Comparative Analyses of Levels of Some Trace Metals in Boreholes and Hand-Dug Wells Water Sources Within and Around Lafia Metropolis

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Abstract: *In this study, the levels of some trace metals (As, Co, Cr, Cd, Pb, Al, Ni and Mn) were determined in boreholes and hand-dug well water sources in Lafia town and its environs using Atomic Absorption Spectrophotometry (AAS). Sampling, preservation of the water samples, pre-concentration and analyses of the trace metals were carried out as prescribed by APHA, AWWA, and WEF Standard Methods for the Examination of Water and Waste Water. In the wet season(WS), the highest mean concentrations(mg/L) of trace metals from boreholes (BH) was Mn(0.7787 $\pm$0.2389) in Lafia West while the least was Pb(0.0049 $\pm$0.0001) in Lafia South. Similarly for hand –dug wells (HDW) in wet season, the highest was Mn(0.6227 $\pm$ 0.0260) in Lafia West while the least was As(0.0106 $\pm$ 0.0001) in Lafia East. In dry season(DS), the highest mean concentration of trace metals from BH was Mn(0.3815 $\pm$ 0.0907) in Lafia West while the least was Cr(0.0042 $\pm$ 0.0001) in Lafia South. Similarly for HDW in dry season, the highest was Mn(0.3588 $\pm$ 0.0762) in Lafia West while the least was Ni(0.0065$\pm$0.0001) in Lafia Central. However Cd and Al were not detected within the two seasons. In all, the analyses revealed the presence of 40%As, 40%Co, 37.5%Cr, 25%Pb, 25%Ni and 97.5%Mn from the total ground water samples. Their mean concentrations were compared with standards of a number of regulatory bodies such as World Health Organization (WHO), National Agency for Food Drug and Control (NAFDAC), National Standard for Drinking Water Quality (NSDWQ for Borehole). In comparison, the results showed higher levels of these metals than the maximum tolerable limits, particularly those of As(0.2710$\pm$0.0001 – 0.0106$\pm$0.0001), Co (0.2406$\pm$0.2114-0.0281$\pm$0.0001), Cr(0.5049$\pm$0.5871-0.0272$\pm$0.0001) for all the water samples throughout the seasons. However those of Pb(0.0423$\pm$0.0537-0.0049$\pm$0.0001),Ni(0.3729$\pm$0.0001-0.0841$\pm$0.0001),Mn(0.7787$\pm$0.2329-0.1049$\pm$0.0322) were within tolerable limits in most cases. The results indicate that these ground water sources were polluted more prominently in wet season; BH (WS)>HDW(WS)>BH(DS)>HDW(DS) in all locations, with specific reference to As, Pb, because of their high toxicities and therefore not safe for drinking.*

I. Introduction

In the development of communities, water plays a vital role; hence a reliable source of water is essential for the existence of both humans and animals. Water supply is mostly derived from precipitation and is often said to be contaminated if it is not suitable for the intended purpose [1,2].

Therefore the presence of heavy metals in water sources has received considerable and special attention for which permissible or recommended limits have been set for water for both domestic and industrial application [3-6].

Assessment of heavy metals is the determination of metal constituents of sample where these constituents make up only a small part of sample generally below or about one hundred parts per million (ppm). The important role of very small amounts of elements in physical, chemical and biological systems has emerged with advances in methods of analysis with increasing sensitivity[7]. The damaging effects of contamination with heavy metals in our environment have become more serious or obvious especially in water [8]. Virtually all metals can produce toxicity when ingested in sufficient quantities but they are several others which are important either because they are pervasive or produce toxicity at low concentration; Pb, Hg, As and Cd are prime examples and serve no biological function. On the other hand, metals like Cr, Cu, Fe, Mn, Se, Mo and Zn though occur in small amounts are essential in our diet because they are key components or constituents of important biological molecules such as enzymes, Hb, Metallic activators, pigments, determinants of osmotic pressure and other biological compounds that are essential to life.

The concern of people globally, on water pollution, as it affects human health is the direct disposal of waste materials into the land surface thereby causing ground water pollution. The waste products or materials occur as individual mounds or it may spread out over the land. If the waste materials contain soluble materials, they will infiltrate thereby causing the ground water to be polluted [9].

In many Nigerian urban centres, the per capita consumption of water which is about 80L/d appears quite low as compared to 115L/d which is considered more appropriate for urban dwellers in a country like Nigeria and even then only 17.2% of Nigerians have access to clean water [10]. In view of the shortfall in the supply of public treated water in urban centres of the nation, most inhabitants have to look for alternative sources of water especially ground water in form of boreholes and hand-dug wells which are untreated. The population of Lafia being the state capital of NasarawaState has increased tremendously since its creation in 1996, with accompanying increase in human activities. One of the economic activities in the state is mineral exploration because of the huge mineral occurrence which the state is fondly tagged "Home of Solid Minerals" and these no doubt affect the soil and water in which life critically depends. Prominent among the minerals in this area are coal, barytes, salts, limestones, cassitterite, columbite, clays, glasssand, lead-zinc and hydrocarbon potential[11].

II. Materials And Methods

2.1 Materials
i)   Distilled water
(ii)   Methyl Isobutyl Ketone (M.I.B.K.)
(iii)   Ammonium PyrolidineDithiocarbamate (APDC) from which 5% was   prepared.
(iv)   Concentrated nitric acid of M & B Analytical Reagent
(v)   Trace metals standards
(vi)   Atomic Absorption Spectrophotometer(AAS)- SOLAAR 32 AA
(vii)   pH Meter- pHep, pH Tester CE of Hanner Instruments Woonsocket: R102895
(viii)   Buffer solution (pH 7.0).

2.2 Geology of the study area
The study area is Lafia metropolis (Figure 1) with about fifty neighbourhoods [56]. Lafia is the capital of NasarawaState which is located in the middle belt region of Nigeria. The state lies between longitudes 7° and 9° 37' E of the Greenwich Meridian and has an altitude of 181.5m above sea level [12].

Lafia is located within the geological Afo Younger Granites complex within the Middle Benue Trough. Afo younger granite complex is the youngest granite complex in Nigeria. The Younger Granites are distinctive series of alkali feldspar granites hosting minerals like cassitterite, columbites as major minerals. Lafia which is the last segment of the Middle Benue Trough is underlined by basement complex rocks and has appreciable layer of sedimentation notable for water retention [13].

2.3 Sample collection and preservation
The samples for this investigation were collected randomly from various hand-dug wells and boreholes using plastic containers from 10 locations or neighbourhoods to generate 40 samples   (10 from hand dug wells, appropriately 12-14m deep and 10 from boreholes, appropriately 45m deep) in each season. The sampling was carried out in the month of September,2011 for wet season and March 2012 for dry season. Samples for the trace metals analyses were preserved by the addition of concentrated nitric acid (HNO_3) to adjust the pH of the sample to below 2 to retard adsorption. The samples were kept in ice packs and transported to the laboratory where they were further preserved in a refrigerator before analysis [15,16].
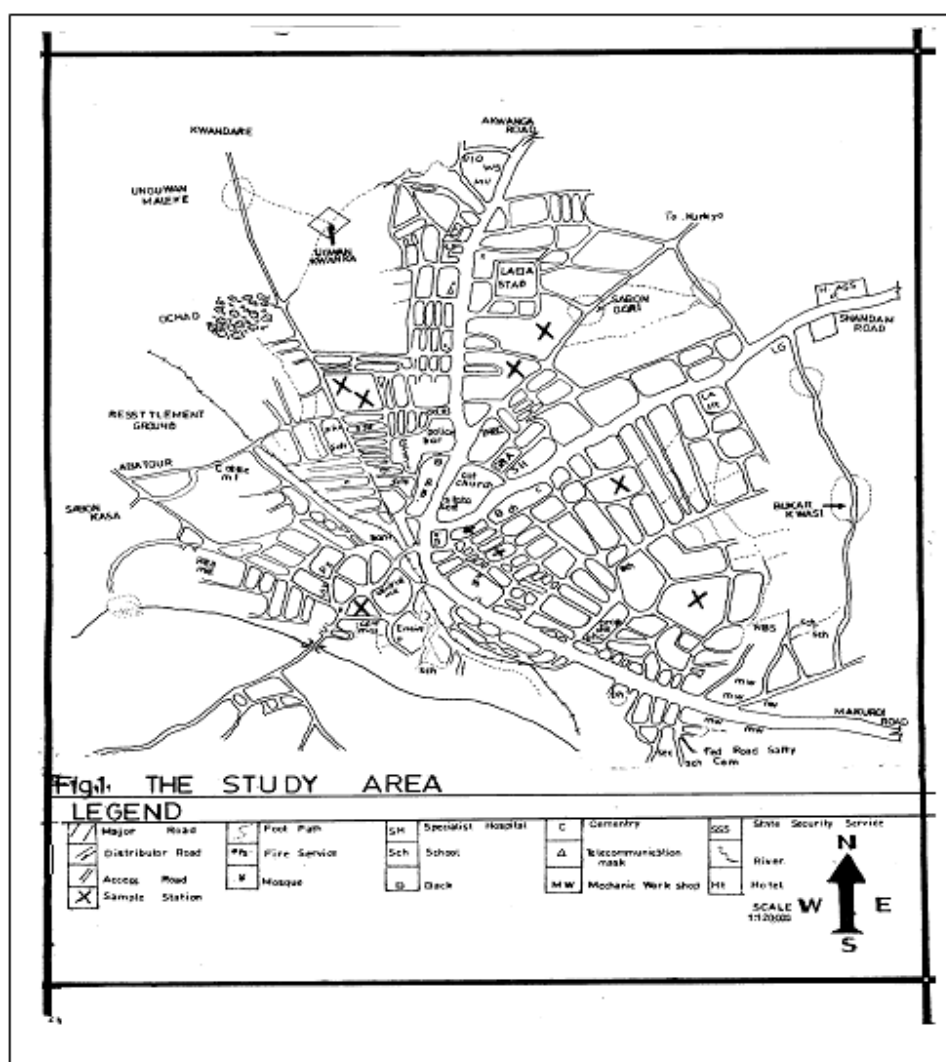
Fig.1 THE STUDY AREA

2.4 pH Determination

The pH of each of the sample was determined at each point of sample location after calibration of the pH meter using buffer solution [17].

2.5 Extraction, preconcentration and analysis of trace metals

The most valuable and commonly used procedure for extractive concentration of trace metals is that employing chelation with ammonium pyrrolidinedithiocarbamate (A.P.D.C.) by extraction into Methyl Isobutyl Ketone (M.I.B.K.). The extraction of charged species from an aqueous solution is not possible unless the charge can be neutralized by chelation. Since metals ions do not tend to dissolve appreciably in organic solvents, their charge must first of all be neutralized to make it "organic like". MIBK is widely used as a solvent in this technique because it has quite low solubility in water making it useful for liquid-liquid extraction.

Thus to 100 mL of each sample measured into 250 mL separating funnel, 4mL of 5% APDC was added, followed by 25 mL Methyl Isobutyl Ketone (M.I.B.K). The separating funnel is stoppered and shaken manually for 5 minutes after which the organic phase separated to the bottom leaving the aqueous phase on top. The process was repeated so as to get enough extract. The organic trace metals extract of each sample was analysed using Atomic Absorption Spectrometry (AAS) against standards at the wavelengths of As (248.3 nm), Co (240.7 nm), Cd (309.3 nm), Cr (248.3 nm), Pb (217.0 nm), Al (248.3 nm), Ni (324.7 nm), Mn (422.7 nm). These standards were prepared in different concentrations; 1ppm, 3 ppm,5 ppm or 10 ppm from 1000 ppm standards. Calibration curves were plotted from which the concentrations of the elements in each sample were extrapolated. Quality control was assured because all the determinations were in triplicate in addition to the use of standard reference materials, procedural blanks, relative standard deviations[18, 19,20].

2.6 Statistical analysis of data

The results obtained were analyzed statistically by using the mean value ($\overline{X}$), coefficient of variation (CV) and standard deviation (S) [21]. Furthermore, correlation tests were used to determine the significant relationship between the mean concentrations of trace metals obtained from BH and HDW using statistical package for social sciences SPSS version 16.

III.   Results And Discussion

3.1 Results

Table 1 shows sample stations and their various locations within ten neighbourhoods.

Tables 2 and 3 presents results of pH determination for BH and HDW for wet and dry seasons.

Tables 4 and 5 show mean concentrations of trace metals campared between BH water samples on one hand and HDW water samples on the other hand for the two seasons. Similarly, Tables 6 and 7show mean concentrations of trace metals compared between BH and HDW on one hand in wet season and that between BH and HDW in dry season. Their corresponding variations (charts) are presented as Figures; 2A-2E, 3A-3E, 4A-4E and 5A-5E. However, Cd and Al were not detected throughout the period.

Table 1: Sample stations and their locations

Location	Neighbourhood
Lafia North	BukanSidi I
	Ombi II
Lafia Central	Millionaires Quarters
	National Supply
Lafia West	TudunGwandara (Alhamis)
	Shinge
Lafia South	Doma Road
	Emir's Palace (KofanFada)
Lafia East	Makurdi Road/Sabo Pegi
	Shendam Road

Table 2: Mean values of pH of water samples from Borehole and hand –dug-well for wet season

	pH(BH)		pH(HDW)	
Location	Mean	CV %	Mean	CV %
Lafia North	6.050+0.9192	15.19	5.800+0.9899	17.07
Lafia Central	5.300+0.1414	2.668	5.100+0.7071	13.86
Lafia West	5.450+0.2121	3.892	4.850+0.3535	7.289
Lafia South	5.300+0.4243	8.006	4.850+2.000	41.24
Lafia East	4.750+0.3536	7.444	4.800+1.697	35.35

KEY: BH   =   Borehole
        HDW   =   Hand-dug-well
        CV   =   Coefficient of variation

Table3: Mean values of pH of water samples from Borehole and hand dug well for dry season

	pH(BH)		pH(HDW)	
Location	Mean	CV %	Mean	CV %
Lafia North	6.600+0.8485	12.86	6.500+0.1414	2.175
Lafia Central	5.750+0.2121	3.689	5.450+1.060	19.45
Lafia West	5.700+0.1414	2.481	5.350+0.6364	11.87
Lafia South	5.300+0.4243	8.006	5.200+1.838	35.35
Lafia East	5.650+0.2121	3.750	5.40+2.404	45.52

KEY: BH   =   Borehole
        HDW   =   Hand-dug-well
        CV   =   Coefficient of variation

Table 4: Comparison of mean concentrations of some trace metals obtained from borehole (BH) water samples for wet and dry seasons

Concentration (mg/L)

	As		Co		Cr		Pb		Ni		Mn	
Location	BH(WS)	BH(DS)	BH(WS)	BH(DS)	BH(WS)	BH(DS)	BH(WS)	BH(DS)	BH(WS)	BH(DS)	BH(WS)	BH(DS)
Lafia North	0.0292±0.0001	0.0140±0.0001	0.1877±0.0001	0.0343±0.0001	0.0283±0.0001	ND	0.0111±0.0001	ND	0.2190±0.0001	0.0210±0.0001	0.2894±0.1414	0.1524±0.0240
Lafia Central	0.0430±0.0001	ND	0.1644±0.0768	ND	ND	0.0309±0.0001	0.0092±0.0001	ND	0.3729±0.0001	0.1756±0.0001	0.4072±0.0935	0.2373±0.0680
Lafia West	0.0905±0.0020	ND	0.1190±0.0001	0.1549±0.0001	0.5049±0.5871	ND	ND	ND	ND	ND	0.7787±0.2389	0.3815±0.0907
Lafia South	0.0292±0.0001	ND	0.1311±0.0001	0.1451±0.0001	0.0272±0.0001	0.0042±0.0001	0.0049±0.0001	ND	0.2129±0.0001	ND	0.2141±0.1414	0.1401±0.0001
Lafia East	0.2710±0.0001	0.1870±0.0001	0.2406±0.2114	0.0740±0.0001	0.4790±0.0001	0.1450±0.0001	0.0082±0.0027	ND	0.3292±0.0001	0.0295±0.0001	0.1709±0.0945	0.0907±0.0473

KEY: BH (WS)   =   Borehole wet season
             BH (DS)=   Borehole dry season
             ND   =   Not Detected

Table 5: Comparison of mean concentrations of some trace metals obtained from hand-dug well (HDW) water samples for wet and dry seasons

	As		Co		Cr		Pb		Ni		Mn	
	HDW(WS)	HDW (DS)	HDW(WS)	HDW (DS)	HDW(WS)	HDW (DS)	HDW(WS)	HDW (DS)	HDW(WS)	HDW (DS)	HDW(WS)	HDW (DS)
Location												
Lafia North	ND	ND	0.0910±0.0001	0.0428±0.0001	ND	ND	0.0202±0.0001	ND	0.0841±0.0001	ND	0.3151±0.0288	0.2833±0.0003
Lafia Central	0.0910±0.0717	0.0721±0.0001	0.1398±0.0001	0.0091±0.0001	0.1663±0.1773	0.0102±0.0001	0.0432±0.0537	0.0432±0.0537	0.1081±0.0001	0.0065±0.0001	0.3109±0.0662	0.1489±0.0407
Lafia West	ND	ND	ND	ND	0.0430±0.0001	ND	ND	ND	ND	ND	0.6227±0.0260	0.3588±0.0762
Lafia South	0.2077±0.0001	0.0987±0.0001	ND	ND	0.2077±0.0001	0.0773±0.0001	ND	ND	ND	ND	0.2529±0.2005	0.2304±0.0236
Lafia East	0.0106±0.0001	0.1102±0.0001	0.0281±0.0001	ND	0.2057±0.0001	ND	ND	ND	ND	ND	0.1049±0.0322	0.1574±0.0002

Concentration (mg/L)

KEY: HDW(WS)   =   Hand-dug well wet season
             HDW(DS)   =   Hand –dug well dry season
             ND   =   Not Detected

Table 6: Comparison of mean concentrations of some trace metals obtained from BH and HDW water samples for wet season

Concentration (mg/L)

	As		Co		Cr		Pb		Ni		Mn	
Location	BH	HDW	BH	HDW	BH	HDW	BH	HDW	BH	HDW	BH	HDW
Lafia North	0.0292±0.0001	ND	0.1877±0.0001	0.0910±0.0001	0.0283±0.0001	ND	0.0111±0.0001	0.0202±0.0001	0.2190±0.0001	0.0841±0.0001	0.2894±0.1414	0.3151±0.0288
Lafia Central	0.0430±0.0001	0.0910±0.0717	0.1644±0.0768	0.1398±0.0001	ND	0.1663±0.1773	0.0092±0.0001	0.0432±0.0537	0.3729±0.0001	0.1081±0.0001	0.4072±0.0935	0.3109±0.0662
Lafia West	0.0905±0.0020	ND	0.1190±0.0001	ND	0.5049±0.587	0.0430±0.0001	ND	ND	ND	ND	0.7787±0.2389	0.6227±0.0260
Lafia South	0.0292±0.0001	0.2077±0.0001	0.1311±0.0001	ND	0.0272±0.0001	0.2077±0.0001	0.0049±0.0001	ND	0.2129±0.0001	ND	0.2141±0.1414	0.2529±0.2005
Lafia East	0.2710±0.0001	0.0106±0.0001	0.2406±0.211	0.0281±0.0001	0.4790±0.0001	0.2057±0.0001	0.0082±0.0027	ND	0.3292±0.0001	ND	0.1709±0.0945	0.1049±0.0322

KEY: BH   =   Borehole,   HDW =   Hand dug well, ND = Not Detected

Table 7: Comparison of mean concentrations of some trace metals obtained from BH and HDW water samples for dry season

Concentration (mg/L)

Location	As BH	As HDW	Co BH	Co HDW	Cr BH	Cr HDW	Pb BH	Pb HDW	Ni BH	Ni HDW	Mn BH	Mn HDW
Lafia North	0.0140±0.0001	ND	0.0343±0.0001	0.0428±0.0001	ND	ND	ND	ND	0.0210±0.0001	ND	0.1524±0.0240	0.2833±0.0003
Lafia Central	ND	0.0721±0.0001	ND	0.0091±0.0001	0.0309±0.0001	0.0102±0.0001	ND	0.0432±0.0537	0.1756±0.0001	0.0065±0.0001	0.2373±0.0680	0.1489±0.0407
Lafia West	ND	ND	0.1549±0.0001	ND	ND	ND	ND	ND	ND	ND	0.3815±0.0907	0.3588±0.0762
Lafia South	ND	0.0987±0.0001	0.1451±0.0001	ND	0.0042±0.0001	0.0773±0.0001	ND	ND	ND	ND	0.1401±0.0001	0.2304±0.0236
Lafia East	0.1870±0.0001	0.1102±0.0001	0.0740±0.0001	ND	0.1450±0.0001	ND	ND	ND	0.0295±0.0001	ND	0.0907±0.0473	0.1574±0.0002

KEY: BH = Borehole, HDW = Hand dug well, ND=Not Detected
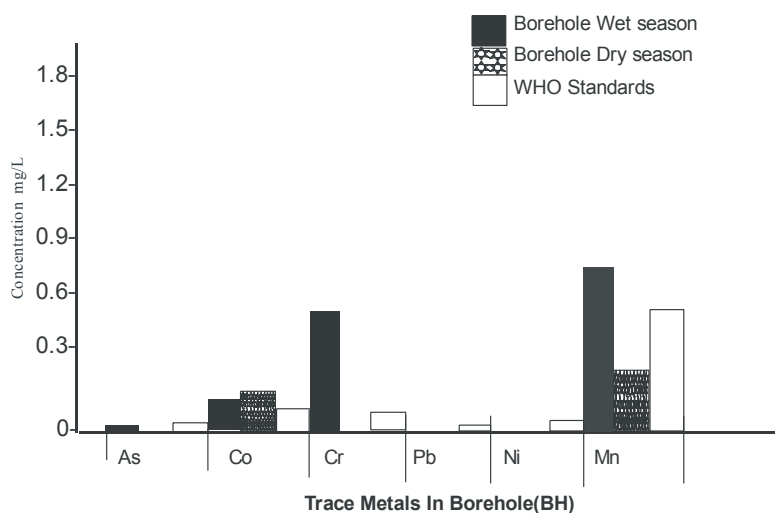
Fig. 2C: Variation of mean concentration of trace metals in borehole for both wet and dry seasons in Lafia West
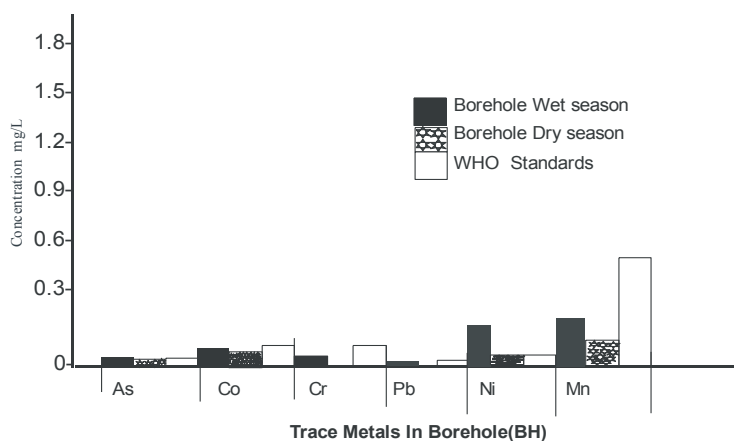
Figure 2A: Variation of mean concentration of trace metals in borehole for both wet and dry seasons in LafiaNorth
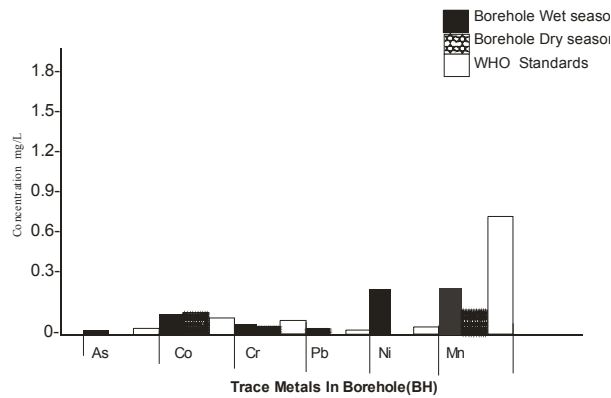
Fig. 2D: Variation of mean concentration of trace metals in borehole for both wet and dry seasons in Lafia South
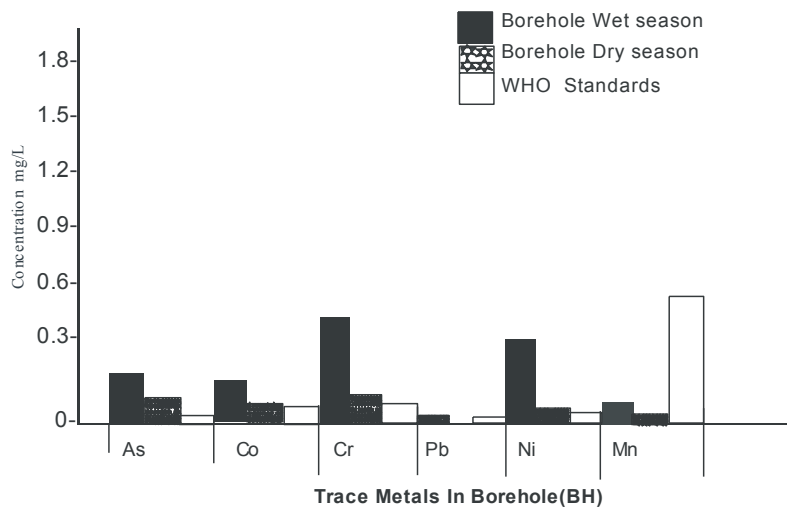
Fig. 2E: Variation of mean concentration of trace metals in borehole for both wet and dry seasons in Lafia East
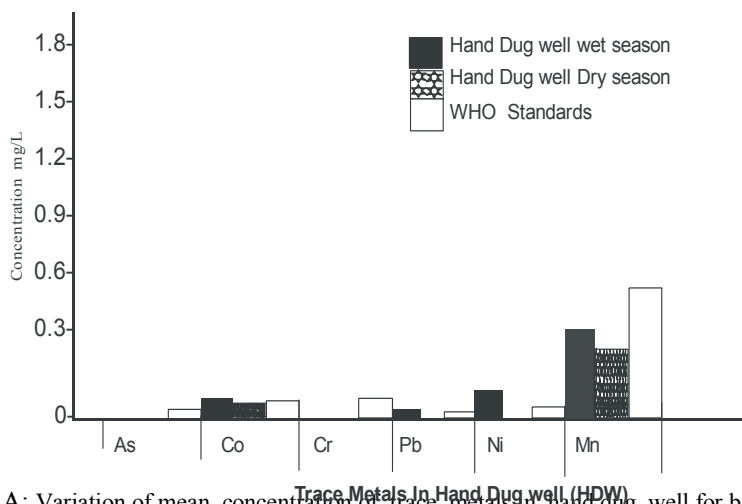
Figure 3A: Variation of mean concentration of trace metals in hand dug well for both wet and dry seasons in Lafia North
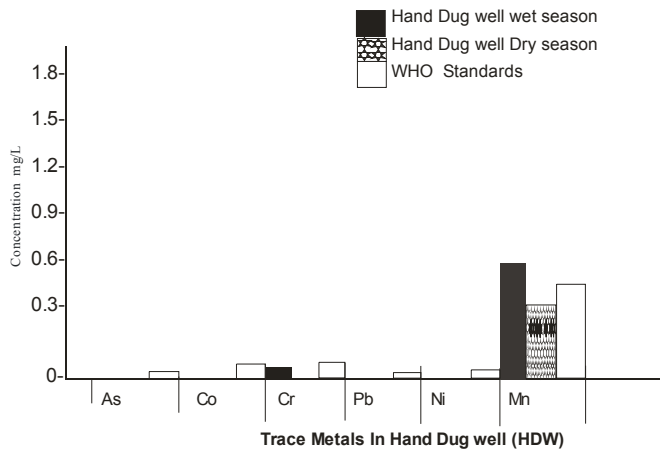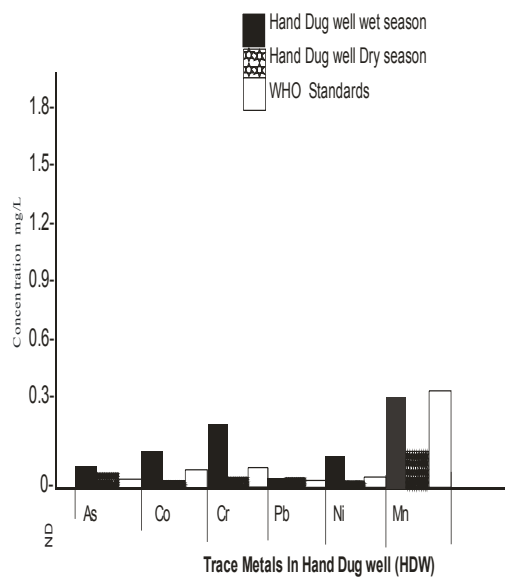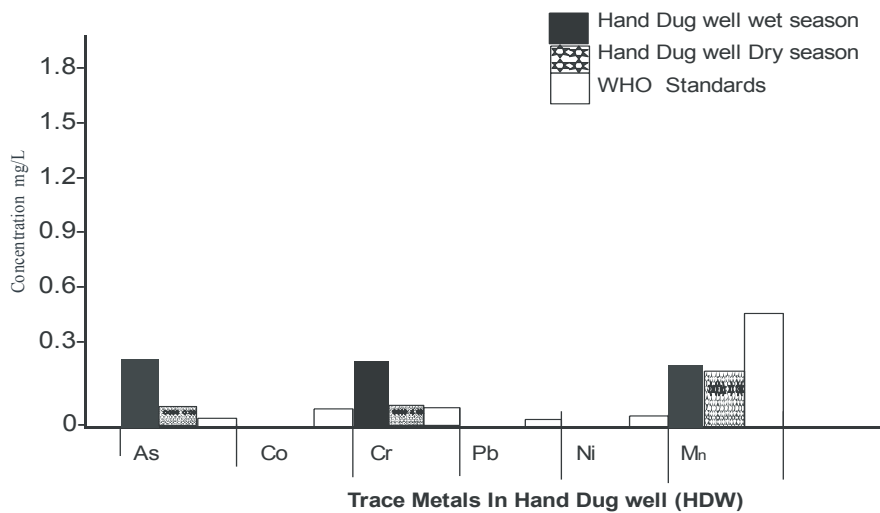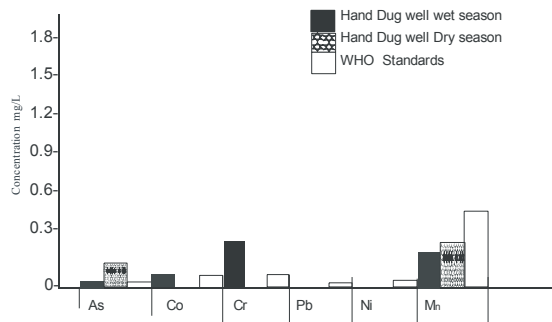
Fig. 3C: Variation of mean concentration of trace metals in hand dug well for both wet and dry seasons in Lafia West

Fig. 3B: Variation of mean concentration of trace metals in hand dug well for both wet and dry seasons in LafiaCentral

Fig. 3E: Variation of mean conc.of trace metals in hand dug well for both wet and dry seasons in Lafia East
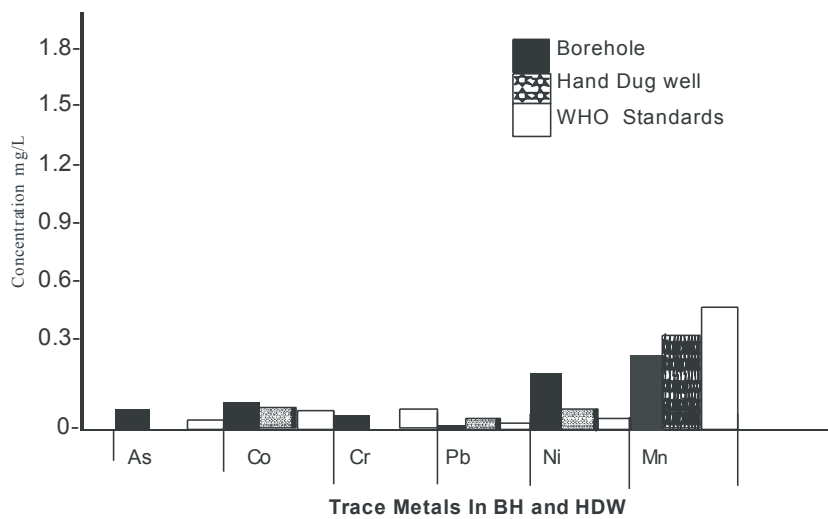
Fig. 4A: Variation of mean concentration of   trace metals in BH and HDW for wet season in Lafia North
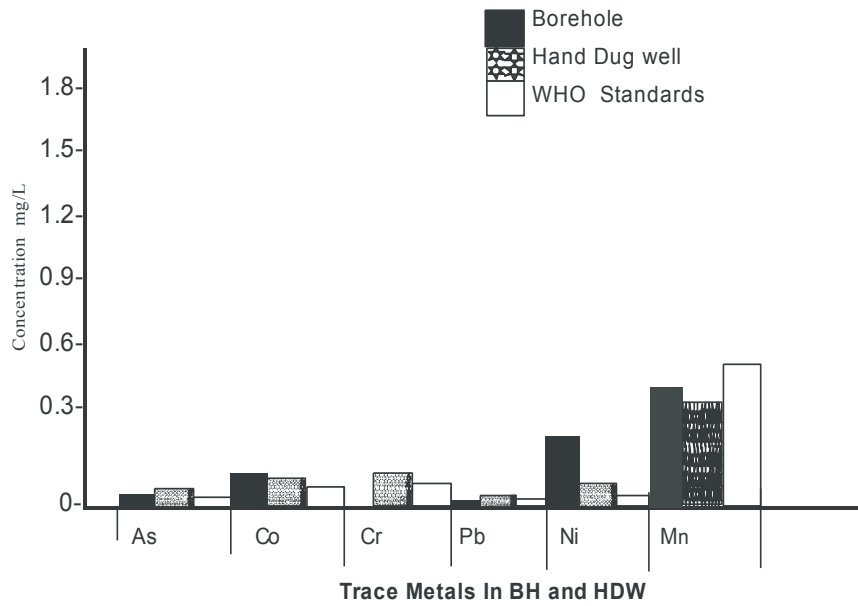
Fig. 4B: Variation of mean concentration of trace metals in BH and HDW for wet season in Lafia Central
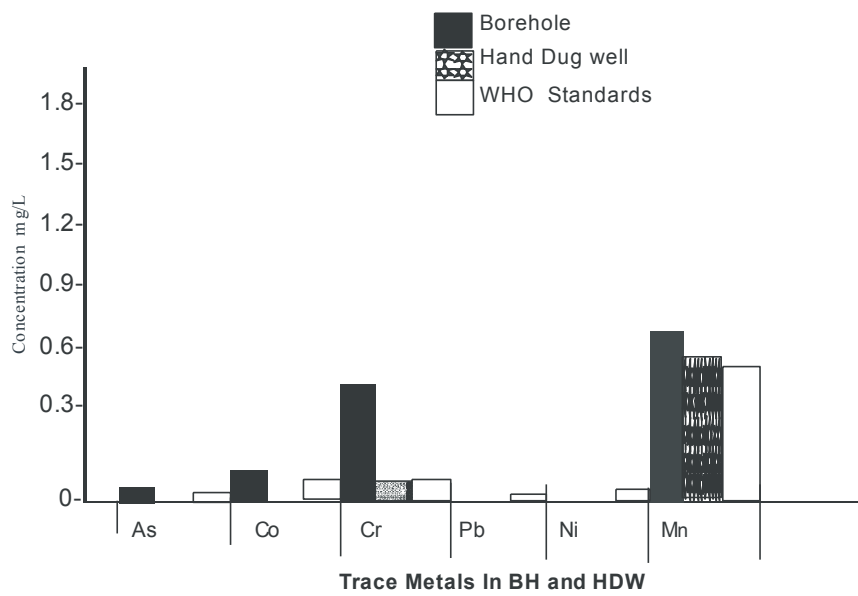

Fig. 4C: Variation of mean concentration of trace metals in BH and HDW for wet season in Lafia West
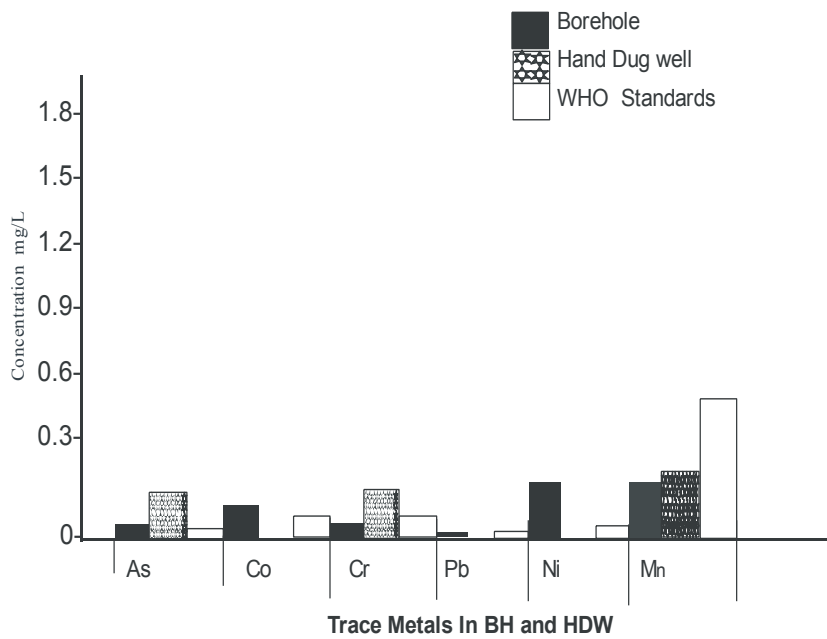
Fig. 4D: Variation of mean concentration of trace metals in BH and HDW for wet season in Lafia South
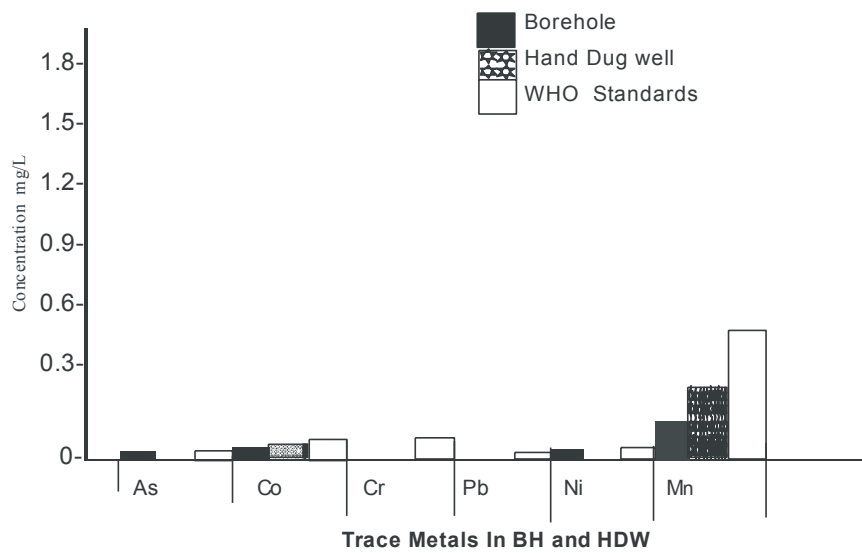

Fig. 5A: Variation of mean concentration of trace metals in BH and HDW for wet season in Lafia North
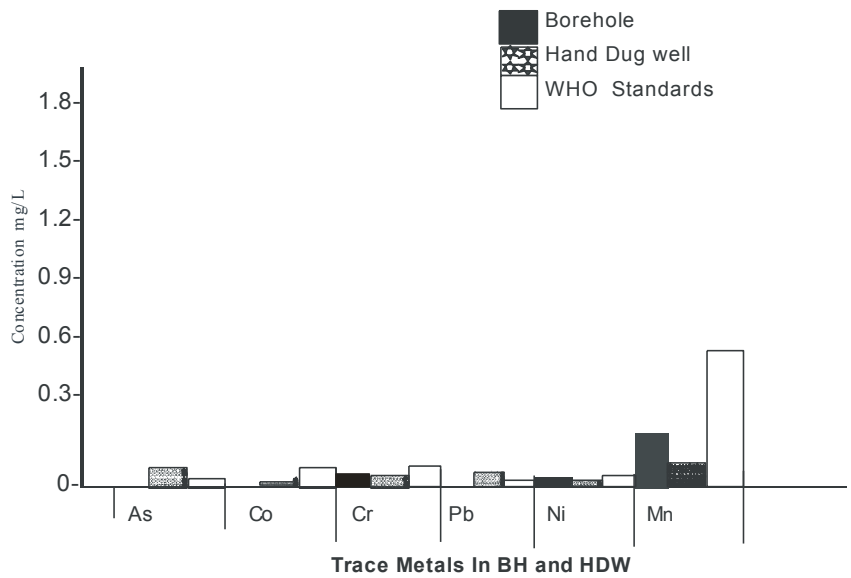
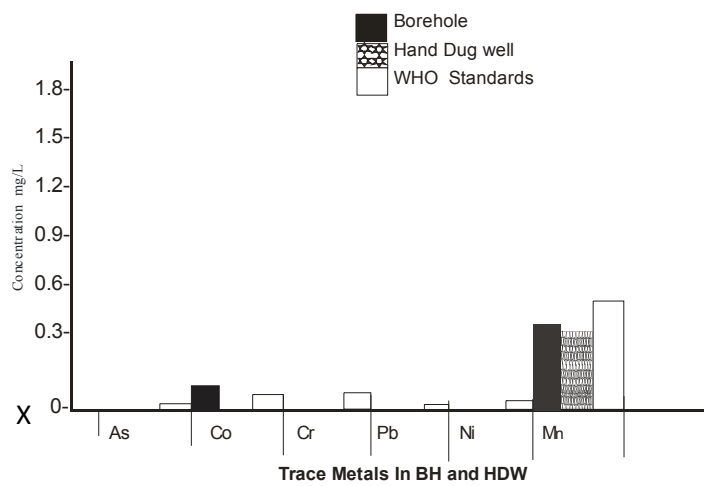Fig. 5B: Variation of mean concentration of trace metals in BH and HDW for dry season in Lafia Central

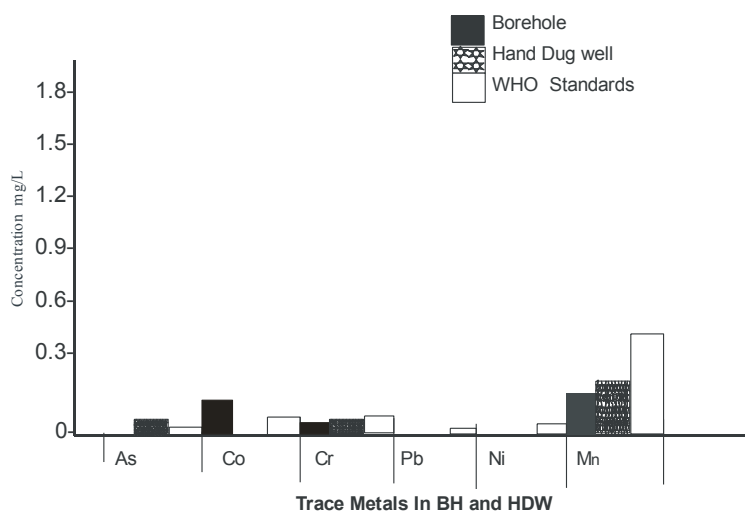Fig. 5C: Variation of mean concentration of trace metals in BH and HDW for dry season in Lafia West

Fig. 5D: Variation of mean concentration of trace metals in BH and HDW for dry season in Lafia South
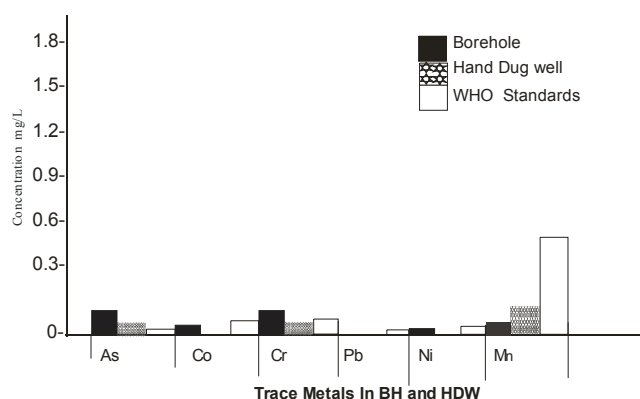
Fig. 5E: Variation of mean concentration of trace metals in BH and HDW for dry season in Lafia East

3.2 Discussion

The results of analyses of some trace metals studied are shown in Tables 4,5,6 and 7. The trace metal with the highest mean concentration during WS was Mn(0.7787 +0.2389 mg/L) for BH in Lafia West while the least concentrated metal for the same season is Pb(0.0049+ 0.0001 mg/L) for BH water samples in Lafia South. Similarly for HDW water samples in wet season, the highest mean concentration was Mn (0.6227+ 0.0260 mg/L) in Lafia West while the least was As (0.0106 +0.0001 mg/L) in Lafia East. In the case of DS, the highest concentrated metal was Mn(0.3815 +0.0907 mg/L) for BH in Lafia West while the least concentrated metal was Cr(0.0042 +0.0001 mg/L) for HDW in Lafia South. Similarly for HDW in dry season, the highest was Mn(0.3580 + 0.0762 mg/L) in Lafia West while the least was Ni(0.0065 +0.0001 mg/L) in Lafia Central.

The following metals were not within the detection limit in both seasons namely Cd, Al. When compared, the level of trace metals for BH and HDW for WS, with the highest variation was found in Cr(116.2%, BH) in Lafia West and Pb(124.3% HDW) in Lafia Central while the least were Ni(0.0268% BH) in Lafia Central; As(0.0481% HDW) and Cr(0.0481% HDW) all in Lafia South. Similarly, the highest variation during the dry season (DS) occurred for Mn(52.15% BH) in Lafia East and Pb(124.3%, HDW) in Lafia Central while the least were As(0.0535% BH and As(0.0907% HDW) all in Lafia East.

In Tables 2 and 3Lafia North had the highest mean pH 6.050 + 0.9192 (slightly acidic) for borehole (BH) during the wet season (WS), while the least pH of 4.750 +0.3536 (moderately acidic) occurred at Lafia East for Borehole (BH). Similarly during, the Dry Season (DS), Lafia North had the highest pH of 6.600 +0 .8485(slightly acidic) for BH while the least pH of 5.200 + 1.838 was recorded for HDW in Lafia South.

These mean pH values, except for BH in Lafia North are not in agreement with the standard guidelines by WHO, NAFDAC (pH 6.5-8.5) indicating that the BH and HDW water samples are not suitable for drinking and other purposes. These values are consistent with the works of Mcbride (1994) which warned that levels of certain soluble metals particularly Al^{3+}, Mn^{2+} at such pH 5.0-5.5 would be high enough to be biologically toxic [22].

The reason may be due to the level of minerals in the area and run-offs of various wastes. Soil pH plays a major function in the sorption of trace metals as it directly controls the solubility and hydrolysis of metal hydroxides, carbonates and phosphates. It also influences ion-pair formation, solubility of organic matter as well as surface charge of Fe, Mn and Al-oxides, organic matter and clay edges [23].

Table 4 compares results generated for BH between the two seasons and variations presented (Fig. 2A-2E). The mean concentrations of all the metals investigated decreased from WS to DS. Similarly in the case of HDW, presented in Table 5, the mean concentration of the five metals investigated decreased generally from WS to DS (Fig. 3A-3E). However the variation is significant in HDW between the two seasons for all the parameters investigated [24].

Tables 6, 7 compares mean concentrations of metals for BH and HDW during wet season on one hand and dry season on the other. The variations are presented graphically in (Fig. 4A-4E) (Table 6), and Fig. 5A-5E (Table 7). In all the locations during the wet season, there is marked difference in mean concentrations between BH and HDW, with BH recording higher values than HDW in all the locations except in Lafia South where the

trend is 50% in favour of HDW and 50% in favour of BH. However, during the dry season, 50% of the samples (BH, HDW) had no trace metals detected. For the remaining 50% of the samples, trace metals in both BH, HDW were detected in equal proportion and low concentrations and significantly low difference between BH and HDW.

In summary, the mean concentrations of trace metals in the BH and HDW water samples were higher during the wet season than dry season. This is most likely due to leaching from already weathered materials which is enhanced during rainy season. Another reason could be due to geological formation (solid minerals) status of Lafia town and increased run-offs of wastes into source waters [25].

IV.   Conclusion

The study presented data on the concentration of trace metals (As, Co, Cr, Pb, Ni, Mn) in ground water sources; Boreholes and Hand dug wells collected from various locations within and around Lafia metropolis. The results revealed that there were indications of trace metals in the following proportion As 40%, Co 40%, Cr 37.5%, Pb 25%, Ni 25%, Mn 97.5% of the total water samples and their contents were found to be higher in some cases than the recommended guideline values by WHO, NAFDAC, NSDWQ (borehole monitoring unit of Federal Ministry of Water Resources). These levels of trace metals could be due to contribution by the geology of Lafia metropolis, which hosts minerals like Columbite, Tantalite, Cassiterite, run-offs of wastes from anthropogenic activities. This means that water sources from BH and HDW are polluted by these metals and will pose danger to consumers. It is well known that minerals are necessary for life performing important function in the metabolism of living organism. On the other hand, when taken in excess both toxicity and necessity vary from element to element and from species to species. Over millions of years, men and other living creatures have become tolerant to these small concentrations of heavy metals and it is more than likely that some forms of life may now be dependent on these poisonous metals as trace elements. Therefore this information onthe levels ofintake of trace metals through water is important in assessing risk to human health arising from increasing environmental pollution.

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