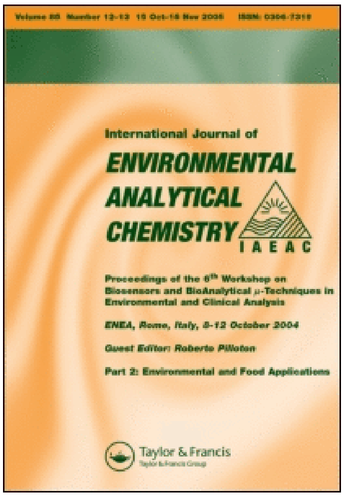

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Abdelali Zouir[ab]; Francesc A. Esteve-Turrillas[a]; Ángel Morales-Rubio[a]; Tarik Chafik[b]; Agustín Pastor[a]; Miguel de la Guardia[a]
[a] Department of Analytical Chemistry, University of Valencia, Valencia, Spain [b] Laboratoire de Génie Chimique et Valorisation des Ressources, Faculté des Sciences et Techniques de Tanger, Université Abdelmalek Essaadi, Tanger, Maroc

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Abdelali Zouir[ab], Francesc A. Esteve-Turrillas[a], Ángel Morales-Rubio[a],
Tarik Chafik[b], Agustín Pastor[a] and Miguel de la Guardia[a]*

[a]*Department of Analytical Chemistry, University of Valencia, Valencia, Spain;*
[b]*Laboratoire de Génie Chimique et Valorisation des Ressources, Faculté des Sciences et Techniques de Tanger, Université Abdelmalek Essaadi, Tanger, Maroc*

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Semipermeable membrane devices (SPMDs) have been used for the evaluation of the contamination of air in both the urban and the industrial area in Tangier (Morocco). Benzene, toluene, ethylbenzene and xylenes (BTEX), 12 polycyclic aromatic hydrocarbons (PAHs) and seven polychlorinated biphenyls (PCBs) were monitored with SPMDs, deployed in six different sites, and determined by using a microwave-assisted extraction with gel permeation chromatography (GPC) clean up for PAHs and PCBs determination; and a head-space direct measurement for BTEX. Gas chromatography with mass spectrometry detection was employed for the identification and quantification of the aforementioned pollutants. From the obtained results, it can be seen that the urban waste deposit and the industrial area of Moghogha present the highest concentrations of BTEX and PAHs, but significantly do not contribute to the contamination of air in the Tangier urban area. PCBs were not found in any of the sampled sites.

Keywords: SPMDs; BTEX; PAHs; PCBs; air contamination; passive sampling

1. Introduction

Benzene, toluene, ethylbenzene and the *ortho*, *meta* and *para*-xylene isomers, so-called BTEX, are organic contaminants emitted into atmosphere from natural and anthropogenic sources and combustion processes of wood, gasoline and fuels [1]. Hence, the urban traffic is considered one of the most important BTEX sources [2], but also their concentration can be increased as a result of solid waste burning practices.

Benzene, toluene, ethylbenzene and xylenes compounds may be analysed in air by using active and passive sampling systems. Most of the contamination studies are based on active sampling by using adsorption tubes with several solid phases as activated charcoal, graphitised carbon or Tenax [3–5]. In the case of passive sampling, devices such as 3M-OVM (Organic Vapours Monitor) [6] or Radiello diffusive samplers [7] can be employed.

Recently, our group has developed a passive sampler for BTEX compounds based on the use of semipermeable membrane devices (SPMD) with BTEX measurement based on head-space (HS) injections in a gas chromatographic system [8].

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*Corresponding author. Email: miguel.delaguardia@uv.es

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On the other hand, polychlorinated biphenyls (PCBs) are common persistent pollutants and polycyclic aromatic hydrocarbons (PAHs) are typical products obtained by the combustion of organic matter which can drastically affect the quality of air [9]. PAHs and PCBs have been commonly sampled in air by using several passive samplers as: polyurethane foam disks, XAD resin samplers, polymer-coated glass samplers or solid phase micro-extraction fibres [10,11]. SPMDs have also been used for the determination of PAHs and PCBs in air, and there are some published models in the literature which permit the correlation between amounts of the contaminants found in SPMDs deployed and the corresponding concentrations in the air of sampling sites [12,13].

Semipermeable membrane devices are made of a low-density polyethylene (LDPE) layflat tube, 70–90 µm wall thickness, filled with high-purity triolein and sealed [14]. Random thermal motions of the LDPE polymer chains form small cavities which allow the diffusion of small hydrophobic pollutants. Triolein is employed to fill the SPMDs because it can dissolve non-polar compounds and because of the similarities between triolein-water and octanol-water partition coefficients [15]. The aforementioned devices provide a low-cost tool to measure the quality of air.

Tangier is a city of 700,000 population, located at the western entrance of the strait of Gibraltar with a big industrial area and an open air solid waste deposit is allocated 5 km far from the city in the south east area where waste is frequently burned (see Figure 1 for details). In addition, the city suffers intense traffic and industrial activities that may harmfully affect air quality. This issue has been addressed in a recent study dedicated to the determination of spatial distribution of major identified air pollutants using passive sampling with Tenax TA inserted into Radiello diffusive tube, followed by a thermal desorption determination and cryo-concentration.

In this study a novel approach, based on the use of inexpensive SPMDs, has been employed for the evaluation of the concentration of BTEX, 12 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene and benzo(a)pyrene) and seven PCB congener indicators (28, 52, 101, 118, 153, 138 and 180). For BTEX determination, a direct treatment of SPMDs in HS-gas chromatography with mass spectrometry (GC-MS) has been used. However for PAHS and PCBs, SPMDs were previously treated in a microwave oven to do the extraction of analytes and obtained extracts were fractioned by gel permeation chromatography (GPC) using dichloromethane. The collected fractions were evaporated and reconstituted in isooctane and thus analysed by GC-MS detection. Correlation of detected contaminant amounts with their concentration in air has been done based on previously established models for concerned molecules uptake during sampling.

2. Experimental

2.1 *Apparatus and reagents*

A Finnigan (Waltham, MS, USA) Trace gas chromatograph equipped with a low bleed Zebron (Newport Beach, CA, USA) ZB-5MS capillary column (30 m × 0.32 mm, 0.25 µm) and a Finnigan Polaris Q ion trap mass spectrometer were used for BTEX, PAHs and PCBs determinations. Direct analysis of BTEX accumulated in SPMDs was performed with the use of a HS2000 HS injector from Finnigan.

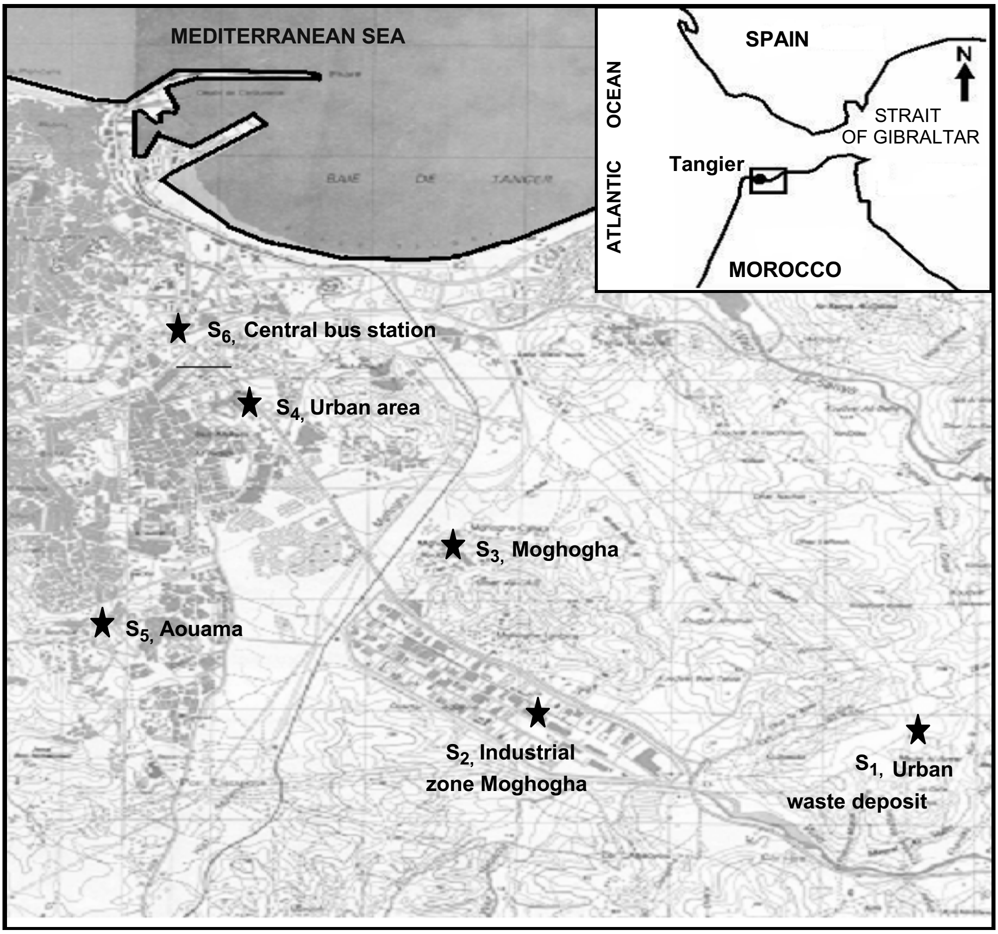

Figure 1. Localisation of sampling sites in Tangier area.

A Milestone Ethos SEL microwave laboratory systems (Sorisole, Italy) was employed for microwave-assisted extraction (MAE) of PAHs and PCBs in SPMDs.

Clean up of PAH and PCB extracts was carried out using a Hewlett–Packard HP1050 (Palo Alto, CA, USA) liquid chromatograph and two Envirogel GPC columns (19 × 150 mm and 19 × 300 mm), employing UV detection at 254 nm and dichloromethane as mobile phase.

Low-density polyethylene layflat tubing, 2.9 cm wide, was obtained from Garciplast (Barcelona, Spain). Triolein 99% was obtained from Sigma Chemicals Co. (St. Louis, MO, USA). A Rovebloc sealer (Barcelona, Spain) was employed to heat-seal the membranes.

Pure solid of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene and benzo(a)pyrene were provided by Sigma-Aldrich (Madrid, Spain) and PCB 28, 52, 101, 118, 153, 138 and 180 solutions were obtained from Dr Ehrenstorfer

(Augbsburg, Germany). Isooctane was employed as solvent in the preparation of PAHs and PCBs calibration curve, with a $50\,\mu g\,L^{-1}$ of PCB-209 employed as internal standard.

Benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, decane, acetone, hexane, dichloromethane and isooctane solvents were obtained from Scharlau (Barcelona, Spain) and Fluka (Steinheim, Germany). Decane was employed as solvent in the preparation of BTEX calibration curve, in order to avoid an excessive evaporation during the HS determination.

2.2 *SPMD preparation*

Low-density polyethylene layflat tubing was cut into segments of 11 cm and one end was heat-sealed, then 0.1 mL triolein was introduced into the membrane, squeezing to form a continuous film, and finally the other end was also heat-sealed (effective length of 10 cm).

The SPMDs were wrapped in separate aluminum foils and stored in a closed vessel at −20°C, to avoid contamination before in-field deployment.

In order to estimate the recovery of the studied compounds from SPMDs, a small number of membranes were spiked with 5 µL PCBs and PAHs standard solution or BTEX standard solution in decane. The standard solution was directly introduced inside the SPMD by using a 10 µL glass syringe and the hole was then heat-sealed. After that, spiked SPMDs were treated in the same way than the deployed ones in the area of study.

2.3 *Sampling*

As indicated in Figure 1, sampling was conducted in Tangier area at six sites (S1, urban waste deposit; S2, industrial zone of Moghogha; S3, Moghogha area; S4, urban area; S5, Aouama urban area and S6, Central bus station). These sites are situated at different distances from the Tangier city centre, industrial area and solid waste deposit.

The SPMDs were deployed 2 m above the ground in the shade in order to avoid unknown effects caused by direct sunlight or rain. Sampling was carried out during 7 days, in October 2007, with a mean ambient air temperature range from 16°C to 23°C.

After the exposure period, the SPMDs were conveniently closed and stored under refrigeration at −20°C. SPMDs were transported in hermetic tubes to avoid possible contaminations during transport and storage before and after sampling. SPMD field blanks were also measured to confirm the absence of contamination.

2.4 *GC-MS determination of PCBs and PAHs*

Exposed SPMDs were softly cleaned with a paper tissue to eliminate dust particles and then introduced in 100 mL Teflon reactors with 30 mL acetone : hexane (1 : 1 v/v) and 0.5 mL internal standard were added. Reactors were closed and irradiated with a 500 W power output, till 90°C for 10 min and this temperature was held for 10 additional minutes. After cooling, reactors were opened and a second extraction with 30 mL fresh acetone : hexane mixture was performed [16]. For each sample, both extracts were mixed and evaporated in a rotatory evaporator and finally reconstituted in 2.5 mL dichloromethane. Extract was filtered with 22 µm PTFE filter and 2 mL were injected

Table 1. Retention time (RT), detector parameters and LOD values for the analysis of BTEX, PCBs and PAHs retained in SPMDs.

Class[a]	Compound	RT (min)	Measurement ions (m/z)	LOD (ng SPMD^{-1})
BTEX	Benzene	2.2	$77+78$	1
	Toluene	3.8	$91+92$	1
	Ethylbenzene	6.7	$91+106$	0.5
	m-Xylene	7.1	$91+106$	0.5
	p-Xylene	7.2	$91+106$	0.5
	o-Xylene	8.5	$91+106$	0.5
PCB	PCB 28	11.4	$256\ (1.40)^{b} \rightarrow 186$	5
	PCB 52	12.6	$292\ (1.35)^{b} \rightarrow 220+222$	5
	PCB 101	15.6	$326\ (1.50)^{b} \rightarrow 254+256$	5
	PCB 118	17.9	$326\ (1.50)^{b} \rightarrow 254+256$	5
	PCB 153	18.7	$360\ (1.40)^{b} \rightarrow 288+290$	5
	PCB 138	19.6	$360\ (1.40)^{b} \rightarrow 288+290$	5
	PCB 180	22.1	$394\ (1.40)^{b} \rightarrow 322+324$	5
PAH	Naphthalene (Nap)	7.5	128	15
	Acenaphthylene (Acy)	14.6	152	15
	Acenaphthene (Ace)	14.8	$153+154$	15
	Fluorene (Flo)	17.6	$165+166$	15
	Phenanthrene (Phe)	22.3	178	15
	Anthracene (Ant)	22.4	178	15
	Fluoranthene (Flu)	27.3	202	15
	Pyrene (Pyr)	28.1	$201+202$	15
	Benzo(a)anthracene (BaA)	34.0	228	15
	Chrysene (Chr)	34.0	228	15
	Benzo(k)fluoranthene (BkF)	38.6	252	15
	Benzo(a)pyrene (BaP)	39.7	252	15

Notes: [a]Each class of pollutant was measured under different chromatographic conditions.
[b]Precursor ion and excitation energy for PCBs tandem mass analysis.

in the GPC system, with a flow rate of 5 mL min^{-1} dichloromethane, and the fraction from 15 to 19 min was collected. The clean extract was evaporated in a rotary evaporator and finally dissolved in 0.5 mL isooctane.

A volume of 1 µL of extract was injected in the GC-MS in splitless mode at 300°C, employing Helium as carrier with a constant flow of 1 mL min^{-1}. Oven temperature program for PAHs was 80°C held for 1 min, increased at a rate of 5°C min^{-1} up to 280°C and finally held for 5 min. Oven temperature programme for PCBs was 110°C held for 1 min, increased at a rate of 15°C min^{-1} up to 150°C and at a second rate of 5°C min^{-1} up to 280°C, and finally held for 5 min. The transfer line and source temperature were 280°C and 250°C, respectively. Detector parameters employed for full scan acquisition of PAHs [17] and tandem mass acquisition of PCBs [18] are shown in Table 1. Calibration curves were prepared in isooctane from 50 to 1000 µg L^{-1} for PAHs and from 1 to 200 µg L^{-1} for PCBs.

2.5 *HS-GC-MS determination of BTEX*

Semipermeable membrane devices were rolled, placed inside 10 mL HS vials and capped hermetically. BTEX HS vapourisation was carried out at 150°C for 20 min.

Syringe temperature was also set at 150°C. A volume of 2 mL HS fraction was injected in the GC-MS in split mode (1 : 10) at 200°C, employing Helium as carrier gas in constant flow mode at 1 mL min^{-1}. The oven temperature programme was 40°C, held for 10 min, increased at a rate of 20°C min^{-1} up to 200°C, and finally held for 2 min. The transfer line and source temperatures were 300°C and 250°C, respectively. A mass scanning range from 75 to 110 *m*/*z* was used for full scan acquisitions. Detector parameters employed for full scan acquisitions of BTEX are shown in Table 1 [1].

Calibration curves were prepared with SPMD spiked with 5 µL of the corresponding BTEX standard. A calibration curve set from 10 to 10,000 ng SPMD^{-1} was used to evaluate the BTEX concentration in unknown samples.

3. Results and discussion

3.1 *Experimental conditions and analytical parameters*

The reference procedure for the extraction of pollutants from SPMDs consists of a dialysis with large volumes of organic solvents (100–900 mL), during long times (6–48 h) [14]. However, based on our group experience, an alternative method, based on MAE has been proposed for the extraction of PAH and PCB compounds from SPMDs [16], with a considerable reduction of analysis time (9 min), organic solvent consumption (100 mL) and waste generation, being a rapid and more environmentally friendly methodology than classical dialysis. Polyethylene oligomers and triolein impurities, also extracted by MAE procedure, can be easily removed from the extract by the use of GPC, that separates PAH and PCBs molecules from the coextracted matrix materials.

Figure 2 shows the chromatograms obtained, at the end of the aforementioned process, for sample S1, a SPMD blank and a standard containing 750 µg L^{-1} of each one of the assayed PAHs. As it can be seen, wide peaks were obtained for benzo(a)anthracene, chrysene, benzo(k)fluoranthene and benzo(a)pyrene which indicate a bad performance state of the employed column, probably due to its intensive use.

Recently, a rapid and fully-automated procedure was developed for the direct determination of BTEX compounds from SPMDs by using a HS injector [8]. This methodology, free from any kind of sample pre-treatment, avoids completely the use of solvents and reduces possible contaminations during the analytical procedure.

As an example of the quality of data available from the aforementioned methodology, Figure 3 shows the chromatograms obtained for a blank, a standard of 50 ng BTEX SPMD^{-1} and for sample S1.

Both methodologies, MAE and HS, have been commonly used by our group during past years, with excellent results. So, the employed methodology is completely useful and analytical parameters such as: pollutant recoveries, limit of detection (LOD), repeatability, reproducibility or linear range are regularly checked.

3.2 *Amounts of pollutants found in SPMDs*

Two SPMDs were deployed in each sampling site to be analysed by both procedures, HS-GC-MS for BTEX determinations and GC-MS after MAE for the determination of PCBs and PAHs. Table 2 shows the amounts of studied pollutants found in each SPMD. PCB compounds evaluated in this study were below LOD.

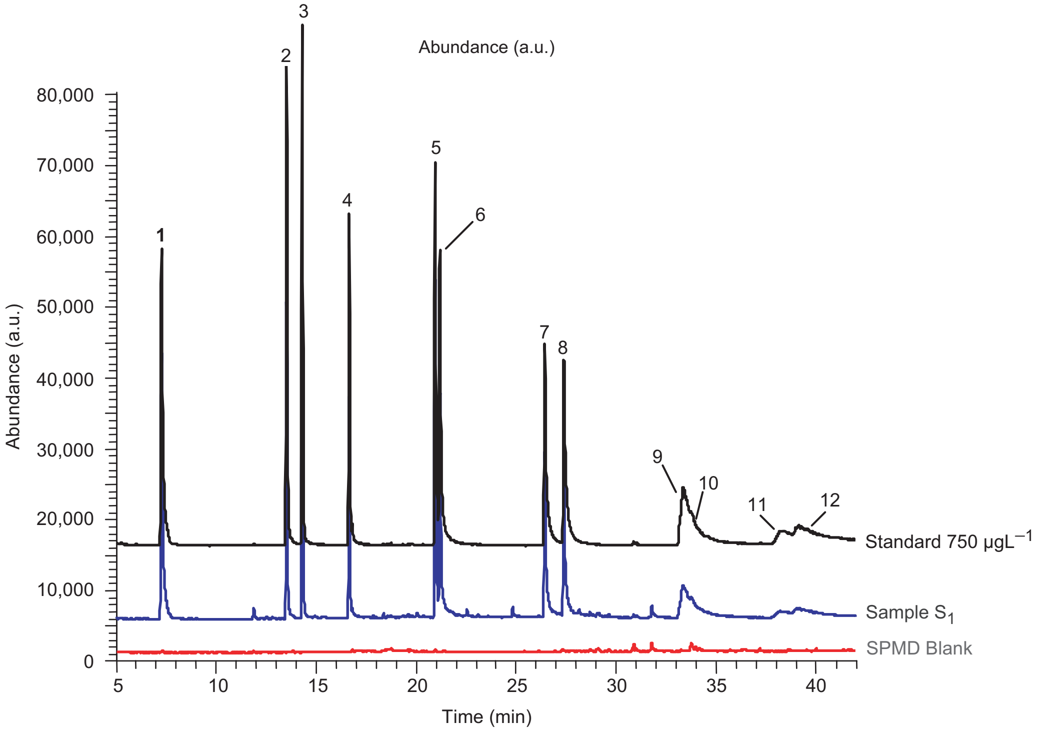

Figure 2. GC-MS chromatograms of sample S1, 750 µg L^{-1} PAHs standard and SPMD blank. Note: Naphthalene (1), Acenaphthylene (2), Acenaphthene (3), Fluorene (4), Phenanthrene (5), Anthracene (6), Fluoranthene (7), Pyrene (8), Benzo(a)anthracene (9), Chrysene (10), Benzo(k)fluoranthene (11), Benzo(a)pyrene (12).

Regarding PAHs, it can be seen that sample S1 (urban waste deposit) and S2 (Moghogha industrial area) were deployed in the most contaminated sites, with PAH amounts found higher than 400 ng for several compounds. On the other hand, sampling sites S5 and S6 were less contaminated, with only four and six PAHs, respectively, at concentrations higher than LOD values and amounts found ranging from 14 to 241 ng.

In the case of BTEX contamination, samples S1 and S2 were also deployed in the most contaminated sites with amounts absorbed by SPMDs from 10 to 67 ng and samples S5 and S6 evidenced the lowest contamination levels, free from benzene and with the lowest values of toluene and ethylbenzene.

3.3 *Correlation of the measured amounts of pollutants with their concentration in air*

The uptake of pollutants from air during sampling with SPMDs is initially linear over time, then moves into a curvilinear stage, and finally can approach equilibrium, as it has been evidenced by previous studies [19].

The equilibrium time for BTEX and the more volatile PAHs is so fast (<1 day), while for the rest of compounds equilibrium can be reached after several weeks [8,13]. In the present work, SPMDs were deployed for 7 days. So, an equilibrium model will

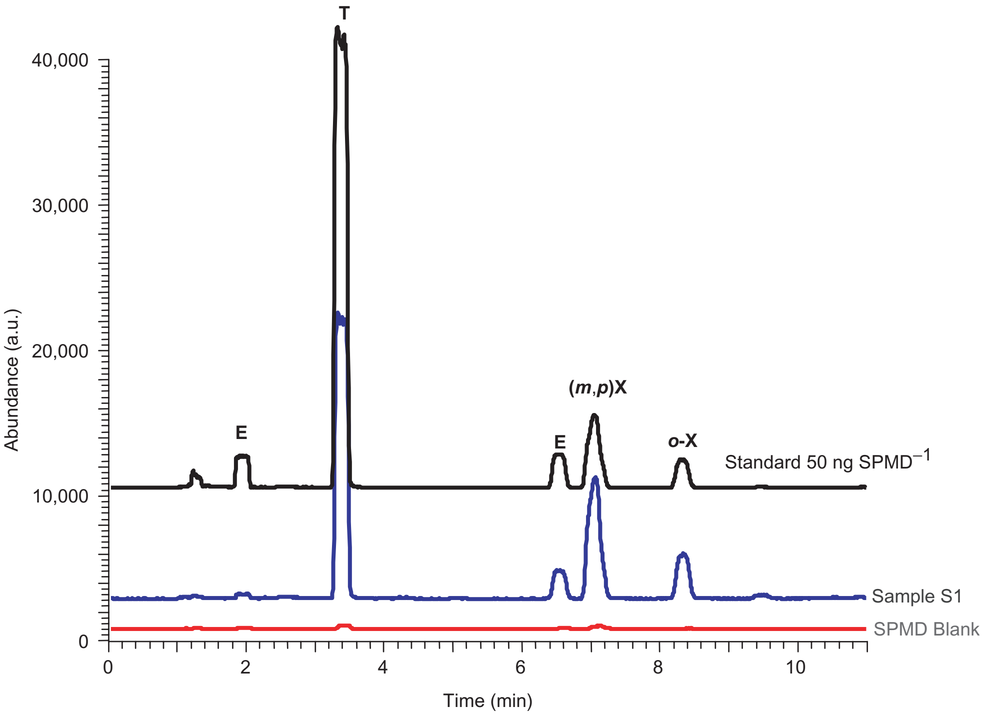

Figure 3. HS-GC-MS chromatogram of sample S1, SPMD standard spiked with 50 ng BTEX and SPMD blank.

Table 2. Amounts of pollutants determined in SPMDs deployed in six sampling sites in Tangier.

	Amount of pollutants (ng SPMD^{-1})					
Compound	S1	S2	S3	S4	S5	S6
Benzene	17	10	6	3	–[a]	–[a]
Toluene	49	40	25	16	13	11
Ethylbenzene	53	25	17	15	12	13
(*m*,*p*)-Xylene	67	65	43	29	26	37
o-Xylene	55	54	19	15	19	37
Nap	651	619	280	173	241	92
Acy	492	164	38	31	–[a]	–[a]
Ace	486	124	91	54	28	15
Flo	55	305	178	112	67	15
Phe	559	528	345	164	201	35
Ant	446	244	127	137	–[a]	–[a]
Flu	420	388	262	251	–[a]	16
Pyr	354	237	118	205	–[a]	28
BaA + Chr	238	212	68	118	–[a]	–[a]
BkF	43	–[a]	–[a]	–[a]	–[a]	–[a]
BaP	55	–[a]	–[a]	–[a]	–[a]	–[a]

Note: [a]Less than the LOD (see Table 1 for details).

Table 3. Calibration parameters employed for BTEX (equilibrium model) [8] and PAHs (lineal model) [13] to relate the amount of contaminants retained in the SPMDs and their time-weighted average concentration in air.

Compound	K_{SA} (m^3)	Compound	$R_{S,1m\ SPMD}$ ($m^3\ d^{-1}$)
Benzene	0.20×10^{-3}	Nap	–[a]
Toluene	0.55×10^{-3}	Acy	–[a]
Ethylbenzene	1.05×10^{-3}	Ace	–[a]
m-Xylene	1.21×10^{-3}	Flo	1.8
p-Xylene	1.21×10^{-3}	Phe	4.4
o-Xylene	1.35×10^{-3}	Ant	4.1
		Flu	4.5
		Pyr	2.0
		BaA	4.1
		Chr	6.1
		BkF	2.1
		BaP	0.6

Note: [a] R_s values were not found in the literature for these compounds.

be performed for sampling of BTEX compounds that have reached the equilibrium and a lineal model for the sampling of PAHs that are still in a lineal uptake. PCB amounts found were lower than LOD values and no correlation to concentration in air could be done.

Sampling rate values for PAHs were obtained from Bartkow *et al.* [13], and SPMD-air distribution factors for BTEX were obtained from our previous study [8]. Table 3 shows the corresponding parameters of these calibration models. In this study we have employed 10 cm devices, 10 times shorter than standard SPMDs. So, the R_S values employed to calculate PAH concentration in air are 10 times lower than those used in the 1 m long SPMDs.

Correlation between the pollutant amount found in SPMDs and the time-weighted average concentration of pollutant in air is shown in Equation (1) for an equilibrium model for BTEX uptake and in Equation (2) a lineal model for PAHs uptake is shown.

$$C_{AIR} = N_{SPMD}/K_{SA} \tag{1}$$

$$C_{AIR} = N_{SPMD}/R_S t \tag{2}$$

where C_{AIR} ($ng\,m^{-3}$) is the concentration of BTEX or PAH in vapour phase in the air; N_{SPMD} (ng) is the BTEX or PAH amount retained in the SPMD; K_{SA} (m^3) is the SPMD-air distribution factor for 10 cm SPMDs; R_S ($m^3\,day^{-1}$) is the sampling rate in non-equilibrium conditions for 10 cm SPMDs and t (days) is the exposure time.

Table 4 shows the air concentration of BTEX and PAH compounds in the selected sampling sites. These values were calculated by using sampling data from Table 2, calibration parameters from Table 3, and Equations (1) and (2).

World Health Organisation [20] established that there is no safe limit for benzene, but the mean ambient air concentrations of benzene and toluene in urban areas are

Table 4. Air concentration of pollutants determined in six sampling sites in Tangier.

	Air concentration[a] ($\mu g\,m^{-3}$)						
BTEX	LOD	S1	S2	S3	S4	S5	S6
Benzene	2.0	87.5	52.0	31.1	17.4	–[b]	–[b]
Toluene	1.0	90.4	73.8	45.1	29.1	23.4	20.2
Ethylbenzene	0.5	50.6	23.5	15.9	14.6	11.1	12.4
($m+p$)-Xylene	0.4	55.1	53.8	35.6	24.2	21.8	30.9
o-Xylene	0.4	40.8	39.7	13.9	10.7	14.0	27.2
PAHs	Air concentration[a] ($ng\,m^{-3}$)						
Flo	1.2	40.1	24.3	14.2	8.9	5.3	1.2
Phe	0.5	18.2	17.2	11.2	5.4	6.5	1.2
Ant	0.5	15.6	8.5	4.5	4.8	–[b]	–[b]
Flu	0.5	13.3	12.3	8.3	8.0	–[b]	0.5
Pyr	1.1	25.3	17.0	8.5	14.7	–[b]	2.0
BaA + Chr	0.5	6.7	6.0	1.9	3.3	–[b]	–[b]
BkF	0.4	2.9	–[b]	–[b]	–[b]	–[b]	–[b]
BaP	1.2	13.2	–[b]	–[b]	–[b]	–[b]	–[b]

Notes: [a]To obtain the reported data, values shown in Table 2 and parameters indicated in Table 3 were used.
[b]Less than the limit of detection.

about 5–20 and 5–150 $\mu g\,m^{-3}$, respectively. The European Union Directive 2000/69/EC recommends and annual mean concentration of 5 $\mu g\,m^{-3}$ benzene [21].

We can conclude that BTEX contamination of the industrial area (S1, S2 and S3) does not affect to the air quality of the city of Tangier, with benzene concentrations lower than 20 $\mu g\,m^{-3}$ and for toluene lower than 30 $\mu g\,m^{-3}$, probably due to the dispersion effect of the characteristic intensive wind in the strait of Gibraltar.

There are no European air quality guidelines for PCBs and PAHs, because direct inhalation exposures constitute a small proportion of the total exposure, if we compare with daily intake of food [21]. However, the annual mean concentration of BaP, used as an indicator of PAH emissions from combustion processes, in European urban areas is in the range 1–10 $ng\,m^{-3}$, being less than 1 $ng\,m^{-3}$ in rural areas [20]. Hence, as shown in Table 4, the PAHs contamination in the sampling site S1 slightly exceeds the mean concentrations indicated by the WHO, with a concentration of 13.2 $ng\,m^{-3}$ BaP in air. However, in the rest of sampling sites, the BaP concentration was less than the LOD, in all the cases. So, it can be concluded that the amount of BaP found in the sampling of the urban waste deposit do not contribute significantly to the global contamination of Tangier's air by PAHs.

4. Conclusion

The use of SPMD passive samplers has been useful for the evaluation of the contamination of air in the urban and industrial areas in Tangier (Morocco). It has been confirmed that the information obtained by using SPMD samplers can provide a good estimation of BTEX and PAH compounds in air.

We can conclude from the results obtained in this study that the industrial area close to Tangier does not significantly contribute to the contamination of urban air, with concentration levels of BTEX and PAH indicators similar to the mean ambient air concentrations in Europe shown by WHO.

Results obtained agree completely with those obtained in June 2007 in the same area by using Radiello diffusive samplers. In the previous study, it was also concluded that near to the industrial area the contamination levels are rather high (with total concentrations of BTEX, expressed in carbon equivalents, of $152.1\,\mu g\,m^{-3}$ in sampling site 1 and $101.7\,\mu g\,m^{-3}$ in site 2), but due to the east wind the contamination is reduced when pollutants reach the Tangier city by dilution (till a level of $39.4\,\mu g\,m^{-3}$ carbon equivalents in site 5). Therefore, it finally confirms that SPMDs can be employed for the sampling of pollutants in air, with results analogous than other sampling devices, with a considerable reduction of the costs.

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