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Physicochemical Characteristics and Heavy Metals Levels in Surface Waters from Aba-lla, Ibadan, Oyo State, Nigeria

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ABSTRACT: Industrial effluents from when released into water bodies, could lead to changes in the physicochemical parameters of water. The physiochemical properties and heavy metal content in surface water from a river, a stream and two wells at the Aba-Ila community in Ibadan, Nigeria were evaluated using standard methods. The results for the physicochemical parameters show that pH values range between 7.1 and 7.6; Dissolved oxygen between 65.2 and 152.3%; Temperature between 26 and 29˚C. Salinity ranged between 0.15 and 0.27 ppt, Alkalinity between 0.56 and 1.28 mg/L, E.C between 301 and 538µS, Total Hardness between 5.32 and 14.50 mg/L and Turbidity between 0.10 and 0.60 NTU. All these parameters were below the WHO permissible limits. All heavy metal concentration in water samples were found to occur above the WHO permissible limits. Self-reported responses of the participants to the questionnaire seem to indicate pollution from cement quarrying site. The quality of surface water in the study area is compromised and polluted in significant proportions. A reduction in release of pollutants and fugitive dust from the factory would be ideal.

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The process of cement production which includes mining, production, distribution and use, have contributed substantially to environmental pollution (Lamare and Singh, 2020). Cement dust is a major by-product of cement production and an important source of pollution ever since the exploitation of limestone quarries for building materials. Cement dust is an important risk factor for respiratory tract diseases; it is emitted at different stages of cement production (Shanshal and Al-Qazaz, 2021). It is known to contain high amounts of particulate matter (PM), sulphur dioxide, nitrogen oxide, carbon dioxide, amongst other hazardous gases, which form a cloud of dust in the surroundings of the cement factory (Hwang *et al*., 2018). Cement manufacturing is the main source of PM emissions, accounting for up to 40% of overall industrial emissions and between 25% and 30% of total PM emissions (Ciobanu *et al.*, 2021). It is estimated that about 500 – 1700kg of particulate matter is emitted daily from a cement factory (Ogedengbe *et al.,* 2011). Particulate matter is one of the major air pollutants in the world, a combination of fine solids and aerosols that are suspended in the air. According to the WHO (2022), low- and middle-income nations experience the greatest exposure to air that includes high levels of pollutants and hazardous quantities of nitrogen dioxide and tiny particulate matter. Particulate matter in cement dust settles in the atmosphere or could be deposited into the nearer water bodies forming compounds and bioaccumulating in aquatic biota. Particles with a diameter of less than 10um have the potential to go deep into the lungs and

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enter the bloodstream. The biggest threat to health comes from particles with a diameter of less than 2.5um, often known as tiny particles or $PM_{2.5}$ (EPA, 2022). This dust when inhaled for a prolonged period, will reportedly lead to the occurrence of respiratory tract infections and ultimately lung diseases (Erah *et al*., 2018).

In water, heavy metals can form compounds which can bio-accumulate directly or indirectly in humans. Theoretically, this implies that all water bodies that are found in the close vicinity of a cement plant should have a high concentration of heavy metals. If this is true, it therefore means that cement plants are responsible for the contamination of water bodies in communities located in their environs, which could lead to health challenges. Hence, the objective of this study was to evaluate the physicochemical characteristics and selected heavy metal levels in surface waters from a river, a stream and two wells at Aba-Ila community in Ibadan, Nigeria.

MATERIALS AND METHODS

Study and Sampling Area: The study area is in Ibadan, Oyo State, Nigeria is the largest city in West Africa and the second largest in Africa, covering an area of 240km^2. The city is located on longitude 3˚5'E and latitude 7˚20'N. It experiences two seasons namely the rainy and dry seasons. The sampling area is located in a village that is about 2km away from a Lafarge Distributing and Quarrying Site called Aba-Ila. The presence of a vegetable oil factory, a brewery and some other industries make it a site that is exposed to numerous anthropogenic activities.

Sample Collection, Preservation, and Handling: Heavy metal samples were collected using sterile 500ml plastic containers in accordance with the specifications provided at the Agronomy Department, University of Ibadan. The samples were taken at the following predetermined sample sites; river Ona runoff (4 sample points), the stream (2 sample points) and two wells in the town. The samples were preserved in ice prior to the time of analysis.

At the sampling sites, temperature and pH readings were taken directly onsite. While two 500mL plastic containers were used to collect water samples at the above listed sample points for the following parameters: Total Dissolved Solids (TDS), Salinity, Electrical Conductivity, Dissolved Oxygen, Turbidity, Total Hardness and Alkalinity. Questionnaires were distributed to interested adults in the town to obtain information on perception of water quality and self-reported health status. Assistance was given in filling the questionnaires in cases where there was a language or other barriers.

Heavy Metal Analysis: The heavy metal samples collected were acidified using Nitric Acid Digestion and an Atomic Absorption Spectrophotometer (Model 210/211 VGP) was used to analyse for the concentrations of lead, cadmium, chromium and nickel at the Agronomy Department, University of Ibadan.

The formula used to calculate the actual results of a diluted and digested sample using AAS is shown below (Schaefer and Vomhof, 1973).

$$Conc. mg/kg = \frac{AAS\ Results\ (m/L)\ x\ DV\ (L)}{Mass\ of\ sample\ (kg)}$$

Where Conc. = Concentration (mg/Kg); AAS results (mg/L); DV = Dilution Volume (L)] and Mass of sample (Kg).

Sample digestion was done as follows. Briefly, to a 100-mL aliquot of well-mixed water sample in a beaker, 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl was added to digest the water sample. The sample was covered with a ribbed watch glass or other suitable covers and heated at 90 to 95ºC until the volume was reduced to 15-20 mL. The beaker was allowed to cool and then its walls and watch glass were washed down with water. The final volume was adjusted to 100 mL with reagent water.

Quality Control and Data Analysis: Samples were analysed in duplicates and data analysed with descriptive statistics. The mean and standard deviation were determined. Significant differences between sites were calculated by the analysis of variance.

RESULTS AND DISCUSSION

Physiochemical Parameters: The measured physiochemical properties of the water from the various sampling points were shown to be lower than the WHO permissible limits (Table 1).

Heavy Metals Concentration: All the heavy metals assayed from the different sampling points had concentrations higher than the WHO permissible limit. Lead had the highest concentration of 12.55mg/L in stream 1, while Cadmium was the lowest with about 0.01 mg/L stream 2 and well 2 (Table 2). The descriptive statistics data shows that the heavy metal concentrations of the water samples collected was highest with Pb, having an average value of 9.05 and a standard deviation of 4.96 for the stream sites. Cadmium was the lowest with average value of 0.02

and a standard deviation of 0.01 in all sampling sites (Table 2). Analysis of variance showed that there was no significant difference between the sampling sites (p> 0.05). The correlation coefficient analysis indicates that Chromium is significantly and positively correlated with Lead. Nickel was negatively correlated with other heavy metal concentrations, but not statistically significant (Table 3). The total number of respondents was 77, out of which 43(55.8%) were males while 34(44.2%) were females. Age distribution revealed that the majority 26(33.8%)] of the total respondents were in the age range of 21-30 while the least 7(9.1) were in the age range 41-50. About 32.5%) of respondents were factory workers (Table 4). Sources of water in Aba-Ila town of Ibadan according to the respondents are rivers (75.3%), well (81.8%), boreholes/pipe-borne waters (71.4%) while rain accounted for (72.7%). It can be deduced that well was the major sources of water in the case study.

Table 1: Physiochemical parameters taken at sample sites in Aba-Ila

	RIVER/R				**STREAM/S**		**WELLS/W**		
	1	**2**	**3**	**4**	**1**	**2**	**1**	**2**	**WHO PL (2012)**
pH	7.61	7.46	7.18	7.85	7.10	7.48	7.22	7.24	6.5 – 8.5
D.O (%)	92.00	65.20	71.40	91.20	95.60	152.30	83.00	83.50	NS
Salinity/ ppt	0.15	0.15	0.15	0.15	0.16	0.16	0.27	0.20	NS
Temperature/ ˚C	26.00	26.50	26.00	27.00	29.00	27.00	28.00	28.00	Ambient
Conductivity/µS	301.00	301.00	306.00	310.00	323.00	316.00	531.00	538.00	1000
Turbidity/ NTU	0.40	0.30	0.20	0.40	0.60	0.50	0.10	0.10	5
Alkalinity/mg/L	0.60	0.56	0.59	0.57	0.71	0.78	1.26	1.28	NS
Total Hardness/mg/L	11.33	6.70	5.32	6.95	9.38	7.50	14.25	14.50	150

NS = not specified; PL = permissible limit

Table 2: Heavy Metal Concentration of the water samples collected

	River			Stream			Wells		
	Range	Mean	*SD*	Range	Mean	*SD*	Range	Mean	*SD*
Pb	2.14	1.88	1.51	7.01	9.05	4.96	0.14	1.22	0.10
Cd	0.00	0.02	0.00	0.02	0.02	0.01	0.01	0.02	0.01
Cr	2.03	2.10	1.44	2.79	6.33	1.97	0.06	2.61	0.04
Ni	0.81	2.90	0.57	1.33	3.20	0.94	0.19	4.63	0.13

Table 3: Correlations between heavy metals

Parameters	**Pb**	**Cd**	**Cr**	**Ni**
Pb	1.00			
Cd	0.375	1.00		
Cr	0.973**	0.262	1.00	
Ni	-0.452	-0.353	-0.254	1.00

*** Significant at p < 0.05*

A few 14(18.2%) of the respondents said they observed change in colour in water sourced from rivers, while most 47(61.0%) of the respondents said they noticed a change in colour in the water fetched from wells. Only about 4(5.2%) of the respondents claimed that change in colour occurred in their water sourced from borehole. Asked about whether the air gets dusty or not, about 80% of the respondents said it did, while over 10 % said it did not and 1.3% was unsure. Indeed, 57% of those that said the air gets dusty claimed it caused difficulty in their breathing while 31.2% denied the claim and 1.3% was unsure.

Asked whether respondents had ever had any nasal or respiratory problems, 34(44.2%) of the survey respondents said they had, 29(37.7%) of the respondents seemed to be free from nasal or respiratory problems while 1(1.3%) were unsure. Furthermore, 32(41.6%) of the respondents adduced their nasal or respiratory problem to the air in their area, 37(48.1%) did not, while 4(5.2%) were unsure. From their observations on visible air pollution, 21(27.3%) of the poll respondents indicated that they had family members with respiratory problems owing to the air in their area while 32(41.6%) of them did not notice that and 20(26.0%) were unsure there was any connection.

A total of 50(65%) respondents worked in the factory environment, out of which 25(32.5%) worked as labourers in the factory while 47(61%) did not work in the factory. Meanwhile, among the factory workers 14(18.2%) of them said their work in the factory had caused them health challenges, 51(66.2%) did not think so, while 5(6.5%) were unsure. Classification based on the kind of health challenges faced by the respondents as a result of working in the factory indicates that 19.5 percent of the factory workers suffered from fever and 13 percent reportedly had general health problems (Figure 1).

Table 4: Demographic characteristics of respondents

Characteristics	Frequency (%)
Age	
21-30	26(33.8)
31-40	17(22.1)
41-50	19(24.7)
51-60	7(9.1)
61and above	8(10.4)
Total	**77(100)**
Sex	
Male	43(55.8)
Female	34(44.2)
Total	**77(100)**
Educational status	
Primary School	10(13.0)
SSCE	39(50.6)
NCE	16(20.8)
HND	6(7.8)
First Degree	2(2.6)
Others	4(5.2)
Total	**77(100)**
Occupation status	
Farming	17(22.1)
Factory workers	25(32.5)
Artisan	4(5.2)
Trading	17(22.1)
Others	14(18.2)
Total	**77(100)**
Employment Status	
Paid employment	31(40.3)
Self-employment	46(59.7)
Total	**77(100)**
Religion	
Christianity	19(24.7)
Islam	34(22.2)
Traditional	24(31.2)
Total	**77(100)**
Ethnicity	
Yoruba	36(46.8)
Islam	22(28.6)
Hausa	19(24.7)
Total	**77(100)**
Marital status	
Single	21(27.3)
Married	47(61.0)
Engaged	7(9.1)
Divorced	2(2.6)
Total	**77(100)**

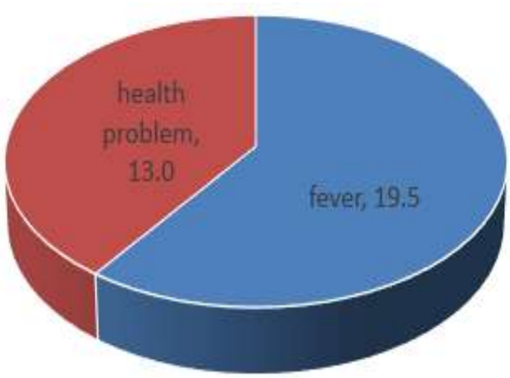

Fig 1: Health Challenges faced by Factory Workers

Development and growing business and housing needs show in increased construction of industries and housing estates. These construction works often utilize cement as an important component. The cement industry itself is a source of income for people especially those living in areas where quarries or cement manufacturing companies are located. The drawback in this is that cement contains key heavy metals (such as Nickel, and Cadmium) that are known to be detrimental to health. The data from this study showed that the concentration of heavy metals lead, cadmium, chromium, and nickel assayed in the different water bodies at Aba Ila community, near the Lafarge quarry site in Ibadan were higher than the WHO permissible limits. Similarly, Gupta and Sharma (2013) reported that traces of chromium and lead were detected with concentrations that were higher than the WHO permissible limit in cement dust emission from the Nokha cement plant in Bikaner, India. This indicates that there is an active pollution of the water bodies in Aba-lla town with heavy metals. In addition, Lead was the highest occurring heavy metal in this study and may be the main pollutant in Aba-Ila town. This corresponds to the report that cement dust released from the Ewekoro Cement Factory, Ogun State, Nigeria led to the deposit of heavy metals like Arsenic, Lead and Nickel in the nearby water bodies (Oluseyi *et al*., 2011). The mean concentration of Lead in the sampling points were significantly different and may be due to the varied proximity of each sampling points to the quarry site or how often these water bodies come in contact with the heavy metals. In contrast, there was a significant difference in the mean concentrations of Cadmium and Chromium in the sampling points. This may be indicative that these heavy metals were from different anthropogenic sources. Lead was positively correlated with Cadmium, irrespective of the sampling point/site, although not statistically significant. Similarly, Cadmium was positively correlated with Chromium. These correlations between the heavy metals may be due to different anthropogenic sources as seen with the presence of different industries in the area. A similar scenario had been reported where the probable source of the heavy metals copper and zinc that were positively correlated, where from different anthropogenic sources (Zrouga *et al*., 2021). On the other hand, there was a significant and positive correlation between Chromium and Lead. Such significant correlation might imply that the source of both heavy metals was the Lafarge quarry. While the quarry may be the main focus of this study, the observations of the probable different sources of the heavy metals may imply that the presence of other industries in the study area may inconspicuously be leading to heavy metal pollution of the water bodies. The data also shows that physiochemical parameters of the sample sites such as pH, dissolved oxygen, Salinity, Temperature, Conductivity, Turbidity, Alkalinity and Total Hardness when compared with the WHO 2012 standards were within the permissible limits. The water bodies were slightly alkaline indicating that the activities of the nearby quarry may have led to an altered pH and alkalinity of the water source.

The major source of water for domestic activities in Aba-lla town is well water. Majority of the respondents had observed changes in the colour of the water fetched from the well, indicating that there may be underground water pollution by these heavy metals. Interestingly, respondents that used borehole water also observed changes in the water colour, further indicating pollution of their water bodies. In this study, air quality is reported to be highly altered as observed by the presence of suspended dust particles in the air. About 80 percent of respondents in this study had reportedly observed that the air in the study area was often dusty. This might be connected to particulate matter released from the quarry site that becomes suspended in the atmosphere. Apart from obstructing the view, these suspended particulate matters are hazardous to health as well as to plants (Kiani *et al*., 2015). Furthermore, cement dust may carry a high content of sulphur dioxide (SO_2), which is a known air pollutant. This gas is known to interfere with and endanger the ecosystem as well as human health. It is associated with breathing difficulty, airways inflammation, corneal haze, eye irritation, pulmonary edema, heart failure, and circulatory collapse (Wang *et al*., 2015). Moreover, majority of respondents in this study had indicated that they have respiratory problems, while others reported that they had family members with respiratory problems due to the air quality in the area. These observations may imply that the area is already heavily polluted and might require urgent intervention measures to avert future complicated health issues. Cement factory workers have been reported to have different forms health problems related to the kind of heavy metals they have been exposed to and at what dose or period of time. These workers are exposed to cement that contain several toxic metals like chromium capable of increasing the risk of related diseases, as such are tagged as independent risk factors in the cement factory workers (Ogunbileje *et al*., 2013). In this study, about 32 % of respondents were workers in the quarry, out of which 18.2% self-reported to have a disease due to working in the quarry, and 13% with general health problems.

Conclusion: The high heavy metal concentrations of the water samples collected from the sample sites is an indication of heavy metal and cement dust pollution in Aba-Ila, making it unfit for domestic use. Slightly alkaline water samples indicate that activities of the nearby quarry may have led to an alteration in the pH and alkalinity of the water source. The physiochemical quality of the water shows that the water is suitable and safe. There is an urgent need for intervention measures to ameliorate water sources in the Aba-Ila Community.

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