

TRANSPORT OF POLLUTANTS THROUGH THE WATER AND SUBSURFACE SOIL USING SIMULATED ACID RAIN.

By

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ABSTRACT

The mobility of heavy metals (Zn, Cd, Pb and Ni) was studied in the laboratory acidic leaching of two different soils around Ibadan with simulated acid rain. The sampling was carried out from two different sites viz: Orogun and Ilupeju respectively. For Orogun site a depth of 128cm was reached (consisting of four horizons). Different length of polyvinyl chloride (PVC) pipes were cut for different soil horizon depth as observed on the field. The PVC pipes were packed with requires masses of soil. This is then leached using simulated acid rain of different pH of 2.0, 4.0, 6.0 and 8.0 after spiking with known volume of standard solution of metals of interest. It was found that simulated acid rain enhanced the mobility of metals in solution. The pH, Cation Exchange Capacity, % clay and organic matter were found to contribute majorly to the mobility of metals. Generally as observed, the mobility of metal was observed to follow the order Zn>Ni>Pb>Cd as the soil is becoming more acidic.

INTRODUCTION

The release of wide range of toxic metals and metalloids into the environment is one of the most dangerous and pernicious pollution. Ever since the tragic deaths at Minamata in Japan due to Mercury poisoning (Hodges, 1977) environment pollution by heavy metals have received considerable attention in industrially developed countries.

Environmental pollution is one of the most serious problems facing humanity today. Air, water, and soil, which are necessary to the survival of all living things, are badly polluted. Badly polluted air can cause illness and even death. Polluted water kills fish and other marine life. Pollution of soil reduces the annual land available for growing food.

Pollution can be defined as the introduction by man into the environment of substance or energy liable to cause hazard to human health, harm to living sources and ecological sources, damage to structure and amenities or interference with legitimate use of the environment. It is the malfunctioning of environment as a result of human activities (Bolt et. al. 1976). These human activities ranges from soil salinisation as a result of irrigation practices to the use of mineral fertilizer on soil, discharge of industrial and household effluents, waste disposal, automobile exhaust, fume, gas flaying, metal mining and metal smelting etc.

Environment may be contaminated or polluted depending on the threshold tolerance level. Contamination should be used where anthropogenic inputs do not appear to cause obvious harmful effects and pollution applies to situation where toxicity has occurred.

Meanwhile, most earlier researches have concentrate on the study of plants macrpnutrients particularly Cu, Fe, Mn, Mo and Zn (Krauskopf, 1972) while interest in As, Be, Cd, Ni Pb, Cr and V as pollutant has only been recently been given attention. Whereas, direct

applicability of simulated acid rain to attenuation and migration of trace contaminants in soil has not been given serious consideration. Lindsay (1972) for example has examined the solubility of Mn, Zn, Cu, Mo and Be as a function of pH. Acid precipitation accelerates the migration of cation from terrestrial ecosystems and increase soil mineral weathering (Tyle, 1978; Singh *et. al.* 1980; Lec and Weber, 1982). The risk of depletion of nutrient pool was pointed out by Mayer and Ulrich (1977) as a result of acid rain.

The relative danger of pollution of soils with biochemically active elements increases as the texture of the soil become heavier and the coefficient of wetting decreases. The assessment of soils for pollution by chemicals should be done in relation to their mobility in the soil (Freiesleben *et. al.* 1986).

Most soils will become acidic if they are exposed for a sufficient length of time to rainwater. Acidification is a natural process and one of the processes of soil formation. Evidence of soil acidification is found in rocks formed million years ago in the carboniferous period. In recent years, however, pollutants in the atmosphere have increased the rate of acidification of soils and freshwater and there has been concern that this has caused the death of tress and fish. The acidifying effect of atmospheric pollutants is often described under the title "acid rain".

The term "acid rain" was first used in the nineteenth century to describe rain in the industrialized part of Northwest England that contained acid pollutants. The acids that give rise to the term "acid rain" were sulphuric, Nitric and hydrochloric acids. Their main source is the combustion of fossil fuels; of the three sulphuric and nitric acids are the most important. Deposition of acid atmospheric pollutants such as sulphuric and nitric acids accelerates the transportation of nutrient cation from terrestrial to aquatic systems and increases soil mineral weathering.

A Laboratory column experiment was performed by Hern *et. al.* (1988) on the effect of simulated acid rain on the CEC of two podzolic soils were leached with acid rain for two years. A small decrease in negative charge with increasing acidity of treatment was observed in the B horizon of both columns although the charge was significant at 9% confidence level for humoferric podzol.

Similarly, the sorption and mobility of Cd and Hg in two soils (sand and peat) were studied by Lodenius *et al.* (1989). Both. Both metals were sorbed strongly to the peat soil. The effect of four elements with different acidity (water, artificial acid rain of pH 5.4 and 3.6 and salt solution), Cd was released at low pH values. A strong leaching was observed after treatment with a neutral salt solution. Increasing acidity in the humus layer and Pb concentration reach up to 50-60 µg/L (Lamerdort 1989), because acidification increases their mobility in soil and allows leaching. Simulated acid rain at pH 3.5 induced leaching of metal ions including Cu, Zn, Mn, Ca, Mg and Cd (Linn and Eliot 1988) also similar correlation was obtained, concentration and fluxes of Mg, Ca Mn, zn and Cd in the soil were significantly increased by addition of acidified through fall water (Bergkvist 1986). The mobility of Zn, Mn, Cd and other trace metals has been reported to increase with soil acidity (Bjor and Teigen, 1980). Even mirror pH decreases have been shown to increase the leaching of Zn, Cd, Ni and Mn significantly for both metal and unpolluted soil layer (Tylor, 1978).

The importance of acidification on the mobility of pollutant cannot be over emphasised as shown in the studies of Berthelsen Bjoern (1994), the mobility of Zn and Cd were found to decrease with decreasing pH while Pb and Cu were not appreciably affected. The reduction in Zn and Cd ceased after termination of the acidification experiment.

Therefore, the objective of this study is to look into mobility (leaching) of pollutants (Pb, Zn, Cd and Ni) from the soil surface to the subsurface soil as to.

- i) Compare the relative mobilities of the above mentioned metals under deionised water leaching as control and simulated acid rain water leaching, and

- ii) Determine which soil properties and physiochemical parameter that controls their movement.

METHODOLOGY.

Materials and Methods

There are various steps in the determination of heavy metals in soils, which include:

- i) Sample location,
- ii) Sampling,
- iii) Sample preparation and pre-treatment
- iv) End determination methods and
- v) Quality assurance protocols

The specific details to be followed in each of these steps depend on the nature of the soil material and the objective of the analysis.

Sampling.

The purpose of analysis is to obtain the quality or composition of a material; and for the analytical results obtained to have any validity or meaning it is essential that adequate sampling is the process of extracting from a large quantity of material a small portion, which is truly representative of the composition of the whole material.

Sampling was carried out at two extreme locations in Ibadan, Oyo State, Nigeria. They are Ilupeju village, along Ibadan – Abeokuta road and Orogun area along old Ibadan Oyo road.

Soil pits dug at the sites to expose the soil profile for proper sampling. At Ilupeju area of Apata soil sample was collected from the topsoil of a depth of 1.5m consisting of four layers. Also at Orogun it consist of six layers and the depth of the pit was 1.54m down the earth. The soil samples were collected in polythene bags. After in necessary pre-treatment the soil was air dried for use in column experiments. The column length corresponds to the length of each soil layer.

Table 1a: Soil profile at Ilupeju (Area of Apata) Ibadan.

Horizon depth (cm)	Description
0 – 29	Loam contains much fibrous roots fine sand, absence of stone fragment clear smooth, regular structureless dark brown 10 yr 3/3 (moist).
29 – 70	Sandy clay, contains little fibrous roots, absence of sand stone, soft, angular, clear and smooth water logging, regular, structureless pale yellow 2-5 yr 7/4 (moist)
70 – 105	Coarse sandy clay, presence of aerial roots contains much gravels, water logging very pale brown 10 yr 3/3(moist)
105 – 150	Clay, blocky, with fair quartz stone, regular, absence of roots water logging, mud land, very sticky and plastic regular light grey 5 yr 7/4 (moist).

Table 2b: Soil Profile Pit at Orogun along old Oyo-Ibadan road.

Horizon depth (cm)	Description
0 – 16	Sand, loam structureless, contains much fibrous roots clear smooth loose and friable absence of stone and granular dark brown 10 yr 3/3(moist)
16 – 33	Sandy loam, few sand stone, contains fibrous root, but fewer than first layer, loose and friable and granular dark reddish brown 25 yr 2.5/3
33 – 48	Sany clay, few gravels, irregular presence of aerial root, few sand

	stones, sticky, yellow 10 yr 8/6 (moist)
48 – 67	Sandy clay contains much gravel, more sand stones, regular much aerial roots, sticky regular, yellowish red 5 yr 4/8(moist)
67 – 128	Sany clay, blocky much sand stone much gravel, few aerial roots sticky, regular yellowish 5 yr 5/8 (moist)
128 – 154	Standy clay blocky, few sand stone few gravels, less aerial roots, not much as above layers, sticky, regular, reddish yellow 5 yr 6/8 (moist).

LEACHING.

A clean PVC plastic was used to design columns. The pipe were designed according to the length of each soil layer; it was able to contain all soil samples up to their various heights in the field. The columns were than packed with various soil from different layer in different pipes, they were tapped gently to allow effective proper packing.

Each soil layer were than packed in accordance with field height. Each of the metal to be determined were added to the first soil layer and were subsequently leached by two types of transport materials, that is, water (control) and prepared simulated acid rain. The first layer from each site received 1000ml transport materials. The leachate obtained from the first was used as input for the second layer and so on till the last soil layer. A portion of leachates coming out of each layer was kept for subsequent analysis.

Part of the leachates from each layer were taken for analysis. The leachate were digested with 2MHNO_3 for two hours in order to remove interference due to organic complexation with the metals.

Duplicate analysis was carried out and each site was samples twice for analysis.

RESULTS AND DISCUSSION

Table 2a: Metal Residue analysis result for Orogun ($\mu\text{g/g}$)

Soil horizon	Cd	Ni	Pb	Zn
1	0.27	5.70	19.20	28.05
2	0.40	14.10	21.10	23.70
3	0.15	5.00	6.70	3.67
4	1.41	13.10	16.90	11.39
5	0.21	18.30	15.00	19.27

Table 2b: Metal Residue analysis result for Ilupeju ($\mu\text{g/g}$)

Soil horizon	Cd	Ni	Pb	Zn
1	0.43	3.80	6.00	5.55
2	0.39	3.50	28.90	38.30
3	0.43	3.8	4.20	44.20
4	0.62	5.0	4.30	44.50

Table 3a: Simulated Acid Rain Leaching result for Orogun Soil (μg)

Soil horizon	CONTROL COLUMN				SPIKE COLUMN				
	PH2	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1		34.432	304.64	474.88	773.12	212.096	471.68	411.52	1055.36
2		95.200	262.08	318.08	220.80	193.432	411.04	324.80	856.20
3		36.288	286.08	207.36	924.48	138.950	382.08	278.40	577.44
4		27.440	356.00	138.40	572.80	77.950	338.75	92.75	505.00

5	15.630	312.40	312.40	273.40	43.852	91.01	61.20	615.38
PH4	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	12.544	34.56	37.56	131.712	109.760	110.720	46.080	143.936
2	12.096	16.80	16.80	111.888	70.784	75.060	36.040	135.968
3	8.064	18.24	39.36	840.960	14.352	22.080	34.080	49.680
4	8.160	8.00	20.00	47.680	8.098	8.035	3.300	47.007
5	6.230	4.30	12.40	53.420	8.185	6.250	6.050	45.848
PH6	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	12.160	10.240	19.20	77.56	12.480	12.160	11.520	89.792
2	15.904	14.560	13.44	76.048	47.096	11.760	18.480	62.664
3	10.848	19.200	29.76	55.104	7.920	14.400	30.720	59.760
4	8.640	6.400	7.20	34.640	10.747	9.980	5.015	64.505
5	6.340	3.200	4.32	10.340	7.745	6.595	4.913	42.677
pH8	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	12.032	20.480	35.84	114.944	16.128	36.480	76.160	126.440
2	8.440	1.340	42.56	85.680	11.088	23.520	50.400	104.272
3	8.544	21.120	63.36	83.232	11.424	26.400	72.960	99.216
4	9.360	6.400	12.80	54.280	8.720	20.080	28.219	74.876
5	5.653	2.710	7.98	43.660	8.532	17.550	19.990	69.909

Table 3b: Simulated Acid Rain Leaching result for Ilupeju Soil (μ g)

Soil horizon	CONTROL COLUMN				SPIKE COLUMN			
pH2	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	110.40	226.40	392.00	86.80	130.80	482.40	86.80	807.01
2	107.20	192.50	352.00	80.00	115.08	425.60	80.00	788.10
pH4	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	26.40	7.68	15.36	16.64	61.60	28.01	16.64	143.50
2	25.90	6.68	20.16	30.24	28.70	8.96	30.24	136.01
pH6	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	23.20	12.80	8.94	107.10	26.40	22.40	51.52	238.00
2	16.60	11.01	6.40	92.30	26.10	14.08	28.00	236.00
pH8	Cd	Ni	Pb	Zn	Cd	Ni	Pb	Zn
1	21.60	15.68	33.28	198.60	26.40	17.92	34.72	242.90
2	20.17	16.80	30.24	176.40	25.90	11.52	34.56	181.60

LEACHATE ANALYSIS.

The data in tables' 3a and 3b represent the mean calculated metal concentration value for the whole study area (Orogun and Ilupeju) respectively. The experimental acidification (pH, 2, 4, 6 and 8) in this short-term study caused significant change in ion leaching through the soil. The behaviour of each layer as a function of pH is presented as follows:

The first horizon shows the highest retention for Cd > Pb > Ni > Zn at pH2.0 this shows

migration of Zn rapidly through the soil but more slowly for Cd. Since equal amount of these metal were used to spike at different pHs, high concentration of Zn was obtained from the leachate. This reflects the metal residue contribution. The migration of the metal decreases down the layer, which was enhanced by organic matter, CEC, and also, as the clay silt increases down the profile so also the adsorption.

The second horizon also at different pHs shows a significant migration change, in ions leaching. The trend was Zn > Ni > Pb > Cd at pH4.0 the order of migration was the same as in pH2.0, at pH6.0 Zn > Ni > Cd > Pb but at pH8.0 Zn > Pb > Ni > Cd. This layer still shows rapid migration for Zn and highest sorption for Pb and Cd.

The third, fourth and fifth horizon shows rapid migration trend in the order Zn > Ni > Pb > Cd throughout the whole pHs. Although the concentration of the metal decreases as we move from pH2.0 > pH4.0 > pH6.0 > pH 8.0 down the strata which correlates with most of the work recorded in the literature as observed at Orogun site table 3a.

For Ilupeju site the migration of the ions is as shown in figure 3b the order of migration at different pHs is as follows Zn > Ni > Cd > Pb. It shows that the least mobile ion here is Pb compared to Cd at Orogun site. This could be as a result of high clay and silt nature of Ilupeju and high percentage of Organic matter which might lead to organic - Pb complexing. Also the concentration of each ion decreases down the horizon with an increase pHs.

CONCLUSION.

The heavy metals (Zn, Ni, Pb and Cd) were generally more mobile in the simulated acid rain than in the deionised water. In the areas under study it was found that out of the four mobile of them all was Cd this may be due to the effect of Ca^{2+} in the leachate, which was used for adjustment of the pH. The tendency of Ca^{2+} replacing Cd^{2+} on the exchangeable site of the soil was predicted (Carallaro and McBride, 1980).

In the simulated acid rain leaching for both Orogun and Ilupeju, there is a rapid decrease in the migration of metals in the leachate from pH2.0 through pH 8.0, although the effect was less observed between pH4.0 to pH8.0 compared to between pH2.0 and pH 4.0 which might be due to buffering capacity of the soil at these pHs and precipitation of this metal.

Generally, an increase in acidity of soil increased the mobility of metals in the soil and it decrease down the strata. At low pH, it was found to increase the leaching of Zn, Ni, Pb and Cd in that order. This trend correlated, with the reports of. Esser and El Bassam (1981) Brummer and Herms (1983) Scokart *et. al.* (1983); and Bjor and Tugan (1980) even significantly from both metal polluted and unpolluted moor layer by Tyler (1973)

Therefore, the relative motilities of elements through the soil are quite variable. However, it should be possible to qualitatively predict the migration of an element through a soil on the basis of the soil's physical and chemical properties. Since pH correlates positively with adsorption in the soil, and factor that would tend to increase pH would improve the migration of metals in the soil, such as organic matter and CEC, etc.

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