AIR QUALITY STATUS OF VOLATILE ORGANIC COMPOUNDS IN HEALTH AND FINANCIAL INSTITUTION MICROENVIRONMENTS IN BENIN CITY, NIGERIA

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ABSTRACT

Volatile organic compounds are considered to be air toxins that affect human health. They have great influence on the troposphere because they affect the formation of ozone. Ambient air samples were collected from indoor and outdoor of five health and financial institution microenvironments. Passive sampling method with diffusion tubes from Drager Safety, Lubeck, Germany, was used. Samples were extracted with carbon disulphide and analyzed with gas chromatographic instrument fitted with flame ionization and thermal conductivity detectors. Samples collected from the Bank outdoor and Microbiology Laboratory indoor have the highest levels of VOCs analyzed for. The most prevalent VOCs was 1,1- dichloropropene followed by methylenechloride, bromoform and ethylbenzene. Statistical analysis showed both strong and positive correlations between the VOCs indicating similarity in their emission sources. Two major factors were identified as VOCs contributing sources in the studied areas. The results obtained for some of the VOCs were found to be lower than the International Standards when compared.

INTRODUCTION

The rapid industrialization, fast urbanization, rapid growth in population, drastic increase in vehicles on the road and other activities of human beings have disturbed the balance of natural atmosphere. There is now a growing concern about the pollution of the atmospheric air by man made activities. Though many of the gaseous pollutants are also emitted by nature (such as volcanic eruptions), anthropogenic activities adversely affect the quality of air, particularly near dense urban areas and near large emission sources. Major primary pollutants by human activities include sulphur oxides, nitrogen oxides, carbon oxides, volatile organic compounds (VOCs), Chlorofluorocarbon (CFCs), particulate matter, toxic metals and radioactive pollutants.

Volatile organic compounds are major components of urban air pollution. These VOCs are particularly reactive and are reported to be important air toxins suspected to increase chronic health problems in exposed populations (Pratt et al, 2000). VOCs also influence climate change mainly through their production of organic aerosols and their involvement in the production of ozone (IPCC, 2001). Ozone is toxic to humans and nature (WHO, 2003) and so, these VOCs have become important issues in environmental research.

Primary sources of VOCs in indoor environments include outdoor air (penetration from outdoors to indoors) as well as indoor sources such as tobacco smoke, fuel combustion, building materials, furnishing, furniture and carpet adhesives, cleaning agents, ventilation systems, cosmetics and the occupants themselves. Indoor materials used in furnishings can act both as source as well as a sink capable of absorbing and re-emitting VOCs. Emission rates are specific for each compound and source and are influenced by factors such as relative humidity, temperature and occupant activities.

According to the United States Environmental Protection Agency (US EPA) TEAM (Total Exposure Assessment methodology) study, the major VOC exposure sources of non-smoking US populations were air fresheners and household and bathroom deodorizers (Wallace, 1996). In a recent study in Mumbay India, (Srivastava et al, 2006), the annual average of benzene concentrations during rush hours in commercial areas and at traffic intersections were $127\mu gm^{-3}$ and $348\mu gm^{-3}$ respectively and even in residential areas, the average concentration was over $40\mu mg^{-3}$. In some European cities, quite high concentrations have also been measured. For example in a medium size Greek city, the annual average benzene concentrations measured at different locations in 2003/2004 were between 10 and $40\mu gm^{-3}$ (Pilidis et al, 2005). In measurements by Hopkins et al (2002), taken on a ship in the Arctic area during August 1999 much lower benzene concentrations were found averaging about 0.1 μgm^{-3}.

It has been estimated that in typical non industrial indoor environments, 50-3000 different VOCs are continuously present in the air (Molhave, 1990). Several studies have shown increased indoor concentration of VOCs when compared to outdoor air levels indicating direct emissions of additional indoor sources or indoor chemical formation for these compounds (Lebret et al, 1984, De Bortoli et al, 1984, Krause et al, 1987, Wallace 1987, Brown et al, 1994). There is wide variety of VOC sources associated with different occupations. Clearly there are also tasks

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and occupations that may lead to exceptional exposures to specific compounds that are not found in the majority of work places. In the study by Ilegan et al (2001), the workplace was the second most important microenvironment contributing to the total VOCs exposure of the working participants in the study involving mostly office workers.

In new or renovated buildings, VOCs such as xylenes, ethyl benzene, trimethylbenzene, decane, undecane and α-pinene as well as carbonyls such as formaldehyde and hexaldehyde may be found in concentrations up to 100 times higher than outdoor levels (Wallace, 1991). Incidentally, as at the time of this study, there was massive renovation, constructions and reconstructions in the University of Benin Teaching Hospital (UBTH). Painting and other renovation activities can result to highly elevated personal exposures to some aromatic and aliphatic VOCs. The Microbiology Laboratory, Operating Theatre and Pharmacy Department in the UBTH operate twenty four hours daily. Workers in these Departments are exposed to the hazardous effects of VOCs as most chemicals used for sample analysis, cleansing agents and gases from air conditioners contained some of these VOCs. The Bank chosen for this study is along a major highway that experiences heavy daily vehicular traffic. Most residents in this axis patronize this Bank and vehicular emissions are also known to contain VOCs. In addition, little or no information about the levels of VOCs in public places such as Operating Theatres in the Hospitals and Bank premises are available. The activities in and around these places contribute VOCs in the microenvironments. It is therefore imperative to ascertain the levels of these VOCs in order to obtain the much needed information on air quality in these microenvironments.

MATERIALS AND METHODS
Sampling Locations

This study focused on variation of some volatile organic compounds in some selected microenvironments in Benin City, Nigeria. Benin City, a southern Nigeria City, is an urban area with a high population density and a high traffic volume as well as some industries. It is located on longitude 6.20^0N and latitude 5.31^0E on geographical scale. Sampling was conducted at four different indoor environments and two outdoor environments. The indoor environments were carefully selected so as to account for different aspects of human's official activities. The environments were a commercial Bank, Teaching Hospital (UBTH), Medical Laboratory, Operating Theatre and Pharmacy Department.

The Bank sampled is United Bank for Africa (UBA). It is situated along Ugbowo - Lagos road Benin City. Both indoor and outdoor air samples were collected from the bank. The Bank is characterized by high human activities and frequent use of air conditioners. The Operating Theatre is located in University of Benin Teaching Hospital, Ugbowo, Benin City. The theatre sampled is the operating room 4 of the accident and emergency section of the hospital. It is the busiest of all the theatres in the hospital characterized by the use of anesthetics, disinfectants and air conditioners. The Microbiology Laboratory is characterized by the use of various solvents like

hypochlorite solution, antiseptics and other chemicals used for blood samples analysis, while the pharmacy section houses different kinds of drugs. Patients with prescriptions from Medical Doctors also collect their drugs from the Pharmacy section.

Data Collection

Ambient air samples were collected by passive sampling using ORSA 5 diffusion tubes from Drager Safety, Lubeck Germany. The tube is cylindrical and about 2cm in length and 0.2mm in diameter. The sampler comprises of a glass tube opened at both ends and filled with activated charcoal. Each end of the tube is blocked with a soft cellulose acetate diffusion barrier. Ambient air is collected by diffusing into the sampler and the VOCs are adsorbed onto the activated charcoal. The tubes were placed horizontally on the wall, held with plaster and exposed at height of 1.5m above the ground which is within the human breathing zone. The sampling was conducted for a seven day period. After the seven day period the tubes were collected and sealed for laboratory analysis.

Sample Preparation

After sampling, the adsorbed VOCs were extracted from the activated charcoal using carbon disulphide. The collection tube was opened by removing one of the porous buffer layers of the glass tube with forceps and the activated charcoal was emptied into a volumetric flask. About 1.5ml of carbon disulphide was added to the samples. The mixture was allowed to stand for 30 minutes with mechanical agitation. The mixture was then filtered into a vial and tightly closed and labeled.

Sample Analysis

The sample extracts were analyzed using claurus 500 gas chromatographic instrument fitted to a flame ionization detector (FID) and thermal conductivity detector (TCD). The gas chromatograph was calibrated using standard solutions of sixteen (16) VOCs. A graph of detector signal versus elution time (min) was prepared (chromatogram containing a number of peaks).

Calculation of Ambient Levels of Analyte

Diffusive samples are based on the diffusion of air pollutants onto an absorbing medium. The driving force is the concentration gradient between the surrounding air and the absorbing surface where the pollutant concentration is zero. The following equation can be used to calculate the ambient concentration of each analyte.

Concentration (C) = $\frac{Q.L}{D.A.t} = \frac{Q}{SR.t}$, Where C = concentration ($\mu g/m^3$), Q = amount absorbed (μg), L = diffusion path (cm), A = cross section (cm^2), D = diffusion coefficient (cm^2/sec), t = exposure time (sec) and S.R = sampling rate (ml/min).

STATISTICAL ANALYSIS

The results obtained from the VOCs analyses were subjected to the following analysis; correlation matrices, factor analysis and cluster analysis to establish relationships among the VOCs.

Correlation Coefficient Matrix

The correlation coefficient r is a measure of the linear relationship between two attributes or columns of data. The value of r can range from -1 to +1 and is independent of the units of measurement. A value of r near 0 indicates little correlation between attributes, a value near +1 or -1 indicates a high level of correlation. When two attributes have a positive correlation coefficient, an increase in the value of one attribute indicates likely increase in the value of the second attribute. A correlation coefficient of less than 0 indicates a negative correlation. That is, when one attribute shows an increase in value, the other attributes tend to show a decrease.

Factor Analysis

Factor analysis is a statistical method used to explain variability among observed variables in terms of fewer unobserved variables called factors. The principal component analysis (PCA) receptor model classifies variables into groups that can then be associated with factors that contribute to pollutant level at receptors. These factors can be identified as emission sources, chemical interactions etc depending on the data that have been submitted to PCA.

Cluster Analysis

Cluster analysis is a statistical method that classifies a set of observation objectively into two or more mutually exclusive group where each group shares common properties. Its object is to sort cases into groups or clusters so that the degree of association is strong between members of the same cluster and weak between members of different clusters. Each data thus describes in terms of the data collected, the class to which its member belong.

RESULTS AND DISCUSSION

The measured concentrations of volatile organic compounds at the different sampling sites (indoor and outdoor) are shown in Table 1.

Table 1: VOCs Concentration ($\mu g/m^3$) in Sampling Sites Outdoor and Indoor Microenvironments

VOCs	Indoor				Outdoor	
	Bank	Pharm. Section	Micro. Lab	Operating Theatre	Pharm/Theatre Walkway	Bank
Carbon tetrachloride	ND	ND	1.323	ND	ND	1.335
Methylene chloride	0.821	ND	1.345	0.886	1.748	1.320
Acetone	ND	ND	ND	ND	ND	0.325
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	0.239
Toluene	ND	ND	ND	ND	ND	0.289
Benzene	ND	ND	0.585	ND	0.634	0.721
1,1- Dichloropropene	ND	ND	2.450	ND	2.516	2.792
Ethyl benzene	ND	ND	1.367	ND	1.794	2.406
m-xylene	ND	ND	0.709	ND	0.867	0.638
p– xylene	ND	ND	0.408	ND	0.675	1.284
o-xylene	ND	ND	0.293	ND	0.581	0.740
Bromoform	ND	ND	1.826	ND	1.919	2.254
Isopropyl benzene	ND	ND	0.452	ND	0.912	0.880
Bromobenzene	ND	ND	0.827	ND	1.072	1.722
2-Chlorotoluene	ND	ND	0.573	ND	0.562	0.561
4- Chlorololuene	0.055	ND	0.463	ND	0.575	0.656

ND = Below the detection limit of the GC/FID TCD instrument.

Carbon tetrachloride (CCl_4) had the maximum concentration of 1.333$\mu g/m^3$ in Bank outdoor environment. The next highest value of CCl_4 (1.323$\mu g/m^3$) was obtained in Microbiology Laboratory indoor environment. The emission sources of CCl_4 in the outdoor environment may include; dry cleaned clothes, refrigerants, pesticides and fire extinguishers. CCl_4 is an important organic compound used in the manufacture of these products. CCl_4 in Microbiology Laboratory could be attributed to the frequent use of sodium hypochlorite solution (bleach) in the laboratory. In 2008, a study of common cleaning products found the presence of carbon tetrachloride in very high concentrations as a result of manufacturers' mixing of surfactants with bleaching agent such as sodium hypochlorite (Odabasi, 2008).

Methylene chloride had the highest concentration of 1.748$\mu g/m^3$ in Pharmacy/Theatre outdoor environment. Its concentration in Bank indoor and outdoor, Microbiology Laboratory indoor, Operating Theatre indoor environments are 0.821, 1.320, 1.345, 0.886$\mu g/m^3$ respectively. Emissions from paints, aerosols, use of cleaning agents like detergents are the possible source of the methylene chloride in these environments.

Acetone, 1, 1, 1- trichloroethane and toluene were detected only in Bank outdoor environment with concentrations of 0.325, 0.239 and 0.289$\mu g/m^3$ respectively. The emission of acetone in this environment is largely from vehicular exhaust as there is regular movement of vehicles in the Bank environment. Other sources may include consumer products like detergents, inks, and nail polish removers. This may be due to high activities of hawkers who sell some of these wares in the prescient. The presence of 1, 1, 1-trichloroethane is probably due to emission from paints, aerosols and dry cleaned clothes because 1, 1, 1-trichloroethane is used as a solvent in these products. The source of toluene in this environment is mainly from paints, vehicular exhaust emission and probably from solvents. According to Barletta et al, (2005), toluene is emitted from vehicles, but painting and industrial processes (solvent application) are likely additional sources. Another possible source of toluene in this

environment could be from cigarette smoking by passers-by.

Benzene had a maximum concentration of $0.721\mu g/m^3$ in Bank outdoor environment. The next highest concentration of $0.631\mu g/m^3$ was obtained in Pharmacy/Theatre outdoor environment. A concentration of $0.585\mu g/m^3$ was obtained in Microbiology indoor environment. Automobile exhaust and fuel evaporation are likely to be responsible for benzene in these outdoor environments. Also, benzene could be emitted from other products like pharmaceuticals, cosmetics and tyres since benzene is a raw material used for the manufacture of chemical intermediates used in turn to manufacture these products. The presence of benzene in Microbiology Laboratory is probably due to the use of pharmaceuticals and also the penetration of automobile exhaust into the indoor environment.

1, 1-dichloropropene had its highest concentration of $2.792\mu g/m^3$ in Bank outdoor environment. The next highest concentration of $2.445\mu g/m^3$ was obtained in Microbiology Laboratory indoor environment. Ethyl benzene was detected in the outdoor environments of Bank and Pharmacy/Theatre walkway with concentrations of 2.406 and $1.7939\mu g/m^3$. The major sources of ethyl benzene in the Bank outdoor environment are probably from vehicular exhaust and smoking of cigarettes by passers-by. Its presence in Pharmacy/Theatre walkway is probably from paints, inks and use of pesticides. Penetration of vehicular exhaust could also be a major contribution. The only indoor environment where ethyl benzene was detected is the Microbiology Laboratory. This may have been due to the use of solvents and penetration of outdoor air and vehicular exhaust.

M, P and o-xylenes were present in all the outdoor environments sampled. Microbiology Laboratory was the only indoor environment where xylene was detected. Bromoform was also detected in the two outdoor environments of Bank and Pharmacy/Theatre walkway with concentrations of 2.254 and $1.919\mu g/m^3$ respectively. 4-chlorotoluene was found in all the environments samples except Pharmacy indoor environment. The presence of all these VOCs in these environments is certainly not unconnected with vehicular exhaust, use of different solvents for sample analysis, gases from air conditioners and wearing of dyed clothes particularly for 4-chloroprpopene that is used as an intermediate for organic chemicals and dyes.

All the VOCs were detected in Bank outdoor environment with a total value of $18.160\mu g/m^3$. This might not be unconnected with the location of the Bank. The Bank is located along a busy highway in Ugbowo, Benin city which is characterized by clusters of filling stations, high traffic density, high human activities which include hawking and sales of consumer products, laundry services and mechanic workshops in addition to biogenic sources such as trees and road dust re-suspension.

The highest VOCs in indoor environment were obtained in Microbiology Laboratory ($12.622\mu g/m^3$). This is certainly the signature of chemicals used for various tests of sample of blood obtained from patients in the hospital. The chemicals used for all the medical requests in respect of patients are mainly organic compounds grouped among the VOCs.
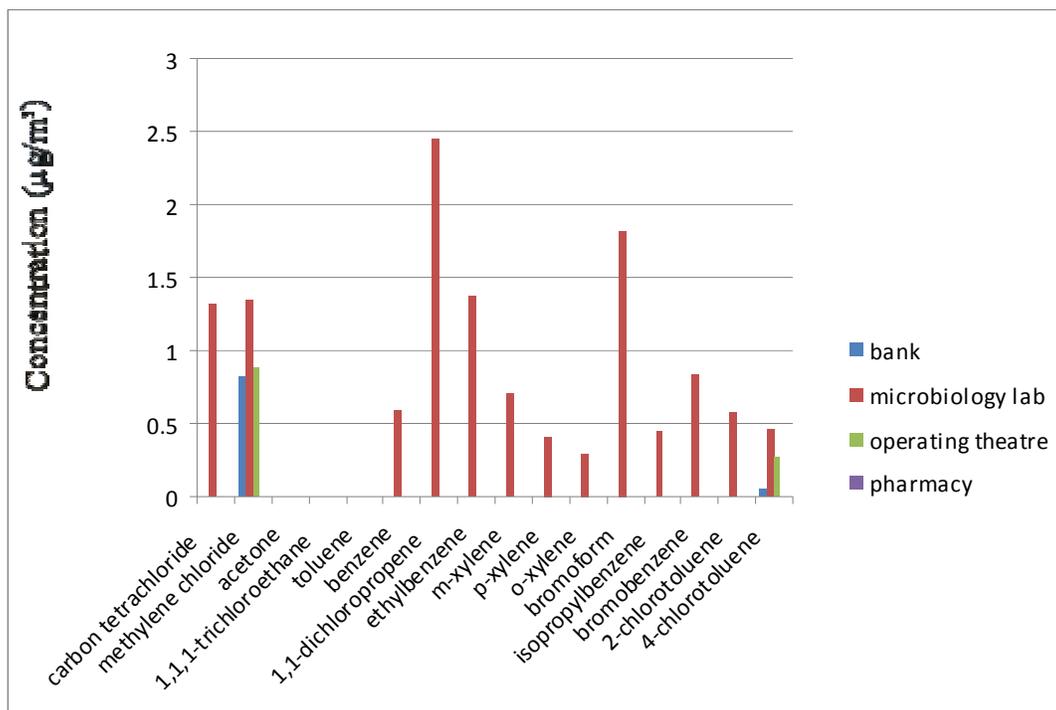

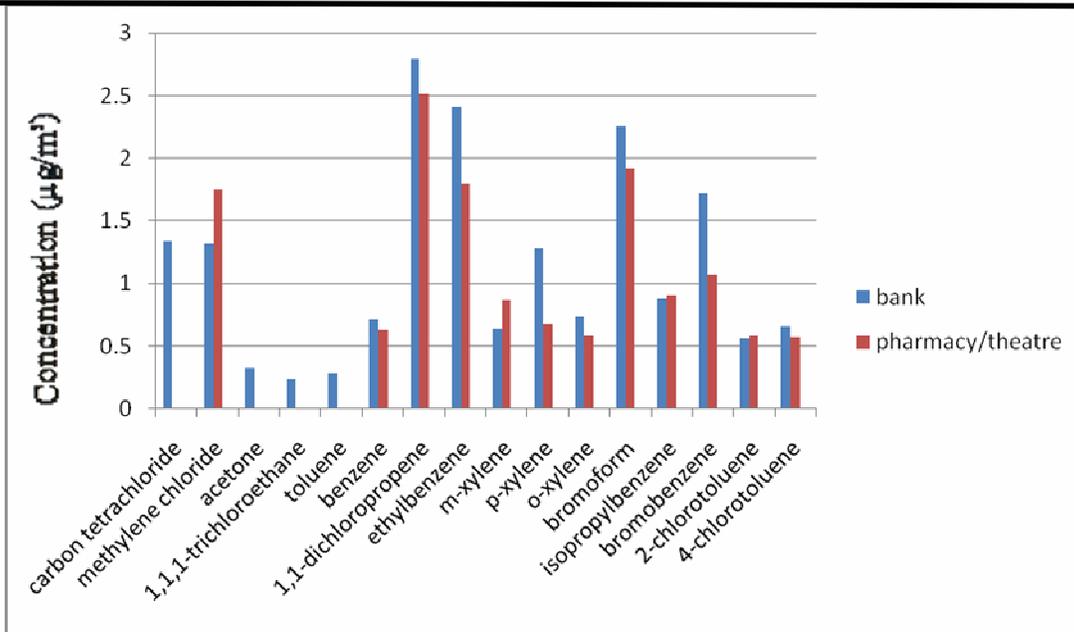**Fig 1: Comparison of Indoor VOCs Concentrations.**

Fig 2: Comparison of Outdoor VOCs Concentrations

It is striking to observe that both indoor environments of the Bank and Operating Theatre contained only methylene chloride and 4-chlorotoluene. Cleaning agents such as detergents are greatly used in these indoor environments particularly in Operating Theatre. The frequency of the use of air conditioners in these two environments is more than any other environment in this study. Cleaning agents and air conditioners contain VOCs such as methylene chloride and 4-chlorotoluene. This might be responsible for the two VOCs found in the two indoor environments.

Correlation Coefficient Matrix

Correlation coefficient matrix was employed in order to determine the relationship between the individual VOCs and sampling locations. Correlation coefficient of 0.5 was taken as significant.

From the results of the correlation coefficient for the sampling sites, Bank indoor environment showed strong correlation with Operating Theater indoor environment ($r = 0.973$). This indicates similar sources of pollutants which are largely from the frequent use of cleaning agents in these environments. Bank indoor environment was weakly correlated with Bank outdoor, Pharmacy/Theatre outdoor and microbiology Laboratory indoor environments, indicating different sources of air pollutants. Bank outdoor environment showed strong correlation with Pharmacy/Theatre outdoor and Microbiology indoor environments($r = 0.863$ and 0.904 respectively), an indication of similar sources of air pollutants mainly from vehicular exhaust as there is regular movement of vehicles in these environments.
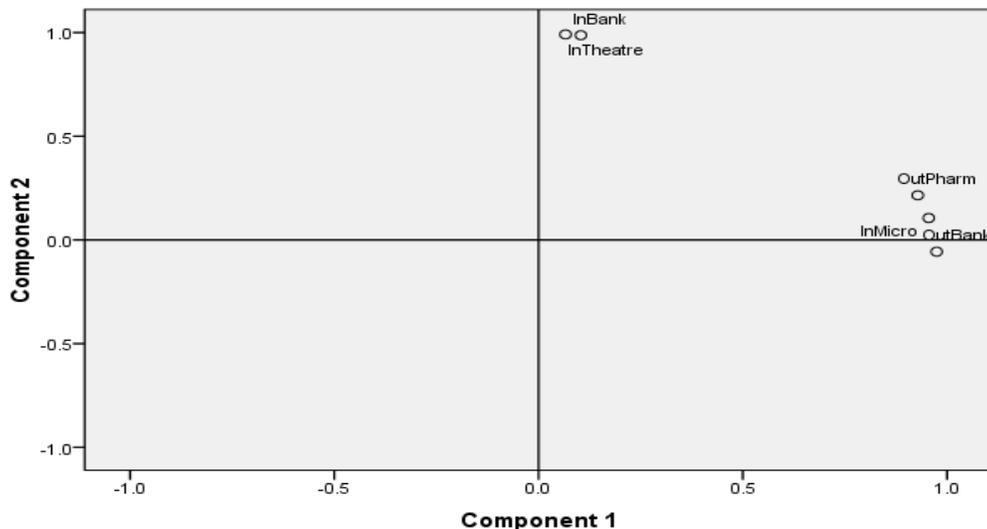

Fig 3: Component Plot in Rotated Space for the Sampling sites.

The results of the correlation coefficient matrix of the VOCs showed carbon tetrachloride to be weakly correlated with methylene chloride and isopropyl benzene (r = 0.261 and 0.445 respectively). This indicates that the emission source of carbon tetrachloride is different from that of methylene chloride and isopropyl benzene. The strong and positive correlations shown by most of the VOCs indicate that their sources are related and not very numerous. These sources may include solvents, paints, adhesives, household cleaners and vehicular emissions.
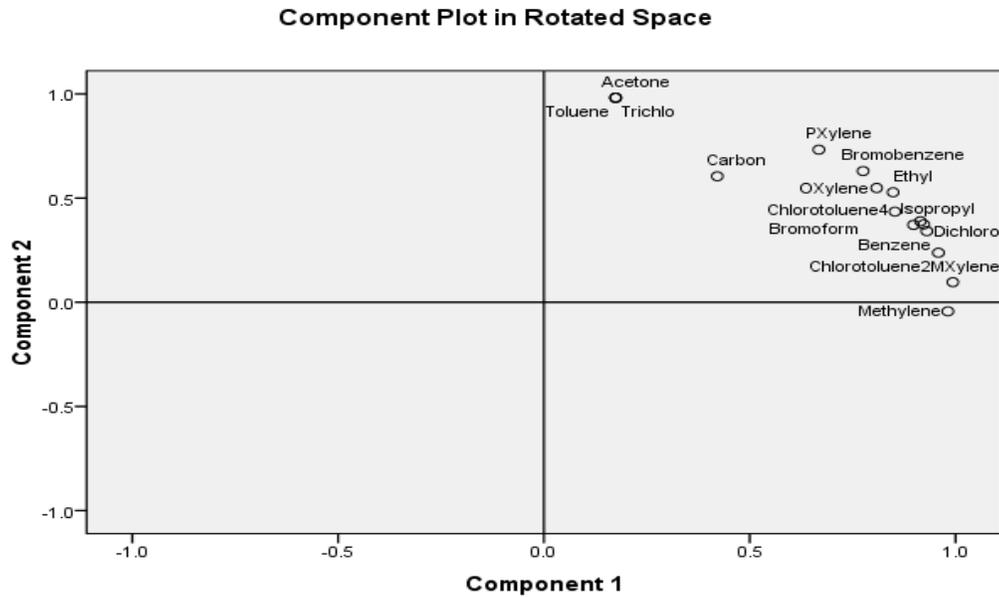

Fig 4: Component Plot in Rotated Space for the VOCs.

3.3: Factor Analysis

Principal component analysis (PCA) was applied to provide an explanation for the inter correlations between variables and for grouping variables into groups that can be associated with factors that contribute to the levels of VOCs. Two major factors were identified as sources responsible for VOCs emission. Factor 1 accounted for 79.22% with high loadings in methylene chloride, benzene, 1,1-dichloropropene, ethyl benzene, m-xylene, o-xylene, bromoform, isopropyl benzene, 2-chlorotoluene and 4-chlorotoluene. These can be attributed to vehicular exhaust emissions, personal activities, gasoline emission and road dust re-suspension. Factor 2 had high loadings in carbon tetrachloride, acetone, 1,1,1-trichloroethane, toluene and p-xylene with 15.89% variance. This can be attributed to the use of solvents, emission from paints and consumer products. Methylene chloride had a negative value in Factor 2 and this shows the presence of additional sources. These observations are in agreement with the results obtained in cluster analysis.

CLUSTER ANALYSIS

The results of the VOCs evaluation were subjected to cluster analysis. The results obtained are shown below in Figs. 5 and 6.
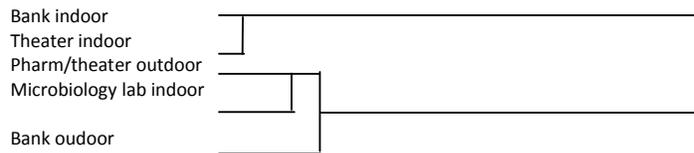

Fig 5: Cluster Analysis for the Sampled Environments

From the statistical result of the sampling sites, there are two major clusters. There is a significant clustering of Bank indoor, Operating Theatre indoor, Pharmacy/Theatre outdoor and Microbiology Laboratory indoor. The results are in agreement with the results of factor analysis that more than one factor made contribution to pollutants at the sampling environments.
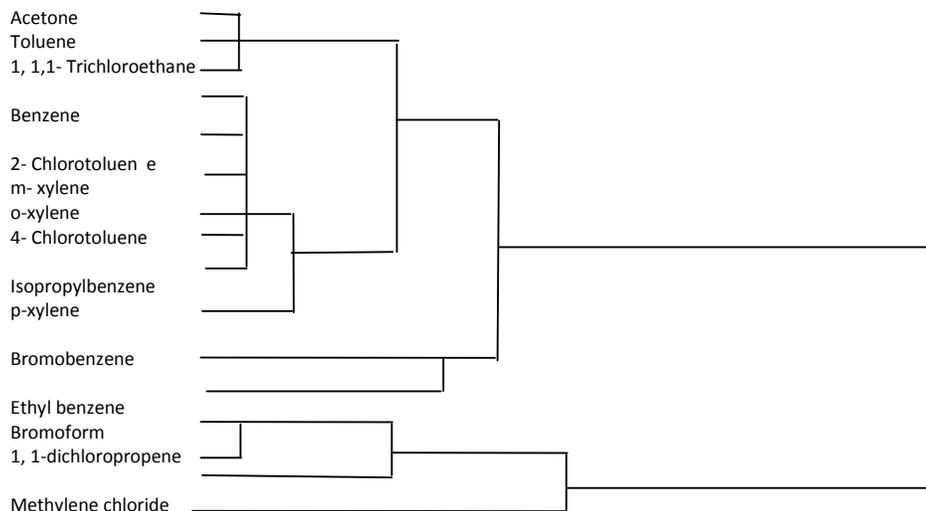
Fig 6: Cluster Analysis of VOCs

Comparison of VOCs with International Standards/Guidelines.

Some of the VOCs obtained in this study were compared with the standards set by Occupational Safety and Health Administration (OSHA) and was found to be below the limit as shown in Table 2.

Comparison of Highest VOCs Measured in this Study with International Standard

VOCs	Occupational Safety and Health Administration Standard(ppm)	Occupational Safety and Health Administration Standard($\mu g/m^3$)	Highest Values Measured in this Study($\mu g/m^3$)
Acetone	1,000	2.4×10^5	0.3249
1,1,1-trichloroethane	350	2.0×10^5	0.2389
Toluene	200	7.5×10^5	0.2885
Benzene	1	3.2×10^5	0.7206
Ethyl benzene	100	4.3×10^5	2.4065
Xylene	100	4.3×10^5	1.2843
isopropyl benzene	50	2.1×10^5	0.9106

Source: (www.osha.gov/index.html)

CONCLUSION

Indoor and outdoor concentrations of VOCs were measured for five different environments namely Bank, Pharmacy Section, Operating Theatre, Pharmacy/Theatre walkway and Microbiology Laboratory) in Benin City. Bank outdoor environment had the highest concentration of VOCs which is due to the location of the Bank, the nature of activities in the environment and the presence of some biogenic sources. The highest VOCs in the indoor environment was obtained in Microbiology Laboratory which is certainly due to the frequency of use of chemical and penetration of outdoor air of VOCs into the indoor environment. The results of VOCs showed positive and strong correlations. The sources and levels of VOCs in the sampled environments are statistically significant ($P \leq 0.05$). The results from PCA and cluster analysis were in agreement.

In conclusion, the measured VOCs in this study are below the standards set by Occupational Safety and Health Administration (OSHA). However, proper control measures should be employed because these pollutants have a tendency to increase over time due to the nature of activities in the locations, the rapid industrialization and fast urbanization in the near future.

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