

Full Length Research Paper

Some trace metal altitudes determination in Asa River using AAS and XRF modus operandi

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The determination of Fe, Mn, Pb, Zn, Cr and Cu concentrations in Asa River using Atomic Absorption Spectrophotometry (AAS) and X – ray fluorescence (XRF) is discussed. Statistical analysis showed there was no significant difference in the concentrations of Cr, Zn, Pb and Cu using the two techniques but significant differences were observed at 5% probability level for Mn and Fe. This was 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. The boxplots were carried out using SPSS and the statistical analysis using ANOVA.

Key words: Atomic Absorption Spectrophotometry, X – ray Fluorescence, micro –particles.

INTRODUCTION

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. Water pollution arising from the presence of foreign substances (organic, inorganic, bacteriological or radiological) which tends to degrade the quality of water (Salami, 2003) has become a serious concern today. These foreign substances in water set the physical and chemical parameters of the water. Some of them may be toxic to the aquatic ecosystem while others may constitute nutrients for aquatic microorganisms (Boukori et al., 1999).

The AAS and XRF techniques have been used extensively individually to determine trace metal levels in water. X – ray fluorescence is able to identify some elements which could not be detected using the AAS technique. Several elements can be identified at the same time using the XRF unlike AAS that requires that lamps be changed for every element to be determined (Eksperiandova et al., 2002).

The Asa River constitutes the bulk of water being used in Ilorin and its environs either treated or otherwise. Somewhere along the course of the River is Asa dam where the water is treated and sent to the public for use.

However there are some industries and establishments located along the course of the River in Ilorin that empty their waste discharges into this river either treated or otherwise. There is conspicuously a soap and detergent Industry, two beverage industries, a major hospital, a major market and a lot of farm practices are carried out along the bank of the River, to mention a few.

MATERIALS AND METHODS

Sample collection and preparation

Water samples were collected from seven different locations along the river based on the ease of accessibility to the river and human activities around the location. The sampling was carried out every month for eighteen months. The water samples were collected in two litre polyethylene bottles. Samples for AAS analysis were acidified prior to analysis with a few drops of HNO₃ to keep the metals in solution.

Detection of Analytes

Florescence X-rays from the samples were detected using a Si (Li) detector (resolution = 175 eV). 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

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

| Mn | Fe | Pb | Cr | Zn | Cu |
|-----------------------|-------------------------|----------------------|----------------------|----------------------|----------------------|
| 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) |
| 1.03 – 5.31 (3.13) | 0.76 – 18.29 (7.26) | 0.02– 0.11 (0.07) | 0.00– 1.10 (0.06) | 0.24– 0.92 (0.54) | 0.03– 0.11 (0.07) |
| 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) |
| 1.47 – 9.12 (5.46) | 4.09 – 8.84 (6.16) | 0.00– 0.13 (0.08) | 0.04 (0.02) | 0.20– 0.56 (0.36) | 0.01– 0.10 (0.05) |
| 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) | 0.02– 0.11 (0.06) |
| 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) | 0.02– 0.11 (0.06) |
| 0.89 – 9.02 (5.03) | 1.97 – 9.52 (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. Range and means of trace metal concentrations (mg l^{-1}) in water across sampling location determined by 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) | 1.39 – 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

using QXAS software from International Atomic Energy Agency (IAEA) Vienna, Austria.

The water sample was shaken for 30 s after which 1 cm^3 of sample was pipetted into a small PTFE vessel and mixed with the solution containing Ga as internal standard ($1 \mu\text{g ml}^{-1}$). 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. This was followed by elemental analysis using Alpha 4 AAS Chem Tech Analytical U.K with graphite atomizer. The analytical quality involved triplicate analysis of the 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 determination. For the XRF, the standard reference material (SRM) used in the XRF was prepared by IAEA, Vienna, Austria.

RESULTS

The trace metal concentration levels determined using the AAS and XRF techniques are shown in Tables 1 and 2 and some known standard concentration levels for metals compared to the results obtained is given in Table 3.

WHO and Canadian standards were culled from: Water

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

| Metal | WHO | EPA | Canada | South Africa | Asa river (AAS) |
|-------|------|-------------|--------|------------------------|-----------------|
| 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 $\mu\text{g/l}$ | 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 |

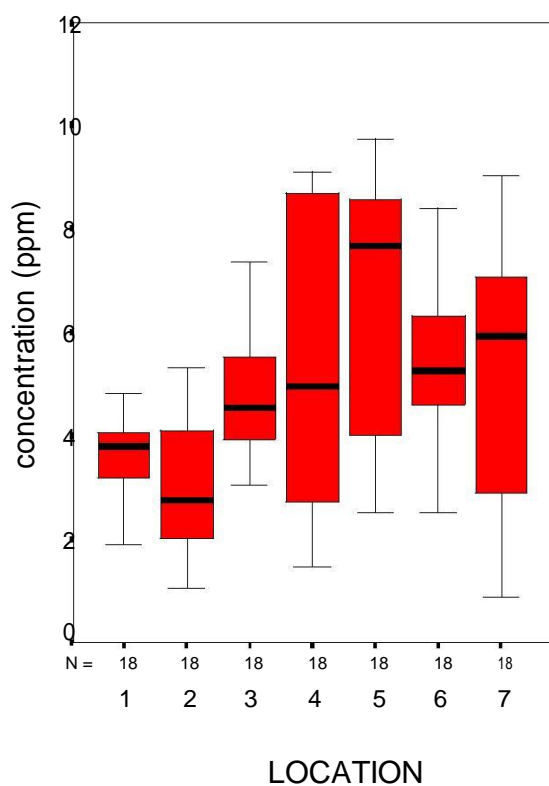


Figure 1. Boxplot Showing the range and mean concentration of Mn in Asa River water over 18 months sampling period.

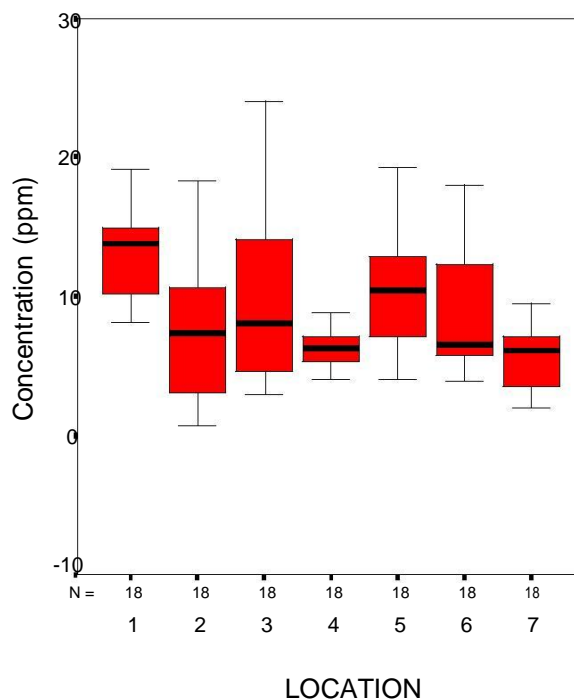


Figure 2. Boxplot Showing the range and mean concentration of Fe in Asa River water over 18 month sampling period.

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.

DISCUSSION

The variation of heavy metals concentrations over the eighteen months of sampling across the seven locations

are illustrated in Figures 1 – 6 above. The trend in the variation of Mn concentration appears to follow the same pattern with the amplitude of variation being almost the same for all the locations suggesting a natural source. From the boxplot Figure 2, 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 (Loring, 1991; Helmke et al., 1995; Hester, 1995). Normalization is carried out to differentiate background levels

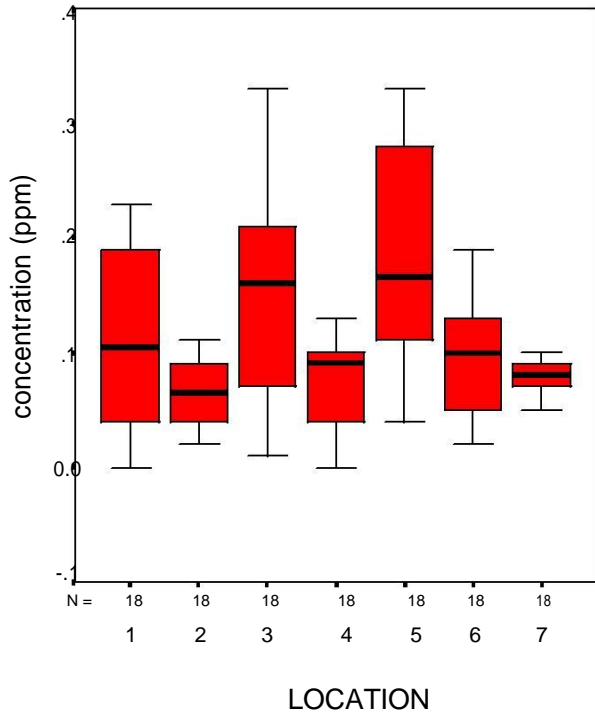


Figure 3. Boxplot Showing the range and mean concentration of Pb in Asa River water over 18 month sampling period.

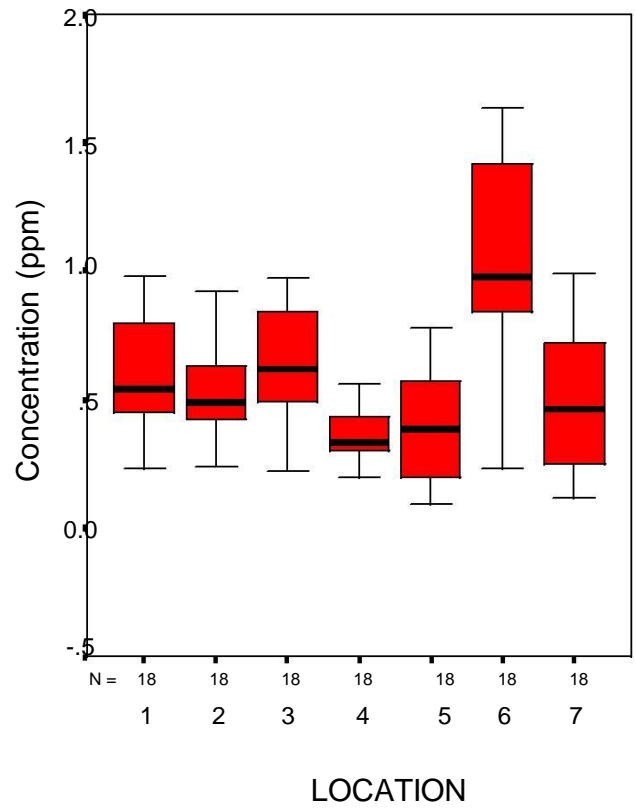


Figure 5. Boxplot Showing the range and mean concentration of Zn in Asa River water over 18 month sampling period.

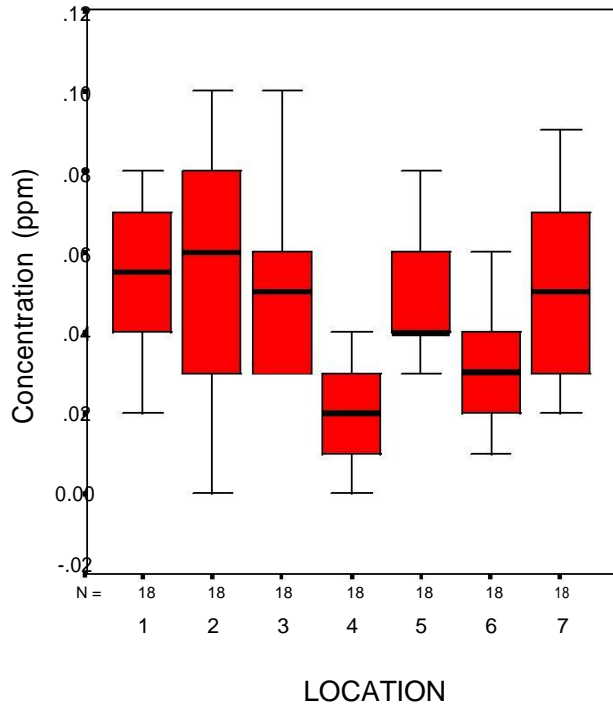


Figure 4. Boxplot Showing the range and mean concentration of Cr in Asa River water over 18 month sampling period.

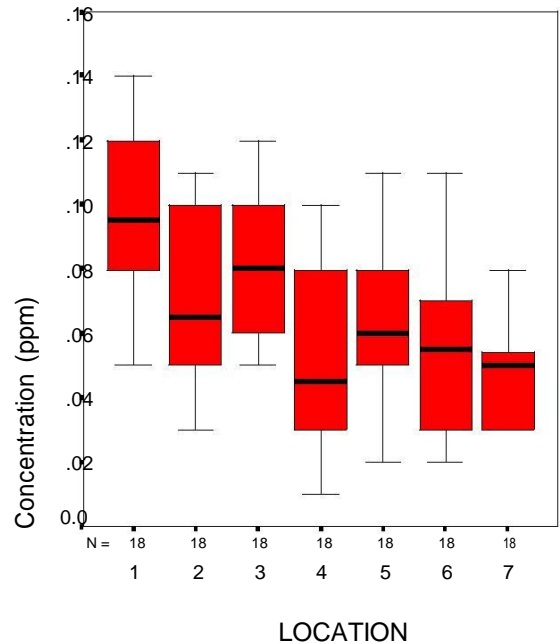


Figure 7. Boxplot Showing the range and mean concentration of Cu in Asa River water over 18 months sampling period.

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 |

and anthropogenic sources. Table 4 is the result obtained using Mn to normalize.

The result confirms anthropogenic inputs for Pb, Cr, Zn and Cu. 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 a distance far from the busy human activities in the town. The basic occupational practice here is farming.

The two methods of analysis, AAS and XRF were found to exhibit no significant differences in concentration for metals that are confirmed to have basically anthropogenic sources. For Mn and Fe that have natural inputs, significant differences were observed using the two methods. The reason suggested 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 analysis. The metals of natural origin are suggested to be trapped in the micropores 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.

Depending on the objectives, either AAS or XRF could be used for water analysis. While AAS would be a better option for qualitative analysis of water samples, the XRF could be employed for gross analysis. The boxplots were carried out using SPSS and the statistical analysis using ANOVA.

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