Canadian Journal of
pure&applied
sciences

BASELINE MONITORING DATA OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN TAKE LAGOS STATE, SOUTHWESTERN - NIGERIA

*Ojiodu CC[1], Okuo, JM[2] and Olumayede EG[3]
[1]Department of Chemical Sciences, Yaba College of Technology, Yaba – Lagos
[2]Department of Chemistry, University of Benin, Edo State
[3]Department of Chemical Sciences, Ondo State University of Science and Technology, Ondo State, Nigeria

ABSTRACT

The present study investigated volatile organic compounds pollution based on the principles of dilution, diffusion and dispersion in a rural fishing community of Take, Lagos state Southwestern, Nigeria. The air samples were collected by passive sampler (ORSA 5). The air samplers were exposed to a height of 1.5-2.0 m and sampling was carried out four times a month for a period of 12 months. The adsorbed VOCs were desorbed with carbondisulphide (CS_2) and the solution analysed using Gas Chromatography (GC) fitted with Flame Ionization Detector (FID). The results from analysis of the air samples collected showed that twenty (26) VOCs were captured in Take area. The VOCs were classified thus: aromatics 43%, halogenated 28%, esters 4%, ketones 13%, alcohols 6%, ethers 6%. There is a significant difference ($P_{value} < 0.05$) between the levels of VOCs in Take area. The meteorological parameters showed significant correlations with the ambient concentrations of VOCs. The principal component analysis revealed that the major sources of VOCs in Take areas are mainly Anthropogenic and three (3) factors were identified as sources of VOCs in the studied area with emissions from the waste dump dominating.

Keywords: Pollution, Baseline, gas chromatography, Sampling, anthropogenic.

INTRODUCTION

Several studies have shown that air pollution is a threat to human health (Muezzinoglu et al., 2001; Ho et al., 2002; Yamamoto, 2000; Ohura et al., 2006; Simona et al., 2009; Zhao et al., 2004). VOCs are known for degrading air quality; their associated oxidants and threatening to both human health and the ecosystem (Molina et al., 2007; Ulman and Chilmonczyk, 2007). The short term adverse effects include conjunctive irritation, nose and throat discomfort, headache and sleeplessness, allergic skin reaction, nausea, fatique and dizziness. While the long term adverse effects include loss of coordination, leukamia, anaemia, cancer and damage to liver, kidney and central nervous system (Kim et al., 2001; Eljarrat and Barcelo, 2003; Environment Australia, 2001; Pohl et al., 2003; Kerbachi et al., 2006). Volatile Organic Compounds are commonly encountered by people as they go about their daily routine. Studies have shown that VOCs enter the human bloodstream through the following means inhalation, ingestion and through the skin (ATSDR, 2001). In Nigeria, air quality status of different environments has been reported (Ukepbor et al., 2010; Olumayede and Okuo, 2011a,b). In a previous study in Nigeria atmosphere, Olumayede et al. (2011a) reported that VOCs concentrations were influenced by economic activities. Similarly, Okuo et al. (2012) reported that ambient VOCs concentrations exhibited a significant correlation with meteorological parameters.

Unfortunately, most of these studies were carried out in an urban atmosphere, while, only Okuo et al. (2011) reported VOC concentration in some health and financial institution Microenvironments in Benin City. In this report, VOCs levels were found to be lower than the international standards when compared.

Take is a community situated at the bank of Lagos Lagoon in Eti - osa Local Government area in Epe division of Lagos state. It is located at longitude 6.36^0 N and latitude 3.59^0. Take have a population of 108 people. The people live in make - shift stalls (houses) which are all lumped together. There are neither streets nor road network in Take. The only source of electricity is the solar power provided by the Lagos state government. Take was selected as a background study because it is an area devoid of vehicular and human activities. The only human activity in Take is fishing. Therefore, there is a need to investigate ambient air pollution by volatile organic compounds in Take areas of Lagos state. The objectives of this study are to: determine the baseline levels of Volatile Organic Compounds in Take areas of Lagos state; determine the contributions of both natural and anthropogenic sources of VOCs emitted in the areas of study.

MATERIALS AND METHODS

Sampling Locations
This study was conducted in Take areas of Lagos state. Take lies within the tropical rainforest region with two

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*Corresponding author email: ojiodu1966@yahoo.com

distinct seasons: wet and dry seasons. The temperature throughout the year ranges between 21^0C and 30^0C. The humidity is relatively high while the rainfall ranges between 150mm - 200mm. The wind speed recorded during the study ranged between 3.20-6.00 ms^{-1}.

Selection of Sampling Site
The samples were collected at five sites within Take area. The sites were carefully chosen based on the following criteria: Cost of equipment, accessibility to the locations, freedom from any obstacle to the free flow of air in the vicinity and security of the sampler. The locations (sites) were chosen to reflect activities in the areas. The geo - referencing was carried out by using GARMIN GPS MAP 76S.

Table 1. Monitoring Locations, their Characteristics and Co - ordinates of Take Area.

Site	CODE	Co-ordinates	Site description
1.	TAK1	N 6^0 36' 16.7" E 3^0 58' 35.0"	A location with make - shift houses lumped together with no human activity.
2.	TAK2	N 6^0 36' 18.2" E 3^0 59' 27.9"	A location with make - shift houses lumped together with no human activity.
3.	TAK3	N 6^0 36' 40.4" E 3^0 59' 43.0"	A location with make - shift houses lumped together with no human activity.
4.	TAK4	N 6^0 36' 32.6" E 4^0 00' 07.6"	A location with make - shift houses lumped together with no human activity.
5.	TAK5	N 6^0 36' 27.4" E 3^0 59' 31.1"	A location with make - shift houses lumped together with no human activity

Sampling Device and Collection of Ambient VOCs
Ambient air samples were collected using ORSA 5 diffusion tubes from Dragger Safety, Lubeck, Germany. The Sampler comprises a glass sampling tube open at both ends and filled with activated charcoal. Each opening in sampling tube is filled with cellulose acetate diffusion barrier. Ambient air diffuses into the sampling tube in a controlled manner. The cross section, tube length and diffusion coefficient are constant and expresses the sampling rate (NIOSH, 1984).
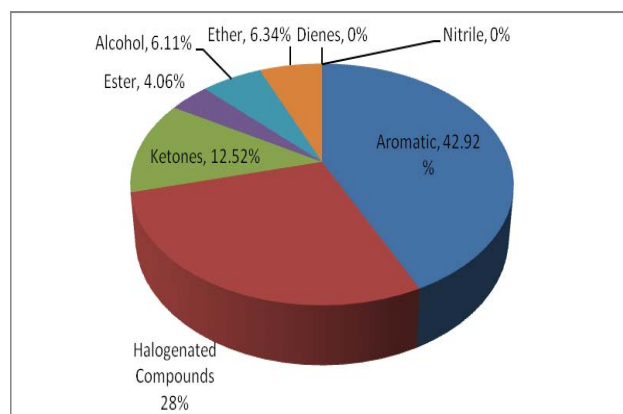

Fig. 1. Percentage Composition of each family of VOCs in Take Area.

Sampling Routine
Samplings were carried out during dry and wet seasons. The samplers were exposed at a height of 1.5 - 2.0 metres. Sampling was done 4 times a month, for a period of 12 months. The samplers were harvested after seven days and taken to the laboratory for analysis. A total of 480 samples were collected for the two seasons. During each round of ambient sampling, meterological parameters such as temperature, wind speed, wind direction and rainfall were also recorded.
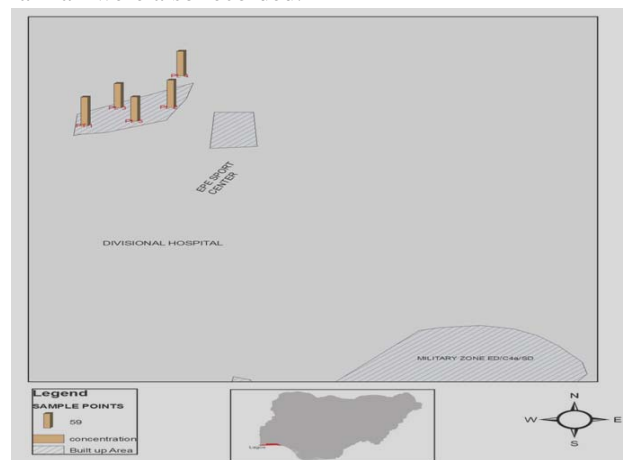

Fig. 2. GIS Map Showing the Sampling sites and in Spatial Distribution of Total VOCs Concentrations at Take Area.

ANALYTICAL METHODS

Extraction Process
After sampling, adsorption tubes were labeled and closed with special caps to avoid contamination and desorption. The samples were placed into tightly closed special plastic bags and kept in a freezer until they were processed. Before analysis, contents of both sections of the adsorbed tubes were placed into two different vials in which they were weighed, 10ml carbondisulphide (CS_2)

was added as the extraction solvent to each tube (ASTM, 1988). Samples were extracted using a magnetic stirrer (Jenweary 1103) for 30min. The extracted samples were then filtered and stored in a freezer until they were analyzed using Gas Chromatographic instrument (GC) fitted with flame ionization detector (FID). The concentrations of the analyte were read from the calibration graph, which was done with standard solution.

Chromatographic Analysis

The extracted solutions were analyzed with gas chromatograph (GC) (Perkin Elmer Clarus 500) equipped with a flame ionization detector (FID). The GC / FID was standardized and calibrated by injecting about 2µL VOC - mix into it. The GC with a capillary column (Elite - V) (40m x 0.18mm x i.d 1.0µm) was used with an initial oven temperature of 35^0C (held for 2min) increased to 60^0C at a rate of 4^0C min^{-1} (held for 0min) and finally to 225^0C at the rate of 40^0C min^{-1}(held for 5min). Helium was used as carrier gas at a constant flow rate of 45ml min^{-1}. The bake time was 8 min at 260^0C. The split ratio is 1: 40 and the injection and detection temperatures were maintained at 250^0C and 280^0C respectively.

Chemical Standards and Instrumental Calibration

External calibration was carried out with a Volatile Organic Calibration Mix containing 40 VOCs in 2000mgL^{-1} in Methanol (Supelco, Bellefonte, USA). The calibration was performed by analyzing diluted standards. The standard solution was prepared by dilution in CS_2 / methanol for gas chromatography. Seven calibration levels of concentration range of 0.1 and 3.0 mg·L^{-1} (0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0) with CS_2 was prepared from stock standard in a clean vial. They were freshly prepared at the moment of calibration. The instrumental calibration was performed by analyzing 2µL of the diluted standards, in order to obtain the relative response value (µv).

STATISTICAL ANALYSIS

Two - way Analysis of Variance (ANOVA) statistical test was used to evaluate significance of the differences in means, we use correlation coefficient (r^2). Sources of emission were determined using correlation coefficient ($p < 0.05$) and the factor analysis (Principal Component Analysis) (SPSS, 2007).

Factor Analysis

The Principal Component Analysis (PCA) are the primary factor analysis techniques that uses eigen value to apportion data sets to identify emission sources, chemical interaction on meterological phenomenon depending on the data sets that have been submitted to PCA. PCA is use to classify variables into groups that can then be associated with factors that contribute to pollutant levels at receptors. Three factors were extracted from Take. The first (F1), second (F2) and third (F3) factors accounted for 52.41, 32.89 and 14.70 % of the total variance.

F1: This factor is highly loaded in xylene, methylene chloride, carbontetrachloride and chloroform. The xylenes were released from waste dumpsite in the area while methylenechloride, carbontetrachloride and chloroform were released from dry cleaning processes and the use of insecticide in homes. Therefore, factor 1 is attributed to waste dumpsite and evaporative emission.

F2: Factor 2 is loaded in xylene, trichloroethane and tetrachloroethane. These solvents are released from the use of insecticides in homes and from waste dumpsite in the studied area. Hence , F2 is an indicator of emissions from evaporative sources and waste dumpsite.

F3: This factor is highly loaded in xylene, 1,2-dichloropropane and carbontetrachloride. Factor 3 is an indication of emission from waste dumpsite and evaporative sources.

Table 2. Measured Mean, Standard Deviation and Maximum values of VOCs at Take Areas (µg/m^3) n = 5.

AROMATICS VOCs	MEAN	STD	MAX.
Benzene	7.62	0.05	7.66
Ethylbenzene	5.26	0.13	5.48
Isopropylbenzene	3.29	0.07	3.40
Napthalene	2.37	0.06	2.46
n-Butylbenzene	2.61	0.08	2.71
n-Propylbenzene	1.97	0.05	2.03
Toluene	2.76	0.01	2.78
m+p-Xylene	18.80	0.08	18.92
o-Xylene	6.34	0.03	6.44
HALOGENATED VOCs BROMIDES			
Bromomethane	6.34	0.03	6.39
Bromoform	3.41	3.99	10.55
CHLORIDES			
Chlorobenzene	2.55	0.03	2.58
Chloroform	2.43	0.16	2.64
Carbontetrachloride	1.63	1.01	3.14
Methylenechloride	4.09	0.16	4.28
Trichloroethane	1.43	0.46	2.08
Trichlorofloromethane	2.41	0.10	2.53
1,2-dichloropropane	2.31	1.27	3.94
2,2-dichloropropane	2.66	1.27	4.05
Tetrachloroethane	2.87	1.86	4.92
KETONE VOCs			
Acetone	8.10	0.03	8.13
4-Methyl-2-Pentanone	4.98	0.06	5.05
ESTER VOC			
Isopropylacetate	4.20	0.04	4.24
ALCOHOL VOC			
Ethanol	6.31	0.09	6.43
ETHER VOC			
Tetrahydrofuran	6.62	0.01	6.62

Table 3. Total Monthly Measured VOCs Values in the Studied Areas (µg/m³).

Months	Urban Area (Ketu-Mile 12) Mean±Sd	Rural Area (Take) Mean±Sd
January	591.53 ± 54.06	64.72 ± 6.39
February	489.87 ± 58.22	64.90 ± 6.86
March	584.56 ± 47.59	64.39 ± 8.09
April	509.18 ± 40.23	66.09 ± 5.20
May	323.28 ± 16.52	28.01 ± 6.34
June	313.12 ± 15.74	27.18 ± 4.75
July	277.97 ± 13.95	26.45 ± 2.31
August	291.99 ± 14.41	26.58 ± 2.42
September	298.75 ± 14.77	27.01 ± 5.08
October	305.62 ± 15.29	27.41 ± 5.32
November	589.02 ± 46.63	64.13 ± 5.39
December	591.73 ± 55.27	62.84 ± 7.04

RESULTS AND DISCUSSION

Twenty- Six (26) VOCs were captured in Take area (Table 1). The VOCs were classified thus: aromatics 42.92%, halogenated 28%, esters 4.06%, ketones 12.52%, alcohols 6.11% and ethers 6.34%. (Fig. 1). The most abundant compounds in Take area were BTEX and halogenated VOCs (Fig. 2). Site 5 has the most abundant BTEX (benzene 7.63, ethylbenzene 5.48, toluene 2.78 and xylenes 25.28 µg/m³, while the lowest BTEX levels were observed at Site 2 (benzene 7.54, ethylbenzene 5.16, tuolene 2.75 and xylenes 25.09µg/m³ (Table 2). This may be due to the principle of diffusion and dispersion of Air within and around Lagos state. The halogenated VOCs species were dominated by bromomethane, chlorobenzene, chloroform, carbon tetrachloride, trichlorofloromethane and 1,2 - dichloropropane. The mean concentrations of halogenated VOCs in the studied background area were 6.34, 2.55, 2.43, 1.63, 2.41, 2.31 µg/m³ respectively. The halogenated VOCs not only results from the use of insecticides, cosmetics and from waste dump sites in the area. (Liu *et al*., 2008). The concentration of xylenes in Take is no doubt a reflection of the presence of dump site in the vicinity of the area. The highest Total Volatile Organic Compound was recorded in the month of April (66.09µg/m³) while the lowest value was in July (26.45µg/m³) (Table 3). This is because during the wet seasons, apart from dilution of the atmosphere, there is a washdown of Atmospheric Air. The Total Volatile Organic Compounds (TVOC) in Ketu - Mile 12 (urban area) is about ten (10) times the values in Take (rural area) (Table 3). Site 1 is the most polluted site in Take, apart from the presence of high human and commercial activities such as hawking of various household, consumer products and materials like footwares, cloths, plastic, detergents, inks, nail polish e.t.c in site 1, the site is located along the major roads

characterized by heavy traffic (Table 4)(Olumayede *et al*., 2012a ; Chang *et al*., 2005; Ohura *et al*., 2006; Hsieh and Tsai, 2003). There is a significant difference (P_{value} < 0.05) between VOCs in the studied background areas (Vasu *et al*., 2009; Liu *et al*., 2008; Srivastava *et al*., 2005). The level of pollution in all the sites in take is similar with site 1 having the highest level of pollution (118.42µg/m³) (Table 4). There is a significant difference (P_{value} > 0.5) between each of meteorological factors such as temperature, relative humidity, wind speed and wind direction. The most prevailing wind direction for the year was the South - South West wind (S - SW). The Principal Component Analysis (PCA) showed that three (3) factors were identified as sources of VOCs in the studied area with emissions from waste dump dominating .

Table 4. Total Volatile Organic Compounds (TVOC), Percentage and Ranking at the Studied Areas (µg/m³).

SITES	Ranking	Percentage %	Mean ± SD n = 10
1	1st	22.18	118.42 ± 17.86
2	2nd	21.08	112.58 ± 16.07
3	4th	18.89	100.89 ± 15.96
4	3rd	18.96	101.25 ± 20.74
5	5th	18.88	100.83 ± 18.14

CONCLUSION

Though, Take is an area devoid of pollution, the sources of pollution are basically from waste dump and evaporative sources, which occur by dilution, dispersion and diffusion of Amospheric air of Lagos-State.

ACKNOWLEDGEMENT

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