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Pitout JDD, Church DL, Gregson DB, Chow BL, McCracken M, Mulvey M, Laupland KB (2007). Molecular epidemiology of CTXM-producing *Escherichia coli* in the Calgary Health Region: emergence of CTX-M-15-producing isolates. *Antimicrob. Agents Chemother.* 51: 1281-1286.

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ARTICLES

Survival Of Enteric Bacteria In Source-Separated Human Urine Used As Fertiliser: Effects Of Temperature And Ammonia

Joseph M. Makaya, Marius K. Somda, Aly Savadogo, Dayéri Dianou, Alfred S. Traoré and Nicolas Barro

Removal Of Azo Dye From Water By Adsorption Using Waste Residue From Alum Manufacturing Process

Haimanot habte, Feleke Zewge and Mesfin Redi

Arsenic Pollution Of Surface And Subsurface Water In Onitsha, Nigeria

A. C. C. Ezeabasili, O. L. Anike, B. U. Okoro and C. M. U-Dominic

Sediment And Nutrient Lost By Runoff From Two Watersheds, Digga District In Blue Nile Basin, Ethiopia

Alemayehu Wudneh, Teklu Erkossa and Prhaba Devi

Physico-Chemical Characteristics Of Surface And Groundwater In Obajana And Its Environs In Kogi State, Central Nigeria

O. K. Musa, E. A. Kudamnya, A. O. Omali and T. I. Akuh

Natural Radioactivity And Environmental Risk Assessment Of Sokoto Phosphate Rock, Northwest Nigeria

Kolo, M. T.

Full Length Research Paper

Survival of enteric bacteria in source-separated human urine used as fertiliser: Effects of temperature and ammonia

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To promote the use of eco-toilets is an alternative to the lack of sanitation and high cost of artificial fertilisers in developing countries. Human urine is the fraction of excreta containing most nitrogen, phosphorus and potassium which are essential nutrients for plant growth. The major concern related to the use of the urine as fertiliser is the possible presence of enteric pathogens. The reduction in the numbers of *Escherichia coli*, *Enterococcus faecalis*, *Salmonella* sp., *Staphylococcus aureus*, *Clostridium perfringens* spores during urine storage was studied in diluted and undiluted urine samples. These experimental samples were stored in ambient air and at temperatures of 25, 35 and 42°C. The initial concentration of ammoniacal nitrogen reduced from 8260 to 1070 mg/L in quarter-diluted urine (1:3), while the pH values remained stable at 8.6 (\pm 0.2). *E. faecalis* survived for 35 days in the quarter-diluted urine at 25°C. Survival times of the tested bacteria were more shortened in ammonia concentrated samples, on storage at 35, 42°C. Except *C. perfringens* spores, *E. faecalis* was the least sensitive to storage conditions as compared to *S. aureus* and the two Gram-negative bacteria tested. Therefore, temperature and ammonia acted synergistically to remove bacteria in the stored urine. Likewise, *C. perfringens* spores were the most persistent bacteria, with only 1-log₁₀ reduction within 100 days storage at ambient temperature. This study shows that a period of at least 30 days of undiluted urine storage at temperatures \geq 25°C is sufficient to sanitize urine, considering only vegetative bacteria. Since urine from eco-toilets may contain other enteric organisms (viruses, protozoa, etc) appearing more persistent in external media, storage time must be lengthened for a satisfactory sanitation.

Key words: Human urine, storage, enteric bacteria, ammonia, temperature, sanitation, fertilizer.

INTRODUCTION

Separating the human excreta at the source can contribute to effective management of wastewater. To do that, urine diversion dry toilets (UDDTs) are the best indicated systems, because they are designed to

separately collect urine and faeces (Mnkeni and Austin, 2009; Münch and Winker, 2009; Dagerskog and Bonzi, 2010). Thus, to promote the use of these eco-toilets, UDDTs represents an alternative to the lack of sanitation

and high cost of artificial fertilisers that affect many people in developing countries. To this end, since 2006, large-scale ecological systems were implemented in many areas in Burkina Faso (Dagerskog and Bonzi, 2010).

Human urine is the fraction of excreta which contains more nutrients, mainly, nitrogen, phosphorus and potassium (Heinonen-Tanski and van Wijk-Sijbesma, 2005), which are essential nutrients for plant growth. Also, fresh urine can contain microorganisms. In individuals suffering from typhoid fever, *Salmonella* can be found in their urine, only in cases of septicemia (Feachem et al., 1983). Recycling urine nutrients in agriculture therefore seems easier and more profitable as compared to faeces.

For health risks associated with the use of urine as fertiliser, the great concern is about enteric pathogens resulting from environmental samples or faecal cross-contamination during urine collection (Esrey et al., 2001; Schönning et al., 2002). In view of that, it is possible to assume that the source-separated human urine can contain enteric organisms. It is possible that applying in soil the untreated urine, may introduce another pathogens transmission route in the environment.

In order to sanitize urine from UDDTs, several treatment options have been proposed (Maurer et al., 2006; Pronk and Koné, 2010). The urine storage in closed containers and then exposed to the ambient air can remove microorganisms. The storage seems to be an appropriate method for the urine sanitation, as its realization is very simple. Apart from pathogens removal, the urine treatment by storage may preserve the useful nutrients for plant growth (Jönsson and Vinnerås, 2007; Pradhan et al., 2009).

The parameters which may influence the survival of microorganisms in urine during storage are mainly temperature, ammonia and pH. The temperature depends on the storage conditions and the climate. Because of high temperatures regularly reported in tropical regions especially in Sahel (Ouédraogo et al., 2007), urine storage time can be shortened, as compared to temperate regions, where storage times of 2-6 months were recommended to sanitize urine satisfactory (at 20°C or higher), including a wide range of bacteria, protozoan (oo) cysts and viruses (Höglund et al., 2002; WHO, 2006; Vinnerås et al., 2008; Chandran et al., 2009).

The pH of fresh urine is usually around 6 (Haneaus et al., 1996), but this value increases to approximately 9 in the collection and storage tanks due to rapid hydrolysis of urea (Jönsson and Vinnerås, 2007). In aqueous solution, the alkaline pH affects the equilibrium between the uncharged ammonia (NH₃) and ammonium (NH₄⁺) in favor of the formation of the NH₃. The microbicidal effects

of NH₃ were shown in several matrices (Jenkins et al., 1998; Nordin et al., 2009). The urine dilution can affect the ammoniacal nitrogen concentrations and therefore these uncharged ammonia (Pecson et al., 2007).

The survival capacity of enteric microorganisms in external environment differs according to microbial groups (Vinnerås et al., 2008; Chandran et al., 2009). Viruses, protozoan oocysts seem to be more persistent in the environment than bacteria. That could justify the choice of *Clostridium perfringens* spores as biological tracers to follow the fate of pathogenic viruses and protozoa in the wastewater (Payment et al., 2001).

This study investigated the effectiveness of the urine treatment by storage on determining the reduction numbers of five indicators or potentially pathogenic bacterial species: *Escherichia coli*, *Salmonella* sp., *Staphylococcus aureus*, *Enterococcus faecalis* and *C. perfringens* spores. The main objective was to evaluate the survival in urine of the above-mentioned bacteria, highlighting the effects of ammonia concentrations and temperatures during storage.

MATERIALS AND METHODS

Isolation of bacteria

Vegetative bacteria were respectively isolated from a polluted soil (*E. coli* and *E. faecalis*), wastewater (*Salmonella* sp.) and pathological exudate (*S. aureus*). To do that, standard methods were used (ISO, 1999, 2000). Isolated bacteria were used in the experiments, for a bacterial suspension. On the other hand, a stock of *C. perfringens* spores was prepared with a dried compost (faeces + soil) taken from an UDDT pit. 30 g of crushed and sieved compost were transferred into 270 mL of saline solution (0.9%). After homogenization, the supernatant was removed and used to prepare decimal dilutions (10⁻¹-10⁻³), 250 mL each. Clostridia spore numbers in dilutions were determined as the described method (Anonymous, 2005), using Tryptone-Sulfite-Neomycin (TSN) Agar. The dilution containing 10⁵ spores/mL was considered as the spore stock solution.

Urine samples preparation

Two-days-old urine from a urinal used by male staff at the Pan African Agency, Water and Sanitation for Africa (WSA) located in Ouagadougou (Burkina Faso) was used to prepare the urine samples. Three (03) matrices were prepared: undiluted urine (1:0), half-diluted urine (1:1) and quarter-diluted urine (1:3). The dilution was done with a sterile water (urine : water).

For the exposure to ambient conditions, each above-mentioned matrix was distributed in 5 L plastic jerry cans (white color) in a volume of 4 L per jerry can. On the other hand, three (03) sets of samples were prepared for storage in an incubator (Binder, Germany) under the following temperatures; 25, 35 or 42°C. Each set of samples was made up of twelve (12) bottles containing in triplicate the three urine matrices (1:0, 1:1, and 1:3) and sterile

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Table 1. Temperatures of the urine during storage at ambient air.

Time* (days)	Temperature per day of measurement (°C)			Temperature in jerry cans (°C)	
	Min.	Max.	Mean	UD = 1:0	UD = 1:1
				Mean ± SD	Mean ± SD
0	22	31.2	25.7	30.0 ± 0.3	29.8 ± 0.2
5	24.2	34	27.7	30.3 ± 0.4	31.0 ± 0.2
10	25.8	36.6	30.8	30.1 ± 0.3	30.1 ± 0.2
15	24	36.5	29.4	30.2 ± 0.1	30.8 ± 0.3
20	24	35.6	29.6	30.4 ± 0.2	30.5 ± 0.0
25	23.2	36.2	29.5	29.5 ± 0.5	30.0 ± 0.1
30	26.7	36.8	30.6	31.0 ± 0.0	30.5 ± 0.2

*Time: Measurements were performed with a time interval of five days, between October 07 and Nov. 06, 2010; UD : Urine diluted.

water (control). These matrices were distributed in 100 mL sterile polyethylene bottles (dark brown color) in a volume of 80 mL each.

Survival tests of bacterial species

Samples stored at ambient

Each sample in jerry can was contaminated either with a bacterial suspension (in which initial concentrations were 10^8 - 10^9 CFU/mL for *E. coli*, *Salmonella* sp. and 10^7 - 10^8 CFU/mL for *S. aureus*, *E. faecalis*) or with a Clostridia spores solution (10^5 cells/mL). Inocula were distributed at a rate of 40 mL per jerry can (1% [vol/vol]). Experiments were performed in duplicate. Contaminated samples were immediately exposed to ambient air (completely out in the sun, at Ouagadougou University site), for 05 months (September 2010-January 2011). Physicochemical and bacteriological parameters in samples were analyzed at regular time intervals (5, 10 days for vegetative bacteria and spores, respectively). Simultaneously, ambient temperatures were recorded daily during the exposure period.

Samples stored in an incubator

Samples in bottles were contaminated with a bacterial suspension (as above-mentioned) at a rate of 1.6 mL per bottle (2% [vol/vol]). Each set of 12 bottles contaminated samples was immediately placed in the incubator under one of these temperatures 25, 35 or 42°C. Bacterial parameters in samples were analyzed within 45 days, for 4 h and 5 days as regular times, respectively for rods and cocci tested bacteria.

Laboratory analyses

Physicochemical analysis

The pH and temperature values in stored samples were measured *in situ* using a multifunctional Inolab 340i pH/Thermo-meter (WTW, Germany). The ammoniacal nitrogen (NH₄-N) was analysed by the Nessler method, using a DR 2400 spectrophotometer HACH (Loveland, Co. USA).

Bacteriological analysis

Stored samples taken at regular time intervals were analyzed for

microbial quantification. Clostridia spores were activated by heat (80°C for 10 min) and then counted in Tryptone-Sulfite-Neomycin (TSN) Agar, according to the method previously described (Anonymous, 2005). *E. faecalis* and *S. aureus* were enumerated respectively in Slanetz & Bartley and Mannitol Salt Agar, after incubation at 37°C for 24 to 48 h (APHA, 2005). *E. coli* and *Salmonella* sp. were counted respectively in Eosin Methylene Blue (EMB) and Salmonella-Shigella (SS) Agar (ISO, 1993, 2001).

Data analysis

For drawing graphs and calculating geometric means, standard deviations, minimum and maximum values of data obtained, the Microsoft Excel package was used.

RESULTS

Storage at ambient

Temperature values

During the samples exposure in the sun, ambient temperatures were recorded. The results showed that minimal and maximal temperatures respectively ranged from 13.9-24.9 and 30.7-38.8°C. The high thermal amplitudes were recorded significantly from November (~20°C), indicating the gaps between daytime and nighttime temperatures in the study area at this period of the year.

Table 1 presents values of daily temperature (sampling days) and those measured in the stored urine, exposed to ambient air. The data show that the differences in temperature between the two matrices of urine are not important. Temperatures in the urine storage containers depend on ambient temperature.

Reduction of vegetative bacteria

The graphs of Figure 1A and B show the reduction of bacterial numbers during samples exposure at ambient

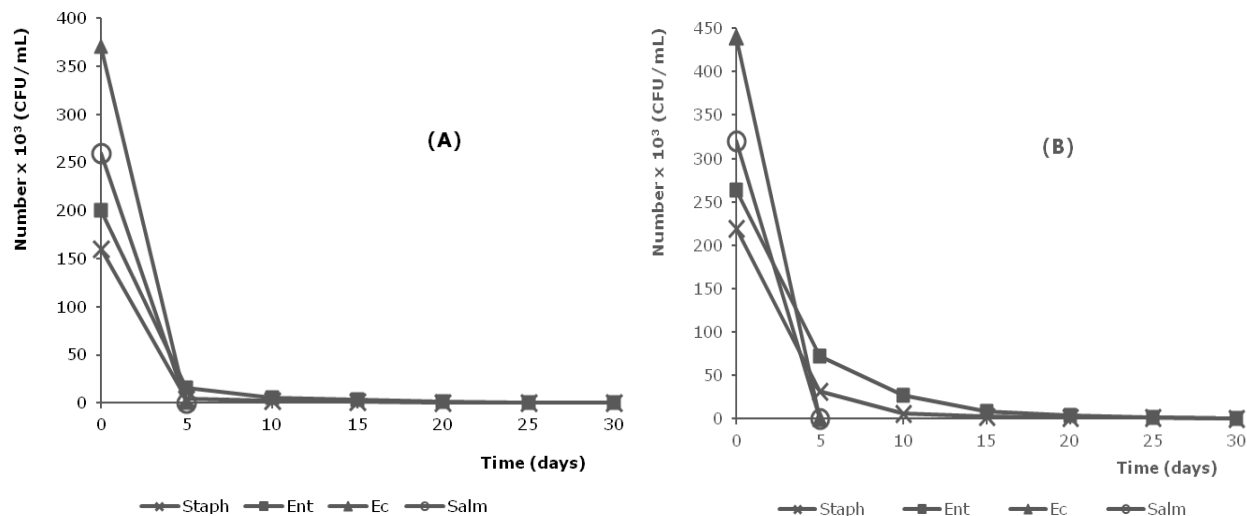


Figure 1. Reduction of bacterial numbers (*E. coli* [▲], *Salmonella* sp. [○], *S. aureus* [X], *E. faecalis* [■]) during samples exposure at ambient temperatures. The initial values were 8260 mg/L $\text{NH}_4\text{-N}$ (pH 8.8) for the undiluted urine (A) and 4450 mg/L (pH 8.7) for the half-diluted urine (B).

temperatures.

The results show that after five (05) days of samples exposure, *E. coli* and *Salmonella* sp. were eliminated (0 CFU/mL) in both diluted and undiluted urine samples. In the undiluted urine samples, *S. aureus* and *E. faecalis* survived ~10 days (Figure 1A), while in the half-diluted urine, they survived around 15 and 20 days, respectively (Figure 1B).

The above data indicate that Gram-negative rods (*E. coli*, *Salmonella* sp.) were more sensitive in urine samples than Gram-positive cocci (*E. faecalis*, *S. aureus*).

Globally, the survival time for each of bacterial species tested was extended in the diluted samples as compared to the undiluted ones.

For the chemical analysis, a low decline of 0.1 pH units was observed in the corresponding pH on diluting the urine by half, while its ammoniacal nitrogen concentration decreased from 8260 to 4450 mg/L. Then, at the end of the experiments (after 30 days of storage), 7730 and 4060 mg/L were respectively the average concentrations of $\text{NH}_4\text{-N}$ obtained in the undiluted urine and the half-diluted samples. These decreases of the ammonia concentration in the stored urine can be due to the nitrogen losses (N) occurring during the tests (measurements).

Reduction of *Clostridia* spores

The results of the reduction of *C. perfringens* spores in urine samples (and control) during the storage are shown in Figure 2. After one hundred (100) days of exposure, 0.85 and 1.07 \log_{10} reductions of *Clostridia* spores were

obtained respectively in the half-diluted urine samples (1:1) and undiluted ones (1:0). In the control (water), spore numbers did not decrease.

The reduced number of *C. perfringens* spores was slightly higher in the undiluted urine than in the half-diluted samples. It is well known that bacterial spores are substantially destroyed by heat ($\geq 100^\circ\text{C}$) and by the tyndallisation process which requires moderate and intermittent temperatures ($\leq 60^\circ\text{C}$). In fact, a moderate heat for 30 min is sufficient to remove the vegetative cells and to trigger the spores transforming in vegetative cells, and then may be destroyed at the next heating (Stanbury et al., 1995).

Storage in controlled environment

Physicochemical parameters

Means (\pm standard deviation) for the pH, ammoniacal nitrogen concentrations and temperature values in stored samples are indicated in Table 2.

Mean values of the initial concentrations of ammoniacal nitrogen were respectively 8260, 4450 and 1070 mg/L in the undiluted (1:0), half-diluted (1:1) and quarter-diluted (1:3) urine samples. At the end of the experiments, we found respectively 7980, 4295 and 1040 mg/L as average concentrations of ammonia. Between the start and the end of the experiments, small decreases in $\text{NH}_4\text{-N}$ concentrations were observed. Apparently, nitrogen (N) losses in the stored urine were lower in the controlled environment (incubator), as compared to the ambient air. The pH was stable, with only a slight decrease (at the most 0.3 pH units) on diluting quarterly the urine, which

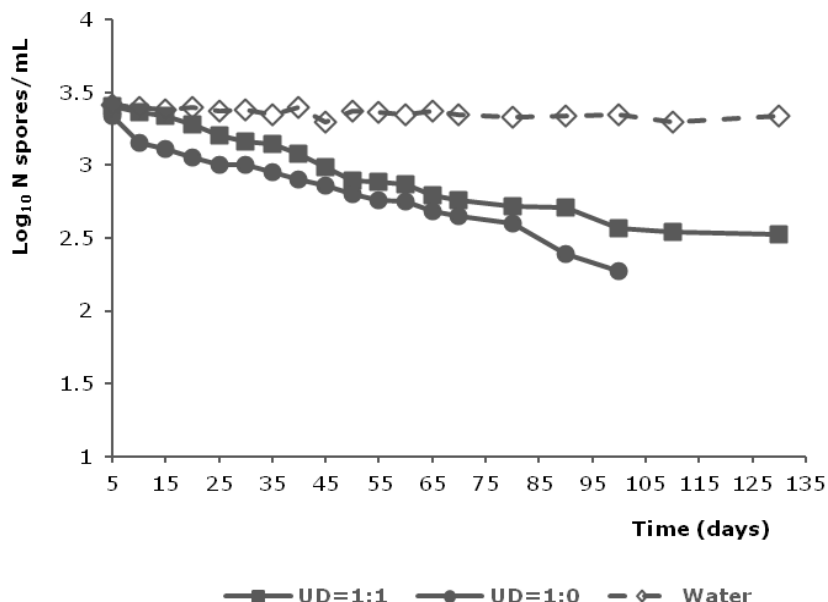


Figure 2. Reduction of *C. perfringens* spores during samples exposure at ambient temperatures. The initial values were 8260 mg/L NH₄-N (pH 8.8) for the undiluted urine (●); 4450 mg/L NH₄-N (pH 8.7) for the half-diluted urine (■) and pH 7.4 for the control (◇).

Table 2. Physicochemical parameters of the urine samples under incubating temperatures.

Sample	NH ₄ -N		Temperature (incubator)					
	(mg/L)		25°C		35°C		42°C	
	Start	End	pH	T (°C)	pH	T (°C)	pH	T (°C)
UD=1:0	8260	7980	8.8±0.0	25.1±0.3	8.6±0.0	35.1±0.2	8.6±0.1	41.3±0.6
UD=1:1	4450	4295	8.7±0.0	25.2±0.1	8.4±0.0	35.2±0.2	8.4±0.0	41.7±0.3
UD=1:3	1070	1040	8.3±0.2	25.2±0.2	8.0±0.0	35.1±0.2	8.0±0.0	41.3±0.1
Control	ND	ND	7.4±0.1	25.1±0.2	7.4±0.0	35.1±0.3	7.4±0.2	41.5±0.0

ND: Not determined; Means ± SD; UD: urine diluted.

indicates its buffer property. The results (Table 2) show that temperatures in samples are similar to those shown on the incubator. Globally, a decrease of 0.2 pH units in urine samples was observed over time, under 25, 35 and 42°C.

Reduction of *E. coli* and *Salmonella* sp. number

Dark colonies with a metallic green sheen of *E. coli* were enumerated on EMB Agar. For *Salmonella* sp., colorless colonies with black centers were counted on SS Agar. The results in Table 3a and b show, regardless of incubation temperatures, 4 h of storage were sufficient to destroy in the undiluted urine, the two tested bacterial species (0 CFU/mL). The above data indicate that the survival of the two bacteria was better in the quarter-

diluted urine (1:3) than in the undiluted (1:0). Similarly, we observed that survival of these bacteria was greater by incubating at 25°C than at 35 and 42°C, since in the case of the quarter-diluted urine samples, *E. coli* survival times were 24, 12 and 4 h respectively at 25, 35 and 42°C of incubation. For the *Salmonella* sp. 28, 16 and 8 h were the survival times obtained respectively in the same conditions as above mentioned. In the control, the reduction of bacterial numbers was particularly fast in function of the incubation temperatures.

Reduction of *E. faecalis* and *S. aureus* numbers

These bacteria were enumerated firstly, after two days of samples storage and then, at regular time intervals of 5 days. Red to maroon colonies of *E. faecalis* were counted

Table 3a. Reduction of *Escherichia coli* numbers in samples under storage conditions.

Time (h)	Number of <i>Escherichia coli</i> x 10 ³ CFU/mL											
	25°C				35°C				42°C			
	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water
0	1030±310	1120±670	1200±330	>300	980±211	1000±110	1070±111	>300	990±28	850±41	1010±38	>300
4	0	1.2±0.3	16.7±4.1	>300	0	1.0±0.1	5.9±1.2	>300	0	0.1±0.0	1.8±0.1	>100
8	0	0.1±0.0	13.6±2.5	>300	0	0	1.4±0.1	>100	0	0	0	<100
12	0	0	10.0±2.6	>300	0	0	0.3±0.2	>100	ND	ND	ND	ND
16	0	0	7.5±1.7	>300	0	0	0	>100	ND	ND	ND	ND
20	ND	ND	5.4±2.5	>100	0	0	0	>100	ND	ND	ND	ND
24	ND	ND	0.7±0.6	>100	ND	ND	ND	ND	ND	ND	ND	ND
28	ND	ND	0	>100	ND	ND	ND	ND	ND	ND	ND	ND
32	ND	ND	0	>100	ND	ND	ND	ND	ND	ND	ND	ND

Table 3b. Reduction of *Salmonella* sp. numbers in samples under storage conditions.

Time (h)	Number of <i>Salmonella</i> sp. x 10 ³ CFU/mL											
	25°C				35°C				42°C			
	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water
0	240±34	330±27	217±56	>300	280±85	341±71	490±141	>300	320±132	460±133	547±169	>300
4	0	1.4±0.4	22.0±5.0	>300	0	1.4±0.1	23.0±5.3	>300	0	0.2±0.0	17.6±4.7	>100
8	0	0.1±0.0	17.9±5.7	>300	0	0	5.0±0.7	>300	0	0	3.5±0.8	>100
12	0	0	11.0±3.8	>300	0	0	1.2±0.2	>300	0	0	0	>100
16	0	0	7.3±3.2	>100	0	0	0.2±0.0	>100	ND	ND	ND	ND
20	ND	ND	3.1±1.9	>100	ND	ND	0	>100	ND	ND	ND	ND
24	ND	ND	0.6±0.3	>100	ND	ND	ND	ND	ND	ND	ND	ND
28	ND	ND	0.1±0.0	>100	ND	ND	ND	ND	ND	ND	ND	ND
32	ND	ND	0	>100	ND	ND	ND	ND	ND	ND	ND	ND

on Slanetz & Bartley agar. For *S. aureus*, yellow colonies with yellow zones were enumerated on Mannitol Salt Agar. Data obtained (Table 3c and d) show that the two tested bacteria have survived at least 5 days in the undiluted urine samples (1:0) under 25°C of incubation, however they

could not survive for up to two days at 42°C in the same samples as mentioned before. In the control, bacterial removal was faster at 42°C than at 25°C. Considering the incubation at 25°C, *E. faecalis* survival time in the quarter-diluted urine was 35 days approximately, however it was less

than 5 days in the undiluted urine samples. For the *S. aureus*, survival times were 15 and 5 days, respectively in the quarter-diluted and the undiluted urine samples. Extended times in the survival of the tested bacteria were observed by incubating in the diluted urine samples.

Table 3c. Reduction of *Enterococcus faecalis* numbers in samples under storage conditions.

Time (days)	Number of <i>Enterococcus faecalis</i> x 10 ³ CFU/mL											
	25°C				35°C				42°C			
	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water
0	96±17	117±14	105±11	>300	103±36	99±15	120±10	>300	86±12.7	97±18	102±40	>100
2	0.8±0.2	9.7±2.2	59±10	>300	0.3±0.1	5.4±0.9	22±7	>300	0	0.4±0.1	2.3±0.6	>100
5	0.2±0.0	4.5±0.4	28.0±1.3	>300	0	1.2±0.4	11.5±0.6	>300	0	0	0.9±0.2	>100
10	0	0.1±0.0	23.0±2.6	>300	0	0.2±0.0	1.5±0.4	<300	0	0	0	99
15	0	0.04±0.0	19.0±2.0	>300	0	0	0.5±0.0	244	ND	ND	ND	ND
20	0	0	5.1±3.2	>100	ND	ND	0	191	ND	ND	ND	ND
25	0	0	1.6±0.7	<100	ND	ND	ND	ND	ND	ND	ND	ND
30	ND	ND	0.2±0.0	<100	ND	ND	ND	ND	ND	ND	ND	ND
35	ND	ND	0.15±0.0	<100	ND	ND	ND	ND	ND	ND	ND	ND
40	ND	ND	0	<100	ND	ND	ND	ND	ND	ND	ND	ND
45	ND	ND	0	26	ND	ND	ND	ND	ND	ND	ND	ND

UD: Urine diluted.

Table 3d. Reduction of *Staphylococcus aureus* numbers in samples under storage conditions.

Time (days)	Number of <i>Staphylococcus aureus</i> x 10 ³ CFU/mL											
	25°C				35°C				42°C			
	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water	UD=1:0	UD=1:1	UD=1:3	Water
0	88±16	107±24	94±20	>100	102±31	100±15	94±30	<300	84±6	90±13	109±14	<100
2	0.6±0.2	09±0.2	3.6±0.9	>100	1.0±0.3	1.6±0.2	3.2±0.9	<300	0	0.2±0.0	0.9±0.2	<100
5	0.1±0.0	0.3±0.1	1.2±0.1	>100	0.2±0.1	0.5±0.1	1.3±0.2	<300	0	0	0.2±0.0	40
10	0	0	0.3±0.0	<100	0	0.1±0.0	0.4±0.0	<100	0	0	0	0
15	0	0	0.1±0.0	<100	0	0	0.1±0.2	<100	ND	ND	ND	ND
20	ND	ND	0	<100	ND	ND	0	<100	ND	ND	ND	ND

UD: Urine diluted.

Overall, Gram-positive cocci particularly *E. faecalis*, were less sensitive in the above described conditions (samples, incubation temperatures) as compared to Gram-negative rods (*E. coli*, *Salmonella* sp.).

DISCUSSION

The chemical results were that ammoniacal nitrogen (NH₄-N) concentrations in samples decreased in function of the urine dilution rate

(Table 2), while pH values remained almost stable, even during the storage. Other previous studies indicated a biocidal effect in urine due to the uncharged ammonia (Jenkins et al., 1998; Nordin et al., 2009). Note that in aqueous solution,

ammoniacal nitrogen is present in both uncharged (NH_3) and ionized (NH_4^+) forms. The uncharged ammonia concentration is proportional to the $\text{NH}_4\text{-N}$ concentration and then, can be calculated, using chemical equations (Erickson, 1985).

Our findings on microbial behaviour show that the destruction of the tested bacteria was faster in the urine samples greatly concentrated in ammonia (Figure 1 and Table 3a to d), thus explaining the biocidal properties of this urine component. It is well known that uncharged ammonia can cross easily biological membranes as compared to ions (NH_4^+ , H_3O^+ , OH^-). Nordin et al. (2009) indicated that inside microorganism, the uncharged ammonia acts by increasing the internal pH to deleterious levels, so destroys cell by causing the dysfunction of the metabolism. Previous studies showed that microbicidal effects of alkaline pH in media (~ 8.8 for the urine) were less significant than these due to the uncharged ammonia (Jenkins et al., 1998; Vinnerås et al., 2008; Nordin et al., 2009). Moreover, a link has been found between the NH_3 membrane permeability and the external temperature (Pecson et al., 2007; Vinnerås et al., 2008). In fact, these authors observed the removal of the NH_3 microbicidal properties at low external temperatures ($\sim 4^\circ\text{C}$) because of the inhibition of its membrane permeability. However, inverse effect was observed by increasing temperature. Likewise, it was shown in this study that the reduction of the bacterial numbers was more rapid in samples incubated at 42°C than those placed at 25°C (Table 3a to d). Accordingly, these results show that temperature and urine intrinsic components, particularly the ammonia act synergistically to sanitize the urine samples.

Moreover, the sensitivity of bacteria during sample storage varied depending on microbial group since, Gram-positive cocci have survived more than Gram-negative rods. The presence or not of a large peptidoglycan layer in the wall of the tested bacteria can explain the difference in bacterial behaviour. In fact, Gram-negative bacteria possess in their wall, a slim peptidoglycan layer, that make them more sensitive to environmental factors like heat shock and ionic strength (Sinton et al., 1994; Madigan and Martinko, 2006).

Usually, to assess the environmental risks due to enteric pathogens, *E. coli* is the common faecal indicator (Finney et al., 2003). Because of its rapid removal in the urine, *E. coli* would not be a suitable faecal indicator for the urine from UDDTs. All the same, *E. faecalis* and *C. perfringens* spores were suggested as suitable indicators of the effectiveness of wastewater treatment (Payment and Franco, 1993; Ashbolt et al., 2001). We have found, for *E. faecalis*, a survival time of 10 days in undiluted urine at 26.5°C as the average of the ambient temperatures. And then, their reduction was faster when temperatures increased (Table 3c). As urine from UDDTs can contain enteric microorganisms such as viruses and protozoan oocysts which are very resistant to the treat-

ment by storage (Höglund et al., 2002; Nordin et al., 2009), so, *E. faecalis* could not be considered as reliable indicator of the effectiveness of the urine treatment by storage.

With respect to our results on *C. perfringens* spores, overall no or small reduction was observed in samples (Figure 2) during the storage. These findings may confirm the statement according to a conservative effect of bacterial spores in alkaline media (Venczel et al., 1997; Gaillard et al., 1998), in so far as the urine pH is ~ 9 .

Only $\sim 1\text{-log}_{10}$ reduction of Clostridia spores was observed within 100 days of storage. These small reduction in spore numbers may be due in part to the low activation of spores. In fact, the occurrence by activating spores is the wall rip, which may exhibit these spore-forming bacteria which has deleterious effects on the environment. Note that spore activating agents can be mechanical (shock), physical (heat) or chemical (acidity). In our case, *C. perfringens* spores were placed in alkaline samples (urine) and then, exposed to ambient (26.5°C). Under these conditions, spore activation cannot occur physically or chemically. Therefore, the mechanically treatment of samples before analyses (homogenization), could be the main cause of spores activation. *C. perfringens* spores have been showed as suitable tracers for determining the fate of viruses and protozoan oocysts in wastewater treatment (Payment et al., 2001; Ashbolt et al., 2001). But, for the treatment of the urine by storage, more data on viruses and protozoan behaviour in this matrix are needed in order to confirm the use of Clostridia spores as tracers in the urine sanitation. Nevertheless, it had been shown that Rotavirus and *Cryptosporidium parvum* oocysts remain viable in urine after 6 months of storage, under very low temperatures (Höglund and Stenström, 1999; Höglund et al., 2002; WHO, 2006).

The ammonia concentrations used for experiments (Table 2), are the same found in the urine collected in fields, by considering large-scale systems (Jönsson and Vinnerås, 2007; Dagerskog and Bonzi, 2010). In these conditions, low $\text{NH}_4\text{-N}$ concentrations observed, can be due to the urine-water mixture that occurred when the UDDTs are used for washing bodies.

On taking into account only the samples incubated at 25°C , the survival times for *E. faecalis* (less sensitive bacteria), were 5, 15 and 35 days respectively in undiluted, half-diluted and quarter-diluted urine. Based on these data, storage times of 30-45 days recommended to sanitize urine from large-scale systems in Ouagadougou (Dagerskog and Bonzi, 2010), seem to be sufficient since in this Sahelian zone, annual average temperatures are above 25°C . Unfortunately, urine collected via UDDTs can contain other enteric microorganisms more persistent in environment than vegetative bacteria.

Also, the volumetric capacities in liquid samples can influence the microorganisms survival. Previous studies had shown that the sensitivity of microbes to the external factors (UV-light, temperature) was more important in the

small volumes than in the high volumes (Lemunier et al., 2005; Pecson et al., 2007; Niwagaba, 2009). Consequently, the urine volumes in containers must be considered for determining the storage time needed to sanitize urine. Although, the effects linked to the matrix volumetric were not studied here, however the ways for the urine collection via UDDTs and the climate variability must be integrated into the process of the urine sanitation by storage, before been applied in soils as fertiliser.

Conclusion

Experimental results have shown that the survival times of the tested bacteria increased during the storage with the urine dilution for which, the direct effect was the reduction of the ammonia concentration. For an effective treatment by storage, adding water into the urine collection containers must be avoided. Also, our findings showed that ammonia and temperature act synergistically to reduce or remove microorganisms in urine, during storage. That is why climatic factors are decisive to estimate the exposure time needed to sanitize urine. On top of that, analyses have shown that the survival capacities of bacteria in the urine, varied depending on bacterial group. Gram-positive cocci, particularly *E. faecalis* which were less sensitive in urine as compared to Gram-negative rods, because of the difference in peptidoglycan layer size. The use of *E. faecalis* as indicator of the effectiveness of the urine treatment seems inappropriate since, *C. perfringens* spores are more resistant to the storage conditions. If the *C. perfringens* spores are suitable tracers for the fate of viruses and protozoan oocysts in wastewater treatment, their use as tracers for the urine treatment (storage) may be possible, in view of their stability. Nevertheless, it would be important to elucidate before the survival potential of viruses and protozoan oocysts in the urine during storage.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

Removal of azo dye from water by adsorption using waste residue from alum manufacturing process

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Adsorption techniques are widely used to remove certain groups of pollutants such as dyes which are not amenable to biodegradation and environmentally very problematic. Although commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents should be investigated. It is well-known that natural materials, waste materials from industry and agriculture, and bio sorbents can be obtained without a cost, therefore could be employed as inexpensive sorbents. Therefore the present investigation reports the adsorptive capacity of an industrial residue for the removal of azo dyes. Batch experiments were carried out for the sorption of the dye onto the adsorbent. The influence of contact time, adsorbent dose, pH and initial dye concentration on the adsorption capacity of the material was studied. Kinetics and adsorption isotherms were also studied to evaluate the rate of dye removal and the capacity of the adsorbent. The equilibrium data best fits freundlich isotherm equation. Adsorption capacity (K_f) and intensity of adsorption (n) as determined by fitting the equilibrium data to freundlich isotherm equation are calculated to be 0.26 and 0.82, respectively. The adsorption process was found to undergo via a pseudo-second-order adsorption kinetics with a rate constant of 3.81×10^{-3} (g / mg / min). The removal of dye was not affected for the initial dye concentration range of 15 to 256 mg/L. An adsorption process; requiring an equilibrium time of 30 h with optimum adsorbent dose of 19 g/L for 77.4% dye removal efficiency was observed at near neutral pH. However, as the pH of water is adjusted from 7 to 9, the dye removal efficiency was greater than 90%. The overall result shows that the industrial by product investigated in this study exhibited a high potential for the removal of dye from aqueous solution.

Key words: Dye, adsorbent, adsorption isotherms, batch adsorption, removal.

INTRODUCTION

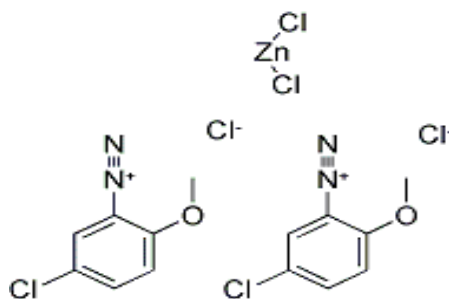
It is estimated that 10,000 different types of dyes and pigments are produced worldwide annually (Wallace,

2001) out of which a large number of dyes are azo compounds (-N=N-), which are linked by an azo bridge.

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Table 1. Percentage composition of the chemical constituents in waste residue.

Chemical composition	Percent (wt. %)	Chemical composition	Percent (wt. %)
Quartz (SiO ₂)	40	K ₂ SO ₄	0.005
Kaolin	8.883	Al ₂ (SO ₄) ₃	1.778
Al(OH) ₃	0.878	CaSO ₄	0.194
Fe ₂ (SO ₄) ₃	0.023	Fe ₂ O ₃	0.001
MgSO ₄	0.008	Na ₂ SO ₄	0.007

**Figure 1.** The molecular structure of the dye.

It is estimated that 10,000 different types of dyes and pigments are produced worldwide annually (Wallace, 2001) out of which a large number of dyes are azo compounds (-N=N-), which are linked by an azo bridge. Azo dyes are used by a wide number of industries. While textile mills predominantly use them, azo dyes can also be found in the food, pharmaceutical, paper and printing, leather, and cosmetics industries (Asamudo et al., 2005). Many of these dyes find their way into the environment via effluent discharges. These compounds retain their color and structural integrity under exposure to sunlight, soil and bacteria; they also exhibit a high resistance to microbial degradation in wastewater treatment systems.

Therefore these compounds have become a major environmental concern (Asamudo et al., 2005). In current dyeing processes, as much as 50% of the dye is lost in the wastewater. This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration and reduction in photosynthesis because of the absorbance of light that enters the water (Slokar and Marechal, 1998).

“Currently there are many dye removal methods, out of these methods ion exchange and adsorptions using natural clays are preferable because of cost effectiveness and ease of operation”. Activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies (Bhattacharyya and Sarma, 2003). However, the disadvantage associated with is its high cost (Babel and Kurniawan, 2003). The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively

inexpensive starting materials is also unjustified for most pollution control applications (Street et al., 1995). Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has been intensified in recent years. Cost is actually an important parameter for comparing the adsorbent materials. A sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. In this paper laboratory investigations were carried out to evaluate the efficiency of the waste residue of aluminum sulfate and sulfuric acid factory to adsorb azo dyes from water.

MATERIALS AND METHODS

The waste residue, generated during the manufacture of aluminum sulfate using kaolin and sulfuric acid, was collected from Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory, which is located at the central part of the Ethiopian Rift Valley Region. Samples were taken from more than 30 batches of aluminum sulfate production residues and then mixed to maintain homogeneity. The waste directly discarded contains about 52% of solid. The chemical compositions of this industrial by product are given in Table 1. The collected waste residues were sundried for one day and ground to fine powder using mortar and the resulting material is considered as untreated media. The chemical composition of the waste material indicates the absence of any hazardous and carcinogenic substances in the material and hence it is suitable to use as a decolorization agent. The dye used for the investigation of the adsorptive capacity of the waste residue was obtained from Akaki textile industry located in Addis Ababa, Ethiopia. The molecular structure of the dye is shown in Figure 1.

Analytical methods and instrumentation

Uv-vis spectrophotometer is selected as an analytical tool to

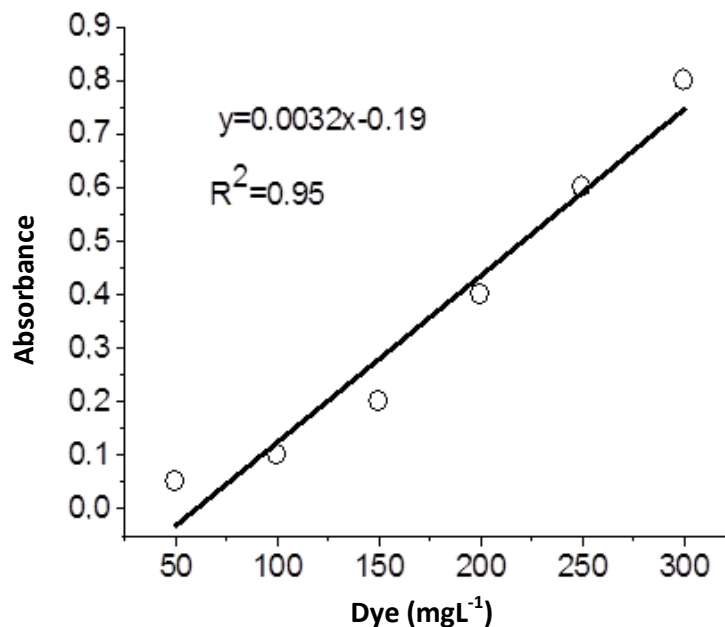


Figure 2. Calibration curve of the dye at its λ_{\max} .

determine the concentration of dye solutions. This selection is made based on the fact that most dyes absorb electromagnetic radiation in the Uv-vis region. Concentration of dye solution was calculated from the absorbance measurements using Lambert Beer's law Equation (1)

$$A = \epsilon cl \quad (1)$$

Where A is absorbance, ϵ is the molar absorptivity, C is the concentration, and l is the path length.

The dye removal capacity of the adsorbent is expressed as follows using Equation 2:

$$\frac{C_i - C_e}{m} \times V \quad (2)$$

Where C_i and C_e are the initial and final dye concentration (mg/L) in the liquid phase respectively, m is the mass of adsorbent (g), and V is the volume of experimental solution (mL).

The percentage of dye removal was calculated using Equation 3:

$$\% \text{ dye adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \quad (3)$$

Batch adsorption studies

After the wavelengths of maximum absorbance ($\lambda_{\max} = 373 \text{ nm}$) of the solutions is determined calibration curve is constructed by dissolving an amount of dye to make 300 mg/L of dye solution. Then the other series of solutions to make the calibration curve are made by taking the corresponding volume of the previously concentrated dye solutions, diluting using distilled water and measuring their absorbance at their respective λ_{\max} . Experimental solutions were prepared by pipetting a known amount of dye into a 1 L conical flask and diluting it with a known amount of distilled water. Batch experiments for decolorization were conducted in 500 mL conical flask containing 300 mL of dye solution at room

temperature ($22 \pm 2^\circ\text{C}$), to evaluate dye removal efficiency and capacity of the media. The media (waste residue) was placed in the flask and then stirred continuously at a constant slow mixing rate with magnetic stirrer during the experiment. The initial dye concentration selected for batch experiments is within the range recommended in the actual textile effluent (Galster and Hansen, 1998). The effect of dose of the media, pH of water and initial concentration of the dye were investigated by varying any one of the process parameters and keeping the other parameters constant. Investigation of the effect of dose experiments was conducted by varying adsorbent doses (1 to 25 g/L) at constant initial dye concentration of 100 mg/L.

The effect of pH was studied by varying the pH from 7–9 either with 0.1 M NaOH or 0.1 M HCl. To investigate the effect of initial dye concentration, experiments were conducted by varying dye concentrations from 50 to 258 mg/L at constant adsorbent dose of 19 g/L. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first order and pseudo-second-order mechanisms. Adsorption kinetics was determined using constant adsorbent dose of 19 g/L corresponding to the initial dye concentration of 100 mg/L. Isotherm experiments were conducted by changing the adsorbent dose from 1 to 43.3 g/L at initial dye concentration of 100 mg/L. For all experiments, the remaining concentration was determined spectrophotometrically at its corresponding λ_{\max} when the equilibrium contact time is reached.

RESULTS AND DISCUSSION

Wave length of maximum absorbance and Calibration curves

The calibration curve (Figure 2) is obtained by preparing dye solution for which the concentration is within the effective concentration range of the dye. The correlation coefficient from the curve shows strong linear relationship between the concentration of the dye solutions and the

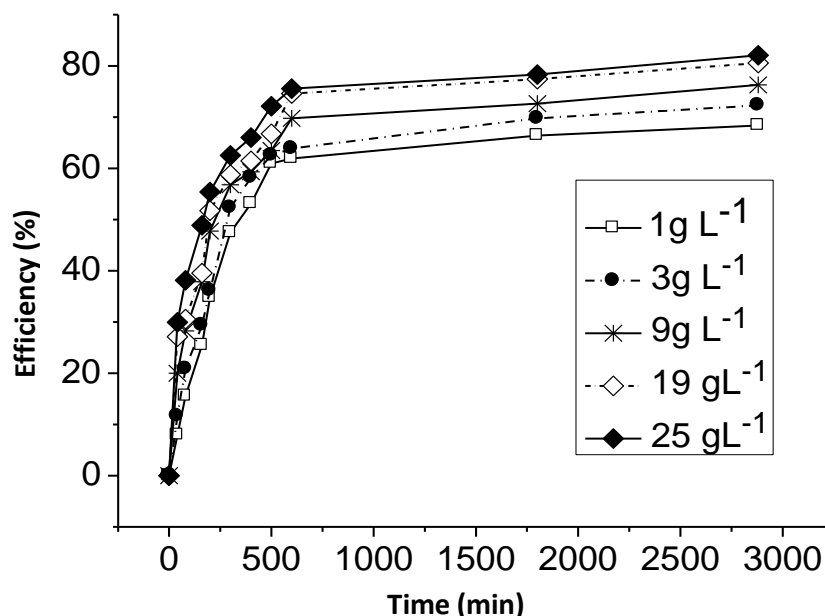


Figure 3. Efficiency of dye removal as a function of time for different doses of untreated media (initial dye concentration = 100 mg /L, pH = 3-4).

absorbance at the dye's wavelength of maximum absorbance.

Effect of dose and contact time

To investigate the effect of dose and contact time, experiments were conducted by varying adsorbent doses (1 to 25 g/L) at constant initial dye concentration of 100 mg/L. Further addition of adsorbent does not provide more increment in the adsorption amount (Figure 3). The results show that the adsorption reached equilibrium after about 30 h. Further increase in contact time did not increase the uptake. In general the decolorization efficiency was increased with dose as reflected by the measured residual dye concentration. The increase in the dye adsorption was due to the increased in availability of dye binding sites resulting from an increase in adsorbent dosage. Higher dose of the media (greater than 19 g/L) will increase the amount of sludge without causing a significant change on the amount of dye removed. On the other hand, the adsorption capacity decreases with increasing dose (Figure 4). To maintain maximum capacity and high removal efficiency, the surface loading (that is the mass ratio of the dye to adsorbent dose) should be lower than the optimum value. A dose of 19 g/L corresponds to the capacity of about 4.74 mg dye /g of adsorbent if there is 90% removal. The surface loading obtained for the dose of 19 g/L in this experiment was 4.1 mg dye /g of adsorbent. Lower capacity of the material is due to the presence of H⁺ ions which may cause the surface to be positively charged and hence reduce its

interaction with the cationic dye. These experimental results suggest that modification of the surface chemistry of the adsorbent may enhance its capacity.

Effect of pH

About 80% of the dried waste residue is quartz. In quartz [SiO₂], Si and O are structural elements; the Si-O bond has about 50% covalent character (Huang and Ostovic, 1978). The siloxane groups, -SiOSi-, interact with water forming -SiOH (Fan et al., 2003). Any oxide surface attains (positive or negative) charge on its surface. The hydroxyl groups can gain or lose proton, resulting in a surface charge that varies with changing pHs. At lower pH, surface sites are protonated and the surface become positively charged. Maximum removal efficiency at pH 7 to 9 and the removal rate increases with an increase in pH in general. At higher pH, the surface hydroxides lose their protons and the surface becomes anionic. This can be the reason for the higher efficiency of the adsorbent for the cationic dye at higher pH value (Figure 5). The other main constituent of the adsorbent mixture is kaolinite (kaolin), a class of natural clay minerals. Here the adsorption capabilities result from a net negative charge on the surface, which gives clay the capability to adsorb positively charged species. Their sorption properties are also due to their high surface area and high porosity (Alkan et al., 2004). Clay mineral exhibits a strong affinity for both heteroatomic cationic and anionic dyes however; the sorption capacity for basic dyes is much higher than for acid dyes because of the ionic

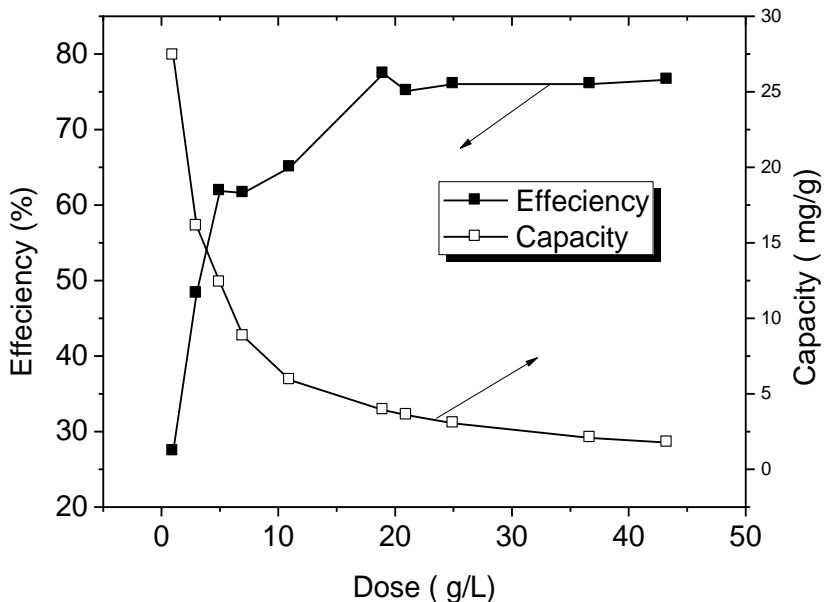


Figure 4. The relationship between adsorbent dose versus percentage of dye removal and adsorbent dose versus removal capacity at fixed dye concentration.

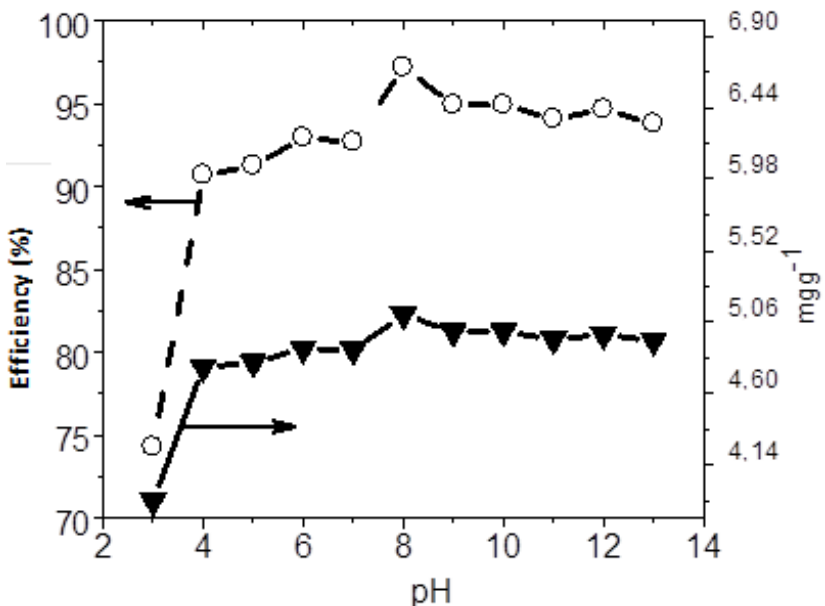


Figure 5. Effect of pH on efficiency and capacity of dye removal at fixed dye concentration and adsorbent dose.

charges on the dyes and character of the clay. Some researchers show that the adsorption of dyes on kaolinite was about 20 times greater than alumina (Harris, 2001). The possible mechanism for the adsorption of the dye for this experimental condition can also be explained based on the theoretical meaning of *pHzpc* (pH of zero point charge). Silica adsorbents have a low *pHzpc* nearly 2

(Rao and Sridharan, 1984). The measured pH for the dye-adsorbent system is 3 to 4 in this particular experiment, that means the surface of the material will have a slight negative charge even at this lower pH; there is a columbic attraction towards the cationic dye. The other possible mechanism for the adsorption of the dyes by quartz can be attributed to the formation of surface

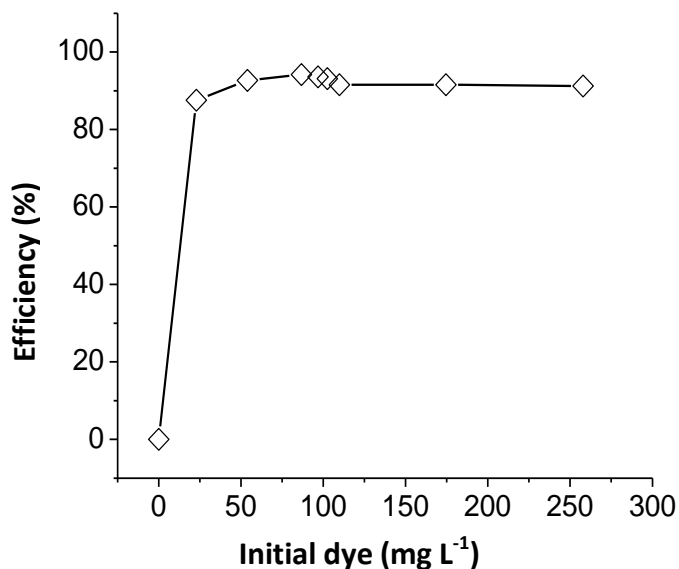


Figure 6. Effect of initial dye concentration on percentage of dye removal at fixed adsorbent dose. (PH = 7 to 9).

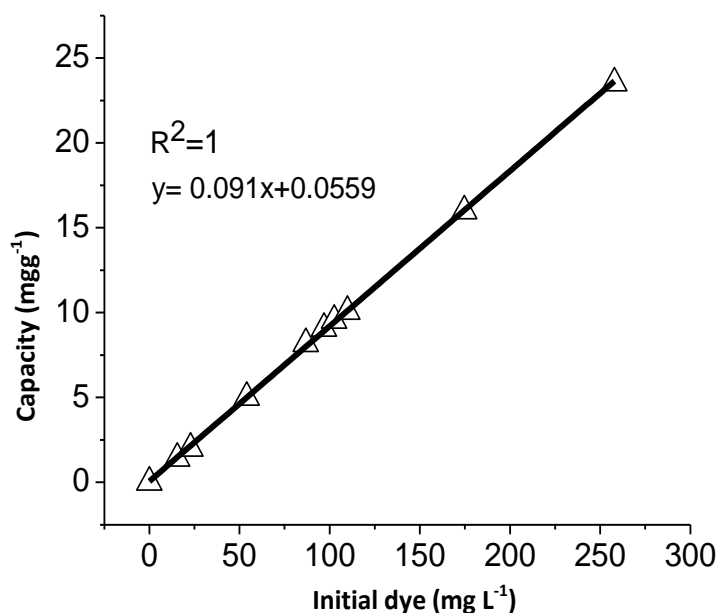


Figure 7. Effect of initial dye concentration on capacity of dye removal at fixed adsorbent dose for (pH = 7 to 9).

hydrogen bonds between the surface hydroxyl groups on the surface of the silica adsorbent and the nitrogen atoms of the dye.

Effect of initial dye concentration

The effect of initial dye concentration at a fixed quantity of

the adsorbent dosage is shown in the following figures. The percentage of dye removal at fixed adsorbent dose increased with increasing initial dye concentration (Figure 6). This is expected because in surface adsorption reactions the equilibrium concentration of a given solute in the solid phase is proportional to the equilibrium concentration in the liquid phase. From Figure 7, it is observed that increasing the initial dye concentration

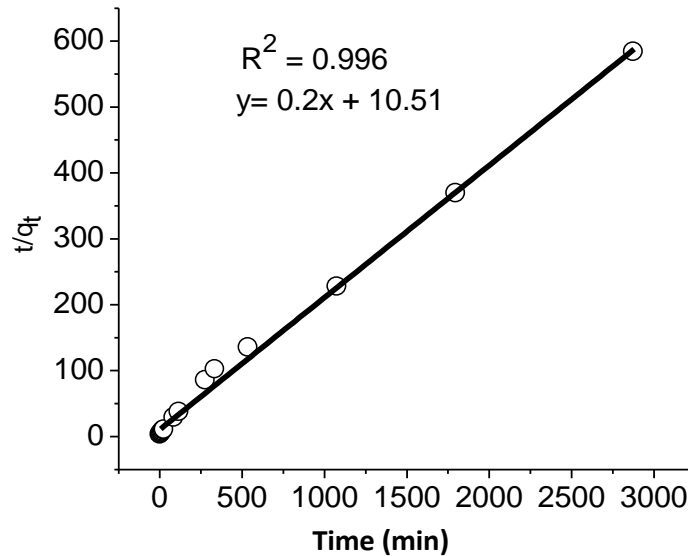


Figure 8. Pseudo-second-order plot of the dye adsorption kinetics on untreated media (pH = 7-9, dose = 10 g/L and an initial dye concentration of 100 mg/L).

increases the removal capacity of the adsorbent. The correlation coefficients of the experiments show that there is a strong linear relationship between the initial concentration of the dye and the removal capacity of the adsorbent. This result indicates that the method is suitable for the treatment of high-strength textile effluent in terms of dye concentration.

Reaction rates

The adsorption kinetics was studied at constant dye and adsorbent concentrations. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms. The uptake of the dye on untreated adsorbent reached equilibrium in 30 h. The kinetics of adsorption was analyzed by using the Lagergren equation as shown below (Yeheyas et al., 2005):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

$$\frac{d(q_e - q_t)}{(q_e - q_t)^2} = -k_2 dt \tag{4}$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation (5) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{5}$$

This is the integrated rate law for a pseudo second-order reaction. Equation (5) can be rearranged to obtain Equation (6), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \tag{6}$$

Where, k_2 (g /mg /min) is the equilibrium rate constant of second-order sorption. The untreated materials can be described very well by the pseudo-second-order rate equation as shown in Figure 8. The correlation coefficient was found as near to unity. The values of q_e and K_2 are 5 (mg/g) and 3.81 (g /mg /min) respectively which are determined by plotting t/q_t against t of Equation (7), and using the slope and y-intercept of the plot. The equilibrium between the adsorbed layer and the solution slightly delayed and this is due to (1) the solute molecules do not diffuse immediately from the bulk of the solution to the interface and (2) the solute molecules do not cross immediately the energy barrier which exists near the interface, and moreover a flow of solute molecules leaving the interface-desorbing-slackens the adsorption.

Adsorption isotherm

The adsorption isotherm of the dye is shown in Figure 9 at a constant temperature ($22 \pm 2^\circ\text{C}$). Langmuir (data not shown) and Freundlich isotherms were used to describe the equilibrium nature of dye adsorption by the adsorbent. The values of n and $\log k_f$ were calculated

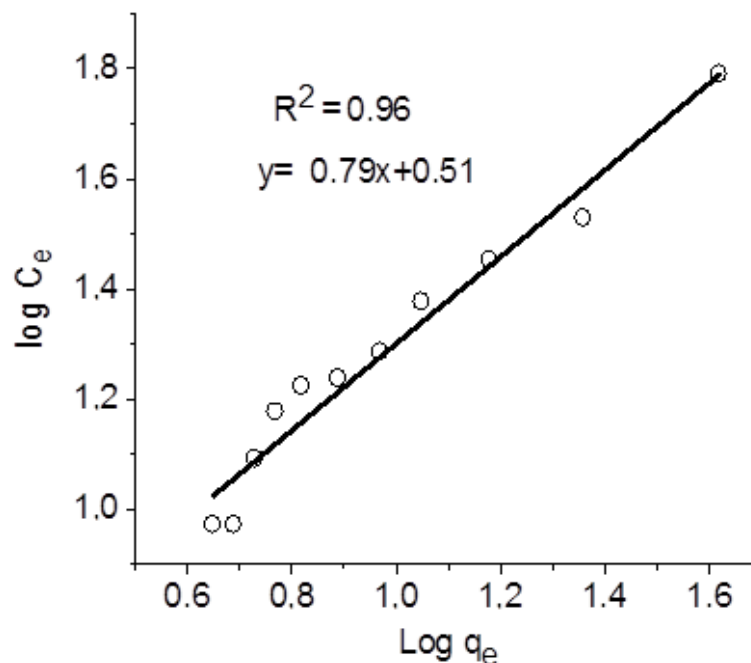


Figure 9. Linearized Freundlich isotherm (initial dye concentration = 103 mg/ L, pH = 7-9, temperature = 24°C).

Table 2. Important adsorption parameters to plot an isotherm for untreated material.

Dose (g/L)	C_e (mg/L)	q_e (mg/g)	$1/q_e$	$1/C_e$	Log q_e	Log C_e
1	61.58	41.53	0.02	0.02	1.62	1.789
3	33.62	23.16	0.04	0.03	1.36	1.527
5	28.25	14.97	0.07	0.04	1.18	1.451
7	23.73	11.34	0.09	0.04	1.05	1.375
9	19.21	9.32	0.11	0.05	0.97	1.284
11	17.23	7.81	0.13	0.06	0.89	1.236
13	16.67	6.65	0.15	0.06	0.82	1.222
15	14.97	5.88	0.17	0.07	0.77	1.175
17	12.43	5.33	0.19	0.08	0.73	1.09
19	9.32	4.94	0.20	0.11	0.69	0.97
25	9.32	3.75	0.27	0.11	0.65	0.97

from the slope and interception of Freundlich plots as listed in Table 2. The adsorption data were analyzed with the help of linear form of Freundlich isotherm. Freundlich model attempts to account for surface heterogeneity (Gupta et al., 1988).

Freundlich isotherm:

$$\text{Log } q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

Where, k_f is roughly a measure of adsorption capacity and $1/n$ is an indicator of adsorption effectiveness; q_e is the amount of dye adsorbed per unit mass of adsorbent

(in mg g^{-1}) and C_e is the equilibrium concentration of dye (in mg l^{-1}). Figure 9 shows a plot of $\log q_e$ vs. $\log C_e$. The constants $1/n$ as the slope and k_f as the intercept. The values of Freundlich isotherm parameters along with the k_f and n were found as 0.26 and 0.82, respectively. It is found that the related correlation coefficient R_2 value for the Freundlich model is near to unity (0.962) and hence the process of decolorization using untreated material is well fitted to the Freundlich isotherm. The Freundlich coefficient, n should have values in the range of $0 < n < 1$ for favorable adsorption (Pola et al., 2003). The data did not fit well to the Langmuir isotherm model (data not shown). The condition for the validity of a Freundlich type

adsorption model is adsorption on heterogeneous surfaces (Gupta et al., 1988). The increase in equilibrium dye removal capacity with residual dye concentration observed during the investigation of effect of initial dye concentration on capacity of dye removal can support the condition of heterogeneous adsorption.

Conclusions

The ability of locally available industrial by product to remove textile dyes from aqueous solutions was investigated employing an adsorption process. The media could remove about 77.4% of the dye from water at 19 g/L dose in pH range of less than 3-4 in the first 30 h. However, the media has an efficiency of 90% when the pH of the adsorbent and adsorbate mixture is between 7 to 9. The removal of dye was not affected by the initial dye concentration range of 15 to 256 mg/L that suggests the industrial by product has high efficiency for high strength textile dye removal. The kinetics of dye adsorption by the industrial by product in the batch study was satisfactorily described by a pseudo second order rate kinetics model, and the experimental data correlated reasonably well with that of the Freundlich adsorption isotherm. The results of these studies indicate that the waste residue is an efficient and low cost adsorbent for dye removal from the aqueous phase.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

Arsenic pollution of surface and subsurface water in Onitsha, Nigeria

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Study on arsenic pollution was conducted in Onitsha town in Anambra State, Nigeria to examine the pollution status of surface and subsurface water. Arsenic concentration in surface water within Onitsha metropolis ranged from 0.2001 mg/L (River Niger upstream) to 1.5883 mg/L (River Niger central drainage surface), while concentration in boreholes lies within the range of 0.0000 mg/L (22.2% of boreholes) and 1.2507 mg/L (creek road), respectively. Arsenic concentration in sampled water from river sources is above the WHO standard (0.01 mg/L) while 87.8% of Arsenic concentration in boreholes adjacent and closest to these rivers and creek is also above the world Health Organization standard (WHO, 2011) of 0.01 mg/L. It is discovered that pollution of surface water is greater than that of the groundwater sources. Major sources of arsenic in Onitsha are refuse dumps, effluent from industries and sewage amongst other sources. Arsenic is known to be the most poisonous metal in existence on earth's surface, its production should be carefully monitored and effluents treated before discharge into the environment.

Key words: Arsenic, water, health.

INTRODUCTION

Water is one of the major means of transport of arsenic in the environment. Soil erosion and leaching have been reported to contribute to the quantity of arsenic in dissolved and suspended form. Soil erosion and agricultural runoff are large contributors to the arsenic concentration in sediments too. Arsenic in its various chemical forms and oxidation states is released into the aquatic environment by natural erosion processes, sewage, refuse and industrial discharges. On release to the aquatic environment, the arsenic species enter into a methylation/ demethylation cycle, while some are bound to the sediments or taken up by biota where they could

undergo metabolic conversion to other organoarsenicals (Islam and Tanaka, 2004). A chemical factory manufacturing several chemicals including the insecticide Paris - green (acetocopper arsenite), was responsible for the contamination of wells in the southern part of Calcutta, India. Over seven thousand people consumed the arsenic-contaminated water for several years, but this fact remained unnoticed until September, 1989. A few died, and some of the victims were hospitalized, while symptoms of arsenic poisoning were evident in many families living in the area. Water samples analyzed for arsenic indicated extremely high levels of contamination,

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with total arsenic concentration ranging from as low as 0.002 to as high as 58 mg/L (Viaraghavan et al., 1999). According to Krishnamurthy (1992), about 1% of Americans consume drinking water that has arsenic levels of 25 ppb or more, and in Utah and California water supplies have been found to contain as much as 500 ppb; also an estimated one-in-a-thousand lifetime risk of dying from cancer induced by normal background levels of arsenic (this equals the risk estimate due to tobacco smoke and radon exposure) (Kosnett, 2005).

Inorganic arsenic is a potent human carcinogen and general toxicant. More than one hundred million people are exposed to elevated concentrations, mainly via drinking water, but also via industrial emissions (Vahter, 2008). Arsenic is metabolized via methylation and reduction reactions, methylarsonic acid and dimethylarsinic acid being the main metabolites excreted in urine. Both inorganic arsenic and its methylated metabolites easily pass the placenta and both experimental and human studies have shown increased risk of impaired foetal growth and increased foetal loss.

Recent studies indicate that prenatal arsenic exposure also increases the risk of adverse effects during early childhood. There is a growing body of evidence that the intrauterine or early childhood exposure to arsenic also induces changes that will become apparent much later in life. One epidemiological study indicated that exposure to arsenic in drinking water during early childhood or in utero was associated with an increased mortality in young adults from both malignant and non-malignant lung disease.

Furthermore, a series of experimental animal studies provide strong support for late effects of arsenic, including various forms of cancer, following intrauterine arsenic exposure. The involved modes of action include epigenetic effects, mainly via DNA hypomethylation, endocrine effects (most classes of steroid hormones), immune suppression, neurotoxicity, and interaction with enzymes critical for foetal development and programming (Vahter, 2008).

The mechanism of toxicity of arsenic is through induction of oxidative stress and impairment of the antioxidant defense mechanism, leading to apoptosis and cell death (Flora et al., 2008). Arsenicosis is the effect of arsenic poisoning, usually over a long period such as from 5 to 20 years.

Drinking arsenic-rich water over a long period results in various health effects including skin problems (such as colour changes on the skin, and hard patches on the palms and soles of the feet), skin cancer, cancers of the bladder, kidney and lung, and diseases of the blood vessels of the legs and feet, and possibly also diabetes, high blood pressure and reproductive disorders. Absorption of arsenic through the skin is minimal and thus hand-washing, bathing, laundry, etc. with water containing arsenic do not pose human health risks. In China (Province of Taiwan) exposure to arsenic via

drinking-water has been shown to cause a severe disease of the blood vessels, which leads to gangrene, known as 'black foot disease'. This disease has not been observed in other parts of the world, and it is possible that malnutrition contributes to its development. However, studies in several countries have demonstrated that arsenic causes other, less severe forms of peripheral vascular disease (WHO fact sheet, 2001). Chronic arsenic toxicity occurred as a large epidemic in Bangladesh (Smith et al., 2000, WHO, 2011). Ogbuagu and Ajiwe (1998) found that Onitsha North and South have the greatest concentration of Industries in Anambra state, and stand a high risk of industrial pollution. He inferred that some of the industries in the state discharge their waste into the environment with little or no treatment.

This study investigates concentration of Arsenic in surface and subsurface water within Onitsha metropolis and possible impact on populace.

Study location

Onitsha is located in Anambra State in Eastern Nigeria and lies within latitudes $5^{\circ}22'$ and $6^{\circ}48'$ and longitudes $6^{\circ}32'$ and $7^{\circ}20'$. Onitsha in Anambra State is located on the east bank of River Niger and covers an area of about 49,000 km². It is one of most important commercial centres in sub-Sahara African, as well as a transit city in Nigeria. It has an estimated population of about one million inhabitants (Figure 1).

The socioeconomic characteristics of Onitsha consist of about 75% labour force that is engaged in tertiary sector, such as, trading and services. The remaining 25% of labour force is engaged in manufacturing and industrial activities. However, Onitsha is a centre for the production of local goods and services, as well as, a market for the sale of foreign goods. The Onitsha main market, which is reputed as the largest market in sub-Saharan Africa, has increased the tempo of commercial activities in the city in recent times.

MATERIALS AND METHODS

Twenty seven (27) water samples (11 of which were from surface water sources and 16 from boreholes) were obtained from the Onitsha metropolitan city. Surface water sampling was conducted at constant depth of 0.5 - 1.0 m in areas where Onitsha main market/ auxiliary drains and industrial effluents enter the rivers. Borehole samples extracted were very close to the Niger river and in most cases less than 10 km away from the bank.

Research work was conducted for period of 2004-2008. Water samples were stored in sterilized 50cl PVC bottles; and acidulated prior to analysis.

Atomic Absorption Spectrometry method was used to determine concentrations of Arsenic in water samples from Onitsha. This method is based upon the absorption of radiant energy, usually in the ultra-violet and visible regions by neutral atoms in the gaseous state. Water sample were stored in 50 ml of PVC bottles, analysis was done using UNICAM 969 model Atomic Absorption

Table 1. Arsenic concentration in sampling points within Onitsha metropolis

Sampled area	Samples Identifier	Concentration (ppm)	pH
River Niger upstream surface	R. Niger Surf.	0.2001	6.1
River Niger upstream riverbed	R. Niger bed	0.9669	
Nwanaene Lake/ drain	Nwanaene	0.6058	5.4
River Niger/Otumoye surface	Otumoye surf.	1.4076	6.1
River Niger/Otumoye riverbed	Otumoye bed	1.0311	
River Niger/Creek road surface	Creek surf.	0.3203	6.1
River Niger/Creek road riverbed	Creek bed	0.6966	
River Niger Downstream surface	R. Niger Surf.	0.3409	6.1
River Niger Downstream riverbed	R. Niger bed	1.5779	
River Niger Central drainage surface	N. central surf.	1.5883	6.1
River Niger central drainage riverbed	N. central bed	0.3625	
Borehole at 20 Niger street, Onitsha	No 20 Niger	0.0188	6.1
Borehole at 2 Niger street, Onitsha	2 nd Niger	0.0000	6.7
Borehole at 9 Abatete/Creek road, Fegge, Fegge	9 Abat.	1.2507	6.1
Borehole at Nigeria Mineral Water Industries, Onitsha	Nig. Min.	0.0026	6.6
Borehole at Royal Queen Table Water, Obosi	Royal Queen	0.0000	7.1
Borehole at Osemaco water, Onitsha	Osemaco	0.0000	7.1
Borehole at Oseokwodu market	Oseokwodu	0.0023	6.8
Borehole at Ivory metal industries, Onitsha	Ivory Metals	0.5140	6.8
Borehole at Akapaka forest avenue	Akapaka	0.0017	7.0
Borehole near Otumonye/ Relef market	Otumonye	0.3060	6.3
Borehole at Enda Table water, Onitsha	Enda	0.0000	6.4
Borehole at St. Joseph drinking water, Bridge Head, Onitsha	Onitsha	0.0000	6.4
Borehole at Banny table water, Nkisi layout, Onitsha	Banny	0.0000	6.8
Borehole at Onitsha South local government area	Onitsha south	0.0008	6.5
Borehole at 35a Ajasa street, Onitsha	35 Ajasa	0.0014	6.1
Borehole at Life Brewery company, Onitsha	Life brewery	0.0038	5.4

Spectrometry. Other chemical utilized were analytical grade chemicals (HNO₃, Sigma chemicals, Australia and standard heavy metal solutions). Samples for heavy metal analysis were digested using nitric acid (65% purity) as described in the APHA methods (APHA, 1999).

RESULTS AND DISCUSSION

Arsenic concentration in surface water within Onitsha metropolis range from 0.2001 mg/L (River Niger upstream surface) to 1.5883 mg/L (River Niger central drainage surface), while concentration in boreholes falls within range of 0.0000 mg/L (22.2% of boreholes that is, 2nd Niger, Royal Queen, Osemaco, Enda, Onitsha, Banny) and 1.2507 mg/L (No. 9 Abbatete/creek road), respectively (Table 1, Figures 2 to 4). Arsenic pollution in these areas are traced to anthropogenic pollution especially industrial pollution, refuse dumps and oil/fuel dumps that get washed down to streams/ rivers of these major cities on daily basis.

One hundred percent of arsenic concentration in river bodies is above the WHO standard while 87.8% of Arsenic concentration in boreholes adjacent and closest to these rivers and creek is over above the world Health Organization standard (WHO, 2011a) of 0.01 mg/L. It is

inferred that river water intrusion into the adjacent soil formation is responsible for the high value of arsenic in the borehole beyond the World Health Organization standard (Al-Juboury, 2009; Igwe et al., 2007) especially as these soils have high permeability coefficients and the pH of these subsurface water are on the average below 7 making for the mobilization of metallic ion like arsenic.

In Nigeria, the World Health Organisation (WHO, 2011b) and the Nigeria Standard for Drinking Water Quality (NSDWQ, 2007) drinking water standard is 0.01 mg/L for Arsenic. Higher range of value is common both in the surface or bottom waters of heavily polluted rivers like River Niger at Onitsha, and their adjacent underground waters.

Degree of pollution of various water sources at Onitsha

In Onitsha, various kinds of pollutants are all over the places; they range from biological to chemical. The most polluted zones are the Nwangene Lake zone where all kinds of sewage and chemical effluent drain into. It is also in this place that the biggest refuse dumps are emptied. This has caused major pollution problems in the River

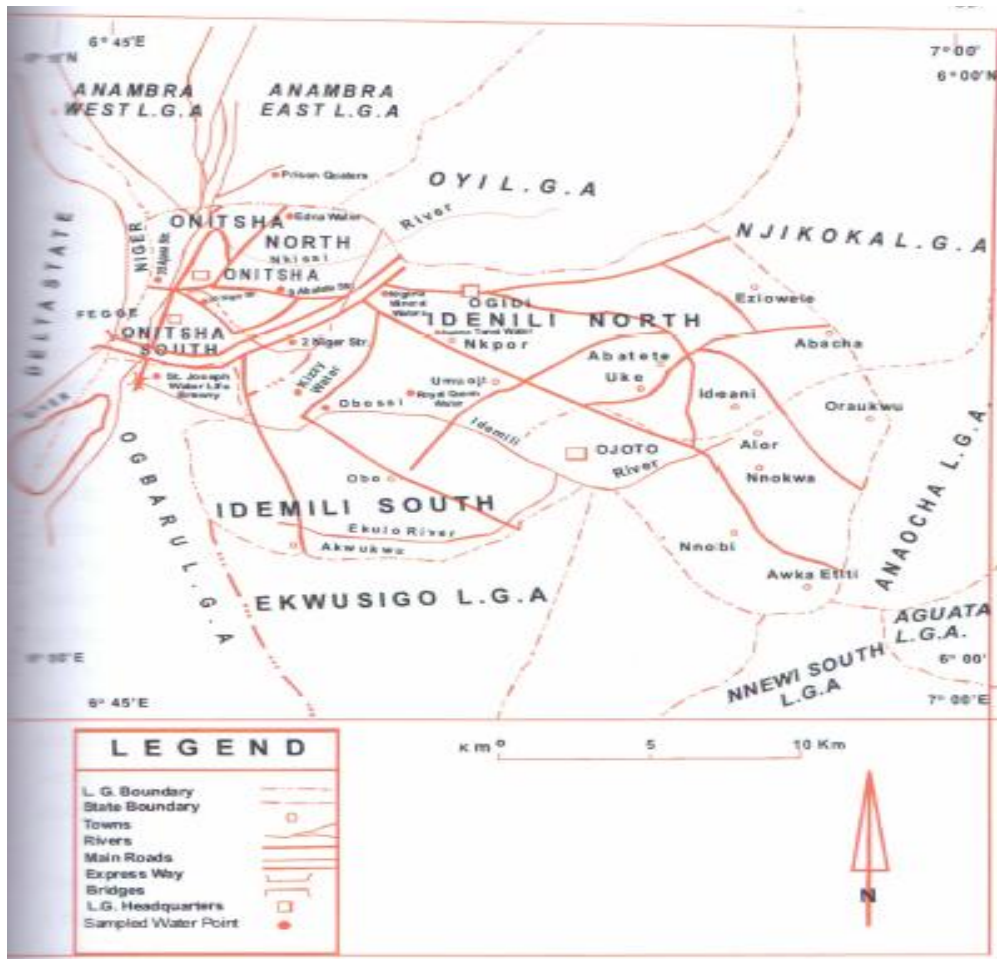


Figure 1. Map of Onitsha Metropolis showing some of the study locations (Source: Adapted from the Federal Survey, 1983).

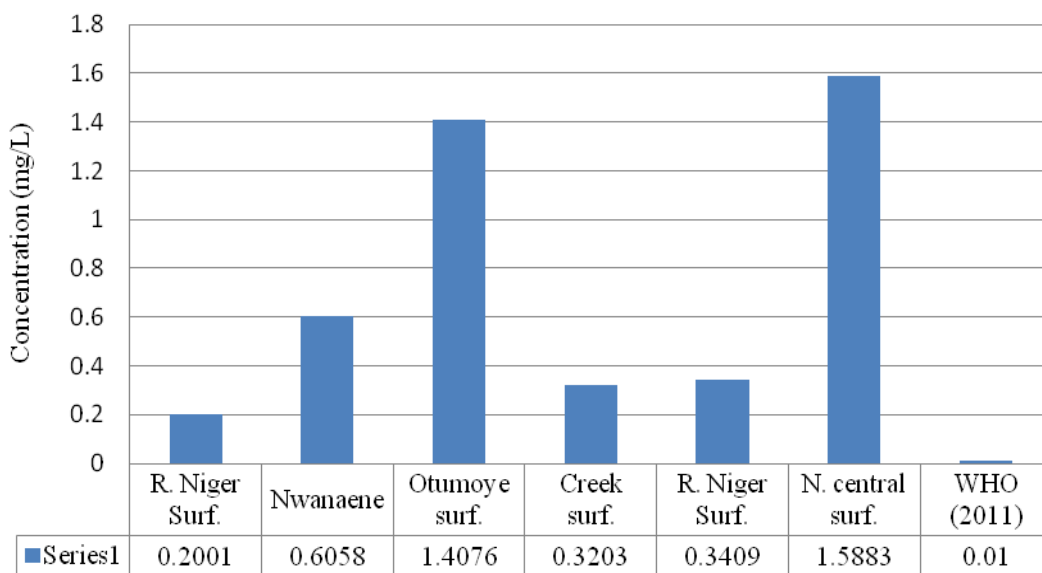


Figure 2. Arsenic concentration in surfaces of water bodies within Onitsha metropolis.

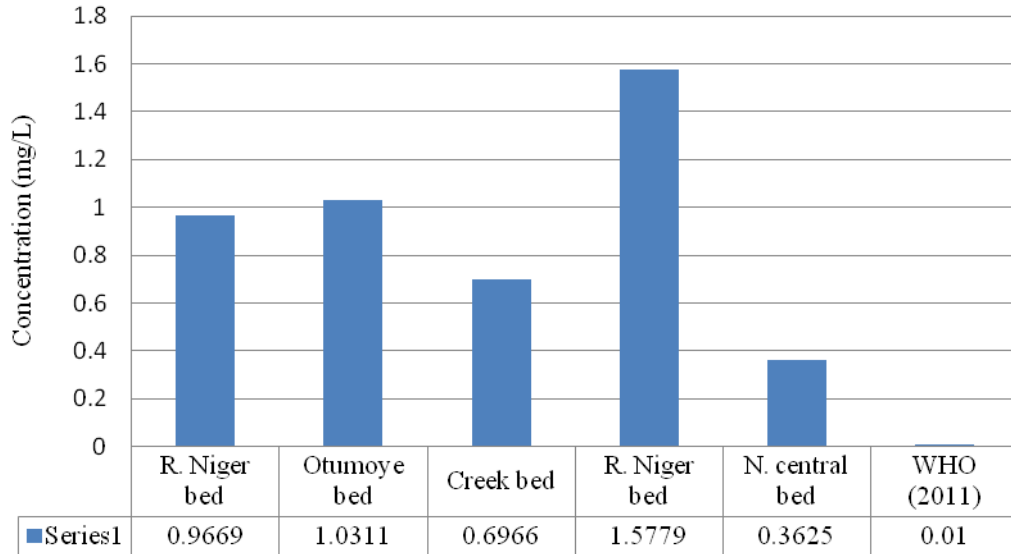


Figure 3. Arsenic concentration in river bed of surface water bodies within Onitsha metropolis.

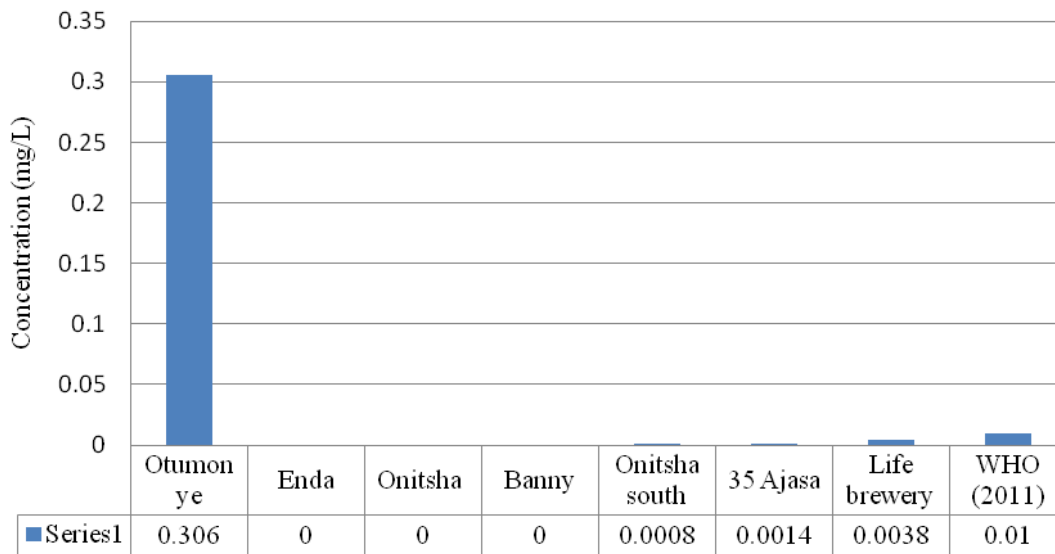


Figure 4a. Arsenic concentration in borehole water Otumoye, Enda, Onitsha, Banny, Onitsha south, 35 Ajasa and Lifebrewery.

Niger where it drains into at Otumoye major drain as can be seen from the results of the tests, but also have polluted boreholes along Creek road and Abatete streets as reported in Table 1 and Figure 4b; the pollution of water bodies in this area can be predicted by the extent of solid and liquid disposals in them. The intrusion of this polluted water is suspected to have stretched up to 100 m radius from the Nwangene Lake and River Niger. It is therefore a serious health hazard for hundreds of inhabitant in the area who use untreated borehole water. The concentration of the heavy metal is much higher than the WHO guidelines.

River Niger water is one of the major sources of water to the people of Onitsha city especially in times of scarcity. Currently all types of wastewater and refuse are disposed in the River Niger. The enormous growth of new industries and urbanization, results in pollution of the river water and the adjoining ground water. Urbanization and technological development results in generation of more and more waste effluents and is discharged into the water bodies resulting in pollution of the surface water. The water borne sewage, storm drainage from Onitsha city streets and effluents from smaller industries combined with flow from municipal outfalls in mounting

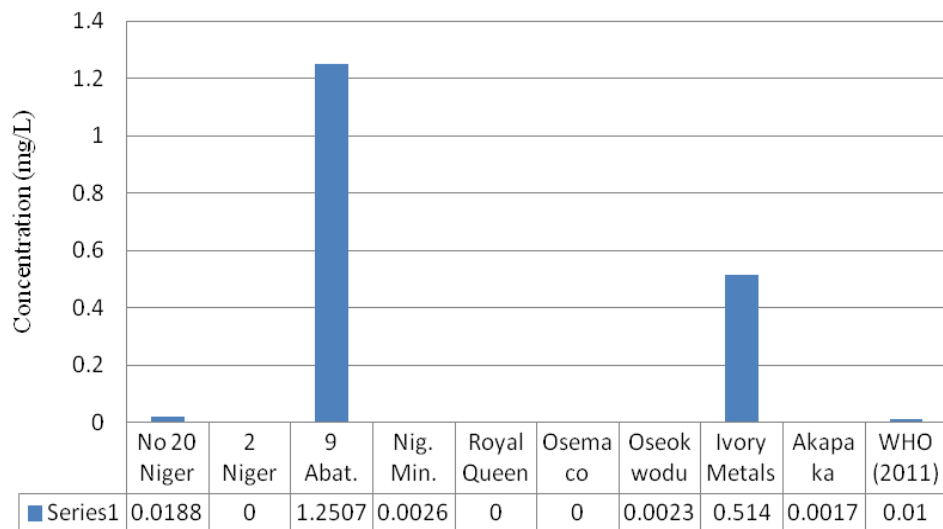


Figure 4b. Arsenic concentration in borehole water of No 20 Niger, 2 Niger, 9 Abat. Nig. Min., Royal Queen, Osemaco, Oseokwodu, Ivory Metals and Akapaka.

volumes along with agricultural runoff from the hinterland ultimately joins the surface water, which drains down the River Niger. Due to inadequacy of public water supply, usage of more ground water for domestic, industrial and agricultural purposes has become very important. Generally, the subsurface water is preferable because of its inherent advantages over surface water.

Major storm water drains in the Onitsha metropolis empties into the River Niger through the main market itself. This also impacts on the quality of water (Figure 2); most results also shows that the bed of the river where the velocity of water is near zero and where a lot of pollutants are supposed to settle are higher than the surface water, which expectedly has self cleansing effects. The general low values of arsenic in most subsurface waters is a thing of joy but it is noticed that consistent pollution activities could aggravate concentration of these dangerous metals with time especially with the rapid increase in urbanization.

Onitsha was a major battle field during the three (3) year Civil War in Nigeria. It is known that Onitsha was contaminated with a wide range of pollutants like hydrocarbons from fuel spillage and leaks, PAHs from fires, explosives, mines, bullets, smokes generating compounds which were not cleared up after the war, this adversely impacts on surface and sub-surface water quality of the environment.

Conclusions and recommendations

Reliable monitoring and surveillance methods are essential for keeping close watch on the health of the environment. Some unacceptable results were recorded for heavy metal loads in the surface and subsurface

water in the area. It is obvious that if the rate of pollution is not abated, common health problems which are already found in at Onitsha would increase. The introduction of modern, sensitive and more reliable methods for testing drinking water for physical, chemical and biological parameters should be explored.

More intense training of health experts in the area in water pollution is a sine qua non. There are enough unpolluted ground water resources to satisfy the needs of the society and these could be exploited while effluents from various sources should be treated before discharge. The proper monitoring of industries through environmental impact assessment and environmental audit reports should be enforced by the Ministry of Environment in Anambra State. Information on increasing presence of heavy metals and their affect on health should be disseminated to various stakeholders, including researchers, policy makers, politicians, and donor agencies.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

Sediment and nutrient lost by runoff from two watersheds, Digga district in Blue Nile basin, Ethiopia

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The study was conducted in two sub watersheds in the Upper Blue Nile Basin in Ethiopia to determine the quantity, quality of sediment lost and its onsite costs in terms of crop yield. Two monitoring stations at the outlets were selected. Discharges were estimated and depth integrated daily runoff samples were collected during the rainy season in 2011. The sediment concentration and nitrogen (N) and phosphorus (P) content was analyzed and related to crop yield using a nutrient response equation for maize (*Zea mays*). The result shows statistically significant differences in sediment concentration of the two watersheds. Suspended sediment concentration was strongly correlated with the discharge from Chekorsa River ($R^2 = 0.7$) but it was very weak for Dapo. There was higher concentration of nutrients in the sediment than the surface soil in both watersheds. Particularly, sediment enrichment ratio of available P was 2.7 and 9 for Dapo and Chekorsa Rivers, respectively. The estimated yield reduction of maize due to N and P loss was about 950 and 1420, and 1015 and 665 kg ha⁻¹ from Dapo and Chekorsa catchments, respectively. Such results are equivalent to an onsite cost to farmers of about 190 and 285 USD ha⁻¹ for Dapo, and 203 and 133 USD ha⁻¹ for Chekorsa catchments in that order. This monetary value can alert farmers and decision makers to take soil and water conservation measures.

Key words: Soil loss, enrichment ratio, nutrient depletion, Blue Nile Basin, sediment.

INTRODUCTION

Soil erosion is a worldwide problem and has become a major global concern since its severe impacts on agriculture and environment (Le Bas and Kozak, 2007; Tenaw and Bekele, 2009). Pimentel et al. (1995) indicated that about 80% of the world's agricultural land suffers moderate to severe erosion. Soil erosion is among the major causes of nutrient depletion and, shortage of basic plant nutrients (Wortmann, 2006; Pimentel et al., 1995) with a devastating impact on overall soil organic matter levels (Van-Camp et al., 2004). According to FAO (1999), Ethiopia is among the countries with high rate of erosion and nutrient depletion rate.

Studies showed soil erosion in Ethiopia is more severe in the highlands. Henao and Baanante (1999) reported NPK loss of more than 60 kg ha⁻¹ based on their study between 1993 and 1995 in Ethiopia and losing fertile topsoil that exacerbated impacts of dry spells and drought in the Upper Blue Nile Basin (Getnet et al., 2009).

Water is the main cause of soil erosion in the highlands of Ethiopia (Dubale, 2001) removing about 1493 Mtyr⁻¹ (Hurni, 1993) whereas in the Abay Basin (the Ethiopian part of the Blue Nile Basin) loss of soil was about 303 Mtyr⁻¹ (Hagos et al., 2009). Nearly 50 and 34% of the total soil loss was estimated to come from cultivated fields in

the central highlands of Ethiopia and Abay Basin, respectively (Hagos et al., 2009; Hurni, 1993).

According to Gruhn et al. (2000), and Desta et al., (2000) soil fertility loss by erosion are the main ways for nutrient outflow from a watershed. Eroded soil was often significantly enriched by plant nutrients than the soil left behind with enrichment ratios ranging from 1.2 to 2.3 (Fenli et al., 2005). It is the characteristics of watershed that influence river nutrient enrichment ratio. Eroded soil by runoff constitutes a large proportion (>60%) of the P transported in surface runoff from surface soil, with enrichment ratio greater than 1 (Scalenghe et al., 2002). The enrichment ratio greater than 1 is related to the high P content in the top 5 cm of the surface soil and the fact that runoff preferentially erodes finer particles including clays with which P is associated (Sharpley et al., 2000).

The losses of the nutrients can limit crop growth and productivity. Soils in all major maize growing regions of Ethiopia are depleted of NPK nutrients, thus demanding high soil amendments (Kebede et al., 1993). Decline in soil fertility due to depletion of NPK nutrients in the country is therefore eradicating production including maize production. Nitrogen is the most limiting nutrient for maize productivity (Kogbe and Adediran, 2003; Alley et al., 2009). As a result of water erosion, organic matter content is highly reduced since its largest part is found in the fertile topsoil and cause decline of production because of low physical structure (Helmecke, 2009).

All physical and economic evidence shows that agricultural land productivity decline is a severe problem in Ethiopia (Berry et al., 2003) and in Africa in general, for example, about 86% of the countries in Africa lose more than 30 kg⁻¹ha⁻¹yr of NPK (Henao and Baanante, 1999). This severe erosion is reducing agricultural land productivity (Berry et al., 2003) particularly, in the Blue Nile basin (Tenaw and Bekele, 2009; Dubale et al., 2009) in which soil erosion is among the major threat (Desta et al., 2000; Bekele and Holden, 1998; Ashagrie, 2009).

Most soil erosion research in Ethiopia focused on its physical, chemical and biological effects (Gorlach et al., 2004) and limited to farm plots (Berry et al., 2003). In Ethiopia, farmers and other decision makers at grass-

roots level cannot easily understand estimated soil and nutrient losses by runoff in terms of scientific units. However, converting the lost soil nutrients by runoff from watersheds into monetary value can easily make them aware of the severity of soil erosion. In other words, the monetary value of lost nutrients can induce and initiate farmers and policy makers to implement land and water management practices. The cost of soil erosion to farmers can be related to loss of productivity due to the lost of nutrients or the cost of fertilizer to compensate for the lost nutrients (Gruhn et al., 2000).

Yield reduction cannot be because of soil nutrient depletion alone but also affected by other physical and biological factors and conditions such as land management, nutrient status, soil microbes, soil depth, etc. To estimate financial cost of lost soil nutrients, it is necessary to consider those factors and conditions prevailing in the specific area (Pimentel et al., 1995). As a result, productivity lost method was preferred to replacement cost for this study.

Depending on the characteristics of watershed, suspended sediment concentration related to discharge can produce different shapes of hysteresis loops (Baca, 2002; Sander et al., 2011). These relationships are normally not homogenous in time, neither within nor between events (Baca, 2002). The most common shapes of the hysteresis effects are clockwise and counter clockwise loop (Sander et al., 2011; Ahanger et al., 2013). The characteristics of watershed that produce hysteresis effects are source of sediment which could be from distant hill slope, or channel or nearby sources, higher rainfall intensities at the beginning of storms, sediment availability, increasing of base flow supply to the river, the duration and interval of storm events (Eder et al., 2010; Baca, 2002; Slattery et al., 2002; Lefrançois et al., 2007)

In this context, the objectives of the research were to estimate the sediment concentration at the outlets of Dapo and Chekorsa watersheds and patten of sediment hysteresis loop, to analyze soil nutrients lost by runoff and consequently river nutrient enrichment ratio, and to estimate the financial cost due to soil erosion at the study

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Abbreviations: AVP, Available phosphorus; BARC, Bako Agricultural Research Center; C/N, carbon/nitrogen; CR, Chekorsa River; CRC, Chekorsa River Catchment; d, ten consecutive days/decade; DDS, Dapo downstream; DFA, discriminate function analysis; DR, Dapo River; DRC, Dapo River catchment; DUS, Dapo upper stream; ER, enrichment ratio; FAO, Food and Agricultural Organization; GDP, gross domestic product; gm/L, gram per liter; INM, integrated soil nutrient management; IWMI, International Water Management Institute; kg/ha/yr, kilogram per hectare per year; L, liter; LD, Lelisa Dimtu; m.a.s.l, meter above sea level; Mg, mega gram; Mha, million hectare; Mm³/d, mega metric cube; Mt⁻¹yr, million tons per year; NBDC, Nile Basin Development Challenge; NH₄-N, ammonium nitrate nitrogen; NO₃-N, nitrate nitrogen; NPK, nitrogen, phosphorus and potassium; OC, organic carbon; PO₄³⁻, phosphate ion; ppm, parts per million; Q, discharge; SPSS, Statistical Package for Social Science; SSC, suspended sediment concentration; SSL, suspended sediment load; SWC, soil and water conservation; t/ha/d, tonnes per hectare per decade; TKN, total Kjeldal nitrogen; tons/ha/yr, tonnes per hectare per year; USLE/RUSLE, revised/universal soil loss equation; WAO, Woreda Agricultural Office.

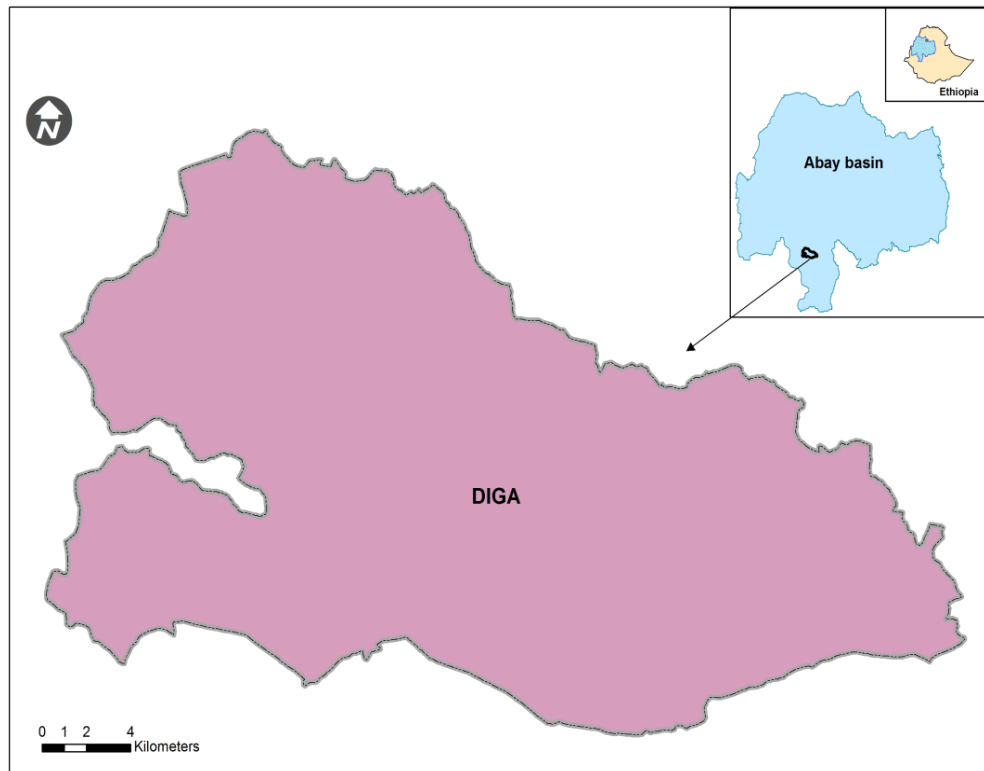


Figure 1. Study location map.

region.

MATERIALS AND METHODS

Description of the study area

The study was conducted in two sub watershed located in Diga district in East Wollega Zone of Oromia Regional State, Ethiopia (Figure 1) from March 2011 to October 2012. The area is characterized by an average annual mono-modal rainfall of 1707 mm which begins late April, and ends in early September, with annual minimum and maximum temperature of 14 and 30°C, respectively (Joshua et al., 2010). Information from Diga District Water Resource Office in 2010 shows that the major livelihood is mixed crop-livestock rain fed agriculture. In middle altitude of the study area, the dominant soil color is red whereas black in the low land (Birhanu Z, 2012) and according to soil map developed by Seleshi et al. (2009) which are classified as Acrisols and Alisols.

Two sub watersheds (Dapo and Chekorsa) were selected by the Nile Basin Development Challenge Program (NBDC) for rainwater management research in the Blue Nile Basin. Zemadim et al. (2010) indicated that the two catchments have an area of 18 and 5.60 km², respectively with their altitude ranging between 1,347 - 2,011 m (Dapo) and 1,266 - 1,430 m (Chekorsa).

Both Dapo River (DR) and Chekorsa River (CR) are tributaries of Didesa River, the largest tributary to the Blue Nile River, in terms of water volume (MWRE, 2010). Both Rivers are supplied by numerous first and second order streams. Similar to Chekorsa River Catchment (CRC), the physiographic, land use and land cover condition in the downstream of Dapo River Catchment (DRC), around the water level gauging site, consists of mango trees and

sparse natural vegetation, maize and grazing areas (Figure 2) (Zemadim et al., 2012). Coupled with the intensive rainfall, Dapo River has cultivation in steep slopes that aggravates soil erosion and plant nutrient depletion (Zemadim et al., 2010). Depleted soil fertility caused by soil erosion and crop uptake is a major limiting factor for crop production and productivity in both catchments (Negassa et al., 2005). In response to the productivity decline, farmers open a new agricultural land which increases deforestation. Maize, sesame and finger millet are the dominant crops in DRC while about one third of the watershed area is covered by forest, mainly located at the most upper land (Figure 3), but no significant forest is left in Chekorsa catchment.

Methods

Selection of runoff sampling site

Hydrologists of the International Water Management Institute (IWMI) selected the bridge on the main highway that goes from Diga to Ghimbi for DRC and the bridge from Arjo Gudatu to Lalisa Dimtu for CRC, where flow monitoring stations were established. The bridges are 4.5 and 3.5 m wide through which Dapo and Chekorsa river flows respectively, and all flows were contained inside the culvert of the bridges.

Discharge measurement

Discharge measurement and sampling was started from the beginning of major runoff in July, 2011 and ended in early September, 2011 when the rainfall ended. Based on Gierke (2002), the flow rate of the river at the outlet was determined using current



Figure 2. Dapo watershed outlet (a) and land use and land cover condition around the outlet (b), at the Diga district, Ethiopia. Photo credit (Brihanu Zemedin, 2011).

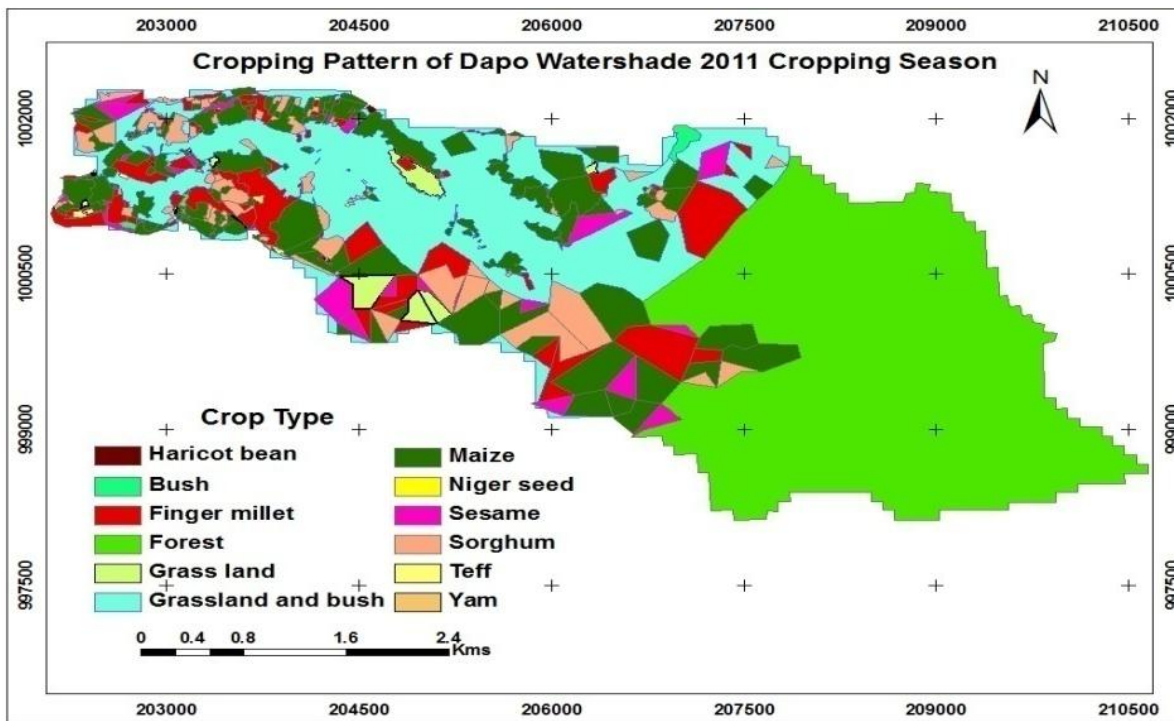


Figure 3. Land use and land cover of Dapo watershed. Source: IWMI (2012).

meter (Model 0012B Surface Display Unit and Model 002 Flow Meter (Figure 4A and B)); the depth of the rivers at the cross-section was measured using 1.5 m wading rod (Figure 4E), and the flow rates and depths (h) were measured across the rivers simultaneously at 9 points spaced at 0.5 m intervals for DR and at 5 points at 0.75 m interval for CR. The cross sectional area of the flow was calculated using the depth records and the average flow rates at each point (Equation 1). Discharge (Q) passing the outlet of the watersheds was calculated using Equation 2.

$$q_i = v_i \cdot a_i \quad (a) \quad Q = \sum_{i=0}^n q_i \quad (b) \quad (1)$$

Where:

q_i = discharge at each cross sectional area ($m^3 \cdot sec^{-1}$); v_i = flow velocity at each cross sectional area ($m \cdot sec^{-1}$); a_i = cross sectional area at each point (m^2); Q = total discharge ($m^3 \cdot sec^{-1}$).

$$Q = c (h + a)^b \quad (2)$$

Where: Q = discharge ($m^3 \cdot sec^{-1}$); h = measured water level (m); a = water level (m) corresponding to $Q = 0$; c = coefficients derived for the relationship corresponding to the station characteristics; b = coefficient derived for the power in relation to the station characteristics.

Discharge rating curves were developed by fitting the measured gauge to discharge into power curve (Equation 4) for the two rivers. And having water levels measured throughout the study period by the staff gauge (Figure 4E), the discharge for each was calculated from the equations of the curves.

Runoff sampling and storage

Depth integrated runoff was collected manually from catchments using one liter plastic bottle three times a day. The daily samples were mixed and two liters were sub sampled and bulked in a 20 L plastic jar for 10 consecutive days. The bulked samples were kept



Figure 4. Current Meter model used for measuring river flow and staff gauge (E) at DR monitoring station. Photo Credit: Brihanu Zemedin (2011).

Table 1. Methods and procedure used for the chemical analysis sediment and water.

Sample	Parameter	Method budget	Reference
Soil	OM	Wet oxidation/Walkley-Black	Jackson (1967)
	TKN	Modified Kjeldahl digestion	Dalal et al (1984)
	NO ₃ -N NH ₄ -N	Magnesium oxide-Devrda's alloy	Maiti (2004)
		Magnesium oxide-Devrda's alloy	Maiti (2004)
	P ₂ O ₅	Alkaline Extraction of Olsen Method	Olsen and Sommers 1982
Texture	Hydrometer	Bouyoucos (1962)	
Water	Dissolved ammonia	Phenate method using Spectrophotometer; Modele Eleco SL-160 double beam UV	Patnaik (2010)
	Dissolved nitrate and phosphorus	Spectrophotometer; Modele Eleco SL-160 Double beam UV	Patnaik (2010)

in the refrigerator at 4°C in a soil laboratory to minimize further chemical and physical changes.

Estimation of sediment load and chemical analysis

Sediment in water sample collected for each consecutive 10 days was allowed to settle down before the clear water at the top was decanted into laboratory beakers. The turbid water remaining at the bottom containing most of the sediment was filtered using filter papers and air dried. Soil loss was calculated based on the sediment concentration and discharge per 10 consecutive days at the gauged sites. The water collected after filtration and that which was stored after decantation were mixed proportionally for chemical analysis (Table 1).

Estimates of nitrogen and phosphorus loss

The quantity of N and P delivered to the outlet of the watersheds with water and suspended sediment was estimated using Equations 3 and 4, respectively. The total N and P lost was estimated by

summation of the amount lost with water in dissolved form and by the quantity lost with suspended sediments (Equation 5). The maize yield loss due to the two essential plant nutrients was estimated according to FAO (1999) method.

$$N_{wi} = N_{cwi} * q_i(a) \text{ and } TN_w = \sum_{i=1}^9 N_{Li} \text{ (b)} \tag{3}$$

$$N_{si} = N_{csi} * SSL \text{ and } TN_s = \sum_{i=1}^9 N_{si} \text{ (b)} \tag{4}$$

$$(TN_w + TN_s)/AGTN = (TN_w + TN_s)/A \tag{5}$$

Where, N_w: nutrient loss with water per ten consecutive days (gm/d) (nitrogen or phosphorus); N_s: nutrient loss with suspended sediment per ten consecutive days (gm/d) (nitrogen or phosphorus); N_{cw}: nutrient concentration in water (gm/L) ((nitrogen or phosphorus); N_{cs}: nutrient concentration in suspended sediment (gm/kg) (nitrogen or phosphorus); SSL: suspended sediment loss (Kg); q: discharge of the rivers per ten consecutive days (L/d); A: area of the catchments (ha); i: ten consecutive days; TN: total nutrient loss (Kg) (nitrogen or phosphorus); grand total nutrient loss (Kg/ha) (nitrogen or phosphorus).

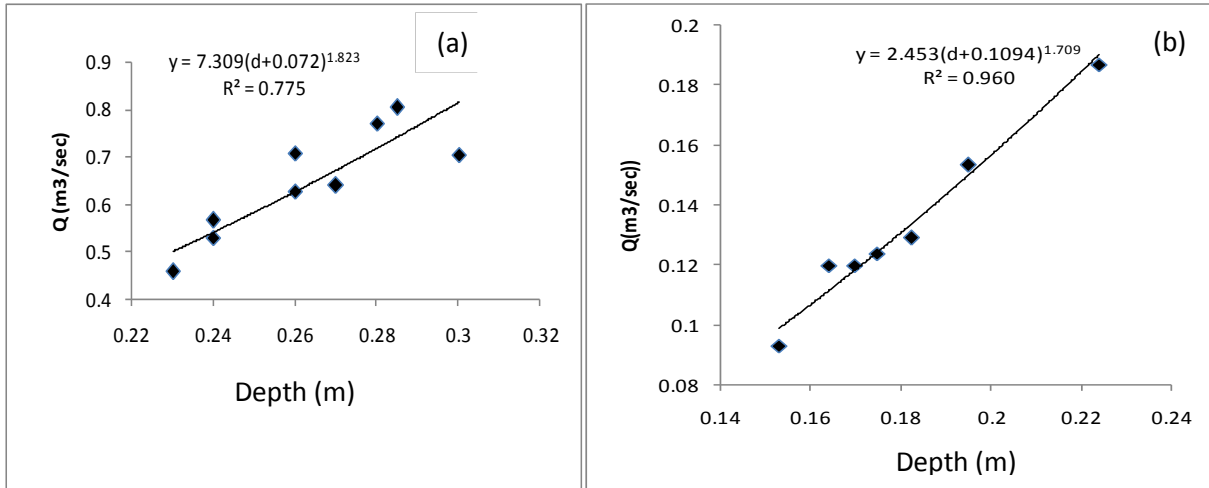


Figure 5. Discharge rating curve for DR (a) and CR (b).

Table 2 Discharge, total suspended sediment and sediment concentration from Dapo River and Chekorsa River.

Parameter	Dapo River				Chekorsa River				t value	p-value
	Mean	SD	CV	R ²	Mean	SD	CV	R ²		
Discharge (Mm ³ /d)	0.64	0.17	26.7	1	0.24	0.043	18.09	1	6.83	0
TSS (tons/d)*	747.86	379	50.7	0.7	434	217	49.82	0.85	2.16	0.05
SSC (gm/L)	1.12	0.36	32	0.3	1.74	0.597	34.29	0.73	2.66	0.02
Soil loss (t/ha/d)	0.42	0.21	50.7	0.7	0.75	0.335	44.82	0.79	2.52	0.023

*TSS: Total suspended sediment loss in tons per 10 consecutive days.

Crop yield reduction due to the loss of nitrogen and phosphorus

Since maize is a major crop in both watersheds, reported research data of maize grain yield response to N and P under similar agro-ecological conditions were obtained from Bako Agricultural Research Center. The yield response curve for N and P was developed by fitting the data into quadratic relation (Rosas, 2011; Naher et al., 2011). The yield reduction due to loss of available N and P were estimated using their respective response curves (Equation 6).

$$Y = ax^2 + bx + C \tag{6}$$

Y: Maize yield per hectare; X: nutrient (N and P) per hectare; a, b and c: constant of quadratic equation.

The local market price of maize which was 3.5 BirrHa⁻¹ (1birr = 17.50USD) was used to convert the reduction in grain yield to financial loss incurred by the farmers.

Data analysis

The data was analyzed using SPSS and presented using Sigma-plot software (version 10). Linear regression analysis was carried out for suspended sediment load (SSL) and suspended sediment concentration (SSC) with hydrological parameters. T-test at 95% confidence limit was used to analyze the differences in sediment

load between the two monitoring stations. Pearson correlation analysis between soil texture percentage and nutrients were also determined.

RESULTS AND DISCUSSIONS

Discharge

Water levels or depth across the width of the rivers and corresponding flows of water resulted in power curves (Figure 5). According to Braca (2008), continuous measurement of flow past a river section is usually time consuming, impractical during flood event and prohibitively expensive. The average discharge estimated using the stage-discharge relationship curve was 0.64 DR and 0.24 Mm³/d for DR and CR, respectively (Table 2).

Suspended sediment and its interaction with discharge

Eroded soil by runoff from watersheds is mostly

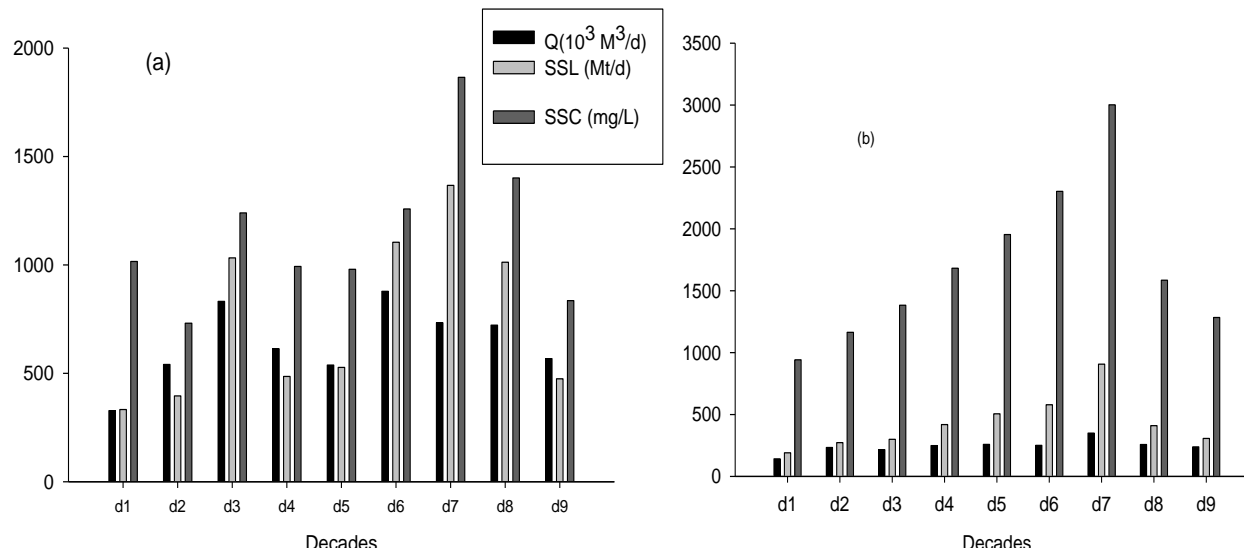


Figure 6. Average discharge and SSC, SSL of Dapo (a) and Chekorsa Rivers (b).

transported by river flow in suspension (Sileshi et al., 2008). The sediment concentration increased with increasing discharge throughout the measurement period for CR (Figure 6b). For DR, the maximum concentration occurred during day 7 after the maximum discharge occurred (Figure 6a). The regression analysis showed SC is strongly related to discharge at CR ($R^2=0.73$) but it was weak at DR weak ($R^2=0.29$) (Table 2). SSC of DR did not remain high with all the discharges throughout the study period. This may be because of the quantity of sediment on a river bed, limited and less sediment availability from the watershed (Ongley, 1996).

Consequently, although the total discharge from DR was about three times greater than that from CR, the amount of sediment lost from the two catchments was similar.

Some possible causes of these variations are soil erodibility, proximity to the waterways, and the difference in riparian zones vegetation (Figure 8), catchments dimensions, land use and cover (GLCUS, 2008), sediment availability (Baca, 2002) and population density, turbulent fluctuations of stream velocity. As shown in Figure 6a, sediment becomes readily available for transportation following the peak discharge that occurred during day 6.

Temporal variability of suspended sediment with discharge

There is significant difference in discharge and sediment transport between ten consecutive days. The discharge to SC (Q-SC) hysteretic loops identified for the two catchments were different (Figure 7a and b) such as it was characterized by anti-clockwise for DR but clockwise

for CR. However, since short-term storm events are important determinants of sediment concentration (Eder et al., 2010), and single events hysteresis analysis must be conducted to confirm this interpretation.

The counter clockwise hysteresis in SC for Dapo watershed may be related to the reduced rainfall and the attendant decrease in discharge up to the fifth ten consecutive days, the delay in sowing time of the major crops in the upstream part as compared to those in the downstream part of the watershed. The eroded sediment from cultivated field had been trapped to its maximum at the riparian zone and then detached and transported after the peak discharge event when the supply of sediment was limited (Figure 8) corroborating the findings of Baca (2012) who conducted a similar study in Slovakia.

The clockwise hysteresis is attributed to the rapid displacement of sediment from source close to the stream. The size of CRC is less than a third of Dapo watershed. Similar result where found by Vanmaercke et al. (2006) in Geba River Catchment of Northern Ethiopia. Clockwise loops most commonly occur when the sediment peak occurs before the water discharge peak and when there is a source of easily erodible sediment which can be rapidly depleted (Hudson, 2002; Picouet et al., 2001; Baca, 2010).

Plant nutrient loss and enrichment ratio

In Chekorsa River, N loss increased towards the end of the rainy season up to three times as compared to at the beginning of the study, whereas P loss increased up to 2 times (Figure 9) although increase in discharge was not significant (Figure 9). On the other hand, it is vice versa

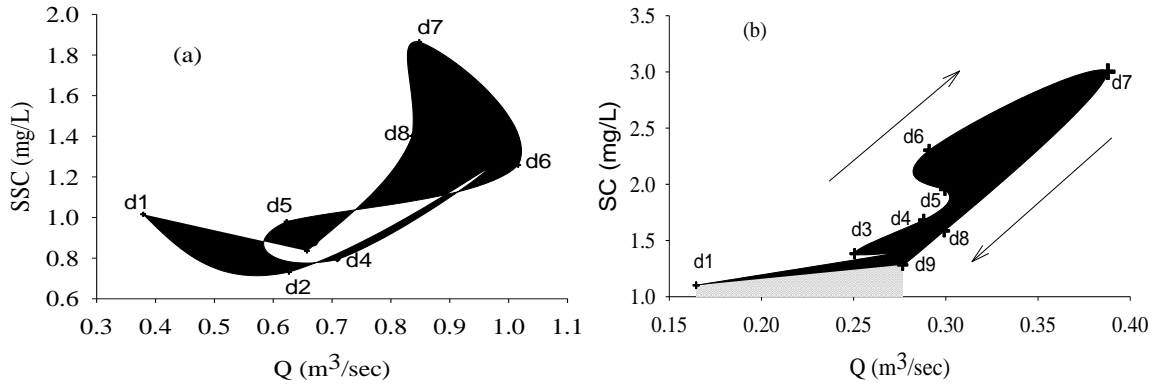


Figure 7. Changes of SSC with decade average discharge of Dapo (a) and Chekorsa Rivers (b).



Figure 8. Accumulated sediment at the edge teff field (a) and vegetation along DR (b).

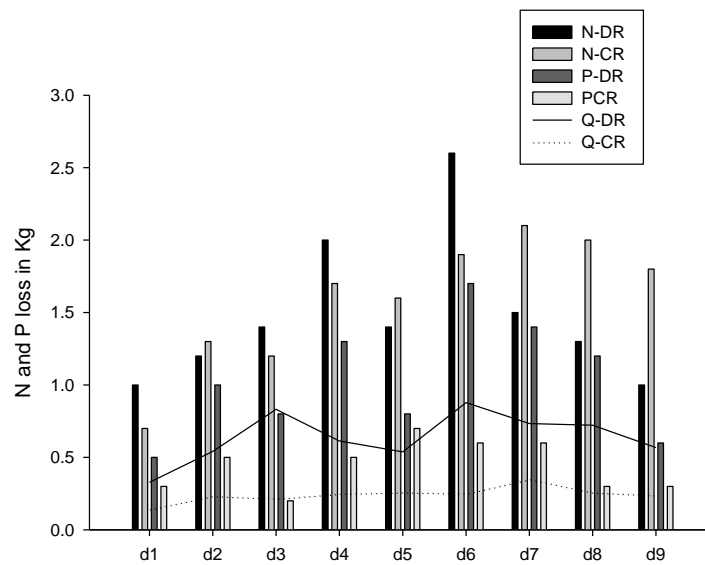


Figure 9. Amount of N and P loss (kg) and discharge ((Q) in Mm³/d) in each decade from DR and CR during the study period.

Table 3. Mean nutrient content of the surface soil of the catchments, and sediment (kg/ton) and enrichment ratio.

Sub areas	Surface soil			Enrichment ratio (: s)		
	Total N	OC	P	Total N	OC	P
Dapo downstream	4.19	57.06	0.013	0.89	1.18	2.69
Dapo upper stream	2.74	26.49	0.022	1.36	2.54	1.62
Chekorsa catchment	2.58	20.47	0.002	0.95	1.5	8.99
DR (Suspended sediment)	3.73	67.2	0.04			
CR (Suspended sediment)	2.44	30.78	0.02			

Table 4. R² regration analysis of nutrient with particle size distribution percentage in the sediment for CR and DR.

TKN	OC		P		Sand (%)		Silt (%)		Clay (%)	
	CR	DR	CR	DR	CR	DR	CR	DR	CR	DR
TKN	0.485	0.43	0.621	0.278	0.074	0.39	0.997	0.14	0.672	0.936
OC			0.981	0.989	0.251	0.1	0.428	0.34	0.964	0.539
P					0.142	0.11	0.565	0.35	0.997	0.523
Sand (%)							0.107	0.91	0.107	0.17
Silt (%)									0.617	0.016
Clay (%)										

TKN, Total Kjeldal nitrogen; OC, organic carbon; CR, Chekorsa River; DR, Dapo River; P, phosphate.

for Dapo River, which is quite similar result found by Liu et al. (2012). The loss of P and particularly N from CR is as higher as that of DR (Figure 9) though the average discharge of CR is as about three times less than DR (Figure 9). It was probably because of an effect remarked by Arheimer and Lide (2000), that is, contribution from rural point sources such as the traditional manuring, the availability of nutrients in the lower parts of a catchment (Chekorsa River catchment is more arable land and dense population), and water has easy access to the rivers and dilution effects by water from upper part of the catchment.

Similarly, the ground water which came as base flow from the upper region of DRC (covered by natural dense forest increase infiltration of rain water into ground water) probably diluted the river. Clay particles have been washed away from both catchments in greatest percentage. For example, if washing of clay particles continues in such a way (Table 4), it would exacerbate pressure on production, since soils with higher clay content have more favorable chemical properties (Hutton et al., 2008) than coarser textured soils.

The concentration of OM, TKN and available P in the eroded sediment were greater than the surface soil. The concentration of available P reaches up to greater than 2.7 and 9 time its initial concentration in some areas of the watershed in the DRC and CRC (Table 3), respectively. This indicates that surface runoff is washing P in large amount to the water body. This may be because of the largest concentration of P in the soil surface layers, and concentrated hydrologic energy on the soil surface (Zaimes and Schultz, 2002). This high P

ER coincides with high clay transport by the rivers, (for example: r² of 0.997) (Table 4). Scalenghe et al. (2002) indicated the highest accumulation of clay has strong relation with P ER because of the preferential loss of P with finer clay sized particle.

Soil erosion selectively washes fine particles such as clay and organic matter leaving coarse sand behind. Sand and silt are comparatively inert and act only as diluents to the more active clay (Page, 1950). Therefore, the higher the clay fraction the greater is the surface area of the soil available for sorption (Hutton et al., 2008).

Surface soil of DRC has greater soil fertility and hence loses much more nutrient than CRC (Table 3). This result also supports why soils with higher fertility status lose much more nutrients relative to those with a lower fertility status. Evans (2006) showed that the amount of nutrient lost was found to be strongly dependent on the nutrient status of the soil.

The severity of nutrient loss

The classifications were based on FAO (1999) calcification for available nutrient loss. The result of classification signifies how much soil erosion alone is contributing for the very high nutrient loss (FAO, 1999; Henao and Baanante, 1999). However, the classification in the report had been based on the nutrient removal including other major means of nutrient removal such as crop residue removal, leaching evapo-transpiration, grazing, etc.

Regarding nitrogen, Table 5 indicates only 35 and 30%

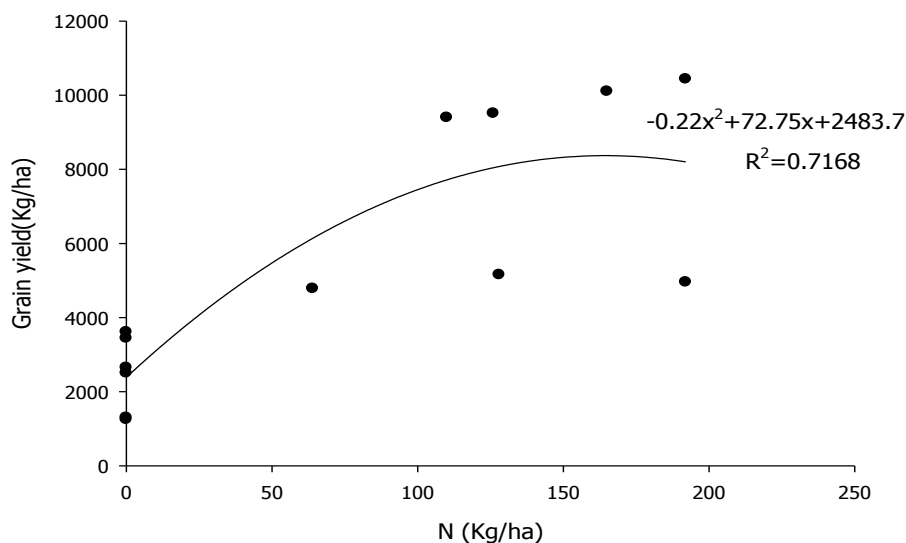
Table 5. Severity classes of the loss available nutrients.

Available	Dapo catchment		Chekorsa catchment		Loss left behind to be classified as high nutrient loss class (%)	
	Total loss	Severity class	Total loss	Severity class	DRC	CRC
N	13.58	Moderate	14.3	Moderate	35.4	30.6
P	9.31	High	4.20	Moderate	---	47.5

Table 6. Estimated monetary value of available nutrient loss by the two Rivers.

Step	Estimated	Dapo catchment		Chekorsa Catchment	
		N	P	N	P
1	Total Lost/ha	13.6	9.3	14.3	4.1
2	Potential grain yield response (Kg/Ha)	3338.1	3905.1	3402.4	3147.6
3	Mean grain yield with no P and N fertilizer*	2389.3	2483.7	2389.3	2483.7
4	Net yield (Kg/ Ha)	948.8	1421.4	1013.1	663.9
5	Total price (Birr/ha)**	3320.8	4974.9	3545.9	2323.7

*Using Figure 12 and 13 equations accordingly. **Since market price of maize at Nekemte is 3.5 birr Ha^{-1} (1 birr = 17.50 USD).

**Figure 10.** Response of maize grain yield to nitrogen application rate.

of high nutrient loss rate class stated by FAO (1999) was left behind in DRC and CRC, respectively, to fall in the high nutrient loss rate class. The soil nutrient loss due to soil erosion alone contributed about 65 and 69% high nutrient loss rate class by FAO (1999). According to FAO (1999), if P_2O_5 losses from cultivated land are between 4 and 7 $\text{kg}^{-1}\text{ha}^{-1}\text{yr}$, such value are considered as high losses. Only by soil erosion, P_2O_5 has already attained the high soil nutrient depletion rate class for Dapo (Table 5). On the other hand, in the CRC, 52.53% has already attained the minimum amount of P_2O_5 loss to be classified as high losses.

Costs of nutrient loss

The estimated macro nutrients (Table 6) and the yield response curve (Figures 10 and 11) were used as a tool to the estimated monetary value of onsite economic cost of the lost nutrients in Table 6. However, estimating total monetary cost of erosion presents many difficulties (GLCUS, 2008) since it involves many different factors (Derek, 1996).

R^2 of Figure 10 shows a wide variation of yield response to the almost equivalent amount of fertilizer rate; that is, 2.3 to 6.5 tha^{-1} . Similarly, Negassa et al.

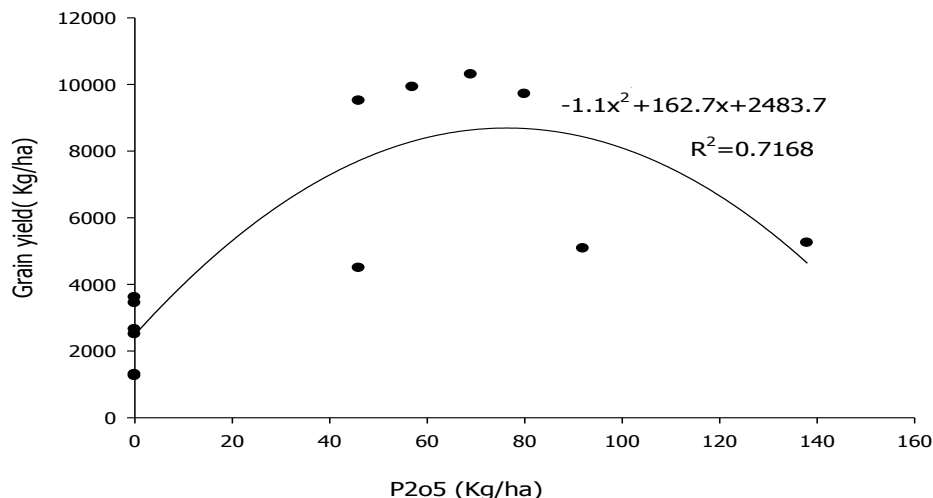


Figure 11. Grain yield response curve of maize to phosphorus rate.

(2005) indicated high variation of maize yields on farmers' fields in the study areas ranging from <1.0 to almost 6.0 t ha^{-1} .

Equations of Figures 10 and 11 represents the yield response curves showing the trend of yield increment for different rates of additional N and P application. Mean grain yield with no N and P fertilizers were $2,389$ and $2,484 \text{ Kg ha}^{-1}$, respectively (Table 6). Therefore, lost net maize grain yield due to the loss of available N and P_2O_5 by runoff were about 949 and $1,421 \text{ kg ha}^{-1}$ from DRC whereas $1,013$ and 664 kg ha^{-1} from CRC (Table 6). Farmers in the study area lost about 190 and 284 USD/ha from Dapo catchment and 203 and 133 USD/ha from Chekorsa catchment due to the loss of N and P, respectively.

Yield decline due to erosion follows a curvilinear, negative exponential (FAO, 1999). Therefore, eventually the current decline of yield can gradually reach a worst period in the future where there is no observation in yield decline. Negassa et al. (2005) also found that the relatively common practice of sole application of low rate of N and P fertilizers has not sustained maize production and productivity in the region because of severe nutrient loss. Therefore, combined application of these nutrients with manure/compost gives a better yield.

Conclusion and recommendations

The results revealed that suspended sediment concentration is strongly related to discharge or flood events for both catchments. The quality of the sediment lost from both sites is similar, though the catchment size and total discharge from Dapo River is about three times greater than Chekorsa, once sediment concentration of the Chekorsa River (varies from 942 to $3,002 \text{ mg/L}$) is higher than one at the Dapo River (ranging from 731 to $1,865 \text{ mg/L}$).

Suspended sediment concentration increases directly coincide with the surge in discharge for Chekorsa River but not for Dapo River. Discharge-suspended sediment concentration produced two types of hysteresis loops, an overlapped anticlockwise hysteresis for Dapo River Catchment and clockwise hysteresis relationships for Chekorsa River. The study reveals the loss of productivity as a result of both dissolved and sediment-sorbed N and P nutrient transported in overland flow delivered to the monitoring station.

In addition, from the result of the study, it is possible to conclude that:

1. Nitrogen and phosphorus losses due to soil erosion are elevated;
2. Clay has eroded more than silt and sand;
3. There is a strong correlation between percentage of clay with phosphate and TKN;
4. The rate of phosphorus loss was nine times in the sediment than that of the surface soil;
5. The monetary value of the lost nutrient may persuade farmers to implement sustainable nutrient practices and soil conservation activities;
6. As recommendation, similar studies must continue in the catchment including event based sediment hysteresis assessment in order to compare it with the weekly based sediment hysteresis.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

Physico-chemical characteristics of surface and groundwater in Obajana and its environs in Kogi state, Central Nigeria

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The present work was aimed at assessing the surface and groundwater quality of the area within and around Obajana using physico-chemical characteristics. Surface and groundwater samples were collected at the peak of dry season in March, 2013, from 24 locations within Obajana and its surrounding areas and were subjected to a comprehensive quality analysis. The following parameters were considered; pH, total dissolved solids, electrical conductivity, turbidity, dissolved oxygen, redox, potassium, sodium, calcium, magnesium, iron, zinc, chloride, nitrate, sulphate and bi-carbonate. Different statistical tools were used to analyse the results. Piper diagrams and Schoeller plots were used to suggest models for predicting water quality. Results from the physico-chemical analysis revealed that the concentrations of the analyzed parameters were within the acceptable limits for drinking water recommended by the World Health Organisation except for iron which had elevated concentration in one location. Surface and groundwater within Obajana and environs are thus considered safe for drinking and domestic use with respect to these analyzed parameters but needs to be protected from the perils of contamination by pollution from the continuous production of cement from the cement company over time. Plots on Piper and Schoeller diagrams indicate a Ca-Mg- HCO₃⁻ water type.

Key words: Obajana, water resources, physico - chemical, cation, anion and pollution.

INTRODUCTION

Water plays a vital role in sustaining life. It is important for domestic, agricultural and industrial use especially in developing countries such as Nigeria. Groundwater is the largest source of fresh water in the world and accounts

for about one third of one percent of the earth's water. It is of major importance to civilization being the largest reserve of drinkable water that can be used by humans. This is due to long retention time and natural filtering

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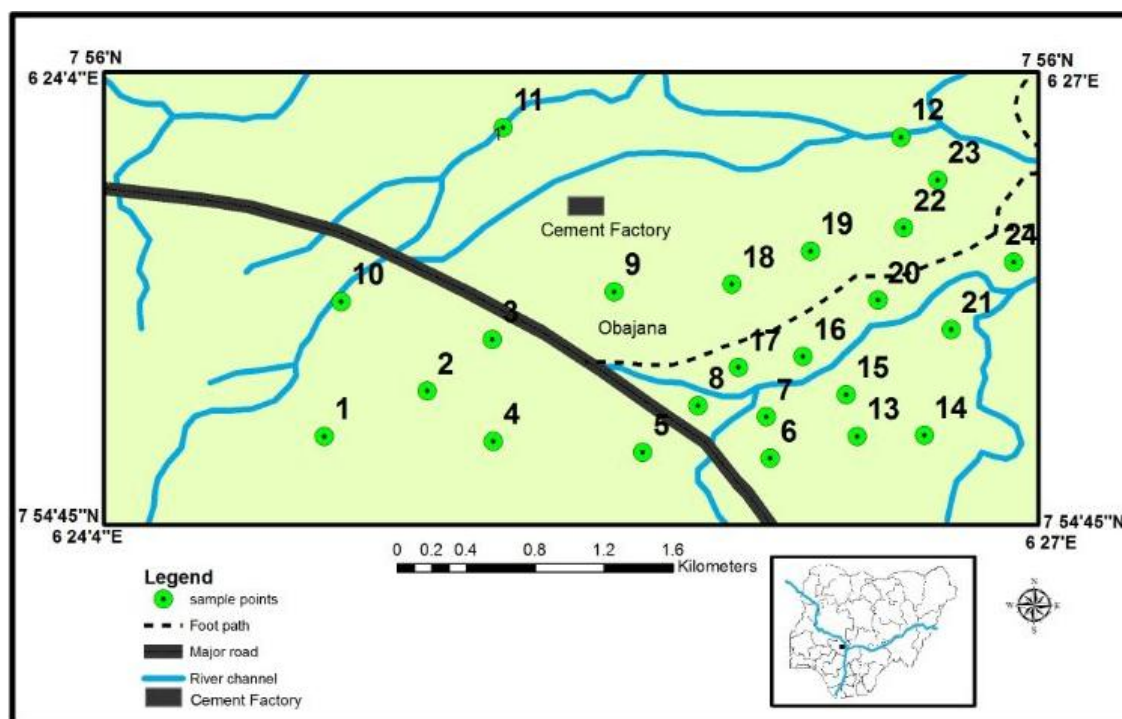


Figure 1. Location map of the study area.

effect of earth materials. It is also an ultimate and most suitable fresh water resource with nearly balanced concentration of the salts for human consumption naturally. Buchanan (1983) and Bouwer (2002): in Omada et al. (2011) quotes, "groundwater accounts for about 98% of the world's fresh water resources". Therefore, increase in the search and use of potable water, is as a result of the speedy expansion in urban population, industrial activities, commercial and agricultural developments.

Quality of surface and groundwater does not depend solely on the clarity but it takes into account the mineral content of the water as well. Groundwater quality is controlled by three main factors; climate, water depth, and soil or sediment. Water in shallow wells is closer to the surface potential sources of contamination, such as fertilizers, sewage and effluents. In contrast, contamination is less likely to occur in deeper groundwater reservoirs because contaminants have to travel greater depths to reach the water.

According to World Health Organization (1996), about 80% of all human diseases are caused by water. Once the groundwater is contaminated, its quality cannot be restored easily, hence there is need to communicate information on the quality of water to the concerned citizens and policy makers, analysis of water is utmost importance. It has become an important process in the assessment and management of water resources in all the countries of the world. Determination of the suitability

of water for drinking and domestic purposes has been the subject of many researches. Egbunike (2007) indicated that though groundwater may be of good quality, it may be contaminated by weathering of feldspars, leaching of clay, sewage pollution, and limestone lenses through which it percolates and flows. Similarly studies carried out in other area of the world include those of Janardhana et al. (2013) in India and Lucie et al. (2010) in Ontario, Canada. In general, quantities of inorganic constituents dissolved in groundwater may vary depending on the local geology or human activities within the immediate environment. The objective of the present work was to ascertain and re-appraise the physical and chemical quality of the water resources in Obajana and environs. Data obtained can be used as base-line for future environmental monitoring in the area.

Location and climate

Obajana lies within longitudes 6°24'E and 6°27'E and latitudes 7°54'N and 7°56'N (Figure 1). It covers an area of approximately 696.81 Km² and has an undulating surface and slopes gently downward in a southwest - northeast trend.

The area is characterized by wet and dry seasons. The wet season starts in April and last until November. The wet season on the average lasts for about 217 days while the dry season starts from November- March and lasts

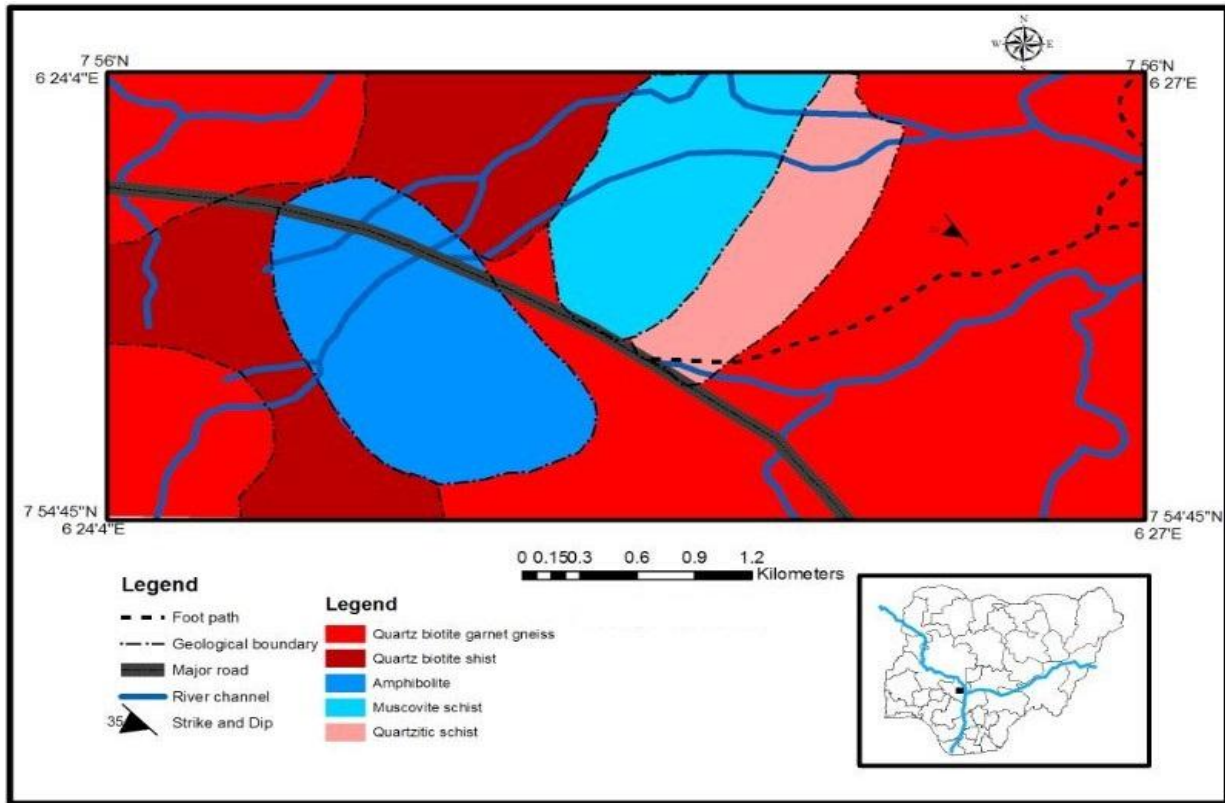


Figure 2. Geological map of the study area (Ameh et al., 2011).

for about 151 days (Walter, 1977). The vegetation is guinea savannah consisting of tall grasses, low trees and shrubs. In the wet season, this vegetation grows to become thick and impenetrable in some parts. In the dry season however, the grasses become dry and are burnt annually.

Geology of the study area

The study area lies within the Benin-Nigeria shield, situated in the Pan-African mobile zone extending between the ancient Basement of West African and Congo Cratons in the region of Late Precambrian to Early Palaeozoic orogenies (Rahaman, 1976; Ekwueme, 2003). The Basement Complex rocks of Nigeria are composed predominantly of migmatite gneiss; slightly migmatized to unmigmatized para-schists and meta-igneous rocks; charnockitic, older granite suites and unmetamorphosed dolerite dykes. (Rahaman, 1976).

The Precambrian Basement rocks of Obajana area, Southwestern Nigeria comprise of schists and gneisses which have been subjected to major supracrustal tectonic events such as the Dahomeyan (3000 ± 200 Ma), Eburnean (1850 ± 250 Ma), Kibaran (1000 ± 100 Ma), and Pan-African (550 ± 100 Ma). The Obajana gneisses (Figure 2) comprise of three types of rocks designated as

quartz-biotite gneiss; quartz-biotite-hornblende-pyroxene gneiss and quartz biotite-garnet gneiss (Rahama, 1976). According to this author, igneous rocks of this area occur as small, circular to oval outcrops and include members of the older granite suite mainly granites, granodiorites and syenites while associated schists in the area are: quartz-biotite schist, amphibolite schist, muscovite schist and quartzitic schist.

METHODOLOGY

A total of twenty four (24) water samples were collected for analysis in April, 2012, before the beginning of the wet season to ensure that effluents from surface run-off did not contaminate the samples taken. Fifteen samples were collected from hand-dug wells, six samples from boreholes and three samples were collected from surface water bodies. The surface water was collected from Angwa Tivi River and Oyo - Iwaa River.

The samples were collected in white plastic containers which were rinsed initially with the water to be sampled before proper sampling, labelling, storage and quality evaluation. *In-situ* test was carried out for the conductivity and pH, using conductivity and pH meters respectively; other parameters studied were total dissolved solids (TDS), and dissolved oxygen (DO). These parameters were measured directly by the use of HANA multi parameter ion specific metre (HI 83200). The concentrations of cations such as Fe^{2+} , Cu^{2+} , Zn^{2+} , K^+ , Na^+ , Mg^+ , and Ca^{2+} were determined by the use of Atomic Absorption Spectrophotometer (Bulk scientific model 210VGP) at the department of soil sciences, Kogi state University, Anyigba. The

Table 1. Physical and chemical composition of groundwater samples taken from hand dug wells.

Parameter	Hand-dug wells															SON MPL
	Locations	L1	L2	L3	L5	L6	L15	L16	L17	L18	L19	L20	L21	L22	L23	
pH	7.0	7.1	6.9	7.2	6.4	6.9	6.8	6.5	6.8	7.0	6.7	6.7	6.8	6.8	6.9	6.5-8.5
TDS (mg/l)	42.0	68.0	134.0	44.0	111.0	73.0	53.0	48.0	35.0	3.0	39.0	49.0	42.0	48.0	72.0	500
EC ($\mu\text{s}/\text{cm}$)	0.047	0.001	226.000	0.014	0.133	0.022	0.038	0.093	0.621	0.034	0.074	0.038	0.058	0.019	0.045	
Turbidity (mg/l)	26	15	41	13	29	118	17	8	35	21	18	18	72	28	41	
DO (mg/l)	7.20	7.40	7.30	8.20	6.50	5.00	5.00	5.00	8.20	4.90	7.00	5.60	6.00	5.89	6.20	
REDOX (mV)	246	454	452	536	312	311	300	300	527	639	617	153	203	202	407	
Major cations and trace elements (mg/L)																
K ⁺	4.13	3.51	0.06	2.00	2.04	5.68	4.13	9.05	5.14	4.03	1.27	2.87	2.54	4.17	8.69	
Mg ²⁺	9.14	2.47	2.57	0.64	4.71	8.04	0.99	2.51	3.59	1.22	3.01	3.82	2.92	4.05	1.38	0.2
Fe ²⁺	0.055	0.123	0.049	0.034	0.007	0.031	0.075	0.032	0.281	0.156	0.041	0.023	0.627	0.072	0.057	0.3
Na ⁺	11.68	5.22	5.12	4.21	6.82	8.11	3.42	5.22	6.53	7.45	4.80	7.92	5.38	5.44	9.36	200
Cu ²⁺	0.002	0.020	0.010	0.002	0.005	ND	0.003	0.012	0.085	ND	0.085	0.001	0.011	ND	0.052	1
Ca ²⁺	12.25	10.22	19.24	8.93	10.87	8.19	10.49	12.22	14.56	22.86	17.21	10.97	7.54	11.45	12.28	
Zn ²⁺	ND	0.035	0.030	0.040	0.030	0.004	0.010	0.062	0.048	0.044	0.041	0.039	0.007	0.004	0.032	3
Anion (mg/L)																
NO ₃ ⁻	0.019	0.117	0.054	ND	0.002	0.195	0.004	0.038	0.051	0.004	0.002	0.142	0.002	0.087	0.002	50
SO ₄ ²⁻	0.245	0.004	0.011	0.004	0.021	0.013	0.106	0.008	0.064	0.011	0.029	0.036	0.021	0.046	0.003	100
Cl ⁻	2.358	1.067	8.140	1.042	0.032	1.081	3.210	2.050	0.050	3.425	2.003	2.011	0.004	4.079	3.013	250
HCO ₃ ⁻	27	66	134	93	37	56	74	18	110	40	61	121	58	107	67	

concentrations of anions such as NO₃⁻ and SO₄²⁻ were determined by the use of spectrophotometer (Model Genesys 20) while those for HCO₃⁻ and Cl⁻ were determined by titration method in the Geochemistry laboratory of the University.

Results of the analysis carried out were processed with the AQUACHEM 4.0 software. This software was used to prepare Piper and Schoeller plots, determine the Hydrochemical facies of the water and carry out some statistical analysis of the data.

RESULTS AND DISCUSSION

Results of the physico-chemical characteristics for Water samples from three streams, 15 hand-dug

wells, and six borehole wells in Obajana and its environs are presented in Tables 1, 2 and 3.

Physical characteristics

The pH values for the sampling points L10, L11 and L12, corresponding to the stream sources ranged from 6.9 to 7.1 with a mean value of 7.00 as shown in Tables 3 and 4 respectively. For the groundwater sources, pH values of water samples from hand-dug wells ranges from 6.4 - 7.2 (represented by sampling points L1, L6, L15, and L24 in Table 1) with a mean value of 6.83, while pH of groundwater samples from boreholes (L4,

L7, L8, L9, L13 and L14) ranges from 6.6 to 7.4 with a mean value of 6.87, as shown in Table 2. The values are however, within the permissible limits of 6.5 - 8.5 set by W.H.O. The present study reveals a pattern of pH values that range from weakly acidic to weakly basic for groundwater and surface water in the area (Table 1).

Results from analysis, also show a similarity in trend between values of total dissolved solids (TDS) and electrical conductivity (EC) in the area under study. The trend decreases in the order; hand-dug wells > stream sources > boreholes (Figure 3a). From stream samples, TDS gives

Table 2. Physical and chemical composition of groundwater samples taken from boreholes.

Parameter	Borehole						SON MPL
	L4	L7	L8	L9	L13	L14	
pH	6.7	7.1	6.8	6.6	6.6	7.4	6.5-8.5
TDS(mg/l)	35.7	42.4	50.7	48.8	64.0	64.5	500
EC (µs/cm)	0.080	0.090	0.040	0.150	0.105	0.070	
Turbidity (mg/l)	18	22	29	27	25	32	
DO (mg/l)	7.6	6.5	7.5	8.3	7.5	6.6	
REDOX (mV)	307	311	324	342	625	298	
Major cations and trace elements (mg/l)							
K ⁺	6.84	5.07	3.73	5.26	3.18	4.82	
Mg ²⁺	3.78	3.22	5.22	2.93	2.88	4.81	0.2
Fe ²⁺	0.014	0.012	0.028	0.013	0.044	0.021	0.3
Na ⁺	4.38	3.22	5.50	4.82	8.32	4.75	200
Cu ²⁺	0.001	0.010	0.006	0.002	0.020	0.001	1.0
Ca ²⁺	9.20	11.60	9.24	10.70	11.62	8.70	
Zn ²⁺	0.052	0.066	0.043	0.047	0.040	0.032	3.0
Anions (mg/l)							
NO ₃ ⁻	0.054	0.003	0.002	0.024	0.004	0.040	50
SO ₄ ²⁻	0.006	0.115	0.131	0.003	0.014	0.207	100
Cl ⁻	6.240	7.180	5.210	5.800	2.500	9.730	250
HCO ₃ ⁻	53	62	92	17	97	69	

Table 3. Physical and chemical characteristics of surface water samples.

Parameter	Surface water			WHO MPL	SON MPL
	L10	L11	L12		
Location	L10	L11	L12		
pH	7.0	6.9	7.1		6.5-8.5
TDS (mg/l)	64.0	67.0	68.0		500
EC (µs/cm)	90.0	75.0	81.0		
Turbidity (mg/l)	32	27	38		
DO (mg/l)	8.1	6.8	7.8		
REDOX (mV)	365	544	511		
Major cations and trace elements (mg/l)					
K ⁺	0.10	0.33	0.43		
Mg ²⁺	4.97	3.87	1.93		0.2
Fe ²⁺	0.101	0.078	0.036		0.3
Na ⁺	1.98	2.29	1.66		200
Cu ²⁺	0.006	0.008	0.007		1.0
Ca ²⁺	22.47	9.62	6.41		
Zn ²⁺	0.011	0.020	ND		3.0
Anions (mg/l)					
NO ₃ ⁻	0.001	0.007	0.016		50
SO ₄ ²⁻	0.745	0.394	0.256		100
Cl ⁻	5.940	1.350	5.500		250
HCO ₃ ⁻	61	92	104		

range of 64 to 68 mg/l and a mean value of 66.33 mg/l. Hand-dug wells recorded a range of 3.0 to 134.0 mg/l

and mean value of 57.4 mg/l. For borehole samples, TDS values range from 35.7 to 64.5 mg/l and a mean value

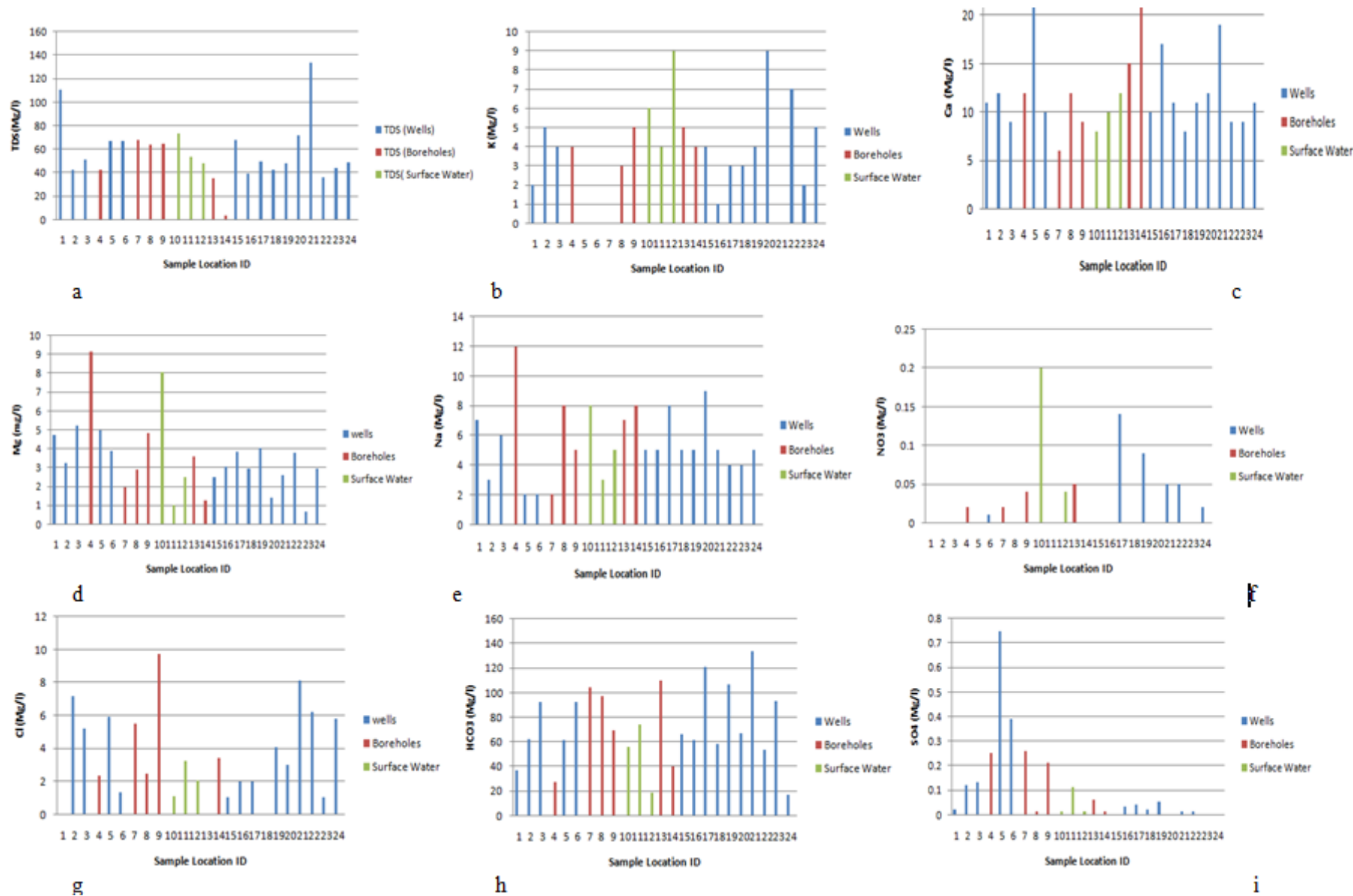


Figure 3. Bar chart representation of concentration of Elements. Compilation: 1- 24 (sample locations) blue graph (wells) red graph (boreholes) green graphs (surface water).

Table 4. Physical and chemical characteristics of surface and groundwater samples.

Parameter	Stream source		Han-dug well source		Borehole source		WHO (2011)	SON (2007)
	Range	Mean	Range	Mean	Range	Mean		
pH	6.9 - 7.1	7	6.4 - 7.2	6.833	6.6 - 7.4	6.87	6.5 - 9	6.5 - 8.5
TDS (mg/l)	64 - 68	66.33	3.0 - 134	57.4	35.7 - 64.5	51.02	1500	500
EC ($\mu\text{s}/\text{cm}$)	75 - 90	82	0.001 - 226.000	15.149	0.04 - 0.15	0.09	250	1000
Turbidity (mg/l)	27 - 38	32.33	8 - 118	33.333	18 - 32	25.5	NA	NA
DO mg/l	6.8 - 8.1	7.57	4.90 - 8.20	6.359	6.5 - 8.3	7.33	NA	NA
REDOX mV	365 - 544	473.33	153 - 639	377.933	298 - 625	367.83	NA	NA
K ⁺ (mg/l)	0.10 - 0.43	0.29	0.06 - 9.05	3.954	3.18 - 6.84	4.82	NA	NA
Mg ²⁺ (mg/l)	1.93 - 4.97	3.59	0.64 - 9.14	3.404	2.88 - 5.22	3.81	150	0.2
Fe ²⁺ (mg/l)	0.036 - 0.101	0.072	0.007 - 0.627	0.111	0.012 - 0.044	0.022	0.3	0.3
Na ⁺ (mg/l)	1.66 - 2.290	1.98	3.42 - 11.68	6.445	3.22 - 8.32	5.165	200	200
Cu ²⁺ (mg/l)	0.006 - 0.008	0.007	0.000 - 0.085	0.019	0.001 - 0.02	0.007	2.0	1.0
Ca ²⁺ (mg/l)	6.41 - 22.47	12.83	7.54 - 22.86	12.619	8.70 - 11.62	10.177	200	NA
Zn ²⁺ (mg/l)	0.000 - 0.020	0.01	0.000 - 0.062	0.028	0.032 - 0.066	0.047	3.0	3.0
NO ₃ ⁻ (mg/l)	0.001 - 0.016	0.008	0.000 - 0.195	0.048	0.002 - 0.054	0.021	50.70	50
SO ₄ ²⁻ (mg/l)	0.256 - 0.745	0.465	0.003 - 0.245	0.041	0.003 - 0.207	0.079	50	100
Cl ⁻ (mg/l)	1.350 - 5.940	4.263	0.004 - 8.140	2.238	2.50 - 9.73	6.11	250	250
HCO ₃ ⁻ (mg/l)	61 - 104	85.67	18 - 134	71.27	17 - 97	65	600	NA

of 51.02 mg/l. All samples analyzed had TDS concentration below SON (2007) (500 mg/l) and WHO (2011) 500 to 1000 mg/l for maximum permissible limit. Mean value of EC for stream water sources was 82 $\mu\text{s}/\text{cm}$, 15.149 $\mu\text{s}/\text{cm}$ for hand-dug wells and borehole sources give 0.09 $\mu\text{s}/\text{cm}$. However, these values suggest that TDS and EC values are lower for groundwater sources than stream water sources. But according to Schoeneich (2001) EC for groundwater in the Crystalline Hydrogeological Province should be the same for surface water. Higher values in the stream/surface water sources could be attributed to slightly high content of Na⁺, Cl⁻, NO₃⁻, and SO₄²⁻. This can also be linked to effluent discharges from industries into the surface water and other anthropogenic activities.

Thus, it can be inferred that range and mean values for the TDS, EC and dissolved oxygen are within the permissible limits of W.H.O and Standard organization of Nigeria, with details represented in Tables 1, 2, 3 and 4. Given the range of values obtained for EC in the Obajana area, groundwater resources available can be classified as low salinity water.

DO of water samples analyzed ranges from 6.8 - 8.1 mg/l with a mean of 7.57 mg/l for surface water, 4.9 - 8.2 mg/l and a mean of 6.359 mg/l for groundwater from hand dug wells, while DO in water samples obtained from boreholes ranges from 6.5 - 8.3 mg/l with mean value of 7.33 mg/l (Tables 1, 2 and 3).

From the results presented in Table 4 above, NA means not available, WHO means World Health Organisation Geneva (2011) and SON means Standard organization of Nigeria (2007).

Chemical characteristics

The result of chemical analysis of the water sample in the study area shows that concentrations of Fe²⁺, Zn²⁺ and Cu²⁺ are all below the permissible limits of the World Health Organisation (2011) and Standard Organization of Nigeria (2007). Guideline values have not been established for potassium and calcium. Potassium (K⁺) concentration in groundwater within the studied area ranges from about 0.06 to 9.05 mg/l with an average of 3.954 mg/l in hand dug wells (Table 1), 3.18 to 6.84 mg/l with an average of 4.82 mg/l in boreholes (Table 2) while surface water had potassium concentration ranging from 0.10 mg/l to 0.43 mg/l with an average of 0.29 mg/l (Table 3). The highest concentration of potassium was observed in samples taken from stream and hand dug wells (Figure 3b). Calcium (Ca²⁺) concentration ranged from 7.54 to 22.86 mg/l with an average of 12.619 mg/l in hand dug wells, 8.70 to 11.62 mg/l with an average of 10.18 mg/l while surface water had concentration ranging from 6.41 to 22.47 mg/l with an average of 12.83. Calcium concentration in groundwater samples analyzed exceeds that of surface water (Figure 3c). This is expected because of the water - rock interaction which has resulted in the dissolution of more calcium from subsurface rocks. Potassium in groundwater results from weathering of orthoclase and microcline. The abundance of potassium and sodium is about the same but potassium is commonly less than one tenth of sodium in natural water because many potassium minerals have higher resistance to weathering.

Magnesium in groundwater within the study area ranges

from 0.64 to 9.14 mg/l for samples from hand dug wells, 2.88 to 5.22 mg/l for borehole samples while surface water (stream) had concentration range of 1.93 to 4.97 mg/l. Magnesium concentration in borehole samples exceeds those of stream and hand dug wells (Figure 3d).

Sodium concentration in all water sources sampled is far below the maximum permissible limit of 200 mg/l recommended by WHO (2011) and SON (2007) (Table 4). Groundwater and surface water within the study area is thus safe for drinking and domestic purposes with respect to their sodium content.

The concentration of iron in all the water samples analyzed were all within the maximum permissible limits of 0.3 mg/l set by SON and WHO except SL22 which has iron concentration of 0.627 mg/l (Table 1). Water from this location is considered unsafe for drinking with respect to its iron concentration. The iron in the groundwater source could have resulted from leaching from lateritic soils of predominantly the gneissic bedrocks. High Fe^{2+} content in water may impact stains on laundered cloth, scaling in metal pipes and affects taste of drinking water (Walter, 1981; Olarewaju et al., 1996).

The study also shows that the concentration of zinc and copper in both surface and groundwater are below the WHO and SON permissible limits of 3 and 1 mg/l set for zinc and copper respectively (Table 4). Water within the study area is thus considered safe for drinking and domestic use with respect to these parameters.

Concentration of cations in groundwater samples reveals that on the average, $\text{Ca}^{2+} > \text{Na}^{2+} > \text{K}^+ > \text{Mg}^{2+}$, while in surface water samples, $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^{2+} > \text{K}^+$. Though, variations exist from one sample point to another. This composition is evident that the water here is derived from source rocks rich in Ca-feldspars, notably plagioclases in the parent rock of metamorphic origin. Thus, water in the area is hard as its cationic content has more concentrations of slightly insoluble Ca^{2+} and Mg^{2+} over the soluble Na^+ and K^+ . The concentrations of cations in all the water samples are below permissible limits for good and safe drinking according to World Health Organisation (1996) and Standard organization of Nigeria (2005).

Anionic concentrations from water samples reveal that HCO_3^- is dominant. It ranges from 61 to 104 mg/l with a mean value of 85.67 mg/l in surface water. In groundwater generally, it ranges from 17 to 134 mg/l with mean values 71.27 mg/l in hand-dug wells and 65 mg/l in boreholes. In all samples, the order of abundance in anionic content is of the order $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ for surface water and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ for groundwater. The high content of HCO_3^- in water from the study area is a reflection of the fact that groundwater is being recharge directly from rainfall sources and not probably any other pollution source.

Nitrate concentration in both water sources analyzed is far below the recommended permissible limit of 50 mg/l

by SON. This is an indication that here has not been much contamination of the water sources by effluents, sewage or agricultural fertilizers.

Piper plots and Schoeller diagram

Plot of the chemical compositions of Groundwater according to Loneragan and Cange (1994), presented in Piper's trilinear diagram is shown in Figure 4. Here, dominant cation and anion fields are classified. A similar plot for the study (Figure 4) using a hydrogeological software AQUACHEM 4.0 reveals that the groundwater is $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{HCO}_3^-$ and bicarbonate water type which represents recently recharged water of meteoric origin that resulted from the dissolution of aluminosilicate minerals. Comparison of the chemical characteristic of groundwater in Obajana and its environs, and the WHO/SON baseline standard for drinking water quality confirms that at the moment, there level of water pollution in water samples from the area is very minimal or almost non-existent.

The Schoeller diagram represents the combination of major and minor constituents of groundwater in the study area (Figure 6) and the result obtained indicates that HCO_3^- is dominant and SO_4 was the least in the following order: HCO_3^- , Ca, Na, Mg, Cl, SO_4^{2-} . This plot again buttresses the composition of major cations and anions present from water samples in the study area, and that they are in consonance with plot from the piper diagram.

The correlation coefficient reveals some relevant hydrochemical relationships; the content of TDS has high positive correlation with Fe^{2+} and so does Zn^{2+} and K^+ (Table 4). This positive correlation indicates that the ions may have been derived from the same source. All other nutrient concentrations in the water samples analyzed either have very weak positive correlation or negative correlations. Negative correlation between most of these nutrient concentrations suggests that they are not of the same source but could have been derived from ion exchange processes between water and rocks. The rock source deduction component of the aquachem 4.0. Software confirms some of the inferences made from the interpretation of the correlation coefficients (Table 5) between the measured parameters. Deductions from this software reveals that sodium in the water is sourced from albite and ion exchange processes, calcium and bicarbonate are sourced from weathering of carbonate and silicate rocks and chloride from rock weathering. Deductions could not be made on the sources of the other parameters because data on some chemical facies needed to do so are lacking.

Conclusion

Water is of immense importance to both rural and urban dwellers of developing nations. Classification of the water

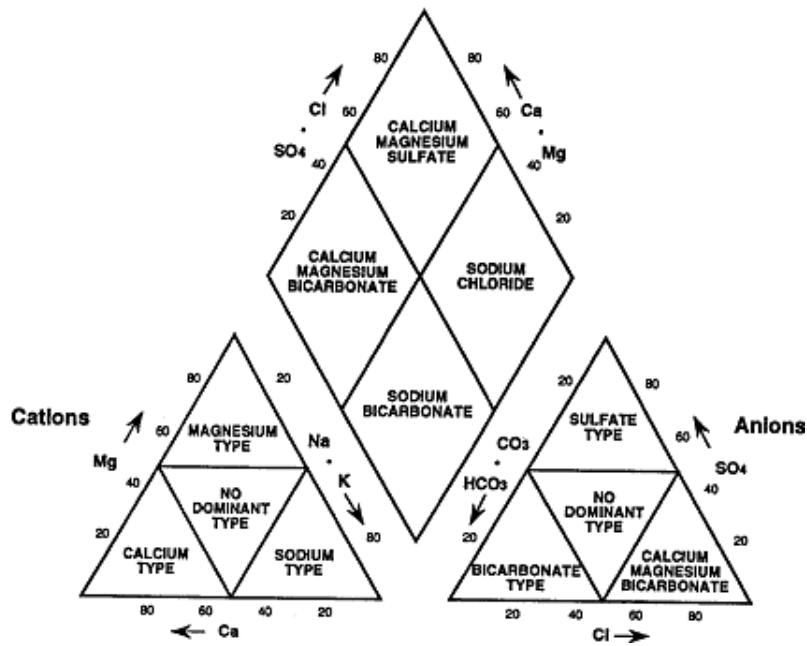


Figure 4. Piper Diagram showing dominant cation and anion fields in the Lower triangles and Hydrochemicals Facies in the upper diamond. Source: Lonergan and Cange (1994).

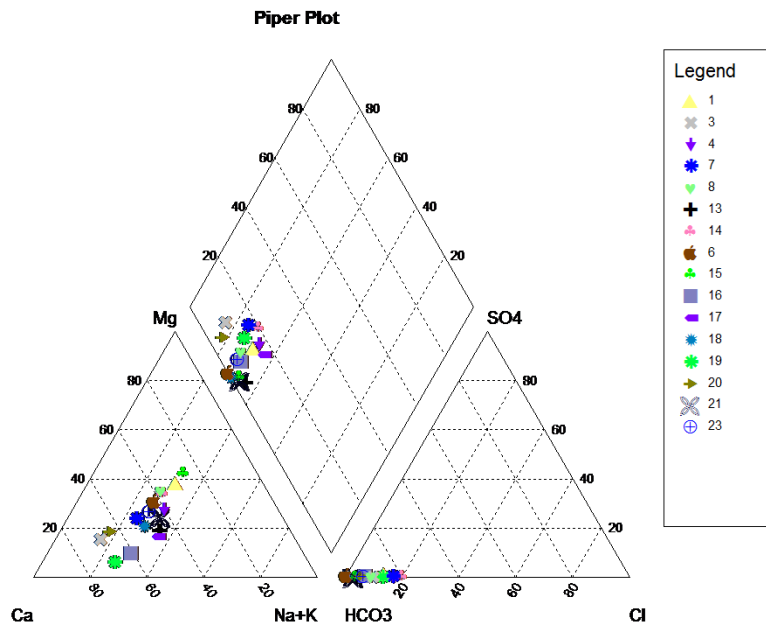


Figure 5. Piper diagram plot for water samples from the study area, where; 1, 2, 3, to 16 represent sample location numbers.

in the study area based on its pH shows that the water is slightly acidic to slightly basic but however falls within the acceptable permissible limit recommended by the World health Organization (2011) and the standard organization of Nigeria (2007). Groundwater in Obajana and environs

has been evaluated for its chemical composition and suitability for drinking.

The abundance of chemical concentrations in surface water within the study area is in the order of $Ca > Mg > Na > K$ for the cations and $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$ for

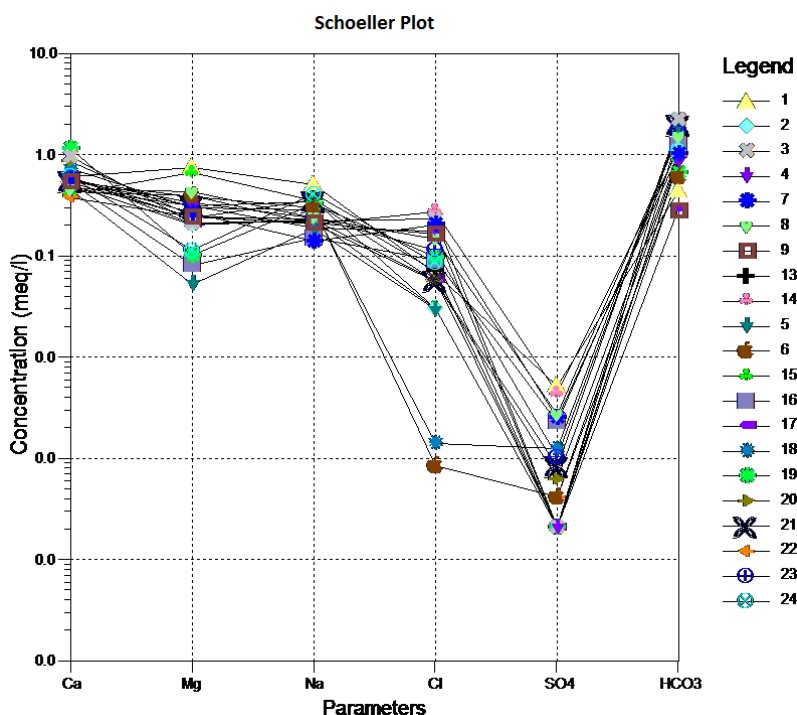


Figure 6. Schoeller diagram for water samples from the study area, where; 1, 2, 3 to 16 represent sample location numbers.

Table 5. Correlation matrix of measured parameters.

	Correlation coefficient												
	DS	Na	K	Ca	Mg	Fe(II)	Cu	Zn	Cl	HCO ₃	NO ₃	SO ₄	O ₂
TDS	1.00	-0.07	-0.34	-0.04	0.11	0.57	-0.39	-0.31	0.13	0.29	0.06	0.08	0.13
Na		1.00	0.40	0.06	0.40	-0.04	0.34	0.17	-0.37	-0.18	0.40	-0.45	-0.26
K			1.00	-0.20	0.02	-0.34	0.19	0.52	-0.03	-0.46	0.18	-0.44	-0.36
Ca				1.00	-0.11	0.35	0.29	-0.08	0.10	-0.04	-0.12	0.23	-0.01
Mg					1.00	-0.11	-0.17	-0.03	-0.03	-0.21	0.38	0.23	0.01
Fe(II)						1.00	-0.13	-0.19	0.33	0.41	-0.07	-0.17	0.08
Cu							1.00	0.20	-0.44	0.12	0.49	-0.24	0.23
Zn								1.00	0.02	-0.18	0.11	-0.46	0.11
Cl									1.00	0.08	-0.32	0.23	0.17
HCO ₃										1.00	0.18	-0.02	0.20
NO ₃											1.00	-0.58	-0.66
SO ₄												1.00	0.42
O ₂													1.00

the anions while the order of abundance for groundwater is Ca > Na > K > Mg for cations and HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻ for the anions. The dominant hydrochemical facies identified here is of the Ca-Mg- HCO₃⁻ type. Groundwater and surface water within the study area is of excellent quality for drinking and domestic use with respect to TDS, pH, magnesium, sulphate, nitrate, chloride, zinc, copper and iron (only has elevated

concentration in one location, L22) as the concentration of these parameters fall within the recommended permissible limits of the world health organization (2011) and the standard organization of Nigeria (2007).

It is however recommended that a well designed groundwater monitoring program be put in place to periodically assess the suitability water for drinking and other domestic purposes. This is to ensure that the

introduction of hazardous contaminants is detected on time and necessary steps taken to avoid health hazards or deaths that may result from drinking such contaminated water.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

Natural radioactivity and environmental risk assessment of Sokoto phosphate rock, Northwest Nigeria

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Phosphate rock samples collected from the phosphate bearing formations of Sokoto State, Northwest Nigeria were assessed for their radiological contents by gamma spectrometric technique (sodium iodide (NaI (TI) detector). The mean activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in all the studied samples were $720.1 \pm 4.2 \text{ Bqkg}^{-1}$, $33.5 \pm 1.4 \text{ Bqkg}^{-1}$, and $315.3 \pm 6.7 \text{ Bqkg}^{-1}$ respectively. Contributions from radium contents to the overall radionuclide activity concentrations were quite significant. The calculated mean value of the absorbed dose rate was found to be 3.6 times the maximum value for the world background level, which shows the severity of radiation risk the public is exposed to in the study areas. The computed values for radiation hazard indices were above the world's proposed safety limits by UNSCEAR, which place the study areas among high background radiation zones. Some restrictive measures and precautionary actions are therefore obligatory for the local farmers and the general public from the view point of radiation protection.

Key words: Natural radioactivity, Sokoto, phosphate rock, radiation hazard, NaI (TI) detector, radiation dose.

INTRODUCTION

Phosphate rocks, which can be of sedimentary, volcanic or biological origin (Sam and Holm, 1995), generally refer to rocks with high concentration of phosphate minerals (Cevik et al., 2010). Phosphate rocks are the starting raw material for all phosphate products and fertilizer production (Khater et al., 2001; Ogunleye et al., 2002). They are also used in the preparation of food and animal feeds, and as a source of phosphorus for agricultural purposes as well as for the manufacturing of certain industrial phosphorus-based chemicals and detergents

(Abbady et al., 2005; Khan et al., 1998). Phosphate rocks contain relatively high amounts of naturally occurring radioactive materials (NORMs) from ^{238}U and ^{232}Th and their respective descendants, and ^{40}K in concentrations that depend on geographical and geological origin. Though the concentrations of NORMs observed in phosphate rocks of all types are similar to those observed normally in soils, uranium and its decay products tends to occur at elevated concentrations in sedimentary phosphates (Harb et al., 2008; Khater et al., 2001). This

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uranium enrichment makes phosphates one of the major sources of technologically enhanced natural radiation (TENORM), (Abbadly et al., 2005), which contributes to human exposure. It is widely believed that the radioactivity associated with phosphate rocks of sedimentary origin is formed by the adsorption and co-precipitation of uranium with calcium (Khater et al., 2001). Phosphate ores are found to occur as phosphorites, $[\text{Ca}_3(\text{PO}_4)_2]$, which are very old marine deposits associated with fossils; and apatite, $\text{Ca}_5[(\text{PO}_4)_3(\text{F})]$, which is of igneous origin (Schmidt, 1993; OSPARCOM, 1997; Abbadly et al., 2005). van Straaten (2002), reported that sedimentary marine phosphate rock deposits accounts for about 75% of the world's phosphate source, which according to Okosun (1989), makes it a great economic base that provides most of the raw materials for the manufacture of phosphate fertilizers and phosphorus based chemicals

Mining and processing of phosphate rock and its use in the manufacturing industry, redistributes the radioactive trace elements and ^{238}U and its decay products throughout the environment and also in the final products, thereby enhancing the concentrations of natural radionuclides in the end products and wastes of the phosphate industry. This constitutes ways in which the workers, the public and the environment are exposed to enhanced radioactivity (IAEA, 2004; UNSCEAR, 1993). Significant radiological investigations have been conducted on phosphate rocks and their products in different countries of the world, which has led to establishment of standards and regulations for the protection of man and his environment from the radiation effects that will arise due to the usage of the rock. Sam et al. (1999) assessed the radiological and chemical constituents of Uro and Kurun rock phosphates from Sudan. Khater et al. (2001), investigated the radiological impacts of natural radioactivity in Abu-Tartor phosphate deposits, Egypt. Saueia et al. (2005) undertook similar investigation for phosphate rock, phosphogypsum and phosphate fertilizers in Brazil. Abbadly et al. (2005), studied the natural radioactivity and dose assessment for phosphate rocks from Wadi El-Mashash and El-Mahamid Mines in Egypt. Cevik et al. (2010), reported the radiological, structural and chemical characteristics of Mardin-Mazidagi phosphate rock in Turkey.

As a result of increasing interest by the Nigerian local farmers in direct application of phosphate rocks to agricultural soils as a substitute for and ready alternative to chemical fertilizer, which is becoming increasingly expensive and out of reach, it becomes important to assess the potential radioactivity exposures of phosphate rocks.

In the present work, gamma spectrometric technique is used to quantify the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K of Sokoto phosphate rocks. The human radiation exposure from the radioactive content of phosphate rock

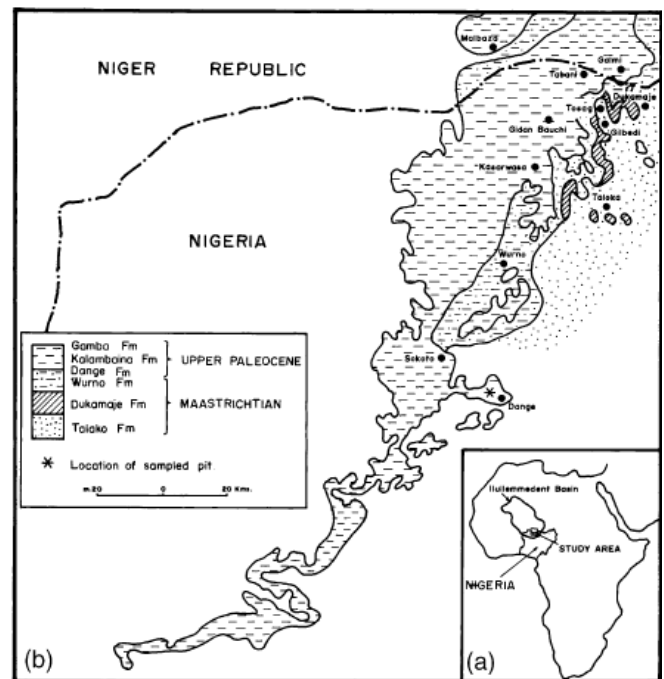


Figure 1. (a) Map of Africa, showing the Sokoto sub-basin, Northwest Nigeria in relation to the Illemmeden basin. Inset: Location of (b). (b) Simplified geological map of the southeastern sector marine and marginal facies of Illemmeden basin, Sokoto sub-basin (Okosun, 1997).

samples was estimated, along with possible environmental implications of direct application of Sokoto phosphate rocks for agricultural purposes.

Sokoto phosphate deposit

The Sokoto basin, Northwest Nigeria is Nigeria's sector of extensive Illemmeden Basin (Figure 1). A phosphate deposit of great significance is located in Sokoto state, northwestern Nigeria, in a paleocene sedimentary sequence. Marine sediments were deposited in Sokoto basin during the maastrichtian-paleocene trans-Saharan transgressions.

The phosphates, whose basic components are from vertebrate remains, are present in the Dange formation which from Paleocene age occur as nodular beds and nodular disseminations in the shales and siltstone of the formation. The Dange formation is phosphate bearing in the entire basin though the concentration differs from place to place. Phosphate rocks are found in commercial deposits in Dukamaje, Dange, Gilbadi, Dankilo-Dange, Wurno, Kindiru, Dillingu and Gada in Sokoto State. Ogunleye et al. (2002) also reported occurrence of phosphate nodules and pellets in Gidan Bauchi, Illela and Kalambiana. Etu-Efeotor (1998), Okosun (1997) and Ogunleye et al. (2002), reported that phosphate deposit thickness in Dukamaje formation range between 1 to 5 m,

Table 1. Mean activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K (Bqkg $^{-1}$) in Sokoto phosphate rock samples.

Sample ID	Number of samples	Activity concentrations (Bqkg $^{-1}$)		
		^{226}Ra	^{232}Th	^{40}K
DNG	3	650.7±3.8 (602.5 - 732.0)	35.7±1.2 (17.0 - 58.6)	264.3±6.4 (111.2 - 392.3)
KDR	3	1073.2±5.9 (1055.7 - 1087.3)	55.9±1.7 (39.2 - 85.3)	380.3±8.3 (310.3 - 459.0)
DLG	3	804.5±3.7 (854.7 - 883.6)	28.9±1.0 (17.7 - 40.8)	394.6±5.6 (375.8 - 428.4)
WRN	3	510.1±4.1 (443.7 - 617.8)	19.5±1.8 (13.2 - 27.7)	272.2±7.7 (202.7 - 362.8)
DNK	3	562.0±3.3 (491.0 - 606.3)	27.4±1.3 (24.7 - 32.2)	265.2±5.3 (110.7 - 404.7)
Av. range	15	720.1±4.2 (443.7 - 1087.3)	33.5±1.4 (13.2 - 85.3)	315.3±6.7 (111.2 - 459.0)

while the phosphate nodules/pellets occur in sizes of 0.1-1cm. Amapu (1998), investigated the agronomic potential of direct application of Sokoto phosphate rock as an alternative phosphate fertilizer for Nigeria's sub-humid Savannah region. Phosphate nodules from Sokoto basin are presently mined superficially by the natives especially women and children during the non-farming season and transported, as a major raw material to feed the Crystal Talc Nigeria, Kagara, Niger State and Federal Superphosphate Fertilizer company plant at Kaduna, Kaduna State, for the production of phosphate fertilizer. They are also blended by the locals and applied directly in the agricultural farms as substitute for fertilizer.

MATERIALS AND METHODS

The Sokoto phosphate deposits occur generally as nodules on the surface, with nodular beds measuring to between 0.2-0.3 m. The phosphate nodules are superficially mined on daily basis mostly by women and children. To measure the natural radioactivity, a total of 15 phosphate rock samples, three each, were collected from five villages which represents the Sokoto phosphate bearing formations. The villages are Dange (DNG), Dankilo (DNK), Wurno (WRN), Kindiru (KDR) and Dillingu (DLG). Phosphate nodules were picked at random from four different points and mixed together thoroughly to give a true representation of each sampling point throughout all the sample locations. The samples, each about 1 kg in weight, were packed in well labelled sampling polyethylene bags, properly tied and sealed to avoid cross contamination of samples, and transported to the laboratory for analysis at the Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Kaduna State.

In the laboratory, the samples were opened and all weeds, stones and other organic and non-phosphate materials, were picked out. The samples were sundried under ambient temperature to almost constant weight for 72 h. The dried samples were crushed into fine powder and sieved through a 2-mm mesh. The dried samples were homogenized, weighed and packed into identical 7.2 cm diameter and 6.0 cm height radon impermeable marinelli beakers which holds between 300-350g of sample. The beakers were then subjected to a triple stage sealing process to ensure the containment of radon-222 (Jamok, 2014), and stored at room temperature for a period of 5 weeks to allow for radioactive equilibrium between the parents and their daughter nuclides (Amin et al., 2013; Ghose et al., 2012; Ibeanu, 2002; Kumar et al., 2003).

The radiometric analysis of the samples was carried out using a gamma spectrometric technique comprising a 7.62 x 7.62 cm NaI

(TI) detector coupled to a computer based multichannel analyzer (MCA) for data acquisition. To effectively reduce the gamma-ray background radiation from the acquired spectrum, the detector is housed in a 6 cm thick lead shield lined with cadmium and copper sheets. The system was set at operating energy range of 0-3000 keV and energy resolution of 661.6 keV peak of ^{137}Cs . For accurate quantitative determination of ^{226}Ra , ^{232}Th and ^{40}K in the samples, the detector calibration is necessary to ensure a good relationship between the respective peak positions of the spectrum and their corresponding gamma-ray energies. RGU-1, RGTh-1 and RGK-1 gamma spectrometric reference materials (gamma sources of known energies) supplied by the International Atomic Energy Agency (IAEA), whose activity is distributed homogeneously within the same volume and container geometry as that of the samples, was used for the energy calibration and absolute photopeak efficiency evaluation of the detector. Each sample was counted for 29,000 s. Knowing that through the period of sample storage, uranium attained circular equilibrium with its daughters, the gamma energy line of 1764 keV (15.6%) for ^{214}Bi used to represent the activity concentration of ^{226}Ra , while the activity concentration of ^{232}Th was evaluated from the average activity of photopeaks of 911.2 keV (25.8%) for ^{228}Ac and 238.6 keV (43.6%) for ^{212}Pb . The ^{40}K activity was determined from its 1460.8 keV (10.66%) single characteristic gamma line. An empty sealed beaker in the same geometry as the samples was first counted in the same manner for 29,000 s to determine the radiation background around the detector environment. The obtained background was used to correct the net peak area of gamma rays of measured radionuclides (Uosif and El-Taher, 2008). The activity concentrations were computed using the equation (Cevik et al., 2010; Khandaker et al., 2012):

$$A(\text{Bq/kg}) = \frac{N}{\varepsilon_{\gamma} \times I_{\gamma} \times M \times t} \quad (1)$$

Where A is the activity concentration of the nuclide, N is the total net count of a specific gamma emission, ε_{γ} is the detection efficiency for the specific gamma emission, I_{γ} is the emission probability, M is the mass of the sample (kg) and t is the counting time.

RESULTS AND DISCUSSION

Phosphate samples collected from the villages visited were analysed for their natural radioactivity concentrations using gamma ray spectrometry. The measured specific activity values for ^{226}Ra , ^{232}Th and ^{40}K along with their statistical uncertainties are summarized in Table 1. These values are actually taken as representing

Table 3. Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K (Bqkg^{-1}) and Ra_{eq} (Bqkg^{-1}) in phosphate samples from different countries.

Country	Activity concentration (Bqkg^{-1})			Ra_{eq} (Bqkg^{-1})	Reference
	^{226}Ra	^{232}Th	^{40}K		
Pakistan (Hazara)	440	50	207	527.4	Khan et al. (1998)
Egypt (El-Mahamid)	567	217.3	217.3	921	Abbady et al. (2005)
Egypt (El-Mashash)	666	329.4	329.4	1182	Abbady et al. (2005)
Tanzania	5022	717	286	6069	Makweba and Holm (1993)
Algeria	619	64	22	712	Olszewska-Wasiolek (1995)
Sudan (Kurun)	393	6.9	141.3	414	Sam et al. (1999)
Tunisia	250	28	167	303	Cevik et al. (2010)
Nigeria (Sokoto)	720.1	33.5	315.3	792.3	Present work

the NORMs level in Sokoto phosphate rocks. The activity concentration levels for NORMs in phosphate rock samples from the five villages range from 44.37 to 1087.3 Bqkg^{-1} , with a mean value of $720.1 \pm 4.2 \text{ Bqkg}^{-1}$ for ^{226}Ra , from 13.2 to 85.3 Bqkg^{-1} with an average value of $33.5 \pm 1.4 \text{ Bqkg}^{-1}$ for ^{232}Th and from 111.2 to 459.0 Bqkg^{-1} with a mean value of $315.3 \pm 6.7 \text{ Bqkg}^{-1}$ for ^{40}K . The results show that the activity levels are higher for phosphate rocks from Kindiru (KDR) village. Generally however, the ^{226}Ra activity concentration values are higher than those of ^{232}Th and ^{40}K indicating that Sokoto phosphates are of sedimentary origin. It can be clearly seen that ^{238}U and its daughters plays a prominent role in contributing to the overall radioactivity content of phosphate rocks (Abbady et al., 2005; Khater et al., 2001). Although the values of radium activity concentration varies within the phosphate rock samples from the five villages, which according to Guimond (1990) and Ivanovich and Harmon (1992), may be due to uranium solubility under oxidation conditions and the percentage of P_2O_5 present, they are generally high. This can pose external radiation risk especially to women and children who mined this commodity on daily basis.

Table 3 give a comparison of activity concentration of natural radioactivity of phosphate rocks from different parts of the world. It can be seen from this table that the activity concentration of ^{226}Ra in this present study is relatively higher than those reported for many countries, except for Tanzania, while the average activity concentration value for ^{40}K falls within the same range as that reported in literature, except for Algeria that is relatively lower. The activity concentration value of ^{232}Th reported for Egypt, Tanzania and Algeria are however higher than that reported in this present study.

Numerous propositional criteria abound in literature for estimating environmental and human hazard due to radiation exposure (Bashir et al., 2013; Sabiha-Javied et al., 2010; Tufail, 2012). ^{226}Ra , ^{232}Th , and ^{40}K are not distributed uniformly within the soils and other environmental samples. A common radiological index, the radium

equivalent activity (Ra_{eq}), which therefore, compare the activity concentrations of the above three radionuclides and their associated radiation hazards, has been defined. This definition is consequent upon an assumption that 370 Bqkg^{-1} of ^{226}Ra , 259 Bqkg^{-1} of ^{232}Th and 4810 Bqkg^{-1} of ^{40}K produce the same gamma dose rate (Abbady, 2005; Cevik et al., 2010; Saueia et al., 2005). Ra_{eq} is calculated using the equation (Beretka and Mathew, 1985; Yu et al., 1992):

$$\text{Ra}_{\text{eq}} (\text{Bqkg}^{-1}) = A_{\text{Ra}} + 1.43A_{\text{Th}} + 0.077A_{\text{K}} \quad (2)$$

Where, A_{Ra} , A_{Th} and A_{K} are the respective activities of ^{226}Ra , ^{232}Th and ^{40}K in Bqkg^{-1} .

The total air absorbed dose rate, D (nGyh^{-1}), 1.0 m above the ground, from outdoor external exposure to natural radioactivity for the population living in the phosphate bearing areas is calculated using the formula (UNSCEAR, 2000):

$$D = 0.462A_{\text{Ra}} + 0.604A_{\text{Th}} + 0.0417A_{\text{K}} \quad (4)$$

Where, A_{Ra} , A_{Th} and A_{K} are the respective average activity concentrations (Bqkg^{-1}) of Ra, Th, and K in the phosphate rock samples.

Jibiri et al. (2007), reported that absorbed dose rates does not give a direct representation of exposure risk of an individual. To estimate the annual effective dose equivalent to an individual from outdoor terrestrial gamma radiation, UNSCEAR (2000), proposed two conversion factors: 0.7 Sv.Gy^{-1} as conversion coefficient from absorbed dose in air to effective dose received by adults, and 0.2 as outdoor occupancy factor, signifying that 80% of time is spent indoors across the world. The annual effective dose equivalent (AE) is estimated using the equation (UNSCEAR, 2000):

$$\text{AE} (\text{mSvyr}^{-1}) = D \times T \times \xi \quad (5)$$

Where, D (nGyh^{-1}) is the absorbed dose rate, T ($= 0.2 \times 24\text{hr} \times 365$) is the outdoor occupancy time, and ξ ($= 0.7 \times 106 \text{ SvGy}^{-1}$) is the conversion factor.

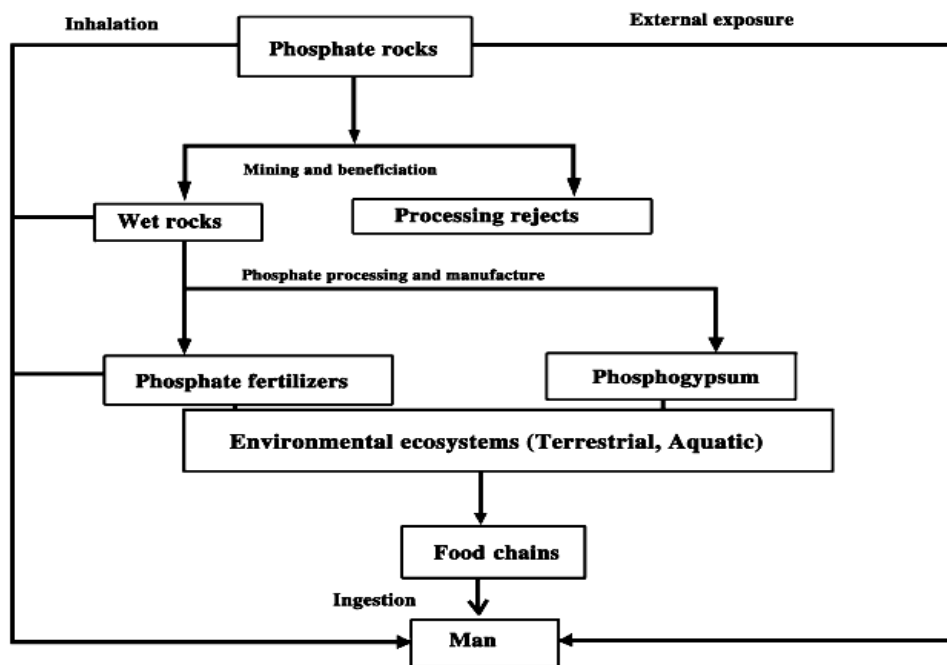


Figure 2. Environmental pathways of natural radionuclides from phosphate rocks.

Table 2. Mean values of total absorbed dose rate (D) and annual effective dose equivalent (AE) of Sokoto phosphate rock sample.

Sample ID	Ra _{eq} (Bq/kg)	D (nGy/h)	AE (mSv/yr)
DNG	722.2 (656.3-778.9)	334.5 (303.2-361.5)	0.4 (0.4-0.4)
KDR	1182.4 (1135.6-1234.0)	547.5 (526.1-570.6)	0.7 (0.6-0.7)
DLG	876.1 (748.3-942.3)	406.9 (347.9-436.9)	0.5 (0.4-0.5)
WRN	558.9 (502.6-664.6)	259.6 (233.1-309.4)	0.3 (0.3-0.4)
DNK	621.7 (545.6-672.8)	288.3 (252.0-312.9)	0.4 (0.3-0.4)
Av. Range	792.3 (502.6-1234.0)	367.3 (233.1-570.6)	0.4 (0.3-0.7)

The two basic environmental pathways by which radiation dose from phosphate rocks are imparted to the general public and phosphate workers in particular are the external and internal exposures represented in Figure 2 (Khater et al., 2001).

The calculated results for radium equivalent activity (Ra_{eq}), total absorbed dose rate in air (D) and the annual effective dose equivalent (AE) are presented in Table 2. Phosphate rock samples from Kindiru (KDR) recorded the maximum value of Ra_{eq} activity (1182.4 Bqkg^{-1}), while phosphate samples from Wuruno (WRN) had the minimum Ra_{eq} activity value of 558.9 Bqkg^{-1} . The mean value of Ra_{eq} across the entire study areas is 792.3 Bqkg^{-1} which is higher than the safety limit of 370 Bqkg^{-1} recommended by the Organization for Economic Cooperation and Development (NEA-OECD, 1979).

The total absorbed doses calculated from the measured activities of phosphate samples varies from 259.6 nGyh^{-1}

for WRN samples to 547.5 nGyh^{-1} for KDR samples, with a mean value of 367.3 nGyh^{-1} . These high dose rate values witnessed across the entire study areas may not be unconnected with the high radium contents of the phosphate rocks. The mean value of the total absorbed dose rate as seen in Table 2 is almost 3.6 times the maximum value of the world's soil background level of 102 nGyh^{-1} proposed by UNSCEAR (2000), which shows the severity of radiation risk the inhabitants of the study areas are exposed to. The computed values for the annual effective dose equivalent in the studied phosphate rock samples as presented in Table 2 varies from 0.3 mSvyr^{-1} for WRN sample to 0.7 mSvyr^{-1} for KDR samples, with a general mean value of 0.4 mSvyr^{-1} . These values are found to be lower than the safety limit of 1 mSvyr^{-1} recommended by the International Commission on Radiological Protection (ICRP-60, 1990). A plot of radium equivalent activity and average dose rates with their res-

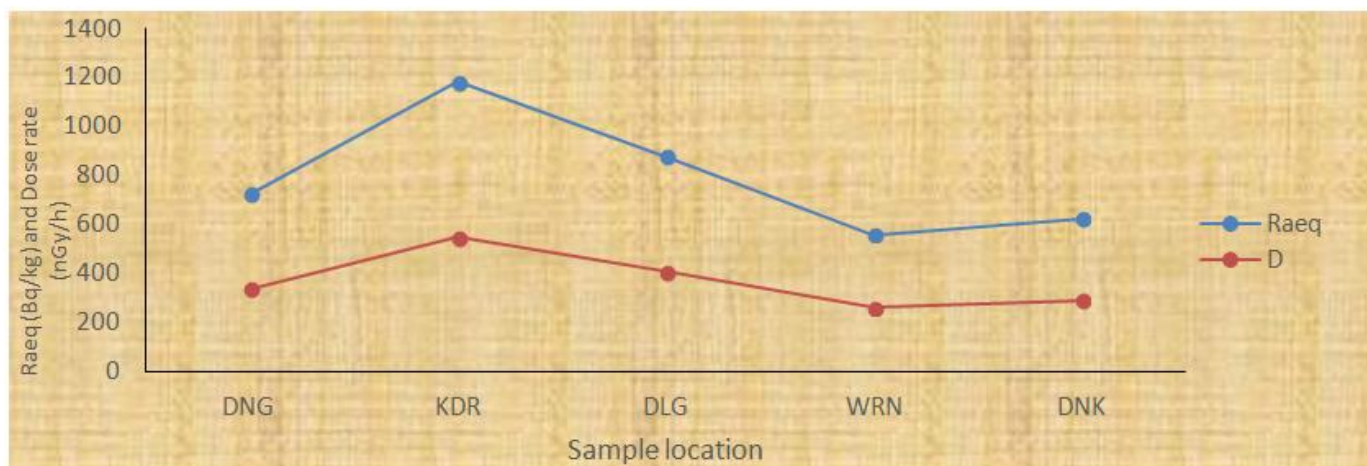


Figure 3. Radium equivalent and average dose rates for phosphate rock samples from different locations.

pective sample locations are shown in Figure 3. These values are higher than the respective recommended safety limits, which presents a serious radiation risk to the inhabitants of the study areas, especially when the untreated phosphate rocks are used generally by the local farmers as substitute for fertilizer. Women and children within the study areas are at greater radiation risk from internal dose due to inhalation of radon and dust during mining and blending of phosphate rocks for direct application to plants. Detail study of this exposure pathway is therefore recommended so as to estimate the occupational radiation dose in these phosphate bearing areas of Sokoto state and to enforce restrictions and precautionary measures where necessary, from the view point of radiation protection.

Conclusion

The results of this preliminary radiological investigation of Sokoto phosphate rocks clearly demonstrates the radiological burden an average member of phosphate bearing communities are exposed to. The obtained results show that ^{238}U and its decay daughters are the primary contributors to the radioactivity level of phosphate bearing formations of Sokoto State. The computed values of external radiation exposure from natural radioactivity of phosphate rocks show that the radioactivity of Sokoto phosphate rock samples is above the proposed safety limit of 1 (370 Bqkg^{-1}), which demonstrates the severity of radiation risk the local farmers are exposed to especially when using the untreated ground phosphates as fertilizer. It is also obvious that phosphate industry, among other geological materials' processing industries, play a significant role in the radiation dose received by the public. The data obtained from this investigation under-

scores the need for in-depth radiological assessment of all the phosphate bearing communities in Sokoto State. Underground water supplies and local building materials from these communities should be investigated for their contribution to the radiation dose incurred by the general public.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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