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Improvement of uptake rate equations depending on meteorological conditions for 25 volatile organic compounds

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ABSTRACT

Stainless steel passive (diffusive) sampling tubes manufactured by Gradko International Ltd. (UK) were filled with Chromosorb 106 (Supelco) and evaluated to determine the uptake rates of 31 VOCs over six months under different meteorological conditions in a suburban area of Ankara, Turkey. The URs have been calculated, and dependence on such meteorological parameters as temperature, relative humidity and wind speed has been established for the 31 VOCs.

The URs of the 31 VOCs measured in this study showed a statistically significant decreasing trend with rising temperature; and weaker, but again statistically significant, increasing trends with increasing relative humidity and wind speed. This study has demonstrated that the URs of VOCs are affected by meteorological parameters, and this dependence should be taken into account when attempting to generate reliable data through passive sampling. A multiple linear regression equation in which temperature, relative humidity and wind speed were used as independent variables was generated for 25 of the 31 tested VOCs.

1. Introduction

Over the past few years, concentrations of volatile organic compounds (VOCs) have increased, particularly in urban locations, due to increased industrialization and rise in population. The various VOCs in ambient air have been well documented, along with suspected mutagens [1], and have been shown to play an important role in the formation of tropospheric ozone and secondary organic particles, and in photochemical reactions [2].

The passive sampling method has been used widely as a cost-effective, simple-to-use and reliable technique for measuring ambient pollutants, and the principle of passive sampling is well established [3,4]. Although passive sampling offers several advantages, one particular drawback in its use is the difficulty of converting mass of VOCs collected on the adsorbent into concentration. An estimation of concentration can be made either theoretically, using Fick's Law, or experimentally, using "uptake rates" (UR) [2,5], as the following equation:

$$\mathrm{UR} = D \times (A/L) \qquad (1)$$

where D is the diffusion coefficient of the compound (cm^2 min^{-1}), A is the cross sectional area of the tube (cm^2) and L is the strength of the diffusion zone (cm).

The experimental approach is based on the URs of VOCs, which are calculated using co-located active and passive samplers, generally under controlled conditions in experimental chambers in laboratories [2,5]. To describe experimental uptake rate (L/min), differential equation derived from Fick's first law is used as follows:

$$\mathrm{UR} = (m_d - m_b)/c \times t \qquad (2)$$

where m_d is the adsorbed mass of compound (µg) during exposure time (t) (min), m_b is the mass of compound (µg) on non-exposed cartridge (a blank) and C (µg L^{-1}) is ambient concentration of the compound.

Significant differences were reported between the experimentally and theoretically calculated VOC concentrations [2,6,7]. Furthermore, VOCs uptake rates, determined in experimental chambers can also be different from URs calculated from collocated active and passive samplers in ambient air, owing to complex variations in meteorological conditions, which cannot be simulated precisely in an experimental chamber.

In this study, the URs of approximately 30 VOCs were determined using the data from collocated active (pumped) and passive samplers in ambient air under real atmospheric conditions, with field measurements conducted in a suburban area for six months. Variations in the URs of the VOCs were investigated as a function of air humidity, wind speed and temperature.

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2. Materials and methods

2.1. Sampling methodology

Active and passive sampling programs were implemented in parallel to determine the URs, with the passive sampling carried out over approximately seven days. The active sampling tubes were replaced with new ones twice a day at 8:30 am and 05:30 pm, and consequently, 14 sets of active samples were collected and analyzed for each set of weekly passive samples.

The study consisted of 26 weekly passive sampling periods. Since the objective of the study was to calculate the URs in real atmospheric conditions, a period that would include different meteorological conditions and both summer and winter climates was chosen for sampling. The field sampling was carried out in the first half of 2008.

Since passive sampling period was about seven days and active samples had to be taken twice a day, a lot of active sampling was performed for each passive set and the average of results obtained from these tubes were compared to the results from passive sampling tubes.

Because of the reasons stated above, it will be helpful to consider active and passive sampling as two distinct systems working in parallel to each other. The uptake rates on passive samplers (ml min^{-1}) were calculated as the ratio of the sorbed mass on the passive sampler (ng) to the exposure time (min) and the average concentration (ng ml^{-1}) obtained from simultaneous active sampling.

2.2. Study site

A sampling cabinet with no temperature control equipment, which was designed by Kuntasal [8], was used to house both the active and passive sampling. The cabinet was located in the Environmental Engineering Department of the Middle East Technical University (METU) Campus in Ankara, Turkey (39.89°N; 32.78°E), which is an area that can be defined as “suburban”. Since settlement and traffic in the METU campus is not very dense, the levels of pollutants measured at the station can be considered as “background” levels for the city of Ankara [8].

2.3. Sampling

The sampling tubes used for both active and passive measurements were filled with 160 mg of Chromosorb 106 (60/80 mesh) adsorbent. Weighing was performed in the laboratory using a 4-digit scale (Sartorius MODEL A210P). The filled tubes were conditioned at 250° C for 4 h using a conditioning oven designed by Kuntasal et al. [9] under a flow of high-purity nitrogen (50 mL min^{-1}). After conditioning, the adsorbent tubes were capped tightly and placed into sealed glass tubes, which were kept refrigerated until sampling.

The passive sampling tubes were placed in shelters and mounted in the active sampling cabinet, which enabled active and passive sampling to be carried out in close proximity to each other at a 20 cm distance. The active tubes were connected to a vacuum pump (SKC, model Universal); and the air flow was kept constant using an ALBORG model GFC171 mass flow controller (MFC).

2.4. Analytical method

After sampling, both the active and passive sampling tubes were analyzed using an Agilent, 6990 GC-FID, equipped with a Unity Thermal Desorption (Markes) System. The TD-GC-FID system was calibrated using a gas mix supplied by the Environment Technology Center (Ottawa, Canada) containing 148 individual VOCs with carbon numbers varying between 2 and 12. Although 148 VOCs ranging from C2 to C12 were identified by the GC-FID, during the calibration process, the Chromosorb 106, due to its sorbent characteristic, allowed for the determination of only those compounds ranging from C5 to C12. The retention time of the compounds was identified both with separated mix liquid VOC mixtures (aromatic, olefin, paraffin and BTEX liquid mixtures) and gas phase mixtures. The surrogate standard, 4-bromofluorobenzene, was loaded in all tubes before sampling. Sample tubes were checked by calculating peak areas before and at the end of the sampling. The difference did not exceed 10% in this study.

Both the active and passive sampling tubes were desorbed at 250 °C for 5 min with a 50 mL min^{-1} flow. Further details on the GC operation parameters are presented in Table 1.

2.5. QA/QC procedure

An extensive QA/QC program, including an estimation of detection limits, precision, blanks, storage stability, desorption efficiency was included in the study. Since two different sampling systems (active and passive) were implemented in the field, different validation procedures were applied in the sampling methodology. The performance characteristics of the passive sampling tube for outdoor measurements were evaluated in accordance with EN-13528-1 and EN13528-2 protocols [10]. The evaluation of the active sampling tubes, on the other hand, was carried out in accordance with TO-17 [11]; however the method was modified slightly when necessary during the experimental studies. The performance parameters such as method detection limit (MDL), desorption efficiency and precision were evaluated for the analytical system. The values of some of the performance parameters for selected VOCs are given in Table 2 and described in detail as follows.

The method detection limit (MDL) for each VOC was calculated from seven replicate measurements of a low concentration sample. Standard deviation values for the seven replicate concentrations were computed and multiplied by Student’s *t*-value for 99% confidence for seven replicate. The detection limit values, which are given in Table 2, were recorded in orders of magnitude that were smaller than the concentrations found in the samples, as expected.

The thermal desorption efficiency was determined by loading sampling tubes with gas phase VOC mixtures containing an 1–13 ng tube^{-1} of each analyte and analyzing them immediately after loading. The thermal desorption efficiency was found to be higher than 95% for all VOCs, aside from methylcyclopentane+2,4-dimethylpetane and m+p-chlorotoluene, which had desorption efficiencies of 85% and 74% respectively. The precision of the method was determined in different ways, including through a replicate analysis of sampling tubes left in the field for one week, and a replicate analysis of the preloaded tubes. The values in Table 2 were obtained from six replicate analyses of tubes preloaded with

Table 1
Gas chromatography system parameters.

Parameter	Value
Carrier gas	Nitrogen
Column	DB-1 (60 m χ 0.32 mm χ 1 μm)
Column flow rate	5.2 mL min^{-1}
Oven temp. program	40 °C hold for 5 min 5 °C/min to 195 °C Hold 10 min

Table 2
Selected method performance parameters for measured VOCs.

Compound name	Anaytical system			Active sampling			Passive sampling		
	MDL ($\mu g\ m^{-3}$)	Desorption efficiency (%)	Precison (%)	Average sample (ng)	Field blank (ng)	Sample/field blank	Average sample (ng)	Field blank (ng)	Sample/field blank
Methylcyclopentane + 2, 4-dimethylpentane	0.05	85.64	2.18	2.3	N.D.	–	1.26	N.D.	–
Benzene	0.05	96.87	1.35	20.88	0.12	174	11.4	0.74	15.40
Cyclohexane + cyclohexene	0.18	100	3.17	2.2	N.D.	–	2.85	N.D.	–
2-Methylhexane	0.06	98.54	4.58	2.3	N.D.	–	1.68	N.D.	–
2,2,3-Trimethylbutane + 2, 3-dimethylpentane	0.06	100	4.34	1.05	N.D.	–	1.23	N.D.	–
3-Methylhexane	0.06	100	3.42	4.02	N.D.	–	2.44	0.23	10.60
1-Heptene	0.06	96	7.81	0.57	N.D.	–	0.67	N.D.	–
2,2,4-Trimethylpentane	0.04	95	6.35	0.86	N.D.	–	0.91	0.09	10.11
n-Heptane + cis-3-heptene	0.06	100	5.22	2.97	N.D.	–	1.91	N.D.	–
Methylcyclohexane	0.06	100	5.48	0.86	N.D.	–	0.44	N.D.	–
Toluene	0.06	94.87	5.85	75.59	N.D.	–	43.46	0.53	82.00
Remaining 19 VOCs	0.01–0.08	75–99	4.2–10.6	1.15–8.1	N.D	–	0.2–10.6	ND–0.4	10–40

N.D.: not detected.

1–13 ng of each analyte. The relative standard deviation was less than 10% for all of the compounds measured in the study.

Two laboratory blanks, comprising unexposed tubes filled with adsorbent, were run on each analysis day to test for the potential contamination of samples after entry to the laboratory. No significant VOC levels were detected in any of these lab blanks.

The field blanks from the passive sampling were left in the field together with real samples for one week; at no point were their caps removed. The active field blanks were left at the site with their caps removed for 5 min, after which the caps were replaced. During the field study, 26 field blanks for passive sampling and 52 tubes for active sampling were analyzed. Since the field blanks were slightly higher than the laboratory blanks the sample chromatograms were corrected for the field blanks.

Both the laboratory and field blank values are given in Table 2, along with the sample-to-blank ratios. In the active sampling the VOC concentrations in the field blanks were below the detection limit for all VOCs. Some of the VOCs had detectable field blank values in the passive samplers, however the sample to blank ratios for all of these VOCs was >10, indicating that the blanks did not contribute significantly to uncertainties in the active and passive VOC samplings.

Breakthrough tests were performed prior to the study by combining three tubes in series. No VOCs were detected in any of the second or third tubes at the end of the 12-h sampling. Two tubes in the series were used in the active sampling throughout the study and both tubes were analyzed, however no VOCs were detected in the second tube in any of the active sampling periods.

Table 3
Calculated average uptake rates of VOCs and their standard deviations.

No	**Compound name**	**Average URs** ($mL\ min^{-1}$)	**S.D.**	**Weekly avg. S.D.**
1	Methylcyclopentane + 2, 4-dimethylpentane	0.33	0.16	0.03
2	Benzene	0.39	0.15	0.03
3	Cyclohexane + cyclohexene	0.41	0.18	0.04
4	2-Methylhexane	0.45	0.15	0.03
5	2,2,3-Trimethylbutane + 2, 3-dimethylpentane	0.51	0.22	0.04
6	3-Methylhexane	0.41	0.23	0.05
7	1-Heptene	0.44	0.25	0.05
8	2,2,4-Trimethylpentane	0.41	0.25	0.06
9	n-Heptane + cis-3-heptene	0.45	0.20	0.06
10	Methylcyclohexane	0.44	0.20	0.06
11	Toluene	0.44	0.13	0.02
12	2-Methylheptane	0.46	0.20	0.06
13	m + p-Chlorotoluene	0.49	0.19	0.06
14	4 + 3-Methylheptane	0.37	0.16	0.06
15	t + c-1,3-DiMethylcyclohexane	0.70	0.76	0.10
16	Octane	0.45	0.28	0.05
17	2,2,5-Trimethylhexane + 1,2, 4-trimethylcyclohexane	0.53	0.32	0.06
18	Ethylbenzene	0.39	0.15	0.03
19	m + p-Xylene	0.40	0.12	0.02
20	Styrene	0.37	0.31	0.05
21	1-Nonene	0.37	0.24	0.07
22	o-xylene	0.35	0.11	0.04
23	n-Nonane	0.39	0.19	0.05
24	Isopropylbenzene	0.61	0.04	0.05
25	n-Propylbenzene	0.40	0.19	0.06
26	3-Ethyltoluene	0.36	0.13	0.06
27	4-Ethyltoluene	0.38	0.16	0.06
28	1,3,5-Trimethylbenzene	0.36	0.09	0.06
29	2-Ethyltoluene	0.35	0.13	0.07
30	1,2,4-Trimethylbenzene	0.41	0.14	0.07
31	n-Decane	0.34	0.17	0.06

3. Results and discussions

The fifty-five target VOCs were monitored during the analysis of the passive and active tubes. The URs were calculated for compounds having concentration higher than the detection limits in passive tubes during six months. This provided dataset of real environmental uptake rates for thirty one VOCs. The average URs of the VOCs measured in this study and their standard deviations (SDs) are presented in Table 3. Standard deviations of URs represented in the table were calculated in two different ways. First SDs were calculated by taking average of all URs generated during sampling campaign. In the second approach, with weekly average SDs, average values of each SDs calculated replicate measurements taken each week. This table is important part of the study, in that it constitutes one of the largest compilations of VOC uptake rates in the literature to date. The URs shown in the table vary between 0.33 and 0.70 mL min^{-1}, which is due to the different affinities of VOCs to the adsorbent used, and the different diffusion rates of the VOCs.

A point worthy of note in Table 3 is the relatively high levels of standard deviation of the URs, which vary between 6% for nonane, and 103% for 1,3-dimethylcyclohexane, indicating a fairly high variability in UR values for all VOCs. However, it should be noted that the standard deviations of URs calculated using data generated from replicate measurements taken each week are significantly smaller than the variability of URs calculated using pooled data. The weekly averages SDs varied between 5% for toluene and 19% for 1-nonene. This difference is shown in Fig. 1, where the coefficients of variations (CV) calculated from the pooled data and from the weekly replicate measurements are plotted. The coefficient of the variation, which is calculated by dividing the arithmetic standard deviation by the arithmetic mean (σ/x), is a simple way of understanding the reproducibility of the data set.

The coefficient of variation in Fig. 1 was calculated in two different ways. First, it was calculated separately for each of the weekly runs (generally seven parallel passive tubes were deployed each week). Then average CV values for all the weeks were calculated, depicted in left side of the bar graph for each compound. In the same figure, the CV calculated from the pooled data is also showed in right site of the bar graph for each compound. For this, the average UR and its standard deviation for all passive tubes and for all weeks were calculated, and the CV of VOCs were calculated by dividing the σ of all data by the mean of all data (the σ given in Table 3 is divided by the mean values of VOCs given in the same table). The figure demonstrates clearly that the CV of the VOCs calculated from the pooled data is considerably higher than the corresponding CV values obtained from the replicate measurements each week. The CV values from weekly replicates vary between 0.029 for o-xylene and 0.19 for 2,2,4-trimethylpentane, whereas the values of CV calculated from the pooled data vary between 0.30 for toluene and 0.84 for styrene. The difference in CV values indicates that the UR values calculated from seven replicate measurements each week are highly reproducible; however the week-to-week variations are large. The URs of VOCs are reliant on a number of meteorological and non-meteorological parameters, such as wind speed, relative humidity, sampling period, etc., and since these parameters may vary significantly from one week to the next, the calculated URs are also subject to these variations. The observed week-to-week variability in the URs of VOCs is an indication of the need to investigate the dependence of URs on meteorological and other factors, and shows that the use of the diffusion coefficients in literature using Fick's Law, which disregards meteorology, may lead to a high uncertainty in passive measurements.

The average URs for the BTEX compounds that were calculated in this study are compared with the corresponding values reported in previous literature in Table 4. Since there are limited URs studies that have used Chromosorb 106 as adsorbent, literature has been compiled for all different types of adsorbents. The comparison is also confined to BTEX compounds, because the URs of other VOCs are scarce in literature.

3.1. Variation uptake rates with sampling durations

Although there is no consensus on the dependence of passive sampling efficiency on sampling time, there is considerable literature stating that such a relation does exist, and that collection efficiency decreases beyond a certain time threshold. This is attributed to desorption of VOC molecules that were initially adsorbed on the adsorbent [12]; however, there is no agreement on the threshold time. Whatever the reason, and regardless of the

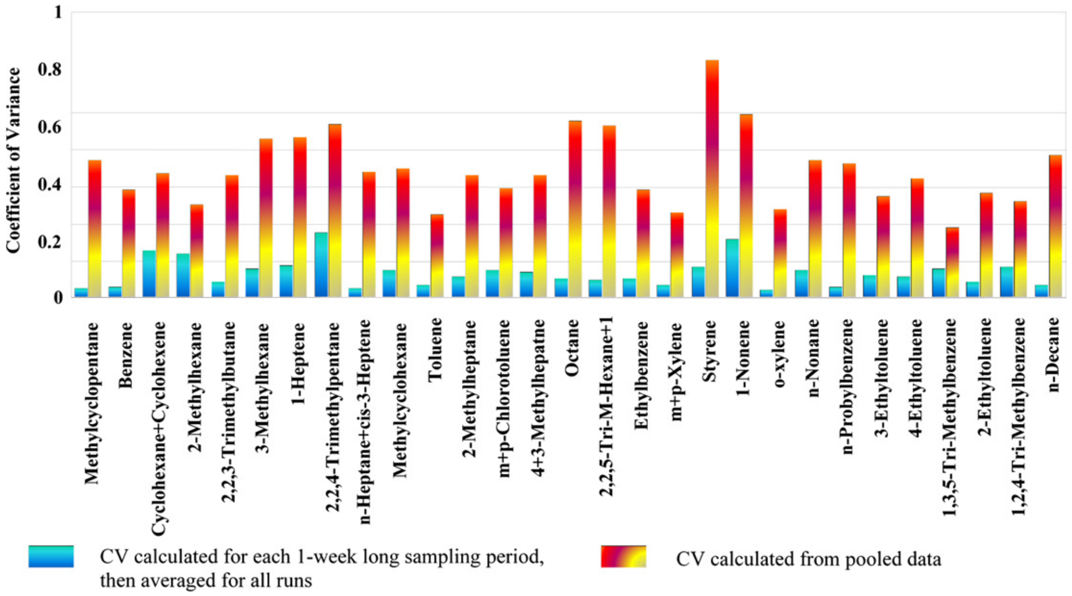

Fig. 1. Coefficient of variance calculated for each set of measurements and for pooled data.

Table 4
Comparison of the BTEX average uptake rates (mL min^{-1}) calculated in this study with the literature.

Compound name	This study	Mowrer et al. [15]	Martin et al.* [16]	Roche et all.* [19]	Hellen et al. [20]	ISO/DIS 16017-2 [21]	Oury et al. [22]	Tolnai et al.* [7]
Benzene	0.39	0.41	0.46 ± 0.10	0.57	0.68 ± 0.19	0.63 ± 0.07	0.27	0.57-0.61
Toluene	0.44	0.45	0.52 ± 0.13	0.51	0.62 ± 0.14	0.56 ± 0.06	0.37	0.42-0.49
Ethylbenzene	0.39	0.55	–	0.45	0.55 ± 0.09	0.5	–	0.51-0.54
m+p-Xylene	0.40	0.55	–	0.43*	0.53 ± 0.10	0.47 ± 0.04	0.42**	0.41-0.58**
o-Xylene	0.35	0.55	0.48 ± 0.11	0.43	0.53 ± 0.10	0.47 ± 0.04	–	0.41-0.48

* Uptake rates values converted from ng ppm^{-1} mL^{-1} to mL min^{-1} using the equation mL min^{-1}=ng ppm^{-1} mL^{-1} × molecular weight^{-1} (mol g^{-1}) × 24.45 l mol^{-1} [15].

** Uptake rate calculated for either m-xylene or p-xylene.

threshold sampling time, if the efficiency of passive sampling decreases over time, then the URs should also decrease in parallel. This possibility of collection efficiency and uptake rate changing over time was investigated in the current study. At the beginning of the sampling 30 passive sampling tubes were co-located with active sampling tubes, and the batch of five samples tubes (quintuple) were taken after 1, 3, 5, 7, 14 and 21 days exposure and analyzed immediately after sampling. The sampling periods varied between 3 and 21 days were repeated 4 times. The uptake rates calculated from different exposure periods and the concentrations calculated using the corresponding uptake rate values for different exposure periods are presented in Fig. 2 for four selected VOCs. The behaviors of remaining VOCs were found to be not significantly different. As can be clearly seen in Fig. 2, URs (and thus concentrations) of VOCs decrease with time. Although the number of data points is small (26), the decrease is statistically significant at a 95% confidence level. The URs of all VOCs did not change significantly in the first week to 10 days, after which a decrease was recorded, and continued to decrease until the exercise was terminated after 21 days. No leveling off was observed either in the concentrations or the URs in the 21 day of the exercise.

Passive sampling is based on molecular diffusion [13] and subsequent adsorption onto the collection media; however adsorption is always accompanied by desorption of VOC molecules from the adsorbent. In the beginning, adsorption overwhelms desorption, and thus VOC mass increases in the passive tube. Desorption gradually increases with increasing VOC mass on the adsorbent and the accumulation of VOCs on the passive sampler slows down. The URs (and concentrations) of VOCs start to decrease when the desorption of analyte molecules from the sampler exceed their adsorption from air [7,14]. The behaviors of the VOCs observed in this exercise suggest that the passive sampling time should be kept below 7–10 days, and VOC concentrations found as a result of sampling periods >20 days may not be a true representation of VOC concentrations in the atmosphere by a factor of 3 to 4.

3.2. Variation uptake rates with meteorological parameters

Changes in uptake rates in passive samplers were investigated as a result of changes in temperature, wind velocity and humidity. As the sampling was carried out between January and July, a reasonable variation in meteorological conditions was experienced during the study. The meteorological parameters included in this study are temperature (T), relative humidity (RH) and wind speed (WS), which are quoted as having the greatest effect on URs [2,4,15]. Hourly data on wind speeds, relative humidity and temperature, obtained from the nearest meteorology station (General Directorate of Meteorology, unpublished data), are presented in Fig. 3.

The weekly average temperature varied between -1 °C and $+20$ °C, during the study, which is typical for Ankara; while the weekly average relative humidity and wind speeds varied between 50% and 86%, and $<1.0\ \mathrm{m\,s^{-1}}$ and $3.0\ \mathrm{m\,s^{-1}}$, respectively. The hourly T, RH and WS were sometimes significantly lower or higher than the average values shown in Fig. 3a, b and c respectively. The comparison of the hourly average values recorded during our study with the typical monthly temperatures measured at the same station between 1975 and 2007 is shown in Fig. 3d. The hourly average values of temperature during the sampling period are indicated with zigzag pattern while the horizontal line shows the long term monthly average temperatures. It is clear that the temperatures measured during the sampling period deviated little from the long-term temperature data obtained from the Ankara Etimesgut meteorological station

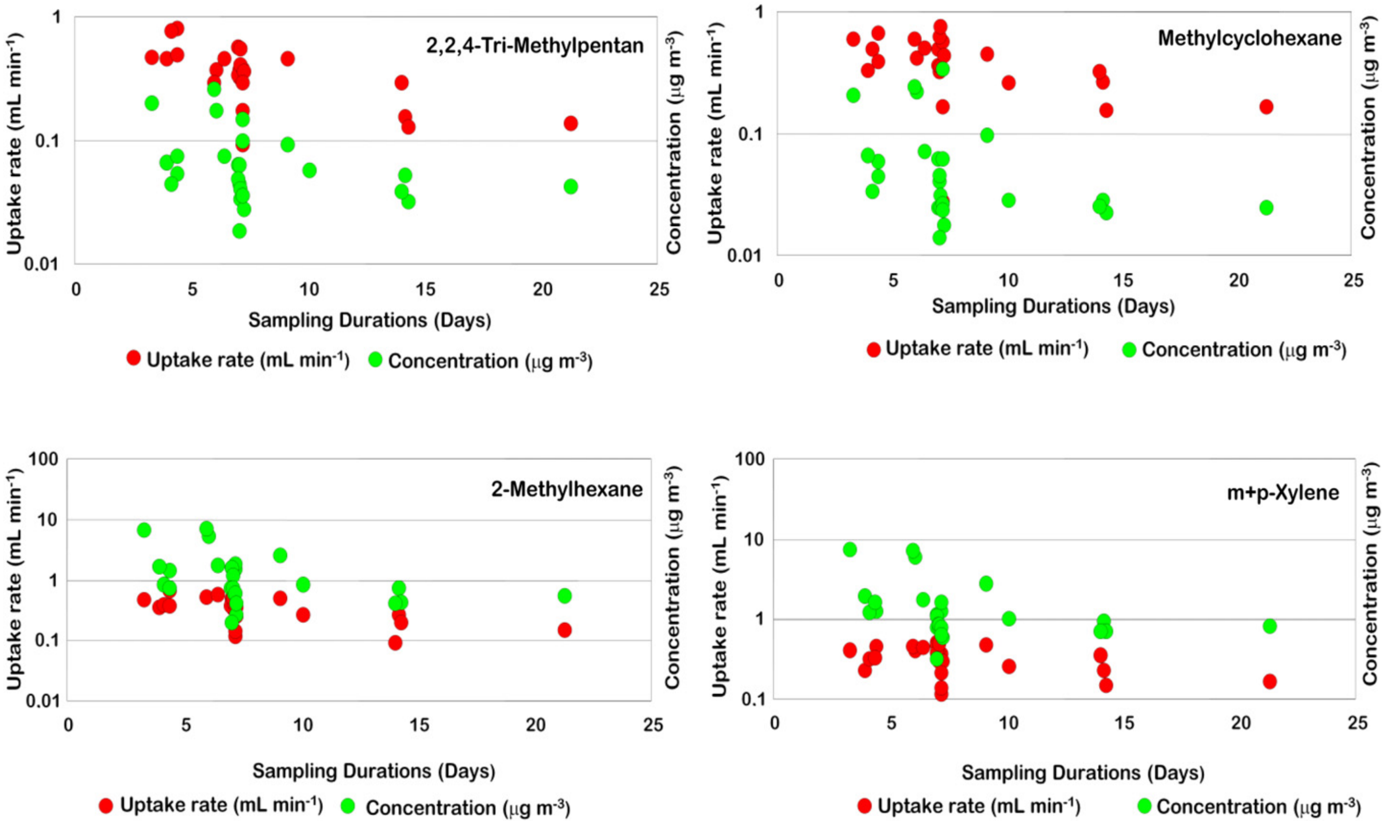

Fig. 2. The relationship among the UR, concentration and sampling period.

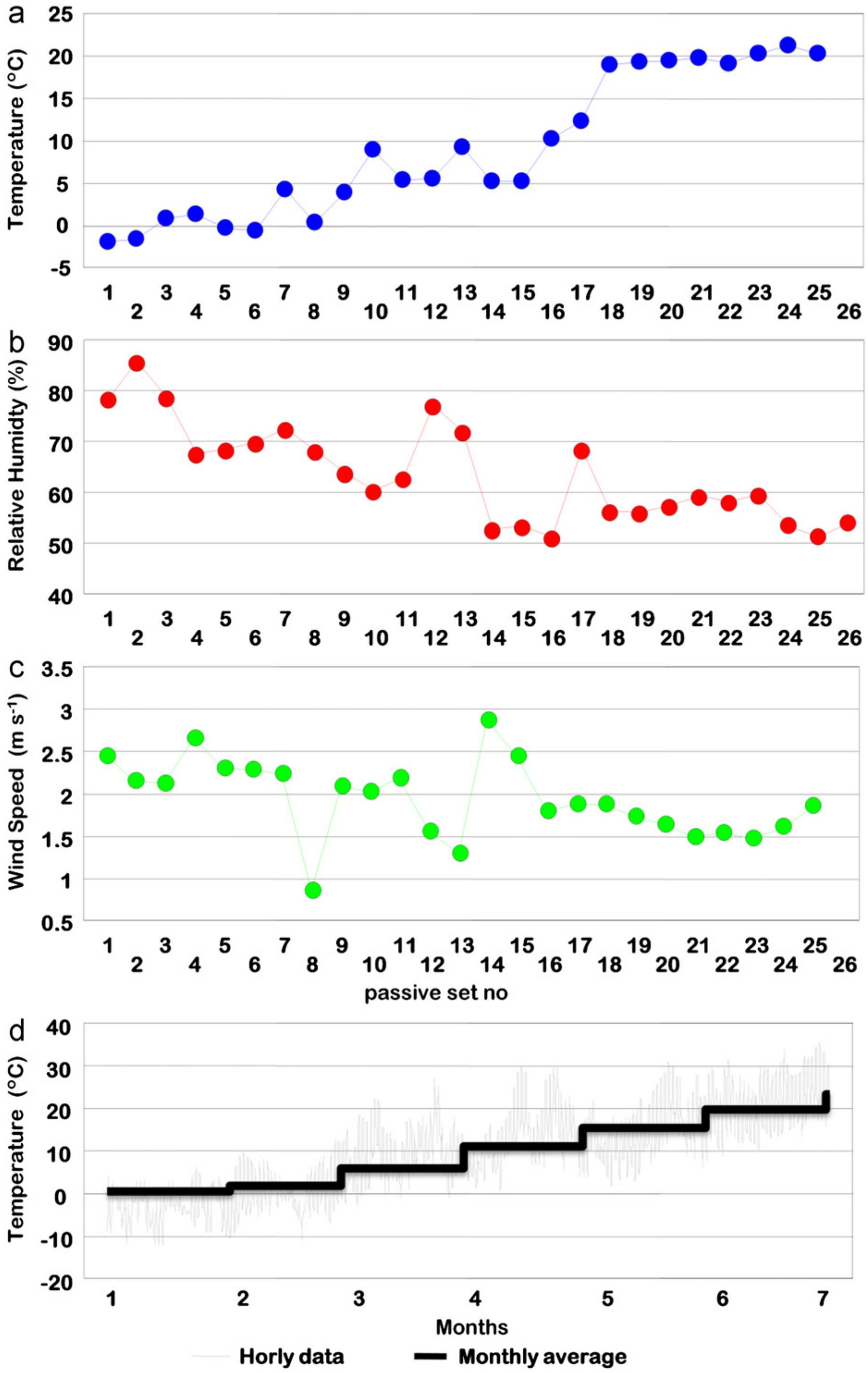

Fig. 3. Meteorological conditions during the study.

(39.57°N; 32.41°E); and the variations in relative humidity and wind speed were also similar.

3.2.1. *Effect of temperature on uptake rates*

The variations in URs of four selected compounds as a result of changes in temperature are depicted in Fig. 4. The URs of all of the VOCs measured in this study (31 in number) decreased with increasing temperature. For four of the VOCs, namely 2,2,3-thrimethylbutane + 2,3-dimethylpentane, n-heptane + cis-3-heptene, 2-m-heptane and isopropylbenzene, the regression equation was statistically significant at a 90% confidence interval. For five of the VOCs (cylohexane + cylohexene, m + p-chlorotoluene, n-nonane, n-propylbenzene and n-decane) the regression relationships between their URs and temperature were statistically significant at a 95% confidence interval; while the regression equations for the remaining 14 VOCs are statistically significant at a 99% confidence interval. This demonstrates clearly that the URs for 23 out of 31 VOCs showed a statistically significant negative relation with temperature. Although the URs of the remaining eight VOCs also decreased with increasing temperature, the regression equation is not statistically significant, with confidence $>90\%$.

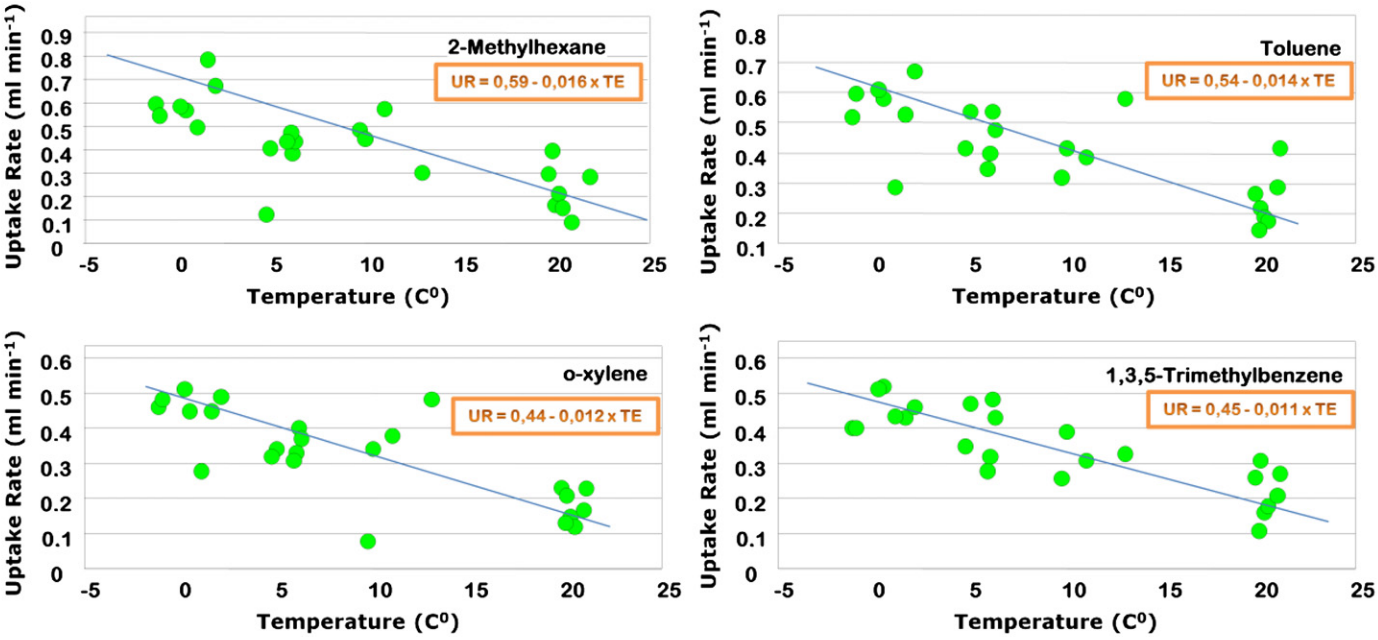

Fig. 4. The relationship between temperature and uptake rates for selected compounds.

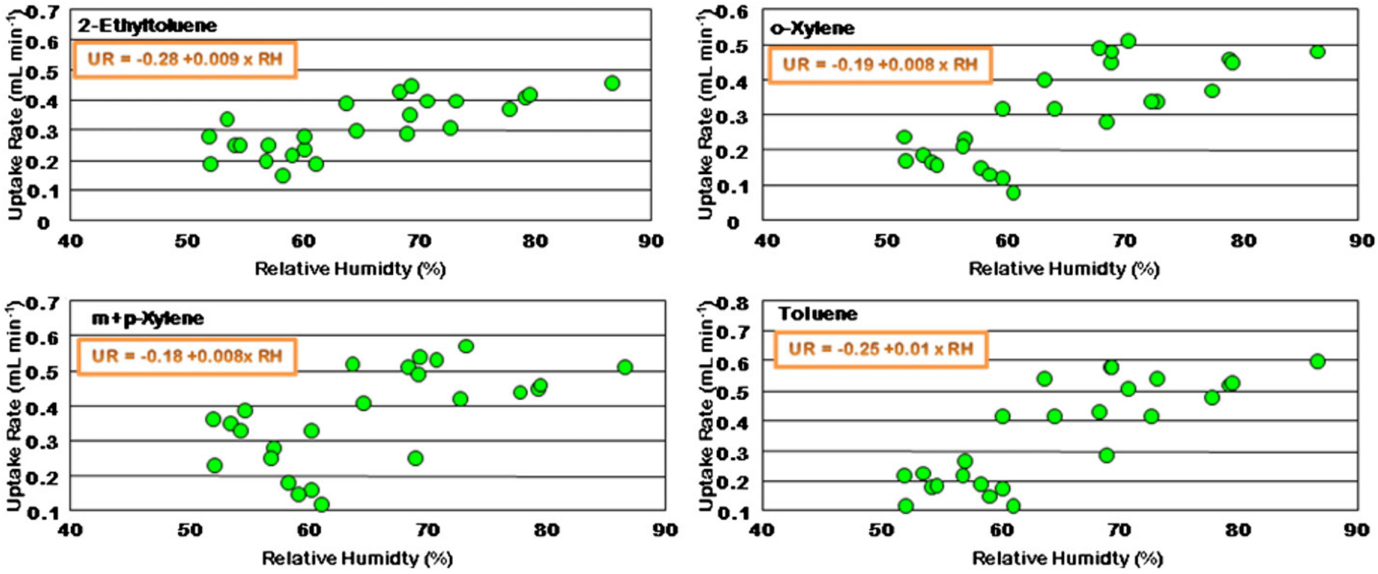

Fig. 5. Variation of uptake rates with relative humidity for selected compounds.

The relationship between UR and temperature is relatively strong (statistically significant at $>99\%$ confidence interval) for the VOCs with well-defined and relatively large (easy to integrate) peaks in the chromatogram. On the other hand, the relationship between UR and temperature is weak if the peak of those particular VOCs in the chromatogram is small and measured with relatively high analytical uncertainty. Although this may be mere coincidence, it may be that the lack of a statistically significant correlation between UR and temperature in these eight VOCs is due to the relatively high uncertainty in measurements of these trace species; and the situation may change if larger quantities of data were used in the regression.

3.2.2. *Effect of relative humidity and wind speed on uptake rates*

The relationship between UR and relative humidity and wind speed are presented in Figs. 5 and 6 respectively, in which it can be seen that the URs of VOCs increased with increasing relative humidity and wind speed.

This behavior is opposite to that observed between URs and temperature. Another point noted in this discussion is that the relationship between URs and these two meteorological parameters are not as strong as the correlation between URs and temperature; however, 19 and 15 of the 31 VOC URs showed statistically significant correlations with relative humidity and wind speed respectively (with 90% and higher confidence).

Although the data suggested a statistically significant correlation between UR and WS, it should be noted that Ankara is a relatively windless city. Approximately 57% of the hourly wind speeds measured during study were lower than 1.0 m s^{-1}, which corresponds to "calm" conditions in meteorology. Such a low wind speed is typical for Ankara and is not specific to our sampling period, but because of general low wind speed in Ankara it was not possible to study the effect of high winds on the UR.

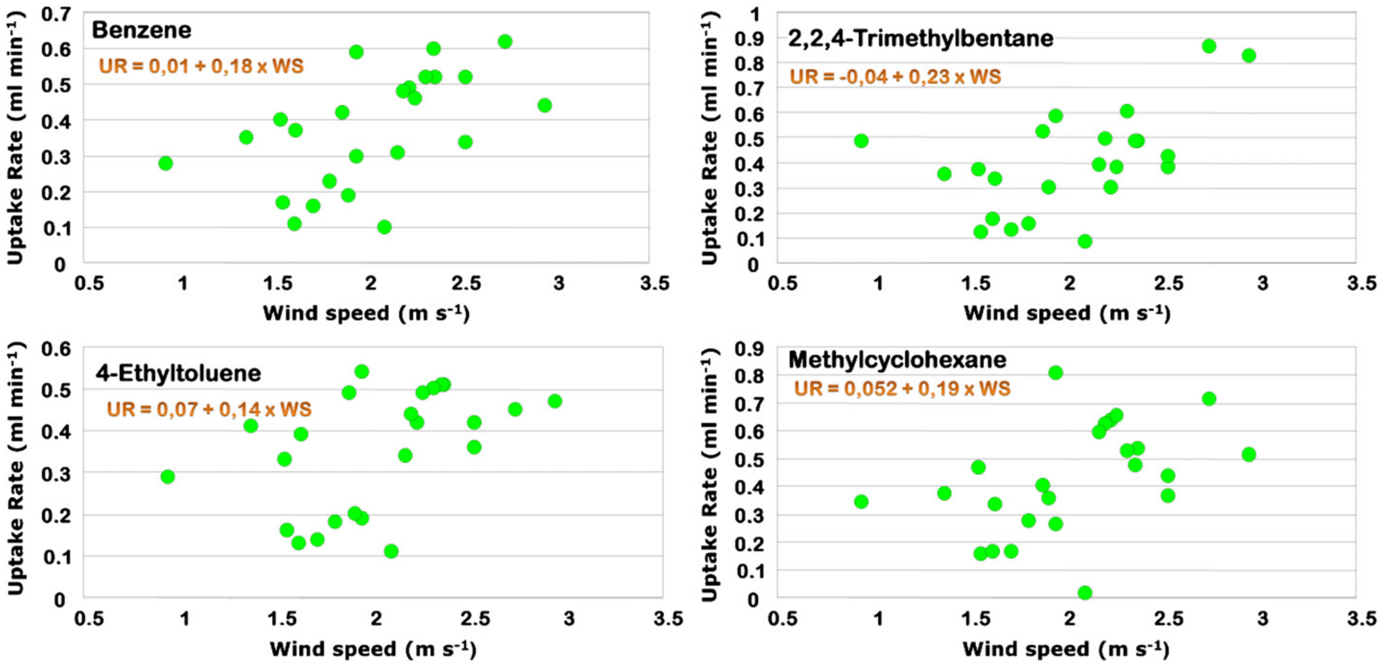

Fig. 6. Variation of uptake rates with wind speed for selected VOCs.

Although the variability in the wind speed was not high enough for a complete investigation of the dependence of URs on WS, even small variations in WS resulted in a statistically significant relationship with the URs of 15 VOCs.

The URs of the 31 VOCs measured in this study showed a general decreasing trend with increasing temperature; and a weaker, but statistically significant increasing trend with increasing relative humidity and wind speed. These findings are in general agreement with the limited studies in literature, conducted either in an exposure chamber or in the field. For example, Ballach et al. [4] observed a negative correlation between the URs of benzene and temperature due to the dependency of the diffusion coefficient on temperature. In this study, a 30% increase of URs was observed between 0.5 and 4.4 m s^{-1} air flows. Cardinala et al. [12] reported that the URs decreased under weak wind speeds, and increased at high wind speeds. An increase in the URs of TEX occurred with increases in temperature, while the benzene UR decreased under the same conditions. Martin et al. [16] carried out experiments to evaluate the benzene URs for Chromosorb 106 in a controlled atmosphere, concluding that there is a negative temperature dependence of the UR of $-2.5\%\ K^{-1}$ due to back diffusion.

3.2.3. *The statistical relationship between uptake rates and the meteorological conditions*

The VOCs can be separated into three groups based on the relationship between their URs and meteorological parameters. The first group consisted of benzene, 2-methylhexane, cyclohexane+cyclohexene, 2,2,4-trimethylpentane, n-heptane+cis-3-heptene, methylcyclohexane, toluene, 2-methylheptane, ethylbenzene, m+p-xylene, o-xylene, n-probylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene and n-decane. The URs of these 18 VOCs showed statistically significant correlations with all three meteorological parameters with $\geq 90\%$ confidence, and were found to be sensitive to variations in temperature, relative humidity and wind speed.

Among these, the URs of cyclohexane+cyclohexene, 2-methylheptane, 1,2,4-trimethylbenzene and n-decane showed a statistically significant relationship with temperature and humidity at $>95\%$ confidence, but their correlation with wind speed was not statistically significant in the same confidence interval. These three VOCs have been included in the second group as a result of the lack of correlation between the UR and wind speed may be due to small variations in the wind speed during the study period, as discussed previously in the manuscript.

The second group consisted of four VOCs: 2,2,3-trimethylbutane+2,3-dimethylpentane, m+p-chlorotoluene, styrene and n-nonane. The URs of these compounds were not sensitive to variations in relative humidity and wind speed, in that the URs showed a statistically significant correlation with temperature, but not with relative humidity and wind speed, at a $\geq 0.90\%$ confidence level.

The third group consisted of eight VOCs: methylcyclopentane+2,4-dimethylpentane, 3-methylhexane, 1-heptene, 4+3-methylheptane, t+c-1,3-dimethylcyclohexane, octane, 2,2,5-trimethylhexane+1,2,4-trimethylcyclohexane and isopropylbenzene. Although the variations in the URs of these VOCs with temperature, humidity and wind speed were in general agreement with the corresponding variations in other VOCs (i.e. their URs increase with increasing temperature and decrease with relative humidity and wind speed), the correlations were not statistically significant, with confidence of $\geq 90\%$.

The URs of the VOCs in the first group all demonstrated a strong dependence on temperature wind speed and relative humidity, which accounted for 48–100% of the variances in the URs of VOCs in this group—much higher than the dependences observed in the other two groups.

Only a small fraction of the variance (between 2% and 24%) in the URs of the VOCs included in the second and third groups can be explained by temperature, wind speed and relative humidity. The only exception to this general trend is observed for the URs of styrene and isopropylbenzene, for which the higher fractions of the variances in their URs may be explained in particular by temperature.

In summary, the inclusion of meteorological factors in the uptake rate and concentration calculations in passive sampling can significantly reduce the uncertainty of data for at least some of the VOCs. It should also be noted that the dependence of VOC URs on meteorology is not the same for all organic compounds.

3.3. Calculation of uptake rates through the use of multiple linear regression

It has been demonstrated clearly in the previous section that URs of most of the VOCs are affected by meteorological parameters, meaning that the values of these parameters should be taken into account in future field studies to determine URs, and thus concentrations. Since the URs of VOCs depend on up to three meteorological parameters investigated in this study, a multiple linear regression approach is obviously needed to determine the value of the UR, to include the effects of temperature, relative humidity and wind speed.

Such a relationship for each VOC is established through a multiple linear regression (MLR) exercise, in which UR is used as a dependent variable; and temperature, relative humidity and wind speed are used as independent variables. Once the MLR expressions are calculated for each VOC, then the URs for a particular sampling campaign can be calculated through the insertion of the temperature, humidity and wind speed data measured during the sampling period. Finally, the UR value, which will be specific for that sampling period, can be used to calculate concentrations of VOCs.

The regression equation for each VOC calculated in the MLR study is given in Table 5. In the MLR study, meteorological parameters, particularly temperature and relative humidity, were found to be auto-correlated, and these two parameters were standardized using the methods developed by Berry and Feldman [17] and Menard [18]. The standardized variables were used in the MLR; and standardization was achieved by calculating the averages of the temperature and relative humidity values and subtracting each value from the average. These standardized temperatures and wind speeds are no longer auto-correlated.

Although 31 VOCs were measured in this study, regression equations are given for only 25, as the statistical r^2 values for the regression equations calculated for the remaining six VOCs were not significantly correlated with any of the three meteorological parameters at a $\geq 90\%$ confidence interval.

3.4. Comparison of the use of regression equations, average uptake rate and Ficks law on measured concentrations of VOCs

It can be stated that the URs of VOCs depend on meteorological parameters, and this dependence should be taken into account when attempting to generate reliable data in passive measurements. However, using measurements based on an MLR approach, as explained in this section, is more difficult than using the simple Fick's Law or average URs, in that the URs need to be calculated using meteorological data for every measurement campaign. If the difference between concentrations calculated using Fick's Law is not substantially different to the concentrations calculated using the MLR approach, then it may be feasible to use Fick's Law and accept the slight error it produces. However, if the concentrations calculated using these two approaches are significantly different from each other, then it may be worthwhile to calculate URs in each campaign using meteorological data and the regression equations given in Table 5.

After the uptake rate study was completed, a new sampling location, again on the university campus but at a different site, was selected to test the magnitude of the influence of meteorology on uptake rates and also the concentrations. At this new sampling location, active and weekly passive VOCs measurements were carried out in June 2008. Active measurement results were used as a reference value. Ambient concentrations were calculated with UR values obtained from different methodologies and these concentration values were compared to the concentrations measured with active sampling in order to investigate the effects of meteorological parameters (WS, *T*, RH) on concentration. Three different URs values are (1) experimentally determined average URs, (2) ideal URs, which is calculated based on Fick's first law of diffusion and sampler geometry and (3) UR values calculated using from MLR approach using the regression equations given in Table 5 and the temperature, relative humidity and wind speeds measured at the new sampling station during the one week sampling campaign. Ideal UR values for VOCs are calculated by the formula of Lugg [23]. Since it was impractical to attempt to demonstrate this effect for all of the 31 VOCs, BTEX were selected. The behaviors of remaining VOCs were not significantly different. The concentration results of this comparison exercise for BTEX compounds are given in Fig. 7.

The most striking result of this exercise was the significant differences in concentrations found using the different approaches. The concentrations of BTEX calculated using the MLR equations and

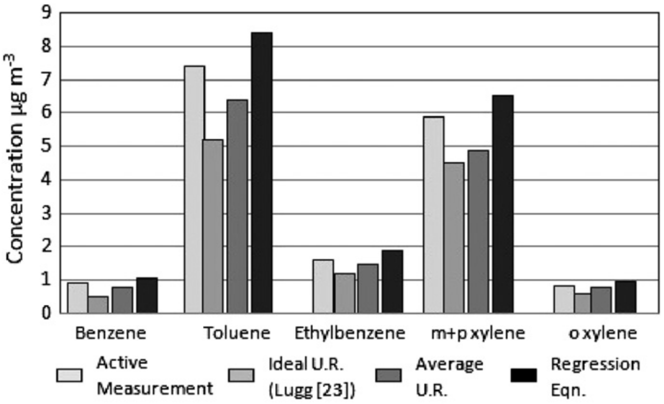

Fig. 7. BTEX concentrations calculated using different methodical approaches.

Table 5
Multiple linear regression equations of the uptake rates depend on the meteorology by means of relative humidity (RH), temperature (*T*) and wind speed (WS).

No	Equations depending on meteorology	R^2	No	Equations depending on meteorology	R^2
1	$-0.048+0.006\mathrm{RH}$	0.265	18	$-0.332+0.007\mathrm{RH}+0.117\mathrm{WS}$	0.408
2	$-0.519+0.008\mathrm{RH}+0.173\mathrm{WS}$	0.544	19	$-0.432+0.008\mathrm{RH}+0.135\mathrm{WS}$	0.561
3	$-0.74+0.013\mathrm{RH}+0.154\mathrm{WS}$	0.417	20	$0.506–0.019T$	0.486
4	$-0.661+0.011\mathrm{RH}+0.191\mathrm{WS}$	0.534	22	$-0.417+0.008\mathrm{RH}+0.12\mathrm{WS}$	0.566
5	$-0.602+0.011\mathrm{RH}+0.173\mathrm{WS}$	0.454	23	$0.479–0.011T$	0.189
6	$-0.362+0.007\mathrm{RH}+0.161\mathrm{WS}$	0.436	25	$-0.299+0.006\mathrm{RH}+0.133\mathrm{WS}$	0.301
8	$-0.04+0.226\mathrm{WS}$	0.271	26	$-0.249+0.006\mathrm{RH}+0.101\mathrm{WS}$	0.377
9	$0.257–0.01T+0.131\mathrm{WS}$	0.565	27	$0.468–0.011T$	0.433
10	$-0.482+0.009\mathrm{RH}+0.183\mathrm{WS}$	0.380	28	$-0.376+0.008\mathrm{RH}+0.103\mathrm{WS}$	0.495
11	$-0.572+0.01\mathrm{RH}+0.165\mathrm{WS}$	0.616	29	$-0.547+0.009\mathrm{RH}+0.14\mathrm{RH}$	0.571
12	$-0.01+0.008\mathrm{RH}$	0.238	30	$0.486–0.011T$	0.363
13	$0.599–0.014T$	0.388	31	$0.398–0.007T$	0.234
17	$0.667–0.015T$	0.220			

meteorological data for that sampling period and for that station were 30% higher than the corresponding concentrations found using the average URs, and approximately 60% higher than the concentrations found using Fick's Law. The concentrations of BTEX found using the average URs of BTEX were only 10–20% higher than the concentrations found using Fick's Law.

The concentration calculated using ideal URs were found lowest value compared to their URs approach. Hence the uses of ideal uptake rates underestimate BTEX concentrations by a factor of half. Furthermore, the measured concentrations of VOCs obtained from the MLR approach were found to be very similar, being only 10–15% higher than the concentrations of BTEX measured with active samples, as a reference value.

This exercise has demonstrated the magnitude of differences in BTEX concentrations of active measurements, with very similar found when using the regression approach. The use of meteorological corrected uptake rate resulted in improved correlation for the active and passive values when compared with other URs approach.

4. Conclusion

The URs for 31 VOC were investigated under different meteorological conditions, and the effect of the exposure time on measured VOC concentrations was assessed.

The results demonstrate that the sampling periods of more than 10 days may result in false measurement of VOC concentrations in the atmosphere. If the exposure time is more than 20 days, the recorded VOCs concentrations may be lower by a factor of 3–4 than the actual levels.

The URs of 23 out of 31 VOCs showed a statistically significant negative relationship with temperature, while 19 out of the 31 VOCs showed a statistically significant relationship with relative humidity, with 90% or higher confidence. Unlike the relationship between URs and temperature, the URs of all VOCs increased with increasing relative humidity. Although the relationship between URs and wind speed is not very strong, the URs of 15 of the 31 VOCs showed a statistically significant relationship with wind speed, with 90% or better confidence. The URs of the 31 VOCs measured in this study showed a general decreasing trend with temperature; and a weaker, but statistically significant increasing trend with increasing relative humidity and wind speed.

In conclusion, it is apparent that the URs of VOCs are indeed dependent on meteorological parameters, and this dependence should be taken into account when attempting to generate reliable data in passive measurements. Multiple linear regression equations, in which VOC concentrations were dependent, and temperature, relative humidity and wind speed were independent parameters, were developed for 25 VOCs. These equations can be useful for reducing uncertainty in passive VOC measurements.

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