Comparison of Some Trace Element Levels Using Two Analytical Methods in Soils and Water from Dadinkowa Dam, Gombe State, Nigeria

A.U. Maigari* and Sambo, M.S.
Department of Chemistry, Federal College of Education (Tech.), P.M.B. 60, Gombe, Gomber State, Nigeria

Abstract: Levels of iron, manganese, copper, lead, cadmium, cobalt, nickel and zinc were determined in soils and water from Dadinkowa dam in Yamaltu / Deba Local government area of Gombe State Nigeria using complexometric analysis and atomic absorption spectroscopy. The results obtained showed that iron had the highest concentration in the soil when analysed by both methods while lead had the lowest concentration for both methods. The trend in concentration of the elements in soil determined by AAS was found to be Fe> Zn> Mn> Cu> Co> Ni> Cd> Pb. While the trend in concentration of the metals in soil for complexometric analysis was found to be Fe> Mn> Zn> Cu> Ni> Co> Cd> Pb. Wilcoxon Signed ranks test was used to analyse for any significant difference between the means of the elements determined by both two analytical methods. The results obtained showed zinc had the highest concentration when determined by complexometric analysis and nickel had the lowest concentration. For AAS, copper had the highest concentration in water while cobalt had the lowest concentration. For water, the trend for complexometric analysis was in the order Zn > Cu > Mn > Fe> Co > Cd > Pb > Ni. For AAS, the trend was found to be Cu > Fe > Zn > Mn > Pb > Ni > Cd > Co. Wilcoxon Signed ranks test was used to analyse for any significant difference between the means of the elements determined by both two analytical methods.

Keywords: atomic absorption, complexometric analysis, metals, analytical methods, wilcoxon sign ranks test

*Corresponding author Email address: aishamaigari@yahoo.com

INTRODUCTION

On-going researches in chemistry and other environmental subject areas are concerned with the study of possible pollution effects arising from man's activities on the environment such as mining, excessive fertilizer and pesticide use, irrigation and pollution by waste materials. Researchers are also probing into the health effects of the pollution on man as a result of using ground and surface waters, plants and livestock exposed to these pollutions. Trace metal pollution is widely reported by Itumoh et al., (2011) as one of the profound alteration of our environment. However, anthropogenic activities like mining and other industrial activities are recognized as some of the sources of metals in the environment (Anglin-Brown *et al.,* 1995; Kosmus *et al.,* 1990 and Ancalucia, 1999) and metals released to the atmosphere from such activities travel for long distances and are deposited onto soil, vegetation and water. These metal ions, which are not degraded, persist and are retained in the ecosystem indefinitely (Monperrus *et al.,* 2005; Pasquini, 2006). Interest in water assessment is due to the enormous importance of water to all categories of living things. It is necessary for the

healthy development of man, animals and plants. Developing countries are witnessing changes in ground water which constitute a major source of portable water. The preference of ground water to surface water must be due to the purification of the latter prior to distribution (McDovel *et al.,*2002). Drinking water plays an important role in the bodily intake of true elements by humans. Even though some trace elements are essential to man, at elevated levels, essential as well a non essential elements can cause morphological abnormalities; reduced growth, increased mortality and mutagenic effects (Adeyeye and Abulude, 2004; Asaolu, 2002). The toxicity of the metals is dependent on their solubility and this in turn depends on the pH and the presence of different types of anions and other cations. Water pollution has been a subject of active investigation for a long time due to their perceived hazardous effects of trace elements (Adeyeye, 2000).

The process of determination of trace metals in soils requires matrix destruction which depends on the dissolution processes and digestion technique was performed through decomposition of complex substance into simple salts and volatile gases under acid solution.

In combined analytical methods, the decomposition of solid samples is an important stage whereby the sample is measured in an aqueous solution and by means of the wide array of analytical methods available such as complexometric analysis, atomic absorption spectroscopy, inductively coupled plasma etc. These combined analytical methods are

favoured for multi element analysis of samples at a very short period. But there is little comparative information available between combined analytical methods, especially complexometric analysis and atomic absorption spectroscopy (Abulude *et al.,* 2006).

The comparative study between ICP-OES and UV-Vis spectrophotometer for detection of heavy metals in soil irrigated with secondary treated wastewater demonstrated the higher trends of heavy metals levels obtained in UV-Vis spectrophotometer as compared to ICP-OES suggesting that lots of interferences with other elements during analysis under UV-Vis spectrophotometer Abulude *et al.,*(2006).

Another study by Pereira *et al.,* (2011) showed no significant difference in the determination of Ca^{2+} and Mg^{2+} between ISE-CT and conventional complexometric titration and flame atomic absorption spectroscopy at 95% confidence level.

GEOLOGY AND RELIEF

Gombe state is part of the central Nigeria highlands; but the flat landscape in the northern and southern parts of the state have isolated hills. While the elevation of the plain is at 600m above sea level, the hills reach between 700m and 800m. The Gongola river the main drainage system, running approximately north south towards the Benue River basin, but with principal tributaries draining from west to east into River Gongola. Gombe state is geologically a part of the upper benue trough, although the state is an entity of its own. However, the state constitutes a major sedimentary basin, with a fill of about 6000m of cretaceous tertiary sedimentary rocks. These rocks are well exposed throughout the state and have been recently explored for oil and gas but without success. The eastern part of the state is geologically older than the west.

River Dadinkowa is found in the eastern part of the state in Yamaltu Deba Local Government area of Gombe State with co-ordinates 10^0 19' 19"N and 11^0 28'54"E. It is a tributary of river of River Gongola, the major river that traverses Gombe state in the north and east through Dukku at Gombe Abba, Nafada and all the eastern LGAs to join River

Benue at Numan. It is the sixth longest river in Nigeria, being about 530km, much of which is in Gombe state. Soils in this area are shallow to deep loamy, sandy clay, loam and vertisols with cracking clays that have weathered from shales.

Dadinkowa dam has a capacity of 800million m^3 with a surface area of 300km^3. It has an irrigation capacity of 44000ha of fertile land for the production of maize, rice and groundnuts twice a year; and vegetables almost year round. Its hydroelectric power generation is expected to be 130GWH. It has the capacity to produce an estimated 20000 tonnes of fresh fish from its artificial lake when fully harnessed. It is the major source of water supply to Gombe town and villages downstream (Maigari *et al.,* 2016).

METHODOLOGY
Sample collection
Water and soil samples were collected between December and February, 2011 early in the morning. Water was sampled using a plastic 2 litre bottle which had been washed thoroughly with detergent, rinsed with distilled water and finally filled with the water, and labelled.

Soil samples were taken near each of the sites in replicates and stored in polythene bags before being transported to the laboratory after proper labelling. Soil samples were air-dried between 24-36 hours and later sieved through a 2mm mesh standard sieve and stored for analysis.

Materials
All reagents used were of analytical grades and deionised distilled water was used for all reagents preparations.

Methodology

Digestion of Soil Samples for Heavy Metals Determination
Two grams of the oven dried roadside soil samples were weighed into a led washed glass beaker. Soil samples were digested by the addition of 20 cm3 of aqua regia mixture of HCl and HNO_3, ratio 3:1) and 10 cm^3 of 30% H_2O_2. The H_2O_2 was added in small portions to avoid any possible over flow leading to loss of material from the beaker. The beakers were covered with watch glass, and heated over a hot plate at 90°C for two hours.

The beaker wall and watch glass were washed with distilled water and the samples were filtered out to separate the insoluble solid from the supernatant liquid. The volume was adjusted to 100 cm^3 with distilled water.

Elemental Analysis of Samples
Determination of Fe, Mn, Cu, Pb, Co, Ni and Zn were made directly on each final solution using Buck Scientific Atomic Absorption spectroscopy (AAS).

Calibration Solution
Standard solutions of each sample Fe, Mn, Cu, Pb, Co,Cd, Ni and Zn were prepared according to the manufacturer procedure for atomic absorption spectroscopy to be used.

Standard EDTA solutions
Disodium dihydrogen diethylenediamine tetraacetate (EDTA) of analytical reagent quality was used. The salt was purified by preparing a saturated solution at room temperature; by weighing 20g of the salt in 200cm^3 of water. Ethanol was slowly added until a permanent

precipitate appeared. The solution was diluted with equal volume of ethanol. The resulting solution precipitate was filtered through a sintered glass funnel, washed with acetone and then dried with diethyl ether. The precipitate was air dried at room temperature overnight in an oven at 80^0C for 24 hours. Solutions of EDTA of the following concentrations were prepared for the experimental work; 0.1M, 0.05M and 0.01M. These contained 37.224g, 18.612g and 3.7224g of the dehydrate per litre of solution in distilled deionised water respectively. The EDTA solution was then standardised by titration using neutralised zinc chloride [18].

Statistical Analysis
The data was statistically analysed using the SPSS version 16 software with a significance level of $p < 0.05$. All collected data were subjected to non- parametric Wilcoxon Sign ranks test.

Table 1: Mean (SD) trace element levels in soil determined by complexometric titration and AAS

ELEMENT	COMPLEXOMETRIC MEAN	AAS MEAN
Fe	11.44(0.13)	11.65(0.46)
Mn	10.46(0.16)	10.92(0.22)
Cu	3.43(0.39)	1.86(0.28)
Pb	1.28(0.01)	0.18(0.01)
Cd	0.50(0.01)	0.65(0.02)
Ni	1.43(0.18)	0.49(0.09)
Co	0.77(0.04)	0.54(0.08)
Zn	10.15(0.86)	11.36(0.19)

TABLE 2: Mean (SD) trace element levels in water determined by complexometric titration and AAS

ELEMENT	COMPLEXOMETRIC MEAN	AAS MEAN
Fe	0.33(0.06)	0.86(0.35)
Mn	0.42(0.09)	0.68(0.34)
Cu	0.73(0.10)	0.92(0.22)
Pb	0.02(0.01)	0.22(0.04)
Cd	0.03(0.02)	0.50(0.13)
Ni	0.03(0.00)	0.59(0.14)
Co	0.40(0.02)	0.48(0.07)
Zn	0.82(0.05)	0.83(0.21)

RESULTS

Iron had a mean of 11.65mg/kg when determined by AAS and 11.44mg/kg for complexometric analysis. Wilcoxon Signed ranks test performed at = 0.05 showed no significant statistical difference between the means of iron obtained by complexometric analysis and atomic absorption spectroscopy in soil from Dadinkowa dam with p= 0.225.

Manganese determined by AAS had a mean of 10.92 and complexometric analysis had a mean of 10.46mg/kg. But statistical analysis showed a significant statistical difference in the means of manganese determined by the two methods with p= 0.043 at = 0.05.

Copper had a mean of 3.43mg/kg when determined by complexometric analysis and a mean of 1.86mg/kg when determined by AAS. Statistics showed a significant statistical difference in the two means of copper determined by the two analytical methods with p= 0.043 at = 0.05.

Lead in soils from Dadinkowa dam were analysed by AAS and complexometric analysis and the means obtained were 0.18 mg/kg and 1.28 mg/kg respectively (Table 1). There was a significant statistical difference in the two means at = 0.05 and p= 0.043.

Cadmium concentration in soils from Dadinkowa dam had a mean of 0.65mg/kg with AAS and 0.50mg/kg for complexometric analysis. There was a significant statistical difference between the means of cadmium obtained by complexometric analysis and AAS with p= 0.043 at = 0.05.

Nickel had a mean of 1.43mg/kg with complexometric analysis and a mean of 0.49mg/kg with AAS. There was a significant statistical difference between the two means with p= 0.043 at = 0.05.

Cobalt had a mean of 0.76mg/kg when determined by complexometric analysis and a mean of 0.54mg/kg when determined by AAS. Statistics showed a significant statistical difference with p= 0.043 at = 0.05.

Soils from Dadinkowa dam had a mean zinc concentration of 11.36mg/kg when determined by AAS and a mean of 10.15mg/kg with complexometric analysis (Table 1). There was a significant statistical difference in the mean of zinc in soil in Dadinkowa dam determined by complexometric analysis and AAS with p= 0.043 at = 0.05.

WATER

Iron was determined by two analytical methods: atomic absorption spectroscopy and complexometric analysis. The mean of iron obtained by AAS in Dadinkowa was 1.88mg/l and the mean for complexometric analysis was found to be 0.02mg/l as shown Table 5. There was a significant statistical difference in the means obtained by the two methods as given by Wilcoxon signed ranks test with p= 0.043 at = 0.05.

Manganese had a mean of 0.42mg/l when analysed by complexometric analysis and a mean of 0.68mg/l with AAS. Statistics showed a significant difference with p= 0.043 at = 0.05.

Copper had a mean of 0.73mg/l when determined by complexometric analysis and 0.92mg/l with AAS. There was no significant statistical difference between the two means with p= 0.080 at = 0.05.

Table 2 shows that lead determined in water from Dadinkowa dam by AAS had a mean of 0.19mg/l while the mean for complexometric analysis was 0.02mg/l. There was a significant statistical difference in the means of lead determined by complexometric analysis and AAS with p= 0.43 at = 0.05.

Cadmium determined by AAS in water from Dadinkowa dam had a mean of 0.50mg/l and the mean for complexometric analysis was found to be 0.03mg/l (Table 2). There was a

significant statistical difference in the means of cadmium determined by complexometric analysis and AAS with p= 0.043 at = 0.05.

Nickel had a mean of 0.03mg/l when determined by complexometric analysis and a mean of 0.59mg/l with AAS. Statistical analysis showed a significant statistical difference with p= 0.043 at = 0.05.

Cobalt had a mean of 0.40 and 0.43mg/l when determined by complexometric and AAS respectively. There was no significant statistical difference with p= 0.109 at   0.05.

AAS determination of zinc in water from Dadinkowa had a mean of 0.83mg/l while the mean for complexometric analysis was 0.82mg/l. There was no significant statistical difference between the two methods used in determining zinc in water in Dadinkowa dam with p= 0.686 at = 0.05.

DISCUSSION

Eight trace elements namely iron (Fe), manganese (Mn), copper (Cu), lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co) and zinc (Zn) were determined in soils and water from Dadinkowa dam in Gombe State, Nigeria using complexometric analysis with EDTA and atomic absorption spectroscopy. The concentrations for the trace metals varied with the two analytical methods used in the determination. For complexometric analysis, iron (Fe) had the highest concentration of 11.44mg/kg. Manganese (Mn) had a concentration of 10.46, then zinc (Zn) with a concentration of 10.15mg/kg. Copper (Cu) had a concentration of 3.43mg/kg then nickel (Ni) with a concentration of 1.43mg/kg. Cobalt had a concentration of 0.76mg/kg, lead(Pb) came next with a concentration of 0.13mg/kg while cadmium had the least concentration of 0.05mg/kg. The trend of concentration of trace metals determined by complexometric analysis can be summarised as Fe> Mn> Zn> Cu> Ni> Co> Pb> Cd.

The trend of the concentration of these trace metals for atomic absorption spectroscopy had iron (Fe) with the highest concentration of 11.65mg/kg. Zinc (Zn) followed with a concentration of 11.36mg/kg. Manganese (Mn) had a concentration of 10.92mg/kg while copper (Cu) had a concentration of 1.86mg/kg. Cobalt (Co) had a concentration of 0.54mg/kg followed by nickel (Ni) with a concentration of 0.49mg/kg. Cadmium (Cd) had a concentration of 0.31mg/kg while lead (Pb) had the least concentration of 0.18mg/kg. The trend of concentration of trace metals determined by AAS can be summarised as Fe> Zn> Mn> Cu> Co> Ni> Cd > Pb.

Statistical analysis showed a significant difference between the mean concentrations of all the trace metals determined by the two methods except for iron (Fe) which showed no significant statistical difference in the two means.

For the concentration of trace elements determined in water by complexometric analysis, zinc (Zn) had the highest concentration with a mean of 0.82mg/l, the copper (Cu) with a concentration of 0.73mg/l. Cobalt (Co) had a concentration of 0.48mg/l and manganese (Mn) had a concentration of 0.42mg/l. Iron (Fe) had a concentration of 0.33mg/l while nickel (Ni) and cadmium (Cd) both had a concentration of 0.03mg/l. Lead (Pb) had the least concentration of 0.02mg/l. The trend of concentration of trace elements determined by complexometric analysis can be summarised as Zn > Cu > Mn > Co > Fe > Cd> Ni > Pb.

The concentration of these metals determined by AAS had copper (Cu) with the highest concentration of 0.92mg/l followed by iron (Fe) with a concentration of 0.86mg/l then zinc (Zn) with a concentration of 0.83mg/l. Manganese (Mn) had a concentration of 0.68mg/l then nickel (Ni) with a concentration of 0.59mg/l and cadmium (Cd) with a concentration of 0.50mg/l. Cobalt (Co) had a concentration of 0.48mg/l while lead (Pb) had

the least concentration of 0.22mg/l. The trend of concentration of metals determined by AAS can be summarised thus: Cu > Fe > Zn > Mn > Ni > Cd > Co > Pb.

Statistical analysis showed a significant difference in the means of concentration of iron, manganese, lead, cadmium and nickel determined by the two analytical methods.

But there was no statistical difference in the means of copper, cobalt and zinc determined by the two methods in water from Dadinkowa dam.

CONCLUSION

Determination of trace elements in water and soil from Dadinkowa dam in Gombe State, Nigeria was done using two analytical methods namely complexometric analysis and atomic absorption spectroscopy. The means obtained by these two methods were compared using wilcoxon sign rank test. There were significant differences in the means of all the elements determined in soil except iron while there were significant statistical difference in the means of iron, manganese, lead,cadmium and nickel determined by the two methods in water. There was no significant statistical difference in the means obtained in water for copper, cobalt and zinc.

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