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Assessment of Herbicide Residues and Heavy Metals in Yawa Dug Wells Water

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Abstract

The present study was carried out to investigate the occurrence and effects of herbicides on human health and the environment in Yawa area of Mubi South Local Government Area. Physiochemical properties were conducted using standard methods. The concentration of heavy metals was determined using atomic absorption spectroscopy (AAS) VGP 210 and pesticide residues were determined according AOAC methods. All the physiochemical parameters investigated did not fall within the permitted values accepted by WHO. It was found that the concentrations of some metals such as Ca, Fe, Mg, and Cu in Wells A and F) detected were slightly higher than WHO limit with few exception that were below required limit. Iron was the most abundant metal detected. The general trend of concentrations of the heavy metals in the water samples from different sources ranges as Fe>Mg>Ca>Cu. Atrazine was found to be present in the following order E >D>A>G >F>B>C. Sample E has the highest value of 0.88±0.001 mg/l and sample C with the lowest value of 0.023±0.001 mg/l. This study has shown that Atrazine is still in use despite the ban on its uses. It is therefore, recommended that government should intensify public sensitisation on the dangers associated with the uses of these pesticides despite their numerous benefits. Periodic assessment of the dug well water in Yawa should be carried out to ascertain the level of pesticide pollution and safety for consumption.

Keywords: Yawa Fulani, Yawa Hosere, herbicide residues, heavy metals, recalcitrant, water contamination, dug well

Introduction

Billions of people are today still living without safe water for their households, schools, farms and workplaces. The rural poor are among people that suffer the most (FAO, 2019). Water supports plants and animals life and it is obtained from ground and surface sources. It can dissolve, absorb and suspend a compound due to its polar nature and hydrogen bonding. Some activities such as indiscriminate disposal of refuge, sewage discharge of domestic and industrial effluent, pharmaceutical product, use of pesticides and use of automobiles have contributed to the pollution of water ways by discharging toxic metals and pesticides into rivers, streams and finally gets into contact with the ground water. Pesticides enter the ground and surface water primarily as a run-off from crops and it is most prevalent in agricultural areas (Babagana *et al.*, 2014).

Pesticides are potentially stable and their recalcitrant metabolites are being formed in the environment before complete herbicide mineralization occurs. Investigation of herbicides such as their occurrence and effects on the environment and human health is significant puzzle which must be obtained (Koplin *et al.*, 1998). Nicotine sulphate was extracted from tobacco leaves in 17th century and used as insecticide (Alan *et al.*, 2017). Pesticides are used for crop protection to improve yield, quality and storage life of foods crops. The pesticide residues, metabolic or break down products present in some environments after its application, spillage or dumping of refuse enter the ground and surface water (Fernandaz and Garcia, 2008). Many of the pesticide residues, especially derivatives of chlorinated pesticide exhibit bioaccumulation that could build up in the body and environment. Chlorinated pesticides are toxic at certain concentration (Chung and Chen, 2011; Chang 2005). Nitrogen and many herbicides-most commonly atrazine ($C_8H_{14}ClN_5$) and its breakdown product metolachlor ($C_{15}H_{22}ClNO_2$) and simazine ($C_7H_{12}ClN_5$) were detected more frequently and at higher concentrations in streams and shallow ground water in agricultural areas than in urban areas (EPA, 2006). These recalcitrant chemicals can be magnified in the food chain as previously reported to in products ranging from meat, poultry, fish and vegetable to water (Chung and Chen, 2011). In addition, heavy metals are essential nutrient required for various biochemical and physiological function in small concentrations but when ingested in large quantity, it leads to health problem such as skin irritations, abdominal pain, vomiting, affect reproduction and development of human and animals. It is against this background that the present study was embarked upon to assess the herbicide residues and heavy metals in the Yawa drinking water from dug wells.

Materials and Methods

The study Area

Yawa is located in Mubi South Local Government Area situated at the Lower Contour of Mandara mountains which separates Nigeria from Cameroon, is located at latitude 10^o 15' 98.34" N and longitude 13^o 29' 97.65" E. The area shares boundary with Maiha Local Government Area to the South, Hong Local Government Area in the west, Michika Local Government Area and Cameroon republic in the East (Peter *et al.*, 2015).

Mubi and its environments exhibit a tropical wet and dry type climate. The wet season runs from months of April to October, while the dry season commences in November and end in March. The annual rainfall is about 900 mm with the highest occurrence in July and August. The temperature regime in Mubi is warm to hot throughout the year because of radiation income which is usually relatively evenly distributed throughout the year. However, there is usually a slightly cool period between November and February with gradual increase from January to March. Adebayo (2004) pointed out that relative humidity is low, however it starts rising as from April and reaches the maximum in August.

Hydrogeology of the area

Ground water in general originate as surface water, but their occurrence and distribution are controlled by geologic factors such as lithology, the texture of the rock an supply to the study area (Ray, 1991). The area have several streams that runs into river Yedzaram. It has several number of hand dug wells which also serve the community as source of drinking water, despite few boreholes which cannot adequately serve community. It is also of interest note that, even though, the stream channels are not perennial, still they serve as the recharge zones in connections with deep seated factors for both the hand dug wells, and the boreholes.

Sample Collection

Seven water samples were collected from different locations of Yawa Fulani and Yawa Hosere of Mubi South Local Government Area (Figure 1) in the month of November 2017 from dug wells which were extensively used for drinking and domestic purposes. The water samples were collected using 1 litre cleaned polyethane bottles and the bottles were rinsed with the sample water before they were filled to the brim. The water samples were immediately transported to the Animal Production Laboratory and Chemistry Laboratory, Adamawa State University, Mubi for analysis.

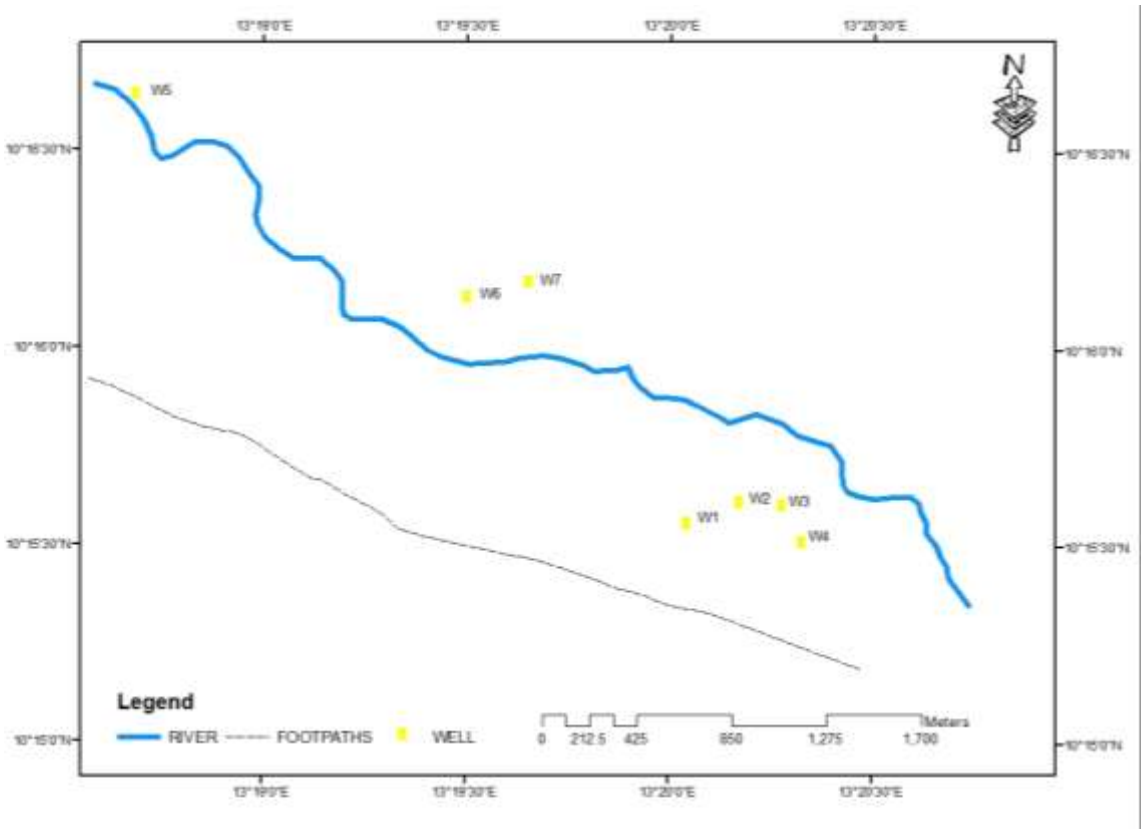

Figure 1: Well water sites at Yawa (Field Work, 2018)

Determination of Physicochemical Parameters of Water

Physicochemical parameters such as pH and temperature were directly evaluated on the point of sample collection, while other parameters were analysed in the laboratory. The pH of the water samples were determined using pocket sized pH meter (pH 107). Temperature was determined using mercury thermometer. Total Dissolved Solids (TDS) of water samples were determined using TDS meter, (Milwaukee Mi 805 pH/ EC/TDS/Temperature portable meters). Turbidity and conductivity of water samples were determined using Lamotte colorimeter as described manufacturer (Lamotte Smart Water Lab).

Determination of Heavy Metals

The stock solution of the metal standard and the samples were prepared and aspirated into a Bulk Scientific 2010 VGP atomic absorption spectrophotometer (AAS), equipped with mono elemental hallow cathode lamps and digital readout the determines the element of interest at specific wave length and lamb current. Water samples were prepared for the analysis of heavy metals as described by Fache (1988). The data generated were statistically analysed using mean and standard deviation.

Preparation and extraction of pesticide residues from water samples

Preparation and extraction of pesticide residues from water samples were conducted using Association of Official Analytical Chemists (AOAC) (2000) with little modification. About 600 ml filtered water samples was transferred into a 1 litre separator and to each 100 ml petroleum ether was added and mixed by shaking for 2 minutes and 10 ml saturated NaCl solution was added until the mixture separates. The mixture was allowed to separate, discarding the aqueous layer and gently solvent layer was washed with two 100 ml portions of water. The solvent layer was removed to make the concentration of the extract to 10 ml by evaporation.

Determinations of pesticides residues

Determination of pesticide residues in water was carried out according to AOAC (2000). The determination of the residues was carried out by injecting 1ml of the 1.0 cm^3 purified exact into the injection port of a HPLC Buck Scientific BLC 10/10 model, HPLC Las Vegas USA equipped with UV/VIS detector set 200-700 nm. The stainless steel column (250 mm x 4.0 mml. d) was parked with ODS 3 V (5 µm particle diameter GL Science, Las Vegas USA) the column temperature of 30°C was maintained. The gradient system consisted of a mixture of acetonitrile and 20 MMKHZ. The flow rate was 1ml/min and the initial composition of the mobile phase, consists of 7% (V/V) solvent a (100% acetonitrile) and 93% of (20MMKHZP 04), maintained for 7 min while solvent A at 25 Min, 20% at 30 min, 25% at 45 min to 70 min. Programming was carried out then continued in the isocratic made as follows: 40% A to 70, 1 to 75.0 min and 7% A at 75, to 90.1 min. The run time was for 17 minutes. Identification of pesticide residues was accomplished using mix AB -2 Nestek, USA reference standards and relative retention time techniques while the residues was determined by comparing the peak heights of the sample of the reference standard of known concentration. The concentration of organochlorines was calculated directly by the chromatography.

Results and Discussion

The physicochemical parameters

The results of Physicochemical Parameters such as pH, Temperature, Conductivity, Total Dissolve Solids (TDS), turbidity and hardness of Dug Wells water samples in Yawa Mubi South Local Government Area is presented in Table 1.

Table 1: Physicochemical Parameters of Dug Wells Samples in Yawa Mubi South Local Government Area of Adamawa State

Samples	pH	Temperature (°C)	Conductivity (µs)	TSB (ppm)	Turbidity (NUT)	Hardness (ppm)
Well A	5.90 ± 0.036^b	28.00 ± 0.50	221.50 ± 3.50^a	230.00 ± 5.5^b	5.00 ± 0.50^c	216.00 ± 20.00^d
B	6.07 ± 0.06^a	$27.00 \pm .033$	206.50 ± 14.66^b	257.50 ± 6.2^a	35.00 ± 12.11^a	122.00 ± 17.79^d
C	6.38 ± 0.05^a	27.50 ± 0.67	275.50 ± 16.04^a	306.50 ± 2.8^a	5.00 ± 0.56^c	324.00 ± 11.14^b
D	6.62 ± 010^c	28.00 ± 0.33	172.50 ± 18.65^c	133.50 ± 0.88^c	8.75 ± 2.24^b	300.50 ± 16.51^a
E	6.67 ± 0.07^a	27.75 ± 0.33	151.00 ± 14.22^d	128.50 ± 1.88^c	28.50 ± 0.85^a	382.00 ± 26.95^a
F	6.64 ± 0.15^a	27.75 ± 0.33	109.50 ± 14.80^e	92.00 ± 2.00^c	29.00 ± 0.24^a	183.50 ± 7.3^c
G	6.71 ± 0.11^c	28.00 ± 0.33	138.50 ± 14.89^e	121.00 ± 1.73^c	10.50 ± 0.58^b	282.00 ± 10.39^c

The pH of the water samples ranges from 5.90±0.23 to 6.78±0.21. The pH values required for drinking is 6.5 to 8.5 (EPA, 2006). According to this, sample G have pH 5.90±0.23 and sample D have pH 6.07±0.23 and sample A, pH 6.38±0.32, which are below the minimum range of WHO standard and this shows that the waters are slightly contaminated. The rest of the samples all fall within the required pH allowed for drinking water (WHO, 2008).

The temperature of the water samples ranges from 27.00±1.41°C to 28.00±1.41 °C. Sample B shows the lowest temperature of 27.00±1.41 °C and samples A, D and G shows the highest value of 28.00±1.41 °C, the differences between the lowest and the highest value is just 1°C.

The electrical conductivity of the water samples ranges from 109.50±19.09 µs to 275.50±28.99 µs Electrical conductivity is a quantitative measure of the ability of electricity to pass through a substance. Sample C shows the highest value and sample F showed the least value. These values obtained shows the sample will all conduct electricity or allow electricity current to pass through. This shows that water are contaminated.

The TDS values obtained ranges from 92.00±2.83 ppm to 306.50±10.61 ppm. Sample F shows the least value and sample C shows the highest value. The permitted limit of TDS is 300-500 ppm as stated by (EPA, 2006). The samples fall below the lowest value of 330 ppm except for sample C (306.56±6.36) lowest the permitted value, which is slightly above sample B and A; 257.50±10.61 µs and 230.00±12.87 µs respectively, while sample D, E and G were 133.50±2.12; 128.50±3.54;121.00±4.24 µs respectively.

The turbidity of drinking water should not be more than 5 NUT as stated by WHO (2008). The water samples shows turbidity ranging from 5.00±1.41 to 35.00±28.28. Only sample A and C falls within the allowed limit by WHO (2008) while the other samples (except A & C) are all far above the allowed limit. This shows that all the samples are not favourable for drinking based on their turbidity. However, turbidity alone is not a single factor for determining quality drinking water. All the water samples studied shows a value below the permitted hardness value of 500 mg/l and sample E shows the least value of 122±39.60 mg/L. When water is hard, it causes scale to form in kettles, pots, steam irons; implying that all water samples studied are good and cannot stuck in the pipes.

Concentration of Heavy Metals

The concentrations of metals observed in the Yewa dug wells water samples is presented in Table 2. Calcium was only found in water samples obtained from Yawa Fulani i.e. sample E-G, Calcium concentration was below detectable limit. Sample A showed the highest value (1.51±0.14 mg/l) of calcium with sample D showing least value (0.28±0.07 mg/l). The value of calcium recorded from the four samples are in a descending order A>C>B>D; 1.51±0.14; 1.23±0.01; 0.80±0.32, mg/l and 0.28±0.07 mg/l respectively. This indicated that people living in Yawa needed supplemental sources of calcium for proper bone formation since the calcium daily recommended intake is 800 mg/day (WHO, 2008). The highest level of Magnesium was found in sample C (2.12±0.04 mg/kg) and from Yawa Hosere which is below the daily intake required metabolism. Copper was only found in two samples but lower than the recommended daily intake (WHO, 2008). The study indicated that the concentration of Cd, Zn, Cr, and Mn are below allowable limit set by WHO (2008). Deficiency in these essential elements such as Zn, Cr and Mn can result to illness, because there are important mineral to the body. While Zn, Cd and Pb are not essential for human even in minute (EPA, 2004).

Table 2: Concentration of Some Metal in Dug Wells Water Samples (mg/L)

Samples	Ca	Cd	Zn	Fe	Mg	Cr	Mn	Pb	Cu
Well A	1.51 ± 0.01[a]	ND	ND	ND	1.56 ± 0.05[b]	ND	ND	ND	0.05 ± 0.01[b]
B	0.80 ± 0.14[c]	ND	ND	6.41 ± 0.01[a]	0.78 ± 0.04[c]	ND	ND	ND	ND
C	1.23 ± 0.01[b]	ND	ND	ND	2.12 ± 0.04[a]	ND	ND	ND	ND
D	0.28 ± 0.02[d]	ND	ND	0.61 ± 0.03[e]	0.63 ± 0.03[d]	ND	ND	ND	ND
E	ND	ND	ND	1.60 ± 0.02[c]	0.32 ± 0.01[f]	ND	ND	ND	ND
F	ND	ND	ND	4.18 ± 0.02[b]	ND	ND	ND	ND	0.08 ± 0.00[a]
G	ND	ND	ND	1.23 ± 0.01[d]	0.40 ± 0.01[e]	ND	ND	ND	ND

Values are mean ± SD of three replicate determinations.

The result for herbicides determined in Yewa dug wells water samples is presented in Table 3. Herbicides were frequently and widely used for the cultivation of farm products. High concentrations of pesticide in water sources have been reported severally in literature which might be due to many environmental factors such as leaching, water runoff, indiscriminate agricultural activities in the area and industrial waste products that flows from drainages into water bodies (Alexander, *et al.*, 2019). The major contributor to measured concentration in ground water for a given herbicide is its metabolite (Koplin *et al.,* 1998). Atrazine is one of the most widely used herbicide for maize cultivation over the world. The use of this atrazine was banned in Germany in 1991. Despite the prohibition of the use atrazine, some countries still make use of it illegally. It is still used in Nigeria. Considering all the water samples studies atrazine's was found to be present, in the following order

E>D>A>G>F>B>C. Sample E has the highest value of 0.88±0.001 mg/L and sample C has the lowest value (0.023±0.001 mg/L). Butachlor were only detected in sample EF and G with sample E showing the highest value of 0013±0.001 mg/l. while trizophos also detected in sample EF and G with sample E showing the highest value of 0.005±0.001 mg/L. Sample E showed the highest value for all the herbicides tested. This indicates the high usage of these herbicides in that locality by the farms. All the herbicides studied were found to be present in all the water samples taken from Yawa Hosere i.e. sample E-G, while only Paraquat, Matalachlor and atrazine where found in sample A-D obtained from Yawa Fulani. This study reveal that there is high level of herbicides usage in Yawa Hosere over Yawa Fulani. According to Koplin *et al.*, (1998) in their study of herbicides in aquifers across Lowa, they found herbicides residues to be prevalent in ground water which was detected in about 75% of the well samples studied. Atrazine was one of the most persistent compounds they found in their research. Their work supports its poor degradability which leads to persistence in drinking water source. The persistence of pesticide residue in the water sources and aquatic animals affects life through deterioration of metabolism and sometimes leading to death (Alexander, *et al.*, 2019). In line with the fore going statement, it is evident that dug well water sources in Yawa area pose a great danger to community health due to its bioaccumulation ability and potential toxicity.

Table 3: Concentration of Herbicide Residue in Dug Well Yawa (mg/L)

Samples	Butachlor	Triphos	Paraquat	Matalachlor	Atrrazine
Well A	ND	ND	0.035 ±	0.065 ± 0.006^{b}	0.056 ± 0.006^{e}
B	ND	ND	0.026 ± 0.005^{d}	0.014 ± 0.003^{f}	0.029 ± 0.006^{g}
C	ND	ND	0.035 ± 0.005^{e}	0.016 ± 0.006^{e}	0.023 ± 0.006^{f}
D	ND	ND	0.016 ± 0.005^{d}	0.026 ± 0.001^{c}	0.073 ± 0.006^{b}
E	0.013 ± 0.001^{a}	0.015 ± 0.001^{a}	0.098 ± 0.006^{f}	0.066 ± 0.001^{a}	0.088 ± 0.001^{a}
F	0.012 ± 0.001^{a}	ND	0.072 ± 0.003^{a}	0.023 ± 0.001^{a}	0.42 ± 0.006^{e}
G	0.001 ± 0.003^{b}	0.011 ± 0.000^{b}	0.042 ± 0.003^{c}	0.016 ± 0.001^{d}	0.047 ± 0.006^{d}

Values are Mean ± SEM of Different Superscript.

Conclusion

In conclusion, the heavy metals detected may not pose environmental hazard to community. The herbicides paraquat, matachalor and atrazine were detected in Yawa drinking water indicating that it is not safe for drinking. It is therefore recommended that Government should enforce none use of prohibited herbicides in the country. The grass root farmer should be enlightened more on the hazardous effect of the herbicides metabolites due to its incomplete mineralization in water on their health and the environment.

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