Article

Assessment of Toxicity and Potential Health Risk of Pesticides and Heavy Metals along Bade Stretch of River Yobe, Nigeria

Mustapha Usman Nasir [1,2] and Taofik Olatunde Uthman [3*]

[1]Department of Chemistry, Nile University of Nigeria, Abuja 900001, Nigeria, [2]Department of Chemistry, Yobe State University, Damaturu 620101, Nigeria, [3]Department of Biochemistry and Biotechnology, Nile University of Nigeria, Abuja 900001, Nigeria
* Correspondence: taosun77@gmail.com

Abstract: Many towns in Bade Local Government Area (LGA), northern Nigeria have been designated as "hotspots" for chronic kidney disease of unknown origin (CKDu). In a bid to unravel this mystery, the present study was conducted to investigate the potential health risks of River Yobe which passes through many towns in the district and serves as the main source of water for domestic and agricultural purposes. The novelty of this work lies in the selection of four towns namely Alagarno, Azbak, Dagona and Gashua which are directly connected to the river for the study. The physicochemical properties of water samples from the river in the four locations were evaluated followed by determination of heavy metal and pesticide concentrations in water, soil, and selected crops (rice and tomatoes) cultivated through irrigation using water from the river. According to the physicochemical analysis, the pH, electrical conductivity, chemical oxygen demand and biochemical oxygen demand levels of water samples from the four towns were above permissible limits in comparison with World Health Organization (WHO) standards. Specifically, the total dissolved solids found in water samples from Dagona and Alagarno as well as turbidity of water samples from Dagona, Azbak and Gashua were above WHO standards. The concentrations of heavy metals and pesticides in water, soil and crops from the four study locations were above limits set by WHO. These findings indicate that anthropogenic activities including refuse dumps along the riverbank as well as release of untreated municipal effluents, pesticides and fertilizer residues from agricultural practices into the river may be responsible for the pollution reported in this study. Consequently, it is hypothesized that the chronic kidney illness afflicting the people of Bade LGA may be connected to poor quality of water from River Yobe and elevated concentrations of toxic heavy metals and pesticides in the crops.

Keywords: Bade, Heavy metals, Pesticides, River Yobe, Toxicity

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Introduction

Environmental pollution is a major global concern as pollutants including pesticides, heavy metals, hazardous chemicals and petroleum products are widely dispersed in water, soil, and air due to increased urbanization and industrialization [1]. Improper disposal of waste also poses a significant health risk by virtue of their potential to pollute essential resources like food, water, air, soil and vegetation which negatively impact on both humans and plants [2]. Pollution of water bodies with heavy metals and pesticides has rendered many water resources hazardous to human and other living systems. Additionally, studies have shown that municipal waste contain pollutants which end up in soils and water as they are leached out of the dumpsite [3].

Heavy metals are a diverse set of elements that weigh more than 5 g/cm^3 with a range of chemical characteristics and functions [4]. They usually have a density of at least five times that of water and can be classified as either essential or non-essential [5]. Deficiencies of essential heavy metals have an impact on both agricultural productivity and human health while non-essential metals can be hazardous even at low concentrations [6]. Heavy metal pollution usually results from a variety of sources including industrial discharges and indiscriminate dumping of refuse [7]. Generally, heavy metals exhibit toxicity when present in excess of the required concentrations due to their environmental persistence and non-biodegradability [8]. Within the ecosystem, heavy metals create a cyclical chain of contamination that negatively impacts soil, water, food, and human health. Many heavy metals, including cadmium, lead, arsenic, mercury, and nickel are found in significant quantities in the environment where they pose serious threats [9]. They are more damaging to plants because they combine with soil and hinder growth, lower nutrient value and interfere with photosynthesis [10].

Pesticides are chemical substances often applied directly on agricultural land to control pests and improve crop yield [11]. These chemicals are also used as insecticides, herbicides, nematicides, fungicides, molluscicides, rodenticides, and mosquito repellents [12,13]. They play important roles in commercial agriculture and food-based industrial processes such as aquaculture, food processing, and storage where they prevent the spread of diseases by vectors [14]. Hence, pesticides have become an essential commodity in modern agriculture by promoting global food security. However, their extensive use has generated serious environmental and health challenges arising from unintended consequences. About 4.19 million metric tons of pesticides were consumed worldwide in 2019, with China consuming the most (1.76 million metric tons), followed by the US, Brazil and Argentina with 408,000 metric tons, 377,000 metric tons and 204,000 metric tons respectively [15]. According to World Health Organization (WHO) data, 20% of developing nations use pesticides in their farming operations with a potential to cause immune system, endocrine and neurological disturbances [16].

The presence of pesticide residues in food and water has become a common feature with a potential to harm natural and human systems [17]. Application of pesticides may leave residues on fruits, vegetables, and other agricultural crops. Generally, majority of farmers are ignorant of the degree of poisoning and risks to human health that may come with pesticide application [18]. Numerous studies have reported the cytotoxic and neurotoxic effects of pesticides, as well as their involvement in DNA damage and gene mutation [19,20]. However, there are serious concerns about the possible harm that pesticides can inflict on humans through dietary consumption. According to population studies, there is a connection between pesticide exposure and serious health consequences such as cardiovascular disease, harm to reproductive and neurological systems, dementia, hormone imbalance, developmental disorders, some forms of cancer as well as kidney, liver and brain damage [21].

In many developed and developing countries, chronic kidney disease usually results from diabetes and hypertension, both of which are linked to unhealthy lifestyle [22]. However, when there is no clear cause of renal failure, a condition known as chronic kidney disease of unknown origin (CKDu) which is characterized by diminishing renal function usually results [23]. Globally, the prevalence of CKDu has increased to epidemic levels affecting countries like El Salvador, Nicaragua, Guatemala, Honduras, Costa Rica, Mexico, Egypt, Sri Lanka, Bangladesh and India [24,25]. Between 1990 and 2007, there was a notable rise in kidney disorders in Sri Lanka, which were subsequently dubbed CKDu. The condition was characterized by chronic interstitial nephritis caused by exposure to potentially toxic agrochemicals through ingestion of contaminated food, drinking water from contaminated wells, inhalation, and direct contact [26].

In Bade Local Government Area of Yobe State, Nigeria, CKDu has experienced an increase in mortality and morbidity. According to reports, CKDu is one of the leading causes of death in this part of the state and it has drawn the attention of decision-makers and community leaders [27]. Based on hospital records, a significant portion of CKDu patients receiving hemodialysis at Maiduguri Teaching Hospital are residents of communities in Bade LGA [27]. This has necessitated the State govern-

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ment to give free dialysis in most tertiary hospitals in the State to lessen the economic burden of the disease in the affected areas. This suggests that the outbreak of CKDu in the area is not by accident and there may be some risk factors at play. Although the exact cause of the pandemic is still unclear, there have been theories that it may have been caused by water or food crops grown in the area. Therefore, the present study was carried out to evaluate the physicochemical properties as well as the level of pesticide and heavy metal contamination in water, soil and crops along Bade stretch River Yobe with a view to assessing its toxicity and potential health risks.

Results and Discussion

Physicochemical properties

The physicochemical properties of water samples from the four sampling towns are presented in Table 1. The data indicate that slight variations exist in water samples from the four locations in terms of pH, EC, TDS, alkalinity, COD and BOD. However, for turbidity, the water sample from Dagona had a significantly high value compared to other locations. Generally, all the parameters evaluated fell short of WHO standards for drinking water. Specifically, water from the four sampling locations had acidic pH values between 6.33 and 6.46 which were lower than the WHO established permissible range [28]. The order of the pH values was Alagarno>Azbak>Gashua>Dagona. EC gives an indication of electrolyte concentration in water and capacity of water to conduct electrical current. This parameter specifies the amount of dissolved minerals in water samples with higher values indicating the presence of contaminants. The EC values recorded in this study fell between 2.16 dS/m and 2.70 dS/m, which were higher than the WHO-recommended threshold. The order of EC values was Dagona>Gashua>Alagarno>Azbak. The EC values recorded in this study agree with that of a previous report for a water body used for similar anthropogenic activities as River Yobe [29].

Table 1. Physicochemical properties of water samples from River Yobe taken in different towns

Parameters	Sampling Towns				
	Dagona	Alagarno	Azbak	Gashua	WHO [28]
pH	$6.33{\pm}0.05^{a}$	$6.46{\pm}0.05^{a}$	$6.43{\pm}0.05^{a}$	$6.42{\pm}0.05^{a}$	6.5-8.5
EC (dS/m)	$2.70{\pm}0.22^{a}$	$2.53{\pm}0.35^{a}$	$2.16{\pm}0.35^{a}$	$2.67{\pm}0.03^{a}$	1.00
Hardness (mg/L)	$31.56{\pm}1.54^{a}$	$46.53{\pm}9.71^{b}$	$64.81{\pm}8.01^{c}$	$28.89{\pm}1.68^{a}$	150
TDS (mg/L)	$625.52{\pm}8.82^{a}$	$610.00{\pm}3.06^{a}$	$552.11{\pm}3.20^{b}$	$521.11{\pm}2.34^{c}$	500
Alkalinity (mg/L)	$86.78{\pm}6.55^{a}$	$91.71{\pm}9.79^{a}$	$84.22{\pm}2.35^{a}$	$93.67{\pm}2.65^{a}$	500
Turbidity (NTU)	$71.77{\pm}0.39^{a}$	$2.52{\pm}0.79^{b}$	$11.31{\pm}0.34^{c}$	$11.12{\pm}0.45^{c}$	5
COD (mg/L)	$179.97{\pm}5.67^{a}$	$173.35{\pm}3.68^{a}$	$159.10{\pm}3.39^{b}$	$148.41{\pm}4.61^{b}$	80
BOD (mg/L)	$4.54{\pm}0.04^{a}$	$3.12{\pm}0.07^{b}$	$2.82{\pm}0.03^{c}$	$3.41{\pm}0.03^{b}$	2

Results are expressed as mean±standard deviation for 3 determinations. Values with different superscripts for each parameter are significantly different (p<0.05).
EC: Electrical Conductivity; TDS: Total Dissolved Solids; COD: Chemical Oxygen Demand; BOD: Biochemical Oxygen Demand

The hardness of water is a measure of the concentration of dissolved calcium and magnesium ions in water. The hardness obtained in the water samples ranged from 28.89 mg/L to 64.81 mg/L with Azbak > Alagarno > Dagona > Gashua. All values fell below the permissible limit of 150 mg/L recommended by WHO. The total concentration of dissolved compounds in water is denoted by TDS comprising majorly inorganic salts and trace amounts of organic compounds. Cations such as calcium, magnesium, potassium, and sodium, as well as anions including carbonates, nitrates, bicarbonates, chlorides, and sulfates are common inorganic salts found in water. The TDS values in the present study ranged from 521.11 mg/L to 625.52 mg/L with Dagona > Alagarno > Azbak > Gashua being the order of results. All TDS readings are higher than the 500 mg/L limit set by WHO. The alkalinity levels obtained for water samples in this study ranged from 84.22 mg/L to 93.67 mg/L which is lower than the WHO standard value of 500 mg/L. The values were arranged in the order Gashua>Alagarno>Dagona>Azbak.

Water becomes turbid due to the presence of suspended particles including silt, clay, and finely separated organic and inorganic materials. Turbidity may also be impacted by algal growth and industrial waste. The turbidity readings obtained in this study fell between 2.52 NTU and 71.77 NTU. All readings, except for Alagarno, were higher than the limit prescribed by WHO. The order of the results was Dagona > Azbak > Gashua > Alagarno. The measured values of BOD for water samples from the four locations fell between 2.82 mg/L and 4.54 mg/L which are above the minimum threshold of 2 mg/L prescribed by WHO. Similarly, the COD levels in the water samples were above the WHO recommended threshold of 80 mg/L. The COD values recorded ranged from 148.41 mg/L to 179.97 mg/L in the order Dagona>Alagarno>Azbak>Gashua.

The observations reported in this study with respect to physicochemical properties may be attributed to the run-off received by River Yobe based on the anthropogenic activities taking place around the river including refuse dumps, untreated municipal effluents as well as pesticides and fertilizer residues from agricultural practices along the riverbank. The acidic pH observed may be a result of the pesticides applied to crops in nearby farms. Studies have shown that water quality is affected by toxicants, and the effect is reflected in the values of one or more of the physicochemical parameters [11]. Heavy rainfall usually brings run-off with high suspended organic matters and other effluents which may be responsible for the high turbidity recorded in this study [30]. The purity of water can be assessed by the levels of BOD and COD [31,32]. The significantly higher values obtained for BOD and COD in this study when compared to WHO standards is an indication of the level of contamination of River Yobe. A possible cause for this may be deposition of organic and chemical compounds occasioned by human activities near the river [33]. Hence, water from the river may not be suitable for irrigation or domestic purposes. In addition, the observed high concentration of TDS in the water samples is a pointer to the fact that there are intense anthropogenic activities along the course of the river which generate run-off with high suspended matter content [33].

Heavy metal concentration

The concentration of heavy metals in water, rice, tomatoes and soil samples from Dagona, Alagarno, Azbak and Gashua are presented in Figures 1 to 4 respectively. The levels of heavy metals in most of the samples were higher than the limit prescribed by WHO. The only exceptions were copper and iron in all the five samples; chromium in rice soil, tomato soil and rice samples; nickel in rice and tomato soil samples and zinc in water, rice and tomato soil samples. In terms of location, the effect of arsenic manifested significantly in Alagarno (water sample), Dagona (rice and tomatoes) and Azbak (rice and tomato soil). For cadmium, Dagona (water and rice), Alagarno (tomatoes) and Gashua (rice and tomato soil) were significantly affected. Chromium significantly affected Dagona (rice and tomatoes), Alagarno (water and tomato soil) and Azbak (rice soil). The effect of copper was significant in Alagarno taking its toll on water, rice and tomato soil samples. For Dagona and Gashua, copper concentration was significant in tomatoes and rice soil samples respectively. For iron, Alagarno recorded the highest concentration in all the tested samples; while for nickel, Dagona (tomatoes), Alagarno (water and rice soil), Azbak (tomato soil) and Gashua (rice) were significantly affected. Lead significantly affected Dagona (tomatoes and tomato soil), Alagarno (rice), Azbak (water) and Gashua (rice soil). Finally, the effect of zinc manifested significantly in Dagona (rice, tomatoes and tomato soil), Azbak (water) and Gashua (rice soil). With respect to samples, zinc recorded the highest concentrations in water (4.32 mg/L), rice (94.13 mg/L), tomatoes (62.19 mg/L), rice soil (186.78 mg/L) and tomato soil (177.36 mg/L). Generally, the concentrations of heavy metals were significant in samples taken from Dagona and Alagarno.

Generally, the levels of heavy metals in the water, crops and soil samples from the four study locations fell outside safety range when compared to WHO standards [34]. This is an indication that water from River Yobe may be responsible for the high concentrations of heavy metals detected in the soil and crop samples since it serves as the only source of water for irrigation

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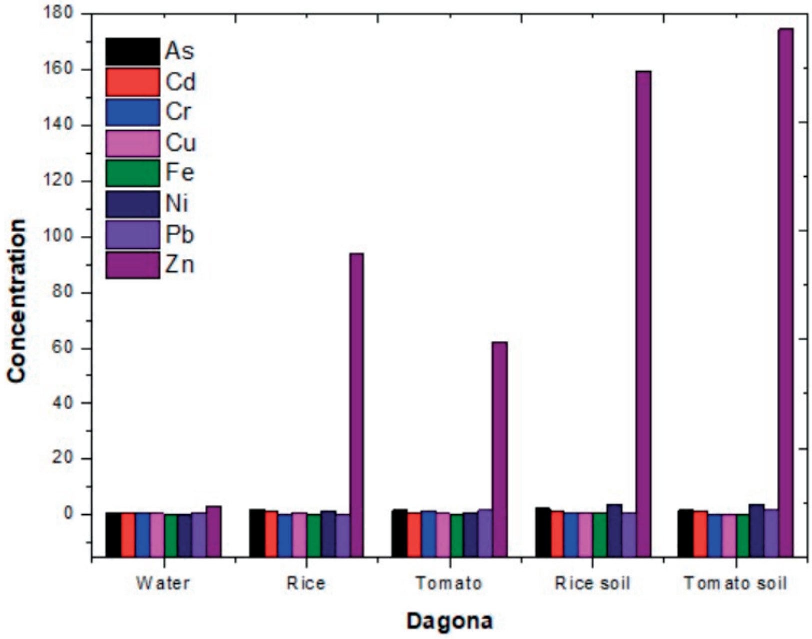

Figure 1. Heavy metal concentrations in water, rice, tomatoes and soil samples from Dagona. Results are mean for 3 determinations.

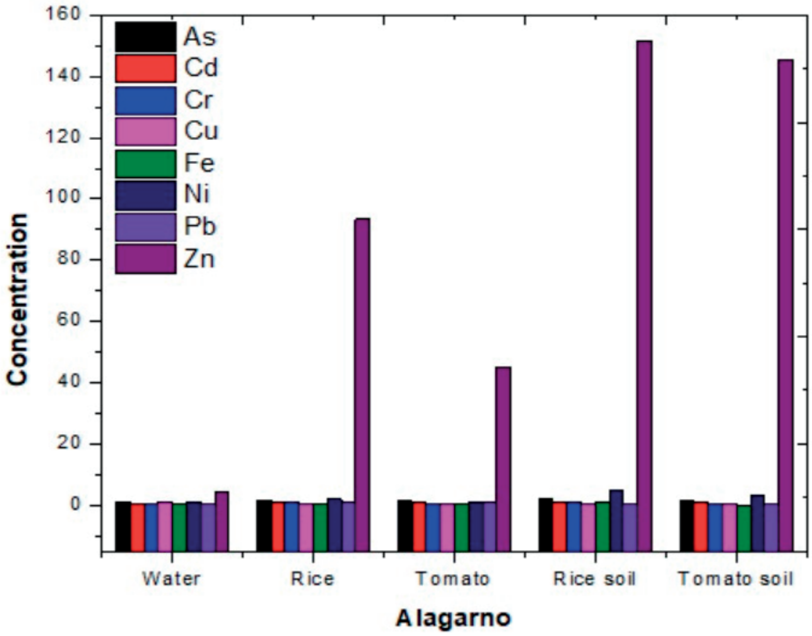

Figure 2. Heavy metal concentrations in water, rice, tomatoes and soil samples from Alagarno. Results are mean for 3 determinations.

in the study area. Exposure of humans to arsenic primarily occurs through consumption of contaminated water, inhalation and absorption through the skin [35,36]. Crops grown on arsenic-contaminated soil and water also serve as potential sources of arsenic exposure. Additionally, arsenic is released by a variety of synthetic products including paints and wood preservatives [37]. Arsenic is a known toxic heavy metal for human beings by virtue of its carcinogenic potential [38]. It has been reported that low to moderate levels of arsenic exposure causes renal dysfunction and neurological complications [39,40]. For instance, long-term arsenic exposure leads to multisystem toxicity arising from accumulation in vital organs including kidneys, lungs, liver and bladder [41-43]. However, the kidneys are very critical because they receive, filter and excrete arsenic-laden blood

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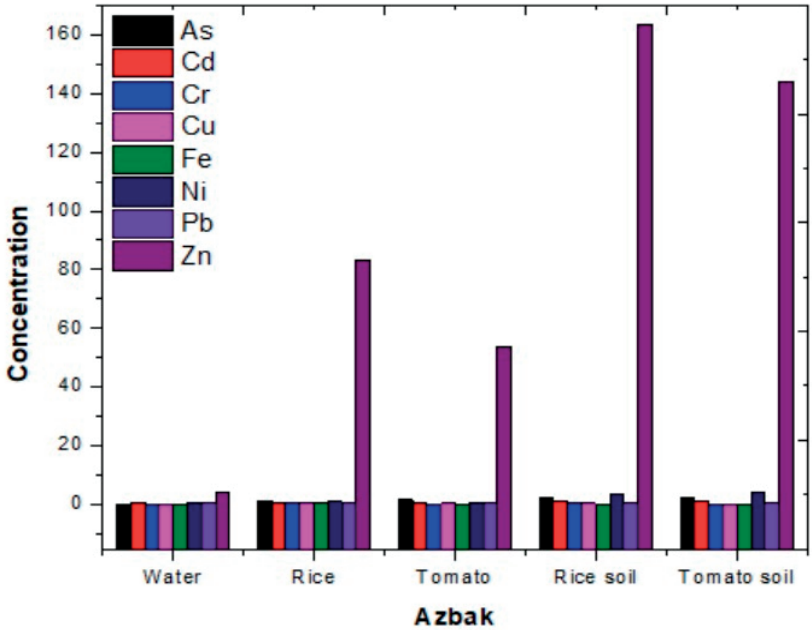

Figure 3. Heavy metal concentrations in water, rice, tomatoes and soil samples from Azbak. Results are mean for 3 determinations.

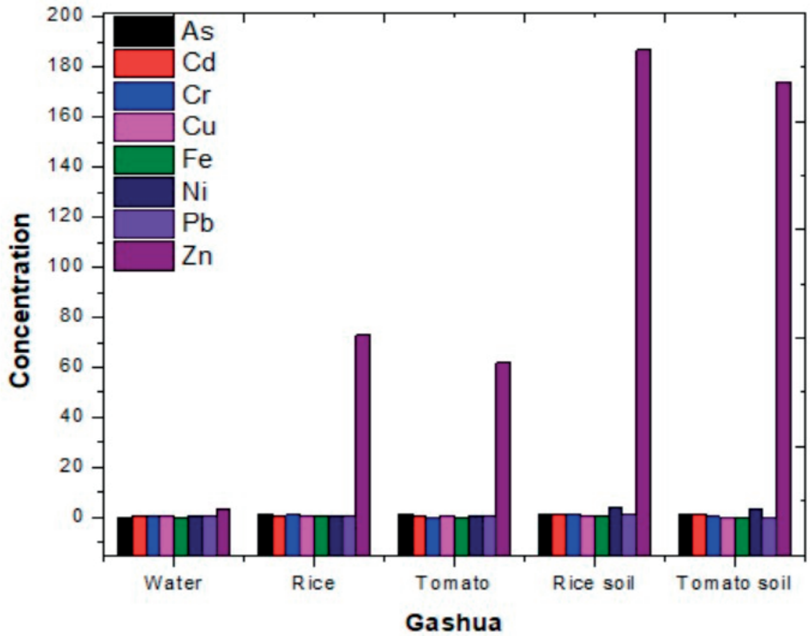

Figure 4. Heavy metal concentrations in water, rice, tomatoes and soil samples from Gashua. Results are mean for 3 determinations.

thereby exposing them to its toxic effects [44,45]. Hence, considering the widespread usage of water from River Yobe particularly for irrigation purposes, the outbreak of CKDu in the study area may not be unconnected to the river.

The primary sources of cadmium emissions in the study locations include block manufacturing, nickel-cadmium batteries, household trash and industrial discharge. Due to its great solubility in water and detrimental effects even at low concentrations, cadmium is regarded as a highly significant pollutant [46]. Exposure to cadmium causes kidney damage by virtue of its interaction with essential elements in the organ to cause functional and morphological changes, ultimately disrupting secondary metabolism [1]. The half-life of Cd exposure is about 30 years, which suggests the possibility of significant accumulation particularly in

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the kidney [45,47]. The relatively long biological half-life of Cd in humans contributes to its accumulation thereby resulting in oxidative stress, mitochondrial dysfunction and disrupts homeostasis of calcium [47]. High concentration of Cd in kidney cells causes irreversible renal death [43]. The nephron part of the kidney is specifically prone to oxidative stress when Cd level is high which eventually leads to renal cell damage, fibrosis, and ultimately chronic kidney disease [44,48].

Several studies have implicated lead as a highly toxic element for humans, animals, and plants. Lead persists in the environment and accumulates in bones, liver, and kidneys through inhalation, waste discharge into water bodies, erosion and mining activities [49]. According to WHO reports, lead toxicity accounts for about 3% of kidney disorders because the organ is responsible for removing lead from the body [50]. At low concentrations, lead elicits major negative health impacts by interfering with processes like cell adhesion, cellular signaling, apoptosis, protein folding, and enzyme regulation [51]. Lead-induced kidney damage is manifested by altered fluid homeostasis arising from a reduction in glomerular filtration rate which promotes various pathological conditions including tubular nephropathy, glomerulosclerosis as well as renal glycosuria and aminoaciduria [52].

Nickel is usually released from natural sources like weathering of rocks and wildfires. However, anthropogenic activities such as casting and battery manufacturing factories as well as stainless-steel kitchen utensils also release nickel in the environment [53]. Studies have shown that kidneys are the major organ for excretion of nickel. Hence, human health deteriorates when exposed to nickel with kidney as the organ most impacted [54]. This justifies previous findings which reported accumulation of the metal in patients with end stage renal disease [55]. This may be attributed to the accumulative capacity of nickel in the kidney brought about by the presence of metallothionein, a metal binding protein with high affinity for nickel [56].

Although zinc is one of the essential trace elements that is crucial to physiological and metabolic processes in many organisms, relatively higher concentration of the element may be harmful to the body, particularly the kidneys [57]. All these observations suggest that the chronic kidney illness afflicting the people of Bade LGA may be connected to poor quality of water from River Yobe which consequently elevated the levels of heavy metal in the adjoining soil and crops.

Transfer factor from soil to rice and tomatoes

Tables 2 and 3 show the transfer factor (TF) values for movement of heavy metals from soil to rice and tomatoes respectively. The data revealed that in Dagona, cadmium, chromium, copper and iron were transferred from the soil to rice and tomatoes by virtue of TF values greater than 1. In Alagarno, chromium, copper and lead were transferred from the soil to both crops. However, in Azbak, tomatoes were greatly affected as manifested by the accumulation of chromium, copper, iron and lead whereas only iron was found in rice. For rice in Gashua, only arsenic and chromium were transferred while chromium, iron and lead were accumulated in tomatoes. Generally, the two crops absorbed arsenic, cadmium, chromium, copper, iron and lead from the soil. The TF values are in the order of Fe > Pb > Cr > Cu > Cd > As for rice and Fe > Cu > Cr > Pb for tomatoes across the four locations. These findings confirm the transfer of these heavy metals from the soil to the two crops. This further corroborates the fact that the chronic kidney disease reported in the study areas may be connected to the elevated levels of heavy metal in the water, rice and tomatoes consumed by the inhabitants. Similar findings were reported in tea plant where cadmium and arsenic were accumulated based on the TF values obtained [58].

Pesticide concentration

The concentrations of pesticides in water, rice, tomatoes and soil samples from the four sampling towns are presented in Table 4. Although pesticide residues were not detected in many of the samples, those detected had higher values than the limit prescribed by WHO [59]. Specifically, it was observed that tomato soil retained considerable concentrations of pesticides, namely Glyphosate, Cyhalothrin, Dichlorvos and Cypermethrin. This may be attributed to the physical and chemical properties of soil. Pesticides can bind to particles and organic matter in the soil, making them more persistent. In addition, the porous nature of soil and continuous usage for several years allow pesticides to penetrate and persist for a relatively long period of time. This

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Table 2. Transfer factor values for movement of heavy metals from soil to rice

Elements	Sampling Towns			
	Dagona	Alagarno	Azbak	Gashua
Arsenic	0.84±0.02	0.63±0.01	0.59±0.01	1.09±0.03
Cadmium	1.11±0.04	0.93±0.02	0.56±0.01	0.66±0.01
Chromium	1.65±0.06	1.05±0.04	0.96±0.02	1.46±0.03
Copper	0.33±0.01	1.24±0.04	0.96±0.03	0.99±0.02
Iron	0.14±0.01	0.81±0.02	1.78±0.04	0.35±0.01
Nickel	0.39±0.01	0.17±0.01	0.29±0.01	0.42±0.01
Lead	0.48±0.01	1.70±0.03	0.54±0.01	0.67±0.01
Zinc	0.59±0.01	0.48±0.01	0.51±0.01	0.50±0.01

Results are expressed as mean ± standard deviation for 3 determinations. TF values greater than 1 indicate accumulation of heavy metals.

Table 3. Transfer factor values for movement of heavy metals from soil to tomatoes

Elements	Sampling Towns			
	Dagona	Alagarno	Azbak	Gashua
Arsenic	0.98±0.02	0.77±0.01	0.73±0.01	0.84±0.01
Cadmium	0.51±0.01	0.94±0.01	0.57±0.01	0.50±0.01
Chromium	3.88±0.07	1.11±0.02	1.96±0.02	3.00±0.03
Copper	4.96±0.08	1.08±0.02	2.60±0.04	0.74±0.01
Iron	6.80±0.09	0.80±0.01	2.58±0.05	2.71±0.02
Nickel	0.28±0.01	0.28±0.01	0.22±0.01	0.26±0.01
Lead	0.90±0.02	2.23±0.03	1.44±0.02	1.57±0.02
Zinc	0.35±0.01	0.31±0.01	0.37±0.01	0.36±0.01

Results are expressed as mean ± standard deviation for 3 determinations. TF values greater than 1 indicate accumulation of metals.

assertion is supported by a previous study which reported that extensive use of pesticides contaminates soil and water, which can be transmitted to crops, thereby posing threat to human beings [10].

One of the major problems associated with the use of pesticides is the possibility of contaminating surface water following run-offs from heavy rainfall. However, this may not be the case always as observed in this study. The relatively low concentration of pesticides in water may be due to the dynamic nature of water, thereby causing pesticides to be diluted, degraded or transported by run-off or infiltration. These factors may contribute to accumulation of pesticides in soil, making it more polluted than water. When used in high quantities, pesticides pollute soil and water, eventually finding their way into the food chain. In addition, commercial use of pesticides for agricultural purposes produces vapors that can become air pollutants [60]. Several studies have documented the adverse effects of pesticide exposure on kidney function and structure. For instance, pesticides have been reported to cause epigenetic effects and pathophysiological changes in kidney function [61]. Other studies revealed that exposure to pesticides led to oxidative stress which impairs the ability of renal cells to generate energy thereby causing cellular injury and eventual kidney damage [62]. Additionally, ingestion of organophosphates results in renal hypoperfusion, damage to renal parenchyma and inflammation [63]. Domestic cleaning agents which may eventually end up in water bodies used for irrigation purpose can cause renal tubular obstruction and inflammation culminating in kidney disease [64]. Epidemiological studies have also confirmed that chronic exposure to pesticides causes kidney damage in human beings [65]. Hence, the chronic kidney illness afflicting the people of Bade LGA may be a result of exposure to pesticides applied to crops grown along River Yobe stretch.

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Table 4. Pesticide concentrations in water, rice, tomatoes and soil samples from the four sampling towns

Parameters	Samples	Sampling Towns				
		Dagona	Alagarno	Azbak	Gashua	WHO [59]
Glyphosate	Water	ND	ND	0.54±0.64	ND	0.1
	Rice	ND	ND	1.23±1.72	0.29±0.50	0.1
	Tomatoes	0.26±0.44	ND	ND	0.74±0.89	0.1
	Rice soil	ND	ND	ND	ND	0.1
	Tomato soil	0.67±0.63	0.95±0.18	0.63±0.71	0.95±1.65	0.1
Chlorpyrifos	Water	ND	ND	ND	ND	0.05
	Rice	ND	ND	ND	ND	0.05
	Tomatoes	ND	ND	ND	ND	0.05
	Rice soil	ND	ND	1.24±2.15	ND	0.05
	Tomato soil	ND	ND	0.82±1.42	2.15±1.60	0.05
Cyhalothrin	Water	ND	ND	ND	ND	0.05
	Rice	ND	ND	ND	ND	0.05
	Tomatoes	ND	ND	ND	0.15±0.26	0.05
	Rice soil	ND	0.81±0.70	0.29±0.50	ND	0.05
	Tomato soil	ND	0.40±0.39	1.33±2.31	0.52±0.45	0.05
Dimethoate	Water	ND	ND	0.35±0.61	ND	0.05
	Rice	ND	ND	ND	0.94±0.82	0.05
	Tomatoes	ND	ND	ND	0.64±0.56	0.05
	Rice soil	ND	ND	0.36±0.63	ND	0.05
	Tomato soil	ND	ND	0.70±1.21	ND	0.05
Dichlorvos	Water	ND	ND	0.56±0.19	ND	0.01
	Rice	ND	ND	ND	ND	0.01
	Tomatoes	ND	0.17±0.29	0.15±0.26	0.17±0.30	0.01
	Rice soil	ND	1.73±1.72	0.50±0.50	ND	0.01
	Tomato soil	0.43±0.74	1.22±1.12	1.67±1.04	0.32±0.33	0.01
Cypermethrin	Water	ND	ND	ND	ND	0.01
	Rice	ND	0.36±0.62	ND	0.29±0.51	0.01
	Tomatoes	ND	0.45±0.78	0.17±0.29	ND	0.01
	Rice soil	ND	1.72±0.71	0.17±0.29	ND	0.01
	Tomato soil	0.11±0.19	0.06±0.10	1.02±0.75	0.25±0.44	0.01

Results are expressed as mean ± standard deviation for 3 determinations. ND means Not Detected. The limits of detection and quantification were estimated as 3 and 10 times the signal-to-noise ratio, respectively, from the chromatogram of the lowest calibration standard.

Materials and Methods

Study area

River Yobe, often called Komadougou Yobe, is a West African river that travels through Nigeria and Niger before emptying into Lake Chad. The river stretches across Bade Local Government Area of Yobe State, Nigeria within the latitude 12o52'25.12"2 and longitude 11o2'49"E. Four towns namely Alagarno, Azbak, Dagona and Gashua were selected for the study (Figure 5).

Collection of experimental samples

Five samples, namely water, rice, rice soil, tomato and tomato soil, were used for the study which was carried out in December,

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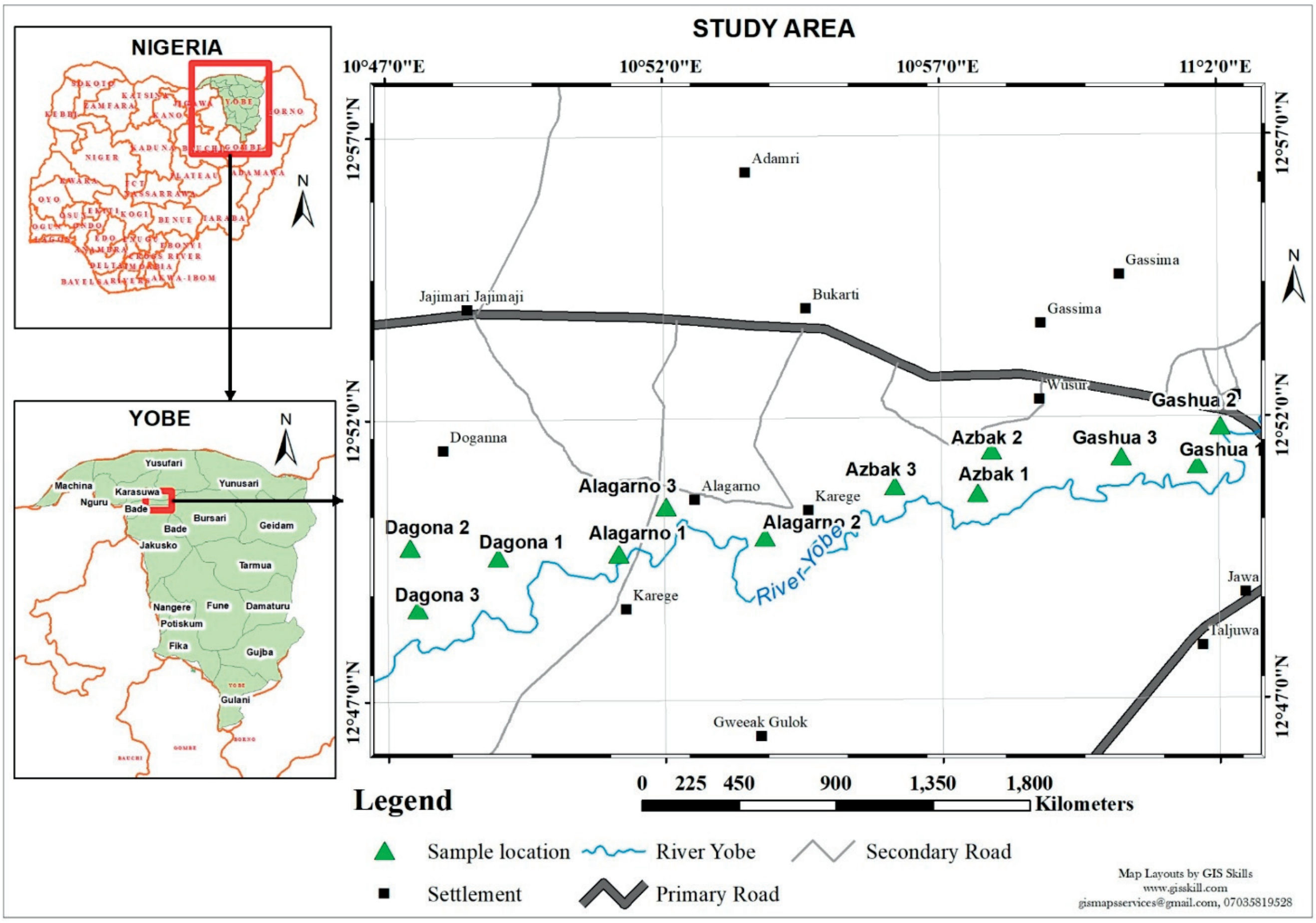

Figure 5. Reference map of Bade LGA showing River Yobe, the four study locations and sampling points.

2024. Water samples were collected from River Yobe in pre-cleaned 1 L plastic bottles in triplicates in each of the four towns at three different points. Samples of tomatoes, rice and their respective soil samples (at a depth of 15 cm) were also collected in triplicates and packaged in Ziplock transparent bags. All samples were immediately transported to the laboratory to preserve their integrity.

Physicochemical analysis of water samples

The water samples collected were homogenously mixed as per each location and subjected to physicochemical analysis according to standard methods [66]. Parameters determined include pH, electrical conductivity (EC), hardness, total dissolved solids (TDS), alkalinity, turbidity, chemical oxygen demand (COD) and biochemical oxygen demand (BOD).

Determination of pH, electrical conductivity and turbidity

pH was determined by inserting the electrode of a pH meter (Mettlar Toledo) into the sample and the reading displayed was recorded. Electrical conductivity was taken with a Conductivity Meter (DDS-307) by dipping the electrode into each sample and the value was recorded upon stability while turbidimeter (WGZ-1B) was used to determine the turbidity of the sample using 2.5% v/v formazin solution.

Determination of total dissolved solids

Each of the samples (100 mL) was filtered using a Whatman No. 1 filter paper and the residue was transferred into a clean,

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dry and pre-weighed evaporating dish (W1). Thereafter, the dish bearing the residue was oven-dried at 105oC repeatedly to a constant weight (W2). TDS was calculated according to Eq. (1).

$$Total\ dissolved\ solids\ (mg/L)\ =\ \frac{W2 - W1}{100} \times 1000 \tag{1}$$

Determination of alkalinity

Each of the samples (50 mL) was transferred into a 250 mL conical flask followed by addition of two drops of methyl orange indicator. The resulting solution was properly mixed and titrated with 0.02 M HCl to determine alkalinity.

Determination of COD

The sample (5 mL) was measured into a 50 mL round bottom flask with anti-bumping materials followed by addition of 0.5 mL mercuric sulphate, 2.0 mL potassium dichromate and 7.5 mL concentrated sulphuric acid. The flask was attached to a reflux condenser and boiled for two hours with gentle swirling for proper mixing. After refluxing, the solution was cooled, and the condenser was carefully washed into the flask using deionized water. Two drops of ferroin indicator were added to the solution and subsequently titrated with ferrous ammonium sulphate until a red colour end point was reached. A blank solution was also prepared using the same process with 5 mL of deionised water instead of the sample.

Determination of BOD

The sample (5 mL) was measured into a dissolved oxygen bottle followed by addition of 5 drops each of manganese sulphate and sodium azide. The resulting coagulated solution was gently shaken before 10 drops of sulphuric acid were added to give a yellow solution. The resulting solution (5 mL) was transferred into a conical flask and titrated with sodium thiosulphate to give dissolved oxygen (DO0). The sample was transferred to a pre-cleaned bottle and incubated for five days to determine the dissolved oxygen after 5 days (DO5). The difference between the two readings gave the BOD.

Preparation of samples

The crop samples (rice and tomato) were thoroughly washed under running tap water to cleanse them of dirt or dust particles and then rinsed with deionized water before they were subjected to standard preparation as previously described with slight modifications [67]. Briefly, the samples were placed separately in crucibles and oven-dried for 12 hours at 60°C after which they were pulverized using an electric blender. The soil samples collected from each town were air-dried overnight and then sieved through a 2 mm screen to achieve fine consistency. The prepared soil samples were kept in Ziplock polythene bags until required for use. All the apparatus used for the experiment were washed with detergents then with a solution of 10% of nitric acid followed by washing with deionized water to prevent contamination.

Digestion of samples and determination of heavy metal concentrations

All the samples were digested using a Master-40-microwave digester, preparatory to atomic absorption spectrometric analysis. Briefly, 0.2 g of soil sample was weighed into the digestion vessel of the equipment followed by addition of 2 mL concentrated hydrochloric acid, 2 mL hydrofluoric acid and 6 mL concentrated nitric acid to digest the sample. For tomatoes, 8 mL of concentrated nitric acid, 1 mL of hydrogen peroxide and 0.5 mL of hydrofluoric acid were added to 0.5 g of the sample in a digestion vessel. For rice, 0.5 g was digested using 6 mL of concentrated nitric acid and 1 mL of hydrogen peroxide. For water, 25 mL was measured into a PTFE (Teflon) beaker and acidified with 2.0 mL of concentrated nitric acid and 6.0 mL of concentrated hydrochloric acid. The beaker was heated on a hot plate inside in a fume extraction hood until the sample was just

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below boiling. The digested soil, crop and water samples were analyzed for heavy metals including Arsenic, Cadmium, Chromium, Copper, Iron, Lead and Zinc using an atomic absorption spectrometer (Buck Scientific, USA). Analytical blanks were prepared for each sample digestion and standards were also prepared for each metal. In each case, a read-out from the screen was taken as the concentration of the selected metals and replicate analysis was carried out for all samples. The limits of detection for the heavy metals are 0.1-0.15 mg/L (As), 0.001-0.002 mg/L (Cd), 0.002 – 0.5 mg/L (Cr), 0.005-0.01 mg/L (Pb), 0.001-0.002 mg/L (Cu), 0.0005-0.001 mg/L (Zn), 0.003-0.005 mg/L (Ni) and 0.01-0.1 mg/L (Fe).

Determination of soil-crop transfer factor

The transfer factor (TF) of metals from soil to crop was determined based on the formula outlined in Eq. (2) [58].

$$TF = C_{crop} / C_{soil} \tag{2}$$

Where C_{crop} and C_{soil} stand for the hazardous metal concentrations in crop and soil respectively. TF greater than 1 indicates a high level of accumulation of metals in the crop [58].

Determination of pesticide concentration

The method of Chang et al. [68] was adopted to determine the concentration of pesticides, namely Glyphosate, Chlorpyrifos, Cyhalothrin, Dimethoate, Dichlorvos and Cypermethrin. Briefly, 5 g of soil/crop and 5 mL of water were separately weighed into different vessels followed by addition of 10 mL acetonitrile and ultrasonically extracted for 20 mins. The resulting solution was centrifuged for 20 mins at 8,000 rpm and left for 12 hours (overnight) before the supernatant was collected. A mixture of petroleum ether and dichloromethane (10 mL each) was added and vortexed for 1 min. The mixture was filtered with Whatman No. 1 filter paper through a funnel containing anhydrous sodium sulphate and activated charcoal. The filtrate was kept in an incubator for 24 hours to evaporate the solvents before collecting the extract in a vial which was subjected to high performance liquid chromatography (Agilent 1200 Infinity Series) to determine the concentrations of pesticides in the samples.

Statistical analysis

Where applicable, data were presented as mean±standard deviation of three replicates. Statistical analysis was performed using Statistical Package for Social Sciences (SPSS; ver. 23.1) software. A p-value of <0.05 was considered statistically significant.

Conclusion

Evidence from this study clearly revealed that River Yobe receives run-off from different activities taking place around the river in the four locations. This may be responsible for the elevated concentrations of heavy metals and pesticides in water samples from the river. One of the limitations of this study is that seasonal variability was not considered as it was conducted in the peak of dry season. However, this may not pose a serious issue considering the high level of water dilution that occurs during the rainy season. Therefore, the impact of both heavy metals and pesticides is likely to be minimal during this period. Also, in the present study, human biomarkers were not examined to establish that consumption of contaminated water and crops in the study locations is responsible for the occurrence of CKDu. However, based on the findings from the present study, water from Bade stretch of River Yobe may be considered unsafe, which renders it unsuitable for irrigation and domestic purposes by virtue of the elevated concentrations of heavy metals and pesticides. Therefore, the chronic kidney illness afflicting the people of Bade LGA in Yobe State, northern Nigeria may be connected to poor quality of water from River Yobe.

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Data Availability: All data are available in the main text or in the Supplementary Information.

Author Contributions: Mustapha Usman Nasir conceived the research, collected the data and wrote the first draft of the manuscript. Taofik Olatunde Uthman designed the research, revised the manuscript and performed the statistical analysis.

Notes: The authors declare no conflict of interest.

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Correspondence and requests for materials should be addressed to Taofik Olatunde Uthman.
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