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Assessment of Pollution into the Densu Delta Wetland Using Instrumental Neutron Activation Analysis

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Abstract: The objective of this work is to assess the levels of trace elements and the extent of pollution in the surface water and sediments from in the Densu delta wetland using INAA, PLI and the help of statistical tools like PCA and CA establish their common sources. Eight samples of surface water, eight samples of sediments were taken for elemental analysis. The samples were analyzed for physical and chemical parameters, as well as trace elements (Al, Cu, V, Mn, Cd, Zn, Cr, Fe and As). The results showed that the surface water in the area can be described as slightly alkaline with pH of 7.5 and high conductivities of 150-3412μS/cm with corresponding TDS of 80-1750 mg/L. Statistical analyses such as Principal Component Analysis (PCA) and Cluster Analysis (CA) were used to identify trace elements pollution in the wetland area. Results from CA and PCA suggest positive relationships between the two analyses. Trace elements were identified as originating from a common source in all the analyses. The PLI calculated for sediments in the study area were found to be below the index limit of 1. This shows that the surface waters are not yet polluted with respect to trace elements but the originality of the ecosystem is threatened.

Key words: Densu delta wetland, hydrochemistry, INAA, pollution load index, principal component, sediments, surface water

INTRODUCTION

In the current world economic paradigms, sustainable socioeconomic development of every community depends much on the sustainability of the available water resources. Water of adequate quantity and quality is required to meet growing household, industrial and agricultural needs. Surface water quality is a very sensitive issue, which transcends national boundaries. It is influenced by many factors, including atmospheric chemistry, the underlying geology, the vegetation (or organic matter decay), and anthropogenic agents.

Human activities have already negatively influenced water quality and aquatic ecosystem functions. This situation has generated great pressure on these ecosystems, resulting in a decrease of water quality and biodiversity, loss of critical habitats, and an overall decrease in the quality of life of local inhabitants (Herrera-Silveira andMorales-Ojeda, 2009). Trace metals are regarded as serious pollutants of aquatic ecosystems, because of their environmental persistence, toxicity, and ability to be incorporated into food chains (Abolude *et al.*, 2009).In aquatic systems, metal pollution can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products (Dawson and Macklin, 1998).

The resultant effect of continuous discharge of wastes in fluvial environments is a build-up of pollutants, including trace metals, in sediments. Bioaccumulation of such metals in sediments has significant environ -mental implications for local communities, as well as for river water quality (Ross and Kaye, 1994, Wright and Mason, 1996).The Densu Delta is fed by the Densu River and its tributaries which have a catchment area of 2500 $km^{2.}$ The Weija dam is situated on the river 11 km upstream of the mouth of the river, this dam serves as one of the two sources of water supply for the Accra Municipality and is also used for irrigation purposes; from Weija the Densu River passes through Oblogo (North-Western) side of the

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Delta, where the main economic activity was stone quarrying which is now turned into a landfill, to Bortianor (south-western) tip. The Oblogo Township is just a few metres from Mendskrom from the main Accra-Takoradi Road; the quarry left a big hole due to the excavation which needed to be filled and then it was filled with waste from the metropolis.

Study area: The area of study is the Densu delta which is also a Ramsar site, which is located in the south-western part of central Accra, the nation's capital. The Densu delta wetland is close to the confluence of the Densu River with the Atlantic Ocean in the Accra Metropolis of Ghana (Fig. 1). It is located approximately 11 km to the South West of Accra and is traversed by the Accra-Takoradi-Axim highway. Some communities of interest in this wetland are Oblogo, Aplaku, Tetegbu, and Bortianor.The wetland is fed mainly by the Densu River, which has been dammed a few kilometres up-stream (Weijadam) to supply water to some parts of Accra. The study area falls within the dry equatorial climate region of Ghana (Teley, 2001)with the climate governed by three district air masses, namely; the monsoon, the harmattan and the equatorial air masses. The site lies in the coastal savannah zone where rainfall is seasonal with two peaks in June and September. Mean annual rainfall for the area is 800 mm.

Highest mean monthly temperatures occur between March and April. Minimum and maximum daily temperatures range from 22.8 to 33.0ºC, respectively. The minimum yearly average is 24.2ºC and maximum yearly average temperature is 31.0ºC. Mean relative humidity is high within a twenty-four hour period with relative humidity occurring in January and highest in August.

The dominant vegetation in this area is shrub and grassland (Teley, 2001). Area under study is generally undulating and relief ranges from 20 to 100 m above sea level. The geology consists of metamorphosed sedimentary rocks, namely; quartzite, schist, and phyllites, which may be incompetent and susceptible to fracturing upon stress. The rocks were first described by (Kesse, 1985), who assigned the name Akwapimianto these rocks.The area is mainly being used for residential purposes (Tigme, 2005).

Stone quarrying, fishing and peasant farming are some economic activities undertaken by majority of the inhabitants at these wetland areas. There are not much industrial activities in these areas but the Bojo White Sand Beach Resort is one that attracts many people from all walks of life to the area.

The Oblogo landfill is situated in the Ga-South District, which has its local administrative capital at Weija. Location of Oblogo site is shown in Fig. 1.

Oblogo town is about 1km off Accra-Winneba road on the way to Weija. The landfill site is located on latitudes 5º33′26″N and 5º33′40″N and longitudes 0º18′45ºw and 0º18′55ºW.

There are no bottom liners for any of the dumping sites (Tigme, 2005). Monitoring boreholes that are to serve as a check on groundwater pollution are absent. Leachate emanating from the dump mainly flow into enclosed sumps (manholes) where it is stored temporarily till it overflows in drainage channels through Oblogo Township and eventually joins River Densu.

MATERIALS AND METHODS

Sampling: Sampling was conducted from August to December, 2008. Samples were collected from all the sampling points (Fig. 1). At each sampling point, water and sediments were collected. Samples of water(SW1, SW2, SW3, to SW8) and sediments (SD1, SD2, SD3, to SD8) were taken from Oblogo were taken along the river to Bortianor. The sampling bottles were pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de-ionized water. At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling was done. The collection of the samples from the river was done with hand gloves. The direction of the flow of the river was faced and the particles in the river was disturbed by the feet and allowed to settle down before sampling. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the water surface. About one litre of the water samples were taken at each sampling site. The water samples were filtered using a pre-conditioned plastic Millipore filter unit equipped with a 0.45 μm filter membrane (Gelman Inst. Co, London). Three sets of water samples were collected at each sampling point. One was used for in situ measurement of pH, Total dissolved solids, Electrical conductivity, etc., the second for analysis of major ions with the ion chromatograph. The third part was acidified with 1% nitric solution. The acidified samples were used for the INAA measurement. The addition of the acid was to keep the metal ions in the dissolved state. The samples were kept over ice in an ice chest and transported to the laboratory. The samples were kept in a refrigerator at about 4ºC until analysis was performed. Sediment collection was also done with pre-cleaned polyethylene shovel and the shovel was used to scoop the sediments from 10 to 15 cm depth with hand gloves and put into pre-cleaned polyethylene bags (Logar *et al*., 2001, Chen *et al*., 1997).

Sample preparation: 0.5 mL of each water samples was pipetted using calibrated Eppendorf tip ejector pipette (Brinkmann Ins., Inc., Westbury, NY) into clean pre-weighed 1.5 mL polyethylene vials, weighed and heat-sealed. Four of these sample vials were placed into a 7.0 mL volume polyethylene vial and heat-sealed. Six replicates were prepared for each sample. However, for short irradiation, only one sample was put in the 7.0 mL vial.

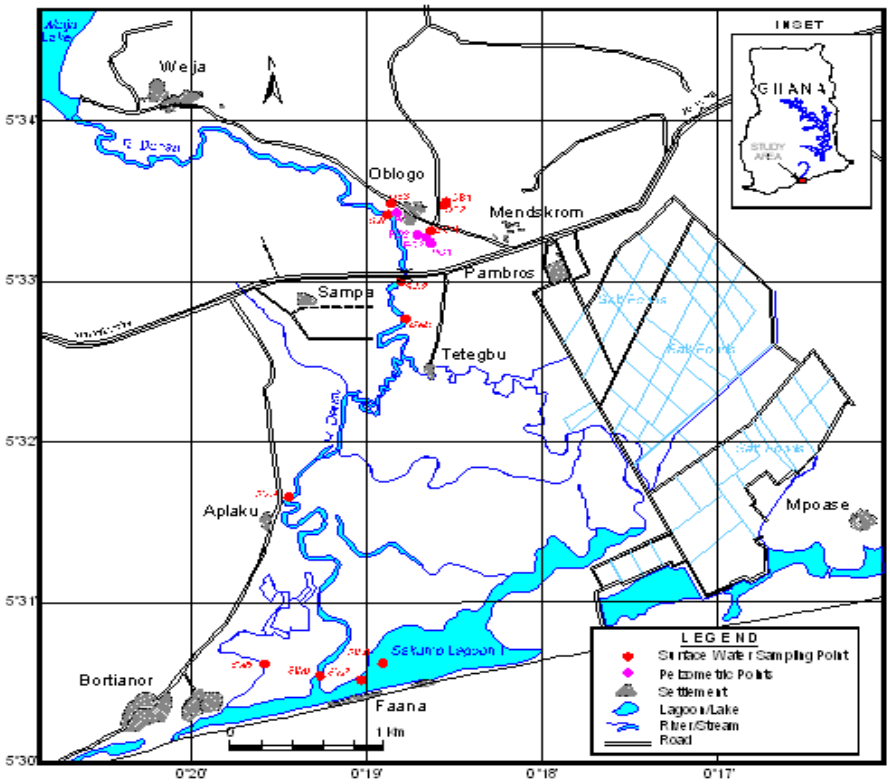

Fig. 1: Location of densu delta wetland showing the study sites: Oblogo, Aplaku, Tetegbu, and Bortianor

Table 1: Statistical summary of physical and chemical parameters

Parameters	Unit	Min	Max	Mean	Median	S.D.	WHO standard
Temp	(oC)	23.3	29.8	26.33	25.55	2.10	22-29
pH	pH units)	6.4	8.1	7.51	7.60	0.43	6.5-8.5
EC	(µs/cm)	150	3412	1636.42	1221.00	1066.76	700
Sal	(ppm)	0.01	14.83	3.80	0.55	4.95	
TDS	(mg/L)	80	1750	705.08	423.50	570.92	1000
Na^+	(mg/L)	37.2	5719	2424.21	2313.50	2279.52	200
K^+	(mg/L)	0.80	390.0	39.90	32.20	79.37	30
Ca^{2+}	(mg/L)	3.39	597.0	46.88	11.81	119.77	
Mg^{2+}	(mg/L)	1.69	183.0	16.78	4.54	37.88	
Cl^-	(mg/L)	212	8600	3906.58	3079.50	3083.78	250
SO_4^{2-}	(mg/L)	5.98	157.5	41.08	35.35	36.29	250
Alk	(mg/L)	27.8	268.0	124.69	131.30	68.56	400
HCO_3^-	(mg/L)	34.8	329.4	153.24	159.70	81.66	
PO_4-P	(mg/L)	0.005	1.30	0.11	0.05	0.26	<0.3
NO_3-N	(mg/L)	0.09	0.71	0.37	0.35	0.18	50
BOD	(mg/L)	0.10	7.01	4.02	4.30	2.95	<3.0
COD	(mg/L)	0.98	80.0	9.60	10.00	15.52	250
Cd	(mg/L)	0.02	0.18	0.11	0.12	0.04	0.05
As	(mg/L)	0.04	0.45	0.17	0.17	0.10	0.005
Zn	(mg/L)	0.05	3.81	2.05	2.04	1.20	
Cr	(mg/L)	0.01	0.08	0.04	0.04	0.03	
Cu	(mg/L)	0.18	8.00	2.53	2.25	1.78	0.05
V	(mg/L)	0.05	3.70	0.53	0.16	0.97	
Al	(mg/L)	3.28	8.21	5.47	5.26	1.29	0.20
Mn	(mg/L)	0.11	6.71	2.62	2.45	1.58	0.50
Fe	(mg/L)	0.31	3.86	1.90	1.68	1.15	0.30

Each sediment sample was air-dried for 3 days in a clean environment. Other organic debris such as shells, micro-organisms were picked from the samples with hand gloves. The samples were crushed using an agate mortar and pestle, sieved using an 85 µm mesh size USA standard sieve (Fisher Scientific Co., USA) and

homogenised. About 100 mg of each sample was weighed into a clean polyethylene film. The films were wrapped and heat-sealed. Six replicate sub-samples were prepared for each sample. The samples were packed into 7.0 mL volume polyethylene capsules for irradiation. Eighteen sub-samples of each sample from all the sampling points and the IAEA Standard Reference Material (SRM) 1,547 Peach leaves and IAEA-Soil-7 were prepared. Six replicate samples of each sample were used for short, medium and long irradiations. The bagged samples were then packed into polyethylene vials and heat-sealed.

Sample irradiation, counting and analysis: Irradiation of the samples was done using the Ghana Research Reactor-1 (GHARR-1) facility operating at half full power of 15 kW and at a neutron flux of 5.0×10^{11} neutrons/cm^{2}s. The scheme for irradiation was chosen according to the half-lives of the elements of interest, sample matrix and the major elements present. The irradiation scheme for the determination of the radionuclides and the nuclear data used are shown in Table 1. The samples were sent into the reactor by means of a pneumatic transfer system operating at a pressure of 1,292.88 mmHg. At the end of their radiation, the capsules were returned from the reactor and assayed according to the scheme adopted. The samples were then placed on top of the detector and the counts were accumulated for a pre-selected time to obtain the spectra intensities. A PC-based gamma ray spectrometry system was used for the measurement. The spectrometry system has been described in detail elsewhere (Dampare *et al.*, 2005). The spectra intensities for the samples were obtained by means of an Ortec Multi-channel Buffer (MCB) emulation software card. The accumulated spectra intensities were analysed both qualitatively and quantitatively.

Contamination factor (CF) and pollution load index (PLI): The Contamination Factor (CF), which gives an indication of the level of contamination, was computed for the sediments using the measured concentrations of the heavy metals and their corresponding values in the world average shale reported by Turekian and Wedepohl (1961). The contamination levels may be classified based on their intensities on a scale ranging from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) (Muller, 1969) The highest number indicates that the metal concentration is 100 times greater than what would be expected in the crust.

The pollution level was computed following the procedure of Pollution Load Index of Tomlinson *et al*. (1980). The PLI Varies from 0 (unpolluted) to 10 (highly polluted):

$$CF = Cm/Cb \quad (1)$$

$$PLI = \sqrt{}(n\&\ (CF1\times CF2 \times CF3 \times CF4\ldots \times CFn)) \quad (2)$$

where, CF = contamination factor; n=numbers; Cm = metal content in polluted sediments; Cb = background value of the metal.

Table 2: Hydrochemical data of surface water [mean of each parameter at various sampling points] from the densu delta wetland taken during the sampling period August-December, 2008

Parameters	Unit	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8
Temp/^{o}C	(oC)	26.27	26.47	26.57	26.3	26.63	26.17	26.03	26.17
pH	pH units	7.37	7.53	7.73	7.73	7.1	7.29	7.7	7.67
EC/µS/cm	(µs/cm)	2234	1909.33	725.33	1986	2523	893.33	1196.33	1624
Sal/ppt	(ppm)	3.28	5.02	0.35	0.34	5.46	4.47	6.34	5.1
TDS	(mg/L)	1160	808.33	209.33	667.33	1272.67	421.67	379	722.33
Na^+	(mg/L)	743	1898.54	66.47	94.9	3419.07	4140.33	5045	3986.33
K^+	(mg/L)	15.55	136.9	8.47	7.18	42.43	18.83	28.23	53.5
Ca^{2+}	(mg/L)	6.11	212.08	14.37	16.95	19.55	25.87	22.3	57.82
Mg^{2+}	(mg/L)	4.19	63.01	6.95	4.61	3.61	7.21	14.59	30.07
Cl^-	(mg/L)	1899.67	2890.33	1293.33	572	4238.67	5686	7295	7377.67
SO_4^{2-}	(mg/L)	29.1	31.54	25.58	33.92	30.13	51.26	28.7	98.46
Alk	(mg/L)	204.67	150	109.27	87.2	111.03	140	74.24	121.1
HCO_3^-	(mg/L)	252.13	181.73	133.6	106.2	144.77	170.8	92.19	144.47
PO_4-P	(mg/L)	0.05	0.07	0.04	0.01	0.01	0.11	0.51	0.1
NO_3^-N	(mg/L)	0.21	0.26	0.23	0.23	0.34	0.56	0.6	0.5
BOD	(mg/L)	0.47	3.43	1.13	1.57	4.7	6.83	6.98	7.01
COD	(mg/L)	30.59	4.72	1.85	2.41	7.52	10.04	9.67	10
Cd	(mg/L)	0.03	0.1	0.13	0.12	0.06	0.11	0.13	0.13
As	(mg/L)	0.1	0.22	0.1	0.23	0.16	0.16	0.19	0.17
Zn	(mg/L)	0.73	2.44	1.26	0.79	3.01	3.62	3.21	3.32
Cr	(mg/L)	0.03	0.03	0.01	0.03	0.03	0.05	0.01	0.06
Cu	(mg/L)	0.62	4.02	2.15	1.66	3.31	1.17	4.62	2.6
V	(mg/L)	0.07	0.46	0.11	0.59	0.07	0.21	0.26	2.32
Al	(mg/L)	4.1	5.19	5.53	4.39	5.41	6.44	7.73	4.98
Mn	(mg/L)	1.51	1.63	3.71	1.89	2.94	2.51	4	2.75
Fe	(mg/L)	1.17	1.71	0.7	0.84	2.27	3.59	2.52	2.38

Principal component analysis (PCA) and factor analysis: These two methods are aimed at finding and interpreting hidden complex and casually determined relationships between features in a data set (Einax *et al.*, 1998). The key idea of PCA is to quantify the significance of variables that explain in the observed groupings and patterns of the inherent properties of the individual objects (in this study, sampling sites). On the basis of the dataset, new factors as the linear combination of original parameters are calculated. Owing to this, all information about the objects gathered in the original multidimensional dataset can be performed in the reduced space and explained by a reduced set of calculated factors called Principal Components (PCs). Identified PCsaccount for the maximum explainable variance of all original property parameters in a descending order (Mazerski, 1997). Factor analysis is a useful tool for extracting latent information, such as not directly observable relationships between variables (Einax *et al.*, 1998). The original data matrix is de composed into the product of a matrix of factor scores plus a residual matrix. In general, the number of extracted factors is less than the number of measured features. So the dimensionality of the original data space can be decreased by means of factor analysis. After rotation of the factor loading matrix (e.g., by VARIMAX rotation and normalized with Kaiser Normalization), the factors can often be interpretedas origins or common sources (Marengo *et al*., 1995).

Cluster analysis (CA): With the cluster analysis, the relationship between various sites in the wetland and water chemistry can be clearly explained and the source of origin of the ions, that is, whether they are anthropogenic or natural, can be evaluated. The dendro*g*ram of the location pattern resulting from CA of measured data.

RESULTS AND DISCUSSION

Hydrochemistry: The Hydrochemical data of surface water determined for the period of sampling were reported in Table 2.The results were analyzed statistically and the summary, which in clues minimum and maximum values; mean and median, as well as standard deviation, has been presented in Table 1.

Water samples are neutral to slightly basic pH of 6.4-8.1 with a mean value of 7.51. The pH values recorded at all sampling points meet the USEPA criteria (6.5-9.0) for freshwater aquatic life (USEPA, 1982). Conductivity (EC) ranges from 150 to 3412.0 µs/cm. Conductivity is a measure of total dissolved solids and ionized species in water and it is a good indicator of major ions inorganic pollution. The range of Total Dissolved Solids (TDS) is from 80 to 1750 mg/L a nd s alinit y ranges from 0.01 to 14.83 ppm. The mean and median values of the Electrical Conductivity (EC) are 1636.42 µs/cm and 1221.00 µs/cm respectively. The standard deviation with respect to the mean is 1066.76µs/cm. The difference may reflect the wide variation in activities and processes prevailing in the surface and sub surface (Amadi and Amadi, 1990).

The conductivity could be used as an indication of pollution in the delta. (Koning and Roos, 1999)Suggested that typical unpolluted rivers have a conductivity of 350 µS/cm while the limit from the WHO standards is 700 µS/cm (WHO, 1998). This indicates that water from the Densu delta have more dissolved ions rom other sources like the landfill, a lot of activities including farming and fishing take place in these wetland areas. Besides, there is a resort centre in Bortianor which is frequented by many tourists especially on weekends, the activities of which could likely impact on the water quality. In addition, a likely contributory factor includes influx of sea water into the river during high tidal periods, and possible sea spray which could also raise the conductivity values.

Sodium levels were found to be very high with a mean of 2424.21; this could be due to its natural abundance in the earth's crust. Naturally Na^+ may originate from rock-water interactions (Chapman, 1996). However other sources like the landfill site, salt mining site which are in the wetland and also proximity to the sea could also have accounted for the high concentrations of sodium.

The potassium ion (K^+) had a mean value of 39.90 and a median of 32.20 which higher than the WHO Limit (1998) for drinking water. The possible source of K^+ could be from potassium salts in fertilizers used by farmers around the delta which have gotten in the wetland due agricultural run-offs.

Table 3: Correlation among selected major cations and anions in surface water samples from densu delta wetland (August-December, 2008).

	Sal	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2}	$^{-}PO_4^{3-}$	NO_3^-
Sal	1.00	0.97	0.77	0.36	0.39	0.88	0.31	0.51	0.62
Na^+		1.00	0.71	0.38	0.37	0.93	0.43	0.53	0.77
K^+			1.00	0.81	0.75	0.63	0.28	0.29	0.30
Ca^{2+}				1.00	0.90	0.34	0.35	0.23	0.23
Mg^{2+}					1.00	0.41	0.37	0.53	0.27
Cl^-						1.00	0.48	0.67	0.86
SO_4^{2-}							1.00	0.21	0.54
PO_4^{3-}								1.00	0.66
NO_3^-									1.00

The mean concentrations of the trace elements in water in the various sampling points are presented in Table 1. It can be seen that all the elements are higher than their various WHO standards. Comparatively the Al concentrations are higher than all other elements. This might also be due to weathering of aluminium based minerals such as alumina in the river bed. The values are higher than domestic water supply of 0 to 0.15 mg/L (Savory and Will, 1991). Arsenic (As) levels in the river have a range of 0.04 to 0.45 mg/L and a mean of 0.17 mg/L, the possible source may be from the landfill, or other anthropogenic activities upstream; this is because the geology of the area does not support availability of these ions; Cadmium (Cd), Zinc(Zn), Chromium(Cr), Vanadium(V), Manganese(Mn), Iron(Fe) and Copper (Cu), have concentrations varied between 0.02 to 0.18, 0.05 and 3., 0.01 to 0.08,0.05 to 3.7,0.11 to 6.71,0.31 to 3.86 and 0.18 to 8.00 mg/L, respectively. Their probable sources have been identified by PCA below.

Correlation matrix: The correlation matrix (Table 3) shows distributions of positive and negative correlations among some selected variables. There is strong positive correlation between Ca^{2+} and Mg^{2+}, also Mg^{2+} and PO_4^{3-}. This suggests contribution from agricultural activities; phosphorus is also derived from solid fertilizers and sewage effluent. there is positive correlation between Na^+, K^+ and salinity indicating that salinity is strongly influenced by salts of Na^+ and K^+, this could be to influx of the sea in the delta during high tides.NO_3^- and Cl^- ions are also correlated positively indicating that all the chloride ions are not from influx of the sea but sources like the landfill and domestic waste from the settlements in the delta, nitrate levels could have originated from the decomposition of domestic waste which is mostly organic (Christensen *et al*., 2001).NO_3^- and PO_4^{3-} as well as SO_4^{2-} andNO_3^- are positively correlated, suggesting that some concentrations of NO_3^- are also from agricultural run-offs from the farms in the delta. The settlement around the bank of the river extensively engages in vegetable farming involving the use of fertilizers and subsequently there is the potential for runoff into the wetland when it rains.

The Pearson correlations coefficients of pH, EC, TDS and trace elements in the surface water are summarized in Table 4. Positive correlations exist between elemental pairs Al-Cd (r = 0.0.52), Al-Cr (r = 0.55), Al-Fe (r = 0.58), Al-Zn (r = 0.72), this suggest a common source for Al and some concentrations of Cd, Cr, Fe and Zn. These may be associated with aluminosilicate minerals from the river bed. Positive correlations also exist between elemental pairs As-Cu (r = 0.0.55), As-V (r = 0.61), Cd-Cu (r = 0.0.57), Cd-V(r = 0.62), Cd-Mn (r = 0.54) suggesting a common source for As, V, Mn and some concentrations of Cu. Meaning that these may be from anthropogenic sources like the landfill and domestic sewage from the settlements around the delta.

Pollution source identification with CA and PCA: R-mode cluster analysis was also performed to visualize physicochemical and elemental groupings in the surface water data sets, and the results are shown in Fig. 2. Elements/parameters belonging to the same cluster/group are likely to have originated from a common source. For the surface water, 4 main clusters were obtained. Cluster 3 contains Sal, Na, Cl, NO_3^-, BOD, Fe, Zn, and it reflects the influence of domestic and agricultural pollution (Omo-Irabor *et al*., 2008) and cluster 4 contains K, Ca, Mg, SO_4, As, Cr, Cu, and V. The CA results largely agree with that of PCA.

As can be seen from Table 5, the main contributions to PC1 probably include both natural and anthropogenic elements. The PC1 which explains 29.73% of the total variance had high positive scores on Na, K, Al, Fe, Zn, BOD, COD, PO_4^{3-}, NO_3^-, Cl^- and Salinity. Most of these ions especially K, Al, Fe, and Zn could have resulted from lithological processes taking place here which include weathering of rocks such as sandstone and shale. There is also evidence of interaction of the wetland with the sea due high levels of Na and Cl. However BOD, COD, PO_4^{3-} and NO_3^- do not have significant lithological origin and thus could likely not be sourced from underlying geology since the bed rock in this area is mostly of the Togo series which consists of mostly sandstones and shales (Osei *et al*., 2010). Thus, run-off from agriculture activities may be responsible for the high concentrations of nitrates in water in the area (Venugopal *et al*., 2009).

Table 4: Correlation among different heavy metals, pH and EC of surface water in the densu delta wetland

	pH	EC	Sal	Al	As	Cd	Cr	Cu	Fe	Mn	V	Zn
pH	1.00											
EC	- 0.37	1.00										
Sal	- 0.51	0.28	1.00									
Al	0.04	- 0.58	0.37	1.00								
As	0.17	0.30	0.18	0.19	1.00							
Cd	0.63	- 0.59	- 0.25	0.52	0.49	1.00						
Cr	- 0.41	0.41	0.34	- 0.42	0.25	- 0.18	1.00					
Cu	0.23	- 0.02	0.25	0.55	0.56	0.57	- 0.33	1.00				
Fe	- 0.47	0.00	0.86	0.58	0.33	0.09	0.43	0.25	1.00			
Mn	0.20	- 0.60	- 0.01	0.75	- 0.12	0.54	- 0.53	0.51	0.20	1.00		
V	0.57	0.02	0.05	- 0.04	0.61	0.62	0.42	0.31	0.18	- 0.05	1.00	
Zn	- 0.26	- 0.21	0.71	0.72	0.36	0.41	0.20	0.60	0.87	0.49	0.27	1.00

Table 5: Loadings of 26 experimental variables on the varimax rotated PCs on five significant varifactors for surface water samples

	PC1	PC2	PC3	PC4	PC5
Temp	- 0.3650	0.0050	0.3340	0.1820	- 0.7120
pH	- 0.5070	0.3190	- 0.5520	0.2660	0.3710
EC	- 0.0110	- 0.1470	0.8940	0.0760	- 0.0180
Sal	0.8990	- 0.2670	0.1800	0.2330	0.0280
TDS	0.1610	- 0.3280	0.8970	0.0320	0.0200
Na	0.9540	- 0.0820	0.1470	0.1870	0.1360
K	0.5470	- 0.1390	0.2720	0.7680	- 0.0640
Ca	0.2020	0.1350	0.0850	0.9390	0.1440
Mg	0.1930	- 0.0380	- 0.2070	0.9170	0.2510
Cl	0.9470	- 0.0380	- 0.1500	0.1780	0.1170
SO_4^{2-}	0.3170	- 0.0190	0.0820	0.1700	0.8100
Alk	- 0.0120	- 0.9490	0.2040	0.0810	- 0.0080
HCO_3	0.0160	- 0.9400	0.2410	0.0490	- 0.0680
PO_4^{3-}	0.5460	- 0.1220	- 0.6890	0.2030	0.2350
NO_3^-	0.8360	0.3210	- 0.2610	- 0.0170	0.3560
BOD	0.7430	0.5120	- 0.0160	0.3080	0.2380
COD	0.5960	- 0.6370	0.1630	- 0.2720	0.1870
Al	0.6480	0.4440	- 0.5540	0.0380	- 0.1710
As	0.1390	0.5820	0.3620	0.4570	0.3320
Cd	- 0.0320	0.7100	- 0.4620	0.3670	0.3100
Cr	0.2050	- 0.2910	0.5900	0.0960	0.6030
Cu	0.2970	0.6490	- 0.0600	0.6040	- 0.2630
Fe	0.9480	0.0330	0.0850	0.0900	0.2230
Mn	0.3510	0.5920	- 0.5500	- 0.1760	- 0.2130
V	- 0.0280	0.2880	0.0060	0.5150	0.7920
Zn	0.8490	0.2830	- 0.0930	0.3430	0.0500
% of Variance	29.731	19.16	16.225	15.13	11.897
Cumulative %	29.731	48.891	65.116	80.245	92.142

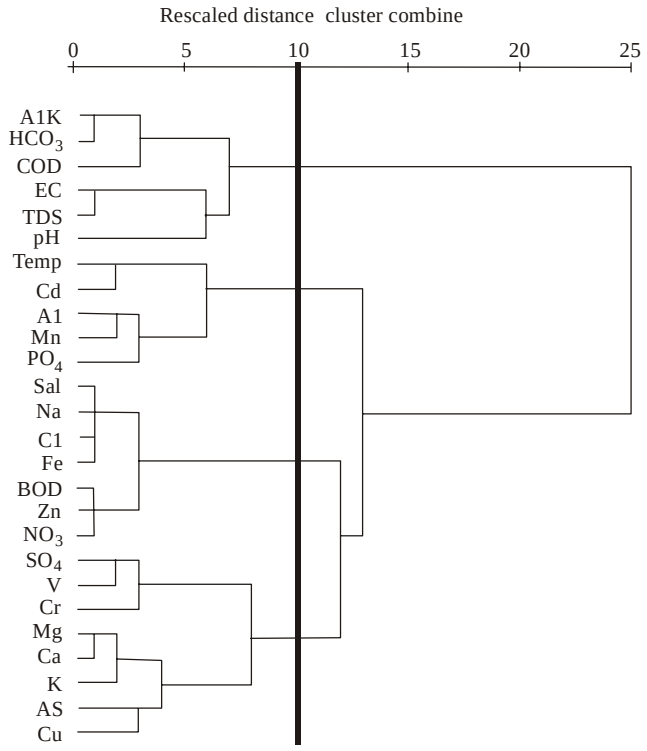

Fig. 2: Dendrogram of water parameters using complete linkage method

Also since these sampling sites are in a close proximity to an unengineered landfill, influence from the landfill leachate cannot be underestimated. PC2, are contributed by predominantly anthropogenic pollution. PC2 explains

19.16% of the total variance and this factor had high positive loadings on BOD, As, Cd, Cu, and Mn.

This is because the geology of the area does not support availability of these ions; the possible source may be from the landfill. Also the Cluster Analysis cluster 3 agrees with PC1 and PC2

PC4 and PC5 are contributed by predominantly natural sources of ions in the delta. PC4 and PC5 explain 15.13% and 11.89 respectively of the total variance. This factor had high positive loadings on K, Ca, Mg, Cu, and V for PC4 and Cr, V and SO_4^{2-} for PC5. PC4 and PC5 also agree with cluster 4. Although there are some variations between the CA and PCA results, a good agreement between the two statistical techniques is evident in all the data set analyzed.A high concentration of these ions is suggestive of lithological processes and seawater intrusion from the ocean into these areas and this agrees with the findings of previous study (Osei *et al*., 2010). From Table 5, temperature contributes negatively to this factor. This clearly indicates that Na and Cl are contributing to the salinity of the water and that there is seawater intrusion. This interaction, however, does not go with high temperature. As such during the rainy season, there is high seawater intrusion.Q-mode CA was performed on the water data set to determine spatial similarities among the various sampling sites in Fig. 3. The Q-mode CA reveals two distinct clusters of sampling sites. Cluster I consists of SW1, SW3, SW4, whilst cluster II comprises SW2, SW5, SW6, SW7 and SW8. The cluster analysis has revealed that sampling sites which fall in a particular cluster have in common certain water parameters.

The similarities and differences within the sampling sites were investigated using the Q-mode PCA. Fig. 4 shows the factor scores of sampling sites on the bi-dimensional plane defined by PC1 and PC2, and two distinct groups realised. Group 1 consists of Oblogo (SW1), Bridge between Oblogo and Tetegbu (SW2), Tetegbu (SW3), Aplaku (SW4) whereas group 2 comprises, Bortianor (SW5, SW6, SW7 and SW8).

With the exception of sites SW2, the PCA shares certain similarities with CA in terms of site groupings. Therefore, the significant agreement between PCA and CA multivariate statistical techniques suggests that the grouping of the sampling points have been done in a very convincing way (Boamponsem *et al*., 2010). Group 1 consists of samples from Oblogo (SW1), Bridge between

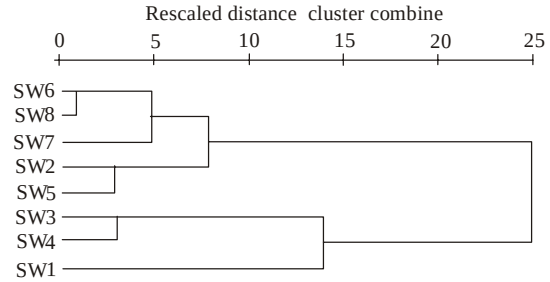

Fig. 3: Dendrogram of sampling sites using complete linkage method

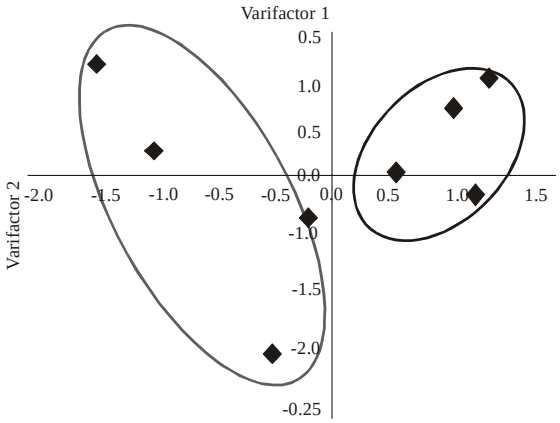

Fig. 4: Scores of surface water quality sites for the sampling period (August-December, 2008) on the bi-dimensional plane defined by the first two varifactors

Oblogo and Tetegbu (SW2), Tetegbu (SW3), Aplaku(SW4) they correspond to a relatively high pollution from both natural and anthropogenic sources. Groups 2 are polluted mainly by influence the sea and anthropogenic sources.

Pollution load index values for all sediments at all sampling locations from Oblogo downstream to the wetland are low and ranged from 0.183 to 0.503, Table 6. In spite of the generally low PLI values detected in the sediments, relatively higher values were observed at sites SD4(Aplaku), SD1 (Oblogo), and SD2 (Bridge between Oblogo and Tetegu). The trend of PLI values in the sediments indicates that the leachate discharge from the landfill activities may be the main source of

Table 6: Contamination factors and pollution load indices

	Cd	As	Zn	Cr	Cu	V	Mn	Fe	Al	PLI
SD1	2.70	0.49	0.07	0.01	0.31	8.19	0.88	0.05	1.85	0.37
SD2	5.70	0.42	0.04	0.00	0.17	8.18	1.50	0.05	1.87	0.35
SD3	5.80	0.15	0.03	0.00	0.15	5.29	0.81	0.05	1.03	0.24
SD4	6.30	0.20	0.11	0.01	0.51	8.27	1.51	0.11	1.94	0.50
SD5	0.50	0.56	0.03	0.00	0.09	4.55	0.49	0.08	0.61	0.18
SD6	0.70	0.57	0.03	0.00	0.09	4.71	0.62	0.11	0.62	0.20
SD7	1.40	0.91	0.03	0.00	0.08	4.95	0.83	0.15	0.72	0.25
SD8	1.60	0.92	0.04	0.00	0.15	0.69	0.90	0.15	0.69	0.29

contamination in the river sediments in SD1-SD3. SD4 (Aplaku), which has the highest PLI value is being influence by high pollution from both natural (lithological processes) and anthropogenic sources (agrogenic, run-offs from domesticwaste).Sediment serves as a sink for element load in water, the values detected in sediment samples compared to water were high. The amount of the metals in water is removed from the water column and subsequently adsorbed to sediment particles (Garbarino *et al*., 1995). Moreover low concentrations of metals in water could be due to that fact that clay and suspended colloids in the water had adsorbed and precipitated the metals from the water solution.

The PLI values are less than the pollution limit of 1 so currently it cannot be said that the delta is polluted. However, improper monitoring and management of the Oblogo landfill could cause a significant rise in pollution levels in the delta.

CONCLUSION

INAA with conventional counting system has been used to analyse water and sediment from Densu delta wetland in Ghana. With the aid of multivariate statistical techniques and PLI, the extent of pollution has been revealed and the possible sources pollutants have also been determined. Elemental concentrations were generally higher in the sediments than in the waters. This could serve as secondary sources of pollution to the overlying water column in the river. The results of the factor analysis performed on the data also appear to explain fairly well the factors that may have accounted for the chemistry of the water in the study area.Based on these findings, it could be concluded that the wetlandwater chemistry is being influenced gradually by the landfill, small scale agricultural activities and sea water encroachment. These impacts could in the immediate future affect the originality of the ecologically important ecosystem.

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