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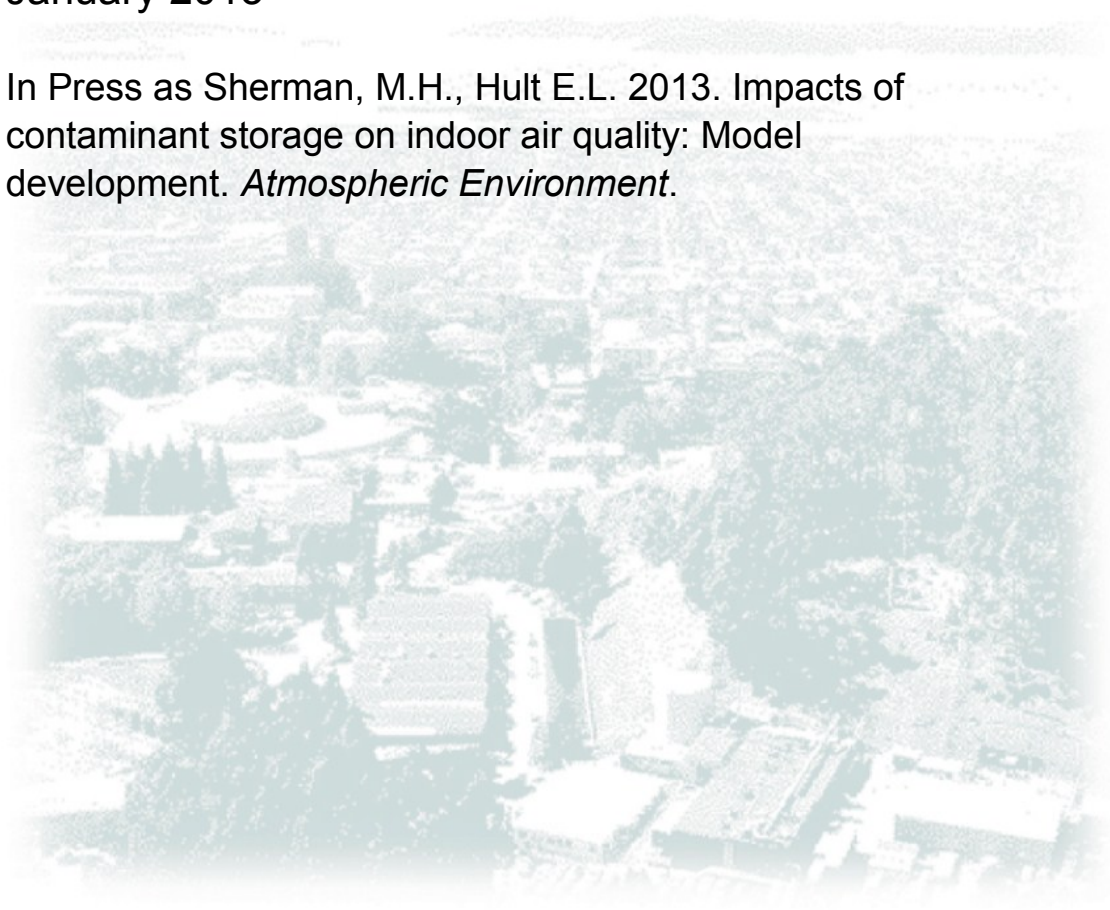
Impacts of contaminant storage on indoor air quality: Model development

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ABSTRACT

A first-order, lumped capacitance model is used to describe the buffering of airborne chemical species by building materials and furnishings in the indoor environment. The model is applied to describe the interaction between formaldehyde in building materials and the concentration of the species in the indoor air. Storage buffering can decrease the effect of ventilation on the indoor concentration, compared to the inverse dependence of indoor concentration on the air exchange rate that is consistent with a constant emission rate source. If the exposure time of an occupant is long relative to the time scale of depletion of the compound from the storage medium, however, the total exposure will depend inversely on the air exchange rate. This lumped capacitance model is also applied to moisture buffering in the indoor environment, which occurs over much shorter depletion timescales of the order of days. This model provides a framework to interpret the impact of storage buffering on time-varying concentrations of chemical species and resulting occupant exposure. Pseudo-steady state behavior is validated using field measurements. Model behavior over longer times is consistent with formaldehyde and moisture concentration measurements in previous studies.

KEYWORDS

Buffering capacity, formaldehyde, moisture

NOMENCLATURE

A	air exchange rate (h^{-1})
C	concentration in indoor air ($\mu\text{g m}^{-3}$)
C_{EL}	concentration in equilibrium layer ($\mu\text{g m}^{-3}$)
C_{eq}	initial concentration in equilibrium layer ($\mu\text{g m}^{-3}$)
C_{∞}	indoor concentration in absence of storage ($\mu\text{g m}^{-3}$)
$C_{material}$	concentration in storage material ($\mu\text{g m}^{-3}$)
C_{out}	outdoor concentration ($\mu\text{g m}^{-3}$)
C_{ss}	steady state concentration ($\mu\text{g m}^{-3}$)
C_0	initial indoor concentration ($\mu\text{g m}^{-3}$)
ΔC	indoor minus outdoor concentration ($\mu\text{g m}^{-3}$)
ER	emission rate ($\mu\text{g m}^{-3} \text{h}^{-1}$)
k	transport coefficient (m/h)
kL	time constant for coupling between air and equilibrium layer (h^{-1})
L	loading factor = ratio of exposed storage material area to V (m^{-1})
S	storage-independent, internal sources plus ΔC_{out} ($\mu\text{g m}^{-3} \text{h}^{-1}$)

t	time (h)
V	volume of inside air (m^3)
V_{material}	volume of storage material (m^3)
A	rate constant for storage to come to equilibrium (h^{-1})
α	storage capacity of compound, equal to $\kappa V_{\text{material}}/V$ (-)
κ	affinity of the compound for the storage material (-)
τ_{∞}	storage depletion time scale (h)
τ_{ss}	repartitioning time scale (h)

1 INTRODUCTION

In determining the concentration of indoor contaminants over time, interaction between the building materials and the concentration of the compounds in the air is often neglected. The time history of the airborne concentrations can be significantly different if such storage is present. This buffering of indoor concentrations resulting from storage can affect occupant exposure to these species, and can influence the effectiveness of various mitigation methods. Doubling the air change rate, for example, is often assumed to halve the steady-state concentration of a contaminant, but that may not be so if there is storage of that contaminant.

Here we discuss how a simplified model can describe the interactions between building materials and chemical species. While the term ‘source’ is often used to describe emitting building materials and furnishings, the term ‘storage materials’ is used here because materials initially uncharged with a contaminant can become loaded over time through interaction with the indoor air. Simplifying assumptions lead to a model that can be used to interpret storage buffering behavior in cases where properties of the storage materials are not well characterized. We will explore how this lumped parameter model behaves for formaldehyde and moisture. Similar models have been applied previously to describe the effects of storage on indoor concentrations of specific compounds (Dunn, 1987; Cummings & Kamel, 1988; Emmerich et al., 2002). This study presents the general form of the model, interpretation of the relevant parameters and timescales, and application to cases of interest. We also use the model to assess the impact of storage on long-term exposure to chemical species.

2 BACKGROUND

Chemical storage in building materials and furnishings has different implications depending on the species of concern. For moisture, one question of interest is to what extent does storage media buffer the humidity levels experienced in the space? For organic compounds, the concern is often how can exposure to such compounds be minimized? As a result, different

strategies have been employed to describe the interaction between airborne species and storage media.

Concerns regarding formaldehyde emissions from pressed wood building materials led to attempts to quantify the emission rate from specific products (Myers, 1984). Although most exposure mitigation strategies continue to assume constant emission rates for indoor air contaminants such as formaldehyde, it has been established that the emission rate of formaldehyde depends on the indoor concentration and thus on the air exchange rate. Equivalent models (Fujii et al., 1973; Berge et al., 1980; Hoetjer & Koerts, 1986) assume that a thin air layer at C_{EL} is in equilibrium with the storage medium concentration $C_{material}$ at all times, $C_{EL}=f(C_{material})$, and that the emission rate per unit volume of the space, ER , is given by:

$$ER = kL(C - C_{EL}) \quad (1)$$

where C is the bulk air concentration and kL [1/s] is the coupling time constant for the air and storage medium. The quantity kL is the product of a transport coefficient k and the loading factor L [m^2/m^3] which is the ratio of exposed storage material area to the room volume. The parameter kL can be interpreted as a time constant for the coupling between the near surface layer and the storage material. Although not all surfaces may initially contain and emit a chemical species, it is likely that over the initial period of repartitioning, additional surface materials will absorb and then re-emit the chemical as surfaces come to equilibrium with the airborne concentration.

This transport process can perhaps be described more accurately as two resistive processes in series (Sparks et al., 1996). The first barrier is between the bulk storage material and the interfacial zone and the second barrier between the interfacial zone and the bulk air concentration. In modeling emission of volatile organic compounds (VOCs) for example from synthetic stain on cabinetry or flooring, resistance between the interfacial zone and the room air tends to dominate. In the upper limit, k is proportional to the surface heat transfer coefficient and has a maximum value of 0.5-3 m/hr (Sparks et al., 1996). In practice, however, there is often a surface coating layer which adds additional resistance between the storage material and the air. This resistance decreases the effective value of k . Such coatings can reduce k to 1/30th of value for the uncoated product, which helps to explain the range of k between 0.01 and 3.3 m/hr reported in product emission tests (Myers, 1984).

The sorption of airborne chemical species onto solid material has been studied in great detail. Axley (1994) recommends that when a chemical species concentration in the storage medium is an order of magnitude less than the saturation concentration, it is appropriate to use the Langmuir isotherm or the linear isotherm model to relate the concentration of the sorbed material to that of the equilibrium layer. To model indoor air contaminants, it is common to use the linear isotherm model, which assumes the concentration at the surface of the storage medium is linearly proportional to the concentration in the equilibrium air layer:

$$C_{material} = \kappa C_{EL} \quad (2)$$

where κ is the affinity of the chemical species for the storage material.

Applying conservation of mass, the evolution of the indoor air concentration is governed by:

$$S - C - AC = kL(\dot{C} - C_{material}/\kappa) \quad (3)$$

where S is the amount of the compound injected into the space due to non-storage sources and outdoor air, and A is the dilution rate. It is clear that the indoor air concentration depends on the change on the storage materials. Accordingly, if the storage material concentration changes significantly over time, the indoor air concentration will change as well.

Due to health concerns regarding chronic exposure to formaldehyde and other volatile organic compounds, there is interest not only in the indoor concentrations of such species but also how concentrations vary over time. It is difficult to quantify the timescale associated with depletion of formaldehyde sources in observational studies because this timescale tends to be long (a year or longer). Additionally, temperature and humidity can cause indoor concentrations to vary seasonally by up to a factor of two (Dingle & Franklin, 2002). Comparing single measurements in different homes, Hun et al. (2010) reported no correlation between house age and indoor air concentration of formaldehyde.

Limited studies have looked at how indoor formaldehyde concentrations vary in the same home over time. Sampling in nearly 300 homes in three subsequent summers, Park and Ikeda (2006) observed a decrease in indoor formaldehyde concentration in homes initially less than 6 months old. Dingle and Franklin (2002) reported the concentration tends to decrease if the home is less than 10 years old. Gilbert et al. (2008) reported higher indoor formaldehyde concentrations in homes where new furniture was introduced in the past 12 months, and Park and Ikeda (2006) noted the level of total VOCs increased by a factor of two in homes that had been renovated in the past year.

Limited efforts have been made to model long-term depletion of formaldehyde in the indoor environment, beyond fitting observations to exponential decay models (Meyer & Hermanns, 1985; Tichenor & Guo, 1991). Time varying volatile organic compound concentrations from building materials have received more attention (Dunn, 1987; Guo & Murray, 2000), in part because the timescales are often much shorter than for formaldehyde—on the order of days rather than years. The following section describes how a simple mass conservation model can be used to illustrate how indoor concentrations of chemical species buffered by storage media may vary over time.

3 Theory

To include absorption and desorption of chemical from materials into the continuity equation, we follow the approach of Dunn (1987), coupling the air space to the simplest, first-order lumped parameter model for the storage medium. A first order model is appropriate when

the storage medium is homogeneous such as pool of liquid or a thin solid. It is also appropriate for a bulk solid when any internal concentration profile is relatively stable. Similar approaches have been used previously to describe VOC (Sparks, et al., 1996) and moisture storage in building materials (Cummings & Kamel, 1988). The storage medium is presumed to have some storage capacity, some coupling with the indoor air and some initial charge. The development of the model can be found in the appendix.

If the capacity of the storage media is large relative to the capacity of the indoor air, the model yields the solution:

$$C(t) = C_{\infty} + (C_{ss} - C_{\infty})e^{-t/\tau_{\infty}} + (C_o - C_{ss})e^{-t/\tau_{ss}}, \quad (4)$$

where

$$C_{ss} \equiv \frac{kLC_{eq} + AC_{\infty}}{kL + A}, \quad (5)$$

C_{eq} is the initial condition of the equilibrium layer and C_{∞} is the true steady-state concentration in the air.

There are two timescales in the resulting solution. τ_{∞} is depletion time scale for the storage medium, which can be related to the material properties as follows:

$$\tau_{\infty} = (1 + \alpha) \left(\frac{1}{A} + \frac{1}{kL} \right), \quad (6)$$

where $\alpha = \kappa V_{material}/V$ is the capacity of storage medium, and

$$\tau_{ss} = 1/(A + kL) \quad (7)$$

is the time scale for the air and different storage media to reach pseudo-steady state equilibrium. C_{∞} is a function of the source storage-independent emission rate of the chemical species and outside conditions (S) and the dilution rate:

$$C_{\infty} \equiv S / A. \quad (8)$$

Considering times that are long compared to the inverse dilution rate ($1/A$), we can use a pseudo-steady-state solution for the problem. For dilution rates in typical buildings, the pseudo-steady-state assumption is valid for timescales of a few hours or longer. With that assumption, we are left with only the depletion time scale:

$$C(t) = C_{\infty} + \frac{kL}{A + kL} (C_{eq} - C_{\infty}) e^{-t/\tau_{\infty}} \quad (9)$$

We have assumed that the storage can be treated as a single first order reservoir and thus the material parameters (C_{eq} , kL , α) are constants. In reality, the indoor environment contains a range of materials and describing the transfer of contaminants between different material surfaces and the air is a complex process (Parthasarathy et al., 2012). We argue that modeling all storage materials as a single reservoir is often sufficient and facilitates the interpretation of analytical solutions. It is possible that two or more storage media in the same space could each

have significant storage capacity and different depletion time scales. The same modeling approach could be modified to include multiple depletion time scales as discussed in the appendix. For real materials, material parameters may well be a function the dilution rate as well as environmental conditions such as temperature or humidity. We are not considering these impacts here.

This model assumes that diffusion of the chemical species within the storage media is not the rate-limiting process. The validity of this assumption depends on the diffusivity of the chemical species within the storage media and the thickness of the media. Some models describing the buffering of airborne chemical species model diffusion within the solid media explicitly (Dunn, 1987; Zhao et al., 2002; Kumar & Little, 2003). Arguing that multiple timescales are present, some emission models include multiple, separate storage layers (Kumar & Little, 2003; Singer et al., 2004). While increasing the degrees of freedom can improve model fit, multiple layers may not be necessary to capture the bulk of the behavior. In modeling of moisture, transport of water through walls often modeled as a diffusive process or an effective penetration depth is assumed (Janssen & Roels, 2009). For daily fluctuations in indoor humidity, it is likely that moisture may not diffuse fully through thick wall materials, however using an effective penetration depth in place of the storage medium thickness may suffice.

If the assumption that chemical concentration is uniform within the storage medium is not valid, the model presented here can often still be applied. In that case, however, the model parameter kL should be interpreted as an *effective* coupling time constant. The effective coupling time constant includes resistance to transport between the equilibrium layer and the storage medium as well as the resistance to transport of the chemical across the storage medium thickness.

4 Results

4.1 *Highly Charged Storage: Example Formaldehyde*

It is generally assumed that the majority of formaldehyde exposure indoors is from emission by building materials. Here, we assume this is the only source of indoor formaldehyde. This represents a case where the formaldehyde storage capacity of materials is large relative to the capacity of the air. This high storage capacity limit is discussed further in the appendix.

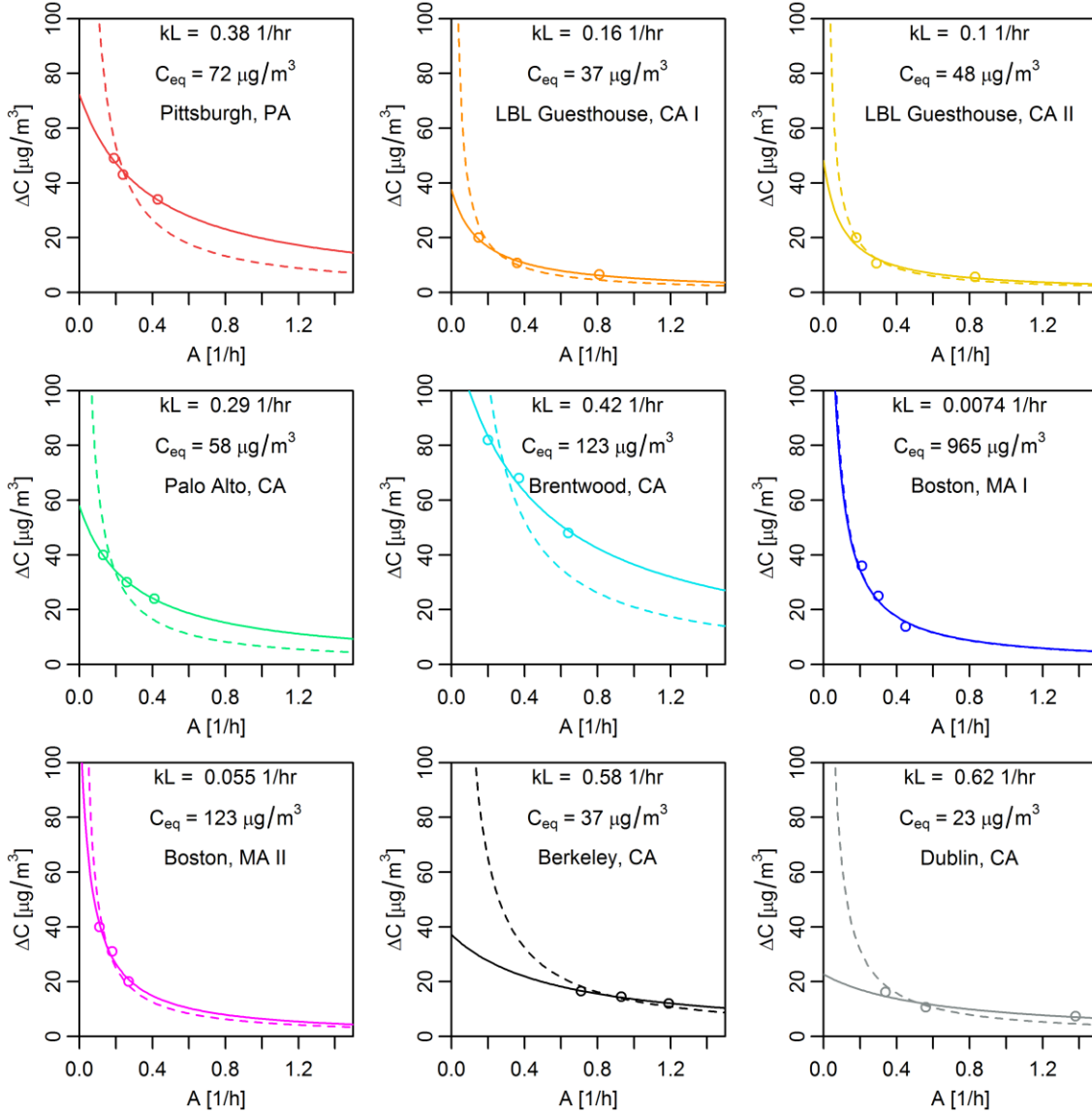


Figure 1: Indoor formaldehyde concentration above outdoor level, ΔC , versus the dilution rate A . Lines show the curve fit using Equation (10) (solid) and Equation (11) (dashed).

Looking at short times compared to the depletion time, the concentration is independent of time and storage capacity:

$$C_{ss} = \frac{kL}{A + kL} C_{eq} \quad (10)$$

Alternatively, the simplest models used to describe the impact of material emissions on indoor contaminant concentrations assume a constant emission rate ER , leading a steady-state concentration with a linear dependence on A :

$$C_{SS,linear} = ER/A. \quad (11)$$

From the non-linear relationship in Equation (10), it is clear that increasing the dilution rate A by increasing ventilation will decrease the concentration, but by a lesser degree than assuming a constant emission rate would predict. Thus, increased ventilation may be a less effective strategy for reducing contaminant concentrations in cases when transport from the storage material is fast relative to the dilution rate. When resistance to transport between storage materials and the air is high (kL small relative to A), the non-linear model reduces to the linear model in Equation (11).

This non-linear behavior is well supported by literature describing the emission of formaldehyde as well as other VOCs. From emission testing data in 20 studies and limited data from homes, Myers (1984) concluded that Equation (10) describes the dependence of formaldehyde concentration on air change rate more accurately than assuming a constant emission rate.

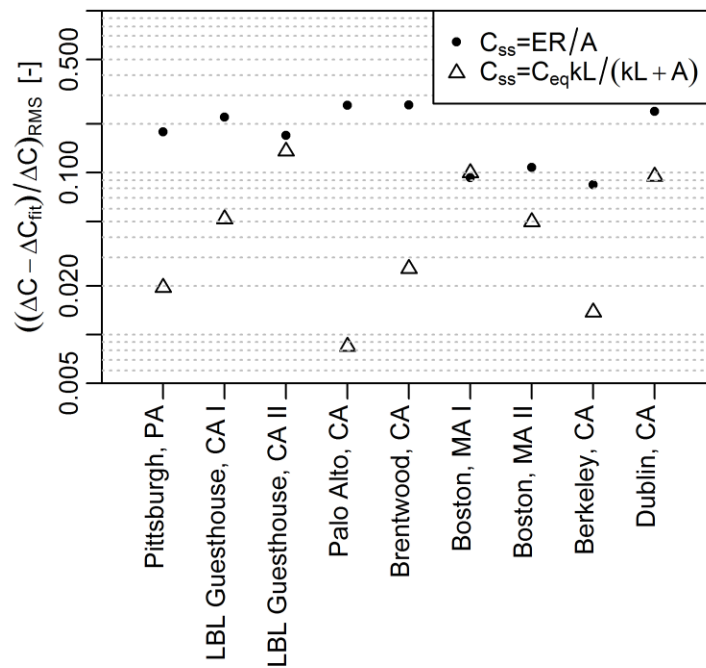


Figure 2: Goodness of fit for modeled pseudo-steady state, indoor formaldehyde concentration compared to observations.

By varying the dilution rate and measuring the resulting pseudo-steady-state indoor concentration, two of the three effective material parameters in the lumped parameter model, C_{eq} and kL but not α , can be determined using Equation (10). To validate the model assumptions leading to Equation (10) and to estimate exposure, results from a field study by Willem et al. (2013) on ventilation control of indoor contaminants are used. Measurements of indoor concentration of formaldehyde sampled at three controlled air exchange rates were obtained at nine inhabited residences. See Willem et al. for details of the experimental procedure. Figure 1 shows the concentration and air exchange rate, compared with both the non-linear model in

Equation (10) and the linear model in Equation (11) fit to the field data. Goodness of fit for the two models is shown in Figure 2, quantified by the RMS deviation between the data and pseudo-steady-state concentration of formaldehyde for each of the two models. For the storage model, the RMS deviation of the model from the observations is 15% or less at each site, versus up to 30% for the constant emission rate model. At the Palo Alto, Brentwood and Pittsburgh sites, Figure 2 shows the storage model is a dramatic improvement over the constant emission rate assumption.

The above pseudo-steady-state analysis considers times small compared to the storage depletion time. As the source depletes, the concentration in the indoor air will be reduced. To determine chronic health risks, it is necessary to integrate the concentration over the long term. If we assume that the relevant exposure is for the entire life of the charged material then we can integrate the concentration for all times:

$$\text{exposure} = \frac{kL}{A+kL} C_{eq} \int_0^{\infty} e^{-t/\tau_{\infty}} dt = (1+\alpha) \frac{C_{eq}}{A}, \quad (12)$$

assuming no new sources are introduced and the air exchange rate remains constant. Therefore, if the exposure time is long relative to the depletion time, the only material properties that matter for chronic exposure are those related to the initial charge of the storage (C_{eq} , α) and not the coupling between the storage material and the air (kL). Chronic exposure is inversely proportional to the dilution rate even though the short-term exposure is not. If designing ventilation guidelines to minimize occupants' overall exposure to formaldehyde, it is important to consider not just the short-term impact of ventilation control on the indoor concentration. The impact of ventilation on the concentration over the exposure time scale is relevant. To minimize exposure in a period comparable to or long relative to τ_{∞} , the quantities α or C_{eq} must be reduced or the air exchange rate A increased.

If the depletion time is long relative to the life of the material (or the occupant), then the assumption that people will be exposed to the complete charge is questionable. In such cases, however, the material can be treated as a constant-emission source. As described in the appendix, this is true for any weakly coupled storage media. When the lifetime of the material (or occupant) in the space is long compared to the depletion time, the exposure to the chemical will be less than given above, specifically

$$\text{exposure} = (1+\alpha) \frac{C_{eq}}{A} \left(1 - e^{-\tau_{lifetime}/\tau_{\infty}}\right) \quad (13)$$

To minimize exposure in during a period that is short relative to the storage depletion time τ_{∞} , C_{ss} must be minimized by reducing kL or C_{eq} (by reducing the initial loading $C_{material}(0)$), or by increasing A . It is unlikely that the assumptions of constant air exchange rate and no introduction of new sources would be met over long time scales, but these assumptions allow us to estimate impacts on exposure, for example, from guidelines specifying whole-house ventilation rates.

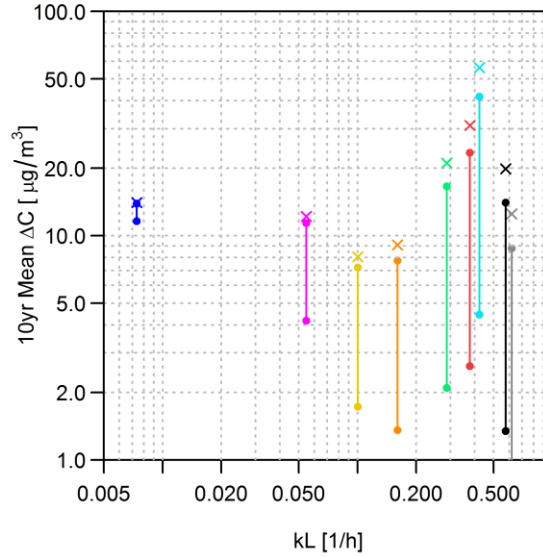


Figure 3: Estimated indoor formaldehyde concentration above outdoor level, ΔC , averaged over the 10 years following measurements. Symbols/colors correspond with Figure 1. The bars corresponds with $\alpha=10^{3.2}$ to $10^{4.5}$. The initial measured concentration (x) is also shown.

According to this model, depletion of formaldehyde storage in building materials and furnishings leads to decreased indoor concentrations and thus decreased exposure of occupants to formaldehyde. Figure 3 shows the estimated mean concentration over a ten-year period for the sites in Figure 1 assuming a constant ventilation rate ($A=0.5 \text{ h}^{-1}$) and that no sources are added or removed. A ten-year period was chosen as an approximation for the timescale for home renovation or furniture replacement. Calculating the mean indoor concentration using Equation (13) requires an estimate of the storage media capacity α , which is not very well determined for formaldehyde. Here, we estimate α as the product of κ , the estimated loading factor L (1 to 4 m^{-1}) and an estimated material thickness (1-5 cm). The Octanol-Air Partition coefficient is used as an estimate for κ , which is $10^{5.2}$ for formaldehyde (EPI Suite, 2011). This leads to the estimated range: $10^{3.2} < \alpha < 10^{4.5}$.

When the coupling is weak between the air and the storage media (low kL in Figure 3), the formaldehyde is tightly bound in the storage media and the mean concentration over the ten-year period is not much below the initial observed concentration. If kL is higher, the indoor concentration may decay significantly over a ten-year period due to depleted storage. However, observed indoor formaldehyde concentrations are rarely less than than $3\text{-}5 \text{ }\mu\text{g}/\text{m}^3$ above the outdoor levels (Dingle & Franklin, 2002; Park & Ikeda, 2006; Hun et al., 2010; Willem et al., 2013). Factors that could contribute to this discrepancy include: multiple storage media with different depletion times, storage capacity not as low as the lower estimate, and the introduction of new sources. It is possible that this model breaks down in the limit of complete depletion, for example, due to formaldehyde generating reactions within building materials.

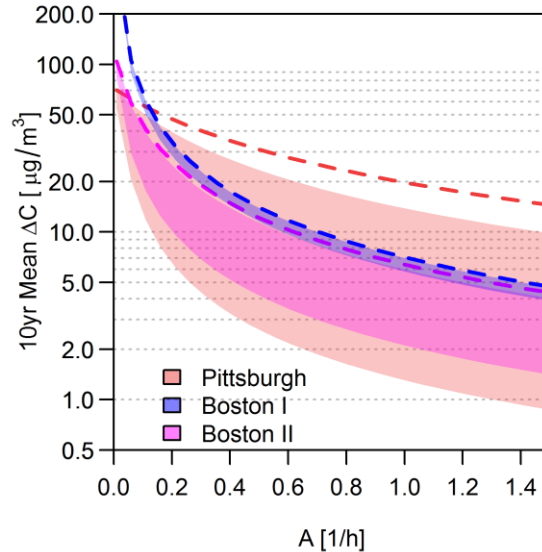


Figure 4: Effect of dilution rate A on formaldehyde exposure for three homes, quantified here by 10 yr mean concentration ΔC . Shaded area indicates the range of the mean formaldehyde concentration as in Figure 3. The dashed lines show the initial concentration from Equation (10).

Figure 4 illustrates the impact of changing the dilution rate on the mean indoor concentration of formaldehyde over a 10-year period at three sites. When kL is small (Boston I), there is a larger benefit to increasing the dilution rate than when kL is larger relative to A (Pittsburgh), but in all cases increasing the dilution rate decreases the expected exposure.

4.2 Periodic Storage: Example Water

Some moisture models attempt to capture the interactions between all moisture-containing materials in a space (Janssen & Roels, 2009). While this may be possible for a very simple experimental approximation of a room, real homes contain a variety of items of different (and largely uncharacterized) materials. The WUFI model simulates moisture transport through composite building envelope cross-sections of a range of materials, but requires the indoor and outdoor humidity to be specified a priori (Karagiozis et al., 2001). With the model presented in this study, we can examine the impact of moisture storage on the moisture concentration in both the storage media and the indoor air. The drying of wet building materials such as wood members follows a similar process as the formaldehyde example.

Far more important for understanding the indoor humidity profile is the fact that most buildings have a large amount of hygroscopic materials. Most fibrous materials can absorb water, as can many inorganic building materials such as concrete. Depending on the forcing cycle of indoor humidity, moisture may not penetrate the entire thickness of the various storage media. This suggests the assumption of lumped capacitance is not always appropriate. If the resistance to chemical transport between the surface and the room air is high relative to the

resistance to transport across the storage material, the then lumped capacitance assumption is valid, but if this ratio is low then the concentration of the chemical will vary across the storage material thickness (El Diasty et al., 1993). For moisture in building materials, this ratio is typically small and so some approaches model the moisture content across the wall thickness explicitly (Karagiozis et al., 2001). To preserve the simplicity of the model, the lumped capacitance assumption can still be used, provided the parameters are treated as effective values. I.e., the effective value of the transport coefficient k in kL will be smaller than for evaporation from a thin film. The forcing cycle can influence these effective transport and storage parameters, and thus the effective parameters may vary seasonally.

Storage materials act as a low-pass filter whose time constant is the depletion time. The available hygro-thermal capacity (α) is equal to the effective storage capacity of the materials and furnishings relative to the storage capacity of the air, sometimes referred to as the moisture buffering capacity. Room scale experiments report that α is between 5 and 20 depending on the quantity of hygroscopic materials, and kL is 0.3 to 0.6 1/h, corresponding to a dilution time of about 1-3 days (Cummings & Kamel, 1988; Yang et al., 2011).

4.3 Depletion Timescales

We have discussed how the chemical storage model can be applied to model different species. Figure 5 shows the depletion and repartitioning timescales for different example cases, as a function of the air-storage coupling kL and the storage capacity α . The H₂O region in Figure 5 corresponds with the range of parameters reported for moisture storage in wall materials (Cummings & Kamel, 1988; Yang et al., 2011). Repartitioning times for moisture are minutes to hours, whereas depletion times are hours to days.

The CH₂O region represents formaldehyde emission from building materials and furnishings. The range of values of kL is calculated from formaldehyde concentration measurements in homes at varied air change rates (Willem et al., 2013), and is consistent with previous values (Myers, 1984). The storage capacity for formaldehyde is estimated as in Section 4.1. For values of kL between 0.1 and 0.6 hr⁻¹, depletion time scales are between 1 and 20 years, consistent with observations in homes. When $kL < 0.1$, due to more tightly sealed materials or lower loading, depletion time scales can be much longer.

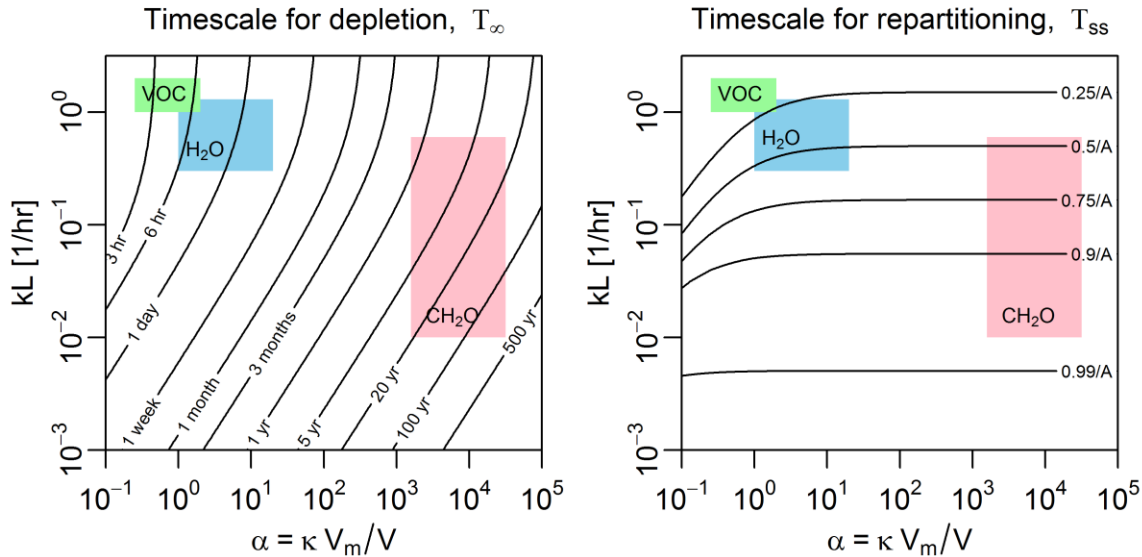


Figure 5: Expected timescales for depletion and repartitioning of VOCs, moisture (H₂O) and formaldehyde (CH₂O). Depletion times vary slightly with the dilution rate and $A=0.5 \text{ hr}^{-1}$ is assumed here.

The VOC region corresponds with parameters reported by Dunn (1987) for an experiment testing emissions from a silicone-based latex acrylic caulk containing C₈ alcohol and butyl propionate. For other VOCs, the storage capacity α may vary depending on the compound volatility and storage volume, and kL will depend on the loading and the extent to which the compound is sealed within the material. Shorter depletion timescales for VOCs are consistent with experiments (Sparks et al., 1996) and observations in residences (Park & Ikeda, 2006).

The timescale for the chemical species to repartition between the air and the storage media is quite short in all cases, relative to the depletion time. The repartitioning timescales for the species listed are between 10 and 100% of the dilution timescale ($1/A$), and are largely independent of the storage capacity.

5 DISCUSSION AND CONCLUSIONS

We used a simple model of chemical storage in materials to explain much of the storage buffering behavior observed in real buildings. This first-order model gives us a better understanding of what to expect when changes are made to physical parameters such as the ventilation rate. The model is applied to describe the highly charged example of formaldehyde storage in building materials and the periodic storage of moisture.

When bringing materials loaded with contaminants indoors, as is often the case for formaldehyde, there is a pseudo-steady state coupling that reduces the impact of changes in ventilation on the contaminant concentration. The model also extends our understanding of the process from this intermediate time scale to longer-term time scales and reproduces behavior

seen in field. Here we find that the total exposure one could get from the material is in fact inversely proportional to the air change rate just as with a contaminant with constant emission rate. The reason for this is that even though the pseudo-steady-state concentration is not lowered as much as a constant emission rate contaminant would be, the source is depleted more quickly.

We have also used this model in a different regime to explore the buffering of indoor humidity from hygroscopic materials. Results explain observations that indoor humidity levels are buffered with a time constant on the order of a day. The large amount of hygroscopic materials that are present in a typical building can absorb 5 to 20 times the quantity of moisture in the indoor air under diurnal forcing. This moisture buffering by storage materials is important to include in models (e.g., for energy use) that include the indoor humidity.

Our model leaves out the higher order terms associated with complex media, but such increased accuracy is not likely to be needed outside of a carefully controlled laboratory experiment. Further field measurements, however, would be useful to confirm or refute this statement. The inclusion of multiple materials with different depletion times may be useful in the modeling of inhabited homes, but longitudinal observational data would be needed to confirm this. In particular, long-term time series data of formaldehyde concentrations and air change rates in the same homes are needed to quantify depletion times but are not currently available. Our model predicts that three parameters characterize a stored source and without measurements over times as large as the depletion time, only two of the parameters can be determined.

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APPENDIX A: Derivation of Lumped Parameter Model

In this section, we will derive a first-order lumped parameter model of chemical storage in materials. This study builds on the solutions of Dunn (1987) to consider relevant physical regimes and timescales, such as the high storage capacity limit.

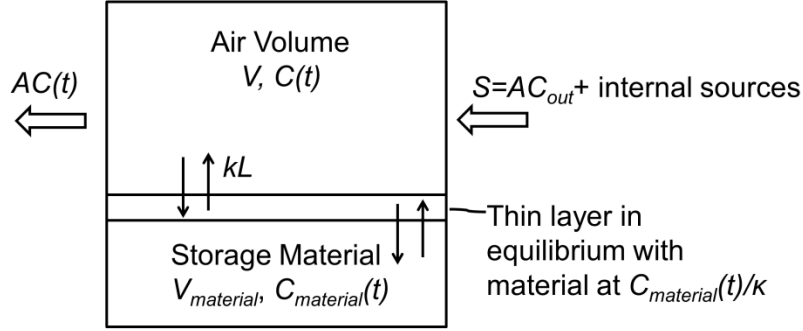


Figure A.1: Schematic of exchange between storage material and air volume.

As described in the main text and illustrated in Figure A.1, we can assume that an infinitesimally thin air layer next to the material is in equilibrium at all times. Therefore, we can express the connection between the material and the bulk air as follows:

$$V_{material}\dot{C}_{material} = kL(C - C_{material}/\kappa)V \quad (\text{A.1})$$

where the un-subscripted values are for the bulk air in the space. If conservation of mass is applied to the air volume:

$$V_{material}\dot{C}_{material} = SV - VAC - V\dot{C} \quad (\text{A.2})$$

then Equations (A.1) and (A.2) can be combined:

$$S - \dot{C} - A(C - C_{out}) = kL(C - C_{material}/\kappa). \quad (\text{A.3})$$

Differentiating Equation (A.3) with respect to time, assuming C_{out} , A , kL and κ are constant:

$$\dot{C} + \frac{\ddot{C} + A\dot{C}}{kL} = \dot{C}_{material}/\kappa \quad (\text{A.4})$$

and then substituting back into Equation (A.2) gives:

$$\frac{\kappa V_{material}}{V} \left[\dot{C} + \frac{\ddot{C} + A\dot{C}}{kL} \right] = S - AC - \dot{C}. \quad (\text{A.5})$$

This yields a second order linear differential equation (LDE) as follows:

$$\frac{1 + \alpha}{\Lambda} \ddot{C} + (1 + \alpha)(1 + A/\Lambda) \dot{C} + AC = S \quad (\text{A.6})$$

where

$$\alpha \equiv \frac{V_{\text{material}} \kappa}{V} \quad (\text{A.7})$$

and

$$\Lambda \equiv \frac{kL(1 + \alpha)}{\alpha}. \quad (\text{A.8})$$

The parameter, A , is the rate constant for the storage medium coming to equilibrium inside a sealed box (i.e., with no dilution or sources).

Similar models have been applied to describe the moisture buffering effect of building materials and furnishings on indoor humidity. In the limit where the coupling between the air and storage is instantaneous ($kL \gg A$), this is equivalent to the single room model discussed by Cummings and Kamel (1988) and the Effective Capacitance Model (Janssen & Roels, 2009). The storage model presented in the current study is mathematically equivalent to the two-room model proposed by Cummings and Kamel, where the moisture storage is modeled as a second room with a specified air exchange rate between the rooms.

A.1 SOLUTION

The solution to Equation (A.6) has the form:

$$C(t) = C_{\infty} + C_+ e^{-\lambda_+ t} + C_- e^{-\lambda_- t}, \quad (\text{A.9})$$

where the eigenvalue solutions to the LDE, λ_+ and λ_- , represent two decay rates:

$$\lambda_{\pm} = (A + \Lambda) \frac{1 \pm \sqrt{1 - \frac{4A\Lambda}{(A + \Lambda)^2(1 + \alpha)}}}{2} \quad (\text{A.10})$$

The first term of the solution in Equation (A.9) is the usual steady state solution, $C_{\infty} = S/A$. The second term is a slower decay representing the depletion (or storage) of the chemical species in the storage medium and thus the approach to the steady state equilibrium. The last term is a faster decay representing the repartitioning of the chemical species between air and material.

To find C_+ and C_- , we need to specify two initial conditions. One initial condition is provided by specifying C at time zero:

$$C_0 = \frac{S}{A} + C_- + C_+ \quad (\text{A.11})$$

The second initial condition is provided by specifying the initial loading of the material. We substitute Equation (A.9) into Equation (A.3) to get:

$$C_{material} / \kappa = \frac{S}{A} + \left(1 + \frac{A - \lambda_-}{\Lambda \alpha / (1 + \alpha)}\right) C_- e^{-\lambda_- t} + \left(1 + \frac{A - \lambda_+}{\Lambda \alpha / (1 + \alpha)}\right) C_+ e^{-\lambda_+ t} \quad (A.12)$$

which, when evaluated at the initial time $t=0$, defines the equilibrium concentration in the material:

$$C_{eq} \equiv C_{material}(0) / \kappa = \frac{S}{A} + \left(1 + \frac{A - \lambda_-}{\Lambda \alpha / (1 + \alpha)}\right) C_- + \left(1 + \frac{A - \lambda_+}{\Lambda \alpha / (1 + \alpha)}\right) C_+ \quad (A.13)$$

Thus

$$C_- = \frac{(C_{eq} - C_o) \Lambda \alpha / (1 + \alpha) - (S / A - C_o)(\lambda_+ - A)}{\lambda_+ - \lambda_-}, \quad (A.14)$$

$$C_+ = -\frac{(C_{eq} - C_o) \Lambda \alpha / (1 + \alpha) + (S / A - C_o)(A - \lambda_-)}{\lambda_+ - \lambda_-}. \quad (A.15)$$

A.2 HIGH STORAGE CAPACITY

When the storage capacity, α , is greater than unity, storage in materials can have a significant impact on the time history of the air concentration. Assuming α to be significantly larger than unity allows some simplifications. First, the fundamental time constant of the material can be simplified:

$$\Lambda \approx kL. \quad (A.16)$$

Furthermore, the two eigenvalues in Equation (A.10) can be found by Taylor expansion of the square root term:

$$A + \Lambda \approx \lambda_+ \gg \lambda_- \approx \left(\frac{A\Lambda}{A + \Lambda} \right) / (1 + \alpha) \quad (A.17)$$

and thus we can simplify our solution:

$$C_- = \frac{\Lambda}{\Lambda + A} (C_{eq} \alpha / (1 + \alpha) + C_o / (1 + \alpha) - S / A) \approx \frac{kL}{kL + A} (C_{eq} - C_o), \quad (A.18)$$

$$C_+ = -\frac{(C_{eq} - C_o) \Lambda \alpha / (1 + \alpha) + S - AC}{\Lambda + A} \approx C_o - \frac{kLC_{eq} + AC_o}{kL + A}. \quad (A.19)$$

which yields

$$C(t) = C_\infty + (C_{SS} - C_\infty)e^{-t/\tau_\infty} + (C_0 - C_{SS})e^{-t/\tau_{SS}}, \quad (\text{A.20})$$

where

$$C_{SS} \equiv \frac{kL C_{eq} + AC_\infty}{kL + A}, \quad (\text{A.21})$$

$$\tau_\infty \equiv (1 + \alpha) \left(\frac{1}{A} + \frac{1}{kL} \right), \quad (\text{A.22})$$

and

$$\tau_{SS} = 1/(A + kL). \quad (\text{A.23})$$

This solution has two decay terms: the first is the slow depletion of the materials to become in equilibrium with the source and air change rate; the second is the faster repartitioning to allow the air to become in equilibrium with the storage medium. If there are other first order removal processes (e.g., reactions, sticking, etc.) we can modify the dilution rate term to include them.

A.3 Weakly Coupled Materials

We are not concerned with storage unless the storage capacity of the storage medium is significantly higher than that of the air. We might similarly wish to limit our investigation to physically meaningful levels of coupling between the storage medium and the air.

In this limit, consider that the material coupling is quite small compared to the air change rate.

$$kL \ll A \quad (\text{A.24})$$

Taking the appropriate limits of the above equations:

$$C_{ss} \approx C_\infty + \frac{kL}{A} C_{eq} \quad (\text{A.25})$$

and

$$C(t) \approx C_\infty + \frac{kL}{A} C_{eq} e^{\frac{-kLt}{1+\alpha}} + (C_0 - C_\infty - \frac{kL}{A} C_{eq}) e^{-At}. \quad (\text{A.26})$$

This is approximately the same as

$$C(t) = C_\infty + S_* / A + (C_0 - C_\infty - S_* / A) e^{-At}, \quad (\text{A.27})$$

where

$$S_* = kL C_{eq} e^{-kLt/(1+\alpha)} \quad (\text{A.28})$$

and S_* represents a slowly decaying emission rate, but otherwise a standard dilution curve.

Therefore, a weakly coupled material can be treated as a simple emission source whose strength

decays slowly and independently of the air change rate. Weakly coupled materials can then be included with a simple modification to the source term.

A.4 COMPLEX MEDIA

So far we have assumed a single, first-order storage medium. In real buildings, there can be multiple materials in the space and each storage material may be made up multiple layers. We can apply the same derivation in theory for the multiple materials and layers and would arrive at a higher order linear, differential equation whose solution would look as follows:

$$C(t) = C_{\infty} + \sum_i C_i e^{-\lambda_i t} \quad (\text{A.29})$$

The *forward* problem (i.e., where we know all the properties of all the layers and materials), is straightforward, but numerically tedious to find the decay rates and coefficients. In practice, we almost never know the properties of the materials in a given space.

In theory, this can be handled by considering the *inverse* problem: taking measurements of the concentration and fitting the equation above to the data. Practically, this can only really be done successfully when there are a small number of well-separated decay rates, given the uncertainties found in field data.

A.4.1 Multiple storage media

Consider a set of independent storage media in a space, each with its own set of characterizing parameters. If we only consider storage of significant capacity, each individual storage medium will have a depletion rate slow compared to the air change rate as shown above. The combined depletion rate cannot be faster. Depending on the number and kinds of media the repartitioning may be made up of many exponential decay terms, but all of them will be as fast as the air change rate or faster. In practical terms only the slowest non-trivial rate of this set will be of interest for understanding the concentration in the air as the other terms will decay away quite quickly.

A.4.2 Layered storage media

Consider a layered material where each layer has a certain capacity and a certain coupling with the layers on either side of it and only the surface layer communicates with the air. If at any layer the coupling becomes weak, the deeper layers are isolated from interacting with air and can be treated as a weakly coupled source. The rest of the layers are not weakly coupled and so there will be a slow set of depletion rates and a faster set of repartitioning rates. Because the non-surface layers do not interact directly with the air, it is possible for some of these repartitioning rates to be slower than the air change rate, but not drastically so.

Therefore, for any type of complex material, there will be a cluster of repartitioning rates in the general vicinity of the air change rate and a cluster of slower depletion rates. For most practical purposes, it is sufficient to use one fast rate and one slow rate—i.e., treat the system as an equivalent single lumped-storage system. This generalization assumes that all weakly coupled materials are treated as a modified source term and also assumes that very short-term behavior is not important.