Evaluation of Heavy Metal Status of Water and Soil at Ikogosi Warm Spring, Ondo State Nigeria.

[1]Adegoke J.A.; [2]Agbaje W.B.;And [3] Isaac , O.O.,

Abstract.

The concentration levels of selected heavy metals, (Cu, Cd, Zn, As and Cr) were determined in the soil (µg/g) and water (ppm) samples collected at Ikogosi Warm Spring, Ekiti State, Nigeria. After digestion, Atomic Absorption Spectrophotometer (AAS) was employed for the determination. The study area was at Latitude of $7^o\ 35^{'}\ 38.9^{''}$, Longitude of $4^o\ 58^{'}\ 52.6^{''}$ and at average elevation of 479m above mean sea level (msl). The average concentrations (µg/g) of the heavy metals in the soil are Cu (5.29), Cd (1.50), Zn (46.72), As (10.50) and Cr (339.78). The average concentrations (ppm) of the heavy metals in the water are Cu (4.8), Cd (0.15), Zn (4.17), Ar (0.57) and Cr (1.46). The mercury was below detection limit for both soil and water samples. In the overall, the average concentration of chromium is the highest in the soil with concentration of 339.78 µg/g (an average of 84.27%) and cadmium having the lowest with value of 1.50 µg/g (an average of 0.37%). When average concentration of heavy metal in the water was considered, copper had the highest level with concentration of 4.80ppm (an average of 43.01%) and cadmium had the lowest concentration with value of 0.15ppm (an average of 1.43%). Comparison of these results showed that, their mean levels are within the standard values obtained in Nigeria and some developed countries.

Key words: Soil, Water, AAS, Heavy metals, Average concentration.

Introduction

The incidence of heavy metal contamination from both natural (geogenic) and anthropogenic sources has increased concern about the health effect of chronic level exposures, particularly people living in urban environment who are more likely to be exposed to this threat. Natural and anthropogenic sources of soil contamination are widely spread and variable (Tahir et al, 2007). Heavy metals occur naturally in rocks. But most of the heavy metals occurrences in urban soils tend to originate from anthropogenic sources such as industrial, urban development and transport activities (Charlesworth et al, 2003, Strivastava et al, 2007). A number of studies (Lee et al, 2006, Yang et al, 2006, Kamarnicki, 2005) have suggested that, there is a possibility that, contaminated soil or dust, ingested either directly or indirectly as a result of hand to mouth activity, may represent a significant way of environment toxic metals to humans, with children representing the main sector of the population at highest risk. Children, especially toddlers, can easily ingest soil or indoor dusts unintentionally when they put contaminated toys in their mouths, pick up foods with dirty hands etc, thus making them susceptible to toxic metals poisoning. In addition, adults may also be exposed to similar threat since inhalation is the most common pathway for toxic metals to enter our body.

Water is regarded internationally as the most fundamental and indispensable of all natural resources. (Ashto and Seetal, 2002).

Interest in water analysis is due to enormous importance of water to all categories of living things. It is necessary for the healthy development of man, animals and plants (Abulude et al, 2007). Water plays an important role in the bodily intake of true element by human. Even though some trace elements are essential to man, at elevated levels, essential and non essential elements can cause morphological abnormalities: reduced growth, increase mortality and mutagenic effects (Nkono and Asubiojo, 1998, Asaolu, 2002). Also, heavy metals are important; some are physiologically essential for plants and animals, though, they exist in trace amount, they have a direct bearing on human health and agricultural productivity and many are significant pollutants in ecosystem throughout the world (Alloway, 1990).

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain, breaking down soils and releasing heavy metals into streams, rivers lakes and ground water. The concentrations of these heavy metals in sediments and water may be traced to the bed rock from which the sediments were derived through which the water flows (Ergin et al, 1991, Mantie et al, 1989).

Environmental water, such as river water, sea water, well water, is used for drinking or agriculture. Many are apprehensive about the influence on humans since substances such as heavy metals from the soil, the water or both, based on the fact that,

[1]Department of Physics, University of Ibadan, Nigeria, [2]Department of Chemical Sciences, Crescent University, Abeokuta, Nigeria, agbaj_ewb@yahoo.com [3]Department of Physics, Olabisi Onabanjo University, Ago-Iwoye, Nigeria

Ikogosi warm spring is a tourist centre which attracts people from different parts of the world. The objective of this   study is to determine the concentration of heavy metals (Cu, Cd, Zn, As and Cr) in the soil and water samples, establish the various anthropogenic sources of these heavy metals by comparing the results obtained with certain standard and suggest remedial ways of controlling the pollution caused by these heavy metals in the study area.

Materials and method

The soil samples used for the study were collected from different geographical coordinates on the site with plastic ladles. Each soil sample was collected at the depth of about 30cm from the surface of the soil to obtain through layer of the soil (Norhayati et al, 2007). Samples were labeled and stored in polythene bags prior to analysis. On each collection point, the geographical latitude, longitude and elevation were recorded with the aid of Hand held GPS. Standard method of sample collection was used for collecting the water samples (Abulude et al, 2007). The samples were kept in a refrigerator (4^0 c) prior to analysis.

The soil samples were first air-dried at room temperature, ground in a ceramic mortar and sieved at 500 microns. About 1g of the pulverized sample was digested with HNO_3, HF and $HClO_4$ as described by Carmody et al, (1973), Mantei and Conrod, (1989), Ergin et al, 1991, Wardas et al, 1996). All the water samples were prepared for analysis by treating a 95.0 ml with concentration HNO_3 (5.0 ml) and filtered through 0.45µm filter (Moodley et al, 2007).

The samples were analysed for Cu, Cd, Zn, As and Cr using a Perkin Elmer model 306 Atomic Absorption Spectrometer. All chemicals used were of analytical reagent grade and deionised water was employed throughout for dilutions and washing. Means and standard deviation of all the values were determined.

Results and Discussions

The results of analysis of soil and water samples are presented in Tables 1 to 4. The mean values in µg/g, of the heavy metal content of the soil were, 5.29±6.88 for copper, 1.50±3.07 for cadmium, 46.72±19.56 for zinc, 10.5±1.76 for arsenic and 339.78±17.96 for chromium. The mean value in ppm of the heavy metal content of the water were, 4.8±1.74 for copper, 0.16±0.1 for cadmium, 4.17±4.87 for zinc, 0.57 ±0.56 for arsenic and 1.46 ±0.8 for chromium.

Copper

Copper in the soil was in the range of 0.2 to 19.8µg/g (Table 1). The lowest copper content was found in sample collected from location 8 and the highest in the one from location 1. The copper content of the nine samples averaged 5.29±6.88µg/g. This value is lower than result reported by Tahir et al, 2007 for soil samples from Dungun town with copper content of 7.4 µg/g, from new Orleans (USA) with copper content of 19 ppm and from Uppsala Sweden (city centre play ground) with copper content of 28.9 µglg. This value is below the critical soil total concentration of 60-125ppm (Rabata-Pendias and Pendias, 1984), suggesting that there is little anthropogenic effect on the study area. Copper can have its way to the soil through various means (Jakienwicz et al, 1998) such as contamination from copper pipes and wires as well as from addition designed to control algal growth. Copper is indispensable for normal development of living organisms, but both its excess and deficiency are harmful. Copper deficiency in the diet may cause anaemia, insufficient growth, fertility problem, nervous system disorders and circulatory system diseases. Its excess may lead to changes in the liver and damage kidneys, brain tissue, coronary vessels and myocardium (McKeague and Wolynetz, 1980).

Cadmium

The mean concentration of cadmium recorded at the study area was 1.5±3.07 µg/g. The lowest concentration was obtained at location 2 with value of 0.2µg/g and the highest at location 6 with value of 2.4µg/g. Thus, the range of concentration of cadmium at the study area is between 0.2 – 2.4 µg/g. The highest value here is the same as the cadmium concentration of 2.4µg/g in the soil samples of new Orleans (USA, school community) but slightly lower than 2.5 µg/g in the soil sample of Dungun town and much higher than value of 0.25µg/g in the soil samples of Uppsala Sweden (city centre play ground) as reported by Tahir et al, 2007.

The major hazard of chromium is its chronic accumulation in Kidneys which causes a disorder known as Itai-Itai disease and bone weakening (Vukojevic etal, 2006, Ademoroti, 1996 and Kjellstrom, 1979). It is obvious from

the overall result that, cadmium has the lowest mean concentration (1.5µg/g) amongst the heavy metal detected at the site of study. This low level of Cd may be related to low anthropogenic distribution in this location. Low concentration of cadmium would be as a result of absence of industries involved in the manufacture of insecticides as well as deposition of aerosols particles from industries.

Zinc

Zinc in the soil was in the range of 14.8 – 76.8 µg/g. The lowest value was obtained from location 5 and the highest from location 6. The zinc content from the nine samples average 46.72 and this is lower than values of 56, 160 and 109 µg/g for soil samples from Dungun town, new Orleans (USA) and Uppsala (Sweden) respectively as reported by Tahir et al, 2007. This level of zinc suggests that, there is little anthropogenic contribution. Zinc is an essential trace element for human, animals and higher plants; it is used in fighting skin problems such as ache, boils and sore throats (Doren and Sheldon, 2002). It is further needed for mitosis and is needed by the tissue of the hair, nails and skin to be in the top form. Deficiency of zinc results in underperforming immune while high intake harms the immune (Golden and Golden, 1981)

Chromium

The mean concentration of chromium recorded at the area of study is 339.78±17.96 µg/g and ranged from 8 – 810 µg/g. The lowest concentration was obtained at location 1 while the highest was obtained at location 6. The highest chromium concentration recorded at the area of study is lower than the upper limit of 1500 µg/g from the normal range of 5 – 1500 µg/g (Rabata et al, 1984). This value of chromium suggests possibility of anthropogenic effect at the area of study. Chromium is used in metal alloys and pigments for paints, cement paper and rubber. Low level exposure can irritate the skin and cause alceration. Long – term exposure can cause damage to kidney, liver circulatory and nerve tissue (Wedeen and Qiran, 1991). Chromium often accumulates in aquatic life, adding to the damage of eating fish that may be exposed to high levels of chromium (Sexana et al, 2006)

Arsenic

The arsenic content in all the soil samples ranged between 7.6 to 14.2µg/g. The lowest and the highest contents were found in samples collected from locations 9 and 2 respectively. The arsenic content of all the locations averaged 10.5±1.76 µg/g. This range of 7.6 – 14.20 µglg content of arsenic is lower than critical soil total concentration of 20 – 50 µg/g and falls within the normal range of 0.1 - 40µg/g in soil (Table 2) (Rabata et al, 1984). This is an indication of low contamination from anthropogenic factors. Indeed, Arsenic (Robbert, 1999, ATSDR Tox FAXs for Arsenic) is the most common cause of acute metal poisoning in adults and is No 1 on the ATSDR's (Agency for Toxic Substances and Disease Registry in Atlanta Georgia) ''Top 20 list'' . Target organs are the blood, kidneys and the central nervous, digestive and skin systems.

A comparison of the heavy metal content of the soil from this study with the world average is shown in Table 2. The data clearly showed that, the level of cadmium was higher than the value for the world average (0.62 µg/g) while concentrations of copper (5.29 µg/g) and zinc (46.72 µg/g) are lower than 25.8 µg/g and 59.8 µg/g respectively, as reported by Tahir et al, 2007.

Heavy metals in water

The result of the heavy metals in the water samples are presented in Table 3 and 4. The distribution of the heavy metals in the water is Zn>>Cr>Ar>Cu>>Cd. Therefore, the metals with the highest and lowest levels are Zinc (4.17±4.87ppm) and Cadmium (0.15±0.1ppm) respectively. Comparison of the mean concentration of these metals with results from Nigeria and other countries showed that, all the metals demonstrated low concentrations (Table 4). In addition, copper level at Ikogosi warm spring is lower than 1.3ppm (the approved minimum standard regulated by U.S Environmental Protection Agency (E P A) and Nebraka Department of Health and Human Services (DHHS) as reported by Sharon et al, 2008.

Conclusion

Results obtained from this study showed that, there are variations in the metal contents of the soil and water from one location to the other. Comparison of the level of contamination showed that, the average metal content of the soil is within the normal range within the soil and the reported world average. The concentrations of the heavy metals in the water at the area of study were

also found to be lower. This is an indication of low contamination of the area of study from anthropogenic sources. Effort should therefore be intensified to guide against pollution of the area. More so that, Ikogosi Warm Spring is a tourist centre.

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Table 1: Concentration of heavy metals in soil (µg/g).

Samples	Cu	Cd	Zn	As	Cr
1	19.8	1.6	54.6	12	8
2	0.8	0.2	72.2	14.2	80
3	4.0	0.8	51	10.6	420
4	2.8	2	40.2	10	740
5	14.2	2	14.8	9.4	80
6	2.0	2.4	76.8	8.2	410
7	2.7	1.6	38.6	12	40
8	0.2	1.2	30.0	10.4	810
9	1.1	1.7	42.3	7.6	470

Table 2: Comparison of heavy metals (µg/g) in soil sample of the study area with existing standards.

	Present study			Existing standards		
Metals	No of samples	Range	Mean ± SD	[a] Normal range in soil	[b] Critical soils total concentration	[c] World – average
Cu	9	0.2 – 19.8	5.29± 6.88	2-250	60-125	25.8
Cd	9	0.2 – 2.4	1.5±3.07	0.01-2.0	3-8	0.62
Zn	9	14.8 – 76.8	46.72±19.56	1-900	70-400	59.8
As	9	7.6 – 14.2	10.5±1.76	0.1-40	20-50	-
Cr	9	8 - 810	339.78±17.96	5-1500	75-100	-

Source: [a-b] Rabata et al, [c] Tahir et al

**Table 3: Concentration of heavy metals in water (ppm).**

| Samples	Cu	Cd	Zn	As	Cr
1	0.72	0.1	4.0	0.96	0.8
2	0.64	0.2	8.0	0.71	1.1
3	0.28	0.2	6.2	0.4	2.4
4	0.3	0.1	ND	0.36	1.8
5	0.31	0.3	2.8	ND	2.4
6	0.68	ND	3.6	0.74	1.0
7	0.42	0.1	0.8	0.91	ND
8	0.48	0.2	6.4	0.4	2.0
9	0.49	0.2	5.7	0.61	1.6

ND: Not Detectable

Table 4: Comparison of heavy metal content of water samples.

	Present work		Heavy metal contents from other countries for comparison			
Metals	Range	Mean±Sd	[a] South Nigeria	[b]Pakistan	[c]Britain	[d]Asano and Kakehashi River valleys (ppb)
Cu	0.28-0.72	0.48±1.74	-	-	-	1.1±0.34-298.99±290.03
Cd	ND-0.3	0.15±0.1	ND-0.2	0-1.12	0-0.06	ND-0.791±0.236
Zn	ND-0.8	4.17±4.87	-	0.1-4.3	0.12-3.81	-
As	ND-0.96	0.57±0.56	0.24-1.30	-	0.04-0.05	-
Cr	ND-2.4	1.46±0.8	0.11-0.12	0-4.1	0.15-0.4	ND-1.35

Source: [a]Nkono and Asubiojo, [b]Danishwan and Shah, [c]Abulude, [d]Kabayashi and Kizu.
ND: Not Detectable.
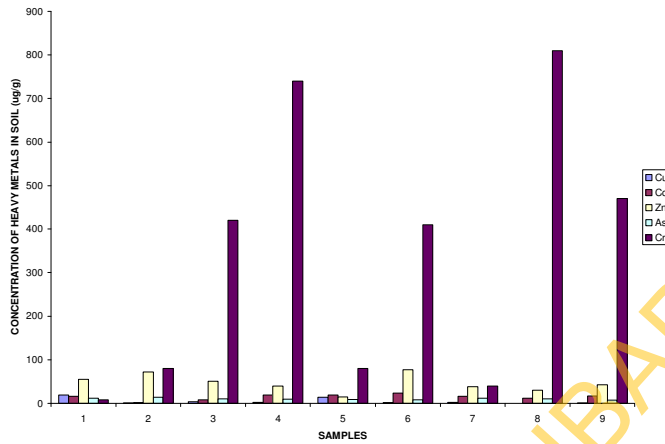
Fig 1: Heavy metal concentration in soil – Cd x 10 (µg/g).
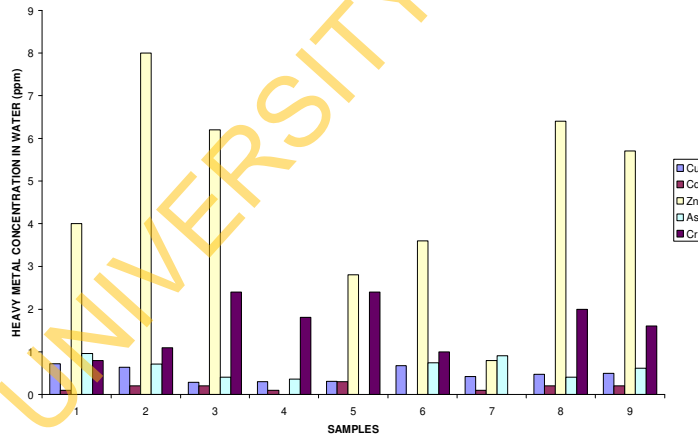
Fig 2: Heavy metal concentration in water (ppm)