Assessment of the levels of toxic and potentially toxic metals in sediments from the weija dam Ghana

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ABSTRACT

This research work aimed at evaluating the degree of metal contamination in the weija lake and the extent to which the quality of the sediment has deteriorated. The dam is a source of drinking water and is also utilized for fishing and irrigation. It however receives agricultural runoff and municipal wastewaters. The concentrations of ten metals (Cu, Co, Cr, Fe, K, Mn, Ni, Pb, V and Zn) in sediments from thirteen sampling points from the Weija dam in Accra, Ghana, were investigated using energy dispersive X-ray fluorescence (EDXRF). Elevated concentrations (in µg/g) of toxic and potentially toxic elements (Cu, 19.80±3.77; Co, <19.80; Cr, 87.62±19.69; Fe, 141245.5±1765.39; K, 25363.08±3740.08; Mn, 433.61±60.71; Ni, 58.65±8.81; Pb, 20.03±1.19; V, 77.35±24.02; and Zn, 19.07±3.41) were recorded in the sediments of the dam. The enrichment factor (Apart from K with EF=1.20 showing minor enrichment) and geoaccumulation index values calculated indicated that these metals were generally from natural sources with insignificant contribution from anthropogenic sources. The geology of the dam, been characterized by granite, shale and phyllite might have contributed to the elevated levels through weathering and leaching. Concentrations of Co were however below detection limit in all the samples. The pollution load index values show that the sediment was unpolluted with respect to Cu, Co, Cr, Fe, K, Mn, Ni, Pb, V and Zn.

Introduction

Pollution of the natural environment by metals is becoming a potential global problem. Heavy metals in particular are indestructible with most of them having toxic effects on living organisms, when they exceed threshold concentrations (Schuurmann and Market, 1998; MacFarlane and Burchett, 2000). They are generally not removed from water as a result of self purification, but accumulate in reservoirs, such as sediments, and enter into the food chain (Loska and Wiechula, 2003).

Sediments, as basic components of the aquatic ecosystem, act as substrates for most aquatic organisms. They serve as sinks and reservoirs for a variety of environmental contaminants. According to *Milenkovic et al,2005*, aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the concentration of the water column. They can incorporate and accumulate many metals added to a body of natural water. Many researchers had studied the pollution history of aquatic ecosystem by core sediments (Karbassi *et al.,* 2005; Lopez and Lluch, 2000). Bellucci *et al.,* 2003 and Weis *et al.,* 2001, have also used sediment cores to study the behavior of metals

In this work, sediments have also been employed for the monitoring and assessment of metal pollution of the Weija dam in Accra, Ghana. This is because sediments are known to remobilize and release metals to the water column under favorable physico-chemical conditions (Harikumar et al, 2009). Accra is a densely populated area with variety of industrial activities (such as metal smelting, pharmaceuticals etc) and agriculture activities (which include maize, cassava, sugarcane and vegetables farming). All these activities release toxic and potentially toxic metals to the environment which may eventually find their way into the weija dam which currently provides drinking water to the Western parts of Accra, as well as fisheries. This research therefore aims at assessing the influence and sources of these toxic and potentially toxic metals on the weija dam.

Materials and methods

The study area

The Weija dam is located at about 17km west of Accra the capital town of Ghana. It is 14 km long, 2.2 km wide and has total surface area of 38 km^2 with mean depth of 5 m [Vanden B.J.P, 1990]. The dam is located between 0° 20' W 0° 25' W and 5° 30' N 5° 45' N. it was created in 1977 as a replacement for an earlier one which was washed away in 1968 by Ghana Water Company Limited through the damming of River Densu mainly to satisfy the demand for potable water supply [Asante K.A, 2005, p171-180].

It is almost at the mouth of the 116 km long Densu river which lies between latitude 5° 30^1N and 6° 20^1N and between longitudes 0^o10^1 and 0° 35^1W. The Densu River takes its source from the Atewa range of hills in the Akim Abuakwa district of the eastern region of Ghana at altitude 0.64km above mean sea level [Akpabli C.K, 2001].

From the source, it flows through the south-eastern direction till it reaches Mangoasi, then changes its course and flows generally southwards till it enters the Gulf of Guinea through the Sakumo lagoon at Botiano, a fishing village which is 16 km west of Accra.

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Geology

About 95% of the basin is underlain by granite and granodiorite of middle precambrian origin, except for the sources and toward the mouth [Akpabli C.K, 2001, p84-94] where they are underlain by the birimian and the Togo series respectively. The birimian is primarily made up of metamorphosed lava, phyllite, schists tuffs and grey wacke. From Weija to the mouth are characterized by quartz, shale and phyllite of the togo series.

Sample collection

A total of 65 sediment samples were collected from 13 points in the whole dam by maintaining a distance of about 100 m using Eckman bottom grab sampler with an attached calibrated cable. At each sampling site, five replicate samples were collected. The sample collection was done from March to April 2010. The sampler was lowered to the bottom of the river at the desired depth where the sediment samples were collected. The top 0-5 cm of the sediments, in each case, were sampled and quickly packed in labeled, pre-cleaned, airtight polyethylene bags. No preservatives were added to the samples. The sediment samples were kept over ice in a thermo-insulated box and transferred into the laboratory for preparation and analysis.

Sample preparation

Sub-samples of the sediment were homogenized using a polyethylene spatula and oven-dried at 105°C overnight. Organic debris, Shelly fragments and macro-organisms were removed from the sample. The dried samples were then crushed using agate mortar and pestle. It was then sieved through a 64 μm-mesh U.S.A standard testing sieve (Fisher Scientific Company, U.S.A). In order to normalize the variations in grain size, the lower particle size fraction was again homogenized by grinding in an agate mortar and stored in pre cleaned polyethylene bags. About 500 mg of each sample were pelletized using a Specac press with a pressure of 2 tons/cm^2 to produce an intermediate thick pellet sample. The pellet produced was kept in a desiccator for at least 24 h to get rid of moisture in the sample.

Reference material

Two standard reference materials; SOIL-7 and NIST-SRM 1646a (estuarine sediments) were prepared in a similar mannar as the samples. These reference materials were used for the validation of the analytical results.

Sample irradiation, counting and analysis

The elemental concentrations were determined using energy dispersive X-ray fluorescence (EDXRF). EDXRF provides a rapid and non-destructive method for the analysis of trace and major elements in geological samples. Under vacuum conditions, all measurements were carried out using an X-ray Generator (Compact 3K5) EDXRF spectrometer with a Mo target, equipped with a liquid- nitrogen-cooled Si (Li) detector. The incident and take-off angles were 45, with a Be window thickness of 12.5 mm. The distance between the sample (exposed diameter of 22 mm) and the detector was 4.5 cm. The energy resolution was 0.165 keV. In order to maximize the EDXRF sensitivities for the wide range of elements in which we were interested, two different combinations of EDXRF parameters (including voltage and current). Applied voltage and current are varied to acquire the require K" or L" energies line. The current was adjusted to maintain similar portions of live detection time. An ORTEC maestro multichannel analyser programme was employed for data collection. Irradiations were made for each sample, being the intermediate thick sample

target for spectrum collection life time of 1500 s. linear least squares fitting of the axil software programme was used for the spectrum deconvolution (IAEA, 2005). Emission transmission method in QXAS package was used to convert spectrum peak areas to concentrations.

Sediment quality assessment

Determination of enrichment factor

In the present study enrichment factor was used to assess the level of contamination and the possible anthropogenic impact in sediments of the Weija Dam. To evaluate the magnitude of contamination in this sediment, the enrichment factors (EF) were computed relative to the abundance of species in source material to that found in the Earth's crust. Although many authors (Baptista Neto *et al*., 2000; Mucha *et al*., 2003) have used conservative elements such as Al and Fe to identify and normalize anomalous metal concentration. Iron has been used in this study to normalize metal contaminant and differentiate natural from anthropogenic components. According to Ergin *et al*. (1991) the metal enrichment factor (EF) is defined as follows:

$$EF = \frac{(X/Fe)\,sediments}{(X/Fe)\,Earth\;Crust}$$

where EF is the enrichment factor, X is the metal studied and X/Fe is the ratio of the concentration of element X to Fe. Many authors prefer to express the metal contamination with respect to average shale to quantify the extent and degree of metal pollution (Muller, 1969; Forstner and Muller, 1973). In this study, crustal abundance values taken from Taylor (1964) was used as background concentrations for the metals; Cu, Co, Cr, Fe, K, Mn, Ni, Pb, V and Zn. According to Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate that the source of metals is entirely crustal materials or natural processes, whereas EF values greater than 1.5 suggest that the metals are more likely to be anthropogenic.

Index of Geoaccumulation (Igeo)

The geoaccumulation index Igeo values calculated for different metals as introduced by Muller (1969) is as follows:

$$Igeo = In\left(\frac{c_n}{1.5 \times Bn}\right)$$

Where Cn is the measured concentration of element n in the sediment sample and Bn is the geochemical background for the element n which is taken from the literature (Taylor,1964). The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations. The seven grades or classes of geo accumulation index proposed by Muller were used in this study.

Pollution Load Index

The extent of pollution by trace metals has been assessed by employing the method based on Pollution Load Index (PLI) developed by Thomilson *et al*, 1980. The relation is shown below

$$PLI = \sqrt[n]{(product\;of\;n\;number\;of\;CF\;value)}$$

Where CF = contamination factor and n= number of metals
PLI provides a simple, comparative means for assessing a site or estuarine quality. A value of zero indicates perfection, a value of one indicates only baseline levels of pollutants present and values above one indicate progressive deterioration of the site (Thomilson et al, 1980).

Results and Discussion

The results of the analysed standard reference materials; estuarine sediment and soil 7 is presented on Table 1. From the results, it was observed that the accuracy of the measurements,

in terms of relative deviation from the IAEA certified values, were all within ±4%. From this, it was realized that, the agreement between the IAEA certified values and the values obtained in this work was generally good.

The average contents of toxic and potentially toxic metals in the sediment of the weija dam are given in Table 2. Mean metal contents in the sediments ranged from 10.18 ±1.97- 51.26 ± 7.56 µg/g (Cu); <42.266 - 305.59 ± 45.95 µg/g (Cr); 6126.01 ± 838.45 -36670 ± 4891µg/g (Fe); 20484 ± 2954-27764 ± 4020 µg/g(K); 233.56 ± 33.84 - 666.74 ± 93.84 µg/g(Mn); 44.88 ±7.20 − 112.72 ± 15.57 µg/g(Ni); 17.21 ± 1.21- 25.47 ± 1.58 µg/g(Pb); <77.411-77.35 ± 24.02 µg/g (V) and 7.35 ± 1.93- 60.07 ± 8.44 µg/g (Zn). Cobolt was below the detection limit of EDXRF.

The highest concentration of total Cu (51.26 ± 7.56 µg/g), Fe (36670 ± 4891µg/g), Mn(666.74 ± 93.84 µg/g), Pb(25.47 ± 1.58 µg/g) and Zn (60.07 ± 8.44 µg/g) were found at site WS3, while the maximum concentration of Cr(305.59 ± 45.95 µg/g) and Ni (112.72 ± 15.57 µg/g) were found at site WS10. Potassium (27764 ± 4020 µg/g) and V (77.35 ± 24.02 µg/g) recorded highest concentrations at WS6 and WS7 respectively.

The mean distribution of metals in the sediment, in µg/g, in decreasing order was Fe(141245.5 ± 1765.39)> K(25363.08 ± 3740.08) >Mn(433.61 ± 60.71)> Cr(87.62 ± 19.69) > V(77.35 ± 24.02) >Ni(58.65 ± 8.81) >Cu(19.80 ± 3.77) >Zn(19.07 ± 3.41). From the above observations, it is clear that Fe showed more pronounced levels of pollution in the sediments. Cobolt was however below the detection limit of EDXRF.

Assessment of pollution by calculating the enrichment factor (EF), geo accumulation index(Igeo) and pollution load index (PLI)

The enrichment factor (EF) values are shown in Table 3. All the EF values obtained for the elements Cu (0.14), Cr (0.35), Mn (0.18), Ni (0.31), Zn (0.11) and V (0.40) were less than 1. This implies that, there was no enrichment and that all the said elements recorded background concentrations. Potassium (EF= 1.21) however indicated minor enrichment.

From Table 3, it can be seen that the geo accumulation index values (Igeo) calculated for the elements Cu, Co, Cr, K, Mn, Ni, V and Zn were all less than zero. They therefore fall in ″class 0″ of the Muller categorization indicating background concentrations. Iron however recorded an Igeo value of 0.51 which fall into the class 1 categorization of Muller indicating uncontamination to moderate contamination. The pollution load index(PLI) calculated for the sediment was also 0.98(i.e <1). From the PLI value, it was realized that, the weija dam sediment was practically unpolluted.

From the EF and Igeo values, the concentration levels recorded for the metals can be said to be originatig mainly from crustal materials or natural processes. The metal vanadium is considered naturally occurring. It is found in about 65 different minerals including camolite, voscoelite, patronite and vanadinite (IPCS, 2001).

Average metal concentrations in the core sediments was compared with standard background values and are summarized in Table 3. In the present study crustal abundance was used as reference lines (Taylor 1972). The mean concentration of Fe(141245.5± 1765.39) and K (25363.08±3740.08), greatly exceeded the average crustal abundance values of 56300 and 20900 respectively. The average concentration of Mn(433.61± 60.71), Cr(87.62±19.69), V(77.35± 24.02), Ni(58.65±8.81), Cu(19.80± 3.77) and Zn(19.07± 3.41) were however lower than

the average crustal abundance values, which indicates that these elements originated mainly from lithogenic sources.

Heavy metal contamination vis-avis ecotoxicology

The ecotoxicological sense of heavy metal contamination in sediments was determined using sediment quality guidelines developed for marine and estuarine ecosystem (Bakan and Ozkoc, 2007) is shown on Table 4.

These effects are as follow:

a) The effect range low (ERL) / effect range median (ERM);

b) The threshold effect level (TEL) / probable effect level (PEL).

Where, ERL and TEL are concentrations below which adverse effects upon sediment dwelling fauna would infrequently be expected whereas, ERM and PEL represent chemical concentration above which adverse effects are likely to occur. Though the concentration of Cu was below the PEL, ERL and ERM values, it however exceeded the TEL value. Chromium was greater than the TEL and ERL values but lower than the PEL ERM values. Lead and Zn however had concentrations below TEL, PEL, ERL and ERM values. Nickel exceeded all the sediment quality guideline values used in this work. This implies that the concentration of Ni in the sediment can trigger adverse effects dwelling fauna.

Conclusions and Recommendations

Recent industrial, Agricultural activities and vehicular emissions in the capital city of Ghana raised concern of environmental pollution with both toxic and potentially toxic metals. The mean distribution of metals in the sediment, in µg/g, in decreasing order was Fe> K>Mn> Cr> V>Ni>Cu >Zn.

From the data provided in this work, apart from K (indicating minor enrichment), the EF calculated for the metals Cu, Co, Cr, Fe, Mn, Ni, Pb, V and Zn showed no enrichment in the sediment of the weija dam. The Igeo calculated for the metals also showed that, the pollution status ranged from background to unpolluted levels. From the low EF and I geo values, the metals can be said to originate from natural sources and that the contribution from anthropogenic sources was insignificant. The PLI value obtained (i.e <1) also supports the fact that the sediment of the weija dam is unpolluted with respect to Cu, Co, Cr, Fe, K, Mn, Ni, Pb, V and Zn.

Apart from Fe and K, the concentrations of all the metals detected were below the average shale value. From the ecotoxicological studies, it was found that all the metals recorded concentrations lower than the PEL, ERL and ERM values except nickel which was above the ERM value.

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Table 1: Comparism of elemental concentrations in reference materials analyzed by EDXRF withcertified/recommended values, n = 5

Element	IAEA-SRM SOIL-7 Concentration (μg/g unless indicated otherwise)		NIST-SRM 1646a (Estuarine Sediments) Concentration (μg/g unless indicated otherwise)	
	This work	Certified value	This work	Certified value
Co	9.0±0.04	(8.9±0.05)*	(5.0)*	(5.0)*
Cr	58.1 ±0.83	(60.0±0.14)*	41.1±2.1	40.9±1.9
Cu	10.2 ±1.6	11.0±2.0	9.95 ±0.31	10.01±0.34
Fe	2.4±0.6	2.5±0.2	1.970±0.291%	2.008±0.039%
K	1.24±0.1	1.2 ±0.1	0.89±0.02%	0.86±0.016%
Mn	632.9±5.0	631.0±22.0	237.3±3.1	234.5±2.8
Pb	58.8±5.6	60±5.0	11.3±1.3	11.7±1.2
Ni	(25±3.0)*	(26±5.0)*	(22.5)*	(23)*
V	67.1±2.6	66.0 ±7.0	43.91±0.90	44.84±0.76
Zn	(105±11.1)*	(104±9)*	48.3 ±0.9	48.9±1.6

*Non certified/ Recommended value

Table 2 Concentration of metals in sediment samples of the Weija Dam (in µg/g)

Element	Cu	Co	Cr	Fe	K	Mn	Ni	Pb	V	Zn
WS1	15.94± 3.00	<94.607	<43.339	14910±202	24030±3510	492.05±70.76	45.59±6.89	17.99±1.06	<125.758	18.85±2.85
WS2	10.29 ± 3.65	<63.990	<51.417	10120± 1372	25822 ± 3782	514.58 ± 71.00	45.27 ± 7.32	17.70 ±1.06	<80.373	10.87 ± 2.18
WS3	51.26 ± 7.56	<194.090	<56.228	36670± 4891	20484 ± 2954	666.74 ± 93.84	79.82 ± 11.45	25.47 ± 1.58	<141.271	60.07 ± 8.44
WS4	23.96 ± 4.43	<118.207	51.69 ± 17.94	19270± 2580	23660 ± 3394	440.16 ± 60.79	63.79 ± 9.14	21.43 ± 1.31	<102.170	25.79 ± 4.14
WS5	15.24 ± 3.84	<104.459	<42.266	13911± 1884	23921 ± 3561	482.59 ± 67.53	53.20 ± 8.33	21.79 ± 1.19	<116.461	38.94 ± 5.48
WS6	15.11 ± 2.90	<75.297	72.34 ± 17.38	10124± 1382	27764 ± 4020	313.15 ± 44.39	54.01 ± 8.35	18.31 ± 1.24	<93.257	10.67 ± 2.19
WS7	10.18 ± 1.97	<53.936	39.45 ± 10.51	10830± 1624	25710 ± 3540	387.11 ± 52.53	49.48 ± 6.96	21.47 ± 0.94	77.35 ± 24.02	28.57 ± 4.23
WS8	12.50 ± 2.43	<53.623	60.99 ± 16.49	6017.16± 819.94	25490 ± 3872	233.56 ± 33.84	44.88 ± 7.20	17.21 ± 1.22	<77.411	9.37 ± 1.71
WS9	21.03 ± 3.67	<105.670	<81.924	15470± 2100	26233 ± 4010	453.49 ± 63.44	58.11 ± 8.42	18.97 ±1.15	<111.63	18.27 ± 2.89
WS10	29.12 ± 4.76	<129.259	305.59 ± 45.49	21730± 2910	25812 ± 3811	476.10 ± 65.91	112.72 ± 15.57	21.61 ± 1.25	<101.913	27.01 ± 3.99
WS11	<9.652	<62.231	69.09 ± 19.88	8432.6 ± 1144.94	27331 ± 4106	431.18 ± 61.09	52.11±8.11	19.59 ± 1.34	<82.648	7.35 ± 1.93
WS12	20.31 ± 3.66	<57.518	38.82 ± 13.47	6126.01 ± 838.45	27032± 3951	236.62 ± 33.77	53.82 ± 8.37	18.93 ± 1.07	<97.147	10.27 ± 2.10
WS13	13.41 ±3.34	<75.427	62.99 ± 16.32	8806.66 ± 1201.78	26431 ± 4110	509.61 ± 70.45	49.69 ± 8.36	19.94 ±1.11	<83.640	8.88 ±2.19
Mean	19.80± 3.77	<91.408	87.62± 19.69	14124.55± 1765.39	25363.08± 3740.08	433.61± 60.71	58.65± 8.81	20.03± 1.19	77.35± 24.02	19.07± 3.41

Table 3 Geo accumulation index and enrichment factor for metals in sediment samples

Elements	Cu	Co	Cr	Fe	K	Mn	Ni	Pb	V	Zn
Concentrations	19.80± 3.77	<91.41	87.62± 19.69	141245.5± 1765.39	25363.08± 3740.08	433.61± 60.71	58.65± 8.81	20.03± 1.19	77.35± 24.02	19.07± 3.41
Geoaccumulation Index(Igeo)	<0.00		<0.00	0.51	<0.00	<0.00	<0.00		<0.00	<0.00
Enrichment Factor (EF)	0.14		0.35	1.00	1.21	0.18	0.31		0.22	0.11
crustal abundance	55	25	100	56300	20900	950	75		135	70

Table 4 Assessment of sediment pollution using different indices of sediment contamination by comparison with effect based sediment quality guideline (SQG)

Element	Concentration of sample	TEL	PEL	ERL	ERM
Cu	19.80±3.77	18.70	110.00	34.00	270.00
Zn	19.07±3.41	124.00	270.00	150.00	410.00
Cr	87.62±19.69	52.30	160.00	81.00	370.00
Pb	20.03±1.19	30.20	110.00	46.70	218.00
Ni	58.65±8.81	15.90	43.00	20.90	51.60