Spectrometric Determination of Lead, Cadmium, Arsenic, Copper and Iron in Drinking Water Samples Across Kogi State, Nigeria.

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ABSTRACT
The aim of the study was to determine the levels of lead, cadmium, arsenic copper and iron in 25 water samples collected from across Kogi State. Atomic absorption spectrometry was used in the determination of copper, iron, lead and cadmium while UV-visible spectrophotometer was employed in the determination of arsenic, based on the formation of Molybdoarsenate. The ranges of mean values obtained for the heavy metals are: Arsenic (0.0014to 0.0252 mg/L), Copper (0.0013to 0.0095 mg/L), Lead (0.0001to 0.024 mg/L), Cadmium (0.003 to 0.072 mg/L) and Iron (0.0068 to 0.1242 mg/L). The results revealed that the River, Stream and Tap water sampled were contaminated with Arsenic (As), whereas, the levels of Fe, Cu and Pb were within the recommended limit set by WHO and NAFDAC. Though the level of cadmium (Cd) falls within acceptable limit in some of water samples, its high concentration in Isanlu should attract the attention of the authority in this area in curbing the growing threat.
Keywords: Kogi, Molybdoarsenate, Arsenic, Stream, Tap water

Introduction
It is known that some heavy metals are essential while some are harmful to human health [1]. According to the WHO, 829, 000 people die each year from drinking unsafe water, lack of adequate sanitation and hygiene, among whom 297, 000 were children under the age of five [2]. This, of course, has made the determination of these heavy metals increasingly important. Heavy metal is a general term applied to a metal or metalloid, which has atomic density greater than 5 g/cm³ (at least 5 times or more than water). Toxic heavy metals are persistent environmental contaminants because they cannot be degraded. To a small extent, they enter the body system through food, air and water. They bio-accumulate over a period of time because they cannot be metabolized [3]. Heavy metal toxicity can lead to damaged or reduced mental and central nervous functioning, damage of vital internal organs and lowering of energy levels in the body [4]. The first three are highly toxic (Lead, Cadmium and Arsenic) and they can cause damaging effects even at low concentrations while the last two (copper and Iron) are only harmful when there is excessive intake [5, 6].

The determination of arsenic is of critical importance and has accordingly received significant attention in recent years, as groundwater is contaminated with high concentrations of arsenic. Exposure to arsenic occurs through oral ingestion and inhalation [7, 8]. The concentration of Cu, Fe, Pb, and Cd in drinking water samples collected from the various local Government Areas in Kogi State was determined by flame atomic absorption spectrometry while determination of arsenic was carried out by spectrophotometric method based on the formation of molybdoarsenate. Absorbance readings were obtained for arsenic concentrations using UV-visible spectrophotometer [9]. Although heavy metal pollution is a reality in Africa, many countries have not yet conducted systematic studies to estimate the impact of the phenomenon. A comparative evaluation of the heavy metals in aquatic environment in Kogi State is lacking. The aim of this research is to determine and compare the levels of cadmium (Cd), lead (Pb), arsenic (As), copper (Cu) and iron (Fe) in different water samples across Kogi State. Therefore, this research is being carried
out with a view to adding more information on the levels of heavy metals in water samples.

**Materials and Methods**

**Study Area**

Kogi state (Figure 1) is located in the central region of Nigeria. It is called the Confluence State because of the confluence of River Niger and River Benue at its capital Lokoja. Agriculture is the major occupation of the people. It is located at an elevation of 55 meters above sea level and has a population of 3, 595, 789. Its coordinates are 7°45’’ N and 6°45’’ E.

![Figure 1: Map of Kogi State](image)

**Sampling and sample treatment**

Twenty-five water samples were collected in 5L polyethylene plastic container using standard water sampling procedure from across Kogi State. This was done by considering the source of water supply that is commonly used by a larger number of people within the area. The main sources where samples were collected are: Rivers, streams, Boreholes and tap water. The twenty one sites studied were River Benue (RB), River Niger (RN), Emachi Stream Ajaka (ESA) River Ofu, Ugwolawo (ROU), Okumoh Borehole, Lokoja (OBL), Inachalo Stream, Idah (ISI), Isanlu Tap water, Yagba (ITY), Ogori Tap water (OT), Kotonkerfi Water Works (KWW), JakuraBorehole, Lokoja (JBL), River Ocheche, Idah (ROI), ASCO Camp Tap water, Lokoja (ACTA), Water Treatment Plant, Abejukolo (WTPA), Ajetachi Borehole, Anyigba (ABA), Anpka Tap water (AT), Otaneji Stream, Ibaji (OSI), River Okura (RO), Bigleo Borehole, Adavi (BBA0, Odole Borehole, Mopa (OBM), Ose Stream, Kabba (OSK), Ayetoro Stream, Ijumu (ASI), River Onyimowa, Bassa (ROB), River Mabolo (RM), Iteme Stream, Dekina (ISD) and Okene Water Works (OWW).

**Sample Treatment**

All samples were pre-treated by boiling and allowed to cool for several hours for solid particles to settle out. This was further decanted and exactly 5000 cm³ was measured and evaporated to dryness on a heating mantle. The residues were dissolved in 50cm³ of IM HNO₃ and stored in a refrigerator.

**Determination of Arsenic Concentration in Water Samples Procedure**

Exactly 3.6 cm³ of water sample was pipetted into a test tube and 5.0 cm³ of ammonium Molybdate - hydrazine mixture with 2 drops of sodium disulphite solution. To the same mixture, 1.0 cm³ of iodine - potassium iodide solution and 0.2 cm³ of NaHCO₃ solution were added and heated in a water bath to 95°C with change of colour to faint blue. On cooling, absorbance readings were taken using UV-visible spectrophotometer at 840nm. The same procedure was repeated with the blank and the remaining standards.

**Results and Discussion**

The results of heavy metal concentrations in River, Stream, Tap and Borehole water are shown in Table 1.
Table 1: Levels of Arsenic (As), Copper (Cu), Cadmium (Cd), Lead (Pb) and Iron (Fe) in Samples taken from Rivers, Streams, Tap water, and Boreholes.

| S.No. | River samples | As   | Cu   | Cd   | Pb   | Fe   |
|-------|---------------|------|------|------|------|------|
| 1     | RB            | 0.0252 | ND   | ND   | 0.0119 | 0.0731 |
| 2     | RNC          | 0.0227 | ND   | ND   | 0.0009 | 0.014 |
| 3     | ROU          | 0.055  | ND   | 0.018 | 0.007  | 0.0237 |
| 4     | ROI          | 0.0069 | 0.018 | ND   | 0.003  | 0.024 |
| 5     | RO           | 0.0017 | ND   | ND   | ND    | 0.0253 |
| 6     | ROB          | 0.0103 | ND   | 0.0096 | 0.031 |
| 7     | RM           | 0.0017 | ND   | 0.006 | ND    | 0.0255 |
| Stream samples |       |      |      |      |      |       |
| 8     | ESA          | ND    | ND   | ND   | 0.0001 | 0.008 |
| 9     | ISI          | 0.0045 | ND   | ND   | ND    | 0.0055 |
| 10    | ASI          | 0.0052 | ND   | 0.027 | ND    | 0.1218 |
| 11    | OSI          | 0.011  | 0.003 | 0.130 | 0.0055 | 0.0253 |
| 12    | ISD          | 0.0017 | ND   | ND   | 0.0022 | 0.0212 |
| 13    | OSK          | 0.0103 | ND   | ND   | 0.024  | 0.0855 |
| Tap Water |       |      |      |      |      |       |
| 14    | ITT          | 0.011  | ND   | 0.072 | ND    | 0.1233 |
| 15    | OT           | 0.0045 | 0.0095 | ND   | 0.0054 | 0.0068 |
| 16    | ACTA         | 0.0014 | ND   | ND   | ND    | 0.016 |
| 17    | WTPA         | 0.0066 | ND   | 0.014 | ND    | 0.0251 |
| 18    | OWW          | 0.0048 | ND   | 0.027 | 0.0096 | 0.1242 |
| 19    | AT           | 0.0034 | ND   | ND   | ND    | 0.0008 | 0.019 |
| Borehole Samples |      |      |      |      |      |       |
| 20    | OBL          | 0.0142 | ND   | ND   | 0.006  | 0.0135 |
| 21    | ABA          | 0.0017 | ND   | 0.007 | 0.0034 | 0.0075 |
| 22    | BBA          | 0.0045 | ND   | ND   | ND    | 0.0084 |
| 23    | OBM          | 0.012  | 0.0013 | 0.033 | 0.0066 | 0.0135 |
| 24    | JBL          | 0.0148 | ND   | ND   | ND    | 0.0253 |
| 25    | KB           | 0.0002 | ND   | 0.001 | ND    | 0.0051 |

ND: Not Detected

Arsenic (As)
For arsenic, it was found that both River Benue and River Niger have a significantly higher concentration compared to ROB, ROI, RO and EM. The reason for this might not be far from the open nature of the two rivers to other streams and smaller rivers as tributaries. While the levels of As in River ROU is significantly greater than those obtained from River Benue and River Niger. Furthermore, the levels of arsenic ranged from 0.0014 to 0.0252 mg/L (Table 1) and has the maximum value a little above the range set by WHO as 0.01 mg/L. Moreover, the only sample where arsenic was not detected was that of Emachi Stream Ajaka, in Igalamela/Odolu local government area. There was no significant difference among the levels of As in all the Stream and tap water samples. However, the levels of As in Borehole water from OBL was significantly greater than those obtained from KB, BBA and ABA. The levels of As in Pasur River ranged from 0.00276 – 0.01673 mg/L [10], falls within the ranged of values obtained in this study.

Lead (Pb)
The concentration range of lead was found to be from 0.0001 to 0.0240 mg/L (Table 1) and this poses significant threat to the consumers in these areas. There was no significant difference among the levels of Pb in the River water collected. The Pb concentration in in Stream OSI was above the recommended limit set by WHO and NAFDAC. While the levels of Pb observed in Tap and Borehole water were below the recommended limit, though care has to be taken to prevent bioaccumulation of Pb in the human body. The levels of Pb obtained in this study were similar to that reported by [10], which ranged from 0.01269 – 0.04267 mg/L and lower than those reported by [11].

Cadmium (Cd)
The levels of cadmium ranged from 0.006 to 0.072 mg/L (Table 1). In this particular analysis, it was discovered that only River ROU (0.018) and RM (0.006) contained Cd. Similarly, Cd was detected in Stream ASI and OSI. In addition, the concentration of cadmium detected in the samples from Isanlu tap water (0.072 g/L) was significantly greater than those recorded in the other tap water samples. However, the Cd levels obtained from WTPA (0.014), OWW (0.027) and ITY (0.072 mg/L) were greater than the recommended limit set by WHO and SON, which might be attributed to the domestic sewage and effluents from industries. Furthermore, cadmium was detected only in Borehole water from ABA and OBM. The levels of Cd obtained in this study is lower than those reported by [11] (0.0026) to (0.0053) mg/L and greater than those reported by [10] in Pasur River in Bangladesh which ranged from 0.00042 – 0.00298 mg/L.

Iron (Fe)
Iron was found in virtually all the samples taken from the state. The levels of Fe, ranged from 0.0068 to 0.1242 mg/L (Table 1). The concentration of Fe, in samples from Isanlu, Ijumu and Okene were particularly higher. Similarly, the levels of Fe, from River RB was significantly greater than those observed in sites RN, ROU, ROI, RO, RM and ROB. More so, in the Stream water analysed, the iron content in
site ISI is significantly greater than those recorded for sites ISD, OSI and ESA. Likewise, the level of Fe in site ASI was significantly higher than those obtained in sites OSK, ISI, ISD, OSI and ESA. In the same vein, the levels of Fe in the Tap water samples collected from OWW and ITY were significantly higher than the values obtained from other sites. Also, the level of Fe in the Borehole water collected from KB was significantly greater than those recorded in the other sites. The level of Fe obtained in this study is lower than those reported for hand-dug wells and Ona River in Itaogbolu area of Akure North Local Government, Ondo State, Nigeria which ranged from 0.1 to 5.3 mg/L [12].

Copper (Cu)
The levels of Cu ranged from 0.0013 to 0.0095 mg/L. Among the River water sampled, Cu was only detected in site ROI while in the Stream water Cu was detected only in site OSI. Similarly, site OT was the only site in which Cu was detected in the Tap water analyzed, whereas in the Borehole water analyzed only site OBM contained Cu.

There was a strong positive correlation between Cd and As, Fe and Pb, Pb and As, in the river samples collected. While in the stream water Cu and As, Pb and As, Fe and Cd were strongly positively correlated, this indicates that they have similar origin. Likewise, in the Tap water, Cd and As, Fe and As, Fe and Cd, Fe and Pb had a strong positive correlation indicating that they have similar origin. In addition, Pb and Cu had a strong positive correlation, whereas Fe and Cd were negatively correlated, this shows that as the concentration of one increases the other decreases.

Conclusion
The results revealed that the River, Stream and Tap water samples were contaminated with Arsenic (As), whereas, the levels of Fe, Cu and Pb were within the recommended limit set by WHO and NAFDAC. The Borehole water was not contaminated by any of these heavy metals. Interestingly, the relatively high concentration of Iron in Isanlu, Ijumu and Okene should be a relief to the dwellers of these areas. Even though, the levels of Pb is within the recommended limit measures should be taken to prevent bioaccumulation in the human body.

Furthermore, People within the state should be cautious in their daily use of water obtained from Rivers as the levels of arsenic (As) in them were above the recommended limit. In the same vein, though the level of cadmium (Cd) falls within acceptable limit in some of the water samples, its high concentration in Isanlu should attract the attention of the authorities of this area in curbing any growing threat.

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