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Comparative study of the adsorption performance of an active multi-sorbent bed tube (Carbotrap, Carbopack X, Carboxen 569) and a Radiello® diffusive sampler for the analysis of VOCs

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ABSTRACT

A simple comparison is made to evaluate the relative performance of active and passive sampling methods for the analysis of volatile organic compounds (VOCs) in ambient air. The active sampling is done through a multi-sorbent bed tube (Carbotrap, Carbopack X, Carboxen 569) created in our laboratory and the passive sampling through the Radiello® diffusive sampler specified for thermal desorption (filled with Carbograph 4). Daily duplicate samples of multi-sorbent bed tubes were taken during a period of 14 days. During the same period of time, quadruplicate samples of Radiello® tubes were taken during 3 days, 4 days, 7 days and 14 days. The sampling was carried out indoors during the months of February and March 2010 and outdoors during the month of July 2010 in La Canonja (Tarragona, Spain). The analysis was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MSD). The analytical performance of the two sampling approaches was evaluated by describing several quality assurance parameters. The results show that the analytical performances of the methodologies studied are quite similar. They display low limits of detection, good precision, accuracy and desorption efficiency, and low levels of breakthrough for multi-sorbent bed tubes. However, the two monitoring methods produced varying air-borne concentration data for most of the studied compounds, and the Radiello® samplers generally gave higher results. Sampling rates (Q_k) were determined experimentally, and their values were higher than those supplied by the producer. As the experimental calculation of Q_k values is generally carried out by the suppliers in exposure chambers with only the target compounds present in the air samples, as well as in concentrations dissimilar to those found in ambient air, the use of constant settled Q_k can lead to inaccurate results in complex samples.

1. Introduction

Odour episodes and environmental air quality are topics of worldwide concern, essentially due to the fact that several atmospheric pollutants, mainly volatile organic compounds (VOCs), are responsible for odorous annoyance of varying degrees of nuisance and represent a threat to human health (irritation of mucous membranes, psychological stress and long-term toxic reactions) and comfort [1–7]. Hence, sensitive, selective, fast and reliable methodologies are needed to sample and analyse pollutants in ambient air.

Thus, many efforts have been devoted to supporting the technological advancement of VOC sampling techniques, and the analytical performances of different sampling approaches to diminish and/or minimize possible errors and limit the experimental bias derived from the sample collection step have been investigated [8–11]. The sampling step is a critical part of ambient air analysis. Thus, the sample must be representative of ambient air, and qualitative and quantitative alterations during sampling, storage and analysis must be prevented [12]. The sampling strategy must allow sample collection during a concrete period of time, giving the results as time-weighted average concentrations. In addition, it must be easy and simple enough to enable facile field sampling [13]. Both active and passive sampling strategies are suitable for determining low concentrations of pollutants in outdoor and indoor ambient air [14–21]. Active sampling has been a traditional sampling technique used to determine pollutants in air [20]. However, the successful application of passive samplers (initially designed to monitor workplace personal air concentrations) to environmental analysis has increased in recent decades [9,16,18,22,23]. A large number of passive samplers are commercially available [24,25] and many international standard methods have been developed for

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application to air monitoring [20]. In addition, the easy operability and low cost of passive samplers make them an ideal tool for the long-term study of average pollution concentrations [26–28].

The comparison between active and passive performances is advised to validate passive samplers for ambient air evaluation [18]. A good agreement between passive and active samplings of pollutants has been found in several studies [26,29–32]. However, changes in uptake rates in passive samplers as a result of changes in temperature, wind velocity, VOC concentrations and humidity may be observed [33,34]. Consequently, comparisons between the adsorption performances of the two methodologies have been widely investigated [29,30,35].

In the present paper, a comparative study between two types of sampling strategies for the active and passive evaluation of VOCs is conducted to establish a reliable sampling methodology for the analysis of ambient air pollutants. Radiello® diffusive samplers for thermal desorption (filled with Carbograph 4) have been evaluated for monitoring several airborne VOCs by comparing their performance with an active multi-sorbent tube developed and validated in our laboratory (Carbotrap, Carbopack X and Carboxen 569) [15]. Generally, the evaluation and sampling rates of diffusive samplers (Q_k) are determined in controlled atmospheres in the laboratory [16,34], sometimes by assessing only one compound at a time. Consequently, in some cases the use of constant settled Q_k can lead to inaccurate results in complex field terms. The experimental results shown in this study are obtained from indoor and outdoor real ambient air samples made up of a mixture of hundreds of compounds. Hence, the data presented would be useful for future studies based on Radiello® diffusive tubes, in order to avoid errors in the calculation of the real concentrations when these samplers are used. The analytical performance of the two sampling methods is evaluated and several quality assurance parameters, such as sensitivity, linearity, precision, accuracy, tube desorption efficiency and breakthrough, are described.

2. Materials and methods

2.1. Chemicals and materials

Standards of VOCs with a purity of no less than 98% were obtained from Aldrich (Milwaukee, WI, USA), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). Methanol for gas chromatography (SupraSolv®) with a purity ≥99.8% was obtained from Merck (Darmstadt, Germany). PerkinElmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanised wool, Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents, Radiello® tubes for thermal desorption SS net (3 μm × 8 μm mesh, 4.8 mm diameter) adsorbent cartridges filled with 350 mg Carbograph 4 (35/50 mesh) (Code 145) and yellow Radiello® diffusive bodies (code 120–2) were obtained from Supelco (Bellefonte, PA, USA).

2.2. Sampling

Sampling was performed in La Canonja (Tarragona, Spain) for indoor (February–March 2010) and outdoor (July 2010) air during an interval of two weeks (Fig. 1). Daily duplicate 24-hour samples of active multi-sorbent bed tubes were taken during a period of 14 days. During the same period of time, quadruplicate samples of Radiello® tubes were taken in 4-day, 3-day, 7-day and 14-day samples to evaluate the performances of the Radiello® tubes depending on the sampling time. In the first week, quadruplicate sets of Radiello® tubes were exposed for 4, 7 and 14 days. On the fifth day of the week, the 4-day quadruplicate set was changed for 4 more Radiello® tubes that were exposed for 3 days. In the second week, the 7-day quadruplicate set was changed for 4 Radiello® tubes that were exposed for 7 more days. The 4- and 3-day sets were sampled as in the first week (Fig. 1).

VOCs were dynamically sampled by connecting custom packed glass multi-sorbent cartridge tubes (Carbotrap 20/40, 70 mg; Carbopack X 40/60, 100 mg and Carboxen 569 20/45, 90 mg) [15] to an air collector pump sampler specially designed in the LCMA-UPC laboratory. The pump sampler was equipped with an inert sampling line and high-precision total volume measurement. Other characteristics include 10 calibration flow levels, high flow stability and inexistent tube contamination during pre-activation processes [36,37]. Sampling flows were of 70 ml min^{-1}, with total sample volumes of approximately 100 l.

Collected ambient air samples, both multi-sorbent and Radiello® tubes, were further analysed by thermal desorption and gas chromatography-mass spectrometry (TD-GC/MSD) [15]. This methodology has been used in previous studies to identify and determine a wide range of VOCs that cause odour nuisance and affect air quality in ambient air [37].

2.3. Preparation and calibration of standard solutions

Stock standard solutions from neat chemicals were prepared through a primary solution with an individual VOC concentration of about 5000 ng μl^{-1}. This solution was prepared by adding 0.05 g of *p*-dichlorobenzene (solid standard) and 50 μl of each liquid neat standard (via a pre-weighed 100 μl Hamilton syringe) into a 10 ml clean flask, and filled with methanol. The solution was further diluted in methanol (via pipette) to obtain VOC standards ranging from 0.001 to 500 ng μl^{-1}. All standards were freshly prepared on the day of use.

The calibration curves (10 calibration points) of the VOC standards were done by spiking the previously prepared standard dilutions into the sorbent tubes (both the multi-sorbent bed and the Radiello® tubes) using a conventional gas chromatography packed column injector. Tubes were connected to the injector through a stainless steel tube and Swagelock adapters. The injector was slightly heated at 30 °C, and a flow stream of 100 ml min^{-1} of Helium was passed though the tubes. 1 μl of each standard dilution was loaded into a tube, with a loading time of 5 min [15].

2.4. Analytical instrumentation

The analysis of VOCs was performed by automatic thermal desorption coupled with a capillary gas chromatography/mass spectrometry detector, using a PerkinElmer ATD 400 (PerkinElmer, Boston, Massachusetts, USA) and a Thermo Quest Trace 2000 GC (ThermoQuest, San Jose, California, USA) interfaced with a Thermo Quest Trace Finnigan MSD.

The methodology, validated for 57 compounds, is described in the literature [15,37]. Thermal primary desorption of the sampling tubes is carried out at 300 °C and 370 °C for multi-sorbent bed and Radiello® tubes, respectively, with a Helium flow rate of 50 ml min^{-1} for 10 min. The double-split applied to the TD system (cold trap inlet and outlet splits of 4 ml min^{-1} and split 7 ml min^{-1}, respectively) allows 12% of the tube analytes to reach the MS detector. The cold trap (15 mg Tenax TA and 15 mg Carbotrap), is maintained at −30 °C. After primary desorption, the cold trap is rapidly heated from −30 °C to 300 °C (secondary desorption), and maintained at this temperature for 10 min. Analytes are then injected onto the capillary column (DB-624, 60 m × 0.25 mm × 1.4 μm) via a transfer line heated at 200 °C. The column oven temperature starts at 40 °C for 1 min, increases to 230 °C at a rate of 6 °C min^{-1} and then is maintained at 230 °C for 5 min. Helium (99.999%) carrier

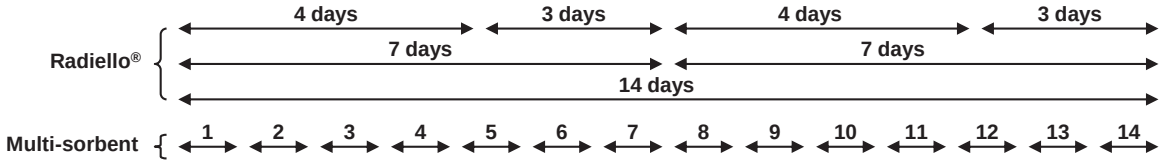

Fig. 1. Sampling strategy. Duplicate samples of multi-sorbent bed tubes were taken during 14 consecutive days. Quadruplicate passive Radiello® tubes were exposed during 3, 4, 7 and 14 days.

gas flow in the analytical column is approximately 1 ml min^{-1} (1.4 bar).

Mass spectral data are acquired over a mass range of 20–300 amu. The qualitative identification of target compounds is based on the match of the retention times and the ion ratios of the target quantification ions and the qualifier ions (Xcalibur 1.4 validated software package). Quantification of field samples is conducted by the external standard method [15]. The concentrations for the Radiello® passive samplers were calculated using the supplier sampling rate values (www.sigma-aldrich.com/radiello), correcting the values for temperature. Thus, only the compounds with these available data were quantified in the Radiello® samplers, even though many more compounds (up to 300) could be identified qualitatively [37]. Hence, the comparison between active and passive samplings could only be referred to these compounds. In addition, sampling rate values were calculated empirically to compare the values given by the supplier with those obtained experimentally.

All concentration values were normalized to standard conditions for temperature and pressure (273 K and 760 mm Hg).

2.5. Quality assurance parameters

The limits of detection, linearity range, precision, accuracy, desorption efficiency and breakthrough values for multi-sorbent bed and Radiello® diffusive tubes are shown in Table 1. The studied compounds show limits of detection (LOD) determined by applying a signal-to-noise ratio of 3, ranging from 1×10^{-5} to 2×10^{-3} μg m^{-3} for active samplers. For passive samplers, detection limits in μg m^{-3} were calculated by introducing the amount of compound of detection limits obtained for the Radiello® sampler to the formula given by the producer to determine the concentration (concentration (μg m^{-3}) = (mass (μg)/(Q_k (ml min^{-1}) × time (min))) × 1,000,000). LOD are given for the range of 3-day to 14-day samples and vary from 2×10^{-5} to 3×10^{-3} μg m^{-3} for 3-day samples and from 1×10^{-5} to 1×10^{-3} μg m^{-3} for 14-day samples.

The linearity has been evaluated within an individual VOC amount range from 0.001 to 5000 ng per tube, with a concrete quantification ion for each compound (Table 1). The linearity was considered acceptable when $r^2 \geq 0.99$, signal to noise ratios > 10, and peaks had a Gaussian shape. Precision was calculated by means of a consecutive analysis of five tubes spiked with the same amount of a standard solution of approximately 100 ng of each studied VOC. The method accuracy for the two types of adsorbent tubes was determined measuring the percentage recovery of the response obtained by the analysis of a tube standard (approximately 200 ng of each studied VOC) through the TD-GC/MS methodology versus the response obtained by direct injection of the same amount of standard under the same split conditions. Additionally, the ratio between the peak abundances obtained from multi-sorbent bed and Radiello® tubes was calculated for tubes spiked with the same amount of standards (approximately 100 ng of each studied VOC).

Desorption efficiency was evaluated in real samples. The desorbed sampling tubes were re-analysed at a higher temperature (350 °C and 400 °C for multi-sorbent bed and Radiello® tubes, respectively) in order to remove any remaining analytes from the tubes. For multi-sorbent bed tubes, the evaluation was done in duplicate samples with a volume of 100 l. The Radiello® diffusive tubes were evaluated in duplicate samples of tubes exposed for 3, 4, 7 and 14 days.

The capacity of a sorbent to retain specific compounds is usually evaluated by measuring the breakthrough volume of a concrete compound on the sorbent. To maximize sampling efficiency, the maximum volume of air of a concrete VOC concentration that can be sampled without loss of adsorbent must be known because, if breakthrough occurs, the sample obtained would not be representative of the concentrations present in ambient air. Breakthrough is the volume of air passing through an adsorbent that causes adsorbate molecules to migrate from the front to the back of the adsorbent bed [12]. Breakthrough values have been calculated for the multi-sorbent bed tubes as the percentage of target compound found in the back tube (in two multi-sorbent bed tubes connected in series) relative to the total mass in both tubes for 90-l samples with sampling rates of 70–90 ml min^{-1} [11].

2.6. Determination of sampling rates (Q_k)

Q_k values for the Radiello® samplers were determined empirically for all studied compounds taking the concentrations obtained from the multi-sorbent bed tubes as reference values, according to the equation given by the Radiello® manufacturers:

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

where C is the concentration of the substance in air (μg m^{-3}); M is the mass of substance absorbed in the Radiello® tube (μg); Q_k is the uptake rate (ml min^{-1}); t is time (min).

Comparing the concentrations that result from the Radiello® tubes and from the active multi-sorbent tubes, and taking as a reference the concentration from the later ones, the new value of Q_k that fits concentrations can be obtained from the equation:

$$Q_{kMS} = Q_{kRD} \frac{C_{RD}}{C_{MS}}$$

Being C_{MS} the concentration obtained with multi-sorbent bed active tubes (μg m^{-3}); C_{RD} the concentration obtained with Radiello® tubes (μg m^{-3}); Q_{kRD} is Q_k published by Radiello® manufacturers (ml min^{-1}); Q_{kMS} is the uptake rate that fits both concentrations (ml min^{-1}).

3. Results and discussion

3.1. Comparative of quality assurance parameters

Multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) coupled to TD-GC/MS was chosen as a reference methodology as it has been validated for a wide range of VOCs, giving excellent results for selectivity, sensitivity, linearity, precision, accuracy, total desorption of the studied compounds, artefact formation, breakthrough, and stability during storage [11,15].

The two sampling methodologies evaluated in the present article to assess air-borne concentrations of VOCs are highly selec-

Table 1
Quality assurance parameters for multi-sorbent bed and Radiello® tubes.

Compounds	Limit of detection[a] ($\mu g\,m^{-3}$)		Linearity range[a] (ng)		Precision[a] (RSD, %)		Accuracy (%)		MS/Rad abundance ratio[b]	Desorption efficiency[c] (%)		Breakthrough[c] (%)	
	MS	Rad[d]	MS	Rad	MS	Rad	MS	Rad		MS	Rad	MS[e]	Rad
tert-Butyl methyl ether	2×10^{-3}	2×10^{-3}–5×10^{-4}	0.8–760	5.8–110	19	23	40	33	1.2	100	100	0	–
n-Hexane	4×10^{-5}	2×10^{-4}–4×10^{-5}	0.1–270	0.3–360	13	5	48	50	0.9	99.93 ± 0.02	99.94 ± 0.03	0.055 ± 0.004	–
1,1,1-Trichloroethane	2×10^{-4}	3×10^{-3}–7×10^{-4}	1.2–790	4.3–430	15	22	40	33	1.2	100	100	0	–
Cyclohexane	1×10^{-4}	3×10^{-4}–1×10^{-4}	0.03–330	0.05–350	9	5	39	41	0.8	99.94 ± 0.01	99.4 ± 0.4	0.09 ± 0.01	–
Benzene	1×10^{-5}	1×10^{-4}–1×10^{-5}	0.001–230	0.07–460	5	5	81	64	1.3	99.1 ± 0.1	90 ± 2	0.1 ± 0.1	–
n-Heptane	1×10^{-4}	2×10^{-4}–3×10^{-5}	0.7–340	0.3–260	5	6	40	40	0.9	99.85 ± 0.01	99.6 ± 0.4	0.051 ± 0.003	–
Trichloroethylene	3×10^{-5}	2×10^{-4}–3×10^{-5}	0.01–350	0.2–470	5	6	58	61	0.9	100	100	0	–
Toluene	1×10^{-4}	1×10^{-4}–2×10^{-5}	0.2–1800	0.09–900	7	5	57	62	0.8	99.91 ± 0.01	99.4 ± 0.3	0.1 ± 0.1	–
n-Octane	8×10^{-4}	1×10^{-4}–3×10^{-5}	0.4–380	0.6–280	8	6	40	40	0.9	99.6 ± 0.1	99.3 ± 0.5	0.07 ± 0.03	–
Tetrachloroethylene	3×10^{-5}	2×10^{-4}–5×10^{-5}	0.01–480	0.2–470	6	8	40	37	1.6	99.9 ± 0.1	100	0	–
Butyl acetate	4×10^{-4}	3×10^{-3}–1×10^{-3}	0.4–350	0.7–470	4	8	50	34	1.5	97 ± 2	99.98 ± 0.03	0.10 ± 0.03	–
Ethylbenzene	1×10^{-4}	1×10^{-4}–2×10^{-5}	0.03–430	0.07–360	5	6	39	38	1.2	99.9300 ± 0.0001	99.6 ± 0.2	0.04 ± 0.03	–
n-Nonane	3×10^{-4}	8×10^{-4}–2×10^{-4}	0.06–350	0.06–300	3	6	40	41	0.9	99.86 ± 0.01	99.3 ± 0.4	0.12 ± 0.04	–
m + *p*-Xylene	4×10^{-5}	1×10^{-4}–2×10^{-5}	0.02–420	0.07–360	5	7	41	42	0.9	99.945 ± 0.002	99.6 ± 0.2	0.1 ± 0.1	–
Styrene	2×10^{-4}	1×10^{-4}–2×10^{-5}	0.03–360	0.07–370	3	7	40	40	1.0	99.4 ± 0.1	97 ± 2	0.1 ± 0.1	–
o-Xylene	5×10^{-5}	2×10^{-5}–1×10^{-5}	0.02–197	0.07–350	5	6	40	41	0.9	99.926 ± 0.002	99.2 ± 0.7	0.1 ± 0.1	–
n-Decane	2×10^{-4}	2×10^{-4}–1×10^{-4}	0.1–590	0.06–300	4	11	39	40	0.9	99.6 ± 0.1	99 ± 1	0.3 ± 0.1	–
1,2,4-Trimethylbenzene	3×10^{-4}	1×10^{-4}–2×10^{-5}	0.06–350	0.4–390	3	3	40	37	1.1	99.89 ± 0.1	99.3 ± 0.4	0.12 ± 0.1	–
p-Dichlorobenzene	3×10^{-4}	1×10^{-4}–3×10^{-5}	0.06–370	0.09–100	5	8	39	40	0.9	100	100	0.9 ± 0.1	–
n-Undecane	3×10^{-4}	3×10^{-4}–1×10^{-4}	0.06–290	0.3–310	4	22	39	35	1.1	98.9 ± 0.4	89 ± 5	0.7 ± 0.1	–

[a] For *m/z*: 73, 57, 97, 56, 78, 100, 130, 65, 43, 166, 73, 106, 57, 106, 104, 91, 71, 105, 146 and 57, for the compounds listed [15].
[b] Ratio between the peak abundances in multi-sorbent bed and Radiello® tubes spiked with the same amount of standards.
[c] $n = 2$ for MS tubes and $n = 8$ for Rad tubes.
[d] Limit of detection range for samples of 3 days to 14 days.
[e] Sample of 90 l [11].

tive procedures as they were developed to retain a wide range of target compounds present in ambient air [[15], www.sigma-aldrich.com/radiello]. The analysis of the sampling tubes with a TD-GC/MS system allows for a good chromatographic separation and a reliable identification of the target compounds through their characteristic mass spectra. In addition, co-elution problems are solved using VOC-characteristic ions in the qualification/quantification step [15]. Thermal desorption is a precise methodology, and all trapped pollutants are cromatographed and directed to the detector in only one run, avoiding sample manipulation and dilution. In addition, solvent use is eliminated [12]. However, the evaluation of terpenes in the Radiello® sampling tubes has been perceived to be unreliable, as decomposition and rearrangement reactions have been observed (see Section 3.5 Terpenes evaluation).

The limits of detection for both methodologies are quite similar (Table 1), in the range of 1×10^{-5} to 3×10^{-3} $\mu g\,m^{-3}$. For Radiello® passive samplers, LOD have been established for periods from 3 days to 14 days of sampling. As it can be observed, the limits of detection for 14-day samples are lower. Hence, this aspect must be taken into account when one is sampling in low concentrated atmospheres.

Linearity ranges for concrete quantification ions (Table 1) range from 3 to 5 orders of magnitude for both tube types. It should be noted that for Radiello® sampling tubes, the chlorinated compounds, namely 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene, show linearity ranges that are an order of magnitude lower than for multi-sorbent bed tubes. The repeatabilities (% relative standard deviation values) are ≤25% in all cases, accomplishing the EPA performance criteria [38]. However, it should be noted that the repeatabilities are slightly higher in the Radiello® diffusive tubes than in the multi-sorbent bed tubes, mainly for *n*-decane and *n*-undecane. Meanwhile, *tert*-butylmethylether and 1,1,1-trichloroethane show repeatabilities of around 20% for the two sampling methodologies.

Accuracy showed recoveries within 39–81% and 33–64% for multi-sorbent bed and Radiello® tubes. The results obtained are quite similar for both sampling methodologies, being around 40–50% for all studied compounds. The causes of these particularly low recoveries could be found in possible leaks in the TD system. Thus, the ratio of the peak abundances obtained from both the multi-sorbent bed and Radiello® tubes spiked with the same amount of VOCs was evaluated. These ratios range between 0.8 and 1.6, with an average value for all studied VOCs of 1.1 ± 0.2. The two sampling approaches studied show a very similar performance.

Desorption efficiencies for the two sampling methodologies are quite similar, at around 99–100%; although the results are slightly higher for multi-sorbent bed tubes. However, it must be taken into consideration that benzene, styrene and *n*-undecane desorption efficiencies for Radiello® tubes are considerably lower than the values obtained for multi-sorbent bed tubes (90 vs. 99.1 for benzene, 97 vs. 99.4 for styrene, and 89 vs. 98.9 for *n*-undecane).

Breakthrough values for the studied VOCs in multi-sorbent bed tubes are in the range of 0–1%. The recommended breakthrough values of typical organic compounds are <5% [38]. Hence, no relevant breakthrough occurs in multi-sorbent bed tubes for the range of concentrations evaluated in the present study, in samples of 90–100 l.

The two sampling methodologies studied have quite similar analytical performances. They show low limits of detection, good precision, accuracy and desorption efficiency. In addition, multi-sorbent bed tubes present very low breakthrough values. Consequently, their effectiveness in the determination and analysis of VOCs should be comparable.

3.2. A comparative of multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569)-Radiello® tube concentrations

Tables 2 and 3 show the average indoor air concentrations of the studied VOCs for the different sampling periods (3, 4 and 7 days), for multi-sorbent bed and Radiello® diffusive tubes. Average individual concentrations of VOCs range from 0.01 to 105 and 0.01 to 119 $\mu g\,m^{-3}$ for multi-sorbent bed and Radiello® tubes, respectively. Generally, only a few of the studied compounds do not show significant differences in the concentrations observed between the two sampling methodologies, although the concentrations obtained with the Radiello® samplers are higher, as shown in Fig. 2. *n*-Hexane, cyclohexane, toluene, *n*-octane, *m* + *p*-xylene and *n*-decane regularly do not show significant differences between the concentrations obtained from the two sampling strategies for the concentration ranges determined (4–105 and 4–119 $\mu g\,m^{-3}$ for these individual VOCs in multi-sorbent bed and Radiello® tubes, respectively).

Tables 4 and 5 show the average outdoor air concentrations of the studied VOCs for the two sampling methodologies evaluated. Average individual concentrations of VOCs range from 0.01 to 3 and from 0.01 to 8 $\mu g\,m^{-3}$ for multi-sorbent bed and Radiello® tubes, respectively. Cyclohexane, trichloroethylene, tetrachloroethylene and styrene regularly do not show significant differences between the concentrations obtained from the two sampling strategies for the concentration ranges determined (0.01–0.7 and 0.01–0.6 $\mu g\,m^{-3}$ for these individual VOCs in multi-sorbent bed and Radiello® tubes, respectively). Fig. 3 shows the differences between the outdoor air concentrations for the two sampling methods for several VOCs. As observed for indoor air, the outdoor concentrations obtained from the Radiello® samplers are higher than the concentrations determined from the multi-sorbent bed tubes.

In this regard, Bruno et al. [26] observed higher concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) for diffusive samplers in outdoor air field measurement studies when the authors compared the Radiello® samplers with GC automatic sampling monitors with FID and PID detectors, as shown in Figs. 8 and 9 of their article. However, they argued that the possible differences observed between the distinct sampling strategies could be attributed to the high experimental error displayed by automatic BTEX analysers. Nonetheless, in the present case, the high reliability of multi-sorbent bed tubes [15,37] cannot be the cause of the differences observed between the two studied sampling strategies.

Table 6 shows the average indoor and outdoor air concentrations of the studied VOCs for a 14-day sampling period, both for multi-sorbent bed and Radiello® diffusive tubes. Average individual concentrations of VOCs range from 0.01 to 93 and 0.03 to 88 $\mu g\,m^{-3}$, and 0.03 to 3 and 0.01 to 7.6 $\mu g\,m^{-3}$ for multi-sorbent bed and Radiello® tubes for indoor and outdoor air, respectively.

A comparison of the studied sampling periods (3, 4, 7 and 14 days) shows that the concentrations obtained for toluene, *n*-octane, *m* + *p*-xylene, *n*-decane, butyl acetate, *o*-xylene and *p*-dichlorobenzene from the two sampling methodologies evaluated are generally comparable when the concentrations determined are higher. However, for trichloroethylene, tetrachloroethylene and styrene, the sampling methodologies are comparable when the concentrations are lower. Thus, the concentrations of VOCs must be taken into account when the Radiello® samplers (Carbograph 4 for thermal desorption) are used and the supplier sampling rate values are applied, as observed in several works [33,34,39,40].

Although the main factors that influence the sampling rate values are wind velocity, temperature, exposure time and VOC concentration [34,40], because temperature and wind velocity were in the range of the expected values (temperature was around 17 °C and 26 °C for February–March and July sampling periods, respec-

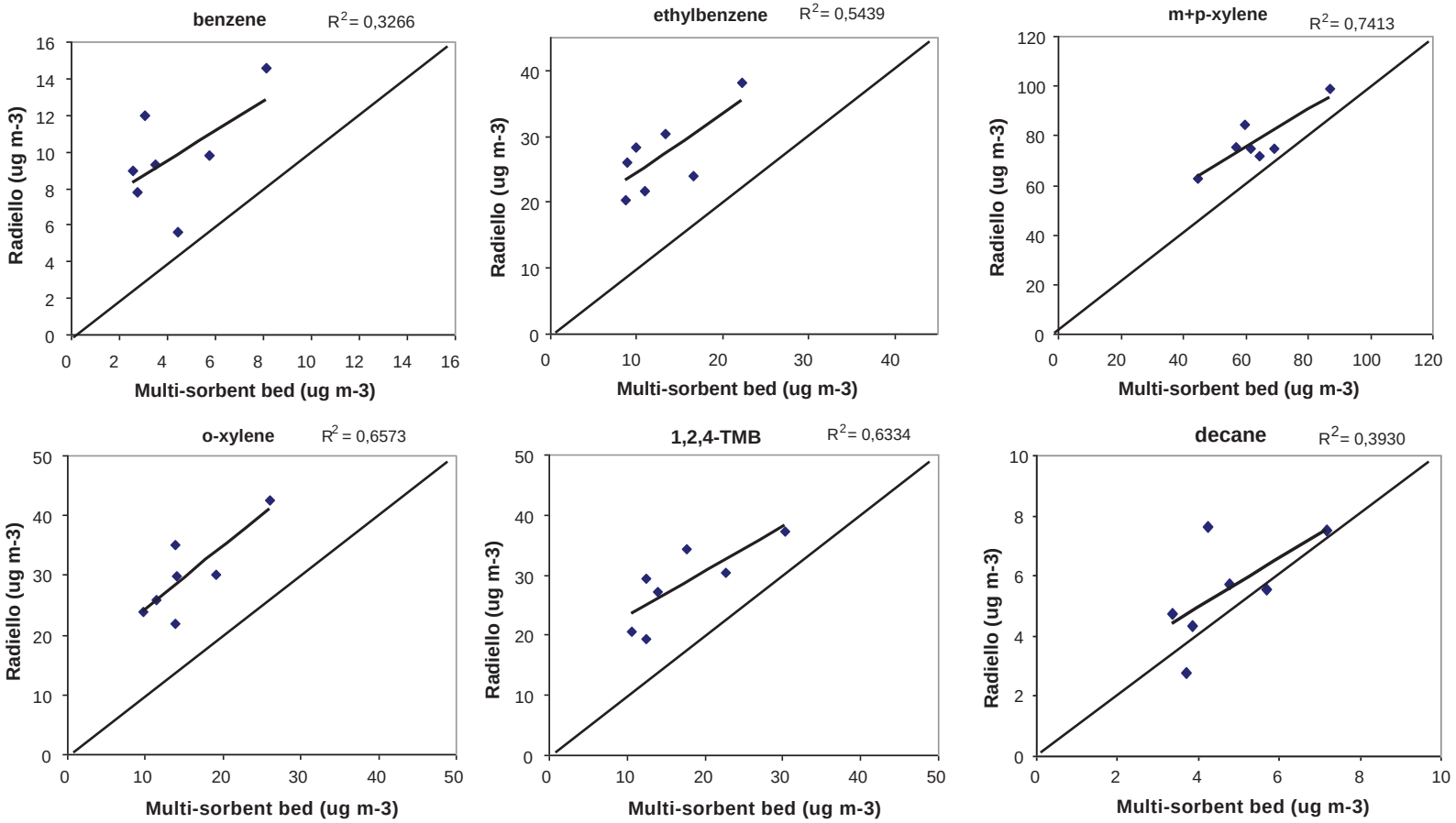

Fig. 2. Comparison of different compound concentrations (μg m^{-3}) using active sampling on a multi-sorbent tube (Carbotrap, Carbopack X and Carboxen 569) and passive sampling on a Radiello cartridge (Carbograph 4) for indoor air.

Table 2
Average ± standard deviation indoor air concentrations (μg m^{-3}) for multi-sorbent bed and radiello tubes for each period sampled (radiello, n = 4; multi-sorbent bed, n = 8 for 4 days periods, n = 6 for 3 days periods, n = 14 for 7 days periods). Compounds are listed by elution order.

Compounds	Week 1					
	MS Days 1–4	Rad Days 1–4	MS Days 5–7	Rad Days 5–7	MS Days 1–7	Rad Days 1–7
tert-Butyl methyl ether	1.5 ± 0.6*	5 ± 1*	1.2 ± 0.4*	2 ± 1*	1.3 ± 0.5*	2.4 ± 0.1*
n-Hexane	18 ± 11	23 ± 3	13 ± 2	14 ± 2	16 ± 9	19 ± 1
1,1,1-Trichloroethane	0.02 ± 0.02*	0.7 ± 0.1*	0.01 ± 0.01*	0.28 ± 0.04*	0.02 ± 0.01*	0.67 ± 0.02*
Cyclohexane	15 ± 11	17 ± 2	6 ± 2	8 ± 1	11 ± 10	11.1 ± 0.4
Benzene	8 ± 8	15 ± 2	3 ± 1*	9 ± 2*	6 ± 7	10 ± 1
n-Heptane	16 ± 13	24 ± 2	10 ± 6*	19 ± 4*	13 ± 11	22 ± 1
Trichloroethylene	0.02 ± 0.02*	0.07 ± 0.02*	0.01 ± 0.01*	0.04 ± 0.01*	0.02 ± 0.02	0.06 ± 0.01
Toluene	105 ± 52	107 ± 4	80 ± 47	86 ± 3	94 ± 50	79 ± 1
n-Octane	8 ± 5	10 ± 1	5 ± 3	8 ± 1	7 ± 5	8.5 ± 0.4
Tetrachloroethylene	0.2 ± 0.1*	0.5 ± 0.1*	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1*	0.6 ± 0.1*
Butyl acetate	0.6 ± 0.5	0.17 ± 0.03	0.2 ± 0.2*	0.08 ± 0.03*	0.4 ± 0.5	0.25 ± 0.01
Ethylbenzene	22 ± 16*	38 ± 3*	9 ± 7*	26 ± 5*	17 ± 15	24 ± 1
n-Nonane	2 ± 2*	5 ± 1*	0.7 ± 0.4*	3 ± 1*	2 ± 2*	8 ± 1*
m + *p*-Xylene	87 ± 42	99 ± 5	45 ± 28	63 ± 6	69 ± 42	75 ± 2
Styrene	2 ± 1*	8 ± 1*	0.7 ± 0.6*	1.9 ± 0.3*	1 ± 1*	2.49 ± 0.04*
o-Xylene	26 ± 16*	43 ± 3*	10 ± 7*	24 ± 4*	19 ± 15*	30 ± 1*
n-Decane	7 ± 2	8 ± 1	4 ± 2	3 ± 1	6 ± 3	6 ± 1
1,2,4-Trimethylbenzene	30 ± 13	37 ± 3	12 ± 6	19 ± 5	23 ± 14	31 ± 2
p-Dichlorobenzene	2 ± 2	1.6 ± 0.3	0.5 ± 0.3	0.7 ± 0.2	2 ± 2*	4.7 ± 0.4*
n-Undecane	3 ± 2*	5 ± 1*	0.8 ± 0.5*	5 ± 2*	2 ± 2*	9 ± 2*

* Significant differences observed between the concentrations obtained from multi-sorbent bed and Radiello tubes (t-test, p < 0.05).

tively, and wind velocity was between 0.3 and 4.9 m s^{-1} for outdoor air), and exposure times were also among those indicated by the supplier, VOC concentration could be an important inducer of possible discrepancies between the supplied sampling rates and the real ones. These could indicate that the sampling rates established by the supplier were calculated with VOC concentrations similar to the concentrations determined. Hence, from the results obtained it can be deduced that, when the supplier sampling rate is used, each compound has a suitable range of concentrations when the data determined would be more accurate and similar to the real concentration values, as stated for benzene in a previous study [33]. Nonetheless, if the sampling is done in locations where the concentrations are far from that range, either higher or lower, the obtained concentrations would be overestimated with the Radiello® diffusive tubes.

On the other hand, the difference in permeability of the diffusive body to the various VOCs [41] and the sorption of the target compounds to this body when it becomes contaminated during field monitoring (mainly due to handling) could also influence the sampling results. More research should be done in order to evaluate these possible interferences.

3.3. Radiello® sampling rate values (Q_k) and exposure time uncertainty

Radiello® sampling rate values available from the supplier (www.sigma-aldrich.com/radiello) were used to quantify the passive Radiello® samples, as mentioned above. The uncertainties (2σ) of these values range from 7.5% to 32.7%, and the values for *n*-decane (22.4%), styrene (24%) and *n*-undecane (32.7%) are

Table 3
Average ± standard deviation indoor air concentrations (μg m^{-3}) for multi-sorbent bed and radiello tubes for each period sampled (radiello, n = 4; multi-sorbent bed, n = 8 for 4 days periods, n = 6 for 3 days periods, n = 14 for 7 days periods). Compounds are listed by elution order.

Compounds	Week 2					
	MS Days 8–11	Rad Days 8–11	MS Days 12–14	Rad Days 12–14	MS Days 8–14	Rad Days 8–14
tert-Butyl methyl ether	1.4 ± 0.4*	3 ± 1*	1.9 ± 0.4	3 ± 1	1.6 ± 0.5*	3 ± 1*
n-Hexane	12 ± 6	15 ± 4	20 ± 3	19 ± 5	16 ± 6*	25 ± 2*
1,1,1-Trichloroethane	0.007 ± 0.002*	0.1 ± 0.1*	0.02 ± 0.02*	0.2 ± 0.1*	0.01 ± 0.01*	0.23 ± 0.04*
Cyclohexane	4 ± 2	4 ± 2	7 ± 6	12 ± 3	5 ± 4*	13 ± 1*
Benzene	3 ± 2*	8 ± 2*	4 ± 2*	9 ± 2*	3 ± 2*	12 ± 1*
n-Heptane	6 ± 5	12 ± 4	7 ± 3*	17 ± 3*	6 ± 4*	24 ± 2*
Trichloroethylene	0.02 ± 0.02	0.05 ± 0.01	0.008 ± 0.002*	0.01 ± 0.01*	0.01 ± 0.02	0.032 ± 0.004
Toluene	98 ± 40	109 ± 8	83 ± 16*	119 ± 7*	92 ± 32	105 ± 3
n-Octane	7 ± 3	11 ± 2	9 ± 3	9 ± 1	8 ± 3	9 ± 1
Tetrachloroethylene	0.04 ± 0.01*	0.10 ± 0.04*	0.03 ± 0.01*	0.05 ± 0.02*	0.03 ± 0.01*	0.18 ± 0.04*
Butyl acetate	0.5 ± 0.3*	0.13 ± 0.05*	0.77 ± 0.02*	0.06 ± 0.03*	0.6 ± 0.3*	0.25 ± 0.03*
Ethylbenzene	11 ± 6*	22 ± 5*	9 ± 4*	20 ± 4*	10 ± 5*	28 ± 2*
n-Nonane	7 ± 7	11 ± 4	1 ± 1*	4 ± 1*	5 ± 6*	13 ± 1*
m + *p*-Xylene	62 ± 21	75 ± 9	57 ± 18	75 ± 6	60 ± 20*	84 ± 4*
Styrene	0.9 ± 0.4*	1.7 ± 0.2*	0.8 ± 0.4*	1.8 ± 0.3*	0.9 ± 0.4*	2.6 ± 0.2*
o-Xylene	14 ± 6*	30 ± 6*	14 ± 6*	22 ± 4*	14 ± 6*	35 ± 2*
n-Decane	4 ± 1*	8 ± 3*	3 ± 2	5 ± 2	4 ± 1	4 ± 1
1,2,4-Trimethylbenzene	14 ± 9*	27 ± 8*	11 ± 5*	21 ± 2*	13 ± 7*	29 ± 3*
p-Dichlorobenzene	0.4 ± 0.2*	0.8 ± 0.3*	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.2*	1.0 ± 0.2*
n-Undecane	0.8 ± 0.3*	4 ± 1*	0.8 ± 0.3*	7 ± 2*	0.8 ± 0.3*	6 ± 2*

* Significant differences observed between the concentrations obtained from multi-sorbent bed and Radiello tubes (t-test, p < 0.05).

Table 4
Average ± standard deviation outdoor air concentrations (μg m^{-3}) for multi-sorbent bed and radiello tubes for each period sampled (radiello, $n = 4$; multi-sorbent bed, $n = 8$ for 4 days periods, $n = 6$ for 3 days periods, $n = 14$ for 7 days periods). Compounds are listed by elution order.

Compounds	Week 1					
	MS Days 1–4	Rad Days 1–4	MS Days 5–7	Rad Days 5–7	MS Days 1–7	Rad Days 1–7
tert-Butyl methyl ether	1.2 ± 0.6*	2.4 ± 0.2*	2 ± 1*	3.3 ± 0.1*	1.4 ± 0.8*	3.1 ± 0.1*
n-Hexane	2 ± 1*	0.8 ± 0.1*	2 ± 1	1.2 ± 0.1	1.9 ± 1.2*	1.17 ± 0.02*
1,1,1-Trichloroethane	0.08 ± 0.05	0.04 ± 0.01	0.054 ± 0.003*	0.04 ± 0.01*	0.07 ± 0.04*	0.03 ± 0.01*
Cyclohexane	0.7 ± 0.2	0.5 ± 0.1	0.7 ± 0.5	0.56 ± 0.03	0.7 ± 0.3	0.5 ± 0.1
Benzene	0.7 ± 0.2*	1.1 ± 0.2*	0.6 ± 0.4*	1.3 ± 0.1*	0.6 ± 0.3*	1.4 ± 0.3*
n-Heptane	0.7 ± 0.3*	1.2 ± 0.1*	0.9 ± 0.7	1.4 ± 0.1	0.8 ± 0.5*	1.53 ± 0.04*
Trichloroethylene	0.03 ± 0.01	0.027 ± 0.004	0.06 ± 0.05	0.047 ± 0.002	0.04 ± 0.03	0.033 ± 0.003
Toluene	3 ± 2	4.0 ± 0.3	3 ± 2*	5.29 ± 0.02*	3 ± 1*	5.0 ± 0.1*
n-Octane	0.3 ± 0.1*	0.49 ± 0.02*	0.9 ± 0.8	1.1 ± 0.1	0.5 ± 0.6	1.0 ± 0.1
Tetrachloroethylene	0.11 ± 0.04	0.10 ± 0.01	0.07 ± 0.03	0.075 ± 0.003	0.09 ± 0.04	0.10 ± 0.01
Butyl acetate	0.13 ± 0.04	0.14 ± 0.02	0.1 ± 0.1	0.13 ± 0.02	0.1 ± 0.1*	0.19 ± 0.01*
Ethylbenzene	1.2 ± 0.5	1.5 ± 0.2	0.8 ± 0.5	0.97 ± 0.03	1.0 ± 0.5*	1.76 ± 0.04*
n-Nonane	0.3 ± 0.1*	0.6 ± 0.1*	0.3 ± 0.2	0.41 ± 0.01	0.3 ± 0.1*	0.36 ± 0.03*
m + *p*-Xylene	1.1 ± 0.3*	1.7 ± 0.2*	1.2 ± 0.6	1.5 ± 0.1	1.1 ± 0.5*	2.3 ± 0.1*
Styrene	0.3 ± 0.2	0.4 ± 0.1	0.2 ± 0.1	0.29 ± 0.03	0.3 ± 0.2	0.39 ± 0.02
o-Xylene	0.4 ± 0.1*	0.6 ± 0.1*	0.4 ± 0.2	0.58 ± 0.02	0.4 ± 0.2*	0.76 ± 0.02*
n-Decane	0.8 ± 0.5	1.0 ± 0.3	0.7 ± 0.4	0.7 ± 0.1	0.8 ± 0.5*	1.3 ± 0.2*
1,2,4-Trimethylbenzene	0.3 ± 0.1*	0.7 ± 0.1*	0.4 ± 0.2*	0.61 ± 0.03*	0.3 ± 0.1*	1.0 ± 0.1*
p-Dichlorobenzene	0.03 ± 0.01	0.052 ± 0.003	0.030 ± 0.003*	0.05 ± 0.01*	0.03 ± 0.01*	0.06 ± 0.01*
n-Undecane	0.7 ± 1.2*	7 ± 1*	0.1 ± 0.1*	1.9 ± 0.4*	0.5 ± 0.9*	8 ± 2*

* Significant differences observed between the concentrations obtained from multi-sorbent bed and Radiello tubes (*t*-test, $p < 0.05$).

remarkable. It has been determined that sampling rate values are the main factor influencing the uncertainty (up to 70%) of the concentrations determined [33], as they are calculated in the laboratory in short time exposures and for concentrations far from those generally found in the environment [42], as well as without the interference of other VOCs present [16]. Concentrations obtained with *n*-undecane are much higher for the Radiello® diffusive tubes for all of the sampling periods (Tables 1–5). In this case, the high level of uncertainty given in the sampling rate can be the cause of this fact. Hence, *n*-undecane evaluation with Radiello® samples can lead to an overestimation of the real concentrations.

The exposure time upper limit for the Radiello® samplers for the studied compounds given by the supplier is generally 14 days (www.sigma-aldrich.com/radiello). However, cyclohexane, *n*-hexane, trichloroethylene and tetrachloroethylene upper limits are set at 7 days, and sampling periods above 7 days could be affected by back diffusion [39]. In indoor air, Radiello® results show higher concentrations for these compounds than multi-sorbent bed tubes, although only *n*-hexane and tetrachloroethylene display significant differences (Table 6). Meanwhile, in outdoor air, the concentrations of these four compounds are generally lower for the Radiello® tubes, and the differences observed are significant only for cyclohexane. Consequently, the data obtained at 14 days for these four compounds is assumed to be comparable with the data determined from the other sampling periods (3, 4 and 7 days). However, as the present study shows that the Radiello® uptake rates are somewhat variable, back diffusion together with competitive effects could have given the correct results in the current case.

Table 5
Average ± standard deviation outdoor air concentrations (μg m^{-3}) for multi-sorbent bed and radiello tubes for each period sampled (radiello, $n = 4$; multi-sorbent bed, $n = 8$ for 4 days periods, $n = 6$ for 3 days periods, $n = 14$ for 7 days periods). Compounds are listed by elution order.

Compounds	Week 2					
	MS Days 8–11	Rad Days 8–11	MS Days 12–14	Rad Days 12–14	MS Days 8–14	Rad Days 8–14
tert-Butyl methyl ether	2 ± 1*	5 ± 1*	0.5 ± 0.4*	1.0 ± 0.1*	1.5 ± 1.2*	3.3 ± 0.1*
n-Hexane	5 ± 3*	2.4 ± 0.2*	0.5 ± 0.1*	0.28 ± 0.01*	3 ± 3*	1.7 ± 0.1*
1,1,1-Trichloroethane	0.04 ± 0.03	0.039 ± 0.003	0.06 ± 0.01*	0.03 ± 0.01*	0.05 ± 0.02*	0.025 ± 0.001*
Cyclohexane	0.6 ± 0.2	0.6 ± 0.1	0.3 ± 0.1	0.18 ± 0.01	0.4 ± 0.2	0.35 ± 0.04
Benzene	0.9 ± 0.3*	1.9 ± 0.3*	0.22 ± 0.02*	0.8 ± 0.2*	0.6 ± 0.4*	1.3 ± 0.2*
n-Heptane	0.9 ± 0.3*	1.5 ± 0.2*	0.3 ± 0.1*	0.36 ± 0.04*	0.6 ± 0.4*	1.20 ± 0.04*
Trichloroethylene	0.02 ± 0.01	0.026 ± 0.003	0.01 ± 0.01	0.014 ± 0.001	0.02 ± 0.01	0.019 ± 0.001
Toluene	3 ± 1*	5 ± 1*	1.2 ± 0.2*	1.5 ± 0.1*	2.1 ± 1.3*	3.7 ± 0.2*
n-Octane	0.5 ± 0.1*	0.8 ± 0.1*	0.13 ± 0.01*	0.20 ± 0.03*	0.3 ± 0.2*	0.65 ± 0.01*
Tetrachloroethylene	0.06 ± 0.02	0.06 ± 0.01	0.07 ± 0.01	0.064 ± 0.004	0.06 ± 0.02	0.072 ± 0.002
Butyl acetate	0.15 ± 0.04	0.17 ± 0.03	0.08 ± 0.03	0.06 ± 0.03	0.1 ± 0.1*	0.18 ± 0.01*
Ethylbenzene	0.6 ± 0.2*	0.9 ± 0.1*	0.3 ± 0.1	0.4 ± 0.1	0.5 ± 0.2*	0.89 ± 0.02*
n-Nonane	0.3 ± 0.1*	0.5 ± 0.1*	0.07 ± 0.02*	0.16 ± 0.02*	0.2 ± 0.1*	0.47 ± 0.04*
m + *p*-Xylene	0.8 ± 0.3*	1.2 ± 0.2*	0.5 ± 0.2	0.7 ± 0.1	0.7 ± 0.3*	1.3 ± 0.1*
Styrene	0.6 ± 0.7	0.5 ± 0.1	0.08 ± 0.04*	0.19 ± 0.03*	0.4 ± 0.6	0.36 ± 0.01
o-Xylene	0.3 ± 0.1*	0.5 ± 0.1*	0.2 ± 0.1*	0.30 ± 0.04*	0.3 ± 0.1*	0.47 ± 0.02*
n-Decane	7 ± 7*	5 ± 1*	0.4 ± 0.1*	0.6 ± 0.1*	4 ± 6	3.8 ± 0.1
1,2,4-Trimethylbenzene	2 ± 2	3 ± 1	0.23 ± 0.04*	0.6 ± 0.1*	1 ± 2*	2.9 ± 0.1*
p-Dichlorobenzene	0.03 ± 0.01	0.04 ± 0.01	0.022 ± 0.004*	0.04 ± 0.01*	0.03 ± 0.01*	0.044 ± 0.002*
n-Undecane	0.3 ± 0.2*	3 ± 1*	0.03 ± 0.01*	2.0 ± 0.3*	0.2 ± 0.2*	3.5 ± 0.3*

* Significant differences observed between the concentrations obtained from multi-sorbent bed and Radiello tubes (*t*-test, $p < 0.05$).

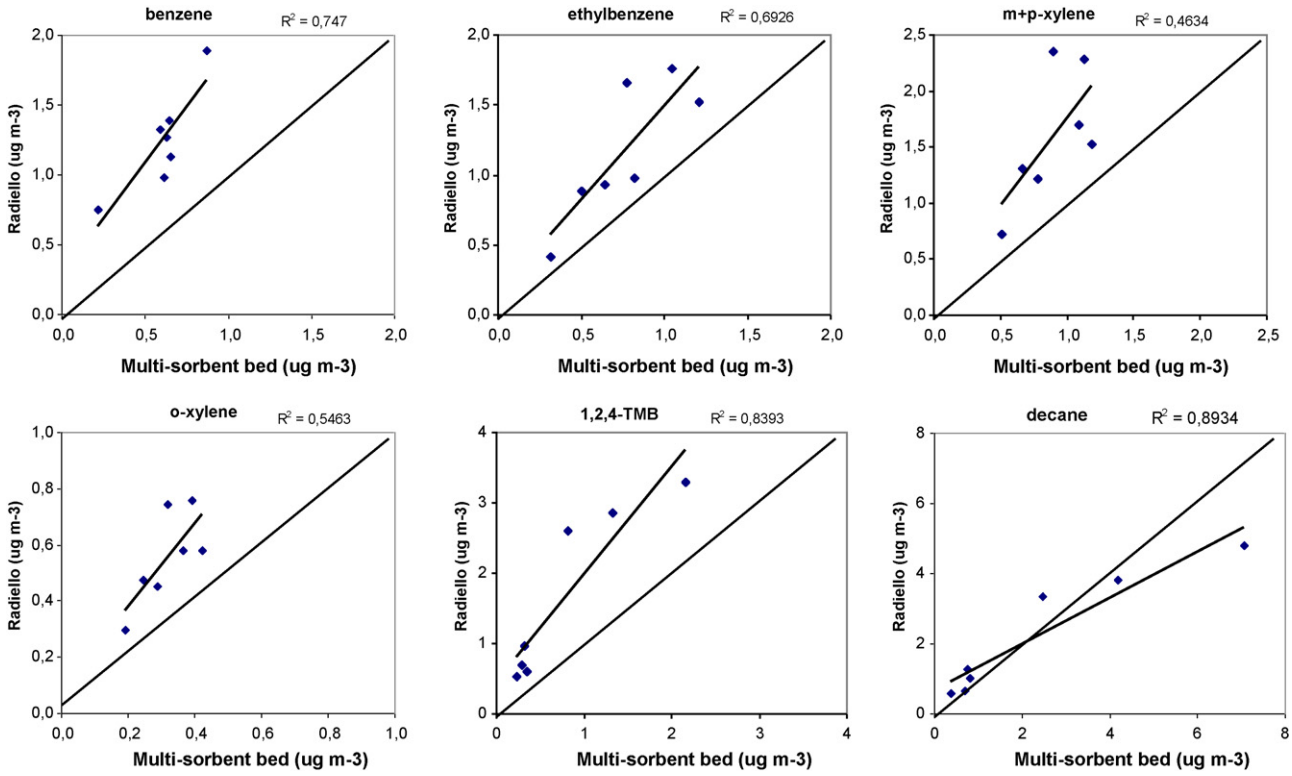

Fig. 3. Comparison of different compound concentrations (μg m^{-3}) using active sampling on a multi-sorbent tube (Carbotrap, Carbopack X and Carboxen 569) and passive sampling on a Radiello cartridge (Carbograph 4) for outdoor air.

Hence, more research is required to ensure that sampling periods of 14 days are safe and would give reliable results for the compounds that have sampling upper limits set at 7 days.

3.4. Experimental sampling rates (Q_k)

Table 7 shows the experimentally obtained Q_k (ml min^{-1}), together with the values given by the supplier. Experimentally obtained Q_k are generally higher than the presented values, as can be expected from the concentrations obtained in the passive samplers. For several compounds, Q_k values could not be determined due to the absence of a trend between active and passive results, mainly due to the fact that all of the results were very similar and created a cloud of points without any tendency. The possible effects of temperature on Q_k were studied through the following equation [33]:

$$Q_k(\text{ml min}^{-1}) = A + \alpha T(^\circ\text{C}),$$

where A and α are constants, and T is temperature in °C. The temperature used is expressed in °C instead of K, after assuming that:

$$Q_k(\text{ml min}^{-1}) = A' + \alpha T(\text{K}) = A' + \alpha[T(^\circ\text{C}) + 273]$$
$$= A' + \alpha 273 + \alpha T(^\circ\text{C}) = A + \alpha T(^\circ\text{C}),$$

and taking into account the restriction of only positive values for the constant A in order to avoid nonsensical negative values for Q_k at 0 °C.

No concluding tendencies could be assumed from the obtained results, and temperature could not be considered to influence Q_k in a decisive way in a decisive way for the temperature range tested.

Chlorinated compounds, such as trichloroethylene and tetrachloroethylene, give calculated Q_k values similar to the ones provided, as well as butyl acetate and *n*-decane. Other compounds, however, only present empirical Q_k values similar to the ones given for determined ambient air concentrations. *n*-Hexane, toluene, *n*-octane and *m* + *p*-xylene show similar Q_k values at higher ambient air concentrations. On the other hand, cyclohexane presents similar Q_k values at lower ambient air concentrations. The use of indoor and outdoor results to calculate Q_k values, *n*-hexane, cyclohexane and *n*-decane gives values close to the supplier Q_k values. These could suggest, as stated previously, that the sampling rates established by the supplier that are comparable to the Q_k obtained experimentally were calculated with VOC concentrations similar to the concentrations obtained in the present study.

In other studies, the Q_k values were calculated experimentally in exposure chambers, with only the target compounds present in the air samples [34,39,40,43]. In these cases, the Q_k obtained are generally similar to the values given by the supplier. However, when Q_k are determined experimentally through real ambient air samples, the obtained values are higher than the supplied values [44]. In the study of Cocheo et al. [44], several models were established for calculating Q_k for BTEX (benzene, toluene, ethylbenzene *m* + *p*-xylene and *o*-xylene) depending on the sampling time for benzene and on the temperature for the remaining compounds. Calculated Q_k values for benzene for 3-14 days samplings were in the range of 26.4–33.0 ml min^{-1}. Furthermore, Q_k values for toluene, ethylbenzene *m* + *p*-xylene and *o*-xylene at 17 °C and 26 °C (the two average sampling temperatures of the present study) were 31.2 and 32.6, 31.2 and 34.4, 30.7 and 33.2, and 29.02 and 31.1 ml min^{-1}, respectively, and all the experimentally determined Q_k were higher than those supplied (26.8, 30.0, 25.7, 26.6 and 24.6 ml min^{-1} for BTEX at 25 °C, respectively). Hence, the use of constant settled Q_k can lead to inaccurate results in complex field terms [16,45,46].

3.5. Terpenes evaluation

The terpenes α-pinene and limonene were also target compounds, as sampling rate values are established by the Radiello® supplier. However, their concentrations could not be determined

Table 6
Average ± standard deviation indoor and outdoor air concentrations (μg m^{-3}) for multi-sorbent bed and radiello tubes for each period sampled (radiello, $n = 4$; multi-sorbent bed, $n = 28$). Compounds are listed by elution order.

Compounds	Indoor air		Outdoor air	
	MS Days 1–14	Rad Days 1–14	MS Days 1–14	Rad Days 1–14
tert-Butyl methyl ether	1.5 ± 0.5*	0.8 ± 0.2*	1 ± 1*	2.6 ± 0.1*
n-Hexane	16 ± 7*	20 ± 1*	3 ± 2	1.54 ± 0.01
1,1,1-Trichloroethane	0.01 ± 0.01*	0.19 ± 0.03*	0.06 ± 0.03*	0.011 ± 0.001*
Cyclohexane	8 ± 8	12.5 ± 0.4	0.6 ± 0.3*	0.42 ± 0.01*
Benzene	4 ± 5	6 ± 1	0.6 ± 0.4	1.0 ± 0.1
n-Heptane	10 ± 9*	25 ± 1*	0.7 ± 0.5*	1.5 ± 0.2*
Trichloroethylene	0.02 ± 0.02	0.03 ± 0.01	0.03 ± 0.03	0.015 ± 0.001
Toluene	93 ± 41	88 ± 2	3 ± 1*	5.1 ± 0.2*
n-Octane	7 ± 4	5.8 ± 0.2	0.5 ± 0.1*	0.96 ± 0.04*
Tetrachloroethylene	0.1 ± 0.1*	0.5 ± 0.1*	0.08 ± 0.03	0.090 ± 0.002
Butyl acetate	0.5 ± 0.4	0.5 ± 0.1	0.1 ± 0.1*	0.207 ± 0.004*
Ethylbenzene	13 ± 11*	31 ± 2*	0.8 ± 0.5*	1.7 ± 0.1*
n-Nonane	3 ± 4*	10 ± 2*	0.2 ± 0.1*	0.6 ± 0.1*
m + *p*-Xylene	64 ± 32	72 ± 5	0.9 ± 0.4*	2.4 ± 0.1*
Styrene	1 ± 1*	2.1 ± 0.1*	0.3 ± 0.5	0.39 ± 0.02
o-Xylene	17 ± 12	26 ± 1	3 ± 5*	0.75 ± 0.04*
n-Decane	5 ± 2	6 ± 1	1 ± 1	3.3 ± 0.4
1,2,4-Trimethylbenzene	18 ± 12*	34 ± 3*	2 ± 2*	2.6 ± 0.4*
p-Dichlorobenzene	1 ± 1	2 ± 1	0.03 ± 0.01*	0.06 ± 0.01*
n-Undecane	1 ± 1*	24 ± 11*	0.3 ± 0.7*	7.6 ± 0.2*

* Significant differences observed between the concentrations obtained from multi-sorbent bed and Radiello tubes (*t*-test, $p < 0.05$).

Table 7
Supplier and calculated Q_k values (ml min^{-1}) for the studied compounds ($n = 7$ for indoor and outdoor values, $n = 14$ for all values (indoor and outdoor values together)). Compounds are listed by elution order.

Compounds	Supplier Qk[a]	Calculated Q_k		
		Indoor air	Outdoor air	All values
tert-Butyl methyl ether	30.0	52.7 ± 15.4	63.0 ± 6.5	58.7 ± 12.1
n-Hexane	25.5	31.2 ± 6.3	14.3 ± 1.7	22.7 ± 9.7
1,1,1-Trichloroethane	20.0	–[b]	11.0 ± 4.5	11.0 ± 4.5
Cyclohexane	27.6	40.7 ± 14.8	21.9 ± 3.4	31.3 ± 14.3
Benzene	26.8	67.5 ± 27.3	58.6 ± 18.8	63.0 ± 23.7
n-Heptane	25.3	57.5 ± 18.9	44.5 ± 7.0	51.0 ± 15.6
Trichloroethylene	27.1	–	24.2 ± 6.6	24.2 ± 6.6
Toluene	30.0	32.3 ± 5.4	50.7 ± 9.6	41.5 ± 12.1
n-Octane	24.1	29.4 ± 6.9	42.7 ± 8.3	36.1 ± 10.1
Tetrachloroethylene	25.4	–	27.2 ± 2.9	27.2 ± 2.9
Butyl acetate	24.5	–	29.2 ± 8.4	29.2 ± 8.4
Ethylbenzene	25.7	57.1 ± 15.2	39.4 ± 8.8	48.3 ± 15.2
n-Nonane	21.0	64.0 ± 24.1	44.7 ± 10.4	54.3 ± 20.8
m + *p*-Xylene	26.6	32.9 ± 4.1	47.1 ± 11.0	40.0 ± 11.4
Styrene	27.1	62.8 ± 13.9	37.0 ± 13.8	48.9 ± 18.9
o-Xylene	24.6	47.4 ± 11.6	43.1 ± 8.4	45.2 ± 10.2
n-Decane	22.3	26.5 ± 9.9	26.8 ± 8.7	26.6 ± 9.2
1,2,4-Trimethylbenzene	21.9	38.6 ± 10.0	53.2 ± 17.9	45.9 ± 16.1
p-Dichlorobenzene	22.0	46.6 ± 22.2	–	46.6 ± 22.2
n-Undecane	12.0	–	–	–

[a] At 25 °C.
[b] The value could not be calculated due to the absence of trend between active and passive results.

by this passive methodology because the calibration curves could not be done properly, as other terpene compounds such as ocimene, camphene, tricyclene and α-phellandrene were identified in the Radiello® tubes that had been spiked only with α-pinene and limonene, suggesting rearrangement reactions. For some adsorbents, such as Tenax TA, it has been noticed that decomposition processes at the surface of the sorbent may degrade adsorbed analytes (e.g. terpenes) during the sample step, when the adsorption of the compounds occur, and during TD-GC analysis [12,47,48]. However, these drawbacks have been observed more often when carbon-type adsorbents are used [49]. In addition, the presence of ozone in ambient air has been found to induce decomposition of terpenes with one, two or more C–C double bonds [50]. The exposure of sorbents to ambient air concentrations of NO_2, O_3 and H_2O during sampling has also been determined as the cause of the decrease in the recovery of terpenes such as α-pinene and limonene [49].

4. Conclusions

The evaluation of the analytical performances of the two sampling approaches (active multi-sorbent bed and passive Radiello® tubes) shows that both methodologies have quite similar analytical behaviours. They display low limits of detection, good precision, accuracy and desorption efficiency, in addition to low levels of breakthrough for multi-sorbent bed tubes. Generally, however, only a few of the studied compounds do not show significant differences in the concentrations observed between the two different sampling methodologies, and the concentrations obtained with the

Radiello® samplers are higher. Furthermore, experimentally determined Q_k values are higher than those supplied by the producer. The suppliers generally calculate the Q_k values experimentally in exposure chambers, with only the target compounds present in the air samples, as well as in concentrations dissimilar from the ones found in ambient air. Hence, the use of constant settled Q_k can lead to inaccurate results in complex samples. It would be advisable to calculate the Q_k values depending on the study case to avoid overestimation of the results. More research is required in order to gain more knowledge of the Radiello® diffusive samplers and their uptake rate behaviour. Moreover, terpenes could not be evaluated properly due to decomposition processes produced during the analysis of the Radiello® samplers.

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