Physico-Chemical and Trace Element Levels in Water from Dams, Rivers and Boreholes in Gombe State, Nigeria

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Abstract The physico-chemical and trace element levels of water samples from Gombe Abba river, Dadinkowa dam, Balanga dam and boreholes from Kwadon used for drinking and irrigation in farms were analysed using complexometric method of analysis. In all the elements sampled, Nickel had the lowest concentration in all the sites sampled with a mean of 0.003±0.00 mg/l in Dadinkowa and Gombe Abba and 0.002±0.00 mg/l for Kwadon and Balanga dam.Copper had the highest concentrations in all the areas sampled with a mean of 0.61±0.32mg/l in Dadinkowa dam, 0.49±0.04mg/l in Gombe Abba river, 0.39±0.01mg/l for Kwadon and 0.30±0.01mg/l for Balanga dams respectively. The levels for the trace elements determined are in the order Cu>Pb>Cd>Ni for Dadinkowa and Gombe Abba while for Kwadon the order is Cu>Ni>Pb=Cd. For Balanga dam, the order is Cu>Cd>Ni>Pb. Statistical analysis using Kruskal-wallis showed no significant difference for all the elements sampled irrespective of location.

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1. Introduction

Human health can be affected by the quality of the food and drink that we take. Water intended for human consumption must be free from organisms and from concentrations of chemical substances that may be hazardous to health. Many trace elements in drinking water are capable of causing human diseases if their concentration exceeds certain permissible limits. World Health Organisation (WHO) places great emphasis on the quality of drinking water and has recommended upper limits for a number of trace elements in drinking water.

1.1. Health Impacts of some Trace Elements

1.1.1. Lead and Its Impact on Human Health

Patients suffer from renal failure were related to contaminant drinking water mainly with lead and cadmium. Lead is a dangerous element; it is harmful even in small amounts. Lead enters the human body in many ways. It can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in various foods, notably fish, which are heavily subject to industrial pollution. Some old homes may have lead water pipes, which can then contaminate drinking water. Most of the lead we take in is removed from our bodies in urine; however, there is still risk of buildup, particularly in children [1].

Exposure to lead is cumulative over time. High concentrations of lead in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys [2]. This damage commonly results in behavior and learning problems (such as hyperactivity), memory and concentration problems, high blood pressure, hearing problems, headaches, slowed growth, reproductive problems in men and women, digestive problems, muscle and joint pain. Studies on lead are numerous because of its hazardous effects. Lead is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Not only does lead poisoning stunt a child's growth, damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children [3].

1.1.2. Cadmium and its Impact on Human Health

Cadmium is generally classified as toxic trace element. It is found in very low concentration in most rocks, as well as in coal and petroleum and often in combination with zinc. Geologic deposits of cadmium can serve as sources to groundwater and surface water, especially when in contact with soft, acidic waters [3].

There is no evidence indicating its essentiality to humans. Cd appears to accumulate with age, especially in the kidney and it is considered also as a cancer and cardiovascular diseases. [4] reported that geochemical implications of Cd in human health related to: bone and renal disease in populations exposed to industrially contaminated drinking water, b) Lung and renal dysfunction in industrial workers exposed to air-borne Cd and (c) Implication in human hypertension.

Galvanized steel is plated with zinc, which is normally contains about 1% Cd. Cd also has specific uses in paint, photography, and nickel-cadmium batteries. Some cases of cadmium poisoning are linked to cadmium-plated food utensils. It is introduced into the environment from paint and pigments, and plastic stabilizers mining and smelting operations and industrial operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. The remaining cadmium emissions are from fossil fuel use, fertilizer application, and sewage sludge disposal. Cadmium may enter drinking water as a result of corrosion of galvanized pipe. Landfill leachates are also an important source of cadmium in the environment.

In low doses, cadmium can produce coughing, headaches, and vomiting. In larger doses, cadmium can accumulate in the liver and kidneys, and can replace calcium in bones, leading to painful bone disorders and to a renal failure. The kidney is considered to be the critical target organ in humans chronically exposed to cadmium by ingestion [5].

Cadmium that is taken into the body usually remains there. Inhaled cadmium is more hazardous than ingested cadmium. A major source of inhaled cadmium is tobacco smoke.

Ingestion of metals such as lead and cadmium may pose great risks to human health.

Cadmium may interfere with the metallothionein ability to regulate zinc and copper concentrations in the body that some patients showed some elevation in zinc in their urine samples. Metallothionein is a protein that binds to excess essential metals to render them unavailable. When cadmium induces metallothione in activity, it binds to copper and zincdisrupting the homeostasis levels [6]. Cadmium is used in industrial manufacture and is a by-product of the metallurgy of zinc. Trace metals such as lead and cadmium will interfere with essential nutrients of similar appearance, such as calcium and zinc. Because of size and charge similarities, lead can substitute for calcium and included in bone. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Once free in the system, lead may cause nephrotoxicity, neurotoxicity, and hypertension. The pollution of drinking water with lead and cadmium arise from industrial sources at the studied areas and renal failures were related to them.

1.1.3. Copper and Its Impact on Human Health

Patients suffer from liver cirrhosis in this study were related to contaminant drinking water mainly with copper and molybdenum. Copper is essential substance to human life, butchronic exposure to contaminant drinking water with copper can result in the development of anemia, liver and kidney damage [7,8]. This disease was a result of drinking water contaminated from corrosion of water pipes made of copper and industrial wastes. Diarrhea in small children could be also occurred due to high copper exposure. The adverse health effects caused by drinking water contaminated with copper are abdominal pain, vomiting, headache, nausea, and diarrhea. Copper in large doses is dangerous to infants and people with certain metabolic disorders. On the other hand, lack of copper intake causes anemia, growth inhibition, and blood circulation problems [2].

Patients who suffered from chronic anemia in this study were related to contaminant drinking water with copper, and cadmium. This study reveals that one heavy metal could have impact on more than one disease for example, copper on liver cirrhosis and chronic anaemia and cadmium in renal failure and chronic anaemia. High doses of copper can cause anaemia, liver and kidney damage, and stomach and intestinal irritation.

Copper normally occurs in drinking water from copper pipes, industrial waste, as well as from additives designed to control algal growth. Chronic exposure to contaminant drinking water with cadmium can result in the development of chronic anaemia [5,6]. Cadmium poisoning has been associated with kidney disease, hypertension, and chronic anaemia [2].

1.1.4. Nickel and Its Impact on Human Health

Patients suffer from hair loss in this study were related to contaminant drinking water with nickel and chromium. Nickel is used as alloys product, nickel-plating for anticorrosion and in the manufacture of batteries. It is regarded as an essential trace metal but toxic in large amount to human health. It is considered as carcinogenic to human. [11] reported that high-dose of nickel in rats and dogs were significantly decreasing their bodyweights.

The pollution of water with nickel and chromium arises from industrial sources and/or agriculture activities at the studied areas. Its toxicity is enhanced in the presence of other metals such as cobalt, copper, iron and zinc in drinking water. Many studies have been published regarding nickel sensitivity in humans. Numerous other studies have been conducted to attempt to establish the relationships between nickel exposure and dermalirritation. This study reports for the first time the relationship between nickel and hair loss. [1] reported worsening of eczema for human exposed to high levels of nickel. Hair loss patients are related to nickel contaminant drinking water and nickel can be related to derma- toxicity in hypersensitive humans.

The results of [1] showed that patients who suffered from renal failure could be related to their contaminated drinking water with lead and cadmium, liver cirrhosis to copper and molybdenum, hair loss to nickel and chromium, and chronic anaemia to contaminant drinking water with copper and cadmium.

2. Materials and Methods

2.1. Sample and Preparations

2.1.1. Sample Collection

Water samples were collected between December 2010 and February, 2011 at two weeks interval early in the morning. Water was obtained randomly to get representative samples using a 2-litre plastic bottle which was washed thoroughly with detergent, rinsed with distilled water and finally filled with the sampled water, and labeled.

2.1.2. Preparations

All reagents used were of analytical grades and deionised distilled water were used for all reagent preparations

2.2. Physicochemical parameters

2.2.1. pH:- [10]

The pH was determined using a pH meter (portable cyberscan 20) which was calibrated using two buffer solutions, pH 7.0 and 4.0. The water was stirred vigorously with $40cm^3$ distilled water for 15 seconds and allowed to stand for 30 minutes. The electrodes were then placed in the slurry and swirled carefully. The pH was then taken.

2.2.2. Electrical Conductivity [10]

Electrical conductivity is a measure of the dissolved salts in a solution. The EC meter (Marton 407 S 214) was calibrated with 0.01 M KCl solution which gives an EC of 1412 µS/cm at 25°C. EC was then measured at 25°C.

2.3. Metal Analysis

Complexometric titration was chosen due to its rare advantage were neither sophisticated equipment, apparatus or electricity is needed. The availability of the reagents for this study makes it easy to manipulate, reliable, selective and sensitive for such environmental samples. Complexometric titration is still in vogue; its usage would assist in modifications in terms of the dye indicators used which is generally selective and elusive of pH range which makes it more specific to the choice of metal in question.

2.3.1. Preparation and standardization of EDTA solutions

The neutral EDTA molecules are not very soluble in water, so aqueous EDTA titrant solution is usually prepared by dissolving the sodium salt of EDTA. The concentration of free EDTA in the solution is decreased by contamination of the solution by metals that may be present in normal glassware. EDTA titrant solutions are generally stored in polythene or borosilicate glass containers.

2.3.2. Standard EDTA Solutions

Disodium dihydrogen diethylenediamine tetraacetate (EDTA) of analytical reagent quality was used. The salt was purified by preparing a saturated solution at room temperature; by weighing 20g of the salt in $200cm^3$ of water. Ethanol was slowly added until a permanent precipitate appeared. The solution was diluted with equal volume of ethanol. The resulting solution precipitate was filtered through a sintered glass funnel, washed with

acetone and then dried with diethyl ether. The precipitate was air dried at room temperature overnight in an oven at 80°C for 24 hours. Solutions of EDTA of the following concentrations were prepared for the experimental work; 0.1M, 0.05M and 0.01M. These contained 37.224g, 18.612g and 3.7224g of the dehydrate per litre of solution in distilled deionised water respectively. The EDTA solution was then standardised by titration using neutralised zinc chloride [11].

2.3.3. Determination of copper using fast sulphon Black F as indicator

Reagents: EDTA solution 0.05M
Indicator solution 0.5%: 0.5g of sulphon Black F was prepared in 100ml of water.

Copper-ion solution 0.05M: 3.11g of A.R. copper sulphate pentahydrate was accurately weighed and dissolved in water to $250cm^3$ in a volumetric flask.

Procedure: $25cm^3$ of the copper ion solution was pipette into a $250cm^3$ conical flask with an equal volume of water and $5cm^3$ of concentrated ammonia solution was added with 5 drops of the indicator solution. The solution was titrated with standard EDTA solution until the colour changed from blue to dark green. Copper ion in the water samples were determined by pipetting $25cm^3$ of the sample into a $250cm^3$ conical flask, diluted with equal volume of distilled water, $5cm^3$ of concentrated ammonia solution and 5 drops of indicator. The mixture was then titrated with the standard EDTA solution until endpoint was reached.

$1 cm^3$ 0.05M EDTA $\equiv$ 3.177mg Cu.

2.3.4. Determination of Lead Using Xylenol Orange as Indicator

Reagents: EDTA solution, 0.05M
Xylenol orange indicator: 0.5g of xylenol orange was dissolved in $100cm^3$ of distilled water.

Lead-ion solution, 0.05M: 4.16g of lead nitrate was accurately and dissolved in water. Few drops of dilute nitric acid was added and then made up to the mark in a $250cm^3$ volumetric flask.

Procedure: $25cm^3$ of the lead-ion solution was pipette into a $250cm^3$ conical flask with an equal volume of water and 3 drops of the indicator solution added. Dilute nitric acid was added until the solution change to yellow. Powdered hexamethylene triamine was added until the colour was intensely red. This ensured the attainment of pH of 6. The solution was titrated with standard EDTA solution until the colour changed to lemon yellow. Lead was determined from the water samples by measuring $25cm^3$ of the water sample into a $250cm^3$ with equal volume of distilled water, 3 drops of indicator, dilute nitric acid, powdered hexamethylene triamine just as above. The solution mixture was titrated with standard EDTA solution until endpoint was realised.

$1 cm^3$ 0.05M $\equiv$ 10.3605mg Pb.

2.3.5. Determination of Cadmium Using Xylenol Orange as Indicator

Reagents: EDTA solution, 0.05M
Xylenol orange indicator: prepared as in lead above

Cadmium ion solution 0.05M: 3.21g of A.R. crystallized cadmium sulphate was dissolved in $250cm^3$ volumetric flask with distilled water.

Procedure: 25cm^3 of the cadmium-ion solution was diluted to 50cm^3 with distilled water and 3 drops of the indicator added. One drop of dilute sulphuric acid was added, where the colour of the solution turned yellow. Powdered hexamine was added with slight agitation, until the colour turned deep red. The solution was then titrated with the EDTA solution slowly near the end point to a colour change from red to yellow. 25cm^3 of the water sample was diluted to 50cm^3 with distilled water and 3 drops of the indicator added. One drop of dilute sulphuric acid was added, powdered hexamine with slight agitation and then titrated with the EDTA solution slowly near the endpoint to a colour change from red to yellow.

1 cm^3 0.05M ≡ 5.621mg Cd.

2.3.6. Determination of Nickel Using Murexide as Indicator

Reagents: EDTA solution, 0.1M

Murexide indicator: 0.5g of powdered murexide was suspended in water, shaken thoroughlyand kept to stabilize.

The saturated supernatant liquid was used for the titration. The old supernatant liquid was decanted daily and the residue treated with water to provide a fresh solution of the indicator.

Nickel-ion solution 0.1M: 4.95g of nickel ammonium sulphate hexahydrate was dissolved in

Water and diluted to 250cm^3 in a volumetric flask. 1M ammonium chloride solution was used procedure: 25cm^3 of the nickel-ion solution was diluted to 100cm^3 with distilled water,5 drops of freshly prepared murexide indicator added and 10cm^3 of 1M ammonium chloride solution was added. Concentrated ammonia solution was added drop wise until the pH was 7. The yellow coloured solution was then titrated with 0.1M EDTA solution until the endpoint was approached. The solution was rendered strongly alkaline by the addition of about 10cm^3 concentrated ammonia solutions, and the titration was continued umtil the colour changed from yellow to bluish-violet. Nickel complexes slowly with EDTA, consequently the EDTA solution was added dropwise near the endpoint. Nickel ions in water samples were determined by pipetting 25cm^3 of water and diluting it to 100cm^3. 5 drops of murexide indicator and 10cm^3 of 1M ammonium chloride solution were added. Concentrated ammonia solution was also added drop wise until the pH was 7. The solution was then titrated with 0.1M EDTA solution until the endpoint was attained.

1cm^3 EDTA ≡ 5.872mg Ni.

3. Results and Discussion

The results of the physicochemical parameters, pH and EC, as well as the concentrations of the trace elements determined in the water sample namely Ni, Cu, Cd and Pb are presented on Table 1 & Table 2 respectively.

Table 1. Mean Values of Physicochemical Parameters of water

SITES	pH	EC (ms/cm)
Dadinkowa	6.99±0.4	3.97±0.5
Gombe Abba	6.97±0.4	0.68±0.3
Kwadon	6.59±0.5	2.08±0.8
Balanga	7.27±0.1	4.88±0.4

Table 2. Mean Concentration of Water Trace Elements from all Sites in mg/l

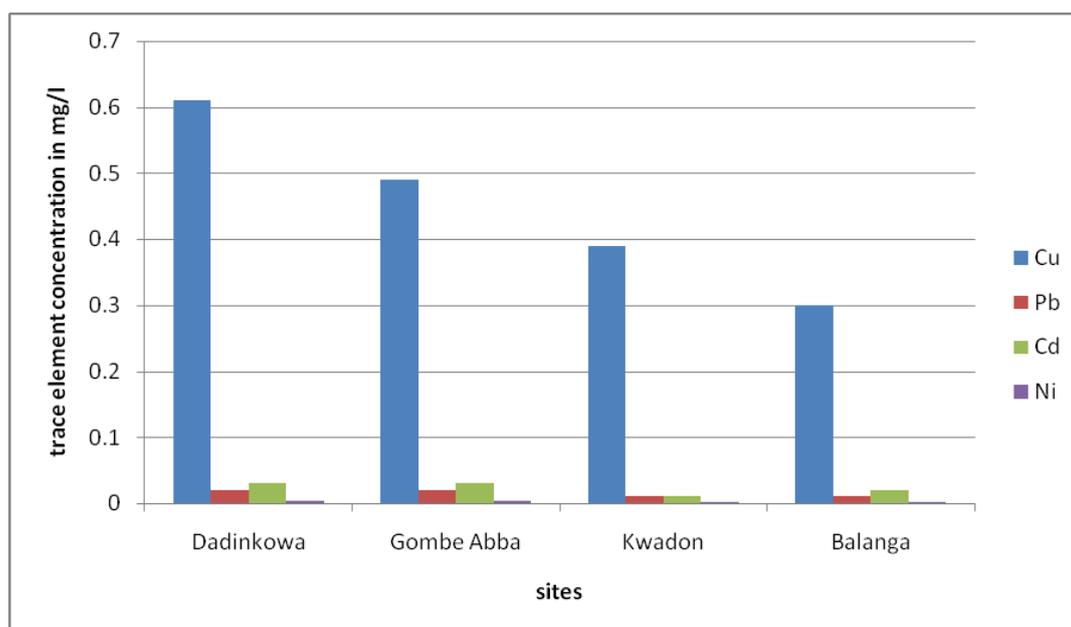| SITES	Cu	Pb	Cd	Ni
Dadinkowa	0.61±0.32	0.02±0.01	0.03±0.02	0.003±0.001
Gombe Abba	0.49±0.04	0.02±0.001	0.03±0.002	0.003±0.000
Kwadon	0.39±0.01	0.01±0.00	0.01±0.000	0.002±0.000
Balanga	0.30±0.01	0.01±0.00	0.02±0.001	0.002±0.000

Figure 1. Variation of trace elements at all sites

The water samples were found to be neutral for Balanga dam with a pH of 7.27±0.1. Dadinkowa dam has a pH of 6.99±0.4, Gombe Abba River has a pH of 6.97±0.4 and the least is 6.59±0.5 for Kwadon boreholes. These ranges of pH are often classified as neutral implying lesser tendency of the water to cause corrosion of metallic materials and hence dissolution of metals from soil.

Electrical conductivity is a measure of the current conducted by ions present in the water as a result of dissolved solids in solution and depends on the

concentration of the ions, the nature of the ions, the temperature of the solution and the viscosity of the solution. The EC recorded for this study were 4.88±0.4µs/cm for Balanga dam, 3.97±0.5 for Dadinkowa dam, 2.08±0.8 for Kwadon boreholes and 0.68±0.3 for Gombe Abba river. These low EC values may be attributed to the nearly neutral pH values of the water samples in all the sites sampled.

For the trace elements, determined, copper had the highest concentration of 0.61±0.32mg/l in Dadinkowa dam, 0.49±0.04mg/l for Gombe Abba River, 0.39±0.01mg/l and 0.30±0.01mg/l for Kwadon boreholes and Balanga dam respectively. The copper concentration in this study are higher than WHO limit of 0.015mg/l in water samples. Kruskal-Wallis test at 0.05 level of confidence showed no significant difference in all the sites sampled.

Lead concentrations were 0.02 ±0.01mg/l for both Dadinkowa dam and Gombe Abba river while the concentration for Kwadon boreholes and Balanga dam was 0.01±0.00mg/l. The concentrations obtained for Dadinkowa and Gombe Abba are slightly above the WHO approved limit of 0.01mg/l while Kwadon boreholes and Balanga dam water had a concentration within the approved limits. Kruskal-Wallis test showed no significant difference in lead concentrations in all the sites sampled.

Cadmium has the second highest concentration after copper with 0.03±0.02mg/l for Dadinkowa dam and Gombe Abba river, 0.02±0.001mg/l for Balanga dam, while water from Kwadon has the least concentration of 0.01±0.00mg/l. the approved WHO limit for cadmium in drinking water is 0.003mg/l. so all the water from the sites sampled are above the approved WHO limit. The high concentration may be attributed to anthropogenic sources. Kruskal-wallis correlation showed no significant difference in the cadmium concentrations for all the sites sampled.

Nickel had the least concentration in all the sites sampled. Dadinkowa dam and Gombe Abba river both have a concentration of 0.003±0.01mg/l while Kwadon boreholes and Balanga dam had a concentration of 0.002±0.000mg/l. All the sites had a mean concentration lower than the WHO [12] approved limit of 0.02mg/l. Kruskal-wallis test showed no significant difference in the mean nickel concentration for water samples from all the sites sampled.

4. Conclusion

The levels for the trace elements determined are in the order Cu>Pb>Cd>Ni for Dadinkowa and Gombe Abba while for Kwadon the order is Cu>Ni>Pb=Cd. For Balanga dam, the order is Cu>Cd>Ni>Pb.statistical analysis using Kruskal-wallis showed no significant difference for all the elements sampled irrespective of location.

All the elements sampled were within the accepted WHO limits except nickel, which exceeded the acceptable limit.

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