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DEPLETION OF LEAD IN THE SOIL OF A BATTERY FACTORY

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Abstract

Lead pollution in soil of a battery making factory at two separate times was studied and reported in this work. Significant changes were noticed in the level of lead in the soil samples between the time of active production and the downtime. This reflects the importance of fallow period in phytoremediation of metal-contaminated soil as a method of environmental clean-up. Atomic absorption spectrophotometer (AAS) was employed in the estimation of lead content in the soil samples for the two periods.

A chemical fractionation of the metal in the soil samples were compared for necessary evaluation. Excessive total concentration of Pb ranging from 15293.12-16295.37µg/g was generally recorded in the first study while a remarkable low level of total Pb concentration ranging from 21.11-54.81µg/g (below the critical concentration established by Federal Environmental Protection Agency (FEPA)) was recorded for the downtime. At first, solid phase speciation of the soils using Tessier procedure showed that the Pb was distributed in the order: organic bound > inorganic bound > residual > occluded by free oxide >exchangeable which at later study showed a redistribution in the order: organic bound > inorganic bound > residual > exchangeable > occluded by free oxide.

Keyword: Lead; Fractionation; Pollution; Atomic Absorption Spectrophotometer;

Introduction

Most of the ions in soil development are essential for plant and animal survival but when such elements as lithium, cadmium, beryllium, gold and lead are present at above natural concentration, they become toxic to human life (White, 1979, Harrison, 1990). Heavy metal contamination of soil through anthropogenic activities constitutes hazard to human health, harm to living creatures and ecological systems (Li, *et al.*, 2005). Fixing the threshold concentration level at which a substance is toxic is extremely difficult. This is because toxicity varies with maturity and general health of the organisms. The risk assessment of trace metals contamination in soils requires knowledge of the control of metal concentration, mobility and speciation. (Wilcke, *et al.*, 2005; Camel, *et al.*, 2001).Some toxic substance mostly found in battery industries includes Pb, Cd, Cu and Ni. (Onawumi and Onawumi, 2004).

John *et al.*, showed that growth of lead responsive crops such as lettuce, spinach leaves and carrot on contaminated soils should be avoided. Consumption of home growth vegetable near secondary lead smelting constitutes a health hazard as leaves and tubers of vegetable with time accumulated significant amount of lead. Jaworska, *et. al.* (2005) in their study on the effect of heavy metal contaminated soil on growth and chemical composition of broad beans and fodder beans noted that heavy metals supplied to the soil in quantities exceeding allowable levels in arable soils strongly weakened growth of both plants studied. Hutchinson. *et al.*, (1974) reported that lead in monthly dust fall collection decreases exponentially with distance. Tobacco has an exceptional capacity to accumulate Pb, Cd, and Zn in high heavy metal exposure conditions, whereas with less heavy metal exposure tobacco was apparently similar to other leaf crops in heavy metal accumulation potential. (WHO/FAO., 1972). According to Angelova *et al.* (2004) the experimental data obtained for the presence of Pb, Cd, and Zn in the different parts of tobacco grown in an industrially polluted region showed that their amounts were mainly due to the heavy metal-continuing aerosols falling from the atmosphere. Part of them, however, got into the soil, and from there penetrated via the root system into the tobacco plants and accumulated in above ground parts.

Accumulation of lead in plant tissues is influenced by the level of lead available in the soil in which the plants are grown. Extensive studies have been done on various methods of remediation ranging from electrokinetic remediation, excavation, planting of metal hyperaccumulators, use of EDTA and citric acid (CA), deposition of accumulation zone, and addition of fixating phases that immobilize the metallic species. extraction of the metallic species. (Kamnev *et al.* 2003; Funaishi, *et. al.*, 2004, Kitagawa, and Ushio, 2004, Kurihara, *et al.*, 2005).

At two different instant in time the soil of a battery producing factory was studied. At first, the factory was in full operation while at another time, three years after the factory had stopped production the same study was repeated to gain an understanding of the depletion of lead in the soil of the factory.

In this study, concentration of lead specie in the metal-contaminated soil of a battery factory as well as its bioavailability in plant, level of exposure of workmen at battery factory and consequence remediation due to a break in production was determined by method of chemical speciation of the soil (Su, and Wong, 2004, Lu *et al.*, 2003). While it is not in the best interest to force a factory causing pollution to closure, knowledge of the extent of damage caused by the activity of the factory may necessitate a drastic decision for purpose of safety of plants, animals and men living in the neighborhood.

Materials and Method

In order to have a good understanding of the concentration, physicochemical forms and bioavailability of this metal in soil, a rapid extraction method proposed by Kuklin, Yu. S. (1980), may not do much good. The concentration of lead was determined by atomic absorption spectrophotometric (AAS) as it was found to be the most acceptable analytical technique for elemental analysis in agricultural and environmental laboratories.

Soil sample were collected randomly from five different locations within 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) and Scrap yard (S5). Duplicate samples were collected from each of the spots mentioned. Soil samples were air dried for seven days, ground in an agate mortar and then sieved with less than 1mm sieve to remove organic debris and large mineral particles (Mclaren and Grawford, 1973). Each of the sieved samples were thoroughly mixed and stored at room temperature in a well labeled polythene bags.

Fractionation of lead in Soil

A chemical fractionation method was applied in the speciation of the soils using Tessier et al. (1979) procedure in the analysis of the five samples collected. This scheme presents extraction of lead in the following forms.

Exchangeable lead

5g of soil was shaken with 50ml of 1M $CaCl_2$ in a 250ml plastic bottled on mechanical shaker for 24hours in other to extract the exchangeable lead. The solution was centrifuged at 1200G for 10minutes. The supernatant solution was collected and heated to dryness in the presence of hydrogen peroxide (H_2O_2) to destroy organic matter, the residue was dissolved in 1M HNO_3. Lead was determined in this extract using atomic absorption spectrophotometer (A.A.S).

Lead Bound Mainly in Inorganic Sites

1g of fresh soil was shaken with 100ml of 0.1M sodium pyrophosphate reagent in a 250ml plastic bottle for 24hours in other to extract lead bound by inorganic site of the soil. The supernatant solution collected after centrifuge was heated to dryness in the presence of hydrogen peroxide, 1M HNO_3 was added to the residue and lead content was determined using A.A.S.

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

Lead Occluded by Free Oxide

Residual soil from pyrophosphate extraction was shaken with 50ml de-ionize 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 of 0.1M oxalic acid, 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 deionized water. The extraction took about 6 hours before completion and content of the basin was centrifuged. The supernatant solution was collected with further washing of the residue with 25ml of oxalate reagent. Lead was determined in this extract with AAS.

Residual Lead

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. Lead was determined in the hydrofluoric acid extract.

Lead Extracted with 1M HNO_3 (Mclaren and Grawford, 1973, Mocko, 2004)

1g of soil was used for total lead extraction by shaking the soil with 50ml 1M HNO_3 for 4hours in a plastic bottle. The solution was centrifuged at 1200G for 15minutes. The supernatant solution was collected for lead determination.

Result and Discussion

The soil fractionation carried out on the samples at two separate times showed that there has been an average of 98% total reduction in lead concentration in the soil of the factory. A close observation of the lead concentration in the different forms in which lead exist in the soil as shown in Table 1 indicate that when the factory is in full operation highest percentage of the lead is bound in organic site which makes it readily available to plants (Fig 1). However, in the case when the factory has stopped production for a period of three years apart from the fact that the concentration has reduced exponentially, the highest lead concentration is bound by organic site which is an indication of rapid recovery of the organic constituent of the soil (Fig 2).The exchangeable lead which like other forms of lead in the soil during days of active operation exceed the recommended critical concentration level (100-400)μg/g, (Alloway,1990) is however reduced below this level of toxicity at the latter time. This also explains that the soil of the factory has fully recovered from lead contamination (Fig 1- Fig 2). It is important to note that result of lead extracted by 1M HNO_3 from each of the sample compared favorably with that of total lead in Tables 1 and 2. The slight higher values obtain from the fractionation method shows that the method is more effective and revealing than the method of digestion using HNO_3. It is preferred when there is a need to know the physicochemical forms in which the metal exists. However, it is more expensive and involving. There is a clear experience of lead pollution at the first analysis carried out on the soil of the factory. Both animals and plant including workers and people leaving or farming in the area close to the factory are exposed to the excessive level of lead in the soil. The result of lead pollution could range from mere ill-health, disease, and death. It is also interesting to note that the depletion of lead in the soil can be highly remarkable within a period of the three year of rest experienced by the soil. The soil can now be put into use by farmers without fear. Plants grown within the factory can now be declared safe for animal and human consumption.

Conclusion

This research study has revealed that there is a significant reduction in the concentration of the different forms of lead in the soil of battery factory as a result of the shutdown of the factory for a period of three years. The state of lead pollution when the factory was in operation was alarming and could have done incalculable damage to health of both animals and plants in the neighborhood. It is suggestive that the factory be moved to another location far from where people live to avoid further pollution of the environment anytime it commence production again.

There is a need for environmental agencies to pay good attention on the activities of the plant and to enforce adequate protection of workers in the factory. The remarkable depletion of lead after three years of production downtime confirms the natural way of correcting the environmental hazard created by the factory and the possibility of total recovery of the soil from pollution. Repeated study may be conducted in the future to assist in developing a depletion model for the soil.

This study has therefore shown that the stoppage in production of battery for some time compared to fallowing period could be a more economic and effective method of remediation of the soil for future safe and productive uses. It is believed that life of the people exposed to this environmental hazard worth more than the economic lose that the company may suffer.

Table 1: Concentration of Lead in the Soil during Active Production Time (μg/g)

Soil Sample	(1) Lead Extracted by 1M-HNO_3	(2) Exchangeable Metal (1M$CaCl_2$)	(3) Lead bound Specifically by Inorganic site (2.5%CHCOOH)	(4) Lead bound by Organic site (0.1M$Na_4P_2O_7$)	(5) Metal Occluded by in digestion Oxalate extract.	(6) Residual Metal (HF)	Total = 2+3+4+5+6
S1	12301.43	1486.78	3407.2	2146.44	1103.96	4427	12571.38
S2	23849.8	1761.09	12053.17	10705.8	1560.22	1876.18	27956.46
S3	51538.67	5043.61	12277.61	23611.28	1460.22	15221.64	57614.36
S4	20159.67	4678.51	10363.61	3241.67	1327.49	1776.18	21387.46
S5	63363.32	2451.37	7097.52	41771.66	1194.67	15761.74	68276.96

Table 2: Concentration of Lead in the Soil at Production Downtime Time (μg/g)

Soil Sample	(1) Lead Extracted by 1M-HNO_3	(2) Exchangeable Metal (1M$CaCl_2$)	(3) Lead bound Specifically by Inorganic site (2.5%CHCOOH)	(4) Lead bound by Organic site (0.1M$Na_4P_2O_7$)	(5) Metal Occluded by in digestion Oxalate extract.	(6) Residual Metal(HF)	Total = 2+3+4+5+6
S1	153.75	25.84	40.33	34.25	32.7	41.44	174.56
S2	186.5	27.73	65.5	46.35	24.93	35.66	200.17
S3	202.32	35.38	57.34	65.35	27.35	39.24	224.66
S4	110.83	22.03	45.89	20.73	15.33	18.2	122.18
S5	225.41	26.2	65	72.5	20.25	57.65	241.6

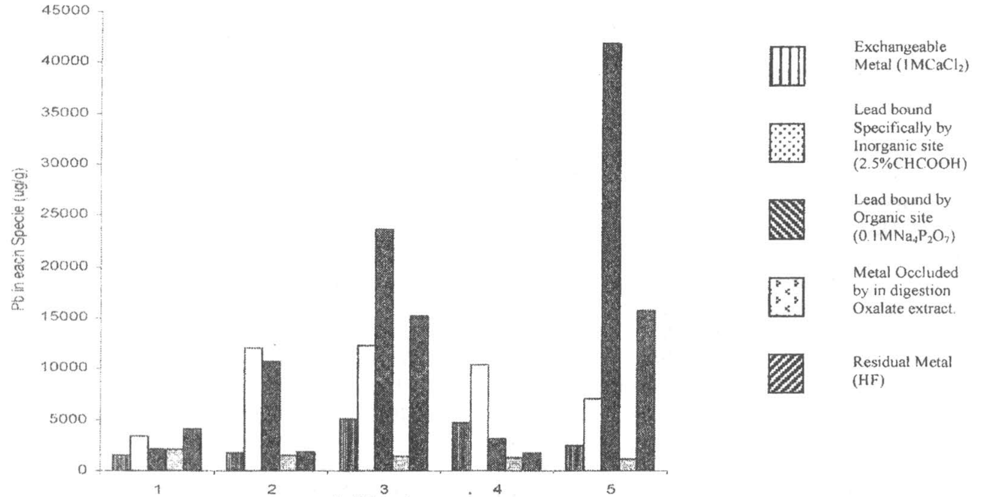

Fig1 : Concentration of Pb associated with the five species of the soil samples taken when in full operation

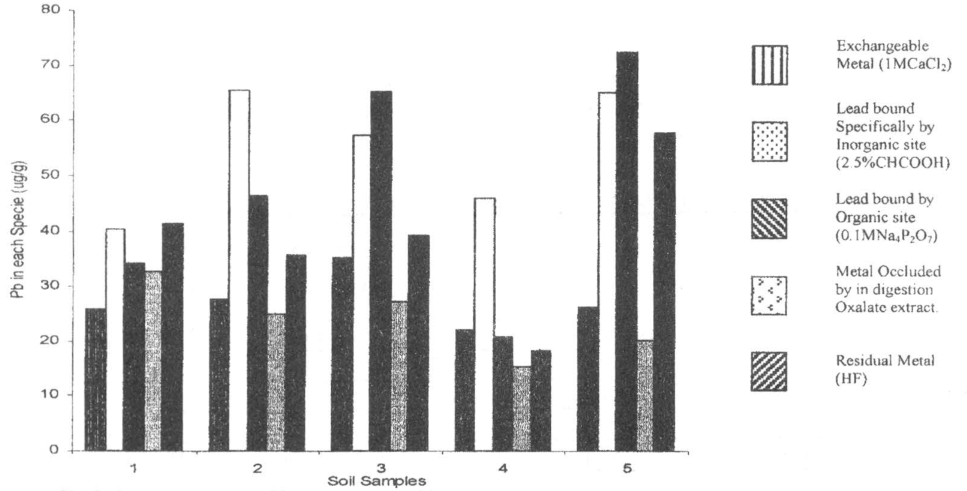

Fig 2: Concentration of Pb associated with the five species of the soil samples taken during the downtime of the factory

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