

Heavy metal geochemistry of stream sediments from parts of the Eastern Niger Delta Basin, South-Eastern Nigeria

Geokemija težkih kovin v rečnem mulju delov Vzhodne kadunje Nigrove delte v jugovzhodni Nigeriji

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Abstract

This study documents the baseline geochemistry of sediments in portions of the Eastern Niger Delta, focusing on the distribution of selected heavy metals (Pb, Zn, Cd, Cr, As and Ni). Concentration levels of metals were determined through Atomic Absorption Spectrophotometry (AAS) and results interpreted with statistical techniques. Interrelations between parameters reveal a control by three dominant geogenic factors. The study shows that heavy metal geochemistry of sediments is related to regional and local geology with minor imprints of anthropogenic activities.

Key words: trace metals, sediments, factor analysis, geogenic, Niger Delta, Nigeria.

Izvleček

Predmet študije je ugotovitev splošnih geokemičnih značilnosti rečnega mulja v nekaterih delih delte vzhodne Nigra s poudarkom na porazdelitvi izbranih težkih kovin (Pb, Zn, Cd, Cr, As in Ni). Vsebino kovin so določili z atomsko absorpcijsko spektrofotometrijo (AAS) in rezultate interpretirali s statističnimi metodami. Medsebojne povezave med spremenljivkami nakazujejo odločilen vpliv treh prevladujočih geogenih dejavnikov. Rezultati raziskave dokazujejo, da je geokemija težkih kovin v rečnem mulju povezana z regionalno in lokalno geologijo ter z lokalnimi vplivi človekovih dejavnosti.

Ključne besede: sledne prvine, rečni mulj, faktorska analiza, geogeni vpliv, Nigrova delta, Nigerija

Introduction

Concentration of heavy or trace metals within geo-environments have received tremendous attention in many research works worldwide;^[1-5]. These have been predicated on a variety of interest including but not limited to the following; (a) their insidious contributions as related to public health concerns (b) their effects on biota growth and diversity and (c) academic interest in establishing baseline data and decipher the fate and dynamics of metal transport within geo-systems.

Chester et al.^[6] conclude that coastal sediments are particularly important traps for trace elements.^[1] observed that marine sediments in coastal regions near large industrial and urban areas contain heavy metals sometimes in amounts higher than their natural background. More than 90 % of transport of most heavy metals in river systems is shown to be as a solid phase in sediments^[7]. Mobilization of these sediments into the major rivers and eventually into reservoirs may concentrate metals at non-background levels.

These metals exist as chemical species or fractions that exhibit different bioavailability and potential risk to human beings. These species and their character have been assessed successfully through statistical and geochemical modelling computer programs^[8-11].

This study attempts to document the heavy metal chemical trend and species availability of sediments in parts of the Eastern Niger Delta basin, south-eastern Nigeria. The natural geochemistries of sediments within the study area are believed to be controlled by geologic rock units through which rivers and streams within the catchment flow. High concentrations of heavy metals may be derived from mineral deposits, rock types with heavy metal concentrations above average crustal rocks as well as from weathering processes that may concentrate metals from rocks which do not contain large amounts of these metals. Contributions from anthropogenic activities may also be imprinted on the geochemical data of the sediments.

Description of study area

The area being described as the Eastern Niger Delta extends eastwards from the shoreline fringe of Ikot Abasi area to the coastal plain physiographic provinces of Calabar area of south-eastern Nigeria. The basin is about 100 km long and about 25 km wide, delimited by longitudes 7° 30'–8° 15' E and latitudes 4° 30'–4° 40' N (Figure 1). The basin spans the shore lines of Akwa- Ibom and Cross River States of south-eastern Nigeria.

Geologically the study area is composed of Tertiary and Quaternary sediments referred to as Coastal Plain Sands of the broader Niger Delta basin^[12]. This formation consists of alternating sequence of gravel, sand, silt, clay and alluvium. Sediment fill within the basin are sourced from three major geologic units on the hinterlands. These units include;

- The Precambrian Oban Massif Complex made up of migmatites-gneisses, granites, schists, para-schists, pegmatites and a host of other ultra-mafic rock suites,^[13]
- Cretaceous sedimentary fill known as the Calabar Flank, composed of limestones, sandstones, shales and marls^[14] and
- The lower Benue Trough (Anambra Basin) of post-Cretaceous sediments with lodes of sulphide deposits.^[15]

Another source of sediments into the study area is the Cross River Delta (Rio Del Rey Basin).^[14, 15]

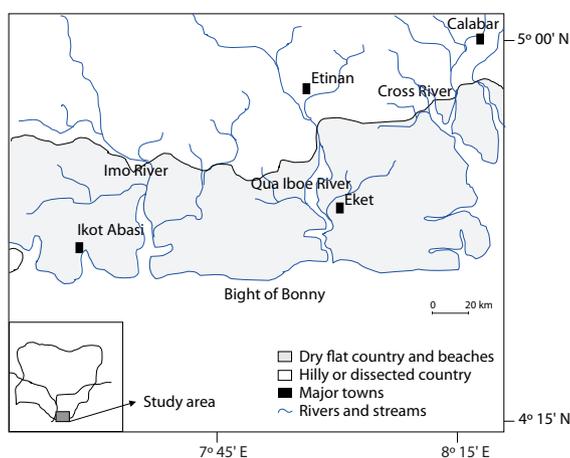


Figure 1: Map of Niger Delta Basin showing sampled rivers; inset index map of Nigeria (modified from Elueze et al., 2009).

Three major rivers (Imo, Qua-Iboe and Cross River) drain the geologic units of the hinterlands alongside their lesser tributaries of other rivers and streams.

Morphologically the area lies within the flat and low-lying terrain of the coastal lowland/Niger Delta region of southern Nigeria with elevations ranging from less than 10 m at the coastal fringe to about 80 m northwards.

The study area receives an average rainfall of about 254 mm annually within two distinct seasons; dry and wet seasons. Mean annual air temperature and relative humidity are 26.8 °C and 84.6 % respectively.^[16]

Methodology

A total of 52 stream sediment samples of about 1.0 kg were collected from the three major rivers and their tributaries within the study area. The samples were collected by hand held au-

ger and hand scooping at shallow depths of 0–30 cm, then stored in clean labelled polythene bags prior to treatment and analysis.

The sediments were air dried and disaggregated in a porcelain mortar using a rubber-end pestle. A nylon sieve was used to obtain the < 63 µm fraction of the samples for further chemical analysis. Element content analyses of replicate samples were carried out by Atomic Absorption Spectrophotometry (AAS) at the Activation Laboratories Ltd., Canada and locally in the quality control laboratory of the Aluminium Smelter Company, Nigeria. Results indicated good coincidence of data and reliability of analyses.

Results and discussion

Table 1 shows a statistical summary of the trace element concentrations of stream sediments sampled from the study area. The table

Table 1: Statistical summary of trace metal concentrations in sediments

River/ Element	w(Pb)/ (mg/kg)	w(Zn)/ (mg/kg)	w(Cd)/ (mg/kg)	w(Cr)/ (mg/kg)	w(As)/ (mg/kg)	w(Ni)/ (mg/kg)
CRS (<i>n</i> = 20)						
Range	27.40–86.40	88.30–117.85	1.20–2.60	0.10–1.70	1.60–2.20	1.20–14.60
Mean	56.51	108.77	1.85	0.97	2.05	7.03
S. D.	22.81	12.90	0.44	0.47	0.93	4.50
QIR (<i>n</i> = 16)						
Range	38.20–68.35	74.20–108.30	1.00–3.20	0.50–1.20	1.30–3.80	1.20–8.40
Mean	53.12	90.55	1.78	0.82	2.56	5.44
S. D.	10.11	11.87	0.72	0.22	0.85	2.15
IMR (<i>n</i> = 16)						
Range	9.00–29.00	31.00–306.00	1.00–1.80	10.00–67.00	30.02–22.00	6.00–28.00
Mean	18.81	65.90	1.40	40.06	6.88	15.73
S. D.	14.14	194.45	0.57	40.31	5.66	15.56
Bight of Bonny	16.41 (7.20–45.5)	647.6 (180–1410)	0.71 (0.30–1.60)	16.71 (6.40–46.10)	–	–
Calabar River	(0.60–30.0)	(0.80–27.0)	–	(0.60–3.30)	–	(1.20–22.50)
Gulf of California	17	88	3	44	7	38
Average shale	20	95	1	90	10	68

CRS – Cross River sediments
QIR – Qua Iboe River sediments
IMR – Imo River sediments

Bight of Bonny^[17]
Calabar River^[4]
Gulf of California^[18]

Average shale^[19]
* values in parentheses indicate ranges
S. D. – Standard deviation

also shows global averages as well as data of studied sediments of similar provenance as a means of comparison.

The trend of dominance of the trace elements for the Cross River and Qua Iboe River sediments was $Zn > Pb > Ni > As > Cd > Cr$ while for Imo River the trend was $Zn > Cr > Pb > Ni > As > Cd$.

Lead (Pb), zinc (Zn) and cadmium (Cd) showed highest mean values from the Cross River, followed by Qua-Iboe and least values in Imo River sediments. On the other hand chromium (Cr), arsenic (As) and nickel (Ni) had highest mean values on the Imo River sediments and lesser in the other two rivers. Mean variances of data from the three rivers were assessed using t-test. At 95 % confidence level values are: CRS/QIR (0.012), CRS/IMR (0.036) and QIR/IMR (0.047). These indicate no significance of variance of data between the rivers. Higher values of Pb, Zn and Cd in the Cross River can be attributed to the catchment of the river. This is mainly the Precambrian basement dominated by ultra-mafic and mafic rock suites that are hosts to most trace and rare metals species as revealed from hydrogeochemical modelling^[10]. Economic activities of mining and quarrying within the basement complex are also responsible for disaggregation and mobilization of sediments with species of these metals. Cross River and Qua Iboe rivers drain most of the urbanized and industrial settlements within the study area. These areas have the presence of large and small scale processing and production outfits, automobile repair and service shops and wide variety of artisanal industries, which may serve as sources of trace metal release from their effluents into the environment. Agriculture is the main occupation of the inhabitants of the study area and possibly past practice resulting in erosion and deposition of sediments within stream channels have affected and may continue to influence stream sediment geochemistry.

Higher Cr, As and Ni concentrations in the Imo River are attributable to the shale dominated sedimentary geology of the lower Benue trough (Anambra basin).

Mean values of heavy metals for sediments from the entire study area were; Pb (34.30 mg/kg), Zn

(80.00 mg/kg), Cd (1.55 mg/kg), Cr (23.10 mg/kg), As (3.90 mg/kg) and Ni (11.60 mg/kg).

Observation reveals the heavy metals to be within ranges and in proximity to levels of sediments of similar provenance and global averages. The values are close to background and below levels that can affect the quality of life of marine biota.^[3]

Factor analysis

Correlation and factor analyses were executed on the heavy metal concentration of sediments in order to identify important and significant inter-relations. The extraction method for factor analysis was based on the maximum likelihood factors. Correlation matrix (Table 2) shows that there exists a strong positive correlation between Cr and Ni (0.86). A moderate negative correlation is seen between Cr and Pb (-0.66). Correlations among all other elements are generally weak ($< \pm 0.50$). Variations in geochemical mobilities of the metals result in a non-uniform distribution pattern with a cumulative distribution function of 0.006.

The raw and unrotated data was subjected to factor analysis (Table 3) and this extracted three factors accounting for over 82 % of total data variance. Cluster of loadings shows that Pb (0.59), Cr (0.93) and Ni (0.93) for factor 1 and Zn (0.67), Cd (0.67) and As (0.72) for factor 2 determines the oblique factors for hierarchical analysis. Only factor loadings with scores greater than ± 0.60 were considered significant and are marked in the factor table.

Factor 1 (Pb, Zn and Cd) extracted about 49 % of total data variance. The loadings reflect signatures of sediments derived from the weathering of sulphide lode deposits found within the lower Benue trough. There is a reported occurrence of galena (PbS) and sphalerite (ZnS) in the Abakaliki area of the lower Benue trough and this area forms part of the drainage basin of the eastern Niger Delta.^[20, 5]

Factor 2 (Cr and Ni) accounts for about 20 % of total data variance and represents inputs of sediments of ultra-mafic origin. This loading can be associated with lineament zones (faults and joints) which may contain sheared ultra-mafic rocks. Cr and Ni coincidence suggest association with meta-basaltic rocks (amphibolites),^[21] and these are common within the adjoining base-

ment complex. Effects of acidic rain water leaching altered rocks of the basement complex and Cretaceous rocks of the Calabar Flank can also be adjudged.^[22] Sandstone has been shown to be a major source of trace elements^[3], thus supporting the role of the Cretaceous Awi sandstones of the Calabar Flank.^[5]

Factor 3 (As), accounts for about 12.5 % of total data variance. This factor suggests litho-geochemical input representative of weathering and mobility of sediments from arsenic or related mineralisation. Cretaceous sediments as well as the poly-metallic sulphide lodes of the lower Benue trough have been reported of Mo-As associations.^[23]

Table 2: Correlation matrix for heavy metals

	Pb	Zn	Cd	Cr	As	Ni
Pb	1					
Zn	0.29	1				
Cd	0.38	0.37	1			
Cr	-0.66	-0.45	-0.38	1		
As	-0.24	-0.23	-0.25	0.22	1	
Ni	-0.33	-0.14	-0.20	0.86	0.03	1

Table 3: Factor loading for sampled sediments

Parameter	Factor 1	Factor 2	Factor 3
Pb	0.708	-0.216	0.034
Zn	0.736	0.285	0.510
Cd	0.688	0.540	0.203
Cr	0.563	0.649	0.421
As	0.535	0.533	0.606
Ni	0.411	0.837	0.116
Eigen value	2.959	1.213	0.753
Total variance (%)	49.311	20.226	12.543
Eigen value cumul.	2.959	4.172	4.925
Cumul. variance (%)	49.311	69.537	82.081

Conclusion

This study has provided an important baseline geochemical data for the eastern sector of the Niger Delta basin. The heavy metals are generally at levels within or in proximity to global

background levels and sediments of similar provenance. The data indicates that regional and local geology are the most important factors controlling heavy metal geochemistry. Possibly localized anthropogenic activities may affect stream sediment geochemistry. Statistical analysis reveals interrelations between metals as indicated by factor loadings to be controlled by three dominant factors of geogenic origin.

References

- [1] Donazzolo, R., Merlin, O. H., Vittur, L. M., Orio, A. O., Pavoni, B., Perin, G., Rabitti, S. (1981): Heavy metal contamination in surface sediments from Gulf of Venice, Italy. *Marine Pollution Bulletin*, vol. 12, no. 12, pp. 417–425.
- [2] Patel, B., Bangera, V. S., Balani, M. C. (1985): Heavy metals in Bombay Harbour area. *Marine Pollution Bulletin*, vol. 16, no. 1, pp. 22–28.
- [3] Preda, M., Cox, M. E. (1999): Trace metals in acid sediments and waters, Pimpama catchment, south-east Queensland, Australia. *Environmental Geology*, vol. 40, no. 6, pp. 755–768.
- [4] Akpan, E. R., Ekpe, U. J., Ibok, U. J. (2002): Heavy metal trends in the Calabar River, Nigeria. *Environmental Geology*, vol. 42, pp. 47–51.
- [5] Elueze, A. A., Ekwere, A. S., Nton, M. E. (2009): Geoenvironmental assessment of the environs of the Aluminium Smelting Company in Ikot Abasi, south-eastern Nigeria. *Journal of Geology and Mining*, vol. 45, no. 2, pp. 115–128.
- [6] Chester, R., Stoner, J. H. (1975): Trace elements from lower Severn Estuary and Bristol Channel. *Marine Pollution Bulletin*, vol. 6, no. 6, pp. 92–95.
- [7] Horowitz, A. J. (1991): *A primer on sediment-trace element chemistry*. Lewis Publishers, Chelsea, Michigan, p. 136.
- [8] Taylor, J. R., Weaver, T. R., McPhail, D. C., Murphy, N. C. (1996): *Characterization and impact assessment of mine tailings in the King River System and delta, Western Tasmania*. Final Rept: Project No. 5 Mt. Lyell Remediation Res. and Demonst. Program.
- [9] Edet, A. E., Merkel, B. J., Offiong, O. E. (2004): Contamination risk assessment of fresh groundwater using the distribution and chemical speciation of some potentially toxic elements in Calabar (southern Nigeria). *Environmental Geology*, vol. 45, pp. 1025–1035.

- [10] Ekwere, A. S. (2010): *Hydrogeological and Hydrogeochemical Framework of the Oban Massif, south-eastern Nigeria*. Ph.D. Thesis, Dept. of Geology, University of Calabar, Calabar, Nigeria.
- [11] Garizi, A. Z., Sheikh, V., Sadodin, A. (2011): Assessment of seasonal variations of chemical characteristics in surface water using multivariate statistical methods. *International Journal of Environmental Science and Technology*, vol. 8, no. 3, pp. 58–592.
- [12] Short, K. C., Stauble, A. J. (1967): Outline of geology of Niger Delta. *AAPG Bulletin*, vol. 52, pp. 761–779.
- [13] Ekwueme, B. N. (2003): *The Precambrian geology and evolution of the Southeastern Nigerian basement complex*. University of Calabar Press, p. 135.
- [14] Reijers, T. J. A. (1996): Selected Chapters on Geology, Sedimentary Geology and Sequence Stratigraphy and three case studies and field guide. *SPDC Publications*, Warri, Nigeria, pp. 197.
- [15] Zaborsky, P. M. (1998): A review of the Cretaceous system in Nigeria. *African Geosciences Review*, vol. 5, pp. 385–483.
- [16] Edet, A, Worden, R. H. (2009): Monitoring of the physical parameters and evaluation of the chemical composition of river and groundwater in Calabar (south-eastern Nigeria). *Environ. Monit. Assess.*, vol. 157, pp. 243–258.
- [17] Ntekim, E. E. U., Ekwere, S. J., Okon, G. A. E. (1992): Trace metal distribution in sediments of the Bight of Bonny, south-eastern Nigeria. *Tropical Journal of Applied Sciences*, vol. 2, pp. 8–13.
- [18] Brumsack, H. J. (1986): The inorganic geochemistry of Cretaceous black shales in comparison to modern upwelling sediments from the Gulf of California. *Geological Society Special Publication*, no. 21, pp. 447–462.
- [19] Wedepohl, K. H. (1971): *Environmental influences on chemical composition of shales and clays*, in Ahrens. L. H., Press, F., Runcom, S. K., and Urey, H. C., eds., *Physics and Chemistry of the Earth*, vol. 8, Oxford, Pergamon Press, pp. 305–335.
- [20] Ekwere, A. S. (2004): *Geoenvironmental assessment of environs of the aluminium smelting company in Ikot Abasi area, south-eastern, Nigeria*. M. Sc dissertation, Department of Geology, University of Ibadan, Nigeria, p. 69.
- [21] Coker, M. D., (1995): *Geochemistry and hydrochemistry of the Oconee River Basin*. Proceedings of the 1995 Georgia Water Resource Conference, University of Georgia, Athens, Georgia, pp. 67–70.
- [22] Edet, A. E., Merkel, B. J., & Offiong, O. E., (2003): Trace element hydrochemical assessment of the Calabar Coastal Plain Aquifer, SE Nigeria using statistical methods. *Environmental Geology*, vol. 44, pp. 137–149.
- [23] Ekwere, A. S. and Elueze, A. A., (2012): Trace element assessment of stream sediments around the Aluminium Smelting Company in Ikot Abasi, south-eastern Nigeria. *Res. Jour. of Appl. Sci. Eng. & Tech.*, vol. 4, no. 4, pp. 256–261.