



Missouri University of Science and Technology
Scholars' Mine

Civil, Architectural and Environmental
Engineering Faculty Research & Creative Works

Civil, Architectural and Environmental
Engineering

01 Jan 2003

Rapid Measurement of Indoor Mass-Transfer Coefficients

Glenn Morrison

Missouri University of Science and Technology, gcm@mst.edu

Zhao Ping

Deborah J. Wiseman

Maneerat Ongwandee

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/civarc_enveng_facwork/23

Follow this and additional works at: https://scholarsmine.mst.edu/civarc_enveng_facwork

 Part of the [Civil Engineering Commons](#)

Recommended Citation

G. Morrison et al., "Rapid Measurement of Indoor Mass-Transfer Coefficients," *Atmospheric Environment*, Elsevier Ltd., Jan 2003.

The definitive version is available at <https://doi.org/10.1016/j.atmosenv.2003.09.034>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Civil, Architectural and Environmental Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Rapid measurement of indoor mass-transfer coefficients

Glenn C. Morrison*, Zhao Ping, Deborah J. Wiseman, Maneerat Ongwandee,
Hong Chang, Julie Portman, Shekhar Regmi

*Department of Civil, Architectural and Environmental Engineering, University of Missouri-Rolla, 233 Butler-Carlton Hall,
Rolla, MO 65409-0030, USA*

Received 31 March 2003; accepted 28 July 2003

Abstract

Indoor air pollutant concentrations can be influenced by how rapidly species are transported to and from surfaces. Consequently, a greater understanding of indoor transport phenomena to surfaces improves estimates of human exposure to indoor air pollutants. Here, we introduce two methods of rapidly and directly measuring species fluxes at indoor surfaces, allowing us to evaluate the transport-limited deposition velocity, v_t (a mass-transfer coefficient). The deposition velocity sensor (DeVS) method employs a small microbalance coated with a pure hydrocarbon, preferably octadecane. We quantify flux (or evaporation rate) of the hydrocarbon into a room by observing the rate of mass loss on the microbalance. The transport-limited deposition velocity, $v_{t, \text{octadecane}}$, is then obtained by combining the flux with the vapor pressure of the hydrocarbon. Simultaneously, $v_{t, \text{ozone}}$ is quantified using the deposition velocity of ozone (DeVO) method, which acts as a standard to calibrate and evaluate DeVS. Specifically, DeVO evaluates ozone transport to surfaces by quantifying the conversion by ozone of nitrite to nitrate on a glass fiber filter. Simultaneous laboratory chamber experiments demonstrates that v_t for octadecane and ozone are strongly correlated, with the values for ozone ~ 1.5 times greater than that for octadecane. In an office experiments, the DeVS method responds within minutes to step changes in conditions such as occupancy, activities and ventilation. At present, the results are in order-of-magnitude agreement with predicted indoor mass-transfer coefficients.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Ozone; Deposition velocity; Pollutant transport; Microbalance; Indoor air

1. Introduction

The concentration of some indoor air pollutants is strongly influenced by the rate of transport to, and irreversible deposition onto surfaces. The transport rate is in turn dependent on indoor air movement and the molecular diffusivity of the pollutant. The characteristics of air movement can change rapidly throughout the day as ventilation systems turn on and off, windows open or close, and even through convective air movement as a result of heat generated by people. Researchers have sought to understand transport through

mathematical modeling (Nazaroff and Cass, 1989; Cano-Ruiz et al., 1993; Haghghat and Zhang, 1999) and measurements (see review in Nazaroff et al., 1993) but these measurements are sparse and often time consuming (Salmon et al., 1990). To capture the influence of indoor conditions on pollutant mass transport, our research seeks to develop methods for rapidly and continuously measuring the location specific, transport-limited deposition velocity, v_t , a mass-transfer coefficient. This parameter, in conjunction with an indoor mass conservation model, the molecular diffusivity and the surface uptake probability, γ , can be used to evaluate indoor pollutant exposure and indoor pollution models. Our goal is to demonstrate proof-of-principle for the idea that a microbalance can be used to rapidly measure indoor mass-transfer

*Corresponding author. Tel.: +1-573-341-7192; fax: +1-573-341-4729.

E-mail address: gcm@umr.edu (G.C. Morrison).

coefficients. The specific objectives of this investigation are to (1) demonstrate that v_t evaluated by hydrocarbon evaporation from a microbalance is of the right order of magnitude, (2) that the microbalance output correlates with v_t derived from a quantitative measure of ozone deposition, and (3) that it can rapidly detect changes in mass-transport conditions.

1.1. Indoor concentrations and exposure estimates

In typical indoor spaces, simple mass-conservation models have proven to be quite accurate in predicting indoor pollutant concentrations (Weschler et al., 1989). Using infiltrated ozone (O_3) as an example of a surface reactive pollutant, the indoor concentration can be estimated by assuming a building represents a steady-state, continuously mixed flow reactor (CMFR):

$$C_{O_3}(\text{bulk indoor air}) = C_{O_3}(\text{outdoor}) \frac{Q}{Q + Av_d}, \quad (1)$$

where $C_{O_3}(\text{bulk indoor air})$ is the volume averaged indoor ozone concentration, $C_{O_3}(\text{outdoor})$ is the outdoor ozone concentration delivered to the building by infiltration, Q is the infiltration rate, A is the total indoor surface area, and v_d is the area-averaged deposition velocity, a mass transfer coefficient. The deposition velocity is defined through the following equation:

$$J = v_d C_{O_3}(\text{bulk indoor air}), \quad (2)$$

where J is the area-averaged flux of ozone to indoor surfaces (Nazaroff et al., 1993).

For infiltrated pollutants with a relatively large deposition velocity, indoor concentrations are substantially lower than the outdoor concentrations.

Cano-Ruiz et al. (1993) showed that v_d is a function of the transport-limited deposition velocity, v_t , a parameter that is independent of surface reactivity. A time-averaged, surface specific v_t has been measured for synthetic aerosols (Thatcher et al., 1996; Thatcher and Nazaroff, 1997), fine mode sulfur particles (Ligocki et al., 1990), nitric acid (Salmon et al., 1990) and radon progeny (Bigu, 1985). More commonly, researchers indirectly measure the area averaged flux, J , by measuring the rate of removal of the pollutant from the air space (Nazaroff et al., 1993). This is because (1) the area-averaged values of mass-transfer coefficients are more readily integrated into existing indoor-air concentration models and (2) the pollutant flux is usually too low to measure an instantaneous surface specific deposition velocity.

The ability to evaluate v_t in real time would greatly advance our understanding of indoor air pollution and exposure. Specifically, real-time measurements during field studies of reactive pollutants can improve models that predict pollutant concentrations and dynamics. Real-time measurements can also allow us to rapidly

evaluate how changes in indoor conditions such as ventilation and occupancy influence indoor pollutant transport to surfaces. To make it possible for a microbalance to be used to generate rapid measurements of v_t for specific pollutants we must first establish that evaporation of a volatile species is analogous to deposition and a surrogate species can be used in place of the pollutant species to measure v_t .

1.2. Evaporation and deposition processes are analogous

The flux of a (now generalized) pollutant in Eq. (2) can be stated another way,

$$J = k(C(\text{bulk air}) - C(\text{surface})), \quad (3)$$

where $C(\text{surface})$ is the concentration of the pollutant adjacent to the surface, and k is a mass-transfer coefficient in the traditional sense (Bird et al., 1960). Note that when the surface acts as perfect sink, then $C(\text{surface}) = 0$ and by comparing Eqs. (2) and (3), $k = v_d$. Since the system is now transport limited, $v_d = v_t$. Therefore, $k = v_t$, and v_t can be evaluated if the flux and the bulk air concentration are known. As a result, $k \equiv v_t$, regardless of the magnitude of the surface and bulk concentrations. Thus the transport-limited deposition velocity can be evaluated if the $C(\text{surface})$ and $C(\text{bulk air})$ are known. As a consequence, the direction of flux is unimportant in evaluating v_t .

1.3. One species can act as a surrogate for measuring v_t for another species (e.g. a pollutant)

A model has been proposed (Lai and Nazaroff, 2000; Morrison and Nazaroff, 2002) that evaluates the absolute and relative magnitude of the gas-phase resistance of mass transport to smooth surfaces. One of the key conclusions of the model is that the transport-limited deposition velocity, v_t , is given by

$$v_t = \frac{u^*}{\Gamma}, \quad (4)$$

where the friction velocity, u^* , is a value related to shear stress within the fluid. Lai and Nazaroff (2000) report that typical indoor values of u^* range from 0.3 to 3 cm s^{-1} . The parameter Γ is a function of the kinematic viscosity of air, ν , and the molecular diffusivity of the species, D . For example, numerical integration of Eq. (15) in Lai and Nazaroff (2000) yields $\Gamma = 13.3$ for ozone in air at 1 atm and 296 K. Correspondingly, $\Gamma = 33.4$ for octadecane, an alkane used in this research to measure v_t . Since u^* is independent of species, it follows that

$$v_{t,A} = v_{t,B} \frac{\Gamma_B}{\Gamma_A}. \quad (5)$$

Therefore, a benign species (B) can be used as a surrogate for measuring the transport-limited deposition

velocity of a pollutant (A). Any pair of compounds will do, but for this example, $v_{t, \text{ozone}} = 2.5(v_{t, \text{octadecane}})$.

1.4. Evaluation of v_t using a microbalance

In this study, we measure v_t in real time by observing how rapidly octadecane evaporates from a quartz crystal microbalance into a room. The advantages of this method are that (1) the measurement is specific to a region of a room around the microbalance, (2) the flux measurement is rapid, and (3) the measurement is continuous. To ensure that the method truly captures mass transport, we compare v_t for octadecane evaporation to v_t derived from ozone deposition to treated filters. Measurements derived from both methods under a variety of mass-transfer conditions should be linearly correlated. However, Eq. (5) can only be directly applied for comparing sources/sinks that are of the same size or same characteristic dimensions. The influence on relative deposition velocity measurements due to the difference in diameters between the two devices will be considered in Section 3.

2. Methods

2.1. Transport-limited DeVS using hydrocarbon evaporation from a microbalance

Shown in Fig. 1, a 10 MHz, 1.4 cm diameter piezoelectric quartz crystal microbalance was positioned within the 1.5 cm hole of a thin aluminum plate so that the face of the microbalance crystal and plate are in the same geometric plane. The hole was centered in the 30×20 cm plate. A second quartz crystal was positioned ~ 0.5 cm behind the sensing crystal as a reference. This reference crystal was covered by a metal sheath to

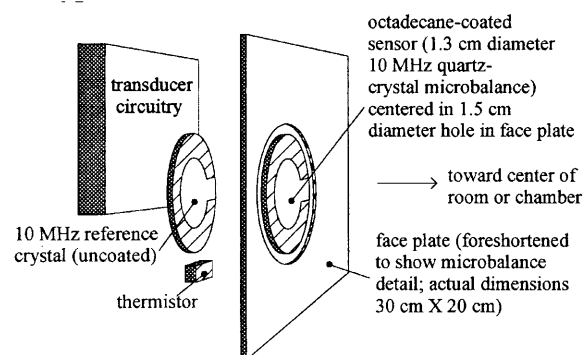


Fig. 1. Schematic of DeVS. A 10 MHz quartz-crystal microbalance is positioned in the center of an aluminum plate with an identical microbalance crystal positioned behind it as a reference. A thermistor next to the microbalances measures temperature. All transducer circuitry is located behind the plate.

prevent accumulation of contaminants on the surface. A thermistor was positioned within 1 cm of the crystals to measure temperature. Transducer circuitry was mounted behind the plate, opposite the side that faces the room for flux measurements. The transducer circuitry combined the frequency from the sense and reference crystals to obtain a beat frequency. Continuous measurements of beat frequency and temperature were collected on a data-acquisition computer system.

The microbalance was coated either (1) by painting a liquid hydrocarbon (e.g. octadecane) onto the microbalance using a small artists brush or (2) by condensing hot hydrocarbon vapors onto the face of the microbalance. Both application techniques produced similar results, but the first technique tends to damage the gold electrode of the microbalance. Therefore, the second technique was used for all reported experiments except where noted. In this technique, the hydrocarbon was placed in a heated evaporating dish. A “heat gun” blower forced evolved vapors onto one face of the microbalance. A brass plate with a hole acted as a mask to ensure that only the gold electrode (0.8 cm in diameter) was coated; the crystal area defined by the gold electrodes is the only sensitive or “active” area. We quantified the condensed hydrocarbon mass by observing the change in frequency of the microbalance (Mandelis and Christofides, 1993). The mass coated on the crystal prior to an experiment was typically between 5 and $10 \mu\text{g}$. Coating compounds tested included C_{14} through C_{22} *n*-alkanes, naphthalene, and acenaphthalene. Octadecane (C_{18}) is presently preferred because (1) it is non-toxic, (2) it is non-polar and thus the mass measurement should not be significantly influenced by changes in humidity and (3) it was found to generate continuous flux measurements for >10 h (Morrison et al., 2002).

For any coated compound, v_t can be evaluated rapidly and continuously because the evaporative flux is directly proportional to the rate of change of the microbalance frequency (or beat frequency), $\Delta f / \Delta t$ (Hz s^{-1}) (Morrison et al., 2002). Mandelis and Christofides (1993) show that the change in frequency, Δf , of a quartz crystal due to mass applied or removed from the surface is given by

$$\Delta f = \frac{-2.3 \times 10^6 F^2 \Delta m}{A}, \quad (6)$$

where F is the base frequency of the microbalance (MHz), Δm is the change in mass (g) on the crystal and A is the active area cm^2 of the crystal. The constant, 2.3×10^6 , is derived from theoretical considerations of the dynamics of induced crystal vibrations. The average flux over time interval Δt of a compound evaporating from the surface is given by

$$J = \frac{\Delta m}{A \Delta t} = v_t C_{\text{Pv}}(\text{coating}), \quad (7)$$

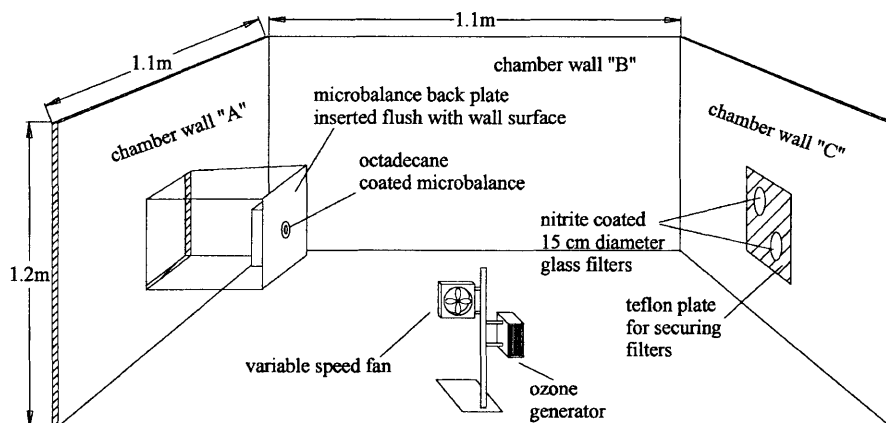


Fig. 2. Schematic of experimental chamber. The octadecane coated microbalance assembly is inserted flush into wall "A" of the laboratory chamber. Two nitrite coated glass filters are attached to a Teflon backplate that is secured directly opposite the microbalance on wall "C". A variable speed fan and an ozone generator are attached to a ring stand in the center of the chamber; air from the fan is directed toward wall "B".

where $C_{Pv}(\text{coating})$ is the concentration of the pure coating compound (e.g. octadecane) adjacent to the surface of the coating derived from the vapor pressure, and assuming that the concentration of the compound in the bulk air of a room is negligible (by Eq. (3) and discussion thereafter). Combining we find that

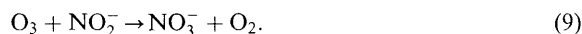
$$v_t = \frac{-1}{2.3 \times 10^6 C_{Pv}(\text{coating}) F^2 \Delta t} \Delta f \quad (8)$$

Because vapor pressure (Baum, 1998) can vary by an order of magnitude over the typical range of indoor temperatures, we continuously measured temperature at the microbalance with the thermistor noted above and incorporated the appropriate value of $C_{Pv}(\text{coating})$ into the calculation of v_t by Eq. (8).

Uncertainty in v_t , octadecane is largely influenced by the term Δf in Eq. (8) because subtraction of two large numbers (frequency of the order 1000 Hz) to arrive at a much smaller number (frequency of the order 10 Hz) can introduce large uncertainties. Based on an analysis of noise and stability (or drift), we have determined that under typical conditions, a value of $\Delta f = 10$ Hz is sufficient to provide a deposition velocity value with 25% uncertainty. This is equivalent to v_t , octadecane = 0.2 cm s^{-1} where the required time interval, Δt , is ~ 200 s.

2.2. Transport-limited deposition velocity for ozone (DeVO) deposition to a reactive surface

In this method, ozone that deposited on a piece of glass-fiber filter was quantified by the amount of nitrite converted to nitrate, by the following reaction:



Preparation of the coated filters was based on Koutrakis et al. (1993) and Wolfson (2003). The coating solution was prepared 100 ml at a time: 1 g NaNO_2 , 1 g of K_2CO_3 , 0.2 g of erythritol $\text{C}_4\text{H}_6(\text{OH})_4$, 70 ml distilled water, 30 ml methanol. This solution was stored at 4°C until needed. In an anaerobic glove box, 12 glass fiber filters (15 cm diameter, Fischer Scientific 09-804-150A) were placed flat on a clean nylon screen. Using a pipette, 5 ml of the coating solution was applied uniformly to completely saturate each filter. These were dried in the glove box for at least 24 h and stored in the glove box to prevent oxidation and contamination. To verify that ozone deposits at the transport-limited rate, we doubled the number of reactive sites on some filters by saturating them with a double-strength coating solution (all components except water and ethanol) and evaluated as discussed below in the chamber exposure experiments.

After a sufficient interval of exposure in the chamber or field test site, the filter was removed and analyzed as follows. Separately, each filter was placed in a sealed plastic bag with 100 ml DI water. The bag and contents were then placed in an ultrasonic cleaning bath for 5 min to enhance the dissolution of the nitrite/nitrate salts. The resulting solution was filtered through a $0.45 \mu\text{m}$ syringe filter and analyzed by ion chromatography (IC). IC parameters were as follows: Dionex-120 with an Ionpac AG9-HC guard and AS9-HC separation column, flow rate of $1.0 \text{ cm}^3 \text{ min}^{-1}$ of a 9.0 mM sodium carbonate. The lower limit of detection (LLD) of nitrate is 0.05 mg l^{-1} and the uncertainty in replicate injections is larger of 0.1% or 0.05 mg l^{-1} .

The transport-limited deposition velocity for ozone using the DeVO system is calculated as follows:

$$v_t, \text{ ozone} = \frac{m_{\text{NO}_3} \text{MW}_{\text{O}_3}}{C_{\text{O}_3} \text{MW}_{\text{NO}_3} A \Delta t} \quad (10)$$

where m_{NO_3} is the mass of nitrate formed on the filter, MW is the molecular weight of the subscripted compound, C_{O_3} is the time-averaged room concentration of ozone during the exposure interval, A is the exposed area of the filter and Δt is the time interval exposed. Eq. (10) was derived assuming that the concentration of ozone adjacent to the reactive surface was near zero (a consequence of low surface resistance to overall mass transfer). The elapsed time, Δt , required to evaluate $v_{t, \text{ozone}}$ was dependent on the LLD of nitrate by IC, the purity of the nitrite salt, and the rate of ozone deposition. The LLD of $v_{t, \text{ozone}}$ for a typical chamber experiment was $\sim 0.05 \text{ cm s}^{-1}$ based on replicate chamber blank filters. Uncertainty in $v_{t, \text{ozone}}$ based on replicate filters in chamber experiments was $\sim 10\%$. However, uncertainty in $v_{t, \text{ozone}}$ was dependent on specific experimental conditions, such as ozone concentration and the magnitude of the mass transfer coefficient.

2.3. Laboratory chamber experiments

The DeVS and DeVO methods were tested in a small chamber to examine the correspondence between the two methods and reproducibility. The test chamber in Fig. 2 is a 1.5 m^3 cube, made of 1.9 cm thick foam insulation panels that were coated on each side with a plastic film. In a typical experiment, the DeVS was installed in the center of one vertical face of the cubic chamber for testing. Two coated DeVO filters were attached to a 30 cm^2 Teflon sheet that was itself centered on the opposite wall of the chamber. To evaluate the two systems simultaneously, it was necessary to position them in different locations (they cannot be co-located). We chose to center each on opposite walls, appealing to symmetry, rather than placing them on the same wall where they may interfere with one another. The chamber was sealed (little or no ventilation). A small, variable output, 15 W fan ($2.9 \text{ m}^3 \text{ min}^{-1}$ at maximum setting) was attached to a ring stand in the middle of the chamber for mixing. The fan was outfitted with an external controller so that fan power/speed can be varied. For consistency, the fan was operated at only five different speed settings (off, 1,2,3,4), corresponding to fan power ranging from 0 to 15 W at approximately equal intervals. Also attached to the ring stand was a small electrostatic precipitator (consumer version) that produced ozone as a byproduct. This device was used as our ozone generator. An ultraviolet light photometric ozone analyzer with a LLD of 0.6 ppbv and a precision of 0.5% was used to measure ozone continuously during these experiments. Ozone concentrations typically rose during the experiment from 0 ppbv to a maximum just prior to when the chamber was opened. Average ozone levels in these experiments ranged from 50 to 150 ppbv.

Experiments conducted in the laboratory chamber include simultaneous evaluations of the two methods under different mixing conditions, DeVS response to changing conditions including humidity, and DeVO response with single and double-strength nitrite coatings. For side-by-side comparisons, a total of 19 individual experiments were performed, each at a single mixing condition, i.e. fan speed was unchanged during the experiment. During some DeVS only experiments, the fan speed was changed throughout the experiment to simulate changing flow conditions in a room. The humidity dependence of the coated and uncoated DeVS device was evaluated by introducing humidified, zero-grade nitrogen at 11 min^{-1} into a 21 glass beaker that covered the face of the DeVS sense crystal. Humidity was controlled by splitting the flow into two streams: one dry, the second directed through two bubblers in series (e.g. $0.21/\text{min}$ directed through the bubbler results in $\sim 20\%$ RH).

To test the hypothesis that ozone was depositing at or near the transport-limited rate, several experiments were performed in which one filter was coated as usual and the second filter (in the same chamber experiment) was coated with twice the amount of nitrite salts. If higher levels of nitrate formed on the double-strength filter this would indicate that transport-limited conditions have not been achieved. DeVS transducer drift was quantified by operating the uncoated microbalance in the chamber for $> 24 \text{ h}$ under typical conditions. Encouraging results from these laboratory studies gave us confidence to perform experiments at a field site.

2.4. Field experiment in a university office

To observe how changes in activity and ventilation influence, v_t , we operated DeVS in a university office under a variety of conditions. The office measured $3 \times 3 \times 6 \text{ m}$. Windows were initially closed and there was no forced ventilation during the experiment. There were two heat sources other than occupants: a steam radiator and a computer. During the experiment, the level of activity in the room was increased by having 3 students and 1 professor enter, 2 at a time, 15 min apart. After entering, they sat still reading or talking. Then they all stood and walked within the room for 15 min. Next the occupants exited. Finally the window and door were opened sequentially. Note that, for this experiment only, the DeVS was coated by painting octadecane onto the crystal face using an artist's paintbrush.

3. Results and discussion

3.1. Laboratory chamber experiments

Figs. 3(a) and (b) show the output of the DeVS as a function of time for chamber experiment in which the

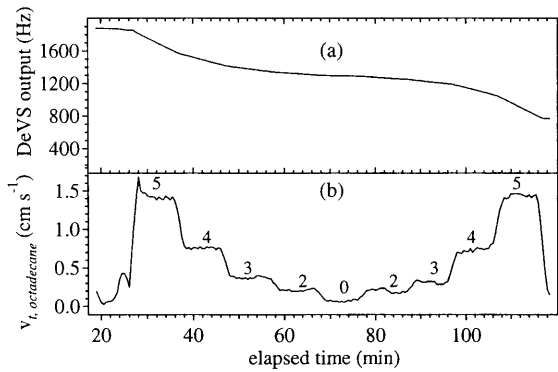


Fig. 3. Output from DeVS for a chamber experiment in which fan speed is adjusted (0–5 represents increasing speeds from off to ~ 15 W output). Shown are the frequency difference between sense and reference microbalance crystals (a) and the resulting transport-limited deposition velocity, $v_{t, \text{octadecane}}$, (b) which is directly proportional to the slope of plot (a).

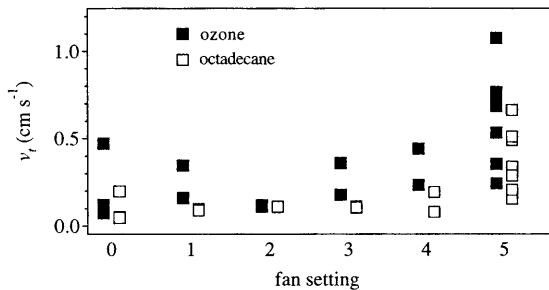


Fig. 4. Transport limited deposition velocity for ozone and octadecane as a function of fan speed setting. At fan speed 5, approximately 15 W of power are delivered to the chamber (heat and momentum). The fan is off at fan speed 0.

fan speed was decreased, then increased, stepwise from setting 4 (approximately 15 W total power input to chamber) to off. As mass evaporates from the balance, the frequency difference between the sense and reference microbalance crystal decreases. The slope of the frequency vs. time plot is proportional to the deposition velocity by Eq. (8).

Shown in Fig. 4 are the time-averaged values of v_t as a function of fan speed for ozone (DeVO) and octadecane (DeVS). The fan speed remains constant during each experiment. We observed a large amount of scatter at higher fan speed for both DeVS and DeVO methods. This suggests that the experimental conditions at a given fan setting are not reproducible. Note also that the spread in the results at setting 0 encompasses the highest value obtained at setting 3. This may mean that some uncontrolled phenomena, such as thermal convection, overwhelms the energy introduced by the fan at those settings. Only on setting 5 does the fan appear to

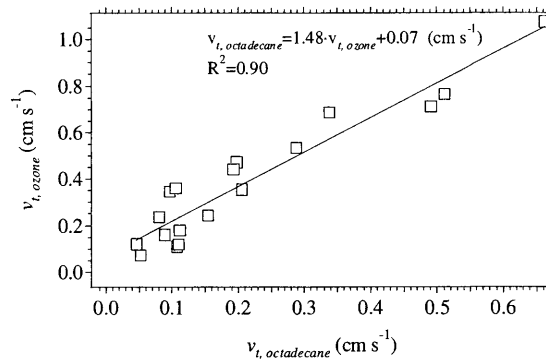


Fig. 5. Correlated transport limited deposition velocities of ozone (DeVO) and octadecane (DeVS) from laboratory chamber experiments. Each point represents the time-averaged value of v_t over the entire experiment, where the elapsed time ranges from 8 to 16 h.

significantly increase the rate of mass transfer over that introduced by other phenomena. Based on air movement induced by fans, we estimated (in Morrison, et al., 2002) that $v_{t, \text{ozone}} = 1.1 \text{ cm s}^{-1}$ and $v_{t, \text{octadecane}} = 0.45 \text{ cm s}^{-1}$ at the highest fan speed. Though variable, the values obtained from DeVO and DeVS devices are of the right order of magnitude.

Despite the variability of experimental conditions, the question of whether these methods adequately measure mass transport is best answered by a side-by-side comparison of the two methods. A comparison of individual experimental v_t values in Fig. 5 demonstrates that v_t for octadecane and ozone are highly correlated. Thus, the conditions that the DeVS and DeVO devices experience in an individual experiment are also correlated, if still somewhat variable. Some of the scatter shown in Fig. 5 may be due to placing the devices on opposite walls. The conditions should be similar, but are not identical.

The slope of the fitted line in Fig. 5 indicates that $v_{t, \text{ozone}}/v_{t, \text{octadecane}}$ is ~ 1.45 . The predicted ratio is ~ 2.5 , based on the model of Lai and Nazaroff (2000) which incorporates the assumption of a fully developed concentration boundary layer in enclosure flow. However, since characteristic dimensions of the octadecane source (DeVS source diameter = 0.8 cm) and ozone sink (DeVO sink diameter = 15 cm) are significantly different, we would not expect their mass-transport properties to be directly comparable through Eq. (5). The characteristic dimension, L , influences mass transport explicitly through the Sherwood number, Sh , a conventional dimensionless parameter for characterizing mass transport:

$$Sh = \frac{v_t L}{D}, \quad (11)$$

where D is the molecular diffusivity of the species transported. Bird et al. (1960) report that $Sh \propto L^a$, where a is typically a positive, non-integer ≤ 1 that depends on the configuration of the source or sink and fluid conditions. Thus, $v_t \propto L^{a-1}$ and as the dimensions of the source or sink become larger, v_t decreases. The ratio, $v_{t, \text{ozone}}/v_{t, \text{octadecane}}$, in our experiments is therefore expected to be somewhat smaller than 2.5. By the same argument, the value of $v_{t, \text{ozone}}$ is expected to be somewhat higher than the average value for the entire chamber or chamber wall. Assuming that mass transport in the chamber can be reasonably modeled by turbulent flow over a flat plate, then $a = 0.8$ (Bird et al., 1960) and $v_{t, \text{ozone}}/v_{t, \text{octadecane}} \sim 1.4$; laminar flow over a flat plate yields $a = 0.5$ and $v_{t, \text{ozone}}/v_{t, \text{octadecane}} \sim 0.6$. Ultimately, the results from either method must be scaled to properly to account for the difference in characteristic lengths if they are to be comparable to predictions based on models such as that by Lai and Nazaroff, 2000. The annular gap around the edge of the coated microbalance may also act to enhance the average evaporation rate by providing an additional transport path for octadecane vapor and perturbing the boundary layer.

The DeVs device in its present configuration is moderately sensitive to changes in humidity. Respectively, the uncoated and coated crystal outputs increase by ~ 80 and 40 Hz for a humidity increase from ~ 20 to 80% RH. We interpret the difference to be due to water condensing on only bare electrode surfaces: both sides for a completely uncoated crystal, but only on the uncoated side of the coated crystal. More importantly, however, we observed no consistent humidity effect on deposition velocity. For constant mass-transfer conditions, the evaporation rate of octadecane at 20% RH was not significantly different from that at 80% RH.

Based on experiments with single and double-strength nitrite coatings on DeVO filters, we conclude that ozone is depositing at the transport-limited rate. Paired filters, one standard and one coated with a double-strength nitrite solution, were evaluated after simultaneous exposure in the chamber at several fan speeds. Fig. 6 demonstrates that the measured deposition velocity was 1.04 ± 0.09 times larger for a filter with twice the nitrite coating.

3.2. Field experiment in office

Shown in Fig. 7 are the results of the office experiment. Note that $v_{t, \text{octadecane}}$, not $v_{t, \text{ozone}}$, is measured in this experiment, but the results are reported as $v_{t, \text{ozone}}$ by using the calibration parameter determined by the slope of the fitted line in Fig. 5. Therefore, the DeVs frequency output is transformed and reported as $v_{t, \text{ozone}}$ (as though it were measured with a 15 cm diameter filter) and plotted as a 2 min running average.

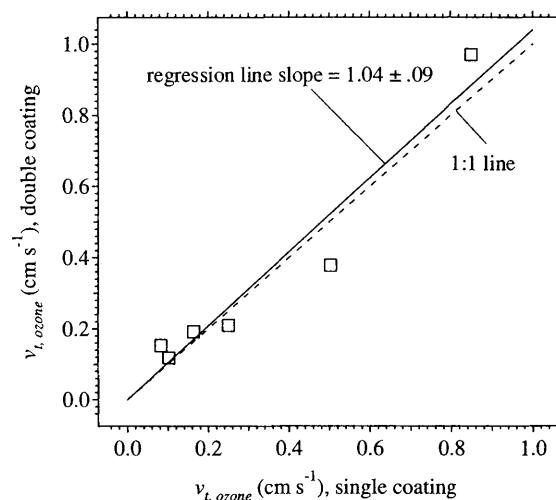


Fig. 6. Comparison of paired filters, one standard and one coated with a double-strength nitrite solution, evaluated after simultaneous exposure in the chamber at several fan speeds. Data falling on the 1:1 line would indicate transport-limited deposition rates on both filters. The slope of the regression line, 1.04 ± 0.09 (forced to zero intercept), indicates that there was no observable difference in ozone deposition rates between single and double coated filters.

The right axis is scaled as the friction velocity ($u^* = v_{t, \text{ozone}} \times \Gamma_{\text{ozone}}$ by Eq. (4) without consideration for scale differences between room and DeVs). Room occupancy, activity and conditions are shown above plot between time interval markings. To the right of the trace is shown the anticipated range of u^* based on Lai and Nazaroff, 2000. The measured value of $v_{t, \text{ozone}}$ ranges between 0.1 and 0.7 cm s^{-1} , which intersects the anticipated range of 0.02 – 0.2 cm s^{-1} . Results larger than the upper range value are not surprising since the diameter of the DeVs or DeVO devices is significantly smaller than that of the characteristic dimension of the room (several meters). In addition, the occupants went out of their way to induce air movement by continuing to walk around the room, often in front of the DeVs itself. However, we were surprised that the presence of stationary occupants reduced $v_{t, \text{ozone}}$, by about 30% as compared to the unoccupied office. This demonstrates that while people generate air movement by thermal convection, they may also act as “wind breaks”, thereby lowering the surface specific flux in some locations. Window and door openings tend to increase the average value of $v_{t, \text{ozone}}$, and the measurement is more variable. It is unclear why there was a downward trend to the data during the first “unoccupied” interval that was not observed in the second “unoccupied” interval.

We also demonstrate in Fig. 7 that the DeVs rapidly detects changes in mass-transfer conditions. The microbalance itself can respond to changes in flux at time scales much smaller than 1 s. However, the rate of

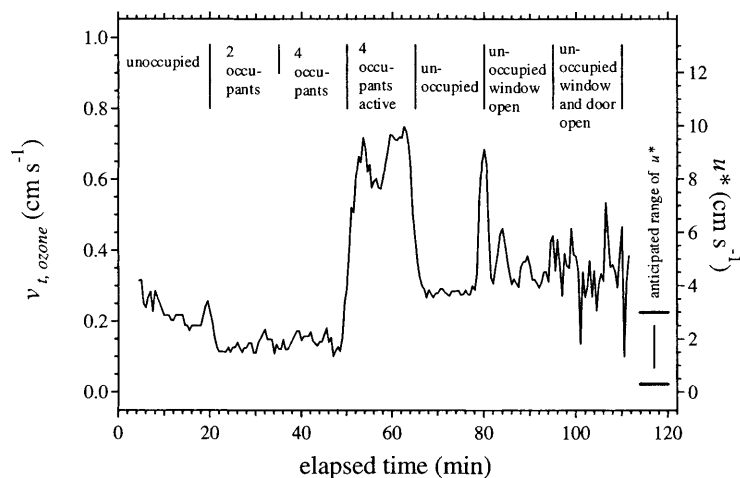


Fig. 7. Continuous DeVS measurement of $v_{t, \text{ozone}}$ in an office with different levels of occupation and activity.

change of flux itself due to a step change in conditions is governed by the time required for a new concentration boundary layer to develop. The characteristic time for a step change in mass-transfer conditions in this experiment was observed to be of the order of 2–4 min. More rapid response to varying conditions is observed during the period in which the window and door are both open, although it is unclear how closely the rapidly changing measurement corresponds to actual changes in conditions.

4. Conclusions

These experiments demonstrate proof of principle for a coated microbalance used as a mass-transfer sensor. In addition, a new method of measuring v_t for ozone is introduced. When validated to our satisfaction, DeVS and DeVO will provide indoor air researchers with tools for evaluating the importance of mass transfer in removing pollutants from (or delivering pollutants to) indoor air. The methods will allow us to generate a parametric survey of indoor mass transfer characteristics due to occupant activities, ventilation, fans, etc. Not only can the method add value to studies of indoor chemical and physical dynamics, the DeVS may be used to directly evaluate mass transfer coefficients for non-polar, low volatility compounds that can be coated on the sensor.

Further improvements are necessary to ensure that DeVS provides accurate measurements of v_t . We have demonstrated that DeVS provides rapid and reasonable values of v_t from first principles. However, it would be preferable if DeVS did not require calibration against other methods and that the output not require scaling to match the dimensions of the room. This would require both that indoor mass transport is well represented by existing models and that the concentration boundary

layer over the DeVS is sufficiently well developed. Future work will include (1) improving the configuration of the DeVS, (2) evaluating both the DeVS and DeVO systems under well-defined mass-transfer conditions, (3) simultaneously evaluating both devices in a wide variety of real indoor settings, (4) comparing the practicality and accuracy of these systems with more traditional direct measures of mass transfer coefficients (e.g. gravimetric determination of the rate of evaporation of naphthalene into a chamber) and with indirect measures of mass-transfer (e.g. hot-wire anemometry), and (5) improving the LLD of both methods.

Acknowledgements

We thank the University of Missouri for supporting this work. We also appreciate helpful suggestions from Dr. Douglas Black of Lawrence Berkeley National Laboratory, and advice on filter preparation and nitrate analysis from Mike Wolfson and Petros Koutrakis at the Harvard School of Public Health. Thanks to Darin Boggs at the University of Missouri for ventilation measurements and Janet Zepernick, Michael Davis and Julie Galloway for review comments.

References

- Baum, E.J., 1998. Chemical Property Estimation. Lewis Publishers, Boca Raton.
- Bigu, J., 1985. Radon daughter and thoron daughter deposition velocity and unattached-fraction under laboratory-controlled conditions and in underground uranium mines. *Journal of Aerosol Science* 16, 157–165.
- Bird, R.B., Stewart, W.E., Lightfoot, E.N., 1960. Transport Phenomena. Wiley, New York.

- Cano-Ruiz, J.A., Kong, D., Balas, R.B., Nazaroff, W.W., 1993. Removal of reactive gases at indoor surfaces: combining mass transport and surface kinetics. *Atmospheric Environment* 27A, 2039–2050.
- Haghighat, F., Zhang, Y., 1999. Modelling of emission of volatile organic compounds from building materials—estimation of gas-phase mass transfer coefficient. *Building and Environment* 34, 377–389.
- Koutrakis, P., Wolfson, J.M., Bunyaviroch, A., Froehlich, S.E., Hirano, K., Mulik, J.D., 1993. Measurement of ambient ozone using a nitrite-coated filter. *Analytical Chemistry* 65, 209–214.
- Lai, A.C.K., Nazaroff, W.W., 2000. Modeling indoor particle deposition from turbulent flow onto smooth surfaces. *Journal of Aerosol Science* 31 (4), 463–476.
- Ligocki, M.P., Liu, H.I.H., Cass, G.R., John, W., 1990. Measurements of particle deposition rates inside Southern California museums. *Aerosol Science and Technology* 13, 85–101.
- Mandelis, A., Christofides, C., 1993. Physics, chemistry and technology of solid state gas sensor devices. In: Winefordner, J.D. (Ed.), *Chemical Analysis*, Vol. 125. Wiley, New York.
- Morrison, G.C., Nazaroff, W.W., 2002. The rate of ozone uptake on carpet: mathematical modeling. *Atmospheric Environment* 36, 1749–1756.
- Morrison, G.C., Ongwadee, M., Chang, H., Portman, J., 2002. Rapid measurements of indoor mass-transfer coefficients. *Indoor Air 2002—Ninth International Conference on Indoor Air Quality and Climate*, Monterey, CA., USA, Vol. 3, pp. 524–529.
- Nazaroff, W.W., Cass, G., 1989. Mass-transport aspects of pollutant removal at indoor surfaces. *Environment International* 15, 567–587.
- Nazaroff, W.W., Gadgil, A.J., Weschler, C.J., 1993. Critique of the use of deposition velocity in modeling indoor air quality. In: Nagda, N.L. (Ed.), *Modeling of Indoor Air Quality and Exposure*, ASTM STP 1205. American Society for Testing and Materials, Philadelphia, pp. 81–104.
- Salmon, L.G., Nazaroff, W.W., Ligocki, M.P., Jones, M.C., Cass, G.R., 1990. Nitric acid concentrations in Southern California museums. *Environmental Science and Technology* 24, 1004–1013.
- Thatcher, T.L., Fairchild, W.A., Nazaroff, W.W., 1996. Particle deposition from natural convection enclosure flow onto smooth surfaces. *Aerosol Science and Technology* 25, 359–374.
- Thatcher, T.L., Nazaroff, W.W., 1997. Effect of small-scale obstructions and surface textures on particle deposition from natural convection flow. *Aerosol Science and Technology* 27 (6), 709–725.
- Weschler, C.J., Shields, H.C., Naik, D.V., 1989. Indoor ozone exposures. *Journal of the Air and Waste Management Association* 39, 1562–1568.
- Wolfson, M., 2003. Personal communication. Procedure for recrystallizing sodium nitrite.