Original Article

Element Content of Surface and Underground Water Sources around a Cement Factory Site in Calabar, Nigeria

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ABSTRACT

Background: Cement production is associated with heavy metal emissions and environmental pollution by cement dust. The degree of contamination of drinking water sources by major and trace elements present in cement dust generated by united cement factory (UNICEM) is still uncertain. This study estimated the element content of ground and surface water samples (hand-dug wells, boreholes and streams) around the factory site to determine the impact of cement dust exposure on the water levels of these elements.

Methods: This study was conducted at UNICEM at Mfamosing, Akamkpa local government area, Cross River State, Nigeria. Drinking water samples (5 from each location) were collected from the cement factory quarry site camp, 3 surrounding communities and Calabar metropolis (45 km away from factory) serving as control. The lead (Pb), copper (Cu), manganes (Mn), iron (Fe), cadmium (Cd), selenium (Se), chromium (Cr), zinc (Zn) and arsenic (As) levels of samples were determined using Atomic Absorption Spectrometry (AAS). Data were analyzed using ANOVA and LSD post hoc at $P = 0.05$.

Results: As and Pb content of samples from camp were above the WHO recommendations of 0.01mg/l and 0.01mg/l respectively. Chromium and cadmium content of all water samples were above and others below WHO recommendations. Water levels of Mn, Fe, Zn, As, Se, Cd, Ca and Si were significantly elevated (though below WHO recommendations) in camp than other locations ($P<0.05$).

Conclusion: Production of cement results in As, Pb, Cr and cd contamination of drinking water sources near the factory. Treatment of all drinking water sources is recommended before public use to avert deleterious health consequences.

Keywords: Cement Dust, Contamination, Drinking Water, Elements.

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INTRODUCTION

Contamination of the environment by major and trace elements is a public health problem, as most of these elements are indestructible, toxic, bio-accumulate and poses a serious threat to human life and the environment [1-3]. Though, most elements are essential for proper functioning of the human biological system [4], humans are not adapted to deal with them at concentrations higher than the reference values that can be tolerated by the human homeostasis [2, 3, 5]. Cement factories have been a major source of heavy metals emission to the environment with several reports showing higher concentrations of heavy metals around cement factories [6-8]. The particulate matter that is emitted from quarrying of limestone to the final process of packaging of cement is deposited on the soil, vegetation and water bodies, which usually serve as drinking water sources in the environment, thus increasing the pollution quotient of the surrounding communities [9]. The quality of water influences the health status of any population; elemental contamination of drinking water sources above the WHO threshold limit for particulate metal concentration has been associated with deleterious health effects including risk for cancers, cardiovascular, renal hepatocellular, neuromuscular, gastrointestinal, skeletal, hematological and immunological diseases [2]. Cement dust deposition in water have been associated with changes in salt content of water leading to serious disruption of aquatic habitat and decrease quality of water used for drinking and irrigation [8]. Elevated concentrations of toxic metals (Pb (1.5 g m-3); Cd (0.004-0.026 g m-3) in

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airborne cement dusts had been reported around the WAPCO cement factory at Sagamu, Nigeria when compared with USA threshold limit of particulate metal concentration [8].

Cement plant's neighborhood pollution depends on location and distances from the cement factory. Toxicity of metals appears to be dependent on dose, route of exposure, duration, and frequency of exposure [10]. Mfanmosing and its environs, which are host communities of united cement factory, have been negatively impacted from cement dust exposure emanating from quarrying, crushing and processing of cement by this factory. However, information on the concentration of the pollutants including essential and non essential elements released into the atmosphere by the manufacturing process of cement especially in drinking water sources, the elemental concentration of drinking water sources in these localities in relation to WHO threshold limit of safe exposure, the deleterious effects of cement dust exposure on man and his environment and the activities of the regulating body monitoring the activities of the cement companies are not readily available. Such information would be beneficial to the public and health authorities in ensuring that adequate preventive measures are instituted to safe guard life and preserve the ecosystem.

This study therefore assessed some element content of drinking water sources from a cement factory quarry site and the surrounding communities to determine the impact of cement dust deposits on the drinking water contents of these elements.

MATERIALS AND METHODS

Study Design

This study was conducted at the United Cement Company (UNICEM) at Mfamosing, Akamkpa local government area, Cross River State, Nigeria. The Mfamosing limestone deposit serves as the major source of raw materials used by UNICEM for the production of ordinary Portland cement (OPC). Since July 2009, the Mfamosing cement plant produces approximately 2.5 million metric tons of cement per annum and currently employs about 350 permanent workers. The factory has four major departments: Production (Crusher, Raw Mill, Kiln, Cement Mill, and Packing Section), Engineering and Maintenance (Mechanical and Electrical Section), Mining, and Administration (Cashier, Administrative Officer, Security, and Marketing Section). The site is close to 200m west to Mbebui village at coordinate 05.04493oN, 008.298995oE, 500m south to Abifan community at coordinate 05.07591oN, 008.52192oE and 200m east to Mfamosing community and 100m east to main quarry site at coordinate 05.06993oN, 008.53908oE [11].

Sample Collection

Drinking water samples from surface and underground water sources (either hand-dug wells, bore-holes or streams, 5 from each location) were collected from quarry site camp 50m away from cement quarry site (2 from stream, 2 from borehole and 1 from hand dug well), 3 surrounding communities; Mbebui, 200m away from quarry site (2 from streams, 2 from borehole and 1 from hand dug well), Mfanmosing l, 100m away from quarry site (2 from streams, 2 from borehole and 1 from hand dug well)and Mfanmosing ll 200m away from quarry site (2 from streams, 2 from borehole and 1 from hand dug well) respectively. Five water samples including water board samples were also collected from Calabar metropolis 45km away from the quarry site (2 from stream, 1 from borehole, 1 from hand dug well and 1 from water board) which served as the control samples. The lead (Pb), copper (Cu), manganes (Mn), iron (Fe), cadmium (Cd), selenium (Se), chromium (Cr), zinc (Zn) and arsenic (As) content of the drinking water samples were determined using Atomic Absorption Spectrometry (AAS).

METHODS

Estimation of Elements by Atomic Absorption Spectrophotometry [12]

Atomic absorption is an absorption spectrophotometric technique in which a metallic atom in the sample absorbs light of a specific wavelength. The element is not appreciably excited in the flame, but is merely dissociated from its chemical bonds and placed in an unexcited state or ground state (neutral atom), thus at this ground state atom absorbs radiation at a very narrow bandwidth corresponding to its own line spectrum and make transitions to higher energy levels The concentration is calculated based on the Beer-Lambert law. Absorbance is directly proportional to the concentration of the analyte present in the sample.

Statistical Analysis

Data analysis was done using the statistical package for social sciences (SPSS version 20.0) (Chicago, INC, USA). Analysis of variance (ANOVA) was used to test significance of variations within and among group means and Fisher's least significant difference (LSD) post hoc test was used for comparison of multiple group means. A probability value $P < 0.05$ was considered statistically significant.

RESULTS

The element content of all drinking water samples from all the different locations studied and the WHO recommended guideline limits were shown in Table 1. The Arsenic and lead content of drinking water samples from camp were above the WHO recommendations, while chromium and cadmium content of all water samples studied were above WHO guideline recommendations. The levels of other elements studied were below the WHO recommendations.

The comparison of element content of drinking water samples from camp, surrounding communities and Calabar metropolis were shown in Table 2. Significant variations were observed in the element content of drinking water sample from all the locations studied (P<0.05).

Table 3 shows the post hoc analysis showing elements levels in water samples from Camp compared to other locations**.** The drinking water levels of Mn, Fe, Zn, As, Se, Cd, Ca and Si were significantly elevated (though below WHO recommendations) in camp compared to other locations studied (P<0.05).

Table 1. Elements levels in water samples studied and WHO recommended limits.

Element	Camp n = 5	Mbebui n = 5	Mfam 1 n = 5	Mfam 2 n = 5	Cal Met n = 5	WHO Limit
Mn (mg/l)	1.532±0.100	0.587±0.042	0.650±0.269	0.492±0.113	0.362±0.172	NH
Fe (mg/l)	0.684±0.096	0.163±0.041	0.161±0.053	0.159±0.042	0.362±0.087	NH
Zn(mg/l)	0.291±0.084	0.101±0.006	0.105±0.010	0.096±0.013	0.096±0.016	NH
Cu (mg/l)	0.178±0.043	0.156±0.017	0.069±0.014	0.169±0.019	0.117±0.072	2mg/l
Pb (mg/l)	0.021±0.006	0.016±0.001	0.006±0.001	0.019±0.002	0.017±0.009	0.01mg/l
Cr (mg/l)	14.290±2.31	17.216±1.11	19.124±2.29	18.684±1.96	13.875±2.79	0.05mg/l
As (mg/l)	0.029±0.004	0.003±0.001	0.006±0.001	0.004±0.001	0.005±0.003	0.01mg/l
Se (mg/l)	0.014±0.002	0.002±0.001	0.002±0.001	0.003±0.001	0.002±0.001	0.04mg/l
Cd (mg/l)	0.022±0.006	0.007±0.001	0.006±0.001	0.008±0.001	0.010±0.005	0.003mg/l
Ca (mg/l)	89.441±6.62	74.204±3.09	50.800±1.85	67.416±3.17	49.385±7.81	NH
Si (mg/l)	0.002±0.001	0.001±0.000	0.001±0.001	0.001±0.000	0.001±0.000	NH

NH = No health concerns at levels found in drinking water, Mfam 1 = Mfanmosing 1
Mfam 2 = Mfanmosing 2, Cal Met = Calabar metropolis.

Table 2. Comparison of elements levels in water samples from Camp, Communities near cement factory and Calabar metropolis.

Element	Camp n = 5	Mbebui n = 5	Mfam 1 n = 5	Mfam 2 n = 5	Cal Met n = 5	F-value	P-value
Mn (mg/l)	1.532±0.100	0.587±0.042	0.650±0.270	0.492±0.113	0.362±0.172	42.47	0.000*
Fe (mg/l)	0.684±0.096	0.163±0.041	0.161±0.053	0.159±0.042	0.362±0.087	56.560	0.000*
Zn(mg/l)	0.291±0.084	0.101±0.006	0.105±0.010	0.096±0.013	0.096±0.016	24.099	0.000*
Cu (mg/l)	0.178±0.043	0.156±0.017	0.069±0.014	0.169±0.019	0.117±0.072	6.288	0.002*
Pb (mg/l)	0.021±0.006	0.016±0.001	0.006±0.001	0.019±0.002	0.017±0.009	6.310	0.002*
Cr (mg/l)	14.290±2.31	17.216±1.11	19.124±2.29	18.684±1.96	13.875±2.79	6.338	0.002*
As (mg/l)	0.029±0.004	0.003±0.001	0.006±0.001	0.004±0.001	0.005±0.003	124.95	0.000*
Se (mg/l)	0.014±0.002	0.002±0.001	0.002±0.001	0.003±0.001	0.002±0.001	87.434	0.000*
Cd (mg/l)	0.022±0.006	0.007±0.001	0.006±0.001	0.008±0.001	0.010±0.005	15.873	0.000*
Ca (mg/l)	89.441±6.62	74.204±3.09	50.800±1.85	67.416±3.17	49.385±7.81	55.033	0.000*
Si (mg/l)	0.002±0.001	0.001±0.000	0.001±0.001	0.001±0.000	0.001±0.000	20.000	0.000*

* = Significant at P<0.05 Mfam 1 = Mfanmosing 1, Mfam 2 = Mfanmosing 2, Cal Met = Calabar metropolis

Table 3. Post hoc analysis showing elements levels in water samples from Camp compared to other locations.

Locations	Element (mg/l)	Mean diff.	F-ratio	*P*-value
Camp/Mbebui	Mn	0.944±0.101	42.470	0.000*
	Fe	0.521±0.043	56.560	0.000*
	Zn	0.190±0.025	24.099	0.000*
	As	0.026±0.001	124.959	0.000*
	Se	0.012±0.001	87.434	0.000*
	Cd	0.015±0.002	15.873	0.000*
	Ca	15.236±3.198	55.033	0.001*
	Si	0.001±0.000	20.000	0.000*
Camp/Mfam 1	Mn	0.882±0.101	42.470	0.000*
	Fe	0.523±0.043	56.560	0.000*
	Zn	0.186±0.025	24.099	0.000*
	Cu	0.108±0.025	6.288	0.003*
	Pb	0.015±0.003	6.310	0.002*
	Cr	-2.927±1.372	6.338	0.016*
	As	0.023±0.001	124.959	0.000*
	Se	0.012±0.001	87.434	0.000*
	Cd	0.016±0.002	15.873	0.000*
	Ca	38.641±3.198	55.033	0.000*
	Si	0.002±0.000	20.000	0.000*
Camp/Mfam 2	Mn	1.040±0.101	42.470	0.000*
	Fe	0.525±0.043	56.560	0.000*
	Zn	0.195±0.025	24.099	0.000*
	Cr	-4.395±1.372	6.338	0.032*
	As	0.025±0.001	124.959	0.000*
	Se	0.011±0.001	87.434	0.000*
	Cd	0.015±0.002	15.873	0.000*
	Ca	22.024±3.198	55.033	0.000*
	Si	0.001±0.000	20.000	0.000*
Camp/Calabar metro.	Mn	1.170±0.101	42.470	0.000*
	Fe	0.322±0.043	56.560	0.000*
	Zn	0.195±0.025	24.099	0.000*
	As	0.024±0.001	124.959	0.000*
	Se	0.011±0.001	87.434	0.000*
	Cd	0.012±0.002	15.873	0.000*
	Ca	40.055±3.198	55.033	0.000*
	Si	0.001±0.000	20.000	0.000*

* = Significant at $P<0.05$ Mfam 1 = Mfanmosing 1, Mfam 2 = Mfanmosing 2,
Cal Met = Calabar metropolis

DISCUSSION

Major and trace elements are naturally present in natural water system. Their occurrence in groundwater and surface water can be due to natural sources such as dissolution of naturally occurring minerals containing trace elements in the soil zone or to human activities such as mining, fuels, smelting of ores and improper disposal of industrial wastes [13]. The detrimental health effects of contamination of drinking water sources have been documented. The impact of cement production on the element content of the drinking water samples near UNICEM cement factory was assessed in this study.

In this study, the element content of drinking water samples obtained from the closest settlement to the cement factory, the quarry camp, exceeded WHO recommended concentration for As and Pb. Their content in water from surrounding communities and Calabar metropolis were within the WHO recommendations. As is usually present in natural waters at concentrations of less than 1–2 µg/l, however, elevated levels are seen in ground water where there are sulfide mineral deposits and sedimentary deposits deriving from volcanic rocks [14]. Thus, high arsenic content of drinking water samples near cement quarry camp may be related to the mining activities of the cement factory with subsequent release of arsenic into the ground water. Arsenic has not been essential in humans. Acute As intoxication has been associated with the ingestion of well water containing very high concentrations (21.0 mg/l). Some of the complications that have been observed in a population ingesting arsenic contaminated drinking water include peripheral neuropathy, hyperpigimentation, hypopigmentation, skin, bladder and lung cancer and peripheral vascular disease [14]. These health effects associated with exposure to arsenic in drinking water samples of these settlement close to the cement factory has not been explored. These people are still ignorant of the health risk posed by their daily consumption of arsenic contaminated water.

Lead is rarely present in tap water because of its dissolution from natural sources; rather, its presence is primarily from corrosive water effects on household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes. The amount of Pb dissolved from the plumbing system depends on several factors, including pH, temperature, water hardness and standing time of the water, with soft, acidic water being the most plumbo solvent. Exposure to high Pb levels has been associated with a wide range of effects, including various neuro developmental effects, mortality (mainly due to cardiovascular diseases), impaired renal function, hypertension, impaired fertility and adverse pregnancy outcomes. Impaired neurodevelopment in children is generally associated with lower blood lead concentrations than the other effects [2, 14]. The detrimental effects of Pb contamination of drinking water on the neurodevelopment and intelligience quotients of children residing in quarry site camp of the cement factory are unimaginable. Contrary to our findings, the lead content of water boreholes from Calabar metropolis has been higher than WHO recommendations [15].The Cr and Cd content of all the water samples studied were above WHO recommendations for element levels in drinking water. Similar observations from other studies have been documented [15-17]. Cadmium has been described as one of air and water pollutant released by cement factories. Besides the cement factory, cadmium is also released to the environment in wastewater, and diffuse pollution is caused by contamination from fertilizers and local air pollution. Another source of cadmium contamination in drinking water may be from leaching from metal fittings and impurities from Zn used in solders and galvanized water pipes [14]. Cadmium contamination of drinking water samples may therefore not solely result from the activities of the cement factories as higher levels were also seen in water samples farther away (control samples) from the cement factory. Ingestion of Cd Pb to bioaccumulation will eventually manifest as cadmium toxicity after prolonged period of exposure. Evidence of bioaccumulation was shown by report of higher serum levels of Cd in occupationally exposed individuals; cement factory workers and residents near cement factory compared to unexposed controls [10]. Occupational exposures to Cd have been associated with renal tubular dysfunction with hypercalciuria, renal stone formation, osteomalacia, and osteoporosis [2, 18]. Cadmium has also been implicated in respiratory and immune dysfunctions [19, 20].

Chromium is widely distributed in the earth crust and chromium III has been described as an essential nutrient. Chromium VI however, has been described as a carcinogen. In epidemiological studies, an association has been found between exposure to chromium (VI) by the inhalation route and lung cancer. Evidence for carcinogenicity via the oral route at high doses has also been reported [14]. Chromium contamination of the drinking water if not curtailed may therefore result in some incidence of cancer because of prolonged and chronic exposure.

The drinking water content of other elements studied (Mn, Fe, Zn, Cu, Se, Ca and Si) in all the locations were within the WHO guideline values for element content in drinking water. Our findings is consistent with other studies who reported trace metals (Cu, Cd, Fe, Pb, Ni, Cr) levels in drinking water samples analysed within WHO allowable limit [17, 21].

Increased levels of Mn, Fe, Zn, Cu, Pb, Cr, As, Se, Cd, Ca and Si (though below WHO recommended limit) were observed in water samples obtained from cement factory quarry site camp when compared with samples obtained from communities around the cement factory and unpolluted sources. Consistent with our findings, water quality parameters of Ebe and Ora rivers collected around the vicinity of the Nigerian cement factory Nkalagu showed increased levels of Fe, Mn, Cd, Pb and As [22]. Heavy metal emissions to the environment among other pollutants have been associated with the activities of cement factories in the course of cement production. Higher levels of heavy metals have been reported around cement factories compared to unpolluted areas by several studies [2, 6-8, 23, 24]. Emitted dusts are naturally eliminated as deposits to the earth surface through dry or wet deposition in rainfall [25, 26]. Cement dust spreads along large area through rain, wind etc., and are accumulated in and on plants, animals, soils and water sources. The damaging effects of dust fall, is characterized by enriched toxic heavy metals such as As, Pb, Ni, Cr, Cu, Zn, Mn and Cd [27, 28]. While some of these elements are essential for humans, at high levels they can also mean a toxicological risk [25, 29].

CONCLUSION

The activities of UNICEM cement factory results in arsenic and lead contamination of surface and underground drinking water sources (hand-dug wells, bore-holes and streams) as shown by the levels of these elements being higher than the WHO recommended limit in water samples collected only from the quarry site camp. Cr and Cd contamination of all drinking water sources in the study area implies that cement production may not be the only source of chromium and cadmium contamination as contamination may arise from household and domestic plumbing. This ugly trend if left unchecked may result in a degenerative negative impact on the environment and health of residents of the area of study. Cement factories should embark on safe environmental practices that would check undue air pollution arising from cement dust.

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The authors declare that there is no conflict of interests.

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