ASSESSMENT OF TRACE METAL CONTAMINATION BY GEOCHEMICAL NORMALISATION IN SEDIMENTS OF TWO LAGOONS: A COMPARATIVE STUDY OF THE KPESHIE AND MUNI LAGOONS, GHANA

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ABSTRACT

Heavy metal contamination status of bottom sediments of two lagoons was compared by the employment of Enrichment Factor (EF) analysis for Iron (Fe), Manganese (Mn), Cupper (Cu), Lead (Pb), Chromium (Cr), Nickel (Ni), Silver (Ag), Zinc (Zn) and Mercury (Hg). Kpeshie Lagoon recorded enrichment (EF ≥ 1) for Cd, Pb, Ag, Hg and Zn, whilst Muni Lagoon recorded enrichment for Cd, Mn, Ag, Hg and Zn as metals of anthropogenic influence. Kpeshie, situated in a highly urbanized area, has 75% spatial distribution of Pb enrichment. The assessment shows that Ag and Hg are the most enriched metals in the sediments of both Lagoons, reaching extremely severe levels. Only Mn showed statistically significant difference in mean concentration of metals for both Lagoons. Pearson correlation matrix indicated that Pb had a strong relation with Ag, Hg and Zn (r = 0.956; p < 0.05) which is significant in Kpeshie. It also had a strong association with Ag and Hg but not with Zn (r = 0.240) in the Muni. The study clearly delineates Pb as a pollutant that designates the urban status of Kpeshie. Its associated metals; Ag, Hg and Zn which may be coming from a common source are from industrialized zones.

Keywords: Trace Metals, Enrichment Factor, sediment, correlation matrix, lagoons

Introduction

Lagoons form part of wetland ecosystems that are made up of soils and water as well as plants and animals. The complex interaction between these components allows wetlands to specialize in the performance of certain ecological or natural functions and generate products of socio-economic importance (Larr *et al*, 2011). Sediments play a significant role in aquatic ecosystems and act as storage reservoirs for all kinds of pollutants which are introduced in to the ecosystem either by anthropogenic or natural processes. Natural trace metal concentrations in estuarine sediments are found at different concentrations depending on the geology of the area. Estuarine sediments also receive significant anthropogenic loads of metals from both point and non-point sources, especially in heavily industralised zones, increasing their natural background concentrations (Esen *et al*, 2010; Remor *et al*, 2018). The sediment compartment embodies the most concentrated physical pool of metals in aquatic environments (Superville *et al*, 2014) with more than 90% of the heavy metal load in aquatic systems said to be bound to suspended particulate matter and sediments (Calmano *et al*, 1993; Superville *et al*, 2014). These metals could be released to the overlying water column through natural and

anthropogenic processes such as bioturbation and dredging, resulting in potential adverse health effects (Daskalakis and O'Cunnor, 1995; Long *et al*, 1995).

More than 50 lagoons and estuaries mark Ghana's 550 km coastline and provides feeding, roosting and nesting sites for thousands of migratory and resident birds; marine turtles; many species of fish; plant genetic materials for research; and a major source of income for especially poor communities. Lagoons are generally classified into 3 main types: leaky lagoons, choked lagoons, and restricted lagoons (Kjerfve, 1994). The Kpeshie lagoon located in the Greater Accra region of Ghana can be classified as a restricted lagoon in that even though it has only one channel to the sea, this channel is quite wide and allow for good water exchange, and a net transport of water to the sea (http://www.sms.si.edu/IRLSpec/Whatsa_lagoon.htm; Kjerfve, 1994). The Kpeshie lagoon, though relatively small in size, contributed significantly to the national fish production stock in the past, however, increasing urbanization and industrialization within its catchment area has resulted in heavy pollution of the lagoon (Addo *et al*, 2011).

The Muni Lagoon on the other hand, is said to be located in a rural setting (Tay *et al*, 2010), and therefore, is expected to receive less industrial and domestic waste discharges. However, there is a gradual increasing urbanization and encroachment of its catchment area by estate developers and salt miners. Urbanization with its attendant commercialization produces pollution from metal sources. These metal contaminants may pose a high risk to the ecosystem on a large scale and hence need to be monitored at regular intervals and that natural versus anthropogenic contribution be distinguished for effective remedial actions against metal pollution.

This is effectively done by employment of geochemical normalization techniques (Nowrouzi and Pourkhabbaz, 2014), which represent actual environmental enrichment rather than the inclusion of natural geochemical background values normally reported as metal concentrations in mg/kg. Few studies were done by Tay *et al*, (2010) on both lagoons but not by metal normalization, and Addo *et al*, (2011), who studied the Kpeshie by using geochemical normalization.

Since these two Lagoons serve as feeding, migration routes, and nursery grounds of many organisms, it is important that sediment contamination by trace metals be evaluated, and that natural versus anthropogenic contribution be distinguished for effective remedial actions against metal pollution.

Experimental

Study area

The Kpeshie Lagoon (Fig. 1), lies on latitude 5˚34'N to 6˚40'N and longitude 0˚00 E to 0˚8'E (Fianko *et al,* 2013). The Lagoon is located between the La Trade Fair (LTF) site to the west and the Teshie Military Barracks to the east. The drainage system of the lagoon has been designed to receive all storm-water from the entire catchments (Addo *et al*, 2011). It used to be an open Lagoon (Addo *et al*, 2011) but can now be described as a restricted lagoon with a narrow channel to the sea. There is another portion of the water body isolated along the La-Palm-Zenith College road. The wetland covers an area of 22 km^2 and comprises sand dune, open lagoon, marshy lands and scrublands (Fianko *et al*, 2013).

Muni Lagoon (Fig. 2), on the other hand, is a shallow saline coastal lagoon situated on the outskirts of Winneba Township, 67 km from the capital Accra, Lat.5° 19'N, Long. 0° 40' W.

It covers an area of 3 km^2 and is fed by the two rivers Muni and Pratu. The Lagoon adjoins the Yenku Forest Reserve, which together with the adjacent degraded forest lands forms the traditional hunting grounds of the Efutu people. The site is mainly important for terns, but a number of waders and herons also occur in significant numbers (Ntiamoa-Baido & Gordon, 1991). Mean monthly temperatures range from minimum of 24°C in July/August to maximum of 28.9 °C in March (Ntiamoa-Baido & Gordon, 1991).
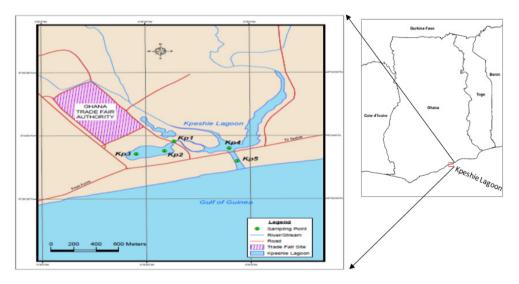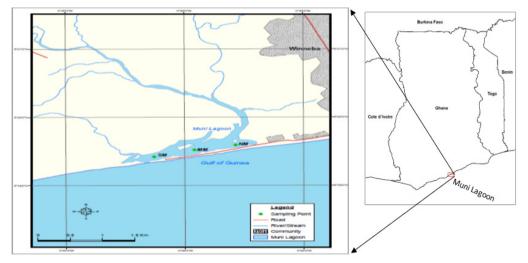

Fig. 1: Location and sampling site for Kpeshie Lagoon with Ghana map insert.

ig. 2: Location and sampling site for Muni Lagoon with Ghana map insert.

Sample collection

Sampling was carried out bi-monthly from October 2016 up to August, 2017 for both Lagoons. The Muni lagoon had three sampling stations; NM, MM and SM whilst the Kpeshie Lagoon had five sampling stations namely; KP1, KP2, KP3, KP4 and KP5. The sampling sites were chosen based on accessibility. Water samples were collected into a 200 ml clean plastic bottle and acidified with concentrated HNO_3 for heavy metal analysis. Sediments were collected using the rod–operated 3.5 litre Ekman grab sampler. A sizeable quantity is then transferred into cleaned polyethylene bags. For Kpeshie Lagoon, sediment sample was not taken for KP1 because of accessibility at the initial stage of the study. All the samples were preserved on ice in an ice-chest and transported to the Environmental Chemistry and Sanitation Engineering Laboratories of the CSIR-Water Research Institute and kept in the refrigerator at < 4°C until analysed.

Sediment digestion

The sediments were air-dried, grounded, homogenized and sieved using 63 μm aperture sieve. This is done because trace elements are disproportionately associated with different particle sizes, the particle-size distribution of a bulk sample can greatly influence metal concentrations of that sample (Salomons & Forstner, 1984).About 0.30 g of the dried-homogenized sediment sample was weighed carefully into Teflon tubes, 8 mls and 2 mls of 65% HNO_3 and HF were respectively added. The samples were digested using Milestone Microwave Digestion System as directed by Standard Methods for the Examination of Water and Wastewater - (APHA, 2017) and digested using US EPA method 3052 (Kington and Walter, 1992). The samples were then

taken out and top up with deionised water to 50mls and analyzed for metals.

Metal analysis

Metals were determined for the sediments by Atomic Absorption Spectrophotometer (AAS), Agilent 240F Series. AAS-flame technique was used for Fe, Mn, Cu, Pb, Cr, Ni, Ag and Zn whilst AAS-Cold vapour technique was used for Hg. The sediment results were then converted to mg/kg before being geochemically normalised.

Geochemical normalisation

Enrichment Factor (EF) is one of environmental parameters used in assessing pollution levels in sediments and environmental impact of metals. It is a relatively simple and easy tool for assessing the enrichment degree and comparing the contamination of different environmental media (Benhaddya & Hadjel, 2013). The EF is a normalisation method proposed by Simex & Helz (1981) to assess the concentration of the metals. It normalizes metal concentration as a ratio to another constituent of the sediments. The geochemical normalization was obtained using Fe as the reference element for the following reasons (Daskalakis & O'Connor, 1995): (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many trace metals; and (3) its natural sediment concentration tends to be uniform. The EF is defined by the Equation (1):

$$EF = \frac{(Me/Fe)_{sample}}{(Me/Fe)_{aveg.shale\ value}} \quad \ldots\ldots\ldots\ldots (1)$$

Where, $(Me/Fe)_{sample}$ is the ratio of metal and Fe concentrations in the sample, and $(Me/Fe)_{aveg.shalevalue}$ is the ratio of metal and Fe concentrations of the average shale values.

The world average shale and the world average soil are among the materials often used to provide background metal levels. Hence the background concentrations of the metals in the average shale as provided by Turekian & Wedepohl (1961) are used in this study.

EF values were interpreted as suggested by Birch (2003) where EF < 1 indicates no enrichment, < 3 is minor; 3 - 5 is moderate; 5 - 10 is moderately severe; 10 - 25 is severe; 25 - 50 is very severe; and > 50 is extremely severe. Enrichment factor (EF) for Fe was not calculated because Fe is the normalizing element.

Quality control
All laboratory wares used were washed with phosphate-free soap, double rinsed with distilled water and left in 10% HNO_3 for 24 hrs. They were removed, rinsed again with double distilled water and dried. Certified Reference Material (CRM), IAEA-356 marine sediment was used and taken through the same process as the sediment samples as a precision check any time samples are being analyzed. Recovery and accuracy for certified and measured values were compared (Table 1).

TABLE 1

Measured and certified concentrations in mg/kg of CRM (IAEA - 356), (n = 4).

Element	Measured	Certified	% Recovery
Ag	7.48±1.40	8.41	88.9
Fe	25,372±924	24,100	105.3
Mn	322±18	312	103.2
Cd	3.56±0.95	4.47	79.6
Cu	329± 14	365	90.1
Cr	47.6± 8.1	69.8	68.2
Ni	41.3 ±6.11	36.9	111.9
Pb	357 ±2.8	347	102.9
Hg	7.77±0.32	7.62	102.0
Zn	806 ±18.1	977	82.5

Results and Discussion

TABLE 2

Mean concentration of bottom sediments in mg/kg for Muni lagoon.

ID	Fe	Mn	Cu	Ni	Cr	Cd	Pb	Ag	Hg	Zn
NM	12258	225.0	6.15	15.1	12.2	0.593	3.85	1.90	1.93	31.4
MM	12279	332.0	6.46	14.2	7.70	0.552	7.23	1.17	2.44	49.9
SM	13525	309.4	10.2	21.6	17.2	0.568	4.68	1.65	1.96	68.1

TABLE 3

Mean concentration of bottom sediments in mg/kg for Kpeshie lagoon.

ID	Fe	Mn	Cu	Ni	Cr	Cd	Pb	Ag	Hg	Zn
KP2	7311	80.2	6.35	**9.34**	4.37	0.569	8.19	3.05	3.20	40.9
KP3	11291	158.6	8.74	**11.56**	22.8	0.799	17.6	5.51	1.68	49.6
KP4	27224	139.5	17.7	7.00	23.7	<0.200	0.511	1.81	5.79	27.2
KP5	16076	119.8	6.53	8.38	10.7	0.337	8.88	1.11	1.90	35.0

Mean Fe concentration ranged between 12258 and 13525 mg/kg dry weight (dw) for Muni lagoon whilst Kpeshie lagoon recorded a mean range between 7311 and 27224 mg/kg dw. The result obtained for Kpeshie was highly variable 15476 mg/kg± 8613 (Table 5), largely influenced by station KP2. The average shale value for Fe is 47200 which is far higher than what was obtained for the two Lagoons, indicating non-anthropogenic input in the sediment of both Lagoons.

This suggests that the presence of Fe in the sediments is principally from natural sources which came from the earth crust. The use of T-test with unequal variance recorded no statistical significant difference between mean concentrations of Fe for Muni and Kpeshie ($p = 0.565$) $p > 0.05$ at the 95% confidence level. Mn for Muni ranged between 225 and 332 mg/kg dw whilst that of Kpeshie Lagoon ranged between 80.2 and 158.6 mg/kg dw. Consequently, the Enrichment Factor (EF) for Muni ranged between 1.02 and 1.50 with a mean of 1.26, higher than that of Kpeshie which ranged between 0.285 and 0.780 with a mean of 0.522 even though the latter is situated in a highly urbanised location. The values in all the stations in Muni showed minor enrichment (EF ≥ 1) whilst that of Kpeshie recorded no enrichment (Table 6), clearly indicating that the presence of Mn in sediments of Kpeshie Lagoon is principally from natural sources.

The minor enrichment in sediments of Muni Lagoon might be as a result of using part of the Lagoon as a receptacle for refuse by the nearby fishing community, as manganese can be released into water bodies as leachate from landfills (Francis & White, 1987), thereby, enriching the water with manganese and subsequently settling in bottom sediments. There was a significant difference between the mean concentrations of Muni and Kpeshie ($p = 0.019$), $p < 0.05$, further indicating that Muni was anthropogenically enriched. Cu for Muni recorded a mean range of 6.15 and 10.20 mg/kg whilst that of Kpeshie recorded values between 6.35 and 17.7 mg/kg. The Threshold Effect Concentration (TEC) (which is a screening value, below which concentrations of contaminants have not been shown to cause an effect on aquatic organisms) for sediments in surface waters set by US Environmental Protection Agency (USEPA) for Cu is 31.6 mg/kg. The mean enrichment factor (< 1.0) for Muni and Kpeshie are 0.628 and 0.666 respectively, suggesting natural geochemical presence of Cu in both sediments of the Lagoons rather than anthropogenic contribution. There was no significant difference between the concentrations of the two Lagoons for Cu, ($p = 0.492$). The mean Ni concentration range for Muni and Kpeshie were between 14.2 and 21.6 mg/kg and 7.00 and 11.56 mg/kg respectively, with a p-value of 0.060. The TEC value set by

USEPA for Ni is 22.7 mg/kg. The EF for Muni and Kpeshie are 0.929 and 0.407 respectively, indicating non-anthropogenic influence. However, station SM for Muni recorded a value of 1.11(Table 6) which is indicative of minor enrichment from anthropogenic influence. This station is very close to a fishing community; therefore, their activities might have contributed to this enrichment, possibly from Cd-Ni base batteries (Hutton *et al*., 1987). These values were relatively lower than similar work by Nowrouzi and Pourkhabbaz (2014) in the Persian Gulf who recorded a mean EF of 1.62 for Ni. Cr recorded mean range between 7.70 and 17.2 mg/kg dw for Muni and between 4.37 and 23.7 mg/kg dw for Kpeshie Lagoon. Muni Lagoon recorded a mean EF of 0.512 against 0.522 for Kpeshie Lagoon, both showing no enrichment, even though station KP3 for Kpeshie shows minor enrichment.

This station might have benefited from direct deposition of Cr related materials from a close by vehicle mechanic workshop. Cd recorded a mean range between 0.552 and 0.593 mg/kg for Muni and between < 0.200 and 0.799 mg/kg for Kpeshie. Addo *et al* (2011), recorded a range between 0.20 and 2.8 mg/kg for Kpeshie Lagoon. Station KP3 of Kpeshie which recorded 0.799 mg/kg is higher than the Threshold Effect Concentration of 0.600 mg/kg. There was however, no significant difference in mean concentration between the two Lagoons (p = 0.526). The mean Cd EF for Muni and Kpeshie were 7.08 and 5.77 respectively indicating moderately severe enrichment for both Lagoons. These values were however lower than the value 16.91, obtained by Nowrouzi & Pourkhabbaz (2014) in the Persian Gulf. However, station KP4 of Kpeshie which recorded an EF factor of 0.578 showed no enrichment for that station. Cd

enrichment is therefore from anthropogenic sources for both Lagoons, possibly from industrial effluents. Station KP4 receives freshwater from a community nearby, leading to the dilution of sediment concentration. This is further shown in the EF values for this station in all metals that exhibit some spatial enrichment (Table 6). The overall mean Pb value recorded for Muni was 5.25 mg/kg as against 8.80 mg/kg for Kpeshie. However, Addo *et al.* (2011), recorded a range between 0.50 and 27.05 mg/kg for Kpeshie lagoon. The TEC for Pb in sediments as given by USEPA is 35mg/kg. The EF for Muni and Kpeshie were respectively 0.977 and 1.34 indicating a minor enrichment of Pb in the Kpeshie Lagoon. There was however, a minor enrichment recorded at station MM of the Muni Lagoon, whilst all the stations except KP4 for Kpeshie were indicative of enrichment of Pb. This enrichment might have been contributed by a series of artisanal related workshops dotted around the catchment area of the Lagoon.

There was no significant difference between the concentrations of the two Lagoons (p = 0.392). Silver (Ag) and Mercury (Hg) were the two metals that indicated extremely severe enrichment in this study. Ag for Muni ranged between 1.17 and 1.90 mg/kg whilst that of Kpeshie ranged between 1.11 and 5.51 mg/kg. Both Lagoons are highly enriched with Ag with Muni recording Enrichment Factor (EF) of 73.1 and Kpeshie an EF factor of 109, indicating very severe enrichment. Silver is a rare but naturally occurring metal, often found deposited as a mineral ore in association with other elements; its bacteriostatic properties made it to be used in filters and other equipment to purify swimming pool water and drinking-water and in the processing of foods, drugs, and beverages (ATSDR, 1990). Silver adsorbs to manganese dioxide, ferric compounds, and

clay minerals, leading to silver deposition into sediments (US EPA, 1980). Silver sorbs readily to phytoplankton and to suspended sediments, especially in the marine environment because of affinity of silver for the chloride ion (Sanders *et al*., 1991). This might have accounted for the Ag concentrations in the sediments of the two coastal Lagoons. Kpeshie which recorded a higher EF value for Ag was influenced by station KP3 which has a mechanic shop close by. The overall mean mercury (Hg) for Muni and Kpeshie Lagoons were 2.11 and 3.14 mg/kg respectively. These values exceed the Probable Effect Limit (PEL) (a value above which toxic effects are likely to occur, and compounds that exceed it are more probably elevated to toxic levels) of 0.486 mg/kg set by USEPA. The EF values for Muni and Kpeshie were 19.6 and 24.0 respectively, indicating severe enrichment for both Lagoons.

However, spatial distribution shows extremely severe enrichment in the case of station KP2 for Kpeshie Lagoon. While local sources may contribute significantly to inorganic Hg deposition in highly industralised regions (Jensen & Invefeldt, 1994), as in the case of Kpeshie lagoon, Hg from the global pool contributes more significantly to the deposition in more remote non-industrialized regions (Guentzel *et al*, 2001), as in the case of Muni Lagoon. Concentration of Zn ranged between 31.4 and 68.1 mg/kg for Muni lagoon, whilst Kpeshie lagoon recorded values between 27.2 and 49.6 mg/kg. These values are far below the PEL value of 315 mg/kg for which aquatic life could be affected. The EF values are 1.95 and 1.23 for Muni and Kpeshie respectively, indicating minor enrichment. The highest spatial enrichment however occurred at station KP2 of the Kpeshie lagoon.

TABLE 4

Minimum, maximum, mean, in mg/kg and EF values for Muni lgoon.

Element	Min	Max	Mean	Stdev	Av.shale value	EF
Fe	12258	13525	12688	725.5	47200	_
Mn	225	332	288.8	56.4	850	1.26
Cu	6.15	10.2	7.60	2.2	45	0.628
Ni	14.2	21.6	17.0	4.06	68	0.929
Cr	7.7	17.2	12.4	4.77	90	0.512
Cd	0.552	0.593	0.571	0.02	0.3	7.08
Pb	3.85	7.23	5.25	1.76	20	0.977
Ag	1.17	1.90	1.57	0.37	0.08	73.1
Hg	1.93	2.44	2.11	0.29	0.4	19.6
Zn	31.4	68.1	49.8	18.34	95	1.95

TABLE 5

Minimum, maximum, mean, in mg/kg and EF values for Kpeshie lagoon.

Element	Min	Max	Mean	Stdev	Av.shale value	EF
Fe	7311	27224	**15476**	8613	47200	_
Mn	80.2	158.6	**124.5**	33.50	850	0.447
Cu	6.35	17.7	**9.82**	5.34	45	0.666
Ni	7.00	11.56	**9.07**	1.92	68	0.407
Cr	4.37	23.7	**15.40**	9.44	90	0.522
Cd	<0.2	0.799	**0.337**	0.23	0.3	5.77
Pb	0.511	17.6	**8.80**	7.00	20	1.34
Ag	1.11	5.51	**2.87**	1.93	0.08	109
Hg	1.68	5.79	**3.14**	1.89	0.4	24.0
Zn	27.2	49.6	**38.2**	9.44	95	1.23

TABLE 6

Enrichment Factors of both Muni and Kpeshie lagoons for each station.

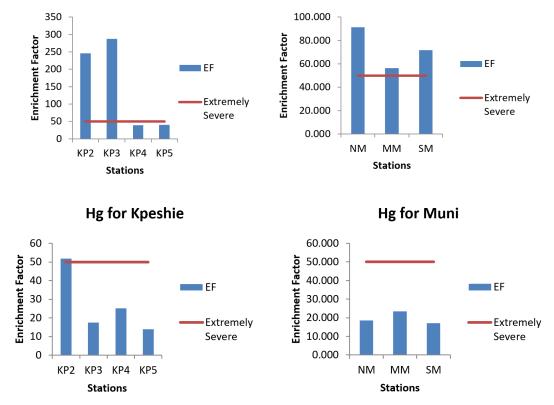| MUNI	Mn	Cu	Ni	Cr	Cd	Pb	Ag	Hg	Zn
NM	1.02	0.526	0.853	0.522	7.608	0.740	91.2	18.6	1.27
MM	1.50	0.552	0.805	0.329	7.073	1.390	56.4	23.5	2.02
SM	1.27	0.789	1.111	0.669	6.602	0.816	71.9	17.1	2.50
KPESHIE									
KP2	0.610	0.912	0.887	0.313	12.2	2.64	246	51.7	2.78
KP3	0.780	0.812	0.711	1.06	11.1	3.68	288	17.5	2.18
KP4	0.285	0.681	0.178	0.457	0.578	0.044	39.2	25.1	0.50
KP5	0.414	0.426	0.362	0.350	3.30	1.30	40.8	14.0	1.08

Fig 3: Spatial distribution of Ag and Hg, showing extremely severe enrichment of sediments in the lagoons.

TABLE 7

Pearson's correlation coefficient between metals for Kpeshie Lagoon.

	Fe	Mn	Cu	Ni	Cr	Cd	Pb	Ag	Hg	Zn
Fe	1									
Mn	0.453	1								
Cu	0.892	0.465	1							
Ni	-0.754	0.234	-0.573	1						
Cr	0.63	0.935	0.732	0.028	1					
Cd	-0.798	0.129	-0.564	0.987*	-0.037	1				
Pb	-0.715	0.288	-0.65	0.966*	0.014	0.916	1			
Ag	-0.521	0.383	-0.194	0.901	0.311	0.92	0.783	1		
Hg	0.738	-0.036	0.868	-0.759	0.306	-0.686	-0.883	-0.408	1	
Zn	-0.822	0.125	-0.643	0.994**	-0.081	0.991**	0.956*	0.872	-0.777	1

Note: * significant at $p < 0.05$; **significant at $p < 0.01$

TABLE 8
Pearson's correlation coefficient between metals for Muni Lagoon.

	Fe	Mn	Cu	Ni	Cr	Cd	Pb	Ag	Hg	Zn
Fe	1									
Mn	0.33	1								
Cu	0.999*	0.381	1							
Ni	0.992	0.209	0.984	1						
Cr	0.874	-0.171	0.846	0.928	1					
Cd	-0.14	-0.981	-0.194	-0.014	0.359	1				
Pb	-0.268	0.821	-0.215	-0.387	-0.703	-0.915	1			
Ag	0.165	-0.877	0.111	0.288	0.623	0.954	-0.994	1		
Hg	-0.441	0.702	-0.392	-0.505	-0.822	-0.827	0.983	-0.958	1	
Zn	0.871	0.751	0.896	0.802	0.522	-0.609	0.24	-0.341	0.057	1

Note: * significant at $p < 0.05$

Correlation matrix

Pearson's correlation coefficient was used to ascertain the sources, the spatial distribution and inter-relationship that exist between metals in the wetlands (Tables 7&8). Elemental association may signify that each paired elements has identical source or common sink in the stream sediments (Fianko et al, 2013). There was a strong positive correlation between Fe and Cu(r= 0.892), Hg(r = 0.738) and negative correlation Ni (r = -0.754), Cd(r = -798), Pb(r = -715), Ag(r = - 0.521) and Zn(r = - 0.822) for the Kpeshie Lagoon, however none of the relationship was significant (at the 95% significant level) (Tables 7&8). For Muni Lagoon, Fe had a strong positive correlation with Cu(r = 0.999; p < 0.05), Ni(r = 0.992), Cr(r = 0.874), Zn(r = 0.871). None of the negative relation was strong. Mn for Kpeshie had a strong positive correlation with Cr(r = 0.935) and weak to moderate positive correlation with the rest of the metals, except Hg (r = -0.035). However, there was a strong positive association between Mn and Pb, Hg, and Zn with (r = 0.821, 0.702 and 0.751) respectively for Muni Lagoon. Cu had a strong

positive correlation with Cr(r = 0.732) and Hg (r = 0.868) and negative correlation with Ni(r = -0.573), Cd(r = -0.564), Pb(r = -0.64) and Zn (r =-0.643) for Kpeshie lagoon. However, for Muni lagoon, Cu had a strong positive relationship with Ni(r =0.984), Cr(0.846) and Zn(0.896), with weak to moderate association with Cd, Pb, and Hg. The correlation between Ni and Cd (r = 0.987; p < 0.05), Pb(r = 0.966; p < 0.05) and Zn(r = 0.994; p < 0.01) were strongly positive and significant with Ag(r = 0.901) being positive but not significant in Kpeshie lagoon. There was strong negative relation with Hg(r = -0.759). Ni however, has a strong correlation with Cr(r = 0.928), Zn(r = 0.802) and Hg(r = -0.505) being negative in the Muni Lagoon. Cr had a strong correlation with Pb(r = -0.703), Ag(r = 0.623), Hg(r = -0.827) and Zn(r = 0.522) in Muni but none of the relationship with these same metals in Kpeshie is strong. In Kpeshie, Cd has a strong association with Pb(r = 0.916), Ag(r = 0.920), Zn (r = 0.991;p < 0.01) and Hg(r = - 0.606) whilst in Muni none of the association was significant with only Ag recording a positive relationship. Cd as a metal is not mined, but is

usually a by-product of the smelting of other metals such as zinc, lead, and copper (Dinis and Fiuza, 2011). Hence, its strong association with Pb and zinc in the sediments of Kpeshie Lagoon, is indicative of coming from the same source. Pb had a strong relation with Ag, Hg and Zn(r = 0.956; p < 0.05) which is significant in Kpeshie. This could be indicative of the enrichment of Pb and Zn coming from a common source. It also had a strong relation with Ag and Hg but not with Zn(r = 0.240) in the Muni. Ag had a strong positive relation with Zn, and Hg had a strong but negative association with Zn in Kpeshie. For Muni, Ag had a strong negative relation with Hg. This clearly shows that the Hg in Muni is not from a gold mining source since Au always have traces of Ag associated with it (GEUS, 2017).

Conclusions

The assessment of Fe, Mn, Cu, Ni, Cr, Cd, Pb, Ag, Hg and Zn did not show any statically clear difference in the mean concentrations of the Kpeshie and Muni Lagoons in a exception of Mn which was statistically significant, with Muni being higher than Kpeshie comparatively. Kpeshie Lagoon recorded enrichment for Cd, Pb, Ag, Hg and Zn which is indicative of anthropogenic influence, whilst Muni recorded Cd, Mn, Ag, Hg and Zn as metals of anthropogenic influence with Mn replacing Pb, even though station MM recorded some Pb enrichment in the scenario. Pb is the dominant metal pollutant in all the stations except one in Kpeshie, with Muni recording enrichment with Pb in station MM only. Hence Pb could be said to be the major pollutant associated with an urbanized zone such as Kpeshie Lagoon and therefore made the Kpeshie Lagoon more polluted with respect to Pb enrichment. Pearson correlation matrix also shows that Pb had a strong relation with two of the most enriched metals, Ag and Hg, as well as Zn(r = 0.956; p < 0.05), which was significant in Kpeshie which indicates that they might be coming from a common source, possibly industries. It also had a strong association with Ag and Hg but not with Zn(r = 0.240) in Muni. The assessment also shows that Ag and Hg are the most enriched metals in the sediments of the two lagoons and should be closely monitored.

References

Addo, M. A, Okley, G. M, Affum, H. A, Acquah, S., Gbadago, J. K., Senu, J. K. & Botwe, B. O. (2011) Water quality and level of some heavy metals in water and sediments of Kpeshie lagoon, La-Accra, Ghana. *Res J Environ Earth Sci* **3** (5), 487 – 497.

APHA (2017) "*Standard Method for the Examination of Water and Wastewater*," 23th Edition, American Public Health Association, Washington D.C.

ATSDR (1990) *Toxicological profile for silver*. Atlanta, GA, US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (TP-90-24).

Benhaddya, M. L. & Hadjel, M. (2013) Spatial distribution and contamination assessment of heavy metals in surface soils of Hassi Messaoud, Algeria. *Environ. Earth Sci.* **71** (3), 1473 – 1486.

Birch, G. F. (2003) A test of normalization methods for marine sediment, including a new post extraction normalization technique. *Hydrobiologia* **492**, 5 – 13.

Daskalakis, K. D. & O'connor, T. P. (1995) Normalization and elemental sedimentcontamination in the Coastal United States. Environmental Science and Technology **29**, 470 – 477.

Dinis, M. & Fiuza, A. (2011) Exposure assessment to heavy metals in the Environment: measures

to eliminate or reduce the exposure to critical receptors. *Geo-Environment and Resources Research Center (CIGAR), Faculty of Engineering, University of Porto, Rua Dr.   Roberto Frias, 4200465, Porto, Portugal.*

ESEN, E., KÜÇÜKSEZGIN, F. & ULUTURHAN, E. (2010) Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. *Environmental Monitoring and Assessment* **160**, 257 - 266. doi: 10.1007/s10661-008-0692-9.

FIANKO, R., LARR, C., OSEI, J., ANIM, K. A., GIBRILLA, A. & ADOMAKO, D. (2013) Evaluation of some heavy metal loading in the Kpeshie lagoon,Ghana. Appl Water Sci *Springer Int*. **3**, 311 – 319.

FRANCIS, C. W. & WHITE, G. H. (1987) Leaching of toxic metals from incinerator ashes. *J Water Pollut Control Fed* **59**, 979 – 986.

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND (2017) *Artisanal and Small-scale mining Handbook for Ghana*. The Danish Ministry of Energy, Utilities and Climate. Copenhagan, Denmark.

GUENTZEL, J., LANDING, W., GILL, G. & POLLMAN, C. (2001) Processes influencing rain fall deposition of mercury in Florida. *Environ Sci Technol*. **35**, 863 - 73.

HUTTON, M., CHANEY, R. L., KRISHNA, C. R., MURTI, M., OLADE, A. & PAGE, A. L.(1987) Group Report. In:Hutchson, T.C. and K.M. Meena, (Eds.), Lead, Mercury, Cadmium and Arsenic in the Environment.John Wiley, New York, pp: 35 - 41.

JENSEN, A. & IVERFELDT, A. (1994) Atmospheric bulk deposition of mercury to thesouthern Baltic Sea area. In: Huckabee J, Watras C, editors. Mercurypollution: integration and synthesis. Boca Raton, FL.: Lewis Publishers; p. 221 – 9.

KINGSTON, H. M. & WALTER, P. J. (1992) Comparison of Microwave versus Conventional Dissolution for Environmental Applications. *Spectroscopy* **7** (9), 20 - 27.

KJERFVE, B. (1994) Coastal Lagoons. in *Coastal Lagoon Processes* B. Kjerfve (ed.). Elsevier-Oceanography Series, 60. Pp 1 – 8.

LAAR, C., BAM EPK, O.S., ANIMA, O. J., BIMI. L., GANYAGLO, S. Y., GIBRILLA, A. & ADOMAKO, D. (2011) Effect of anthropogenic activities on an ecologically important wetland in Ghana. *Journal of Biodiversity and Environmental Sciences* **1** (6), 9 – 21.

LONG, E. R., MACDONALD, D. D., SMITH, S. L. & CALDER, F. D. (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management **19**, 18 - 97.

NOWROUZI, M. & POURKHABBAZ, A. (2014) Application of geoaccumulation index and enrichment-factor for assessing metal contamination in thesediments of Hara Biosphere   Reserve, Iran. *Chemical Speciation and Bioavailability,* **26** (2).

NTIMOAH-BAIDOO, Y. & GORDON, C. (1991) Coastal Wetlands Management Plans: Ghana. A Report Prepared for The World Bank and The Environmental Protection Council, Ghana. No. 51166.

REMOR, M. B., SAMPAIO, S. C., DERIJK, S., BOAS, M. A.v., GOTARDO, J. T., PINTO, E. T. & SCHARDONG, F. A. (2018) Sediment geochemistry of the urban Lake Paulo   Gorski. *Int. J. Sediment Res*. **33**, 406 – 414.

SALOMONS, W. & FORSTNER, U. (1984) metals in the hydropsyche: berlin, springer-verlag, 349p.

SANDERS, J., RIEDEL, G. & ABBE, G. (1991) Factors controlling the spatialand temporal variability of trace metal concentrations in *Crassostreavirginica*(Gmelin). In: Elliot M, Ducrotoy J, eds. *Estuaries andcoasts: spatial and temporal intercomparisons.* Proceedings of the Estuarine and Coastal Sciences Association Symposium, 4–8 September 1989, University of Caen, France.

SIMEX, S. A. & HELZ, G. R. (1981) Regional geochemistry of traceelements in Checapeake Bay. *Environ. Geol.* **3** (6), 315 – 323.

SUPERVILLE, P - J., PRYGIEL, E., MAGNIER, A., LESVEN, L., GAO, Y., BAEYENS, W. (2014) Daily variations of Zn and Pb concentrations in the Deûle River in relation to the resuspension of heavily polluted sediments. *Sci Total Environ.* **470 – 471**, 600 – 7.

TAY, C., ASMAH, R. & BINEY, C. A. (2010) A comparative study of the pollution status of Sakumono II and Muni Lagoons in Ghana. *Water Science and Technology* **62.5**, 1067 - 1075.

TUREKIAN, K. K. & WEDEPOHL, K. H. (1961) Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Am.Boll.* **72**, 175 – 192.

USEPA (1980) *Ambient water quality criteria for silver*. Washington, DC, US Environmental Protection Agency (440/5-80-071).

WINDOM, H. L., SCHROPP, S. J., CALDER, F. D., RYAN, J. D., SMITH, R. G., BURNEY, L.c., LEWIS, F. G. & RAWLINSON, C. H. (1989) Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environmental Science and Technology* **23**, 314e320.