AMBIENT VOLATILE ORGANIC COMPOUNDS (VOCS) POLLUTION IN ISOLO INDUSTRIAL AREA OF LAGOS STATE, SOUTHWESTERN – NIGERIA

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Abstract

Air pollution by volatile organic compounds is based on the principles of dilution, diffusion and dispersion. 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 (CS2) 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-six (26) VOCs were captured in Isolo Industrial area. The VOCs were classified thus: aromatics 41%, halogenated 42%, esters 3%, ketones 8%, alcohols 4%, and ethers 2%. There is a significant difference ($P < 0.05$) between the levels of VOCs in Isolo 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. Evaporative, vehicular/petroleum product, solvent and Industrial emission were identified as sources of VOCs in the studied industrial area with industrial emissions dominating.

Keywords: *Pollution, Ambient, Gas Chromatography, Industrial, Anthropogenic*.

Introduction

Volatile Organic Compounds (VOCs) are carbon - based compounds that have vapour pressure to significantly vaporize and enter the atmosphere (US, EPA, 2003; EU, 2000; 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 and Chilmonczy, 2007). 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). It was observed that VOCs are products from different industries, refineries and other chemical and non-chemical industries (Cetin *et al*., 2003). The most abundant VOCs in an industrial site depend on the sampled site (Marr *et al*., 2005). VOCs emissions from industrial activities are influenced by surrounding traffic sources (Liu *et al*., 2008). Generally, volatile organic compounds (VOCs) emission results from natural and anthropogenic (man-made) sources. Although, natural sources of VOCs emission are more overall, (Guenther *et al*., 1995) there are anthropogenic sources of VOCs in populated and industrialized areas that are contributors to air quality. The major anthropogenic sources of VOCs are in industrial processes, oil refining and distribution from vehicles, the use of solvents containing products and industrialized and agricultural sources (Schiffman *et al*., 2001; Klemp *et al*., 2002). It was stated that accidental spillage of VOCs by the industries that uses organic solvent have been known to emit VOCs such as methylisocyanate which is

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extremely disastrous to human and animals health living within the industrial area (US EPA, 2003). Majority of the VOCs released into the environment by the industries affect both human and animal health. The use of all kinds of artificial panels such as plywood, laminated wood floor by some furniture industries contributes to severe formaldehyde contamination in the environment (Wieslander *et al*., 2007). VOCs are important class of air pollutants commonly found in the urban and industrial atmosphere (Derwent *et al*., 2000). There is growing evidence that chronic exposure to VOCs have adverse health effects on human (Rumcher *et al*., 2004; Suh *et al*., 2000). 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*., 2002; Kerbachi *et al*., 2006).

Study Area

Lagos state with a population of 8 million compared with 8 – 9 million in London, 8 million in New-York and 7 million in Paris, is one of the world's mega-cities. It is the most populous and industrialized city in Africa and its population far exceed the entire population of some countries. It is the nation's economy nerve centre with over 2000 industries. Currently, over 200,000 vehicles are registered annually (NPC, 2009; LASG, 2006).

Figure 1 Base-Map of Isolo Industrial Area Showing Spatial Distribution of Sampling Sites

Isolo industrial area is situated at Oshodi-Isolo Local Government area of Lagos state. It is in Ikeja division of Lagos state. Isolo industrial area is located on longitude 6.31^0N and latitude 3.19^0E. Its population which the Local Government area estimated at 521,509

people according to the 2006 final census results (NPC, 2009). Conspicuous in these area are various types of industries which include textile, pharmaceutical, soap and detergent, food and beverage, paint, printing and publishing etc. There are also clusters of filling stations, commercial stores, eatries, Motor parks, official and residential house. The land-use pattern of Isolo industrial area is mixed, residential and industrial. Therefore, there is need to investigate ambient air pollution by volatile organic compounds in Isolo industrial area of Lagos state. Volatile Organic Compounds are commonly encountered by people as they go about their daily routine. This study was conducted in Isolo industrial area of Lagos state, namely Abimbola Street, Johnson Wax, IIasamaja Market, Chesebrough way, Isolo- Apapa Road, IIe-iwe meta, Rotary Road, Isolo Road, Afprint, and Aswani Market. Isolo 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}. The main objectives of this study are to: determine the baseline levels of Volatile Organic Compounds in Isolo industrial area of Lagos state; the contributions of both natural and anthropogenic sources to VOCs emission in the area of study.

Methodology

Selection of Sampling Site

The samples were collected at ten sites within Isolo industrial 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 (mainly industrial). The geo-referencing was carried out by using GARMIN GPS MAP 76S.

Collection of Ambient VOCs

Ambient air samples were collected using ORSA 5 diffusion tubes from Dragger Safety, Lubeck, Germany. 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, 2007). The diffusive (passive) sampler fulfilled many of the logistical requirements of an ideal ambient air monitor. A validation processes for diffusive sampler had been performed (Brown *et al.,* 1999; Pfeffer *et al.,* 1995). 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 was also recorded.

Extraction and Sample Analyses

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, 1998). Samples were extracted using a magnetic stirrer (Jenweary, 1103) for 30min. The extracted samples were 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, 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.

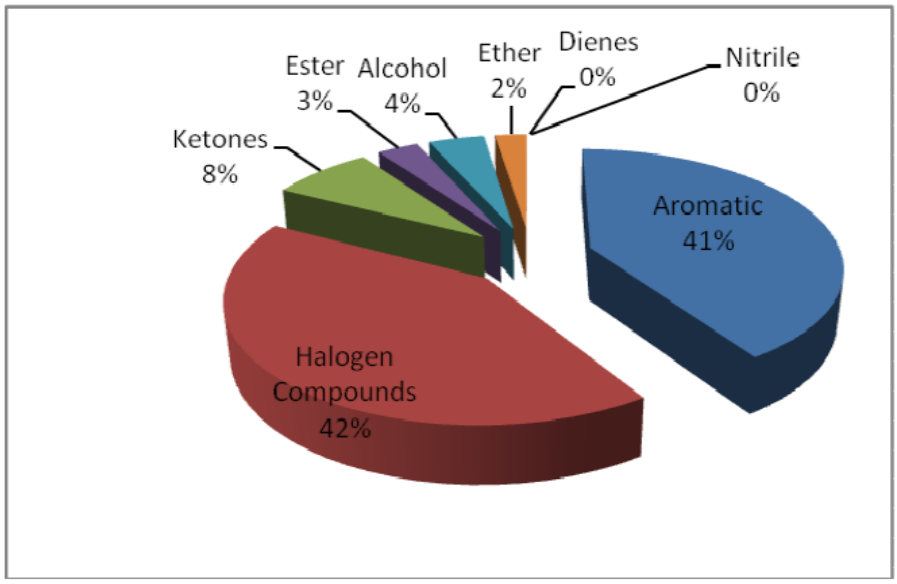

Figure 2 Percentage by Composition of each family of VOCs at Isolo Industrial Area

Statistical Analysis

Two-way Analysis of Variance (ANOVA) statistical test was used to evaluate significance of the differences in means; we use correlation coefficient (r2). Sources of emission were determined using correlation coefficient ($p < 0.05$) and the factor analysis (Principal Component Analysis) (SPSS, 2007).

Factor Analysis

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. Factor 2 suggests vehicular and petroleum products emission.

F3: Factor 3 is highly loaded in ethanol, acetone and chloroform. These compounds are used as solvent in textile and paint industries in the study 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 study 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.

Results and Discussion

Twenty - Six (26) VOCs were captured in Isolo industrial area. The VOCs in the industrial area were classified thus: aromatics 41%, halogenated VOCs 42%, esters 3%, ketones 8%, alcohols 4%, ethers 2% (Figure 1). The most abundant compounds in the Isolo industrial area were Benzene, tuolene, ethylbenzene and xylene (BTEX) and halogenated VOCs. The maximum BETX levels observed at Isolo industrial area are 14.11, 14.37, 9.99 and 49.89µg/m^3 respectively. It is an area with high industrial activities such as petrochemical processes, storage and distribution of chemicals, combustion processes, solvent usage and high traffic density. This result is in agreement with other studies conducted by Kolabokas *et al.,*2001 and Gariazo *et al.,* 2005. The halogenated VOCs species were dominated by bromomethane, chlorobenzene, chloroform, carbon tetrachloride, trichlorofloromethane and 1,2 - dichloropropane. The mean concentrations of these halogenated VOCs in the studied industrial area were 10.24, 18.70, 15.16, 18.00, 15.18 and 14.15 µg/m^3 respectively. The alogenated VOCs not only results from industrial sources but also from surrounding traffic. The high concentration of ethanol 16.66; Acetone 17.02 and Chloroform 15.22 µg/m^3 in Isolo industrial area is no doubt a reflection of the presence of textile industries in the areas (Table 1). Isolo-Apapa road appears to be the most polluted site with highest total VOC of 393.71µg/m^3 (Table 2). 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 (Chang *et al.,*2005; Ohura *et al.,* 2006) (Figure 2). It is evident that, in addition to traffic emissions, industrial activities enhance the concentration levels of VOCs in the industrial area. It is not surprising that Aswani Market is the least polluted site with a total VOC of 382.92µg/m^3 because it is one day [Tuesdays] market that takes place once a week after which follows immediately cleanup of the market. There is a significant difference ($P < 0.05$) between VOCs in the studied industrial area (Srivastava *et al.,* 2004; Vasu *et al.,* 2009). Ikeja Industrial area has mean total VOC concentrations of 5669.47µg/m^3 while Isolo Industrial area 3899.16 µg/m^3 (Okuo *et al.,* 2012).

The result of the levels of VOCs in the industrial area suggests 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 ($P < 0.05$) between each of meteorological factors such as temperature, relative humidity, and 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 5.70ms^{-1} occurred in August when TVOC is low (Table 3). Seven (7) VOCs 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% (Ojiodu *et al.,* 2012) are the major contributors to ambient air pollution in Isolo industrial areas in Lagos State. Evaporative, vehicular/petroleum product, solvent and Industrial emission were identified as sources of VOCs in the studied industrial area with industrial missions dominating.

Figure 3 GIS Base - Map of Isolo Industrial Area Showing Spatial Distribution of Total VOCs Concentrations.

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

	Mean	Std	Min	Max
AROMATIC VOCs				
Benzene	13.43	1.14	10.42	14.11
EthylBenzene	9.38	1.33	9.15	9.99
IsopropylBenzene	18.43	0.29	17.89	18.88
Napthalene	14.55	0.10	14.43	14.77
n-ButylBenzene	18.97	0.15	18.82	19.31
n-PropylBenzene	15.14	0.09	15.02	15.27
Toluene	14.03	0.16	13.77	14.37
m+p -Xylene	31.30	0.21	30.99	31.64
o-Xylene	17.91	0.25	17.36	18.25
HALOGENATED VOC BROMIDES				
Bromomethane	10.24	0.13	10.07	10.42
Bromoform	16.23	0.18	15.91	16.51
CHLORIDES				
ChloroBenzene	18.70	0.13	18.47	18.91
Chloroform	15.16	0.04	15.10	15.22
Carbontetrachlorid	18.00	0.20	17.69	18.28
Methylene Chloride	13.17	0.10	13.05	13.37
Trichloroethane	12.10	0.08	12.03	12.30
Trichlorofloromethane	15.18	0.36	14.75	15.64
1,2-Dichloropropane	14.15	0.05	14.09	14.23
2,2- Dichloropropane	15.30	0.07	15.24	15.46
Tetrachloroethane	14.48	0.29	13.96	14.79
KETONE VOCs				
Acetone	16.87	0.18	16.42	17.02
4-Methyl-2-Pentanone	13.00	0.38	12.21	13.36
ESTER VOC				
Isopropylacetate	12.19	0.19	11.87	12.46
ALCOHOL VOC				
Ethanol	16.58	0.04	16.51	16.66
ETHER VOC				
Tetrahydrofuran	9.36	0.03	9.30	9.41

Table 2 Total Volatile Organic Compounds (TVOC), Percentage and Ranking at the Studied Areas ($\mu g/m^3$)

Sites	Isolo Mean ± SD [n = 10]	Percentage	Ranking
1	388.99 ± 27.24	9.976	8TH
2	389.82 ± 34.16	9.998	6TH
3	389.31 ± 24.17	9.984	7TH
4	391.42 ± 30.36	10.039	4TH
5	393.71 ± 34.10	10.097	1ST
6	388.58 ± 18.63	9.966	9TH
7	391.47 ± 22.74	10.040	3RD
8	392.32 ± 24.96	10.062	2ND
9	390.68 ± 27.17	10.020	5TH
10	382.92 ± 28.58	9.821	10TH
TVOC	3899.16$\mu g/m^3$		

Table 3 Tvocs, Windspeed, Rainfall, Relative Humidity and Temperature

Month	Isolo	Temp (^oC)	Relative Humidity (%)	Wind Speed (ms^{-1})	Rainfall (mm)	Wind Direction
May-10	87.68	27.8	86	6.00	159.30	S
Jun-10	86.95	26.3	87	4.50	367.70	S
Jul-10	84.72	25.1	89	4.50	130.80	SW
Aug-10	85.55	25.1	88	5.70	190.60	SW
Sep-10	86.22	26.2	90	4.20	253.70	SW
Oct-10	86.96	26.7	84	3.70	122.80	SW
Nov-10	304.48	27.8	81	3.50	126.70	SW
Dec-10	305.59	28.0	77	3.20	76.70	S
Jan-11	305.13	29.2	61	3.30	38.00	SW
Feb-11	306.28	30.2	72	5.20	52.50	SW
Mar-11	305.00	29.3	77	4.60	69.00	S
Apr-11	253.86	29.2	79	5.50	136.20	S

Conclusion

Though, traffic source influenced VOCs pollution in Isolo industrial area but industrial emission dominates it. Therefore, the VOCs in the studied industrial areas of Lagos state needed to be monitored continuously as the level of VOCs obtained increase tremendously because of the increasing rate of urbanization and industrialization.

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