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### Baseline

Distribution and enrichment of trace metals in marine sediments from the Eastern Equatorial Atlantic, off the Coast of Ghana in the Gulf of Guinea

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#### ABSTRACT

We present results of a preliminary geochemical assessment of Cd, Pb, V, As, Ni, Cu, Zn, Mg, Al, K, Ca, and Fe in marine sediments from the Eastern Equatorial Atlantic, off the Coast of Ghana. Samples were taken along 4 regions G1, G2, G3 and G4 at approximately 25 m, 100 m, and 250 m, 500 m and 1000 m depths. Elemental compositions were assessed through the estimation of Al-normalized enrichment factors and geochemical accumulation indices, and the concentrations determined to produce any potential toxic effects to biota. Significant enrichment of the bottom sediments with Cd, Ni and As were observed at some locations with sediments showing signs of heavy pollution with As at region G4. Apart from Ni, V and As which were beyond threshold effects levels at most regions, all other metals were below probable effect levels. Both natural and anthropogenic processes controlled trace metal accumulation and distribution in the Ghanaian coastal environment.

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The increasing demands on mineral resources globally have resulted in the release of enormous amounts of metals and several other pollutants into the world's oceans. Natural geochemical cycling of trace metals into different environmental compartments have been altered profoundly mainly as a result of increasing urbanization and industrialization in coastal cities worldwide. Enrichment of trace metals in marine sediments are of critical concern due to their toxicity to biological systems as well as associated public health risks. Unlike other contaminants, metals are non-degradable and may persist in the environments over billions of years with potentials of becoming bioaccumulated and biomagnified up the food chain (Kontas, 2007). Metals such as Fe, Cu, and Zn for instance may become toxic at high concentrations (Merian, 1991) while As, Cd, and Pb which have no important biological roles tend to be teratogenic, carcinogenic or mutagenic (Yoshida et al., 2006).

Situated in the Guinea Current Large Marine Ecosystem region of the Eastern Equatorial Atlantic, the coastline of Ghana measures about 550 km long, and stretches from longitude 3°06'W to 1°10'E and latitudes 4°30' to 6°6'N (Koranteng, 1995). The continental shelf which narrows in width progressively towards the east drops sharply into the Cote d'Ivoire escarpment just beyond the

\* Corresponding author. E-mail address: edemmahu@gmail.com (E. Mahu). 145-250 m depth contour (Koranteng, 1995). Just as many parts of the world, the coastal zone of Ghana is a home to over 80% of the country's industries, with the western part being the hub of commercial oil exploration and drilling. Majority of the industries in the coastal zone have introduced significant levels of trace metals into the marine environment through the discharge of untreated effluents either directly or via estuaries (Armah and Amlalo, 1998). Apart from a study carried out by Nyarko et al. (2011) in the Jubilee Oil field of the Ghanaian continental shelf which showed some significant contamination of the sediments with barium (Ba), all available literature show that, this area of the Equatorial Atlantic Region is among the poorly studied in terms of trace metal accumulation and distribution. This paper thus presents the results of a preliminary geochemical assessment of some selected trace and lithogenic metals in coastal and deep sea sediments sampled across this area of the Eastern Equatorial Atlantic.

Twenty (20) surface sediments were taken off four (4) regions, G1, G2, G3 and G4 during an R/V Fridtjoff Nansen oceanographic cruise in 2010 and 2012 in the Ghanaian continental shelf (Fig. 1). Region G1 is located to the easternmost part of the coast-line where Volta, the largest river in the country empties into the sea. The Volta River drains major farm lands and many rural residential areas before joining the Gulf of Guinea. Region G2 also in the east coast is located off the city of Tema which is among the most urbanized and industrialized areas of the country. Regions







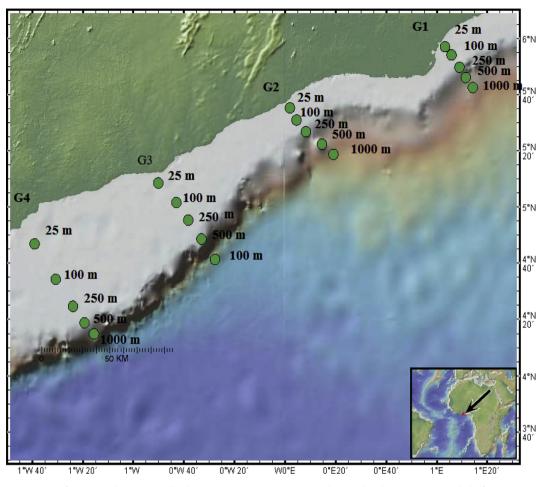


Fig. 1. Map showing sampling locations at regions G1, G2, G3 and G4 in the Ghanaian continental Shelf.

G3 and G4 are situated on the western coastline, where Rivers Ankobra (to the left of G3) and Tano (to the left of G4) join the Eastern Equatorial Atlantic. These two Rivers drain important inland alluvial gold mining areas whose effluences are mostly transported into the ocean. Additionally, commercial oil exploration and exploitation activities are currently ongoing in the deeper areas of region G4. The regions are about 100 km spaced from each other. Samples were taken at depths of about 25 m, 100 m, 250 m, 500 m and 1000 m at each region using a Van Veen Grab with adjustable opening of 0.1  $m^2$ . The fractions below 63  $\mu m$ mesh size were analyzed for Cd, Pb, V, As, Ni, Cu, Zn, and lithogenic elements Mg, Al, K, Ca, and Fe. Sediments were digested according to the protocols outlined in USEPA method 3050B with slight modifications. About 0.1 g of homogenized freeze dried sediment sample was weighed into pre-washed and dried Teflon bombs. 2 mL guartz distilled 6 N hydrochloric acid and 2 mL of 14 N nitric acid was added to each sample, covered and heated in temperature baths for about an hour. The mixture was cooled, transferred into pre-weighed Teflon beakers followed by subsequent addition of 2 mL 26 N hydrofluoric acid and 5 mL nitric acid and evaporated to dryness. A final solution of 2 mL nitric acid in 8 mL milli Q (18 megaohm Milli-Q, Millipore Systems<sup>®</sup>) water was made and pipetted into low density polyethylene bottles. The BCSS-1 certified standard reference material (CRM) and method blanks were prepared using the same procedure. Elemental quantification was carried out using a Perkin-Elmer Element 2 high resolution Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Moss Landing Marine Laboratories in the United States of America. Five (5)%, 25% and 100% standard solutions for calibration were prepared from multi-element stock solution (Sigma Aldrich). To meet the analytical requirements of trace metals analysis in environmental samples using the ICP-MS, the quality control and quality assurance procedures outlined in USEPA method SW-846 6020A were strictly followed. These included sample and standards preparation, tuning of the ICP-MS with a tuning solution containing all elements representing the mass regions of interest prior to calibration, three (3) initial blank calibrations using nitric acid, and an initial calibration verification (ICV) using standards containing all target elements. An initial blank calibration (ICB) using nitric acid was made immediately after the ICV. A continuous calibration verification (CCV) using standards and a continuous calibration blank (CCB) followed every 10 batch of samples analyzed, and at the end of the analytical run. Rhodium internal standard stock solution was added to each sample and quality control samples as a yield tracer. Method blanks and CRM (triplicates) were analyzed in addition to samples. Recoveries (%) varied with respect to each metal and were in the range of 88-118% for Ni, Cu, Zn, As, Cd and V; and 90–107% for Al, Mg, K, Ca (Table 1). The average values of the variation coefficients obtained were less than 10% which can be considered satisfactory for environmental analysis (Morillo et al., 2004). Principal component analysis (PCA) followed by a direct oblimin rotation was carried out in SPSS 13.0. The aim of the PCA was to reduce the number of variables to a smaller set of orthogonal factors making it easier to interpret by displaying the correlations existing among the original variables (Stella et al., 2002).

All trace and major elements analyzed (Cd, Pb, V, As, Ni, Cu, Zn, Mg, Al, K Ca, and Fe) in the study were detected in sediment

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