LEVELS OF Mn, Fe, Ni, Cu, Zn AND Cd, IN EFFLUENT FROM A SEWAGE TREATMENT OXIDATION POND AND A RECEIVING STREAM- A PRELIMINARY STUDY

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Abstract

This study reports the results of preliminary investigation of heavy metal levels-Ni, Cd, Fe, Zn, Cu and Mn; pH; temperature and electrical conductivity in effluents from a sewage treatment oxidation pond and its receiving stream.

The heavy metal concentrations were determined with Inductively Coupled Plasma-Mass Spectrometry (ICP–MS). The overall mean levels of Ni, Cd, Zn, Cu, Fe and Mn were 1.92 ± 0.66 µg/L, 11.99 ± 3.45 µg/L, 0.43 ± 0.32 mg/L, 0.18 ± 0.08 mg/L, 7.26 ± 1.32 mg/L and 0.43 ± 0.26 mg/L in the effluent samples and 1.64 ± 0.55 µg/L, 4.74 ± 3.73 µg/L, 0.19 ± 0.01 mg/L, 0.13 ± 0.07 mg/L, 4.34 ± 1.00 mg/L and 0.24 ± 0.24 mg/L in the receiving stream respectively. Thus, higher levels of these metals were generally found in the effluent samples compared with the reference sample and the receiving stream. The discharge of effluents from the sewage treatment oxidation pond into the receiving stream is therefore a major source of heavy metal pollution of the stream apart from diffuse and natural sources of these metals.

The mean levels of Cd, Fe and Mn obtained for the receiving stream exceeded the WHO guideline criteria of 3.0 µg/L, 1.0 mg/L and 0.5 mg/L respectively for drinking water, while the mean levels of Zn and Mn in the receiving stream exceeded the WHO guideline criteria of 20 µg/L and 0.18 mg/L respectively for protection of aquatic ecosystem.

Although, the overall mean temperature values of 26.8 ± 0.52 °C obtained for the receiving stream is normal, the pH levels fall below the WHO range of 7.0-8.5 for drinking water.

The pH and heavy metal concentrations of the effluents indicate their potential environmental hazard on the general ecology of the receiving stream. This calls for proper management of the effluent from the oxidation pond prior to its discharge into the receiving stream.

Keywords: Heavy metals, oxidation pond, effluent, influent, receiving stream

1. Introduction

Pollution is caused when a change in the physical, chemical or biological condition in the environment harmfully affects the quality of human life including effect on other animals' life and plants (Lowel and Thompson, 1992 and Okoye *et al.*, 2002).

Water and soil pollution by heavy metals has become a question of considerable public and scientific concern in the light of evidence of their extreme toxicity to human health and to biological ecosystems (Katsuro *et al.*, 2004). The occurrence of heavy metals in industrial and municipal sewage effluents constitute a major source of the heavy metals entering aquatic media. Hence there should be regular assessment of these sewage effluents to ensure that adequate measures are taken to reduce pollution level to the very minimum. Contamination of the environment by heavy metals is viewed as an international problem because of the effects on the ecosystem in most countries. In Nigeria, the situation is no better by the activities of most industries and populace towards waste disposal and management which usually leads to the increasing

level of pollution of the environment. Sewage discharge is a major component of water pollution, which is compounded in areas where wastewater treatments are inefficient. Such is the case of the Obafemi Awolowo University sewage treatment oxidation ponds, which were constructed as aerobic/anaerobic sewage treatment plant. This allows natural treatment of sewage without added chemicals hence inadequate removal of contaminant in the wastewater before it is finally discharged into the receiving stream.

Electrical conductivity (EC) is a useful indicator of the mineralisation in a water sample. The effects of high EC may include disturbances of salt and water balance and high salt concentrations in waste effluents; however, it can increase the salinity of the receiving water, which may result in adverse ecological effects on aquatic biota (Fried, 1991). Some of the adverse ecological effects of high salt concentrations include heart problem, high blood pressure and renal disease (DWAF, 1998).

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Temperatures at which samples are collected and at which physico-chemical measurements are made are important for data correlation and interpretation purposes. High temperature may increase the toxicity of many substances such as heavy metals in waters for domestic use (Fatoki and Awofolu, 2003).

The pH of a water body determines the chemical species of many metals and thereby alters their availability and toxicity in aquatic environment (DWAF, 1990). Metals like Cd and Zn are most likely to have increased detrimental environmental effects as a result of lowered pH (Fatoki and Awofolu, 2003 and DWAF, 1990). In addition to microbial activities within an aquatic medium, temperature and pH are two important factors that govern the methylation of elements such as Pb and Hg (Van loon, 1982 and Dojlildo and Best, 1993).

Metals like Zn, Cu, Fe and Cd are common pollutants, which are widely distributed, in aquatic environment. Their sources are mainly from atmospheric deposition (Merian, 1991); industrial effluents Asami, 1974 and Prater, 1975); domestic effluents (Dean et al., 1972 and Preuss and Kollmann, 1974); urban storm water run off (Sartor et al., 1974 and Filed and Larger, 1975) and spoil heaps (Heitfeld and Schottler, 1973 and Fatoki and Mathabatah 2001).

Zn and Cu are required for metabolic activities but at high concentrations they can constitute nuisance to the natural environment and its inhabitants. Copper is one of several metals that is essential to life (Scheinberg, 1991). Plant and animals rapidly accumulate it. Cd has been found to be toxic to fish and other aquatic organisms (Woodworth and Pascoe, 1982). Toxicity effect of Cd in man includes Kidney damage (Herber, 1988) and pain bones (Kjellstoem, 1986). The mutagenic, carcinogenic and teratogenic effects of cadmium have also been reported in the literature (Heinrich, 1988; Friberg et al., 1896 and Fischer, 1987).

This paper reports the results of monitoring of Fe, Cd, Zn, Cu, Mn and Ni as well as pH. Temperature and Electrical conductivity in the sewage treatment oxidation pond of the Obafemi Awolowo University, Ile-Ife, Nigeria and its receiving stream. This receiving stream serves as a source of water to some communities downstream which is used for a variety of purposes like irrigation, drinking and other domestic uses without prior treatment. The present preliminary study on the metals is significant in that some of these metals at large doses may prove lethal to aquatic flora, fauna and ultimately humans who are usually at the top of the food chain. The receiving stream serves as a 'convenient' means of cleaning the highly loaded sewage lagoon and carries wastes away from its discharge point. The need to know the quality of the water from the receiving stream has informed this study. The study will also provide information on the performance efficiency of the sewage lagoon.

2. Materials and Methods

(a) Study area and sampling points

The Obafemi Awolowo University Campus has two sewage treatment oxidation ponds X and Y (Figure 1) for the treatment of the domestic sewage generated from the University community. Sewage and wastewater are collected and channeled through sewers into the two alternately operated oxidation pond for treatment. The wastewater is allowed about two weeks detention time after which effluent from the pond is charged into the receiving stream. There is no form of activated sludge operation and the ponds are not artificially aerated although some anaerobic digestive process may operate due to activities of algae, bacteria and other microorganism. Pond Y was operational during the period of this study; hence samples were collected from the pond, its influent and effluent as well as the receiving stream.

The sample locations from the influent and effluent of the sewage treatment plant and the receiving stream are as shown in Fig. 1. The sampling sites were chosen to reflect the impact of contamination or pollution from the sewage treatment plant on the receiving stream in order to predict the likely effects on aquatic biota and consequently health effect on people that depend on the water from either the receiving stream or the adjoining Opa River.

The sampling sites have been designated S1 to S8; S1 to S4 are sites for influent and effluent of the sewage treatment plant while S5 is the merging point of the effluent and the receiving stream; S6, S7 and S8 were located downstream at 20 m, 100 m and 350 m respectively. SR represents the reference point, located about 30 m upstream before discharge of the effluent into the stream and serves as control. Samples were collected at strategic points from the study area (as shown in Fig. 1) for a period of six months from January, 2003 to June, 2003.

(b) Sample Collection

Wastewater and fresh water samples were collected in polythene containers previously cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 72 hours before finally rinsing with deionized water prior to usage. During sampling, sample bottles were rinsed with the sample several times before they were finally filled with the sample. Samples for metal analyses were preserved with 5 mL concentrated HNO_3. The samples were then kept at about 4 °C prior to analysis (Fatoki and Awofolu, 2003).

(c) Determination of Temperature, pH and Electrical Conductivity

Temperature, pH and Electrical Conductivity were determined in un-acidified water samples.
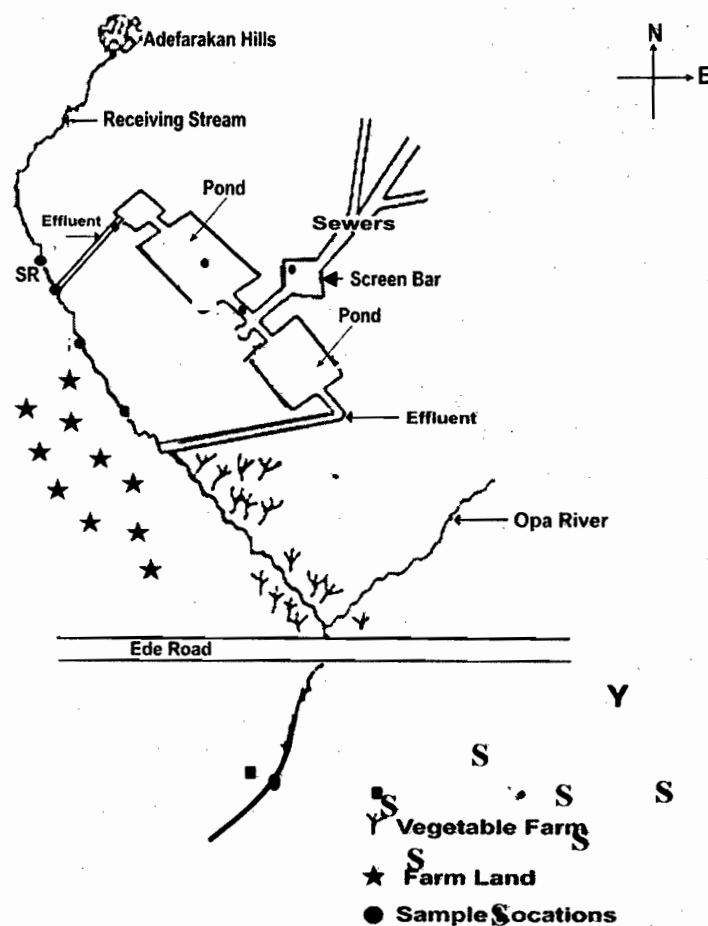
Fig. 1: A sketch diagram of the study area

Temperature was taken on site using mercury in glass thermometer with 0.1 °C graduations. pH values were measured with a digital pH meter model H18519 (Hanna Instrument), which was periodically calibrated using buffers of pH 4 and 10, while electrical conductivity (EC) of samples was measured using a METTLER TOLEDO MC 126 conductivity meter. This instrument was calibrated with METTLER TOLEDO conductivity standard of value 1413 mS/cm at 25 °C and operated as per the instrument manual.

(d) Sample Preparation for heavy metal determination

The water samples were digested by the open beaker digestion method using nitric-perchloric hydrofluoric acid digestion method described by Carrondo (1979). 10 mL aliquot of water sample was taken for analysis in a Teflon beaker (previously soaked in 10% nitric acid for 72 h and rinsed with de-ionized water) and 30.0 mL of concentrated HNO_3 was added and the sample was evaporated to dryness on a hot plate in a

fume cupboard. This was allowed to cool and 5.0 mL of conc.HNO_3, 2.0 mL of 60 % perchloric acid $HClO_4$ and 6.0 mL of 40 % HF were added. The mixture was evaporated to dryness at a temperature not exceeding 280 °C. Furthermore, 2.0 mL of HNO_3 and 2.0 mL of $HClO_4$ acid were added and evaporated to ensure that silicon and fluoride were removed. Again the beaker was cooled and 20.0 mL of 5% v/v HNO_3 was added to dissolve the salts. The solution was transferred to 25.0 mL standard flask and made up to mark with de-ionized water washing from the digestion beaker. A blank experiment was carried out for background correction using de-ionized water and following the procedure described above without the sample.

(e) Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Analyses of Metals

Solutions of the worked up samples were analysed using Finnigan MAT Element2 High Resolution Inductively Coupled Plasma-Mass Spectrophotometer (HRICP-MS) (Finnigan MAT

GmbH, Bremen, Germany) at the Department of Chemistry, University of Botswana, Gaborone, Botswana. The instrument was operated with the following conditions: RF Power 1.158kW; nebulizer gas (Air) flow rate 1.0 L/min.; cool gas flow rate 14.89 L/min.; and detector voltage 2398 V. The isotopes of the elements determined were; ^{111}Cd, ^{56}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, and ^{55}Mn.

3. Results and discussions

The results obtained in this preliminary study are summarized and presented in Tables 1 to 4 and are the means of data from nine sampling points (including a control sample) with sampling dates.

Temperature varied between 27.5 °C (S4) in January and 34.0 °C (S3) in February for the influent and effluent samples. In the receiving stream however, temperature varied between 25.0 °C (S6 & S7) in January and April and 29.5 °C (S8) in May (Table 1) while in the reference samples, temperature varied between 24.0 °C and 26.0 °C. The results show that the discharge of effluent from the oxidation pond into the stream contributed to higher temperature obtained in the stream from the discharge point downstream. This may impair the domestic use of water from the stream, as it has been reported that high temperature may increase the toxicity of many substances such as heavy metals in waters (Fatoki and Awofolu, 2003).

The pH values ranged from 4.7 to 6.9 in the oxidation pond influent and effluent and from 5.9 to 7.3 in the receiving stream. The pH of the reference sample ranged from 6.2 to 7.2. Generally, the influent, effluent and the receiving stream were acidic. In most cases the values of pH obtained in the influent and effluent samples fell outside the stipulated Nigerian Federal Ministry of Environment (FMEnv), formerly Federal Environmental Protection Agency (FEPA) pH tolerance limit of between 6.0-9.0 for effluent discharge through sewers into a stream (FEPA, 1990). The pH values from the point of discharge of effluent into the receiving stream and downstream (S5-S8) (Table 1) fell below the WHO range of 7.0-8.5 for drinking water (DWAF, 1990). Based on these criteria, water from the receiving stream is not safe for drinking and recreational purposes.

Electrical conductivity varied between 566 and 1985 μS/cm in the influent and effluent samples and between 391 and 1250 μS/cm in the receiving stream. In the reference sample (SR), electrical conductivity varied between 394 in January and 820 μS/cm in March (Table 1). There were indications from these results that the effluent discharge from the sewage treatment oxidation pond generally led to increase in the electrical conductivity reported for the receiving stream. The effects of high EC may include disturbances of salt and water balance and eventually lead to increase in the salinity of the receiving water, which may result in adverse ecological effects on aquatic biota (Fried, 1991). Some of the adverse ecological effects of high salt concentrations include; heart problem, high blood pressure and renal disease (DWAF, 1998).

Fig. 2 (a, b and c respectively) shows site variability for temperature, pH and electrical conductivity in the study area. Generally the figure showed enhanced levels of temperature and EC in influent and effluent samples and the receiving stream compared to the reference sample. The result of pH however, is lower and highly acidic in the influent and effluent compared with the reference sample and the receiving stream. The higher overall pH level of 6.85 ± 0.36 in the reference sample (Fig. 2b) compared to other sites is expected and can be adjudged acceptable for this fresh water sample as the level agreed with the EU pH protection limits of 6-9 for fisheries and aquatic life (Chapman and Kimstach, 1996). The results from this figure showed that the effluents discharged from the sewage lagoon led to increase in the levels of EC and temperature in the receiving stream.

Concentrations of Ni ranged from 1.19 ± 0.08 μg/L in May (S1, S4) to 3.96 ± 0.29 μg/L in January (S3) for the influent and effluents of the sewage treatment oxidation pond and from from 1.06 ± 0.08 μg/L in March (S7) to 3.44 ± 0.25 μg/L in January (S8) for samples in the receiving stream after the discharge of effluents (S5-S8) (Table 2). In the reference sample, Ni concentration was lowest compared to other sites and ranged from 0.17±0.01 μg/L in May to 0.82 ± 0:07 μg/L in January (Table 2).

The average concentration of Ni in this study ranged from 1.27 ± 0.14 μg/L to 3.08 ± 0.62 μg/L; 1.21 ± 0.06 μg/L to 2.66 ± 0.54 μg/L and from 0.17 ± 0.01 μg/L to 0.82 ± 0.07 μg/L in influent and effluent, receiving stream and reference samples respectively (Table 2 a, b & c). Generally, the relatively high concentrations obtained for Ni in the receiving stream (S5-S8) compared with those of the reference sample (SR) was observed to be as a result of the discharge of effluents from the sewage into the stream.

Nickel can be extremely toxic to man even at low concentrations in domestic water supply when consumed (Stoeppler, 1991 and Gauglhofer and Bianchi, 1991), it has as well been shown to have mutagenic, carcinogenic and teratogenic effects (Frieberg *et al.*, 1896 and Fishbein, 1987) hence the need for its effective removal from water during the sewage treatment. However, the levels obtained in the influent and effluent samples fell below 1 mg/L limit set by Nigeria Federal Ministry of Environment (FMEnv) for effluents to be discharged into surface water. Hence Ni does not constitute any threat to the aquatic biota and people that depend on the receiving stream downstream.

The levels of Cd in the samples analyzed are presented in Table 2. Concentrations of Cd in the influent and effluent samples varied between 2.59 ± 0.25 μg/L in

Table 1: Variations of Temperature, pH, and Electrical Conductivity in the Study Area.

Date Sampling Site	Temperature ^oC						pH						Electrical Conductivity (μS/cm)					
	23rd Jan 2003	26th Feb 2003	22nd Mar 2003	29th April 2003	19th May 2003	9th June 2003	23rd Jan 2003	26th Feb 2003	22nd Mar 2003	29th April 2003	19th May 2003	9th June 2003	23rd Jan 2003	26th Feb 2003	22nd Mar 2003	29th April 2003	19th May 2003	9th June 2003
(a) Influent and Effluent from the Sewage Treatment Oxidation Pond																		
S1	29.0	29.5	29.0	29.0	30.0	30.0	6.1	6.4	5.6	6.7	6.9	4.7	708	1985	1535	1185	1034.5	1755
S2	28.5	29.5	29.0	29.5	30.5	31.0	6.1	6.9	6.4	6.4	6.7	4.9	788	1930	1515	1240	985	1805
S3	28.5	34.0	33.0	31.0	32.0	30.0	6.2	5.9	5.7	6.2	6.6	6.1	566	1330	1325	775	975	1235
S4	27.5	33.0	29.0	29.0	30.5	28.0	5.9	6.2	5.8	6.2	6.3	6.9	707	1321	1550	881.50	945	975
Average	28.38 ± 0.63	31.50 ± 2.35	30.0 ± 2.00	29.63 ± 0.95	30.75 ± 0.87	27.75 ± 1.23	6.06 ± 0.14	6.36 ± 0.45	5.87 ± 0.36	6.36 ± 0.23	6.61 ± 0.23	5.68 ± 1.03	689.75 ± 88.94	1641.5 ± 365.59	1481.3 ± 105.15	1020.9 ± 227.18	984.88 ± 37.19	1442.5 ± 404.42
(b) Receiving Stream																		
S5	26.5	27.5	26.5	26.0	26.5	28.0	6.4	6.9	6.8	6.4	6.8	7.23	497	959	1250	685	863.50	823.50
S6	25.5	27.0	26.0	25.0	26.5	26.0	5.9	6.6	6.8	6.5	6.9	6.58	496	850	1230	634	848	560
S7	25.5	27.0	26.0	25.0	26.0	25.5	6.0	7.0	6.9	6.6	7.0	7.04	397	846	1250	620.50	845.50	502
S8	28.0	29.0	29.0	29.0	29.5	27.5	6.0	7.0	7.3	6.6	7.1	6.99	391	910	975	682.50	905	721
Average	26.38 ± 1.18	27.63 ± 0.95	26.88 ± 1.44	26.25 ± 1.89	27.25 ± 1.55	26.75 ± 1.19	6.07 ± 0.19	6.88 ± 0.21	6.97 ± 0.23	6.51 ± 0.10	6.97 ± 0.09	6.96 ± 0.27	445.25 ± 59.23	891.25 ± 53.82	1176.3 ± 134.50	655.50 ± 33.10	865.50 ± 27.51	651.63 ± 147.35
(c) Reference																		
SR	25.5	26.0	25.5	24.0	26.0	25.0	6.2	7.1	7.0	6.6	7.0	7.2	394	700	820	615.50	577	448.50

Table 2: Concentrations (μg/L) of Nickel and Cadmium in the Sewage treatment oxidation pond and the receiving stream

Date / Sampling Site	Nickel (μg/L)						Cadmium (μg/L)					
	23rd Jan. 2003	26th Feb. 2003	22nd Mar. 2003	29th April 2003	19th May 2003	9th June 2003	23rd Jan. 2003	26th Feb. 2003	22nd Mar. 2003	29th April 2003	19th May 2003	9th June 2003
(a) Influent and Effluent of the Sewage Treatment Oxidation Pond												
S1	2.55 ± 0.17	2.21 ± 0.26	2.26 ± 0.19	1.89 ± 0.16	1.19 ± 0.08	1.49 ± 0.15	25.97 ± 2.11	22.04 ± 2.50	11.14 ± 1.16	15.43 ± 1.25	14.25 ± 1.57	15.02 ± 1.02
S2	2.91 ± 0.25	2.11 ± 0.19	2.49 ± 0.19	1.94 ± 0.15	1.48 ± 0.12	1.44 ± 0.12	16.36 ± 1.03	15.24 ± 1.25	9.49 ± 0.75	10.39 ± 0.85	13.79 ± 0.85	12.25 ± 1.12
S3	3.96 ± 0.29	1.82 ± 0.17	1.92 ± 0.16	1.53 ± 0.09	1.22 ± 0.11	1.34 ± 0.12	17.06 ± 2.13	14.17 ± 1.61	9.53 ± 0.57	6.96 ± 0.55	5.62 ± 0.52	12.22 ± 0.93
S4	2.82 ± 0.22	1.79 ± 0.16	1.84 ± 0.15	1.36 ± 0.15	1.19 ± 0.09	1.29 ± 0.16	9.09 ± 0.76	10.33 ± 1.22	8.99 ± 0.92	5.72 ± 0.52	2.59 ± 0.25	5.11 ± 0.58
Average	3.08 ± 0.62	1.98 ± 0.21	2.13 ± 0.30	1.68 ± 0.28	1.27 ± 0.14	1.35 ± 0.09	17.12 ± 6.91	15.45 ± 4.88	9.79 ± 0.93	9.63 ± 4.43	8.81 ± 5.61	11.15 ± 4.24
(b) Receiving stream												
S5	2.45 ± 0.21	1.73 ± 0.13	1.84 ± 0.15	1.34 ± 0.12	1.27 ± 0.11	1.25 ± 0.09	9.07 ± 0.54	9.47 ± 0.65	7.28 ± 0.52	1.33 ± 0.25	0.65 ± 0.04	5.50 ± 0.44
S6	2.57 ± 0.18	1.71 ± 0.14	1.78 ± 0.13	1.32 ± 0.11	1.20 ± 0.09	1.20 ± 0.08	8.25 ± 0.58	8.55 ± 0.81	7.28 ± 0.77	0.70 ± 0.02	0.55 ± 0.01	2.16 ± 0.02
S7	2.19 ± 0.16	1.58 ± 0.13	1.06 ± 0.08	1.29 ± 0.13	1.13 ± 0.15	1.19 ± 0.07	5.28 ± 0.75	8.00 ± 0.52	6.84 ± 0.53	0.50 ± 0.02	0.5 ± 0.02	0.79 ± 0.04
S8	3.44 ± 0.25	1.94 ± 0.15	2.19 ± 0.22	1.30 ± 0.16	1.24 ± 0.13	1.24 ± 0.13	6.87 ± 0.57	12.06 ± 1.48	7.49 ± 0.58	1.37 ± 0.23	2.56 ± 0.14	0.66 ± 0.03
Average	2.66 ± 0.54	1.74 ± 0.15	1.72 ± 0.47	1.31 ± 0.02	1.21 ± 0.06	1.22 ± 0.03	7.37 ± 1.66	9.52 ± 1.80	7.22 ± 0.22	0.98 ± 0.44	1.07 ± 1.00	2.28 ± 1.25
(c) Reference												
sR	0.82 ± 0.07	0.53 ± 0.07	0.59 ± 0.06	0.28 ± 0.02	0.17 ± 0.01	0.18 ± 0.02	<0.5	2.86 ± 0.36	2.62 ± 0.22	<0.5	<0.5	<0.5

Concentrations are Mean Values ± SD for n = 3

Table 3: Concentrations of Zinc and Copper in the Sewage treatment oxidation pond and the receiving stream

Date Sampling Site	Zinc (mg/L)						Copper (mg/L)					
	23rd Jan. 2003	26th Feb. 2003	22nd Mar. 2003	29th April 2003	19th May 2003	9th June 2003	23rd Jan. 2003	26th Feb. 2003	22nd Mar. 2003	29th April 2003	19th May 2003	9th June 2003
(a) Influent and Effluent of the Sewage Treatment Oxidation Pond												
S1	0.84 ± 0.02	1.47 ± 0.03	0.60 ± 0.01	0.27 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	0.23 ± 0.01	0.37 ± 0.009	0.13 ± 0.006	0.20 ± 0.01	0.20 ± 0.01	0.09 ± 0.004
S2	0.66 ± 0.01	0.78 ± 0.02	0.72 ± 0.01	0.39 ± 0.02	0.15 ± 0.01	0.12 ± 0.01	0.29 ± 0.008	0.25 ± 0.01	0.13 ± 0.006	0.22 ± 0.007	0.17 ± 0.008	0.09 ± 0.004
S3	0.54 ± 0.02	0.76 ± 0.02	0.64 ± 0.01	0.19 ± 0.01	0.15 ± 0.01	0.10 ± 0.008	0.28 ± 0.006	0.24 ± 0.01	0.14 ± 0.006	0.19 ± 0.006	0.10 ± 0.006	0.04 ± 0.002
S4	0.41 ± 0.02	0.55 ± 0.01	0.51 ± 0.01	0.17 ± 0.01	0.09 ± 0.007	0.07 ± 0.006	0.23 ± 0.008	0.23 ± 0.009	0.13 ± 0.008	0.18 ± 0.006	0.08 ± 0.005	0.04 ± 0.002
Average	0.61 ± 0.18	0.89 ± 0.40	0.62 ± 0.09	0.26 ± 0.10	0.13 ± 0.02	0.11 ± 0.02	0.26 ± 0.03	0.2 ± 0.06	0.13 ± 0.005	0.20 ± 0.02	0.14 ± 0.05	0.07 ± 0.02
(b) Receiving Stream												
S5	0.37 ± 0.02	0.30 ± 0.01	0.39 ± 0.02	0.17 ± 0.01	0.07 ± 0.005	0.06 ± 0.004	0.23 ± 0.01	0.23 ± 0.008	0.14 ± 0.007	0.13 ± 0.006	0.10 ± 0.005	0.04 ± 0.002
S6	0.25 ± 0.01	0.17 ± 0.01	0.11 ± 0.01	0.13 ± 0.008	0.07 ± 0.004	0.05 ± 0.003	0.21 ± 0.009	0.21 ± 0.008	0.13 ± 0.006	0.09 ± 0.004	0.07 ± 0.003	0.04 ± 0.002
S7	0.21 ± 0.01	0.17 ± 0.01	0.09 ± 0.007	0.09 ± 0.007	0.04 ± 0.003	0.04 ± 0.003	0.21 ± 0.008	0.20 ± 0.008	0.12 ± 0.006	0.08 ± 0.003	0.05 ± 0.002	0.03 ± 0.001
S8	0.67 ± 0.02	0.31 ± 0.01	0.60 ± 0.01	0.12 ± 0.01	0.05 ± 0.004	0.05 ± 0.003	0.24 ± 0.006	0.21 ± 0.005	0.14 ± 0.008	0.14 ± 0.004	0.13 ± 0.006	0.05 ± 0.003
Average	0.38 ± 0.20	0.24 ± 0.08	0.30 ± 0.24	0.13 ± 0.03	0.06 ± 0.02	0.05 ± 0.008	0.22 ± 0.02	0.21 ± 0.01	0.13 ± 0.00	0.11 ± 0.03	0.09 ± 0.04	0.04 ± 0.007
(c) Reference				(µg/L)					(µg/L)			
SR	32.38 ± 2.94	50.13 ± 4.97	17.52 ± 1.39	22.51 ± 2.81	12.79 ± 1.63	15.25 ± 1.62	13.93 ± 1.07	10.79 ± 1.32	19.13 ± 1.07	8.31 ± 1.12	8.89 ± 0.12	6.74 ± 0.56

Concentrations are Mean Values ± SD for n = 3.

Table 4: Concentrations (μg/L) of Iron and Manganese in the Sewage treatment oxidation pond and the receiving stream

| Sampling Site	Iron (μg/L)						Manganese (μg/L)					
Month	January 2003	Feb. 2003	March 2003	April 2003	May 2003	June 2003	January 2003	Feb. 2003	March 2003	April 2003	May 2003	June 2003
(a) Influent and Effluent of the Sewage Treatment Oxidation Pond												
S1	9.23 ± 0.89	11.52 ± 0.96	5.75 ± 0.46	6.45 ± 0.56	9.05 ± 0.63	9.05 ± 0.82	0.49 ± 0.03	0.84 ± 0.06	0.83 ± 0.03	0.41 ± 0.02	0.33 ± 0.04	0.27 ± 0.03
S2	8.81 ± 0.77	7.77 ± 0.55	5.60 ± 0.71	6.50 ± 0.62	7.95 ± 0.82	11.35 ± 0.99	0.46 ± 0.04	1.04 ± 0.10	0.51 ± 0.03	0.35 ± 0.03	0.18 ± 0.02	0.20 ± 0.02
S3	6.90 ± 0.71	6.55 ± 0.56	6.00 ± 0.83	6.32 ± 0.49	9.35 ± 0.78	8.25 ± 0.79	0.49 ± 0.05	0.94 ± 0.07	0.44 ± 0.02	0.23 ± 0.01	0.13 ± 0.12	0.16 ± 0.01
S4	5.00 ± 0.93	4.11 ± 0.34	4.27 ± 0.33	4.89 ± 0.36	6.39 ± 0.41	7.14 ± 0.66	0.31 ± 0.01	0.65 ± 0.05	0.49 ± 0.05	0.22 ± 0.03	0.13 ± 0.01	0.14 ± 0.01
Average	**7.49 ± 1.94**	**7.49 ± 3.29**	**5.41 ± 0.77**	**6.04 ± 0.77**	**8.19 ± 1.34**	**8.95 ± 1.78**	**0.44 ± 0.09**	**0.87 ± 0.07**	**0.57 ± 0.18**	**0.30 ± 0.09**	**0.19 ± 0.09**	**0.19 ± 0.06**
(b) Receiving Stream												
S5	4.92 ± 0.37	3.99 ± 0.27	3.18 ± 0.29	4.08 ± 0.54	5.55 ± 0.39	6.17 ± 0.55	0.14 ± 0.02	0.60 ± 0.03	0.40 ± 0.03	0.21 ± 0.01	0.08 ± 0.002	0.11 ± 0.01
S6	4.20 ± 0.33	3.93 ± 0.19	3.01 ± 0.41	3.36 ± 0.27	4.59 ± 0.52	5.20 ± 0.38	0.09 ± 0.03	0.45 ± 0.06	0.39 ± 0.05	0.09 ± 0.006	0.07 ± 0.001	0.10 ± 0.01
S7	2.95 ± 0.14	3.75 ± 0.18	2.82 ± 0.17	3.10 ± 0.22	4.20 ± 0.37	3.25 ± 0.21	0.03 ± 0.01	0.20 ± 0.01	0.35 ± 0.02	0.06 ± 0.001	0.05 ± 0.002	0.08 ± 0.004
S8	3.70 ± 0.29	8.35 ± 0.68	2.88 ± 0.15	3.55 ± 0.36	6.06 ± 0.53	6.83 ± 0.52	0.15 ± 0.03	1.39 ± 0.09	0.34 ± 0.02	0.12 ± 0.02	0.12 ± 0.02	0.16 ± 0.01
Average	**3.94 ± 0.83**	**5.13 ± 2.48**	**2.97 ± 0.16**	**3.52 ± 0.41**	**5.10 ± 0.86**	**5.36 ± 1.56**	**0.10 ± 0.06**	**0.68 ± 0.51**	**0.37 ± 0.03**	**0.12 ± 0.06**	**0.08 ± 0.03**	**0.11 ± 0.03**
(c) Reference												
SR	2.85 ± 0.11	2.25 ± 0.13	1.23 ± 0.09	1.38 ± 1.14	1.28 ± 0.08	1.10 ± 0.07	0.02 ± 0.003	0.15 ± 0.01	0.11 ± 0.01	0.05 ± 0.002	0.04 ± 0.001	0.07 ± 0.002

Concentrations are Mean Values ± SD for n = 3
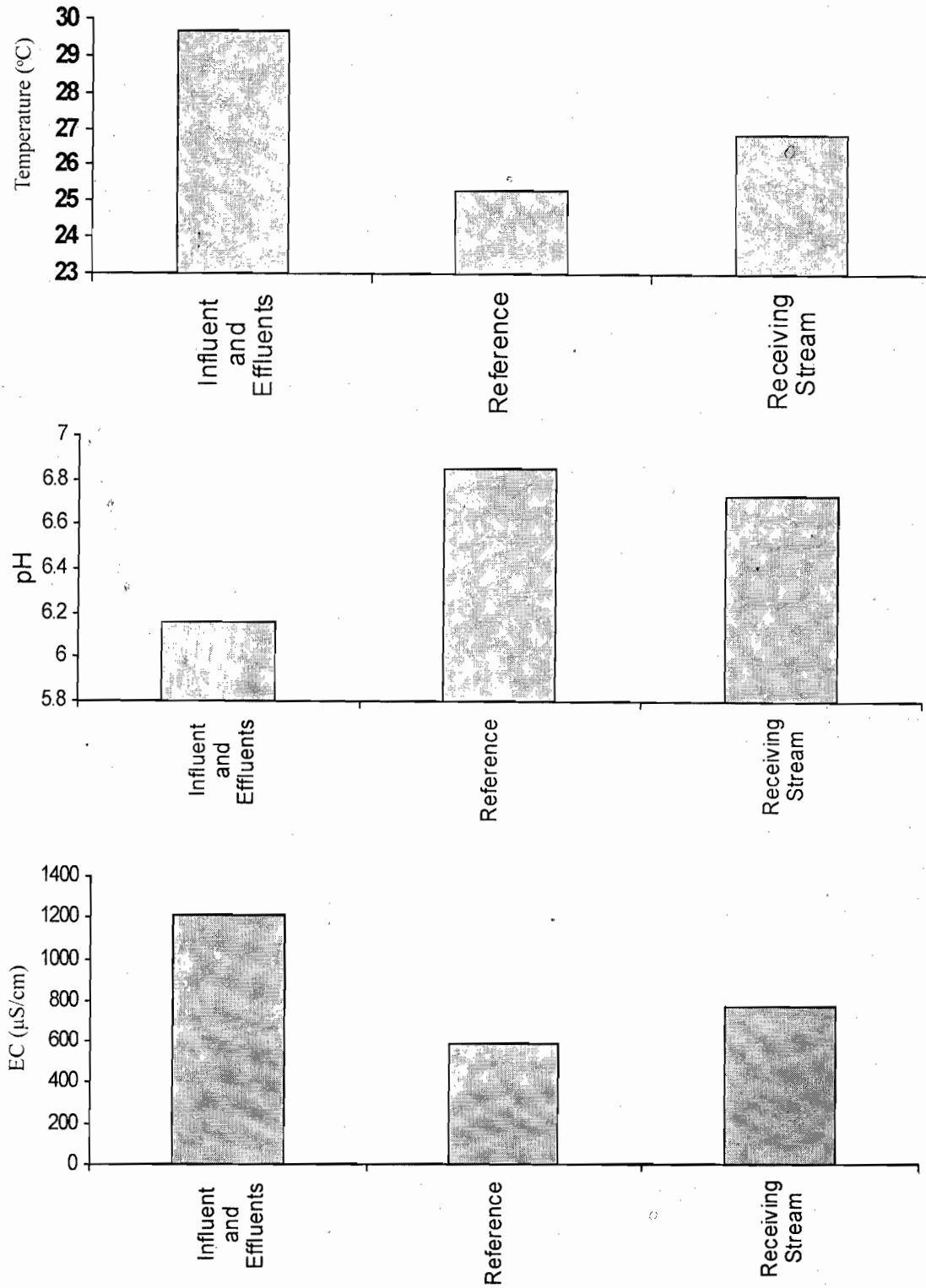
Figure 2: Variability of Temperature, pH and Electrical Conductivity across the sites of the study Area

(a)　　Temperature
(b)　　pH
(c)　　Electrical Conductivity (EC)

May (S4) and 25.97 ± 2.11 µg/L in January (S1). In the receiving stream Cd ranged from 0.50 ± 0.02 µg/L in April and May (S7) to 12.06 ± 1.48 µg/L in February (S8) but in the reference samples concentrations of between 0.5 µg/L and 2.86 ± 0.36 µg/L were obtained.

Average of Cd in the influent and effluent samples had an upper concentration which ranged from 8.81 ± 5.61 µg/L in May to 17.12 ± 6.91 µg/L in January; while in the receiving stream the maximum average concentration of Cd was 9.52 ± 1.80 µg/L in April. (Table 2).

The WHO maximum allowable concentration of cadmium in drinking water is 3 µg/L (WHO, 1992; USEPA, 1986 and Salido and Jones, 1999). The overall mean concentration of cadmium in this study for the receiving stream (4.74 ± 3.37 µg/L) exceeded this limit. In view of the fact that major use of water from the receiving stream and the adjoining Opa river is domestic, the high levels of Cd in the stream and the adjoining river give cause for a great concern because cadmium is extremely toxic, causes adverse health effect such as renal disease and cancer (Fatoki and Awofolu, 2003 and Friberg *et al.*, 1896) and has been implicated in the disruption of endocrine system (Susan *et al.*, 2001).

The results of Zn and Cu analyses in the sewage lagoon, the receiving stream and reference samples are shown in Table 3. The levels of Zn ranged from 0.08 ± 0.006 mg/L in June (S4) to 1.47 ± 0.03 mg/L in February (S1), in the influent and effluent samples and in the receiving stream (S5-S8), concentration of Zn ranged from 0.04 ± 0.003 mg/L in May (S7) to 0.67 ± 0.01 mg/L in January (S8). The reference samples gave Zn levels that ranged from 0.01 ± 0.01 mg/L in May to 0.05 ± 0.04 mg/L in February. The average concentration of Zn in the influent and effluent sample ranged from 0.10 ± 0.02 mg/L in June to 0.89 ± 0.40 mg/L in February and from 0.05 ± 0.01 mg/L in June to 0.38 ± 0.20 mg/L in January for samples in the receiving stream.

Levels of Zn in all the stream samples analysed fell below the 5 mg/L highest desirable level of Zn in drinking water (WHO, 1984), hence use of such water from the receiving stream for domestic purposes may not pose any danger based on this criterion. However, Zn levels in the stream may be of problem from aquatic ecosystems standpoint, as their levels exceeded the 20 m (Fatoki *et al.*, 2002). Thus waters from the stream are unsuitable for use of the aquatic ecosystem and could be very detrimental to fish and other aquatic biota. Zinc is one of the trace metals that are essential to humans but could be toxic even at low concentration (Foster *et al.*, 1980). Ingesting extreme amounts of zinc can impair immune function and cause nausea,

headaches, vomiting, dehydration, fatigue, possible kidney failure and prostate cancer (Michael and Standford, 2003).

Concentrations of Cu detected in waste water samples from the influent and effluent of the oxidation pond ranged from 0.04 ± 0.02 mg/L (S4) in June to 0.37 ± 0.09 mg/L (S1) in February, while levels in the receiving stream (S5-S8) ranged from 0.03 ± 0.01 mg/L (S7) in June to 0.24 ± 0.06 mg/L (S8) in January (Table 3). The levels in the reference sample were much lower and ranged from 6.74 ±m! p±mGopGoAverage concentration of Cu in the influent and effluent samples varied between 0.06 ± 0.03 mg/L in June and 0.27 ± 0.6 mg/L in February, while in the receiving stream (S5-S8) average concentration varied between 0.04 ± 0.007 mg/L in June and 0.22 ± 0.02 mg/L in January (Table 3).

Levels of Cu in the receiving stream fell below the 1mg/L stipulated level for Cu in water for domestic use by the Nigeria Federal Ministry of the Environment, therefore Cu is not likely to be a problem for the domestic use of water from the stream based on this criterion. Also, the levels of Cu in the influent and effluent samples fell below the 1 mg/L FMEnv limit for the discharge of effluents into surface water. However, there is need to ensure that the Cu do not exceed this limit as a result of continuous influx wastes into the sewage lagoon, because copper like other metals when discharged into safe water body can enter the food chain, be bio-accumulated in aquatic biota and hence become a threat to man.

Generally, cadmium, zinc and nickel are classified as highly toxic and considered responsible for health hazards, whereas copper is less toxic in nature (Michael and Standford, 2003). The result for these metals showed that the levels were higher in the influent and effluent from the sewage lagoon than those of the receiving stream and the reference sample. Higher levels of these metals reported in the receiving stream compared to the reference sample upstream showed that the receiving stream was impacted by heavy metals pollution through point source discharge from the sewage treatment oxidation pond.

The levels of Fe in influent and effluent samples varied between 4.11 ± 0.34 mg/L as observed in February (S4) and 11.52 ± 0.96 mg/L in February (S1); in the receiving stream (S5-S8) concentration of Fe varied between 2.82 ± 0.17 mg/L (S7) in March and 8.35 ± 0.68 mg/L (S8) in February. On the other hand the reference samples gave concentration range of between 1.10 ± 0.07 mg/L in June and 2.85 ± 0.11 mg/L in January (Table 4).

As shown in Table 4, average concentration of Fe in the influent and effluent samples ranged from 5.41 ± 0.77 mg/L in March to 8.95 ± 1.78 mg/L in June, while in the receiving stream (S5-S8), average levels

ranged from 2.97 ± 0.16 mg/L in March to 5.36 ± 1.56 mg/L in June.

The FMEnv tolerance limit for Fe in effluent for discharge through public sewers into streams is 20 mg/L. This limit was not exceed by the effluent discharged into the receiving stream, but levels of Fe in the water from the receiving steam exceeded the 1.0 mg/L WHO maximum permissible value of Fe for drinking water. Although Fe is not classified as a toxic metal, its concentration and chemical form can influence the speciation of Pb and hence its toxicity. Fe and Mn normally act as metal scavengers, due to their tendency to form colloidal particulate hydrous oxides (Stumn and Morgan, 1971 and Mill, 1980) which have strong adsorption affinities for certain metals like Pd and Cd (Gadde and Laitinen, 1974). In this way dissolved Cd can be transferred onto the particulate phase, hence becoming less bioavailable. Levels of Mn detected in the influent and effluent samples, varied between 0.13 ± 0.01 mg/L in May (S3, S4) and 1.04 ± 0.10 mg/L in February (S2), and between 0.03 ± 0.01 mg/L (S7) in January and 1.39 ± 0.09 mg/L in February (S8) in the receiving stream. Levels in the reference sample varied between 0.02 ± 0.003 mg/L in January and 0.15 ± 0.01 mg/L in February (Table 4). In humans, manganese toxicity represents a serious health hazard, resulting in severe pathologies of the central nervous systems, hence there is need to control the levels of Mn flowing into the steam through the effluent discharge.

The average concentration of Mn in the influent and effluent samples varied between 0.19 ± 0.06 mg/L in June and 0.87 ± 0.07 mg/L in February and between 0.08 ± 0.03 mg/L in May and 0.68 ± 0.51 in February, in the receiving stream (Table 4). The limit of Mn in water meant for aquatic ecosystem use is 0.18 mg/L (DWAF, 1998) and WHO provisional guideline value for drinking water is 0.5 mg/L (WHO, 1984). These two limits are exceeded in most cases in the receiving stream (except reference samples), this gives cause for concern, therefore, the stream will be unsuitable for drinking and maintenance of the aquatic ecosystem.

Cluster analysis is very useful in establishing the elemental associations within sites in a given study area. The results of cluster analysis of the six metals with sites are presented in Fig. 3 (a, b, c, d, e and f) for Cd, Cu, Fe, Mn, Ni and Zn respectively.

This analysis was done in an attempt to find out which of the metals are associated and common to various sampling sites within the study area using the SAS software package. Generally two main groups are evident that are correlated under which are some sub-groups. Cadmium association in the sampling sites showed closest correlations between sites S6 & S8; S7 & S4; S4&S5 and S1&S2; S2&S3; and may imply common source for them; whilst for Copper, the closest inter-elemental clustering was

obtained between sites S6&S7; S5&S8; S3&S4 whereas a weak association of Cu was observed between sites S1&S2. Iron showed correlations at sites S5&S6; S5&S4 and weak association at sites S8, S7, S2, S1 and S3 which may suggest different sources for Iron in these sites. The results of cluster analysis for Mn, Ni and Zn at the eight sites studied also showed strong association with two prominent association and sources evident. The cluster analysis results point to elemental composition from the study sites in the study area originating from two major sources. The two major sources of metal pollution in this study are likely to be point sources from the sewage treatment oxidation pond and agricultural runoff. Other sources may include contribution from natural sources, such as weathering of rocks and land which eventually get eroded through surface runoff into the receiving stream.

4. Conclusion

Levels of Cd, Fe, Ni, Cu, Zn, and Mn in the effluent of a sewage treatment oxidation pond as well as the receiving stream have been determined in this study by ICP-MS after triple acid digestion. The high levels of Cd, Fe,, Zn, and Mn obtained may have deleterious effects on the health of rural communities in the vicinity of the stream that use water from the stream directly for domestic purposes without treatment. Significant pollution of the receiving stream was also indicated for pH as their levels fell below the WHO range of 7.0-8.5 set for drinking water. The high enrichment of the toxic metals in the receiving stream should give cause for concern because of their potential adverse effects on floral, fauna and human health.

The sewage treatment oxidation pond seems to do very little in the way of reducing levels of metals in the sewage before it is discharged into the receiving stream. The relevant authorities should therefore attend to proper management and control of the effluent from the sewage lagoon before its discharge into the receiving stream.

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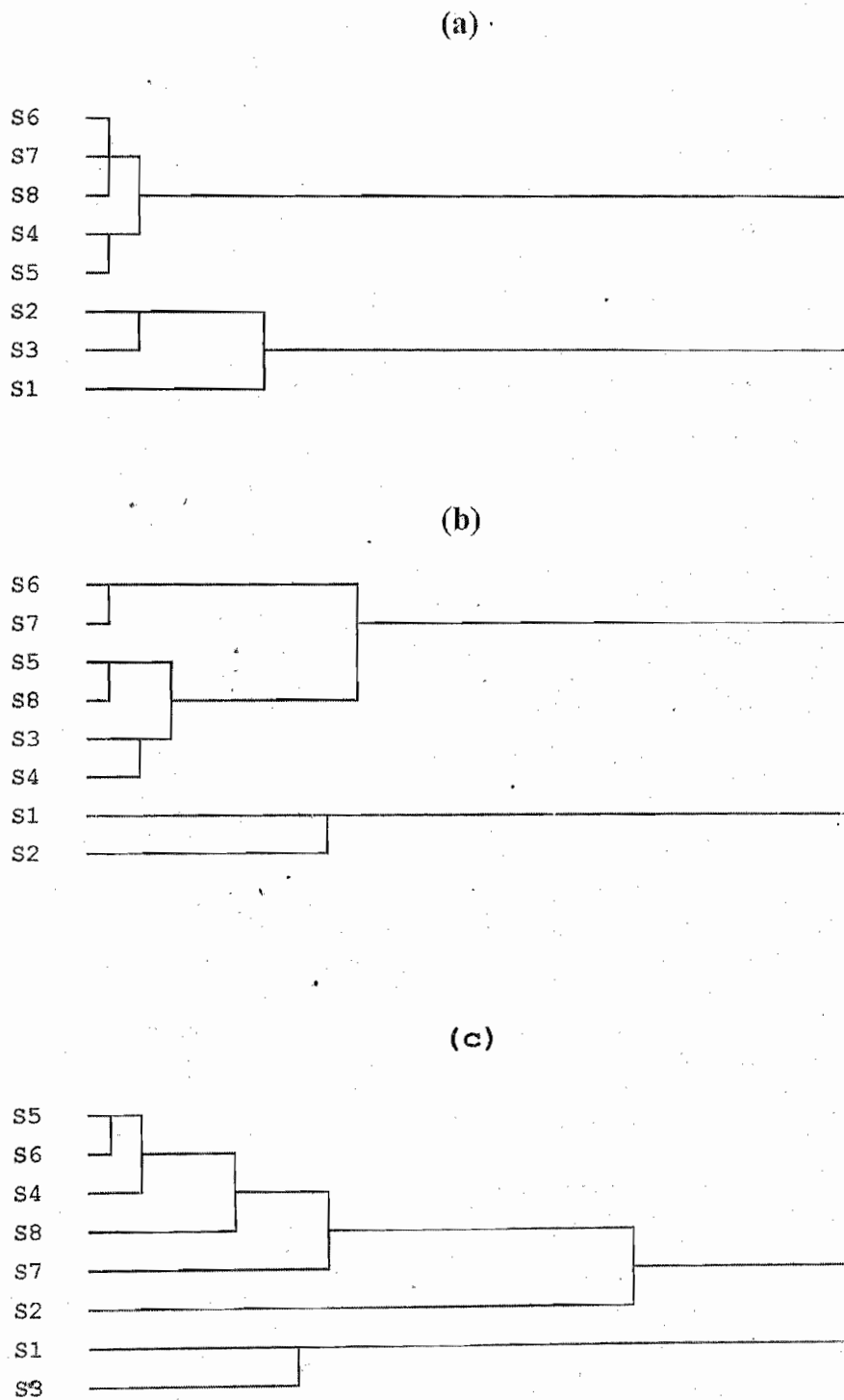**(a)**

(b)

(c)

Fig. 3: Cluster analysis of metal with sample collection sites- (a) = Cd, (b) = Cu, (c) =Fe
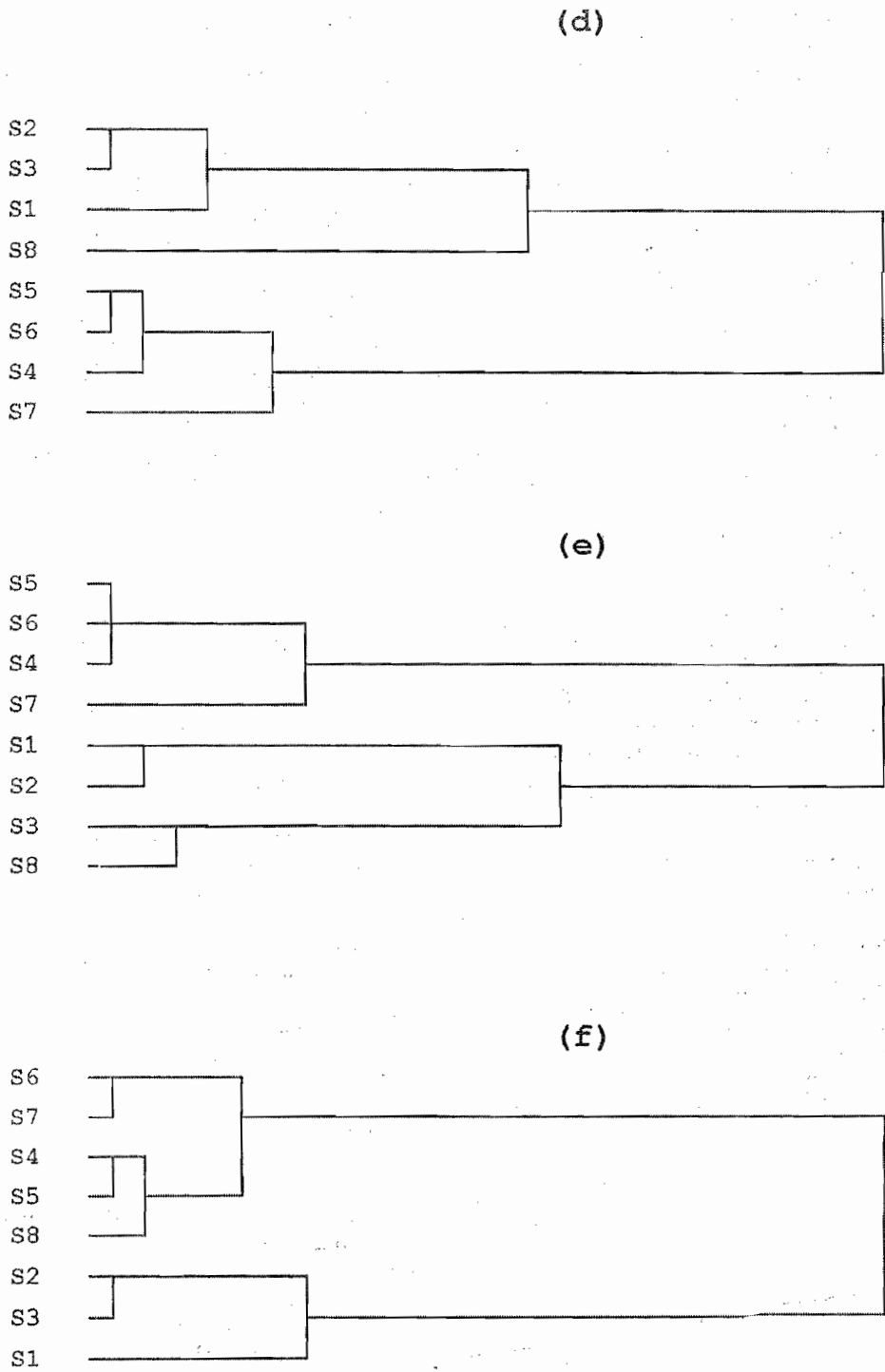
(d)

(e)

(f)

Fig. 3: Cluster analysis of metal with sample collection sites- (d) = Mn, (e) = Ni, (f) = Zn

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