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METAL CONCENTRATIONS IN THE WATER AND BEDROCK OF OGUN RIVER, NIGERIA
ความเข้มข้นของโลหะในน้ำและหินชั้นล่างของแม่น้ำโอกัน ประเทศไนจีเรีย

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Abstract

Parts of the Ogun River basin namely Mokoloki, Brewery, Akomoje, Akin Olugbade, Lafenwa, Oyan, Arakanga, and Kara were surveyed to determine the effects of bedrock metals on the water quality of the river. Physicochemical analyses were done on the bedrock and water samples obtained while bedrock trace metal analyses were determined using the Inductively Coupled Plasma Optical Emission Spectrometry. Water trace metal analyses were carried out by Atomic Absorption Spectrometry (AAS). Data obtained were subjected to the Duncan Multiple Range Test (DMRT). Results obtained showed that Cadmium (Cd) (0.425-1.990 ppm for bedrock samples and 0.005-0.011 mg L^{-1} for water samples) exceeded internationally acceptable limits. Also, Lead (Pb) value for water samples (0.005 - 0.217 mg L^{-1} was reported to be higher than the internationally acceptable limits. Other values obtained for bedrock, and water samples (trace metal analysis), were lower than the internationally acceptable limits.

Keywords: metal concentration, bedrock, water quality, Ogun River

บทคัดย่อ

ทำการสำรวจลุ่มน้ำโอกันซึ่งโมโกโลกิ บริวเวอรี อโคโมจิ อคิน โอลักเบด ลาเฟนวา โอยัน อาราคันกา และคารา เพื่อหาผลของโลหะในหินพื้นล่างที่มีต่อคุณภาพน้ำในแม่น้ำ วิเคราะห์ลักษณะทางฟิสิกส์เคมีของตัวอย่างหินพื้นล่างและน้ำ โลหะปริมาณน้อยในหินพื้นล่างวิเคราะห์โดยใช้เครื่อง Inductively coupled plasma optical emission spectrometry วิเคราะห์โลหะในน้ำโดยใช้เครื่อง atomic absorption ข้อมูลที่ได้ทดสอบด้วย Dulcan multiple range ผลการศึกษาพบว่าแคดเมียมในตัวอย่างหินพื้นล่าง (0.425-1.99 ppm) และในตัวอย่างน้ำ (0.005-0.217 มก./ล.) เกินขีดยอมรับได้ของระหว่างประเทศ ค่าตะกั่วในตัวอย่างน้ำ (0.005-0.217 มก./ล.) สูงกว่าขีดยอมรับได้ของระหว่างประเทศ ค่าอื่นๆ ที่ได้จากตัวอย่างหินพื้นล่างและตัวอย่างน้ำต่ำกว่าขีดยอมรับได้ของระหว่างประเทศ

คำสำคัญ: ความเข้มข้นของโลหะ, หินชั้นล่าง, คุณภาพน้ำ, แม่น้ำโอกัน

Introduction

Metals in bedrock are exposed to the environment via weathering as a result of some agents of erosion such as rainfall and

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wind. When this happens, they are washed into the water bodies where they increase the metal load or concentration. Most of these metals like Copper (Cu), Chromium (Cr), Zinc (Zn), Mercury (Hg) etc settle down on the sediment bed since sediment serves as an ultimate sink for heavy metals[1]. Bedrock weathering and tectonic activities have been the largest sources of trace metals entering surface waters. According to CCME [2] sediments play a major role in the transport and fate of pollutants. Toxic metals are either attached or adsorbed to sediments. Due to turbulence and resuspension, heavy metals are released into the water bodies thus causing increased metal concentration in water. The implication of this is that cost of water treatment increases and there is gradual decrease in aquatic population since some aquatic organisms are susceptible to elevated concentrations of certain metals in water.

Water is indeed life and thus the most important natural resource without which life would be non- existent. Availability of safe and reliable source of water is an essential prerequisite for sustained development. Its usage constitutes a major criterion towards sustainable growth and development of a region and its economy[3]. Water pollution is of grave consequence because both terrestrial and aquatic life can be poisoned; it may cause disease due to the presence of some hazardous substances, may distort the water quality, add odours and significantly, hinder economic activities.

Ayeni et al[4] stated that understanding and monitoring surface water quality of a region remains a better tool towards promoting sustainable development of water resources within the societal economic and conservational contextual need. They further emphasized that, of great importance is the assessment of the human activities that are capable of changing the quality of river water within an urban area. Though these trace elements are usually present in the environment, they are potentially extremely toxic and not only would they affect the biota at a water soluble concentration at less than 1 part per million (ppm), humans can be grossly affected. Larcoque and Rasmussen[5] stated that the geosphere (the soild earth) is the original source of all metals except those that enter the atmosphere from space in the form of meteorites and cosmic dust. They further stressed that the geosphere as well as the hydrosphere may constitute sinks for metals.

Materials and Experimental Methods

This study is therefore to determine the effects of bedrock metals on the water quality of the river.

Study Area: The Ogun-River, located in Ogun-State, South West of Nigeria lies between latitude 6°35' and 8°58' North with Longitude 2°40' and 4°10' East. It rises from Iganran Hills, east of Shaki, Oyo state, South West, Nigeria (latitude 07°40' N and Longitude 03°20' E)[6]. The entire river basin (Ogun River) occupies an area of approximately 23,700 km^2 [7].

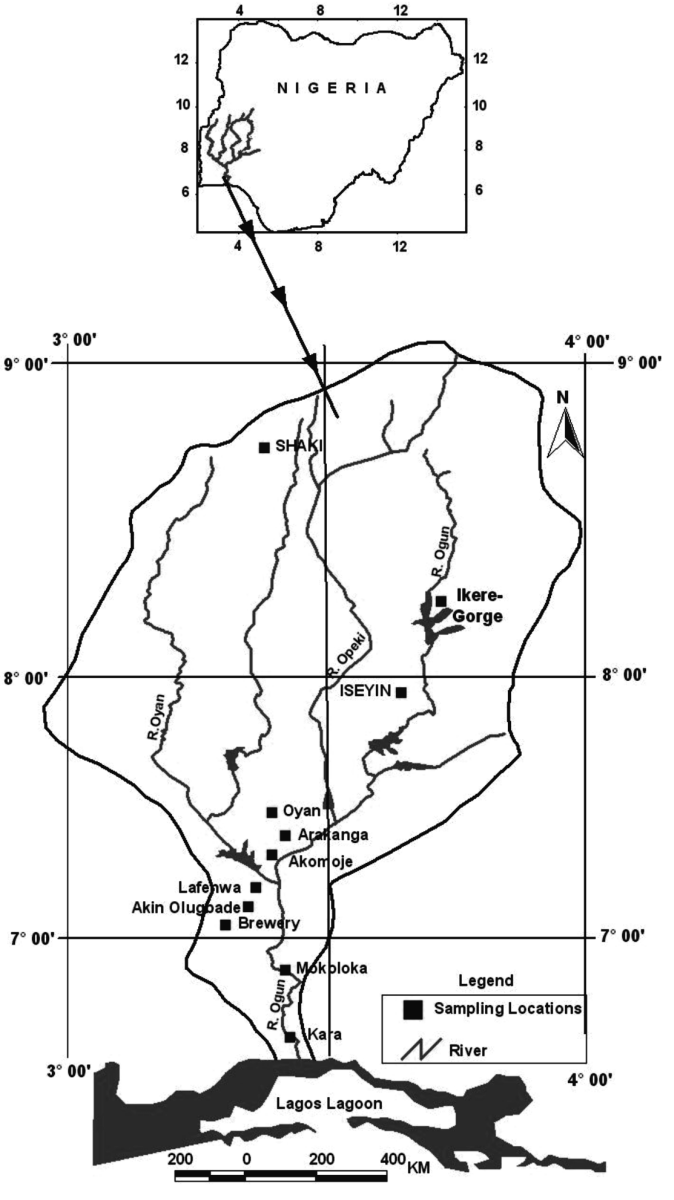

Figure 1 Location of the Ogun River

Sampling Area: Areas sampled along the Ogun-River course include; Mokoloki, Brewery, Akomoje, Akin-Olugbade, Lafenwa, Oyan, Arakanga and Kara were surveyed.

Bedrock samples were collected using hammer and chisel. The samples were then stored in a polythene bags and stored in a cooler from where they were transported to the laboratory for analysis. The bedrock samples were air dried to remove moisture after which they were pulverized and sieved using a 2mm sieve to obtain fine powder. The finer particles were stored in polythene sachets from where they were sent for trace metal analysis at Actlab, Canada using the Inductively Coupled Plasma Optical Emission Spectrometry. Water samples were collected in a 2 liter plastic can and stored in an ice chested cooler for onward transportation to the laboratory. Parameters like pH, temperature and conductivity were measured in-situ using Hanna Combo (HI 98129). Total solids for the water samples were determined using evaporation method while filtration method was used to obtain total dissolved solids. Total suspended solids were determined mathematically using the formula TSS = TS-TDS where TSS= Total Suspended Solids, TS=Total Solids and TDS= Total Dissolved Solids. Alkalinity of the water samples collected were determined using titration method. Trace metals such as Cu, Cd, Zn and Pb were determined using Atomic Absorption Spectrometry (AAS). The water samples were first digested using concentrated Hydrochloric acid after which they were transferred into 2ml screw capped plastic bottles for AAS analysis. A total of forty bedrock and forty water samples were collected from different sections of the Ogun River course between April and October, 2008

Results

From the water physicochemical analysis conducted, it was observed that the highest pH obtained at Mokoloki (8.83) while the lowest was at Brewery (7.50). Conductivity values ranged from 0.04-7.41 mS cm^{-1} while the highest value for total dissolved solids was obtained at Brewery with Mokoloki recording the lowest value for total dissolved solids. Alkalinity values ranged from 34.50 mg L^{-1} in Akin Olugbade to 89 mg L^{-1} at Oyan. More water hardness and Cl^- values were reported at Akin Olugbade than all the other locations sampled while NO_3^- values ranged from 5.05 mg L^{-1} to 16.59 mg L^{-1}. Trace metal values showed that Lafenwa had the highest Pb concentration of 0.217 mg L^{-1} while Arakanga Pb value was reported to be the lowest. Similarly, the highest Cd value was obtained from Lafenwa (0.010 mg L^{-1}).

Arakanga water Pb value was observed to be the lowest (0.005 mg L^{-1}). Zn was not detected in the water samples of Brewery and Lafenwa while the highest Zn concentrations were observed at Akin-Olugbade and Oyan respectively. Trace metal values obtained from Mokoloki were observed to be the highest for Silver (Ag), Cd, Manganese (Mn), Nickel (Ni), Pb, Zn, Arsenic (As), Beryllium (Be), Cr, Hg and Antimony (Sb) while Brewery bedrock value had the highest values for Cu, Aluminium (Al), Barium (Ba) and Scandium (Sc).

Discussion

Water pH values from Table 1 for all the areas sampled were alkaline. According to Hydrological Sciences[8], in a lake or pond, water pH is affected by its age and the chemicals discharged by communities and industries. Most lakes are basic (alkaline) when they are first formed and become more acidic with time due to the build-up of organic materials. As organic substances decay, carbon dioxide (CO_2) forms and combines with water to produce a weak acid, called "carbonic" acid. Large amounts of carbonic acid lower water's pH[8]. Since most fishes survive between pH 5.0-9.0 [8], the pH range of the locations samples along the Ogun River course (7.50 - 8.83) is considered to be tolerant for the growth and development of aquatic species.

The highest water conductivity of 0.36 mS cm^{-1} from this study as seen in Table 1 was obtained at Akin Olugbade. High conductivity is an indication that more dissolved substances are present in a particular location. Conductivity in water is affected by the presence of inorganic dissolved solids, such as chloride, nitrate, sulfate and phosphate anions (i.e., ions that carry a negative charge) or sodium, magnesium, calcium, iron and aluminum cations (i.e., ions that carry a positive charge). Some factors that affect conductivity in streams and rivers include temperature and the local geology of an area. The warmer the water, the higher the conductivity while streams that run through areas with granite bedrock tend to have lower conductivity because granite is composed of more inert materials that do not ionize, or dissolve into ionic compounds, when washed into the water. Streams that run through areas with clay soils tend to have higher conductivity because of the presence of materials that ionize when washed into the water.

Table 1 Physicochemical analysis of water samples from the study area

Location	Parameters									
	pH	Conductivity ($mS\ cm^{-1}$)	Temp (°C)	TS ($mg\ L^{-1}$)	TSS ($mg\ L^{-1}$)	TDS ($mg\ L^{-1}$)	Alkalinity ($mg\ L^{-1}$)	Hardness ($mg\ L^{-1}$)	Cl^- ($mg\ L^{-1}$)	NO_3^- ($mg\ L^{-1}$)
Mokoloki	8.83^{a}	0.09^{e}	30.25^{a}	1.12^{a}	1.10^{a}	0.02^{e}	14.50^{f}	29.00^{h}	18.00^{g}	5.05^{d}
Brewery	7.50^{bc}	0.22^{f}	29.00^{bc}	0.72^{d}	0.16^{e}	0.56^{a}	44.00^{c}	90.50^{b}	18.50^{fg}	5.18^{d}
Akomoje	8.22^{ab}	0.08^{f}	29.25^{b}	0.83^{c}	0.72^{e}	0.11^{d}	35.50^{e}	36.00^{g}	21.00^{e}	10.10^{b}
Akin-Olugbade	7.54^{bc}	0.36^{a}	26.25^{d}	0.24^{g}	0.15^{e}	0.09^{d}	34.50^{e}	98.00^{a}	45.50^{a}	16.59^{a}
Lafenwa	7.45^{bc}	0.14^{d}	29.00^{bc}	0.42^{f}	0.21^{d}	0.21^{c}	50.00^{d}	60.00^{e}	21.50^{cd}	5.19^{d}
Oyan	7.47^{bc}	0.30^{b}	29.00^{bc}	0.16^{h}	0.05^{f}	0.11^{d}	89.00^{a}	89.00^{c}	34.00^{b}	7.23^{c}
Arakanga	8.14^{ab}	0.09^{e}	30.50^{a}	1.00^{b}	0.96^{b}	0.04^{e}	45.00^{c}	45.00^{f}	22.00^{d}	7.22^{c}
Kara	7.84^{abc}	0.04^{f}	28.45^{c}	0.48^{e}	0.25^{c}	0.23^{b}	64.50^{b}	64.50^{d}	19.00^{f}	10.15^{b}

Note: TS = Total Solids, TSS = Total Suspended Solids, TDS = Total Dissolved Solids. Values with identical letters were not significantly different from each other at 95% confidence

All water Pb values obtained from the locations as seen in Table 2 were higher than the WHO standard[9] of 0.001 mg L^{-1}. This corroborates with earlier research results obtained by Jaji et al [6] and Asonye et al [10]. In humans, exposure to Pb can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in oxic biochemical effects in humans which in turn cause problems in synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joint and reproductive system, and acute or chronic damage to the nervous system.

All water Cd values as seen in Table 2 were higher than the WHO standard [9] of 0.003 mg L^{-1}. Various sources of Cd into the Ogun River include municipal dumping of Cd rich wastes into the river water as observed in Lafenwa area which had a Cd concentration as high as 0.01 mg L^{-1}.

Table 2 Trace metal contents in water samples from the study area

Location	Parameters (mg L^{-1})			
	Pb	Cu	Cd	Zn
Mokoloki	0.031 ^{f}	0.011 ^{d}	0.006 ^{d}	0.084 ^{b}
Brewery	0.096 ^{b}	0.012 ^{d}	0.005 ^{d}	0.000 ^{e}
Akomoje	0.052 ^{e}	0.011 ^{d}	0.011 ^{a}	0.018 ^{d}
Akin- Olugbade	0.071 ^{d}	0.087 ^{b}	0.009 ^{bc}	0.096 ^{a}
Lafenwa	0.217 ^{a}	0.032 ^{c}	0.010 ^{ab}	0.000 ^{e}
Oyan	0.076 ^{c}	0.006 ^{e}	0.008 ^{c}	0.096 ^{a}
Arakanga	0.005 ^{g}	0.018 ^{a}	0.005 ^{d}	0.060 ^{c}
Kara	0.052 ^{e}	0.115 ^{d}	0.009 ^{bc}	0.018 ^{d}

Note: Values with identical letters were not significantly different from each other at 95% confidence level when subjected to Duncan Multiple Range Test.

Cd bedrock values as seen in Table 3 were lower than the Abundant Element in Average Crustal Rock (AEACR) standard of 0.1ppm except that from Mokoloki (1.99 ppm). Long-term human exposure to Cd results in renal disfunction. High exposure could also lead to obstructive lung disease and can be linked with long cancer. Zn values from Mokoloki (454 ppm) and Brewery (136 ppm) in Table 3 were observed to be higher than the (AEACR) value of 80 ppm. This indicates that Zn is present in these areas at a high concentration. Although Zn is a very essential requirement for a healthy body, excess Zn can be harmful, and cause Zn toxicity. Excessive absorption of Zn can also suppress Cu and iron absorption. The free Zn ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. High As concentration (Table 3) was also observed at Mokoloki (34 ppm). This was seventeen times higher that the AEACR standard of 2 ppm. Chronic exposure to inorganic As may lead to hypertension, involuntary muscular dysfunction (including incontinence), diabetes, neuropathy, depression, obesity and any other condition related to the altered role of intercellular voltage-dependent potassium channels, including cutaneous hyperpigmentation. Be value from Mokoloki (5.6 ppm) as seen in Table 3 was also observed to be higher than the AEACR standard of 2.0 ppm. All Pb bedrock values from Table 3 were higher than the AEACR standard of 10.1 ppm.

Table 3 Trace metal content in bedrocks obtained from the study area. (ppm)

Parameters	Mokoloki	Brewery	Akomoje	Akin Olugbade	Lafenwa	Oyan	Arakanga	Kara
Ag	0.200^{a}	0.175^{ab}	0.185^{ab}	0.180^{ab}	0.170^{b}	0.185^{ab}	0.180^{ab}	0.170^{b}
Cd	1.990^{a}	0.675^{b}	0.475^{c}	0.470^{c}	0.425^{d}	0.470^{c}	0.480^{c}	0.465^{c}
Cu	5.00^{c}	38.0^{a}	2.00^{e}	3.00^{d}	2.00^{e}	7.00^{b}	7.00^{b}	5.00^{c}
Mn	326.00^{a}	271.00^{b}	17.00^{h}	25.00^{g}	217.00^{e}	225.00^{d}	231.00^{c}	51.50^{f}
Ni	69.00^{a}	35.00^{b}	0.94^{h}	1.00^{g}	5.00^{e}	16.00^{c}	7.00^{d}	3.00^{f}
Pb	9.750^{a}	1.930^{f}	6.000^{b}	1.970^{f}	4.000^{d}	5.000^{c}	6.000^{b}	3.000^{e}
Zn	454.0^{a}	136.00^{b}	5.00^{h}	8.00^{g}	75.00^{c}	61.00^{d}	25.00^{e}	61.00^{d}
Al	1.120^{b}	2.040^{a}	0.100^{d}	0.150^{d}	0.585^{c}	1.105^{b}	0.560^{c}	0.580^{c}
As	34.00^{a}	1.945^{b}	1.910^{c}	1.945^{b}	1.950^{b}	1.955^{b}	1.945^{b}	1.960^{b}
Ba	55.00^{e}	111.00^{a}	31.00^{g}	21.00^{h}	74.00^{d}	84.00^{c}	88.00^{b}	52.00^{f}
Be	5.600^{a}	0.475^{bc}	0.450^{d}	0.465^{bcd}	0.460^{cd}	0.475^{bc}	0.465^{bcd}	0.450^{d}
Cr	100.0^{a}	70.00^{b}	2.000^{l}	5.000^{f}	9.000^{e}	9.000^{e}	19.00^{d}	40.50^{c}
Ga	10.00^{b}	20.0^{a}	9.66^{de}	9.67^{de}	9.68^{e}	9.7^{cd}	9.78^{c}	9.85^{c}
Hg	2.000^{a}	0.950^{d}	0.960^{bcd}	0.945^{d}	0.945^{d}	0.965^{bcd}	0.980^{b}	0.955^{cd}
Sb	11.00^{a}	2.000^{b}	1.970^{cd}	1.980^{bc}	1.950^{cd}	1.960^{cd}	1.945^{d}	1.945^{d}
Sc	5.000^{b}	11.00^{a}	0.950^{f}	0.975^{e}	3.000^{c}	3.000^{c}	1.000^{d}	1.000^{d}

Note: values with identical letters are not significantly different at 95% confidence level when subjected to Duncan Multiple Range Test

Table 4 Exchangeable bases for bedrocks obtained from the study area

Location	Ca %	Mg%	Na%	K%
Mokoloki	0.065 [e]	0.088 [e]	0.0295 [ef]	0.080 [d]
Kere-Gorge	0.040 [f]	0.020 [fg]	0.020 [g]	0.040 [f]
Iseyin	0.020 [g]	0.009 [g]	0.015 [h]	0.010 [g]
Brewery	0.060 [e]	1.115 [a]	0.050 [a]	1.486 [a]
Akomoje	0.150 [c]	0.010 [g]	0.030 [f]	0.068 [de]
Akin Olugbade	0.040 [f]	0.020 [fg]	0.040 [d]	0.050 [f]
Lafenwa	0.220 [b]	0.360 [c]	0.060 [a]	0.590 [b]
Oyan	0.070 [e]	0.405 [b]	0.054 [b]	0.580 [b]
Arakanga	3.745 [a]	0.260 [d]	0.032 [e]	0.100 [c]
Kara	0.120 [d]	0.030 [f]	0.032 [e]	0.055 [f]

Note: Values with identical letters were not significantly different from each other at 95% confidence

Conclusion

Mokoloki Bedrock had the highest trace metal value for Ag, Cd, Mn, Ni, Pb, Zn, As, Be, Cr, Hg and Sb (11 out of the 16 elements analyzed). Most of these metal concentrations exceeded the AEACR standards thus; this indicates that Mokoloki bedrock has high trace metal contents which when released into the river water, could result in high trace metal concentration in the Ogun River as observed in the Cd analysis where both bedrock and water values obtained were higher than the AEACR and WHO [(9)] standards respectively. Uranium toxicity could also occur in the Ogun River water if Uranium values in bedrocks sampled are higher than the AEACR standard. This could increase the Ogun River water concentration via weathering or mining along the Ogun River course.

Recommendations

Monitoring of the Ogun River water and bedrock should be done regularly in order to obtain adequate information/ database on the quality of the Ogun River. Indiscriminate dumping of mining wastes into the Ogun River should be discouraged since the trace metal content of some bedrock could be high and can lead to elevated metal concentrations in the Ogun River water.

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