

BTEXs emissions from waste municipal located at Medea City in Northern Algeria

Yacine MOUSSAOUI¹, Yacine KERCHICH², Angelo CECINATO³

¹ Univ Ouargla, Faculté des Mathématiques et des Sciences de la Matière,
Dept. De Chimie, Ouargla 30 000 (Algérie)

²Laboratory of Environmental Sciences and Techniques, National Polytechnic School, BP 132, El-Harrach,
Algiers, Algeria

³Istituto sull'Inquinamento Atmosferico del C.N.R., Area della Ricerca di Roma, Via Salaria Km 29.300,
C.P. 10, 00016, Monterotondo Scalo, RM, Italy

E-mail : moussaoui.yacine@univ-ouargla.dz

ملخص: طبقت في هذه الدراسة طريقة انتقال الهواء عن طريق الانتشار وهذا لجمع الهواء الملوث داخل أنبوب زجاجي مملوء بالفحم المنشط ذو النوعية العالية قصد تحديد تركيز الملوثات العضوية الآتية: البنزين، التلوثين، إيثيل البنزين، (ميتا + بارا)-إكزيلان، (أورتو)-إكزيلان المنتشرة في هواء المفرغة النفايات العمومية في مدينة المدية. دامت عملية جمع الهواء شهر في المرحلة الأولى و شهرين في المرحلة الثانية، تمت عملية استرجاع الملوثات العضوية الطيارة، المد مصة على الفحم المنشط باستخدام تنائي كبريت الكربون كمثل. لتحليل الهواء استعملنا تقنية الكروماتوغرافية المقرونة بمطيافية الكتلة التي من خلالها قمنا بالدراسة النوعية بواسطة عملية مسح شامل للطيف والدراسة الكمية بواسطة تقنية قياس الأيون المشخص. التركيبية المثوية للتحليل النصف الكمي للمركبات العضوية الطيارة الموجودة في العينة المدروسة هي كالتالي: البنزين (7,82)، التلوثين (12,57)، (ميتا + بارا)-إكزيلان (6,05)، ن-نونان (1,22)، 1,3, 4-ثلاثي مثيل البنزين (1,13)، ن-ديكان (2,21)، ليمونان (14,32)، ن-انديكان (2,71)، ن-دوديكان (2,35). وجد البنزين و التلوثين بنسبة عالية بلغت 15,90 و 20,26 مغ/م³ على التوالي.

الكلمات المفتاحية: طريقة أخذ العينات السلبي، مفرغة النفايات العمومية، GC/sVOC MS، sXEBT، Analyst-I.

Résumé : Les niveaux atmosphériques des BTEX ont été évalués par exposition des échantillonneurs passifs de type Analyst-I. Après exposition, les COVs collectés ont été extraits avec du disulfure de carbone, et la caractérisation chimique a été effectuée en utilisant la chromatographie en phase gazeuse couplée à la spectromètre de masse (GC/MS). L'analyse des COVs par GC/MS a été conduite en mode SIM (sélection des ions cibles) et en mode SCAN (mode de balayage total), les teneurs de benzène et toluène étaient respectivement 15,90 et 20,26 $\mu\text{g m}^{-3}$ respectivement. Tandis que, la concentration de l'éthylbenzène dans l'air atmosphérique de la décharge était de 3,21 $\mu\text{g m}^{-3}$ et celle de la somme des isomères de xylènes concentration était de 8,59 $\mu\text{g m}^{-3}$. Parmi les COVs identifiés dans la décharge, les BTEX et le limonène sont les plus abondants, ils représentent environ 45% des COVs totaux

MOTS CLES : Echantillonnage passif, COVs, BTEXs, Analyst-I, GC/MS, Décharge publique.

ABSTRACT

BTEXs have been monitored in waste municipal, by using ANALYST-I as the diffusive samplers. After exposition to the air, the VOC collection device was extracted with carbon disulfide, and chemical characterization was performed by applying gas chromatography coupled with mass spectrometer detection (GC-MS). According to VOC diffusive sampling and the GC-MSD determination (operated in both selected-ion-detection and full scan modes), the contents of benzene and toluene in the air were 15.90 and 20.26 $\mu\text{g m}^{-3}$ respectively. The concentration of ethylbenzene in air atmosphere of the waste landfill was 3.21 $\mu\text{g m}^{-3}$ and the total xylenes isomers concentration was 8.59 $\mu\text{g m}^{-3}$. Within VOCs identified in air atmosphere of the waste landfill, BTEXs and limonene are the most abundant they account approximately 45 % of the total VOCs.

KEY WORD: passive sampling, VOCs, BTEXs, Analyst-I, GC/MS, waste municipal.

1 Introduction

Hundreds of different volatile organic compounds (VOCs) occur in emissions and in the air, they are ubiquitous in the air we breathe [1, 2]. They include a multitude of components causing a variety of adverse health effects such as asthma, dizziness, fatigue, eye, nose and throat irritation. In addition, nausea and similar non specific symptoms have been associated with VOCs [3-5].

According to the environmental toxicity, the BTEXs series (benzene, toluene, ethylbenzene and xylenes), carbonyl compounds (formaldehyde, acetaldehyde and acrolein) and organic halogens (used as monomer and anesthetic mixture) are the most important VOCs [6, 7].

In addition to these later, the air composition is dominated by some biogenic VOCs or contaminated fragrances including terpenes compounds [8].

Previous studies demonstrated that: vehicular exhausts, industrial emissions and biomass burning are the major sources of VOCs [9-14].

Because of the complex and multi-source exposure, as well as the continuously renewing formula of consumer products, a number of compounds need to be identified and quantified routinely in order to expand our knowledge about the VOCs occurrence and possible health effects both in indoor and outdoor air [15-21].

The collection of VOCs from air can be obtained by active or passive techniques. Passive samplers are well established for indoor and outdoor air measurements at concentrations usually detected in the environment [22, 23].

“Passive sampler” is defined as any device capable of capturing gases or vapors from the atmosphere at rates controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane. Thus, it does not involve the movement of air through the device by active aspiration. In addition, the sampler itself is usually very small and hence is lightweight and not intrusive. However, the use of passive samplers presents also some limitations, the most important one being the need of determining the virtual aspiration rate of the device itself, which varies with the compound nature and exposure time [22, 23].

An investigation was conducted between March and May 2011 in the waste landfill of Medea to characterize VOCs emission from this waste municipal and estimate the concentration of BTEXs emitted in the air.

2 Materials and methods

2.1 Theory of passive air samplers

The basic equation that describes the passive sampler sampling mechanism is based on Fick's first law. The *Analyst* passive sampler has been developed in 2000 [22, 23]. The sampler can be used for industrial, indoor, outdoor, and personal exposure monitoring. The device consists of a glass cylinder (20 mm i.d., 20 mm diffusion path length) closed at the base and threaded near the opening. The plastic cap of the sampler holds a Teflon-lined rubber septum. The adsorbent, situated on the bottom of the vial within a stainless-steel viewing ring, is graphitized charcoal (ca. 80 m²/g, 20-40 mesh, 150 mg). A finely woven stainless steel net is situated on the viewing ring, and is kept in place by another stainless-steel ring. The removable stainless-steel net, positioned in a threaded aluminum ring, is screwed into the mouth of the device during the sampling time. This extra barrier results in avoidance of random additional effects of eddy diffusion. The device design allows to use it as “extraction vial”, so further transfer and manipulation of the adsorbent is unnecessary (Figure 1).

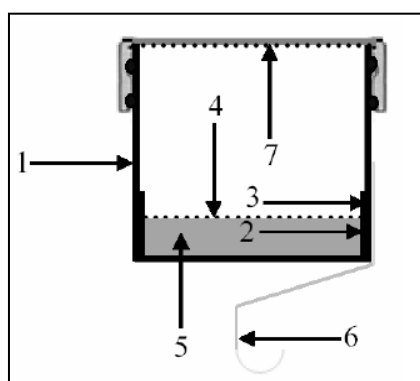


Figure 1: Structure of the Analyst-I passive sampler. 1: Glass cylinder (20 mm i.d. x 20 mm diffusive path length), 2: Retaining stainless-steel ring, 3: Viewing stainless-steel ring, 4: Stainless-steel mesh, 5: Adsorbent bed (80 m²/g, 20-40 mesh, 150 mg), 6: Hook, 7: Removable aluminum and stainless-steel mesh shield.

The daily mean VOC concentration, C ($\mu\text{g}/\text{m}^3$), during the exposure time, t (min), was calculated by the further equation:

$$C = 10^6 M/Kt$$

Where, M is the amount of VOCs in μg , and K is the sampling rate for VOCs.

The sampling rate (K) is evaluated from laboratory experiments. Table 1 shows the uptake rate (mL/min) from some volatile organic compounds.

Table 1: Uptake rates of some VOCs

Compounds	Sampling rate (mL/min)
Benzene	8.93
Toluene	7.96
Ethylbenzene	6.93
<i>m/p</i> -Xylene	6.93
<i>o</i> -Xylene	6.93
1,2,3-Trimethylbenzene	6.51
<i>n</i> -Heptane	7.76
<i>n</i> -Octane	7.15
<i>n</i> -Nonane	6.46
<i>n</i> -Decane	5.99
<i>n</i> -Undecane	5.71
<i>n</i> -Dodecane	5.47

2.2 Reagents

A certified mixture of benzene, toluene, ethylbenzene, *m*-xylenes, *p*-xylene, and *o*-xylene (EPA TO-1 Toxic Organic Mix 1A, 2 mg/mL each in methanol) was purchased from Supelco (Sigma Aldrich, Milan, Italy). 2-fluorotoluene (Supelco) was chosen as internal standard compound. Carbone disulfide, CS_2 (Fluka). The passive samplers (Analyst type, purchased from Marbaglass, Rome, Italy) were just unsealed from the twin-layer aluminum envelopes and used as received.

2.3 Site sampling and deployment

Passive samples were displayed at four points in the waste municipal, located at about 6.4 km far from Medea City ($36^\circ 45' 21.81''\text{N}$, $3^\circ 28' 20.85''\text{E}$), which is 87 km far from Algiers. The exposition time selected for passive sampling was equal to 45 days, from 21 April to 05 May 2011. The site sampling covers an area of more than 7.5 ha. The waste municipal receives a waste daily, the current volume of waste discharged at the landfill cannot be determined, as the waste is burned daily either by scavengers or by all fires as consequence of landfill gas emissions. The detailed position of site sampling is shown in the Figure 2.

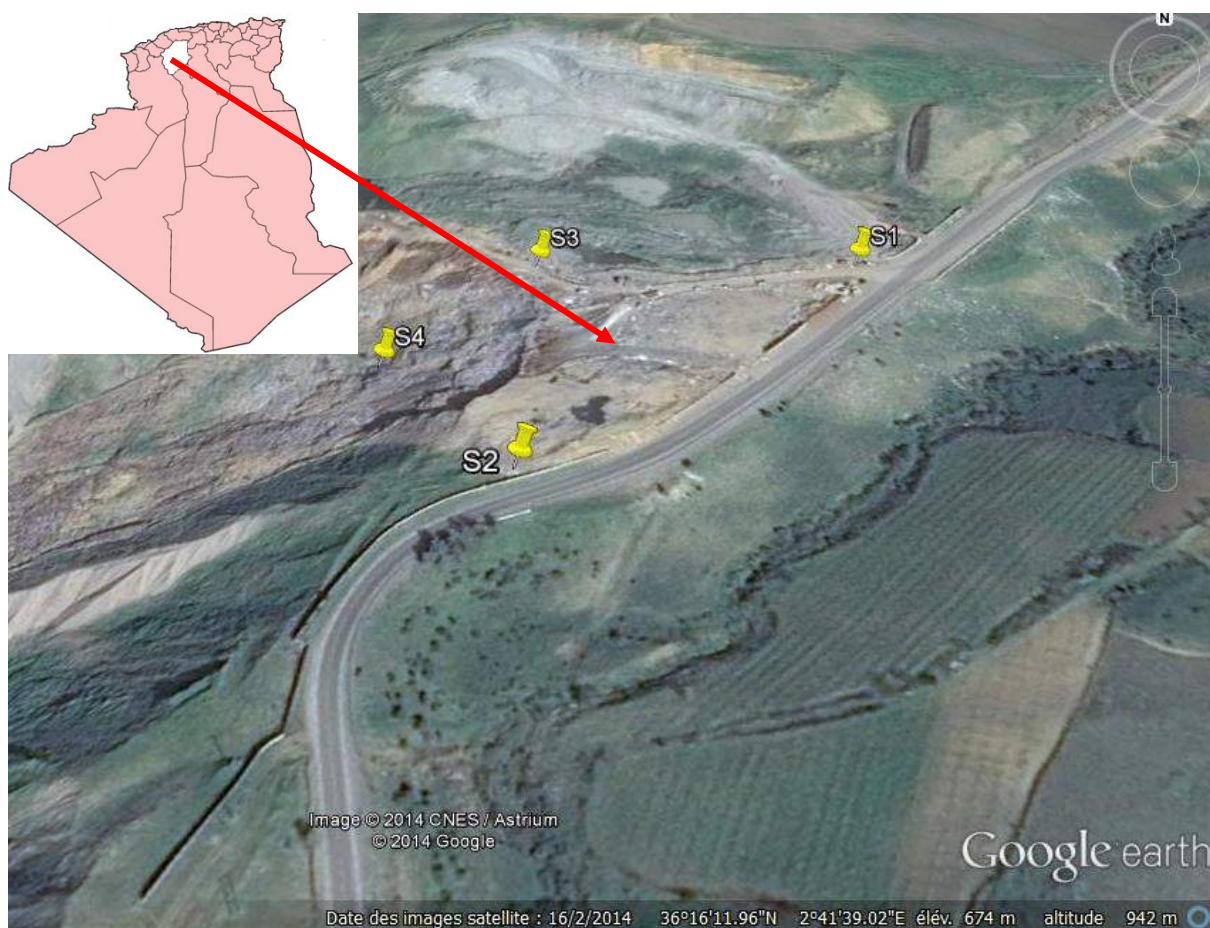


Figure 2: Detailed position on site sampling: on the left in the corner of this figure the Map of Algeria, where Medea is white colored; the rest de position of sampling in the waste municipal (S1, S2, S3 and S4 site sampling)

3 Chemical Processing and Analysis

3.1 Extraction and analysis

Analyst-I type devices were used as passive samplers for the determination of VOCs. After sampling, the VOCs adsorbed on the samplers were solvent extracted by adding 1 mL of CS_2 in septum screwed-vial, the samples were allowed to stand at room temperature for 2 hour under slight shaking, then the solutions were directly subjected to GC analysis.

2 to 5 μL of the extract were analyzed by using a HP 5890 gas chromatograph coupled with a HP 5970B mass-selective detector (Hewlett- Packard, Palo Alto, CA, USA). The MSD was operated in electron impact mode with the following conditions: ionization potential = 70 eV; source temperature = 230 $^\circ\text{C}$; transfer line temperature = 280 $^\circ\text{C}$, M/Z scan range = 20 \div 250, frequency = 3 scans per second. The signals were acquired and processed by a dedicated software purchased from Hewlett-Packard.

The compounds identification was carried out through comparing the features of peaks eluted with those of authentic analyte standards. GC retention times, and mass spectra derived from reference (NIST) and home-made libraries were used for the purpose. Whenever necessary, interpretation of mass spectrometric fragmentation patterns helped as for identification. Analyses were performed both in *scan* and *SIM* modes. In the latter case, the ion fragments $m/z = 78, 91, 109, 91, 91, 91$ were chosen for identification and quantification of benzene, toluene, 2-flourotoluene, ethylbenzene, *m+p*-xylenes and *o*-xylene, respectively. Two or three auxiliary traces were recorded to confirm identification, including molecular ion.

A methylphenyl polysiloxane-type capillary column (HP5-MS, 0.32 mm i.d., 30 m length, 0.25 μm film thickness) was chosen for separation, and helium as carrier gas. The injection port temperature

was maintained at 250°C. The column temperature was run according to the following program: $T_1 = 40^\circ\text{C}$, 8 min, then $+2^\circ\text{C min}^{-1}$ up to $T_2 = 200^\circ\text{C}$, finally 10 min isothermal.

3.2 Assurance and control quality

All analytical procedures were monitored using strict quality assurance and control measures.

Laboratory and field blanks consisted of charcoal coconut glass tubes and Analyst I passive samplers that were run in each sampling campaigns. Three laboratory blanks and eight field blanks were analyzed in total.

The method limit of detection (LOD) for BTEX was determined as equal to three times the standard deviation of the signal obtained from three replicate measurements of blanks, divided by the slope of the calibration curve. LODs as low as 0.05 to $1 \mu\text{g}/\text{m}^3$ were achieved for the BTEX. All analytical results were above the corresponding LODs. For the analyte recovery assessment three blanks of both active and passive sampling devices were spiked with the target VOCs from 0.04 to 35 mg/L. Recoveries ranged from $80\pm 5\%$ to $110\pm 3\%$.

4 Results and discussion

Table 2 reports the BTEXs identified and quantified at waste landfill of Medea. Figure 3 shows the chromatogram GC/MS in SIM mode of BTEXs. Among BTEXs, toluene and benzene were the most abundant compound affecting the oil laboratory (15.90 and $20.26 \mu\text{g m}^{-3}$ respectively). Low concentrations of ethylbenzene was also detected ($3.21 \mu\text{g.m}^{-3}$), while total xylene (*m*-, *p*-, and *o*-isomers) was as high as $8 \mu\text{g.m}^{-3}$. The benzene concentration was very high, exceeding tenth of times the limit guidelines established by the Union European ($5 \mu\text{g.m}^{-3}$).

The whole spectrum of VOCs affecting the air in the waste landfill is provided in Table 3, which reports also the corresponding percentages of principal VOC identified, and the figure 4 shows that the GC/MS chromatogram in SCAM mode of whole VOCs identified at waste landfill of Medea.

Sixty four compounds were found in the atmospheres of the waste municipal of Medea as the most abundant VOCs. Within all VOCs identified at the municipal waste, two biogenic volatile organic compound (α -pinene and limonene) were detected and four microbiogenic volatile organic compounds were also identified (Acetic acid, Benzonitrile, Trans-1-methyl-2-indanol and Cycloazaheptene), others VOCs identified are as source emission as anthropogenic origin.

Among them limonene, benzene, toluene, total xylenes and ethylbenzene accounted cumulatively for more than 46 % of the total; in particular, limonene was the most important one. Limonene is widely used in scented deodorizers, cleaning products, tobacco, food, and flavor applications [24] (Batterman, 2006).

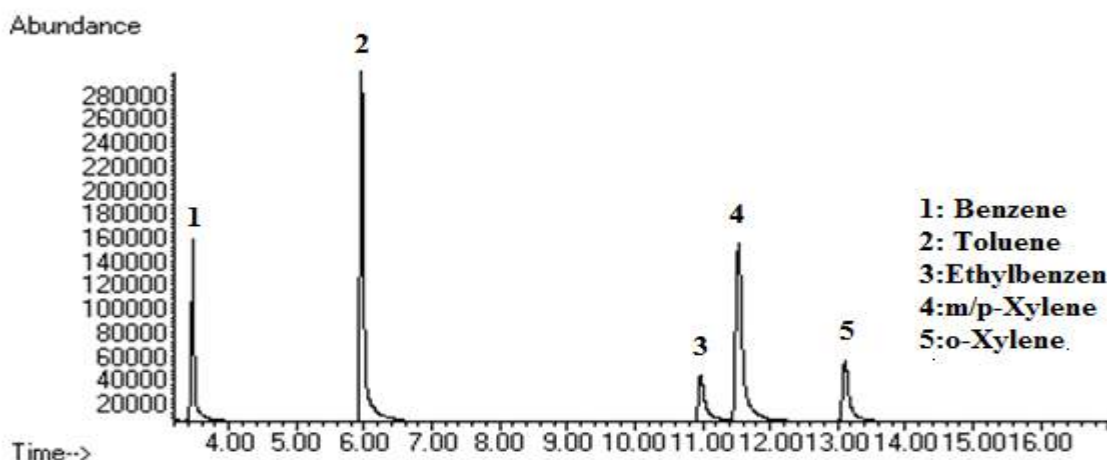


Figure 3: Chromatogram GC/MS of BTEXs in SIM mode

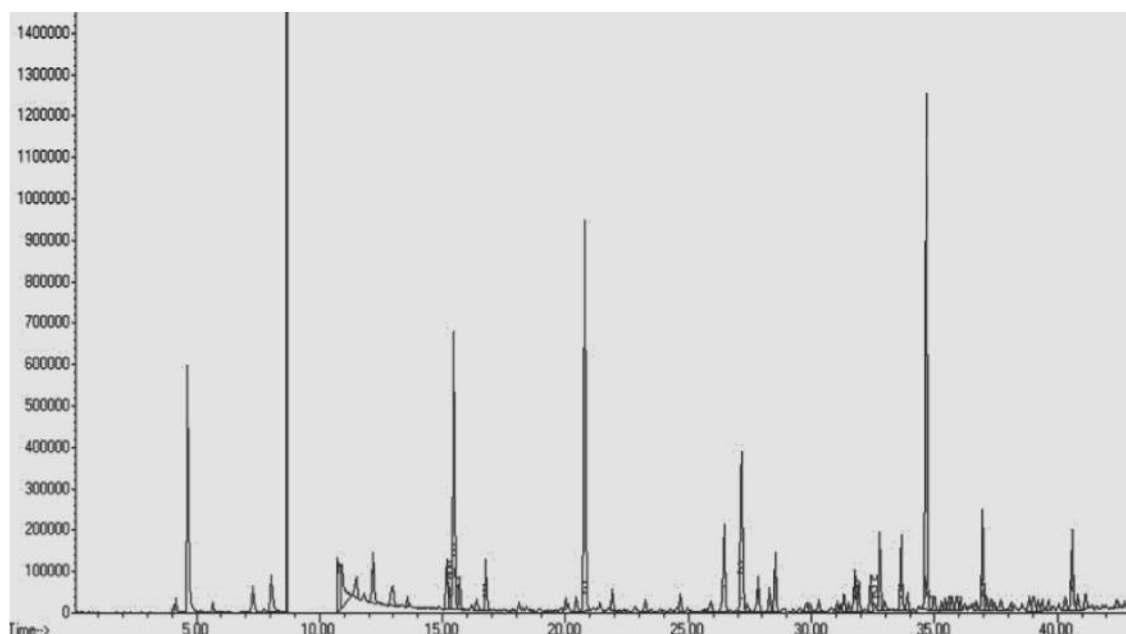


Figure 4: Chromatogram GC/MS of VOCS in SCAN mode

Table 2: Average concentrations of BTEXs ($\mu\text{g.m}^{-3}$)

Compounds	Retention time (min)	Molecular ion	Base peak	C ($\mu\text{g.m}^{-3}$)
Benzene	15.46	78	78	15.90
Toluene	20.78	92	91	20.26
Ethylbenzene	26.45	106	91	3.21
<i>m/p</i> -Xylene	27.15	106	91	7.36
<i>o</i> -Xylene	28.52	106	91	1.23

Table 3: Major VOCs identified at waste municipal of Medea

No.	Compounds	RT (min)	% of total
1	<i>n</i> -Butane	5.66	0.28
2	2-Methylbutane	7.28	1.08
3	<i>n</i> -Pentane	8.03	1.66
4	<i>n</i> -Hexane	12.18	1.78
5	Acetic acid	12.96	1.13
6	Cyclohexane	15.16	1.39
7	2-Methylhexane	15.26	0.71
8	Benzene	15.46	7.82
9	3-Methylhexane	15.69	0.92
10	1-Heptene	16.38	0.44
11	<i>n</i> -Heptane	16.76	1.40
12	2-Methylheptane	20.05	0.26
13	3-Methylheptane	20.43	0.58
14	Toluene	20.78	12.57
15	<i>n</i> -Octane	21.90	0.76
16	Tetrachloroethylene	23.25	0.48
17	2-Undecene	24.67	0.61
18	4-Methyloctane	25.91	0.65
19	Ethylbenzene	26.44	3.07
20	<i>m/p</i> -Xylene	27.14	6.05

21	1-Nonene	27.40	0.32
22	<i>n</i> -Nonane	27.83	1.22
23	Styrene	28.29	0.79
24	<i>o</i> -Xylene	28.52	1.85
25	1-Methylethylbenzene	29.80	0.44
26	Propylcyclohexane	29.95	0.32
27	α -Pinene	30.30	0.41
28	4-Methylnonane	31.06	0.31
29	Propylbenzene	31.33	0.51
30	3-Methylnonane	31.52	0.24
31	1-Ethyl-2-Methylbenzene	31.76	1.52
32	1,2,4-Trimethylbenzene	31.91	0.86
33	1,3,4-Trimethylbenzene	32.40	1.13
34	<i>n</i> -Decane	32.78	2.21
35	Benzonitrile	32.97	0.38
36	1,2,3-Trimethylbenzene	33.64	2.24
37	2,3,4-Trimethylhexane	33.90	0.64
38	Limonene	34.66	14.32
39	1,2,4-Trimethylbenzene	34.99	0.68
40	5-Methyldecane	35.29	0.30
41	Cyclopropylbenzene	35.44	0.41
42	2-Methyldecane	35.58	0.39
43	1-Methyl-2-Propylbenzene	35.71	0.49
44	Tetracyclo[5.2.1.0(1,6)]decan-6-ene	35.91	0.67
45	1-Ethyl-3,5-dimethylbenzene	36.07	0.39
46	3-Tetradecene	36.67	0.27
47	<i>n</i> -Undecane	36.96	2.71
48	1-Ethyl-2,3-dimethylbenzene	37.10	0.57
49	4-Ethyl-1,2-dimethylbenzene	37.30	0.47
50	Trans-1-methyl-2-indanol	37.71	0.55
51	2,3-Dimethylundecane	38.13	0.32
52	1,2,3,5-Tetramethylbenzene	38.88	0.60
53	1,2,4,5-Tetramethylbenzene	39.03	0.82
54	4-Methylundecane	39.22	0.33
55	2-Ethyl-1,4-dimethylbenzene	40.32	0.64
56	<i>n</i> -Dodecane	40.59	2.35
57	Cycloazaheptene	40.82	0.53
58	2,6-Dimethylundecane	41.14	0.58
59	Heptylcyclohexane	42.43	0.39
60	<i>n</i> -Tridecane	43.84	1.60
61	2,6,10-Trimethyldodecane	46.26	0.29
62	1-Pentadecene	46.60	0.26
63	<i>n</i> -Tetradecane	46.79	1.13
64	<i>n</i> -Pentadecane	49.51	0.63

As shown in Table 4, the benzene and toluene contents at the waste municipal of Medea measured in this study were significantly higher than those measured at Nan Ji Do waste municipal (Seoul, Korea) in autumn 2000, Woon Jung Dong waste municipal (Gwang Ju, Korea) in autumn 2002, Sam Poong Dong waste municipal (Kyung San, Korea) in winter 2003, Hoei Chun Dong waste municipal (Jeju, Korea) in summer 2003, Dae Gu waste municipal (Jeju, Korea) in winter 2004, and at the waste municipal of Montcada i Reixac (Barcelona, Spain), both in winter and summer 2010. On the other hand, they were lower than those measured at Oued Smar waste municipal (Algiers, Algeria). However the ratio of Benzene to sum of BTX (benzene, toluene and total xylenes) recorded in this study was higher than other ratios Benzene to sum of BTX recorded at different sites of waste municipal reported by the Table 4.

Table 4: Concentrations of BTEXs ($\mu\text{g}/\text{m}^3$) measured in various studies at waste municipal

	Benzene ($\mu\text{g m}^{-3}$)	Toluene ($\mu\text{g m}^{-3}$)	Σ Xylenes ($\mu\text{g m}^{-3}$)	BTX ($\mu\text{g m}^{-3}$)	Benzene/BTX
Municipal waste of Nan Ji Do, Korea, 20 Sep. - 4 Oct. 2000 [25]	0.72	6.32	0.82	7.86	0.09
Municipal waste of Woon Jung Dong, Korea, 9-11 Dec 2002 [25]	2.44	110	32	144.44	0.01
Municipal waste of Sam Poong Dong, Korea, 14-15 Jan. 2003 [25]	0.80	6.03	1.48	8.31	0.09
Municipal waste of Hoei Chun Dong, Korea, 22-23 July 2003 [25]	0.72	8.88	20.72	30.32	0.02
Municipal Waste of Dae Gu, Korea 13-16 January 2004 [26]	0.99 \pm 1.10	8.58 \pm 5.26	0.46 \pm 0.44	10.03	0.1
Municipal Waste of Montcada i Reixac Barcelona, Spain, Winter 2010 [27]	0.6	5.3	3.9	9.80	0.06
Municipal Waste of Montcada i Reixac Barcelona, Spain, Summer 2010 [27]	0.5	5.4	2.9	8.80	0.05
Municipal Waste of Oued Smar, Algiers, Algeria 5 June 1998[8]	71	253	69	393	0.18
This study	115.90	220.26	8.59	44.75	0.35

4.1 BTEXs Sources

The toluene, *m/p*-xylene and *o*-xylene ratios vs. benzene were calculated at municipal waste for this study and for various studies investigated in air tunnel in Algiers and Rome, to draw insights about the sources of VOCs. In fact, when the three ratios, in the order, approach the values of 2.7, 1.8 and 0.9, respectively, the automobile exhaust as source emission is clearly confirmed. According to Table 5, the toluene, *m/p*-xylene and *o*-xylene to benzene ratios for air tunnel of Oued Ouchayeh (Algiers, Algeria), investigated by passive samplers, using Analyst-I for two month and Radiello for 24 hours were lower than those proposed by technical literature. In contrast, the toluene, *m/p*-xylene and *o*-xylene to benzene ratios for air tunnel at Rome (Italy), investigated by an active sampler for few minutes were very high than those proposed by technical literature. In fact, in the tunnel it was supposed that automobile exhaust is the predominant emission: although the value of ratios were significantly lower than those reported in the literature, however at least two factors could modify their values in the case of the using the passive sampling. Indeed, benzene, toluene and xylenes exhibit different reactivities vs. OH radical. Since the Analyst sampler requires considerable time in order to the equilibrium be established (at least 2 weeks), the most reactive congeners could be partly degraded. It will be necessary, in further investigations, to estimate new values of BTEX diagnostics ratios for passive sampling by Analyst or similar devices, in agreement with the respective application times. However, when the tunnel was investigated by Radiello, the value of the calculated ratios approach at least those proposed by the literature, because the exposition time was very lower in comparison with the time used in case of Analyst-I at the same Tunnel. The high value of the toluene, *m/p*-xylene and *o*-xylene to benzene ratios for air tunnel at Rome (Italy), could be explain by using the thermal desorption tube as an active sampler and also the outcome of toluene and xylenes from other sources (especially old emissions). In our study, it's appeared clearly, when the value of ratios were very lower in comparison with those proposed by the technical literature (calculated for fresh emission of automobile exhaust) that the benzene, toluene and Xylenes (*o*-, *m*-, *p*-) have gas emission from a municipal waste as origin source.

Since that the concentration of benzene recorded in this study and approached $16 \mu\text{g m}^{-3}$, where exceeding more than tenth of times the limit guidelines established by the Union European, when this latter recommended the an annual concentration of benzene equal to $5 \mu\text{g.m}^{-3}$ as a limit value to

be not exceeded. This fact, let to think of the health of workers in the landfill that are daily exposed to this level for a long time, especially since benzene is a carcinogen class A.

Table 5: Values of the toluene, *m/p*-xylene and *o*-xylene vs. benzene concentration ratios calculated at various studies.

	This study	*Oued Ouchayeh Tunnel, Algiers	**Oued Ouchayeh Tunnel, Algiers	***Tunnel at Rome, Italy	Automotive exhaust
Toluene/benzene	1.27	2.1	2.37	5.40	2.7 [28]
<i>m/p</i> -Xylene/benzene	0.46	0.7	1.65	3.85	1.8 [29]
<i>o</i> -Xylene/benzene	0.08	0.4	0.37	1.56	0.9 [30]

*Passive sampling for two month in the Tunnel of Oued Ouchayeh, Algiers using Analyst-I [31]

**Passive sampling for 24 hours in the Tunnel of Oued Ouchayeh, Algiers using Radiello [32]

***Active sampling for few minutes using thermal desorption tube in the big Tunnel at Rome, Italy [33]

5. Conclusion

The diffusive sampling method was successfully applied to monitor BTEXs and estimate the ambient air of the municipal waste of Medea, Algeria.

High benzene concentrations were observed, which often exceeded by far the limits set by EU Directive.

Limonene, benzene, toluene, total xylenes and ethylbenzene were the most abundant VOCs identified at the waste municipal of Medea, They accounted cumulatively more than 46 % of the total VOCs.

The diagnostic ratio of toluene, *m/p*-xylene and *o*-xylene ratios vs. Benzene, evaluated for the waste municipal of Medea, demonstrated clearly the gas emission from the waste municipal of Medea as the source origin of BTXs recorded in the air atmospheres of this investigated site.

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