

RISK ASSESSMENT OF CADMIUM CONTAMINATED SOIL IN A BATTERY MANUFACTURING FACTORY IN NIGERIA.

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ABSTRACT

Risk assessment of trace metal contamination in soil involves the understanding of its chemical form and concentration. In this study the chemical species, distribution and bioavailability of cadmium in the soil within a battery factory in Ibadan, Nigeria was investigated. The result indicates that total concentration of cadmium (12.62-37.35mg/kg) within the factory site exceeds the threshold limit established by Federal environmental protection agency (FEPA) by a factor of 4.54. Solid phase speciation of the soil showed that cadmium was distributed in order: residual > organic bound > occluded by free oxide > inorganic bound > exchangeable. Cd content that could be exchange with other useful ion in the soil however falls between the standard normal ranges. The threat posed by presence of cadmium is indicative by its concentration level distribution in other species.

INTRODUCTION

Cothorn (1991) has observed that quantitative risk assessment is a new, emerging and potentially useful method for comparing the risks to human health and environmental degradation due to natural and anthropogenic contamination. Environmental contaminants are transported in the air, water, soil and dust and enter human being by ingestion and dermal routes (DeRosa, *et al* 1991).

Heavy metals are found useful to plants and animals when they occur in compound form and within safe threshold. Often time adverse contributions from casting, smelting and other metal processing plants are hazardous waste in high concentration. A wide use of cadmium is in the production of a range of batteries (Onawumi, *et al*, 2004). Major routes of exposure of human being to cadmium which has been identified as a toxic element are through inhalation of its dust and fumes (usually cadmium oxide), the ingestion of cadmium salt and the consumption of vegetables homegrown on Cd contaminated soil (Millis *et al* 2004). Other notable pathway of cadmium to man are foods grains and cereals (Cherian and Gover, 1998).

Soils and plants are major sink for contaminants in the terrestrial environment and form the basis of food chain through which toxic substance may be transmitted to man (Little, 1977). Accumulation of cadmium in plant tissue is the result of the level of Cd available in the soil in which the plant is grown (Alloway, 1990). For instance it was reported that in the local rice consumed by multiparous women in Fuchu, Japan after the World War II, cadmium was found to play an etiological role in the

disease called itai-itai (ouch-ouch) which affected them (Ademoroti, 1996). After absorption into the body, Cd has a strong affinity for liver and kidney. Cadmium like some other heavy metals is highly water soluble and may be readily absorbed by plants. Cadmium, lead and nickel have been shown to cause reduction in photosynthesis and transpiration of detached leaves of corn and sunflower (Ibrahim, *et al*. 1981). Blume, *et al.*, (1983) reported that cadmium and mercury are more readily taken up from soil by plants than lead hence their liberation unto land used for growing food crops. Other potential sources of cadmium contamination are found in the production of paints pigment –alloy, solder, and electroplating. Feid (1992) adduced that the amount of cadmium ingested varies with such factors as the cadmium-content of the soil and the quantity in the infected organ and meat such as liver and kidney that are eaten.

Soil is an open system that undergoes continual exchange of matter and energy with the atmosphere, hydrosphere and biosphere. This means whatever affect water and air will also affect soil, plant and animal. Mobility and bioavailability of heavy metals in the soil solution is only dependent on the total concentration, but also related to their chemical species reflecting the interaction between solid and solution phase of soil (Camerlynck, 1982). Soil pH has been considered an important factor controlling the uptake of cadmium by plants.

The risk of exposure to toxic material or wastes decreases exponentially with distance from the source of the pollution (Hutchinson, *et al*, 1974). Concentration has been found to increase with time of

release of this toxic material. Onawumi, *et al.* (2007) have found that there is significant reduction in the level of lead in soil as a result of stoppage of operations at a battery factory. According to the empirical observation reported in NAS (1983), as the dosage of a chemical increase, the toxic response also increases. There is therefore the need to assess the possible risk that the presence of different species of cadmium in the soil may cause.

Material and Method

Different methods of extraction process for various heavy metals have been reported. The forms of metals in soils have generally been investigated using either single-step extractions or sequential extraction procedure (Iu, *et al.* 2003). In this work a sequential extraction procedure as used by Tessier *et al.* 1979 was adopted.

Soil sample were collected randomly from a battery factory area using an urger from 0 – 15cm depth of the soil. Sampling points ranges from Administrative block (S1), Back of bag house (S2), Battery breaking (S3), Slag place (S4), Scrap yard (S5) and Sample point (S6) which represented the control point taken at the back of Department of Law, University of Ibadan, Ibadan. Soil samples were air dried for seven days. It was ground in an agate mortar and then sieved with less than 1mm sieve to remove organic debris and large mineral particles. Each of the sieved samples was thoroughly mixed and stored in a well labeled polythene bags for subsequent analysis. This scheme presents extraction of cadmium in the following forms.

Exchangeable Cadmium

5g of soil was used for the extraction of exchangeable cadmium using 50ml of 1M CaCl₂ in a 250ml plastic bottled on mechanical shaker for 24hours. The solution was centrifuged at 1200G for 10minutes. The supernant solution was collected and heated to dryness in the presence of hydrogen peroxide (H₂O₂) to destroy organic matter and the residue was dissolved in 1M HNO₃. Cadmium was determined in this extract using atomic absorption spectrophotometer (A.A.S).

Cadmium Bound Mainly in Inorganic Sites

To the soil residue from the above extraction was added 50ml of 2.5% acetic acid (pH=5.0) for the extraction of cadmium bound by inorganic site. This was shaken for 24 hours on a mechanical shaker. The resulting solution was centrifuged and the supernatant was heated to dryness by adding 5ml of 50% H₂O₂. The residue was dissolved in 10ml 1M HNO₃ for subsequent analysis.

Cadmium Bound Mainly in Organic Sites

1g fresh soil was used for this extraction and it was shaken with 100ml sodium pyrophosphate (0.1M) reagent in a 250ml plastic bottle for 24hours. The supernant solution collected after centrifuge was heated to dryness in the presence of hydrogen peroxide, 1M HNO₃ was added to the residue, organically bound cadmium was determined using A.A.S.

A fresh sample of soil was used for this extraction because smaller quantity was required.

Cadmium Occluded by Free Oxide

Residual soil from pyrophosphate extraction was shaken with 50ml de-ionized water and the water was discarded. The soil was washed with a small amount of water into a 100mm diameter evaporating basin. This was evaporated to dryness on a boiling water bath, 50ml of a mixture of oxalic acid (0.1M), 33ml and 17ml of 0.175M ammonium Oxalate at pH of 3.25 was added. The liquid level in the basin was maintained during extraction with de-ionized water. The extraction took about 6 hour before completion and the content of the basin was centrifuged. The supernatant solution was collected with further washing of the residue with 25ml of oxalate reagent. Cadmium was determined in this extract with A.A.S.

Residual Cadmium

Residue from the oxalate extraction was evaporated to dryness and ignited at 600°C in a muffle furnace. The residue was cooled, weighed and ground. The ground residue was digested with hydrofluoric acid using teflon beaker on a hot plate. Cadmium was determined in the hydrofluoric acid extract.

Table 1: Cadmium in the soil specie expressed as percentage of total concentration

Soil Sample	(1) Exchangeable Metal (1M-CaCl ₂) µg/g (% of TC)	(2) Cadmium bound Specifically by Inorganic site (2.5%CH ₃ COOH) µg/g (% of TC)	(3) Cadmium bound by Organic site (0.1M-Na ₄ P ₂ O ₇) µg/g (% of TC)	(4) Metal Occluded by in digestion Oxalate extract. µg/g (% of TC)	(5) Residual Metal (HF) µg/g (% of TC)
S1	0.0069	4.8988	66.1626	8.1839	20.7478
S2	0.0137	51.6345	17.8498	9.7114	20.7906
S3	0.0103	18.9362	1.4262	21.1547	58.4726
S4	0.0138	20.8395	0.0118	8.6543	70.4806
S5	0.0067	24.7292	7.9650	30.5954	36.7037
S6*	0.0212	15.5196	0.0163	11.7622	72.6970

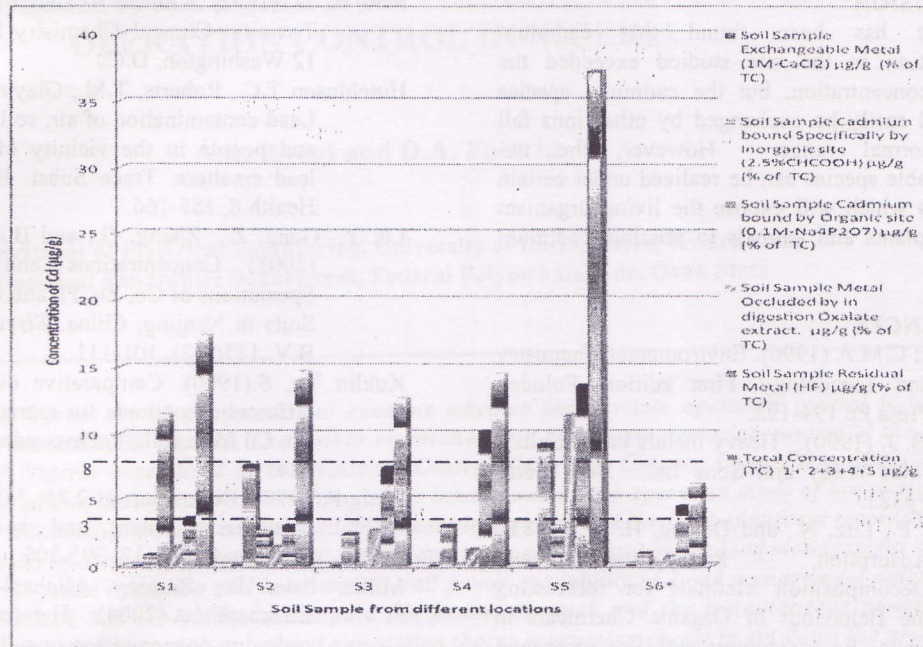


Figure 1: Concentration of Cadmium in the Soil Sample

RESULT AND DISCUSSION

Table 1 shows the percentage of different species of cadmium from the test soils. For the purpose of comparing the results were express as percentage of total concentration of the species for each of the samples. From Table 1, the percentage of the total concentration of cadmium that could easily be exchanged for other useful ions by plants falls between 0.00672 and 0.0212 percent which was within the normal concentration (0.001-0.0025µg/g) as shown in Figure 1. In all the samples, residue has the highest concentration of cadmium. Residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature. At the administrative block (S1) of the factory, 60% of the cadmium present is mainly bound by organic site that is the percent cadmium bound to various forms of organic matter. Organic matter can be degraded, leading to a release of soluble cadmium which may be absorbed by plants or made available to other living organisms. In the overall, the total cadmium from the control site (S6) is the lowest compared to the samples from the manufacturing sites.

The distance of the activity centers from the main factory, the topography and the quantity of deposit of contaminant present at each center have been found to correlate significantly with the total contaminants in the soil being studied. The result indicates that total concentration of cadmium (12.62-37.35mg/kg) within the factory site exceeds

the threshold limit established by Federal environmental protection agency (FEPA) by a factor of 4.54. The possible accumulation of cadmium above the minimum critical concentration level (4mg/kg) in plant due to natural and anthropogenic activities of cadmium in soil exposes plants and animals that feed on them to high level of food poisoning. The solid phase speciation of the soil also showed that cadmium was distributed in order: residual > organic bound> occluded by free oxide > inorganic bound > exchangeable. Cd content that could be exchange with other useful ion in the soil however falls between the standard normal ranges. Environmental impact of cadmium in the affected area is relatively significant when compared with similar analysis conducted on the soil sample (S6) used as control (see Figure 1). The hazard posed by presence of cadmium is indicative by its concentration level distribution in the factory area.

In this work, distance, duration of exposure, nature, volume of toxic waste released and level of activities at work centers were identified as risk factors which determine the level of exposure to the toxic element under study. For the six locations which were considered in the study, the samples taken were studied for concentration relative to that of battery making centre (Main Factory) where the concentration of cadmium is highest. The nature and level of activities carried out at different work centers could be traced to the concentration level of cadmium at the factory.

CONCLUSION

It has been found that cadmium concentration in the site studied exceeded the allowed concentration, but the cadmium species that could easily be exchanged by other ions fall below normal range. However, the un-exchangeable species can be realized under certain conditions which will expose the living organism i.e. both plants and animals to possible cadmium risk.

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