

WATER QUALITY ASSESSMENT OF OSUN RIVER: STUDIES ON INORGANIC NUTRIENTS

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Abstract. The present investigation provides data of some ions, namely Na^+ , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- , CN^- and PO_4^{3-} on water samples of river Osun, selected rivers in the region and groundwaters. The pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH) and total carbon (IV) oxide (TCO_2) have also been determined to assess the chemical status and pollution levels of these water sources. The higher values of certain parameters with respect to the acceptable standard limits for drinking water indicate the pollution in both groundwater and river water samples of the study area, and make the waters unsuitable for various applications. The high pollution river water source showed higher levels of phosphate, nitrate and ammonium ions ($P < 0.05$). There is no significant difference ($P < 0.05$) between the mean concentrations of other inorganic nutrients in the high and low pollution water source types. The correlation coefficient between quality parameter pairs of river water and groundwater samples are determined and the significance of these parameters in both types of water sources are discussed.

Keywords: atomic absorption spectrophotometer and flame photometry, inorganic nutrients, rivers, technicon's autoanalyzer, water quality assessment

1. Introduction

The importance of environmental quality in Osun State (Southwestern Nigeria) generally, and in Osogbo (an urban area) in particular has recently attracted a great deal of interest. The population density of the study area in 1991 was about 183,223; in 1996 about 209,139 and in 1998 about 557,707. By the next millennium, it may exceed 1 million [NPC, 1991]. Water and land, the vital resources of life, are increasingly being polluted in the wake of popular growth, poor land use system, agricultural activities, industrialization and anthropogenic impact on the study area.

The effect of poor water quality on human health was noted for the first time in 1854 by John Snow, when he traced the outbreak of cholera epidemic in London to the Thames river water which was grossly polluted with raw sewage. Since then, the science of water quality progressed. In the third world countries, 80% of all diseases are directly related to poor drinking water and unsanitary conditions (Sharma *et al.*, 1995). The industrial units located at the outskirts in cities, intens-



ive agricultural practices and indiscriminate disposal of domestic and municipal wastes are the sources for the river water and groundwater pollution. Thus constant monitoring of river water and groundwater quality is needed so as to record any alteration in the quality and outbreak of health disorders.

Due to urbanization, rapid population growth in Osogbo, the State Capital of Osun State, Nigeria, the extent of surface water pollution along the downstream of the river ranges from moderate to serious. The principal objective of the present study is to examine the chemical status and pollution levels of the waters of the study area with respect to ions, namely Na^+ , Ca^{2+} , NH_4^+ , Cl^- , CN^- , PO_4^{3-} and NO_3^- and pH values, temperature, total dissolved solids, total hardness, electrical conductivity and total carbon (IV) oxide, and hence to ascertain the nutrient value of these elements in water.

2. Materials and Methods

2.1. SAMPLING

A short term field survey of Osun river was carried out in order to locate the important sources of pollution. Stations for the collection of river water samples include locations along all the tributaries that enter the river as well as the main stem of the river (Figure 1). The river was sampled on three occasions: May 28, 1998; June 30, 1998 and August 26, 1998.

Station 1, which is river Asaba (RAI) is located on the north branch of the river, just upstream of river Osun. Station 2 is river Ogbaagba (RO2), located on the north-west side of the river while stations 3 and 4 (i.e. WE3 and WE4 respectively) are groundwater stations, located near river Osun; these wells are at the same water table with Osun river, and serve as the current water supply for residents and businesses of people in the area. Station 5 is the river Osun (RS5), located on the western part of Osogbo town, the capital of Osun State, Nigeria. Stations 6 and 7 are rivers Okoko and Ajibu (i.e. RK6 and RB7 respectively), also tributaries to river Osun, and are located on the south-east branch of the river. These stations serve as the main source of water for people residing downstream. Station 8 is river Elekunkun (RE8), located on east branch of the river.

River water samples were taken from the surface of the river (upper 50 cm) and groundwater samples at two well locations near the river Osun using a 2 dm³ capacity teflon container that had been pre-rinsed with organic solvents and acid leached. Samples were taken at each station (Figure 1) nine times over the course of a 24-hr period; that is about three hours apart. All sampling stations were located between 150 and 200 m away from industrial or municipal discharge points. Storage and treatment of water samples were done according to Fresenius *et al.*, 1988 and APHA (1989).

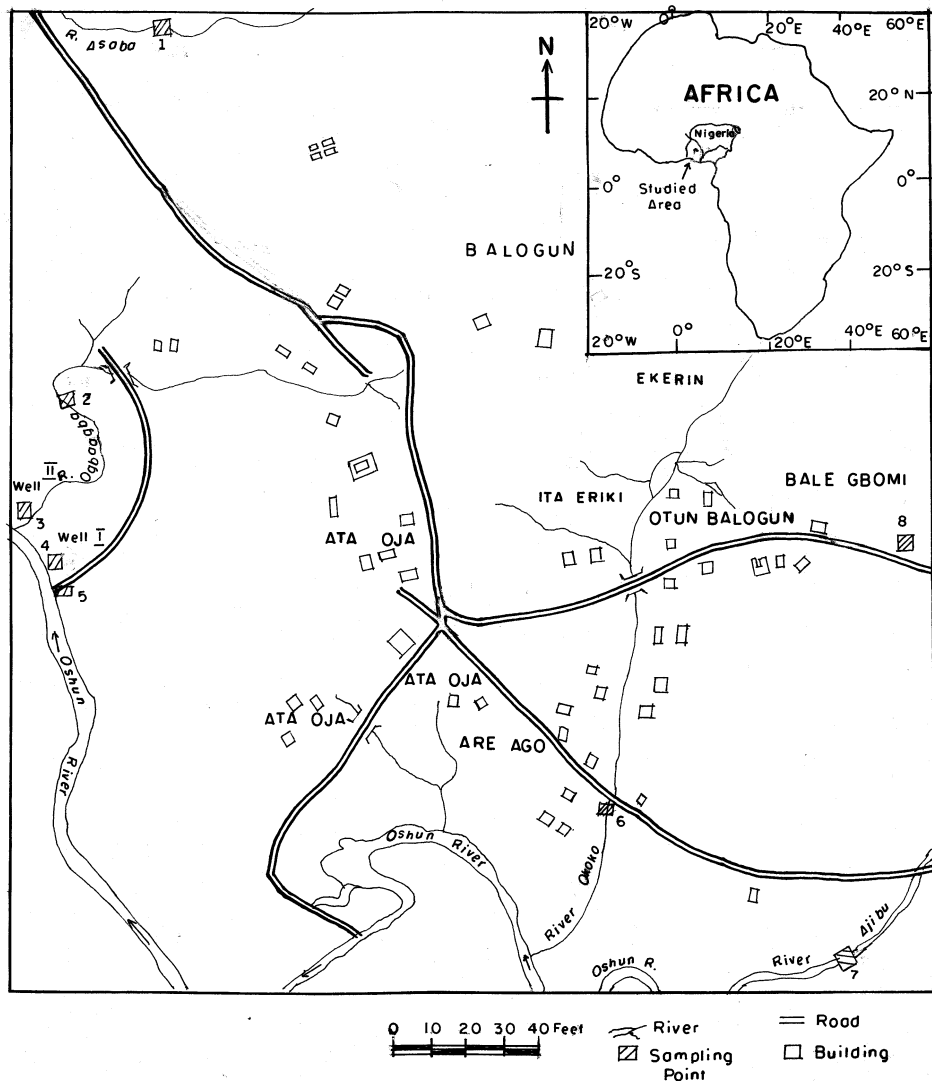


Figure 1. Map of Osogbo showing sampling locations.

2.2. ANALYTICAL METHODS

The pH, electrical conductivity and temperature were measured at sampling site using potable meters. The water samples were analyzed for phosphate, cyanide, nitrate and ammonia (measured as ammonium ion) concentrations using a Technicon AA 11 Autoanalyzer (Technicon Instrument Corporation, Tarrytown, New York, U.S.A.) while the concentrations of total dissolved solids, total hardness, total carbon (IV) oxide and chloride were determined by using the standard methods [APHA, 1989; Trivedi and Goyal, 1986; Suess, 1982; Jain and Bhatia, 1987].

2.3. METAL IONS ANALYSIS

The water samples (500 cm³) were acidified with 10 cm³ of concentrated nitric acid and concentrated to 25 cm³ using evaporation method (Parker, 1972). After chelation, extraction and subsequent mineralization, calcium ion was determined by atomic adsorption spectrophotometer and sodium ion was determined by flame photometry. The instruments were operated as per the instrument's manual. The blank was used for zeroing the instruments before each analysis.

2.4. ANALYTICAL PRECISION

The reproducibility of the analytical procedures were checked by carrying out a duplicate analysis. Duplicate results did not differ by more than 5% of the mean. Replicability of sampling was determined by collection of multiple samples at station 5. Briefly, 9 samples were collected over a two-hour period and were combined to give three samples that were time averaged over the collection interval. These samples were analyzed in duplicate for water quality parameters. The overall variability ranged from 2.68% r.s.d. for temperature to 16.5% r.s.d. for phosphate ion concentration with the average sampling variability being 10.5%.

3. Results and Discussion

The sampling locations including two wells are shown in Figure 1. The determined values of quality parameters of the water samples are given in Tables I–IV, while Table V shows the recommended water quality criteria. The analytical results given in these tables are the means (and standard deviations) and the ranges of data for 9 samples taken from each location for the three sampling dates. The present investigation of the water samples studied indicates that the water is alkaline in nature. Though it has no direct effect on human health, the recommended value (Table V) for drinking purpose is 7.0 to 8.5 [WHO, 1984 and ISI, 1983]. The average pH values (Table I and II) varied from 6.35 (WE4) to 7.62 (RK6) during May survey; 5.91 (WE4) to 7.44 (RS5) during June survey and 7.13 (WE4) to 8.90 (RA1) during August survey. The pH values of most of the water samples studied on the three surveys fell within the permissible limit except for samples WE4 (6.35) collected during May survey; WE3 (6.09) and WE4 (5.91) collected during June survey that were acidic. The low pH values may be partly due to high content of humic acids in the groundwater. Also sample RAI (pH = 8.90) collected during August survey has a pH value that is greater than the upper limit of 8.5. This might be due to exposure to air (surface water) which results in loss of carbon (IV) oxide and thus gives rise to high pH observed with the sample. Temperature is a measure of the degree of hotness or coldness of a substance. Its determination is important because of its effect on other physical phenomena such as rate of biochemical and chemical reactions in the water body, reduction in solubility of gases and amplifications of

TABLE I
Values of physico-chemical parameters of river water samples for the three sampling dates

Sampling data	Sample code	Tempt. (°C)	pH	EC, 20 °C ($\mu\text{mhos cm}^{-1}$)	TDS (mg dm^{-3})	TH (mg dm^{-3} CaCO ₃)	TCO ₂ (mg dm^{-3})
May 28 1998	RA1	28.0 ^a (0.34)	7.24(1.22)	1820(270)	138(24.5)	140(24.5)	4.99(1.24)
		27.4 ^b –28.5 ^c		590–4990	89.0–167	48.6–515	2.14–7.54
	RO2	28.2(0.29)	7.26(1.18)	4980(990)	334(65.5)	157(35.6)	10.0(2.15)
		27.0–28.6		1650–9730	115–401	36.8–509	0.25–14.9
	RS5	28.4(0.45)	7.33(1.28)	7700(1560)	172(26.8)	144(25.9)	6.08(1.22)
		27.4–29.8		2820–13400	65.6–257	78.5–405	2.20–19.7
	RK6	27.8(0.33)	7.62(1.22)	5100(1020)	398(59.7)	160(23.8)	9.04(2.08)
		27.5–28.6		630–11600	106–494	54.8–458	1.78–16.5
	RB7	27.5(0.44)	7.42(1.27)	1300(280)	190(24.7)	84.6(17.8)	4.69(0.98)
		27.0–28.4		350–5910	48.2–219	27.5–399	1.15–15.8
	RE8	27.6(0.52)	7.10(0.86)	1100(410)	148(20.7)	110(25.3)	7.64(2.14)
		26.4–28.8		140–6320	35.8–276	28.2–417	1.42–14.6
June 30, 1998	RA1	28.7(0.46)	7.21(0.94)	2120(380)	192(30.7)	116(21.9)	8.99(2.34)
		26.6–29.4		450–8740	101–366	37.9–320	4.92–15.1
	RO2	28.0(0.40)	6.94(1.32)	3550(870)	264(44.2)	268(39.5)	13.0(2.90)
		27.2–28.8		880–9060	108–496	101–609	7.05–14.9
	RS5	28.9(0.48)	7.44(0.79)	5180(930)	156(18.7)	72.8(11.6)	3.85(0.96)
		27.8–29.6		120–1030	97.6–487	44.2–387	1.67–10.8
	RK6	28.0(0.45)	7.29(0.92)	3940(780)	244(40.2)	325(58.5)	12.6(2.75)
		27.0–29.5		180–8770	99.6–526	261–615	6.59–15.5
	RB7	27.6(0.59)	7.12(0.88)	1400(190)	258(41.3)	96.6(18.4)	2.60(0.82)
		26.6–28.4		230–5480	115–494	44.6–315	0.91–9.96
	RE8	27.6(0.66)	6.84(0.90)	1260(230)	146(20.5)	84.2(21.6)	6.02(1.40)
		26.0–29.6		520–9320	37.8–474	23.5–490	2.11–13.9
August 26, 1998	RA1	29.4(0.78)	8.90(1.52)	1490(250)	238(38.1)	92.6(17.9)	3.99(1.20)
		26.2–29.9		640–7990	195–502	29.7–112	1.64–8.97
	RO2	28.8(0.35)	8.33(1.44)	2220(360)	414(52.5)	128(26.9)	6.94(1.50)
		27.4–29.8		480–8050	122–697	60.2–517	0.99–13.3
	RS5	29.4(0.60)	7.58(1.63)	3630(850)	204(23.5)	68.5(14.9)	5.62(1.44)
		27.2–29.8		940–1120	95.0–452	35.6–285	1.52–12.6
	RK6	28.4(0.44)	8.32(1.11)	2860(590)	552(80.6)	288(54.7)	7.70(1.92)
		26.6–29.2		520–8610	161–894	192–677	2.08–14.7
	RB7	28.0(0.25)	7.59(0.94)	1080(130)	262(39.7)	236(45.9)	2.55(0.54)
		27.6–28.4		201–5730	106–588	110–534	0.27–8.18
	RE8	28.6(0.82)	7.55(0.83)	980(190)	188(24.9)	80.9(17.7)	6.47(1.30)
		26.4–30.2		110–6500	74.6–499	25.6–396	1.70–12.8

Values in parenthesis are the standard deviation, σ_{n-1} ; ^a means of duplicate analysis and 9 sampling; ^b minimum value; ^c maximum value, n.d. = not detected.

TABLE II
Values of physico-chemical parameters of groundwater samples for the three sampling dates

Sampling data	Sample code	Tempt. (°C)	pH	EC, 20 °C ($\mu\text{mhos cm}^{-1}$)	TDS (mg dm^{-3})	TH (mg dm^{-3} CaCO ₃)	TCO ₂ (mg dm^{-3})
May 28. 1998	WE3	28.8 ^a (0.38)	6.56(0.98)	3940(850)	510(71.4)	528(111)	14.9(3.18)
		28.0–29.6		1750–7600	202–740	187–879	4.35–16.8
	WE4	29.0(0.43)	6.35(0.86)	4050(730)	732(140)	1170(190)	10.8(4.05)
		28.0–29.4		1120–10200	329–897	589–1260	5.44–15.1
June 30. 1998	WE3	29.4(0.55)	6.09(0.76)	4380(660)	480(63.4)	499(75.6)	13.9(3.50)
		27.4–29.8		1110–10700	176–678	160–753	9.60–15.4
	WE4	29.6–(0.36)	5.91(0.66)	4630(970)	592(83.8)	896(136)	4.90(1.13)
		28.4–29.9		690–8910	161–749	319–1002	1.04–11.8
August 26. 1998	WE3	28.8(0.32)	8.06(0.95)	3740(720)	402(72.4)	488(73.2)	12.6(2.80)
		28.0–29.2		140–9550	212–752	26–813	3.25–15.4
	WE4	29.6(0.54)	7.13(1.10)	3750(600)	476(60.6)	716(82.9)	11.2(2.96)
		27.8–30.0		640–7690	120–610	24–999	4.86–14.8

Values in parenthesis are the standard deviation, σ_{n-1} ; ^ameans of duplicate analysis and 9 sampling; ^bminimum value; ^cmaximum value.

tastes and odours of water. The temperature of the water samples analyzed ranged from 27.5 (RB7) to 29.0 °C (WE4) during May survey; 27.6 (RB7 and RE8) to 29.6 °C (WE4) during June survey and 28.0 °C (RB7) to 29.6 °C (WE4) during August survey, and were within the maximum permissible limit (Tables I and II).

The electrical conductivity is a valuable indicator of the amount of material dissolved in water; and its values ranged from 1100 (RE8) to 7700 $\mu\text{mhos cm}^{-1}$ (RS5) during May sampling; 1260 (RE8) to 5180 $\mu\text{mhos cm}^{-1}$ (RS5) during June sampling and 980 (RE8) to 3750 $\mu\text{mhos cm}^{-1}$ (WE4) during August sampling with a wide range of fluctuations at different locations (Table I and II). The recommended value (Table V) of electrical conductivity for a potable water is 2500 $\mu\text{mhos cm}^{-1}$ [WHO, 1988]. The high electrical conductivity values in water samples RO2 (4980 $\mu\text{mhos cm}^{-1}$); RS5 (7700 $\mu\text{mhos cm}^{-1}$) and RK6 (5100 $\mu\text{mhos cm}^{-1}$) collected during May survey; and WE3 (4380 $\mu\text{mhos cm}^{-1}$); WE4 (4630 $\mu\text{mhos cm}^{-1}$); RS5 (5180 $\mu\text{mhos cm}^{-1}$) collected during June survey, showed they are unfit for human consumption. Total dissolved solids (TDS) indicates the general nature of water quality or salinity. Water samples containing more than 500 mg dm^{-3} of TDS is considered undesirable for domestic uses but unavoidable cases of 1500 mg dm^{-3} is also allowed. Hence 500 mg dm^{-3} is the desirable limit and 1500 mg dm^{-3} is the maximum permissible limit [ICMR, 1975]. In the present investigation, the TDS values varied from 138 (RAI) to 732 mg dm^{-3} (WE4) during May survey; 146 (RE8) to 592 mg dm^{-3} (WE4) during June survey and 188 (RE8) to

TABLE III
Concentration (mg dm^{-3}) values of ions in the river water samples for the three sampling dates

Sampling date	Sample code	PO_4^{3-}	NO_3^-	CN^-	Cl^-	NH_3 (NH_4^+)	Ca^{2+}	Na^+	
May 28, 1998	RA1	0.82 ^a (0.29)	32.8(6.89)	0.03(0.01)	70.3(15.1)	0.56(0.10)	27.8(5.67)	22.8(4.66)	
		0.22 ^b -1.14 ^c	17.8-44.2	N.D.-0.06	20.1-115	N.D.-1.06	6.97-37.5	5.82-33.6	
	RO2	0.46(0.14)	30.8(6.54)		39.7(6.52)	7.76(1.68)	18.7(4.55)	17.6(3.64)	
		0.18-0.64	14.8-40.9	$< 5.0 \times 10^{-3}$	12.8-89.4	1.52-10.2	4.64-25.3	4.04-29.6	
	RS5	0.99(0.36)	39.7(6.04)	0.07(0.03)	415(70.8)	10.8(1.98)	37.6(5.77)	35.7(7.78)	
		0.45-1.25	17.1-43.3	N.D.-0.09	116-687	2.45-13.9	8.24-50.5	11.1-50.6	
	RK6	0.35(0.15)	23.1(4.23)	$< 5.0 \times 10^{-3}$	183(37.8)	0.54(0.22)	33.8(6.41)	27.6(6.24)	
		0.06-0.62	9.04-35.1		33.6-298	N.D.-1.63	7.75-49.1	8.11-34.2	
	RB7	0.59(0.18)	20.5(3.55)	$< 5.0 \times 10^{-3}$	291(50.3)	5.66(1.16)	14.3(2.86)	20.6(3.70)	
		0.24-0.86	7.58-32.6		78.6-308	1.33-9.64	2.64-20.7	6.01-36.7	
	RE8	0.72(0.35)	23.9(4.61)	$< 5.0 \times 10^{-3}$	188(37.5)	10.6(2.41)	17.4(4.65)	19.1(4.44)	
		0.36-0.94	16.5-34.5		64.1-218	1.98-15.7	3.69-28.5	3.81-25.2	
	June 30, 1998	RA1	0.66(0.22)	31.9(7.98)	0.06(0.01)	110(22.9)	0.26(0.04)	19.2(3.78)	31.8(7.04)
			N.D-0.80	15.6-42.4	0.02-0.08	30.4-220	0.09-0.41	2.11-30.7	8.88-40.7
RO2		0.25(0.07)	35.8(6.05)	$< 5.0 \times 10^{-3}$	28.5(7.22)	5.06(1.33)	22.6(4.20)	10.7(2.82)	
		N.D-0.44	11.4-43.9		7.05-49.7	N.D-9.17	5.08-43.5	3.21-18.9	
RS5		1.12(0.46)	36.9(7.64)	0.05(0.02)	309(60.7)	15.6(3.16)	68.7(14.5)	50.1(10.4)	
		0.58-1.49	12.2-43.6	N.D-0.09	88.3-478	2.89-19.7	18.9-77.4	12.6-71.4	
RK6		0.53(0.28)	24.8(5.53)	$< 5.0 \times 10^{-3}$	139(28.4)	0.73(0.23)	44.1(9.82)	30.9(7.18)	
		0.19-0.94	10.9-37.8		50.8-245	N.D-1.90	10.2-60.8	5.67-48.1	
RB7		0.74(0.24)	27.4(7.42)	$< 5.0 \times 10^{-3}$	285(57.5)	8.36(1.96)	21.6(5.32)	27.8(6.30)	
		0.48-0.99	6.10-31.8		105-369	1.47-11.9	5.30-37.4	9.66-39.5	
RE8		0.40(0.14)	21.7(5.34)	0.07(0.02)	215(43.8)	7.09(1.88)	21.8(4.14)	22.2(4.21)	
		0.29-0.63	10.5-37.6	0.02-0.10	70.1-325	1.45-11.7	2.82-29.3	7.18-37.6	
August 26, 1998		RA1	0.76(0.33)	20.4(4.66)		115(24.5)	0.39(0.09)	17.5(4.03)	25.3(3.85)
			N.D-0.90	9.21-35.7	$< 5.0 \times 10^{-3}$	40.9-231	N.D-0.68	6.44-30.8	8.04-45.7
	RO2	0.33(0.09)	22.1(5.05)		33.6(8.38)	8.57(1.78)	20.9(4.97)	18.9(4.61)	
		N.D-0.45	9.90-26.8	$< 5.0 \times 10^{-3}$	10.7-66.9	2.61-13.2	10.6-40.5	2.60-29.8	
	RS5	1.48(0.39)	31.0(8.15)	0.04(0.01)	355(69.4)	14.9(2.98)	40.6(8.75)	49.2(9.48)	
		0.91-1.75	10.1-42.1	N.D-0.08	115-479	3.64-22.5	15.6-66.4	18.2-75.4	
	RK6	0.44(0.12)	23.6(3.26)		205(43.9)	1.59(0.45)	27.7(5.26)	34.6(8.30)	
		N.D-0.55	10.5-37.7	$< 5.0 \times 10^{-3}$	87.5-352	N.D-2.09	11.1-39.2	11.0-58.6	
	RB7	0.52(0.16)	21.3(4.24)	$< 5.0 \times 10^{-3}$	117(25.2)	9.46(2.52)	19.8(4.66)	13.8(2.17)	
		0.11-0.69	8.15-32.4		20.6-239	2.35-12.8	9.16-28.5	1.02-18.9	
	RE8	0.29(0.08)	25.2(4.50)		270(61.3)	5.98(1.46)	30.4(7.99)	29.4(6.06)	
		N.D-0.48	10.0-30.9	$< 5.0 \times 10^{-3}$	110-417	1.72-9.28	17.5-52.8	4.63-46.0	

Values in parenthesis are the standard deviation, σ_{n-1} ; ^a means of duplicate analysis and 9 sampling; ^b minimum value; ^c maximum value; N.D. = not detected.

TABLE IV
Concentration (mg dm^{-3}) values of ions in the groundwater samples for the three sampling dates

Sampling date	Sample code	PO_4^{3-}	NO_3^-	CN^-	Cl^-	NH_3 (NH_4^+)	Ca^{2+}	Na^+
May 28, 1998	WE3	0.12 ^a (0.06)	17.1(2.56)	$< 5.0 \times 10^{-3}$	119(23.6)	0.05(0.01)	20.6(3.88)	21.8(4.58)
		0.03 ^b -0.20 ^c	5.72-22.8		52.9-197	N.D-0.12	5.07-32.6	5.70-33.9
	WE4	0.23(0.09)	16.5(2.13)	$< 5.0 \times 10^{-3}$	253(49.7)	0.06(0.02)	29.5(6.78)	9.08(2.72)
		N.D-0.36	2.48-27.5		40.6-374	0.03-0.14	10.1-43.2	1.23-15.8
June 30, 1998	WE3	0.09(0.03)	19.6(2.83)	$< 5.0 \times 10^{-3}$	198(38.6)	0.15(0.03)	24.2(3.87)	15.4(3.93)
		N.D-0.17	4.05-28.9		77.1-249	N.D-0.46	7.22-51.2	2.63-29.4
	WE4	0.10(0.02)	15.4(2.05)	$< 5.0 \times 10^{-3}$	149(29.3)	0.08(0.02)	20.9(3.43)	19.7(4.20)
		0.04-0.16	3.33-21.5		15.9-234	N.D-0.21	4.66-27.8	1.08-22.9
August 26, 1998	WE3	0.17(0.02)	19.3(0.08)	$< 5.0 \times 10^{-3}$	208(49.5)	0.09(0.03)	22.1(4.20)	24.8(5.90)
		N.D-0.38	1.98-25.2		101-302	0.02-0.36	9.09-37.8	8.63-30.5
	WE4	0.22(0.06)	16.9(2.11)	$< 5.0 \times 10^{-3}$	269(57.1)	0.14(0.05)	16.7(3.67)	13.7(4.15)
		0.07-0.42	5.11-24.8		30.7-335	0.06-0.26	3.07-24.6	1.78-21.9

Values in parenthesis are the standard deviations, σ_{n-1} ; ^a means of duplicate analysis and 9 sampling; ^b minimum value; ^c maximum value; N.D = not detected.

TABLE V
Recommended water quality criteria

Quality Factor	Desirabbe limit	Maximum permissible limit	Organization/Body
Temperature	30	34	-
Range of pH	7.0-8.5	6.5-9.2	WHO, ISI, ICMR
Total Dissolved Solids (TDS), mg dm^{-3}	500	1500	ICMR
Total Hardness (TH), mg dm^{-3} CaCO_3	100	500	EPA, ICMR
Electrical Conductivity, $\mu\text{m hos/cm}$	750	2500	WHO
Total Carbon (IV) oxide (TCO_2), mg dm^{-3}	-	15.0	WHO
Nitrate ion, mg dm^{-3}	25	50	EC
	-	45	WHO
Cyanide ion, mg dm^{-3}	-	0.05	WHO
Chloride ion, mg dm^{-3}	250	600	WHO
Phosphate ion, mg dm^{-3}	0.35	6.1	EC
	1.0	-	WHO
Sodium ion, mg dm^{-3}	50	175	WHO
Calcium ion, mg dm^{-3}	75	200	ICMR
Ammonium ion, mg dm^{-3}	10	-	WHO

EC, European Community; WHO, World Health Organisation; ICMR, Indian Council of Medical Research; ISI, Indian Standard Institution; EPA, Environmental Protection Agency.

552 mg dm⁻³ (RK6) during August survey (Table Ia and II). The high level of TDS in WE4 (732 mg dm⁻³) collected during May survey may be an indication of seepage of filthy surface waters into the groundwater or weathering of rocks and soil beneath the ground surface as water percolates through them.

Hardness of water depends mainly upon the amounts of calcium or magnesium salts or both. The limits of Ca and Mg ions in potable water range from 75 to 2000 mg dm⁻³ and 50 to 100 mg dm⁻³ respectively [ICMR, 19750]. In the present study, the Ca ion content of the water samples ranged from 14.3 (RB7) to 37.6 mg dm⁻³ (RS5) during May survey; 19.2 (RA1) to 68.7 mg dm⁻³ (RS5) during June survey and 16.7 (WE4) to 40.6 mg dm⁻³ (RS5) during August survey and were well within the maximum permissible limit (Tables III and IV). The total hardness (TH) varied from 84.6 (RB7) to 1170 mg dm⁻³ CaCO₃ (WE4) during May survey; 72.8 (RS5) to 896 mg dm⁻³ CaCO₃ (WE4) during June survey and 68.5 (RS5) to 716 mg dm⁻³ CaCO₃ (WE4) during August survey (Tables I and II). The recommended limits of TH (Table V) in drinking water are 100 mg dm⁻³ CaCO₃ as desirable limit and 500 mg dm⁻³ CaCO₃ as maximum permissible limit [ICMR, 1975]. The high values of TH in WE4 (1170 and 896 mg dm⁻³ CaCO₃ for May and June surveys respectively) may be due to the presence of high salt water content in the well. The high salt water content in the well could be due to dissolution of gypsum (CaSO₄.2H₂O) or other salt sources as water percolates through them. Waters for public supplies should not contain significant quantities of organic or any other weak acid except carbon (IV) oxide [APHA, 1989]. The presence of carbon (IV) oxide in water body can lead to depletion of dissolved oxygen (DO), and low DO value indicates the high pollution nature; and this will affect the life of the aquatic animals that need DO to survive. The total carbon (IV) oxide in the water samples ranged from 4.69 (RB7) to 14.9 mg dm⁻³ (WE3) during May survey; 2.60 (RB7) to 13.9 mg dm⁻³ (WE3) during June survey and 2.55 (RB7) to 12.6 mg dm⁻³ (WE3) during August survey (Tables I and II) and were within the permissible limit of 15.0 mg dm⁻³ for potable water [WHO, 1988].

The maximum concentrations of nitrate and cyanide ions for public water supplies are 45.0 and 0.05 mg dm⁻³ respectively [WHO, 1988]. The guidelines (GL) for drinking water quality of European Community provide reference value of 25 mg dm⁻³ and maximum admissible limit of 50 mg dm⁻³ for nitrate [EC, 1980]. The concentrations (Tables III and IV) of nitrate and cyanide in both river water and groundwater samples of the study area were within the maximum permissible limits. This indicates that there was no danger due to nitrate and cyanide ions to the consumers. Chloride ion impacts a salty taste to water. The limit for domestic purposes is fixed at 250 mg dm⁻³ (EPA, 1989). In the present study, chloride ion content (Tables III and IV) in both river water and groundwater samples ranged from 39.7 (RO2) to 415 mg dm⁻³ (RS5) during May survey; 28.5 (RO2) to 309 mg dm⁻³ (RS5) during June survey and 33.6 (RO2) to 355 mg dm⁻³ (RS5) during August survey. The high chloride ions of RS5 (415, 309 and 355 mg dm⁻³ during May, June and August surveys respectively); RB7 (291, 285 mg dm⁻³ during May

TABLE VI

Statistical^a assessment of inorganic nutrient contents of waters from two different sources

Source	PO ₄ ³⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Ca ²	Na ⁺
High-Pollution river water source (18 samples)	0.64	27.4	187	6.33	28.0	27.1
Mean (mg dm ⁻³)	50.0	22.3	61.5	78.0	47.5	39.5
R.S.D. (%)						
Low-Pollution groundwater sources (6 samples)						
Mean (mg dm ⁻³)	0.16	17.5	199	0.10	22.3	17.4
R.S.D. (%)	37.5	9.43	29.1	40.0	19.2	33.2
t-values	3.50	3.75	-0.24	2.95	0.99	2.03

^a Critical value of |t| for 22 d.f is 2.07 at 95% confidence level.

d.f. is degree of freedom.

R.S.D. is relative standard deviation.

and June surveys respectively) and RE8 (270 mg dm⁻³ during August survey) showed they were unfit for domestic purposes. The phosphate ion content (Tables III and IV) in the water samples studied lies below the permissible limit of 1.0 mg dm⁻³ for domestic applications except for Osun river water sample (RS5) where it exceeded the permissible limit (RS5: 1.12 and 1.48 mg dm⁻³ during June and August surveys respectively). The high phosphate ion content of Osun river (RS5) might be due to leaching of Agricultural wastes into the river and/or the use of phosphate additives in detergent formulations, which get leached into water bodies through wastewaters generated industrially, domestically or municipally and/or from cloth dyeng and garment industries operating in the study area.

The sodium, calcium ions and ammonia (measured as ammonium ion) contents (Tables III and IV) in both the river water and groundwater samples for the three surveys of the study area were well within the desirable limits of 50 mg dm⁻³; 75 mg dm⁻³ and 10.0 mg dm⁻³ respectively for domestic applications, except for river water sample of Osun (RS5) where the ammonia levels were exceeded during the three surveys (RS5: 10.8, 15.6 and 14.9 mg dm⁻³ during May, June and August surveys respectively). The high level of ammonia might be due to the leaching of fertilizer residues used on Agricultural farms into the river system.

The mean inorganic nutrient contents of river waters (high pollution water source) were compared with those of groundwaters (low pollution water source) using the student-t' test (Table VI). The values for the student's 't' calculated from these data (P < 0.05) showed the difference between the water samples from the high and low pollution water sources for phosphate, nitrate and ammonium ions. The

TABLE VII

Correlation coefficient between quality parameter pairs of the water samples from two different sources

Quality parameter pairs	Coefficient of correlation (r^a)	
	High-Pollution river water source	Low-Pollution groundwater source
pH – TCO ₂	-0.28	0.35
Na ⁺ – TH	-0.28	-0.69
Na ⁺ – NO ₃ ⁻	0.38	-0.29
Na ⁺ – PO ₄ ³⁻	0.73	-0.51
Na ⁺ – Cl ⁻	0.68	-0.66
Ca ²⁺ – Cl ⁻	0.45	0.16
Ca ²⁺ – PO ₄ ³⁻	0.49	0.14
NH ₄ ⁺ – NO ₃ ⁻	0.32	0.84
Ca ²⁺ – TDS	-0.14	0.66
Ca ²⁺ – TH	0.01	0.51
EC – TDS	0.13	0.39
NH ₄ ⁺ – PO ₄ ³⁻	0.53	-0.08

^a Critical values of $|r|$ for 16 and 4 d.f. are 0.47 and 0.81 respectively at 95% confidence level.
d.f is degree of freedom.

high concentration levels of phosphate, nitrate and ammonium ions from the high pollution river water source could be attributed to the leaching of fertilizer residues from Agricultural farms and the use of phosphate additives in detergent formulations, which can be eroded into the river system during the disposal of wastewaters generated municipally, domestically or industrially. Other inorganic nutrients were not significantly different ($P < 0.05$) in the two water source types.

The correlation coefficients between the quality parameter pairs of both the river water and groundwater samples are calculated in order to indicate the nature and the sources of the polluting substances. As seen In Table VII, significant correlation ($P < 0.05$; 16 d.f) does occur between Na⁺/PO₄³⁻; Na⁺/Cl⁻; Ca²⁺/PO₄³⁻ and NH₄⁺/PO₄³⁻ in the high pollution river water source while significant correlation ($P < 0.05$; 4 d.f) occurs between NH₄⁺/NO₃⁻ in the low pollution groundwater source, thus suggesting a common source for the polluting substances. There is low correlation ($P < 0.05$; 16 and 4 d.f) between other quality parameter pairs of both river and groundwater samples, thus suggesting a non-common source of the polluting substances. The probable sources of the pollutants in both water source types varied widely and may include leachates from wastewaters generated municipally, domestically and industrially and/or wastes from intensive Agricultural practices, the major occupation of the people in the study area.

It has been evident from our findings that the causes and sources of water pollution in the study area are due to agricultural land use, anthropogenic activities and industrialization. The major occupation in the study area is Farming. This is seen as the main source for the high ammonia (measured as NH_4^+) and phosphate ion concentrations. Domestic and industrial discharges into the river are probably responsible for the observed high concentration values of electrical conductivity, total hardness, total dissolved solids and chloride ion. Proper treatment of effluent from industrial processes to the acceptable levels, discouraging stagnation of domestic sewage on the ground surface, availability of sewage treatment plant along with proper sewerage system and thorough analysis and study of any water sources before being used for domestic applications are therefore recommended to minimize the health risk.

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