

# Investigation of the extent of Heavy Metal Pollution in Sediments and Sludge Using Atomic Absorption Spectroscopy (AAS)

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**Abstract** The method of Atomic Absorption Spectroscopy has been employed to analyze three heavy elements; Cu, Fe and Mn in cored samples from the underlying sediments from Ahmadu Bello University Water Dam. Additionally, the variations observed for Fe and Mn further showed the capability of the AAS technique to distinguish small difference in concentrations of these elements in samples collected from nearly the same environment. By the results presented in this work for Mn, Fe and Cu, the chemical baseline data have been further enriched for these elements in the A.B.U Water Dam.

**Keywords** Trace Element, Atomic Absorption Spectroscopy, Heavy Metals, Sediments, Pollution, Water Dam

## 1. Introduction

Heavy metals are considered as a group of major pollutants of marine ecosystem, particularly those elements which are toxic to marine organisms and human beings of which As, Cd, Fe, Cr, Ni, Hg, Se, Zn, Cu and Mn are generally held to be most important.

In the assessment of the pollution situation of these elements in the source of water supply to Ahmadu Bello University Community, in Zaria, Nigeria, knowledge of their present levels in the sediment and suspended matter (sludge) of River Kubanni is necessary. Besides, the analysis of heavy metals in the sediments underlying the A.B.U Water Dam is important as it will help enrich the baseline data for the area under study. Three of heavy metals, i.e. Cu, Mn, and Fe, whose cathode lamps are readily available, due to the researchers' funding limitation, were eventually analyzed in 34 sediment and 3 sludge samples.

Atomic absorption spectroscopy requires the following two essential conditions:

- A source of electromagnetic radiation of the resonance frequency i.e. light which can be absorbed by atoms in the ground state.
- A population of ground state atoms able to absorb the light of the correct resonance frequency.

When a magnetic light wave of energy

$$E = E_0 \exp[i(\omega t - kx)] \quad (1)$$

Where  $\omega = 2\pi\nu$  = angular frequency

$K = 2\pi/\lambda$  = wave number

travels through an absorbing sample with absorption coefficient  $\alpha$  and length  $L$ , the intensity  $I_0$  of the incident wave decreases to:

$$I = I_0 \exp(-\alpha L) \quad (2)$$

If  $\alpha L \ll 1$ ,

The relative attenuation can be expressed as

$$\exp(-\alpha L) = 1 - \alpha L$$

Therefore

$$I = I_0(1 - \alpha L)$$

hence

$$\alpha L = I_0 - \frac{I}{I_0} \quad (3)$$

In order to measure  $\alpha$ , one has to measure a small difference of two large quantities, which becomes less and less accurate with decreasing  $\alpha L$ .

In AAS, lines are classified to their integrated coefficients.

Absorbance  $A$  is defined as:

$$A = \log(I_0/I) \quad (4)$$

At a time temperature  $T$  (in K), the ratio of the number of atoms  $N_u$  in an excited (upper) state 'a' to the number of atoms  $N_i$  in the ground state is given by the Maxwell-Boltzman expression;

$$\frac{N_u}{N_i} = \frac{g_u}{g_i} \exp[-(E_u - E_i)/KT] \quad (5)$$

Where

$E_u$  and  $E_i$  are the energies of the excited and ground states respectively.

$g_u$  and  $g_i$  are the statistical weights of the respective states.  $K$  is the Boltzman's constant.

Putting equation (9) in equation (12) we have;

$$A = \log \left[ \frac{I_0}{I_0 \exp(-\alpha L)} \right] = \log e^{\alpha L} = \alpha L \log e$$

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$$\text{Therefore } A = 0.4343 \alpha L \quad (6)$$

This implies that the abundance is directly proportional to the absorption coefficient and therefore to the concentration of the analyte.

Without dilution;

$$\text{Conc. of element of interest} = \frac{\text{amount in ppm(\% of sol.)}}{\text{weight of sample (g)}}$$

## 2. Methodology

Samples were collected during the dry season by making use of plastic cylindrical covers. This was done by squeezing the cover to sediments under water until the desired depth was achieved. This was done at different sample points across the dam labelled appropriately. The sediments collected were then sectioned into plastic bags according to depths and taken to the laboratory where the samples were kept in the oven at 60°C for one week until the samples were completely dried. Sludges were also collected from the base of the sedimentation tank from the water treatment section of the dam. The sludges were collected into plastic bags and kept in the oven alongside the sediments to ensure dryness. Dried samples were then homogenized by grinding using the Agate Mortar and pestle. Homogeneity of the samples was further ensured by making each sample to undergo traditional quartering technique by making each sample to go through several sub-divisions. The grinded samples were then kept in sealed bottles awaiting analysis procedures. The grinding was done until fine powder of ca 150 – 200 mesh was obtained. 1.0 gramme of each sample were weighted into PTEE (Polytetrafluoroethylene) beakers and moistened with distilled water.

In this study, interest is not based on silicon determination hence the method of dissolution is one based on Hydrofluoric acid addition with the help of which silicon can be lost from the matrix. It is of advantage if silicon is to be removed during the acid attack procedure such advantages include the following:

(i) Resultant solutions are far more stable. Silica bearing solutions tend to hydrolyze and precipitate on standing for long period.

(ii) Silicon and fluorine cause interference with some photometric determinations.

(iii) The corrosive action of HF is removed, permitting manipulations with normal laboratory glass ware.

(iv) Such procedures reduce the salt content of resultant solutions. This is important as the method of atomic absorption spectroscopy is being used for determinations.

5ml of Nitric acid was then added to the sample in the PTEE beaker after which 10ml of Hydrofluoric acid was then added. The resulting solution was then placed on a sand bath at about 60°C in a vacuum cupboard until dryness was achieved. In some cases, fresh additions of the reagents were necessary for complete loss of silica. The reason for the addition of distilled water and Nitric acid is to soften the matrix and to reduce a likely vigorous reaction between the HF and

the sample.

The dried sample were then recovered from the vacuum cupboard and made into solution by adding concentrated Hydrochloric acid and distilled water 1:1 (v/v). It was ensured that all samples were taken up into solution and kept in labelled plastic bottled and ready for analysis.

### 2.1. Preparation of Standard Solution for AAS

A single element standard solution was prepared for each element of interest. This was done by dissolving the high-grade metal or appropriate compound of the element in a small volume of conc. HNO<sub>3</sub> acid. About 1mg/ml (1000ppm) each of Cu, Mn and Fe standard solution was prepared as stocks from which subsequent dilutions suiting the instrument calibration ranges for the elements of interest were made. The standard used as check for the analysis using AAS is the International Atomic Energy Agency's (IAEA) Lake Sediment (SL). The digestion and dissolution was also done for this standard as was done for the samples. The concentration of elements in the IAEA SL- standard is shown in Table 3.

## 3. Results

AAS Analysis was done for three elements; copper, manganese and Iron. The table below shows the concentration ranges and the corresponding wavelength for each element being analysed.

**Table 1.** Conc. Range and Wavelength for Mn, Fe and Cu

Element	Range in (ppm)	Wavelength Å
Mn	1.5 – 3.0	2795
Fe	2.5 – 5.0	2483
Cu	2.5 – 5.0	3244

## 4. Discussion

The result for the concentration ranges of Copper, Iron and Manganese in the sediments, sludge and in the Standard Reference Material (SL-1) are presented in Tables 2 and 3. From the tables, one observes that the concentrations for Cu, Fe and Mn in both the sludge and underlying sediments are less than those for the Standard Reference Material (SL) which has been prepared to represent sediments exhibiting normal concentrations for elements in the list.

There is therefore no obvious pollution by Cu, Fe and Mn in the sediment. In other words, the Cu, Fe and Mn contents belong to the natural background values.

3-D plots for the distribution for the three elements are displayed in Figures 1, 2 and 3. The result for the distribution of Iron in A.B.U Water Dam is shown in Table 2 and the 3-D plots for the distribution is shown in Figure 1. From the plot, it is observed that the highest concentration of Iron is along the North-Western end of the dam. This may be due to accumulation of more waste taking place along that side of the dam. The result for the distribution of Manganese in A.B.U

Water Dam is shown in Table 2 and the 3-D plot for the distribution is shown in Figure 2. From this interesting plot, the concentration of Manganese is observed to be higher at the source end of the Dam which could be due to the sudden slowing down in the speed of the water thereby causing it to deposit most of its contents at the entry point.

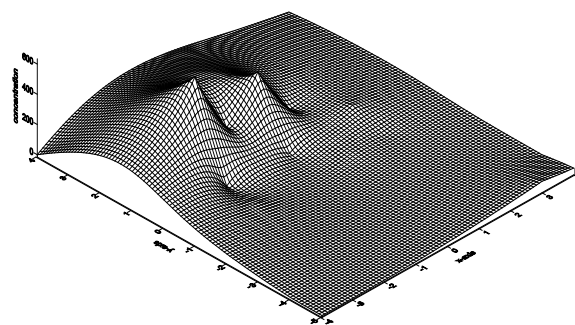
From figure 3, it is observed that the concentration of Copper across the dam is almost constant except for very few troughs or variations.

**Table 2.** Distribution of Copper at various Sample Points

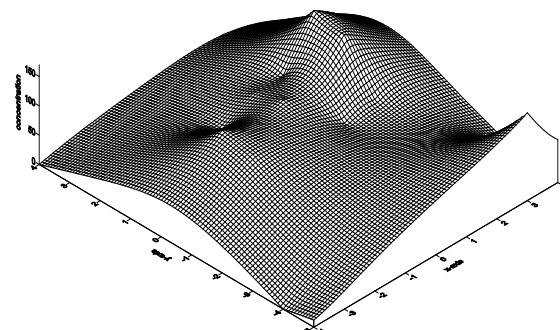
Sample	Depth (cm)	Conc. of Cu (ppm)	Conc. of Fe	Conc. of Mn
A1	2.0	10.0	36.5	110
A2	4.0	10.0	38.0	130
A3	6.0	10.0	24.2	100
B1	2.0	10.0	9.5	110
B2	4.0	10.0	29.5	90
B3	6.0	10.0	12.2	130
C1	2.0	0.0	15.5	70
C2	4.0	10.0	8.5	60
C3	6.0	10.0	14.8	90
D1	2.0	10.0	11.0	80
D2	4.0	10.0	26.0	60
D3	6.0	10.0	35.0	60
E1	2.0	10.0	27.5	120
E2	4.0	10.0	24.9	60
F1	2.0	0.0	635.0	80
F2	4.0	0.0	224.0	170
G1	2.0	10.0	179.0	60
G2	4.0	10.0	603.5	50
G3	6.0	0.0	23375.0	60
H1	2.0	10.0	430.5	90
H2	4.0	10.0	4890.0	80
H3	6.0	10.0	777.5	70
H4	8.0	10.0	3375.0	60
I1	2.0	10.0	61.5	90
I2	4.0	10.0	37.5	80
I3	6.0	10.0	109.5	100
J1	2.0	10.0	-	170
J2	4.0	10.0	54.5	80
K1	2.0	10.0	91.5	160
K2	4.0	10.0	64.5	180
K3	6.0	10.0	55.0	150
L1	2.0	10.0	60.5	150
L2	4.0	10.0	102.0	170
L3	6.0	10.0	99.0	100

**Table 3.** Sludge and Lake sediment concentration for the elements

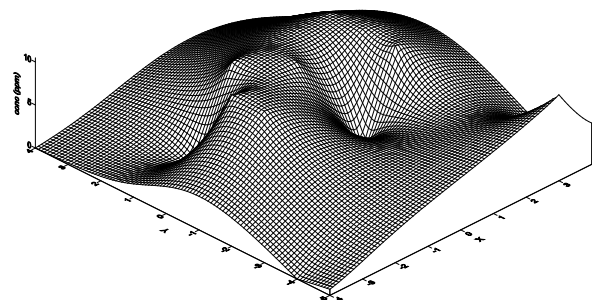
	Cu(ppm)	Fe(ppm)	Mn
S1	20	5.0	130
S2	10	0.0	110
S3	20	-	-
SS1	10	530	-
SS2	675	-	-
SLI - 1	0.0	375	4750
SLI - 2	0.0	-	2750
SLI - 3	-	-	3000
SLI - 4	0.0	760	4000
SLI - 5	0.0	440	3000
SLI - 6	0.0	430	3000
SLI - 7	0.0	740	3250



**Figure 1.** 3D plot of the Fe Distribution in ABU Water Dam



**Figure 2.** 3D plot of the Mn Distribution in ABU Water Dam



**Figure 3.** 3D plot of the Cu Distribution in ABU Water Dam

## 5. Conclusions

The overall conclusion that could be drawn from this work is that for the three elements Copper, Iron and Manganese which were analysed in the underlying sediment, there seems

to be no serious indication of pollution arising from their accumulation over the period of this study.

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