BASELINE LEVELS OF VOLATILE ORGANIC COMPOUNDS (VOCs) POLLUTION IN A MACROENVIRONMENT: A CASE STUDY OF YABA COLLEGE OF TECHNOLOGY CAMPUS, LAGOS - STATE, SOUTHWESTERN NIGERIA

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Abstract
The concept of air pollution is based on the principles of dilution, diffusion and dispersion. 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). Eighteen - thirty (18-30) VOCs were captured in the atmosphere of Yaba College of Technology Campus. They are classified thus: - Aromatics (23 - 48%), Halogenated (bromides, chlorides) (21 - 53%), Ketones (6 - 24%), Ethers (0 - 4%), Alcohol (6 - 10%), Dienes (0 - 1%), Ester (1-10%) and Nitriles (0- 5%). The most abundant VOCs were BTEX (Benzene 15.80 $\mu g/m^3$, Toluene 16.01 $\mu g/m^3$, Ethylbenzene 9.98 $\mu g/m^3$ and Xylenes 46.08 $\mu g/m^3$) and the halogenated VOCs: Chloroform 47.51$\mu g/m^3$, Carbon tetrachloride 63.40$\mu g/m^3$, Trichlorofloromethane 30.55$\mu g/m^3$. Xylenes has the highest measured mean concentration in all the ten sites especially in Biology Laboratory (41.6$\mu g/m^3$) and Bakassi Outside (46.08$\mu g/m^3$). There is a significant difference ($P_{value} < 0.05$) between the levels of VOCs within and outside the studied areas. The meteorological parameters showed significant correlations with the ambient concentrations of VOCs. The principal component analysis revealed that the major sources of VOCs in studied areas are mainly Anthropogenic and the major contributors to ambient air pollution are Isopropylbenzene 49.23%, Butylbenzene 31.74%, Propylbenzene 11.74%, Toluene 3.94%, Naphthalene 1.61% and Xylene 1.14%.

Keywords: Pollution, Ambient, Gas Chromatography, Macroenvironment, Anthropogenic.

Introduction

An environment consisting of two or more institutions is known as a Macro-environment. Such institutions could be financial, academic, industrial etc. Since human activities are involved in macro-environment, Volatile Organic Compounds (VOCs) are emitted into the environment thereby causing adverse effect on the environment. 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 (VOCs) in ambient air arises from human, industrial and vehicular activities of man. They are carbon-based compounds that have vapour pressure to significantly vaporize and enter the atmosphere (U.S. EPA, 2005; 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 Chilmonczyk, 2007). Recent studies have shown that the major sources of VOCs in ambient air in a macro-environment were as follows: as solvent (which include paints, adhesives, aerosols, metal cleaning and printing) and road transport. Substantial VOCs come from processes such as painting (evaporation of solvents), printing, oil production and combustion processes (flaring and venting of gas), oil refining (flaring and fugitive emissions) distribution of oil or refining products (evaporation from storage, displacement losses when heating of gas) dry cleaning (final drying of clothes), use of aerosol sprays (both in the product and from the propellant), inefficient combustion of bituminous coal in domestic grates, production of alcoholic drinks (breweries and distilleries) and arable farming (crop growing, silage manufacture, sludge spreading. VOCs are commonly monitored by continuous sampling and analysis, 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). Several studies have determined the levels of VOCs in Urban and industrial atmosphere (Ohura et al, 2006; Simona et al, 2009; Ojiodu et al, 2012a,b). Yaba College of Technology a cradle of higher education in Nigeria is situated in Yaba Local Government Area of Lagos State. It is located on longitude 03^0 22'E and latitude 06^0 30'N and bounded to the North by Fadeyi, to the South by Fola Agoro, to the East by Shomolu and to the West by Herbert Macaulay Way (Omona et al, 2007). The Campus is structured into eight schools and thirty four academic departments have all its programmes fully accredited by National Board for Technical Education (NBTE). The present student population is about 15,000 while the total staff strength is about 1600. Yabatech Campus environment is known to be divided into academic and residence areas. Being a macro-environment, we have Banks, Eatries, Business centres, Dry cleaning shops, Automobile workshops, residential buildings, Bukertaril etc. There is a rapid growth in students' populations over time and an increase in human, commercial and vehicular activities within the campus thereby leading to increase in Volatile Organic Compounds levels in the environment. The main objectives of this study is to: determine the baseline levels of Volatile Organic Compounds in Yaba College of Technology Campus, Lagos State, identify the VOCs pollutants, determine the contributions of both natural and anthropogenic sources to VOCs emission in the areas of study and to make recommendations on ways to reducing VOCs in the study area.

Materials and Methods

Sampling Locations

This study was conducted in Yaba College of Technology Campus, Lagos state. Samples were collected at the Administrative Building (Inside), Administrative Building (Outside), Biology Laboratory, Mechanical Workshop, Students Union Government (SUG) Building, Food Village, Bakassi Hall (Inside), Bakassi Hall (Outside), Medical Centre (Inside) (Injection Room) and Medical Centre (Outside). These sites lie within the tropical rainforest region with two distinct seasons: wet and dry seasons. The temperature throughout the year ranges between 26.600C and 30.200C. Humidity is relatively high while the rainfall ranges between 0.00mm - 476.90mm. The wind speed recorded during the study ranged between 3.20 - 11ms^{-1}.

Selection of Sampling Site

The samples were collected at ten sites within Yaba College of Technology, Campus. 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).

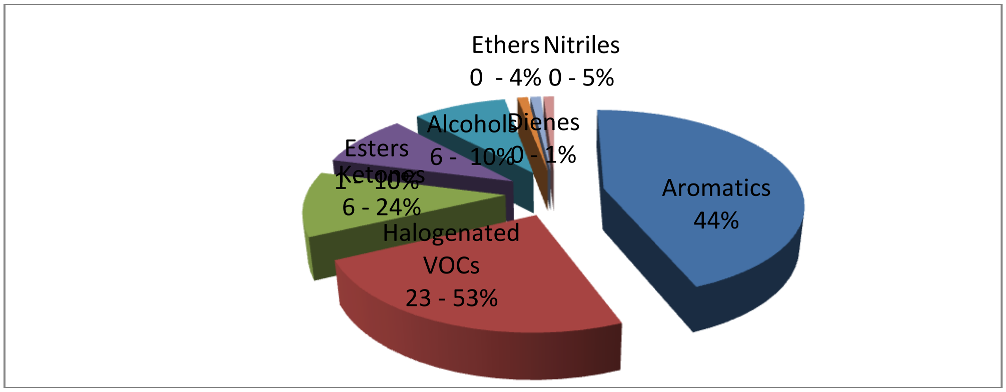

Fig. 1: Percentage Composition of each family of VOCs in the Studied Area.

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 480 samples were collected for the two seasons. During each round of ambient sampling, meteorological parameters such as temperature, wind speed, wind direction and rainfall were also recorded.

Table 1: Monitoring locations, their characteristics and co-ordinates at the studied area

Site	Code	Co-Ordinates	Description
1.	YTAI	N 06° 30' 57.9" E 03° 22' 32.29"	This site is inside the Administrative building. A location where administrative activities is carried out.
2.	YTAO	N 06° 30' 58.4" E 03° 22' 32.49"	Located outside the Administrative building. It is a location with little human activities.
3.	YTBL	N 06° 30' 59.7" E 03° 22' 29.04"	Created at the biology laboratory. A location where students receive lectures and carry out biology practicals.
4.	YTMW	N 06° 31' 00.03 E 03° 22' 28.00"	This is the mechanical workshop. It is a location where servicing and repairing of automobile take place.
5.	YTSB	N 06° 31' 08.7" E 03° 22' 27.2"	The site is situated at Students Union building. It has high human activities like photocopying, browsing, typesetting. It also has food vendors' shops.
6.	YTFV	N 06° 31' 10.2" E 03° 22' 29.8"	Situated at food village where commercial activities like cooking and selling of food took place.
7.	YTBI	N 06° 31' 08.6" E 03° 22' 30.5"	The site is created inside Bakassi hall of residence. A location with household activities like cooking, bathing and washing.
8.	YTBH	N 06° 31' 08.0" E03° 22' 29.3"	Created outside Bakassi hall of residence. A location with commercial activities like selling of

			household items and stationeries.
9.	YTMI	N 06° 31' 08.81" E 03° 22' 37.77"	This site is created inside the medical centre. This is the injection room.
10.	YTMC	N 06° 31' 08.95" E03° 22' 37.41"	Medical Centre outside i.e. Quadrangle of Medical Centre. A site where those that need medical attention are being attended to.

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 8min at 260^0C. The split ratio is 1: 4 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).

Statistical Analysis

The mean concentrations of VOCs collected from various locations in Yabatech Campus were analyzed using Statistical Package for Social Science (SPSS) (SPSS, 2007).

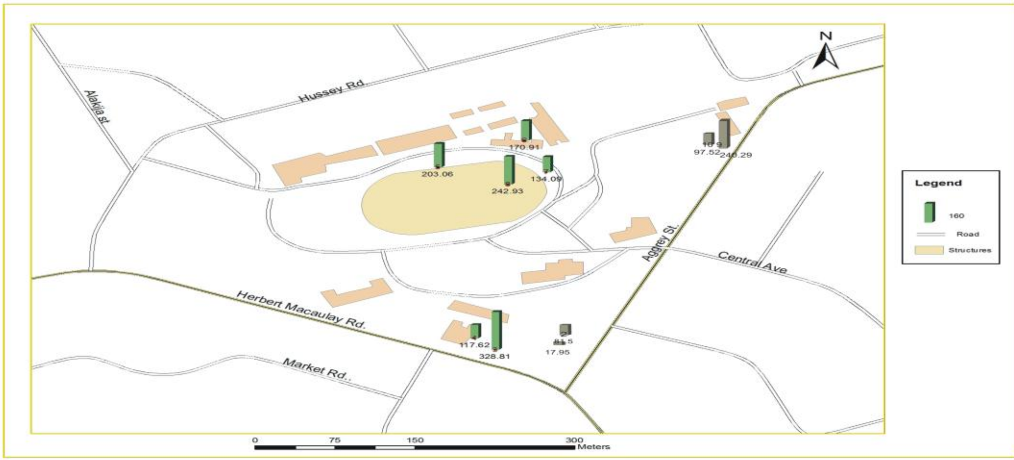

Fig 2: GIS Map of Yabatech showing the level of TVOCs at each sampling site.

Results and Discussion

Table 2: Measured Mean, Standard Deviation, Minimum and Maximum Concentrations

AROMATICS VOCS	MEAN	STD	MIN	MAX
Benzene	30.47	7.19	0.06	43.19
Ethylbenzene	18.96	6.23	0.02	21.76
Isopropylbenzene	9.63	0.65	0.01	15.12
Napthalene	15.69	8.61	0.01	21.59
n-Butylbenzene	18.58	4.94	5.12	21.07
n-Propylbenzene				
Toluene	23.02	7.07	0.03	38.37
m+p-Xylene	70.88	4.72	3.05	97.01
o-Xylene	39.43	8.68	1.06	56.81
HALOGENATED VOCS				
BROMIDES				
Bromomethane	28.66	6.47	9.6	34.19
Bromoform	19.71	6.06	4.94	23.96
CHLORIDES				
Chlorobenzene	30.94	1.26	29.53	32.94
Chloroform	29.98	2..85	0.05	47.51
Carbontetrachloride	17.28	1.05	0.03	63.40
Methylchloride	22.91	2.97	1.79	32.12
Trichloroethane	20.71	0.82	1.96	28.53
Trichlorofloromethane	21.49	1.20	5.78	30.55
1,2-dichloropropane	8.23	2.34	0.03	14.34
2,2- dichloropropane	13.49	8.73	0.01	19.59
1,3- dichloropropane	11.08	2.01	0.02	13.87
Tetrachloroethane	13.90	8.93	0.01	20.77
KETONE VOCS				
Acetone	45.96	3.89	1.02	61.52
2-Hexanone	32.98	5.34	3.86	37.09
4-Methyl-2-pentanone	11.97	3.74	0.01	19.16
ESTER VOC				
Isopropylacetate	17.21	6.73	1.34	20.78

ALCOHOL VOC				
Ethanol	29.53	5.05	1.75	39.59
ETHER VOC				
Tetrahydrofuran	26.30	5.12	0.01	39.32
DIENES VOC				
Chloroprene	15.76	1.08	0.03	37.95
NITRILE VOC				
Acetonitrile	11.32	2.37	0.01	16.17

Air pollution by Volatile Organic Compounds (VOCs) in Yaba College of Technology Campus was studied to understand the class, composition and concentration distribution of VOCs (Fig. 2). Eighteen to thirty (18 - 30) VOCs were captured at various sites in atmosphere of the Campus (Ojiodu et al, 2012). The highest number of VOCs (30) were captured at Mechanical Workshop, Students Union Government Building (SUG), Food Village, Bakassi Hall (Inside), Bakassi Hall (Outside), Medical Centre (Inside) (Injection Room) and Medical Centre (Outside) while the least (18 VOCs) was captured at the Administrative Building (inside) (Table 2). The VOCs were classified thus: Aromatic 23 - 48%, Halogenated 21 - 53%, Ketones 6 - 24%, Esters 1 - 10%, Alcohols 6 -10%, Ether 0 - 4%, Dienes 0 - 1%, Nitrile 0 - 5%(Fig. 1). The most abundant compounds were the aromatics (BTEX) and halogenated VOCs. Bakassi Hall (Outside) has the most abundant BTEX (Benzene 15.80 µg/m^3, Toluene 16.01 µg/m^3, Ethylbenzene 9.98 µg/m^3 and Xylenes 46.08 µg/m^3) (Table 1). This can be attributed to the use of devices (stoves and generators) that uses gasoline as fuels while the lowest BTEX levels were observed at Administrative Building (Inside) (Benzene 0.06 µg/m^3, Toluene 0.03 µg/m^3, Ethylbenzene 0.02 µg/m^3 and Xylene 4.11 µg/m^3). The maximum BTEX levels were observed at Mechanical Workshop and Students Union Building 43.19, 38.37, 25.92, and 155.35 µg/m^3 (Table 2). The high concentration may be attributed to the high commercial activities by lockup shops around the Students Union Building near the food village such as Buying and selling food stuff, household materials including stationeries, dry cleaning, and photocopying, browsing, regular use of combustion generators etc. and the use of petroleum products in the Mechanical workshop. This result is so in agreement with studies conducted by Ojiodu (2012); Okuo et al, 2012a, b. The halogenated VOCs were dominated by tri-chloro-fluoro-methane, chloroform and carbon tetrachloride. These halogenated VOCs are mostly abundant at the Biology Laboratory and Medical Centre (Inside) (Table 2). This is caused by the frequent use of these VOCs as solvents and for the preservation of specimen. There is a high concentration of ketones especially acetone with the highest value recorded at the Biology laboratory. This is due to its constant use as solvents in the laboratory and also by the use of body sprays and cosmetics by almost everyone in the college (Chang et al*,* 2005; Nazaroff and Wieschsler, 2004; Ohura et al, 2006; Hsieh and Tsai, 2003). A high concentration of alcohols and ethers is observed throughout the college which is as a result of use of personal care like cosmetics, hair sprays, nail paints etc. The presence of ester VOCs in the college is an evidence of the general painting of all the buildings in the College during the period of sampling. The chloroform and dienes present at the Student Union Building is no doubt a reflection of the extensive use of plastic products like plates, buckets, spoons for the selling and buying of food. The acetonitrile is sourced from biological waste products generated from Biology Laboratory during the practical classess. The Total Volatile Organic Compound (TVOCs) gives an indication of pollution strength and allows for comparison of the variability of VOCs at different sites. Biology Laboratory 328.81µg/m^3 appears to be the most polluted sites in the studied area while Administrative Building (Inside) appears to be the least polluted with total VOCs of 17.95µg/m^3 (Table 3). There is a significant difference ($P_{value} < 0.05$) between VOCs in the studied sites (Vasu et al., 2009; Liu et al*,* 2008). There is a significant difference ($P_{value} > 0.5$) between each of meteorological factors such as temperature, relative humidity, and wind speed and wind direction.

The results of the meteorological factors show that the ambient air in the studied areas were characterized by low wind speed with high TVOC with a corresponding high temperature, humidity and in some cases low rainfall. The most prevailing wind direction for the year was the South - South West wind (S - SW) (Table 4).

Table 3: Total Volatile Organic Compound (TVOCs) in each sampling site

S/N	SAMPLING SITES	TVOCs ($\mu g/m^3$)(No of VOCs)	RANKING
1.	Administrative Building (Inside)	17.95 (18)	10th
2.	Administrative Building(Outside)	81.50 (22)	9th
3.	Biology Laboratory	328.81(28)	1st
4.	Mechanical Workshop	117.62(30)	7th
5.	Students Union Building	203.06(30)	4th
6.	Food Village	170.91(30)	5th
7.	Bakassi Hall(Inside)	97.52(30)	6th
8.	Bakassi Hall(Outside)	242.93(30)	2nd
9.	Medical Centre(Inside)	240.29(30)	3rd
10.	Medical Centre(Outside)	134.09(30)	8th

Table 4: Wind speed, Relative Humidity, Temperature and Rainfall

MONTH	TEMP(^{0}C)	RELATIVE HUMIDITY(%)	WIND SPEEDms^{-1}	RAINFALL(mm)	WIND DIRECTION
Nov-10	27.80	81	3.50	126.70	SW
Dec-10	28.00	77	3.20	76.70	S
Jan-11	29.20	74	3.30	0.00	SW
Feb-11	30.20	80	5.20	87.20	SW
Mar-11	29.30	77	4.60	21.60	S
Apr-11	29.20	76	3.70	74.70	SW
May-11	28.80	80	3.50	170.6	SW
Jun-11	27.20	87	4.00	251.9	S
Jul-11	26.60	86	11.0	476.9	SW
Aug-11	26.80	86	9.5	43.70	SW
Sep -11	26.90	87	4.2	175.30	S
Oct-11	27.2	86	6.9	209.30	S

Source: Nigerian Meteorological Agency (NIMET), Oshodi, Lagos – State.

The Principal Component Analysis showed that six VOCs which include Isopropylbenzene 49.23%, Butylbenzene 31.74%, Propylbenzene 11.74%, Toluene 3.94%, Naphthalene 1.61% and Xylene 1.14% were the major contributors to ambient air pollution in Yaba College of Technology Campus (Ojiodu et al, 2012c). The results of the meteorological factors show that the ambient air in the studied areas were characterized by low wind speed with high TVOC with a corresponding high temperature, humidity and in some cases low rainfall.

Conclusion

The sources of VOCs in the studied area need to be monitored continuously as the level of VOCs obtained increase tremendously because of the increasing rate of commercial and high human activities within the Campus.

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