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CORRELATION AND PARTITIONING OF SOME HEAVY METALS IN AQUATIC MEDIA AROUND A MAKE SHIFT CRUDE OIL REFINING AREA

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Abstract

The major aim of the present study was to evaluate the concentration levels of some heavy metals and their relationships between the bottom sediments, its overlaying (bottom) water and the surface water of the study area in Andoni local Government of Rivers State, Nigeria (Long.7 ° 20′ 48.639″E and Lat.4 29 20.169N) using standard methods of analysis. The mean result showed variation patterns ($P<0.05$) of the metals in each of the medium as - surface water – Mg>N=Cu=Zn>Pb=Cd>V; bottom water – Mg>Cu>Ni=Zn>Pb=Cd>V and bottom sediments – Mg=Zn>Pb>Cd>Cu=Ni>V, while that of the media for each metal is Sediment >> Bottom water=Surface water. The sediments of the study area had more positive significant correlations among metal pairs than others indicating that metals were more bound to the sediments than in the water columns. V-Cd, V-Pb and V-Ni showed significant positive correlations in the water columns indicating that their input sources may likely be the same, which could have been from petroleum related activities. The level of contamination of the study area is relatively high when compared to related studies within and outside the region. It is therefore recommended that the activities of this make-shift refining of crude oil in the area should be stopped by the relevant regulatory agencies and also further studies on other media should be carried out.

Key words: Environmental safety, Contamination, Sediments, Quality, Water columns

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Introduction

Heavy metals are regarded as major contaminants of the aquatic environment due to the persistency, toxicity and ability to accumulate in most substrates. Several workers have reported the concentration and partitioning of heavy metals in water columns (Obire et al. 2005), sediments (Osuji and Onojake, 2004) and both water and sediments (Addo et al. 2011, Howard and Briggs, 2012). The outcome of most of these reports is that the aquatic environment is regarded as dumping grounds in most less developed countries (Obire et al. 2005, Samir et al. 2006, Howard and Briggs, 2012).

The unregulated waste discharge has led to the pollution of the aquatic ecosystem due to the immobilisation of toxic materials which in most cases include heavy metals. The toxicity of most of these metals has been attributed mainly to capability of the ions to form stable complexes with the active sites of proteins (Moyer, 2014). Masoud et al. (2005) has reported that "factors such as pH, redox potential, total organic carbon and cation exchange capacity (CEC) were identified as some of the major indices controlling the levels of metals in a river system". Similarly, other related factors that control metal activities in an aquatic ecosystem are bottom and suspended sediment compositions and the hydrodynamics of the water columns (Akcay et al.2003, Abdel- Ghani and Elchaghaby, 2007). Different types of changes are bound to occur as the metals are immobilized from these substrates (Akcay et al.2003, Abdel- Ghani and Elchaghaby, 2007), which of course affects their availability in the water columns and the sediments (Marchand et al. 2006, Nicolau et al. 2006, Pekey, 2006, Nouri et al. 2011).

Sediments of aquatic environment have significant roles in mobilisation of dissolved heavy metals, although they can also be a source of metal pollution by immobilisation through biogeochemical features of the aquatic ecosystem. Several studies have indicated that due to temporal and spatial variability in water column, it is always problematic to obtain representative samples to actually show the true concentration of contaminants in surface water (Osuji and Onojake, 2004, Ezekiel et al. 2011, Howard and Briggs, 2012, Ephraim and Ajayi, 2014). Similarly, sediments accumulate pollutants which interweaves with the water columns, hence the analysis of chemical parameters in sediments in relation to its immediate overlaying water columns can permit proper quantification of contaminants that may either be detected or undetected in the water columns (Boreretzen and Albu, 2002, Obire et al. 2005). It is for these reason and coupled with the activities of the make shift crude oil refinery of the study area, that we set out to evaluate the concentration levels of some heavy metals and their relationships between the bottom sediments, its overlaying (bottom) water and the surface water.

Study area

The study area which is closed to the make shift crude oil refining area (source point) is located at the South-West fringe of the Andoni Local Government Area, Rivers State, precisely between Long.7^{o} 20′ 48.639″E and Lat.4 29 20.169N. The River is tidal in nature and drains the adjoining mangrove on both sides; it empties into the Andoni River (Okwaan Obolo), one of the major rivers draining the Eastern Niger Delta into the Atlantic Ocean. Generally, the area is low-lying; it is about 5m below sea level. The area is typical of the Niger Delta ecosystem that is supported by saline soil with potential of Hydrogen (pH) value of between 4 for freshly deposited soft silt low tide and 7 for transitional swamps at high tide. Six sampling stations (SSA, SSB, SSC, SSD, SSE and SSF) hereafter referred to as A, B, C, D, E and F was chosen within the study area as indicated in Figure 1. The first sampling station (SSA) is located some kilometers away - upstream from the source point (SSC) with GPS coordinates 7^{o} 21′ 53.592″E and 4^{o} 28′ 50.374″N. Mangrove plant species here is densely populated with sights of crabs, mudskipper, periwinkles and birds. The surface mud at this station was normal-not stained with oil, but careful observation could reveal very thin oil sheen on the surface of the river at this station. The second sample station (SSB) lies within 7^{o} 21′ 37.046″E and 4^{o} 28′ 42.957″N. Oil sheen was seen on the surface of the river, especially during low tide. Mangrove plants were sparsely dense with dotted aquatic fauna such as juvenile periwinkle, crabs, mudskipper, etc. in the mangrove mudflats. The mud here is oil-stained, but no direct inlet of spilled oil into the water body was observed.

Sample station C is the source point where the raw crude oil and some crudely refined products find their way into the river – either via surface run-off or seepage whenever there was a large spill. It is within 7^{o} 21′ 23.353″E and 4^{o} 28′ 50.945″N. The surface mud here is darkened from oil stain and greasy, with scanty mangrove plants, withered leaves, prop roots and stems. No aquatic organism was spotted as oil sheen was seen on the surface of river water and the adjourning mudflats.

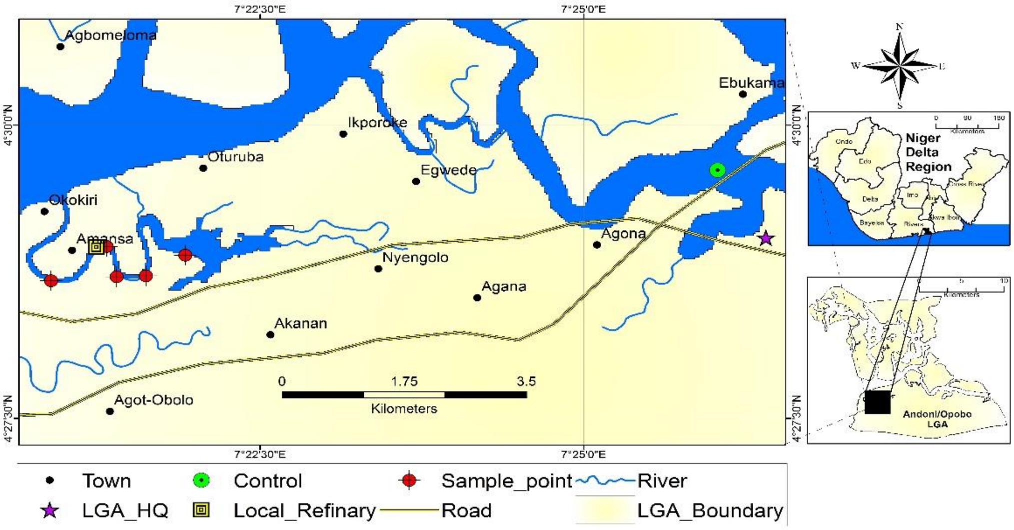

Figure 1: Map of the study area showing sample stations

Sample station (SSD) is located downstream from SSC with GPS coordinates 7^{o} 21′ 13.654″E and 4^{o} 28′ 38.963″N. Oil sheen was seen on the surface of the river, surface sediments at both side are badly oil-stained as aquatic fauna and flora are very scanty and unhealthy. Sample station E (SSE) is downstream from SSA, with GPS coordinates 7^{o} 20′ 53.685″E and 4^{o} 28′ 40.675″N. This station has relatively buoyant aquatic flora and fauna; which can be attributed to its location which is almost at the mouth of the river vis-à-vis its interaction with fresh and relatively uncontaminated water from the larger Andoni River which drains this point first. Oil sheen is seen on the surface of the river water at this station only during ebb tide.

A sample station (SSF) was chosen as control point at an unimpacted Creek which is far away from the test stations in the same Local Government Area, specifically around the Ngo axis, the mangrove at this station is dense and green with an abundance of aquatic fauna (crabs, periwinkles, mudskippers, birds, reptiles and other aquatic invertebrates). The mangrove mud here is not stained with oil and oil sheen was not seen on the surface of the water here.

Materials and Methods

Water and sediment samples were collected by the method of Ezekiel et al. (2011); each sample was concurrently collected in triplicates from each station once in the dry and wet seasons between 2012 -2013. The surface water samples were taken just below the surface at each sampling stations, while the bottom water samples were taken at about 10ft depth of the column. Each sample were placed into a polyethylene bottle and labeled according to the sampling sites. Each of the water samples were acidified to pH <2 using 10% analytical grade HNO_3.

The sediment samples were emptied into polyethylene bags, labeled according to the sampling sites and placed in a separate sample chest with ice, thereafter, transported to the laboratory, same day for each sampling trip. In the laboratory sediment samples were sun dried for 48 hours, then macerated into a powdery form and sieved with a 1.0mm sieve. The sieved samples were stored in well-labelled smaller plastic containers with cover, from where samples were withdrawn for metal analysis.

100 ml each of the water samples were digested, while 0.5g sediment samples were digested by the nitric acid-perchloric acid method (Howard and Briggs, 2012). Samples were allowed to cool and thereafter filtered into a 100.0ml standard flask and were later made up to the mark with distilled water. Aliquot portions of the digests were aspirated into Buck Scientific (205A) Atomic absorption spectrophotometer one at a time (Okafor and Opuene, 2007).

Quality assurance

To ensure accuracy and precision of the data obtained from sampling to final quantification of the metals in the samples, appropriate quality control and assurance measures were undertaken all through the study period.

Statistical analysis

Data was analysed using Microsoft office Excell 2003 and SPSS version 20, while mean separation of the metals within and between the media was done with Duncan Multiple Range Test (DMRT) at 95% confidence level.

Results

The mean levels of the metals Cu, Zn, Mg, Ni, V, Cd and Pb in the bottom sediments and water columns of the study area as presented in Figure 1, that indicated Mg to be the highest in the three media and V the least. The sediment load of each of the metal were higher ($P<0.05$) than those of the water columns, whereas there were no significant difference of the metals between both columns of water from the study area. Zn and Mg were significantly higher in the wet season than in the dry season for sediments, Cu was significantly higher in the dry season than in the wet season in bottom water while there was no significant seasonal difference for all the metals in the surface water. Comparative study of the result of the test stations (SSA –E) and the control station (SSF) for all the metals indicates that Zn, Mg and Cd in both bottom and surface water were higher in the control station than in the test stations, whereas in the sediments all the metals were higher in the test stations than in the control stations (Figures 2 – 5). The mean variation patterns ($P<0.05$) of the metals in each of the medium is as follows surface water – Mg>Ni=Cu=Zn>Pb=Cd>V; Bottom water – Mg>Cu>Ni=Zn>Pb=Cd>V and bottom sediments – Mg=Zn>Pb>Cd>Cu=Ni>V (Figure 1), while that of the media for each metal is Sediment >> Bottom water=Surface water.

The correlational analysis of the metals between media pairs (bottom and surface water, bottom sediment and water and bottom sediment and surface water) showed some significant relationships (Table 1). Li et al. (2012) has observed that "heavy metals in the environment usually have complicated relationship among them" while Rafiei et al. (2010) noted that "heavy metals showing very high correlation may indicate same origin and controlling factors". Cd had the highest correlation coefficient for the three media pairs $r = 0.982$, 0.723 and 0.688 respectively (Table 1). The determination coefficient (R^2) of these significant relationships (Table 1) indicates that each medium depends on each other in a pair for the metal values which is unlike those without significant relationships. The highest log transformed partition coefficient observed in this study is Cd in bottom sediment and water 4.16 and was followed by that in bottom sediment and surface water 4.22 (Table 1). The Pearson product moment correlation coefficients of heavy metals in the media showed several metal pair correlations ($P<0.05$) (Table 2). Bottom sediments had more positive correlations than others. For the three media pair Cu-Zn are common.

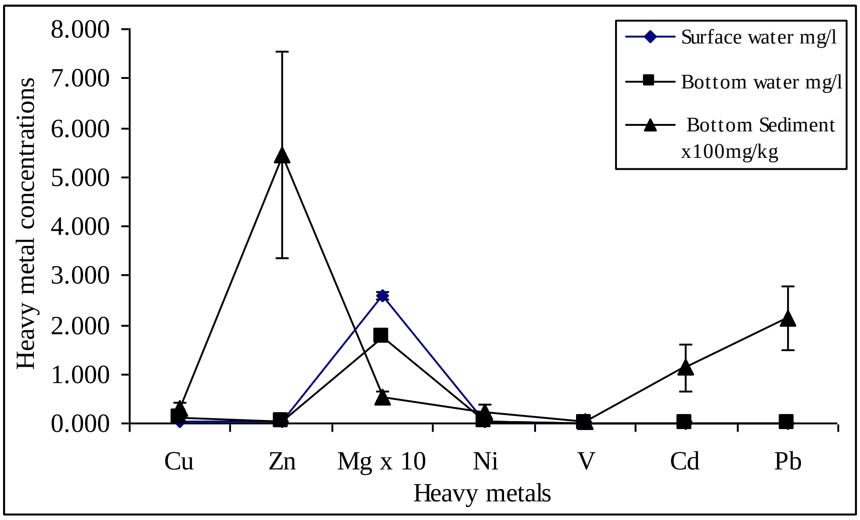

Figure 2: Mean heavy metals levels in the bottom sediments and the water columns of the test stations from the study area.

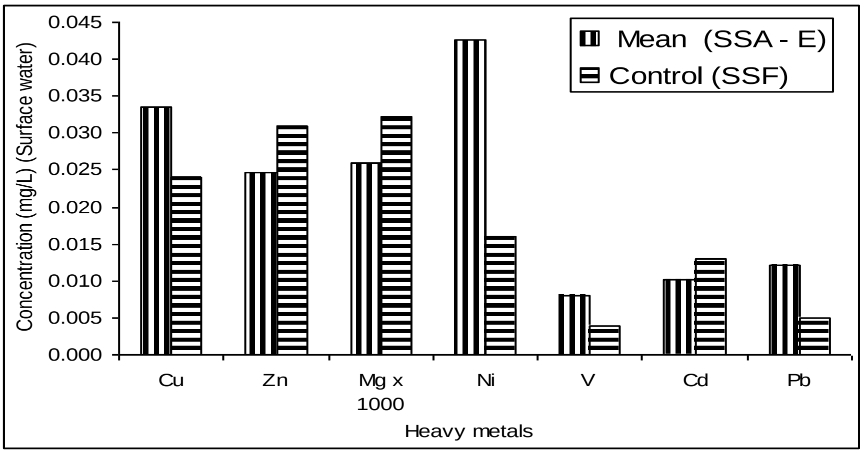

Figure 3: Comparison of the mean heavy metals levels in the surface water of the test stations and the control station.

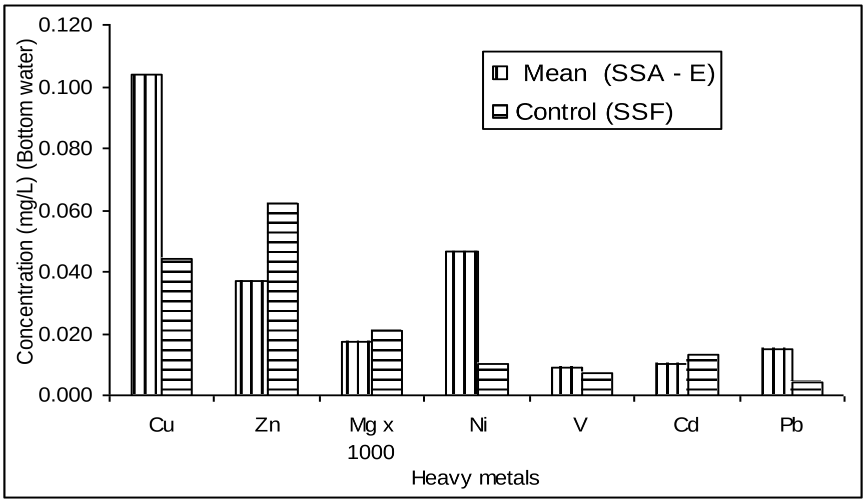

Figure 4: Comparison of the mean heavy metals levels in the bottom water of the test stations and the control station.

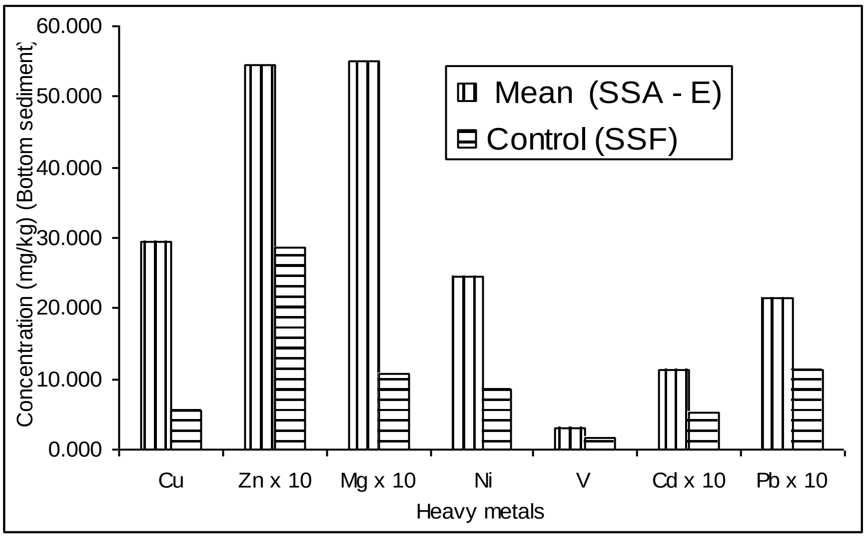

Figure 5: Comparison of the mean heavy metals levels in the bottom sediments of the test stations and the control station

Table 1: Some significant relationships of the metals in the media showing their r, R^2, kd and Logkd

Media pair	**Metals**	**Relationship**	**Correlation coefficient (r)**	**Determination coefficient (R^2)**	**Partition coefficient (Kd)**	**LogKd**
[Bottom sediment (y) and bottom water (x)]	Mg	y = -23.781x + 905.4	0.555	30.8%	31.8	1.5
	Cd	y = 3699.6x + 64.48	0.723	52.3%	14295.7	4.16
[Bottom sediment (y) and surface water (x)]	Cd	y = 3573.3x + 66.42	0.688	47.3%	16757.1	4.22
[Bottom water (y) and surface water (x)]	Cu	y = 2.449x + 0.015	0.672	-	2.195	0.34
	Zn	y = 1.390x + 0.006	0.799	-	1.78	0.25
	Ni	y = 1.066x - 0.0001	0.838	45.2%	1.037	0.016
	V	y = 1.292x - 0.0005	0.897	63.9%	1.448	0.161
	Cd	y = 0.997x + 0.0002	0.982	70.1%	1.128	0.052
	Pb	y = 1.068x + 0.0013	0.709	80.4%	1.107	0.044

Table 2: Pearson product moment correlation coefficients between metal levels in the various media

Metals	Sediment	Surface water	Bottom water
Pb – Mg	**0.583***	-0.638*	-0.680*
Zn – Pb	**0.921****	-0.677*	-
Cu – Ni	**0.661***	-	-
Cu – Pb		-	0.978**
Cu – Zn	**0.784****	-0.642*	-0.591*
Cu – Mg	-	-0.597	-0.647*
Cu- Cd	**0.915****	-0.730**	-
Mg – Ni	**0.840****	-0.834**	-
Mg – Cd	**0.552***	-	-
V – Cd	-	0.790**	0.757**
V – Pb	-	0.590*	-
V – Ni	-	-	0.835**

** Correlation is significant at the 0.01 level 0.684, * Correlation is significant at the 0.05 level 0.553

Discussion

The results of the study on correlation and partitioning of some heavy metals in the bottom sediments and water columns from the study area have shown variability in the levels of the metals in the different media. For instance the sediment load of each metal was significantly higher than those of the water columns. This affirms the observation of other researchers that sediments act as sinks to pollutants (Isidori et al. 2004, Marchand et al. 2006, Pekey, 2006, Samir et al. 2006). This is unlike the water columns that are tidal in nature according to the hydrodynamics of the area; even if the water is stagnant some of these pollutants will ultimately find their way to the bottom, thereby making the sediment host to most pollutants. Another possible reason could be due to the physicochemical nature of the overlaying water and the sediments. For instance high levels of Fe in sediments has been attributed to high levels of dissolved oxygen and pH in the water that leads to mobilisation of $Fe(OH)_3$ in the bottom sediments (Masoud et al. 2005). Again the activities of microorganisms in both media are other factors, for example assimilation of trace metals by organisms and later relocation and discharges as waste material and body adsorption**.** The reason why there were no significant differences between the water columns may be due to the hydrodynamics of the Atlantic ocean and also other runoffs; but some of the metals e.g. Cu, Zn, Ni, V and Pb, where higher in the bottom water than in the surface, though not significant. This could be due to the closeness to the sediments.

Copper ranged from 0.017 to 0.051mg/L in the surface water and 0.044 to 0.132mg/L in the bottom water while in the bottom sediments the range is 7.85 to 47.82mg/kg. These values are lower than that obtained in the surface waters and sediments of the upper reaches of Sombriero River (Howard and Briggs, 2012); again that of the bottom sediments are lower than those of Lake Edku, Egypt (Masoud et al. 2005), Bangalore Urban lakes (Aboud et al. 2009) and soils around an oilfield area by Karbassi et al. (2015). Copper correlated with all the metals studied apart from Vanadium. This could be due to its relationships with these metals in its diver's forms. For instance in all the media copper correlated with Zn, this may be due to their divalent status. Copper mobilisation in sediments may be due to biogeochemical processes **(**Banas et al. 2010**)**. The data could be seen from the fact that dissolved copper in water maybe due to a resuspension or immobilisation from the bottom sediments. Masoud et al. (2005) has suggested that "such approach could be subjected to further steps, mainly of adsorption and co-precipitation phenomenon of dissolved species on to suspended matter".

The mean level of Cd in surface water ranged from 0.005 to 0.026 mg/L and 0.004 – 0.028mg/L in the bottom water while that in the sediment varied between 60.76 and 147.25mg/kg. The values obtained in surface water is in consonance with the tolerance level of <0.1mg/l for wastewater (USEPA, 2008) and 0.033mg/l being the Criterion Maximum Concentration (CMC) for salt waters (USEPA, 2016). Cd levels in the bottom sediment were above those reported by Masoud et al. (2005), Naji and Ismail (2011), Howard and Briggs (2012) and Karbassi et al. (2015). Cadmium has been observed to be toxic to fish and other aquatic resources; hence it has often been used as an important index in aquatic monitoring studies (Patil et al. 2005). Also Cd poses a threat to human health due to its activities against the endocrine system in human beings (Awofulu et al. 2005). By way of comparison between the three media, the high level of Cd in the sediment is due to that fact that it acts as a receptacle to pollutants in aquatic environment (Samir et al. 2006). In addition to discharges of make shift refining, other likely sources of Cd into an aquatic environment could be natural sources like runoff from agricultural fields where phosphate fertilizer might be in use, and also from Ni-Cd based batteries (Patil et al. 2005).

The level of lead in surface water ranged from 0.005 to 0.1mg/L, 0.004 – 0.02mg/L for bottom water and between 118.73 to 292.76mg/kg in bottom sediment. Pb levels in the water columns were lower than those of the bottom sediments, which implies that in addition to the pH of the water columns that influences dissolution and availability of metals (Masoud et al.2005), sediments also influences the level of Pb in the water columns. Lead correlated with Mg in all three media which means there must a relationship of the different forms of these metals in these media. Lead has been observed to be toxic to human health as it impairs the proper functioning of the brain, hence this leads to aggressive behaviours in young persons (Ramadan, 2003). The routes of Pb toxicity to humans are through inhalation from the air, Pb contaminated pipe-borne water and from contaminated fish stuff. The toxicity of Pb is due to the fact that it behaves like Ca in some metabolic pathways thereby inhibiting many enzymatic processes where Ca is involved (Brochin, et al. 2008, Flora et al. 2012). Pb levels in the water columns of this study are comparable to those of Addo et al. (2011) but those of the sediments are higher than those of Masoud et al. (2005), Omaka et al. (2011), Naji and Ismail (2011), Howard and Briggs (2012) and Karbassi et al. (2015).

The mean Zn level in the surface water is from 0.021 to 0.033mg/L and 0.027-0.062mg/L in the bottom water, while that in the bottom sediment ranged from 289.411 – 867.52mg/kg. The level of Zn in the water columns of this study is in consonance with 0.09mg/l being the Criterion Maximum Concentration (CMC) for salt waters (USEPA, 2009). This implies that there is no detrimental effect on the aquatic ecosystem. However, the high level of Zn in the sediments of station F which is the control could be due to excessive surface runoff from domestic and other sources. Unlike other metals, Zn is less toxic to man but more toxic to aquatic fish (Vosylien and Jankait, 2006). Zinc correlated positively with lead and copper in the bottom sediment. The level of Zn in the surface waters of this study is lower than that reported in an earlier study (Howard and Briggs, 2012), Addo et al. (2011) in the Kpeshi lagoon, Ghana, but the sediment loads are higher than both studies, likewise those of Okafor and Opuene (2007) and Ephraim and Ajayi (2014).

Ni in the surface water varied from 0.016 to 0.068 mg/L and 0.11 – 0.79mg/L in the bottom water, while sediment values of Ni ranged from 11.26 to 42.59 mg/kg with a mean value of 24.53mg/kg. It has been reported that more attention has been focused on the toxicity of Ni in low concentration, such as the fact that Ni can cause allergic reaction and that certain Ni compounds may be carcinogenic (Cempel and Nikel, 2005) but later on Ni was observed to be a biologically significant element at low concentration to humans (Wintz et al.2002). Ni levels of 0.015 to 0.020mg/l in water bodies has been observed to be safe (Salnikow and Denkhaus, 2002), but the levels in this study are higher, indicating that the water columns are contaminated. Hence there is the possibility of the contamination of aquatic resources, as the toxicity of rainbow trout by Ni has been reported by Pane et al. (2003). The sediment load of Ni of this study is comparable to that reported by Ephraim and Ajayi (2014) but lower than those of Addo et al. (2011), Howard and Briggs (2012), Karbassi et al. (2015) but higher than those of Okafor and Opuene (2007) and Masoud et al. 2005).

Vanadium in surface water varied from 0.003 to 0.015mg/L and 0.002 to 0.018mg/L in the bottom water while that of the sediment is 1.652 to 5.711mg/kg. V levels in the water columns of this study are higher than those reported in an earlier study (Howard and Briggs, 2012), but those of the sediments are lower and also lower than the soils around oilfield area by Karbassi et al. (2015) and those reported by (EL-Moselhy, 2006) in some riverine areas of Egypt. At high concentrations, Vanadium complexes can be toxic but at lower concentrations they reduce the growth of cancer cells and ameliorate human diabetes mellitus (USEPA, 2011, Korbecki, 2012). EL-Moselhy, (2006), Nadal et al. (2004) among others have stated that "the main source of vanadium in to coastal areas is the petroleum activities and fuel burns". This is in consonance with the fact that Station C which is the source point station had the highest V values in the water columns of this study. It has been averred that V exists in divers' forms but the pentavalent form is the most soluble, and is the primary agent of transport in surface water (EL-Moselhy, (2006). This might be the reason why there were positive correlations of V with Cd, Pb and Ni in the water columns and also a positive correlation coefficient between the water columns. Other significant inputs of V in the aquatic ecosystem are the dumping of sewage sludge, discharge of domestic wastewater and the industrial effluents specially fertilizers containing materials with high vanadium content (Abd El-Azim and El-Moselhy, 2005).

Magnesium levels in the three media of this study are higher than all the other metals with a mean value of 25.94mg/L and 17.48mg/L and 550.17mg/kg in the surface water, bottom water and sediments respectively. Unlike all other metals of this study, Mg levels in the surface water are greater than that of the bottom water. This could be due to it being the second highest cation in sea water after sodium (Nessim, 2015) and its reactivity that increases with oxygen levels that is more in the surface water than in the bottom water. Mg correlated significantly with Pb in all the three media and also with Ni in sediment. Mg levels in the sediments of this study is higher than those given by Ledo et al. (2004), Adefemi (2013) and Montalvo et al. (2014). Magnesium is essential for all organisms and is not toxic under circumstances normal. Deficiencies of magnesium are much more common than problems concerned with toxicity.

Conclusion

The study has shown that bottom sediments accumulate heavy metals than the water columns. The variation patterns ($P<0.05$) of the metals in each of the medium is surface water – Mg>N=Cu=Zn>Pb=Cd>V; bottom water – Mg>Cu>Ni=Zn>Pb=Cd>V and bottom sediments – Mg=Zn>pb>Cd>Cu=Ni>V and that of the media is Sediment >> Bottom water=Surface water. Correlation matrices constructed for each medium showed the surface water column to have more negative significant correlations, implying that more of these metals are taken out from the surface water into the bottom water and sediments. The sediments of the study had more positive significant correlations among metal pairs than others indicating that metals are more bound to the sediments than in the water columns thereby corroborating its higher loads of these metals than the other media. Again the positive significant correlation of V-Cd, V-Pb and V-Ni in the water columns indicates that their input sources may likely be the same, which could have been from petroleum related activities. The level of contamination of the study area is relatively high when compared to related studies within and outside the region. It is therefore recommended that the activities of the make-shift refining of crude oil in the area be stopped by the relevant regulatory agencies also further studies on other media be carried out.

References

Abdel-Ghani, N. T. and Elchaghaby, G. A., 2007. Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *International Journal of Environmental Science and Technology*, 4 (4), 451-456. DOI: :https://doi.org/10.1007/BF03325980

Abd El-Azim, H. and El-Moselhy, Kh. M., 2005. Determination and partitioning of metals in sediments along the Suez Canal by sequential extraction. *J. Mar. Sys.*, 56, 363 - 374. https://doi.org/10.1016/j.jmarsys.2004.12.001 (accessed on: 16 May 2016)

Addo, M. A., Okley, G. M., Affum, H. A., Acquah, S. and Gbadag, J. K., 2011. Water quality and level of some heavy metals in water and sediments of Kpeshie Lagoon, La-Accra, Ghana. *Research Journal of Environmental and Earth Sciences*, 3(5), 487-497. https://scholar.google.com/scholar? (accessed on: 16 May 2016)

Aboud, S. J. and Nandini, N., 2009 . Heavy metals analysis and sediment quality values in urban lakes. *American Journal of Environmental Science*, 5(6), 678-687. https://www.researchgate.net/profile/Aboud_Jumbe2/publication/49590016 (accessed on: 09 May 2016)

Akcay, H., Oguz, A. and Karapire, C., 2003. Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research*, 37 (4), 813-822. https://doi.org/10.1016/S0043-1354(02)00392-5

Awofulu, O. R., Mbolekwa, Z., Mtshemia, V. and Fatoki, O.S., 2005. Levels of trace metals and sediment from Tyume River and its effects on an irrigated farmland. *Water South Africa*, 31(1), 87-94. DOI: http://dx.doi.org/10.4314/wsa.v31i1.5124

Banas, D., Marin, B., Skraber, S., Chopin, E.I.B. and Zanella, A., 2010. Copper mobilization affected by weather conditions in a storm water detention system receiving runoff waters from vineyard soils (Champagne, France). *Environmental Pollution*. 158, 476–482. DOI:10:1016/j.envpol:2009.08.034.

Borretzen, P. and Albu, B., 2002. Fixation of Cs to marine sediments estimated by a stochastic modeling approach. *Journal of Environmental Radioactivity*, 61(1),1-20. https://doi.org/10.1016/S0265-931X(01)00107-2

Brochin, R., Leone, S., Phillips, D., Shepard, N., Zisa, D. and Angerio., A. 2008. The cellular effect of lead poisoning and its clinical picture. *George University Journal of Health Sciences*, 5 (2), 1-8. https://blogs.commons.georgetown.edu/journal-of-health-sciences/issues-2/previous-volumes/vol-5-december 2008 (accessed on: 16 May 2016)

Cempel, M. and Nikel, G., 2006. Nickel: A review of its sources and environmental toxicology. *Polish Journal of Environmental studies*. 15 (3), 375-382. https://scholar.google.com/scholar? (accessed on: 10 May 2016)

Defew, L., Mair, J., and Guzman, H., 2004. "An assessment of metal contamination in mangrove sediments and leaves from Punta Mala Bay, Pacific Panama". *Marine Pollution Bulletin*, 50 (50), 547-552. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

EL-Moselhy, K. H. M., 2006. Distribution of vanadium in bottom sediments from the marine coastal area of the Egyptian seas. *Egyptian Journal of Aquatic Research*, 32(1), 12-21. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

Ephraim, B. E. and Ajayi, I. O., 2014. Geo environmental assessments of heavy metals in surface sediments from some creeks of the Great Kwa River, Southeastern Nigeria. *Journal of Environment and Earth Sciences*, 4 (21), 15 – 26. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

Ezekiel, E. N., Hart, A. I. and Abowei, J. F. N., 2011. The sediment physical and chemical characteristics in Sombreiro River, Niger Delta, Nigeria. *Research Journal of Environmental. Earth Sciences*, 3(4), 341-349. https://scholar.google.com/scholar? (accessed on: 10 May 2016)

Flora, G., Gupta, D., and Tiwari, A., 2012. Toxicity of lead: A review with recent updates. *Interdisciplinary toxicology*. 5(2), 47–58. DOI: 10:2478/v10102-012-0009-2

Howard, I. C. and Briggs, A. O., 2012. Metal pollution indices of surface sediment and water from the Upper Reaches of Sombriero River, Niger Delta, Nigeria. *Our Nature*, 10, 206-216. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

Isidori, M., Lavorga, M., Nardelli, A. and Parrella, A., 2004. Integrated environmental assessment of Volturno River in South Italy. *Science of the Total Environment*, 7, 123-134. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

Karbassi, A. R, Tajziehchi, S. and Afshar, S., 2015. An investigation on heavy metals in soils around oil field area. *Global Journal of Environmental Science Management*, 1 (4), 275 -282. DOI:10.7508/gjesm.2015.04.002

Korbecki, J., Baranowska-Bosiacka, I., Gutowska, I. and Chlubek, D., 2012. Biochemical and medical importance of vanadium compounds - Review. *ACTA Biochemical Polinica* 59 (2), 195–200. Online at: www.actabp.pl (accessed on: 10 May 2016)

Ledo, H., Rivas, Z., Gutiérrez, J., Gutiérrez, E., Ojeda, J. and Avila, H., 2004. Baseline of Ca, Mg, Fe, Mn and Al Concentrations in Catatumbo River Surficial Sediments. *Water, Air, and Soil Pollution*, 155(1), 117-135. URL: https://scholar.google.com/scholar? (accessed on: 10 May 2016)

Li, X., Liu, L., Wang, Y., Luo., G. and Chen, X., 2012. Integrated assessment of heavy metal contamination in sediments from a coastal industrial basin, NE China. *PLoS ONE.*, **7,** 1-10. DOI: 10.1371/journal.pone.0039690

Marchand, C., Lalliet Verges, E., Baltzer, F., Alberic, P., Cossa, D., and Baillif, P., 2006. Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana. *Marine. Chemistry*, 98, 1-17. DOI: 10.1016/j.marchem.2005.06.001

Masoud, M. A., Elewa, A.E.S. Ali, A.E. and Mohamed, E.A., 2005. Distribution of some metal concentrations in water and sediments of lake Edku, Egypt. *Bulletin of the Chemists and Technologists of Macedonia*, 24(1), 21-34. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

Montalvo, C., Aguilar, C. A., AmAddor, L. E. Cerón, J. G., Cerón, R. M., Anguebes, F., and Cordova, A. V., 2014. Metal contents in sediments (Cd, Cu, Mg, Fe, Mn) as Indicators of Pollution of Palizada River, Mexico. *Environment and Pollution*, 3(4), 89 – 98. doi:10.5539/ep.v3n4p89

Moyer, T. P. 2014. Toxic metals in " Teitz fundamentals of clinical chemistry and molecular diagnostics" 7h edn. Sawyer, B. G (Editor). Suanders Elsevier. U.S.A. p 592. ISBN: 978-1-4557-4165-6

Nadal, M., Schuhmacher, M, and Domingo, J. L., 2004. Metal pollution of soils and vegetation in an area with petrochemical industry. *Science of the Total Environment* 321, 59–69. https://scholar.google.com/scholar? (accessed on: 16 May 2016)

Naji, A. and Ismail, A., 2011. Assessment of metals contamination in Klang river surface sediments by suing different Indexes. *Environment Asia.* 4(1), 30-38. https://scholar.google.com/scholar? (accessed on: 15 May 2016)

Nessim, R. B., Tadros, H. R. Z., Abou Taleb, A.E.A and Moawad, M. N., 2015. Chemistry of the Egyptian Mediterranean coastal waters. *Egyptian Journal of Aquatic Research.* 41, 1-10. https://doi.org/10.1016/j.ejar.2015.01.004

Nicolau, R., Galera, C. A., and Lucas, Y., 2006. Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river. *Chemosphere*, 63 (3), 469 - 476 . https://scholar.google.com/scholar? (accessed on: 15 May 2016)

Nouri, J., Lorestani, B., Yousefi, N., Khorasani, N., Hasani, A. H., Seif, S. and Cheraghi, M., 2011. Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead–zinc mine (Hamedan, Iran). *Environmental Earth Sciences*, 62 (3), 639-644 . DOI : 10.1007/s12665-010-0553-z

Obire, O., Tamuno, D. C. and Wemedo, S. A., 2007. Bacteriological water quality of ELechi Creek in Port Harcourt, Nigeria. *Journal of Applied Sciences and Environmental Management.* 9 (1), 79-84. https://www.ajol.info/index.php/jasem/article/view/17260 (accessed on: 14 May 2016)

Okafor, E.C. and Opuene, K., 2007. Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments. *International Journal of Environmental Science and Technology*, 4(2), 233-240. https://www.environmental-expert.com/Files/19294/articles/12547/10-mar.pdf (accessed on: 14 May 2016)

Omaka, N. O., Igidi, J. O., Iyke, F. N. and Itumoh, E. J., 2011. The impacts of oil spill and soil factors on trace metals in sediments (soils) of Abakaliki and Afikpo, Nigeria. *Journal of Emerging Trends in Engineering and Applied Sciences*, 2(4), 648-657. https://journals.co.za/content/sl_jeteas/2/4/EJC156637 (accessed on: 14 May 2016)

Osuji, L. C. and Onojake, C. M., 2004. The Ebocha-8 Oil spillage II. Fate of associated heavy metals six months after. *African Journal of Environmental Assessment and Management*, 9, 78-87. https://scholar.google.com/scholar? (accessed on: 14 May 2016)

Pane, E .F., Richard, J. G. and Wood, C.M., 2003. Acute water borne nickel toxicity in the rainbow trout (*Oncorhychus mykiss*) occurs by respiratory rather than ions regulatory mechanism. *Aquatic Toxicology*, 63(1), 65-82. URL: https://scholar.google.com/scholar? (accessed on: 09 May 2016)

Pekey, H., 2006. Heavy metals pollution assessment in sediments of the Izmit Bay, Turkey. *Environmental Monitoring Assessement*, 123, 219-231. DOI : 10.1007/s10661-006-9192-y

Patil, S.S., Yardi, D. and Auti R.G., 2005. Conservation and management of lake: A case study of Salim Ali Lake. Paper published on national conference on wetlands biodiversity organized by Department of Zoology St. Aloysius College, Elthuruth in association with Limnologists Association of Kerala and IAAB, Hyderabad, pp.193-196.

Rafiei, B., Bakhtiari-Nejad, M., Hashemi, M. and Khodaei, A. S., 2010. Distribution of heavy metals around the Dashkasan Au mine. *International Journal of Environmental Research*, 4, 647-654. 82. URL: https://scholar.google.com/scholar? (accessed on: 09 May 2016)

Ramadan, A. A., 2003. Heavy metal pollution and biomonitoring plants in Lake Manzala, Egypt. *Pakistan Journal of Biological Sciences*, 6(13), 1108-1117. URL: http://www.pjbs.org. (accessed on: 09 May 2016)

Salnikow, K. and Denkhaus, E., 2002. Nickel essentiality, Toxicity and carcinogenicity. *Critical Review of Oncology and Haematology,* 42(1), 35-56. URL: https://scholar.google.com/scholar? (accessed on: 09 June 2016)

Samir, M. N., Mohamed, A.O. and Shaif, M. K. 2006. Environmental assessment of heavy metal pollution in bottom sediments of Aden Port, Yemen. *International Journal of Ocean and Oceanography,* 1(1), 99-109. URL: http://www.ripublication.com/ijoo.htm (accessed on: 10 June 2016)

Vosylien, M. Z. and Jankait, A., 2006. Effect of heavy metal model mixture on rainbow trout biological parameters. *Ekologija*. 4, 12-17. URL: https://scholar.google.com/scholar? (accessed on: 10 June 2016)

United States Environmental Protection Agency (USEPA), 2008. Method of chemical analysis of water and wastewater, EPA/600/4-79/020, 374.3.1-375.4.3. (assessed on: 18 May , 2016).

United States Environmental Protection Agency (USEPA), 2009. National Recommended Water Quality Criteria. Office of water/ office of science and technology (4304T) 65FR31682 (assessed on: 18 May, 2016).

United States Environmental Protection Agency (USEPA), 2011. USEPA Regional Screening Level (RSL) Summary Table: November 2011, (assessed on: 18 May, 2016).

United States Environmental Protection Agency (USEPA), 2016. Quality Criteria for Water. Office of Water Regulation and Standards, Washington DC, USEPA- CAS No.7440439 .(assessed on: 5 August, 2016).

Wintz, M., Fox, T. and Vulpe, C., 2002. Functional genomics and gene regulation in bio metal research. *Bulletin of Environmental Contamination and Toxicology,* 30, 765 – 768. https://scholar.google.com/scholar? (accessed on: 14 June 2016)