Lead, Mercury, Cadmium and Arsenic in the Environment
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CHAPTER 18

Dispersion of Cadmium, Lead and Zinc in Soils and Sediments of a Humid Tropical Ecosystem in Nigeria

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ABSTRACT

Primary ores and naturally enriched rocks constitute one of the main sources of anomalous metal concentrations in the environment. In the search for economic mineral deposits, geochemists have delineated areas where excesses of such heavy metals may be hazardous to plants and/or animals.

Several studies on the cycling of cadmium, lead and zinc have focused largely on their pathways from industrial point sources and on their biological fluxes, while relatively little is known about the factors influencing their mobility, redistribution and 'early' pathways in rock–soil–sediment systems (geochemical cycle). A better understanding of such processes may aid in our assessment of the environmental impact of these heavy metal contaminants and the nature of metal uptake by plants. It can also lead to a better understanding of the potential influences of man on local and global cycles of these elements. Data are particularly limited for tropical regions where the high temperatures and rainfall may have specific influences.

Studies on the distribution of cadmium, lead and zinc in soils overlying background and mineralized bedrocks show that, during ferralitic weathering, these metals are released through oxidation and leaching. Cadmium and Pb are generally enriched in the topsoil while Zn is depleted. Within the subsoil, Cd and Zn are characterized by enhanced levels within the B_1 horizon in association with Fe-Mn sesquioxides whereas Pb is accumulated nearer the surface within the B_2 horizon. The dominant pathway for their dispersal is by aqueous transportation by downward percolating rainwater and readjustments of the groundwater table. In mineralized soils, the accumulations of Cd and Pb in the topsoil can reach toxic proportions.

Stream sediments are composites of rock and soil material eroded upstream of the catchment area. Because of the intensity of tropical weathering and metal solubility in water, Zn and Cd enter the streams mostly as solutes which are later precipitated in the sediments. In contrast, Pb shows a rather restricted dispersion train which may suggest transportation mainly as suspended sediment derived from the erosion of anomalous seepage-area soils.

The 'natural' geochemical cycles of Cd, Pb and Zn in tropical environments are generally similar, although their mobility characteristics and chemical forms in surficial materials differ. Considering the flux of these heavy metals from the soil to the streams, it is estimated that the rate of geochemical cycling is more rapid for Zn and Cd than for Pb. This longer residence time for Pb than for Cd or Zn is parallelled in studies done in temperate regions.

INTRODUCTION

In the search for mineral deposits geochemists have delineated areas where excesses of certain trace elements, such as cadmium, lead, zinc, molybdenum and selenium may be harmful to plants and/or animals (Warren *et al.*, 1971; Fletcher *et al.*, 1973; Thornton and Webb, 1981). Other workers, during similar investigations, have attempted to establish the factors influencing the mobility, redistribution and chemical forms of trace elements in rock–soil–plant systems, thereby contributing to our understanding of metal cycling in the environment (Jenne, 1968; Fletcher and Doyle, 1974; Olade *et al.*, 1978; Olorunfemi, 1984).

Cadmium, lead and zinc represent a coherent group of metals both from the metallogenic viewpoint, and as contaminants of the environment (Thornton and Webb, 1981; Peterson and Alloway, 1979; Davies, 1981). Previous studies on the biogeochemical cycling of these metals have focused largely on the pathways from industrial point sources, most commonly within either temperate or sub-tropical ecosystems (Wilkins, 1978; Warren, 1981; Martin and Coughtrey, 1982; Khan and Frankland, 1983). According to Peterson and Alloway (1979), an assessment of the environmental impact of heavy metal contaminants can only be better achieved if the main steps in their geochemical pathways within the various natural ecosystems are understood. However, a great majority of studies have been done in temperate regions, while both arid and humid tropical regions here received little attention.

The tropical rainforest is unique and highly activating due to a combination of extreme climatic conditions, luxuriant vegetative growth and attendant effects of intense weathering, leaching and soil erosion. Although there have been a number of synoptic studies on the nutrient status of tropical soils and the nature of plant communities, relatively little is known about the biogeochemical cycling of trace elements in tropical ecosystems.

This chapter describes the geochemical dispersion of cadmium, lead and zinc in surficial materials from background and anomalous areas within a humid tropical environment. The technique of regional geochemical reconnaissance based on stream sediment sampling is used as a tool in the study of the regional distribution of trace elements (Webb and Thornton, 1981).

DESCRIPTION OF STUDY AREAS

Over 60% of tropical West Africa is underlain by crystalline igneous and metamorphic rocks, mostly of Precambrian age. They comprise a complex assemblage of gneisses, migmatites, metasediments and granitic rocks which have been subjected to several episodes of deformation and metamorphism. Sedimentary rocks of Cretaceous–Tertiary age are largely confined to the coastal areas and interior basins (Figure 18.1), and they are mostly shales and sandstones with minor limestones. The only areas with known lead–zinc deposits, where mining activity has been intermittent, are along a 600 km long metallogenic belt within Cretaceous sediments of Nigeria's Benue Trough.

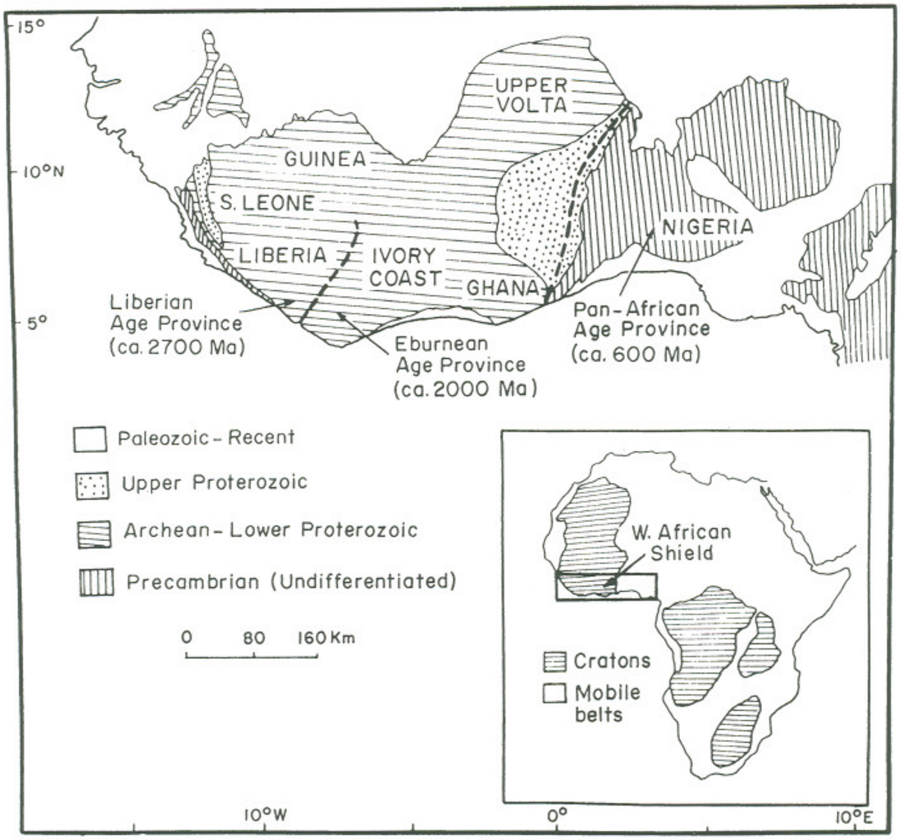


Figure 18.1 Generalized geology of West Africa

The present study on the dispersion of Cd, Pb and Zn is focused on areas around the lead–zinc mines where soils and stream sediments have developed from naturally enriched parent materials, including black shales, hydrothermally mineralized rocks and mine dumps. The heavy metal content of rocks, soils and stream sediments from uncontaminated areas overlying the crystalline basement and sedimentary rocks are presented for comparison.

The main study area around Abakaliki is one of the well known lead–zinc mineralized districts in Africa (Hawkes and Webb, 1954). The host rocks are black, carbonaceous shales with nodules of calcareous matter. Extensive weathering has generally converted the black shales to a bleached pale grey colour. Mineralization consists of several occurrences of hydrothermal vein deposits which have been mined intermittently for decades. However, because of the small-scale mining, contamination of the environment by mining activity is very limited and areas with undisturbed mineralization can still be found. Principal ore minerals are galena and sphalerite with minor chalcopyrite. The sphalerite is enriched in Cd while the galena is argentiferous (Olade, 1976).

DISCUSSION

Background Data for Rocks and Ores

The overall abundance of trace elements in surficial materials depend initially on their concentrations in bedrocks and mineralized zones. Background concentrations of Cd, Pb and Zn in rocks from the Nigerian Basement Complex and sedimentary areas, particularly the Abakaliki area are shown in Table 18.1. The metal contents for the crystalline rocks are generally within the range for crustal rocks, except for the group of anomalous alkaline granites (Younger Granites) which contain enhanced values of these elements. They are genetically associated with zinc–tin–niobium mineralization.

The Cretaceous black shales which are host to the lead–zinc mineralization contain slightly enhanced background values of Cd, Pb and Zn although they compare favourably with those for black shales elsewhere (Doyle *et al.*, 1973). However, close to mineralized zones, the metal contents of the shales show strong enrichment due to primary dispersion effects. Cadmium concentrations in the sphalerites from the mineralized zones are high, with values exceeding 2500 ppm (Table 18.1). On the basis of the metal contents in the bedrocks, the inherited levels of Cd and Pb in soils and sediments are likely to be anomalous near mineralization depending on the nature of weathering and other environmental factors. Data for Nigerian soil composition are given in Table 18.2.

Table 18.1 Trace element contents (ppm) of tropical rocks (Nigeria). Data from Olade (1976)

	Cd	Pb	Zn
Gneisses	0.25 (0.1–0.4)*	46 (28–65)	72 (45–92)
Granites	0.15 (0.1–0.3)	20 (12–30)	54 (45–64)
Anomalous granites	0.45 (0.2–1.5)	32 (10–54)	250 (70–800)
Shales	1.5 (0.5–4)	32 (20–36)	95 (80–115)
Black Shales	6.5 (5–12)	80 (60–115)	175 (160–220)
Sphalerite (Benue valley)	(2100–2600)	–	–
Average crustal rocks	0.2	13	70

* Range

Table 18.2 Trace element contents (ppm) of tropical soils (Nigeria)

	Cd	Pb	Zn
Background soils (crystalline rocks)	0.35 (0.2–0.8)*	42 (16–124)	74 (10–158)
Background soils (black shales)	4.5 (2–12)	78 (35–150)	118 (80–270)
Mineralized soils (black shales)	(12–30)	(2200–7500)	(500–1800)

* Range

Metal Dispersion in Sediments

Approximately 350 stream sediment samples were collected within the Abakaliki area with an overall sample density of about one per km^2 (Olade *et al.*, 1978). Samples were air dried, disaggregated and sieved to <100 mesh and analysed for Zn, Pb, Cd, Mn and Fe by atomic absorption spectrophotometry after hot nitric acid digestion. Data are given in Table 18.3. Organic matter content and pH of the sediments were also determined.

High concentrations of lead (more than 100 ppm and up to 1000 ppm) occur in sediments from areas contaminated by exposed mineralization and mining. The dispersion pattern of Pb is limited as the anomalies are confined to the mineralized zones. Anomalous Zn values (200 and up to 2000 ppm)

Table 18.3 Trace element contents (ppm) of stream sediments in the Abakaliki area of Nigeria. Values are based on nitric acid digestions ($n = 350$)

	Mean	Range
Cd	3.5	(1–20)
Pb	50	(10–99)
Zn	112	(20–2178)
Cu	21	(8–260)
Mn	1183	(20–10 000)
Fe	5.2	(0.8–16.0)
pH	5.9	(4.6–8.5)
Organic matter	6.4%	(1.3%–14.4%)

also outline the known mineralized areas with a dispersion pattern that is more extensive than that of Pb.

Several other localities contain isolated but anomalous values not related to mineralization. Cadmium levels are generally very low (<2 ppm) except close to mineralized zones where values up to 20 ppm are encountered (Table 18.3).

R-mode factor analysis was used to obtain inter-element relationships and factors controlling metal dispersion patterns. The following metal associations for a 3-factor model which accounts for 70% of total data variability were obtained.

Factor 1: Organic matter, Pb, Cu, Cd.

Factor 2: Zn, Fe, Mn

Factor 3: pH, Mn

Factor 1 which accounts for 60% of total variance is most strongly related to organic matter and may reflect metallo-organic complexing of ore elements. Zn–Fe–Mn which are closely associated in the second factor indicates Fe–Mn oxide co-precipitation with Zn in sediments, whereas the strong association of pH–Mn in Factor 3 may represent the effect of increased pH on Mn precipitation.

Metal Distribution in Soils

Distribution of heavy metals within soil profiles provides an insight into their behaviour during weathering and availability to plants. Due to high temperatures and heavy rainfall, the predominant soils of humid tropical regions are ferralsols (Young, 1976). They are usually characterized by very intense and complete weathering and leaching of the parent materials to kaolinite and Fe–Al oxides. The high ratio of precipitation to evaporation generally favours downward percolations, as it does in temperate region podsols. Due to very high rainfalls the humid tropical environment provides the optimum conditions for metal dispersion.

Soil differentiation with depth in ferralitic soils usually occurs by the development of four distinct horizons. The A horizon is usually restricted to a relatively thin layer of sandy to loamy soil with small to moderate amounts of organic matter at the top. The B_2 and B_1 'horizons' which may reach several metres in thickness consist of an upper reddish-brown ferruginous gravelly horizon and a lower yellowish kaolinitic horizon, respectively. Iron-rich layers or concretions (laterite) may occur anywhere within the B_1 or B_2 horizons. The C horizon is commonly made up of a mixture of clay and partially weathered parent material.

In order to establish the geochemical behaviour of Cd, Pb and Zn in ferralitic weathering, uncontaminated soil profiles overlying crystalline and sedimentary rocks, as well as those from mineralized but undisturbed areas, were sampled and analysed by AAS after nitric acid digestion. Results show that, although the absolute concentrations of these metals differ due to lithologic control, the dispersion patterns are generally similar (Figures 18.2 and 18.3).

In Profile 1, cadmium shows a slight enrichment in the topsoil, with values decreasing in the highly-leached B_2 horizon. Within the B_1 horizon with abundant clay, Cd increases in concentration and shows highest values within an Fe-rich layer (Figure 18.2). Zinc shows a similar pattern except for the relative depletion within the top soil. In contrast, lead is relatively enhanced within the top soil and B_2 horizon while it shows strong depletion within the B_1 horizon and slight enhancement near the base in association with Al-hydroxides. In Profile 2 with a fragmental soil overlying a weathered carbonaceous shale, Pb and to lesser extent Cd are enriched in the A horizon while Zn is impoverished (Figure 18.3a).

In the weathering profile overlying a mineralized zone which has not been disturbed by mining activity (Figure 18.3b), cadmium and zinc are characterized by fairly high levels reaching toxic proportions, but are depleted relative to parent material. On the other hand, Pb shows strong accumulation within the topsoil and B_2 horizon partly as a result of the formation of lead sulphates and carbonates. The slight enrichment of Zn and Cd within the B_1 horizon may also be attributed to the formation of secondary minerals (Figure 18.3b).

Factors Controlling Dispersion of Metals in Tropical Soils and Sediments

The concentrations of metals within tropical soils are strongly controlled

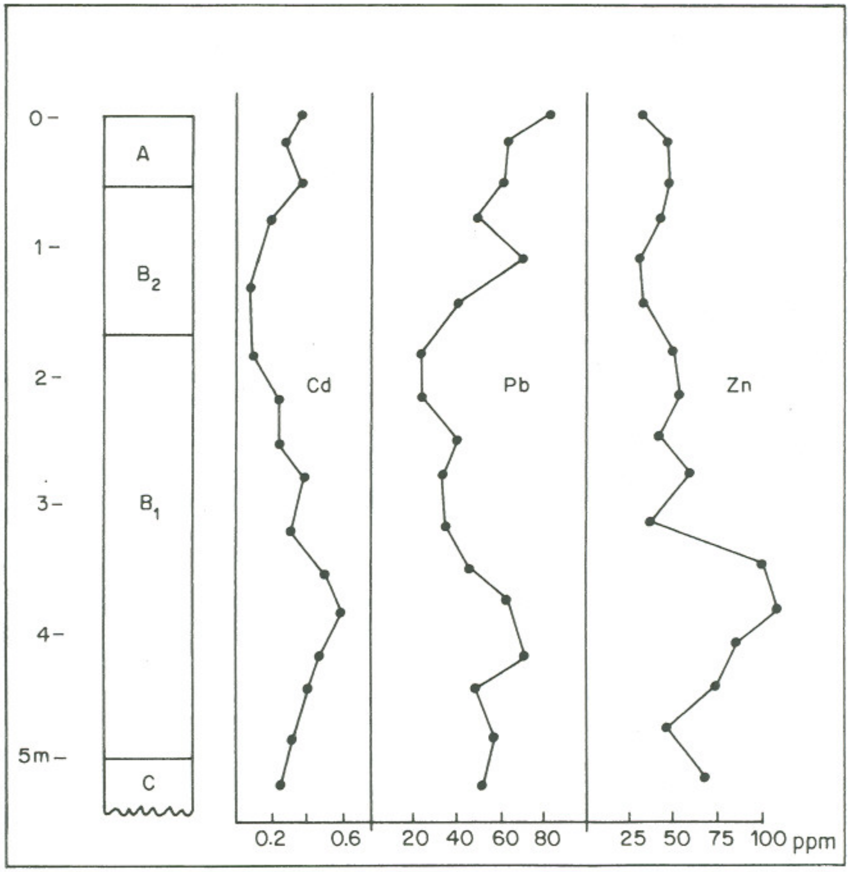
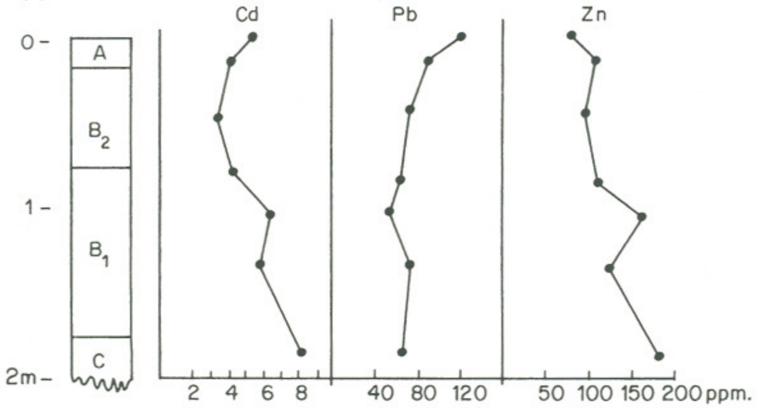


Figure 18.2 Metal distribution in weathering soil profile over crystalline rocks (profile 1)

by the geochemical characteristics of the underlying rock and the nature of weathering processes. Ferralitic weathering, which is prevalent in the humid tropics, results in oxidation and intense leaching of major and trace metals. The high ratio of precipitation to evaporation permits free drainage and transportation of metals down the profile. Among the major elements, silica is partially or totally leached while iron and alumina concentrate within the profile as oxides and hydroxides.

However, the degree of trace element re-distribution is usually dependent on the mobility characteristics and the effects of other environmental parameters such as organic matter content, Fe–Mn co-precipitation and formation of insoluble precipitates.

(a) Profile 2



(b) Profile 3

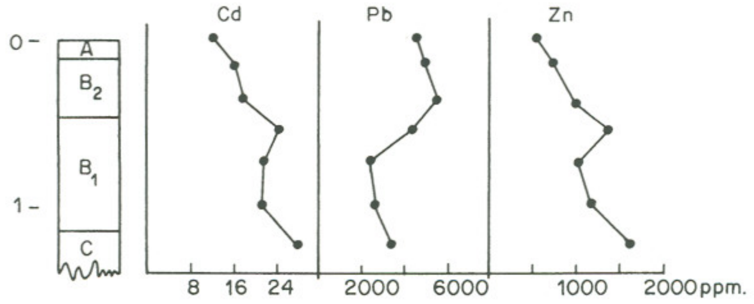


Figure 18.3 Metal dispersion in soil profile overlying (a) uncontaminated and (b) mineralized carbonaceous shale

Cadmium tends to be fairly mobile during tropical weathering and is redistributed within the soil profile. There is evidence from our results that, despite its mobility, it shows slight enrichment within the topsoil as well as in clayey zones rich in soluble Fe hydroxides, but is strongly leached within Al-rich zones. The most likely forms of Cd in tropical soils are as soluble or insoluble organo-metallic complexes and co-precipitates with Fe–Mn hydroxides. The relatively high Eh values in freely-drained humid tropical soils tend to promote formation and sorptive ability of Fe–Mn sesquioxides particularly with increasing pH conditions. Within stream sediments, results of R-mode factor analysis suggest that Cd, along with Pb and Cu, are strongly associated with finely divided organic matter in carbonaceous shale parent rock. However, in soils overlying mineralized zones Cd shows a very strong association with Zn and both are precipitated as secondary minerals.

Lead most often accumulates within the topsoil due to its relatively poor mobility and strong tendency to form metallo-organic complexes. Lead shows little or no association with Fe–Mn precipitates, but tends to readily form secondary lead sulphates and carbonates in soils overlying mineralization. In stream sediments Pb is closely associated with organic matter.

Zinc is a relatively mobile element both in soils and stream sediments and is most commonly depleted in the topsoil. The dispersion train of Zn is long, although there is strong evidence of co-precipitation with Fe–Mn hydroxides in the surficial environment. In mineralized soils, Zn is generally depleted in the soils relative to the underlying parent material, and enrichment due to precipitation of insoluble secondary minerals is common.

Stream sediments are largely derived from rock and soil material eroded from upstream in the catchment area. The major pathways for heavy metals are by sedimentation of particles and by sorption of dissolved metals from surface waters or groundwater seepages in contact with the stream sediments (Warren, 1981). The three main kinds of particles transported by stream are bed load, suspended sediment load and solutes (Davies, 1981). Considering the intensity of tropical weathering and metal solubility in aqueous medium, Zn and to a lesser extent Cd and Pb enter the streams as solutes which are later precipitated in the sediments. However, Pb shows a rather restricted dispersion train which may suggest that it is also partly transported as suspended sediment derived from erosion of anomalous bank or seepage-area soils containing insoluble secondary minerals (Ukpong and Olade, 1979). It is also possible that the sediments contain clastically dispersed mine debris.

In conclusion, detailed and more quantitative data on weathering rates, soil inventory, and the inputs from the biological cycle are required. Because of the rural setting of most communities within tropical Africa, the input of heavy metal contaminants into the environment from industrial activities is still minimal although growing steadily.

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