



## Ambient Air Levels of Aromatic Organic Compounds in the Urban Area of Algiers, Algeria

YACINE KERCHICH\*, RABAH KERBACHI and HICHAM KHATRAOUI

National Polytechnic School of Algiers, BP 182, El Harrach, 16200 Algiers, Algeria

\*Corresponding author: E-mail: r\_kerbachi@yahoo.fr

(Received: 16 March 2010;

Accepted: 27 August 2010)

AJC-9049

The sampling by "Radiello" diffusion sampler of volatils organic compounds in the ambient air of Algiers reveals the presence of BTEX in all 71 sites sampling chosen. Three representative types of sites were chosen for sample collection at roadside, urban background and semi-rural areas. The samples were taken in two seasons (winter and summer). The following monocyclic aromatic hydrocarbons were found: benzene, toluene, ethylbenzene and (*o*-,*m*-,*p*-)xylene, also referred to as BTEX. Near the road traffic, benzene and toluene mean concentrations were 1.94 and 4.57  $\mu\text{g}/\text{m}^3$ , respectively, with benzene concentration values higher than 18.29  $\mu\text{g}/\text{m}^3$  observed. At the urban site, the average benzene concentration don't exceeds the European regulatory limit of 10  $\mu\text{g}/\text{m}^3$  while the compositional ratios of toluene to benzene and (*o*-,*m*-,*p*-)xylene to ethylbenzene are within the typical range of values observed in urban atmospheres worldwide. The seasonal variation indicates a decrease in concentration during summer due of the conditions that favour the depletion of VOC by photochemical degradation. It was found that Algiers source of pollution by aromatic hydrocarbons is related to car traffic emissions.

**Key Words:** Air pollution, Road traffic, BTEX compounds, GC-FID, VOC, Algeria.

### INTRODUCTION

The monitoring of aromatic hydrocarbons in air has been and continues to be a major subject of research for many years. These compounds are an important class of air pollutants found in many urban and industrial areas. They represent *ca.* 30 % of the total ambient non methane hydrocarbons (NMHCs) in modern urban environment<sup>1</sup>. The major source of monocyclic aromatic hydrocarbons (MAHs) in these areas is anthropogenic production<sup>2</sup>. In urban districts, automobiles are the predominant source of benzene, toluene, ethylbenzene as well as the isomers of xylene, commonly called BTEXs<sup>3</sup>. These compounds are added to fuels to increase octane number and are therefore emitted to the urban atmosphere as components of automobile exhaust gases and by gasoline evaporation and spillage<sup>4</sup>. Additional sources of these monocyclic aromatic hydrocarbons are solvent evaporation, emission from the chemical industry, waste incinerators, composting facilities<sup>5</sup> and household chemicals<sup>6</sup>.

Apart from contributing to urban pollution themselves by their carcinogenic and mutagenic effects on living organisms and human health, like benzene, they are toxic for the human species<sup>7</sup>. They play an important role in the formation of ground-level ozone and photochemical oxidants associated with urban smog<sup>8</sup>. Several studies showed that the highest emissions are closely related to the use of gasoline in non-catalytic cars<sup>9,10</sup>.

Algiers, the capital of Algeria, an area in North Africa at southern Mediterranean. Algiers is a relatively big city with about 3.5 million inhabitants and a large car fleet of approximately one million vehicles (2009), either 22 % of the total national car fleet. In this city, the relatively high rate of car use, 35 vehicles per every 100 inhabitants, is among the highest in developing countries. However, this automobile park is old, the average age is 11 years and has poor maintenance. Recent years, the rate of the car fleet renewal in Algeria has increased to reach 5 % per year. Furthermore, the major part of this car fleet is not equipped with catalytic converters. In Algiers, the urban and inter-urban traffic play an important role in the pollution of the air. It is important to emphasize that there is no heavy industry in the vicinity of the city. According to refineries' officials, present gasoline content varies from 35 to 40 % for aromatics and from 2.5 to 3.0 % for benzene<sup>11</sup>.

Ambient VOC are commonly monitored by on-line gas chromatography (GC), or indirectly after sampling, on passivated canisters or on solid adsorbents. They are afterwards analyzed by thermal desorption (ATD) followed by gas chromatography coupled to a flame ionization detector (GC-FID) or a mass spectrometer detector (GC-MS)<sup>12-15</sup>.

Due to the ubiquity of their emission sources, the BTEX can also be detected even in rural areas<sup>16</sup>. The atmospheric lifetimes of the BTEX are shorter than those of the semi-volatile organic compounds (SOCs). The BTEX can only be transported

over a maximum of a few hundreds kilometres<sup>17</sup>. Therefore, biomonitoring of air pollutants such as the BTEX is done on a regional scale. In Algeria, as in Africa and the southern Mediterranean countries there is not enough information about air pollution in urban cities.

This paper presents results of the BTEXs concentration levels measured at several different locations, urban and roadside areas in Algiers using a passive sampling method. Additionally, the seasonal variations of the pollution were also considered.

## EXPERIMENTAL

**Radiello diffusive sampler:** The Radiello sampler (Fig. 1) used in the passive sampling method consists of a stainless-steel net coaxial cylindrical cartridge (60 mm long, 4.8 mm in diameter, 100 mesh hole size). It is filled with  $530 \pm 30$  mg of 35-50 mesh activated carbon housed in a cylindrical diffusive body made of polycarbonate and microporous polyethylene (60 mm long, 16 mm diameter, 1.7 mm wall thickness and  $25 \pm 5$   $\mu\text{m}$  pore size). Two cellulose acetate caps are soldered with an epoxy adhesive to the cylinder ends. In the case of ambient measurements, the Radiello sampler is screwed on the equilateral triangle plate equipped with an attaching clip. All ready-to-use radial diffusive sampler components are commercially available to the Fondazione Salvatore Maugeri<sup>18</sup>.

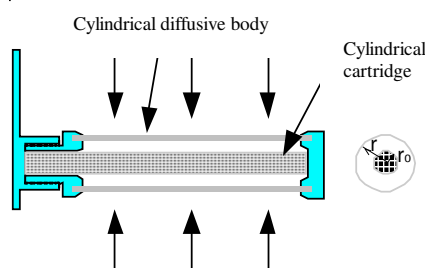


Fig. 1. Diffusive sampling principle

During the sampling procedure, the BTEXs molecules diffuse through the cylindrical membrane towards the cartridge in which they are adsorbed by activated carbon. The diffusion of BTEXs molecules is controlled by the coefficient of molecular diffusion of compound in air, the geometry of the sampler, the porosity of the membrane and the gradients between the BTEXs concentrations in ambient air and at the cartridge area where it is adsorbed on activated carbon. The concentration of pollutants in air is calculated by applying eqn. 1 derived from Fick's first law:

$$C [\mu\text{g m}^{-3}] = \frac{M [\mu\text{g}]}{Q_K [\text{mL min}^{-1}] \cdot t [\text{min}]} \cdot 1,000,000 \quad (1)$$

where  $Q_K$  is the uptake rate,  $t$  the sampling time and  $m$  the BTEXs masses sampling in the cartridge. The sampling rate values of BTEXs at 298 K and 1 013 hPa given by the manufacturer Radiello are: benzene: 80 mL/min, toluene: 74 mL/min, ethylbenzene: 68 mL/min, *m*-xylene: 70 mL/min, *p*-xylene: 70 mL/min, *o*-xylene: 65 mL/min.

Considering the results of previous works on the performances of Radiello diffusive sampler for benzene, toluene, ethylbenzene and xylenes (BTEX) measurements<sup>19,20</sup> and the

sampling time of 7 days appears to be favoured for the estimation of the annual mean concentrations of BTEXs in ambient air.

The variation of the sampling rate according to the effect of temperature (in Kelvin) is given by the following eqn. 2:

$$Q_K = Q_{298} \left( \frac{K}{298} \right)^{1.5} \quad (2)$$

where  $Q_K$  is the sampling rate at the temperature  $K$  and  $Q_{298}$  is the reference value at 298 K. This produces a variation of  $\pm 5\%$  for  $10^\circ\text{C}$  variation (upwards or downwards) from 298 K.

Sampling rate is independent of humidity<sup>21</sup> in the range 15-90% and of wind velocity between 0.1 and  $10 \text{ m s}^{-1}$ .

**Study area and sampling sites:** The studied area in the city of Algiers consists of 27 municipalities with a total surface area of  $181.75 \text{ km}^2$  and an average population density of  $9483 \text{ people/km}^2$  which forms the major urban area in northern Algiers, *ca.* 59% of the total population of the city and 64.9% of its area (Office of National Statistics Algeria, 2006). The city is located along the Mediterranean sea, latitude  $36^\circ 77' 63'' \text{N}$  and longitude  $3^\circ 05' 85'' \text{E}$ .

The climate of the city is typically characterized by a cold and moisty weather during October/April, a hot and dry weather during May/September (Office of National Meteorology Algeria, 2007). The average yearly temperature is  $18^\circ\text{C}$  and the average yearly precipitation is *ca.* 800 mm. Municipalities studied counts a total length of road of *ca.* 256 km, a density of  $1.40 \text{ km/km}^2$  and represents the heart of most commercial and administrative activities of the city.

**Sampling approach and strategy:** Based upon location of urban areas, mobile sources of emissions and the main roads near residences, the approach with a grid-based sampling design was used to monitor the spatial variation of BTEX, *i.e.* 22 sampling areas (either 41 sites) were selected in center of Algiers, which represent an area  $0.96 \text{ km}^2$  and 16 sampling areas (either 30 sites) were chosen in the East coast of Algiers, an area of  $0.60 \text{ km}^2$  (Fig. 2).

This allocation provides an overview on the spatial variation of pollution in the city of Algiers. Sampling sites were placed in the main residential areas to enhance the use of the collected data for evaluating personal exposure related to background pollution. In this sense, it seems logical that a high density mesh fits tightly and conversely, a low population density, correspond a mesh expanded. Samplers placed close to emission sources, were located at distances not exceeding 5 meters from a road. The urban background sites are located at minimum 50 meters from any source of pollution. The samplers were placed 3 m above ground level to reduce the possibility of undesired manipulation. Samplers were hung on utility or telephone poles and streetlight posts, *etc.* Ambient temperature was measured and recorded during sampling operations. Up to 4 sampling points were installed in some municipalities. The road traffic sites and the urban background sites were respectively designed Pi and Fi. The total number of nearby sites and urban background is respectively 28 and 43.

**Weather conditions and periods sampling:** Two campaigns were conducted during the period 2005-2006, one during the summer (71 samples from 24th July to 1st August 2005) and the last during winter (71 samples from 7th February to 15th

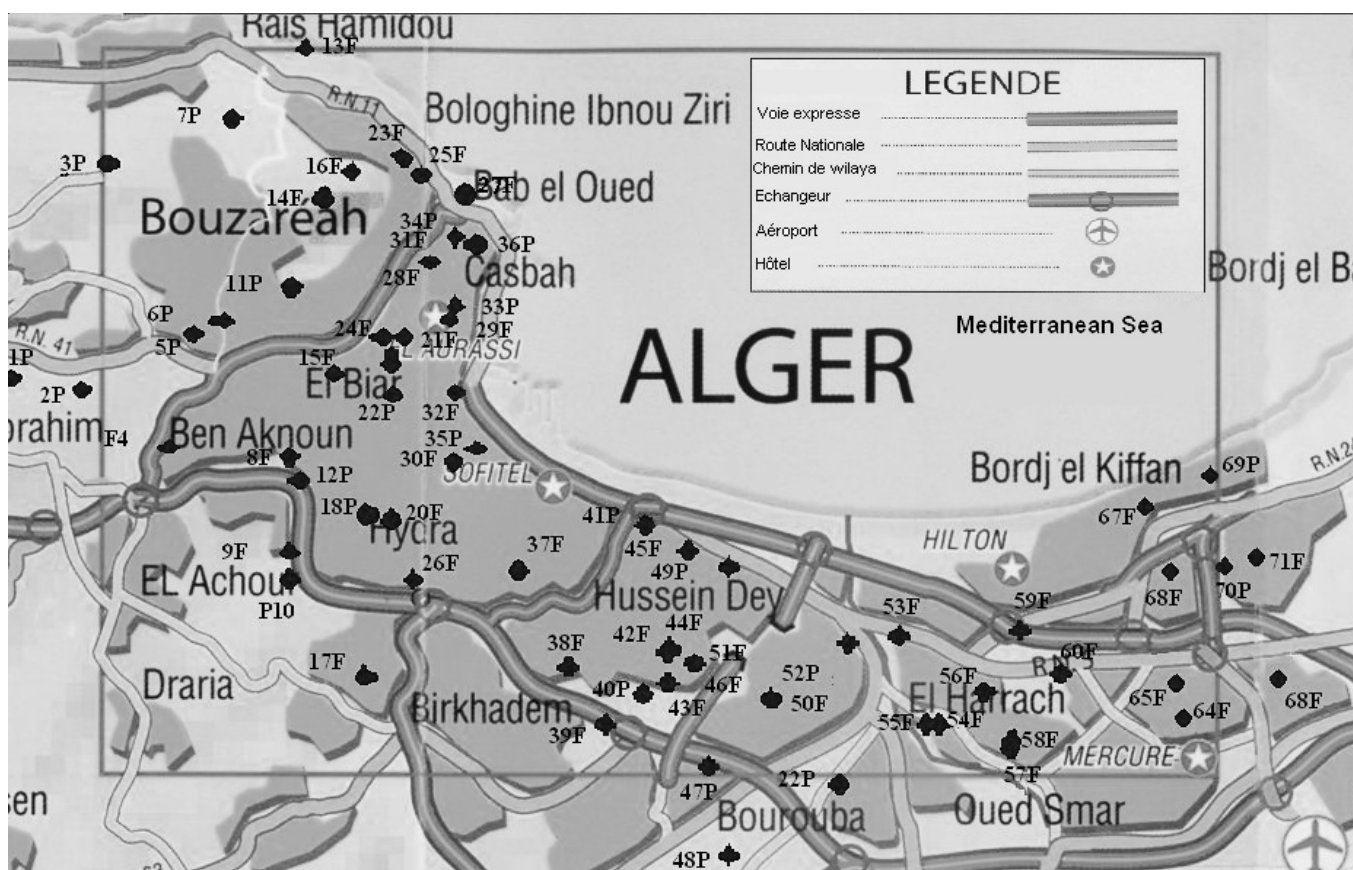


Fig. 2. Localization of the municipalities of the studied area

February 2006). For each campaign the proposed sampling period was 7 days in order to collect sufficient mass for the determination and to smooth out temporal variability. Hourly meteorological data were obtained from the International Airport weather station located at *ca.* 12 km South-East of the capital city of Algiers. The data were then extracted to match each sampling period. The dominant winds directions during sampling period in summer (July) were coming from the north or the north-east (18.5 %, 23.8 % respectively) while those of the sampling campaigns in winter (February) were coming from the north, west and south-west (10.3, 12.1 and 15.2 %, respectively). The average wind speed was  $3.50 \text{ m s}^{-1}$  and  $3.51 \text{ m s}^{-1}$  for the July and February samplings, respectively. The samplers were deployed by 2 field team members within 8 h to ensure simultaneous sampling at all the sampling sites. Two field blanks were deployed in each area during each sampling campaign.

**Limitation of the study:** The major limiting step of this study is the limited or restricted number of sampling campaigns, which would not allow for analysis of seasonal or meteorological effects on spatial variability. Few sampling tubes have been used during the preliminary studies on the nearby sites. These studies were supposed to be necessary to carry out in order to confirm the presence of the pollutants and to validate the analytical method.

Moreover, a risk assessment study would be necessary to further evaluate the potential for harmful health effects based on the results of the spatial variation study.

**Analytical methods:** For the analysis of the BTEX, the activated carbon sample were desorbed using 2 mL  $\text{CS}_2$  (Fluka,  $\geq 99.5\%$ ) and allowed to stand with an occasional shaking for 0.5 h. The extracted substance was analyzed by gas chromatography GC-FID with 1-chlorooctane as an internal standard. The gas chromatography GC-17A from Shimadzu was equipped with a capillary column Supelco BP5, length 15 m, diameter 0.53 mm. The temperature program was: initial temperature  $35^\circ\text{C}$  (0 min), first temperature rising rate  $3^\circ\text{C}/\text{min}$  up to  $50^\circ\text{C}$ ; second temperature rising rate  $5^\circ\text{C}/\text{min}$  up to  $100^\circ\text{C}$ ; third temperature rising rate  $20^\circ\text{C}/\text{min}$  up to  $220^\circ\text{C}$ . Other operating conditions of the GC analyzer were: injector temperature  $250^\circ\text{C}$ ; detector temperature  $250^\circ\text{C}$ . The identification of the BTEXs was based on comparison with pure standard. A  $5 \mu\text{L}$  of sample extract was used for one injection. Each sample was injected twice and the average results were reported. Tube blanks were analyzed in the same way as the samples and all results were corrected. Further details concerning the methods are described in Fondazione Salvatore Maugeri-IRCCS, Italy. With the technique used, it happens even to separate the two isomers *m*, *p*-xylene. However and as is often reported in the literature, we are giving the concentrations of both isomers together. All the results were expressed in  $\mu\text{g}/\text{N m}^3$ . Normal conditions as defined by EC directives are  $T = 293 \text{ K}$  and  $P = 101.3 \text{ kPa}$ . The precision (ratio between the standard deviation and the average value) based on repeated injections of each sample is in the range from 8 to 13 % for all the analytes.

## RESULTS AND DISCUSSION

**BTEX concentrations:** Average concentrations of BTEX, are given in Table-1. Hence, a statistical summary of the data on the BTEX levels in the city of Algiers from July 2005 to February 2006, a total of 142 sites of sampling (Fig. 2) is shown in Table-1. Due to the lack of appropriate standards, only BTEX have been quantitatively evaluated. The BTEX found at nearby (road traffic) and background sites were generally related to the automobile exhaust gas emissions in the urban area and this result fits with other studies<sup>22-26</sup>. In urban areas, the BTEX represent up to 60 % of the main non-methane VOCs<sup>26</sup> and can therefore be considered as an efficient indicator of organic compound pollution generated by road traffic. As expected, the highest concentrations of the individual aromatic compounds are observed at nearby sites which are directly exposed to road traffic emissions. The results clearly indicate the predominance of toluene among all the other investigated BTEX, since it shows the highest average concentration namely  $46.2 \mu\text{g m}^{-3}$  for nearby points and  $9.78 \mu\text{g m}^{-3}$  for background sites (Table-1). This major presence has also been reported in other studies conducted in urban atmospheres<sup>26-28</sup>. The highest levels of BTEX were recorded in sampling sites 41, 49, 51, 52, 63 and 69, which were located in a heavy traffic street (with more than 10,000 vehicles per day) and street intersections subject to important traffic jam. For the background, the highest levels of BTEX were recorded in points 39, 55, 61, 65 and 71. These sites are well exposed to winds which transport the pollutants generated by road No. 5 leading to the centrum of Algiers and the Southern belt connecting Rouiba to Benaknoun (about 50.000 veh./day), and main streets such as Tripoli street-Hussein Dey. Points 13, 23 and 26 showed the lowest concentrations of BTEX, not a surprising result indeed since these points were located in residential neighborhoods. Besides, the highest levels of ethylbenzene were registered in points 39, 57, 61 and 65. It can be seen that the urban BTEX are two to three times lower than those measured at the road traffic sites (Table-2). It is believed that high BTEX levels recorded in Algiers are the results of incomplete combustion in old car engines and the non-existence of catalytic converters in most cars together with the poor vehicle maintenance routine. According to the directive 2000/69/EC, the annual mean benzene concentrations in ambient air must not exceed  $5 \mu\text{g m}^{-3}$ .

The concentration of benzene in the road traffic sites, exceeded this limit value in points 41, 48, 51, 52 and 63, with a mean max registered value of  $12.45 \mu\text{g m}^{-3}$ , whereas other points as 40 and 63 were very close to this limit ( $5.08$  and  $4.58 \mu\text{g m}^{-3}$ , respectively). Therefore, these points could be excluded when considering the exceedances of benzene regulations since according to the same above mentioned Directive, the location of the sampling point must be taken away enough from the emission source to be able to be representative. Also, these concentration levels are not very high compared to situations in European cities with much higher traffic density. For example, in case of benzene the mean concentrations less than  $15 \mu\text{g m}^{-3}$  have been measured at Canyons street in Düsseldorf and Essen<sup>29</sup>, Paris<sup>30</sup> and in Rome<sup>31</sup>. Regarding to toluene levels and although they are not regulated by European legislation, who establishes a guideline value for

TABLE-1  
MEAN CONCENTRATIONS ( $\mu\text{g m}^{-3}$ ) OF BENZENE, TOLUENE,  
ETHYLBENZENE AND XYLENES, FOR THE 71 SITES

Sampling point	Benzene	Toluene	Ethylbenzene	( <i>m,p</i> )-Xylene	<i>o</i> -Xylene	Total BTEX
1P	0.41	1.39	0.17	0.82	n.d.	2.78
2P	1.47	3.64	0.51	1.98	0.68	8.27
3P	1.70	3.27	0.47	1.54	0.26	7.23
4F	0.28	1.07	0.14	0.54	n.d.	2.03
5P	0.64	1.08	0.10	0.66	0.12	2.59
6P	0.37	1.76	0.15	0.68	n.d.	2.95
7P	0.66	0.87	0.07	0.26	n.d.	1.86
8F	0.87	0.17	n.d.	n.d.	n.d.	1.04
9F	1.11	0.42	n.d.	0.09	n.d.	1.62
10P	0.22	1.12	0.10	0.37	0.14	1.93
11P	0.40	1.04	0.05	0.24	n.d.	1.72
12P	0.58	1.56	0.29	1.14	0.36	3.93
13F	0.08	0.83	n.d.	n.d.	n.d.	0.91
14P	0.30	1.26	0.13	0.42	n.d.	2.10
15F	0.89	0.63	n.d.	0.15	n.d.	1.67
16F	0.41	1.12	0.46	0.54	0.06	2.58
17F	0.77	0.92	0.15	0.48	0.09	2.41
18P	0.84	2.12	0.32	1.20	0.40	4.87
19P	1.07	1.93	0.39	1.33	0.33	5.03
20F	0.27	0.64	0.06	0.92	n.d.	1.89
21F	0.14	0.56	0.27	0.32	n.d.	1.29
22P	1.11	1.92	0.32	1.18	0.36	4.88
23F	0.20	0.63	n.d.	0.12	n.d.	0.95
24F	0.47	1.89	0.21	0.80	0.15	3.51
25F	1.01	1.36	0.22	0.80	0.22	3.60
26F	0.17	0.49	n.d.	0.17	n.d.	0.83
27P	0.30	0.90	1.57	0.39	0.06	3.21
28F	0.75	2.59	0.43	1.63	0.52	5.92
29F	0.29	0.73	n.d.	0.60	n.d.	1.62
30F	0.68	1.17	0.18	0.59	0.08	2.69
31F	0.14	1.13	n.d.	0.18	n.d.	1.45
32F	0.63	2.56	0.36	1.27	0.40	5.22
33P	1.33	3.20	0.44	1.67	0.49	7.12
34P	0.76	1.19	0.16	0.60	0.12	2.81
35P	1.16	2.44	0.42	1.51	0.57	6.10
36P	1.03	2.27	0.34	1.28	0.42	5.34
37F	0.46	2.74	0.07	0.53	n.d.	3.79
38F	0.65	1.13	0.15	0.73	0.24	2.90
39F	1.81	8.89	2.03	1.52	0.03	14.27
40P	4.58	9.85	0.87	0.55	1.09	16.95
41P	18.29	46.20	10.24	2.38	2.05	79.17
42F	2.89	5.12	0.44	n.d.	n.d.	8.44
43F	1.58	4.94	0.07	2.93	0.83	10.34
44F	2.35	4.71	0.35	0.30	0.08	7.79
45F	2.40	5.24	0.58	0.90	0.44	9.55
46F	1.55	3.97	0.31	0.15	0.15	6.14
47P	2.70	n.d.	n.d.	-	n.d.	2.70
48P	2.70	n.d.	1.13	1.46	n.d.	5.29
49P	6.27	13.47	8.81	0.37	4.36	33.27
50F	2.35	7.38	0.64	1.14	0.96	12.47
51P	8.41	7.85	6.70	-	n.d.	22.96
52P	7.36	21.40	5.69	4.41	4.62	43.48
53F	1.95	3.17	0.19	0.46	0.20	5.96
54F	1.56	2.06	0.93	1.09	0.16	5.79
55F	3.15	5.97	0.96	2.91	0.25	13.24
56F	1.38	1.92	0.31	0.39	0.20	4.20
57F	1.53	2.84	1.97	0.26	0.40	6.99
58F	1.57	4.26	n.d.	n.d.	n.d.	5.84
59F	1.14	2.91	0.25	0.18	0.16	4.64
60F	2.03	7.30	0.13	0.18	0.41	10.05
61F	2.92	4.74	3.02	3.41	0.13	14.23
62F	1.47	7.63	0.59	1.08	0.14	10.91

63P	12.45	18.85	n.d.	0.16	n.d.	31.47
64F	0.85	4.27	n.d.	0.82	n.d.	5.94
65F	0.80	9.78	1.34	4.69	n.d.	16.61
66F	0.58	5.38	0.76	0.84	0.36	7.92
67F	0.14	1.96	0.63	0.10	0.11	2.93
68F	3.55	6.07	0.67	1.65	0.05	11.98
69P	5.08	19.45	10.26	4.15	n.d.	38.95
70P	2.76	n.d.	n.d.	n.d.	n.d.	2.76
71F	3.28	7.30	0.97	1.95	0.74	14.24
Mean	1.94	4.57	1.20	1.07	0.55	8.59
(S.D.)	2.86	6.76	2.34	1.04	0.94	12.05
Median	1.07	2.355	0.375	0.765	0.255	5.03
Min.	0.08	0.17	0.05	0.09	0.03	0.83
Max.	18.29	46.2	10.26	4.69	4.62	79.17

S.D. = Standard deviation; n.d. = undetectable

the protection of human health of  $260 \mu\text{g m}^{-3}$  expressed as weekly average. Level which, indeed remains far above the levels registered in this study.

The mean concentrations of other compounds measured such as ethylbenzene, (*o*-,*m*-,*p*-)xylene, for all the considered samples were 1.20 (2.34), 1.07(1.04) and 0.55 (0.94)  $\mu\text{g m}^{-3}$ , respectively. The mean concentrations for background sites were 0.60, 0.96, 0.28 and for nearby sites were 1.99, 1.23, 0.97 (Table-2).

TABLE-2  
MEAN LEVELS OF BTEX ( $\mu\text{g/m}^{-3}$ )

Type of sampling site	Benzene	Toluene	Ethylbenzene	( <i>m,p</i> -)Xylene	<i>o</i> -Xylene	BTEX
Urban background sites	1.23	3.27	0.60	0.96	0.28	6.01
Road traffic sites	3.03	6.80	1.99	1.23	0.97	12.56

The concentrations of BTEX recorded in this study were in the range of those found for VOC in Algiers city and in other European urban areas<sup>11</sup>. For comparison, urban BTEX concentrations for different cities around the world are shown in Table-3. In general, values in Algiers are slightly higher

TABLE-3  
BTEX LEVELS ( $\mu\text{g m}^{-3}$ ) AMBIENT AIR OF VARIOUS CITIES WORLDWIDE

Cities	Benzene	Toluene	Ethylbenzene	( <i>m,p</i> -)Xylene	<i>o</i> -Xylene	Ref.
Roma	35.5	99.7	17.6	54.1	25.1	31
Bombay (India)	13.7	11.1	0.4	1.3	2.2	35
United Kingdom	1.23-6.23	2.30-13.8	0.71-3.84	1.68-11.8	0.88-5.73	1
Yokohama (Japan)	1.7-3.7	4.7-34.3	0.5-3.8	1.0-2.0	0.1-0.8	27
Seoul (South Korea)	3.2	24.5	3.0	10	3.5	36
Berlin (Germany)	6.9	13.8	2.8	7.5	2.9	8
London (England)	2.7	7.2	1.4	3.7	1.5	8
Sao Paulo (Brazil) Urban and road site	4.6	44.8	13.3	26.1	6.9	37
Santiago (Chili)	19.5	83.5	-	46.9	16.5	38
Germany	1.13-1.62	4.46-4.98	-	1.20-1.76	-	39
Guangzhou, Nanhai and Macau (South China) Urban and road sites	20-51.5	39.1-85.9	3-24.1	14.2-95.6 ( <i>o,m,p</i> -Xylenes)	1.6	40
Helsinki	2.1	6.6	1.3	4.1	0.6-1.9	41
13 sites in 8 states (USA)	0.8-3.6	1.5-10.5	0.6-2.4	1.8-5.2	2.74	42
La Coruña	3.43	23.6	3.34	5.08	3.7	43
Toulouse	2.0	6.6	-	1.2	-	44
Athens	13.3-26.0	-	-	-	0.55	45
Pamplona-Northern Spain	2.84	13.26	2.15	6.01 ( <i>o,m,p</i> -Xylenes)	-	46
Algiers	1.94	4.57	1.20	1.07	-	Present study

than urban concentrations measured in large cities in industrialized countries but are similar or less than those measured in big cities of some developing countries. These differences can be explained<sup>32</sup> by the particular characteristics of the studied cities, the sampling sites, the sampling periods and the main city activities as well as the differences associated with vehicles, such as vehicle fuel composition, *etc.* However, considering the size of the cities, the concentration levels in Algiers are relatively high and suggest that measurements alleviating these levels must be considered by regulatory or government agencies. In Algeria, air quality standards have not yet been set for air pollution. As a consequence, a higher level of exposure to hazardous gases is observed for pedestrians, people living near main roads and busy intersections or other areas with high traffic density. The health impact is illustrated through the lifetime benzene-related cancer risk which has been calculated using the US EPA unit risk factor<sup>33</sup> and found to be *ca.*  $2 \times 10^{-4}$  at roadside. It is interesting to notice that in the some background sites, the aromatic compound *o*-xylene has not been detected and ethylbenzene did not appear in many samples. This result can be explained by the main removal mechanism of atmospheric higher molecular weight aromatics by the reaction with OH-radicals. The reaction rates for the ethylbenzene and *o*-xylene are 6 and 10 times higher, respectively than those for benzene<sup>34</sup>. During the summer sampling period, this removal process can be faster due to a higher atmospheric content of OH-radicals. It should be noticed also, that during the summer, road traffic decreases slightly compared to the winter period.

**Toluene to benzene and xylene to ethylbenzene mixing ratios:** For the entire duration of sampling, the characteristic benzene:toluene:ethylbenzene:xylene ratio for road traffic sites was 1.62 : 2.82 : 1.00 : 0.74. Most of the 71 sampling points displayed similar ratios although slightly higher compared to the nearby sites (1.52 : 3.41 : 1.00 : 1.10). This suggests that BTEX have a common origin as the main sources are motor vehicles. The non-background ratios recorded in this study

have shown some resemblance with those reported in roadside studies<sup>47</sup>. These ratios were also similar to those reported in La Coruña by Fernández-Martínez *et al.*<sup>43</sup> and Parra *et al.*<sup>46</sup>. However, a different behaviour was found in the background sampling sites.

The ratio of toluene to benzene, for the most sampling sites, is in the average range of 0.20-12.33 with the highest observed ratio of 14.31.

In the background and road traffic sites, these ratios were in the average range of 1.32-14.31 and 0.93-5.07 respectively. Generally, the values of toluene/benzene (T/B) ratios reported in the literature are: 1.7-9.3<sup>26</sup>; 3-12<sup>27</sup>; 0.7-3.8<sup>48</sup>. The lowest T/B ratios occur at background monitoring stations<sup>26,48</sup> and during the summer<sup>48</sup>. In many US cities, the average ratio of  $1.77 \pm 0.4$  is observed<sup>34</sup>. In Algeria, benzene content of leaded gasoline is *ca.* 2.5% and the total aromatic content is 36 % with a gasoline total aromatic to benzene ratio of 14. Considering that the urban BTEX constitutes *ca.* 70 % of the concentration of all aromatics in the atmosphere, the urban ambient air total ratio of aromatic to benzene is *ca.* 3.46. One significant aspect of this result is that it shows that benzene is released into the atmosphere not only as a component of unburned fuel, but also as a by-product of the dealkylation reaction as well.

In the investigated area of the center of Algiers, the (*m*, *p*)-xylene to ethylbenzene mixing ratio is 3.39. This ratio is close to that found<sup>11</sup> in greater urban area such as Algiers with a ratio 2.9. Munich<sup>49</sup> with a ratio of 3.4. Sydney<sup>50</sup> with a ratio of 3.0 and in different cities of UK<sup>1</sup> with a ratio of 2.9. Since *m*-xylene and *p*-xylene have a much higher rates of oxidation by atmospheric OH-radical<sup>51</sup>. The (*m*-*p*)-xylene/ethylbenzene ratio in urban atmospheres is lower than that found in vehicle exhausts or in traffic tunnel measurements. The monitoring of this ratio is interesting and could prove useful indicator for urban photochemical pollution studies.

On the other hand, the compositional patterns of the BTEX expressed as a percent of the total is benzene = 0.24 %, toluene = 0.54 %, ethylbenzene = 0.16 %, xylene = 0.18 % for road traffic sites and benzene = 0.21 %, toluene = 0.54 %, ethylbenzene = 0.10 %, xylene = 0.21 % for urban background.

**Seasonal variation of BTEX:** Table-4 illustrates the seasonal variations of the mean concentrations of BTEX in all the monitored stations (two sampling campaigns). As shown in it, there is a large and statistically significant variation in BTEX levels. Most of the results (Table-4) show that the concentrations of total BTEX significantly differ among sampling periods  $8.77 \mu\text{g m}^{-3}$  in winter and  $6.07 \mu\text{g m}^{-3}$  in summer. Generally, BTEX concentrations were higher in winter and autumn than in spring and summer, as found in many other cities<sup>42,46,52,53</sup>. Several factors can affect the concentrations of BTEX. Thus, BTEX concentrations reach a maximum in the winter due to higher atmospheric stability and minimum in summer, when atmospheric dispersion is more important. Moreover, chemical removal of BTEX by OH radicals is faster in summer than in winter since more sunlight and higher temperatures produce higher chemical removal reaction rates<sup>28</sup>. Besides, the seasonal toluene/benzene ratios corresponding to road traffic station in winter and summer was compared.

TABLE-4  
SEASONAL VARIATIONS OF BTEX CONCENTRATIONS  
( $\mu\text{g m}^{-3}$ ) AND METEOROLOGICAL PARAMETERS

	Summer ( $\mu\text{g m}^{-3}$ )	Winter ( $\mu\text{g m}^{-3}$ )
T (°C)	25.3	10.0
RH (%)	65.5	76.3
Precip. (mm)	0	102.11
Wind speed ( $\text{m s}^{-1}$ )	3.10	3.51
Benzene	1,39	2.11
Toluene	3.44	4.39
Ethylbenzene	0.51	1.22
( <i>p,m</i> )-Xylene	0.93	0.69
<i>o</i> -Xylene	0.22	0.69
Total BTEX	6.07	8.77

It can be seen that the ratios generally followed a similar pattern, with higher values during winter (Fig. 3) as observed elsewhere<sup>28</sup>. At the same time, the seasonal ratios relative to background sites follow different behaviour (Table-5). On the other hand, it was found that the ratios benzene/ethylbenzene and toluene/ethylbenzene in most of the road traffic sites were higher in summer. This finding could be related to the higher reactivity of ethylbenzene compared to that of benzene and toluene, which allows a major loss of this pollutant in this season and therefore higher benzene/ethylbenzene and toluene/ethylbenzene ratios. Although this fact cannot immediately affect the emissions, it might be responsible for the decrease of ethylbenzene in background areas, as the higher distance from the emission point allows a major reaction of this compound and, consequently, the increases of both B/E and T/E in these areas.

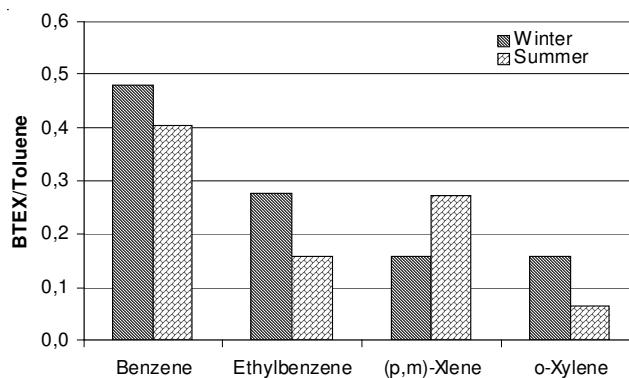


Fig. 3. BTEX to toluene ratio in winter and summer

TABLE-5  
SEASONAL VARIATION OF BTEX ( $\mu\text{g/m}^3$ )  
AT URBAN BACKGROUND SITES

	Summer	Winter
( <i>p,m</i> )-Xylene	0.79	0.53
B/E	2.37	1.92
Benzene	1.07	1.06
Ethylbenzene	0.45	0.55
<i>o</i> -Xylene	0.1	0.31
T/B	3.29	2.94
T/E	7.78	5.67
Toluene	3.53	3.12
Total BTEX	5.95	6.30
X/E	1.97	1.52

With respect to xylene/ethylbenzene ratio, ratios found in road traffic sites (Table-6) were significantly higher in summer than in winter. Since the atmospheric reactivity of xylenes is also high. Considerable variation (Table-4) was observed between temperature and solar radiation and concentration of hydrocarbons.

TABLE-6  
SEASONAL VARIATION OF BTEX ( $\mu\text{g}/\text{m}^3$ )  
IN ROAD TRAFFIC SITES

	Summer	Winter
Benzene	1.92	2.72
Toluene	3.30	6.03
Ethylbenzene	0.60	2.06
( <i>p,m</i> )-Xylene	0.65	1.03
<i>o</i> -Xylene	0.41	0.50
Total BTEX	6.22	11.71
B/E	3.20	1.32
X/E	1.76	0.74
T/E	5.50	2.92
T/B	1.71	3.52

These results are consistent with the effects of photochemical reactions explained above. On the other hand, there is little other source of contribution in urban areas in Algeria since the domestic burning and heating use only natural gas energy and do not contribute to increase winter concentrations of aromatic pollutants. Likewise, a significant positive correlation (Table-4) was found between relative humidity and BTEX concentrations, since winter periods are associated with higher humidity values in the area. Regarding the low wind speeds during the study period, does not seem to have fostered dispersion of pollutants.

## Conclusion

Analysis of ambient air samples in the different road traffic and urban background sites in Algiers city have shown the presence large amount of volatile compounds. The concentration levels of ambient BTEX in ambient air are mainly influenced by road traffic. Large spatial variations of urban BTEX concentrations were detected between the different sampling sites. In the background and road traffic sites, the benzene and toluene average range concentrations are 0.08-3.55  $\mu\text{g}/\text{m}^3$  and 0.4-18.29  $\mu\text{g}/\text{m}^3$ , respectively. The benzene content level is in the same order of magnitude as that found in other urban areas throughout the world. The data obtained showed also that street level concentrations were up to 2 times higher than those found in the background sites. The ratios of benzene to toluene and other ratios found, indicate that the main sources of pollution are emissions from road traffic.

Thus, the passive sampling technique allows for a comprehensive overview of the distribution of air pollution throughout the city. The results show temporal variations between summer and winter values. The concentrations are lower in summer, corresponding to periods with high temperatures and low relative humidity, conditions that favour the depletion of BTEX by photochemical degradation. It can be concluded, that measures of sampling on only two periods (winter and summer) may sometimes not be sufficient for estimating the pollution in large urban areas or for exposure assessment. Also, these

results, we obligate to say that a sharp reduction emissions of air pollutants from traffic seems be necessary, which can be partially achieved through improved vehicle control and maintenance and mandating the use of catalytic converters in all vehicles and the use of cleaner fuels natural gas and liquefied propane gas (LPG). As BTEX compounds are major pollutants of vehicle exhaust, there is the need to strengthen standards for vehicle emissions in Algeria. Also, more intensive studies are necessary to study the distribution of pollutants inside cities and the buildings' influence that have on the dispersion of pollutants within the city and expand the current monitoring air quality network for better measures of air pollution which will help develop better control and allow epidemiological studies to assess the impact of air pollution on the population at Greater Algiers.

Finally, this work provides pollution levels that are typical of other major cities in North Africa, as Tunis (Tunisia) and Casablanca (Marocco), which show large similarities with Algiers in terms of traffic, climate and of socio-economic level.

## ACKNOWLEDGEMENTS

The authors thank Jean-pouleau, Laboratory of Air quality manager-eneris and his staff for their technical assistance and availability. Thanks are also due to A. Khoudir and Prof. N. Moulay for their support and reviewing the manuscript.

## REFERENCES

1. R.G. Derwent, T.J. Davies, M. Delaney, G.J. Dollard, R.A. Field, P. Dumitrean, P.D. Nason, B.M.R. Jones and S.A. Pepler, *Atmos. Environ.*, **34**, 297 (2000).
2. M.A. Dearth, C.A. Glerczak and W.O. Slegl, *Environ. Sci. Technol.*, **26**, 1573 (1992).
3. S.A. Edgerton, M.W. Holdren, D.L. Smith and J.J. Shah, *J. Air Pollut. Contr. Assoc.*, **39**, 729 (1989).
4. A.I. Clark, L.E. McOntire, R. Perry and J.N. Lester, *Environ. Pollut.*, **7B**, 141 (1984).
5. B.D. Eitzer, *Environ. Sci. Technol.*, **29**, 896 (1995).
6. T.M. Sack, D.H. Steele, K. Hammerstrom and J. Remmers, *Atmos. Environ.*, **26A**, 1063 (1992).
7. US EPA, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analysis. US EPA, Quality Assurance Division, Environmental Monitoring Systems Laboratory, June (1984).
8. A. Monod, B.C. Sive, P. Avino, T. Chen, D.R. Blake and F.S. Rowland, *Atmos. Environ.*, **35**, 135, 149 (2001).
9. J. Colls, *Air Pollution*, E & FN Spon, London, pp. 58-59 (1997).
10. J.E. Sigsby Jr., S. Tejada, W. Ray, J.M. Lang and J.W. Duncan, *Environ. Sci. Technol.*, **21**, 466 (1987).
11. R. Kerbach, M. Boughedaoui, L. Bounoua and M. Keddad, *Atmos. Environ.*, **40**, 3995 (2006).
12. US EPA, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography. US EPA, Quality Assurance Division, Environmental Monitoring Systems Laboratory, June (1984).
13. U.S. EPA TO-14A. Compendium of Methods for the determination of Toxic Organic Compounds in Ambient Air: Determination of Volatile Organic Compounds in Ambient Air Using SUMMA Polished Canister Sampling and Gas Chromatography (GC) Analysis-collection by passivated pre-evacuated canister and analysis by GC/ECD, NPD, or FID. US-Environmental Protection Agency, Method TO-14A, Second edition, EPA/625/R-96/010b, edn. 2 (1999).
14. U.S. EPA TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Determination of Volatile Organic Compounds (VOCs) in Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS). US Environmental Protection Agency, Method TO-15, EPA/625/R-96/010b, edn. 2 (1999).

15. M. Clément, S. Arzel, B. Le Bot, R. Seux and M. Millet, *Chemosphere*, **40**, 49 (2000).
16. J. Dewulf and H. Van Langenhove, *Atmos. Environ.*, **31**, 3291 (1997).
17. R. Keymeulen, M. Görgényi, K. Héberger, A. Priksane and H. Van Langenhove, *Atmos. Environ.*, **35**, 6327 (2001).
18. F.S. Maugeri, Instruction Manual for Radiello Sampler, version 1/2003. <http://www.radiello.com>.
19. A. Pennequin-Cardinal, H. Plaisance, N. Locoge, O. Ramalho, S. Kirchner and J.-C. Galloo, *Talanta*, **65**, 1233 (2005).
20. A. Pennequin-Cardinal, H. Plaisance, N. Locoge, O. Ramalho, S. Kirchner and J.-C. Galloo, *Atmos. Environ.*, **39**, 2535 (2005).
21. G.A. Lugg, *Anal. Chem.*, **40**, 1072 (1968).
22. B. Zielinska, J.C. Sagebiel, G. Harshfield, A.W. Gertler, W.R. Pierson, *Atmos. Environ.*, **30**, 2269 (1996).
23. L. Löfgren and G. Petersson, *Chemosphere*, **24**, 135 (1992).
24. K. Sexton and H. Westberg, *Atmos. Environ.*, **18**, 1125 (1984).
25. E. Grosjean, R.A. Rasmussen and D. Grosjean, *Atmos. Environ.*, **32**, 3371 (1998).
26. S.C. Lee, M.Y. Chiu, K.F. Ho, S.C. Zou and X. Wang, *Chemosphere*, **48**, 375 (2002).
27. N. Yamamoto, H. Okayasu, S. Murayama, S. Mori, K. Hunahashi and K. Suzuki, *Atmos. Environ.*, **34**, 4441 (2000).
28. K.F. Ho, S.C. Lee, H. Guo and W.Y. Tsai, *Sci. Total Environ.*, **322**, 155 (2004).
29. H.U. Pfeffer, J. Friesel, G. Elbers, R. Beier and K. Ellermann, *Sci. Total Environ.*, **169**, 7 (1995).
30. A. Coursimault, J. Donati and H. Viellard, *Sci. Total Environ.*, **169**, 17 (1995).
31. D. Brocco, R. Fratarcangeli, L. Lepore, M. Petricca and I. Ventrone, *Atmos. Environ.*, **31**, 557 (1997).
32. I.L. Gee and C.J. Sollars, *Chemosphere*, **36**, 2497 (1998).
33. US EPA, 1990. Cancer risk from outdoor exposure to air toxics. EPA-450/1-90-004a.
34. H.B. Singh, J.L. Salas, B.K. Cantrell and R.M. Redmond, *Atmos. Environ.*, **19**, 1911 (1985).
35. A.M. Mohan Rao, G.G. Pandit, P. Sain, S. Sharma, T.M. Krishna-moorthy and K.S.V. Nambi, *Atmos. Environ.*, **31**, 1077 (1997).
36. K. Na and Y.P. Kim, *Atmos. Environ.*, **35**, 2603 (2001).
37. M. Colón, J.D. Pleil, T.A. Hartlage, M.L. Guardani and M.H. Martins, *Atmos. Environ.*, **35**, 4017 (2001).
38. T.-Y. Chen, I.J. Simpson, D.R. Blake and F.S. Rowland, *Geophys. Res. Lett.*, **28**, 2193 (2001).
39. P. Schneider, I. Gebefügi, K. Richter, G. Wölke, J. Schnelle, H.-E. Wichmann and J. Heinrich, *Sci. Total Environ.*, **267**, 41 (2001).
40. X.-M. Wang, G.-Y. Sheng, J.-M. Fu, C.-Y. Chan, S.-C. Lee, L.Y. Chan and Z.-S. Wang, *Atmos. Environ.*, **37**, 5141 (2002).
41. H. Hellén, H. Hakola, T. Laurila, V. Hiltunen and T. Koskentalo, *Sci. Total Environ.*, **298**, 64 (2002).
42. J.F. Pankow, W. Luo, D.A. Bender, L.M. Isabelle, J.S. Hollingsworth, C. Chen, W.E. Asher and J.S. Zogorski, *Atmos. Environ.*, **37**, 5023 (2003).
43. G. Fernández-Martínez, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez and E. Fernández-Fernández, *Water Air Soil Pollut.*, **129**, 267 (2001).
44. V. Simon, M. Baer, L. Torres, S. Olivier, M. Meybeck and J.P. Della Massa, *Sci. Total Environ.*, **334-335**, 177 (2004).
45. C. Chatzis, E.C. Alexopoulos and A. Linos, *Sci. Total Environ.*, **349**, 72 (2005).
46. M.A. Parra, D. Elustondo, R. Bermejo and J.M. Santamaría, *Sci. Total Environ.*, **407**, 999 (2009).
47. M.F. Mohamed, D. Kang and V.P. Aneja, *Chemosphere*, **47**, 863 (2002).
48. G.A. Pilidis, S.P. Karakitsios and P.A. Kassomenos, *Atmos. Environ.*, **39**, 6051 (2005).
49. B. Rappenglueck and P. Fabian, *Atmos. Environ.*, **33**, 3843 (1999).
50. P.F. Nelson, S.M. Quigley and M.Y. Smith, *Atmos. Environ.*, **17**, 439 (1983).
51. R. Atkinson, *J. Phys. Chem.*, Reference Data, Monograph 1, pp. 1-246 (1989).
52. S.A. Batterman, C.-Y. Peng and J. Braun, *Atmos. Environ.*, **36**, 6015 (2002).
53. K.A. Kourtidis, I. Ziomas, C. Zerefos, E. Kosmidis, P. Symeonidis, E. Christophilopoulos, S. Karathanassis and A. Mploutsos, *Atmos. Environ.*, **36**, 5355 (2002).