Spatial considerations in the transport of pollutants to indoor surfaces

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Abstract

Spatial distributions in surface flux and concentrations complicate the measurement of surface mass-transfer coefficients can bias the resulting estimates of indoor exposure. To better understand these phenomena, we quantify the spatial distribution of ozone flux and mass-transfer coefficients to indoor surfaces in several field locations using NaNO₂ coated filters. The 8-hour average transport-limited deposition velocity for ozone, $v_{t,ozone}$, ranged from 0.06 cm s⁻¹ on a wall to 0.78 cm s⁻¹ near an operating ventilation supply vent in an apartment. A narrower distribution and a lower spatial average was observed with the recirculation system off. Qualitatively, we observed 1) a tighter distribution of flux for filters placed near one-another, 2) higher values near sources of air movement such as supply vents and computers, 3) consistent results in a single location over 5 days. Measurements obtained with devices such as coated filters will exceed the “true” value of $v_{t,ozone}$ by a factor dependent on the size of the device, size of the room and the flow conditions within the room. Based on a
preliminary understanding of phenomena that influence these measurements, a combination of techniques should be used simultaneously for correction of measurement bias: time-averaged measurements, using two different sizes of devices such as coated filters, and a continuous measurement, such as evaporation of a hydrocarbon from a microbalance.

Keywords: mass-transfer, pollutant transport, pollutant deposition, indoor air, spatial measurement

1. Introduction

The transport-limited deposition velocity, $v_t$, is a mass-transfer coefficient that can be used directly in the analysis of pollutant flux to indoor surfaces. Flux is defined as the product of $v_t$, and the concentration gradient across a boundary layer that has developed over a surface. Mathematically, the local, instantaneous flux, $J(s,t)$, to or from a surface is given by,

$$J(s,t) = v_t(s,t)[C_b(s,t) - C_s(s,t)]$$

where $s$ denotes surface location or coordinates, $t$ is time, $C_b(s,t)$ is the concentration at the outer edge of the concentration boundary layer that has developed over a reactive surface, and $C_s(s,t)$ is the near-surface gas concentration of the pollutant. As the flux to a surface increases, indoor concentrations decrease and vice versa. In understanding indoor systems, Eq (1) can sometimes be simplified because the magnitude of $C_s(s,t)$ depends on dynamics taking place at the surface. For example, nitric acid deposition to an indoor surface is nearly completely irreversible, and as a result $C_s(s,t)$ is effectively zero. In
contrast, for emission from a solvent spill, $C_s(s,t)$ is the saturation concentration of the solvent.

In a mass-conservation model of indoor air concentrations, the area-integrated flux is the total instantaneous mass rate of change in a room due to surface interactions. Therefore, it is desirable to quantify the underlying parameters, such as $v_t(s,t)$, that control fluxes. The term $v_t(s,t)$ is independent of concentrations for dilute systems. Instead $v_t(s,t)$ depends on the flow conditions near the surface and the gaseous pollutant diffusivity. Thus $v_t(s,t)$ can be determined from location specific measurement (Morrison et al., 2003) or model calculations of flow conditions (Nazaroff and Cass, 1987). However, (Nazaroff et al., 1993) cautioned that deposition rates are strongly dependent on flow conditions which will vary greatly among building types and ventilation and that using average deposition velocities for a room or building may be inappropriate since the local values may vary considerably. Thus, to improve the usefulness of the concept of deposition velocity for indoor air quality modeling and exposure assessment, we require a better understanding of the magnitude and variability of air/surface pollutant transport.

This research is directed to measuring the spatial distribution of ozone surface flux in several field settings. We combine these results with a theoretical consideration of bias resulting from using measurement devices which necessarily have smaller dimensions than the room dimensions to arrive at the spatial distribution of transport-limited deposition velocities. The distribution, in turn, allows us to qualitatively evaluate building characteristics that influence $v_t$. We estimate how spatial distribution of transport
influences uncertainty in models used to predict indoor concentrations. In addition, we make procedural recommendations for future mass-transport measurements in buildings.

1.1 Theory: spatial variability in mass transport

To demonstrate the importance of measuring the spatial distribution of transport phenomena, we first consider the infiltration of a surface reactive pollutant into a building, where concentrations and transport conditions are not uniformly distributed throughout a room. The steady-state, volume-averaged core concentration, $\bar{C}_b$, is here derived by balancing the mass rates of sources (infiltration) and sinks (exfiltration and surface flux):

$$\bar{C}_b = \frac{1}{Q} \int_s v_t(s)(C_b(s) - C_s)ds$$

(2)

where $C_o$ is the outdoor concentration, $Q$ is volumetric infiltration rate and the integration takes place over a surface, $s$. If each of these parameters ($v_t$, $C_b$, $C_s$) is spatially dependent, then the use of an area-averaged value of $\hat{v}_t$ for modeling is not appropriate because, $v_t$, cannot be separated from the product within the integral. Only if $(C_b - C_s)$ is independent of $s$ or nearly constant in $s$, will it be possible to isolate area-average value of the transport-limited deposition velocity, $\hat{v}_t$:

$$\bar{C}_b = C_o - \frac{Q}{A} \int_s v_t(s)ds = C_o - \frac{(C_b - C_s)\hat{v}_t A}{Q}$$

(3)

where $A$ is the total surface area of the room. Only for this unique case is it accurate to report or use $\hat{v}_t$. 
To estimate error introduced by this type of method, spatial distributions in concentrations and transport would be necessary, but are not readily available. The spatial-distribution measurements to be reported here provide some guidance in estimating uncertainties in measuring and using $\hat{v}_t$.

1.2. Spatial scales and measurement of $v_t$

Care must be taken when interpreting results from spatial-distribution measurements because the size of the collecting/emitting surface can influence the outcome. The stagnant-film theory model of mass transfer can be used to demonstrate this size dependent effect. Due to surface emission or deposition flux, a concentration gradient and boundary layer will develop over the measurement surface, but not necessarily over the surrounding walls. The flux in this case is equal to the product of a concentration gradient and a mass-transfer coefficient, itself equal to the diffusion coefficient, $D$, divided by the thickness of the stagnant film, $\delta$. All else being equal, as the film thickness increases the flux and the mass-transfer coefficient decrease. Non-stagnant concentration boundary layers also exhibit this behavior: the thicker the concentration boundary layer over a surface, the lower the flux and the lower the resulting mass-transfer coefficient.

This issue of device dimensions is addressed by considering the concentration boundary layer that has developed over a device used to measure the mass-transfer coefficient. See Fig. 1a and 1b for a two-dimensional representation of a case in which the pollutant, e.g. ozone, is consumed readily by the measuring surface but not with the surrounding walls. For example, deposition of ozone to a disk coated with a reactive media (see Methods section) is used to determine the time-averaged local mass-transfer
coefficient on a wall. A concentration boundary layer will develop over the disk with varying thickness depending on the fluid-mechanical nature and direction of flow as well as the distance from the edge of the disk. The value of $v_t$ derived from disk 1 is proportional to the thickness of the boundary layer, $\delta_t$. If the researcher uses a larger disk, Fig 1b, the mean thickness of the concentration boundary layer will be greater, $\delta_2$. Given the same time interval for evaporation, the time-integrated flux will be larger for disk 1 than for disk 2 and $v_t$ derived from disk 1 will be larger than that derived from disk 2.

Preferably, the size of the device should not matter. This will be the case for measurements of a pollutant that tends to be consumed by all surfaces, such as acid gases, where the appropriate boundary layer for measurement should look something like Fig 1c; in this figure, the concentration boundary layer develops over a wall and corner and no sensing surface is present. For this case, a continuous concentration boundary layer develops over all indoor surfaces whether a collecting surface is present or not. Since $\delta_3 > \delta_2 > \delta_t$, a measurement as shown in Fig 1a and 1b always over-predicts $v_t$. Unlike the ozone example, placing a collector as shown in Fig. 1d should not influence the thickness of the boundary layer. Since $\delta_3 = \delta_4$, flux measured in Fig 1d will represent the true length-averaged flux regardless of the length $L_4$. The value of $v_t$ derived from disk 4 is the “true” value to be used for modeling indoor dynamics.

1.3. Deviation of measured $v_t$ from “true” $v_t$

Since the pollutant or surrogate species used for measuring $v_t$ may not react rapidly with surfaces, a correction factor is necessary to generate the “true” value of $v_t$. The relative influence of the dimensions of the flux surface on the resulting value of $v_t$
can be estimated by scrutinizing mass-transfer correlations for boundary layers in relevant aerodynamic systems (Table 1). For example, for developing flow (turbulent) over a planar surface the local value, $v_t(x)$ is

$$v_t(x) = 0.0296x^{-1}D Re_x^{4/5} Sc^{1/3}$$

where $x$ is the distance along the surface from the upstream edge, $Re_x$ is the Reynolds number ($xu/\nu$), $Sc$ is the Schmidt number ($\nu/D$), $u$ is the bulk velocity and $\nu$ is the kinematic viscosity. Thus, $v_t$ is proportional to $x^{-0.2}$. Each of the turbulent systems shown in Table 1 exhibits this weak dependence on dimension, suggesting that a size correction factor is small. This would be advantageous because the larger the correction factor, the larger the potential for error due to the correction. For example, for a measuring device dimension, $L_1$, of 0.15 m and a typical room dimension, $L_c$, of 2.5 m, the measured value of $v_t$ will be roughly $(0.15/2.5)^{-0.2}$ or 1.8 times greater than the “true” value. Although this may only apply to turbulent systems, measurements (Nazaroff et al., 1990) have indicated that indoor air movement can often be described as “homogeneously turbulent” and it may be reasonable to simply apply this correction factor based on the dimensions of the flux device and the room as suggested by (Morrison et al., 2003). Results derived from ozone deposition to coated filters, described in Methods, will be adjusted in this way by assuming homogeneous turbulence.

The generalized correction factor, $f_L$, for spatial differences is

$$f_L = \frac{v_t(L_1)}{v_t(L_c)} = \left(\frac{L_1}{L_c}\right)^a$$

where the superscript $a$ is equal to -0.2 for turbulent conditions. In contrast, for air flow that is not turbulent (Nazaroff and Cass, 1987), the appropriate correction may be
obtained from correlations appropriate to the existing fluid-mechanical conditions. From Table 1, it is apparent that $a$ takes different values depending on the fluid-mechanical conditions and the system. Fig. 2 shows how the fraction, $f_L$, in Eq. (5) decreases as the ratio $L_1/L_c$ decreases for laminar and turbulent duct flow. The error is minimized as the linear dimension of the measuring surface (see inset of Fig. 2) approaches the dimension of the room itself, assuming the correlations for duct flow can be extrapolated to indoor systems. A large absolute value of $a$ is suggested for transition flow in a duct ($a = -1.1$) and laminar flow between parallel plates ($a = -1.33$). The correction factor becomes exceedingly large for these systems.

2. Methods

2.1 Analytical

The local surface flux of ozone is quantified, using the DeVO method of (Morrison et al., 2003), by determining the rate at which nitrite ions on a prepared filter are converted to nitrate by the following reaction:

$$O_3 + NO_2^- \rightarrow NO_3^- + O_2$$  (6)

For each experiment, a coating solution of 100ml was prepared, including 1g of sodium nitrite, 1g of potassium carbonate, 0.2 g of erythritol (hygroscopic agent similar to glycerol) in a solvent of 70ml deionized water and 30ml of methanol. This solution was stored in a refrigerator at 4°C. Twelve glass fiber filters, 15 cm in diameter, were placed on horizontal nylon screens in an anaerobic glovebox. 5ml of the coating solution was applied onto each filter by 5ml pipette. The filters were then dried completely in the glovebox for 1 to 2 days and stored there until needed.
After an experimental exposure interval, discussed below, each sample filter was placed in a sealed plastic bag and ultrasonically extracted for 5 min with 100 ml deionized water. The extracts were filtered through 0.45 µm nylon syringe filter and 5 ml of the extract was injected into an ion chromatography system for analysis. The time-averaged mass transport-limited deposition velocity to the filter, \( \bar{v}_{t, \text{ozone}, \text{filter}} \), is derived by assuming that a) the bulk ozone concentration is uniform throughout the room and b) the ozone concentration near the filter surface is almost zero due to low surface resistance to the overall mass transfer process. This transport limited behavior was verified by (Morrison et al., 2003).

\[
\bar{v}_{t, \text{ozone}, \text{filter}} = \frac{m_{\text{NO}_3} M_{\text{O}_3}}{C_{\text{O}_3} M_{\text{NO}_3} A \Delta t}
\]

where \( m_{\text{NO}_3} \) is the mass of nitrate formed on the filter (g), \( M_{\text{O}_3} \) is the molecular weight of ozone (g mol\(^{-1}\)), \( M_{\text{NO}_3} \) is the molecular weight of the nitrate ion (g mol\(^{-1}\)), \( C_{\text{O}_3} \) is the time-averaged room concentration of ozone during the exposure interval (µg m\(^{-3}\)), \( A \) is the exposed area of the filter (m\(^{2}\) or cm\(^{2}\)) and \( \Delta t \) is the time interval exposed (h or s). The elapsed time, \( \Delta t \), needed to quantify \( \bar{v}_{t, \text{ozone}, \text{filter}} \) depends on the lower detection limit of detection (LLD) of nitrate by IC, the purity of the nitrite salt, and the rate of ozone deposition. The LLD of \( \bar{v}_{t, \text{ozone}, \text{filter}} \) for the chamber experiment was 0.05 cm s\(^{-1}\) based on replicate chamber blank filters for which the standard deviation was 3.6 µg NO\(_3\)-. Therefore, the practical detection limit can be taken as 36 µg per filter. This is equivalent to exposure of filters to 20 ppb ozone in the air for 5 hrs, 13 ppb in the air for 8 hrs with

\( \bar{v}_{t, \text{ozone}, \text{filter}} = 0.05 \text{ cm s}^{-1}. \)
Field measurements of $\bar{v}_{t,\text{ozone, filter}}$ were converted to a “true” value of $\bar{v}_{t,\text{ozone}}$ by assuming that fluid mechanical conditions reflected homogeneous turbulence. Using the correction factor defined by Eq (5),

$$\bar{v}_{t,\text{ozone}} = \frac{\bar{v}_{t,\text{ozone, filter}}}{f_L}$$  \hspace{1cm} (8)

where $a = -0.2$ and $L_c = 2.5 \text{ m}$, using the room height as the characteristic length, $L_c$. These values are not corrected for systematic error associated with time-averaging (Morrison and Wiseman, 2005). Uncertainty in reported $\bar{v}_{t,\text{ozone}}$ values is ± 0.03 cm s$^{-1}$.  

2.2 Field Experiments  

*Laboratory and Office.* In a 10.1 m $\times$ 7.4 m laboratory, two DeVO filters, centers separated by 15 cm, were installed on a foam board false wall that was itself supported by an electronics rack at the location marked (*) in Figure 3a. The sampling inlet of the ozone analyzer was located in the center of the lab. The two filters were exposed to air in this way for 12 h and the experiment was repeated three times over a period of five days. The spatial distribution of $\bar{v}_{t,\text{ozone}}$ in this laboratory was evaluated in one experiment with nine more filters positioned at approximately equally spaced wall locations, also exposed for 12 h. One set of measurements was performed in a laboratory space serving as an office for 10 graduate students. As in the laboratory experiment, two filters were placed near one another at a central location, * in Fig 3b, and 9 other filters were distributed evenly around the perimeter of the room. The experiments were performed during the daytime to take advantage of higher natural ozone concentrations, which improved sensitivity of the DeVO method. The time interval, $\Delta t$, was 12 hrs.
Apartment. In an apartment (Figures 4a and 4b), two separate measurements of the spatial distribution of $v_{t,\text{ozone}}$ were obtained using nine DeVO filters spaced equally on walls in the living room and dining area. One additional filter was placed on the ceiling near a recirculation supply vent. To improve sensitivity, the window and door were kept open throughout the experimental period, increasing the average indoor concentration of ozone. Measurements were obtained with recirculation vents on (Fig 4a) and off (Fig 4b), respectively. The sampling inlet of ozone analyzer was located in the center of the living room.

2.3 Influence of transport distribution on predicted mean flux

Using the results of these experiments, an estimate is made of the range of error associated with using an area-averaged value, $\hat{v}_t$, instead of the true distribution to determine overall surface flux. Since the spatial distribution of ozone concentrations is not readily available, we assume that this distribution is similar to the spatial distribution of flux. For example, let $\hat{v}_t = 0.2 \text{ cm s}^{-1}$ with a maximum of 0.3 cm s$^{-1}$ and a minimum of 0.1 cm s$^{-1}$. For this situation, we assume that for a volume-averaged ozone concentration $= 20 \mu g \text{ m}^{-3}$, the maximum local concentration at the edge of a concentration boundary layer will be 30 $\mu g \text{ m}^{-3}$, and the minimum will be 10 $\mu g \text{ m}^{-3}$. The range of error is determined using Eq. (2) and by allowing $v_t$ and $C_b$ to be correlated and anti-correlated.

For the purposes of deriving the extremes of uncertainty, we assume that the ozone surface reaction probability, $\gamma$, equals 1, i.e. the surfaces are highly reactive.

3. Results

Laboratory and Office. Figures 3a and 3b show the spatial distribution of $v_{t,\text{ozone}}$ measured in a working laboratory and an office area respectively. The diameter of the
circles is proportional to the transport-limited deposition velocity at the indicated locations. In the laboratory, the $\overline{v}_{t,ozone}$ values near hoods, computers and on wide sidewalks or columns were greater than the $\overline{v}_{t,ozone}$ values under cabinets, in corners and on central columns. This may be because mean air velocities are lower in the latter locations. Relatively consistent results were obtained at the position denoted by the asterisk, where three repeated measurements were obtained over the period of 5 days (see Figure 5).

Figure 3b shows the spatial distribution of $\overline{v}_{t,ozone}$ measured in the occupied office space. The average of spatial measurements were not significantly different between the lab, 0.14 cm s$^{-1}$, or office, 0.15 cm s$^{-1}$ nor were the standard deviations significantly different between the lab, 0.04 cm s$^{-1}$, or office, 0.06 cm s$^{-1}$.

**Apartment.** Figures 4a and 4b show the spatial distribution of $\overline{v}_{t,ozone}$ in an apartment with the window and door open and the recirculation fans on (4a) and off (4b). With the recirculation fans on, the $\overline{v}_{t,ozone}$ values at the location near the vent and window are very large due to high air velocities at these locations. The $\overline{v}_{t,ozone}$ values at the location between two recirculation vents are much smaller and may be relatively stagnant locations. The average of measured values of $\overline{v}_{t,ozone}$ is nearly double with the recirculation fan on, 0.18 cm s$^{-1}$, than with the fan off, 0.10 cm s$^{-1}$. The standard deviation for results with recirculation on, 0.21 cm s$^{-1}$ is much greater than with the fan off, 0.03 cm s$^{-1}$. By excluding the near-vent filter measurement, the average and standard deviation of filters are nearly indistinguishable between fan-on and fan-off experiments. Although the average value of $\overline{v}_{t,ozone}$ was higher with the recirculation fans on, some of the filter
locations experienced lower individual mass-transfer rates. Figure 5 demonstrates that colocated measurements (separated by 15 cm) result in flux that is within 20% of one another, whereas the range of values measured in other locations throughout the room is much greater. Most of the results from the laboratory studies and from the apartment are within the expected range of values of $\bar{v}_{t,\text{ozone}}$ (Nazaroff et al., 1993).

**Distribution and the influence on predicted indoor concentrations.**

Using the $\bar{v}_{t,\text{ozone}}$ spatial distribution as a guide, we generated a series of possible flux distributions for hypothetical rooms. Beginning with the apartment (no recirculation) results, and assuming that the outer boundary layer ozone concentration is spatially uniform, the estimated area-averaged flux is $0.0193 \text{ } \mu g \text{ } m^{-2}$. If the boundary layer ozone concentration distribution positively correlates with $\bar{v}_{t,\text{ozone}}$, the predicted area-averaged flux is $0.0186 \text{ } \mu g \text{ } m^{-2}$. If the outer boundary layer ozone concentration distribution inversely-correlates with $\bar{v}_{t,\text{ozone}}$, the predicted area-averaged flux is $0.0173 \text{ } \mu g \text{ } m^{-2}$.

Therefore, we observe a deviation of 4 to 11% compared with a uniform distribution assumption. Applying the same operation on the apartment results (with recirculation), the estimated deviation is 45 to 57%. Analyzing flux distributions in the laboratory and office, we find deviations ranging from 6 to 14%. In all cases, allowing the boundary layer concentration distribution to correlate with $v_t$, results in area-averaged flux that is lower than allowing the boundary layer concentration of ozone to be spatially uniform.

**4. Discussion**

**4.1 Spatial distribution of flux**

The laboratory, office and apartment results demonstrate that there can be a wide distribution of surface flux in a single room. As anticipated, areas near vents and other
sources of air movement tend to exhibit higher relative values of $\overline{v}_{t, \text{ozone}}$. Both measurements near operating computers ($0.19$ and $0.22$ cm s$^{-1}$) were roughly twice the value measured under cabinets or at most desks ($0.09$ – $0.14$ cm s$^{-1}$). The flux near the apartment recirculation register is demonstrated to be nearly $7$ times greater than the average of all other spatial measurements in the apartment. Yet, excluding this measurement, the distribution of fluxes appear similar between the two apartment experiments. Flux on walls in unobstructed areas in the laboratory appears to be higher than in other locations; this effect was not observed in the apartment.

Filters located within ~ $1$ meter of one another are observed to measure roughly the same flux, even in repeated measurements over $5$ days. This finding suggests that there exists a limited number of measurement locations required to evaluate the distribution in a room. For example, an uninterrupted expanse of wall may require only a few measurements, and only a few “under-cabinet” measurements may be needed. Complicated geometry or locations near registers and windows likely require a higher density of measurements.

It is important to recall that a key, and most likely erroneous, assumption in the determination of local $\overline{v}_{t, \text{ozone}}$ is that the bulk concentration is uniform. If not, then these values of $\overline{v}_{t, \text{ozone}}$ only reflect the relative flux to those locations, not the true values of $\overline{v}_{t, \text{ozone}}$. Mass-transfer coefficient measurement methods that employ the evaporation of a pure substance side-step the bulk concentration distribution problem because $C_b$ can be ignored in Eq. (2) as being insignificant compared to $C_s$.

This uncertainty in the spatial distribution of concentration and transport intensity will also limit certainty in quantifying surface flux that is used in exposure models. A
good method of determining the surface source/sink term of these models is to measure inlet and outlet pollutant concentrations of a building while accounting for all other sources and sinks (Weschler et al., 1989). The area-averaged flux derived from this method is accurate for that building at that time, but internal transport or concentration distributions are not constant. Using our measured flux distribution as a guide, we can see that indoor surface flux predictions may be in error by up to 50% for highly surface-reactive species. If surfaces are the primary pollutant sink, then exposure estimates can be fairly uncertain. In the case of ozone, the surface reaction probability is moderate, meaning that the uncertainty in the surface-sink term, and exposure, will generally be smaller or perhaps negligible.

4.2 Recommendations for field measurements

Having established that a distinct spatial variation in flux to indoor surfaces exists, how should future measurements be performed? There are several key issues that must be addressed before collecting indoor flux data. The analyses from sections 1.2 and 1.3 demonstrate that the development of a concentration boundary layer over the measuring surface depends on the species measured. If a depositing species reacts completely with other indoor surfaces, then the “natural” boundary layer will not be disturbed and consideration of the fluid-mechanical state is unnecessary. Otherwise, some method of determining the fluid-mechanical state may need to be employed. In either case, the spatial distribution of concentration must be considered. Finally, an evaluation of temporal influences on flux (Morrison and Wiseman, 2005) suggests that a semi-instantaneous measure of surface flux may be necessary to avoid bias resulting from time-varying transport conditions. In lieu of an ideal, well-instrumented method, a
combination of techniques would likely provide sufficient information about spatial and
temporal distributions and simultaneously provide for error correction. In general, at least
one continuous/instantaneous measure of conditions, such as microbalance flux or air
velocity (Morrison et al., 2003), and two sizes of deposition/emission flux surfaces
maybe employed simultaneously. Combined, these methods allow the researcher to de-
convolute errors imposed by the independent limitations of each device. With these as
considerations in mind, we discuss four different scenarios for determining the transport
limited deposition velocity of various species.

4.2.1 Deposition of ozone and spatial distribution of $\bar{v}_{t,\text{ozone}}$.

In this example, we consider mass-transfer analyses in a room (see Fig. 2 inset)
that is similar to the methods employed for the spatial distribution shown in Figs. 3 and 4.
Distributed around the room are several small filters ($L_1$) coated with NaNO$_2$ for
determining a time-averaged flux of ozone at those locations. In addition several larger
NaNO$_2$ filters ($L_2$) are located near, but not immediately adjacent to, the smaller filters.
The gas-phase concentration of ozone is measured continuously using a photometric
ozone analyzer in the center of the room. Using Eq. (7) a location specific $\bar{v}_{t,\text{ozone}}$ for each
filter is obtained after 8 hours. A micro-balance based evaporative flux instrument
providing an instantaneous, local result is deployed on one wall (cross-hatched circle).
This evaporative method, a.k.a. DeVS, is described in detail in Morrison et al. (2003).
Briefly, octadecane evaporates from a quartz-crystal microbalance and the flux is
converted into an instantaneous mass-transfer coefficient using Eq. 1. Error correction
can now be applied in a two step fashion:
1) Because the flow characteristics are unknown, the coefficient $a$ in Eq. (5) is unknown. Instead, results from the small ($L_1$) and large ($L_2$) filters are combined to estimate the value of $a$ by rearranging Eq. (5), and replacing $L_c$ with $L_2$:

$$a = \ln \left( \frac{\overline{V}_{t,L_1}}{\overline{V}_{t,L_2}} \right) \frac{L_1}{L_2}$$  \hspace{1cm} (9)

This is used to correct, at each location, for the error which is due to the limited size of the filters used to determine ozone flux. For each location, Eq. (5) is solved for $f_L$, using the characteristic dimension, e.g. height, of the room, $L_c$.

It should be noted that determination of $a$ inherently corrects for uncertainty in the relative reactivity of the surface, parameterized by the surface reaction probability, $\gamma$. For species with a low surface reaction probability, e.g. a solvent, $a$ is the maximum value associated with the fluid mechanical conditions. For species with a high surface reaction probability, e.g. nitric acid, $a$ should be near zero. Species of moderate surface reactivity, e.g. ozone, the value of $a$ will fall somewhere in-between the high and low reactivity cases.

Error due to time-averaging can now be corrected by using the continuous $v_t$ measurement. A value for the correction factor, $f_t$ is obtained from Eq. (16) of (Morrison and Wiseman, 2005). The corrected value at location 1 is now,

$$\overline{V}_{t,1,corrected} = \frac{\overline{V}_{t,L_1}}{f_t f_L}$$ \hspace{1cm} (10)

The absolute value at the continuous measurement location must also be corrected for its small dimensions:

$$v_{t,corrected}(t) = \frac{v_t(t)}{f_L}$$ \hspace{1cm} (11)
Note that no spatial measurement of ozone concentrations was recommended. It is unclear how to make this field measurement in practice without disturbing the system with a forest of sample tubing. Spectroscopic methods (Drescher et al., 1996) may not be sensitive enough to resolve ozone spatially at typical ppb indoor mixing ratios.

4.2.2 Deposition of nitric acid and spatial distribution of $\bar{V}_{t,\text{HNO}_3}$.

In this example, distributed filters are used to collect nitric acid, a species that is expected to deposit irreversibly with all indoor surfaces. With such a high reaction probability, the act of collecting nitric acid does not influence the existing concentration boundary layer and consideration of fluid-mechanical conditions is unnecessary. Therefore, the size of the collecting surface is unimportant. Yet, a continuous measurement afforded by the DeVS device is still required. Morrison and Wiseman (2005) show that for depositing species with high reaction probabilities, bias associated with time-varying conditions is maximized.

4.2.3 Deposition of carbon dioxide used to determine spatial distribution of $\bar{V}_{t,\text{ozone}}$.

As explained in Morrison and Wiseman (2005), it is not necessary to use ozone itself to determine $\bar{V}_{t,\text{ozone}}$. Instead a surrogate species can be used in combination with a correction factor to determine the mass-transfer coefficient of a target species. In this example, filters coated with LiOH are used to collect carbon dioxide by the reaction

$$\text{LiOH} + \text{CO}_2 \rightarrow \text{LiHCO}_3 \quad (12)$$

Titration of the extracted filters provide information used to determine flux and $\bar{V}_{t,\text{CO}_2}$.

Because CO$_2$ does not deposit to any substantial degree on indoor surfaces, i.e. a low surface reaction probability, two sizes of filters are again used (as in 4.2.1) to correct for
boundary layers of uncertain thickness that develop over the filters. Using Eq. 15 of Morrison and Wiseman (2005), \( \bar{v}_{t,\text{ozone}} \) can be evaluated at each filter location

\[
\bar{v}_{t,\text{ozone}} = \bar{v}_{t,\text{CO_2}} \left( \frac{D_{\text{CO_2}}}{D_{\text{ozone}}} \right)^{0.67}
\]  

(13)

where \( D \) is the diffusion coefficient of the subscripted compound. The analysis of (Morrison and Wiseman, 2005) suggests that time-varying conditions may bias results even for some surface unreactive compounds such as \( \text{CO}_2 \). Therefore, the DeVS device is deployed in this example as well. Since \( \text{CO}_2 \) mixing ratios are generally in the >500 ppm range, a spatial measurement (Drescher et al., 1996) may be possible, but cumbersome.

4.2.3 Emission of octadecane used to determine spatial distribution of \( \bar{v}_{t,\text{ozone}} \)

In this example, we suggest employing a surrogate species, once again, to determine \( \bar{v}_{t,\text{ozone}} \). However, the emission of an evaporating hydrocarbon from a surface is employed instead of deposition, since both processes are mirror images under the same fluid-mechanical conditions. To enhance our understanding of both spatial and temporal distributions within a room, we employ a suite of microbalance based DeVS devices coated with octadecane (Morrison et al., 2003). To account for uncertainty in fluid-mechanical conditions, half of the DeVS devices are coated with octadecane to a diameter of 15 cm; the rest of the units are coated to a diameter of 30 cm. These values are arbitrary, and just used to illustrate the system. This is effectively the same as using two different filter sizes as suggested in 4.2.1 and 4.2.3. There is no need to measure the spatial distribution of gas-phase octadecane concentrations because the evaporation rate is so small that the outer boundary layer concentration is effectively zero and near surface concentration depends only on the temperature of the coating.
Will these corrected methods provide robust values needed for indoor air quality modeling and exposure assessment? Until the experimental evidence is in hand, these recommendations are tentative. The fact that it is impossible to co-locate collecting/emitting surfaces makes the corrections, Eqs. (10) and (11), somewhat uncertain but better than no correction, since our results show that a 20% uncertainty in co-located DeVO filters is to be expected.

8. Conclusions

The measurement accuracy of heat and mass-transfer coefficients in practice is limited. By measuring spatial distributions in indoor settings, we demonstrate that fluxes vary widely with location. Spatial gradients in concentration and flux make simple exposure analysis less certain. Error associated with the use of devices of dimensions smaller than the size of the room is more severe than that due to uncertainty in the spatial concentration of the depositing species. Researchers tempted to map out the spatial distribution of mass-transfer coefficients with small filters or other devices may observe much larger mass-transfer coefficients than the “true” values. Before initiating a study of this sort, the device size, room-surface reaction probability of the species collected, and flow conditions must all be considered so that a reasonable estimate of the mass-transfer coefficient can be obtained with thoughtful error correction. The two-step procedure for error correction recommended here should generate a best-estimate of the local mass-transfer coefficient.

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References


Figure and Table Captions

Fig. 1. Concentration boundary layer development over indoor surfaces with and without measurement devices: (a) collecting/emitting device of length $L_1$ develops a boundary layer with a center thickness $\delta_1$; (b) collecting/emitting device of length $L_2$ develops a boundary layer with a center thickness $\delta_2$; (c) boundary layer over walls (at corner) for a highly surface reactive species such as a gas-phase acid; (d) boundary layer over walls (at corner) for a highly surface reactive species, including collecting surface with length $L_4$.

Fig. 2. The ratio, $f_L$, for turbulent and laminar duct flow vs the ratio $L_1/L_2$. Inset: room outfitted with two different sizes of time-averaged flux measurement disks $\Theta$, a continuous flux measuring device $\Theta$, and a gas-measurement method.

Fig 3. Spatial distribution of $v_{t,ozone}$ in (a) a working laboratory and (b) a laboratory room used as student offices. The diameter of the circle corresponds to the intensity of ozone flux at that location.

Fig 4. Spatial distribution of $\overline{v}_{t,ozone}$ in an apartment with (a) the recirculation fan on and (b) the recirculation fan off. The diameter of the circle corresponds to the intensity of ozone flux at that location.

Fig 5. Co-located measurements of $\overline{v}_{t,ozone}$ on a central column in a working laboratory over a 10 day period and distribution of $\overline{v}_{t,ozone}$ throughout a room on a single day.

Table 1. Mass-transfer correlations for various configurations and flow conditions.
Figure 1

(a) \[ \delta_1 \]

(b) \[ \delta_2 \]

(c) \[ \delta_3 \]

(d) \[ \delta_4 \]

Figure 2

\[ f_L \]

laminar

\[ \text{turbulent} \]
Figure 3

(a) Room layout with measurement locations and intensities indicated.

(b) Room layout with ventilation exhaust and supply points marked.

Legend:
- ○ measurement location and intensity
- □ ventilation exhaust
- ✗ ventilation supply

Dimensions:
- 7.4 m, 7.5 m, 10.1 m, 11.3 m

Locations:
- Window
- Desk
- Computer
- Sink
- Cabinet
- Column
- Ventilation exhaust
- Ventilation supply
- Ozone analyzer

Note: The numbers indicate distances in meters.
Figure 4

- **Diagram a**: Living room window with measurements of 0.17 and 0.06. Kitchen with measurements of 0.11.
- **Diagram b**: Living room window with measurements of 0.12 and 0.06. Kitchen with measurements of 0.09.

- Measurement location and intensity.
- Ventilation supply.

Figure 5

- **Graph**: Ozone concentration (cm s⁻¹) from May 1 to May 13, 2003.
- Co-located filters in laboratory.
- Filters distributed around perimeter of laboratory.
- Co-located filters in office.
- Filters distributed around perimeter of office.
Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>fluid mechanical region</th>
<th>Local ( v_{lx} = )</th>
<th>Length average ( v_{l,L} = )</th>
<th>( \frac{v_l(L_1)}{v_l(L_2)} = \left( \frac{L_1}{L_2} \right)^n )</th>
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</thead>
<tbody>
<tr>
<td>Duct</td>
<td>laminar</td>
<td>Eq. 3.48-3.49 Kakaç⁷</td>
<td>0.332x⁻¹DRe⁺³/² Sc⁺¹/³</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>transition</td>
<td>Eq. 4.31-4.35 Kakaç⁷</td>
<td>0.664L⁻¹DRe⁺¹/² Sc⁺¹/³</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>turbulent</td>
<td>0.023x⁻¹DRe⁺⁰·⁸ Sc⁺¹/³</td>
<td>0.02376L⁻¹DRe⁺⁴/⁵ Sc⁺¹/³</td>
<td>-0.2</td>
</tr>
<tr>
<td>Planar</td>
<td>laminar</td>
<td>0.332x⁻¹DRe⁺¹/² Sc⁺¹/³</td>
<td>0.664L⁻¹DRe⁺¹/² Sc⁺¹/³</td>
<td>-0.5</td>
</tr>
<tr>
<td>surface</td>
<td>turbulent</td>
<td>0.0296x⁻¹DRe⁺⁴/⁵ Sc⁺¹/³</td>
<td>0.02376L⁻¹DRe⁺⁴/⁵ Sc⁺¹/³</td>
<td>-0.2</td>
</tr>
<tr>
<td>Parallel</td>
<td>laminar</td>
<td>2xDRe⁺¹/³ Sc⁺¹/³</td>
<td>4xDRe⁺¹/³ Sc⁺¹/³</td>
<td>-1.33</td>
</tr>
<tr>
<td>plates</td>
<td>transition</td>
<td>( \frac{2x}{\Gamma(4/3)(\frac{6x}{D_h})^{1/3}} )</td>
<td>( \frac{4x}{3\Gamma(4/3)(\frac{6x}{D_h})^{1/3}} )</td>
<td>-0.67</td>
</tr>
<tr>
<td></td>
<td>turbulent</td>
<td>Eq. 4.104 Kakaç⁷</td>
<td>Eq. 4.105-4.106 Kakaç⁷</td>
<td>-0.16 to 0.26</td>
</tr>
</tbody>
</table>

Notes:
Reynolds number, \( Re_{L,x} = uL/\nu \), where \( u \) is the net fluid velocity, \( L \) is the characteristic length (e.g. height of room or length of flux surface) or \( x \) is the distance along the surface, \( \nu \) is the kinematic viscosity. \( D_h \) is the hydraulic diameter of the system, duct or parallel plates. Schmidt number, \( Sc = \nu/D \), where \( D \) is the diffusion coefficient of the transporting species. Correlations all derived from (Shah and Bhatti, 1987)

⁷For brevity these equations are not shown in this table but are found in Shah and Bhatti (Shah and Bhatti, 1987)