Investigation of the Occurrence and Levels of Some Heavy Metals In Spring Water from Bazza, Pella And Yadim Areas of Adamawa State

Abstract:

Analytical studies was carried out on spring water samples collected from Bazza (Michika L.G.A), Pella (Hong L.G.A) and Yadim (Fufore L.G.A) in Adamawa state of Nigeria in other to investigate the occurrence and concentration levels of some heavy metals using the Atomic Absorption Spectrophotometer (AAS).The results obtained revealed that cadmium, chromium and lead were absent in the water samples while Iron, Manganese, Zinc and Copper were found to be present in the water samples with their mean concentration in the following ranges Iron (0.39 – 0.82mgL^{-1}), Copper (0.05 – 0.20mgL^{-1}), Manganese (0.01-0.04mgL^{-1}), and Zinc (0.87-0.94mgL^{-1}). From the results, Zinc has the highest concentration while Manganese has the least. The values of Fe, Cu, Mn, and Zn were found to be within the acceptable range of standard values for heavy metals in water set by NAFDAC (2001), SON (2007) and WHO (2011)

Key words: Heavy metals, AAS, Pollution, NAFDAC, SON, WHO

INTRODUCTION

Water is a unique and one of the most essential substances on earth. This is because most chemical activities and life processes depends on water for their sustenance. The presence of oxygen which is highly electronegative in a water molecule gives it a unique polar chemical behavior, making water able to dissolve or suspend many substances and in some cases, water participate as a major reactant in chemical reactions or act as a medium through which a chemical reaction can occur. This ability however, makes water a potential reservoir for all kinds of contaminants which can be organic or inorganic, biodegradable or non biodegradable. Thus in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities (Mendie, 2005).

The sources of water can be broadly classified into two main classes; Surface water and Underground water. Of the two, surface water is the most common since it is any water that travels or is stored on the top of the ground which is open to the atmosphere and is subject to runoff from the land. Sources include water that is in rivers, lakes, streams, reservoirs, cisterns, even the oceans and other controlled catchments. Runoff is the water that runs in gutters, off roofs, etc. when it rains. This is surface water too. Runoff is a problem because it carries bad things like car oil, road salt, and trash into the water bodies. Controlled catchments are areas from which nearly 100 percent of precipitation is collected as run off. Rooftops are the most easily recognized type of controlled catchments (Clasen and Bastable, 2003). Ground water is a little harder to understand than surface water. Groundwater, water that lies hidden beneath the earth‟s surface, is an important resource. Although it makes up only 4 percent of the total amount of water on earth, it constitutes 95 percent of the fresh water that is suitable for human consumption (Wright *et al*., 2004). In the water cycle, some of the precipitation sinks into the ground and goes into water sheds, aquifers and springs. The amount of water that seeps into the ground depends on how steep the land is and what is under the ground. For example: a sandy environment will allow more water to sink in than places that have lots of rocks. When the water seeps down, it will reach a layer of ground that already has water in it. That is the saturated zone. The highest point in the saturated zone is called the water table. The water table can rise and lower depending on the seasons and the amount of rainfall. Groundwater flows through layers of sand, clay, rock and gravel. These serves as filters that cleanse the water, and since underground water is not exposed, things that fall into surface water can't fall into it. This means that ground water stays cleaner than water on the surface. The major sources of underground water are well water, boreholes and spring waters.

A water body can be polluted when a large amount of contaminants or harmful materials are disposed either directly or indirectly into it, making it unfit for intended use, and poses severe threat to the aquatic life therein. These contaminants varies based on the nature of the materials which can be either solid or liquid, organic or inorganic, biodegradable or non biodegradable, and can also vary based on the sources of the waste which include industrial or domestic effluents, sewage water, solid waste disposal, and dissolved inorganic chemicals like herbicide, insecticides and fertilizers; which can be washed by rain into the streams in form of run-off which has adverse effects on aquatic life. Similarly, rain can wash these inorganic substances which seep through the soil and eventually get to the ground water level where it settled there (this is the major channel through which underground water can be polluted).

Of all the water sources mentioned in this study, ground water is the least exposed, cleaner and safer than surface water, and most people assume that it is safe for both domestic and industrial use with little or no treatment. However, studies conducted by Momodu and Anyakora (2010), assessed the quality of underground water in a neighborhood in Surulere, Lagos state. About forty nine well and borehole water samples were analyzed using Atomic Absorption Spectrophotometer for their Aluminium, Cadmium and Lead content and their levels compared with WHO specified maximum contaminant level. From the results obtained, none of the samples analyzed contained Aluminium in concentrations above the MCL, however, the metal was found to be present in 93.88% of the samples analyzed. Over 38% of the samples had Cadmium present in them and 32.65% of the samples had Cadmium concentrations above the MCL. Almost 60% of the samples had detectable level of Lead while 36.73% of the sample had Lead concentration above the MCL. In general 97.96% of all samples analyzed contained one or more of the three heavy metals studied each in varying concentrations. The results obtained from this study suggest a significant risk to this population given the toxicity of these metals and the fact that for many, hand dug wells and bore holes are the only sources of their water supply in this environment.

Between the wide diversity of contaminants affecting water sources, heavy metals receive particular concern considering their toxicity even at low concentrations (Marcovecchio *et al.,* 2007). The term “Heavy Metals” refer to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Most of these metals found their way into the water bodies either through natural processes such as eroded minerals within sediments, leaching of ore deposits and volcanism extruded products, or Human and animal activities such as solid waste disposal, industrial or domestic effluents, harbor channel dredging. Some of the metals are essential to sustain life-calcium, magnesium, potassium and sodium must be present for normal body functions. Also, cobalt, copper, iron, manganese, molybdenum and zinc are needed at low levels as catalyst for enzyme activities (Adepoju-Bello *et al*., 2009). Since such metals can be toxic even at low concentration and are capable of bioaccumulation, then excess exposure to these metals can result into health complications and therefore should be minimized to the bearable limit.

The study areas constitute three villages which are; Bazza, in Michika Local Government Area located at latitude $10^{o}57'$N and longitude $13^{0}32'$E, Pella, in Hong LGA located at latitude $10^{0}23'$N and longitude $12^{0}93'$E, and Yadim, in FuFore LGA located at latitude $9^{0}33'$N and longitude $12^{0}44'$E in Adamawa State of Nigeria. The state capital is Jimeta-Yola which is located within located within latitude $90^{0}11'$N to $90^{0}20'$N and longitude $12^{0}23'$E and covers an area of about 305Km^2. The mean annual rainfall in Yola is 859.3 and 917.9mm in Yola (Ishaku, 1995). The major occupation of the inhabitants of these villages is peasant farming where they produce food crops for their immediate needs, using crude and semi-mechanized farm tools, herbicides and fertilizers. They depend on these springs for their sources of water for farming purposes such as irrigation and spray of chemicals, and for domestic use. The locals visit the sites mostly during the dry season for recreational and relaxation purposes, and also to clean themselves and wash their clothes. Similarly, the Yadim waterfalls is also visited by both Tourists and locals for similar reasons as mentioned above, thereby making the sites a potential dumpsite for waste matters and contaminants.

The overdependence of both human and animal activities on these spring water sources thus makes them susceptible to pollution. There is thus a need to assess the quality of these water sources in comparison with the permissible standard by the World Health Organization (WHO), Standard Organization of Nigeria (SON), and National Agency for Food and Drugs Administration and Control (NAFDAC).

MATERIALS AND METHODS

Water Sampling

Spring water samples were collected from 30 different sampling points across the three sampling sites stated in the study area. The samples were collected between the months of March and April, 2014. The samples were collected by lowering a clean 50ml plastic sampling bottle about 15-20cm deep and allow to overflow before withdrawal. Ten (10) sampling points were used for each of the three sampling sites with about 10m distance from successive points. In other to keep the required cation species in solution, stop microbial growth and to avoid interference during analysis, the samples were digested using Aqua regia. 5ml of Aqua regia (a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3) was added to 50ml of water in a 250 ml conical flask. The mixture was evaporated to half its volume on a hot plate after which it was allowed to cool and then filtered.

Storage and Preservation

Water samples were analyzed immediately after collection and digestion. Where analysis could not commence immediately, the samples were stored at 4^0C.

Standards Preparation

Standard 1000ppm stock solutions were prepared for the metals to be analyzed (Pb, Zn, Cr, Cd, Cu, Fe and Mn) by dissolving in a 1litre volumetric flask, 1.5985g, 2.0320g, 5.1250g, 4.3960g, 3.5883g, 4.3960g, and 3.9307g of Lead nitrate {$Pb(NO_3)_2$}, Cadmium chloride ($CdCl_2.2^1/_2H_2O$), Chromium (III) chloride hexahydrate ($CrCl_3.6H_2O$), Zinc sulphate hexahydrate ($ZnSO_4.6H_2O$), Manganese chloride tetrahydrate ($MnCl_2.4H_2O$), Ammonium ferrous sulphate hexahydrate ($(NH_4)_2SO_4FeSO_4.6H_2O$), and Cupric sulphate pentahydrate ($CuSO_4.5H_2O$) respectively with 5% nitric acid. The mixture was then shaken and made up to the 1litre mark for each of the metal. Calibration curves for each of the target metal ions were obtained from the stock solutions.

Sample Analysis

The sample were analysed for the presence of Pb, Zn, Cr, Cd, Cu, Fe and Mn ions using Atomic Absorption Spectrophotometer Buck Scientific 210VGP model and calibration curves for this analysis. The wavelengths of maximum absorption for the metals were 213.9nm, 248.3nm, 324.7nm, 228.9nm, 279.5nm, 357.9nm and 283.2nm for Zn, Fe, Cu, Cd, Mn, Cr, and Pb respectively. The digested samples were analysed thrice each and the average absorbance recorded by the instrument were obtained and extrapolated from the calibration curves in the unit of concentration, mgL^{-1}.

RESULTS AND DISCUSSION

Calibration curves were obtained using varying concentrations of the standard stock solutions for the target metals. The regression data for the calibration curves are shown in Table 1, where all the seven calibration curves obtained were linear with their Pearson product-moment correlation coefficients ranging from 0.92 to 1.00 which suggest that the measure of the strength of linear association between the variables is strong. The results were expressed as mean concentrations ± standard deviation (SD) as shown in Table 2.

All the 30 water samples analyzed from the three locations does not contain detectable level of Cd, Pb, and Cr. However, zinc (Zn) was detected in 8 of the samples collected at Yadim (with their mean concentration ranging from 0.87-0.94mgL^{-1}) but was not detected in the other two locations. These values are below the permissible limits set by Both NAFDAC and SON. Zinc is an essential element which is generally considered to be non-toxic. Drinking water is not considered an important nutritional source of this element. Water containing zinc at concentrations above 5.0 mg/L tends to be opalescent, develops a greasy film when boiled, and has an undesirable astringent taste (Wright *et al*., 2004).

Similarly, Manganese (Mn), was detected in 8 of the samples collected at Pella (with mean concentrations ranging from 0.01-0.04mgL^{-1}) but was not detected at the other two locations. These values are also below the permissible limits set by WHO, SON, and NAFDAC. But the presence of Manganese in drinking water can cause a number of health problems notable among which is neurological disorder. At concentrations above 0.15 mg/L, manganese stains plumbing fixtures and laundry and produces undesirable taste in drinks. Manganese may cause microbial growths in the distribution system. Even at concentrations below 0.05 mg/L, manganese may form black coatings on water distribution pipes. The element manganese is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans. Manganese is most often present as the dioxide, carbonate or silicates. Manganese is most often a concern for systems that use a groundwater source (Rajesh *et al*., 2004).

Detectable levels of Fe, and Cu were found in all the three locations, with Yadim having the highest concentration of Iron (with mean concentration of iron ranging from 0.67-0.82gL^{-1})

while Pella has the least concentration of Iron (with mean concentration ranging from 0.39-0.61mgL^{-1}). The Nigerian regulating bodies both set the limit for iron to be 0.3mg/L. At concentrations slightly above the permissible limits, iron can make water taste bad and can cause staining of laundry and plumbing fixtures. Iron is an essential element in human nutrition, and deficiency can result in impaired mental development in children, reduced work performance in adults and, in severe cases, anemia or impaired oxygen delivery. Iron is the fourth most abundant element in the earth's crust and the most abundant heavy metal. It is present in the environment mainly as Fe(II) or Fe(III). . Iron is generally present in surface waters as salts containing Fe(III) when the pH is above 7. Most of those salts are insoluble and settle out or are adsorbed onto surfaces Therefore; the concentration of iron in well-aerated waters is seldom high. Under reducing conditions, which may exist in some groundwater, lakes or reservoirs, and in the absence of sulphide and carbonate, high concentrations of soluble Fe(II) may be found. The presence of iron in natural waters can be attributed to the weathering of rocks and minerals, acidic mine water drainage, landfill leaches, sewage effluents and iron-related industries (Rajesh *et al*., 2004).

On the other hand, Bazza has the highest concentration of copper (with mean concentration ranging from 0.15-0.20mgL^{-1}) while Yadim has the least concentration of copper (with mean concentration ranging from 0.05-0.07mgL^{-1}). Copper is an essential element in the human metabolism, whose deficiency results into clinical disorders notable among which include gastrointestinal disorder, and nutritional anemia in infants. At concentrations above 1mg/L, copper makes water taste okay. Large doses of copper may result in adverse health effects. Copper occurs in nature as a metal and in minerals. (Rajesh *et al*., 2004).

CONCLUSION

The results reveal detectable levels of four out of seven heavy metals studied across the three sites. Even though the heavy metals detected were all within the acceptable limits, they pose a serious threat on the inhabitants of these villages because heavy metals are capable of Bio-accumulating over a long period of time and can result into serious health issues, and also to the fact that those spring water bodies are the major sources of their water supply in those environments.

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APPENDIX

Table 1: Regression data for calibration curves

Metal ions	Regression equation	Correlation coefficient ®	Coefficient of determination (R^2)
Pb^{2+}	y = 0.008x + 0.032	1.00	0.997
Zn^{2+}	y = 0.044x + 0.845	0.92	0.838
Cr^{3+}	y = 0.001x + 0.005	1.00	0.998
Cd^{2+}	y = 0.039x + 0.503	0.96	0.929
Cu^{2+}	y = 0.080x + 0.025	1.00	0.996
Fe^{2+}	y = 0.021x - 0.051	0.94	0.890
Mn^{2+}	y = 0.032x + 0.206	0.93	0.869

Table 2: Results of the concentration of Heavy metal ions in Bazza, Pella, and Yadim spring water samples

		Concentration of Heavy metals in mgL^{-1}						
Sampling Area	**Code**	**Zn**	**Cd**	**Cr**	**Pb**	**Mn**	**Fe**	**Cu**
Bazza	Bz1	-	-	-	-	-	0.73±0.02	0.18±0.01
	Bz2	-	-	-	-	-	0.62±0.01	0.16±0.01
	Bz3	-	-	-	-	-	0.70±0.02	-
	Bz4	-	-	-	-	-	0.68±0.03	0.17±0.04
	Bz5	-	-	-	-	-	0.68±0.02	0.18±0.02
	Bz6	-	-	-	-	-	0.71±0.04	0.20±0.04
	Bz7	-	-	-	-	-	0.71±0.02	0.17±0.01

	Bz8	-	-	-	-	-	0.65±0.01	0.15±0.03
	Bz9	-	-	-	-	-	-	0.19±0.09
	Bz10	-	-	-	-	-	0.57±0.03	0.18±0.02
Pella	Pl1	-	-	-	-	0.01±0.01	0.61±0.02	0.14±0.04
	Pl2	-	-	-	-	0.03±0.01	0.39±0.01	0.14±0.03
	Pl3	-	-	-	-	0.03±0.05	0.57±0.01	0.12±0.01
	Pl4	-	-	-	-	-	0.54±0.05	0.10±0.03
	Pl5	-	-	-	-	0.03±0.02	0.48±0.03	0.13±0.01
	Pl6	-	-	-	-	-	0.45±0.02	0.11±0.02
	Pl7	-	-	-	-	0.04±0.02	0.51±0.02	0.13±0.02
	Pl8	-	-	-	-	0.01±0.04	0.58±0.01	0.12±0.04
	Pl9	-	-	-	-	0.03±0.03	0.51±0.01	0.10±0.05
	Pl10	-	-	-	-	0.04±0.01	0.61±0.03	-
Yadim	Yd1	0.91±0.07	-	-	-	-	0.80±0.08	0.07±0.02
	Yd2	0.94±0.05	-	-	-	-	0.75±0.01	0.06±0.02
	Yd3	0.81±0.01	-	-	-	-	0.79±0.06	-
	Yd4	-	-	-	-	-	0.67±0.01	0.05±0.03
	Yd5	0.92±0.02	-	-	-	-	0.77±0.06	0.07±0.01
	Yd6	0.87±0.03	-	-	-	-	0.81±0.05	0.06±0.01
	Yd7	0.89±0.01	-	-	-	-	-	0.05±0.04
	Yd8	0.79±0.04	-	-	-	-	0.80±0.01	0.07±0.03
	Yd9	0.91±0.05	-	-	-	-	0.79±0.04	0.06±0.03
	Yd10	-	-	-	-	-	0.82±0.03	0.06±0.01

- Not detected

Table 3: permissible Limits of Heavy Metals in water

Heavy Metals	**WHO (mgL^{-1})**	**SON (mgL^{-1})**	**NAFDAC (mgL^{-1})**
Zn	-	3.0	5.0
Cd	0.003	0.003	0.003
Cr	0.05	0.05	0.05
Pb	0.01	0.01	0.01
Mn	0.4	0.2	2.0
Fe	-	0.3	0.3

Cu	2.0	1.0	1.0

WHO – World Health Organization (2011)

SON – Standard Organization of Nigeria (2007)

NAFDAC – National Agency for Food and Drugs Administration and Control (2001)