Sediment Quality of Effluent Discharge Channels from Six Industrial Sites in Lagos, Nigeria

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ABSTRACT: Concentrations of eight metals namely, Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb were examined in the surface sediments of discharge channels of six industries in Lagos using x-ray fluorescence spectrometry.These channels drain into the Isolo Canal which empties into the Lagos Lagoon and eventually into the Atlantic Ocean. This study was conducted to detect any contamination levels within the sedimentsand possibly determine their sources. Sediment samples were collected over a period of six months.The results provided evidence of large differences in total metal concentrations in the sediment samples from the six industrial sites. Box plots of the average absolute deviation from median emphasized that metal concentrations were not homogeneously distributed similarly, calculation of the *F* ratio confirmed location effect on the concentration of the various metals investigated. The trace metals Cr, Mn, Co, Ni and Cu might be entirely from crustal materials or natural weathering processes whilea significant amount of Zn and Pb are from anthropogenic sources.

Key words: Effluent, Pollution, Sediment, Metals, Industries, Lagos

INTRODUCTION

Sediments can be sensitive indicators for monitoring contaminants in aquatic environments (Ergin *et al*., 1991; Balls *et al*., 1997; Atgin *et al*., 2000). They are polluted with different kinds of hazardous and toxic substances including heavy metals and are important for the water quality (Pekey *et al*., 2004; Hsu *et al*., 2007). These accumulate in sediments via several pathways, including disposal of liquid effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban, industrial, and agricultural activities as well as atmospheric deposition (Harikumar *et al*., 2009).

Heavy metals from industrial and urban discharges are deposited in different components of the aquatic ecosystem, such as sediments, soils and biota. Heavy metals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Ramos *et al*., 1999; Tam and Wong, 2000; Mucha *et al*., 2003). Sediment analysis allows contaminants that are adsorbed by particulate matter, which escape detection by water analysis, to be identified (Geaney, 2005). The presence of these metals in aquatic systems originates from the natural interactions between the water, sediments and atmosphere with which the water is in contact. The

concentrations fluctuate as a result of natural hydrodynamic chemical and biological forces. Man, through industrialization and technology, has developed the capacity to alter these natural interactions to the extent that the very waters and the aquatic life therein have been threatened to a devastating point (Carman *et al*., 2007). In most circumstances, the major contribution of anthropogenic metals in a marine coastal area is of terrestrial origin, i.e. from mining, industrial, and urban development and other human practices near rivers and estuaries (Kucuksezgin *et al*., 2006), and these havea negative impact on several biological processes and there is no doubt that these will continue to affect the functioning of highly productive coastal ecosystems. Contamination caused by trace metals affects both ocean waters, those of the continental shelf and the coastal zone where, besides having a longer residence time, metal concentrations are higher due to input and transport by river runoff and the proximity to industrial and urban zones (Guzman and Garcia, 2002; Mucha *et al*., 2003).

It is widely recognized that marine ecosystems can become contaminated by trace metals from numerous and diverse sources and have been considered as an important indicator for environmental

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pollution; they act as permanent or temporary traps for material spread into the environment (DeGregori *et al*., 1996; Harikumar *et al*., 2009; Balkis *et al*., 2010). Trace metal levels can be indicators of the concentrations of other pollutants to which they are potentially related (Mateu *et al*., 1996), and have frequently been analyzed to identify sources of trace metal in the aquatic environment because of the high accumulation rates exhibited (Atgýn *et al*., 2000; Greaney, 2005). Most of the metals are retained by the surfaces of particles.They are preferentially transported, deposited, and eventually buried with fine-grained sediments (Perin *et al*., 1997; Balkis *et al*., 2010). The non-residual fraction of the sediment is considered to be mobile and therefore, is likely to become available to aquatic organisms (Waldichuk, 1985).

Anthropogenic derived inputs can accumulate in local sediments up to five orders of magnitude above the overlying water (Bryan and Langston, 1992; Ladipo and Ajibola, 2009).With such concentrations (Defew *et al*., 2004) showed that the bioavailability of even a minute fraction of the total sediment metal assumes considerable importance. This is especially true to burrowing and filter feeding organisms. This effort has prompted this research, to characterize sediments of effluent discharge channels of some industries in Lagos.The present paper aims at the degree of metal contamination of the surface sediments of these channels that eventually lead to the Lagos lagoon.

MATERIALS & METHODS

Ilupeju industrial area is located close to the densely populated Oshodi and Mushin residential areas of Lagos. Several industries are sited here out of which six were selected for investigation on the basis of the type of effluent discharges. The six industries coded as PZ, SMB, NCP, MTP, NSF and LYS are located in closed proximity; PZZ are manufacturers of household products such soaps, toothpaste, body creams etc.; SMB is a pharmaceutical industry; NCP manufactures paper and toiletries; MTP are manufacturers of plastics and polybags; NSF is a textile industry and LYS is a steel industry. All these industries have effluent channels that discharge into the Isolo Canal, which drain into the lagoon and finally to the Atlantic Ocean. Six surface sediment samples were collected on monthly basis along each industrial channel in the study area between April and October 2005. Sediment samples from sampling points were collected with the aid of a stainless steel grab of the Van-Veen type, sampling an area of $0.5\ m^2$.Samples were collected 0-10 cm deep from the surface.All of the sediment samples were stored in polyethylene bags immediately after collection and prior to undergoing analysis in a

laboratory. The samples were dried in a well-ventilated oven at 105° C (Ahmed *et al*., 2006;Lez-Maci´as *et al*., 2006). Large debris and fragments of shells were removed before grounding. All of the sediment samples were then ground in an agate mortar to obtain fine particles (<125 µm). Samples collected were homogenized and composited to obtain a single sample for each channel per month. A total of forty-two samples were thus analyzed.

Pellets of 19 mm diameter were prepared from 0.3-0.5 g of sample by mixing sample with an organic binder (polystyrene dissolved in toluene) and pressed afterwards at 10 tons with a SPECAC hydraulic press. Measurements are performed using an annular 25 mCi ^{109}Cd as the excitation source, that emits Ag-K X-rays (22.1 keV), in which case all elements with lower characteristic excitation energies are accessible for detection in the samples. The system consists furthermore of a Canberra Si(Li) detector, with a resolution of 170 eV for the 5.90 keV line, coupled to a computer controlled MCA-card (Trump 8K). The setup provides for dead time correction and pile-up rejection. Sensitivity calibration of the system was performed with thick foils of pure metals (Ti, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Sn, Ta, Pb) and stable chemical compounds (K_2CO_3, $CaCO_3$, Ce_2O_3, WO_3, ThO_2, U_3O_8). The spectra for the samples are collected for 3000 s with the ^{109}Cd source and 2000 s for the ^{55}Fe source and the spectra are then evaluated using the AXIL-QXAS program (Benasconi, 1996).

A thick foil of pure Mo was used as target material for absorption correction. The Mo was placed at 4 mm above the sample position and the intensity of Mo K peak was measured in the presence and absence of the sample for 100s in each case. The contribution of the Zr K_β line to the Mo K_α peak was subtracted in the various measurements. The Mo absorption line was used for the evaluation of the absorption of the samples. It was used as an input by the program for the evaluation of the residual material of the sample under consideration and for the determination of its elemental composition.

Descriptive statistics was performed on the data and because of variation in the quality of sediments over the months of investigation it is of utmost importance to use methods available for detecting and describing the distribution of the metals in the sediments from the various sampling sites.Thus Analysis of Variance (ANOVA) was used at 95% confidence level.The comparison between the actual variation of the group averages and that of the standard deviation of the estimated means is expressed in terms of the *F* ratio. This was computed from the ratio of the mean sum squared deviation of each

group's mean from the overall mean and the mean sum of the squared deviations of each item's group mean. The average absolute deviation from the median for each metal from each site were also obtained and presented as Box Plots. The p-values for each metal were also determined. The ANOVA results, when used in conjunction with the Box plots, provided statistical evidence that the heavy metals were not homogeneously distributed in all the sediments. The Statistical Package for the Social Sciences, version 13 was used to assess the statistical uniqueness of metal concentrations at each of the sample sites (SPSS Inc., 2003).

RESULTS & DISCUSSION

Though the amount and type of pollutant discharged into the environment may differ from one industry to another, it is evident from the present study that the industries in this work did not treat their effluents before finally discharging them into the environment (Ajibola and Ladipo, 2009). The metal concentration in the sediments obtained from the various locations like the water samples were found to be high and in most cases higher than the values obtained for the water and effluent samples (Ajibola and Ladipo, 2009). The total mean concentration of the metals in the sediment indicates that the sediments serve as reservoir for these metals. The results also provided evidence of large differences in total metal concentrations in the sediment samples from the six sites. Chromium enters aquatic systems through aerial deposition or surface runoff, and, subsequently, its association with particulate matter results in its deposition in bed sediments. The average Cr concentration in soils was reported to be 40-50 mg/kg (Adriano, 2001). Chromium exists commonly in two oxidation states Cr(VI) and Cr(III). Chromium (VI) is known to be more toxic than Cr(III). In natural environments with presence of reduced dissolved Fe(II) Cr(VI) will be reduced to Cr(III) (Marcussen*et al*., 2008). When Cr (VI) enters the food chain, it is toxic to humans (Muwanga and Barifaijo, 2006). The concentrations of Cr in all the sediments are presented in Table 1. All the sediment samples had high Cr concentrations that exceed the average reported by Adriano (2001). Sediments samples collected from MTP and NSF recorded the highest concentrations of 270 and 356 mg/kg respectively, with the NSF having the highest mean. Variations in the concentrations of the metals examined reflect anthropogenic input from the industries. The NSF samples showed the highest variation followed by the MTP samples. The average absolute deviation from the median is plotted for each metal and presented in Fig. 1. The result also showed that MTP and NSF had the highest average absolute

deviation from the median. This means that the distribution of Cr within this period showed some positive skewness. The result of ANOVA also revealed that there is significant difference in the concentration of Cr between the sample locations as shown by the *F* ratio is 0.98 (p = 0.446). This indicates that the industrial discharges from these industries are the likely cause of this difference.

The Mn concentrations in all the sediments were high with large variations (Table 1). The LYS sediments had the highest concentration, 411 mg/mg and the highest standard deviation (96.3) followed by the SMB sediments with 370 mg/kg and standard deviation of 82.8. The values obtained for the average absolute deviation from the median showed that the distribution of Mn in all the sediments deviated from the normal distribution (Fig. 1). The *F* ratio for Mn in these sediment samples is 1.05 (p = 0.404). This also indicates that the accumulation of Mn in the sediments was also as a result of the industrial activities carried out by the different industries. The NCP sediments recorded the highest Fe mean value (246000 mg/kg) and showed the least variation of all the locations (Table 1). The PZZ sediments recorded the lowest concentration of Fe, 6600 mg/kg. The average absolute dispersion from the median in all cases is relatively low with the highest being the LYS sediments, while NCP recorded the lowest. This result suggests that the distribution of Fe in the sediments is close to being normal. The large value of *F* (7.84) indicates there was contribution by the different industries, however, the low value p (p = 0.000) indicates that the difference between these industries is not significant. Again this showed that the concentration of Fe in the sediment was not entirely as a result of discharges from these industries.

The average abundance of Co in soils/sediments is around 8 mg/kg (Adriano, 2001). All of the analyzed sediments have concentrations above this acceptable range. Cobalt is relatively non-toxic animals and man and deficiency of Co is of far greater concern than potential toxic levels in plants. The NCP samples recorded the highest mean 84.4 mg/kg and lowest mean was obtained for samples collected from PZZ 46.5 mg/kg (Table 1). The variation in the concentration of Co in the sediments showed anthropogenic input. Result from ANOVA showed that MTP sediments had the least average absolute dispersion from the median followed by the PZZ sediments. The *F* ratio of the mean Co concentrations for the different locations is 3.11 and p = 0.02 (Fig. 1). There is a significant difference in the variation of Co among these sites again indicating that this difference is as result of discharges from these industries.
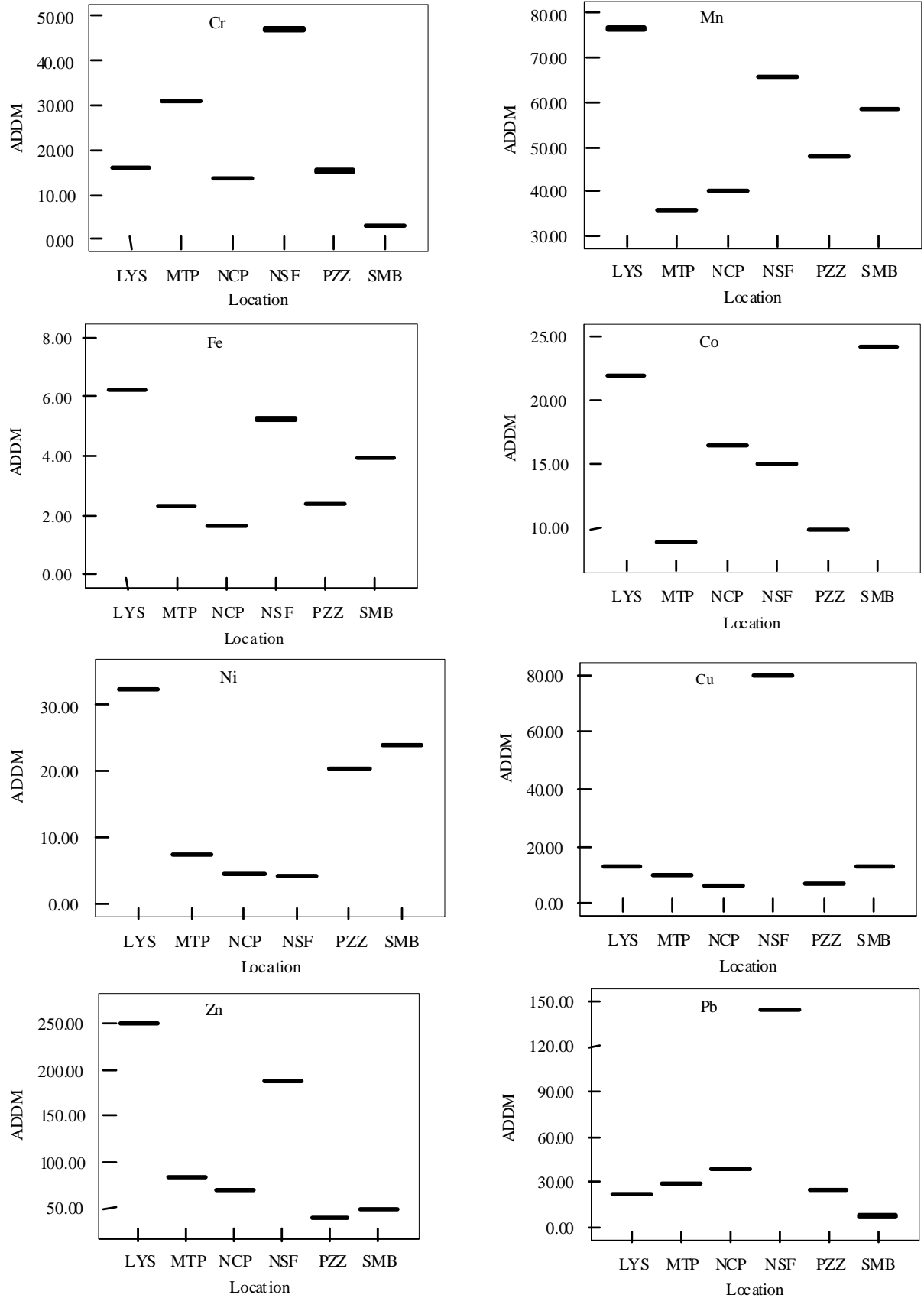
Fig. 1. Box plots showing the Average absolute deviation from the median at 95% confidence level for all the metals (ADDM is the Average Deviation from median)

Table 1. Descriptive statistics of metals in surface sedimentsof the discharge channels

Location	Min-Max Concentration (mg/kg)	Mean (mg/kg)	Standard deviation	Median (mg/kg)
Chromium				
PZZ	104-183	144.43	23.8	146
SMB	134-148	139.71	4.5	140
NCP	140-175	161.28	17.4	164
MTP	141-270	180.43	45.4	167
NSF	103-356	167.86	86.3	145
LYS	115-187	145.71	22.7	139
Manganese				
PZZ	59-312	198.14	75.8	214
SMB	139-370	224.63	82.8	188
NCP	210-339	267.71	49.7	258
MTP	124-259	200.14	46.9	189
NSF	121-302	208.2	79.1	181
LYS	152-411	250.57	96.3	238
Iron				
PZZ	6600-117000	69000	343	69000
SMB	102000-233000	152700	5450	142000
NCP	184000-283000	246300	3010	250000
MTP	79200-194000	121300	3620	116000
NSF	63100-235000	130400	6950	106000
LYS	91500-354000	178600	8910	171000
Cobalt				
PZZ	23.8-66.2	46.50	13.5	46.2
SMB	43.9-124	75.47	30.2	47.3
NCP	60.9-125	84.40	22.6	84.1
MTP	39.9-87.1	51.14	16.5	45.2
NSF	34.1-92.9	53.53	22.6	42.2
LYS	37.1-119	71.77	28.5	60.5
Nickel				
PZZ	15.4-90.0	41.17	28.0	26.6
SMB	21.70-94.5	53.84	29.6	47.3
NCP	23.0-46.4	29.71	7.83	26.4
MTP	23.3-57.6	33.26	11.8	27.4
NSF	14.7-30.6	21.96	5.45	21.8
LYS	55.3-158	107.14	40.7	128
Copper				
PZZ	9.4-35.5	22.44	8.77	20
SMB	28.4-74.8	51.91	16.8	53
NCP	24.3-50.6	38.09	8.79	37
MTP	41.7-87.8	59.54	14.7	58.8
NSF	73.1-387	161.39	114	124
LYS	47.1-104	73.36	18.1	74.4
Zinc				
PZZ	93.6-219	140.77	53.7	114
SMB	106-283	173.14	63.2	158
NCP	75.2-334	208.03	89.1	186
MTP	304-680	410.71	130	356
NSF	140-827	365.43	258	215
LYS	270-1400	613.57	383	599
Lead				
PZZ	7.54-123	55.65	45.8	45.8
SMB	38.30-72	56.33	10.6	56
NCP	63.4-215	125.97	51.5	125
MTP	83.6-237	124.09	52.7	102
NSF	139-735	346	204	259
LYS	43.5-102	69.34	27.1	56.2

The average Cu content in soils/sediments is considered to be about 30 mg/kg. The Cu analyses in the present study are not within acceptable range, except for the samples from PZZ, 22.44 mg/kg; NCP 38.09 mg/kg is only slightly above this average (Table 1). The NSF sediments showed the highest concentration, 387 mg/kg and standard deviation of 114. The high Cu value in the NSF sediments seems to be related to textile activities. Result for the average absolute deviation from median also shows that the distribution of Cu in the NSF sediments was not normal. The NSF sediments have the highest value of 79.5 while the SMB and LYS sediments have a distance second of 12.7. The *F* ratio for this metal is 7.23 (p = 0.00). The statistical result obtained for Cu is similar to that obtained for Fe. The large value of *F* indicates there was contribution by the different industries; however, the low value p indicates that the difference between these industries is not significant. Again this showed that the concentration of Cu in the sediment was not entirely as a result of discharges from these industries. Although copper toxicity in humans is rare, aquatic organisms are potentially at risk from Cu exposures (Adriano, 2001).

The average Ni concentration in soils/sediments is reported as 20 mg/kg. The LYS sediments recorded the highest concentration of 158 mg/kg and standard deviation (Table 1). Although Ni is relatively less toxic to invertebrates, it can be toxic to aquatic organisms such as reduction in skeletal calcification and diffusion capacity of gills (Moore, 1991). The sediments from the LYS may therefore affect fish when eventually discharged into the canal. The distribution of Ni in the sediments is not normal from values obtained for the average absolute deviation from the median. Again result was obtained for the F ratio is similar to those obtained for Fe and Cu. Here *F* ratio is 11.41 and p = 0.00. This suggests a form of association between these metals in the sediments.

The average concentration of Zn in soils/ sediments is 90 mg/kg. The sediments collected from LYS (a steel industry) had highest mean concentrations of Zn (613 mg/kg), followed by those from MTP, manufacturers of polybags (Table 1). LYS and NSF sediments recorded the highest standard deviations of 383 and 258 respectively. The average absolute deviations from median for all the sediments are relatively high with LYS and NSF again recording the highest (251 and 187 respectively). The *F* ratio is 5.58 and p is 0.00 again similar to results obtained for Fe, Cu, and Ni.

The Pb levels in sediments around the NSF are highest, 139-735 mg/kg, followed by those collected from the MTP (83.6-237 mg/kg) and NCP (63.4-215 mg/

kg). The distribution of Pb in all the sediments deviated from a normal distribution with the NSF sediments deviating the most with a value of 144 (Table 1). The highest variations in the concentration of Pb were also found in these sites with NSF recording 346 mg/kg. *F* ratio obtained for Pb is 10.45 (p = 0.00). Although Pb is expected to have low phytotoxicity because of its strong affinity to organic matter, when environmental conditions e.g. change in pH, it may become mobile. Assessment of sediment contamination by the contamination factor (C_f^i), degree of contamination (C_d) and enrichment factor (EF) were carried out for all the locations. Contamination factor ()described as the contamination of a given toxic substance in a basin suggested by Hakanson (1980) was used and is given by

$$C_f^i = \bar{C}_f^i = \frac{\bar{C}_{0-1}^i}{C_n^i}$$

where C_n^i is the reference value of the substance obtained from Hakanson (1980) and Pekey*et al.* (2004); $\bar{C}_{0-1}^i$ is the mean content of the substance in sample. The following terminologies are used to describe the contamination factor: C_f^i< 1 low contamination factor; 1 d" < 3 moderate contamination factor; 3 d" < 6 considerable contamination factor; e" 6 very high contamination factor. Degree of contamination (C_d) is defined as the sum of all the contamination factors of a given basin:

$$C_d = \sum_{i=1}^n C_f^i = \sum_{i=1}^n \frac{C_{0-1}^i}{C_n^i}$$

For degree contamination the following terminologies have been used: C_d< 7 low degree of contamination; 7 d" C_d< 14 moderate degree of contamination; 14 d" C_d< 28 considerable degree of contamination; C_d e" 28 very high degree of contamination. The results calculated for C_f^i and C_d is given in Table 2. The contamination factor () values for Cr in all sites are moderate with the order MTP > NSF > NCP > LYS > PZZ > SMB. The values obtained for Mn show low contamination factor in all the sites. The contamination factors for Co were moderate for PZZ, MTP, NSF and LYS while SMB and NCP recorded considerable contamination factors. The values for Ni are low for all the sites except for LYS where a moderate contamination factor was observed. The sediments of PZZ, SMB and NCP gave low contamination factors while MTP, NSF and LYS were moderately contaminated with Cu. The contamination factors for Zn range from moderately contaminated at PZZ, SMB and NCP through considerable contamination at MTP and NSF

to very high contamination factor at LYS. Lead also varied between moderately contamination factor at SMB, NCP and LYS to moderate contamination factor at PZZ and MTP and very high contamination factor at NSF. The C_d values indicate moderately contaminated sediments at PZZ, SMB and NCP, while considerable degree of contamination was recorded in an increasing order at MTP, LYS and NSF suggesting anthropogenic pollution at all the sites with NSF being the most polluted.

Metal enrichment factor (EF) which is an index used to evaluate anthropogenic influences of heavy metals in sediments and generally defined as the observed metal to Fe ratio in the sample divided by the background metal/Fe ratio was used to determine the sources of pollution. This is given by the expression:

$$EF = \frac{(M/Fe)\ sample}{(M/Fe)\ Crust}$$

Commonly geochemical normalization of heavy metals data to a conservative element such as Al or Fe, whose levels are unaffected by contaminant inputs, is employed in order to identify anomalous metal concentration (Zhang *et al.*, 2007; Balkis*et al.*, 2010). The $0.5 < EF < 1.5$ suggests that the trace metals may be entirely from crustal materials or natural weathering processes. $EF > 1.5$ suggests that a significant portion of trace metals are provided by other sources. The results for EF values are given in Table 3.The EF values Cr, Mn, Co, Ni and Cu were found to be equal to or less than 1.5 suggesting that these trace metals might be entirely from crustal materials or natural weathering processes. EF values obtained for Zn in most locations and Pb in all locations were greater than 1.5 suggesting that a significant amount of these trace metals is from anthropogenic sources.

Table 2. Contamination factors C_f^i and degree of contamination (C_d) of surface sediments of the discharge channels

Site	C_f^i							C_d
	Cr	Mn	Co	Ni	Cu	Zn	Pb	
PZZ	1.44	0.21	1.86	0.55	0.41	2.01	3.60	10.08
SMB	1.40	0.24	3.02	0.72	0.94	2.47	1.66	10.45
NCP	1.61	0.28	3.38	0.39	0.69	2.97	2.30	11.62
MTP	1.80	0.21	2.04	0.44	1.08	5.87	4.61	16.05
NSF	1.68	0.22	2.14	0.29	2.93	5.22	11.95	24.43
LYS	1.46	0.26	2.87	1.43	1.33	8.76	1.75	17.86

Table 3. EF values of the metals in surface sediments of the discharge channels

Site	Cr	Mn	Co	Ni	Cu	Zn	Pb
PZZ	1.18	0.17	1.50	0.44	0.33	1.64	3.60
SMB	0.52	0.09	1.11	0.26	0.35	0.91	1.66
NCP	0.37	0.06	0.77	0.09	0.16	0.68	2.30
MTP	0.84	0.10	0.95	0.21	0.50	2.72	4.61
NSF	0.72	0.09	0.92	0.13	1.27	2.25	11.95
LYS	0.46	0.08	0.90	0.45	0.42	2.76	1.75

CONCLUSION

The concentrations of metals were found in some sites were found to exceed those commonly found in soil/sediments. It was found from statistical treatment of the data that the accumulation of these metals in the sediments was in some cases as a result of discharge of untreated effluent to the environmentand none of the variables has normal distribution. The trace metals Cr, Mn, Co, Ni and Cu might be entirely from crustal materials or natural weathering processes whilea significant amount of Zn and Pb are from anthropogenic sources. Therefore, the risk of bound contaminants being spread into the environment, e.g. during situations of high water discharge of flood as a result of rainfall will grow with the increasing amount of sediment trapped in these effluent channels. This in turn is a risk to fish and benthic animals in the major Isolo Canal that receives these discharges.

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