VOLATILE ORGANIC COMPOUNDS (VOCs) POLLUTANTS IN TWO INDUSTRIAL AREAS IN LAGOS STATE, NIGERIA

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Abstract
VOCs are important class of air pollutants because they are ubiquitous and associated with increased short and long - term health risks in the industrial areas and environs. The air samples were collected by passive sampler (ORSA 5) from two contrastive industrial areas such as Ikeja and Isolo industrial areas. The air samplers were exposed to a height of 1.5 - 2.0m 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). Twenty - Six (26) VOCs were captured in the Atmosphere of each of the studied areas. Seven (7) VOCs each were identified as the major contributors to ambient air pollution in Ikeja and Isolo industrial areas. There is a significant difference ($P_{value} < 0.05$) between the levels of VOCs in the studied areas. The meteorological parameters showed significant correlations with the ambient concentrations of VOCs. The monthly mean concentrations of the atmosphere total volatile organic compounds (TVOCs) in the studied areas show significant difference. The Principal Component Analysis (PCA) showed that the major sources of VOCs are mainly anthropogenic and four factors each were identified as sources of VOCs in each of the studied industrial areas with industrial emissions dominating in industrial areas.

Keywords: Pollutants, Contrastive, Gas Chromatography, Industrial, Anthropogenic.

Introduction

VOCs are important class of toxics air pollutants because they are ubiquitous and associated with increased short and long - term health risks in the industrial areas and environs for two distinct reasons. Firstly, they are precursors required for the photochemical production of atmospheric Ozone. Secondly, they include species that are individually carcinogenic and mutagenic in their own right (Pratt *et al,* 2000). The impact of any pollutant can be reduced by one of the following four ways which include (i) dilution of its concentration before it reaches any sensitive receptor (ii) collect the pollutant and dispose it in a way that prevents it from reaching most sensitive receptor (iii) collect and recycle the pollutant for some useful purposes (iv) Produce or prevent the emissions from occurring in the first place (Goodwin *et. al,* 1999). VOC pollutants are numerous including alkanes, alkenes, aldehydes and aromatics which vary in reactivity. The major oxidant responsible for their removal from the atmosphere is the hydroxyl radical (PORG, 1997). Volatile Organic Compounds are commonly encountered by people as they go about their daily routine. VOCs are carbon - based compounds that have vapour pressure to significantly vaporize and enter the atmosphere (U.S EPA, 2005; EU, 2005; Estate Management, 2009). Studies have shown that VOCs enter the human bloodstream through the following means inhalation, ingestion and through the

skin (ATSDR, 2001). They play an important role in the chemistry of the atmosphere; their role in the formation of photochemical smog and their associated oxidants, degrading air quality and threatening both human health and ecosystem (Molina *et al,* 2007). VOCs in industrial areas emanate from industrial activities of various industrial units and the products associated with them. These industrial units include ceramic and tile, lime and cement, energy, rendering, metal plating, refineries, slaughter houses, metal foundries, food industries, detergents, dry cleaners, dyeing industries, tanneries, dairies, oil mills, fisheries, hydrometallurgical processes, aluminum recycling, piggeries, poultry raising, breweries, cosmetics, canning industries, pharmaceuticals, wood processing units, paper mills, production of construction materials etc. The commulative risk from exposure to multiple VOCs and other air pollutants is not well known in Lagos and its industrial areas and limited evidence suggests that the minority population residing in industrial of Lagos state have disproportionately higher exposures (Kinney *et al,* 2002). It is generally believed that Children, Pregnant women and the elderly are at greater risk for developing disease from lower levels of exposure (Freedom *et al*, 2001).

The two Contrastive areas in this study are Ikeja and Isolo industrial areas. They are both located in Ikeja division of Lagos State on longitude 6.31 - 6.360N and latitude 3.19 - 3.20^0 E. The population within the Local Government was estimated at 313,196 - 521,509 people according to the 2006 final census result (NPC, 2009). Conspicuous in these areas are various types of industries which include paint, food and beverage, pharmaceutical, textile, soap, and detergent, heavy chemical, paper, paint, printing and publishing, cosmetic, breweries etc. There are also clusters of filling stations, shoppingmoore, eatries, motor parks, official and residential houses. The land - use pattern at Ikeja and Isolo industrial areas are mostly in dustrial and partly residential (Ojiodu, 2012)

The main objectives of this study are to: determine the types of VOCs Pollutants and the percentage contribution to pollution in the study area, the contributions of both natural and anthropogenic sources to VOCs emission in the areas of study.

Materials and Method

Sampling Locations

This study was conducted in Ikeja and Isolo industrial areas of Lagos state. Ikeja and Isolo areas lies within the tropical rainforest region with two distinct seasons: wet and dry seasons. The temperature throughout the year ranges between 21^0C and 30^0C. 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

10 samples were collected at ten sites from each of the studied areas. The sites were carefully chosen based on the following criteria: Cost of equipment, accessibility to the locations, freedom from any obstacle to 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.

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). The diffusive (passive) sampler fulfilled many of the logistical requirements of an ideal ambient air monitor

(Brown, 1999). A validation processes for diffusive sampler had been performed (Pfeffer *et. al*, 1995; ASTM, 1988).

Principle of the method

The sampling is performed through diffusion. The analyte is adsorbed on the activated charcoal and the surface of the charcoal attracts and holds the gases (adsorbate) by physical adsorption.

Sampling Routine

Sampling was 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 960 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.

Table 1: Monitoring Locations, their Characteristics and Co - ordinates at Ikeja Industrial Area

Site	Code	Co-ordinates	Site Description
1.	IKEI	N 6^0 36′ 40.5″ E 3^0 21′ 13.6″	This site is created at oregun road by Eleganza Industries. A location with heavy traffic density.
2.	IKOR	N 6^0 36′ 33.9″ E 3^0 21′ 16.7″	Created at Oregun road by Seven - Up Bottling Company, PLC. A location with clusters of filling stations and commercial activities such as hawking of household items.
3.	IKOA	N 6^0 36′ 07.0″ E 3^0 20′ 16.7″	Oba -Akran. This site is at Vitafoam, PLC. A location with high vehicular activities.
4.	IKOB	N 6^0 36′ 07.5″ E 3^0 20′ 10.4″	Created at Obasa junction.
5.	IKNP	N 6^0 36′ 05.2″ E 3^0 20′ 07.8″	This site created at Obasa road. A location with commercial activities such as hawking of cosmetic products, plastic and textile materials, footwears, food items.
6.	IKIP	N 6^0 36′ 13.0″ E 3^0 20′ 13.1″	Created at Oba-Akran road by International paints for West Africa, PLC. (IPWA). A location with high traffic density.
7.	IKGI	N 6^0 36′ 28.3″ E 3^0 20′ 10.4″	This site is at Oba – Akran road by Guinness Nigeria, PLC. A location with high vehicular activities.
8.	IKAJ	N 6^0 36′ 26.0″ E 3^0 20′ 19.1″	Created at Adeniyi Jones by Dilux paint. A location with commercial activities such as hawking of household items.
9.	IKOS	N 6^0 36′ 23.7″ E 3^0 20′ 31.9″	Olorunbe site. This location is made up of residential buildings with commercial stores such as pharmaceutical and paint shops
10.	IKAS	N 6^0 36′ 00.6″ E 3^0 20′ 26.2″	This site is created at Ajao street, off Obafemi Awolowo road. A location with commercial stores and business centres.

Table 2: Monitoring Locations, their Characteristics and Co - ordinates at Isolo Industrial Area

Site	Code	Co-ordinates	Site Description
1	ISLT	N 6^0 31′ 42.3″ E 3^0 19′ 49.9″	Created at Abimbola street by Limca junction. A location with many road intersections and high traffic density.
2	ISJW	N 6^0 31′ 29.9″	Abimbola site created at Abimbola street by Johnsonwax

		E 3^0 19′ 48.2″	Industries, PLC. A location with high traffic density.
3	ISIM	N 6^0 31′ 26.3″ E 3^0 19′ 54.1″	Ilasamaja International market site. A location where various types of products such as agricultural, household, petrochemicals, pharmaceuticals etc. are sold.
4	ISCB	N 6^0 31′ 35.2″ E 3^0 19′ 58.5″	Created at Limca /Chesebrough way. A location with many road intersections and high traffic density.
5	ISMD	N 6^0 31′ 44.9″ E 3^0 20′ 02.5″	Isolo-Apapa site. Created at Isolo - Apapa Express by mandilas. A very busy road with high human and vehicular density.
6	ISIJ	N 6^0 31′ 23.8″ E 3^0 20′ 22.6″	Created at ile-iwe meta junction Bus-stop. A location with many road intersections.
7	ISRT	N 6^0 31′ 55.4″ E 3^0 19′ 54.1″	Rotary site. A site located at Rotary road. A location with many commercial shops with road side mechanics.
8	ISIS	N 6^0 31′ 48.8″ E 3^0 19′ 48.9″	Created at Isolo road. A location with high commercial and vehicular activities.
9	ISAF	N 6^0 31′ 59.5″ E 3^0 20′ 07.7″	This site is located at Oshodi - Apapa Express road by Afprint, PLC. A location with high traffic density.
10	ISAM	N 6^0 31′ 26.3″ E 3^0 19′ 58.1″	Created at Isolo way by Aswani - market. A location where textile and plastic materials are sold.

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 0.18 mm 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 2500C 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, U.S.A.). 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). The calibration results curve shows good linearity, with determination regression coefficient (r^2) greater than 0.999 for all the compounds.

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. It involves the classification of variables into groups that can then be associated with factors that contribute to pollutant levels at receptors.

Four factors were extracted from the data acquired at Ikeja Industrial areas. The first factor (F1) explained 38.35% of the total variance, second factor (F2) accounted for 30.69%, third (F3) and fourth (F4) factors were responsible for 23.0 and 7.69% of the total variance.

F1: This factor is loaded in xylene, isopropyl acelate, n - butylbenzene, n-propylbenzene and methylene chloride. The chemicals are used as solvent in paint, soap and detergent, cosmetic, pharmaceutical, paper and printing industries and also from hawkers of household materials like cloths, perfume and gift items like dinner sets. These chemicals are also released from vehicles in the studied area (Graham et. al, 2004). Therefore, factor 1 may be attributed to a combination of industrial solvent usage and vehicular emission.

F2: The high loading of factor 3 in ethanol, acetone, naphthalene and 4-methyl-2 pentanone. These are solvents used in paint, cosmetics and textile industries in the studied area (Wallace, 2001). Hence, factor 3 may be attributed to industrial solvent usage.

F3: Ethanol, benzene and ethylbenzene released from breweries, vehicules and people involved in gluing operations and tobacco smokers in the studied area is loaded in factor 3. Therefore, factor 3 is an indication of industrial and vehicular emission.

F4: Factor 4 accounted for 13.59% of the variance in the data. It was highly loaded in trichloroethane, 1, 2-dichloropropane and isopropyl acetate. These chemicals are used as solvents in cosmetics and paint industries in studied area. The source of factor 4 might be a combination of solvent usage and industrial emission. Similarly, four factors were identified as contributing to the

measured values in Isolo industrial area. The first (FI), second (F2), third (F3) and fourth (F4) factors accounted for 40.52, 25.26, 15.24 and 13.16 % of the total variance.

F1: This factor is highly loaded in ethylbenzene, isopropylbenzene, naphthalene, tuolene, trichloroethane and chloroform. These chemicals are used in cosmetics and paint industries and in the area. They are also released from petroleum products from petrol stations located in the area. Therefore, factor 1 is attributed to emissions from industrial solvent usage and petroleum products.

F2: Ethylbenzene, ethanol, chlorobenene and xylene is loaded in factor 2. These compounds are released from vehicle exhaust and petroleum products from petrol stations in the vicinity of the studied area (Rappengluck and Fabian, 1999). Factor 2 suggests vehicular and petroleum products emission.

F3: Factor 3 is highly loaded in ethanol, acetone and chloroform. These compounds are use as solvent in textile and paint industries in the studied area. Therefore, factor 3 is attributed to industrial solvent usage.

F4: Tetrachloroethane and trichlorofloromethane is loaded in factor 4. These are solvents used in paint and textile industries in the studied area. They are also released from refrigerator and air conditioner workshops in the area. Factor 4 is due to industrial solvent usage and evaporative emission.

The principal component analysis revealed that the major sources of VOCs in both Ikeja and Isolo industrial areas are mainly Anthropogenic and four (4) factors each were identified as sources of VOCs in the studied area with emissions from industries and traffic dominating.

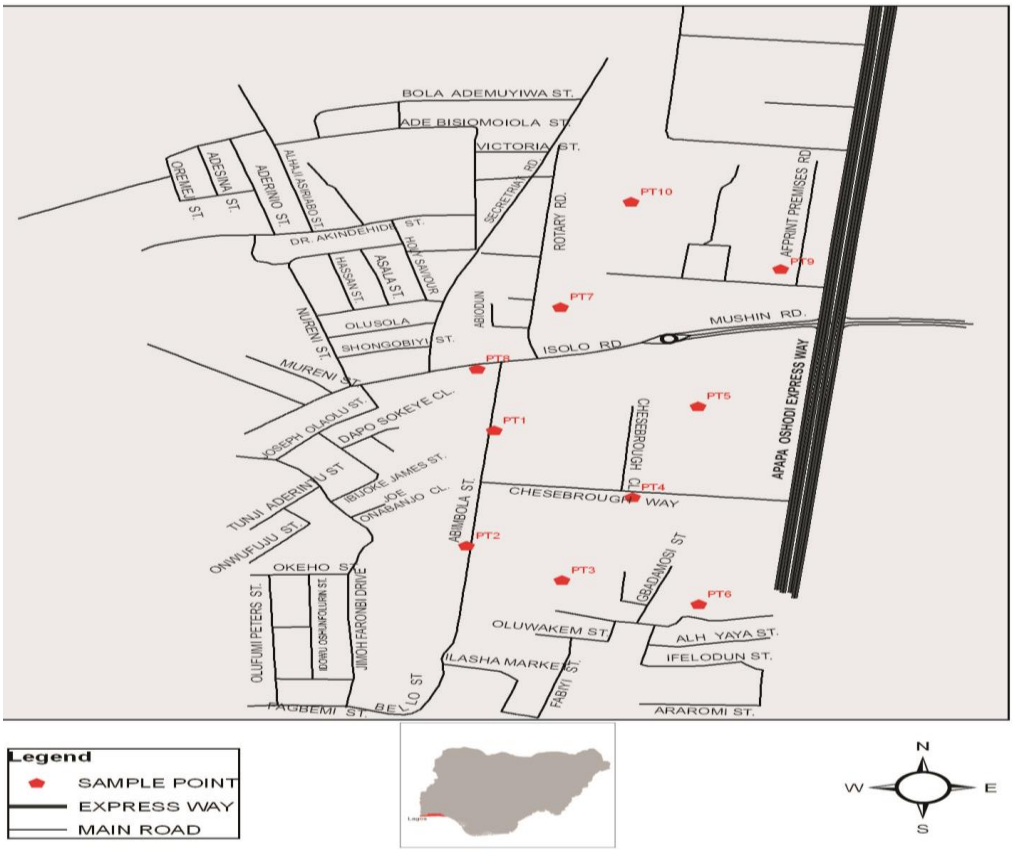

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Fig. 2: GIS map showing the sampling sites in isolo industrial area results and discussion

Table 3: Mean, Standard Deviation and Maximum Concentration of VOCs at Ikeja (n = 10) an Isolo Area (μgm^{-3}) (n = 10)

	Ikeja			Isolo		
	Mean	Std	Max.	Mean	Std	Max.
AROMATICS VOCS						
Benzene	27.04	0.96	31.85	13.43	1.14	14.11
Ethylbenzene	12.04	0.2	16.4	9.38	1.33	9.99
Isopropylbenzene	13.62	0.5	16.31	18.43	0.29	18.88
Napthalene	14.99	0.51	17.34	14.55	0.1	14.77
n-Butylbenzene	16.16	0.24	16.59	18.97	0.15	19.31
n-Propylbenzene	14.87	1.51	18.91	15.14	0.09	15.27
Toluene	22.28	1.04	26.14	14.03	0.16	14.37
m+ p – Xylene	63.67	0.08	73.69	31.3	0.21	31.64
o-Xylene	45.95	9.12	55.7	17.9	0.25	18.35
HALOGENATED						

VOCS						
BROMIDES						
Bromomethanez	26.34	0.77	27.84	10.24	0.13	34.19
Bromoform	15.17	5.44	15.5	16.23	0.18	23.24
CHLORIDES						
Chlorobenzene	22.08	1.01	23.14	18.7	0.13	10.42
Chloroform	26.87	0.55	27.89	15.16	0.04	16.51
Carbontetrachloride	21.38	1.03	21.31	18	0.2	18.91
Methylene chloride	20.13	1.42	17.96	13.17	0.1	15.22
Trichloroethane	15.45	0.85	15.71	12.1	0.08	15.22
Trichlorofloromethane	15.65	0.79	17.77	15.18	0.36	18.28
	16.1	1.05	17.66	14.15	0.05	13.37
2,2-dichloropropane	15.85	0.29	15.69	15.3	0.07	12.3
1,3-dichloropropane	ND	ND	ND	ND	ND	ND
Tetrachloroethane	14.34	0.14	14.55	14.48	0.29	15.64
KETONE VOCS						
Acetone	25.26	2.5	27.15	16.87	0.18.	15.46
2-Hexanone	ND	ND	ND	ND	ND	ND
4-Methyl-2-pentanone	12.18	0.32	12.69	12.19	0.19	17.02
NITRILE VOC						
Acetonitrile	ND	ND	ND	ND	ND	ND

Table 4: Total Variance (eigen values)

	Initial Eigen Values					
	Ikeja			Isolo		
Component	Total	% of Variance	Cumulative %	Total	% of variance	Cumulative %
Row 1.	151.09	61.9	61.89	1.618	66.36	66.361
2	51.127	20.904	82.8	0.326	13.39	79.753
3	21.647	8.864	91.67	0.161	6.604	86.357
4	13.49	5.526	97.19	0.126	5.154	91.511
5	3.26	1.336	99.11	0.095	3.894	95.405
6	1.425	0.184	99.67	0.043	1.767	97.172
7	1.365	0.559	99.88	0.041	1.662	98.834

Table 5: Total Volatile Organic Compounds (TVOC) at the Studied Areas (μgm^{-3})

SITES	IKEJA Mean ± SD (n = 10)	ISOLO Mean ± SD (n = 10)
1	550.6 ± 0.07	388.99 ± 27.24

2	561.05 ± 21.11	389.82 ± 34.16
3	583.56 ± 27.11	389.31 ± 24.17
4	569.14 ± 38.04	391.42 ± 30.36
5	583.56 ± 34.18	393.71 ± 34.10
6	584.78 ± 28.10	388.58 ± 18.63
7	565.33 ± 19.17	391.47 ± 22.74
8	553.84 ± 31.08	392.32 ± 24.96
9	540.81 ± 26.02	390.68 ± 27.17
10	571.80 ± 31.28	382.92 ± 28.58
TVOC	5669.47	3899.16

Twenty - Six (26) VOCs each were captured in Ikeja and Isolo industrial areas. The VOCs were classified thus: aromatics 41- 44%, halogenated 37- 42%, esters 3%, ketones 7-8%, alcohols 4-5%, ethers 2-4% (Table 3). Seven (7) VOCs each are the major contributors to pollution in Ikeja and Isolo industrial areas, such VOC Pollutants and their percentage contribution to pollution is as follows: xylenes 61.90%, isopropylbenzene 20.90%, isopropyl acetate 8.47%, n - Butylbenzene 5.53%, tuolene 1.34%, n - propylbenzene 0.58% and methylene chloride 0.56% (eigen value ≥ 1). The other nineteen (19) VOCs were able to contribute 0.12% to pollution in the area (Table 4). Similarly, in Isolo we have: ethylbenzene 66.36%, ethanol 13.39%, chloroform 6.60%, 2,2-dichloropropane 5.15%, xylene 3.89%, isopropyl acetate 1.77% and tetrachloroethane 1.66% the major contributors to air pollution in the area (Fig. 4). The other nineteen (19) VOCs were able to contribute 1.17% to pollution in Isolo. Ikeja (5669.47µg m^{-3}) is more polluted than Isolo (3899.16µg m^{-3}) industrial areas of Lagos state (Table 5). The total volatile organic compound (TVOC) in Ikeja is twice the value in Isolo (Table 4). This may be due to more industries and more vehicular traffic in Ikeja because of peoples patronage of such industries (Chang *et al* , 2005; Ohura *et al*, 2006; Hsieh *et. al*, 2003). The most polluted sites in Ikeja is IPWA site along Oba Akran avenue (site 6) while Isolo - Apapa express road (site 5) is the most polluted site in Isolo (Okuo *et al,* 2012). The most abundant VOCs in the studied areas were BTEX and halogenated VOCs. The halogenated VOCs in the studied areas were dominated by bromomethane, chlorobenzene, chloroform, carbon tetrachloride, trichlorofloromethane and 1, 2 - dichloropropane (Table 3). Ikeja Industrial area has the highest BTEX and halogenated VOCs. The BTEX levels in Ikeja (Benzene 27.04, tuolene 22.28, ethylbenzene 12.04, 109.62 μgm^{-3}) while the halogenated VOCs (bromomethane 26.34, chlorobenzene 22.08, chloroform 26.87 carbon tetrachloride 21.38, trichlorofloromethane 15.65 and 1, 2 - dichloropropane 16.10 μgm^{-3}). Eleganza site has the most abundant BTEX (benzene 31.85, ethylbenzene 16.40, toluene 26.53 and xylenes 127.27 μgm^{-3}) (Table 3). Isolo - Apapa road has the most abundant BTEX in Isolo (benzene 14.11, ethylbenzene 9.99, toluene 14.10 and xylenes 49.89 μgm^{-3}) (Fig.2). The halogenated VOCs in the studied areas were dominated by bromomethane, chlorobenzene, chloroform, carbon tetrachloride, trichlorofloromethane and 1, 2 - dichloropropane (Table 3). The high concentration of ethanol in Oba - Akran 30.06 μgm^{-3} and Guinness 32.91μgm^{-3} both in Ikeja Industrial area is no doubt a reflection of the presence of brewery industries in the areas. The principal component analysis revealed that the major sources of VOCs in both Ikeja and Isolo industrial areas are mainly Anthropogenic and four (4) factors each were identified as sources of VOCs in the studied area with emissions from industries and traffic dominating.

Conclusion

Though, Ikeja has more industries than Isolo but the type of pollutants differs.

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