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Original article

Presence of volatile organic compound (VOCs) in the atmosphere of Ilupeju industrial area, Lagos state, Southwestern - Nigeria

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ABSTRACT

Air pollution is the introduction of chemicals, particulate matter or biological materials that cause harm or discomfort to human or other living organisms. The atmosphere has always served as a disposal area. 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 showed that twenty - Six (26) VOCs were captured in the Industrial area. The VOCs in the industrial area were classified thus: aromatics 43%, halogenated 40%, esters 2%, ketones 6%, alcohols 5%, ethers 4%. There is a significant difference (Pvalue < 0.05) between the levels of VOCs in Ilupeju industrial 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 the industrial area are mainly anthropogenic and Six (6) factors were identified as sources of VOCs in the studied industrial areas with industrial emissions dominating.

1. Introduction

The main environmental problems in industrial areas throughout the world is air pollution. Air pollution is the introduction of chemicals, particulate matter or biological materials that cause harm or discomfort to human or other living organisms. The atmosphere has always served as a disposal area. Air pollutants are not only one of the central environmental problems of the century but also presents serious health problems to the industrial world and economic cost to its citizens. Volatile Organic Compounds are Commonly encountered by people as they go about their daily routine. Volatile Organic Compounds (VOCs) are carbon - based compounds that have vapour pressure to significantly vaporize and enter the atmosphere (U. S EPA, 2003; Estate Management, 2009). Studies have shown that VOCs enter the human bloodstream through the following means inhalation, ingestion and through the skin (ATSDR, 2001). VOCs 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; Ulman et al. 2007). Volatile Organic Compounds are products from petrochemical industries, refineries and other chemical, non- chemical industries(Cetin et al. 2003; Ergas et al. 2007). The most abundant VOCs in an industrial sample depends on the site of sampling (Maria et al., 2009). Industrial pollution, human and vehicular activities are some of the significant sources of primary air pollutants in the industrialized world especially for VOC components(Hesterberg et al., 2009). They are commonly monitored by continuous sampling and analysis by chromatography, by sampling on passivated canisters, or by dynamic or diffusive adsorption on solid adsorbents and analyzed by thermal desorption and gas chromatography with mass spectrometry (MS) or flame ionization detection (FID)(Tanimoto et al. 2007; Demeestere et al. 2007). Various studies have been conducted by several authors at different industrial cities in order to understand the air borne VOCs distribution and the source correlations(Chang et al. 2005; Ohura et al. 2006; Ojiodu et al. 2012; Ojiodu et al. 2013). VOCs emissions from industrial activities is influenced by surrounding traffic sources (Liu et al., 2008). Air pollution problems relating to volatile organic compounds in the ambient air has been proven to have short and long term consequences to residents living in the cities like Lagos particularly to those in the industrialized areas and environs (Krzyanowski et al. 2005; MCEA, 2003). 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 et al. 2003 ; Kerbachi et al. 2006). The main objectives of this study is to : examine the presence of VOCs in the study Area, determine the baseline levels of Volatile Organic Compounds in Ilupeju industrial area of Lagos state; evaluate the contributions of both natural and anthropogenic sources to VOCs emission in the area of study.

2. Materials and methods

2.1. Study area

This study was conducted in Ilupeju Industrial area of Lagos state. Ilupeju 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}. Ilupeju Industrial area is situated at Mushin Local Government area in Ikeja division of Lagos state. It is located on longitude 6.33^0N and latitude 3.2^0E. It's population within the Local Government was estimated at 430,144 people according to the 2006 final census results (NPC, 2009). Conspicuous in these area are various types of industries which include food and beverage, pharmaceutical, textile, paint, printing and publishing, soap and detergent, building and construction industries etc. There are also clusters of filling stations, eatries, official and residential houses, commercial stores, and Motor parks. The land - use pattern of Ilupeju industrial area is mixed industrial and residential.

Fig. 1. GIS Base - Map of Ilupeju Industrial Area Showing Spatial Distribution of Sampling Sites.

2.2. Selection of sampling site

The samples were collected at ten sites within the studied area. 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.

2.3. 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).

2.4. Sampling routine

Sampling 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.

2.5. 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.

2.6. 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} 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.

2.7. 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 $mg{\cdot}L^{-1}$ (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).

2.8. 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) .

2.9. Factor analysis

Six factors were extracted from Ilupeju Industrial area.. The first factor (F1) explained 21.87% while the second (F2), third (F3), forth (F4), fifth (F5) and sixth (F6) factors accounted for 18.91, 16.36, 14.59, 10.91 and 5.97% of the total variance. F1: This factor is highly loaded in trichloroethane, isopropylbenzene, tetrahydrofuran, ethylbenzene,ethanol and acetone. These compounds are widely used in the textile, paint, soap and detergent industries in Ilupeju and are also released from cement depots and vehicles in the studied area. Therefore, factor 1 is attributed to vehicular and Industrial solvent usage. F2 and F3: Trichloroethane, ethanol, trichlorofloromethane, acetone and benzene which are highly loaded in factors 2 and 3 are evaporatives from dry cleaning shops and electrical appliances such as air conditioners and refrigerators. Moreover, these compounds are used as solvent in textiles, cosmetics, paints industries in the studied area. Factors 2 and 3 is an indication of contributions from evaporative emissions and industrial solvent usage. F4: This factor is highly loaded in tetrachloroethane, 1,2-dichloropropane and trichloroethane. These are solvents used in cosmetics and paint industries in the sampled area. Factor 4 may be attributed to industrial solvent usage. However, high loading of chlorobenzene, carbontetrachloride, xylene and tetrachloroethane in factors 5 and 6 is an indication of emissions from vehicular and Industrial solvent usage.

3. Results and discussion

Twenty - Six (26) VOCs were captured in Ilupeju industrial area (Table 1). The VOCs in the industrial area were classified thus: aromatics 43%, halogenated 40%, esters 2%, ketones 6%, alcohols 5%, ethers 4% (Fig 2). The most abundant compounds in the Ilupeju industrial area (Fig. 1) were: BTEX Benzene 17.94 at Macmillian publishers, Tuolene 16.51 at Afolabi Lessi street, Ethylbenzene 14. 92 at Warehouse Bus- stop and Xylene 89.21 $\mu g/m^3$ both at Haier thermocool and Industrial Cresent (Table 1). These are areas with high industrial activities such as petrochemical processes, storage and distribution of chemicals, combustion processes, solvent usage and high traffic density. This results is in agreement with other studies (Kolabokas et al. 2001; Marr et al. 2005; Gariazzo et al. 2005). The halogenated VOCs species in were dominated by bromomethane, chlorobenzene, chloroform, carbon tetrachloride, trichlorofloromethane and 1, 2 - dichloropropane. The maximum concentrations of these halogenated

VOCs in the studied industrial area were 24.38, 19.94, 22.83, 16.73, 13.24 and 12.76μg/m^3 at Warehouse Bus - stop, Afolabi- lessi street, Bishop street, Industrial cresent, Warehouse Bus- stop and Town planning way respectively(Fig 2). These sites are characterized by high traffic density and industrial activities. The halogenated VOCs not only results from industrial source but also from surrounding traffic (Liu et al. 2008 ; Ojiodu et al. 2012; Ojiodu et al. 2013) . The high concentration of Methylene chloride in Warehouse Bus - stop 12.69, Industrial way 12.68, Industrial Avenue 12.69, Haier thermocool 12.70 and Macmillian publishers 12.70μg/m^3 is no doubt a reflection of the presence of printing and publishing industries in the areas. High concentrations of acetone , ethanol and tetrahydrofuran were also observed in these areas. Industrial way (9.08μg/m^3) has the highest concentration of ester VOCs in the studied industrial area (Table 1). This may be attributed to paint, textile, cosmetic and pharmaceutical industries in the area. In addition, it is a location with high traffic density with human activities such hawking of cloths, footwares, cosmetics , food, plastic items e.t.c. Apart from the presence of various industries such as paint, textile, ceramic, brewery, paper etc around the vicinity of these site, it is located along the major roads characterized by heavy traffic because of peoples patronage of such industries[14-15]. It is evident that, in addition to traffic emissions, industrial activities enhances the concentration levels of VOCs in the industrial area. There is a significant difference (Pvalue < 0.05) between VOCs in the studied industrial area (Srivastava et al. 2005 ; Liu et al. 2008 ; Vasu et al. 2009 ; The most polluted site in Ilupeju Industrial area is the Industrial Cresent with a TVOCs of 531.81μg/m^3 while the least polluted site is the Town planning way (432.46μg/m^3)(Table 2). Ilupeju has mean total VOC concentrations of 4059.62μg/m^3 compared to 5669.47μg/m^3 of Ikeja Industrial area (Okuo et al., 2012) . The result of the levels of VOCs in the industrial area suggest that at low wind speed, the TVOC has direct relationship with meteorological factors such as temperature and humidity. The low wind speed has been explained as being responsible for poor dispersion and dilution of pollutants like CO in Benin City (Ukpebor et al., 2005). There is a significant difference (Pvalue > 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 lowest windspeed 3.20ms^{-1} occurred during December when TVOC was high and the highest wind speed 6.00ms^{-1} occurred in May when TVOC is low(Table 3). The Principal Component Analysis (PCA) showed that six (6) factors were identified as sources of VOCs in the studied industrial area with industrial emissions dominating (Table 3).

5. Conclusion

It was observed that the Ilupeju industrial Areas might not only encounter emissions from the industrial sources but was also influenced by the vehicular and evaporative emissions in the vicinity of the Area

Table 1
Measured Mean Concentration of VOCs at Ilupeju Industrial Area (μg/m^3) n = 10.

	Industrial Avenue	Town Plann.way	Ware-House B/Stp	Afolabi Lessi street	Industrial Way	Industrial Estate	Haier Thermocl.	Industrial Crescent	Bishop street	Macmillian Publishers	Mean	STD	Min.	Max
Aromatic VOCs														
Benzene	17.80	17.92	17.94	17.69	17.80	17.84	17.93	17.85	17.85	17.94	17.87	0.08	17.69	17.94
Ethyl benzene	14.72	14.82	14.92	14.73	14.60	14.68	14.74	14.88	14.85	14.59	14.77	0.11	14.59	14.92
Isopropylbenzene	12.22	12.21	12.22	12.21	12.17	12.11	12.21	12.32	12.20	12.17	12.20	0.06	12.11	12.32
Naphthalene	13.25	13.33	13.35	13.41	13.34	13.41	13.40	13.38	13.40	13.32	13.35	0.05	13.25	13.41
N-butylbenzene	11.03	11.08	10.97	10.97	10.99	11.08	11.05	11.14	11.02	11.11	11.04	0.06	10.97	11.14
N-propylbenzene	13.33	13.43	13.47	13.72	13.41	13.46	13.35	13.35	13.37	13.52	13.44	0.12	13.33	13.72
Toluene	16.36	16.40	16.50	16.51	16.44	16.45	16.37	16.34	16.37	16.50	16.41	0.06	16.34	16.51
M+P-xylene	62.68	62.64	62.73	62.64	62.81	62.78	62.79	62.84	62.58	62.81	62.73	0.09	62.58	62.84
O-xylene	26.36	26.39	26.45	26.44	26.42	26.34	26.42	26.37	26.37	26.37	26.39	0.04	26.34	26.45
Halogenated VOCs														
Bromides														
Bromomethane	24.32	24.31	24.38	24.22	24.24	24.28	24.26	24.25	24.33	24.28	24.29	0.05	24.22	24.38
Bromoform	10.70	10.82	10.66	10.67	10.67	10.62	10.58	10.54	10.65	10.77	10.66	0.09	10.54	10.82
Chlorides														
Chlorobenzene	19.94	19.72	19.93	19.46	19.79	19.86	19.94	19.89	19.84	19.89	19.83	0.15	19.46	19.94
Chloroform	22.69	22.64	22.69	22.69	22.61	22.72	22.72	22.74	22.83	22.65	22.70	0.06	22.61	22.83
Carbonterachloride	16.68	16.63	16.66	16.54	16.62	16.56	16.68	16.73	16.69	16.65	16.64	0.06	16.54	16.73
Methylene chloride	12.69	12.68	12.69	12.60	12.61	12.60	12.70	12.67	12.64	12.63	12.66	0.03	12.60	12.70
Trichloroethane	10.88	10.85	10.79	10.82	10.88	10.93	11.18	11.10	10.98	10.91	10.91	0.12	10.79	11.18
Trichlorofloromethane	13.10	13.14	13.24	13.22	13.16	13.03	13.08	13.08	13.04	13.12	13.12	0.07	13.03	13.24
,2-dichloropropane	12.69	12.76	12.68	12.65	12.71	12.66	12.71	12.62	12.64	12.74	12.69	0.04	12.62	12.76
2,2-dichloropropane	14.27	14.28	14.16	14.17	14.23	14.25	14.20	14.18	14.28	14.20	14.23	0.05	14.16	14.28
Tetrachloroethane	14.60	14.69	14.62	14.66	14.63	14.59	14.71	14.59	14.27	14.76	14.61	0.14	14.27	14.76
Ketone VOCs														
Acetone	17.21	17.17	17.18	17.15	17.12	17.18	17.25	17.26	17.22	17.29	17.20	0.05	17.12	17.29
4-methyl-2-pentanone	9.50	9.68	9.57	9.67	9.59	9.68	9.58	9.49	9.59	9.60	9.61	0.07	9.49	9.68
Ester VOC														
Isopropylacetate	8.96	8.99	8.99	9.03	9.08	9.01	8.99	8.94	8.97	8.93	8.99	0.04	8.93	9.08
Alcohol VOC														
Ethanol	21.06	21.14	21.05	21.08	21.17	21.08	21.07	21.15	21.12	21.16	21.11	0.04	21.05	21.17
Ether VOC														
Tetrahydrofuran	15.74	15.74	15.73	15.72	15.72	15.63	15.80	15.76	15.64	15.68	15.71	0.05	15.63	15.80

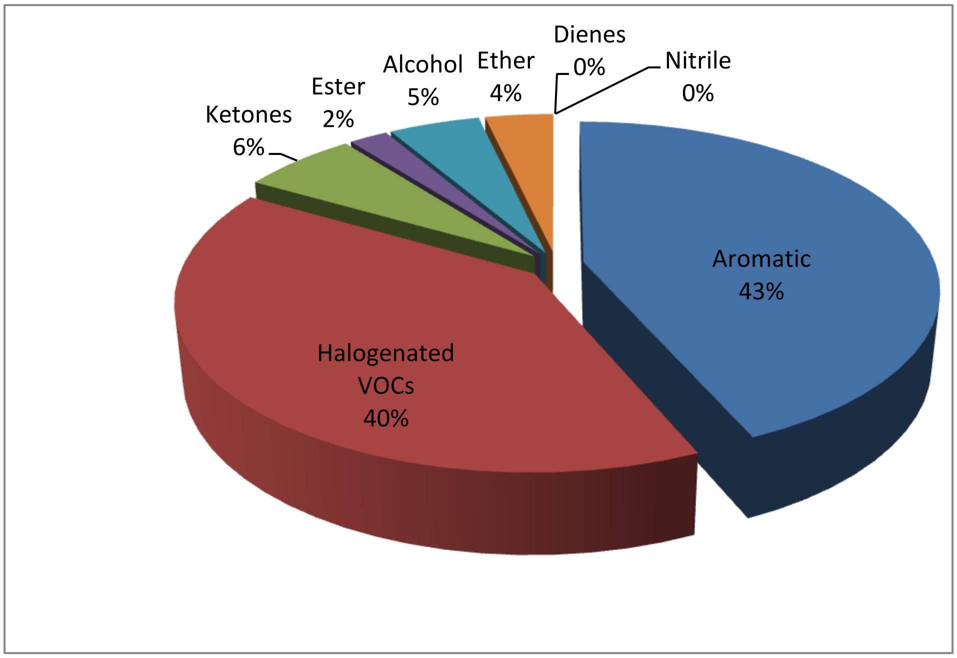

Fig. 2. *Percentage Composition of each family of VOCs in Ilupeju Industrial Area.*

Table 2
Total Volatile Organic Compounds (TVOC in μg/m³), Percentage and Ranking at Ilupeju Industrial Area (μg/m³).

Sites	**Mean ± SD (n = 10)**	**Ranking**	***Percentage (%)***
Industrial Avenue	433.46 ± 19.26	5th	10.677
Town Planning Way	432.46 ± 24.18	10th	10.653
Warehouse Bus - Stop	433.57 ± 30.16	4th	10.680
Afolabi Lessi Street	432.67 ± 26.06	9th	10.658
Industrial Way	432.78 ± 29.01	7th	10.660
Industrial Estate	432.83 ± 27.54	6th	10.662
Haier Thermacool	453.71 ± 37.06	2nd	11.176
Industrial Cresent	531.81 ± 26.12	1st	13.010
Bishop Street	432.74 ± 36.09	8th	10.659
Macmillian Publishers	433.59 ± 34.13	3rd	10.681
TVOC	4059.62		

Fig. 3. GIS Base-Map of Ilupeju Industrial Area Showing Spatial Distribution of Total VOCs.

Table 3
Tvocs, windspeed,rainfall, relative humidity, temperature.

Month	Ilupeju	Temp(^{0}C)	Relative	Humidity(%)	Wind Speedms^{-1}	Rainfall(mm)	Wind Direction
May-10	110.83	27.80	86		6.00	159.30	S
Jun-10	109.93	26.30	87		4.50	367.70	S
Jul-10	108.52	25.10	89		4.50	130.80	SW
Aug-10	189.11	25.10	88		5.70	190.60	SW
Sep-10	111.64	26.20	90		4.20	253.70	SW
Oct-10	110.03	26.70	84		3.70	122.80	SW
Nov-10	322.67	27.80	81		3.50	126.70	SW
Dec-10	355.67	28.00	77		3.20	76.70	S
Jan-11	323.69	29.20	61		3.30	38.00	SW
Feb-11	323.98	30.20	72		5.20	52.50	SW
Mar-11	322.68	29.30	77		4.60	69.00	S
Apr-11	208.24	29.20	79		5.50	136.20	S

SOURCE: NIGERIAN METEROLOGICAL AGENCY, 2010/2011..

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