Pak. J. Sci. Ind. Res. 2005 **48**(1) 28-36

Determination and Seasonal Variation of Heavy Metals in Algae and Sediments in Sewers from Industrial Areas in Lagos State, Nigeria

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(received June 25, 2004; revised September 14, 2004; accepted November 25, 2004)

Abstract. The level of heavy metals (Cd, Pb, Cu and Zn) in algae and sediments in sewers from industrial areas was determined by atomic absorption spectrophotometry (AAS). In order to evaluate the metal load of the sewers, as a result of discharged effluents, algae and sediments were collected from three major industrial areas in Lagos, Nigeria during the two main seasons (rainy and dry). Using total digestion, the mean concentration of Cd, Pb, Cu and Zn in algae at Oshodi/Isolo industrial area for the two seasons respectively ranged from 0.04-0.15 µg/g, 0.32-1.86 µg/g, 0.42-1.52 µg/g and 0.10-1.80 µg/g, while those in sediments ranged from not detectable (ND)-0.10 µg/g, 0.12-1.32 µg/g, 0.21-2.65 µg/g and 0.18-1.74 µg/g, respectively. At Iganmu industrial area, the range in algae was ND-0.21 µg/g, 0.20-1.84 µg/g, 0.17-1.90 µg/g and 0.05-1.87 µg/g, while those in sediments was 0.04-0.50 µg/g, 0.22-1.85 µg/g, 0.15-1.78 µg/g and 0.48-2.86 µg/g in the same metal order. The range in algae at Ikeja industrial area was 0.05-0.18 µg/g, 0.08-0.82 µg/g, 0.51-1.40 µg/g and 0.24-2.80 µg/g, while the sediments recorded a range of 0.04-0.60 µg/g, 0.16-0.90 µg/g, 0.24-2.35 µg/g and 0.23-2.84 µg/g, in the respective metal order. Levels of the metals were higher in most samples during the dry season and there were significant differences in the metal concentrations from industrial and residential areas.

Keywords: heavy metals, sewer, algae, sediment, atomic absorption spectrophotometry (AAS)

Introduction

The concept of 'save environment' is rapidly gaining vast attention in many developing countries of the world, especially in Africa and South East Asia. However, one of the major impediments to the realization of this concept is due, partly, to inadequate and ineffective monitoring of proper waste treatment and disposal by industries and to non-compliance of waste treatment legislations by the industries where such exist. Most of these industries still consider waste treatment as a profit reduction venture. These scenarios exist in Lagos State, the industrial nerve center and former capital of Nigeria, where over 60% of the industries are located. A sizeable percentage of these industries are the chemical and allied industries. Trace metals, such as Cd, Pb, Cu and Zn, are the common pollutants. These are widely distributed in the environment with sources mainly from the weathering of minerals and soils (O'Neil, 1993; Merian, 1991). However, there has been a greater input to the amount of these metals in the environment as a result of human activities. These inputs are mostly from industrial discharges, domestic effluents, urban runoffs and atmospheric deposition.

Some of these metals, especially Cd, Pb, Zn and Hg, have been found to be harmful even in small quantities (Borgmann, 1983; Tyler, 1981), hence usually monitored for health purposes. Cadmium is one of the most toxic elements with reported carcinogenic effects in humans (Goering *et al.,* 1994). It accumulates mainly in the kidney and liver, and its high concentration has been found to cause chronic kidney dysfunction. It induces cell injury and death by interfering with calcium regulation in biological systems. Copper is among some of the heavy metals that are essential to life but could be toxic at elevated levels. It is toxic at low concentration in water and is known to cause brain damage in mammals (DWAF, 1996). Provisional health-based guideline value of 2 mg/l for copper was proposed and concentration above 5 mg/l can give rise to problems of taste (IPCS, 1998). United States Environmental Protection Agency classified lead as potentially hazardous and toxic to most forms of life (USEPA, 1986). It has been found to be responsible for quite a number of ailments in humans, e.g., chronic neurological disorder, especially in foetus and children. Although Zn has been found to have low toxicity to man, yet prolonged consumption of large doses can result in some health complications such as fatigue, dizziness, and neutropenia (Hess and Schmid, 2002). Health-based guideline value was not derived for zinc, however, drinking water containing zinc at levels above 3 mg/l may not be acceptable to consumers (WHO, 1996).

The determination and evaluation of environmental metal burden have been carried out by using potable water (Garcia *et al.,* 1999; Gulson *et al.,* 1997; Holynska *et al.,* 1996), fresh

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and marine waters (Fiaccabrino *et al.,* 1998; Batterham *et al.,* 1997; Fatoki, 1993), air (Cerda *et al.,* 1999), soil and sediments (Borgmann *et al.,* 2001; van Staden and van der Merwe, 2000; Mellor and Bevan, 1999), algal samples (Kut *et al.,* 2000; Carrilho and Glibert, 2000), and plants (Murphy *et al.,* 2000) by using various methods. However, there has been greater interest in the use of algal species as pollution indicators, mostly present in aquatic environments (Kaewsarn and Qiming, 2001; Tam *et al.,* 1997; Chan *et al.,* 1991). Unicellular green algae have been reported as potential biological materials for removing heavy metals from industrial effluents (Wong *et al.,* 2000; Wong and Pak, 1992; Akzu and Kutsal, 1990). This is due to their hyper-accumulating capacity of metals. They are, therefore, being studied as potential phyto-remediating agents of trace metals in water and sediments. They are able to accumulate metals in thousand-folds higher than the concentration in surrounding water (Bryan and Langston, 1992). The accumulated metals were found to only affect the reproductive activities (stasis) of these plants but are not fatal to them. They also satisfy all the basic requirements of organisms used as bioindicators. These include their sedentary nature, sensitivity to environmental variations, rapid response to pollutants, easy identification and collection, and wide distribution (Lovett-Doust *et al.,* 1994).

The present study was aimed at the determination and evaluation of trace metals (Cd, Pb, Cu and Zn) in common algal species and in sediments from sewers in industrial areas of Lagos State, Nigeria. This is with a view of assessing the environmental metal burden as a result of the perceived inadequate waste treatment and management of the industries and to stimulate the necessary governmental authorities of the need to intensify their monitoring and compliance activities.

Materials and Methods

Sampling area and sampling protocol. Algal samples were collected randomly from sewers using pre-washed stainless steel spoon, rinsed with 1% dilute HNO_3 and then with double distilled water. The samples were placed in clean polyethylene containers, labelled and taken to the laboratory where they were kept refrigerated at 4 °C before analysis so as to preserve them. Sediment samples were also collected randomly from sewers at each site by using a separate and clean stainless steel spoon. The spoon was properly washed, rinsed first with 1% dilute HNO_3 and then with double distilled water. They were placed in clean polyethylene containers, labelled and taken to the laboratory where they were kept frozen at -18 °C in order to preserve the integrity of sediment samples and to avoid possible biological activities before analysis. Freezing has long been an acceptable preservation method for sediments collected for the determination of organic and inorganic constituents. It has been shown that rapid deep-freezing can best maintain sample integrity and thus enable investigation for concentrations of the contaminants (Forstner, 2004).

There are two major dry and rainy seasons in Nigeria. The dry period is characterized by hot climatic/atmospheric temperature, which varies relatively between 30-40 °C and spans between November and April, climaxing in February/March. The rainy season spans between May and October, climaxing in June/July. Consequently, both the algae and the sediment samples were collected in February and June 2000 representing the dry and rainy periods, respectively.

Algae and sediment samples were collected from sewers of three different major roads on which a variety of chemical industries are located within each of the selected industrial areas. Samples were also collected from sewers in residential areas within the respective Local Government Authority of the industrial areas. A total of three major industrial areas were sampled. The different sampling sites and their respective industrial areas are presented in Table 1.

Reagents. All chemicals, purchased from Aldrich Chemical Company, were of analytical grade. Metal standard solutions were prepared from 1000 mg/l stock solutions of the respective metals. All the glassware was properly washed with detergent, rinsed with water, soaked overnight in dilute nitric acid and then rinsed with distilled water before use.

Instrumentation. The analysis was performed with Pye-Unicam Philips (PU900X) atomic absorption spectrophotometer with a digital readout unit and a standard single slot burner head. The operational conditions specified in the instrumentation manual were followed.

Chemical analysis. The algal samples were carefully rinsed with double distilled water to remove any attached particles.

Table 1. List of industrial areas and designation of sampling sites

Industrial areas	Sampling sites	Designation
Oshodi/Isolo	Aswani Road	I
	Ademola Road	II
	Abimbola Road	III
Iganmu	Abebe Road	IV
	Industrial close	V
	Moshood Abiola Way	VI
Ikeja	Acme Road	VII
	Adeniyi Jones Avenue	VIII
	Oba Akran Road	IX

These were then air dried in the oven at 25 °C for about 48 h. Low temperature at 25 °C was used because low temperature drying prevents loss of volatile constituents, avoids chemical changes in labile components, particles of the dried sediments remain dispersed, and aggregation of the particles is minimized. Also, it avoids charring of the filamentous lower plants. The dried plant sample was gently pulverised and 0.5 g weighed into a 100 ml beaker. This was digested using 5 ml of nitric acid and then about 2 ml of perchloric acid in a fume-hood to a final volume of about 2 ml (adapted method, van Loon, 1982). Double distilled 10 ml water was used to rinse the sides of the beaker and the solution was filtered into 50 ml standard flask using 0.45 µm Millipore filter kit (Millipore Corp., Bedford, MA, USA). Triplicate analysis of each sample was carried out and the results were expressed as the mean of the triplicate digestion.

Sediment samples were also air-dried in a circulating oven at 25 °C for 48 h. 0.5 g of the sediment was weighed into a 100 ml beaker and 5 ml concentrated HNO_3 was added. This was digested at low heat on a hot plate for about 20 min in the fume-cupboard until the brown fumes subsided. The digest was allowed to cool and 2, 3 and 5 ml $HClO_4$, HNO_3 and HF, respectively, were added. This was then digested until the content was about 2 ml. The digest was allowed to cool and 5 ml of double distilled water was used to rinse the sides of the beaker. The content was filtered using 0.45 µm Millipore filter kit into a 50 ml standard flask and made up to the mark. The metal concentration was expressed as the mean of the triplicate digestion.

Quality assurance. This was carried out by using the spiking procedure in the absence of standard reference materials. The weighed samples were spiked with 0.02 ppm of Cd and Pb and 0.5 ppm of Cu and Zn. They were taken through the same digestion protocol for the lower plant and sediment samples as described above. Triplicate analysis of this process was carried out and the recoveries of the spiked elements were determined.

Statistical analysis. The results of the elements determined in the samples were subjected to statistical evaluation using the Pearson correlation coefficients.

$$r^2 = \frac{\sum x_i y_i - \sum x_i \sum y_i}{[n\sum x_i^2 - (\sum x_i)^2]\,[\sum y_i^2 - (\sum y_i)^2]}$$

Results and Discussion

Industrial areas from where samples were collected together with their sampling sites and designations are presented in Table 1. Results of the quality assurance of metals for the algal and sediment samples are presented in Table 2. The percentage recovery of the spiked elements in algae was between 93.8 to 96.0% while that of the sediments was in the range of 91.7 to 95.8%. The concentration of metals in algae and sediments for both the dry and rainy seasons at Oshodi/Isolo, Iganmu and Ikeja industrial areas are presented in Fig. 1a, b; 2a, b; and 3a, b, respectively.

Variation patterns of the metal values in the algal and sediment samples are shown in Fig. 4a, b; 5a, b; and 6a, b for Oshodi/Isolo, Iganmu and Ikeja industrial areas, respectively. The high percentage recoveries obtained from the spiked algal and sediment samples indicate the reliability of the analytical processes employed in this study.

The range and mean concentrations of Cd, Pb, Cu and Zn in algae at Oshodi/Isolo industrial area for the two seasons was 0.04-0.15 µg/g, 0.09 µg/g; 0.32-1.86 µg/g, 0.98 µg/g; 0.42-1.52 µg/g, 1.02 µg/g; and 0.10-1.80 µg/g, 1.12 µg/g, respectively. The range and mean concentrations of the elements in sediments in this area, in the same metal order were not detectable (ND)-0.10 µg/g, 0.05 µg/g; 0.12-1.32 µg/g, 0.78 µg/g; 0.21-2.65 µg/g, 1.27 µg/g; and 0.18-1.74 µg/g, 0.73 µg/g, respectively. The mean concentrations of metals at the residential areas (Table 3) for the two seasons were 0.02, 0.03, 0.06 and 0.12 µg/g in algae; 0.03, 0.07, 0.09 and 0.34 µg/g in sediments for the elements Cd, Pb, Cu and Zn in that order.

The range and mean concentrations of the metals (Cd, Pb, Cu and Zn) in algae at Iganmu industrial area were ND-0.21 µg/g, 0.08 µg/g; 0.20-1.84 µg/g, 1.12 µg/g; 0.17-1.90 µg/g, 0.93 µg/g; and 0.05-1.87 µg/g, 0.87 µg/g, respectively. The range and mean concentration in sediments for this area, also in the same metal order, were 0.04-0.50 µg/g, 0.13 µg/g; 0.22-1.85 µg/g, 0.99 µg/g; 0.15-1.78 µg/g, 0.88 µg/g; and 0.48-2.86 µg/g, 1.42 µg/g. The mean metal concentrations for the two seasons in algae at the residential areas were 0.02, 0.07, 0.05 and 0.07 µg/g for Cd, Pb, Cu and Zn, respectively, while those in sediments, in the same order were 0.05, 0.07, 0.08 and 0.08 µg/g.

Table 2. Percentage recoveries* of trace metals from spiked algae and sediment samples

Metals	% Recovery (algae)	% Recovery (sediments)
Pb	95.6 ± 0.4	92.4 ± 0.2
Cd	93.8 ± 0.2	91.7 ± 0.3
Cu	95.2 ± 0.3	95.8 ± 0.1
Zn	96.0 ± 0.1	94.2 ± 0.2

*average of three replicate analyses; ±: standard deviation

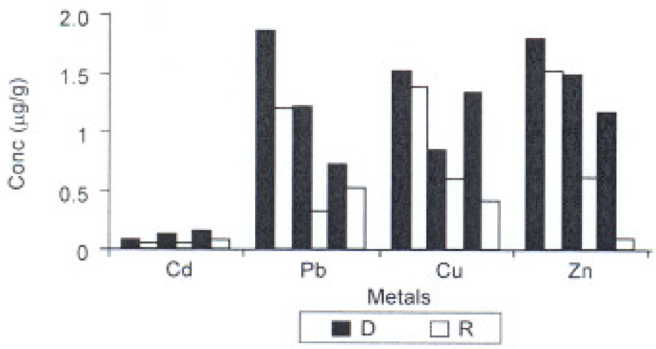

Fig. 1a. Concentration of heavy metals in algae (dry weight) at Oshodi/Isolo industrial area; D: dry season, R: rainy season.

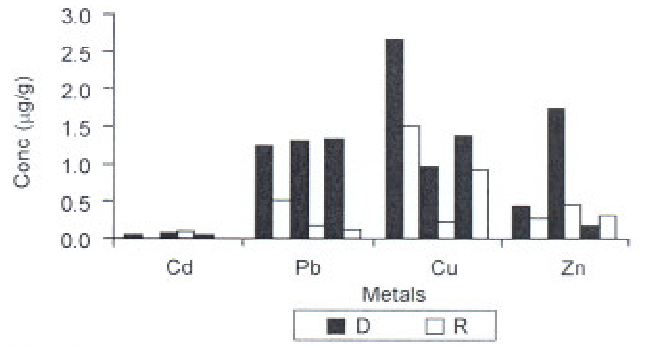

Fig. 1b. Concentration of heavy metals in sediments (dry weight) at Oshodi/Isolo industrial area; D: dry season, R: rainy season.

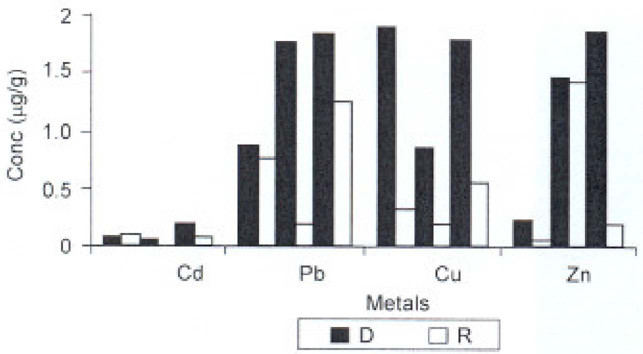

Fig. 2a. Concentration of heavy metals in algae (dry weight) at Iganmu industrial area; D: dry season, R: rainy season.

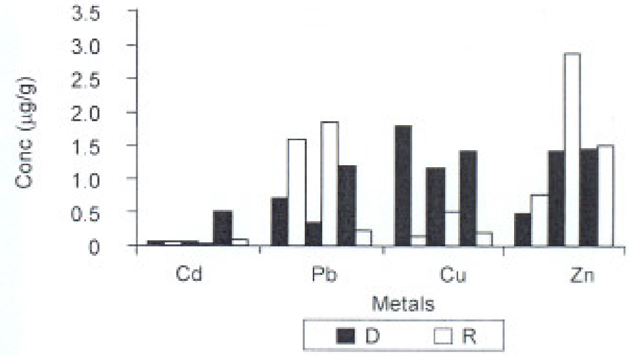

Fig. 2b. Concentration of heavy metals in sediments (dry weight) at Iganmu industrial area; D: dry season, R: rainy season.

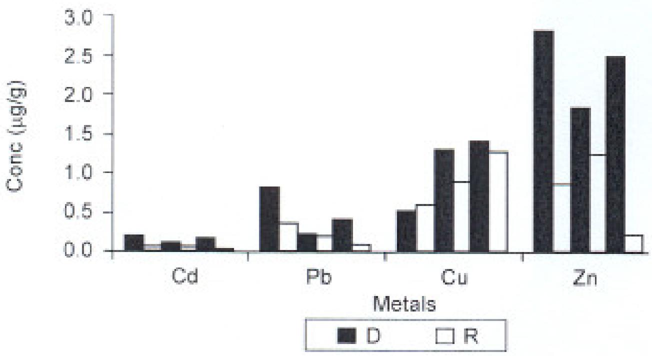

Fig. 3a. Concentration of heavy metals in algae (dry weight) at Ikeja industrial area; D: dry season, R: rainy season.

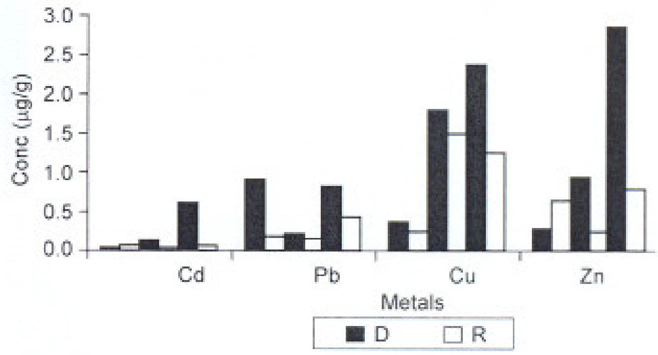

Fig. 3b. Concentration of heavy metals in sediments (dry weight) at Ikeja industrial area; D: dry season, R: rainy season.

At Ikeja industrial area, the range and mean concentrations of the metals (Cd, Pb, Cu and Zn) in algae for the sites and seasons were 0.05-0.18 µg/g, 0.10 µg/g; 0.08-0.82 µg/g, 0.40 µg/g; 0.51-1.40 µg/g, 1.00 µg/g; and 0.24-2.80 µg/g, 1.58 µg/g, respectively. Those for sediments in the same metal order were 0.04-0.60 µg/g, 0.15 µg/g; 0.16-0.90 µg/g, 0.50 µg/g; 0.24-2.35 µg/g, 1.24 µg/g; and 0.23-2.84 µg/g, 0.95 µg/g.

Samples from the residential areas at Ikeja recorded the presence but low concentrations of all the analysed metals when compared to values from the industrial areas. The mean concentration of metals for the two seasons following the above order in algae were ND, 0.14, 0.30 and 0.15 µg/g, while those in sediments were 0.07, 0.05, 0.33 and 0.46 µg/g.

Generally, highest concentrations of 0.21, 1.86, 1.90 and 2.80 µg/g of Cd, Pb, Cu and Zn, respectively, were obtained in algae while those in sediments were 0.60, 1.85, 2.65 and 2.86 µg/g, respectively, in the same metal order. There were significant differences in the mean metal concentrations

Table 3. Mean concentrations of metals (μg/g) in samples at residential areas for the two seasons

Metals	Samples					
	Algae			Sediments		
	Oshidi	Iganmu	Ikeja	Oshodi	Iganmu	Ikeja
Cd	0.02	0.02	ND	0.03	0.05	0.07
Pb	0.03	0.07	0.14	0.07	0.07	0.05
Cu	0.06	0.05	0.30	0.09	0.08	0.33
Zn	0.12	0.07	0.15	0.34	0.08	0.46

*three replicate analyses; ND: not detected

found in the algal and sediment samples from the three industrial areas when compared with their respective residential areas.

Although there were instances where individual metal level found in a sample from an industrial area was lower than those obtained from the residential areas at Oshodi/Isolo industrial area, relatively higher concentrations of Cu and Zn were detected in the samples than those of Cd and Pb. This is most likely due to the effluents coming from textile industries in this area which are released into the sewers, since Cu and Zn salts are known to be used in textile manufacturing processes.

Seasonal variation pattern of the metals revealed that their concentrations were higher during the dry seasons for algal samples with the exception of site III (Fig. 4a). Similar pattern was also shown by the sediment samples at this site with the exception of Cd at site II and Zn at site III (Fig. 4b).

At Iganmu industrial area, higher concentrations of all the elements were recorded in algae during the dry season with the exception of Cd at site IV (Fig. 5a). Similar distribution was shown by cadmium, copper and lead (except at site IV) in the sediment samples (Fig. 5b). A reverse distribution pattern was, however, displayed by Zn with higher concentration of the element during the rainy season.

At Ikeja industrial area, higher metal concentration was observed in algal samples at all sites during the dry season with the exception of Cu at site VII (Fig. 6a), while in sediment samples (Fig. 6b), only Cd and Zn at site VII showed higher concentrations during the rainy season.

Sediments are known to be the sink for heavy metals (Stephens *et al.*, 2001; Ankley *et al.*, 1996; Luoma 1989) where they concentrate according to the level of pollution. Algae that inhabit the sewers are also directly exposed to these trace metals from the effluents. Algae have been reported as accumulators of metals (Wong *et al.*, 2000; Cetinkaya *et al.*, 1999; de la Taboada *et al.*, 1998). The higher metal values, therefore, found in them, relative to that in the surrounding sediments are the possible indication of their accumulating capacity of heavy metals.

The higher values of the metals found in this lower plant during the dry season could be attributed to the nature of effluents being discharged into the sewers. During this period, effluent colours are usually deep in intensity and likely to contain higher concentrations of metals. Moreover, the volume of water flowing through the sewers during this season is usually lower than that during the rainy season. This possible dilution factor of the effluents might be responsible for the lower metal values obtained for the algal samples and some of the sediment samples during the rainy season. Generally, Cu and Zn were detected in both the algal and sediment samples in all the samples analysed.

Lead was also detected in most of the samples with the exception of samples from residential areas at the Oshodi/Isolo

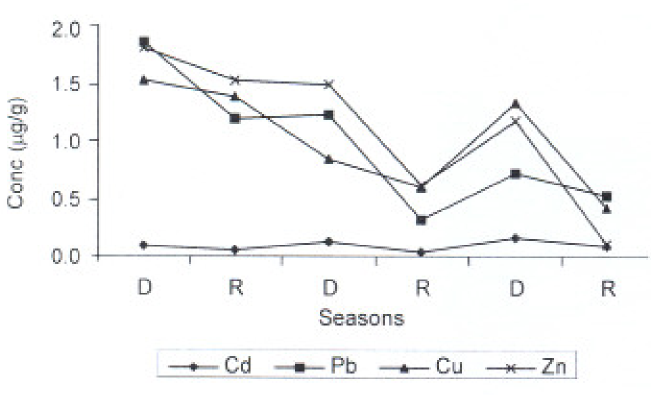

Fig. 4a. Seasonal variation of heavy metals in algal samples at Oshodi/Isolo industrial areas; D: dry season, R: rainy season.

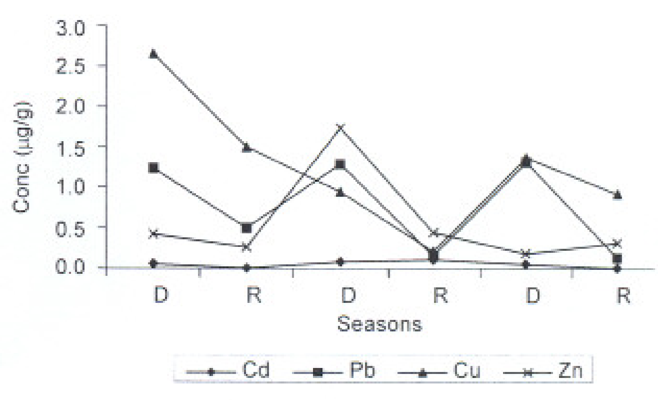

Fig. 4b. Seasonal variation of heavy metals in sediment samples at Oshodi/Isolo industrial areas; D: dry season, R: rainy season.

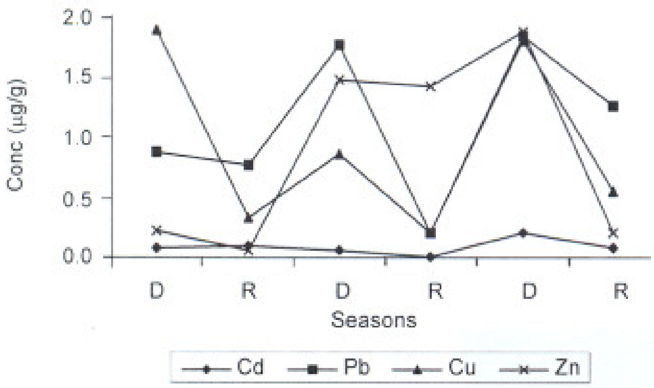

Fig. 5a. Seasonal variation of heavy metals in algal samples at Iganmu industrial areas; D: dry season, R: rainy season.

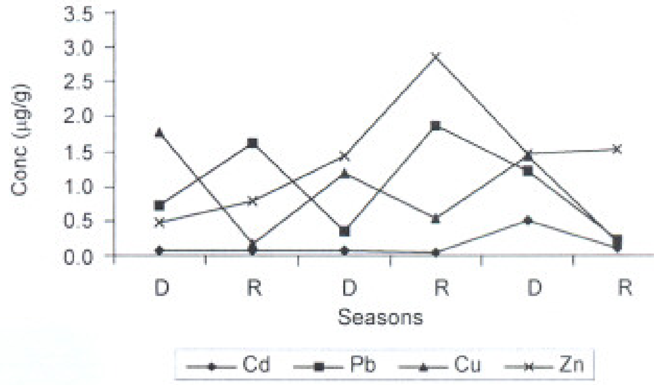

Fig. 5b. Seasonal variation of heavy metals in sediment samples at Iganmu industrial areas; D: dry season, R: rainy season.

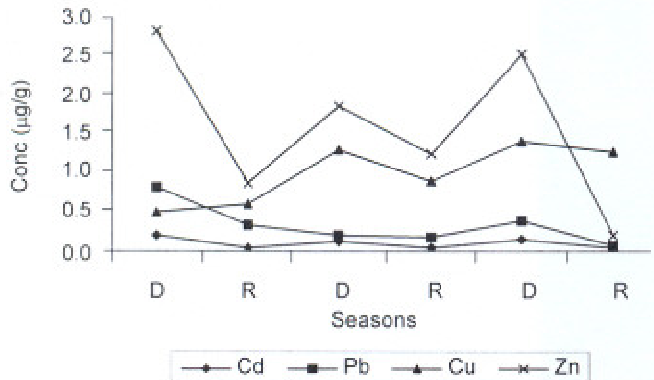

Fig. 6a. Seasonal variation of heavy metals in algal samples at Ikeja industrial areas; D: dry season, R: rainy season.

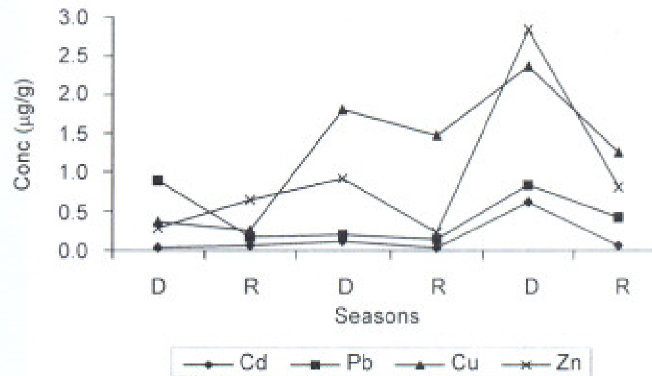

Fig. 6b. Seasonal variation of heavy metals in sediment samples at Ikeja industrial areas; D: dry season, R: rainy season.

industrial areas. Most probable sources of this metal were from effluents discharged into sewers by paint, battery, plastic and chemical industries within the sampled areas. Copper and zinc salts are known to be used in textile manufacturing processes. Effluents discharged by textile industries from the sampled areas are, therefore, most likely to contain these metals. Other sources include copper wire, plastics, and copper alloy industries with respect to copper, and electroplating, smelter, waste combustion and steel processing with respect to zinc. Although possible atmospheric deposition of metals from sources such as roadsides, automobile exhaust, etc., as contributing factors to the amount obtained, may not be ruled out (Harrop *et al.,* 1990). Copper and zinc are regarded as essential elements, however, their concentrations above the threshold levels could be toxic.

Recorded amounts of Cd were lower when compared to other analysed metals and was not detected in some of the algal and sediment samples. Possible sources of Cd and Pb in effluents are most likely from battery, paint, metal smelter and other chemical industries from the sampled areas. The metal values obtained in both the algal and sediment samples in each industrial area were subjected to statistical evaluation using the Pearson correlation coefficient. This was with a view to checking possible relationship between the metals in the samples. Average correlation of Pb ($r = 0.64$) was observed between algal and sediment samples, while a relatively significant correlation of Cu was obtained ($r = 0.81$) between the two samples at Oshodi/Isolo industrial areas. At Iganmu industrial area, Cd and Cu were highly correlated in the two samples with $r = 0.88$, and $r = 0.91$, respectively, while Zn and Pb were averagely correlated with values of 0.60 and 0.50, respectively. Significant correlation was also obtained with Pb and Cu at Ikeja industrial areas with values of 0.69 and 0.91, respectively. These correlations are indications of common sources of the metals in both samples. Generally, lower mean values of the analysed metals in sediments were obtained when compared with concentration range of 0.1-1.4 µg/g Cd, 9.0-61.9 µg/g Pb, 4219-15182 µg/g Cu, and 18.8-

126 μg/g Zn, reported in harbour sediments (Fatoki and Mathabata, 2001), 0.07-3.83 mg/kg Cd, 4.47-420 mg/kg Pb, 2.30-107 mg/kg Cu, and 9.75-2050 mg/kg Zn, reported in river sediments (Ouyang *et al.,* 2002) and mean concentration of 4.82 μg/g Cd, 28.1 μg/g Pb, 7.21 μg/g Cu, and 11.3 μg/g Zn reported in mangrove sediments (Shriadah, 1999).

The lower metal values obtained in sediments might be due to the continuous flow of effluents through the sewer which tend to "wash" off the sediments, only to be deposited in the larger fresh and marine environment. Consequently, accumulation and concentration of the metals within the sediment core in the sewers might not be significant compared to the high rate of sedimentation and lower undercurrent flow associated with sediments in the larger water bodies.

The results showed significant differences in the metal load in both algal and sediment samples analyzed from the industrial areas and those from their respective residential areas. The detection of metals such as Pb and Cd at residential areas might be due to atmospheric deposition of metal particulates possibly from automobile exhausts and Cd based waste materials such as batteries in some of the sewers. It is not uncommon to find wastes of various types of metal based materials such as batteries, iron rods, food cans, etc., in sewers at residential areas in Lagos.

Comparative assessment of the amount of metals obtained in sediment samples in all the sites was also made with standard guidelines. The Canadian Environmental Protection Authority guidelines for trace elements in sediments specifies maximum concentration of 3, 8, 22 and 40 μg/g for Cd, Pb, Cu and Zn, respectively (CEPA, 1976). The proposed South Africa guidelines as used by Maritz and Swanepool (1998), in the interpretation of their results on dredged silt suggested an amount of 10, 500, 500 and 750 μg/g in the same metal order as above. Both the individual and mean values of analysed metals in sediments were lower than those specified by both guidelines. Consequently, metal concentrations in sediments from sewers are not expected to be of environmental concern, however, regular monitoring of the metal load of the effluents from point sources is recommended. This is with a view to ensuring adequate protection and safety of the aquatic environment.

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