

Article

Diffusive Uptake Rates of Volatile Organic Compounds on Standard ATD Tubes for Environmental and Workplace Applications

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Abstract: Passive sampling for airborne volatile organic compounds (VOCs) has gained popularity; however, diffusive uptake rates (UR s) have been experimentally determined for only a small subset of VOCs. This study aims to develop empirical models that can interpolate effective UR s (UR_{eff}) for a wide range of VOCs. The modelling was based on the standard automated thermal desorption (ATD) tubes packed with Tenax TA and targeted the sampling efficiency (α), defined as the ratio between the ideal UR (UR_{ideal}) and UR_{eff} . Available experimentally determined UR s were compiled from literature. Method detection limits were determined on a thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) system. The 8-h UR_{eff} can be modeled with retention volumes or boiling points (BP s) and the biases were within $\pm 20\%$. The α for 7-day UR_{eff} can be estimated by the model: $\alpha = 0.3626 \ln(BP) - 1.2324$. The 8-h and 7-day UR_{eff} values were then compiled for 75 VOCs commonly encountered in the environmental and occupational settings. The TD analytical method showed high precision, linearity and sensitivity, suitable for measuring indoor and outdoor VOCs. The approach and data presented here are anticipated to ease passive monitoring of VOCs for the general users.

Keywords: uptake rate; passive sampling; volatile organic compound; thermal desorption; sorbent tube

1. Introduction

Volatile organic compound (VOC) contamination represents a health concern in indoor, outdoor and occupational environments [1,2]. Current exposure and risk assessment of VOCs requires representative exposure measurements, which are achieved by large sample sizes and frequent and long-term sampling [3]. For example, the U.S. Environmental Protection Agency (EPA) requires monitoring programs to collect air samples once every 6 or 12 days [4]. Sample sizes of several hundred are common in large survey studies, e.g., Relationship of Indoor, Outdoor and Personal Air (RIOPA) study [5], National Health and Nutrition Examination Surveys (NAHANES) [6] and urban air toxics studies [7]. Thus, there is a critical need for simple, low-cost and reliable VOC measurement methods to realistically evaluate public health risks and regulation compliance.

Passive sampling is a widely used sampling technique for determining time-weighted average concentrations of airborne VOCs [8,9]. There are three major types of passive samplers: axial tube-type sampler, badge sampler and radial sampler. The stainless-steel automated thermal desorption (ATD) tube has been widely employed since it offers some clear advantages compared to other methods [10]. First, the field sampling is very easy: the methods only requires removal and replacement of sealing caps and does not require a pump as opposed to the active sampling method. Second, these small samplers are easy and inexpensive for shipping and storage, in comparison to bulky canisters favored by the U.S. EPA [4]. Third, the laboratory analysis of ATD tubes is simple with the latest thermal

desorption-gas chromatography/mass spectrometry (TD-GC/MS) instrumentation. The major ATD systems—e.g., Markes International, PerkinElmer and Gerstel—are all equipped with an internal standard addition module that allows analyzing tubes with minimum or no sample preparation. Fourth, ATD tube-type samplers are preferred over badge samplers for the high sensitivity, low background, no need for extraction solvents and reusability for over 100 desorption times. In summary, passive sampling with ATD tubes can reduce field and lab staff's burden, save the cost and obtain high quality analytical performance.

The most challenging step in passive sampling is to determine the sampling rates or diffusive uptake rates (UR s) [11]. ATD tubes offer the greatest flexibility for users to select sorbents and determine tube configuration but at the same time, add complexity to the UR determination. Many studies have determined UR s from the diffusion theory [12], in laboratory chambers [13–16] and by comparing active and passive sampling in the field [17,18]. Many factors influence UR s, including sorbent selection, tube configuration, exposure duration and environmental conditions. The effective UR (UR_{eff}) is preferred as theoretically derived UR s display large biases in the field [19]. Unfortunately, only a small subset of VOCs has their UR_{eff} values determined and validated in laboratory and/or field. The determination requires complex instruments, well-controlled laboratory environments and time-consuming field tests, making it impractical for the general users to determine UR s experimentally.

The stainless-steel ATD tubes are the most popular, industry standard tubes for VOC sampling. Use of ATD tubes could be traced back to 1970s and tens of studies have applied and/or validated the passive sampling using ATD tubes. Many organizations have established standards based on ATD tubes [20,21], e.g., ISO 16017-2 [22], ASTM D6196 [23], EPA325b [24] and TO-17 [25] methods. However, even the most comprehensive reviews and compilations cover UR s for limited numbers of compounds for each specific tube configuration and these UR s were determined mainly for occupational applications. Current analytical laboratories are capable of analyzing tens of compounds, as standard mixtures containing >70 compounds are commercially available and GC/MS can be calibrated to analyze these compounds in one single injection. It is then an imperative task to determine UR_{eff} values for new compounds without laboratory or field experiments. This study aims to develop models that can estimate UR_{eff} values with available UR measurements and physicochemical properties. We then determine the method detection limits (MDLs) with the state-of-the-art TD-GC/MS system for a wide range of VOCs commonly found in community and occupational settings. We also make recommendations for passive sampling with ATD tubes.

2. Methods

2.1. The Passive Diffusion Theory

The theory for the passive diffusion process, primarily defined by the Fick's First Law, has been well established and studied [19,26]. For a specific VOC, the ideal uptake rate (UR_{ideal} , in mL/min) is determined as:

$$UR_{ideal} = D \frac{A}{L} \times 60 \quad (1)$$

where D = the diffusion coefficient of the compound (cm^2/s), A = the cross-sectional area of the tube (cm^2), L = the air gap between the sampling end of the tube and the surface of sorbent (cm) and 60 = the conversion coefficient from mL/s to mL/min. D is a physical property of the chemical that can be experimentally determined or modelled. UR_{ideal} can be theoretically calculated for any compound given a certain tube geometry of A/L . In reality, the UR_{eff} differs considerably from the UR_{ideal} due to volatility of the chemical, weak sorbent, back diffusion and sorbent saturation during long-term sampling [19,27]. UR_{eff} is a percentage of UR_{ideal} and this percentage can be defined as the sampling efficiency α :

$$UR_{eff} = \alpha UR_{ideal} \quad (2)$$

The key is to determine α for any given exposure duration, e.g., 8 h or 7 days.

2.2. Standard ATD Tubes

The standard ATD sorbent tube has a dimension of 89 mm long \times 6.4 mm o.d. \times 5 mm i.d. When in use, the sampler has, from the sampling end, a diffusion cap, an air gap, a retaining gauze mesh, a sorbent bed, another retaining gauze and a spring (Figure 1). Note:

- (1) The air gap (L) is 15 mm between the sampling end and sorbent surface when a diffusion cap is fitted. The UR changes with or without the diffusion cap, as it changes the air gap [28]. It is recommended to use the diffusion cap during passive sampling, as it prevents the convective transport of chemical molecules.
- (2) The cross-sectional diffusion area (A) is 0.196 cm². The retaining gauze has a pore size of 80 mesh and the wire is 0.21 mm in diameter, giving an effective area of 46% of the full area by calculation. Previous studies [15,18] assumed full cross-sectional diffusion area without considering the effective area on the retaining gauze. This assumption is questionable; however, it does not impact the determination of UR_{eff} , since UR_{eff} is not determined directly from the tube geometry, rather, by experiments or modelling as presented later.
- (3) The sorbent tube is packed with only one sorbent for the passive sampling purpose. The multisorbent configuration is not necessary, as the later sorbent layers do not contact compounds. Tenax TA is the most common sorbent due to its high thermal stability, low inherent artifacts and degradation, hydrophobicity and accommodation for wide volatility [29,30]. It also allows efficient desorption and displays optimal GC performance when used as a chromatographic stationary phase. An ATD tube is typically packed with 150–250 mg of Tenax TA, allowing both active and passive sampling.

Thus, this study estimates UR_{eff} values for standard ATD tubes packed with 200 mg of Tenax TA, with $L = 1.5$ cm and $A = 0.196$ cm². These parameters agree with those listed in a previous study [15]. The standard tubes are commercially available from a number of vendors, e.g., Markes International Inc. (Llantrisant, UK), PerkinElmer Inc. (Waltham, MA, USA), Sigma-Aldrich (St. Louis, MO, USA) and Camsco Inc. (Houston, TX, USA).

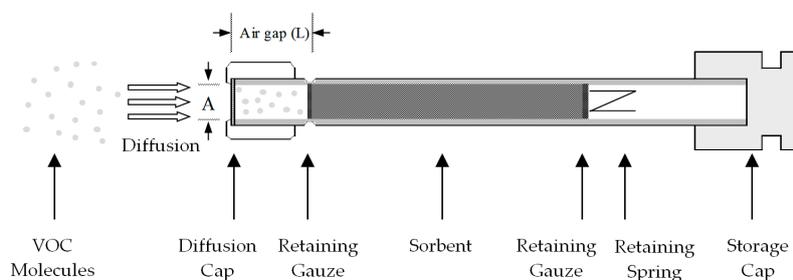


Figure 1. Structure and geometry of the standard automated thermal desorption (ATD) tube type passive sampler. VOC: volatile organic compound.

2.3. Diffusion Coefficients

Diffusion coefficients (D_s) can be obtained from many chemical properties handbooks. U.S. EPA developed a user-friendly on-line diffusion coefficient calculator [31]. This online tool uses three models to estimate the D for a chemical based on its molecular structure and boiling point [32]. The three models give very close estimates and thus the average of three estimates was used in this study. D does not change with respect to chemical concentrations or the sorbent but is dependent on temperature. D_T at any absolute temperature (T) is calculated as a function of D_{298} at 25 °C (298 K):

$$D_T = D_{298} (T/298)^{1.75} \quad (3)$$

2.4. Modeling Short-Term Effective Uptake Rates

For short-term (8 h) sampling in workplaces, the work by European Standards, Measurements and Testing Programme (SMT) shows that α has an empirical linear relationship with logarithm retention volume (V_g , in L) [33]:

$$8h-\alpha = 0.154 \text{Log}_{10}V_g + 0.4 \quad (4)$$

V_g values are available for many common VOCs in the latest ASTM protocol [23]. If it is unavailable, V_g can be experimentally determined following an established protocol [34]. Brown and Purnell's fundamental work shows that $\text{Log}_{10}V_g$ and boiling point (BP , in $^{\circ}\text{C}$) are highly correlated for most VOCs [35]. We then fitted $\text{Log}_{10}V_g$ against BP using the V_g data in the ASTM protocol. $\text{Log}_{10}V_g$ and BP displayed close relationships for alkanes, aromatics, chlorinated compounds, acetates and acrylates:

$$\text{Log}_{10}V_g = 0.0283 \times BP - 1.2559 \quad (5)$$

The regression line showed high linearity ($R^2 = 0.98$, Figure 2). Thus, V_g can be interpolated for these chemical groups if direct V_g measurements are unavailable.

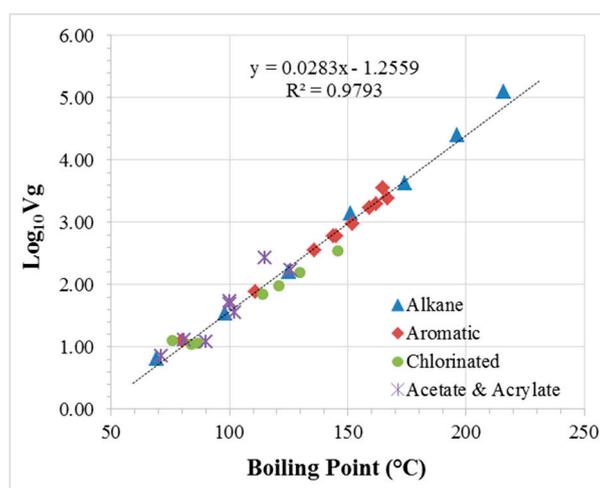


Figure 2. Relationship between $\text{Log}_{10}V_g$ and boiling points ($^{\circ}\text{C}$). Note: Only applies to alkanes, aromatics, chlorinated compounds, acetates and acrylates.

The performance of modeling $8h-UR_{eff}$ using Equations (4) was then evaluated by comparing modeled UR_{eff} against measured UR_{eff} . This comparison used 25 compounds that had both measured $8h-UR_{eff}$ and V_g values from the ASTM protocol [23]. We also evaluated model performance for 47 compounds whose V_g values were unavailable but could be modeled by Equation (5). The measured $8h-UR_{eff}$ values were taken from the manufacturer's application note [36], which summarized UR s from over 10 data sources. All the data were summarized in Table A1. A relative bias of $\pm 20\%$ was considered acceptable.

2.5. Modeling Long-Term Effective Uptake Rates

For long-term (7 days) environmental sampling, we used UR s from Walgraeve et al.'s study [18]. This study determined $7d-UR_{eff}$ values on standard Tenax TA ATD tubes for a total of 25 VOCs commonly found in indoor and outdoor air (Table A2). Most of the VOC measurements were below $10 \mu\text{g}/\text{m}^3$, with a few up to $150 \mu\text{g}/\text{m}^3$. Although many studies measured UR s in chamber, a recent study recommended field calibration [37]. We propose the following three models:

Model (1) assumes $7d-\alpha$ to be a constant across all the compounds for a given exposure duration. With calculated UR_{ideal} and measured UR_{eff} , we can derive $7d-\alpha$ by regressing UR_{eff} against UR_{ideal} .

The UR_{eff} for another compound will then be calculated by multiplying its UR_{ideal} by $7d-\alpha$. This approach has been reported in two previous studies [38,39].

Model (2) assumes $7d-\alpha$ to be a variable dependent on volatility and exposure duration. This is particularly true when much lower UR_{eff} values have been observed for more volatile compounds and on weak sorbents like Tenax during long-term sampling periods [40,41]. Similar to Equation (4), we propose that $7d-\alpha$ be expressed as a linear function of BP :

$$7d-\alpha = \beta_0 + \beta_1 BP \quad (6)$$

Model (3) is similar to Model (2) but we propose that $7d-\alpha$ be expressed as a linear function of $\ln(BP)$:

$$7d-\alpha = \beta_0 + \beta_1 \ln(BP) \quad (7)$$

The $7d-\alpha$ was calculated by dividing UR_{eff} by UR_{ideal} for each compound. To fit Model (1), we regressed UR_{eff} against UR_{ideal} without constant. To fit Models (2) and (3), we regressed $7d-\alpha$ against BP or $\ln(BP)$, respectively. We found a low UR_{eff} for α -pinene and treated it as an outlier and excluded it from Model (1) fitting. The low UR_{eff} of α -pinene might be caused by decomposition on Tenax during sampling [42] and storage [43]. We also excluded hexanal as the relationship between $\log_{10} Vg$ and BP was not established for aldehydes due to lack of data [35]. We conducted regression analyses in Microsoft Excel and SAS (Version 9.4, SAS Institute Inc., Cary, NC, USA). The best-fit models were selected by checking the regression lines and regression R^2 . The linear relationship was confirmed by checking the pattern of residual points in the linear regression residual plot.

2.6. Determination of MDLs

Laboratory performance tests were conducted to determine the method detection limits (MDLs) of passive VOC sampling using ATD tubes followed by TD-GC/MS analysis. VOC standard solutions were prepared using EPA 524 VOC Mix (Part #: 502111, Sigma-Aldrich), EPA 524 Rev. 4 Update Mix, Part #: 47427-U, Sigma-Aldrich), C7–C17 alkanes (Part #: 49451-U, Sigma-Aldrich) and individual pure chemicals from Sigma-Aldrich. These compounds included aromatic, halogenated, aliphatic and terpenoid compounds, most listed as hazardous air pollutants (HAPs) by the U.S. EPA. Series solutions were prepared at 0.2, 0.5, 1.0, 5.0, 10, 40 and 200 $\mu\text{g}/\text{mL}$ in methanol.

A Tenax TA ATD tube (Catalog No. C1-AXXX-5003, Markes International, Llantrisant, UK) was spiked with 1.0 μL of the solution on a calibration solution loading rig (Model: CSLR, Markes International, Llantrisant, UK) with a helium purge flow of 60 mL/min . After the spiking, the tube was retained on the rig for 3 min to ensure all the analytes were delivered and most of the solvent was purged. The spiked tubes were then placed in the autosampler of a TD system (ULTRA 2 + UNITY 2, Markes International, Llantrisant, UK). The TD was connected to a GC/MS system (Agilent 7890A/5975C, Agilent, Santa Clara, CA, USA). Conditions of the TD-GC/MS analysis were summarized in Table 1. An HP-5MS Ultra Inert GC column was used as it had low bleeding, good separation and fast elution [44]. After analysis, a list of 75 target compounds were identified and confirmed using NIST 2005 Spectral Library in ChemStation.

The calibration was established by analyzing all the 7 concentrations for each compound. The linearity was assessed by the R^2 of the linear regression line. We also calculated the relative standard deviation (RSD , in %) of 7 relative response factors ($RRFs$). RRF at a calibration level is determined as follows:

$$RRF = \frac{A_S \cdot C_{IS}}{A_{IS} \cdot C_S} \quad (8)$$

where A_S = peak area for quantitation ion of the target compound; A_{IS} = peak area for quantitation ion of the assigned internal standard compound; C_S = concentration of the target compound;

C_{IS} = concentration of the assigned internal standard compound. The *RSD* of *RRFs* calculated at 7 calibration levels was then calculated as:

$$RSD \text{ (in \%)} = \text{Standard deviation of (7 } RRFs) / \text{Mean (7 } RRFs) \times 100\% \quad (9)$$

An R^2 of ≥ 0.99 and *RSD* of $\leq 30\%$ were considered acceptable [4]. Duplicate analyses were conducted for each calibration level to determine the duplicate precision, expressed as percent difference:

$$\text{Duplicate precision (\%)} = \frac{|X_1 - X_2|}{\bar{X}} \times 100\% \quad (10)$$

where X_1 = First measurement value; X_2 = Second measurement value; and \bar{X} = Average of the two values. The lowest concentration of 0.2 $\mu\text{g/mL}$ was analyzed 7 times to determine the MDL. The MDL was calculated by multiplying standard deviation of 7 determined masses by 3.14, the one-sided student's *T* value at 99% confidence corresponding to 7 spikes analyzed.

Table 1. Thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) conditions.

Instrument	Parameter	Settings
Thermal Desorption (TD)	Dry purge flow rate	20 mL/min
	Dry purge time	1 min
	Desorption temperature	260 °C
	Desorption flow rate	50 mL/min
	Desorption time	5 min
	Split ratio	6.3:1
	Trap low	40 °C
	Heating rate	40 °C/s
	Trap high	280 °C
	Trap hold	3 min
Gas Chromatography (GC)	Injector	Splitless
	Column	HP-5MSUI, 30 m \times 250 μm \times 0.25 μm
	Flow rate	1.2 mL/min
	Temperature program	35 °C hold for 3 min; 15 °C/min to 95 °C, hold for 2 min; 15 °C/min to 140 °C, no hold; 35 °C/min to 220 °C, no hold; 40 °C/min to 300 °C, hold for 4 min
	Total run time	20.29 min
Mass Spectrometry (MS)	Mass mode and range	Scan mode, solvent delay 1.5 min 1.5–20.29 min: 35–350 amu, 4.5 scans/s, 0.1 <i>m/z</i> step size
	MS quad temperature	150 °C
	MS source temperature	230 °C

The tube preparation, cleaning and handling strictly followed the manufacturer's instructions. The MS was tuned following the tuning procedure before the analysis. A number of blank tubes were analyzed to check if the tubes had background contamination.

3. Results

3.1. Effective Uptake Rates (UR_{eff}) for Short-Term Workplace Sampling

Short-term UR_{eff} on Tenax ATD tubes can be modeled using available V_g or BP values with acceptable biases. In Figure 3, Modeled $8h-UR_{eff}$ values based on V_g values were all within $\pm 20\%$ of the measured $8h-UR_{eff}$ values, except for C9–C12 alkanes (Table A1). If direct V_g values were unavailable, $8h-UR_{eff}$ values were modeled using BP and the modeled values were within $\pm 20\%$ of the measured $8h-UR_{eff}$ values for most compounds. Besides the chemical groups referred by Figure 2, we found $8h-UR_{eff}$ values estimated by Equations (4) and (5) also applied to ketones and α -pinene. The models did not work for C9–C16 straight-chain alkanes or naphthalene though.

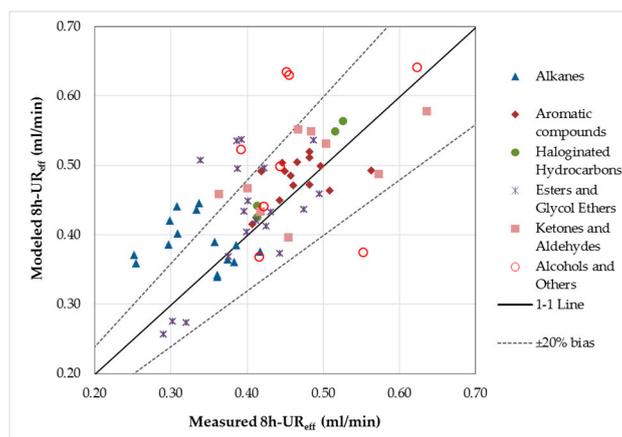


Figure 3. Comparison of modeled and measured 8h-UR_{eff} values in occupational sampling.

3.2. Effective Uptake Rates for Long-Term Environmental Sampling

Models for estimating long-term UR_{eff} in environmental sampling are compared in Figure 4. In Model (1), the 7d-UR_{eff} had an average sampling efficiency (α) of 0.49 (Figure 4A), meaning UR_{eff} is only half of the UR_{ideal} on average. However, the scatter plot between UR_{eff} and UR_{ideal} did not show a simple linear relationship. In contrast, Models (2) and (3) indicated a good linear relationship between 7d- α and BP (in °C, Figure 4B,C). Comparing the R² of Models (2) and (3) showed that Model (3), i.e., Ln(BP) as a predicting variable, gave better fitting. The points of residual plot from Model (3) were randomly distributed (Figure A1), confirming that a linear relationship between 7d- α and LnBP was appropriate. We also tried BP in absolute temperature as a predicting variable in Model (3) but obtained a lower R² of 0.80. Thus, the 7-day passive sampling efficiency can be calculated using the following empirical equation:

$$7d-\alpha = 0.3626 \text{ Ln}(BP) - 1.2324 \tag{11}$$

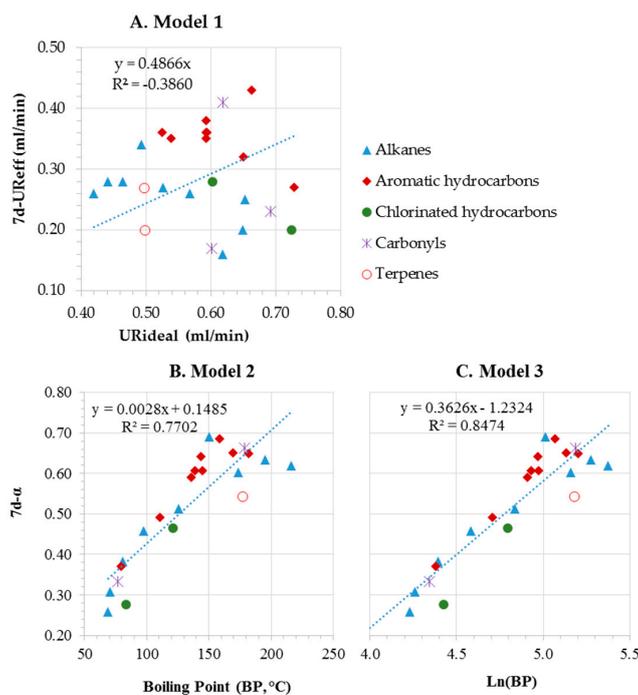


Figure 4. Comparison of three models for estimating 7d-UR_{eff} or 7d- α values in environmental sampling.

Then the UR_{eff} is calculated for a VOC by Equation (2). Equation (11) suggests that more volatile chemicals will have large loss during long-term passive sampling, which agreed with the literature [28,40,45].

3.3. Compilation of Ideal and Effective URs

For the convenience of use, we calculated diffusion coefficients at 25 °C (D_{298}) for 75 common VOCs and then determined their 7d- and 8h- UR_{eff} values, as summarized in Table 2. UR_{eff} values of other compounds can be derived using Equations (4), (5) and (11). In short-term workplace sampling, the median 8h- UR_{eff} is 0.47 mL/min (min–max: 0.25–0.68 mL/min), corresponding to 0.23 L (0.12–0.33 L) of sampling volumes. In long-term environmental sampling, the median 7d- UR_{eff} is 0.32 mL/min (0.13–0.43 mL/min), resulting in a median sampling volume of 3.2 L (1.3–4.3 L) at 25 °C.

Table 2. Physiochemical properties and uptake rates of 75 common volatile organic compounds (VOCs).

VOCs	CAS #	MW ¹ (g/mol)	BP ² (°C)	V _g ³ (L)	D ⁴ (cm ² /s)	UR _{ideal} ⁵ (mL/min)	8h-UR _{eff} ⁶ (mL/min)	7d-UR _{eff} ⁷ (mL/min)
Acrylonitrile	107-13-1	53.1	77		0.1120	0.88	0.48	0.30
trans-1,2-Dichloroethylene	156-60-5	96.9	48		0.0958	0.75	0.31	0.13
Methyl tert-butyl ether	1634-04-4	88.1	55		0.0803	0.63	0.28	0.14
1,1-Dichloroethane	75-34-3	99.0	57		0.0927	0.73	0.33	0.17
Propionitrile	107-12-0	55.1	97		0.1080	0.85	0.54	0.36
Methacrylonitrile	126-98-7	67.1	91		0.0967	0.76	0.46	0.31
cis-1,2-Dichloroethylene	156-59-2	96.9	60		0.0956	0.75	0.35	0.19
Methyl acrylate	96-33-3	86.1	80	13	0.0918	0.72	0.43	0.26
2,2-Dichloropropane	594-20-7	113.0	96		0.0805	0.63	0.40	0.27
Chloroform	67-66-3	119.4	61		0.0917	0.72	0.34	0.19
Tetrahydrofuran	109-99-9	72.1	66		0.0978	0.77	0.38	0.22
1,1,1-Trichloroethane	71-55-6	133.4	75		0.0826	0.65	0.35	0.22
1,2-Dichloroethane	107-06-2	99.0	83	11	0.0923	0.73	0.41	0.20
1,1-Dichloropropene	563-58-6	111.0	78		0.0854	0.67	0.37	0.23
Benzene	71-43-2	78.1	80	13	0.0928	0.73	0.41	0.27
Carbon tetrachloride	56-23-5	153.8	76	12	0.0809	0.64	0.59	0.22
1,2-Dichloropropane	78-87-5	113.0	95		0.0830	0.65	0.41	0.27
Trichloroethylene	79-01-6	131.4	87	11	0.0846	0.67	0.37	0.28
Dibromomethane	74-95-3	173.8	97		0.0953	0.75	0.47	0.32
Bromodichloromethane	75-27-4	163.8	87		0.0880	0.69	0.41	0.27
2,5-Dimethylfuran	625-86-5	96.0	93		0.0781	0.62	0.38	0.25
Methyl methacrylate	80-62-6	100.1	100	55	0.0825	0.65	0.43	0.28
trans-1,3-Dichloropropene (E)	10061-02-6	111.0	108		0.0850	0.67	0.45	0.31
cis-1,3-Dichloropropene(z)	10061-01-5	111.0	108		0.0850	0.67	0.45	0.31
Toluene	108-88-3	92.1	111	76	0.0829	0.65	0.44	0.32
1,1,2-Trichloroethane	79-00-5	133.4	113		0.0821	0.65	0.45	0.31
1,3-Dichloropropane	142-28-9	113.0	121		0.0826	0.65	0.48	0.33
Ethyl methacrylate	97-63-2	114.1	118		0.0744	0.59	0.42	0.29
Dibromochloromethane	124-48-1	208.3	118		0.0850	0.67	0.48	0.33
n-Octane	111-65-9	114.2	126	160	0.0671	0.53	0.36	0.27
1,2-Dibromoethane	106-93-4	187.9	131		0.0480	0.38	0.29	0.20
Tetrachloroethene	127-18-4	165.8	121		0.0767	0.60	0.43	0.28
Chlorobenzene	108-90-7	112.6	131	52	0.0796	0.63	0.42	0.34
1,1,1,2-Tetrachloroethane	630-20-6	167.8	131	156	0.0749	0.59	0.44	0.32
Ethylbenzene	100-41-4	106.2	136	360	0.0756	0.60	0.46	0.35
m-Xylene	108-38-3	106.2	144	600	0.0756	0.60	0.42	0.36
p-Xylene	106-42-3	106.2	144	600	0.0756	0.60	0.42	0.36
Bromoform	75-25-2	252.7	150		0.0826	0.65	0.56	0.38
Styrene	100-42-5	104.1	145	600	0.0757	0.60	0.56	0.36
o-Xylene	95-47-6	106.2	144	600	0.0756	0.60	0.42	0.34
n-Nonane	111-84-2	128.3	151	1400	0.0628	0.49	0.40	0.34
1,1,2,2-Tetrachloroethane	79-34-5	167.8	147	340	0.0747	0.59	0.46	0.34
1,2,3-Trichloropropane	96-18-4	147.4	154		0.0749	0.59	0.52	0.35
Cumene	98-82-8	120.2	153		0.0687	0.54	0.46	0.32
trans-1,4-Dichloro-2-butene	110-57-6	125.0	126		0.0752	0.59	0.45	0.31
Bromobenzene	108-86-1	157.0	156		0.0789	0.62	0.52	0.37
α-Pinene	7785-70-8	136.2	155		0.0602	0.47	0.42	0.28
2-Chlorotoluene	95-49-8	126.6	158		0.0730	0.58	0.51	0.35
n-Propylbenzene	103-65-1	120.2	158		0.0669	0.53	0.48	0.36

Table 2. Cont.

VOCs	CAS #	MW ¹ (g/mol)	BP ² (°C)	Vg ³ (L)	D ⁴ (cm ² /s)	UR _{ideal} ⁵ (mL/min)	8h-UR _{eff} ⁶ (mL/min)	7d-UR _{eff} ⁷ (mL/min)
4-chlorotoluene	106-43-4	126.6	162		0.0730	0.58	0.52	0.35
1,3,5-Trimethylbenzene	108-67-8	120.2	165	3600	0.0698	0.55	0.48	0.34
Pentachloroethane	76-01-7	202.3	162		0.0692	0.55	0.50	0.33
Phenol	108-95-2	94.1	182	480	0.0844	0.66	0.54	0.43
<i>tert</i> -Butylbenzene	98-06-6	134.2	169		0.0643	0.51	0.48	0.32
1,2,4-Trimethylbenzene	95-63-6	120.2	168	3600	0.0686	0.54	0.44	0.35
<i>n</i> -Decane	124-18-5	142.3	174	4200	0.0592	0.47	0.40	0.28
1,3-Dichlorobenzene	541-73-1	147.0	173		0.0723	0.57	0.55	0.36
<i>sec</i> -Butylbenzene	135-98-8	134.2	174		0.0643	0.51	0.49	0.32
1,4-Dichlorobenzene	106-46-7	147.0	173		0.0723	0.57	0.54	0.36
<i>p</i> -Isopropyltoluene	99-87-6	134.2	177		0.0642	0.51	0.49	0.33
<i>d</i> -Limonene	5989-27-5	136.2	176		0.0632	0.50	0.48	0.27
1,2-Dichlorobenzene	95-50-1	147.0	180		0.0722	0.57	0.56	0.37
<i>n</i> -Butylbenzene	104-51-8	134.2	183		0.0642	0.51	0.51	0.33
Hexachloroethane	67-72-1	236.7	187		0.0647	0.51	0.52	0.34
1,2-Dibromo-3-chloropropane	96-12-8	236.3	196		0.0709	0.56	0.59	0.38
Nitrobenzene	98-95-3	123.1	210	28,000	0.0771	0.61	0.66	0.43
<i>n</i> -Undecane	1120-21-4	156.3	196	25,000	0.0562	0.44	0.31	0.28
1,2,4-Trichlorobenzene	120-82-1	181.4	214		0.0668	0.53	0.60	0.38
Naphthalene	91-20-3	128.2	218		0.0691	0.54	0.49	0.39
<i>n</i> -Dodecane	112-40-3	170.3	216	126,000	0.0535	0.42	0.30	0.26
1,2,3-Trichlorobenzene	87-61-6	181.4	218		0.0668	0.53	0.61	0.38
Hexachlorobutadiene	87-68-3	260.8	215		0.0595	0.47	0.54	0.34
<i>n</i> -Tridecane	629-50-5	184.0	234		0.0512	0.40	0.31	0.30
<i>n</i> -Tetradecane	629-59-4	198.0	254		0.0506	0.40	0.30	0.31
<i>n</i> -Pentadecane	629-62-9	212.0	271		0.0473	0.37	0.25	0.30

¹ MW: molecular weight, from [46]; ² BP: boiling point, from [46]; ³ Vg: retention volume, from [23]; ⁴ D: diffusion coefficient, from [31]; ⁵ Calculated by Equation (1); ⁶ Values in bold are measured 8-h effective uptake rates from [36]; other values are calculated using Equations (2), (4) and (5); ⁷ Values in bold are measured 7-day effective uptake rates from [18]; other values are calculated using Equations (2) and (11).

3.4. Analytical Performance and MDLs

The retention times (RTs) ranged from 1.907 min to 14.118 min for the 75 target compounds (Table 3). These RTs had variations within ± 0.1 min. Blank tubes did not show any target VOCs except for trace levels of benzene, toluene, ethyl benzene and xylenes (BTEX, <0.1 ng). The average duplicate precision over the calibration range was within 10% for most compounds. The high percent differences for a few compounds were mainly caused by poor precisions at low concentrations. The R² of linear calibration curves were all above 0.99 and most were above 0.999. RSDs of linear curves were all within 30% except for a few polar compounds, e.g., tetrahydrofuran, phenol and nitrobenzene. The MDLs ranged from 0.02 to 0.16 ng and this range indicated that the spiked amount (0.2 ng) met the criterion that it should be between MDL and 10-fold MDL [4]. Based on the 8-h and 7-day sampling rates, the MDLs can be expressed as 0.01 to 0.05 $\mu\text{g}/\text{m}^3$ for 7-day environmental sampling and 0.08 to 0.86 $\mu\text{g}/\text{m}^3$ for 8-h workplace sampling. The sample quantitation limits (SQLs) can be derived from MDLs as an SQL is defined as 3.18 times the MDL concentration [4].

Table 3. Performance of laboratory analysis of automated thermal desorption (ATD) tubes.

VOCs	RT ¹ (min)	Precision ² (%)	R ²	RSD ³ (%)	MDL ⁴ (ng)	MDL_8h ⁵ (µg/m ³)	MDL_7d ⁶ (µg/m ³)
Acrylonitrile	1.907	8.6	0.9992	18.9	0.13	0.56	0.042
<i>trans</i> -1,2-Dichloroethylene	2.074	9.3	0.9991	11.7	0.03	0.21	0.024
Methyl tert-butyl ether	2.100	5.4	0.9999	11.5	0.05	0.37	0.035
1,1-Dichloroethane	2.157	5.6	0.9990	8.0	0.03	0.22	0.020
Propionitrile	2.168	8.7	0.9988	9.3	0.03	0.12	0.008
Methacrylonitrile	2.314	7.9	0.9994	7.8	0.13	0.60	0.043
<i>cis</i> -1,2-Dichloroethylene	2.370	8.2	0.9993	9.0	0.03	0.18	0.016
Methyl acrylate	2.430	7.9	0.9994	7.9	0.03	0.14	0.011
2,2-Dichloropropane	2.430	3.7	0.9999	7.6	0.06	0.32	0.023
Chloroform	2.456	8.1	0.9993	7.4	0.04	0.22	0.019
Tetrahydrofuran	2.558	10.3	0.9988	97.0	0.02	0.12	0.010
1,1,1-Trichloroethane	2.749	2.9	0.9998	17.3	0.04	0.26	0.020
1,2-Dichloroethane	2.786	5.6	0.9991	7.4	0.04	0.20	0.020
1,1-Dichloropropene	2.873	5.9	0.9999	6.4	0.04	0.22	0.016
Benzene	2.940	5.8	0.9998	22.2	0.03	0.16	0.012
Carbon tetrachloride	2.951	1.8	1.0000	4.3	0.04	0.14	0.018
1,2-Dichloropropane	3.480	8.4	0.9976	18.3	0.06	0.32	0.023
Trichloroethylene	3.491	6.2	0.9986	8.0	0.03	0.15	0.010
Dibromomethane	3.517	5.5	0.9991	6.8	0.03	0.13	0.009
Bromodichloromethane	3.600	4.7	0.9990	8.1	0.03	0.13	0.009
2,5-Dimethylfuran	3.630	5.4	0.9995	5.8	0.06	0.33	0.024
Methyl methacrylate	3.716	9.4	0.9988	9.3	0.08	0.37	0.027
<i>trans</i> -1,3-Dichloropropene (E)	4.170	7.5	0.9995	7.5	0.05	0.23	0.016
<i>cis</i> -1,3-Dichloropropene (Z)	4.601	7.0	0.9996	6.4	0.04	0.18	0.013
Toluene	4.612	5.6	0.9996	13.1	0.06	0.26	0.017
1,1,2-Trichloroethane	4.694	6.2	0.9999	7.2	0.04	0.18	0.012
1,3-Dichloropropane	4.927	6.5	1.0000	6.9	0.03	0.14	0.010
Ethyl methacrylate	4.976	5.2	0.9999	10.2	0.06	0.28	0.020
Dibromochloromethane	5.077	5.3	1.0000	7.8	0.02	0.09	0.006
<i>n</i> -Octane	5.167	7.1	1.0000	18.7	0.07	0.43	0.027
1,2-Dibromoethane	5.260	6.3	1.0000	7.0	0.05	0.33	0.023
Tetrachloroethene	5.324	4.3	0.9998	7.2	0.02	0.10	0.007
Chlorobenzene	5.916	2.7	0.9999	7.2	0.02	0.11	0.006
1,1,1,2-Tetrachloroethane	5.980	2.1	1.0000	6.8	0.03	0.15	0.010
Ethylbenzene	6.160	7.7	0.9993	8.2	0.03	0.16	0.010
<i>m</i> -Xylene	6.284	4.9	0.9978	10.5	0.07	0.35	0.019
<i>p</i> -Xylene	6.284	4.9	0.9978	10.5	0.07	0.35	0.019
Bromoform	6.505	5.9	0.9999	13.0	0.05	0.19	0.013
Styrene	6.599	6.9	1.0000	10.0	0.05	0.17	0.013
<i>o</i> -Xylene	6.632	7.6	0.9996	9.4	0.05	0.23	0.013
<i>n</i> -Nonane	6.722	11.6	0.9991	17.7	0.04	0.22	0.012
1,1,2,2-Tetrachloroethane	6.910	9.0	1.0000	10.1	0.04	0.16	0.011
1,2,3-Trichloropropane	7.011	7.7	1.0000	8.4	0.05	0.20	0.014
Cumene	7.086	8.7	0.9996	7.5	0.03	0.14	0.009
<i>trans</i> -1,4-Dichloro-2-butene	7.131	10.6	0.9999	16.7	0.05	0.23	0.016
Bromobenzene	7.176	9.2	0.9999	6.4	0.06	0.25	0.016
α -Pinene	7.232	10.6	0.9998	8.1	0.04	0.20	0.014
2-Chlorotoluene	7.483	8.5	0.9999	7.0	0.06	0.26	0.018
<i>n</i> -Propylbenzene	7.517	10.1	0.9995	9.5	0.06	0.26	0.017
4-chlorotoluene	7.570	9.0	0.9999	7.7	0.05	0.21	0.015
1,3,5-Trimethylbenzene	7.746	9.0	1.0000	7.4	0.04	0.19	0.013
Pentachloroethane	7.869	6.7	0.9998	13.7	0.05	0.20	0.014
Phenol	7.899	26.6	0.9999	30.9	0.16	0.60	0.036
<i>tert</i> -Butylbenzene	8.158	2.5	0.9996	6.6	0.06	0.25	0.018
1,2,4-Trimethylbenzene	8.169	9.4	0.9995	7.2	0.06	0.31	0.018
<i>n</i> -Decane	8.244	17.7	0.9998	49.6	0.07	0.34	0.023
1,3-Dichlorobenzene	8.387	5.7	0.9998	8.7	0.04	0.15	0.011
<i>sec</i> -Butylbenzene	8.484	6.5	0.9984	10.3	0.04	0.18	0.013
1,4-Dichlorobenzene	8.507	6.4	0.9999	6.9	0.05	0.19	0.013
<i>p</i> -Isopropyltoluene	8.747	4.5	0.9998	9.9	0.04	0.16	0.012
<i>d</i> -Limonene	8.833	9.3	0.9995	14.5	0.12	0.53	0.046
1,2-Dichlorobenzene	8.964	4.1	0.9999	7.7	0.04	0.13	0.010
<i>n</i> -Butylbenzene	9.384	6.6	0.9994	10.3	0.04	0.16	0.012
Hexachloroethane	9.733	14.5	0.9997	13.9	0.04	0.15	0.011
1,2-Dibromo-3-chloropropane	9.894	6.5	0.9999	19.5	0.05	0.16	0.012
Nitrobenzene	9.976	13.0	0.9997	29.9	0.13	0.42	0.031
<i>n</i> -Undecane	10.145	9.2	0.9993	11.1	0.05	0.34	0.018
1,2,4-Trichlorobenzene	11.431	7.8	0.9997	8.7	0.06	0.20	0.015
Naphthalene	11.532	9.5	0.9975	12.9	0.08	0.35	0.021
<i>n</i> -Dodecane	11.674	14.7	0.9974	13.0	0.05	0.32	0.017
1,2,3-Trichlorobenzene	11.933	7.8	1.0000	7.5	0.08	0.27	0.020
Hexachlorobutadiene	11.978	8.0	1.0000	7.8	0.06	0.24	0.018
<i>n</i> -Tridecane	12.799	12.3	0.9978	13.6	0.06	0.41	0.020
<i>n</i> -Tetradecane	13.549	15.6	0.9960	25.5	0.10	0.67	0.031
<i>n</i> -Pentadecane	14.118	19.8	0.9944	26.2	0.10	0.85	0.034

¹ RT: retention time; ² Precision: duplicate precision; ³ RSD: relative standard deviation; ⁴ MDL: method detection limit; ⁵ MDL_8h: 8-h MDL; ⁶ MDL_7d: 7-day MDL.

4. Discussion

We developed empirical models that can estimate UR_{eff} values for a wide range of VOCs. Previous work developed Freundlich isotherm models [47,48], multilayer saturation models [12,49] and several computer programs [50,51]. However, the complexity and unavailability of parameters or programs impede the easy adoption of these models. Our models were an attempt to simplify the modeling process with reasonable biases. The relative biases of modeled $7d-UR_{eff}$ values were within 20% except for 1,2-dichloroethane (36%), in comparison to measured UR_{eff} values (Table A2). The relative biases of modeled $8h-UR_{eff}$ values were mostly within $\pm 20\%$ from measured values too. These biases were acceptable, considering the 16–69% variation of UR s under different environmental conditions [37], inter-laboratory variation of 40% [52] and U.S. EPA's criterion of $\leq 30\%$ for accuracy [25].

The laboratory analysis using TD-GC/MS shows excellent performance. The high reproducibility, linearity and sensitivity meet requirements by the U.S. EPA [4]. In particular, the MDLs are comparable with or superior to reported MDLs using tube-type passive samplers [44,53]. The sensitivity is sufficient for concentrations commonly found in indoor environments [7,54] and ambient air [55].

The empirical models are applicable under certain conditions. The samplers should be standard Tenax TA ATD tubes. Models only apply to nonpolar chemicals and a few polar chemical groups, including aromatics, branched alkanes and cycloalkanes, chlorinated compounds, acetates, acrylates and ketones. Models do not apply to alcohols, acids, anhydrides, higher amines, or chlorobenzene as their retention volumes on the ATD tube and boiling points did not show simple linear relationship [35]. The measured and modeled UR_{eff} values are valid for 8-h and 7-day sampling in occupational and environmental settings, respectively. ATD tubes are not recommended for very short passive sampling, given the considerable variability of the UR during the first hours [27,56]. According to requirements for determining the retention volumes [34] and ASTM's sampling protocols [23], ATD tubes can be used for 4–8 h passive sampling of job-related chemicals at a concentration range of $100 \mu\text{g}/\text{m}^3$ – $100 \text{mg}/\text{m}^3$ in workplaces.

In environmental applications, the sampling duration must be sufficient to collect enough mass measurable by GC/MS [11]. Although the current TD-GC/MS is sensitive enough for even <1 day samples, 7-day integrated samples are preferred in practice for several reasons. The total sample volume of $\sim 3 \text{L}$ is appropriate for the generally low levels of VOCs in environmental settings. The 7-day sampling reflects the long-term exposure and accounts for weekday and weekend variations. UR_{eff} values in Table 2 are the best estimates for 7-day sampling as they were modelled from 7-day UR data. The applicable concentration range is from the detection limit to $10 \mu\text{g}/\text{m}^3$ based on the original measurements. ASTM states that uptake rates are valid for a concentration range of $1 \mu\text{g}/\text{m}^3$ – $1 \text{mg}/\text{m}^3$ for individual compounds for 4-week exposure time. Combining these two ranges, the $7d-UR_{eff}$ values are valid for a concentration range from the detection limit to $1 \text{mg}/\text{m}^3$ for individual compounds.

Several limitations should be recognized in our modeling approach. Our models were applicable to the specific sampling durations and a specific ATD tube configuration. Laboratory, field and theoretical validations are needed for other sampling methods that involve different sorbents, exposure durations, concentration ranges and/or microenvironments. The $7d-UR_{eff}$ values were modeled based on measured UR_{eff} data from only one study. We conducted an extensive search but only found this study measured UR_{eff} for over 20 VOCs. We assumed that the diffusion geometry is the same for all the standard tubes. In reality, within-vendor and between-vendor variations may exist in the diffusion cap, air gap, tube inside diameter and retaining gauze. The simplified models did not include other influential parameters, such as air velocity, humidity, chemical concentration, interference and competition of chemicals and degradation and artifacts [19]. They also bypassed complex calculations involving other physicochemical properties, chemical-adsorbent interaction and adsorption isotherm. For example, terpenes, aromatics, acetates and alkanes displayed different UR change patterns with respect to exposure time [40]. The efficiency of passive samplers is strongly influenced by adsorption isotherms, such as Langmuir, Freundlich and Dubinin-Radushkevich isotherms [48]. The scarcity and

inconsistency of UR data warrants more laboratory and field measurements and future development and validation of practical models for estimating the UR_{eff} accurately.

Future measurement and modeling work should be extended to standard ATD tubes packed with other sorbents, or to different sampling durations. Some available UR datasets using ATD tubes include: (1) 24-h UR s on Carbopack X solid sorbent for 27 VOCs determined in laboratory chamber [16]; (2) 4-day UR s on Tenax TA and Carbopack B for 10 VOCs determined in laboratory chamber [37]; and (3) 4- to 10-day UR s on Carbopack B for 68 VOCs determined by field tests [38]. Depending on the analyte/sorbent combination, the adsorption behavior might be completely different and new models should be developed. Future work should also consider other passive samplers, e.g., 3M OVM, SKC, GABIE and Radiello samplers. The advantage of these other samplers is their fixed geometry and configuration, in contrast to the flexibility of ATD tubes. We anticipate the need for a user friendly software program or an online database that is capable of generating effective uptake rates given input parameters such as sampler type, sorbent, target compound and exposure duration. The database will not only promote the popularity of passive sampling techniques but ensure valid measurements.

5. Conclusions

This study developed and confirmed empirical models that can determine effective uptake rates (UR_{eff}) on the standard ATD tubes for a wide range of VOCs commonly detected in the environment. It fills an important data gap in the passive air sampling research. For short-term passive sampling (4–8 h) in occupational settings, UR_{eff} values can be modeled with available retention volumes or boiling points for aromatics, branched alkanes and cycloalkanes, chlorinated compounds, esters and ketones but not for alcohols. For long-term passive sampling (7 days) in environmental settings, the sampling efficiency (α) can be calculated from a function of boiling point for alkanes, aromatics, chlorinated compounds, carbonyls and terpenes. Ideal UR s calculated by the Fick's Law and tube geometry typically overestimate the actual sampling rate and cause biases. In the order of preference, we recommend using laboratory determined UR s followed by field validations, field determined UR s and modelled UR s under the same conditions. We suggest extending research on measuring and modeling effective uptake rates to ease the use of passive sampling among the general users.

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Conflicts of Interest: The authors declare no conflict of interest. The authors declare that they have no relevant or material financial interests that relate to the research described in this paper. The authors make no endorsement of any of the products, brands, trademarks, or companies they mentioned in this paper.

Appendix A

Table A1. Physical and chemical properties, diffusion parameters, measured and modeled uptake rates of volatile organic compounds measured in workplaces.

VOCs	CAS#	MW (g/mol)	BP ¹ (°C)	D_{298} ² (cm ² /sec)	UR_{ideal} ³ (mL/min)	$8h-UR$ ⁴ (ng/ppm·min)	$8h-UR$ (mL/min)	V_g ⁵ (L)	Log ₁₀ V_g	α ⁶	Pred. UR ⁷ (mL/min)	Bias ⁸ (%)
Alkanes												
<i>n</i> -Heptane	142-82-5	100.2	98	0.0723	0.568	1.57	0.383	34	1.53	0.636	0.361	−5.8
<i>n</i> -Octane	111-65-9	114.2	126	0.0671	0.527	1.67	0.357	160	2.20	0.739	0.390	9.0
<i>n</i> -Nonane	111-84-2	128.3	151	0.0628	0.493	1.75	0.334	1400	3.15	0.885	0.436	30.8
<i>n</i> -Decane	124-18-5	142.3	174	0.0592	0.465	1.96	0.337	4200	3.62	0.958	0.445	32.2
<i>n</i> -Undecane	1120-21-4	156.3	196	0.0562	0.441	1.97	0.308	25,000	4.40	1.000	0.441	43.2
<i>n</i> -Dodecane	112-40-3	170.3	216	0.0535	0.420	2.08	0.299	126,000	5.10	1.000	0.420	40.7
<i>n</i> -Tridecane	629-50-5	184.4	235	0.0512	0.402	2.33	0.309		5.40	1.000	0.402	30.1
<i>n</i> -Tetradecane	629-59-4	198.4	253	0.0492	0.386	2.41	0.297		5.91	1.000	0.386	30.1
<i>n</i> -Pentadecane	629-62-9	212.4	270	0.0473	0.371	2.19	0.252		6.39	1.000	0.371	47.4
<i>n</i> -Hexadecane	544-76-3	226.5	287	0.0457	0.359	2.36	0.255		6.88	1.000	0.359	40.9
Cyclohexane	110-82-7	86.2	81	0.0832	0.653	1.32	0.375		1.03	0.558	0.365	−2.6
Methylcyclohexane	108-87-2	98.2	101.1	0.0759	0.596	1.55	0.386		1.60	0.646	0.385	−0.2
2-Methylhexane	591-76-4	100.2	90	0.0724	0.569	1.48	0.361		1.28	0.597	0.340	−5.9
3-Methylhexane	589-34-4	100.2	91	0.0724	0.569	1.48	0.361		1.31	0.602	0.342	−5.2
2-Methylheptane	592-28-8	114.2	116	0.0672	0.528	1.95	0.417		2.02	0.711	0.375	−10.1
Aromatic compounds												
Benzene	71-43-2	78.1	80.1	0.0928	0.729	1.3	0.407	12.5	1.10	0.569	0.415	1.9
Toluene	108-88-3	92.1	111	0.0829	0.651	1.67	0.443	76	1.88	0.690	0.449	1.3
Ethylbenzene	100-41-4	106.2	136	0.0756	0.594	2.00	0.461	360	2.56	0.794	0.471	2.3
<i>m</i> -Xylene	108-38-3	106.2	139	0.0756	0.594	1.82	0.419	600	2.78	0.828	0.492	17.3
<i>p</i> -Xylene	106-42-3	106.2	139	0.0756	0.594	1.82	0.419	600	2.78	0.828	0.492	17.3
<i>o</i> -Xylene	95-47-6	106.2	144	0.0756	0.594	1.82	0.419	600	2.78	0.828	0.492	17.3
Styrene	100-42-5	104.1	145	0.0757	0.595	2.40	0.563	600	2.78	0.828	0.492	−12.6
Isopropylbenzene	98-82-8	120.2	153	0.0687	0.540	2.50	0.509	960	2.98	0.859	0.464	−8.8
Propylbenzene	103-65-1	120.2	158	0.0669	0.525	2.37	0.482	1700	3.23	0.897	0.472	−2.2
1,3,5-Trimethylbenzene	108-67-8	120.2	165	0.0698	0.548	2.37	0.482	3600	3.56	0.948	0.520	7.8
1,2,4-Trimethylbenzene	95-63-6	120.2	168	0.0686	0.539	2.37	0.482	3600	3.56	0.948	0.511	5.9
<i>o</i> -Ethyltoluene	611-14-3	120.2	165	0.0686	0.539	2.44	0.496		3.41	0.925	0.499	0.5
<i>m</i> -Ethyltoluene	620-14-4	120.2	159	0.0687	0.540	2.25	0.458		3.24	0.899	0.485	6.0
<i>p</i> -Ethyltoluene	622-96-8	120.2	161.7	0.0686	0.539	2.21	0.450		3.32	0.911	0.491	9.2
1,3-Dimethyl-4-ethylbenzene	874-41-9	134.2	185	0.0641	0.503	2.45	0.446		3.98	1.000	0.503	12.8
1,4-Diethylbenzene	105-05-5	134.2	184	0.0642	0.504	2.56	0.466		3.95	1.000	0.504	8.1
Naphthalene	91-20-3	128.2	218	0.0691	0.543	2.14	0.408		4.92	1.000	0.543	32.9

Table A1. Cont.

VOCs	CAS#	MW (g/mol)	BP ¹ (°C)	D ₂₉₈ ² (cm ² /sec)	UR _{ideal} ³ (mL/min)	8h-UR ⁴ (ng/ppm·min)	8h-UR (mL/min)	V _g ⁵ (L)	Log ₁₀ V _g	α ⁶	Pred. UR ⁷ (mL/min)	Bias ⁸ (%)
Halogenated Hydrocarbons												
Tetrachloroethylene	127-18-4	165.8	121	0.0767	0.602	2.80	0.413	96	1.98	0.705	0.425	2.9
Benzyl chloride	100-44-7	126.6	178.9	0.0728	0.572	2.72	0.525		3.81	0.986	0.564	7.3
Tetrachloroethene	127-18-4	165.8	121.1	0.0767	0.602	2.80	0.413		2.17	0.734	0.442	7.0
Bromobenzene	108-86-1	157.0	156	0.0789	0.620	3.31	0.515		3.16	0.886	0.549	6.5
Esters and Glycol Ethers												
Ethyl acetate	141-78-6	88.1	77.1	0.0892	0.701	1.60	0.444	7	0.86	0.532	0.373	−16.1
<i>n</i> -Butyl acetate	123-86-4	116.2	125.6	0.0738	0.580	2.26	0.476		2.29	0.753	0.436	−8.3
Isobutyl acetate	110-19-0	116.2	117.2	0.0739	0.580	1.91	0.402	265	2.42	0.773	0.449	11.6
<i>sec</i> -Butyl acetate	105-46-4	116.2	112.2	0.074	0.581	1.90	0.400		1.91	0.695	0.404	1.0
<i>tert</i> -Butyl acetate	540-88-5	116.2	97.8	0.0742	0.583	1.79	0.377		1.50	0.632	0.368	−2.3
Methyl acrylate	96-33-3	86.1	80	0.0918	0.721	1.500	0.426	13	1.11	0.572	0.412	−3.3
Methyl methacrylate	80-62-6	100.1	100	0.0825	0.648	1.77	0.432	55	1.74	0.668	0.433	0.1
Butyl acrylate	141-32-2	128.2	145	0.0697	0.547	2.60	0.496		2.84	0.838	0.459	−7.5
Ethylhexyl acrylate	1322-13-0	184.3	227.7	0.0552	0.434	2.99	0.397		5.19	1.000	0.434	9.3
Halothane	151-67-7	197.4	50	0.0824	0.647	2.59	0.321		0.15	0.423	0.273	−14.8
Enflurane	13838-16-9	184.5	56	0.078	0.613	2.29	0.303		0.32	0.449	0.275	−9.4
Isoflurane	26675-46-7	184.5	49	0.0782	0.614	2.20	0.292		0.12	0.418	0.257	−11.9
2-Methoxyethyl acetane	110-49-6	118.1	145	0.077	0.605	1.64	0.339		2.84	0.838	0.507	49.3
2-Ethoxyethyl acetate	111-15-9	132.2	156.1	0.0711	0.558	2.10	0.389		3.16	0.887	0.495	27.4
2-Ethoxyethanol	110-80-5	90.1	135	0.0859	0.675	1.80	0.488		2.56	0.794	0.536	9.7
2-Propoxyethanol	2807-30-9	104.1	153	0.0781	0.613	1.65	0.387		3.07	0.873	0.536	38.2
2-Butoxyethanol	117-76-2	118.2	171	0.0718	0.564	1.90	0.393		3.58	0.952	0.537	36.5
1-Methoxypropan-2-ol	107-98-2	90.1	121	0.0862	0.677	1.56	0.423		2.16	0.733	0.496	17.3
2-Methoxypropan-2-ol	72360-66-8	90.1	94.8	0.0865	0.679	1.52	0.412		1.42	0.618	0.420	1.9
Ketones and Aldehydes												
Butan-2-one	78-93-3	72.1	75.6	0.0943	0.741	1.34	0.454		0.87	0.534	0.396	−12.9
Methyl isobutyl ketone	108-10-1	100.2	118	0.0766	0.602	1.71	0.417		2.08	0.720	0.433	3.8
Cyclohexanone	108-94-1	98.2	155.6	0.0786	0.617	2.30	0.573	340	2.53	0.790	0.488	−14.9
2-Methylcyclohexanone	583-60-8	112.2	162.8	0.0739	0.580	2.31	0.504		3.35	0.916	0.532	5.6
3-Methylcyclohexanone	591-24-2	112.2	170	0.0738	0.580	2.22	0.484		3.55	0.947	0.549	13.5
4-Methylcyclohexanone	589-92-4	112.2	171	0.0738	0.580	2.14	0.466		3.58	0.952	0.552	18.3
Furfural	98-01-1	96.1	162	0.0889	0.698	2.5	0.636	600	2.78	0.828	0.578	−9.1
Hexanal	66-25-1	100.2	131	0.0765	0.601	1.64	0.400		2.45	0.777	0.467	16.6
Decanal	112-31-2	156.2	209	0.0584	0.459	2.32	0.363		4.66	1.000	0.459	26.3

Table A1. Cont.

VOCs	CAS#	MW (g/mol)	BP ¹ (°C)	D_{298} ² (cm ² /sec)	UR_{ideal} ³ (mL/min)	$8h-UR$ ⁴ (ng/ppm·min)	$8h-UR$ (mL/min)	V_g ⁵ (L)	Log ₁₀ V_g	α ⁶	Pred. UR ⁷ (mL/min)	Bias ⁸ (%)
Alcohols and Others												
Isobutanol	78-83-1	74.1	108	0.0910	0.715	1.260	0.416	6	0.75	0.515	0.368	−11.4
Furfuryl alcohol	98-00-0	98.1	170	0.0862	0.677	2.5	0.623		3.55	0.947	0.641	2.9
Tetrahydrofurfuryl alcohol	97-99-4	102.1	178	0.0817	0.642	1.9	0.455		3.78	0.982	0.630	38.6
Allyl glycidyl ether	106-92-3	114.2	154	0.0759	0.596	1.83	0.392		3.10	0.877	0.523	33.5
Butyl glycidyl ether	2426-08-6	130.2	164	0.069	0.542	2.36	0.443		3.38	0.921	0.499	12.6
<i>n</i> -Methylpyrrolidone	872-50-4	99.1	204	0.0808	0.635	1.83	0.451		4.52	1.000	0.635	40.6
<i>n</i> -Vinylpyrrolidone	88-12-0	111.1	95	0.0771	0.606	2.51	0.552		1.42	0.619	0.375	− 32.1
α -Pinene	80-56-8	136.2	156	0.0634	0.498	2.35	0.422		3.16	0.886	0.441	4.6

Notes: ¹ BP: boiling point, from [46]; ² D_{298} : diffusion coefficient at 298K, from [31]; ³ UR_{ideal} : ideal uptake rate, calculated from Equation (1); ⁴ $8h-UR$: Measured 8-h effective uptake rate, from [36]; ⁵ V_g : retention volume, taken from [23] or calculated by Equation (5) if missing; ⁶ α : sampling efficiency, calculated using Equation (4). $\alpha = 1$ if the calculated value exceeds 1; ⁷ Pred. UR : predicted UR , calculated using Equation (2); ⁸ %Bias: Percent bias of predicted $8h-UR$ from measured $8h-UR$. Values of <−20% or >20% were in bold highlighted.

Table A2. Data used to model 7-day effective uptake rates.

VOCs	CAS#	BP ¹ (°C)	D ₂₉₈ ² (cm ² /s)	UR _{ideal} ³ (mL/min)	7d-UR _{eff} ⁴ (Obs.) (mL/min)	7d-α ⁵ (Obs.)	7d-UR _{eff} ⁶ (Mod.) (mL/min)	Bias ⁷ (%)
<i>n</i> -Hexane	110-54-3	69	0.0788	0.619	0.16	0.259	0.190	18.7
<i>n</i> -Heptane	142-82-5	98	0.0723	0.568	0.26	0.458	0.246	-5.5
<i>n</i> -Octane	111-65-9	126	0.0671	0.527	0.27	0.512	0.275	2.0
<i>n</i> -Nonane	111-84-2	150.8	0.0628	0.493	0.34	0.689	0.289	-14.9
<i>n</i> -Decane	124-18-5	174.1	0.0592	0.465	0.28	0.602	0.297	6.0
<i>n</i> -Undecane	1120-21-4	195.5	0.0562	0.441	0.28	0.634	0.300	7.2
<i>n</i> -Dodecane	112-40-3	216.3	0.0535	0.420	0.26	0.619	0.301	15.7
Methylcyclopentane	96-37-7	71	0.0827	0.650	0.20	0.308	0.206	3.0
Cyclohexane	110-82-7	81	0.0832	0.653	0.25	0.383	0.238	-4.8
Benzene	71-43-2	80.1	0.0928	0.729	0.27	0.370	0.263	-2.8
Toluene	108-88-3	111	0.0829	0.651	0.32	0.491	0.311	-2.9
Ethylbenzene	100-41-4	136	0.0756	0.594	0.35	0.589	0.327	-6.7
<i>m</i> & <i>p</i> -Xylene	108-38-3	139	0.0756	0.594	0.36	0.606	0.331	-8.0
<i>o</i> -Xylene	95-47-6	144	0.0756	0.594	0.38	0.640	0.339	-10.9
Propylbenzene	103-65-1	159.2	0.0669	0.525	0.36	0.685	0.319	-11.5
1,2,4-Trimethylbenzene	95-63-6	169.5	0.0686	0.539	0.35	0.650	0.339	-3.2
Styrene	100-42-5	145	0.0757	0.595	0.36	0.606	0.341	-5.4
Phenol	108-95-2	182	0.0844	0.663	0.43	0.649	0.434	0.9
Benzaldehyde	100-52-7	179	0.0788	0.619	0.41	0.662	0.401	-2.1
Ethyl acetate	141-78-6	77	0.0881	0.692	0.23	0.332	0.239	4.1
Hexanal	66-25-1	130.5	0.0765	0.601	0.17	0.283	n.a.	n.a.
1,2-Dichloroethane	107-06-2	83.5	0.0922	0.724	0.20	0.276	0.272	35.8
Tetrachloroethylene	127-18-4	121	0.0767	0.602	0.28	0.465	0.306	9.3
α-Pinene	80-56-8	155	0.0634	0.498	0.20	0.402	n.a.	n.a.
<i>d</i> -Limonene	5989-27-5	177	0.0632	0.496	0.27	0.544	0.320	18.5

Note: ¹ BP: boiling point, from [46]; ² D₂₉₈: diffusion coefficient at 298K, from [31]; ³ UR_{ideal}: ideal uptake rate, calculated from Equation (1); ⁴ 7d-UR_{eff} (obs.): observed 7-day effective uptake rate, taken from [18]; ⁵ 7d-α (obs.): observed 7-day sampling efficiency, calculated from Equation (2); ⁶ 7d-UR_{eff} (mod.): modeled 7-day effective uptake rate, calculated using Equations (6) and (2); ⁷ %Bias: Percent bias of 7d-UR_{eff} (mod.) from 7d-UR_{eff} (obs.).

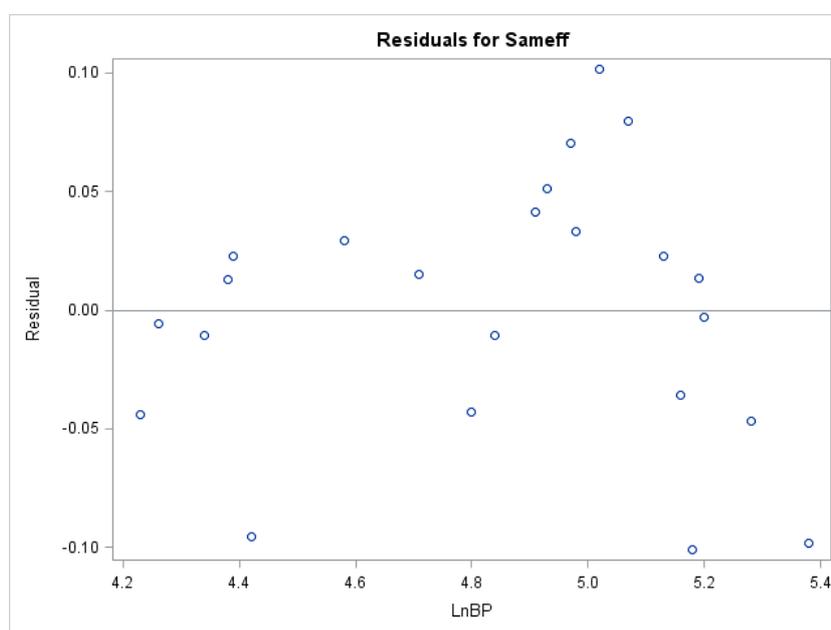


Figure A1. Residual plot of linear regression of 7d-α (Sameff) against LnBP.

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