DETERMINATION OF OXYGENATES AND SELECTED ORGANIC MICROPOLLUTANTS IN SUBSURFACE WATER OF OIL SPILLAGE PRONE AREAS IN LAGOS STATE USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE

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ABSTRACT

Gas Chromatography /Mass Spectrometry method of analysis was used to determine the presence and quantitative values of selected Oxygenates and Organic micropollutants in underground water of oil spillage prone areas in Lagos State Nigeria. The analysis involved six samples of water with three collected from each sampled sites. The water samples were analyzed using GC/MS to determine the presence and concentrations of various oxygenates such as MTBE, Benzene, Methanol, Ethanol, t-Butanol and some other organic micropollutants. From the results obtained, the presence of the oxygenates and micropolloutants were confirmed and the quantitative values of some, especially the carcinogenic ones were above recommended values by environmental protection agencies like EPA, WHO, and NESREA.

KEYWORDS: Gas Chromatography /Mass Spectrometry, Organic micropollutants, Oxygenates.

INTRODUCTION

Globally, there is an increased demand for portable water and has necessitated the interest in a need for wastewater treatment as an alternative source of portable water for human consumption. In the treatment given to these waste water, the removal of organic micropollutants (OMPs) like disinfection by-products (DBPs), oxygenates, endocrine disrupting compounds (EDCs), pharmaceutical active compounds (PhACs) and body care by-products are important concern [1]. Also in most developing countries, where scarcity of good portable water is high, a major concern is contamination of groundwater by organic micropollutants.

By definition, OMPs are organic compounds that find their ways into the environment, thus causing pollution to the environment [2]. These organic compounds are referenced to as micropollutants due to their concentrations in the environment, often in the range of nanogram per litre (ng/l) to microgram per litre (µg/l) in solutions. Further, they are also identified as contaminants that are bioactive and persistent and cannot be fully eliminated with traditional waste treatment methods and therefore, are not completely biodegradable. Examples of organic micropollutants are pesticides, pharmaceuticals, hormones, personal care products, plasticizers, flame-retardants, fuel additives and other industrial organic pollutants (e.g. bisphenol-A) [3].

Subsurface water is water that occurs beneath the surface of the earth and is found in all or some of the void spaces in the soils. It is so called to differentiate it from surface water found in water bodies like oceans or streams and can otherwise be referred to as groundwater [4]. Generally, the safety of drinking water is dependent upon the quality of water resources and like in most African countries, study shows that more than 60% of the people of Danube river basin in Europe use groundwater for their domestic purposes [5]. The pollution of such water sources by organic micropollutants might have effect on the people using it especially the unregulated type or when the regulated which is subject to control is not complied with. Also as a result of the OMPs occurring mostly at specific places and subject to factors like social status of people, economic power, industrialization, and population of the area, the introduction of legislations serve as interventions both at national and international level.

The presence of pharmaceuticals, endocrine disrupting compounds, surfactants, phthalates, per-and poly-fluoroalkyl substances, personal care products, artificial sweeteners, and pesticides in groundwater was reported in different part of India [6]. Many cities in Nigeria are not exempted from the use of groundwater to meet up with the water demand of the increasing population. This need necessitated many research on water in the country to be investigation on water parameters, often mainly physico-chemical and biological parameters. On the other hand, the presence of organic micropollutants like that discovered in India groundwater cannot be ruled out due to all these products equally being in use in Nigeria. In addition, Nigeria groundwater is likely to also be prone to contamination due to pollutants from petroleum fractions and products, termed oxygenates because of high activity level using crude oil and its products in the country. As specification, some locations in Nigeria have special characteristics that necessitate further investigations on the pollution status of the groundwater in respect of OMPs contamination. An example of such location

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is Lagos State, with some of its towns being places of high activity area for crude oil and its products business. For such areas, in addition to groundwater physico-chemical parameters alteration due to normal domestic activities, the water is also likely susceptible to OMPs pollution from crude oil activities.

The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) are the leading environmental agencies that have contributed to curtailing exposure to organic contaminants. WHO has since 1980s, recommended a "total diet study" (TDS) approach, to which many countries approved and followed for assessing the exposure of their citizens [7]. The OMPs are equally included in the priority list of contaminants in United States EPA and European framework directives [8]. Despite the issued guidelines for humanly safe drinking water concentrations for several pollutants, the increase in portable water pollution by OMPs is still alarming. Study carried out by Ren et al [9] found 51 organic micropollutant compounds in Yangtze River Delta in China, while that of Chau et al [10] determined 1153 micropollutants to grasp a pollution picture of microcontaminants in an aquatic environment using solid-phase extraction (SPE), LC-TOF-MS and GC-MS analysis. Equally, Shao et al [11] studied the toxicity of 10 organic micropollutants for their aquatic risk implications and found all capable of causing toxicity on zebrafish embryos, thus posing a potential risk in the Danube River and Rhine River.

Organic micropollutants that result in the introduction of carcinogens into the environment cause alteration of the chemistry of life, and eventual death of organisms in such environment. Such organic micropollutants are majorly from petroleum refining and treatment for upmost utilization and its products. These categories of OMPs are hazardous and are majorly benzene family and ether oxygenates. Oxygenates are alcohols and ethers that are added to gasoline to comply with air emission regulations, and as an octane enhancers. The most widely used oxygenate is methyl tertiary-butyl ether (MTBE). MTBE accounts for more than 85% of oxygenate usage. Other oxygenates include other ethers and alcohols (Rhodes and Verstuft [12].

Common oxygenates are as shown in the figure below;

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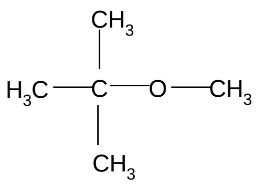
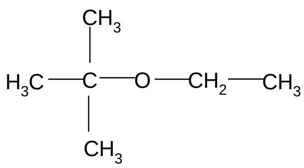
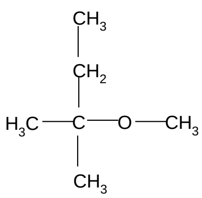


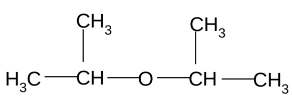
Methyl tert-butyl ether (MTBE)



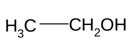
Ethyl tert-butyl ether (ETBE)



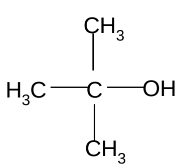
tert-Amyl methyl ether (TAME)



Diisopropyl ether (DIPE)



Ethanol



tert-Butyl alcohol (TBA)

There is a growing concern about organic micropollutants with carcinogenic nature because of their high solubility in water, gradient flow rate, and toxicity hazards. The need for the concern is due to the rate of increase in illnesses or diseases which could alter the chemistry of life and eventually resulting to death. Examples of such diseases are hormonal imbalance, mutation, malfunctioning of organs to growth of foreign body otherwise called cancer.

According to World Health Organization (WHO), cancer accounts for 13 percent of all deaths registered globally and 70 percent of that figure occurs in middle and low income countries. In Nigeria, about 10,000 cancer deaths are recorded annually while 250,000 new cases are recorded yearly [13].

Although, the health implications of consumption of drinking water containing a cocktail of organic micropollutants are unknown, or difficult to predict, but The U.S. Environmental Protection Agency tentatively considers organic micropollutant like MTBE a "possible human carcinogen" and has set health advisory levels for MTBE in drinking water at 20-40 parts-per-billion [14]. Therefore, removal of these pollutants in the drinking water treatment is desirable [2].

In Nigeria, where many rely on subsurface water for domestic use, Lagos State is a territory surrounded by water and has topography of coastal beaches, extensive inland lagoons, marshes, creeks and mangrove wetlands at elevation of 0 to 2 meters. It is equally an upland area with moderately drained soils and elevation range of 2 to 50 meters above sea level, but

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unfortunate the water in the lagoon and ocean surrounding the state are not fit for human consumption, therefore, the large expanse of water surrounding Lagos is not portable. This deficiency factor thus makes the people of Lagos State to depend majorly on groundwater from the Coastal Plain Sands Aquifer, which is often readily available due to high rainfall of about 2 meters annually as source of water.

Equally, the rapid population growth rate of Lagos has increased the demand for water especially for household usage and this has resulted to residents looking to the most readily accessible water source, groundwater. The result of this is the increased number of boreholes sited in the State resulting to unplanned and uncontrolled groundwater exploitation [15].

The need for reuse of water in Lagos State calls for ensuring that the concentrations of organic micropollutants in portable water are within permissible limits. In an attempt to achieve the minimum recommended concentration, many studies have been done to bring up appropriate method. The common method for the removal of organic micropollutants from wastewater is the conventional activated sludge treatment (CAS), but other improved methods are membrane reactor (MBR) with advantage of complete suspended solids removal and increased sludge age, post-ozonation or activated carbon adsorption often used for discharge to sensitive receiving waters advanced treatment. Siegrist and Joss recommended plants nanofiltration (NF) and reverse osmosis (RO) for the ability to efficiently reject micropollutants due to size exclusions, electrostatic, and hydrophobic effects. Also, it was equally recommended that to remove micropollutants fully, additional post-ozone or the addition of powdered activated carbon (PAC) needs to be introduced to reduce NDMA precursors [16].

Other studies have equally contributed to the literature of water treatment and micropollutant removal from portable water. Liu et al [17] in their study on preparation of nanofiltration membranes for high rejection of organic micropollutants and low rejection of divalent cations opined that a simultaneous high rejection of trace organic compounds (TrOCs) and low rejection of divalent cations (Ca^{2+}/ Mg^{2+}) is better for nanofilteration (NF) for drinking water. To them, their recommendation is based on the fact that the target desired for drinking water treatment cannot be attained using the commercial NF membranes currently in use [17]. Ojajuni et al [18] applied membrane processes to water

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and wastewater treatment in their study of removal of organic micropollutants using membrane-assisted processes. Also, a study on screening of organic micropollutants in raw and drinking water in the Yangtze River Delta in China by Ren et al. [9], shows that the major differences in concentrations and composition profiles of organic micropollutants were observed with the dominating group being pesticides in some samples and poly- and perfluoroalkyl substances (PFASs) in others. Overall, in the study on Yangtze River Delta in China, a total of 51 compounds were detected with an average total concentration of 730 $\pm$160 ngL^{-1} [9]. Despite all efforts to limit the pollution of the environment with OMPs, several individuals are yet to comply with the regulations. Therefore, to ensure water safety for drinking and domestic purposes, the knowledge on the concentration levels of organic micropollutants in water body must be ensured to be within acceptable permissible limit. In view of this, we investigated the presence, quantitative values and type of fuel additive organic micropollutants in subsurface water in some oil-spillage prone communities in Lagos State.

MATERIALS AND METHODS

Reagents and Chemicals

All reagents were of analytical-reagent grade. Dichloromethane (HPLC grade, Loba chemie) was used for the extraction of the water samples. Phenyl Methyl Siloxane was used for the stationary phase of the GC while the carrier gas was Helium. Perfluorotributylamine (PFTBA) was used to auto-tuned the MS. Methanol, Ethanol, MTBE and 1-Butanol solvents were used for the calibration of the instrument.

Sampling

Samples were collected from two Local Government areas in Lagos State part of Nigeria. The two sites were chosen because of similar characteristics of being prone to oil spillage as a result of closeness of one to waterway used for transportation of crude oil product and the other, due to high rate of oil pipes vandalism.

Instrumentation

GC-MS Instrumentation

Analysis of Methyl tert butyl ether (MTBE) and volatile organic solvents was done by operating MSD in the dual selective ion mode (SIM)/scan mode (*m/z* 45 – 400) to allow for better sensitivity and analytical precision.

Agilent 7820A gas chromatograph coupled to 5975C inert mass spectrometer (with triple

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axis detector) with electron-impact source (Agilent Technologies) was used. The stationary phase of separation of the compounds was HP-5 capillary column coated with 5% Phenyl Methyl Siloxane (30m length x 0.32mm diameter x 0.25µm film thickness) (Agilent Technologies). The carrier gas was Helium used at constant flow of 1.5 mL/min at an initial nominal pressure of 1.56 psi and average velocity of 44.411 cm/sec. 1µL of the samples were injected in split mode with split ratio 10:1 at a flow of 15 mL/min and injection temperature of 250 °C. Purge flow to spilt vent was 0.002 mL/min and total flow of 16.502 mL/min; gas saver mode was switched off. Oven was initially programmed at 40 °C (5 min) then ramped at 8 °C/min to 180 °C (0 min) and finally ramped at 30 °C/min to 250 °C (0.17 min). Run time was 25.003 min with a 2 min solvent delay. The mass spectrometer was operated in electron-impact ionization mode at 70eV with ion source temperature of 230 °C, quadrupled temperature of 150 °C and transfer line temperature of 300 °C.

Prior to analysis, the MS was auto-tuned to perfluorotributylamine (PFTBA) using already established criteria to check the abundance of *m/z* 69, 219, 502 and other instrument optimal & sensitivity conditions.

After calibrating with the appropriate solvent standard (a cocktail of methanol, ethanol, MTBE, and 1-butanol solvents) purchased from JHD Chemicals, the samples were analyzed and corresponding volatile organics concentration obtained are stated in the results.

RESULTS AND DISCUSSIONS

The presence of organic micropollutants was confirmed in all the sampled subsurface water in both areas A and B, with that of area B lower. Figures 1-6 shows the GC/MS chromatograms of the extracted water samples. The quantitative values (concentrations) of these organic micropollutants obtained as compared with NESREA, WHO, and EPA standards are as shown in Table 1. The result shows that Benzene was high in all the sampled subsurface water, while Toluene was high in only two subsurface waters. Ethylbenzene was present in all sampled subsurface water, but their concentrations were below the target standard. The three forms of xylenes were discovered but were below the standards target. The chlorinated hydrocarbons determined were found to be absent. As fuel additives, MTBE, Methanol, Ethanol, and t-Butanol were discovered in all the subsurface water with MTBE having quantitative values

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higher than the recommendations of the standard Agencies.

In view of our obtained results, we opine that the recommendation of EPA, with respect to MTBE usage since 1979 [14] should be revisited and reviewed due to the high quantitative values of MTBE in all the sampled subsurface water in Lagos State, implying that the chemical is still highly in use.

Table 1: Concentrations for each Organic micropollutants and Oxygenates obtained from the underground water samples from the two areas under study.

	AREA A			AREA B			ORGANIZATION TARGET STANDARDS		
Compounds	Underground water 1 in (mg/l)	Underground Water 2 in (mg/l)	Underground Water 3 in (mg/l)	Underground Water 1 in (mg/l)	Underground Water 2 in (mg/l)	Underground Water 3 in (mg/l)	NESREA	WHO	EPA
MTBE	25.153	25.815	27.349	1.267	1.251	1.300	Nil	Nil	20-40ppm
Methanol	4.827	0.5801	0.4524	1.6076	1.0843	0.6897	Nil	Nil	Nil
Ethanol	0.2705	0.2375	0.2630	0.1716	0.1475	0.1057	Nil	Nil	Nil
t-Butanol	0.3340	0.4290	0.5830	0.3060	0.5800	0.6060	Nil	Nil	Nil
Benzene	664.991	1829.190	1724.820	43.888	204.284	277.403	0.2	0.1	1.0
Toluene	524.893	159.524	69.792	2.342	4.502	2.011	0.2	0.001	Nil
Ethylbenzene	34.347	34.423	34.382	1.717	1.719	1.717	0.2	0.001	Nil
m/p-Xylene	17.037	17.035	17.009	0.000	0.000	0.000	0.2	0.005	Nil
o-Xylene	0.000	0.000	0.000	1.579	1.579	0.000	0.2	0.005	Nil
Chlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.01	1.0	1.0
1,2 dichlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.01	1.0	1.0
1,3-dichlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.01	1.0	1.0
1,4-dichlorobenzene	0.000	0.000	0.000	0.000	0.000	0.000	0.01	1.0	1.0
Total Volatile Organics (mg/l)	1266.421	2065.986	1873.351	50.793	213.334	282.431			

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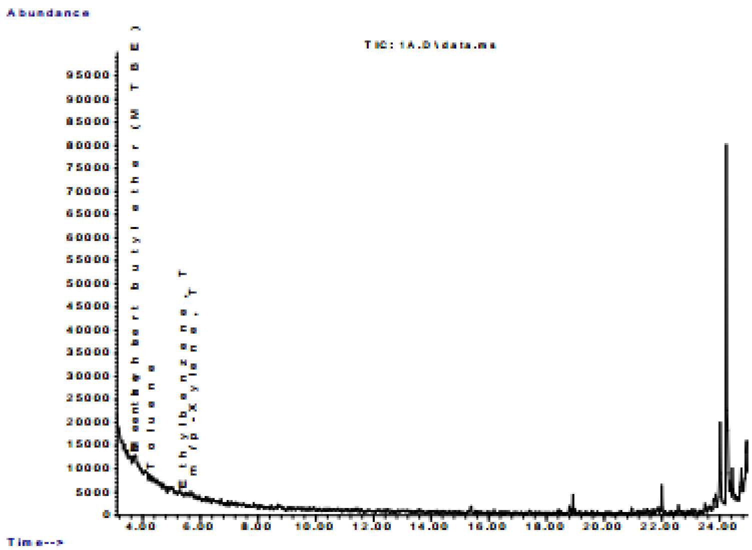

Fig 1 Chromatogram for concentrations of Oxygenates and Organic micropollutants for subsurface water 1 in area A studied.

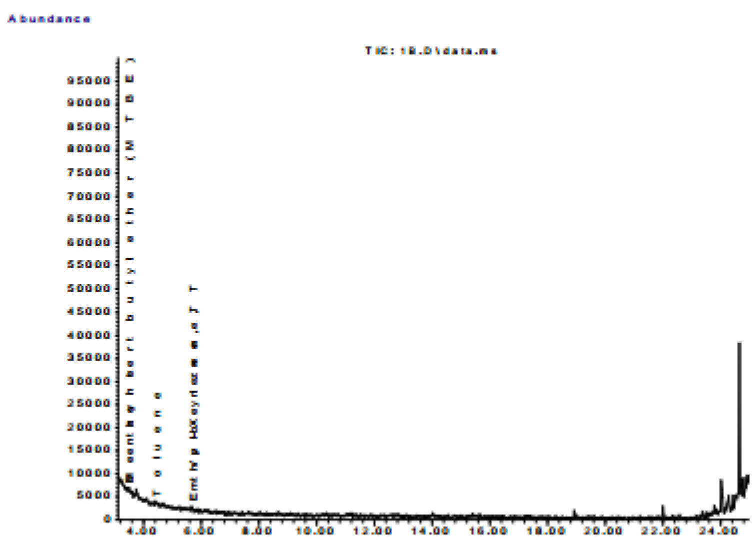

Fig 2 Chromatogram showing concentrations of Oxygenates and Organic

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Micropollutants obtained for subsurface water 2 in area A studied.

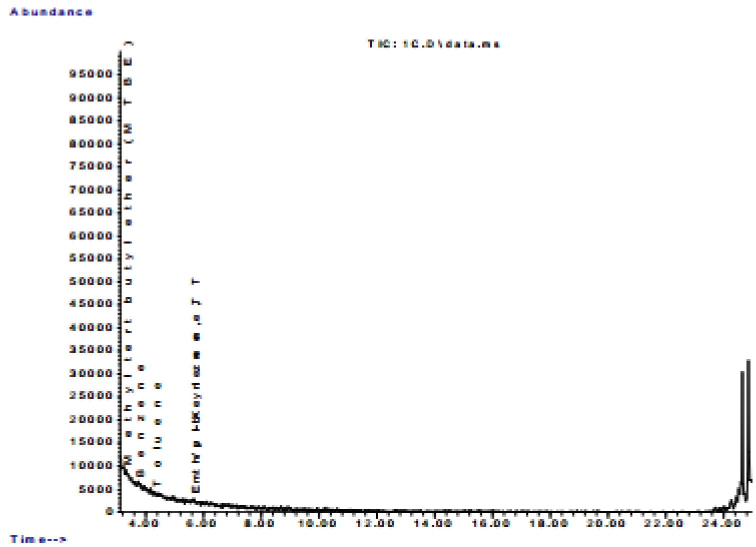

Fig 3 Chromatogram for concentrations of Oxygenates and Organic

micropollutants for subsurface water 3 in area A studied.

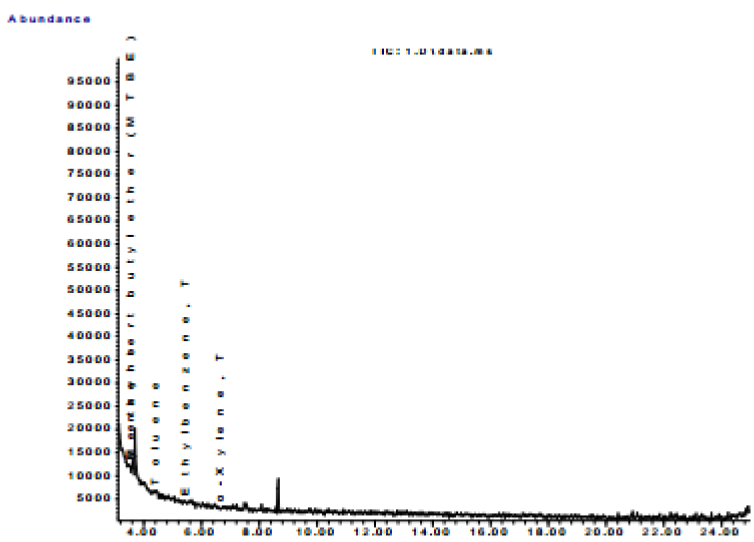

Fig 4 Chromatogram obtained for concentrations of Oxygenates and Organic

micropollutants for subsurface water 1 in area B studied.

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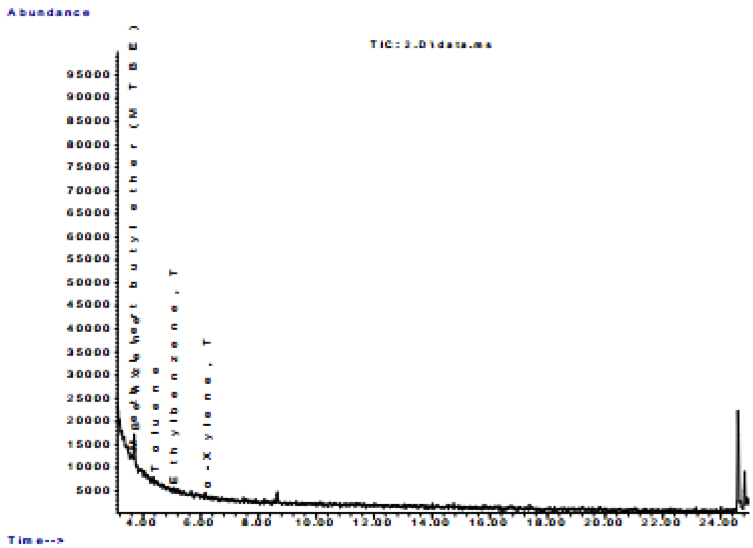

Fig 5 Chromatogram showing concentrations of Oxygenates and Organic micropollutants for subsurface water 2 in area B studied.

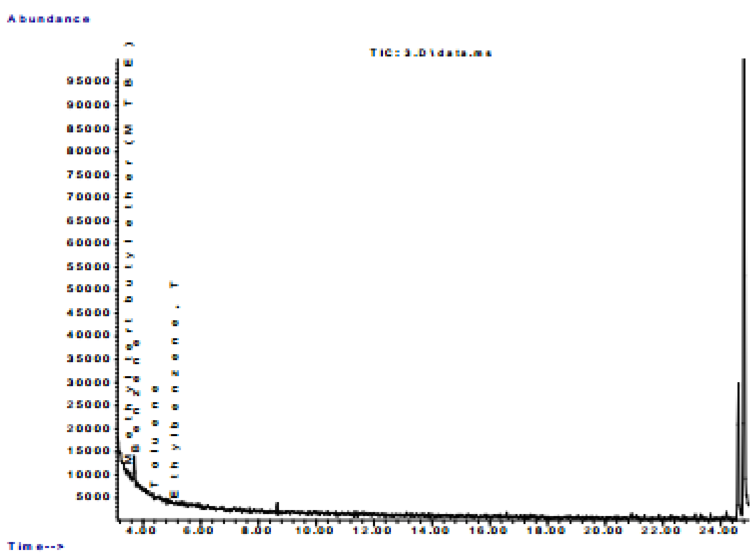

Fig 6 Chromatogram obtained for concentrations of Oxygenates and Organic Micropollutants for subsurface water 3 in area B studied.

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CONCLUSION

The presence of organic micropollutants in the sampled subsurface water was confirmed and their quantitative values when compared to recommendations of Environmental agencies shows some to be above standard while others below. The organic micropolluants found to be above are majorly those that are or likely to be carcinogenic in nature, thus there is need for concern on the use of these chemicals despite the recommendation of abolishment by environmental agencies.

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