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Proceedings: Atanda, O. A. Awoderu, V. A. and Dina, S. O. (1977) Plant protection in the Sahelian Zone of Nigeria. In Proc. Of the Government Consultation on Crop and Post-Harvest protection needs in the Sahel, FAO Headquarters, Rome 13 – 17 December, 1976 AGP/CPS/76/WP55pp 20 – 25.

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Abundances of Nitrates and Coliform with Regards to Water Quality In Some Parts of Ibadan, Southwest, Nigeria.

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ABSTRACT

Water pollution has been reported throughout the world and Nigeria is not an exception. A very wide range of pollutants have been recognized, including Nitrogen species and bacteria. Nitrate (NO_3) is the main form of Nitrogen which occurs in water and is becoming increasingly widespread because of agriculture activities, the disposal of sewage and wastes. This study thus focused on the assessment of the water samples in Ibadan, Southwest, Nigeria based on these two pollutants (NO_3) and Colform) and possibility of natural de-nitrification in the study area. The surface and groundwater in Ibadan have been polluted by municipal, industrial wastewater, agricultural activities among others. The nitrate and coliform concentrations at thirty sampling points within Ibadan ranged from 5.89 to 250mg/l and 74-1000cfu/100mg/l respectively. The concentration of nitrate and caliform exceeded the WHO limit of 10mg/l and 0cfu/100mg/l in 93% and 100% of the sampled locations respectively. High nitrate and caliform levels were observed in water from wells from the undeveloped part of the study area. The decrease in nitrate concentration viz a viz an increase in both HCO_3- and pH along the groundwater flow direction confirmed the possibility of nitrate removal or natural de-nitrification in the study area.

Key words: Water; Nitrate; Pollution; Coliform; De-nitrification.

Introduction

Groundwater pollution in a number of aquifers throughout the world has been reported, and a very wide range of pollutants including N species, heavy metals, chlorinated hydrocarbons, phenols, cyanides, pesticides, major inorganic species and bacteria has been recognized. Nitrate (NO_3) is the main form of N which occurs in groundwater while Coliforms which is a form of bacteria is the commonest in water. The concentration of coliform bacteria is commonly used as a general bacteriological indicator of water quality standards. The coliforms are a functional group of intestinal bacterial from warm blooded animals. It is used here as an indicator for feacal contamination and a tracer for more highly pathogenic bacteria which occur at lower concentraion. Both are becoming increasingly widespread because of agricultural activites, disposal of sewage and domestic wastes. High solubility of nitrate and its anionic form increase its mobility in groundwater. In strongly oxidizing groundwater, nitrate is the stable form of dissolved nitrogen. It moves in groundwater with no transformation and little or no retardation (Freeze and Cherry, 1979).

Ibadan is one of the fast-growing industrialized cities in Africa (Fig1). The population of the city has also increased tremendously in recent times. In conjuction with the fast developement, water use has also increased. This region became heavily populated and large industrial centres and intense agricultural developed. Most of the municipal and industrial wastes are disposed directly into the rivers. Neither sewage nor solid waste is controlled. The groundwater of Ibadan, Southwest Nigeria has been polluted by municipal and industrial wastewater disposal into the River and irrigation channels, storage of the domestic wastewater in septic tanks and agricultural activities.

STUDY LOCATION AND GEO-ENVIRONMENTAL SETTING

The study area falls within the Northern part of Ibadan metropolis and located on longitude 3°45'-4 03' and latitude 6° 45'-7°30' (Fig 1). The study area falls within the humid and subhumid tropical climate of Southwestern Nigeria with two distinct season: the wet season which occurs between March and October with an average annual rainfall of about 1.250mm and dry season from November to February characterized by dry, dusty and relatively cold NE-SW trade winds. Ibadan metropolis is characterized by high population density. However, like many urban centres in developing countries, Ibadan metropolis is characterized by poor environment planning such as lack of proper sewage and waste disposal systems, lack of adequate water supply and sanitary conditions and direct discharge of domestic sewage water and dumping of domestic refuse into the drainage channels are common practices especially within the congested central portion of the city. Geologically, the study area is characterized by Precambrian Basement Complex composed of quartzites, gneisses and migmatite as the major rock types which are intruded by pegmatites, quartz veins, apiltes and dolerite dkyes (Olayinka *et al.*, 1999 Tijani *et al.*, 2004). These intrussions occur as ridges and inselbergs around the adjoining plains and valleys. The overburden is dominated by weathered saprolite units and the thickness depends on the underlying bedrock. Groundwater occurences are essentially unconfined to semi - confined which depends on the phreatic weathered regolith and presence of joints and fractures in the fresh rock. Morphologically, the unmodified drainage channels form dendritic patterns and run in a southerly direction through much of the city centre (Fig.2). Water flows are irregular during the dry seasons, while population pressure had resulted in built-up areas closer to the stream banks and attendant human activities with increasing run-off constituting constant danger in terms of flooding during the peak of the rainy season

Methodology

Water samples were collected from groundwater and streams within the study area to determine the abundances of nitrates and coliform with regards to their quality (Fig.1). In situ measurements and laboratory analyses were carried out. Groundwater samples were collected from hang dug wells and streams. Temperature *(T)*, pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured in the field. Nitrate analyses of the water samples were carried out using an automated hydrazine reduction method performed on a continous flow analyzer system (ALPHA/AWWA/WEF 1995). Nitrate is reduced to nitrite by hydrazine sulphate in the presence of Copper sulphate. The resulting nitrite plus any nitrite originally present in the sample is diazotized with Sulphanilamide and forms a colored complex with N- (1-naphthyl) - ethylenadia - mine dichloride. The colored complex is measured colorimetrically at 520nm. This method is applicable to samples having nitrate concentrations between 1 to 50mg/L.

Waters samples having nitrate concentrations greater than 50mg/L were diluted to fall within the range of the calibration curve.

30 samples were collected from groundwater. Sampling wells were selected to represent the entire study area. The water samples were collected in sterilized 1.0ml bottles and transported immediately to the laboratory to determine concentration of coliform bacteria. The filtration processes for bacteriological analyses were made within 2 hours from collection. Indicators were determinded using classic methods of water filtration (1.0ml of samples and/or its dilutions) on sterile membrance filters (GN-6 Mertical, pore size 0.45 lm, Pall), with incubation on Endo- Agar LES (BBL) for 24 hours at 35p C for total coliform. All counted colonies were adjusted to 100- ml volume of water.

Results and Discussions

30 groundwater samples were analysed to determine the concentration of Nitrate, coliform and other cations and anions around Ibadan Southwest Nigeria. Other parameters like pH, dissolved oxygen, temperature and total dissolved solids were also determined. Table 1 shows that nitrate ranges between 5.89 to 250mg/l with the mean of 72.61mg/l. coliform ranges between 74 and 1000cfu/100ml with average of 323.3mgl/l, TDS ranges between 50mg/l with an average of 399.5mg/l. pH, dissolved oxygen and temperature show mean values of 7.01, 4.53 and 26.43°C respectively. The Dissolved Oxygen concentration was 3.3 to 7.3mg/l. TDS ranges between 300 and 1500mg/l. Cations and Anions follow the following order; $Na^{+} > Ca^{2+} > K^{+} > Mg^{2+}$ and $Cl^{-} >$ and $NO_3^{-} > HCO_3^{-} > SO_4^{2-}$ respectively. The summary is shown in Table 2.

Pattern of Nitrate pollution

The concentrations of nitrates found in thirty groundwater samples were listed in Table 1. Nitrate and coliform were detected at concentrations exceeding WHO (2004) and EPA (2005) standards (10mg/l and 0Cfu/100mg/l) in 93% and 100% of water samples respectively. Based on the percentile analysis of the nitrate and coliform concentrations (Table 3) 36.67% and 33.3% of the water samples contained concentrations between 11-45mg/l and 250-500cfu/100mg/l respectively and represent the highest percentage. The lowest percentage which is 6.67% fall within <10mg/l for nitrate and 13.33% which represent 101-150cfu/mg/l for coliform. (Fig2). The average nitrate concentration for the study area was 75mg/l, and 93% of all the samples exceeded the upper limit of 10mg/l (WHO @2004, EPA 2005). Examination of the current pattern of nitrate pollution clearly showed that high nitrate and caliform concentratin were found in shallow wells and those sited close to the septic tanks and other municipal wastes as well as agricultural areas (Table 3). Generally, low nitrate concentrations tended to be from those wells from the developed part of the city. Improper construction, sitting, installation, and maintenance of the septic tanks, as well as factors such as depth to groundwater, climate, geology of the site, and septic tanik density influence the potential of septic tanks to pollute groundwater. The improper location of wells with respect to septic tanks will increase the potential for the leaching of effluents to the well and groundwater system (Piskin 1973).

Correlation analysis of major constituents

From the correlation analysis in Table 4, three main observations can be summarized as follows;

1. The strong positive relationship between NO , SO CL and coliform. All of these constituents indicated pollution and their sources were probably from septic tanks and applications of the chemical fertilizer $(NH_4)_2SO_4$ in the farm around the study area. NH within a nitorgen fertilizer is transformed in the soil into NO and H by the following nitrification process:

$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$

2. The negative relationship between NO_3 on one side and other parameters such as TDS, Na^+, K^+, Mg and Ca . This confirmed the anthropogenic source of nitrate which is different from other ions whose sources are likely from the bedrock (geology) of the study area.

3. The strong negative correlation (-0.61) between NO_3 and HCO_3^- compared to the insignificant relationship with Na^+, K^+, Ca^{2+} and Mg^{2+} (-0.18, -0.02, -0.18 and 0.18 respectively). This revealed that the presence of HCO_3^- in the ~~groundwater of the study area is closely linked to the~~ removal of NO_3 from the system as a bi-product of the heterotrophic de-nitrification process and not to natural dissoltion from soil or rock (Trudell et al., 1986; Van Beek and Van Puffelen, 1987).

$5C + 4NO_3 + 2H_2O = 2N_2 + 4HCO_3 + CO_2$ (Kolle *et al.* 1983)

Evidence of De-nitrification in the groundwater system

In order to determine whether the de-nitrification process is already taking place in the groundwater aquifer of the study area some of the water parameters such as HCO_3^- pH and SO_4 were plotted along the groundwater flow directions. To ensure existence of de-nitrification, there must be presence of elctron donor and acceptor and organic carbon (OC) as an electron donor. SO_4^{2-} was found to decrease along the direction of groundwater flow (Fig 4) contrary to what should be the case if the electron donor was sulfide (Korom, 1992). Organic carbon (OC) can be supplied to groundwater in two ways. One is where organic carbon is artificially injected into the acquifer while the other is when groundwater interacts with surface water or the root of vegetation. Generally, the majority of all groundwater have dissolved organic carbon (DOC) < 2mg/l (Thurman, 1985).

Change of NO3 and HCO3

There was negative correlation between HCO_3^- which is the main product of the heterotrophic de-nitrification reaction and NO_3^-. The HCO_3 concentraion increases (produced) while NO_3 concentration decreases (removed) along the flow direction of groundwater (Fig 4). This can be properly explained by the equation above.

Change of pH

The pH increases along the flow of groundwater direction while the concentration of NO_3 decreases along the same direction and this also could be attributed to the removal of nitrate by de-nitrification (Fig 4).

Conclusion

All the parameters analyzed in the groundwater around Ibadan were within both WHO and EPA standards for drinking water except coliform and nitrate. Nitrate and Coliform were detected at concentrations exceeding WHO (2004) and EPA (2005) standards (10mg/l and 0cfu/100mg/l) in 93% and 100% of water samples respectively.

The decreases in nitrate concentrations viz a viz an increase in both HCO_3^- and pH along the groundwater flow direction confirmed nitrate removal or natural de-nitrification in the study area groundwater aquifer. High nitrate concentrations in water supplies are potential hazards to infant health. The consumption of waters with high nitrate concentrations decreases the oxygen carrying capacity of the blood while coliform is responsible for most of the water borne diseases.

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IOC

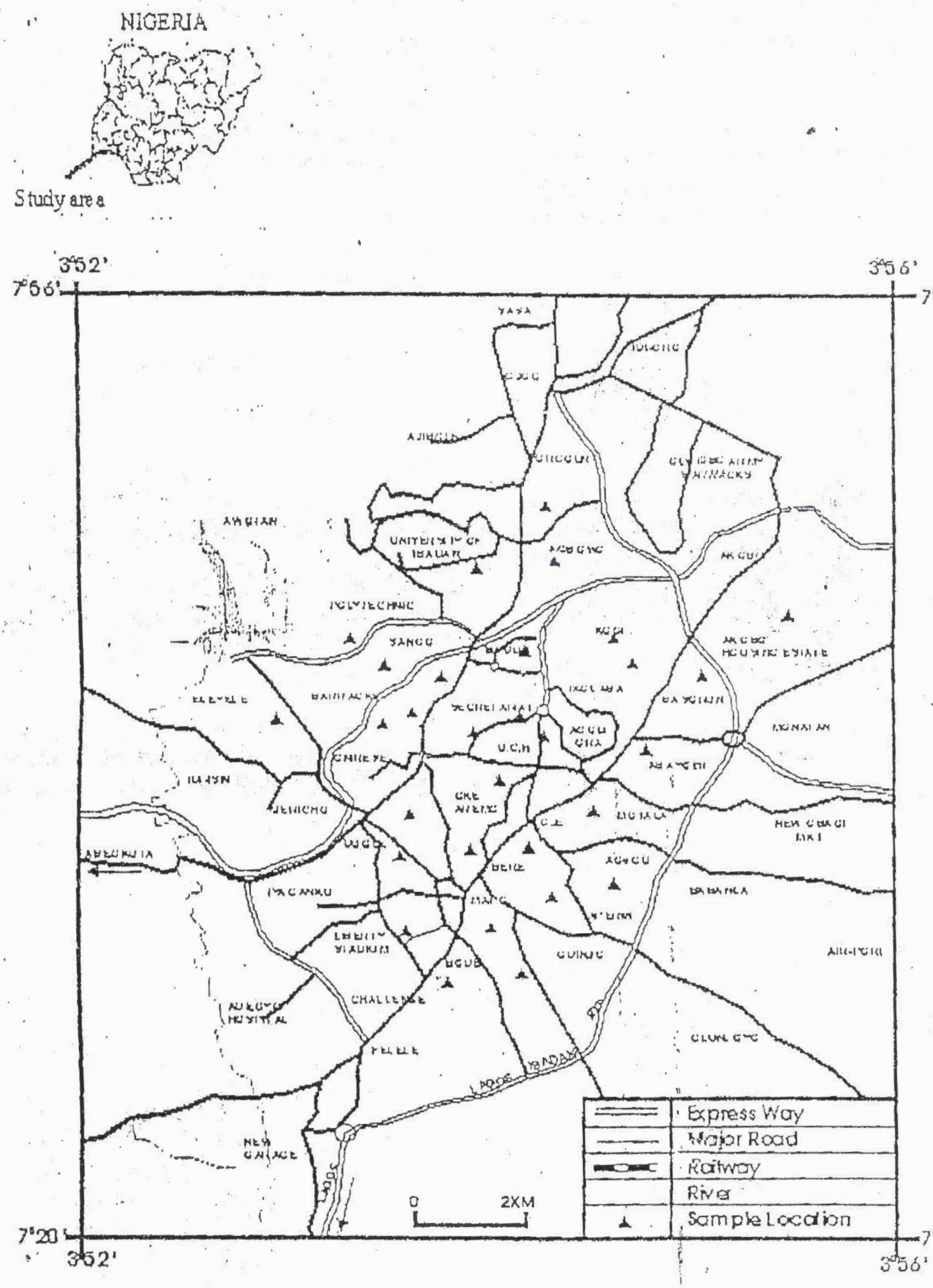

Fig 1: Map of the study area showing sample points

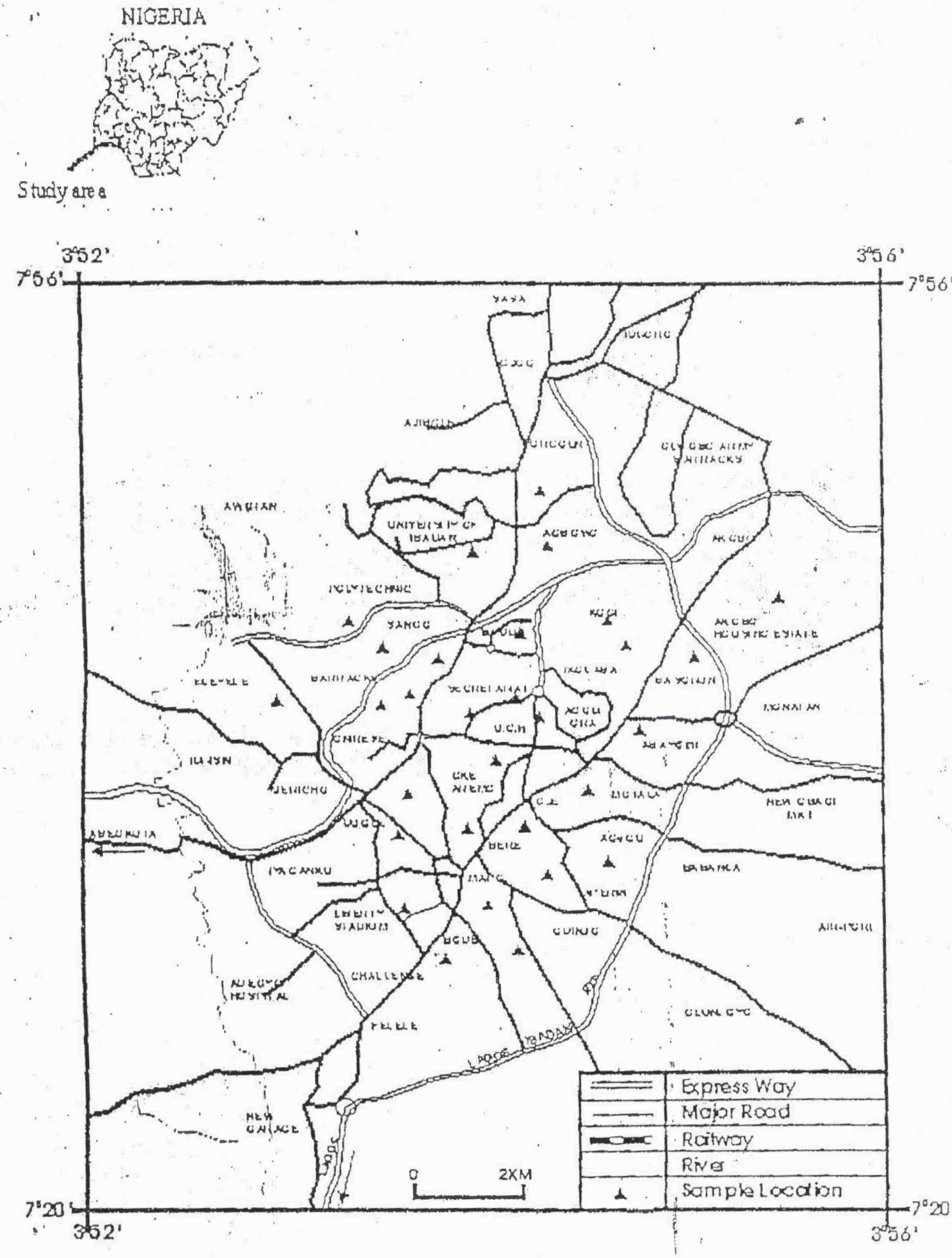

Fig 1: Map of the study area showing sample points

Table1. Results of Physico-chemical analysis in water samples

mple	Coliform	Nitrate	TDS	DO	pH	Temp °C	HCO_3	Cl	SO_4	Ca	K	Na	Mg
1	80	32	300	3.7	6.2	25	28	127	33	9.6	10.9	18	4.2
2	120	74	800	3.6	6.4	26	77	72	34	12.2	11.8	23.8	3.5
3	100	65	850	3.5	7.4	27	54	181	19	12.5	12.6	28	5.3
4	160	52	500	3.9	7	25	53	85	18	8.4	11.4	38	4.4
5	150	28	900	4.2	6.8	29	54	101	34	12.2	10.8	25	4.6
6	80	20	600	4.8	7.2	28	22	82	24	12.5	9.3	27	2.6
7	280	90	280	3.9	6.9	25	64	70	10	8.4	6.4	38	4.2
V8	74	5.89	1000	4.8	6.8	25	75	127	12	12.2	8.9	23.6	4.4
V9	280	23.43	200	3.8	6.5	26	74	28	19	5.2	10.1	55	5.4
V10	440	28.82	1200	3.3	7.2	25	50	106	25	12.4	11.2	46	4.8
V11	120	11.85	120	4.6	7.4	28	51	95.5	10	19.6	10.9	25	3.8
V12	280	37.24	280	3.4	7.8	27	62	136	10	12.6	6.3	50	4.2
V13	80	7.84	50	3.6	7.6	22	36	54.5	26	10.8	5.68	66	3.6
W14	160	43.22	160	4.8	6.9	27	78	127	14	17.6	8.74	65	4.0
W15	120	17.51	120	4.4	6.8	26	29	37.5	18	18.5	6.49	55	3.0
W16	90	12.41	90	5.2	7.1	25	52	69.5	14	27.9	7.8	36	3.8
W17	180	35	180	6.6	6.9	28	30	85	10	20.5	10.9	35	3.6
W18	550	120	550	6.8	6.8	30	28	212	22	18.6	11.6	21	3.4
W19	155	89	155	7.2	7.3	28	48	132517		47.4	11.4	11	2.5
W20	450	87	450	3.5	7.3	25	62	172525		48.4	8.5	53.4	4.5
W21	300	98	80	3.6	6.9	26	21	54.5	33	36.4	17.5	34	3.4
W22	800	150	120	4.6	6.8	27	20.6	120545		24.4	12.4	42	4.3
W23	850	220	100	4.8	7.2	26	37.2	75.5	16	26.8	11	32	2.8
W24	500	56	160	5.6	7.4	30	20	82.5	25	14.4	10.5	38	2.4
W25	900	213	150	7.3	6.5	25	11.5	77.2	15	9.3	12.5	42	1.8
W26	600	125	280	4.5	6.8	26	12	53	34	16.3	17.6	53.4	2.2
W27	280	65	70	3.8	7.3	25	28	137	25	26.2	36.3	21	3.2
W28	1000	250	440	3.3	7.4	26	43	73.0	18	8.5	16.4	34	6.4
W29	200	56	300	4.6	6.9	27	56	23.7	23	8.6	24.4	54	4.6
W30	320	65	1500	4.2	6.8	28	98	78.6	32	6.8	14.6	42	3.4

*All parameters in mg/l except coliform that is in cfu/100ml

Table 2: Summary of Physico-chemical results of water samples

Parameters	Min	Max	Mean	ST.Dev.	WHO (2004)	EPA (2005)
pH	6.2	7.8	7.01	0.37	6.5-7.5	6.5-7.5
TDS	50	1000	399.5	373.4	1000	500
DO	3.3	7.3	4.53	1.14		
Temp	25	30	26.43	1.72		
Ca	5.2	48.4	17.57	10.99	200	75
K	5.68	36.3	12.16	5.98		
Na	11	66	37.7	14.18	200	200
Mg	1.8	5.4	3.81	1.02	200	50
HCO3	11.5	98	45.8	22.03		
Cl	23.7	212	95.88	44.53	250	250
SO4	1O	45	22	8.98	400	250
NO3	5.89	250	72.61	64.25	10	10
Coliform	74	1000	323.3	269.6	0	0

Table 3: Percentile Analysis of Nitrate and Coliform in water samples

Nitrate			Coliform		
Concentration (mg/l)	No of samples	Percentile	Concentration Cfu/100ml	No of samples	Percentile
<10	2	6.67%	0-100	06	20%
11-45	11	36.67%	101-150	04	13.33%
46-70	05	16.67%	151-500	14	46.66%
71-100	05	16.67%	501-1000	06	20%
101-200	04	13.33%			
201-250	03	10%			
Total	30	100	Total	30	100

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W17	180	35	180	6.6	6.9	28	30	85	10	20.5	10.9	35	3.6
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Ca	5.2	48.4	17.57	10.99	200	75
K	5.68	36.3	12.16	5.98		
Na	11	66	37.7	14.18	200	200
Mg	1.8	5.4	3.81	1.02	200	50
HCO3	11.5	98	45.8	22.03		
Cl	23.7	212	95.88	44.53	250	250
SO4	1O	45	22	8.98	400	250
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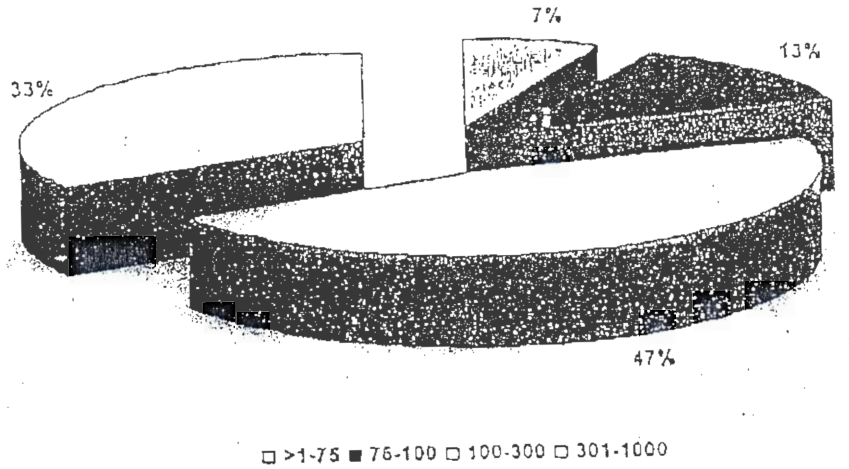
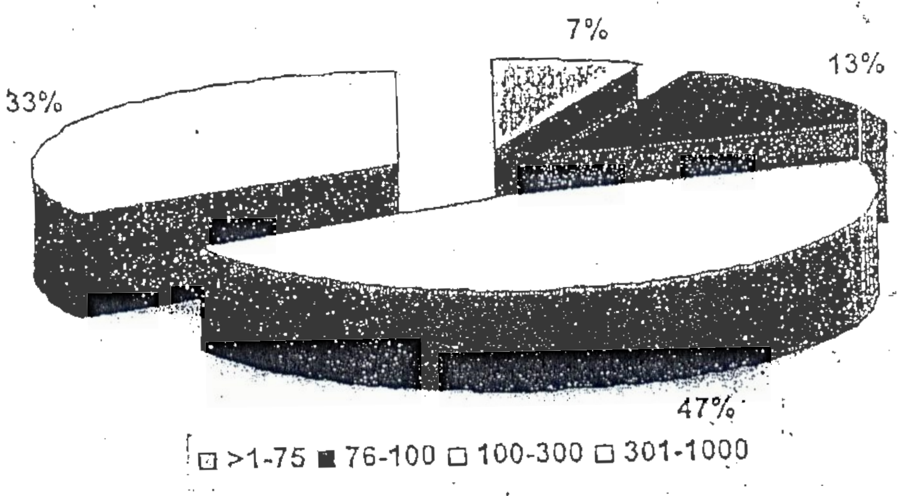
46-70	05	16.67%	151-500	14	46.66%
71-100	05	16.67%	501-1000	06	20%
101-200	04	13.33%			
201-250	03	10%			
Total	30	100	Total	30	100



Nitrate



Coliform

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Fig 3: Distribution of Nitrate and Coliform in different percentages. Nitrate in mg/l, coliform in cfu/100ml