and sample collection

Site selection, sample collection and sample treatment have been described (Lalor 1995). A total of 445 soil samples were collected during the period 1988-1995. One hundred and sixty five sites were sampled during an island-wide survey at an average sample density of 1 per 8 x 8 km^2. 281 additional soil samples were collected at a density of 2x2 km^2 in the parish of St. Elizabeth and at a sample density of 1 per 150x150 m^2 in the Hope Mine residential area. The sampling depth was between 5 and 30 cm. Sample sites were located on the 1:12,500 scale topographic series maps of Jamaica and the exact geographical position was recorded using a global positioning system. At one in every four sites, a duplicate sample was collected (about 3 metres from the original site). This provided information on the geochemical variability within a site.

The data reported here were obtained from the <150 µm soil sample fraction. This fraction is now an internationally recommended standard for multielement and multipurpose regional geochemical surveys of soils and stream sediments and is used in a broad spectrum of applications, ranging from mineral exploration to environmental studies and agriculture (Darnley *et al.* 1995). The exclusion of "barren" diluents such as quartz grains results in a higher proportion of values above the analytical detection limits and therefore better definition of areas of interest. There is also a marked reduction in sample preparation time and reduced wear on equipment, which reduce research cost.

In Jamaica the <150 µm fraction of soil samples usually represents > 50% of the soil sample (Simpson *et al.* 1991) so that adequate amounts are normally available. The concentrations of trace elements in the A and B soil horizons collected over most representative rock types in Jamaica are very similar and the main variance in the geochemical signature for A and B horizon soils, as shown by multielement plots normalized to continental crust, is between sites and not within them (Williams *et al.* 1992). This insensitivity of concentration to sample depth means that, for the present purposes, it is not essential to accurately identify the particular soil profile from which the sample is taken and in this case the sampling method is very robust.

Analytical methods

The soil samples were analyzed for Cd using Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectrophotometry (AAS). INAA was employed for multielement analysis including cadmium using the UWI SLOWPOKE-2 reactor (Lalor *et al.* 1990). The detection limit for Cd was about 4 mg kg^{-1}. Two Certified Reference Materials Soil-5 and Soil-7, obtained from the International Atomic Energy Agency were used to check accuracy and monitor precision which were both better than ± 10%.

The soil samples with lower concentrations of Cd (< 5-10 mg kg^{-1}) were analyzed by Flame Atomic Absorption Spectrophotometry (AAS). Soil samples of about 1.0 g, accurately weighed, were digested with an aqua regia reagent, evaporated to 0.5 ml and made up to 10 ml with high purity deionized water. Aluminium chloride (1.25 % Al) was used as a matrix modifier. The calibration curves were prepared in the appropriate concentration range with matrix modifier added. The detection limit was about 0.3 mg kg^{-1}. The analytical accuracy was checked by using standard solutions of the Canadian Certified Reference Materials (GSD, 1992a) and in-house standards and was usually better than ± 5%. The overall precision was better than ± 10%.

The GRASS 4.0 geographical information system was used for data analysis, interpretation and map production.

RESULTS AND DISCUSSION

A simplified geological map of Jamaica including the place names used in the text can be found in **figure 1**.

In non-contaminated, non-cultivated soils, cadmium concentrations are largely governed by the amount of cadmium in the parent material. Cadmium levels in soils are expected to vary from about 0.06 mg kg^{-1} in pristine soils to several hundred mg kg^{-1} in the vicinity of some smelters (Waldron 1980). Residual soils developed from shales have been reported (Lund *et al.*, 1981) as having the highest concentrations with a mean of 7.5 mg kg^{-1}, whereas soils derived from sandstones and basalts have the lowest concentrations with a mean of 0.84 mg kg^{-1}. Alluvial soils with parent materials from mixed sources have intermediate Cd levels of 1.5 mg kg^{-1} (Adriano 1986). The average in Jamaican soils is 20 mg kg^{-1} compared with a world average of less than 1 mg kg^{-1} (Alloway 1990).

The range of Cd in non-mineralized Jamaican soils varies from less than 0.3 mg kg^{-1} (the detection limit of the present AAS technique) to over 400 mg kg^{-1}. These values are unusually high compared with the range for world soils of 0.005 - 2.9 mg kg^{-1} and the highest are comparable to the several hundred mg kg^{-1} found in the vicinity of some smelters (Waldron 1980).

The island-wide distribution of cadmium in soil is shown in **figure 2**. Four principal associations between rock type, overlying soil and Cd concentrations are readily recognized.

The lowest concentrations of cadmium are found mainly in the soils of the Cretaceous inliers in Hanover and in the Blue Mountain range, and in mixed parent materials of the Wagwater

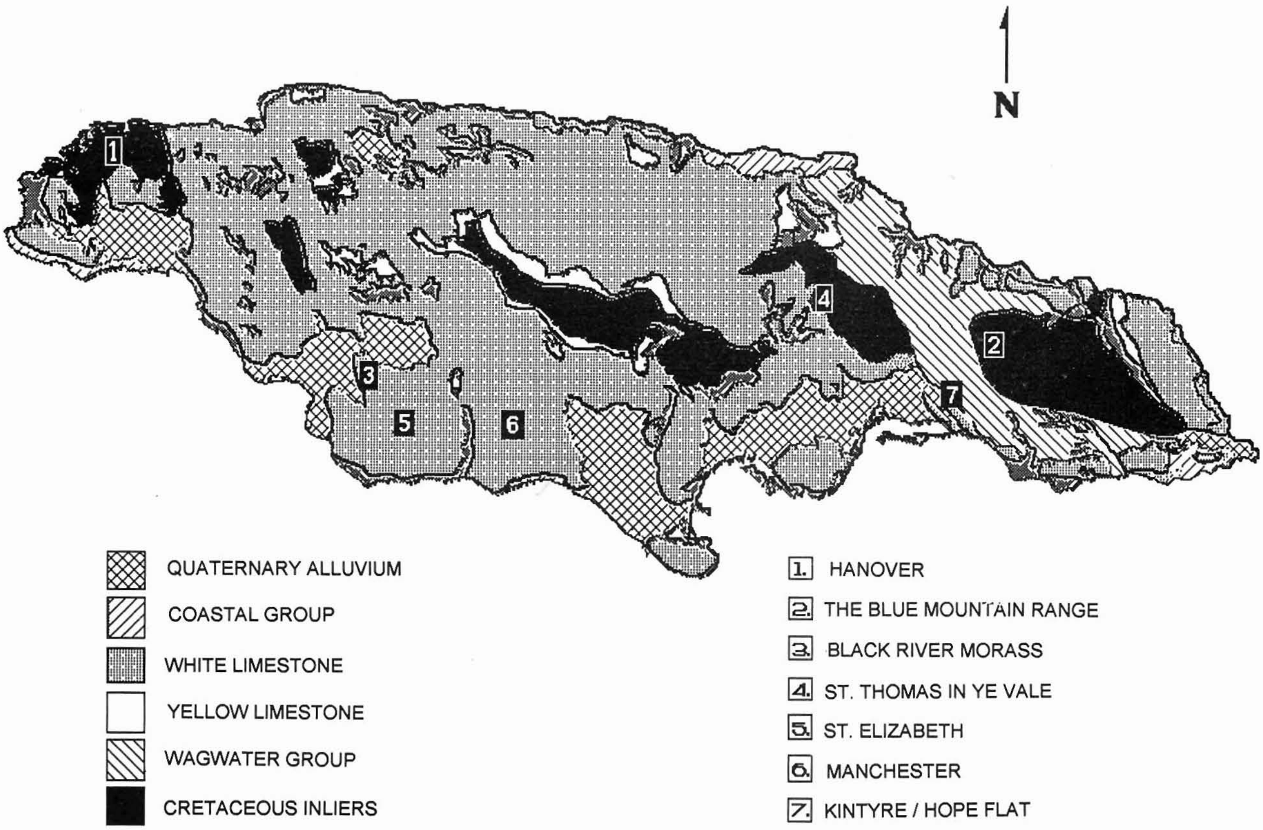

Fig. 1. Simplified geological map of Jamaica with place names used in the text

Formation. These values are typically below 0.90 mg kg^{-1}. The alluvial soils exhibit a mean concentration of 2.5 mg kg^{-1}, but the Black River Morass and St. Thomas-in-the-Vale Basin areas are significantly enriched. Both of these locations are adjacent to major bauxite deposits, which could signature the Cd. It is also possible that there is enrichment of Cd in the organic-rich substrate which contributes to the levels in the Black River region. The rendzinas or black marl soils underlain by White Limestone Group rocks and the soils underlain by the Coastal Group rocks, have intermediate Cd levels with mean concentrations of 5 and 3.7 mg kg^{-1} respectively.

The highest values, which average 35 mg kg^{-1} Cd, are generally associated with the *Terra Rossa* soils overlying the White Limestone Group notably in the borough of Manchester and St. Elizabeth but with extensions into adjoining regions. Extremely high levels (307 and 409 mg kg^{-1}) were found in Manchester within a bauxite mining zone. Such enrichment, by up to three orders of magnitude relative to bedrock, probably constitutes one of the most significant potential heavy metal hazards associated with the soils of Jamaica.

Correlations between cadmium and selected elements

Cadmium concentrations in Jamaican soils are significantly correlated with several of the other elements also found in bauxitic soils. **Table I** shows linear correlation coefficients between Cd and a selection of elements.

The near zero correlation with elements such as lead and copper reflects the limited control of base metal mineralization on the soil distribution of cadmium and the negative correlation with the alkaline earth metals is a reminder of the resistate nature of the bauxitic soils. The high correlation with Zn in these soils suggests the coincident enrichment of Cd and Zn.

TABLE I. LINEAR CORRELATION COEFFICIENTS BETWEEN CADMIUM AND SELECTED ELEMENTS (Lalor 1995)

	Zn	U	Al	Cr	Th	Fe	Hg	REE	I	Pb	Cu	Mg	Ca
Cd	0.69	0.50	0.42	0.42	0.37	0.35	0.32	0.43-0.33	0.11	0.07	0	-0.17	-0.08

The origin of Jamaican bauxites is not universally agreed. The purity of the white limestones is so high that there is some doubt that the observed concentrations of aluminium, iron, and a group of minor elements, could have been produced by the

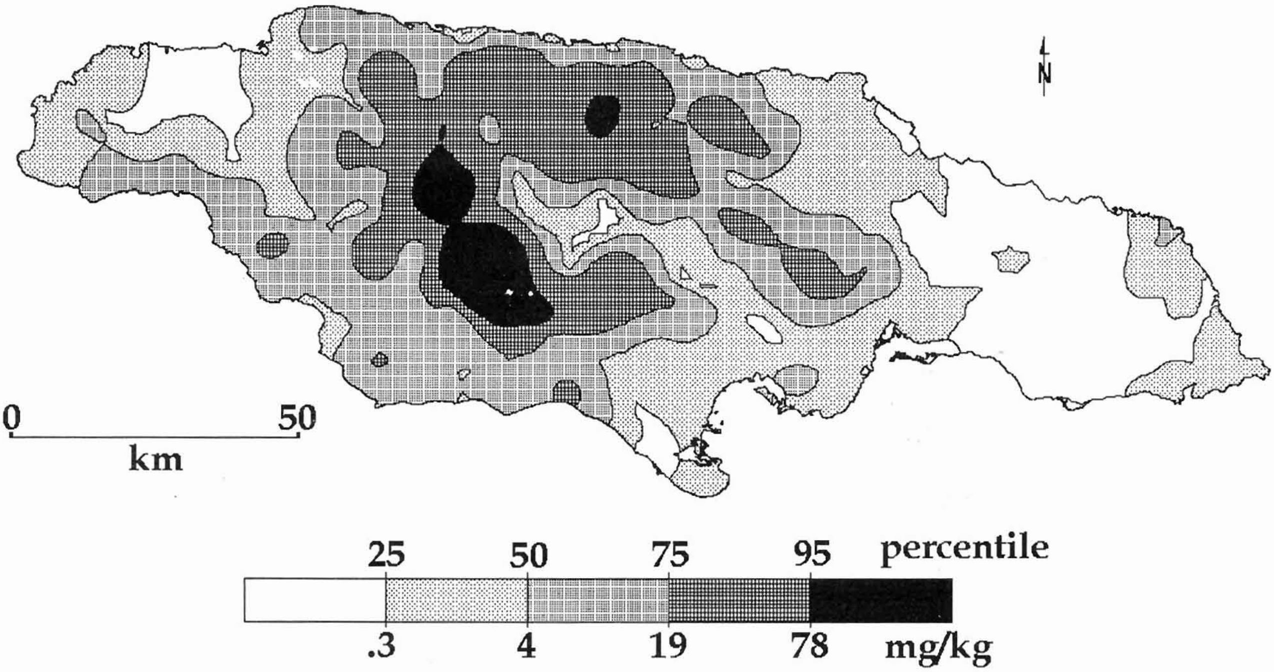

Fig. 2. Island-wide distribution of cadmium in Jamaican soils

dissolution of the limestone. Moreover, the true Caribbean-type bauxites are located only in Jamaica and the peninsular arm of Hispaniola where they are thought to represent the diagenetically reworked products of volcanic ash from volcanic centres in Central Hispaniola. These points lead to the view that Jamaican bauxites may have originated similarly (Lyew-Ayee 1986). The correlation between the Cd and Zn concentrations reported here may support this theory and a detailed comparison of the compositions of the bauxites in Haiti and Jamaica is planned along with depth profile studies in the deep bauxite deposits and at the bauxite/limestone interface. But, whatever the origin, the enrichment of cadmium is most probably associated with ferric-alumino-phosphatic compounds in the bauxite soils which tend to immobilize Cd and Zn.

In soil, Cd is generally adsorbed onto amorphous oxides of Al, Fe, Mn and soil organic matter. The carbonate provides the main control of Cd^{2+} activity in the soil solution and Cd phosphates may also influence Cd^{2+} activity in calcareous soils (Lindsay 1979). The bauxitic or *Terra Rossa* soils in Jamaica situa-ted on porous limestone rocks and subject to seasonal heavy rain fall, will tend to have a range of pH/Eh conditions. These conditions favour solution of Cd from surficial oxidized soils during periods of high rainfall with re-precipitation, and therefore higher concentration lower down in the soil profile under more alkaline conditions, as $CdCO_3$. This is especially likely near the interface with the permeable limestone bedrock. The overall effect of the process may be a very significant contribution to natural soil enrichment of Cd, compared with similar soils in temperate latitudes.

Comparison of soils and stream sediments

The Cretaceous Inliers and Wagwater Group were examined by geochemical survey exploration methods based on the <150 μm fraction of stream sediment samples. Sampling was done at an average density of one sample per 1 x 1 km^2 and cadmium was included in a suite of pathfinder elements for gold (GSD 1992b). Most of the cadmium levels in the stream sediments lie below 1.5 mg kg^{-1} with a few outliers extending up to a maximum value of 20 mg kg^{-1}.

The stream sediment samples in which Cd significantly exceeds 1.5 mg kg^{-1} appear to have been collected over outcrops of: White Limestone Group and Yellow Limestone Group rocks; White Limestone Group rocks to the east of the Marchmont Inlier; Yellow Limestone Group rocks to the south of the Central Inlier, White Limestone Group rocks to the north of the Blue Mountains inlier, and around the margins of the outcrop of the Hanover Inlier. These results are generally consistent with the results of the present work and the sample density difference in the two studies is probably sufficient to account for the small local differences between the soil and sediment maps to the north of the Blue Mountains where the locations of higher Cd values (>1.5 mg kg^{-1}) in stream sediments appear to be at sites for which soil samples are absent.

The Hope Mine area

The Hope Mine is a lead-zinc-copper mine with traces of silver and gold, associated with an altered calc-alkaline andesite in the Wagwater Group, which contains sediments and volcanics. It was an interarc graben during the early Tertiary. Unsorted ore and mine waste, including fine grain ore grade products from mineral processing operations, are to be found in several locations including a school for four to six year old children. The area has been now the subject of intensive study and remediation (Anglin-

Brown *et al.* 1995). In this area, lead has been a great concern, but cadmium con-centrations as high as 478 mg kg^{-1} have been recorded in the soils and, therefore, should also be of concern. These Cd concentrations, interestingly, are not remarkably higher than the highest values found in Manchester.

Potential risk from exposure to cadmium

Cadmium in soil can be ingested through food (and tobacco) grown on the soil, directly from dust, and from drinking water into which it has leached. The plant uptake/soil cadmium relationship is complex and depends on soil pH and other factors.

Under normal soil conditions, plants take up only small quantities of cadmium from the soil but it is phytotoxic at much lower concentrations than metals such as Zn, Pb or Cu (Adriano 1986, Kabata-Pendias and Pendias 1984). Because it is available to plants from both air and soil sources, its concentration can increase rapidly in plants grown in polluted areas. Leafy vegetables and root vegetables are the most likely pathway to man because plants usually concentrate Cd in these parts (Kabata-Pendias and Pendias 1984). In countries for which data are available, the mean dietary intake is 15-50% of the provisional tolerable intake.

The effects of soil cadmium on humans depend on complex factors. Contamination of soils to the extent of only 0.9-1.5 mg kg^{-1} from a tungsten dressing plant in China caused significant health problems ascribed to acid soil which enhances the mobility of the element and its high consumption in the locally grown vegetables (HMSO 1995). On the other hand, in the village of Shipham in England, a stream sediment survey discovered cadmium with a maximum concentration as high as 618 mg kg^{-1} but there was no clear evidence of cadmium-caused health problems. In this case, the Cd was largely unavailable due to a high pH limestone environment and encapsulation of Pb(Cd) sulphides by an insoluble phosphate mineral. Also much of the food was imported to the village (Morgan and Simms 1988). **Table II** contains information on some soil variables in the high cadmium region in Jamaica.

TABLE II. SOIL VARIABLES IN HIGH CADMIUM REGION

Soil variables	pH range	Soil depth	Organic matter	Soil type
Parameters	6-8	Typical 0.1-1m Bauxitic soils up to 100m	0.5-3.5%	Mainly *Terra rossa* clay

In the regions of higher cadmium concentrations the soils are generally *Terra rossa* and occur in deep pockets surrounded by the limestone bedrock. The pH of these soils is between 6 and 8 and *in vitro* sequential extractions with sodium acetate/acetic acid buffers show that little cadmium is extracted above pH 6. The soil pH and strong adsorption to aluminium and iron minerals may inhibit the availability to plants and animals.

Fortunately, despite high levels of Cd (and other heavy metals) in Jamaican soils in many areas, heavy metal concentrations in water and stream sediments are very low (Lalor *et al.* 1995). The underlying limestone base itself probably protects the underground water from contamination by potentially hazardous metals by precipitating carbonate and hydroxide compounds from solution as rainwater leaches the soil. There is no evidence that cadmium is entering the drinking water. This is important because cadmium in drinking water is particularly hazardous. The U.S. Environmental Protection Agency has established a Maximum Contaminant Level in drinking water of 10 μg per litre and a goal of one half this.

No cases of Cd phytoxicity or poisoning of animals or humans have been reported in Jamaica but it is possible that the correlations with cadmium have not been recognized. About 1000 new cases of end stage renal disease are reported annually for Jamaica (Douglas 1997); this represents some 370 new cases per million per year, which appears to be significantly higher than the cases that occur in other Caribbean territories for which data are available. (Santiago-Delpin 1991).

CONCLUSIONS

The concentration of cadmium in soils mainly over the White Limestones in Jamaica is remarkably high. Although no links have been suggested yet between morbidity and Cd in soils in Jamaica, some concentrations are so high that these may become hazards. This could be mitigated by a low bioavailability of the element due to the species present, the near neutral pH values of the soils, and to the alkaline underlying bedrock, but this remains to be demonstrated.

At the very least, the relevant areas need to be more closely defined, potential food uptake assessed, and it must be considered that any future changes in land use or other conditions may increase the risk of harm. Further study and evaluation are needed to understand the cadmium occurrence and distribution and the extent of anthropogenic inputs. An examination of source-pathway-target relationships will help to assess and minimize the exposure of humans and animals to this potential hazard.

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