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Article

Development of a New Passive Sampling Method for the Measurement of Atmospheric Linear and Cyclic Volatile Methyl Siloxanes

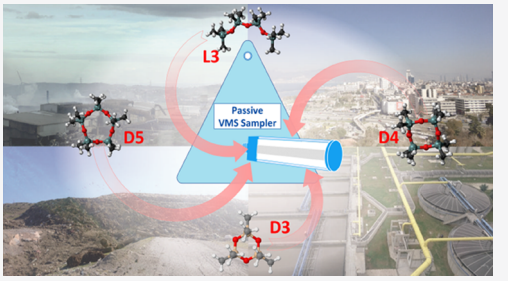
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ABSTRACT: A new passive sampling method was developed and characterized to measure atmospheric volatile methyl siloxanes (VMS). The infrastructure of a commercial passive air sampler (PAS) was used along with XAD-2 resin as the adsorbent. Experimental sampling rates (SR) determined using collocated active and passive samplers ranged between 0.0363 (L5) and 0.0561 (D3) m^3/day and agreed well with the theoretical ones. VMS uptake was highly linear for eight weeks. The precision of the method was very good (<10%). Compared to the other PASs used for VMS, the new method has several advantages (i.e., the sampler is much smaller, it has commercially available components, and the solvent requirement, equipment needed for extraction, and steps for sample preparation are minimal) while achieving similar or lower method detection limits. The developed method was applied to investigate the spatial distribution and possible sources of atmospheric VMS in the Izmir region. Field sampling covered 42 sites representing different source and land use areas. ΣVMS concentrations ranged between 41.4 and 981 ng/m^3. The dominant VMS was D5 followed by D3 and D4. Spatial distributions indicated that the main VMS sources in the area were urban areas, wastewater treatment plants, and landfills where the VMS-containing products are used and disposed.



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INTRODUCTION

Linear and cyclic volatile methyl siloxanes (VMS) are used as additives in personal care products, cleaning materials, and many industrial products.[1−3] Previous studies suggested that VMS have toxic and endocrine-disrupting features, and therefore, they may harm the environment and threaten human health.[4] However, there are studies suggesting that their toxic and endocrine-disrupting properties may be overestimated, and more research is needed on this subject.[5,6] VMS are emitted to the atmosphere via evaporation from VMS-containing products and to surface waters by wastewater discharges. VMS are distributed in the environment by dispersion, dilution, and water-air, soil-air, water-sediment, and plant-air exchange.[7] Once they are released, VMS are predicted to be distributed predominantly in air where they have relatively short half-lives due to reaction with OH radicals.[7] They may be subject to long-range atmospheric transport, but they have low potential to contaminate the North and South poles.[4] Even though VMS were detected in distant locations, such as poles, their presence was attributed to the effect of local sources rather than long-range atmospheric transport.[8,9]

VMS are produced in very high quantities, up to 10 million tons annually.[6] Due to their high vapor pressures, VMS readily volatilize from materials and products. Therefore, they are present in the atmosphere and indoor air at relatively high levels. Despite the uncertainties surrounding their toxicity and long-range transport potential, there has been an increased concern on their levels in air.[6] Consequently, several studies have investigated the VMS levels in the atmosphere[9−13] and indoor air.[14,15]

Two methods have been utilized to measure VMS concentrations in air: active air sampling and passive air sampling.[10,11] Commercial solid-phase extraction cartridges, sorbent (XAD-2, Tenax, and activated carbon)-filled tubes, and polyurethane foam (PUF) cartridges are used in active air sampling for VMS.[11,16] Both high- and low-volume samplers are used in active sampling with sample volumes ranging from a few liters to a few hundred cubic meters.[11,16] Air samples are also collected using passive air samplers (PAS) consisting of sorbent-impregnated polyurethane foam (SIP) disks,[11] XAD-2-filled mesh cylinders,[17] and Tenax-filled thermal desorption tubes.[18] While active sampling can be used for short-term (daily or diurnal) measurements, passive sampling could be used to provide the spatial distribution of VMS levels in a specific region. High equipment cost and electricity are required for active sampling that limit its use at multiple sites. However, passive sampling is low-cost, and no electricity is needed.[11] Although

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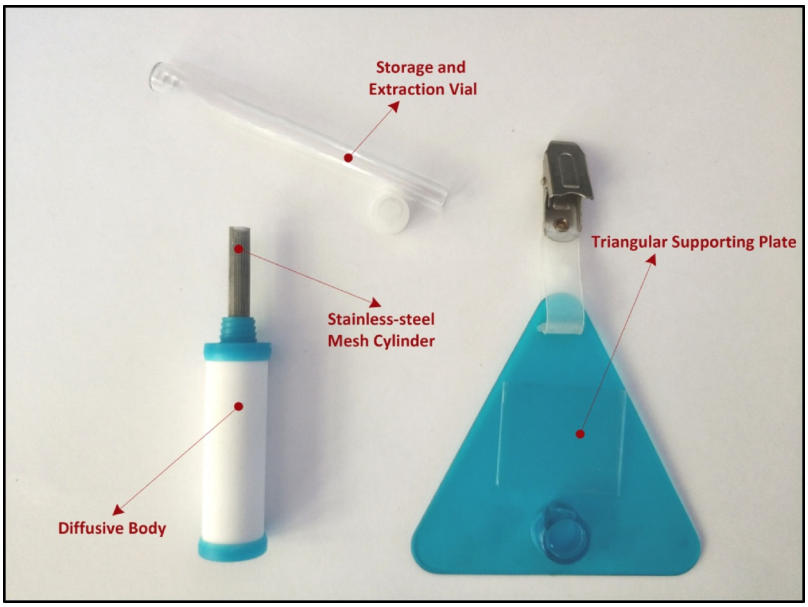


Figure 1. Components of the passive air sampler.

passive samplers have several advantages, most of the currently used samplers are relatively large, and they require large solvent volumes and lengthy sample preparation procedures (i.e., extraction, cleanup, and solvent volume reduction). Therefore, simpler methods are still needed to overcome these disadvantages.

The objectives of this study were (i) to develop and characterize a new passive sampling method for measuring atmospheric VMS and (ii) to investigate the spatial distribution and possible sources of atmospheric VMS in Izmir, Turkey. The infrastructure of a commercial passive sampler was used as the sampler, while polyurethane-divinylbenzene copolymeric resin (XAD-2) was used as the adsorbent. Sampling rates (SRs) of VMS for the PAS were determined experimentally with the help of active samplers operated simultaneously. The developed method was also used to determine the spatial distribution of atmospheric VMS levels in the Izmir region.

EXPERIMENTAL SECTION

Passive Sampler Calibration. The approach used by McLagan et al.[19] to develop a passive sampling method for gaseous mercury was adapted and used in the present study. A commercial passive air sampler that is available for volatile organic compounds (VOC) (Radiello, Code 130) was modified and used (Figure 1). The Radiello VOC sampler uses a mesh cylinder filled with activated carbon (AC). The sampler was modified by replacing the AC with XAD-2 resin. Specifically, a mesh cylinder (stainless steel, a height of 60 mm, a diameter of 5.8 mm, a mesh size of 165, and 47% open area) was filled with 439 ± 5 mg of XAD-2 resin. The cylinder is then placed within a commercially available, white Radiello diffusive body (high-density polyethylene, a porous section height of 47 mm, a porous barrier thickness of 1.7 mm, and a diameter of 16 mm). This diffusive body is then screwed into a supporting plate (Figure 1).

The passive air sampler was calibrated during indoor air experiments using the VMS amounts on the samplers and VMS concentrations measured by collocated active air samplers. Active air samples were collected using a sampling train consisting of an adsorbent tube, a flow meter (rotameter), a valve, and a vacuum pump. VMS compounds were collected with a glass tube filled with XAD-2 resin (528 ± 22 mg) (Figure S1). The calibration study was conducted in an office room in the Dokuz Eylul University, Department of Environmental Engineering. Variable indoor VMS levels during the calibration experiments were provided by personal care products (PCPs) (i.e., shampoo, shower gel, liquid soap, toothpaste, various makeup products, deodorant, hair spray, and hand cream) that were included and exposed to room air. The experimental conditions included no products (for 5 days) or different numbers of products (25 days) to provide variable air concentrations. Thirty daily samplings were conducted to determine sampling rates for the PAS. Sampling duration was 24 h for collocated active and passive samplers. The sampling flow rate for active sampling was 250 mL/min, and the total sample volume was 0.36 m^3. The average indoor air temperature was 21.4 ± 1.3 °C during the calibration experiments.

Determination of Uptake Profiles and Precision in the Atmosphere and Indoor Air. An 8-week passive sampling program was conducted indoors and outdoors in the district of Buca, Izmir to determine the uptake profiles and precision of the PAS. Indoor sampling took place in an apartment, while outdoor sampling was conducted at the balcony of the apartment. The door to the balcony was closed during the deployment. A total of 32 PASs were deployed (16 indoor, 16 atmospheric) initially, and duplicate indoor and outdoor air samples were collected each week during the 8-week period.

Atmospheric Passive Sampling Study in the Izmir Region. The PAS method developed in the present study was used to determine the spatial variation and potential sources of atmospheric VMS in the Izmir region. Passive sampling was carried out for 1 month (between November 4 and December 5, 2019) at 42 sampling sites representing different source and land use areas (wastewater treatment plant, solid waste landfill, and urban, rural, suburban, and industrial areas) (Figure S2). PASs were deployed using protective shelters (Radiello, outdoor shelter) during atmospheric sampling. Sampling sites were located at densely populated urban areas, around the Cigli wastewater treatment plant, the Harmandali landfill, the

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Tinaztepe campus of the Dokuz Eylul University, the Aliaga industrial region (iron-steel industries, ship dismantling facilities, a petroleum refinery, and a petrochemical plant), and forested areas at Bergama-Kozak.

Preparation for Sampling and Analysis. XAD-2-filled stainless steel mesh cylinders used for passive air sampling were cleaned three times in acetone-hexane (1:1) for 10 min in an ultrasonic bath. Then, the cylinders were dried by passing through high-purity N_2 for 45 min. XAD-2 used for active air sampling was also cleaned three times in acetone-hexane (1:1) for 10 min in an ultrasonic bath. Glass wool plugs were inserted into the active sampling glass tubes. Then, the tubes were filled with XAD-2-solvent slurry. XAD-2-filled glass tubes were dried by passing a high-purity N_2 stream through the cartridge for 30 min.

After the sampling, XAD-2-filled mesh cylinders were inserted into their storage and extraction vials and transferred to the laboratory (Figure 1). An extraction solvent was added to the vial (2 mL of hexane), and it was soaked in overnight, spiked with 20 μL of internal standard solution containing 2000 ng of tetrakis(trimethylsilyloxy)silane (M4Q), and then extracted for 10 min by sonication. For active samples, XAD-2 was transferred from the glass sampling tube to a 40 mL amber vial. Then, 5 mL of hexane was added as the extraction solvent, and it was kept overnight. Extraction was conducted by sonicating the samples for 10 min after they were spiked with 50 μL of internal standard solution containing 5000 ng of M4Q. Then, for both active and passive samples, 1 mL of sample extracts was placed in 2 mL GC vials for analysis.

Instrumental Analysis. All samples were analyzed for 7 VMS compounds (D3, D4, D5, D6, L3, L4, and L5) using an Agilent 6890N GC−MS (Agilent 5973 inert MSD) at electron impact ionization and selected ion monitoring mode (SIM). The following target and qualifier ions were monitored for VMS analysis: m/z 281, 147 (M4Q); 207, 208 (D3); 221, 222 (L3); 281, 282 (D4); 207, 295 (L4); 355, 267 (D5); 281, 369 (L5); 341, 429 (D6). An HP5-MS-UI capillary column (30 m, 0.25 mm, and 0.25 μm) was utilized for the analysis with helium as the carrier gas. The injection mode was pulsed splitless, and the injection volume was 1 μL. The initial oven temperature was held at 40 °C for 3 min and raised to 160 °C at 10 °C/min and to 300 °C at 30 °C/min and was held for 3 min. The injector, ion source, and quadrupole temperatures were 200, 230, and 150 °C, respectively.

Quality Assurance/Quality Control. Accurate quantification of VMS in environmental samples is crucial to assess their effects on the environment. Therefore, the use of VMS-containing materials (i.e., silicon-containing septa and personal care products) during sampling, sample preparation, extraction, and analysis was avoided. Samplers were stored in desiccators and in their containers (Teflon-lined capped glass tubes containing silica gel and granulated activated carbon) both before and after sampling until they were analyzed. Glassware used in the VMS experiments was washed with acetone and hexane and dried at 105 °C. The contact time of samples with laboratory indoor air was minimized to prevent possible contamination. Three blank samples for each sample batch were prepared to detect any contamination from sample processing.

The recovery efficiency of M4Q was determined to be 105.3 ± 11.8% (average ± SD) for active air sampling and 100.1 ± 11.1% for passive air samples (indoor calibration) (Table S1). The recovery efficiency of M4Q was 89.0 ± 3.7 and 88.2 ± 5.1% for passive samples collected during indoor and outdoor uptake profile experiments, respectively, while it was 90.3 ± 2.7% for the atmospheric samples collected in the Izmir region.

The definition of the method detection limit (MDL) was MDL = mean blank value + 3SD. Instrumental detection limits (IDL) were estimated from the calibration curve, based on the area of a peak with a signal to noise ratio of 3. The IDL was utilized for the analytes that were not detectable in blanks. The quantifiable VMS amounts ranged between 0.03 (L3) and 0.20 pg (D3 and D6) for 1 μL injection. Samples above the MDL were corrected by subtracting the average blank amounts. Blank amounts were <10% of the sample amounts, ranging between 0.1 (D5) and 5.9% (D3), 0.9 (D5) and 6.9% (D4), and 5.2 (D5) and 9.8% (D3) for indoor active, indoor passive, and atmospheric passive samples, respectively.

The solvent amounts used for extraction were also tested by subsequent extractions. VMS amounts were below the MDL in second extracts, showing that solvent amounts used were sufficient for extraction.

In active sampling, a backup XAD-2 tube was placed into the sampling train to determine if there was any breakthrough. VMS amounts found in the backup columns were low and ranged between 0.2% (D5) and 5.5% (L4), indicating that breakthrough was insignificant (Table S2).

One gram samples (n = 3 for each component) of the diffusive body, the triangular supporting plate, and shelters (both clean and used in the field) were soaked in 5 mL of hexane overnight, extracted by sonication, and analyzed for their VMS contents. For all samples and VMS compounds, amounts were below the MDL, indicating that PAS components do not act as contamination sources or sorb VMS in air.

RESULTS AND DISCUSSION

Characterization of the Passive Sampling Method. *Agreement between the Replicates.* Uptake profiles and precision of the PAS were evaluated through an 8-week passive sampling program that included indoor and atmospheric samples. Table S3 presents the mean relative standard deviations (RSDs) for duplicate indoor and atmospheric samples. RSDs were generally lower for indoor samples. They varied from 2.9% (L5) to 11.4% (D6) and 2.7% (D4) to 6.7% (D6) for atmospheric and indoor samples, respectively. These low RSD values indicated that the precision of the developed method was very good.

Uptake Curves and Deployment Times. Uptake profiles of indoor and ambient air passive samplers deployed for 8 weeks are illustrated for D5 in Figure 2, while the remaining compounds are presented in Figure S3. VMS masses on the PAS were substantially higher for indoor air samples, especially for cyclic VMS. Average indoor/outdoor ratios were 3.3, 1.9, 5.9, 23.1, 8.8, 4.7, and 10.0 for L3, L4, L5, D3, D4, D5, and D6, respectively. The uptake curves for all VMS demonstrated highly linear relationships between sorbed amounts (ng) and deployment time (weeks) for both the indoor and outdoor samples (r^2 = 0.95−0.99, $p < 0.01$). This linearity indicated that the sorbent had not approached its equilibrium uptake capacity during the 8-week deployment period.

Since none of the VMS reached equilibrium with XAD-2 within 56 days, the longest deployment period for the PAS could not be determined (Figure S3). Also, it was not possible to calculate the partition coefficients between XAD-2 and air ($K_{XAD\text{-}air}$). The approach used by Krogseth et al.[17] was adapted to further evaluate the sorption characteristics of VMS to the

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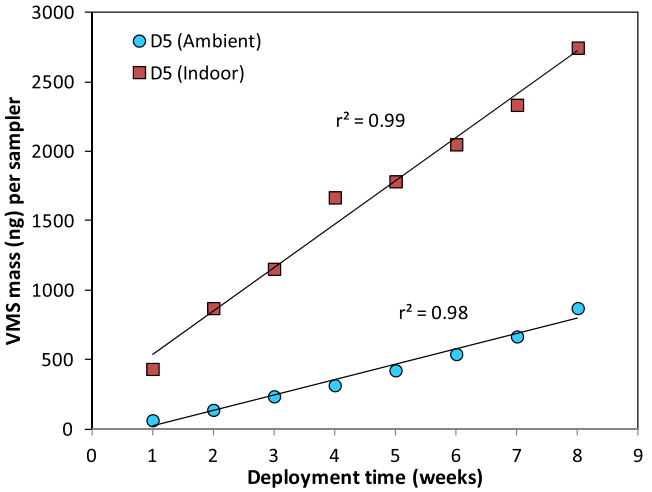


Figure 2. Uptake profiles of indoor and ambient air passive samplers deployed for 8 weeks. $p < 0.01$, for both correlations.

PAS used in the present study. A lower limit for $K_{XAD\text{-}air}$ (L/g) was calculated by dividing the VMS concentration in XAD (C_{XAD}, ng/g) at the end of the deployment period (8 weeks) by the mean VMS concentrations in air (C_{air}, ng/L) during that period. Seven C_{air} values were determined (for both indoor and outdoor) using the VMS amounts on the 1-, 2-, 3-, 4-, 5-, 6-, and 7-week deployed PAS, temperature-adjusted experimental sampling rates (18.3 and 24 °C for outdoor and indoor samples, respectively), and deployment times. Then, mean C_{air} values were obtained by averaging these values. The sorbent density (640 g/L) was used to convert the $K_{XAD\text{-}air}$ (L/g) to a unitless value.[20] The lower limit for log $K_{XAD\text{-}air}$ values was similar for all congeners, and they ranged between 6.36−6.59 and 6.34−6.63 for indoor and atmospheric samples, respectively, indicating that the samplers had not reached equilibrium (Table S4). A very similar range was reported for XAD-PAS (log $K_{XAD\text{-}air}$ = 6.47−6.51).[17]

A polyparameter linear free-energy relationship (pp-LFER) for XAD and solute descriptors for VMS were used to predict $K_{XAD\text{-}air}$ for VMS.[20,21] Predicted values were adjusted to the average temperatures using sorption enthalpies and the van't Hoff equation.[20] The estimated log $K_{XAD\text{-}air}$ ranged between 4.80−6.90 and 4.97−7.16 for indoor and atmospheric temperatures, respectively, and they were lower than the experimentally determined minimum values except for L5 and D6 (Table S4). The times required to reach 25% (t_{25}) and 95% (t_{95}) equilibrium could be estimated using XAD-2 mass (0.439 g), the experimentally determined sampling rates, and the $K_{XAD\text{-}air}$ estimated by the pp-LFER approach.[20] It was suggested that the time t_{25} could be considered as the upper limit of the linear uptake phase.[20] The t_{25} and t_{95} for VMS ranged between 0.2 (D3) and 78 days (D6) and from 2.3 (D3) to 809 days (D6), respectively (Table S4). Estimated t_{25} values for both indoor and outdoor deployed PASs were generally lower than the observed linear uptake period of 56 days for most of the VMS, while estimated t_{95} values were <56 days for D3, L3, and D4. These indicated that the pp-LFER approach underestimates $K_{XAD\text{-}air}$ values especially for D3, L3, and D4, and equilibrium VMS amounts on XAD are higher than predicted.

Experimental and Theoretical Sampling Rates. Experimental sampling rates were determined through a 30-day indoor sampling program that was conducted using collocated passive and active air samplers. The summary of indoor VMS concentrations measured by active sampling is presented in Table S5. Generally, cyclic VMS (cVMS) were observed at higher concentrations compared to linear VMS (lVMS). D5 was determined as the dominant compound for indoor air concentrations. The highest average concentration was measured for D5 (87,389 ng/m^3), while the lowest average concentration was for L3 (134 ng/m^3). The measured VMS levels were highly variable, and maximum/minimum concentrations ratios varied between 11 (D4) and 426 (L3). The lowest VMS levels were observed when there were no PCPs in the room. Average concentrations were 4.3 (D4) to 43.5 (L4) times lower when there were no PCPs.

Experimental sampling rates (SR_{Exp}) for the PAS were calculated using

$$SR_{Exp} = \frac{m}{Ct} \quad (1)$$

where m is the amount of the analyte collected by the PAS (ng), C is the mean actively measured concentration over the sampling period (ng/m^3), and t is the deployment time (days).[19] The SR_{Exp} is the average of the individual values calculated for each sampling. The relationship between the air concentrations and VMS masses collected on the PAS is shown in Figure 3. Alternatively, SR_{Exp} was derived as the slope of a linear regression line between m/t and C. Because all VMS concentrations in samples were blank-corrected, the regressions were forced through zero.[19] Correlations for all VMS were highly linear (r^2 = 0.91−0.99, $p < 0.01$) (Figure S4).

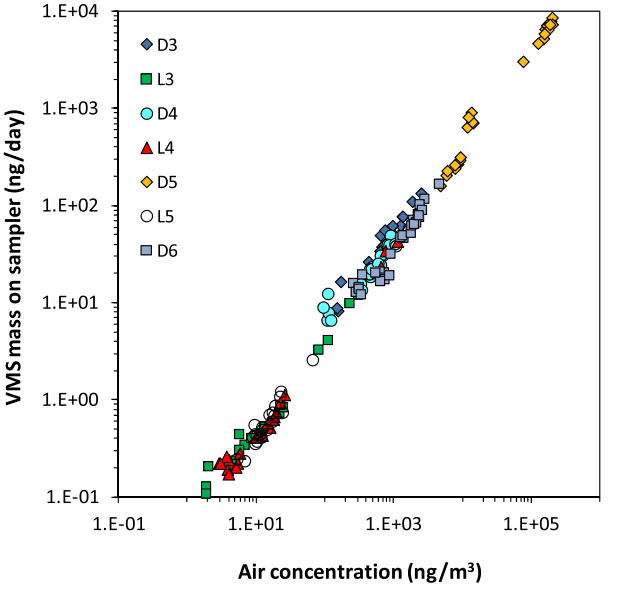


Figure 3. Relationships between the indoor VMS concentrations and sorbed amounts on passive samplers.

Theoretical sampling rates (SR_{Theo}, mL/min) were calculated for each VMS compound according to the following equation derived by McLagan et al.[19] for the Radiello cartridges used in the present study

$$ST_{Theo} = D_a(T, P) \times 2\pi h/[\ln(r_a/r_{d-out}) + v^{-1.33} \times \ln(r_{d-out}/r_{d-in}) + \ln(r_{d-in}/r_s)] \quad (2)$$

where D_a (T, P) is the molecular diffusion coefficient of siloxanes in air (cm^2/min), which is a function of temperature T and

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pressure P, h is the height of the diffusive barrier (4.7 cm), and r_a (18 mm), $r_{d\text{-}out}$ (8 mm), $r_{d\text{-}in}$ (6.3 mm), and r_s (2.9 mm) are the radii corresponding to the outside of the air-side boundary layer, the diffusive barrier, the internal air space, and the sorbent cylinder, respectively (Figure S5). The term $v^{-1.33}$ accounts for the tortuous path through the porous diffusive barrier, with v being the porosity (dimensionless). A porosity of 0.496 ± 0.001 for the Radiello diffusive barrier was determined via Hg intrusion porosimetry and reported recently by McLagan et al.[19] SR values obtained in mL/min were then converted to m^3/day.

Molecular diffusion coefficients (D_a, cm^2/min) were estimated by the following equation[22]

$$D_a = 10^{-3} \times 60 \times \{T^{1.75} \times [(1/m_{air}) + (1/m)]^{1/2}\}/P \times [V_{air}^{1/3} + V^{1/3}]^2 \quad (3)$$

where T is the absolute temperature (K), m_{air} is the average molecular mass of air (28.97 g/mol), m is the molecular mass of the chemical of interest (g/mol), P is the gas-phase pressure (atm), V_{air} is the molar volume of air (20.1 cm^3/mol), V is the molar volume of the chemical of interest (cm^3/mol), and 60 is the conversion factor from seconds to minutes.

Experimental SRs determined with the two methods (average values determined with eq 1 and the slope method) and the theoretical ones (eq 2) are presented in Table 1. Experimental SRs determined by the slope method had lower uncertainties than those determined using eq 1, as it was apparent from their standard errors and standard deviations. Experimental SRs determined with average and slope methods agreed well (r^2 = 0.92, slope of the regression line = 0.98, and $p < 0.01$). Experimental SRs (slope method) ranged between 0.0363 (L5) and 0.0561 (D3) m^3/day. These SRs for VMS were two orders of magnitude higher than those reported for Tenax-PAS (0.00014−0.00030 m^3/day),[23] while they were substantially lower than those reported for XAD-PAS (0.42−0.50 m^3/day)[17] and SIP-PAS (3.3−5.7 m^3/day).[11]

Table 1. Experimental and Theoretical Sampling Rates (SR, m^3/Day) for VMSs (at 21.4 ± 1.3 °C)[a]

	experimental (slope)		experimental (average)		theoretical	
	SR	SE	SR	SD	SR	SD
D3	0.0561	0.0014	0.0587	0.0126	0.0630	0.0003
L3	0.0435	0.0002	0.0498	0.0185	0.0551	0.0003
D4	0.0458	0.0012	0.0530	0.0183	0.0527	0.0003
L4	0.0389	0.0007	0.0443	0.0135	0.0487	0.0002
D5	0.0399	0.0005	0.0415	0.0099	0.0469	0.0002
L5	0.0363	0.0003	0.0413	0.0069	0.0440	0.0002
D6	0.0370	0.0008	0.0376	0.0084	0.0429	0.0002

[a]SE, standard error; SD, standard deviation; hexamethylcyclotrisiloxane (D3), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (L4), decamethylcyclopentasiloxane (D5), dodecamethylpentasiloxane (L5), and dodecamethylcyclohexasiloxane (D6).

The linear regressions between theoretical and estimated SRs were highly linear with r^2 = 0.92 and $p < 0.01$. The slope of the regression line was ∼1.0, indicating a very good overall agreement between the experimental and theoretical SRs (Figure S6). The good agreement between the experimental and theoretical SRs suggests that SRs for VMS compounds that were not included in the present study could be determined using eq 2.

The sampling efficiency (SE) was defined as the ratio of the SR_{Exp} to SR_{Theo}. It was suggested that an SE close to 1.0 indicates that the analyte uptake is controlled by the sorbent side rather than the air side.[23,24] SE ranged from 0.79 (L3) to 0.89 (D3), suggesting that VMS uptake is primarily controlled by XAD-2.

The effect of temperature on sampling rates was not determined in the present study. However, according to eq 3, sampling rates are a function of temperature, and they are proportional to $T^{1.75}$. Therefore, SRs could be adjusted for the temperature

$$SR_T = SR_{T,ref} \times \left(\frac{T}{T_{ref}}\right)^{1.75} \quad (4)$$

where SR_T is the sampling rate at the temperature T (K) and $SR_{T,ref}$ is the sampling rate at the reference temperature. According to eq 4, the sampling rate has a variation of ±6.1% for a 10 °C temperature difference. McLagan et al.[25] recently evaluated the effect of temperature (between −15 and + 35 °C) on the SR in the laboratory for their gaseous mercury PAS, having the same infrastructure of a commercial sampler that was also used in the present study (Radiello white diffusive body and protective shelter). It was reported that the SR increases by 0.7% for every 1 °C increase in temperature. This corresponds to ±7% variation in the SR for a 10 °C temperature difference that is in good agreement with the variation (±6.1%) estimated using eq 4.

Indoor concentrations are substantially higher than atmospheric levels, and they could be adjusted to provide a wide range. Atmospheric passive sampling requires at least one week sampling duration (see the subsection "Method Detection Limits for VMS") and multiple concurrent daily active samples. However, because of high indoor levels, daily sampling is possible, reducing the sample number and experimental time substantially. Therefore, experimental SRs were determined through indoor experiments in the present study. As a result, the effect of wind speed and relative humidity could not be investigated. However, the sampler manufacturer reports in their user manual that the SR is invariant for VOCs with humidity and wind speed within the ranges of 15−90% and 0.1−10 m/s, respectively.[26] McLagan et al.[25] measured the SRs of a PAS for gaseous Hg in the laboratory under varying wind speeds (calm to 6 m/s) and relative humidities (44 to 80%) using the white diffusive body (Radiello) and shelter configuration that were also used in the present study. It was reported that relative humidity had no impact on the SR. However, the SR increased slightly with wind speed. The SR increased by 0.003 m^3/day or 2.5% of the previously calibrated SR for every 1.0 m/s increase for wind speeds over 1.0 m/s.[25] These results and a recent literature review by Huang et al.[27] indicated that using both diffusive barriers and protective shields substantially reduce the effect of wind speed on the SR.

For the field sampling program of the present study, temperature data were provided from 15 meteorological stations in the study region. Average temperature during the sampling period ranged between 13.4 and 18.3 °C, and the overall average was 16.4 ± 1.2 °C. Temperature data from the closest station (within 5 km) was used to adjust the sampling rates for individual sampling sites. Temperature correction for SRs (eq 4) ranged between −1.8 and −4.7% (average ± SD, −3.3 ± 0.8%). As the effect of wind speed was not tested, no correction was

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Table 2. Method Detection Limits (MDLs) (ng/m^3) for Active and Passive VMS Sampling

	this study				literature			
	active sampling	passive sampling			SIP-PAS[a]	SIP-PAS[b]	XAD-PAS[c]	Tenax-PAS[d]
	1 day	1 day	7 days	30 days	30 days	90 days	90 days	20 days
D3	32.3	129	29.9	6.0	0.79	1.1	24.2	
L3	0.11	0.72	0.10	0.02	0.02	0.011		
D4	10.5	66.5	9.5	2.2	6.2	2.5	14.7	0.62
L4	0.08	0.79	0.11	0.03	0.04			
D5	6.6	118	16.9	3.9	5.4	7.1	11.3	0.42
L5	0.07	1.2	0.17	0.04	0.06			
D6	6.4	55.0	7.9	1.8	4.8	2.3	15.0	1.22

[a]Ahrens et al.[11] [b]Genualdi et al.[28] [c]Krogseth et al.[17] [d]Li et al.[23]

applied for SRs. Average wind speed ranged between 1.52 and 3.95 m/s (average ± SD, 2.49 ± 0.86 m/s). These were within the wind speed range (0.1−10 m/s) that the SRs are invariant, according to the PAS manufacturer.[26] If the slight increase determined by McLagan et al.[25] over 1.0 m/s is assumed to be valid for VMS, then the increase in SRs due to wind speed ranges between +1.3 and +7.4% (average ± SD, +3.7 ± 2.2%), suggesting that the effect of wind speed on SRs was minor under field sampling conditions of the present study.

Method Detection Limits for VMS. The definition of the method detection limit (MDL) was MDL = mean blank value + 3SD. MDLs ranged between 0.03 (L3 and L4) and 11.7 ng/sample (D3). MDLs in terms of air concentration (ng/m^3) were calculated by dividing the MDLs in terms of analyte mass (ng) by corresponding sampling volumes (m^3) determined using the SRs derived by the slope method and sampling duration (t). MDLs were calculated for different sampling durations (1 day, 1 week, and 1 month), and they are presented in Table 2. For 1-day active sampling, MDL ranges from 0.07 (L5) to 32.3 ng/m^3 (D3). MDLs ranged between 0.72 (L3) and 129 ng/m^3 (D3) for 1-day passive sampling. MDLs for one-week passive sampling approached to those for daily active sampling. MDLs for 1-month deployment period are substantially lower, varying between 0.02 (L3) and 6.0 ng/m^3 (D3). Table 2 also compares the MDLs determined in the present study to those reported in the literature. For 1 month, MDLs for the PAS used in the present study were generally lower than the ones reported for SIP-PAS, the most commonly used passive sampling method for VMS.[11,28] MDLs were also much lower than those reported for XAD-PAS.[17] However, they were higher than those determined for a recently developed method (Tenax-PAS).[23] As a result of their larger SRs, SIP-PAS and XAD-PAS could sample much higher air volumes. However, they use much larger solvent volumes and additional sample preparation steps resulting in higher blank amounts and higher MDLs.

Compared to atmospheric VMS concentrations, elevated indoor levels were measured during the calibration experiments in the present study even when there were no PCPs in the room (Table S5). Similar or higher indoor air VMS concentrations were reported within the ranges of 350−52,000 (L3) and 2400−440,000 (D5) in the UK, 80−5400 (L3) and 1700−730,000 (D5) in Italy, and 23−500 (D4) and 970−56,000 (D5) ng/m^3 in Chicago, USA.[10,14] Considering these indoor concentrations and the MDLs, the PAS method developed in the present study could be used for relatively short deployment periods (i.e., daily) to measure indoor air concentrations. Relatively high atmospheric concentrations near VMS sources (i.e., WWTPs and landfills) could also be measured daily. For lower VMS levels, one week or longer deployment periods may be needed. In the present study, it was shown that a one-month deployment period was sufficient to detect VMS even in the rural sites where the lowest levels were observed.

Comparison with SIP-PAS, XAD-PAS, and Tenax-PAS. The newly developed method in the present study has several advantages over the currently used passive sampling methods for VMS:

- The sampler is much smaller (SIP-PAS contains a 14 cm disk placed inside a stainless steel chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm, XAD-PAS contains a mesh cylinder filled with ∼10 g of XAD-2 and has a height of 10 cm and a diameter of 2 cm, placed inside a shelter with 10 cm diameter and 17.7 cm height, the sampler of the present study is a stainless steel mesh cylinder containing 0.439 g of XAD-2 and has a height of 6 cm and a diameter of 0.58 cm, placed inside a 1.6 cm diameter diffusive body) and easier to deploy, transport, and store.
- The PAS used in this study is based on components of a commercially available sampler, while XAD-PAS is not.
- The solvent volumes used for preparation for sampling and sample extraction are much smaller (only 2 mL for extraction).
- Equipment requirement needed for extraction is minimal (sonicator) compared to XAD-PAS and SIP-PAS (i.e., Soxhlet extractor and pressurized liquid extraction system).
- No sample concentration (volume reduction) and cleanup are needed.
- As a result of low solvent volume used for extraction and no additional sample preparation steps, contamination is minimized, and lower blank values are obtained.
- Tenax-PAS has also similar advantages over SIP-PAS and XAD-PAS since VMS are introduced to GC−MS by thermal desorption and no sample preparation steps are required. However, SRs for Tenax-PAS are two orders of magnitude lower than the current method. Also, the sampler was not tested for D3, L3, L4, L4, and L5, and the agreement between the theoretical and experimental SRs was poor.[23]

Evaluation of Possible Sampling Artifacts. It was demonstrated that isotopically labeled ^{13}C-D5 degrades to form ^{13}C-D4, while ^{13}C-D6 degrades to ^{13}C-D5 and ^{13}C-D4 on two types of active sampling cartridges (ENV+ and ABN) when stored for 14 days at room temperature or at −20 °C. Higher degradation observed on the ENV+ sorbent was attributed to the acidic phenolic substituent within the divinylbenzene structure of the

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sorbent, enhancing the degradation of cVMS via hydrolysis under humid conditions.[29] Based on the observed higher concentrations and concentration ratios (D4/D5) for VMS on passive samplers compared to active samplers, Warner et al.[29] have suggested that there are potential issues related to cVMS stability on passive samplers over long deployment periods.

VMS degradation during storage was not assessed in the present study. The possibility of VMS degradation collected on XAD-PAS was evaluated by Krogseth et al.[17] through storage experiments. Ten XAD-PAS were exposed to indoor air for 45 days and stored at −20 °C. Duplicate samples were extracted and analyzed after 0, 7, 14, 21, and 28 days of storage. Then, the recovery relative to day zero was determined. Based on linear regression, no significant losses were observed (at the 95% confidence level) in the VMS amounts with time. The losses were 0.2, 0.05, 0.09, 0.4, 0.01, 0.04, and 0.5% per day for D3, D4, D5, D6, L3, L4, and L5, respectively. Insignificant VMS losses from the XAD-PAS suggested that hydrolysis reactions hypothesized for ENV+ resin do not occur on the XAD-2 resin within the specified time period.[17] It should be noted that degradation losses determined by Krogseth et al.[17] at −20 °C under laboratory conditions may not represent the losses during the field deployment due to different conditions (i.e., temperature, humidity, and oxidant levels). On the other hand, losses due to storage are conservative estimates as it is assumed that the complete sampled amount is present at the start of the deployment that is not valid for field deployments.[17]

In the present study, the sampling period for indoor calibration experiments was short (1 day), and all samples were extracted and analyzed within one day. Therefore, it was assumed that degradation losses during sampling and sample storage were not significant for calibration experiments. Field samples were also extracted and analyzed immediately upon their collection; thus, degradation losses for sample storage were insignificant. However, since exact conditions, mechanisms, and degradation rates in the field are not known, possible degradations during 1-month field deployment could not be assessed, and this issue needs to be further investigated.

Atmospheric VMS Concentrations in the Izmir Region.

Atmospheric VMS Levels. Spatial distribution and possible sources of atmospheric VMS in the Izmir region were investigated using the PAS method developed in the present study. The sampling program included the urban areas (n = 12), the Cigli WWTP (n = 6), the Harmandali solid waste landfill (n = 8), the Aliaga industrial region (n = 10), and suburban (n = 3) and rural areas (n = 3). The average atmospheric ΣVMS concentration in the Izmir region was measured to be 338 ± 278 ng/m^3, and the range was 41.4−981 ng/m^3 (Table S6). The dominant compound was D5 followed by D3 and D4 with average concentrations of 231, 48.5, and 38.9 ng/m^3, respectively. Linear VMS were measured in substantially lower concentrations compared to cVMS with average concentrations ranging between 0.9 (L4) and 1.6 (L3) ng/m^3.

ΣVMS levels measured in the present study were within the ranges reported in the literature. Similar to the present study, substantially higher concentrations were reported for urban locations and sites near wastewater treatment plants (WWTPs) than the rural sites. Rauert et al.[30] measured ΣcVMS ranges of 1.6−120, 0.33−169, and 91−413 ng/m^3 for polar, background, and urban sites, respectively. However, much lower levels (maximum 8 ng/m^3) were observed at urban and industrial sites in Portugal.[12] Atmospheric ΣVMS levels in Turkey ranged between 12.7 and 212 ng/m^3 at an urban site in Izmir,[31] while a range of 41.7 to 433 ng/m^3 was measured in the Kucuk Menderes river basin.[32] Shoeib et al.[33] measured VMS concentrations in the vicinity of a WWTP and reported elevated average atmospheric cVMS concentrations, 3000 ± 730 and 1700 ± 170 ng/m^3 during summer and winter periods, respectively. They concluded that WWTPs are major sources of VMS to the atmosphere. When other urban areas are considered, ΣVMS concentration was measured to be 92 ng/m^3 in Sydney, Australia, while it was 413 ng/m^3 in Paris, France.[28] All compared literature ΣVMS concentrations included the same seven compounds (L3, L4, L5, D3, D4, D5, and D6). Similar to the present study, cVMS levels were substantially higher than lVMS, and D5 was reported as the dominant compound.

Spatial Distributions and Possible Sources. Average ΣVMS concentrations were 572, 488, 351, 132, 80, and 44 ng/m^3 in urban, landfill, WWTP, suburban, industrial, and rural areas, respectively (Figures 4 and 5 and Figure S7).

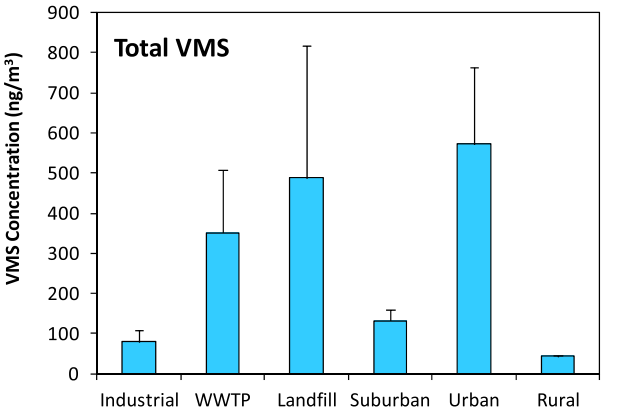


Figure 4. Average atmospheric ΣVMS concentrations for different areas. Error bars indicate 1 SD.

D5, D6, L4, and L5 had their highest concentrations in urban areas. The highest D3 levels were measured at WWTP sites, while the highest D4 and L3 levels were found in the landfill area. For most of the VMS compounds, the lowest concentrations were observed in the rural area except for L5 and D6 that were the lowest in the industrial area (Figure S8).

Previous studies on soil, ambient air, stack-gas sampling, and biomonitoring have indicated that the Aliaga industrial region in Turkey is heavily polluted by several persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polybrominated diphenyl ethers (PBDEs).[34−39] These POPs are mainly emitted by scrap-processing iron-steel plants located in the region. It was suggested that POPs contained in ferrous scrap are evaporated and emitted during steel production or they are formed in part by thermal processes.[36] However, ΣVMS levels measured in the industrial sites of the present study were substantially lower than urban levels. They were slightly higher than rural levels and lower than suburban levels. These results indicated that unlike other organic compounds, VMS are not emitted in substantial quantities by the industrial sources in the Aliaga region (Figure S7).

Average D3 concentrations were 108, 63.1, 43.1, 23.0, 18.9, and 8.61 ng/m^3 at WWTP, urban, landfill, suburban, industrial, and rural areas, respectively. The highest D3 concentrations

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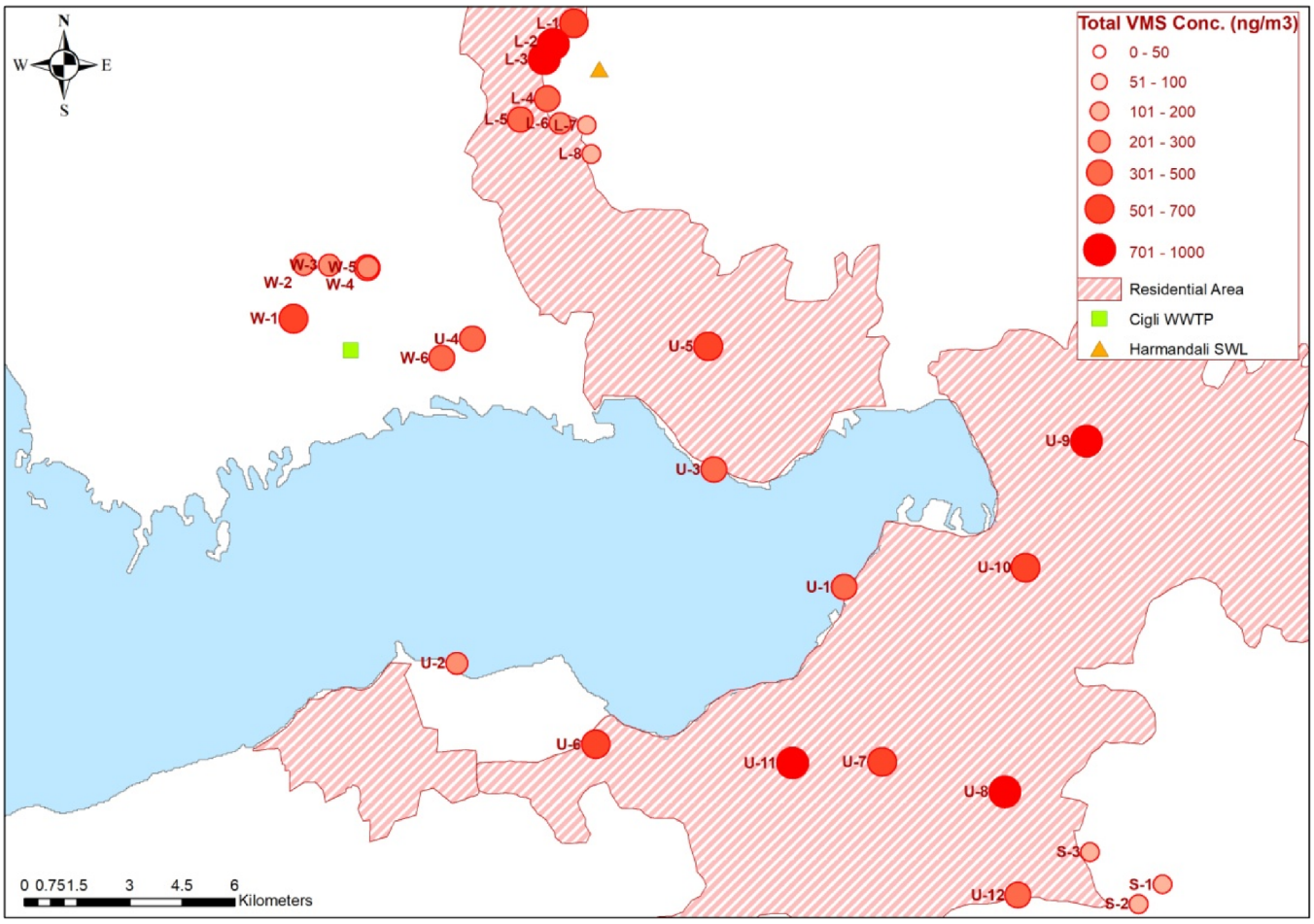


Figure 5. Distribution of ΣVMS concentrations (ng/m^3) in Izmir urban areas.

were observed around the WWTP, while the lowest ones were observed in rural areas (Figures S9 and S10). Previous studies have indicated that WWTPs are substantial sources of VMS into the surface waters and the atmosphere.[33,40,41] It was suggested that D3 may be formed through the degradation of higher-molecular-weight cyclic VMS in wastewater.[41] This mechanism may explain the occurrence of the highest atmospheric D3 levels around the WWTP in the present study.

Average concentrations of D4 were 102, 36.9, 32.1, 19.2, 14.2, and 3.59 ng/m^3 at the landfill, WWTP, urban, suburban, industrial, and rural areas, respectively. The highest levels of D4 were measured around the landfill area, while its lowest levels were observed in the rural area (Figures S11 and S12). Previous studies have also reported that D4 was the dominating compound in landfill gases.[42] D4 is found mainly in household cleaning and hair care products.[15] The residuals of these products may be contained in the landfill waste and evaporate to air. High D4 levels observed in the present study and in the literature suggest that landfills may be important sources of this compound.

Average concentrations of D5, the most dominant VMS, were 447, 321, 188, 70.9, 38.9, and 18.9 ng/m^3 at urban, landfill, WWTP, suburban, industrial, and rural sites, respectively (Figures S13 and S14). D5 was reported as the most dominant cVMS in almost all examined personal care products (PCPs) in the literature.[15,43] In parallel with this, atmospheric levels of D5 in the present study could be associated with the use of PCPs in densely populated urban areas and their disposal in landfills and WWTPs.

Average concentrations of D6 were 24.2, 17.6, 15.4, 14.4, 12.3, and 6.8 ng/m^3 at the urban, suburban, landfill, WWTP, rural, and industrial sampling sites, respectively. The highest levels of D6 were seen at the urban area (Figures S15 and S16). Similar to D5, D6 is also commonly found in PCPs,[15] and its spatial distribution was associated with the use and disposal of PCPs. However, D6 variability among the different sampling sites was not as pronounced as D5, and relatively high concentrations were observed at suburban and rural sites. D5/D6 ratios were 20.0, 18.3, 13.4, 5.9, 4.4, and 1.6 at the landfill, urban, WWTP, industrial, suburban, and rural sites, respectively. This could be attributed to the longer atmospheric half-life of D6 (3.0−6.1 days) compared to D5 (2.0−3.6 days) that was determined recently based on global measurements.[44]

Average L3 concentrations from high to low were 3.55, 1.84, 1.27, 0.55, 0.38, and 0.13 ng/m^3, at the landfill, urban, WWTP, industrial, suburban, and rural areas, respectively (Figures S17 and S18). The spatial distribution of L3 suggested that it is mainly emitted by use and disposal of PCPs.

Average concentrations of L4 were 1.53, 1.34, 0.73, 0.38, 0.36, and 0.17 ng/m^3 at the urban, landfill, WWTP, suburban, industrial, and rural areas, respectively. L4 was seen at the highest levels in the urban area and it is mainly emitted by the use and disposal of L4 containing household, industrial and personal care products (Figures S19 and S20).

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Average L5 levels were 2.25, 1.35, 1.01, 0.55, 0.44, and 0.36 ng/m^3 at the urban, landfill, WWTP, rural, suburban, and industrial areas, respectively. The highest levels were observed in urban areas (Figures S21 and S22). Similar to other lVMS, spatial distribution of L5 suggested that its main sources are the use and disposal of VMS-containing products in densely populated areas.

In summary, a new high-precision PAS method was developed and calibrated to measure the atmospheric VMS levels. Experimental SRs agreed well with the theoretical ones, indicating that the method could also be used for uncalibrated VMS compounds. Compared to the commonly used PASs for VMS, the new method has several advantages (i.e., the sampler is much smaller, it has commercially available components, and the solvent requirement, equipment needed for extraction, and steps for sample preparation are minimal) while achieving similar or lower MDLs. VMS uptake by the PAS was shown to be highly linear for eight weeks. However, additional studies are required to establish the maximum deployment period. The developed method was used to investigate the VMS in the Izmir atmosphere, and it was shown that the major VMS sources in the region were urban areas, wastewater treatment plants, and landfills.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c00227.

Additional figures and tables as noted in the text (PDF)

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Notes

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■ REFERENCES

(1) Dudzina, T.; von Goetz, N.; Bogdal, C.; Biesterbos, J. W. H.; Hungerbühler, K. Concentrations of cyclic volatile methylsiloxanes in European cosmetics and personal care products: Prerequisite for human and environmental exposure assessment. *Environ. Int.* **2014**, *62*, 86−94.

(2) Horii, Y.; Kannan, K. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. *Arch. Environ. Contam. Toxicol.* **2008**, *55*, 701−710.

(3) Graiver, D.; Farminer, K. W.; Narayan, R. A Review of the Fate and Effects of Silicones in the Environment. *J. Polym. Environ.* **2003**, *11*, 129−136.

(4) Wang, D. G.; Alaee, M.; Steer, H.; Tait, T.; Williams, Z.; Brimble, S.; Svoboda, L.; Barresi, E.; DeJong, M.; Schachtschneider, J.; Kaminski, E.; Norwood, W.; Sverko, E. Determination of cyclic volatile methylsiloxanes in water, sediment, soil, biota, and biosolid using large-volume injection-gas chromatography-mass spectrometry. *Chemosphere* **2013**, *93*, 741−748.

(5) Dekant, W.; Klaunig, J. E. Toxicology of decamethylcyclopentasiloxane (D5). *Regul. Toxicol. Pharmacol.* **2016**, *74*, S67−S76.

(6) Mojsiewicz-Pieńkowska, K.; Krenczkowska, D. Evolution of consciousness of exposure to siloxanes-review of publications. *Chemosphere* **2018**, *191*, 204−217.

(7) Kim, J.; Mackay, D.; Whelan, M. J. Predicted persistence and response times of linear and cyclic volatile methylsiloxanes in global and local environments. *Chemosphere* **2018**, *195*, 325−335.

(8) Warner, N. A.; Evenset, A.; Christensen, G.; Gabrielsen, G. W.; Borgå, K.; Leknes, H. Volatile Siloxanes in the European Arctic: Assessment of Sources and Spatial Distribution. *Environ. Sci. Technol.* **2010**, *44*, 7705−7710.

(9) Krogseth, I. S.; Kierkegaard, A.; McLachlan, M. S.; Breivik, K.; Hansen, K. M.; Schlabach, M. Occurrence and Seasonality of Cyclic Volatile Methyl Siloxanes in Arctic Air. *Environ. Sci. Technol.* **2012**, *47*, 502−509.

(10) Yucuis, R. A.; Stanier, C. O.; Hornbuckle, K. C. Cyclic siloxanes in air, including identification of high levels in Chicago and distinct diurnal variation. *Chemosphere* **2013**, *92*, 905−910.

(11) Ahrens, L.; Harner, T.; Shoeib, M. Temporal Variations of Cyclic and Linear Volatile Methylsiloxanes in the Atmosphere Using Passive Samplers and High-Volume Air Samplers. *Environ. Sci. Technol.* **2014**, *48*, 9374−9381.

(12) Ratola, N.; Ramos, S.; Homem, V.; Silva, J. A.; Jiménez-Guerrero, P.; Amigo, J. M.; Santos, L.; Alves, A. Using air, soil and vegetation to assess the environmental behaviour of siloxanes. *Environ. Sci. Pollut. Res.* **2016**, *23*, 3273−3284.

(13) Rauert, C.; Shoieb, M.; Schuster, J. K.; Eng, A.; Harner, T. Atmospheric concentrations and trends of poly- and perfluoroalkyl substances (PFAS) and volatile methyl siloxanes (VMS) over 7 years of sampling in the Global Atmospheric Passive Sampling (GAPS) network. *Environ. Pollut.* **2018**, *238*, 94−102.

(14) Pieri, F.; Katsoyiannis, A.; Martellini, T.; Hughes, D.; Jones, K. C.; Cincinelli, A. Occurrence of linear and cyclic volatile methyl siloxanes in indoor air samples (UK and Italy) and their isotopic characterization. *Environ. Int.* **2013**, *59*, 363−371.

(15) Tran, T. M.; Hoang, A. Q.; Le, S. T.; Minh, T. B.; Kannan, K. A review of contamination status, emission sources, and human exposure to volatile methyl siloxanes (VMSs) in indoor environments. *Sci. Total Environ.* **2019**, *691*, 584−594.

(16) Lamaa, L.; Ferronato, C.; Fine, L.; Jaber, F.; Chovelon, J. M. Evaluation of adsorbents for volatile methyl siloxanes sampling based on the determination of their breakthrough volume. *Talanta* **2013**, *115*, 881−886.

(17) Krogseth, I. S.; Zhang, X.; Lei, Y. D.; Wania, F.; Breivik, K. Calibration and Application of a Passive Air Sampler (XAD-PAS) for Volatile Methyl Siloxanes. *Environ. Sci. Technol.* **2013**, *47*, 4463−4470.

(18) Li, Q.; Lan, Y.; Liu, Z.; Wang, X.; Wang, X.; Hu, J.; Geng, H. Cyclic volatile methylsiloxanes (cVMSs) in the air of the wastewater treatment plants in Dalian, China - Levels, emissions, and trends. *Chemosphere* **2020**, *256*, 127064.

(19) McLagan, D. S.; Mitchell, C. P. J.; Huang, H.; Lei, Y. D.; Cole, A. S.; Steffen, A.; Hung, H.; Wania, F. A High-Precision Passive Air Sampler for Gaseous Mercury. *Environ. Sci. Technol. Lett.* **2015**, *3*, 24−29.

(20) Hayward, S. J.; Lei, Y. D.; Wania, F. Sorption of a diverse set of organic chemical vapors onto XAD-2 resin: Measurement, prediction and implications for air sampling. *Atmos. Environ.* **2011**, *45*, 296−302.
(21) Ulrich, N.; Endo, S.; Brown, T. N.; Watanabe, N.; Bronner, G.; Abraham, M. H.; Goss, K.-U., *UFZ-LSER database v 3.2.1 [http://www.ufz.de/lserd]*. Research-UFZ, H. C. f. E., Ed. UFZ Helmholtz: Leipzig, Germany, 2017.
(22) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry*. 2nd ed.; Wiley, New York, 2003.
(23) Li, Q.; Wang, X.; Wang, X.; Lan, Y.; Hu, J. Tube-type passive sampling of cyclic volatile methyl siloxanes (cVMSs) and benzene series simultaneously in indoor air: uptake rate determination and field application. *J. Environ. Monit.* **2020**, *22*, 973−980.
(24) Walgraeve, C.; Demeestere, K.; Dewulf, J.; Van Huffel, K.; Van Langenhove, H. Diffusive sampling of 25 volatile organic compounds in indoor air: Uptake rate determination and application in Flemish homes for the elderly. *Atmos. Environ.* **2011**, *45*, 5828−5836.
(25) McLagan, D. S.; Mitchell, C. P. J.; Huang, H.; Abdul Hussain, B.; Lei, Y. D.; Wania, F. The effects of meteorological parameters and diffusive barrier reuse on the sampling rate of a passive air sampler for gaseous mercury. *Atmos. Meas. Tech.* **2017**, *10*, 3651−3660.
(26) Radiello 2019. *Radiello User Manual*; Supelco, Inc: https://www.restek.com/pdfs/radiello-manual.pdf
(27) Huang, C.; Shan, W.; Xiao, H. Recent Advances in Passive Air Sampling of Volatile Organic Compounds. *Aerosol Air Qual. Res.* **2018**, *18*, 602−622.
(28) Genualdi, S.; Harner, T.; Cheng, Y.; MacLeod, M.; Hansen, K. M.; van Egmond, R.; Shoeib, M.; Lee, S. C. Global Distribution of Linear and Cyclic Volatile Methyl Siloxanes in Air. *Environ. Sci. Technol.* **2011**, *45*, 3349−3354.
(29) Warner, N. A.; Nikiforov, V.; Krogseth, I. S.; Bjørneby, S. M.; Kierkegaard, A.; Bohlin-Nizzetto, P. Reducing sampling artifacts in active air sampling methodology for remote monitoring and atmospheric fate assessment of cyclic volatile methylsiloxanes. *Chemosphere* **2020**, *255*, 126967.
(30) Rauert, C.; Harner, T.; Schuster, J. K.; Eng, A.; Fillmann, G.; Castillo, L. E.; Fentanes, O.; Villa Ibarra, M.; Miglioranza, K. S. B.; Moreno Rivadeneira, I.; Pozo, K.; Aristizábal Zuluaga, B. H. Atmospheric Concentrations of New Persistent Organic Pollutants and Emerging Chemicals of Concern in the Group of Latin America and Caribbean (GRULAC) Region. *Environ. Sci. Technol.* **2018**, *52*, 7240−7249.
(31) Dumanoglu, Y.; Yaman, B.; Odabasi, M., Seasonal Variations of Cyclic and Linear Volatile Methylsiloxanes in An Urban Atmosphere. In *38th International Symposium on Halogenated Persistent Organic Pollutants (POPs) & 10th International PCB Workshop-DIOXIN 2018*; Vrije Universiteit Brussel: Krakow, Poland, 2018.
(32) Yaman, B.; Erkuzu, H.; Okan, F.; Odabasi, M. Spatial variations of linear and cyclic volatile methyl siloxanes in a river basin and their air-water exchange. *Atmos. Meas. Tech.* **2020**, *11*, 2308−2316.
(33) Shoeib, M.; Schuster, J.; Rauert, C.; Su, K.; Smyth, S. A.; Harner, T. Emission of poly and perfluoroalkyl substances, UV-filters and siloxanes to air from wastewater treatment plants. *Environ. Pollut.* **2016**, *218*, 595−604.
(34) Cetin, B.; Yatkin, S.; Bayram, A.; Odabasi, M. Ambient concentrations and source apportionment of PCBs and trace elements around an industrial area in Izmir, Turkey. *CHEMOSPHERE* **2007**, *69*, 1267−1277.
(35) Bozlaker, A.; Odabasi, M.; Muezzinoglu, A. Dry deposition and soil-air gas exchange of polychlorinated biphenyls (PCBs) in an industrial area. *Environ. Pollut.* **2008**, *156*, 784−793.
(36) Odabasi, M.; Bayram, A.; Elbir, T.; Seyfioglu, R.; Dumanoglu, Y.; Bozlaker, A.; Demircioglu, H.; Altiok, H.; Yatkin, S.; Cetin, B. Electric Arc Furnaces for Steel-Making: Hot Spots for Persistent Organic Pollutants. *Environ. Sci. Technol.* **2009**, *43*, 5205−5211.
(37) Kaya, E.; Dumanoglu, Y.; Kara, M.; Altiok, H.; Bayram, A.; Elbir, T.; Odabasi, M. Spatial and temporal variation and air-soil exchange of atmospheric PAHs and PCBs in an industrial region. *Atmos. Meas. Tech.* **2012**, *3*, 435−449.
(38) Odabasi, M.; Dumanoglu, Y.; Kara, M.; Altiok, H.; Elbir, T.; Bayram, A. Polychlorinated naphthalene (PCN) emissions from scrap processing steel plants with electric-arc furnaces. *Sci. Total Environ.* **2017**, *574*, 1305−1312.
(39) Odabasi, M.; Ozgunerge Falay, E.; Tuna, G.; Altiok, H.; Kara, M.; Dumanoglu, Y.; Bayram, A.; Tolunay, D.; Elbir, T. Biomonitoring the Spatial and Historical Variations of Persistent Organic Pollutants (POPs) in an Industrial Region. *Environ. Sci. Technol.* **2015**, *49*, 2105−2114.
(40) Cheng, Y.; Shoeib, M.; Ahrens, L.; Harner, T.; Ma, J. Wastewater treatment plants and landfills emit volatile methyl siloxanes (VMSs) to the atmosphere: Investigations using a new passive air sampler. *Environ. Pollut.* **2011**, *159*, 2380−2386.
(41) Horii, Y.; Minomo, K.; Ohtsuka, N.; Motegi, M.; Nojiri, K.; Kannan, K. Distribution characteristics of volatile methylsiloxanes in Tokyo Bay watershed in Japan: Analysis of surface waters by purge and trap method. *Sci. Total Environ.* **2017**, *586*, 56−65.
(42) Rasi, S.; Lehtinen, J.; Rintala, J. Determination of organic silicon compounds in biogas from wastewater treatments plants, landfills, and co-digestion plants. *Renewable Energy* **2010**, *35*, 2666−2673.
(43) Capela, D.; Alves, A.; Homem, V.; Santos, L. From the shop to the drain - Volatile methylsiloxanes in cosmetics and personal care products. *Environ. Int.* **2016**, *92-93*, 50−62.
(44) Xu, S.; Warner, N.; Bohlin-Nizzetto, P.; Durham, J.; McNett, D. Long-range transport potential and atmospheric persistence of cyclic volatile methylsiloxanes based on global measurements. *Chemosphere* **2019**, *228*, 460−468.

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