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Determination of Trace Elements in the Sakumo Wetland Sediments

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Abstract: The objective of this research was to determine the current pollution status of the Sakumo wetland with the aim of identifying factors affecting the long-term integrity of the wetland ecosystem. Sediment samples from the Sakumo wetland were analysed for Cd, Co, Cr, Cu, Fe, Ni, Mn and Zn using Instrumental Neutron Activation Analysis (INAA) coupled with the conventional counting system. The sediment materials exhibited higher concentrations of trace elements Cd (maximum; 0.041 mg/kg), Co (maximum; 0.64 mg/kg), Cr (maximum; 30.73 mg/kg), Cu (maximum; 22.89 mg/kg), Ni (maximum; 11.69 mg/kg) and Zn (maximum; 6.52 mg/kg). In some of the lagoon sediments compared with their levels in world average soils, the average concentrations of the trace elements in general are below or within levels in world average soils/uncontaminated soils. Concentrations of Ni showed positive correlation with Cr whilst Co correlated positively with Cr and Zn. However, lack of correlation between Fe and Cd, suggests that the influence of these parameters on the distribution of trace metals is not important.

Key words: Analysis, contamination, heavy metals, pearson correlation, sediment, spectrophotometry

INTRODUCTION

Sediment is a long-term sink for trace elements. Trace elements can accumulate in sediments; thus, posing significant and persistent threat to organisms which feed on the sediments. Trace elements are normally produced from a variety of natural and anthropogenic sources. However, in aquatic ecosystems, metal pollution can also result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, industrial, municipal or residential waste products (Dawson and Macklin, 1998). The resultant effect of the continuous discharge of such wastes in the environment is a build-up of pollutants including trace elements.

Trace elements are important determinants of sediment quality because of their potential toxicity to living organisms (Förstner and Wittman, 1979). Some of the trace element (e.g., Zn and Cu) usually present within the aquatic ecosystem are essential for proper metabolism in living organisms yet toxic when they occur in high concentrations. Others such as Cd and Cr are non-essential and toxic even at relatively low concentrations. Hence, their concentration in the environment is of major importance to since the accumulation of such metals in the wetland sediment has both direct and indirect consequences on both aquatic and human life.

As concentrations in sediment can exceed those of the overlying water by between three and five orders of magnitude (Bryan and Langston, 1992), the bioavailability of even minute fractions of the total sediment metal concentrations assumes considerable importance. Trace elements and many persistent organic pollutants bind predominantly to suspended material, and finally accumulate in the sediment. Analysis of sediment thus, provides an excellent picture of the extent of pollution within a defined area.

There is more concern about long-term effects, for example linked to accumulation of the chemical in the sediments of rivers and reservoirs, or where industrial discharge continues over a long period. Polluted aquatic sediments can cause environmental damage by releasing these trace elements to surrounding waters, directly contaminating aquatic plants and animals living in such environmnts and ingesting the sediments as food (Marcus, 1991). Hence, the objective of this research is to determine the concentration and distribution of trace metals in rivers and streams draining into the Sakumo wetland.

The study area: The Sakumo wetland lies due east of Accra between Teshie-Nungua and Tema Township in the Greater Accra region of Ghana (Fig. 1). The wetland lies between latitude 5º35′ N to 6º40′ N and longitude 0º00′ W to 0º10′ W with an altitude of 86.9 m (286ft) and an average elevation of 45.7m. The effective catchment area of the Sakumo Ramsar Site is approximately 27,634ha but

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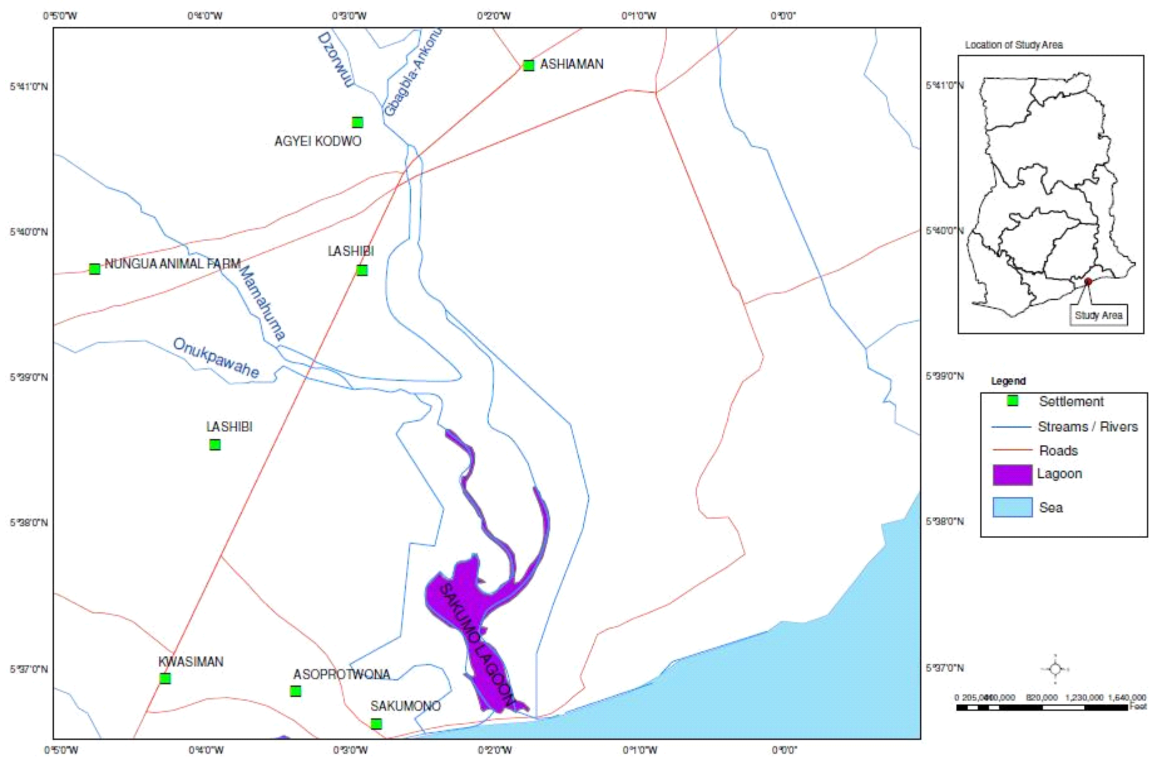

Fig. 1: Map of Sakumo wetland

the water bodies including the lagoon, reservoirs and area liable to flooding is 812 ha. The wetland is a habitat to about thirteen (13) fish species belonging to thirteen (13) genera and eight (8) families with *Sarotherodon melanotheron* also known as the Black-Chin tilapia (name for the black coloration often present under the chin) consisting of about 97% (Koranteng, 1995). The predominant soils consist of black calcareous, heavy plastic clays suitable for mechanised irrigated cultivation of rice and vegetables. In unorganised communities such as the Sakumo catchment, effects due to human and industrial activies have adversely affected the wetland environment.

Sample collection: Sediment materials were sampled from the Sakumo wetland in the Ga-East municipality of Ghana between September and November of 2009. The wetland was divided into five sections with fifteen sampling points established. Sediment were scraped with a hand auger between 0-10 cm depth within a 1x1 m square and stored in a 500 mL polythene bags. A control site (Lebanon Dam) was chosen within the wetland which drains into the lagoon.

Sample preparation: The sediment samples were air-dried and all clods and crumbs were removed. The dried sediments were ground in a mortar and passed through a 180 μm sieve to remove coarse particles. The fine powder sediments were then sub-sampled in preparation for chemical analysis.

Sample analysis: Neutron Activation Analysis was used to analyse the metals Ca, Cu, Mg, Mn, Na, K, V. Samples and standards (IAEA reference soil 7) were wrapped in plastic bags and irradiated at the Ghana Research Reactor 1 (GHARR-1) (Fig. 2). GHARR-1 is a 30KW tank-in-pool reactor using light water as moderator and coolant. The fuel source is highly enriched Uranium (90.2%-Al alloy) with metal beryllium as reflectors. The reactor is cooled by natural convection. Samples were sent into one of the available inner irradiation sites by means of a pneumatic transfer system (rabbit system). At the inner irradiation sites, the samples are irradiated with a thermal flux of 5×10^{11} n/cm^{2}s when the reactor operated at 15 Kw. The metals Ca, Cu, Mg Mn, V classified as short lived radioisotopes were analysed using ti = 2 min, td = 10 s and tc = 10 min. Cd, is classified as medium-lived hence, analysed using the scheme ti = 1 h, td = 24 h, tc = 2h. The samples were analysed using irradiation schemes by optimising irradiation time (ti), decay time (td) and counting time (tc) based on the $t_{1/2}$ of respective elements. The metals were identified using the γ-ray

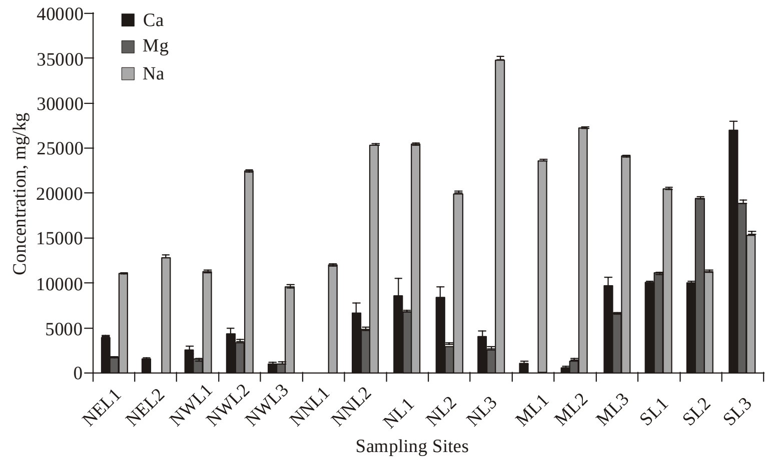

Fig. 2: Bar chart of Ca, Mg and Na concentrations in the Sakumo wetland sediments with standard error

energies that were detected by a high purity Germanium (HPGe) detector and quantified using the Maestro 32 software. The quantitative analysis was done by converting the counts as area under the photopeak of the radionuclides by the comparator method.

Sediment samples were digested in a mixture of concentrated nitric acid (HNO_3), concentrated Hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) according to the Standard examination of water and wastewaters for the analysis of heavy metals (APHA, 1992) for the determination of Fe, Cr, Co, Ni and Zn. A reagent blank was run for each set of six samples. The extracts were analyzed by atomic absorption spectrophotometer (Varian AA240FS). The measurements were made using a hollow cathode lamp of at wavelengths of 232.0, 240.7, 357.9, 253.7 and 213.9 nm, respectively. The slit width was adjusted for all the heavy metals between 0.2 and 1 nm. The values of the detection limits for Cr, Co, Fe, Ni and Zn were 0.001, 0.003, 0.006, 0.010 and 0.001 mg/kg, respectively. Standard solutions were frequently run to check the sensitivity of the instrument (APHA, 1992).

RESULTS AND DISCUSSION

Background levels of Cd in sediments were extremely low, with values less than 0.2 mg/kg, most commonly quoted (Bryan and Langston, 1992; Salomons and Forstner, 1984). Cadimum values were generally low in the sediments with concentrations varying from <0.002 to 0.04 mg/kg (Fig. 4). The low solubility of cadmium for example, could be attributed to the fact that, the cadmium mineral, octavite ($CdCO_3$), which controls the solubility of cadmium in sediments under conditions of high pH and reducing conditions, allows the formation of insoluble precipitate with sulphide mineral greenockite (CdS) (Alloway, 1995). In addition, replacement of Ca^{2+} cations by Cd^{2+} may also occur on the surface layer of calcite when it comes into contact with solutions containing cadmium. There is evidence to show that Cd can be absorbed from surface sediments, suspended particular matter and water (Bryan and Langston, 1992; Schwartz *et al*., 1980). It is known to be one of the more mobile, and hence bioavailable, trace metals (Jensen and Bro-Rasmussen, 1990).

Measured concentration of Cr ranged between 16.32 to 30.73 mg/kg (Fig. 4). Background concentrations of Cr in sediment are usually less than 50 mg/kg (Salomons and Forstner, 1984; Bryan and Langston, 1992). Elevations above this background range are nearly always due to anthropogenic discharge. Fe was found in the sediments in significant quantities with concentrations varying from 63.9 to 172 mg/kg (Fig. 3). These high Fe concentrations in the sediment could be attributed to human activities such as the discharge of untreated sewage, use of the metals in industrial processes as well as the ability of the sediment to also act as a sink for the metal. The highest concentrations of iron were observed in the wetland sediments in areas with fine-grained silts. This may be due to the clayey material that forms the bottom of the lagoon bed in the area.

Concentration of Mn varied from 31.76 to 902.6 mg/kg (Fig. 3). Mn is frequently associated with iron deposits in reducing environments. Mn in the sediments could be attributed to detrital materials, ferromanganganese minerals, clay minerals and accessory sulphide minerals.

Finally, of equal concern are the levels of hydrogen sulphide observed in the sediments surrounding the dump. Most of the sediment was black and anoxic, hydrogen sulphide bubbling to the seawater. Oxygen levels are thus poor, possibly none existent, The effects of oxygen

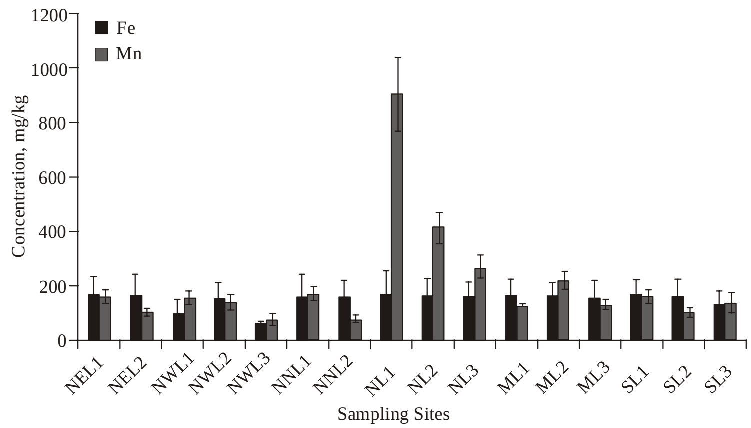

Fig. 3: Bar chart of Fe and Mn concentrations in the Sakumo wetland sediments with standard error

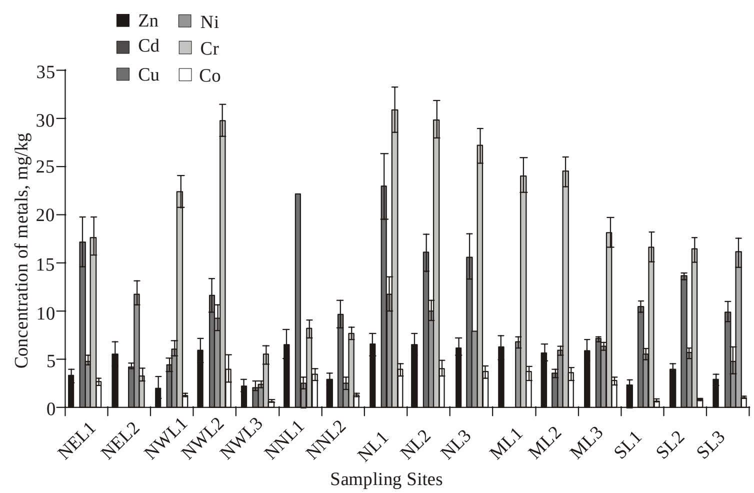

Fig. 4: Bar chart of Zn, Cd, Cu Ni Cr and Co concentrations in the Sakumo wetland sediments with standard error

depletion are much more marked in coastal areas of the sea, such as this, and can result in substantial losses (in terms of both numbers and species diversity) to fish and marine invertebrate populations (UNEP, 1995).

Concentrations of copper (Cu) varied from <0.003 to 22.89 mg/kg (Fig. 4). The enrichment of Cu in the study area may however, be due to its association with organic matter thereby increasing its production in the environment. The enrichment of biogenic element Cu in the sediments may be due to its association with organic matter thereby increasing planktonic production in the mangrove environment. Cu has biological importance for making frustles of plants which contributes to high planktonic production through increase of organic. Co and Ni could be due to the discharge of agricultural and industrial. Cobalt concentrations varied from 0.64 to 4 mg/kg whilst nickel concentration ranged from 1.51 to 11.69 mg/kg (Fig 4). The source of cobalt pollution is mainly from industrial waste. Co contamination in the sediments is also associated with the burning of the metal during industrial processing (Barałkiewicz and Siepak, 1999) whilst high concentrations of nickel were measured in areas polluted by sewage (refuse dumps).

In order to ascertain sources that affect heavy metals distribution in the wetland sediments, interelemental association was evaluated using the Pearson correlation coefficient and the results are presented in Table 1. Elemental association may signify that each paired elements has identical source or common sink in the stream sediments (Singh *et al*., 2002; Nyangababo *et al*., 2005b). Strong positive correlation was observed between Ni and Cd, Cr, Mn. Co and Zn showed significant correlation whereas weak/negative or no significant correlation existed between Cd and Cr, Co Cu; Cu and Cd, Co, Cr; Fe and Cd; Cr and Cu, Ni; Zn and Cd (Table 1). These weak correlations suggest that the trace elements are not specifically associated with each other and hence are insignificant in the distribution of the elements in the wetland. Examples of metal-containing pesticides include simple inorganic

Table 1: Pearson correlation of heavy metals contents (mg/kg) of sediments from the Sakumo wetland

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
Cd	1.00							
Co	- 0.11	1.00						
Cr	- 0.50	0.60	1.00					
Cu	0.08	0.27	0.12	1.00				
Fe	- 0.01	0.45	0.29	0.31	1.00			
Mn	- 0.34	0.60	0.65	0.50	0.23	1.00		
Ni	- 0.65	0.61	0.92	0.26	0.25	0.72	1.00	
Zn	- 0.02	0.90	0.46	0.23	0.53	0.48	0.48	1.00

compounds such as zinc chloride, zinc sulphate, zinc phosphide, copper oxide, copper oxychloride, copper sulphate and barium carbonate (ATSDR, 1997). Finally, of equal concern are the levels of hydrogen sulphide observed in the sediments surrounding the dump. Most of the sediment was black and anoxic, hydrogen sulphide bubbling to the seawater. Oxygen levels are thus poor, possibly none existent, The effects of oxygen depletion are much more marked in coastal areas of the sea, such as this, and can result in substantial losses (in terms of both numbers and species diversity) to fish and marine invertebrate populations (UNEP, 1995).

CONCLUSION

Cadmium, chromium, cobalt, iron, manganese and zinc had the highest concentrations and the greatest range of concentrations in the lagoon sediments compared to sediments from the feeder streams and control site (Lebanon dam), indicating possible enrichment of these elements in the industrialized and urbanized areas. The concentrations measured may not necessarily have negative impacts on the environment, but suggest that industrial and agricultural activities are leading to increased levels of these elements in the wetland sediments and could possibly exceed background levels if not monitored.

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