

Variation Characteristics of Volatile Organic Compounds in an Urban Atmosphere in Nigeria

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Abstract

The living patterns of people may create different variations in concentrations of air pollutants in urban setting. Ambient VOCs measured in the Nigerian urban center of Benin City were analyzed and evaluated for variation characteristics; spatial, seasonal, and diurnal patterns of air pollutants. For this purpose samples were collected (from June 2009 to May 2010) at seven locations selected to represent local activities in the city. To determine the diurnal pattern of VOCs, four hourly samplings were carried out at six-day intervals. Samples were analyzed using gas chromatography. Among the VOC species detected are 4 alkanes, 6 aromatic compounds, 4 chlorinated hydrocarbons, and 1 ketone. The results showed that ambient VOC levels in the atmosphere of Benin City are driven by high traffic; hence high concentrations were observed in most traffic junctions sampled. The examination of the average of total VOC accumulation showed significant spatial and seasonal variability ($p < 0.01$) in all sites. The diurnal pattern showed higher concentrations in the morning, and then evening, indicating that fresh emissions impact the air mass in the city. Analyses of the weekly variations of the pollutants showed the weekday's maxima and the weekend's minima, an indication of traffic influence.

Keywords: air pollution, urban pollution, monthly variation, seasonal variation

Introduction

Since the emergence of the pollution prevention concept many years ago, there has been a growing concern about air quality in urban areas. To improve urban air quality, environmental policy makers express widespread interest in controlling and regulating major gaseous pollutants such as O₃, CO, NO, NO₂, SO₂, and volatile organic compounds (VOCs). Pollution due to volatile organic compounds is known to have deleterious effects on human health [1-4]. Some VOCs have been linked with increases in diseases such as lung cancer and leukemia. Similarly, studies of the relationship between VOC profiles and emis-

sion sources in ozone episode regions have shown that ozone formation is VOC limited [5]. Volatile organic compounds are produced in all processes of incomplete combustion of organic substances, the use of petrochemical solvents, and vaporizations of petroleum products [6, 7]. The complexity of VOC behavior, rapid changes in sources, and the number of concentrations as a function of time of the day, location, and season may help characterize the sources of their emissions as well as refine human exposure parameters used in epidemiological studies [8].

Nigeria belongs to the oil producing and exporting countries (OPEC). This implies that large-scale oil productions and utilization activities would take place in the country. In addition, there has been a tremendous increase in the level of industrial activities and vehicular traffic in most

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

Site	Site Code	Co-ordinates	Site Description
1	BNAR	N06° 20' 52.1" E005° 40' 18.2"	Created along Ramat park, close to a petroleum depot and two breweries
2.	BNUG	N06° 24' 10.1 E005° 36' 32.2"	Ugbowo monitoring site created at the University of Benin main gate and close to fuel dispensing stations along the expressway to the western part of the country
3.	BNNB	N06° 20' 57.3" E005° 37' 25.1"	Site three created at New Benin bus terminal. A location with high traffic density and petroleum product dispensing stations
4.	BNRR	N06° 38' 45.1" E005° 37' 20.1"	Created at King's Square with many road intersections and high traffic density
5.	BNSP	N06° 17' 44.6" E005° 38' 8.9"	Created along Sapele road, close to Santana Market
6.	BNEN	N06° 19' 28.4" E005° 35' 99.3"	Ekenwan site close to the University of Benin postgraduate student hostel
7	BNOL	N06° 19' 17.8" E005° 38' 12.5"	3 rd East Circular road site with many road intersections
8	BNAU	N06° 19' 42.6" E005° 36' 86.7"	Upper Adesuwa in GRA, close to the Word of Faith secondary school
9	BNSP	N06° 18' 28.4" E005° 38' 16.5"	Upper Sakponba junction, a bus stop with many shops
10	BNEK	N06° 38' 45.1" E005° 46' 00.5"	Odighi, a background site created close to a village square

Nigerian cities. Most of the industrial processes involved the use of chemicals that are prone to emit VOCs into the atmosphere. Besides, most urban centers in the country are characterized by high populations and traffic densities, so also by mixed resident/industrial buildings. The preliminary ambient VOCs that resulted from our previous studies [9, 10] reported significant spatial variations in hydrocarbon distribution and combustion-related emissions from vehicular exhausts as the main source in the city.

The work presented in this paper is intended to provide more comprehensive information about variation characteristics; seasonal and spatial variations, as well as diurnal pattern of abundant atmospheric VOCs within the urban center of Benin City, southern Nigeria. The study is the first of its kind in a systematic study of VOCs in an air quality study of the Nigerian atmosphere. It is hopeful that the data obtained will be helpful for better policy formulation.

Methodology

Sampling Locations

Benin City in southern Nigeria is located between longitude 6.20°N and latitude 5.31°E. It is one of the urban centers in the southern part of the country with about 1.3 million inhabitants [11]. It is the administrative headquarters of Edo states; hence, it is an urban residential area with high

population and steady traffic density, especially during weekdays. The city lies within such areas that receive rainfall of between 2000 mm and 3000 mm annually. Sun is high throughout the year; hence the high temperature ranges from 30°C to 35°C.

Description of Sampling Sites

Nine sampling sites were selected within the City, and background sites were carefully chosen for this study. The sampling sites were chosen to reflect activities in the areas (mainly residential, commercial, motor park, and industrial). The locations were also selected based on the following criteria: cost of equipment, accessibility of the locations, and freedom from any obstacle to free flow of the air in the vicinity. The geo-referencing was done using a GARMIN GPS MAP765 chart-plotting receiver. The descriptions, their characteristics, and co-ordinates are given Table 1.

Collection of Ambient VOCs Using Active Sampler

Ambient air samples were collected by charcoal tubes (Dräger-NIOSH) containing 150 mg of activated carbon in two successive sections [12]. A low-volume sampling pump (Acuro, Dräger, Lubeck, Germany) was used to draw the air. The average sampling flow rate was 0.51 min⁻¹. The tube was connected in front of the inlet of the adsorption

tube to absorb the gases in air before entering the adsorption tube.

Sampling Routine

The ambient air samples were collected using an active sampling method at a height of 1.5 meters from ground level. Samples were collected at each site every four hours from 6 a.m to 6 p.m, four times per month. The sampling periods covered both dry and wet seasons.

Extraction

After sampling, adsorption tubes were labeled and closed with special caps to avoid contamination and desorption. The samples were placed in 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 in two different vials in which they were weighed, 10 ml carbon disulfide (CS_2) was added as the extraction solvent and was reweighed [12]. Samples were extracted in an ultrasonic bath for 15 min. Then they were centrifuged for another 15 min to obtain a clear phase at the top. The extracted samples were stored in a freezer until analyzed.

Analysis

The extracted solutions were analyzed with an Aligent 6890N gas chromatograph (GC) equipped with a selective detector (Aligent 5973 inert mass selector detector). The chromatograph column was HP-INNOWax, 30×25 mm Internal Diameter × 0.25 μm film and total chromatopack software. The carrier gas was helium at 0.1 cm^3/min at 250°C and 36 $cm \cdot s^{-1}$ linear velocity with a split ratio of 1:20. The inlet temperature was 240°C. The temperature program was: initial oven temperature 40°C, hold for 3 minutes, 40°C to 120°C at 5°C/min, hold for 1 min and the final hold is 15 minutes. Ionization mode of the mass spectrometer was electron impact (EI) at condition of 76 eV. Ion source, quadropole, and GC/MSD interface temperatures were 230, 150, and 280°C. The mass selector detector (MSD) was run in selected ion monitoring. The mass spectrometers acquired data in scan with an m/z interval from 10 to 250 a.m.u.

The peaks obtained were identified based on their relative retention times and qualifier ions using the automatic mass spectral deconvolution and identification system (AMDIS) linked to the US National Institute of Standards and Technology (NIST) Library mass spectral database. Compounds were identified based on their retention times (within ± 0.05 minutes of the retention time of calibration standard).

The concentrations of the identified compounds were read from the calibration graph, which was done with standard solution prepared externally. The standard is a volatile organic calibration mix containing 54 VOCs at 2000 $mg \cdot l^{-1}$ in methanol (Supelco, Bellefonte, U.S.A.). The standard solution was prepared by dilution in CS_2 /methanol for gas chromatography. Ten calibration levels of concentration range

0.02-20.0 $\mu g \cdot ml^{-1}$ were prepared from stock standard with CS_2 in a clean vial. They were freshly prepared at the moment of calibration.

Instrumental calibration was performed by analyzing 1 μl of the diluted standards. The calibration curve shows good linearity, with determination coefficients (r^2) greater than 0.999 for all compounds. The lowest calibration level for each compound was taken as the instrumental quantification limit for that compound.

Quality Control and Assurance

Quality control includes the determination of instrument repeatability and analyzes the blank activated carbon tubes, as process blank. The extraction solvent (CS_2) was also analyzed to determine if there were any contaminants. None of the compounds included in this study were detected in CS_2 and in process blanks. Back-up sections of adsorbent tubes were also extracted and analyzed. VOC amounts in the back-up sections were below the detection limits, indicating that breakthrough was not a problem. No internal standard was used because of good repeatability shown by the method.

Statistical Method

In order to test the significance of the interaction between period and the mean total VOC obtained at different locations, a two-way analysis of variance (ANOVA) statistical test was used. The significance probability of the test is controlled at a specified level ($p < 0.05$). To evaluate significance of the differences in means, we used correlation coefficient (r^2).

Results and Discussion

General Characteristic and Ambient Concentrations of Abundant VOCs

A total of fifteen volatile organic compound species were successfully identified and quantified in ambient air of Benin City, among which were four alkanes, 6 aromatic compounds, 4 chlorinated hydrocarbons, and 1 ketone.

Levels of VOCs in Atmospheric Air

Table 2 summarizes the mean and maximum of individual VOC loads measured together with their standard deviations in the air of Benin City. Among the aliphatics, 3-methyl pentane had its highest average concentration of 2.09 $\mu g \cdot m^{-3}$ at Ugbowo site, with a maximum value of 8.47 $\mu g \cdot m^{-3}$ at ring road. Other alkanes such as butane, 2,2-methylbutane, isopentane, and undecane had highest mean concentrations of 1.24, 0.98, 1.25, and 2.63 $\mu g \cdot m^{-3}$ at the Ring Road, Sapele Road, GRA, and 3rd East Circular Road, respectively.

In the aromatic class, Benzene had the maximum value of 9.35 $\mu g \cdot cm^{-3}$ and the highest mean value of 2.89 $\mu g \cdot m^{-3}$

Table 2. Mean concentrations of abundant VOC species in the atmosphere of Benin City.

VOCs ($\mu\text{g}\cdot\text{m}^{-3}$)	3 rd East Circular Road Mean (Max.)	EKenwa Mean (Max.)	GRA Mean (Max.)	New Benin Mean (Max.)	Ramat ark Mean (Max.)	Ring Road Mean (Max.)	Sapele Road Mean (Max.)	Sakponba Junction Mean (Max.)	Ugbowo Mean (Max.)	Odighi Mean (Max.)
3- Methylpentane	0.57 (2.30)	0.52(3.43)	1.29 (4.10)	1.37 (2.28)	0.20 (0.52)	0.95(8.47)	0.41 (0.61)	0.73 (2.78)	2.09 (4.45)	0.16(0.27)
Butane	0.93 (3.50)	0.54 (1.86)	0.92 (0.67)	0.24 (1.14)	0.55 (0.83)	1.24(3.23)	0.01(0.07)	0.25(2.87)	0.05(0.10)	ND
2,2- Dimethylbutane	0.04 (0.90)	0.43 (1.76)	0.22 (0.49)	0.14 (1.10)	0.23 (0.34)	0.55(0.90)	0.98 (1.76)	0.58 (1.20)	0.17 (0.37)	0.09(0.25)
Iso-pentane	0.89 (1.73)	0.85 (1.73)	1.25 (6.54)	0.88 (1.73)	0.45 (1.73)	0.85(1.73)	0.89 (1.73)	1.11 (4.49)	0.89(2.00)	0.03(0.06)
Undecane	2.63(4.89)	0.45(3.43)	0.02 (0.10)	0.02 (0.10)	0.01 (0.04)	0.01(0.04)	0.09 (0.80)	0.06 (1.74)	0.71 (1.74)	0.01 (0.02)
Benzene	10.4 (16.6)	1.70 (3.61)	2.20 (4.05)	1.82 (2.78)	2.14 (4.39)	2.89(4.54)	1.90(3.92)	1.97(9.35)	2.14(3.46)	0.18(0.89)
Toluene	5.59 (6.64)	3.32(17.43)	3.09 (8.29)	4.57 (15.6)	11.6 (19.1)	11.1(16.7)	6.05 7.57	5.17(18.78)	9.30(17.4)	0.68(2.44)
Ethyl benzene	2.19(4.10)	2.84(6.70)	5.10 (7.52)	1.33 (4.10)	1.09 (7.51)	3.87(6.13)	5.83(15.5)	5.32(7.62)	2.30(5.12)	1.12 (1.96)
P+m xylenes	0.51 (1.59)	2.92 (7.05)	1.33 (2.76)	2.30 (4.14)	3.12 (5.71)	4.08(6.13)	8.36(14.2)	4.01(7.62)	4.73 (7.05)	0.44(0.90)
Oxylenes	0.26 (0.72)	1.22 (6.27)	1.05 (1.89)	3.88 (2.56)	1.09 (4.06)	2.42(4.65)	1.89 (3.93)	0.15(0.75)	4.51 (6.53)	0.17(0.43)
1,2,4 -Trimethylbenzene	0.16(1.17)	1.54(6.12)	0.17 (0.50)	6.88 (20.1)	0.56 (1.04)	0.82(1.44)	0.38 (3.74)	0.51(5.34)	0.18(0.39)	0.01 (0.01)
Methylene chloride	1.03 (3.03)	1.73(5.16)	0.73 (1.25)	0.97 (6.19)	0.78 (1.43)	0.51(1.50)	0.87 (1.68)	0.17(1.68)	0.64(1.15)	ND
1,2 - dichloroethane	1.62(1.66)	0.20(1.16)	0.11(0.93)	0.50 (1.78)	1.08 (3.23)	0.14(0.64)	1.76 (3.56)	0.91 (3.50)	0.26 (0.49)	ND
1,1,1-Trichloroethyne	0.63 (3.22)	0.18 (0.97)	0.12(0.32)	0.51 (1.33)	0.59(2.32)	0.32 (1.27)	0.99(1.41)	0.74 (2.42)	0.36(0.94)	ND
Chloroform	0.13 (0.35)	0.20 (1.81)	0.02 (0.05)	0.82(2.47)	0.01(0.10)	0.33 (1.15)	0.00(0.01)	0.52(1.89)	0.27(0.05)	0.01(0.02)
Acetone	0.12 (0.35)	0.76 (1.79)	0.52(1.67)	2.29(5.30)	1.77(7.23)	0.34 (1.43)	0.76(1.31)	0.65(6.74)	0.69(1.21)	1.07(1.81)

at Sakponba Junction and Ring Road, respectively. Toluene had a maximum of $18.78 \mu\text{g}\cdot\text{m}^{-3}$ at Sakponba Junction, with the highest mean concentration of $11.6 \mu\text{g}\cdot\text{m}^{-3}$ observed at Ramat Park, a site close to industries. (m+p)-xylene, a diesel-related component had a fairly high concentration with a maximum of $14.3 \mu\text{g}\cdot\text{m}^{-3}$ and a mean value of $8.36 \mu\text{g}\cdot\text{m}^{-3}$ at Sapele Road. This may be attributed to heavy trucks plying this site to the Warri petroleum loading point.

The chlorinated VOC species were dominated by methylene chloride, carbon tetrachloride, and chloroform. The highest mean concentrations of these four species were 1.73, 1.76, and $0.82 \mu\text{g}\cdot\text{m}^{-3}$ at Ekenwan, Sapele Road, and New Benin, respectively. The maximum concentrations were 3.03, 3.56, 1.41, and $2.47 \mu\text{g}\cdot\text{m}^{-3}$, respectively. The differences among these values show the influence of the activities taking place in the surrounding atmospheric VOC levels.

Total Volatile Organic Compound (TVOC)

The total concentration of VOCs was obtained by summarizing the concentrations of individual species detected in each sampling site. This gives an indication of pollution strength and allows for comparison of the variability of VOCs at the different sites. Fig. 1 shows the variation in total VOC (TVOC) levels at the various urban sampling sites and background sites.

Fig. 2 shows the proportion by composition of each family of hydrocarbons. As can be seen, the aromatic group provided the largest VOCs in all sites, except the background site where the largest contribution is from the ketones group. This observation points to the fact that bio-

genic or biomass sources dominate the background site while additional sources impact air masses of urban sites.

Spatial and Temporal Trends of Atmospheric VOCs in Benin City

The temporal and spatial variations of the measured VOCs were analyzed to present novel information about the detailed structure of air quality situation in the sampled centers. The specific-site monthly average of total volatile organic compounds observed in the nine sampling sites of Benin City and background sites (Table 3) were analyzed for spatial and temporal variations.

The results of two-way factor ANOVA analysis of the Monthly average of total volatile organic compounds reveal significant ($P < 0.05$) temporal and spatial variations of TVOC concentrations (Table 4). Factors responsible for the spatial variation in urban air pollution, which could also be responsible for observed spatial VOCs distribution in Benin City, include: direct emission rate, emission strength, emission conditions, and atmospheric dispersion [13, 14].

Another notable observation in Table 4 is the seasonal behavior of total VOCs. In Nigeria, the wet season includes June, July, August, September, and October while the dry season includes, November, December, January, February, March, and April. The temperature in the wet season is usually between 20°C and 30°C , while the temperature in the dry season is usually between 32°C and 37°C . The seasonal variation in temperature no doubt greatly influences the pollutant concentration in the atmosphere. The high values during the months of December and April are at traffic intersections. These months were festival periods when

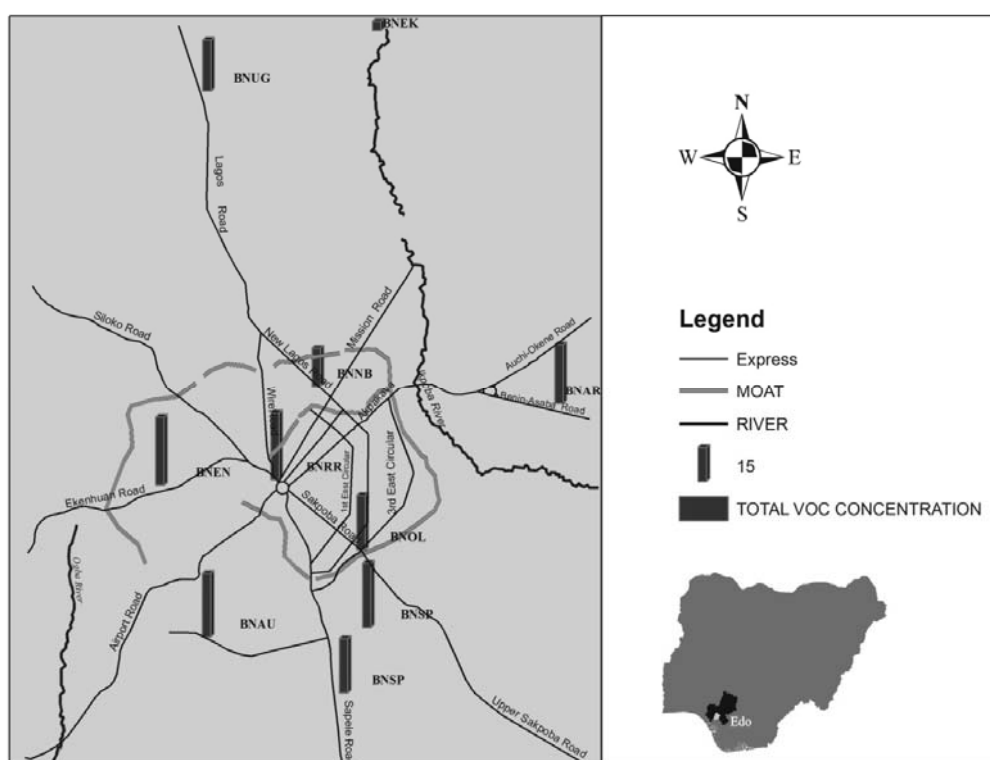


Fig. 1. GIS base-map of Benin City showing spatial distribution of total volatile organic compound concentrations.

there were significant differences in traffic flow. However, the observed slight decrease in the month of August corresponds to a decrease in traffic due to school vacation during the month to early September.

The plots provided some insight concerning the pollution episode in the urban sampling sites of Benin City.

A comparison of concentration time-series plots for the background site and the urban sampling sites clearly showed that major pollution episodes occurred in most of the sampled sites during dry season months. The episode periods were characterized by significantly elevated VOCs. This observation is expected as the background site (a remote

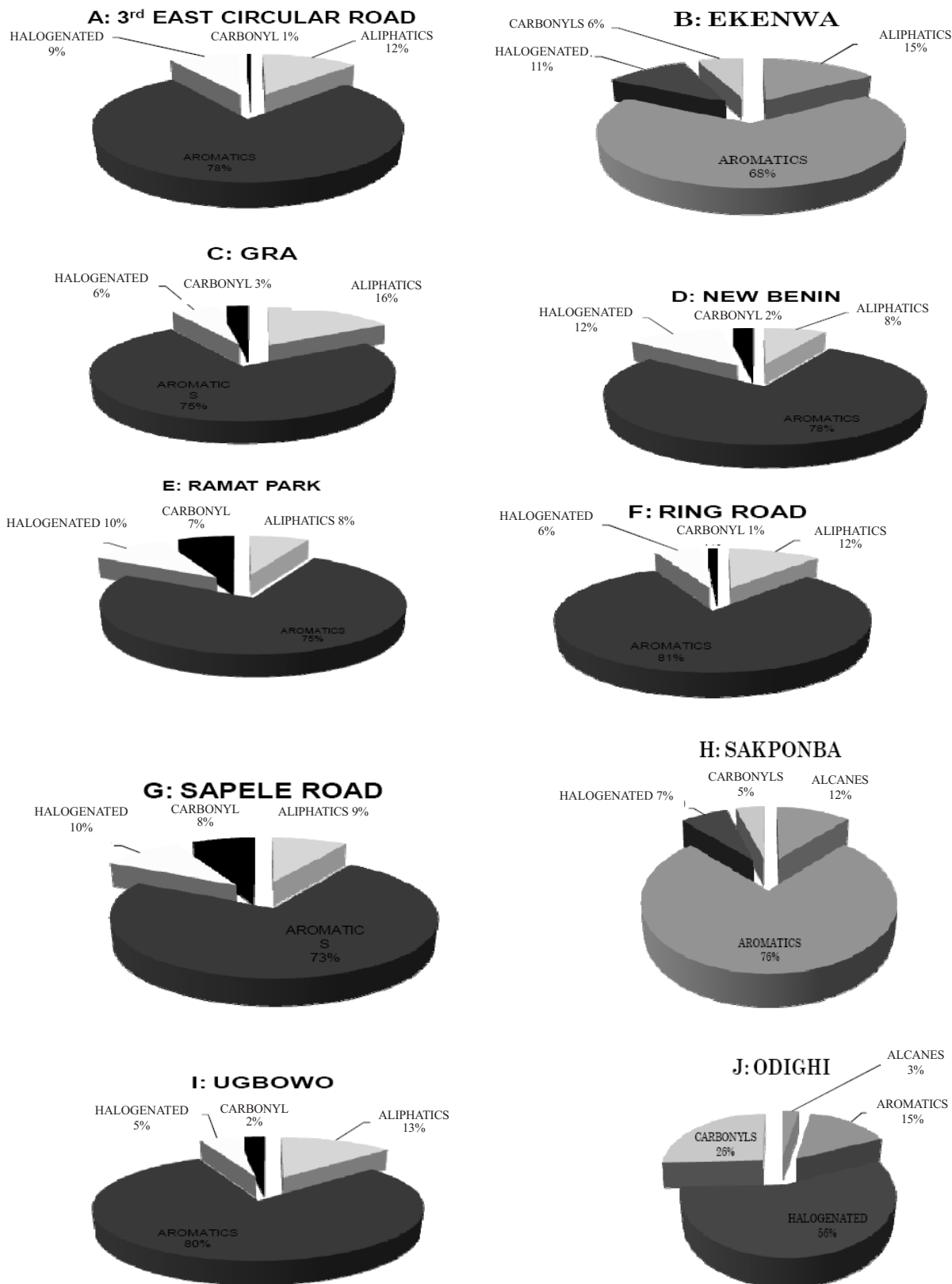


Fig. 2. The percentage by composition of each family of hydrocarbons at the sampling sites.

Table 3. Time-weighted mean \pm SD of ambient VOC concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) measured at sampling sites of Benin City.

Months	3 rd East Circular Road	Ekenwa	GRA	New Benin	Ramat Park	Ring Road	Ugbowo	Sakponba	Sapele Road	Odighi
June 2009	23.72 \pm 9.24	15.83 \pm 3.30	16.22 \pm 1.80	23.68 \pm 2.17	14.77 \pm 2.40	35.08 \pm 3.14	24.3 \pm 2.24	27.52 \pm 2.45	33.49 \pm 1.75	3.67 \pm 0.50
July 2009	23.04 \pm 6.66	14.01 \pm 2.99	16.1 \pm 1.70	23.92 \pm 1.34	15.23 \pm 2.99	23.36 \pm 1.97	24.14 \pm 1.38	25.00 \pm 5.64	16.18 \pm 2.28	3.64 \pm 0.44
August 2009	17.88 \pm 1.56	20.61 \pm 3.71	16.01 \pm 1.09	24.15 \pm 1.76	14.28 \pm 2.71	19.99 \pm 2.62	22.48 \pm 1.49	16.82 \pm 2.64	14.01 \pm 0.98	3.90 \pm 0.49
September 2009	17.04 \pm 1.67	16.21 \pm 4.28	16.38 \pm 1.28	23.68 \pm 1.77	14.09 \pm 1.13	18.16 \pm 1.86	19.86 \pm 1.27	16.40 \pm 1.99	14.92 \pm 1.09	4.05 \pm 0.55
October 2009	16.19 \pm 1.56	15.51 \pm 1.59	17.11 \pm 1.40	23.1 \pm 1.32	12.86 \pm 1.27	16.9 \pm 1.97	22.89 \pm 1.54	23.10 \pm 5.36	16.6 \pm 1.23	3.07 \pm 0.90
November 2009	24.47 \pm 5.10	15.69 \pm 1.33	17.31 \pm 1.44	23.13 \pm 4.21	15.63 \pm 3.55	31.48 \pm 3.31	29.81 \pm 1.73	25.33 \pm 2.32	34.84 \pm 3.69	4.60 \pm 0.90
December 2009	35.32 \pm 1.77	24.81 \pm 5.09	20.24 \pm 1.99	35.33 \pm 2.00	32.88 \pm 2.41	35.91 \pm 2.35	31.9 \pm 2.02	24.42 \pm 1.67	41.3 \pm 10.16	4.42 \pm 1.07
January 2010	36.38 \pm 5.77	36.25 \pm 1.75	21.95 \pm 1.39	36.62 \pm 2.32	30.49 \pm 1.53	40.86 \pm 5.89	37.05 \pm 2.28	26.41 \pm 2.67	41.77 \pm 5.87	4.28 \pm 1.39
February 2010	35.87 \pm 2.25	17.29 \pm 7.12	17.78 \pm 1.69	35.43 \pm 1.90	31.79 \pm 3.21	36.83 \pm 3.93	36.47 \pm 2.94	22.20 \pm 2.65	34.82 \pm 5.46	3.98 \pm 1.06
March 2010	32.95 \pm 3.27	21.78 \pm 5.03	16 \pm 1.39	34.51 \pm 2.20	31.52 \pm 3.08	35.54 \pm 2.45	33.63 \pm 3.83	23.05 \pm 3.28	32.24 \pm 4.11	4.69 \pm 0.66
April 2010	30.82 \pm 2.59	20.23 \pm 7.72	15.46 \pm 1.71	35.07 \pm 1.92	31.73 \pm 3.08	35.56 \pm 1.29	35.1 \pm 5.23	32.92 \pm 4.84	33.37 \pm 3.58	4.55 \pm 0.16
May 2010	30.65 \pm 2.01	15.26 \pm 1.89	17.59 \pm 1.87	34.23 \pm 2.14	31.48 \pm 2.81	35.94 \pm 1.74	30.68 \pm 4.89	35.37 \pm 3.16	31.41 \pm 2.06	3.18 \pm 0.95

Table 4. Two-way ANOVA of the average total VOC concentrations.

Source	DF	SS	MS	F _{CAL}	P-value
Location	6	1,577.60	262.934	16.84	0.0000
Month	11	3,297.43	299.767	19.20	0.0000
Error	66	1,030.48	15.613		
Total	83	5,905.52			

Table 5. The average total VOC concentrations.

	Wet season ($\mu\text{g}\cdot\text{m}^{-3}$)	Dry season ($\mu\text{g}\cdot\text{m}^{-3}$)	Dry/ Wet ratio	Correlation coefficient (r^2)
3 rd East Circular road	20.39	33.66	1.65	0.193
Enkenwa	16.32	22.60	1.21	0.483
GRA	16.52	18.17	1.09	-0.547
New Benin	23.61	35.19	1.49	0.598
Ramat Park	14.47	31.6	2.18	-0.218
Ring Road	21.67	36.77	1.69	0.637
Ugbowo	23.91	34.13	1.42	-0.547
Sakponba	24.05	27.41	1.0	-0.426
Sapele Road	21.67	35.81	1.65	-0.547
Odighi	4.21	3.81	0.90	

location) is assumed to be devoid of any known anthropogenic source.

Generally, serious air pollution episodes in urban environments have been attributed to sudden increases in pollutants emissions, and unfavorable metrological conditions [15].

Table 5 shows that the dry/wet ratio in most sites exceeded 1.0, this likely due to variations of VOC emission strengths in different seasons. However, the linear correlation coefficients (r^2) calculated in most sites were not significant (negative value). This might suggest the combined contributions from different sources. For example, at Ramat Park (a site close to a brewery with moderate traffic and primarily considered as an industrial site), correlation coefficient ($r^2=-0.037$) was calculated.

The high statistical correlation coefficient ($r^2>0.5$) observed in New Benin and Ring Road sampling sites shows that there was consistency in emission sources. This is not surprising, as the sites are bus stops experiencing regular traffic.

Time-Series Plot

The concentration of time-series plots for the measured VOCs in the nine urban sites of Benin City and the background sites are shown in Fig. 3.

The observed high concentrations between October and December in most traffic junctions and market areas (Ramat Park, Sapele Road, and Ring Road) may be attributed to increases in vehicular movement, visiting the market in preparation for festival during the period. However, the increase observed in the month of June at Odighi village no doubt reflects the increase in farming activities during the period, which involved the use of some pesticides.

Diurnal Variation of VOCs

The living patterns of people may create different variations in concentration of air pollutants in urban settings [19]. It is imperative to have thorough knowledge of the

variations in the concentrations of the VOCs with respect to the time of day. In Nigeria, it is customary to classify the day into three time zones: morning (from dawn to noon), afternoon (noon to 4 p.m), and evening (4 p.m to 7 p.m). The diurnal variation of VOC concentrations were analyzed by computing the mean values as a function of the time of day. Fig. 4 depicts the monthly diurnal trend of TVOCs at various urban sites of Benin City.

Surprisingly, the results of monthly diurnal analysis show no clear behavior throughout the year in all sampling sites of this study. This finding is in contrast to those reported in other studies, which found that VOC concentrations follow a distinctive diurnal trend [16-18]. The diurnal profiles indicate that fresh emissions of VOC concentrations

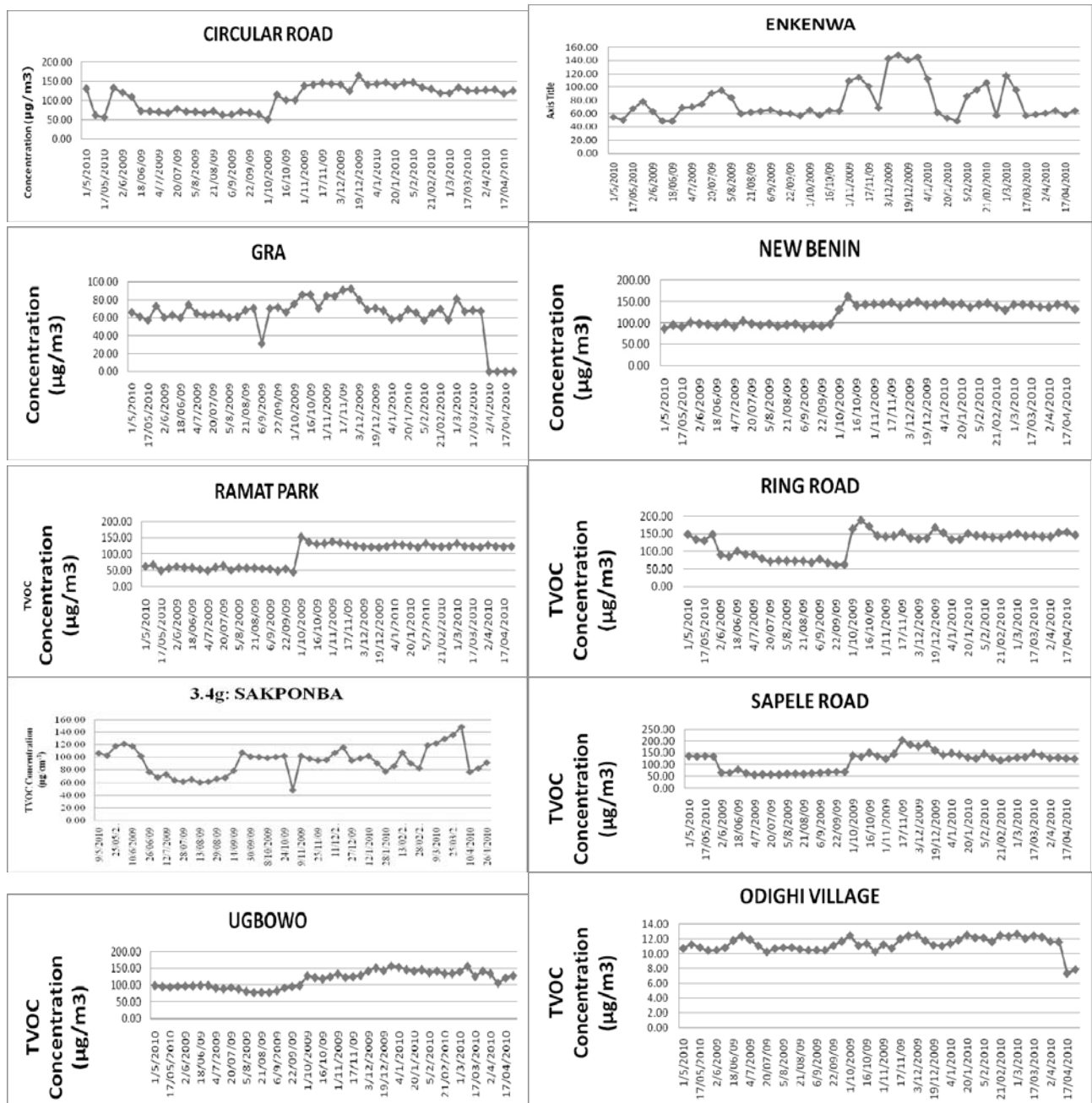


Fig. 3. Concentrations of time-series plots of VOCs in different sampling sites of Benin City and the background site.

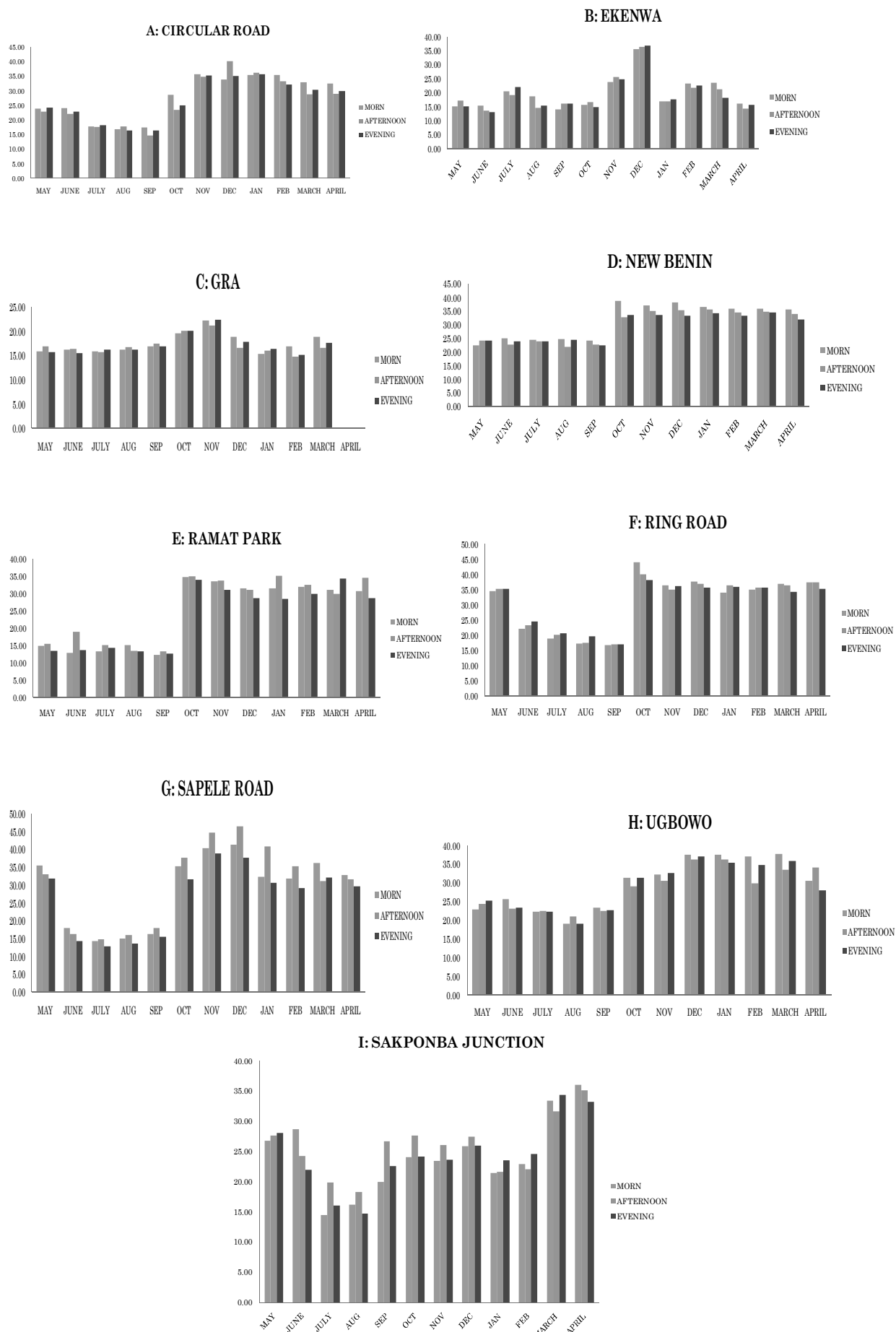


Fig. 4. Diurnal variations of monthly TVOC concentrations at nine urban sampling sites of Benin City.

are impacting the atmosphere of the study centers. The absence of the diurnal trend suggests the possibility of contributions from sources other than vehicular emissions, which are not uniform throughout the year. The observed afternoon peak at Sapele road, Ramat Park, and Sakponba sites between September and December, however, may be attributed to the fact that these sites are surrounded by a market. These months are usually characterized by increased market activities in preparation for festivals. The observed unclear diurnal total VOC trend in New Benin and Ring Road sites may be attributed to the fact that both sites are a bus stop surrounded by a market. Consequently, the traffic volume is high all day.

Conclusions

The VOC concentrations in ambient air of Benin City were studied to understand the composition and concentration distribution. Fifteen species of VOCs were detected in the samples from seven sampling sites of Benin City. The concentrations of VOCs at the seven sites of Benin City showed obviously diurnal and seasonal variations. The total volatile organic compound concentrations during the dry season were high at all sites, while the concentrations in wet season were relatively low. The monthly total volatile organic compounds showed no clear diurnal pattern throughout the year. The diurnal profiles indicate that fresh emissions of VOC concentrations are impacting the atmosphere of this city.

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