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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 springs water samples collected from Bazza (Michika 4 L.G.A), Pella (Hong L.G.A) and Yadim (Fufore L.G.A) in Adamawa state of Nigeria in order to 5 investigate the occurrence and concentration levels of some heavy metals using the Atomic 6 Absorption Spectrophotometer (AAS). The results obtained revealed that cadmium, chromium 7 and lead were absent in the water samples while Iron, Manganese, Zinc and Copper were found 8 9 to be present in the water samples with their mean concentration in the following ranges Iron $(0.39 - 0.82 \text{mgL}^{-1})$, Copper $(0.05 - 0.20 \text{mgL}^{-1})$, Manganese $(0.01 - 0.04 \text{mgL}^{-1})$, and Zinc $(0.87 - 0.20 \text{mgL}^{-1})$. 10 0.94mgL⁻¹). From the results, Zinc has the highest concentration while Manganese has the least. 11 The values of Cu, Mn, and Zn were found to be within the acceptable range of standard values 12 for heavy metals in water set by NAFDAC (2001), SON (2007) and WHO (2011), While the 13 studied samples contain higher concentration of Fe than the acceptable range of NAFDAC 14 (2001) and SON (2007). 15

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

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INTRODUCTION

20 Water is the unique and the most essential substance on earth. This is because most chemical activities and life processes depends on water for their sustenance. The presence of oxygen 21 22 which is highly electronegative in a water molecule gives it a unique polar chemical behavior, making water able to dissolve or suspend many substances in some cases. In addition water 23 participates as a major reactant in chemical reactions or act as a medium through which a 24 chemical reaction can occur. This ability however, makes water a potential reservoir for all kinds 25 of contaminants which can be organic or inorganic, biodegradable or non biodegradable. Thus in 26 nature, water is not pure as it acquires contaminants from its surrounding and those arising from 27 natural sources as well as humans, animals and other biological activities (Mendie, 2005). 28

29 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 30 31 threat to the aquatic life therein. Groundwater represents the second source of fresh water worldwide and has a great importance. Groundwater flows through layers of sand, clay, rock and 32 gravel. These serves as filters that cleanse the water, and since underground water is not exposed, 33 things that fall into surface water can't fall into it. This means that groundwater stays cleaner 34 than water on the surface. Of all the water sources, groundwater is the least exposed, cleaner and 35 safer than surface water, and most people assume that it is safe for both domestic and industrial 36 use with little or no treatment. However, studies conducted by Momodu and Anyakora (2010), 37 assessed the quality of underground water in a neighborhood in Surulere, Lagos state and found 38 39 detectable concentrations of Al, Cd and Pb. About 32.65% and 36.73 of samples contain Cd and Pb above the Maximum allowable limit, respectively. In general, 97.96% of all samples analyzed 40 contained one or more of the three heavy metals studied each in varying concentrations. The 41 results obtained from this study suggest a significant risk to this population given the toxicity of 42 these metals and the fact that for many, hand dug wells and bore holes are the only sources of 43 44 their water supply in this environment.

Between the wide diversity of contaminants affecting water sources, heavy metals receive 45 particular concern considering their toxicity even at low concentrations (Marcovecchio et al., 46 47 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. Most of these metals found their way into 48 the water bodies either through natural processes such as eroded minerals within sediments, 49 leaching of ore deposits and volcanism extruded products, or human and animal activities such 50 51 as solid waste disposal, industrial or domestic effluents, harbor channel dredging. Some heavy metals are essential to sustain life; Fe, Mn, Co, Cu, Mo and Zn are needed at low levels as 52 catalyst for enzyme activities in humans (Adepoju-Bello et al., 2009). Since such metals can be 53 toxic even at low concentration and are capable of bioaccumulation, then excess exposure to 54 these metals can result into health complications and therefore should be minimized to the 55 bearable limit. 56

57 The study areas constitute three villages which are; Bazza, in Michika Local Government 58 Area located at latitude $10^{\circ}57'N$ and longitude $13^{\circ}32'E$, Pella, in Hong LGA located at latitude

10°23'N and longitude 12°93'E, and Yadim, in FuFore LGA located at latitude 9°33'N and 59 longitude 12⁰44'E in Adamawa State of Nigeria. The major occupation of the inhabitants of these 60 villages is peasant farming where they produce food crops for their immediate needs, using crude 61 and semi-mechanized farm tools, herbicides and fertilizers. They depend on these springs for 62 their sources of water for farming purposes such as irrigation and spray of chemicals, and for 63 domestic use. The locals visit the sites mostly during the dry season for recreational and 64 65 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, 66 thereby making the sites a potential dumpsite for waste matters and contaminants. 67

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69 The overdependence of both human and animal activities on these spring water sources 70 thus makes them susceptible to pollution. There is thus a need to assess the quality of these water 71 sources in comparison with the permissible standard by the World Health Organization (WHO), 72 Standard Organization of Nigeria (SON), and National Agency for Food and Drugs 73 Administration and Control (NAFDAC).

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MATERIALS AND METHODS

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77 Water Sampling

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Spring water samples were collected from 30 different sampling points across the three sampling 79 sites stated in the study area. The samples were collected between the months of March and 80 April, 2014. The samples were collected by lowering a clean 50ml plastic sampling bottle about 81 82 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 83 84 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 85 86 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 87 allowed to cool and then filtered. 88

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90 Storage and Preservation

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

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95 Standards Preparation

96 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, 97 Lead nitrate $\{Pb(NO_3)_2\}$, Cadmium chloride 3.5883g, 4.3960g, and 3.9307g of 98 (CdCl₂.2¹/₂H₂O), Chromium (III) chloride hexahydrate (CrCl₃.6H₂O), Zinc sulphate hexahydrate 99 100 (ZnSO₄.6H₂O), Manganese chloride tetrahydrate (MnCl₂.4H₂O), Ammonium ferrous sulphate hexahydrate (NH₄)₂SO₄FeSO₄.6H₂O), and Cupric sulphate pentahydrate (CuSO₄.5H₂O) 101 respectively with 5% nitric acid. The mixture was then shaken and made up to the 11itre mark for 102 each of the metal. Calibration curves for each of the target metal ions were obtained from the 103 104 stock solutions.

105 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.

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114 **RESULTS AND DISCUSSION**

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116 Calibration curves were obtained using varying concentrations of the standard stock solutions for 117 the target metals. The regression data for the calibration curves are shown in Table 1, where all 118 the seven calibration curves obtained were linear with their Pearson product-moment correlation 119 coefficients ranging from 0.92 to 1.00 which suggest that the measure of the strength of linear 120 association between the variables is strong. The results were expressed as mean concentrations \pm 121 standard deviation (SD) as shown in Table 2.

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123 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 124 (with their mean concentration ranging from 0.79-0.94 mgL⁻¹) but was not detected in the other 125 two locations. These values are below the permissible limits set by Both NAFDAC and SON. 126 Zinc is an essential element which is generally considered to be non-toxic. Drinking water is not 127 considered an important nutritional source of this element. Water containing zinc at 128 129 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). 130

Similarly, Manganese (Mn), was detected in 8 of the samples collected at Pella (with 131 mean concentrations ranging from 0.01-0.04mgL⁻¹) but was not detected at the other two 132 locations. These values are also below the permissible limits set by WHO, SON, and NAFDAC. 133 But the presence of Manganese in drinking water can cause a number of health problems notable 134 among which is neurological disorder. At concentrations above 0.15 mg/L, manganese stains 135 plumbing fixtures and laundry and produces undesirable taste in drinks. Manganese may cause 136 microbial growths in the distribution system. Even at concentrations below 0.05 mg/L, 137 138 manganese may form black coatings on water distribution pipes. Manganese is most often a concern for systems that use a groundwater source (Rajesh et al., 2004). 139

Detectable levels of Fe, and Cu were found in all the three locations, with Yadim having 140 the highest concentration of Iron (with mean concentration of iron ranging from 0.67-0.82gL⁻¹) 141 while Pella has the least concentration of Iron (with mean concentration ranging from 0.39-142 0.61mgL^{-1}). The Nigerian regulating bodies both set the limit for iron to be 0.3 mg/L. At 143 concentrations slightly above the permissible limits, iron can make water taste bad and can cause 144 staining of laundry and plumbing fixtures. Iron is an essential element in human nutrition, and 145 deficiency can result in impaired mental development in children, reduced work performance in 146 147 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 148 mainly as Fe(II) or Fe(III). Iron is generally present in surface waters as salts containing Fe(III) 149

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 many minerals. (Rajesh *et al.*, 2004).

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165 CONCLUSION

The results reveal detectable levels of four out of seven heavy metals studied across the three sites. Even though the heavy metals detected except Fe 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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 point-of use. Tropical Medicine and International Health, 9 (1): 106-117.
- 196
- 197
- 198 APPENDIX
- 199
- 200 Table 1: Regression data for calibration curves

Metal ions	Regression	Correlation	Coefficient of	
	equation	coefficient ®	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

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

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203 samples

Concentration of Heavy metals in mgL ⁻¹								
Sampling Area	Code	Zn	Cd	Cr	Pb	Mn	Fe	Cu
Bazza	Bz1	-	-	-	-	\sim	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	-		V	1	-	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	>	X	-	-	-	-	0.19±0.09
	Bz10			-	-	-	0.57±0.03	0.18±0.02
Pella	P11		-	-	-	0.01±0.01	0.61±0.02	0.14±0.04
	P12		-	-	-	0.03±0.01	0.39±0.01	0.14±0.03
	P13		-	-	-	0.03±0.05	0.57±0.01	0.12±0.01
	Pl4		-	-	-	-	0.54±0.05	0.10±0.03
	P15	-	-	-	-	0.03±0.02	0.48±0.03	0.13±0.01
	P16	-	-	-	-	-	0.45±0.02	0.11±0.02
	P17	-	-	-	-	0.04±0.02	0.51±0.02	0.13±0.02
	P18	-	-	-	-	0.01±0.04	0.58±0.01	0.12±0.04
	P19	-	-	-	-	0.03±0.03	0.51±0.01	0.10±0.05
	P110	-	-	-	-	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	-	-	-	-	$0.77 {\pm} 0.06$	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

204 - Not detected

205 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

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- **WHO** World Health Organization (2011)
- 208 SON Standard Organization of Nigeria (2007)
- 209 NAFDAC National Agency for Food and Drugs Administration and Control (2001)