Heavy Metal Assessment of Groundwaters in the Vicinities of Dumpsites in Calabar Metropolis, South-Eastern Nigeria

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Abstract: Assessment of heavy metal contents in groundwater in vicinities of dumpsites within the Calabar metropolis was carried out. The dumpsites included those located at Akai-Effa, Anantigha, Bogobiri, LEMNA road and Marina beach. The choice of dumpsites was guided by magnitude of operation, history and longevity as related to possible metal speciation, leachate fate and disperssivity. Studied heavy metals included; Fe, Mn, Cu, Zn, Pb, Cd, Cr, Ni, Co and As. Results and interpretation revealed generally the highest concentration of selected metals to be in the vicinities of the Akai-Effa dumpsite (an abandoned and reclaimed automobile repair and scrap metal dumpsite with a long history of operation). This was followed by the Bogobiri dumpsite with a relatively shorter period of operation but a history of frequent incineration of refuse. Hydrochemical modelling indicated the aqueous species of metals to be predominantly free mobile ions, oxides and hydroxides. Other multi-element complexes were also identified at varying degrees of dominance and these were largely hydrated arsenates. Metal speciation in groundwater was adjudged to be controlled by dumpsites longevity, refuse type and associated activities. Current levels and speciation trend create a need for temporal and spatial monitoring for possible hazard prognosis and human health concerns.

Keywords: Calabar, Dumpsite, Heavy Metal, Nigeria, Speciation

1. Introduction

The impacts of wastes generation, disposal and management strategies in relation to human health and the geo-environment has been a major concern in most parts of the world in recent times. Most affected within the geo-system are soils, surface and groundwater systems with attendant effect on plant, animal and human populations. These solid wastes especially industrial and municipal solid wastes "MSW" have been shown to be major sources of environmental pollution through the introduction of chemical components at levels above the environmental threshold. The magnitude of pollution is however attributed to several factors such as catchment geology and mineralogy, biological and biogeochemical cycling, soil physicochemical conditions and the series of reactive transport processes of both surface and groundwaters.

Asides natural processes, virtually all human activities also have the potential to contribute and produce heavy metals as side effects. This remains a major concern as heavy metal contents associated with these wastes may adversely affect plant growth, soil organisms, water quality and consequently animal and human health [1], [2] and [3]. This has been a major issue especially in developing communities where optimum waste disposal technologies are scarce or completely absent.

This current research which is a pioneer work in the study area, focuses on the concentration levels of some heavy metals; Fe, Mn, Pb, Cu, Zn, Cd, Cr, Co, As and Ni in groundwaters in the vicinities of dumpsites within the study area. An attempt is also made to ascertain the saturation levels, speciation and availabilities of the mineral species of the heavy metals in the groundwaters.

Description of the Study Area

The study area Calabar is one of the fastest growing socio-economic hubs south of the River Niger on the western coast of Africa (Fig. 1). This has been occasioned by the thriving tourism potentials and a fast developing sea port in the area. Economic activities are at their climax currently, as compared with the last few decades. Increased industrial population, a boom in the hospitality sector and the sprouting of other numerous subsidiary commercial ventures has led to

increased generation of industrial and municipal waste as well as several environmentally non-friendly activities.
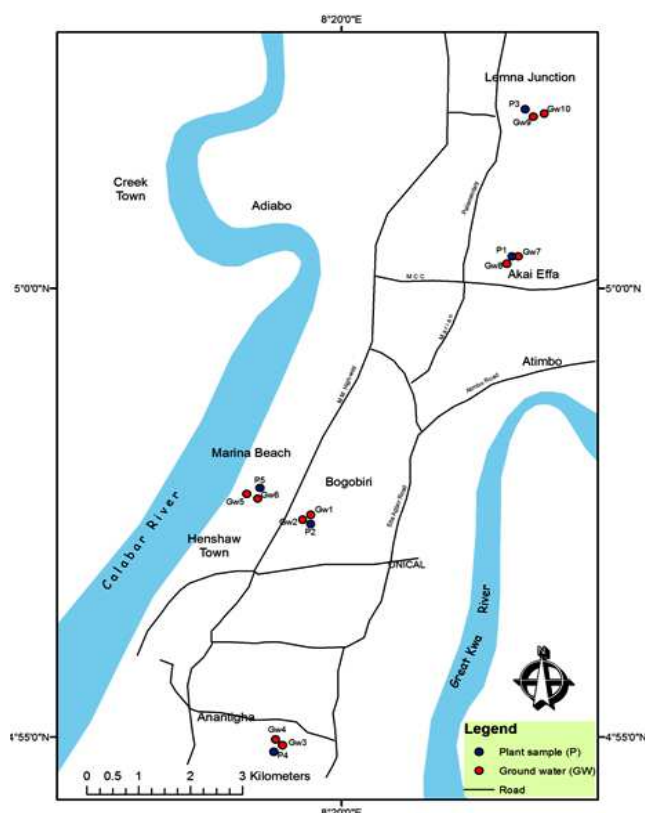

Fig. 1. Map of study area showing sample locations.

The study area comprises two administrative political units; Calabar Municipality and Calabar-South Local Council making up the larger Calabar Metropolis. Geographically the area is delimited by latitudes 4° 15 - 5° 15 North and longitudes 8° 15 - 8° 25 East (Fig. 1). Annual rainfall records indicates an average of about 254mm within two distinct seasons; the wet and dry seasons. Mean annual temperature and relative humidity are 26.8° C and 84.6% respectively. Geology of the area is built on the Tertiary - Quaternary sediments of the Niger Delta basin [4]. This basin consists of alternating sequences of gravels, sands, silts, clays and alluviums which are dominantly derived from the adjoining Precambrian basement (Oban Massif) complex and Cretaceous rocks (Calabar Flank). The basement complex is made up of gneisses, granites, schists, pegmatites and host of ultra-mafic suites [5], while Calabar Flank is characterised by units of limestone, sandstones, shales and marls [6]. Topographic variations extend from less than 10m in the south to about 80m in the north of the study area.

Hydrogeological investigations shows that three aquiferous units characterise the sub-surface of the study area extending from a depth of about 80 - 180 m below surface. The southern fringe of the study area is composed of two relatively shallow water-bearing horizons, spanning a depth of 80 – 120m.

Within the north-central portion of Calabar metropolis, three aquiferous units are recognised with a depth range of 120 – 180m. The first aquiferous unit generally lies at a depth of ± 120m and is underlain by a structural impedance of shale impervious unit. The two lower aquiferous units extend below from about 120 – 180m and most functional wells and boreholes within this area are sourced from these two lower units.

Further to the northern axis of the study area the impervious shale unit thins out towards the near-surface and two aquiferous units are recognized below this at depths of about 150 – 180m.

2. Methodology

Four groundwater samples were collected from the vicinities of five municipal solid waste dumpsites in Calabar. These dumpsites are spread across the study area and are either operational or abandoned with varying longevity of operational histories. The dumpsite environs are generally enveloped by residential and commercial buildings and estates. Table 1 shows the dumpsites, their locations, operational history and major refuse types.

Table 1. Sampling locations and associated refuse types.

Dumpsites	Coordinates	Status/history	Refuse type
Bogobiri	N0457 29.6 E0819 43.3	Operational for over fifteen years, frequent open incineration of refuse	Municipal/ domestic wastes. Scrap metals and automobile wastes.
LEMNA road	N05 0155.8 E0822 03.0	Operational for about ten years	General municipal waste (biodegradable to non-biodegradable) largest dumpsite.
Anatigha	N0454.54.4 E0819.23.3	Operational for over fifteen years	Municipal wastes, slaughter effluents etc.
Marina	N0457.42.4 E0819.00.7	Operational for over twenty years	Municipal wastes, shipyard sludge, scrap metals etc.
Akai-Effa	N0500.22.2 E0821.50.7	Abandoned and reclaimed. Operated for over fifteen years	Auto-metal scraps, automobile effluents, scrap metals, domestic waste etc.

Two water samples were collected from each sampling location in 75cl polyethylene bottles which were doubly rinsed with aliquots of the water prior to sample collection. Standard field precautions were ensured to avoid sample

contamination and in-situ parameters (temperature and pH) were measured using a multi-parameter water quality probe meter: model PHT-027. The samples from each location were preserved by acidifying to pH ca.2 with 0.5ml of concentrated HNO_3 acid prior to trace metals analyses. Samples were prepared according to standard laboratory techniques and heavy metal concentrations were by Atomic Absorption Spectrophotometry with AAS model: UNICAM 939. Instrumental analyse were carried out in the quality control laboratory of the Aluminium Smelter Company of Nigeria (ALSCON), Ikot Abasi, Nigeria.

3. Results and Discussion

Statistical summary of heavy metal contents in the sampled groundwaters are as presented in Table 2. The table (2) shows the range and mean values of heavy metal concentrations in comparison with acceptable limits for potable water. Initial assessment reveals mean heavy metals dominance in the order Mn>Fe>Cu>Zn>Cd>Cr>Ni>Pb>Co> As across all sampling locations.

Table 2. Statistical summary of results of analysed groundwaters; values in mg/l except pH.

Parameter		Anantigha (n=4)	Bogobiri (n=4)	LEMNA (n=4)	Akai-Effa (n=4)	Marina (n=4)	WHO (2001)
Fe	Mean	0.134	0.044	0.463	0.698	0.121	0.3
	Range	0.088 – 0.170	0.034 – 0.049	0.398 – 0.512	0.694 -0.712	0.092 – 0.146	
Mn	Mean	0.573	0.702	0.006	1.524	0.440	0.5
	Range	0.434 – 0.682	0.684 – 0.721	0.005 – 0.007	1.426 – 1.591	0.434 – 0.455	
Pb	Mean	0.045	0.032	0.029	0.033	0.023	0.05
	Range	0.008 – 0.080	0.028 – 0.034	0.027 – 0.030	0.030 – 0.034	0.018 – 0.026	
Zn	Mean	0.119	0.111	0.073	0.322	0.084	5.0
	Range	0.114 – 0.124	0.104 – 0.118	0.062 – 0.080	0.314 – 0.339	0.076 – 0.092	
Cu	Mean	0.214	0.127	0.248	0.267	0.144	2.0
	Range	0.196 – 0.229	0.094 – 0.167	0.196 – 0.297	0.218 – 0.312	0.138 – 0.152	
Cd	Mean	0.140	0.112	0.068	0.299	0.067	0.005
	Range	0.108 – 0.170	0.108 – 0.115	0.065 – 0.072	0.292 – 0.304	0.054 – 0.082	
Cr	Mean	0.021	0.050	0.050	0.065	0.010	0.05
	Range	0.018 – 0.024	0.042 – 0.054	0.044 – 0.060	0.054 – 0.072	0.009 – 0.012	
Co	Mean	0.014	0.005	0.005	0.013	0.008	
	Range	0.008 – 0.018	0.004 – 0.006	0.004 – 0.005	0.009 – 0.016	0.007 – 0.009	
As	Mean	0.001	0.011	0.001	0.012	0.002	0.01
	Range	0.001 – 0.002	0.003 – 0.020	0.001 – 0.002	0.004 – 0.020	0.001 – 0.003	
Ni	Mean	0.044	0.060	0.005	0.072	0.007	0.02
	Range	0.036 – 0.050	0.048 – 0.068	0.004 – 0.006	0.066 – 0.084	0.006 – 0.008	
pH	Mean	5.90	5.75	6.45	6.10	7.50	6.5-8.5

Iron (Fe) concentration values ranged from 0.034 – 0.712mg/l with a mean value of 0.292mg/l across the sampling locations. Higher mean values of 0.463mg/l and 0.698mg/l were recorded at LEMNA road and Akai-Effa dumpsites respectively. These values are above the acceptable limits of 0.3mg/l of [7] standard. Manganese (Mn) ranged from 0.005 – 1.591mg/l with a mean value of 0.649mg/l. Higher mean values were recorded at Bogobiri and Akai-Effa dumpsites. Concentrations of Pb ranged from 0.008 – 0.080mg/l and a mean value of 0.032mg/l. Anantigha dumpsite had the highest mean for Pb concentration (0.045mg/l). Zinc (Zn) ranged from 0.062 – 0.339mg/l with a mean of 0.142mg/l for the sampled waters. Highest mean concentration was recorded around the Akai-Effa dumpsite. Cu, Cd, Cr and Co had mean values of 0.2, 0.137, 0.039 and 0.009mg/l respectively. These set of elements had their highest mean values reported at the Akai-Effa dumpsite except Co which had its highest mean concentration at Anantigha dumpsite. Arsenic (As) and nickel (Ni) had ranges of 0.001 – 0.020mg/l and 0.004 – 0.084mg/l and mean values of 0.005 and 0.038mg/l respectively across the sampled locations.

From assessment, it was noticed that total heavy metal weight concentration across the dumpsites is in the order; Akai-Effa > Bogobiri > LEMNA road > Anantigha > Marina. The Akai-Effa dumpsite shows the highest concentration of most of the heavy metals (Fe, Mn, Cu, Zn, Cd, Cr, As and Ni. This abandoned dumpsite which has been reclaimed served as a major automobile repair estate in the past. The dumping of automobile-metal scrap parts, automobile discharges and effluents is viewed as a contributing source of metals in the sampled waters within the location. Most of the metal concentrations within this location are above the WHO (2001) acceptable limits. Fe was higher by 233%, Mn by 305%, Cd by 5,980%, Cr by 130% and Ni by 360%. However inputs of geogenic sourcing from aquifer matrix and sediments are not excluded as a contributing factor to metal contents. The high concentration of cadmium raises some concern as these metals is readily taken up by leafy vegetables [8] and can be injurious to humans at levels beyond bio-assimilation.

Next to the Akai-Effa groundwater metal concentrations is the Bogobiri dumpsite. This dumpsite has a history of incessant incineration of waste. During combustion of waste, volume reduction may be up to 85%, thus increasing the concentrations of the metals originally in the waste.

According to [9], trace elements are mainly enriched in fine-grained fractions of ashes. The resulting ashes may be readily dissolved and associated metals make entrant into the groundwater system through recharge zones, increasing the background levels.

Total heavy metals concentrations are comparatively less in the other three locations and generally at low levels. Metal concentrations appear to be controlled by dumpsite longevity, waste types and other associated activities.

Metal Speciation Trend

Assessment of mineral species, saturation levels and availability was carried out through geochemical modelling using the visual MINTEQ computer program. Predicted species of metals and their percentage dominance for the sampled waters are presented in Table 3. Assessment shows that iron (Fe) occurred as multiple species which included; Fe $(OH)_{2\ (aq)}$, Fe^{2+}, Fe $(OH)^+$ and Fe $(OH)^{3-}$. Fe^{2+} was predicted to be the predominant species (88%). The probable sources of iron are minerals such as chlorite, siderite, pyrite and goethite. These mineral species are common minerals in the rocks that provide sediments to the study area [10]. However these species are unlikely to contribute significantly soluble ion concentrations, but water chemistry is predicted to be strongly influenced by other assemblages [11].

Manganese existed as $Mn(OH)_4^{2-}$ (pyrochroite), Mn^{2+}, $Mn_2(OH)_3^+$, $Mn_2(OH)^{3+}$ and $Mn(OH)$ with Mn^{2+} being predicted as the predominant species (82%). Manganese may be hosted naturally by siderite, rhodochrosite and from trace concentrations in pyrite and these mineral species are recognised in the rocks that provide sediments to the study area [10]. Relatively high aqueous concentrations of Mn are believed to be primarily related to the low pH of the groundwaters.

Lead species were $Pb(OH)_{2(aq)}$,(litharge) $Pb(OH)_3^-$ (massicot), Pb^{2+}, $Pb_2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$ and $Pb(OH)^+$. The predicted predominant species were Pb^{2+} and $Pb(OH)^+$ making up about 89% of total lead in sampled waters.

The predicted species of copper were $Cu(OH)_{2(aq)}$ (tenorite), $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, Cu^{2+}, $Cu_2(OH)_4^{2-}$ and $Cu(OH)^+$. Speciation of copper is known to be controlled pH and redox (Taylor et al., 1996). Despite the many possible aqueous species of copper, the predicted predominant one was Cu^{2+} with about 87% dominance. Natural sources of aqueous copper may be from detrital chalcopyrite associated with sediments within the catchment geology.

Multiple aqueous species of zinc predicted included; $Zn(OH)_{2(aq)}$, Zn_2OH^{3+} (zincite), $Zn(OH)_3^-$, $ZnOH^+$, $Zn(OH)_4^{2-}$ and Zn^{2+}. In all the sampled water Zn^{2+} was predicted to be the predominant species constituting about 85% of total zinc concentration.

Cadmium (Cd) species included; $Cd(OH)_{2(aq)}$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, Cd^{2+}, Cd_2OH^{3+} and $CdOH^+$ with their speciation being pH dependent. Cd^{2+} ion was predicted to be the predominant species (79%) and followed by $Cd_2 (OH)^{-3}$ (11%) across all sampled waters

Aqueous species of cobalt (Co) were; $Co(OH)_{2(aq)}$, $Co(OH)_3^-$, Co^{2+}, $Co_4(OH)_4^{4+}$, $Co(OH)^+$ and that of chromium (Cr); Cr^{2+} and $Cr(OH)^+$. Their predominant species were Co^{2+} (90%) and Cr^{2+} (82%) respectively.

Arsenic (As) occurred mainly as oxidised species; As_2O_5, $H_2AsO_4^-$, H_3AsO_4 and $HAsO_4^{2-}$. The predicted predominant species was $H_2AsO_4^-$ with about 78% dominance of total arsenic concentration.

Predicted species of nickel (Ni) included; $Ni(OH)_{2(aq)}$, $Ni(OH)_3^-$, Ni^{2+} and $NiOH^+$. The predominant species was Ni^{2+} with an 82% dominance of total concentration.

Table 3. *Major chemical species of trace elements.*

Element	Mass fraction, w%	Dominant species
As	78.26	$H_2 AsO_4^-$
	9.19	$H_3 AsO_4$
	1.53	$HAsO_4^{-2}$
Cd	78.92	Cd^{+2}
	11.08	$Cd_2 (OH)^{-3}$
Co	79.94	Co^{+2}
Cr	81.64	Cr^{+2}
	8.38	$Cr(OH^+)$
Cu	87.48	Cu^{+2}
	0.68	$Cu_2 OH^{+3}$
	1.72	$Cu_2 (OH)_2^{+2}$
Fe	87.92	Fe^{+2}
	9.68	$Fe(OH)_3$
Mn	82.46	Mn^{+2}
Ni	82.20	Ni^{+2}
Pb	79.93	Pb^{+2}
	8.69	$Pb(OH)^+$
Zn	84.97	Zn^{+2}

Several metallic complex species were also predicted from the modelling output. These included mostly hydrated and non-hydrated arsenates of metals; $Cu_3(AsO_4)_2:2H_2O$, $Mn_3(AsO_4)2:8H_2O$, $Ni_3(AsO_4)_2:8H_2O$, $Pb_3(AsO_4)$, $Zn_3(AsO_4)_2:2.5H_2O$.

The saturation states of the predicted mineral species were calculated as part of the output from the modelling program. This indicates mineral species that might be dissolving or precipitating into or from the water, thus controlling its composition. It is pertinent to note that the results of these calculations are based on an equilibrium model and as such are only an indication, as kinetic factors may inhibit approach to equilibrium.

Assessment of saturation indices of the various aqueous single and multi-metallic species of metals in the sampled waters shows concentrations to be generally at under-saturation levels. However tenorite $(Cu.H^+(H_2O)$ and hydrated copper-arsenate $(Cu_3(AsO_4)_2:2H_2O)$ showed oversaturation with indices of 0.799 and 8.50 respectively. Signatures of the oversaturated copper-arsenate species was recorded from the modelling of waters from the Akai-Effa dumpsite.

According to [12] free metal species are the most bio-available and toxic form of trace elements in natural waters. The predominance of aqueous free metallic species of trace elements (Fe, Mn, Pb, Cu, Zn, Cd, Cr, Ni, Co and As) under the prevalent pH conditions poses a concern on their

bioavailability and toxicity. However their relatively low concentrations and the presence of limiting mineral phases [13] may reduce the risk to water potability.

4. Conclusion

Current studies have shown the importance of heavy metal contamination in components of the geo-system. The approach to understanding their effects is becoming more systematic [14]. Such studies provide requisite information for natural resource and environmental management at municipal, states and federal government levels.

This research has assessed the impact of dumpsites and operations on groundwater quality in proximity. Data from analysis indicates availability of selected heavy metal to be controlled by refuse type, longevity of dumpsites and associated operation activities. Highest concentrations of analysed metals are recorded in groundwater around Akai-Effa (an abandoned automobile and scrap metal dumpsite of prolonged operational history). Groundwater around Bogobiri dumpsite also had elevated metal contents reckoned to availability induced by ash from incineration of refuse. Hydrochemical modelling reveals aqueous species of heavy metals to be dominantly free mobile ions, oxides and hydroxides. Other aqueous complexes include hydrated arsenates.

Results and indications suggest a need for establishing a monitoring program for heavy metals in groundwater and other geologic components around the dumpsites. This will serve to curb the potential risk on the environment and human health from potentially toxic metals speciation.

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