

ASSESSMENT OF A GROUNDWATER QUALITY FOR DRINKING PURPOSE IN ILORIN, NIGERIA

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Abstract:

Groundwater is a major source of water supply in Nigeria where there is an inadequate supply of water for domestic, industrial and agricultural uses. This paper examines the suitability of water samples from a target hand dug well (TW) in a residential area in Ilorin, Nigeria for drinking purpose. The samples were characterized to determine physico - chemical properties over eight weeks due to the observed, oily, greenish blue water discharged from the groundwater source. Another well in the neighborhood was investigated as a control (C). Concentration of selected anions, cations and the presence of hydrocarbons were established in the contaminated well with focus on nutrients and hydrocarbons related to sewer, paint and petroleum compounds to establish the possibility of leakages from sewers, the auto repair/painting workshop and the petroleum products pipeline which are located uphill of the well. The results of physico -chemical characterization carried out on the TW showed pH: 7.3 – 7.9; turbidity: 1.2 – 4.5 NTU; total hardness; 175.30 – 222.02 mg/l; TDS: 90 – 125 mg/l. Concentration of cations and anions ranged between 0.16 – 0.24 for Fe; Mn: 0.01 – 0.06; Zn: 0.18 – 0.45; NO₃²⁻: 5.95 – 12.76; SO₄²⁻: 192.1 – 235.85; Cl⁻: 230.63 - 283.32 all in mg/l. A Gas Chromatography Mass Spectroscopic analysis (GC-MS) carried out on the water samples from TW showed that, 24.83% of the peaks are within 90 – 100% quality range which confirms the compounds suggested from the installed NIST11 library are correct within minimal error limit.

Key words: Groundwater, pipeline, nutrients, GC – MS, Sewer, hydrocarbons

INTRODUCTION

Water is very essential for life support. Quality, quantity and availability of potable water is a very important environmental issue and, this makes monitoring of water quality and decision – making a challenge for the environmental engineer. Several methods are discussed in literature on drinking water quality criteria and decision- making. The fuzzy synthetic evaluation model gives the certainty levels for the acceptability of water based on the prescribed limit of various regulatory bodies (Chang *et al.*, 2004; Dahiya *et al.*, 2007) The Oregon water quality index is used to express water quality by integrating measurements of eight water quality variables, temperature, dissolved oxygen, BOD, pH, ammonia + nitrate nitrogen, total phosphorous, total solids and fecal coliform (Cude, 2001), Factor analysis: a multivariate statistical method (Liu *et al.*, 2003), A

generalized water quality index for Taiwan (Liou *et al.*, 2004), the application of Canadian Council of Ministers of the Environment Water Quality Index (CCMEWQI) (Lumb *et al.*, 2006) etc., have been employed over time in groundwater assessment with each having its drawbacks.

Groundwater is one of the indispensable, most natural resources for drinking water in developing countries especially where the public water supply is inadequate. The composition of groundwater is influenced by many processes; wet and dry depositions of atmospheric salts, evapotranspiration, water – soil and water-rock interactions (Liu *et al.*, 2003; Umezawa *et al.*, 2009; Frische *et al.*, 2010; Jain *et al.*, 2010). It is used for diverse purposes ranging from domestic to, industrial, agricultural etc., and, these activities generate wastes which are discharged to land and, ultimately find their ways into groundwater by leaching (Srinivas *et al.*, 2015).

Over the years, the effect of groundwater pollution has been on the increase as a result of man's activities. These activities have been known to add to the environment, pollutants such as, trace metals, nutrients, hydrocarbons to mention a few that have ended up negatively changing water quality as a result of increased loading of pollutants in response to changes in land use (Buck *et al.*, 2006). The measurement of groundwater quality parameters is very important at regular intervals as there is a need to monitor the quantity and availability for different purposes and the quality which had over time acted as precursors to various waterborne home epidemics (Srinivas *et al.*, 2015).

Trace elements and especially heavy metals are toxic, (when present above certain concentrations) persistent and they possess and cause bioaccumulation problems. They could be from natural and anthropogenic sources (Pekey *et al.*, 2004). Determination of metals in natural waters provides a foundation for informed action by environmental interest groups and regulators and a starting point for further study. Trace metals are important, with some serving as micro – nutrients (Zn, Fe) while some can be toxic at high concentrations (Pb, Cu, Cr, Cd) (Chase *et al.*, 2011). Trace metal concentrations can be determined using the Atomic Absorption Spectrophotometer (AAS), Inductively Coupled Plasma- Mass Spectrophotometer (ICPMS) amongst other techniques.

Nutrients can occur naturally in water however, elevated concentrations would usually originate from the activities of man and animals (directly related) such as, artificial fertilizers, manure (animal waste) and septic – system leakages. Nutrients could be present as, nitrate, nitrite, ammonia, total nitrogen, orthophosphate and total phosphorous. Phosphorous is most commonly found as phosphate and it plays a key role in biochemical processes and eutrophication of surface water (Galhardo and Masini, 2000; Umezawa *et al.*, 2009; Robinson, 2015).

Nitrate has been identified as a common, surface and groundwater contaminant that could result in health hazard in the infant and eutrophication of a water body. Abandoned landfill, or industrial sites (eg military facilities involved in the production and demolition of explosives, propellants and pyrotechnics) have been known to contribute significantly to levels of nitrogen in groundwater.

In the past, nitrates in groundwater was linked to agricultural processes however, recent studies have illustrated other non – agricultural sources of nitrates in groundwater. These sources include sewage and mains leakages, septic tanks, industrial spillages, contaminated land, fertilizers etc (Wakida and Lerner, 2005). The World Health Organization (WHO) and European Union (EU) standards for nitrate in drinking water has been put as 50 mg-NO₃/l and 10 mg- N/ l respectively.

Sulphate is widely distributed in nature and may be present in natural waters in concentration ranging from a few hundred to thousands of mg/l as it occurs naturally in numerous minerals. It is of significant concern because, it is indirectly responsible for serious problems associated with the handling and treatment of wastewater (odour and sewer corrosion). The amount of sulphate in water is used to determine the magnitude of problems that can arise from reduction of sulphates to hydrogen sulphide under anaerobic conditions. Aromatic organic compounds, such as BTEX (benzene, toluene, ethylbenzene and xylene) or PAHs (polycyclic aromatic hydrocarbons) are frequently detected in groundwater. Some are in the form of solvents frequently encountered in many industrial operations while, some are ubiquitous contaminants resulting from burning of fossil fuels and other organic compounds. They include the possibility of transport across phases by volatilization, sorption and dissolution phenomena. However, under specific conditions, slow biodegradation phenomena might occur, both in aerobic and anaerobic

conditions, which can lead to the transformation of these compounds into simpler and less hazardous molecules (Canzano *et al.*, 2014).

pH is very important because certain chemical processes can only take place when reaction proceeds at a certain pH and, it is a measure of the acidity or basicity of a substance and serves as an indicator that compares some of the most water-soluble ions. In aqueous solutions, pH is controlled primarily by the hydrolysis of salts of strong bases and weak acids or vice versa.

In May 2015, somewhere along the petroleum products pipeline road area of Ilorin, Nigeria, a hand dug well (TW) in a home, discharged water with a greenish blue colour which stained ceramics (with an oily feel).

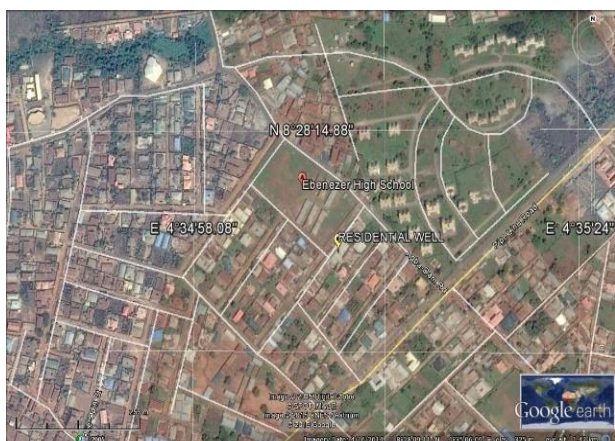


Fig 1: Arial view of sample location

This informed a study to characterize the water from the well to establish what the possible inflow into the well could have been. The aim of this study is to assess the quality of a groundwater source as a potable watersupply.

The specific objectives are to:

- carry out the physico-chemical characterization of water samples from TW and C and, compare with established standards in literature;

- Study the quality of analyzed water samples and;
- Establish the suitability of ground water as a potable water supply in the home.

EXPERIMENTAL PROCEDURE

Materials and Methods

Sampling location

The well under review (TW) is sited in a residential area, off pipeline road, Ilorin, Nigeria. It is located along latitude ($8^{\circ} 28' 14.88''N$), longitude ($4^{\circ} 34' 58.08'' E$) with a control C in the same estate (Google earth, 2015). Some notable sites around the sample locations include, the pipeline road, major mechanic/painting and auto panel beater workshops uphill of the sample site (Fig 3)

Sampling: Water sample was collected over a period of 8 weeks in triplicates from TW and C site (fig 3) into pre – washed, polyethylene bottles. For trace metal determination, water samples were collected in acid – leached, polyethylene bottles and preserved with a few drops of concentrated nitric acid to ensure that the metal ions remained in solution while the samples for anion determinations were filtered and, all collected samples were refrigerated prior to analysis.

Apparatus/equipment/ reagents

Weighing balance: Ohaus Pro Model AV313 with a capacity of 310 g and readability of 0.001g; UV-VIS Spectrophotometer (Schimadzu UV-1800); 210/211 VGP Atomic Absorption Spectrophotometer PG990; Hanna Multi parameter instrument HI 9812-5, Gas Chromatograph from Agilent USA, hyphenated to a mass spectrometer 5975C. All reagents used were of analytical grade and distilled water was used for all preparations as required.

Sulphate determination

Turbidimetric method was employed in the determination of SO_4^{2-} . The method is based on the principle of, the formation of barium sulphate in colloidal form by a sulphate in the presence of barium chloride.

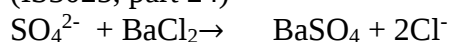
Conditioning Reagent

This was prepared by mixing 50ml glycerol with a solution containing 30ml concentrated HCl, 300ml distilled water, 100ml of 95% ethanol and 75g NaCl.

Standard Sodium Sulphate Solution

0.1479 g of anhydrous sodium sulphate (Na_2SO_4) was dissolved in distilled water and diluted to 1 litre. This solution was used to prepare calibration curve.

Procedure: From the standard solution prepared, smaller concentrations were prepared by serial dilution and to this was added required quantity of conditioning reagent and barium chloride with continuous stirring. The absorbance and hence concentration of sulphate ion was then determined using the UV Spectrophotometer following standard methods from literature (IS3025, part 24)



Nitrate

Standard solution was prepared by dissolving 0.7218g of dry KNO_3 in distilled water and diluted to 1000ml and preserved with 2ml chloroform, which was then used to prepare calibration curve by dilution and chloride concentrations were determined from the curve.

Chloride

4.17g of $\text{Hg}(\text{SCN})_2$ was dissolved in 500 ml methanol, it was then diluted to 1 litre with

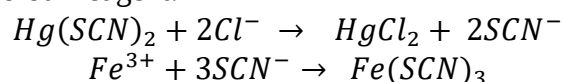
methanol and filtered using Whatman 45 filter paper.

Ferric Nitrate Solution: 20 % ferric nitrate solution is prepared by dissolving 202 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 500 ml distilled water, 31.5 ml conc HNO_3 was added, this was thoroughly mixed and diluted to 1litre.

Colour reagent: 150ml of mercuric thiocyanate solution was added to 150 ml of ferric nitrate solution, this was also mixed and diluted to 1litre with distilled water.

NaCl standard

Standard NaCl solution was prepared by appropriately dissolving with distilled water. To 25 ml of each of the standards, 10ml of the colour reagent was added and gently shaken for some minutes, Absorbance was read using the UV-visible spectrophotometer. This was used in preparing a standard calibration curve from where the concentration of chloride in samples was determined using the same volume of the sample (as the standard) and the colour reagent.



Total Hardness

The sample was first adjusted to a pH of 10 using a buffer solution. The sample is then titrated to its equivalence point using a standard EDTA solution. The calmagite indicator initially turned red in the presence of magnesium, then turns blue when enough EDTA solution had been added to combine with all calcium and magnesium ions. The total hardness of the sample was calculated using the volume of EDTA solution added when the indicator changes color, as well as the EDTA concentration, in mg/l .

Trace metals

Collected water samples were digested following standard methods from literature

prior to analysis for trace metals(Jain *et al.*, 2010; Tyagi *et al.*, 2014).Trace metal analysis was carried out using Atomic Absorption Spectrophotometer model, PG990 from the Centre for Energy Research and Development. Obafemi Awolowo University, Ile Ife. Nigeria. Air – acetylene flame was used and the operations were carried out in accordance with the manufacturer’s guideline.

pH and TDS: these were measured using Hanna Multi parameter instrument HI 9812-5.

RESULTS

Result of physico-chemical carried out on TW and C are as shown in table 1. The range, mean and standard deviation are tabulated and tabulated against the BIS, WHO and EPA standards.

Table 1: Target and Control Water Quality Data Against BIS, WHO and EPA standards

Parameters	BIS Standard		WHO Standard	Water Quality Data	
	Desirable limit	Permissible limit	Desirable limit	Min – Max (TW)	Min – Max (C)
Ph	6.5 – 8.5	No relaxation	6.5-8.5	7.3 – 7.9 ± 0.23 (7.6)	6.8 -7.4 ± 0.16 (7.2)
Turbidity NTU	1	5	1.5	1.2 - 4.5 ± 1.15 (3.1)	0.2 - 0.5 ± 0.03 (0.28)
Total Hardness mg/l	200	500		175.30 -222.02 ± 18.69 (196.69)	102.90 – 175.01 ± 20.53 (163.07)
TDS mg/l	500	2000		90.00 - 132.00 ± 13.88 (111.75)	45.17 - 82.59 ± 9.47 (67.42)
Fe mg/l	0.3	No relaxation	0.1	0.16 - 0.29 ± 0.04 (0.21)	0.18 – 0.26 ± 0.04 (0.23)
Mn mg/l	0.1	0.3	0.05	0.01 - 0.06 ± 0.02 (0.03)	0.01 - 0.04 ± 0.02 (0.02)
Zn mg/l	5	No relaxation	-	0.18 - 0.45 ± 0.09 (0.29)	0.10 - 0.50 ± 0.03 (0.22)
NO ₃ ²⁻ mg/l	45	No relaxation	50	5.95 - 12.76 ± 2.02 (8.35)	6.7 – 9.52 ± 1.05 (8.54)
SO ₄ ²⁻ mg/l	200	400	250	192.1 - 251.75 ± 19.34 (224.78)	170.49 – 223.14 ± 20.11 (189.76)
Cl mg/l	250	1000	200	230.63 – 283.32 ± 16.52 (256.46)	185.21 – 212.03 ± 13.45 (194.09)

***BIS: Bureau of Indian standards**
TW: Target Hand Dug Well

****WHO: World Health Organization**
C: Control Well

3.1 pH and Turbidity

The pH of TW ranged between 7.3 and 7.9 while pH for C ranged between 6.8 and 7.4. all were within the desirable limits by both BIS and WHO. Turbidity in TW ranged between 1.2 - 4.5 NTU. All values are above the

desirable limit by both BIS and WHO as shown on table 1. Turbidity in the control well (C) in the same area ranged between 0.2 – 0.5 NTU. This suggests a point source leakage into TW.

3.2 Total Hardness (TH)

Total Hardness in TW ranged between 175.30 – 222.02 mg/l while for C, it ranged between 102.90 – 175.02 mg/l. The increase above the desired value of 200 mg/l in some of the samples from TW may be attributable to the influx into the groundwater source as evidenced by the increase in turbidity above location C.

3.3 Total Dissolved Solids (TDS)

TDS in TW ranged between 90 – 132 mg/l while it ranged between 45.17 – 82.59 mg/l in C. The values are all within desirable limit of 500 mg/l.

3.4 Trace Metals (TM)

Concentration of Iron (Fe) in TW ranged between 0.16 - 0.29 mg/l in TW and ranged between 0.81 – 0.26 mg/l in C. All were within the desirable limits by BIS however, they were all outside the 0.1 mg/l limit by WHO. Fe is naturally occurring micro-nutrient in soil and rocks and, it could have gotten into the water through weathering. There is no significant difference in concentration of Fe across the two wells in the neighborhood.

Concentration of Manganese (Mn) in TW ranged between 0.01 – 0.06 mg/l and between 0.01 – 0.06 mg/l in C. They are all within the desirable limits by both BIS and WHO and, there is no significant difference in concentration across the two wells.

Concentration of Zinc (Zn) in TW ranged between 0.18 – 0.45 mg/l and between 0.10 and 0.50 mg/l in C. The concentrations are well below desirable limits by BIS and, there is no significant difference in concentration across the two wells.

3.5 Anions in water samples

Concentration of nitrate (NO_3^{2-}) in TW ranged between 5.95 and 12.76 mg/l in TW and

between 6.70 – 9.52 in C. These are all well below the desirable limits of 45 and 50 mg/l by BIS and WHO respectively. This rules out possible influx from leaking sewers as source of TW pollution.

Concentration of sulphate ions ranged between 192.1 -251.75 mg/l in TW and between 170.49 -223.14 mg/l in C. A few of the samples had concentrations slightly above the desirable by BIS but the values are within the permissible values by BIS. The values are however within the desirable by WHO.

Concentration of chloride in TW ranged between 230.63 – 283.32 mg/l and between 185.21 – 212.03 mg/l in C. TW has chloride levels above the desirable limit of 200 mg/l suggested by WHO throughout the sampling period. Concentrations above 250 mg/l were also above the desirable limit of 250 mg/l by BIS though these are still within the 1000mg/l permissible limit by BIS. A significant difference is noticed in the concentrations across location suggesting that the influx into TW had affected the chloride concentration in the groundwater.

3.6 Hydrocarbons

Hydrocarbons in the water sample was leached into n- hexane and presence of these was determined using Gas Chromatography-Mass Spectrophotometer (GC-MS).Based on the analysis carried out, the following were the findings

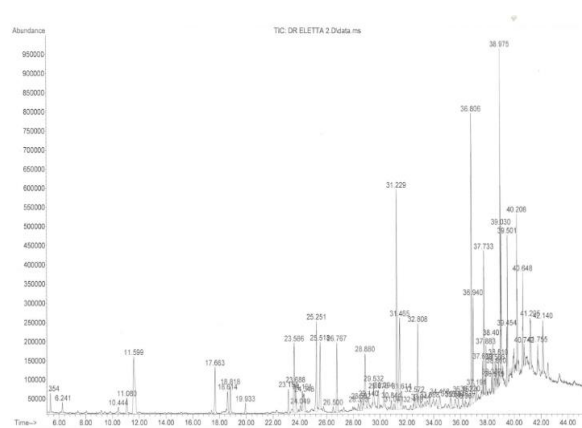


Fig2a : Spectra of Sample from TW

GC-MS analysis of hydrocarbons leached from water sample from TW showed sixty – six (66) peaks (using RTE integrator) as seen in the figure 2a. However, of the 66 peaks, only seven (7) have peak qualities within 90 – 100 % quality and these are shown on table 2. The installed Library NIST11 library has over 70,000 compounds with which it compares the peak. For a pure substance, it would give peaks of 100 % purity while for others, suggestion of compounds closest to the peak is made by the MS and that is why only those peaks with 90 – 100 % quality are considered as true representative of compounds in the sample. Identified compounds in TW include; Decane, with 90% peak quality, Cyclopentasiloxane and 5-octadecene, 91 % peak quality; p-xylene and Tetradecane, 93 % peak quality; Cyclohexane, octyl with 94 % peak quality and Hexadecane with 96 % peak quality. Hexadecane with the highest peak quality is insoluble in water and it is reported to be a petroleum hydrocarbon.

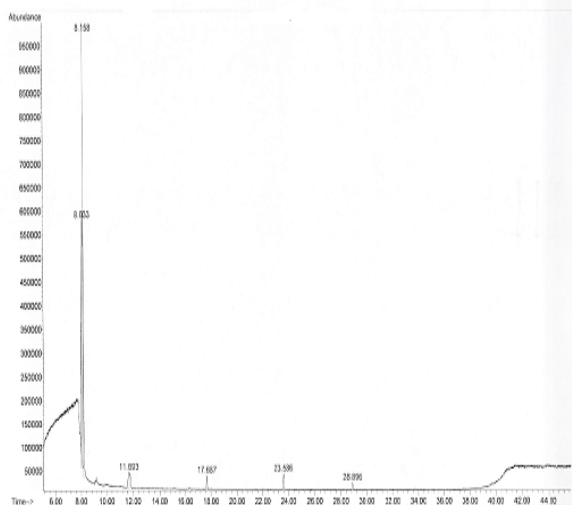


Fig2b: Spectra of Sample From the Control (C)

-MS analysis of sample from the control well had six peaks (using RTE integrator) as shown in fig 2b and of these, only two of the peaks had 90 – 100 % quality (table 3).

DISCUSSION

Arial view of Agba housing Estate where the study sites are is shown in figure 1, figures 2a and b show the spectral for the GC MS

analysis of TW and C. Fig 3 shows the survey map of the sample area, TW is shown as A on the map, the control well is located at B while C shows location of the mechanic / paint workshops. The target hand dug well was observed to suddenly produce water with very light greenish blue at the beginning to a deeper shade observed around the fourth week of discharge. Currently, the water has lost all colour in TW while water from the control remained colourless through the study.

The pH, TDS, Total hardness; Fe, Zn, Mn, sulphate, nitrate concentrations all fall within the permissible BIS limits for drinking water however, high turbidity and chloride concentrations were observed at TW which are significantly different from what obtains in samples from C, which is close to TW confirming some influx into TW that could be responsible for the elevated values. All the investigated parameters for C were contained within the permissible limits of BIS.

The hydrocarbons detected in TW confirms point source discharge into the water. Compounds that compared 90% and above in the spectra with compounds in the NIIST library are reported as the correctly identified compounds. Even though several hydrocarbons are observed in the spectra for TW, only those with quality of the peak between 90 – 100 % were considered as this determines how close to the suggested compound in the library this is. The sum of the percentages corresponding to this range is 24. 83 % for TW (Table 2). Only two (2) of the 6 peaks in the spectra for C had 90 % and above quality and, they are compounds which are predominant in soil. The suggestions from the NIST11. library used represent only 9.13 % of the hydrocarbons in the sample from the control (Table 3).

CONCLUSION

The water discharged from the well left greenish blue oily stain on ceramics and most of the hydrocarbons identified using GC-MS

have been found to be insoluble in water. Many of them have been linked from literature to petroleum and paints and considering the fact that there is a pipeline uphill of the sample location and extensive painting of cars is carried out uphill of the well there is the likelihood of a massive spill that was leached into the well especially with the stoppage within four weeks of the discharge. Ampling was continued for four extra weeks while the use of the well for drinking and cooking purposes has been stopped.

Nitrate levels in both TW and C were not significantly different and, they all were within the desirable limits by BIS and WHO. This, coupled with the fact that the water quality changed with time without evacuation of the sewer system confirms leakage into TW is not from this source. There is significant difference in the turbidity of the water in TW

and C. This confirms the fact that, water in TW had been contaminated via anthropogenic sources since there are in the same neighborhood.

It can be concluded that, there was hydrocarbon leakage into TW as shown in the spectra for TW however, the source could not be ascertained. The abrupt stop noticed in the coloured discharge suggests the source had been observed and taken care of. The relatively high concentration of chloride ions observed in TW could not be accounted for since, the source of the leakage could not be identified. For now, periodic discharge of water in the well is being carried out by pumping while, an alternative source of water supply has been provided to the home. Spontaneous check on the TW is to be conducted sometime to confirm the leakage is an accident and not a repeated occurrence.

Table 2: Hydrocarbons of significance in spectrain sample from home

SN	Retention Time	Area %	Compound	Qual	Remark
1	5.323	1.86	p-xylene	93	Insoluble in water and hazardous but have been found in groundwater(Canzano <i>et al.</i> , 2014).
2	11.065	3.14	Decane	90	Insoluble in water with gasoline like odour
3	17.663	3.14	Cyclopentasiloxane	91	Synthetically manufactured
4	25.519	4.10	Tetradecane	93	Gasoline like odour
5	26.768	1.90	Cyclohexane,octyl	94	
6	31.237	4.95	5-octadecene	91	
7	31.465	5.74	Hexadecane	96	Insoluble in water and petroleum hydrocarbon (Ulrich <i>et al.</i> , 2009)

Table 3: Hydrocarbons of significance in spectra in sample from control

SN	Retention Time	Area %	Compound	Qual	Remark
1	11.693	5.25	Tetrasiloxan-1-ol	90	
2	23.586	3.98	Cyclohexasiloxane, dodecamethyl	91	

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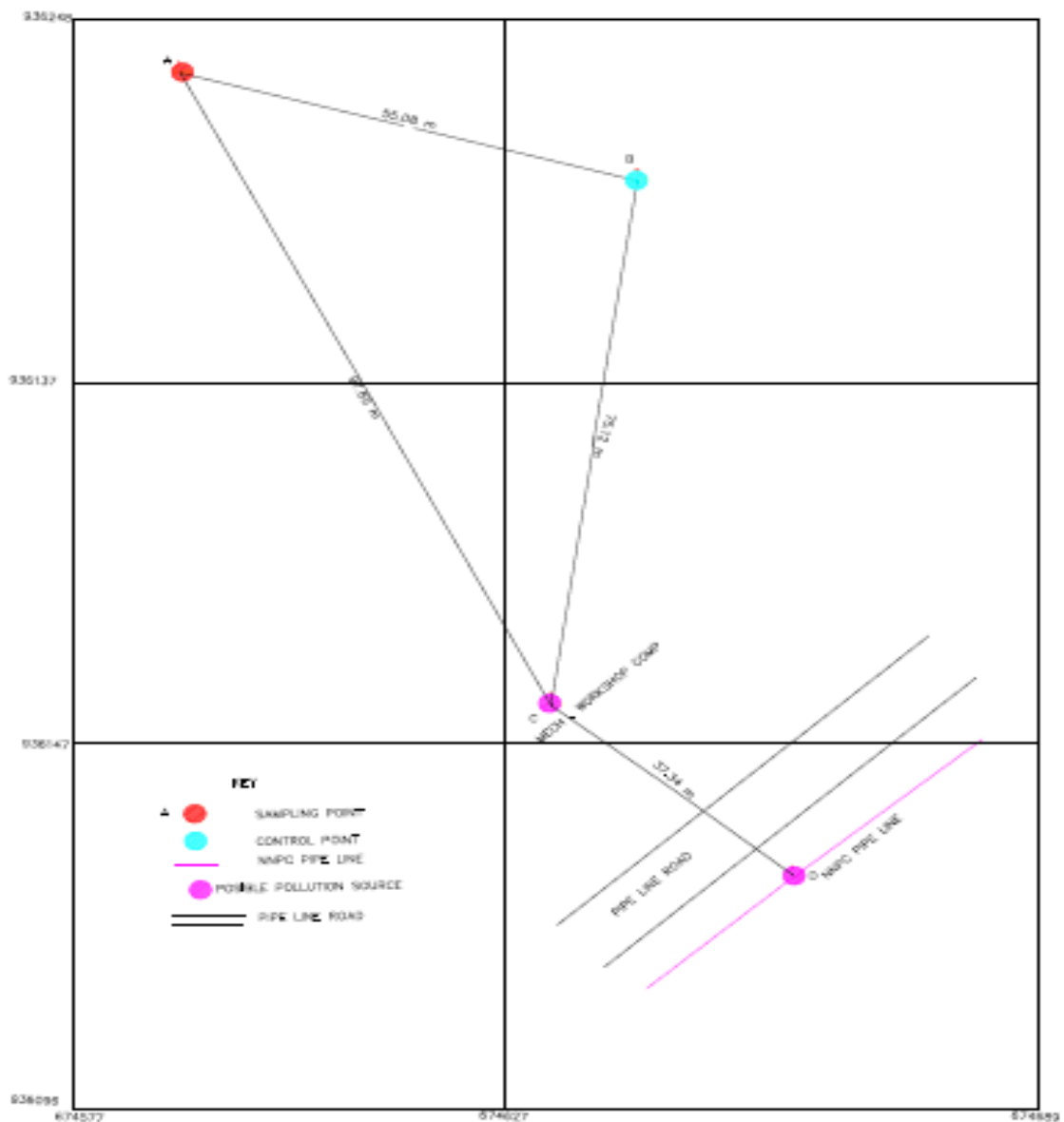


Fig 3: Survey map of sample locations and possible sources of pollution