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Comparative Studies of Ambient Air Quality for Volatile Organic Compounds in Benin City Using Active and Passive Sampling Methods

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Abstract

Ambient air quality in Benin city was evaluated for their volatile organic compounds concentrations using both active and passive sampling methods. Air samples were collected from six locations comprising industrial, residential and commercial areas with heavy traffic on a four hourly basis for active sampling and a seven day period for the passive sampling. Collected samples were desorbed and analysed for volatile organic compounds using gas chromatography with flame ionization detector. A total of 42 VOCs; mainly aliphatic, aromatic, halogenated and oxygenated components were identified using both sampling methods. The result indicated that there is a significant difference between both active and passive sampling methods.

Keywords: Volatile Organic Compounds, Active and Passive Sampling Methods, Gas Chromatography, Air quality, Concentrations.

Introduction

One of the major problems facing cities across the world today is air pollution. The significance of air pollution to human health has been recognized as a major public

health challenge in cities (Edet, 2003)[1].Volatile organic compounds (VOCs) belong to a class of gaseous organic pollutants with boiling points between 50^{o}C to 260^{o}C (WHO, 1989)[2]. VOCs have received widespread attention in recent decades due to their toxicity, carcinogenic and mutagenic properties, photochemical generation of oxidants and stability in the environment (Wolska *et al,* 2003)[3]. VOCs are produced in all processes of incomplete combustion of hydrocarbons from automobile exhausts, use of photochemical solvents and vapourization of petroleum products (Leinick *et al,* 1993; Sims et al., 1983)[4,5], indiscriminate dumping of refuse, open bush burning of solid waste, etc. They are important indicators of air quality, because they are associated with increased long-term health risks (Adagate *et al,* 2004)[6].

Different sampling techniques have been identified for VOCs measurement prominent among which are active and passive sampling (Prado *et al,* 1996; Periago *et al,* 1997 and Batterman *et al,* 2002)[7-9]. Active sampling includes pumping of controlled air flow into the sample for a specific sampling period. A flow meter measuring the flow rate and volume of air is required. While in passive sampling, the analytes flow through the collecting medium without any force obeying Fick's first law (Giorecki and Namienisk 2002)[10]. Passive sampling provides more advantages such as simplicity and low cost. However, one of the disadvantages associated with the use of passive sampling method is the comparatively low sampling rate, which requires longer sampling time for low concentration VOC environments (Pekey and Arslanbas, 2008)[11]. In both techniques, adsorbents are used to trap VOCs as much as possible for analysis with sufficient accuracy (Woolfenden, 2007) [12].

Benin City is a commercially and industrially active capital city with a number of government parastatals, petroleum and allied industries. It serves as a transit city linking the western and eastern parts of the country through different road networks. Hence, it usually experiences huge traffic flow. No previous work has been carried out on volatile organic compounds levels in ambient air in the city. Thus, the objectives of this work are to identify, evaluate and compare VOCs levels in ambient air in Benin City using both active and passive sampling methods.

Methodology

The Study Area

The study was conducted in Benin City, Edo state, Southern Nigeria. It is a city approximately 25 miles north of the Benin River and situated 200 miles by road east of Lagos; the commercial capital of Nigeria. It has a population of about 1,147,188 inhabitants (Columbia Encyclopedia, 2005)[13]. It is located at latitude 6.32^{0}N and longitude 5.63^{0}E. The climate is semi-humid equatorial with two distinct seasons (wet and dry). Benin City has a high relative humidity and intense rainfall occurring between April and September.

Description of Sampling Sites

Sampling was performed at six different locations within Benin City. Table 1 represents the sampling sites, their descriptions and co-ordinates. The geo-referencing

was done by using GARMIN GPS MAP 765 chart plotting receiver. The map of Benin city showing all the sampling sites is shown in Figure 1.

Table 1: Monitoring locations, their characteristics and co-ordinates in Benin City.

Site	Site code	Coordinates	Site Description
1	BNAR	NO6^0 20' 52.1" EOO5^0 40 18.2"	Along Ramat park, close to a petroleum depot and two breweries.
2	BNUG	NO6^0 24' 10.1" EOO5^0 36' 32.2"	Ugbowo monitoring site located at the University of Benin main gate and close to a fuel dispersing station along the express way to the western part of the country.
3	BNNB	NO6^0 20' 57.3" EOO5^0 57' 25.1"	Located at new Benin bus terminal.
4	BNRR	NO6^0 38' 45.1" EOO5^0 37 20.1"	Located at the king's square with many road intersections and high traffic density.
5	BNEN	NO6^0 `9' 28.4" EOO5^0 35 99.3"	Ekenwan site close to University of Benin postgraduate student hostel.
6	BNSP	NO6^0 16' 28.4" EOO5^0 38 16.5"	Upper Sakpoba junction, a bus stop with shops.

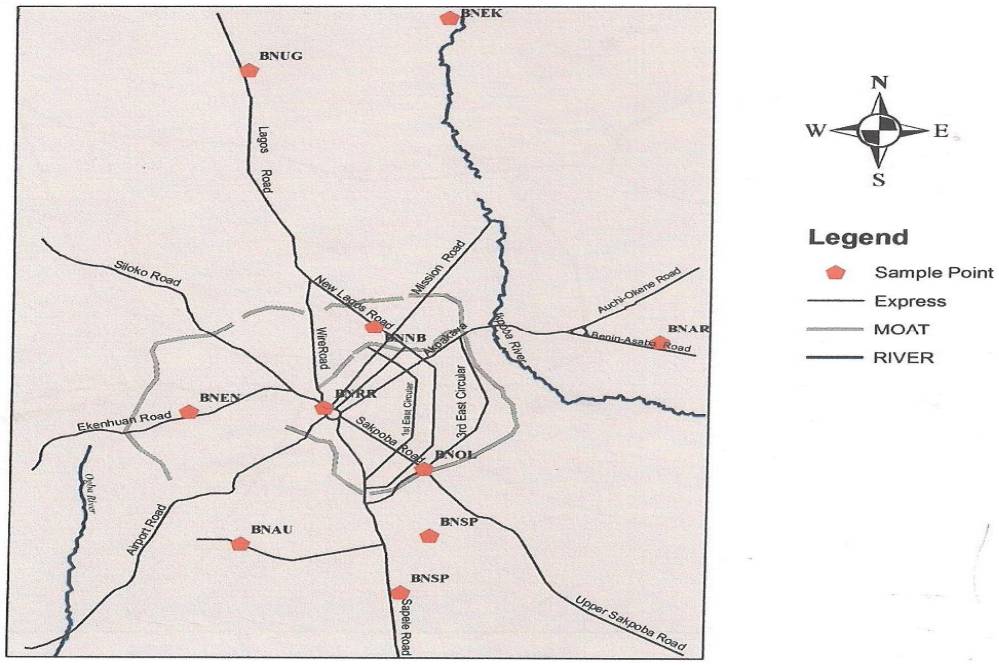

Figure 1: Map of Benin City showing the sampling locations.

Sample Collection and Analysis

For active sampling, ambient air samples were drawn into an active air sampler (Drager-NIOSH) containing 150mg of activated carbon in two successive sections

(ASTM 1988). The tube is equipped with a low volume sampling pump at an average sampling flow rate of 0.51 min^{-1}.The sampler was placed at a height of 1.5m above the ground level and air samples were collected on a four (4) hourly bases from 12am to 6pm at each site. In the case of passive sampling, air samples were collected using ORSA 5 diffusion tubes placed at a height of about 1.5–2.0m above ground level at each of the sampling sites for seven days. The sampler consists of a glass sampling tube open at both ends and filled with activated charcoal. Adsorbed air samples were then extracted with 10ml carbon disulphide and placed in ultrasonic bath for 15mins. This was followed by centrifugation for another 15mins to obtain a clear supernatant. The extracted solutions were analyzed with gas chromatography (GC) equipped with a flame ionization detector (Agilent 6890N). The chromatograph column was HP–INNO wax, 30×25 mm internal diameter×0.25µm film and total chromatopack software. The carrier gas was helium with a purity of 99.99% at a constant flow of 0.01ml min^{-1} and 36cms^{-1} linear velocity with split ratio of 1:20. The inlet temperature was 240^0C. A 2µl volume was injected by applying a hot split less injection techniques. Temperature program is as follows: initial oven temperature 40^0C, hold for 3 minutes, 40^0C to 120 ^{0}C at 5^0c/min, hold for 1min and final hold for 15 minutes.

Chemical Reagents

Volatile organic calibration mixture containing 54 VOCs was purchased from Spelco (Bellefonte, U.S.A) and was used for calibration. Pure helium gas (99.99% purity) and chromatography grade were used as the carrier gas in gas chromatography analysis. All reagents were used without further purification.

Compounds Quantification and Identification

The relative concentrations of the identified VOCs were determined from the retention time and peak areas using the standard method (Cao, 2005)[14]. The lowest calibration level for each compound was taken as the instruments quantification limit (LOQ) for that compound and the precision was estimated as 5%.

Compounds were identified based on their retention times (within ± 0.05 minutes of the retention time of calibration standard), target and qualifier ions. The peaks obtained were identified based on their relative retention times and ion ratios using Automatic Mass Spectral Deconvolution and Identification system (AMDIS) linked to the to the US National Institute of Standard and Technology (NIST) library mass spectral database, the compounds in chromatographic elution order and retention time as followed:

Table 2: The Retention Time, Correlation Coefficient and Standard deviation of Identified compounds in Active Sampling Method.

S/ No.	Identified compounds	Retention time (t_r) (mm)	Correlation coefficient (r^2)	Standard Deviation
1	Acetone	0.937	0.999900	0.77
2	Methylene chloride	5.17	0.999810	0.53
3	Butane	6.65	0.999780	0.42
4	2,2-dimethylbutane	7.66	0.999659	0.20
5	1,1,1- trichloroethane	8.64	0.999693	0.43
6	Benzene	9.27	0.999608	0.42
7	3-methylpentane	11.48	0.999302	0.67
8	Chloroform	13.06	0.999736	0.28
9	Toluene	13.59	0.998413	3.59
10	Carbon tetrachloride	14.06	0.95887	0.39
11	1,2–Dichloroethane	14.44	0.99935	0.40
12.	Isopentane	15. 31	0.99796	0.21
13.	Undecane	17.32	0.99765	0.67
14	Ethylbenzene	17.35	0.998121	1.67
15.	(m+p)-xylene	17.68	0.995785	0.90
16.	o-xylene	18.58	0.993700	1.71
17.	1,2,4-trimethylbenzene	22.14	0.995870	2.56

Table 3: The Retention Time, Correlation Coefficient and Standard Deviation of Identified compounds in the Passive Sampling Method.

S/ No	Identified Compound	Retention Time	Correlation Coefficient	Standard Deviation
1	Acetone	0.941	0.999900	0.28
2	Chloroform	1.262	0.999810	0.39
3	Benzene	1.516	0.999780	0.26
4	Bromomethane	1.519	0.999659	0.27
5	Toluene	1.633	0.999693	0.81
6	1,1,1-trichloroethane	7.322	0.999608	0.09
7	4-methyl-2-pentanone	10.452	0.999302	0.04
8	Ethylbenzene	11.243	0.999736	0.46
9	m-xylene	15.010	0.998413	0.21
10	p-xylene	18.633	0.958870	0.27
11	o-xylene	19.114	0.999350	0.51
12	Chlorobenzene	20.304	0.99796	0.11
13	Ethanol	21.104	0.998121	0.20
14	Carbon tetrachloride	22.110	0.995785	0.18
15	Trichlorofluoromethane	22.202	0.993700	0.07
16	Methylene chloride	22.158	0.997083	0.33

17	Isopropyl chloride	23.119	0.995870	0.11
18	Tetrahydrofuran	23.684	0.998476	0.22
19	Naphthalene	24.007	0.995438	0.01
20	n-propylbenzene	25.115	0.992342	0.16
21	1,2-dichloroethane	25.625	0.934570	0.48
22	n-butylbenzene	26.358	0.994360	0.01
23	2,2-dichloropropane	26.829	0.965748	0.06
24	Tetrachloroethane	27.958	0.995436	0.06
25	Bromoform	28.061	0.953460	0.02
26	Isopropylacetate	29.876	0.942379	0.08

Quality Assurance

Laboratory and field blanks analysis were carried out during each sampling period. Extraction solvent (CS_2) was also analyzed. None of the compounds included in this study was detected in CS_2 and in process blanks.

Results and Discussion

A total of seventeen VOCs species were captured and quantified in the ambient air using the active sampling method; among which were five aliphatics, six aromatics, five halogenated and one oxygenated compounds (Table 4). In the passive method, a total number of twenty five VOCs were detected, among which were ten halogenated hydrocarbons, twelve aromatics and four oxygenated compounds (Table 5). No aliphatic component was detected with the passive sampling method. The relatively high volatile nature of the aliphatic VOCs might be responsible for their absence in the passive sampling method.

Table 4: List of Captured VOCs using Active sampling method.

Aliphatics	Aromatics	Halogenated	Oxygenated
Butane	Benzene	Methylene chloride	Acetone
2,2- dimethylbutane	Toluene	Carbon tetrachloride	
3-methylpentane	Ethylbenzene	1,2- dichloroethane	
Isopentane	(p+m)-xylene	Chloroform	
Undecane	o-xylene	1,1,1-trichloroethane	
	1,2,4-trimethylbenzene		

Table 5: List of Captured VOCs using Passive sampling method.

Aromatics	Halogenated	Oxygenated
Benzene	Chloroform	Isopropylacetate
Toluene	Methylene chloride	Ethanol
m-xylene	Carbon tetrachloride	4-methyl-2-pentanone
p-xylene	Bromomethane	Acetone
o-xylene	2,2dichloropropane	
Chlorobenzene	Tetrachloroethane	

Naphthalene	1,1,1,-trichloroethane	
Tetrahydrofuran	Trichlorofluoromethane	
Ethylbenzene	1,2- dichloromethane	
n-propylbenzene		
n-butyl benzene		
isopropyl benzene		

Average Concentration (µgm^{-3}) of Detected VOCs in the Atmosphere of Benin City Using Active Sampling Method

Table 6 showed the average concentrations of ambient VOCs species measured in the city using the active sampling method. Among the aliphatic components, 3-methyl pentane had the highest average concentration of 2.09µgm^{-3} at Ugbowo site where there is a heavy traffic and near a fuel dispensing station. Other aliphatics such as butane, 2,2-dimethylbutane, isopentane and undecane had highest mean concentrations of 1.24, 0.58, 1.11, and 0.71µgm^{-3} at Ring road, Upper Sakpoba, and Ugbowo site respectively. In the aromatic groups, benzene had the highest average concentration of 2.89µgm^{-3} at Ring road. Benzene is a carcinogenic compound causing leukemia. The World Health Organization estimated that a lifetime exposure of 1 µg/m^3 benzene through inhalation leads to about six additional cases of leukemia per million inhabitants (WHO, 1999)[15]. With the mean value of all sites at 2.11µgm^{-3} and a city population of 1,147,188 inhabitants, this implies six additional cases of leukaemia in the population under study (provided all other indoor and outdoor sources of inhalation are negligible). Toluene had the highest mean concentration of 11.6 µgm^{-3} observed at Ramat park, a site close to brewery industries. The (m+p)-xylene, a diesel related component had a fairly high concentration with a mean value of 4.73 µgm^{-3} at Ugbowo. This might be attributed to high traffic flow in this area. The chlorinated VOC species were dominated by methylene chloride, carbon tetrachloride and chloroform. The highest mean concentrations of these three species were 1.73, 1.32 and 0.82 µgm^{-3} at Ekenwan, Upper Sakpoba and New Benin respectively. The result of this study is comparable with 0.48-4.35 µgm^{-3} range obtained from other studies in different cities across the world (Chan *et al,* 2002; Saito *et al,* 2009 and Tiwari *et al,* 2010)[16-18].

Average Concentration (µgm^{-3}) of Detected VOCs in the Atmosphere of Benin City Using Passive Sampling Method

The average concentrations of detected VOCs measured in the city using this method is presented in Table 7. Among the aromatics, toluene had the highest mean value of 3.27µgm^{-3} at Ramat Park, a site close to industries. The mean value of 1.73µg/m^{-3} was obtained for benzene at Ring road. The mean value of benzene for all the six sampling sites is 1.30µgm^{-3}. The m–xylene, p-xylene and o-xylene had a mean value of 1.74, 1.42 and 1.82 µgm^{-3} at Ugbowo. Ethylbenzene had its highest mean value of 2.14µgm^{-3} at upper Sakpoba road. The halogenated VOCS were mostly dominated by chloroform, carbon tetrachloride, methylene chloride and trichlorofluoromethane with

mean values of 1.12, 0.78, 1.10 and 1.28 μgm^{-3} respectively at Ring road; a site with many commercial activities. Ethanol, with a mean value of 0.73 μgm^{-3}, at Ramat park, a site situated between two breweries and a petroleum depot. Acetone, another oxygenated VOC had the highest mean concentration of 1.01μgm^{-3} at Upper Sakpoba and the least value of 0.32μgm^{-3} at New Benin. Naphthalene and 2-methyl-2-pentanone had the least average concentrations among the detectable VOCs in all the sampling sites.

Comparison of Active and Passive Sampling Methods of VOCs Measurement in Benin City

A total of ten VOCs; comprising four aromatics, five halogenated and one oxygenated components were common in both sampling methods (Table 8). Of all the sampling sites, Ring road and Ramat Park had the highest overall mean VOC concentration of 22.25 and 20.77μgm^{-3} respectively using active sampling method while 9.04 and 8.93μgm^{-3} were obtained using passive sampling method. The least mean value of 12.47μgm^{-3} (active) and 7.93μgm^{-3} (passive) was obtained at Ekenwan site. Variations in these locations might be attributed to heavy traffic volume, presence of petroleum depot and fuel dispensing stations. Based on the F-test carried out on the two sampling methods (Table 9), the result indicated a significant difference between the two sampling methods since the F-calculated is greater than the F-tabulated (at 95% confidence level) at each of the sampling sites.

Table 6: The Average Concentration (μgm^{-3}) of Detected VOCs in the Atmosphere of Benin City Using Active Sampling Method.

VOCs (μgm^{-3})	Ekenwan	New Benin	Ramat park	Ring road	Upper Sakpoba	Ugbowo	Mean value of all sites
3-methyl pentane	0.52	1.37	0.20	0.95	0.73	2.09	0.98
Butane	0.54	0.24	0.55	1.24	0.25	0.05	0.48
2,2 – dimethylbutane	0.43	0.14	0.23	0.55	0.58	0.17	0.35
Isopentane	0.85	0.88	0.45	0.85	1.11	0.89	0.84
Undecane	0.45	0.02	0.01	0.01	0.06	0.71	0.21
Benzene	1.70	1.82	2.14	2.89	1.97	2.14	2.11
Toluene	3.32	4.57	11.6	11.1	5.17	9.30	7.51
Ethylbenzene	2.84	1.33	1.09	3.87	5.32	2.30	2.79
(p+m) xylenes	2.92	2.30	3.12	4.08	4.01	4.73	3.53
O-xylene	1.22	3.88	1.09	2.42	0.15	4.51	2.22
1,2,4 trimethyl benzene	1.54	6.88	0.56	0.82	0.51	0.18	1.75

Methylene chloride	1.73	0.97	0.78	0.51	0.17	0.64	0.80
1,2- Dichloroe thane	0.20	0.50	1.08	0.14	0.91	0.26	0.52
Carbon Tetrachloride	0.32	0.47	0.62	0.23	1.32	0.51	0.58
1,1,1-trichloroe thane	0.18	0.51	0.59	0.32	0.74	0.51	0.48
Chloroform	0.20	0.82	0.01	0.33	0.52	0.27	0.36
Acetone	0.76	2.29	1.77	0.34	0.65	0.69	1.08

Table 7: The Average Concentration (µgm^{-3}) of Detected VOCs in Atmosphere of Benin City Using Passive.

Sampling Method

VOCs (µgm-3)	**Ekenwan**	**New Benin**	**Ramat Park**	**Ring road**	**Upper Sakpoba**	**Ugbowo**	**Mean value of all sites**
Benzene	1.00	1.26	1.47	1.73	1.03	1.31	1.300
Toluene	1.20	1.38	3.27	2.20	1.23	1.43	1.790
Ethylbenzene	1.63	0.98	1.01	1.84	2.14	I.43	1.510
m-xylene	1.35	1.12	1.23	1.39	1.28	1.74	1.350
p-xylene	1.20	1.07	1.04	1.21	1.77	1.42	1.290
o-xylene	1.28	1.46	1.03	1.39	0.30	1.82	1.210
Naphthalene	ND	0.05	0.02	0.02	0.02	0.01	0.020
Tetrahydrofuran	0.61	0.04	0.16	0.06	0.37	0.10	0.220
n-propylbenzene	0.17	0.32	0.11	0.16	0.18	0.71	0.280
n-butylbenzene	ND	0.47	0.23	0.14	0.17	0.31	0.220
Isopropylbenzene	ND	ND	ND	ND	0.01	ND	0.002
Chlorobenzene	0.22	0.35	0.16	0.21	0.47	0.19	0.270
Chloroform	1.01	1.08	0.11	1.12	1.09	0.84	0.880
Carbon tetrachloride	0.40	0.28	0.52	0.41	0.78	0.32	0.450
Methylene chloride	1.10	0.53	0.52	1.10	0.32	0.47	0.670
Bromoform	ND	ND	0.04	ND	ND	ND	0.007
1,1,1–trichloroethane	0.23	0.02	0.01	ND	ND	0.02	0.047
Trichlorofluoromethane	1.35	0.59	1.24	1.38	0.28	0.55	0.898
1,2-dichloropropane	0.18	0.27	0.16	0.17	0.21	0.46	0.242
Tetrachloroethane	0.13	ND	0.10	ND	ND	ND	0.038
Acetone	0.90	0.32	0.83	0.92	1.01	0.48	0.605
4-methyl-2pentanone	ND	ND	0.03	0.01	ND	ND	0.007
Isopropyl acetate	0.17	0.04	ND	0.02	0.15	ND	0.058
Ethanol ND: Not Detected	0.20	0.32	0.73	0.39	0.20	0.42	0.377

Table 8: Comparison of Active and Passive Sampling Methods of VOCs measurement in the atmosphere of Benin City.

VOCs (µgm-3) Active (Passive)	Ekenwan A (P)	New Benin A (P)	Ramat park A (P)	Ring road A (P)	U. Sakpoba A (P)	Ugbowo A (P)
Benzene	1.70(1.00)	1.82(1.26)	2.14(1.47)	2.89(1.73)	1.97(1.03)	2.14(1.31)
Toluene	3.32(1.20)	4.57(1.38)	11.60(3.27)	11.10(2.20)	5.17(1.23)	9.30(1.43)
O-xylene	1.22(1.28)	3.88(1.46)	1.09(1.03)	2.42(1.39)	0.15(0.30)	4.51(1.82)
Ethylbenzene	2.84(1.63)	1.33(0.98)	1.09(1.01)	3.87(1.84)	5.32(2.14)	2.30(1.43)
Carbon tetrachloride	0.32(0.40)	0.47(0.28)	0.62(0.52)	0.23(0.41)	1.32(0.78)	0.51(0.32)
Methylene chloride	1.73(1.10)	0.97(0.53)	0.78(0.52)	0.51(1.10)	0.17(0.32)	0.64(0.47)
1,1,1-trichloroethane	0.18(0.23)	0.51(0.02)	0.59(0.01)	0.32(-)	0.74(-)	0.36(0.02)
1,2-dichloroe thane	0.20(0.18)	0.50(0.27)	1.08(0.16)	0.14(0.17)	0.91(0.21)	0.26(0.46)
Chloroform	0.20(1.01)	0.82(1.08)	0.01(0.11)	0.33(1.12)	0.52(1.09)	0.27(0.84)
Acetone	0.76(0.90)	2.29(0.32)	1.77(0.83)	0.34(0.92)	0.65(1.01)	0.69(0.48)
Mean	1.25(0.89)	1.72(0.76)	2.08(0.89)	2.21		

Active sampling method P- Passive sampling method.

Table 9: Test for Significance difference between Active and Passive Sampling. Methods (F-Test)

F-Test	Ekenwan	New Benin	Ramat park	Ring road	Upper Sakpoba	Ugbowo
F-calculated	31.62	56.96	159.96	467.7	88.64	526.26
F-tab at 95% confidence limit	3.18	3.18	3.18	3.18	3.18	3.18

Toluene/Benzene (T/B) Ratio As An Indicator Of Pollutant Source

For this study, Toluene/benzene (T/B) ratio is observed to be higher than 1 in all the sampling sites using both sampling methods (Table 10). T/B ratio approaching a value of 1 indicates traffic-originated emission sources, and the value increases with the closeness of the pollution source (Gelencsér *et al.* 1997)[19]. Ugbowo sampling site had the highest T/B ratio value of 4.34 (active sampling). This might be attributed to its proximity to a fuel dispensing station and the heavy traffic on this expressway. Ekenwan sampling site has the least T/B ratio value of 1.95 (active sampling). This site is close to the postgraduate students hall of residence with relatively low traffic volume. Generally, T/B ratio obtained by active sampling method is higher than those of passive sampling method. High volatility or relatively high vapour pressure of the VOCs might be responsible for their low capturing by the passive sampling method. The T/B ratio obtained in this study agrees with those obtained in other studies (Tiwari *et al*, 2010)[18].

Table 10: Toluene/Benzene (T/B) ratio for both active and passive sampling methods.

T/B ratio	Ekenwan	New Benin	Ramat	Ring road	Upper Sakpoba	Ugbowo
Active sampling	1.95	2.51	5.42	3.84	2.62	4.34
Passive sampling	1.20	1.09	2.22	1.27	1.19	1.09

Conclusion

The VOC concentrations in ambient air of Benin City were studied using both active and passive sampling techniques to understand the composition and concentration distribution. Comparison of the active and passive sampling methods indicates that industrial activities and vehicular emission were the major contributors of VOC species at all the sampling sites. Both active and passive methods are suitable methods for VOCs analysis but active sampling method is more accurate and versatile. However, passive method captured more aromatic and halogenated VOCs than active method at lower concentrations. It is noteworthy from the statistical test that there exists a huge significant difference in the two methods of VOCs measurements.

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