Research Journal of Applied Sciences 2 (4): 416-419, 2007

Some Trace Metal Levels in Asa River, Ilorin, Nigeria Using AAS and XRF Techniques

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Abstract: Determination of Fe, Mn, Pb, Zn, Cr and Cu concentrations in Asa River water is discussed. Two different methods of analysis are compared. Atomic Absorption Spectrophotometry (AAS) and X-ray fluorescence (XRF) were employed. A statistical analysis carried out showed that there was no significant difference in the concentrations of Cr, Zn, Pb and Cu using the two techniques. Significant differences were observed at 5% probability level for Mn and Fe using the two techniques. This has been attributed to differences in sample preparation as the two metals have been observed to be mainly of natural origin. It is suggested that they could have been trapped in the micro particles in water since no digestion was carried out prior to XRF analysis.

Key words: Ilnn, AAS, XRF, vital resources, environmental pollution

INTRODUCTION

The vital resources of life; water and land are being increasingly stressed through the action or inaction of man leading to environmental pollution (Ibe *et al.*, 1992). Water may be temporarily or permanently impaired in quality as a result of these actions and inactions.

Water pollution has been defined as the presence of foreign substances (organic, inorganic, bacteriological or radiological) which tends to degrade the quality of water (Salami, 2003).

These compounds set the physical and chemical parameters of the water. Some of these are toxic to the aquatic ecosystem while others constitutes nutrient for the aquatic microorganism (Boukari *et al.*, 1999).

The AAS and XRF techniques have between used extensively individually to determine trace metal levels in water. The XRF has been found from literature to be able to identify some elements which could not be analysed using AAS technique. Several elements can be identified at once using the XRF unlike the AAS that requires that lamps be changed for every element to be determined (Ekspriandova *et al.*, 2002).

MATERIALS AND METHODS

Sample collection and preparation: Samples for trace metal analysis were collected from seven different locations based on the ease of accessibility to the river and activities around the locations. The sampling was carried out every month for eighteen months. The water samples were collected in 2 L polyethylene bottles. Samples for were acidified prior to analysis with a few drops of conc HNO_3 to keep the metals in solution.

Analytical methodology: Florescence X-rays from the samples were detected using a Si (Li) detector (resolution = 175eV). The signals were amplified and processed through a multichannel analyzer. The spectrum was stored using GENIE 2 K software and the analysis was carried out using QXAS software from International Atomic Energy Agency (IAEA) Vienna, Austria.

The water sample was shaken for 30 sec after which 1 mL of sample was pipetted into a small PTFE vessel and mixed with the solution containing 1 μg of Ga as internal standard (1 $\mu g\ mL^{-1}$). An aliquot of 50 to 100 μL of standardized sample was transferred onto a quartz disc, dried under reduced pressure and measured (IAEA-TECDOC, 1996).

For the AAS analysis, the samples were digested using HNO_3 and HCl following standard methods from literature. This was followed by elemental analysis using Alpha 4 AAS Chem Tech Analytical U.K with graphite atomizer.

Determination of precision and accuracy: The analytical quality involved triplicate analysis of samples and blanks. The accuracy of the analytical techniques was evaluated by preparing standards and analyzing these alongside the samples and this was used in the preparation of calibration curve for the AAS. For XRF, the Standard Reference Materials (SRM) used in the XRF were prepared by IAEA. Vienna, Austria.

RESULTS AND DISCUSSION

In this study, some trace metal concentration levels were measured using the AAS and XRF techniques and the findings are as shown in Tables 1 and 2 and some known standards are shown on Table 3.

Table 1: Range and means of trace metal concentrations (mg l^{-1}) in water across sampling location determined by AAS

Location	Mn	Fe	Pb	Cr	Zn	Cu
1	1.90-4.81 (3.62)	8.06-19.10 (13.14)	0.00-0.23 (0.11)	0.02-0.08 (0.05)	0.23-0.98 (0.61)	0.05-0.14 (0.10)
2	1.03-5.31 (3.13)	0.76-18.29 (7.26)	0.02-0.11 (0.07)	0.00-2.10 (0.06)	0.24-0.92 (0.54)	0.03-0.11 (0.07)
3	3.07-7.37 (4.81)	3.03-24.06 (9.63)	0.01-0.33 (0.15)	0.03-0.10 (0.05)	0.22-0.97 (0.64)	0.05-0.12 (0.08)
4	1.47-9.12 (5.46)	4.09-08.84 (6.16)	0.00-0.13 (0.08)	0.0 0.04 (0.02)	0.20-0.56 (0.36)5	0.01-0.10 (0.05)
5	2.52-9.76 (6.80)	4.06-19.30 (10.34)	0.04-0.33 (0.19)	0.03-0.08 (0.05)	0.09-0.78 (0.40)6	0.02-0.11 (0.06)
6	2.49-8.42 (5.42)	3.97-18.03 (9.09)	0.02-0.19 (0.10)	0.01-0.06 (0.03)	0.23-1.63 (1.04)7	0.02-0.11 (0.06)
7	0.89-9.02 (5.03)	1.97-09.52 (5.64)	0.05-0.10 (0.08)	0.02-0.09 (0.05)	0.1-0.99 (0.52)	0.03-0.08 (0.05)

Table 2: Concentration (mg l^{-1}) of trace metals in water samples using XRF

Location	Mn	Fe	Pb	Cr	Zn	Cu
1	0.32-0.76 (0.46)	1.15-6.05 (3.44)	0.10-0.17 (0.11)	Nd-0.01 (0.01)	0.30-0.69 (0.42)	0.02-0.10 (0.06)
2	0.13-0.54 (0.29)	0.17-1.05 (0.58)	0.07-0.13 (0.10)	Nd-0.35 (0.10)	0.04-1.54 (0.47)	0.03-0.12 (0.700)
3	0.14-0.56 (0.32)	1.29-5.32 (2.63)	0.07-0.24 (0.12)	Nd-0.06 (0.01)	0.03-1.08 (0.23)	0.03-0.09 (0.06)
4	0.56-0.68 (0.57)	0.63-2.13 (1.35)	0.05-0.15 (0.08)	Nd-0.12 (0.02)	0.03-0.21 (0.13)	0.02-0.08 (0.04)
5	0.07-0.66 (0.28)	3.06-4.29 (3.46)	0.05-0.21 (0.13)	Nd-0.29 (0.05)	0.06-1.64 (0.50)	0.03-0.10 (0.06)
6	0.10-0.54 (0.32)	!.39-2.90 (1.98)	0.04-0.14 (0.09)	Nd-0.01 (0.01)	0.04-1.23 (0.41)	0.03-0.12 (0.05)
7	0.07-0.56 (0.34)	0.46-2.86 (1.67)	0.03-0.11 (0.06)	Nd-<0.01 (<0.01)	0.03-0.18 (0.08)	0.04-0.10(0.06)

ND: below detection limit

Table 3: Maximum allowable concentrations (mg l^{-1}) of trace metals in drinking water against average trace metal concentration in Asa river water

Metals	WHO	EPA	Canadian	SouthAfrican	Asa river
Mn	0.10	0.50	0.05	0.05	0.89-9.76
Fe	0.30	0.10	0.30	0.10	0.76-24.06
Pb	0.05	-	0.05	0-10 μg L^{-1}	0.00-0.33
Cr	0.05	-	0.05	-	0.00-2.10
Zn	5.00	5.0-15.00	5.00	3.00	0.09-1.63
Cu	1.00	0.05-1.50	0.05	0-1.00	0.01-0.14

WHO and Candian standards were culled from: Water quality assessments, UNESCO/WHO/UNEP, 1992; EPA standards were from;"Environmental Protection Criteria 1972", Washington D.C., 1973; South African standards were from: Department of Water Affairs and Forestry (1996c) South African water quality guidelines

Table 4: Normalization of total trace metal concentrations in water

Location	Mn	Fe	Pb	Cr	Zn	Cu
1	1	2.63	0.03	0.01	0.17	0.03
2	1	2.31	0.02	0.02	0.17	0.02
3	1	2.80	0.03	0.01	0.13	0.01
4	1	1.03	0.02	0.004	0.07	0.01
5	1	1.52	0.03	0.01	0.06	0.01
6	1	1.68	0.02	0.01	0.19	0.01
7	1	1.02	0.02	0.01	0.10	0.02

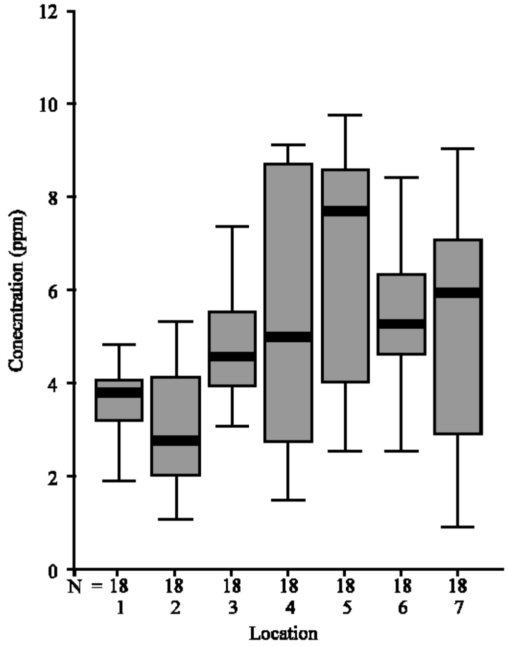

Fig. 1: Boxplot showing the range and mean concentration of Mn in Asa River water over 18 months sampling period

The variation of heavy metals concentrations over the eighteen months of sampling across the seven locations are illustrated in Fig. 1-6. The trend in the variation of Mn concentration appears to follow the same pattern appear to follow basically the same pattern with the amplitude of variation being almost the same for all the locations suggesting a natural source. From the boxplot Fig. 1, iron was found not to have regular variation across location. A statistical analysis carried out showed significant variations across location and time suggesting natural and anthropogenic input. Lead, chromium, zinc and copper were also found to vary significantly across time suggesting some anthropogenic inputs. Aluminium, manganese and iron have been used by some researchers to normalize heavy metal data (Helmke *et al*., 1995; Loring, 1991). Normalization is carried out to differentiate background levels and anthropogenic sources. Table 4 is the result obtained using Mn to normalize.

The result confirms anthropogenic inputs for Pb, Cr, Zn and Cu. From the result, Fe in locations 4 and 7 are found to be basically from natural sources. Location 4 is behind a bottling company while location 7 is located at an outskirt far from the busy activities of the town. The basic practice here is farming.

The two methods of analysis, AAS and XRF were found to exhibit no significant differences in

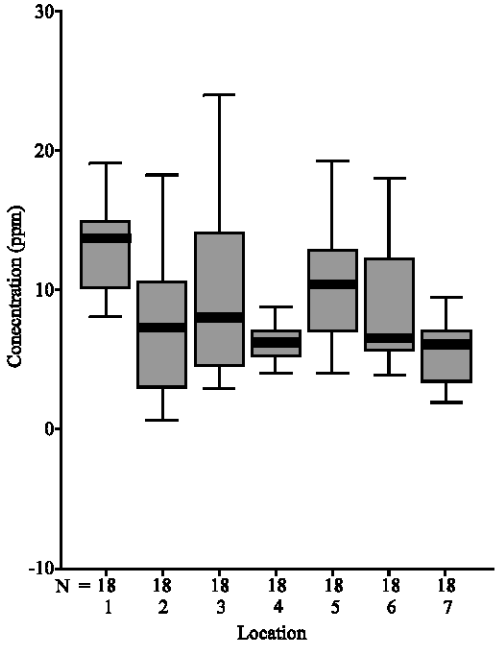

Fig. 2: Boxplot showing the range and mean concentration of Fe in Asa River water over 18 months sampling period

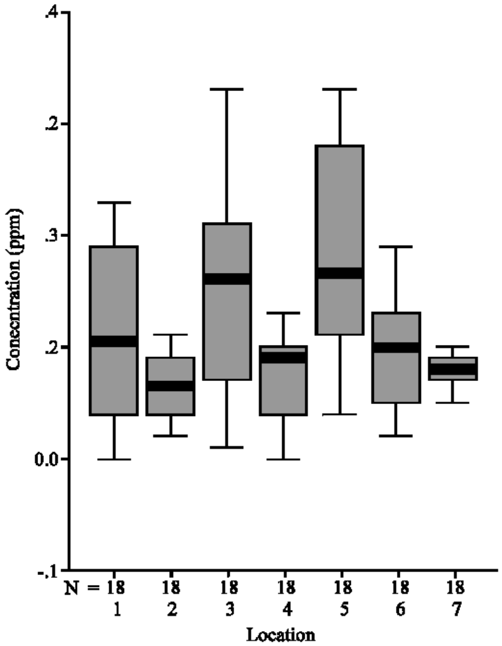

Fig. 3: Boxplot showing the range and mean concentration of Pb in Asa River water over 18 months sampling period

concentration for metals that are confirmed to have basically anthropogenic sources. For Mn and Fe that

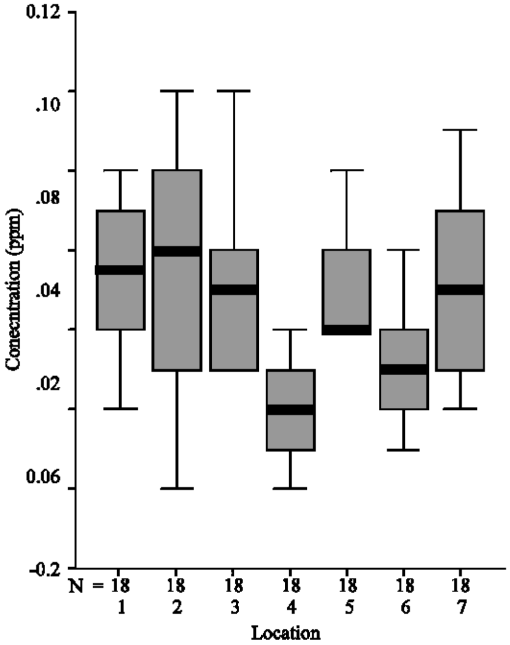

Fig. 4: Boxplot showing the range and mean oncentration of Cr in Asa River water over 18 months sampling period

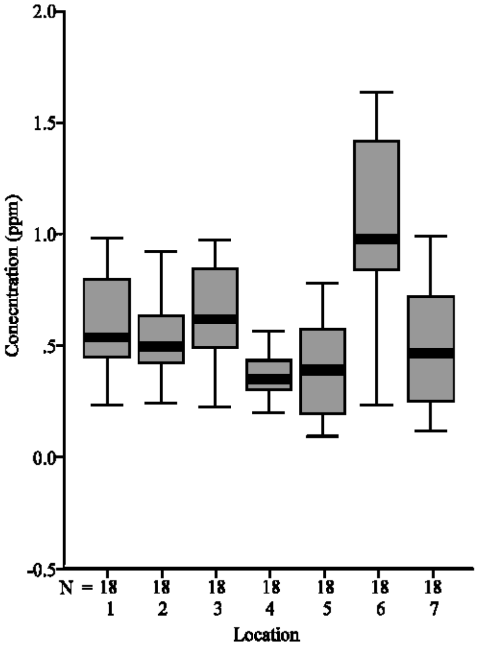

Fig. 5: Boxplot showing the range and mean concentration of Zn in Asa River water over 18 months sampling period

have natural inputs basically, significant differences were observed using the two methods. The reason suggested

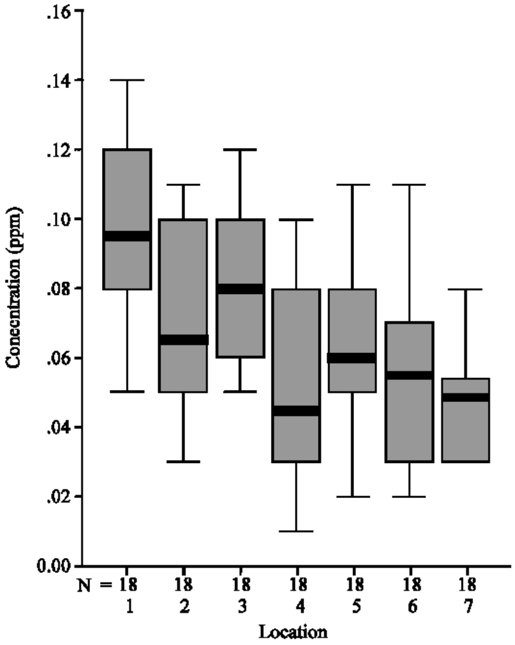

Fig. 6: Boxplot Showing the range and mean concentration of Cu in Asa River water over 18 months sampling period

for this is the fact that, while the samples were digested prior to AAS analysis, the samples used for the XRF analysis did not undergo any prior treatment to anlysis. The metals of natural origin are suggested to be trapped in the macropores and therefore not readily available for detection using the XRF technique. The XRF however offered the added advantage of knowing the other metals present at trace and ultra trace levels without a need for change of lamps as in AAS before detection.

Depending on the objectives, either AAS or XRF could be used for water analysis. While ASS would be a better option for qualitative analysis of water samples, the XRF could be employed for gross analysis.

ACKNOWLEDGEMENT

I would like to appreciate the Association of African Universities (AAU) for financial assistance under the small grants for thesis and dissertation. I am also grateful to Prof H.B Olaniyi of the Department of Physics and Dr A.O Oladipo, Mr A Ajele of the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife. Nigeria, for the assistance rendered in running the XRF and AAS, respectively.

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