

EVALUATION OF SOME METALS IN THE INDUSTRIAL WASTES FROM A PAINT INDUSTRY AND THEIR ENVIRONMENTAL POLLUTION IMPLICATIONS

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Abstract: The effluent and sludge samples as well as their precipitates from Peacock Paint Industry in Etinan were analysed for the presence and concentrations of five metals, namely Zn, Pb, Cd, Cu and Cr using Atomic Absorption spectrophotometer (Pye Unicam, Model SP—9, 1981). Also analysed for the same metals were soil samples in the immediate environment which received the effluent and sludge wastes from the factory. The results obtained showed very high concentrations of the five metals in the precipitates and soils receiving paint wastes compared with those in the effluent and sludge samples. Correlation coefficients of metals between pairs of samples were also computed and used to establish any relationship existing between the metals in the different samples. The data obtained from the four sets of samples (effluent, sludge, precipitate and soil) are compared with data obtained from analysis of typical background soil samples. The pollution implication of these metals are also discussed based on the background values, international standards and previous findings.

Introduction

Environmental pollution may result from industrial and commercial activities when substances resulting from these activities enter the environment and attain levels which may cause discomfort and/or harm to man and his environment. The pollution of these environments has been found to result from man's determination to match desire with production through the establishment of various industries with potentials to pollute the environments Udosen, *et al.* 1987. Industry, big or small, is a source of pollution of land, water and air. According to Vagale (1983), industrial pollution may result from noise, dust, gaseous, liquid and soil wastes as well as heat, and vibration.

Paint wastes are always in the form of effluent and sludge and according to Moriber (1974), in the case of the sludge, one is no longer faced with a water pollution problem but a solid waste disposal situation. However, leaching may result in the contamination of the soil and underground water with toxic and hazardous materials notably heavy metals. The waste-water from the paint industry often arises from rinsing of mixing tanks, filling equipment, cleaning of floor and spill as well as plant sinks (Dawson, 1979). The Peacock Paint Industry at Etinan (Akwa Ibom State) produces two classes of paints, namely, the water-based and solvent-based paints. The manufacturing waste-water from these two types of paints may contain substantial quantities of hazardous substances arising from the raw materials for the manufacturing process particularly pigments which are generally rich in heavy metals such as Pb, Zn, Cd, Cr and Cu.

There has been a general tendency of irresponsible waste disposal by industrial establishments in Nigeria. Ajai and Osibanjo (1981), Martins (1978), and Jegede (1977) amongst others have observed that most industries still choose the cheapest which are not necessarily adequate disposal methods. According to Martins (1978), at least six factories in Iganu and Apapa threw solid wastes carelessly about their premises. The situation may not be different in Akwa Ibom State as most of the few industries lack adequate waste disposal facilities. For instance, the Peacock Paint Industry in Etinan located far away from the Qua Iboe River (Fig. 1), discharges its waste into an artificial valley, a few metres away from the factory building.

The effects of heavy metals on industrial wastes have been elaborately investigated by Martin, *et al.* (1982). According to them, environmental contamination by heavy metals such as Cd, Pb, Zn, and Cu has aroused great concern in the last decade because these metals can constitute a hazard to man and other organisms when accumulated within the biological system. According to Ibok, *et al.* (1989), the most affected of these biological systems are the natural waters which often receive industrial effluents replete with metals such as Hg, Zn, Co, Sb, Cd, Pb and Cr into our environments. Writing on water quality surveillance and treatment, Oni (1987) asserted that the effect of dumping industrial wastes on land filled sites has been found in shallow wells and in later years in deep wells. Goldsmith and Hildyard (1988) contended that lead in paint, particularly the older high-lead varieties has caused numerous fatalities including death.

Table 1: Ranges and Mean Concentrations of Metals in samples. Ranges are in parenthesis (ppm).

Metals	Effluent	Sludge	Precipitate	Soil Receiving paint wastes	Background soil
Zn	4.35 (2.90-6.00)	0.48 (0.24-0.85)	325.68 (81.16-530.88)	189.04 (125-237.16)	85.46 (80-91.28)
Pb	1.06 (0.91-2.00)	0.35 (0.31-0.40)	219.04 (81.48-480.48)	126.05 (10-295.68)	5.64 (5.00-6.16)
Cd	0.17 (0.00-0.34)	0.39 (0.31-0.47)	16.11 (3.14-25.12)	10.15 (3.00-25.12)	2.55 (2.00-3.14)
Cu	0.29 (0.06-0.50)	0.04 (0.00-0.06)	37.58 (3.78-71.82)	39.74 (81.25-70.56)	25.59 (25-26.50)
Cr	0.48 (0.00-1.00)	3.55 (0.71-7.14)	39.87 (19.60-71.40)	69.83 (30.10-128.52)	26.53 (25-28.56)

Table 2: Pearson Correlation Coefficient (r) for the Paint effluents and Precipitate Samples

	Zn	Pb	Cd	Cu	Cr
<i>Paint Effluent</i>					
Zn	1.00	0.66	-0.02	0.61	-0.05
Pb		1.00	0.44	0.84	-0.12
Cd			1.00	0.25	0.17
Cu				1.00	-0.47
Cr					1.00
<i>Precipitates</i>					
Zn	0.32	0.29	-0.12	-0.09	0.31
Pb		0.39	0.48	0.52	0.37
Cd			-0.08	-0.005	0.001
Cu				0.17	-0.10
Cr					0.70

Table 3: Pearson Correlation coefficient (r) for the Paint Effluents and Soils Receiving Paint Wastes.

	Zn	Pb	Cd	Cu	Cr
<i>Paint Effluents</i>					
Zn	1.00	0.66	-0.02	0.61	-0.05
Pb		1.00	0.44	0.84	-0.12
Cd			1.00	0.25	0.17
Cu				1.00	-0.47
Cr					1.00
<i>Soils Receiving Paint Wastes</i>					
Zn	0.31	0.33	0.40	0.37	0.28
Pb		0.40	0.36	0.40	0.35
Cd			-0.07	-0.16	-0.07
Cu				0.03	-0.05
Cr					0.56

Apparently systematic environmental pollution monitoring for the paint industry has not been reported inspite of a serious need for it. There is therefore a justification for the present work to find out levels of heavy metals (Zn, Pb, Cd, Cu and Cr) in the soils (of the artificial valley) into which the paint wastes are discharged especially as villagers still carry out farming there.

Materials and Methods

Sampling was carried out within and outside the factory building at designated points. Samples collected included factory effluents and sludges as well as precipitate and soil samples. Altogether three sampling points were selected: 2 tanks located inside and outside the factory building respectively and the artificial valley (which receives the factory wastes).

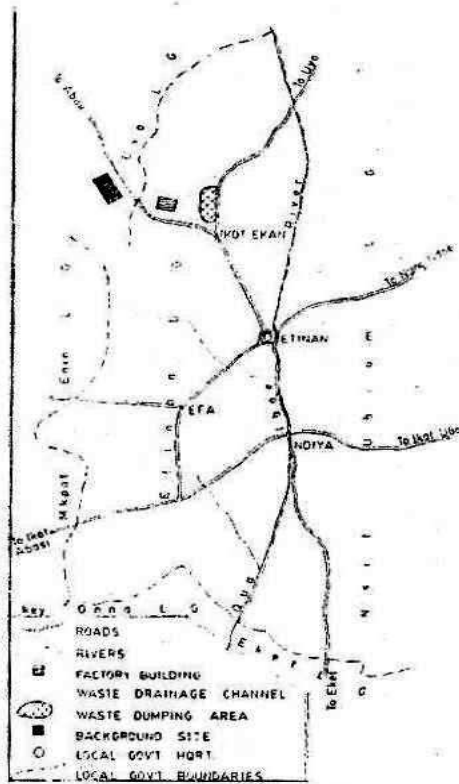


Fig. 1: Map of the study area showing sampling locations.

Similarly, soil samples were collected about 500 metres west of the factory premises to provide baseline information (Fig. 1). All sampling were carried out fortnightly for 5 months between August 1988 and December, 1988.

Effluent and sludge samples from the production units (Fig. 2) were collected from two tanks located within and outside the factory building using 200cm³ pre-washed and rinsed polythene bottles (Hanson, 1973; Reeves and Brooks, 1978). Samples from these two tanks were then mixed and homogenised.

The collection of precipitate samples was carried out within the valley using a plastic trowel since the samples were surface deposits. Samples were collected at about 10 metres interval from the point of effluent and sludge discharge which is about 50 metres away from the factory building. Ten precipitate samples corresponding to the sampling points were collected in calico cloth bags.

For the collection of soil samples within the valley (about 200 metres long, east of the factory house), triangular grids were constructed. The same was true for the background soil samples. Ten triangular grids were mapped out in the valley and background sites and samples collected within these grids were mixed, homogenised and put into calico cloth bags. Soil samples were collected at the depth of 20cm (Ward, *et al*, 1974).

Immediately after collection, samples were transferred to the laboratory for pre-treatment and analysis. The effluent and sludge samples (about 50

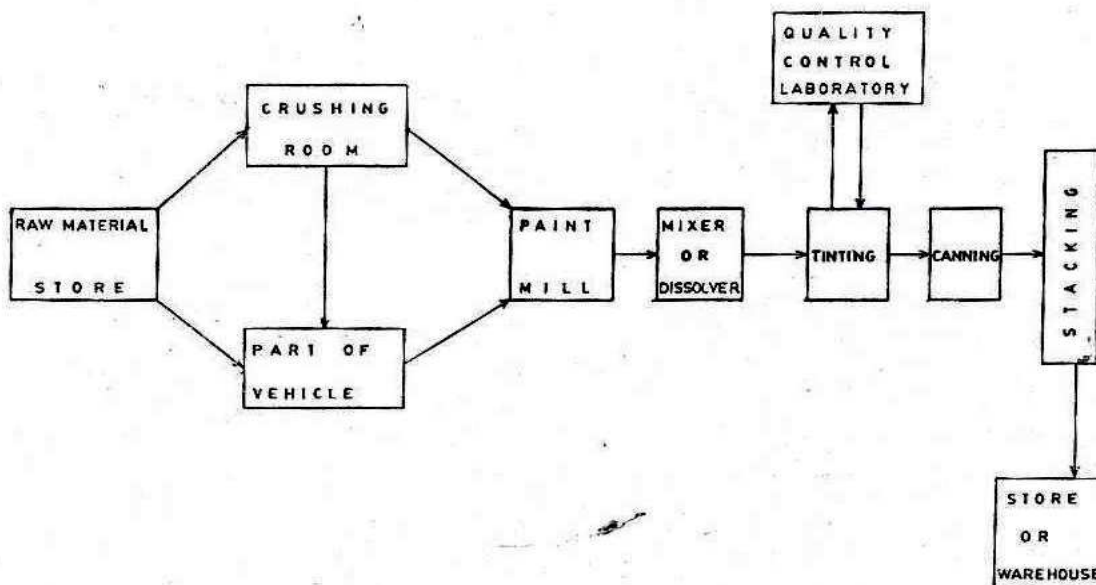


Fig. 2: A flowsheet of major production line in Peacock Paint Industry.

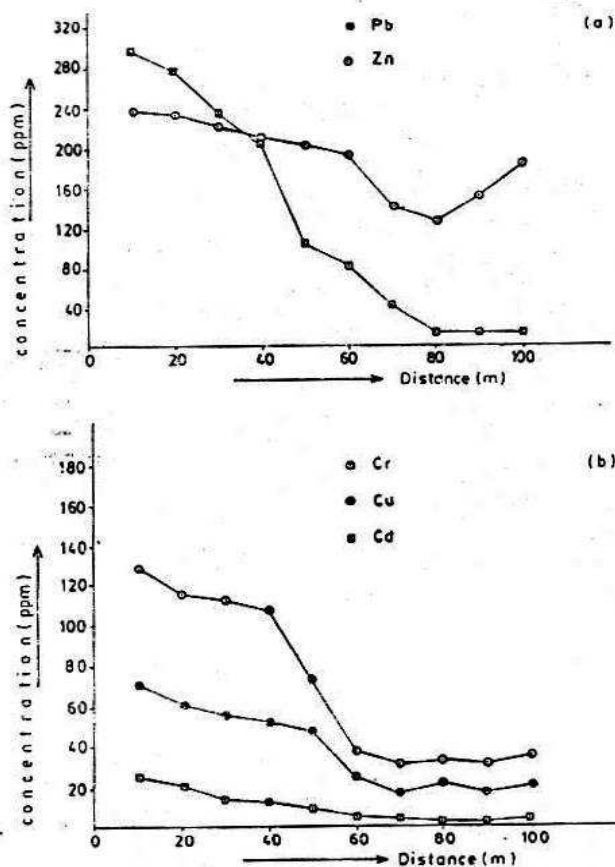


Fig. 3 (a) Variation in concentrations of Pb and Zn in soil receiving paint waste.
(b) Variation in concentrations of Cr, Cu and Cd in soil receiving paint waste.

cm³) were transferred to an evaporating dish and evaporated on a steam bath to about 20 cm³. 8M HNO₃ (12 cm³) was then added and evaporated on a hot plate to near dryness in each case. The residue was quantitatively transferred using two aliquots of 10 and 15 cm³ of HNO₃ into a 250 cm³ conical flask. HClO₄ (20 cm³) was added and boiled until the solution became clear and white fumes of HClO₄ appeared. It was then cooled, and deionised water (about 50 cm³) was added and the solution filtered (AWWA, 1980). The filtrate was quantitatively transferred to a 100 cm³ volumetric flask with two portions of water (5 cm³). The solution was diluted to the mark and mixed thoroughly. Portions of this solution were taken and used for the estimation of the required metal using Atomic Absorption spectrophotometer (Pye Unicam, Model Sp-9, 1981).

In the case of the precipitate and soil samples, air-drying and later, oven-drying at a temperature of 105°C for 6 hours was effected. Drying was carried out to eliminate organic matter among other unde-

sirable materials. After this, the samples were disaggregated using mortar and sieved with a 20 mesh screen. Each sample (about 5.0g) was placed in a teflon beaker and 4MNO₃ (10 cm³) and analar H₂O₂ (20 cm³) were gradually added to aid further oxidation of any organic matter (AWWA, 1980). The solution was then left to digest under reflux on a hot sand bath. After refluxing for 1 hour (Whiteside, 1979), the samples were removed and transferred to an evaporating dish and left to evaporate to dryness at a temperature of 120°C on a hot plate. The samples were finally removed and leached with 6M HCl (5 cm³) and made up to 10 cm³ mark in a standard volumetric flask with deionised water. Solutions of the samples were taken and aspirated into Atomic Absorption Spectrophotometer and the absorbances obtained from the automatic printout in the instrument were used in calculating the concentrations of the metals in the different samples.

Results and Discussion

The ranges and mean concentrations of the five metals Zn, Pb, Cd, Cu and Cr in all the five samples are summarised in Table 1. The ranges for all the metals are generally low in the effluent, sludge and background samples but remarkably higher in the precipitates and soils receiving paint wastes. The mean concentrations for Cd, Cu and Cr are very low (0.5 ppm) in effluent samples compared with Zn and Pb. In the corresponding sludge samples, the concentrations of the metals except Cr are equally low, Cu being significantly much lower (Table 1). A comparison of the concentrations of these metals in the effluent and sludge samples shows them to be higher in the former for Pb, Zn and Cu; and lower for Cd, and Cr; a situation which may have arisen from the fact that the solid sludges are probably removed and dumped in a ravine in Uyo.

Variations over space of the concentrations of Zn, Pb, Cd, Cu and Cr in the soils of the valley receiving the paint wastes are shown in Fig. 2 (a, b). Zn and Pb concentrations in these soils appear to follow a similar distribution pattern (Fig. 2a). However, Pb metal appears to be more absorbed by the soil than Zn at the same point as evidenced by the sharp reduction in the concentration of Pb as the distance increases against that of Zn (Fig. 2a). On the other hand Cd, Cu, and Cr show a different distribution pattern. Cu concentrations tend to fluctuate more with distance from the point of discharge of the wastes (Fig. 2b).

A more significant result was obtained by the calculation of correlation coefficients of metal concentrations between pairs of samples of interest under investigation notably effluent/precipitate samples and effluent/soils receiving paint wastes.

The results are presented in Tables 2 and 3. Based on the results and the correlation coefficients, the pollution implications of the metals are discussed.

Zinc

There is a clear correlation pattern for zinc with the other metals in paint effluent. For instance, Zn shows a somewhat high positive correlation with Pb and Cu but a negative correlation with Cd and Cr in the effluent samples, while in the precipitate samples there is no inter-element correlation of any kind. This presupposes a loss of these metals through evaporation since the effluent, particularly of the gloss paint is highly volatile. It also suggests an increase in concentration of metals in the precipitate samples. There is also no positive correlation between the concentration of Zn in the effluent and that in the precipitate. However with time and as the manufacturing of paint and subsequent discharge of wastes into the valley continue the correlation may become significant.

Zn, although useful as a metabolic antagonist of metals such as Cu, Fe and Cd has also been known to induce vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea, lethargy, dizziness and lack of muscular co-ordination in man when taken in excess (W.H.O. 1984). The metal should therefore not be introduced into the environment indiscriminately. Zinc found in the samples analysed may have come from paint pigments such as Zinc Chromate ($ZnCrO_4$) and Zinc oxide (ZnO) in addition to natural occurrence, and since soil is the ultimate sink for Zn and other metals such as Cd, Pb and Cu (Martin, *et al*, 1982), the retention of this metal in the soil may likely have a long term pollution consequence. However, if solid organic matter such as the Lumic acid in humus containing functional groups such as $-COOH$, $-OH$ and $>C=O$ is present, Zn complexes with it and this reduces the concentration of Zn in the soil solution (Bohn, *et al* 1979; Greenland & Hayes, 1981). On the whole Zn in this environment is not yet considered a hazard since the mean concentration in almost all the samples are below the natural level (1–300 ppm), (Levinson, 1974; and Bohn, *et al*, 1979).

Lead

There is a high positive correlation of this metal with Cu in the effluent sample ($r = 0.84$) compared with that in the corresponding precipitate sample ($r = 0.52$), (Table 2). Although the correlation of this metal with Cd in the two samples are not very significant, yet the values are worthy of note. The correlation coefficient for lead in the two samples is low. Lead occurs naturally as a minor constituent of soil and plant even in areas of no industrial activity to the extent that analysis of any soil or plant often shows

evidence of its presence. In our study the mean concentration of Pb in the background sample was 5.64 ppm while the mean lead concentration in the corresponding samples of soil receiving paint wastes, was 126.05 ppm. The remarkable difference which exists between lead concentration in these two sets of samples may be attributable to the pb present in the paint wastes which must have resulted from the use of pigments containing lead e.g. Lead Chromate ($PbCrO_4$), Lead Sulphate ($PbSO_4$), white Lead [$PbCO \cdot Pb(OH)_2$], red Lead (Pb_3O_4), or from the use of Lead additives. When compared with background value (5.64 ppm) and the natural level in the soil (2–200 ppm), (Bohn, *et al*, 1979), mean concentrations of 219.04 ppm in the precipitate samples and 126.05 ppm in soils receiving paint wastes are high. Since pb has been known to be a cumulative, toxic metal capable of inducing abdominal pains, vomiting, drowsiness or paralysis, convulsion, dysfunction in kidneys, reproductive system, Liver, the brain and central nervous system (Goldsmith and Hildyard, 1988), then there should be a check on the discharge of any pb-laden waste into the environment. However, in order to completely establish the pollution potential of Lead in this environment, other parameters such as pH, alkalinity and acidity should be determined. There are however no reports of injurious effects of lead on vegetation nor is lead taken up by plants from the soil (Treshow, 1978).

Cadmium

There is no significant correlation between Cadmium and any other metal although the correlation coefficients between Cd and pb in the effluent and precipitate samples are appreciable. The inter-element correlation between Cd and Cu and between Cd and Cr is not very significant. There is also no correlation between Cd in the effluent precipitate samples.

Cadmium may occur in the soil, not only through industrial processes but also through the application of fertilizers containing Cd. According to Voogt *et al*, (1980), unlike most other heavy metals, Cd can be taken up by several plants such as wheat, maize, rice, spinach or tobacco. It is capable of accumulating in food chains and the accumulation depends on certain factors such as low pH and high temperature. Secondly Cd uptake is irreversible and its excretion only occurs very slowly. Above all, although Cd is very hazardous and of no use to biological systems, it often enters many chemical and biological processes such as photosynthesis and translocation through repeated application of certain phosphatic fertilizers (Williams and David, 1973; Korte, 1983).

The presence of Cd in the samples analysed is suspected to be from the use of pigments containing Cd such as Cdse as well as from superphosphate fer-

tilizers since natural occurrence is rare (W.H.O., 1984). Korte (1983), gives the background level of Cd in the soil as 0.01–1.0 ppm, while the nature level is 0.01–7.0 ppm (Bohn, *et al*, 1979). Therefore, a concentration of up to 10.15 ppm recorded in the study suggests a possible Cd pollution when compared to the background value of 2.55 ppm. This deduction is made based on reports by Voogt *et al*, (1980), which showed that itai-itai disease resulted from consumption of rice containing between 0.45–4.0 ppm Cd whereas the soil contained 2–3 ppm. Secondly Cd_2^+ is relatively soluble and capable of being retained in the soil at any pH (Bohn, *et al*, 1979).

Copper

Copper shows high correlation with Zn and pb in paint effluent ($p < 0.10$ and $p < 0.01$) respectively but moderately high correlation with pb only in the precipitate samples. There is no significant correlation between Cu in effluent and the precipitate samples.

Copper sometimes occurs naturally and is also found in living organisms. It is sometimes a component of paint pigment such as phthalocyanine blue [$Cu(C_8H_7N_2)_4$] and its presence in the environment is risky since all copper salts are poisonous (Burser and Efimov, 1984). Although all copper salts are said to be poisonous, yet copper is an essential element in human metabolism and has a powerful emetic action. However, intake of excessively large doses by man leads to severe mucosal irritation and corrosion, widespread capillary damage and central nervous system irritation followed by depression. Severe gastroin testinal irritation and possible necrotic changes in the liver and kidney could also occur (WHO, 1984). Since copper and its compounds are naturally ubiquitous in the environment, addition of more copper into the environment may not be desirable. The copper levels in the samples including the soils receiving paint wastes could not be said to be high when compared with the level of this metal in the background soils (25.59 ppm) and the natural occurrence in soils (2–100 ppm).

Chromium

Chromium exhibits a more fluctuating trend with respect to its correlation coefficients between metals within the samples and its inter-element relationship. However there is a high correlation between Chromium in the effluent and Chromium in the precipitate samples (Table 2).

One of the major sources of Cr is industrial discharge although contamination occasionally arises from the use of sewage sludge when added to land. Of the two major forms of Cr, the hexavalent Cr is toxic while the trivalent form is essential for human

beings although it is usually poorly absorbed (Hale, 1977). The high Cr content in the soils receiving paint wastes may be due to Cr present in the paint pigments such as Lead or Zinc chromate, basic lead chromate or Chromic Oxide. Since hexavalent Cr at 10 mg/kg of body weight will result in liver necrosis, nephritis and death (W.H.O, 1984), the discharge of Cr-laden wastes into the environment should be checked. A glance at the mean concentrations of Cr in the precipitates and soils receiving paint wastes reveals a pollutional trend compared with the background (Table 1).

In the case of paint effluent and soils receiving paint wastes there is some correlation between Zn, Pb, Cd, Cu and Cr in the paint effluent and the soils receiving paint wastes, although that of Cr is much less significant than the rest (Table 3). Similarly there is a marked inter-element relationship between Zn and other elements in the soils receiving paint wastes. There is still a high correlation between concentration of Cr in effluent and that in the soils receiving paint wastes.

Conclusion and Recommendation

From the above results on the distribution of metals in the different samples, it is clear that whereas certain metals tend to be associated with one another, others do not. The probability of contamination of the soils by these metals arises from the fact that Cu^{2+} and Zn^{2+} ions are known to be more soluble in aerobic soils than other transition metals and their availability increases with soil acidity (Bohn, *et al*, 1979). On the other hand Cd^{2+} is relatively soluble and usually available to plants with high retention capability — relatively independent of pH. Pb^{2+} is usually less available to plants especially if the pH is high while little is known about the Chemistry of CrO_4^{2-} in soils and according to Bohn *et al* (1979), the ranges of metal concentrations that have been considered toxic are Cd (0.01–7.0 ppm); Cu (2–100 ppm); Pb (2–200 ppm); Zn (10–300 ppm); and Cr (5–1000 ppm) in total soil. Also according to Greenland and Hayes (1981), analyses of 42 sewage sludges from England and Wales gave the following ranges in concentrations of the five metals in ppm of dry matter: Cd (60–1500); Cr (40–8800); Cu (200–8000); Pb (120–3000); and Zn (700–49,000). These results show that concentrations of the metals depend on the types and sources of samples. Since nature has not been able to degrade some of these heavy metals, they often bioaccumulate and become concentrated along the trophic level.

In this investigation the levels of metal in the samples (Table 1) follow the following sequence below:

- Zn: precipitate \gg soil receiving wastes $>$ background soil \gg effluent $>$ sludge.
 Pb: precipitate \gg soil receiving wastes $>$ background soil \gg effluent $>$ sludge.
 Cd: precipitate $>$ soil receiving wastes $>$ background soil $>$ sludge $>$ effluent.
 Cu: Soil receiving wastes $>$ precipitate $>$ background soil $>$ sludge $>$ effluent.
 Cr: Soil receiving wastes $>$ precipitate $>$ background soil $>$ sludge $>$ effluent.

The above summary shows that most of the metals were concentrated in the precipitates and soils receiving the industrial wastes compared with the concentration of these metals in the background soils (Fig. 5). There is therefore the need to treat the paint wastes before discharge into the environment. Alternatively, the paint wastes could be recycled to recover some useful materials and water for other industrial processes rather than dumping them into a ravine from where neighbouring inhabitants get their water when taps in the town are dry.

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