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Application of Passive Sampling Technique for Monitoring of BTEX Concentration in Urban Air: Field Comparison of Different Types of Passive Samplers

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Abstract

Urban air background concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) were measured in 2007 in the Tricity area (Gdansk, Gdynia, and Sopot) and Tczew applying two types of passive samplers: Home-made permeation passive samplers and two diffusive passive samplers Orsa 5 (National Dräger) and Radiello (FS Maugeri). Differences between the time-weighted annual averages concentrations of BTEX obtained with two types of passive samplers were found in each of the sampling sites. The obtained results indicate that the BTEX concentrations measured in the urban air in the Tricity area and Tczew are slightly dependent on season; they are higher in winter and spring than in summer. However, the average values for benzene concentrations in the ambient air were low enough to satisfy the requirements of the European Directive 2000/69EC of the European Parliament, which stipulates a limit of 5 μg/m^3. The study brought useful data regarding the BTEX air concentrations in the investigated region. Good capability of passive samplers to show fluctuations in BTEX concentrations in atmospheric air was confirmed, which makes them applicable for air monitoring on the local scale.

Introduction

Volatile organic compounds (VOCs) have a significant effect on air quality. They are emitted into the atmosphere from controlled as well as from non-controlled sources. Due to high volatility and high vapor pressure, they are predominant in the atmosphere. They can be transported to areas far away from emission sources and increase risk to human health. The common occurrence and properties make this a risk to populations that are exposed to VOCs (1,2). The most abundant pollutants among the VOCs emitted into the atmosphere are monoaromatic hydrocarbons: benzene, toluene, ethylbenzene, and xylenes (BTEX) (3), which are also markers for human exposure to VOCs (4,5). Exposure of the population to benzene and other VOCs has been the subject of much interest in the scientific community due to the toxicity of these compounds (6).

Measurements of VOCs in the air are required to determine the sources and mechanisms of atmospheric pollution and pollutant transport, to study their health effects, and to monitor regulatory compliance. The knowledge of BTEX concentration in atmospheric air allows the assessment of present and future conditions of the atmosphere and can help explain changes in the environment due to human activity.

Tricity is one of the most urbanized and industrialized regions in the northern part of Poland and consists of three cities: Gdansk, Gdynia, and Sopot. The quality of the atmospheric air in the Tricity area is affected by emissions from the industry, including the Gdansk Oil Refinery, Phosphorus Fertilizer Manufacturing Plant, sulphur-processing plants, Heat and Power Generating Station and the large Port of Gdansk, Port of Gdynia, and the Northern Port (trans-shipment terminals). The significant increase in the number of petrol stations in Tricity area and increased traffic in the Tricity agglomeration could undoubtedly have negative effects on atmospheric air quality. The number of automotive vehicles registered in Pomeranian Province in 2000–2006 increased by 28%. Taking all this into account, it can be stated that within a few years the air quality in the Tricity area can deteriorate. In our research, we have made an attempt to supplement the information on air quality in Tricity area by constant measuring of BTEX concentrations. It can help localize the areas where the air quality is deteriorating; this could be a signal to take action in reducing pollutant emissions to the atmosphere. The obtained BTEX concentrations will be used to check compliance with the air quality directives (7). The data would be basic factors in identifying emission sources of BTEX in Tricity agglomeration.

Conventional methods employed in monitoring atmospheric air are based on the use of sorption tubes or evacuated canisters. They require relatively skilled personnel and/or a significant upfront investment in the equipment. As a result, large-scale atmospheric air quality monitoring is usually prohibitively expensive. Thus, passive sampling has been becoming an increasingly pop-

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ular technique for the assessment of air quality. Passive sampling provides a simple and cost-effective method of collecting a large number of samples and involves the measurement of the concentration of any analyte as a weighted average over the sampling time. The concentration of the analyte is integrated over the whole exposure time, making such a method immune to accidental or extreme variations of the pollutants concentrations. Information obtained in this way is suitable for creating a long-term overview on pollutants concentration levels (8,9).

Due to the diversity of passive samplers available on the market, an attempt has been made to assess the applicability of these samplers at different sampling rates of analytes based on different phenomena (diffusion and permeation) of mass transport for continuous urban air quality control.

Experimental

Materials and method

Passive samplers

For isolation and enrichment of the analytes from atmospheric air, two types of passive samplers (permeation and diffusion type) were used: a home-made (H-M), badge-type permeation passive sampler equipped with a silicone membrane of 50-µm thickness (SSP-M100, Speciality Silicone Products, Ballston Spa, NY). Active carbon was used as a sorbent in the samplers (40–60 mesh, Gryfskand, Poland). The design of the samplers, developed at the Gdansk University of Technology (Poland), was described in detail elsewhere (10). Diffusion samplers used were: an Orsa 5, a tube type diffusive passive sampler with a short and axial diffusion path and a protective membrane made of cellulose acetate with which shell charcoal was used as a sorption medium (11); and a Radiello, a radial diffusive passive sampler, designed and developed by the Fondazione Salvatore Maugieri (Padova, Italy). This sampling system is made up of a cylindrical adsorbing cartridge housed coaxially inside a cylindrical diffusive body of polycarbonate and microporous polyethylene. It combines different characteristics common to both types: the diffusive surface is the cylinder itself, the sampling area is large, and the diffusion length is short. Diffusion is radial, and the analyte passes across a microporous cylinder before reaching an inner stainless steel net cylinder containing 300 mg of Carbograph 4 as an adsorbent (thermally desorbable adsorbent). Due to the high sampling rate, care must be taken not to saturate the sorbent with the component of interest (12). Radiello diffusive samplers filled with a thermally desorbable adsorbent have been evaluated for the monitoring of BTEX according to the European standard EN 13528-2 as a reference passive sampler (13).

Sampling

Characteristics of sampling sites and sampling periods

To evaluate the atmospheric average urban background BTEX concentration in the Tricity area, twelve one-month passive sampling campaigns were conducted (in the case of Orsa 5 passive sampler and home-made permeative passive sampler). To avoid saturation of the sorbent, Radiello passive sampler's exposure time was shortened to two weeks; and consequently, twenty-four exposures were conducted.

Sampling period was from January to December 2007. This period was chosen because it represents varying seasonal climatic conditions. The atmospheric air was sampled at 10 measurement stations located in the metropolitan area of the Tricity. Figure 1 presents a map of the Tricity and its surrounding area with monitoring stations indicated.

During each of the monitoring campaigns, two samplers of each type were placed at each measurement station 20 cm from one another. The samplers were placed 3 m above ground level in specially designed shelter made of stainless steel to protect them from the changing atmospheric conditions (precipitation and wind). Moreover, during each measurement series, also one non-working sampler was individually placed at each station in order to provide a blank value for each type of sampler. The atmospheric conditions in the Tricity in 2007 are presented in Table I.

After each sampling campaign, the passive samplers were closed and separated from the atmosphere in a way appropriate for a given type of a sampler. The Orsa 5 samplers were sealed by putting them into a glass container (each sampler separately). In the case of Radiello passive samplers, the sorption medium was removed from the cylindrical diffusive body and put in a glass tube tightly sealed with a polyethylene stopper. The home-made

Table I. Meteorological Conditions in Tricity Area in 2007

	Average meteorological conditions				
Sampling period	Duration	Temp. (°C)	Relative humidity (%)	Wind speed (m/s)	Atmospheric pressure (h Pa)
1	January	4.0	82.9	3.9	1000
2	February	–0.4	82.9	2.8	1006
3	March	6.3	78.1	2.7	1009
4	April	8.3	63.0	2.6	1014
5	Mai	11.9	71.3	2.1	1011
6	June	18.5	75.4	1.8	1005
7	July	17.1	78.5	2.3	1002
8	August	18.5	77.5	2.1	1005
9	September	15.8	79.4	2.1	1008
10	October	12.2	79.8	2.0	1012
11	November	7.4	82.3	2.0	1015
12	December	2.9	87.9	2.6	1001

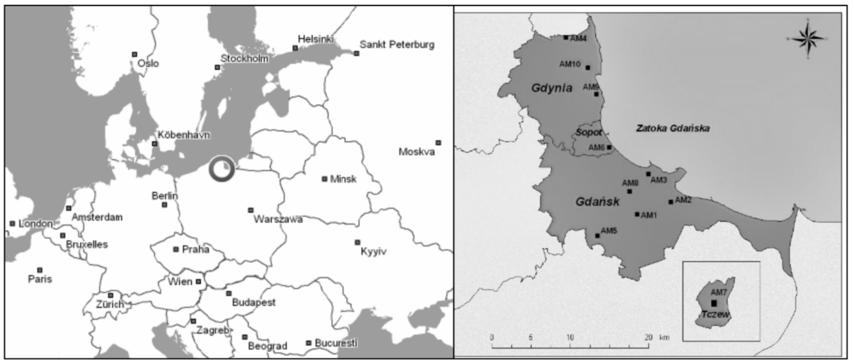

Figure 1. Map of the sampling sites.

permeation passive samplers were sealed with a polyethylene lid to protect them from contamination and to avoid any desorption. All samplers were then brought to the laboratory and stored in a freezer until analysis. The samplers were analyzed within a week since sampling.

Samples analysis

Solvent extraction of analytes from carbon bed and chromatographic conditions

In the case of Orsa 5 passive samplers and home-made permeation passive samplers, all experiments were performed using an HP 5890 gas chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with an FID detector (280°C) and a splitless injector (the inlet temperature 200°C, injection volume 2 µL). The chromatographic column was J&W DB1 (30 m × 0.32 mm; 5 µm), and the carrier gas was helium at 2.2 mL/min. Oven temperature program was: hold for 1 min at 40°C, ramp to 120°C at 15°C/min, ramp to 220°C at 10°C/min, and hold 5 min. Before the analysis, samplers were taken from the freezer, and the adsorbent from each was transferred into Teflon-capped 1.8-mL glass vials. The analytes were liberated from the sorbent bed by extraction with 1 mL CS_2. To confirm identity of BTEX compounds, randomly selected CS_2 extracts were analyzed by means of gas chromatography–mass selective detector (GC–MSD).

Determination of recovery from active carbon

Analyte recovery was determined for each component of interest. Ten 300-mg samples of active carbon placed in 1.8-mL Teflon-capped vials were spiked with known amounts of the analytes. After 24 h, the samples were extracted with CS_2 and analyzed by gas chromatography with flame ionization detection (GC–FID). The recovery coefficients obtained were taken into account in all determinations of the mass of the analyte trapped on the active carbon. Recoveries were as follows: benzene 96% ± 3, toluene 96% ± 3, ethylbenzene 97% ± 3, *p,m*-xylene 97% ± 3, and *o*-xylene 97% ± 3.

Thermal desorption

For the Radiello diffusive samplers, the analytes were liberated from the sorbent bed using a two-step thermal desorption. All experiments were performed using a Agilent Technologies 6890 GC coupled with 5873 network inert mass spectrometer (MS) and with thermal desorber (Unity Markes International, Limited Version 2.00, South Queensferry, UK).

The sorption medium of the Radiello passive sampler was removed from the sealed glass tube and placed into stainless-steel tubes (89 mm × 6.4 mm o.d.), which were then loaded into a Unity thermal desorber. In the first step, the tube with sorbent was heated to 300°C and kept at this temperature for 20 min while pure helium gas at 45 mL/min was passed through the tube to desorb analytes and focused them in a cold trap kept at –10°C. The cold trap was packed with Tenax TA (37 mg) and Carbotrap (27 mg). In the second step (cold trap desorption), the helium flow was inverted, and the trap was heated to 300°C. The analytes were quickly desorbed from the trap and transferred into the chromatographic column. The chromatographic column was HP1 MS (30 m × 0.25 mm; 1 µm), and the carrier gas was helium at 1 mL/min. A split flow of 10 mL/min was applied in this step. Oven temperature program was: 50°C, ramp to 280°C at 7°C/min, and hold 5 min. Ionization mode of the MS was electron impact (EI). The ion source, quadruple, and GC–MSD interface temperatures were 230°C, 150°C, and 300°C, respectively. The MSD was run in full-scan and selected ion monitoring modes. Compounds were identified based on their retention times, and target and qualifier ions: benzene, 78, 77, 51; toluene, 91, 92, 65; ethylbenzene, 106, 91, 65; and xylenes, 106, 91, 79.

The results of gas chromatographic determination (GC–FID and TD-GC–MS) were corrected for the blank values. All the reagents and materials being in contact with the sample, and the standards were randomly tested for contamination.

Table II. The Equations Used To Calculate TWA Concentrations of Particular BTEX in Atmospheric Air

Radiello diffusive passive sampler

$$C = \frac{M}{Q_k \times t} \times 10^6$$

C	concentration of analyte (μg/m^3)
M	mass of analyte (μg) determined by GC
Q_k	uptake rate (mL/min)
t	sampling time (min)

Orsa 5 diffusive passive sampler

$$C = \frac{K_{ORSA} \times M}{D_A \times D_i \times t} \times 10^3$$

C	concentration of analyte (μg/m^3)
K_{Orsa}	device constant of sampler (cm^{-1})
M	mass of analyte (ng) determined by GC
D_A	desorption efficiency of the analyte
D_i	diffusion coefficient specific for the analyte (cm^2/s)
t	sampling time (s)

Home-made permeation passive sampler

$$C = \frac{K \times M}{t} \times 10^6$$

C	concentration of analyte (μg/m3)
k	calibration constants of the samplers (min/cm^3)
M	mass of analyte (mg) determined by GC
t	sampling time (min)

Table III. Correlation Coefficients (R^2) Between the Average BTEX Concentrations Recorded on Different Season

	Spring			Summer			Fall			Winter		
	R*	O†	H-M‡	R	O	H-M	R	O	H-M	R	O	H-M
B/T	0.240	0.498	0.361	0.385	0.319	0.329	0.337	0.183	0.134	0.376	0.177	0.134
B/E	0.131	0.406	0.389	0.334	0.461	0.522	0.088	0.0869	0.166	0.146	0.267	0.137
T/E	0.349	0.707	0.278	0.324	0.530	0.515	0.493	0.360	0.192	0.373	0.476	0.230
T/m.p-X	0.531	0.550	0.280	0.297	0.308	0.418	0.514	0.101	0.0929	0.419	0.397	0.375

* Radiello passive sampler. † Orsa 5 passive sampler. ‡ Home-made permeation passive sampler.

Chemical standards

External calibration was carried out with a volatile calibration mix (VCM) containing 13 VOCs (including BTEX) at 2000 µg/mL^3 (Supelco). Six standard solutions were prepared by dilution of calibration mix in methanol for gas chromatography (Merck). For solvent extraction, concentration of standard solutions ranged between 1.0–25.0 µg/mL^3, and in the case of thermal desorption ranged between 50.0–2000 µg/mL^3. Calibration solutions were freshly prepared at the moment of calibration.

Calibration of TD-GC–MS system

Blank Radiello sorbent tubes were spiked with 1 µL of the calibration standards. Pure helium at a flow rate of 50 mL/min was passed through the tube for 5 min to purge the solvent from the tube and, immediately the analytical process was run to calibrate the analytical system (TD-GC–MS).

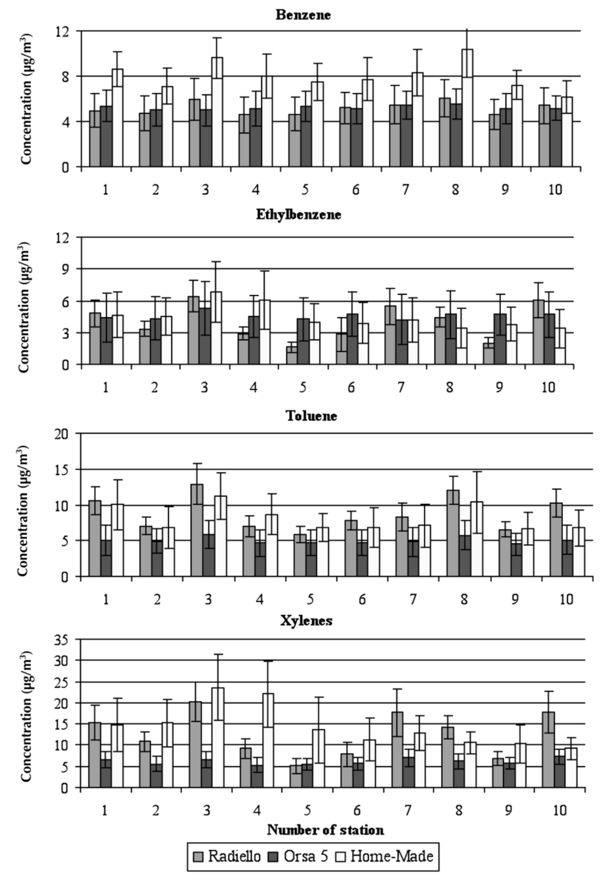

Figure 2. The time-weighted annual average concentration of BTEX at various sampling sites in the metropolitan area of Tricity area and Tczew.

BTEX concentration calculation

Application of passive samplers under real conditions to monitor and assess air quality requires the knowledge of parameters responsible for uptake rate of analytes. They are sampling rate (SR) for diffusion type samplers and calibration constants (*k*) for permeative samplers. When they are known, time-weighted average concentrations can be determined by measuring the amount of an analyte trapped in a specified exposure time. For diffusive passive samplers (Radiello and Orsa 5), the BTEX sampling rates (SR) are specified by manufacturers. However, only in the case of Radiello passive samplers, the uptake rate values (SR) supplied by the manufacturers were determined at 25ºC and 1013 hPa in a controlled atmosphere; so, they was recalculated to the actual mean sampling temperature (Table I).

For permeative passive samplers equipped with PDMS semipermeable membrane, calibration constants (k) of the compounds were determined experimentally by exposure of the samplers in standard gas mixtures (10,14). TWA concentrations of particular BTEX were calculated using the equations presented in Table II.

Quality control and quality assurance

The uncertainty of determination of the analyte concentration by passive sampling technique is affected mainly by the sampling rate uncertainty. However, environmental parameters, such as temperature, humidity and air velocity, might also play a significant role (8). Uncertainty affects method's limit of detection (MDL), which is a function of the sampling rate (SR) or calibration constant (k), the sampling time, blank values of unexposed samplers, the reproducibility, the sensitivity and selectivity of the applied detector, and the selectivity of the column used for GC analysis.

The quality assurance and quality control (QA/QC) procedures included the analysis of field blanks, parallel samples, and triplicate measurements of CS_2 extracts. Precision estimated from replicate analyses of the standards and samples was within ± 10%. For field blanks, unexposed passive samplers were analyzed for the BTEX under conditions identical to those used in the analysis of samplers exposed to atmospheric air.

The method limit of detection (MDL) was calculated based on equations presented in Table II (for each analyte and each type of passive samplers), where m is the mass of the analyte collected on the sorbent bed, and the average mass obtained from the unexposed samplers (blanks) was used.

The MDL for benzene for Orsa 5 and permeative passive samplers for one-month exposure was 0.6 µg/m^3 and for remaining monitored compounds were 0.3 µg/m^3. Consequently, method quantification limit (MQL) for benzene for Orsa 5 and home-made permeative passive samplers was 1.7 µg/m^3 and for remaining monitored compounds were 1.0 µg/m^3. In general, BTEX concentrations for Orsa 5 and home-made permeative passive samplers were substantially higher in the samples than in the field blanks.

Table IV. The Obtained Values of Mean Ratios Between the Selected Compounds*

Comp.	Average			Max			Min		
ratio	R† (SD)	O‡ (SD)	H-M§ (SD)	R	O	H-M	R	O	H-M
ΣX/T	1.38 (0.61)	1.56 (0.80)	2.6 (2.3)	2.43	3.19	3.57	0.83	1.39	1.92
B/T	0.66 (0.36)	1.5 (1.2)	2.0 (2.7)	0.83	2.03	3.10	0.49	1.27	1.28
E/T	0.44 (0.22)	0.91 (0.34)	0.75 (0.63)	0.81	1.10	1.07	0.29	0.85	0.70
B/ΣX	0.60 (0.50)	0.95 (0.46)	0.91 (0.81)	1.22	1.45	2.29	0.31	0.63	0.45
E/ΣX	0.32 (0.10)	0.69 (0.35)	0.34 (0.24)	0.37	1.01	0.56	0.30	0.32	0.27

*The standard deviation SD of the average values is given in brackets.
†Radiello passive sampler.
‡Orsa 5 passive sampler.
§Home-Made permeation passive sampler.

Results and Discussion

BTEX concentrations in urban air

In analytical processes, a significant role is played by a sampling step. In atmospheric air quality assessment, the selection of sampling sites will decide if the sample is representative and if it reflects the real state of the air monitored. So as to get reliable information on the assessment of atmospheric air pollution with BTEX in the Tricity area, the measuring sites should be representative of the real state of the environment. Atmospheric air was sampled at 10 monitoring stations run by the Agency of Regional Air Quality Monitoring Foundation (ARMAAG), located in the metropolitan areas of the Tricity and Tczew. Network of ARMAAG measuring stations was established on the basis of many years' studies including meteorological conditions, population density, and database of pollutants emissions from point and area sources. In sampling site selection, special care was also taken to avoid any direct effect of stationary sources of pollutants (lack of point and linear sources of emission in the direct vicinity of the sampling sites). Selected monitoring sites are classified as background sites where the sampled air is well-mixed.

According to European legislation, the reference period for measuring benzene concentration in urban air is one year (7). Therefore, in assessment of air quality in the Tricity area with respect to BTEX concentration, annual average concentrations were determined for each type of dosimeter separately and compared with EU and Polish permissible levels. The obtained results for 10 individual measurement stations and for each type of passive sampler used are presented on Figure 2. The time-weighted annual average concentrations of BTEX were taken as the averages of the average monthly values obtained in measuring campaigns for each station, separately. Because each station was equipped with two passive samplers of each type, the mean annual value for Orsa 5 and home-made permeative passive samplers resulted from averaging 24 values, and for Radiello passive samplers the mean annual value resulted from averaging 48 values. The obtained results indicate that there were no significant differences in annual benzene concentrations between the stations. The time-weighted annual average concentration of benzene determined applying the Radiello and Orsa 5 passive samplers was in both cases 5.2 ± 1.3 µg/m^3 and only slightly exceeded the permissible level of 5 µg/m^3. For the home-made permeation passive sampler, the benzene concentration was 7.2 ± 1.6 µg/m^3 and was about 40% higher than the permissible value but still within the tolerance range recommended by EU regulations (7).

Much higher fluctuations in the concentration were observed for the remaining compounds from the BTEX group. The lowest concentrations of all the examined compounds were observed at measurement station 5 located in an open area far away from busy roads and local emission sources, and the highest values were located at measurement station 3. Elevated concentrations of BTEX at station 3 could be related to the location of this site in the vicinity of major roads and streets. The high concentration

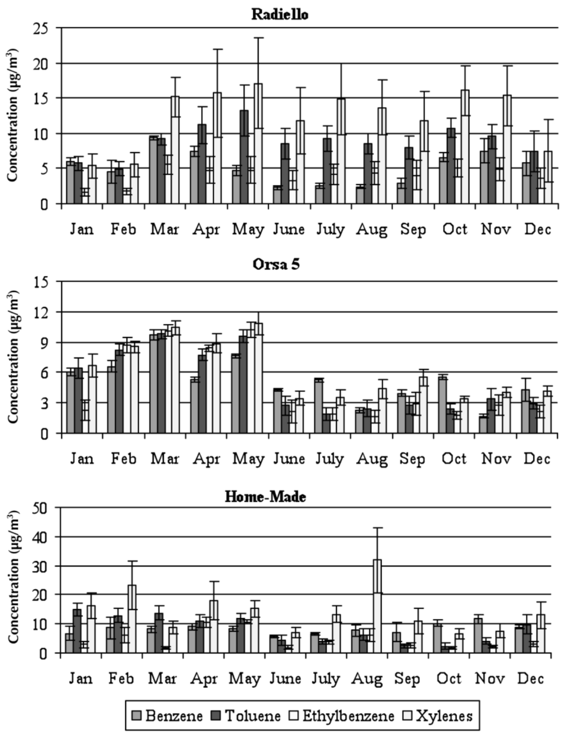

Figure 3. Monthly fluctuations in average concentrations of BTEX in the atmospheric air in the metropolitan area of Tricity in 2007.

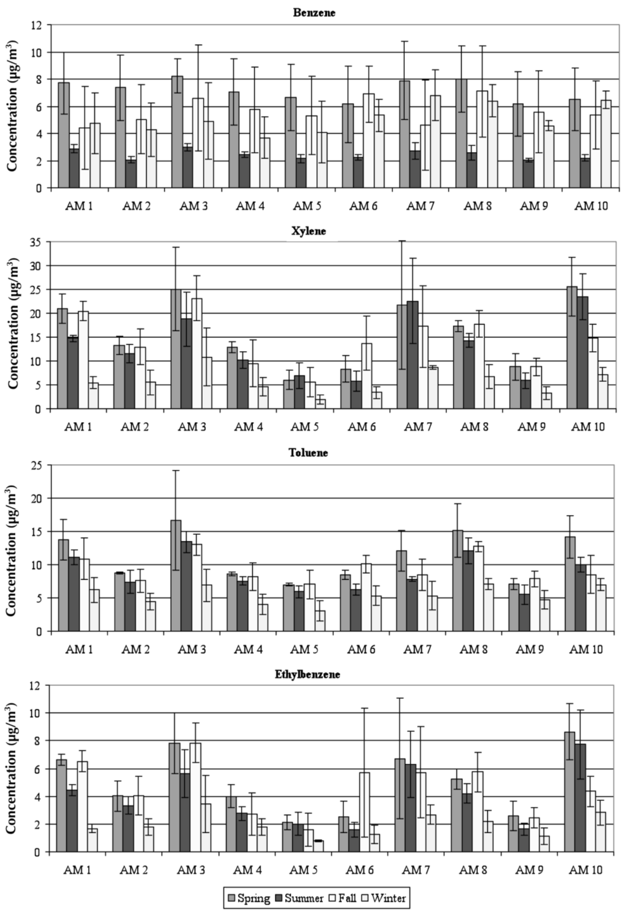

Figure 4. Seasonal variations in the time-weighted average BTEX concentrations at each monitoring station (obtained by applying Radiello passive samplers).

of BTEX at station 3 and 8 could be attributed to very high traffic intensity, slow movement of vehicles due to congestion, and frequent idling of them. It is interesting that despite the differences in the BTEX concentration values obtained with different types of passive samplers, the concentration profiles of the monitored compounds for particular stations are similar (Figure 2). Monthly fluctuations in average concentrations of BTEX in the atmospheric air in the metropolitan area of Tricity in 2007 are presented on Figure 3. In addition, to present the temporal trends in BTEX concentrations in the Tricity area the seasonal variations in BTEX concentrations at each monitoring station (obtained by applying Radiello passive samplers) are presented on Figure 4. The benzene concentrations ranged from 2.0 to 8.2 μg/m^3 with the highest values at monitoring station 3 and 8. As expected, the highest concentrations for benzene were observed in the spring season and the lowest during summer season. The large seasonal differences in benzene concentrations were not accompanied by large differences in concentrations between the stations during the same season. This also results from the data showing fluctuations in monthly average benzene concentrations. Figure 5A–5B shows monthly average concentration of benzene for two month in which the contractions were the highest (March) and the lowest (July). Similarly to seasonal changes in concentrations of the compounds monitored, monthly average concentrations of benzene in March and July did not show any significant differences between stations. However, differences in concentrations obtained with different passive samplers were quite significant. From the results obtained it can be concluded that benzene is nearly equally distributed in the air of Tricity metropolitan area.

As can be seen from Figure 4 for the other pollutants (toluene, ethylbenzene, and xylenes) the highest concentrations were also observed in spring; however, for those compounds fluctuations in concentration levels between monitoring stations were much higher. This suggests that toluene, ethylbenzene, and xylenes must be emitted from some other local sources.

It should be also emphasized that, climatic conditions in the area of the Tricity agglomeration make that heating season is elongated. This can cause the increased concentration of the monitored compounds in the spring season.

Additionally, to show the possible spatial trends, concentrations of benzene and toluene during the year 2007 at each monitoring station and for each type of passive sampler are presented in Figure 6. It was also found that the largest differences in concentrations of benzene were at measuring stations 3 and 1 and of toluene at station 9 and 10. Even though all monitoring stations are located away from potential direct emission sources, there is the spatial variation of BTEX concentration. This can result from differences in dispersion of pollutants in the Tricity agglomeration due to differences in topography. The concentration of pollutants can be also be influenced by local meteorological conditions.

Our study confirmed good capability of passive samplers to show temporal and spatial fluctuations in BTEX concentrations in atmospheric air, which makes them applicable for air monitoring with respect to BTEX compounds on a local scale.

Field comparison of the passive samplers: diffusive samplers and permeative samplers

This research on the quality of the atmospheric air in the metropolitan area of the Tricity is based on two types of passive samplers that apply the phenomenon of free mass transport in analyte transport (15): diffusion through a static layer of air in the passive diffusive samplers, Radiello and Orsa 5, and analyte

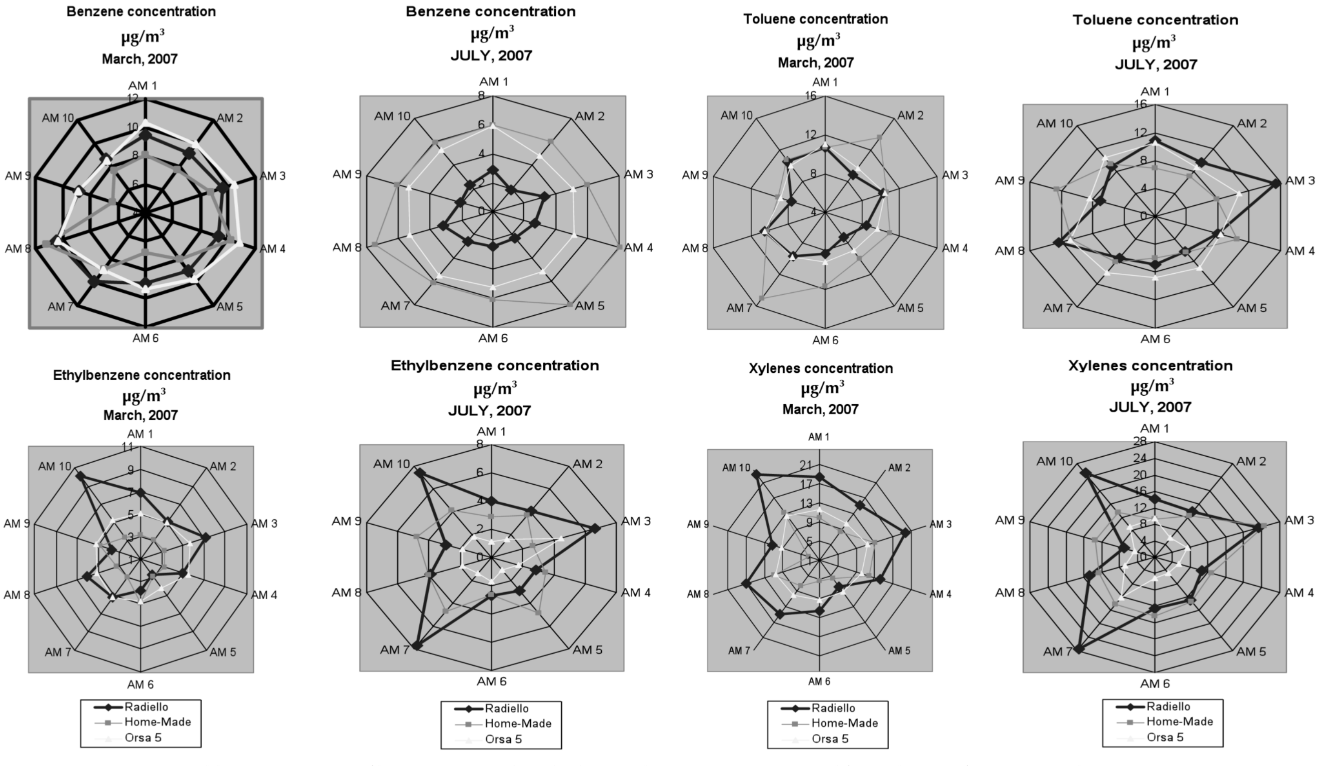

Figure 5. Average monthly concentrations of benzene in March and July at each monitoring station and for each type of passive sampler.

permeation through a non-porous membrane in passive permeation samplers home-made passive sampler.

So far, the Orsa 5 and home-made permeation passive samplers have been used mostly to examine the quality of indoor air, as personal samplers or to monitor air quality in these work places where environmental conditions such as temperature, humidity and air flow surrounding the sampler are known and stable. Only the Radiello sampler is commonly used in research on the quality of atmospheric air (16,17). That is why the concentrations obtained with this sampler have been used as the reference values to assess the operation of the two other passive samplers.

The insignificance of the difference between BTEX TWA concentrations determined using Radiello passive samplers and using Orsa 5 or home-made permeation passive samplers was examined by means of the linear regression method (18–20). (The BTEX concentrations determined applied with the use of Radiello passive samplers were plotted vs. those by means of Orsa 5 or home-made permeation passive samplers). For the difference between the two values to be insignificant, the dependence should be linear ($y = bx + a$), the line should pass through the origin of the coordinate system, and the slope should be close to unity. In other words, the parameters used for the validation of the proposed approach to compare TWA concentrations are the slope b, the intercept a and the regression coefficient r. It was found that at the probability level P = 95% and for f = n – 2 = 46 degrees of freedom. All of the previous conditions were fulfilled in the case of Orsa 5 passive sampler; ($t_{b\ \mathrm{Orsa\ 5}}$ ((1 – b)/s_b) = 1.256 ≤ t_{cr} = 2.014; $t_{a\ \mathrm{Orsa\ 5}}$ (a – 0)/s_a) = 1.694 ≤ t_{cr} = 2.014; $r_{\mathrm{Orsa\ 5}}$ = 0.786 ≥ r_{cr} = 0.27). Thus, the slope b and the intercept a were not significantly different from the expected values of β_0=1 for the slope and α_0=0 for the intercept, which means that the differences between the BTEX concentrations determined using Radiello and Orsa 5 passive samplers were statistically insignificant. In the case of home-made permeation passive sampler, it was found that the slope b was not significantly different from the expected values ($t_{b\ \mathrm{H\text{-}M}}$ ((1 – b)/s_b) = 1.221 ≤ t_{cr} = 2.014); however, the difference between the intercept a and α_0 = 0 was statistically significant ($t_{a\ \mathrm{H\text{-}M}}$ (a – 0)/s_a) = 3.536 ≥ t_{cr} = 2.014; $r_{\mathrm{H\text{-}M}}$ = 0.727 ≥ r_{cr} = 0.27). The regression coefficient r in both cases for Orsa 5 and home-made permeative passive samplers is higher than r_{cr} at the probability level P = 95% and for f = n – 2 = 46 degrees of freedom.

On the other hand, Figure 7A presents the comparison of the obtained average annual BTEX concentrations for each type of passive sampler with the extended uncertainty values (U, for k = 2). From Figure 7A, it can be concluded that the concentrations of benzene, ethylbenzene, and xylenes obtained using any of the three kinds of passive samplers fell within the expanded uncertainty ranges for the remaining values, which indicates that these values belong to the same group. Only for toluene did the concentrations obtained by the Orsa 5 not fall within the expanded uncertainty ranges of the Radiello passive samplers.

Relative differences between the time-weighted annual average concentrations of benzene, toluene, ethylbenzene, and xylene determined using the Radiello and Orsa 5 passive samplers were 1.5%, 47%, 15%, and 24%, respectively; and between Radiello and home-made permeation passive samplers were 40%, 26%, 42%, and 19%, respectively.

The greater differences observed in the case of the permeation sampler than in the case of the Orsa 5 sampler may result from the fact that in the former, influence of temperature on calibration constant (k) and, hence, on sampling rate was not taken into account. The calibration constants of the permeation passive samplers (k – parameter responsible for the sampling rate in the gaseous phase) were determined at a constant temperature of 25°C, and the influence of temperature on the k constant has been not examined in a very wide range of temperatures (10,21). It is also

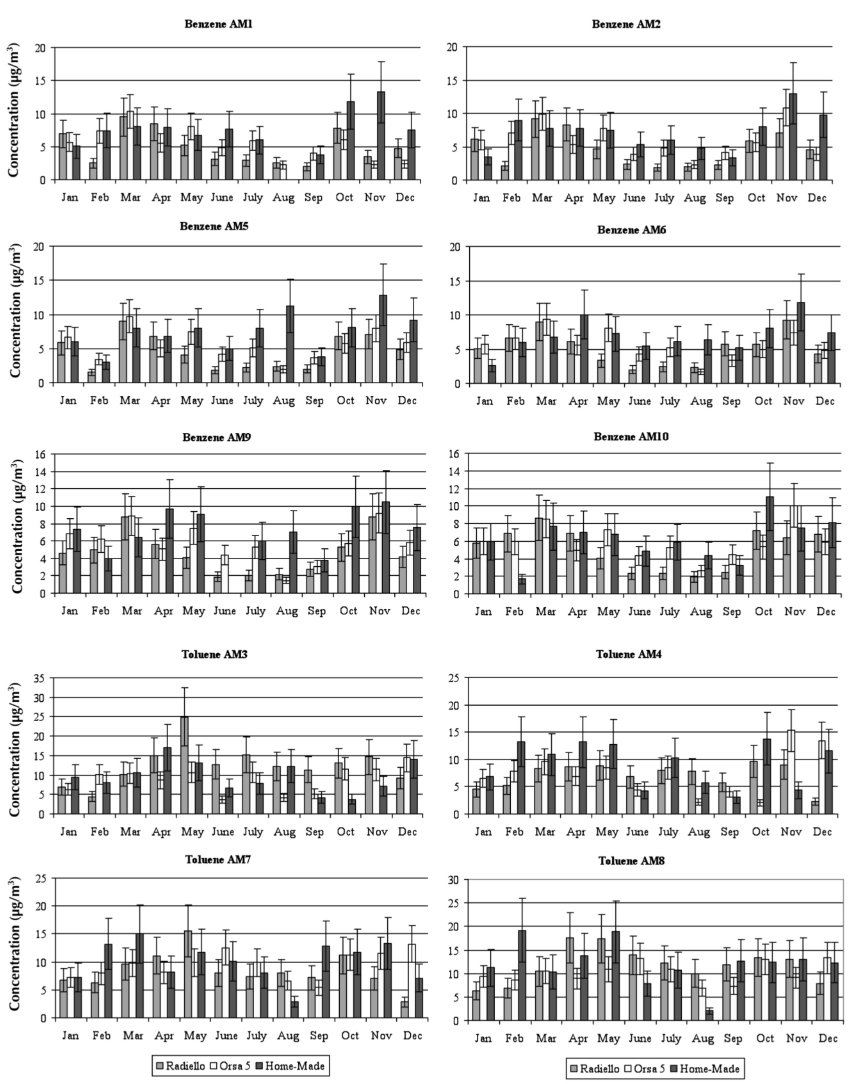

Figure 6A. Temporal and spatial trends in concentrations of benzene and toluene during the year 2007 at each monitoring stations and for each type of passive sampler.

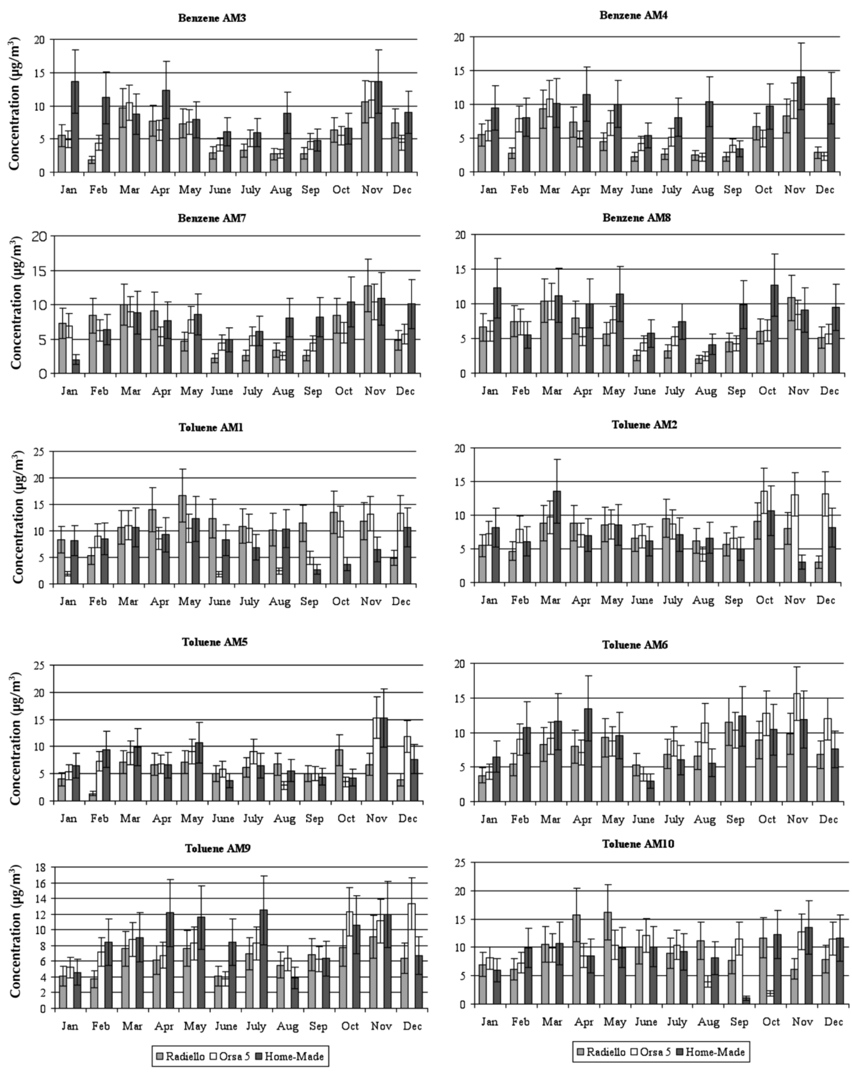

Figure 6B. Temporal and spatial trends in concentrations of benzene and toluene during the year 2007 at each monitoring stations and for each type of passive sampler.

necessary to remember that the monitored compounds are present in the atmospheric air at low concentrations, whereby 30–40% differences are acceptable for most of the environmental analytical tasks.

Despite the differences in the obtained values of annual average BTEX concentrations, all the types of passive samplers can be used to monitor atmospheric air quality with regard to BTEX compounds.

Correlation analysis

One of the aims of this research was to identify BTEX emission sources to the atmospheric air in the Tricity area. In order to find the occurrence of different source of BTEX, correlations between concentrations of individual compounds from BTEX group were calculated. The results obtained for different seasons and types of passive sampers are presented in Table III. Correlations between the most important target compounds were looked for: if two compounds show a strong correlation, a common source could be assigned to them (22).

Low correlation coefficient values (R^2) obtained for the linear plots of toluene concentration versus benzene concentration [benzene vs. toluene (B–T)] for each season and type of passive sampler suggest a lack of correlations between the concentrations of these compounds (B–T).

This indicates that road traffic is not the only source of these compounds in the atmospheric air of the Tricity area. The existence of other sources may also be found by examining the correlations between the remaining BTEX analytes: toluene vs. ethylbenzene (T–E); toluene vs. *m,p*-xylenes (T–X) (Table III).

The ratios between the concentrations of analyzed compounds obtained in this work are shown in Table IV. The obtained values of mean ratios between the selected compounds are different from those available in the literature on urban areas, in which road traffic is the main source of BTEX. The values range between 2 and 9 for different European cities (23,24). It also confirms the existence of other additional sources of BTEX emission in the Tricity area such as industrial activities and residential heating systems.

The benzene to toluene ratios for 10 monitoring stations are presented on Figure 7B. As it can be seen from Figure 7B, some groups of monitoring stations had similar benzene to toluene ratios, which can indicate identical sources of these compounds in the atmospheric air in those places.

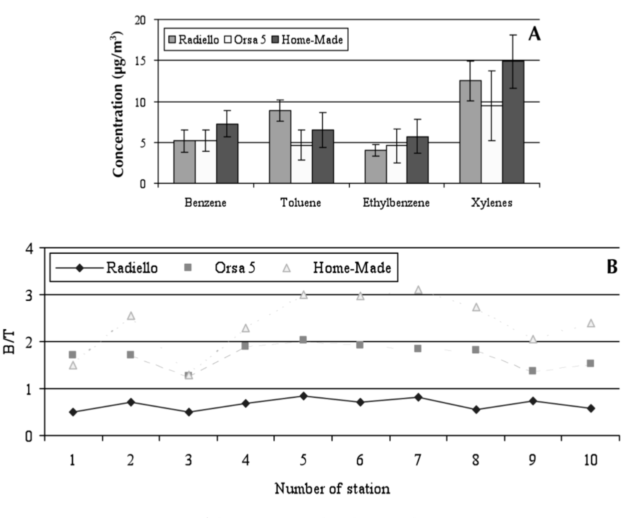

Figure 7. Comparison of the time-weighted annual average BTEX concentrations in the atmospheric air obtained with three types of passive samplers (A). Changes of benzene to toluene ratios with monitoring stations (B).

Conclusion

Passive sampling of analytes from gaseous matrices has numerous advantages. It is much cheaper and easier in operation than active sampling; samplers can be operated unattended for prolonged periods of time without the unavoidable annoyance of active sampling.

The obtained time-weighted annual average concentrations of benzene for the selected passive samplers only slightly exceed the permissible value for the benzene recommended by the EU directive. The values are within the range of the annual tolerance margin, 8 µg/m^3, for average weighted benzene concentration. The obtained data also suggest that the emissions from automotive vehicles are not the only source of BTEX emission in the metropolitan area of Tricity. The lack of correlation between the concentrations of benzene and toluene and the weak correlations between the remaining monitored compounds support some hypotheses that industrial plants located in the metropolitan area of Tricity could have significant effect on BTEX concentrations in the atmospheric air.

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References

1. R. Atkinson. Atmospheric Chemistry of VOCs and NOx. *Atmos. Environ.* **34:** 2063–2101 (2000).
2. B.J. Finlayson-Pitts and Jr. J.N. Pitts. Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. *Science* **276:** 1045–1052 (1997).
3. D. Brocco, R. Fratarcangeli, L. Lepore, M. Petricca, and L. Venturne. Determination of aromatic hydrocarbons in urban air of Rome. *Chemosphere* **31:** 557–566 (1997).
4. C.C. Chan, H. Ozkaynak, J.D. Spendgler, and L. Sheldon. Driver exposure to volatile organic compounds, CO, ozone, and NO2 under different driving conditions. *Environ. Sci. Technol.* **25:** 964–972 (1991).
5. C.P. Weisel, N.J. Nicholas, and P.J. Lioy. Exposure to emission from gasoline within automobile cabins. *J. Expos. Anal. Epidemiol.* **2:** 79–96 (1992).
6. J. Begerow, E. Jermann, T. Keles, T. Koch, and L. Dunemann. Screening method for determination of 28 volatile organics compounds in indoor and outdoor air at environmental concentration using dual-column capillary gas chromatography with tandem electron-capture-flame ionization detection. *J. Chromatogr. A* **749:** 181–191 (1996).
7. European Commission, 2000. Directive 2000/69/EC of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air.
8. J. Namiesnik, B. Zabiegała, A. Kot-Wasik, M. Partyka, and A. Wasik. Passive sampling and/or extraction techniques in environmental analysis: a review. *Anal. Bioanal. Chem.* **381:** 279–301 (2005).
9. A. Kot-Wasik, B. Zabiegała, M. Urbanowicz, E. Dominiak, A. Wasik, and J. Namiesnik. Advances in passive sampling in environmental studies. *Anal. Chim. Acta* **602:** 141–163 (2007).
10. B. Zabiegała, T. Górecki, and J. Namiesnik. Calibration of permeation passive samplers with silicone membranes based on physicochemical properties of the analytes. *Anal. Chem.* **75:** 3182–3192 (2003).
11. J. Begerow, E. Jermann, T. Keles, T. Koch, and L. Dunemann. Performance of two different types of passive samplers for the GC/ECD-FID determination of environmental VOC levels in air. *Fresenius J. Anal. Chem.* **363:** 399–403 (1999).
12. B. Oury, F. Lhuillier, J.C. Protois, and Y. Moréle. Behavior of the Gabie, 3M 3500, Perkin Elmer Tenax TA, and Radiello 145 Diffusive samplers exposed over a long time to a low concentration of VOCs. *J. Occup. Environ. Hygiene* **3:** 547–557 (2006).
13. European standard EN 13528-2 Ambient Air Quality. Diffusive samplers for the determination of concentration of gases and vapours. Part 2: Specific requirements and test.
14. B. Zabiegała, M. Partyka, T. Górecki, and J. Namiesnik. Application of the chromatographic retention index system for the estimation of the calibration constants of permeation passive samplers with polydimethylsiloxane membranes. *J. Chromatogr. A* **1117:** 19–30 (2006).
15. B. Kozdron-Zabiegała, J. Namiesnik, and A. Przyjazny. Use of passive dosimeters for evaluation of the quality of indoor and outdoor air. *Indoor Environ.* **4:** 189–203 (1995).
16. B. Strandberg, A.L. Sunesson, M. Sundgren, J.O. Levin, G. Sällsten, and L. Barregard. Field evaluation of two diffusive samplers and two adsorbent media to determine 1,3 butadiene and benzene levels in air. *Atmos. Environ.* **40:** 7686–7695 (2006).
17. A. Pennequin-Cardinal, H. Plaisance, N. Locoge, O. Ramalho, S. Kirchner, and J.C. Galloo. Performances of the Radiello diffusive sampler for BTEX measurements: influence of environmental conditions and determination of modelled sampling rates. *Atmos. Environ.* **39:** 2535–2544 (2005).
18. L. Brüggemann and R.Wennrich. Evaluation of measurement uncertainty for analytical procedures using a linear calibration function. *Accred. Qual. Assur.* **7:** 269–273 (2002).
19. J. Van Loco, M. Elskens, C. Croux, and H. Beernaert H. *Accred. Qual. Assur.* **7:** 281–285 (2002).
20. K. Heydorn and T. Anglov. Calibration uncertainty. *Accred. Qual. Assur.* **7:** 153–158 (2002).
21. B. Zabiegała, T. Górecki, E. Przyk, and J. Namiesnik. Permeation passive sampling as a tool for the evaluation of indoor air quality. *Atmos. Environ.* **36:** 2907–2916 (2002).
22. G. Fernández-Martínez, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, and E. Fernández-Fernández. Measurement of Volatile Organic Compounds in Urban Air of La Coruña, Spain. *Water, Air, Soil Pollut.* **129:** 267–288 (2001).
23. R.A. Field, M.E. Goldstone, J.N. Lester, and R. Perry. The sources and behavior of tropospheric anthropogenic volatile hydrocarbons. *Atmos. Environ.* **26A:** 2983–2996 (1992).
24. Th. Knobloch, A. Asperger, and W. Engewald. Volatile organic compounds in urban atmospheres: Long-term measurements of ambient air concentrations in differently loaded regions of Leipzig. *Fresenius J. Anal. Chem.* **359:** 189–197 (1997).

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