Modeling Sorption Transport in Rooms and Sorption Filtration Systems for Building Air Quality Analysis

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Abstract

Adsorption, desorption and chemisorption are known to impact the dispersal of volatile organic and chemically reactive compounds in buildings. These same three processes may be used to advantage to control the levels of these compounds indoors using building sorption filtration devices. To add to the understanding of these processes, to provide the means to predict the impact of these processes on human exposure and to provide the tools needed to design gaseous filtration systems to mitigate the exposure to these compounds, a general approach to modeling the dynamics of these processes is presented. Equations are presented to account for the elemental advection, diffusion, sorption, and chemical transport steps affecting single component sorption dynamics in rooms and sorption filtration systems. These element equations are based on general principles and formulated in terms of fundamental physical parameters that may be determined using standard procedures. Models to predict room and sorption filtration system dynamics are formulated using assemblages of these element equations and a series of simplified models of these systems are derived. Initial applications to model single-component sorption transport in rooms and sorption filtration systems indicate that the approach has the potential to provide accurate predictions providing the sorption and chemical characteristics of the sorbate-sorbent system being considered are well-characterized. This potential is, however, compromised by the lack (or present uncertainty) of fundamental data relating to sorption equilibrium, porous diffusion, surface chemistry, and boundary layer mass transport.

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Introduction

Experimental and theoretical research in the past decade has demonstrated that sorption transport in rooms can significantly influence the dispersal of air pollutants in buildings (Neretnieks et al., 1981; Seifert and Schmahl 1987; Nielsen 1988; Silberstein 1989; Axley and Lorenzetti 1992; Christiansson et al. 1992; Neretnieks, Christiansson et al. 1993). During this same period, other research results were reported that indicate sorption filtration can effectively control levels of VOCs, ozone, and sulfur dioxide in buildings (Graham and Bayait, 1990; Kinkhead 1990; Liu 1990; Liu 1991; Axley and Lorenzetti 1992; Liu 1992; Weschler et al. 1992; Muller 1993; Yu and Neretnieks 1993) – contradicting earlier studies that suggested a more limited potential (Neretnieks et al. 1981; Ramanathan et al. 1988; Ramanathan et al. 1989; Viner et al. 1991). Yet methods to model sorption transport in rooms, for exposure analysis, and to model sorption filtration devices, for use with multi-zone contaminant dispersal analysis procedures, have been slow in forthcoming.

This paper reviews the theoretical bases of sorption models developed for single-component, multizone contaminant dispersal and sorption filtration system analysis (Axley 1990; Axley 1991; Axley 1991; Axley and Lorenzetti 1992) and presents new work to extend these models to account for surface chemical transformations. These models are based upon fundamental principles of sorption transport and, as such, are closely related to models put forward by Professor Neretnieks' research group in Sweden (Christiansson et al. 1992; Neretnieks et al. 1993; Yu and Neretnieks 1993). The models are organized into generic model families that account for (a) the equilibrium limits of reversible sorption processes with or without (b) boundary layer diffusion transport at the sorbent surface, (c)

diffusion transport within the sorbent proper (d) chemical transformation at active sites, and (e), for filtration devices, convective transport within the filtration media. Individual members of each family are distinguished by the sorption equilibrium relationship (sorption isotherm) and, for those case involving chemisorption, the chemical rate expression used in their formulation.

To proceed, some fundamental principles of sorption transport will be reviewed and, from these, elemental equations for each of the relevant transport processes involved will be presented. Models governing the sorption dynamics in rooms and filtration devices will then be formulated from these elemental relations and examples of their application will be considered.

Fundamental Principles

Adsorption, the separation of a substance from one phase – indoor air in the present context – and its accumulation on the surface of another phase – here, building materials or sorption filtration media – is just one of several steps that together determine the nature of *sorption dynamics* within buildings. In general, these steps include:

1. *bulk advection (convection)* of the adsorbate species from remote areas to areas containing the sorbent;
2. *external diffusion* of the adsorbate through air-phase boundary layers separating the sorbent's exposed surface from the bulk air-phase;
3. *internal diffusion* of the adsorbate through interstitial sorbent pores to interior *active sites;*
4. *adsorption* of the sorbate to the active sites;
5. *chemical transformation* of the sorbate, manifested by electron sharing or exchange, to effect either a strong bond to the sorbent or to produce product species;
6. *desorption* of the sorbate or product species from the active sites to the interstitial air-phase;
7. *internal diffusion* of the adsorbate or product species through the porous interstices of the sorbent to the sorbent's exposed surface;
8. *external diffusion* of the adsorbate or product species outward through air-phase boundary layers; and
9. *bulk advection (convection)* of the adsorbate or product species from the areas containing the sorbent to remote locations within the building or HVAC system.

Sorbate species affected by the fifth step are said to be *chemisorbed* otherwise the sorbate species is said to by *physically adsorbed*, the former being a relatively irreversible process while the latter not. *Chemisorption* is, presumably, responsible for the transport of the large variety of chemically active indoor air pollutants known to be *scavenged* or *deposited* on indoor surfaces including ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitrogen monoxide (NO), nitric acid (HNO_3), etc. Surface removal rates of these species are commonly modeled using the so-called *deposition velocity* concepts based on the assumption that removal rates are related directly to the bulk air-phase species concentration – a *first order approximation*. The mechanistic details of these removal processes remain unclear at this time, consequently, the deposition velocity, first order approximation should be questioned (Nazaroff et al., 1992; Weschler et al., 1992). We will consider this issue further.

Advecture Transport and the Element Assembly Approach

Our purpose here is to develop models for sorption transport that may be used for practical indoor air quality analysis of whole building systems. Consequently, the transport of adsorbent species due to infiltration, exfiltration, and interroom *advection* and that due to *convective* transport in HVAC systems including, possibly, sorption filtration devices must be considered.

The advective transport within the building proper and the convective transport within air handling HVAC subsystems may be modeled directly using available macroscopic contaminant dispersal analysis theory to account for flow transport, homogeneous (bulk-phase) transformations, other heterogeneous (surface-related) transformations, and arbitrary source dynamics. This theory transforms the central continuum problem of determining the temporal (t) and spatial (x, y, z) variation of air pollutant concentrations $C(x, y, z, t)$ (g-species/g-air) into a spatially-discrete, but temporally-continuous problem of determining the variation of air pollutant concentrations $\{C(+)\}$ – the *system concentration vector* – at discrete locations or *nodes* within the building and/or HVAC subsystem(s). As a result, the dispersal of contaminants within the building/ HVAC airflow system are approximated by systems of differential equations – the *system equations* – of the form:

$$[W]\{C\} + [M]\frac{d\{C\}}{dt} = E(t) \tag{1}$$

where, for a system idealized with n discrete points, $[W]$ is the n by n *transport matrix* (mass-air/time) that may, in general, vary in time and depend on discrete concentrations, $[M]$ is the n by n *capacitance matrix* (mass-air) that may also vary in time and depend on discrete concentrations, and $E(t)$ is the n by 1 *excitation vector* (mass-species/time) that accounts for both internal sources and contaminant mass transport from outdoors.

Element Equations

The *assembly* approach to this theory assembles equations governing the dispersal within the system from *element* or *component* models, that describe local mass transport processes, defined in terms of equations of the general form (Axley 1989):

$$\{w^e\} = [W^e]\{C^e\} + [M^e]\frac{d\{C^e\}}{dt} + \{R^e\} \tag{2}$$

For a specific element or component "e", w^e is the *element mass flow rate vector* (g-species/s), C^e is the *element concentration vector*, a subset of the system concentration vector. The arrays W^e and M^e may, in general, vary with time and depend on the element concentration vector. The removal vector R^e admits the possibility of species removal or generation at the element level.

For example, the conventional multi-zone theory based upon building idealizations consisting of well-mixed zones linked by discrete airflow paths containing, possibly, simple filtration devices (Sinden 1978; Sandberg 1984) may be implemented using assemblages of a *well-mixed zone element* and a *simple flow/filtration element*. The well-mixed zone element equation for element (zone) "e" is a simple scalar relation (represented here in expanded matrix notation for consistency):

$$\{w^e\} = M_{air}[1]\frac{d\{C^e\}}{dt} + \{R^e(t)\} \tag{3}$$

that relates the mass flow rate of an air pollutant species into accumulation, w^e, to the product of mass of air contained within the zone, M_{air}, and the time rate of change of the species concentration in the zone C^e associated with an arbitrary node (location) in the zone (i.e., given the assumption of well-mixed

conditions in the zone). The removal term, $R^e(t)$, accounts for a known time-varying contaminant removal rate – an unlikely possibility, usually – or if negative, a known time-varying contaminant generation rate – the more likely possibility.

The simple flow/filtration element for the discrete flow path "e" that accounts for flow from node "i" to "j" is a set of two relations:

$$\begin{Bmatrix} w_i^e \\ w_j^e \end{Bmatrix} = w_{air}\begin{bmatrix} 1 & 0 \\ -(1-\eta) & 0 \end{bmatrix}\begin{Bmatrix} C_i^e \\ C_j^e \end{Bmatrix} + \begin{Bmatrix} R_i^e \\ R_j^e \end{Bmatrix} ; \tag{4}$$

for airflow from i to j

that relates the species mass flow rate from node i into the element, w_i^e, to the product of the mass flow rate of air in the flow path, w_{air}, and the node concentration, C_i^e. The species mass flow rate from node j *into* the element, w_j^e, is related to the product $-w_{air}(1-\eta)C_j^e$ where η is the efficiency of the filter, if any, contained in the flow path. The removal terms, again, provide a means to account for known time-varying contaminant removal rates or if negative, time-varying contaminant generation rates.

To account for the spatial variation and time delays of contaminant transport in ducts, where airflow is reasonably approximated as a one-dimensional flow regime, element equations may be formulated using Finite Element approximations to the one-dimensional, convection-diffusion equations governing the dispersal (Axley 1989). Using this approach, the duct would be discretized into number of segments or *finite elements* each having a chosen number of nodes; an approximate form of the spatial variation of concentration within each finite element – the *shape functions* – would be defined in terms of the nodal concentrations; and, through the application of a minimization principle, element equations of the form given above, Equation 2, would be formulated. For two-node elements based on linear shape functions the following equations result:

$$\begin{Bmatrix} w_i^e \\ w_j^e \end{Bmatrix} = \begin{bmatrix} \frac{\rho A \mathscr{D}}{\delta x^e}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + \frac{w_{air}}{2}\begin{bmatrix} 1 & 1 \\ -1 & -1 \end{bmatrix} \end{bmatrix}$$

$$+ \phi\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}\end{bmatrix}\begin{Bmatrix} C_i^e \\ C_j^e \end{Bmatrix} \tag{5}$$

$$+ \frac{\rho A \delta x^e}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\frac{d}{dt}\begin{Bmatrix} C_i^e \\ C_j^e \end{Bmatrix} + \begin{Bmatrix} R_i^e \\ R_j^e \end{Bmatrix}$$

where a lumped (diagonal) capacitance is used here for simplicity, ρ is the density of air flowing in the duct, A is the cross-sectional area of the duct, $\mathscr{D}$ is the (effective) diffusivity of the contaminant, δx^e is the length of the duct segment/element "e", ϕ is the so-called *upwind parameter* ($0 \le \phi \le 1$) used to control the numerical characteristics of the resulting equations, and all other variables are defined as before. This element equation simplifies to that corresponding to a simple flow element (i.e., Equation 3 with $\eta = 0$) when the diffusivity and element length are negligible and the upwind parameter is set to 1.0.

Finite element equations, similar to this relation, may be used to account for the convection-diffusion transport in packed-bed filtration devices (Hossain and Yonge, 1992). From a practical point of view, finite element approximations to these continuous transport processes are attractive for the simple reason that they assume the form of the general element equation, Equation 2, and, as such, can be directly assembled with other transport elements to model complex transport dynamics. In addition, finite element approximations allow nonuniform spacing of nodes, a technique that may be used to advantage to capture sharp concentration gradients, and have proven to provide accurate results (Hossain and Yonge, 1992).

System Equations and Assembly

Additional *element equations* formulated to account for the diffusion, sorption, and chemical transformation steps outlined above, based on fundamental principles of sorption transport, will be presented in the following sections. These element equations may be combined – *assembled* – to form *system equations* that govern a variety of contaminant dispersal problems in whole-building systems or selected subsystems (e.g., an HVAC sorption filtration system) that involve sorption transport. The assembly process may be defined rigorously in terms of algebraic transformations that impose constraints of species mass conservation at system nodes (Axley 1989). For our purposes here, however, we may use a *direct assembly* approach wherein system equations are formed directly from the element equations by accounting for the contribution to species mass flow of each element for each system node.

Sorption

The existing sorption science and technology literature is directed toward either industrial sorption

separation applications (Yang 1987; Satterfield 1991) or for large scale air and water pollution control (Noll et al. 1992). As such, it may be directly applied to building sorption filtration systems. However, to model sorption transport in rooms requires adaptation of the theory. Much of the detail of this development has been published elsewhere (Axley 1991; Axley and Lorenzetti 1992); the presentation here will be limited to key results and new extensions.

The sorption of a species A to an active site $S - {}^\star$ may be represented as:

$$A + S - {}^\star \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} A \cdot S - {}^\star + \Delta H \qquad (6)$$
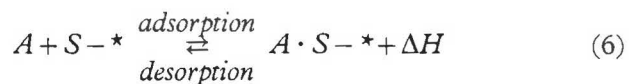
where $A \cdot S - {}^\star$ is the species bound to the active site and ΔH is the heat of adsorption. Ironically, the rate of adsorption or desorption is, most often, practically instantaneous relative to the other transport steps outlined above and need not be modeled explicitly. The equilibrium limits of this transformation are, however, all-important and will prove central to all following considerations.

Single-component Sorption

For closed *single-component* systems under steady conditions the rate of adsorption will eventually come to equal the rate of desorption and the concentration of the adsorbate in the air-phase C and the sorbed-phase C_s (g-species/g-sorbent) will remain constant at their respective equilibrium values C_e and C_{se}. For isothermal conditions at atmospheric pressure, equilibrium relations between these variables – *adsorption isotherms* – may be represented as:

$$C_{se} = f(C_e) \qquad (7)$$

where the function f is unique for each adsorbate-adsorbent system. Some isotherm models are presented in Table 1 (see, for example, Yang 1987; Noll et al., 1992) for details.

For the sorption of trace concentration air-pollutants on building materials, the Langmuir model or its low-concentration asymptote, the Linear model, are reasonable first candidates. For sorption of water or other contaminants with concentrations within one order of magnitude of their saturated values, the BET model should be considered. The Polanyi DR and Freundlich models are often employed for industrial sorbents that exhibit highly

Table 1 Representative adsorption isotherm models

Model	$C_{se} = f(C_e)$	Model Parameters
Linear	$C_{se} = K_p C_e$	K_p is the Partition Constant.
Langmuir	$C_{se} = \dfrac{C_{so} K_L C_e}{1 + K_L C_e}$	C_{so} is the molecular mono-layer sorbent concentration. K_L is the Langmuir Constant.
BET	$C_{se} = \dfrac{C_{so} K_{BET} \hat{C}_e}{(1 - \hat{C}_e)(1 - \hat{C}_e + K_{BET} \hat{C}_e)}$	K_{BET} is the BET Constant. $\hat{C}_e$ is the ratio of the equilibrium to the saturation concentration C_{sat}.
Polanyi DR	$C_{se} = C'_{so} \exp\left(-D \left[\ln\left(\dfrac{C_{sat}}{C_e}\right) \right]^2 \right)$	D is the Dubinin-Radushkevich parameter. C'_{so} is the sorbed concentration for complete filling of micropores.
Freundlich	$C_{se} = K_F C_e^{(1/n)}$	K_F is the Freundlich constant. n is the Freundlich exponent.

nonlinear equilibrium behavior although the former is the model of choice for sorption of VOCs on granulated activated carbon where capillary condensation in microporous interstices – *pore filling* – is important. Although these two models may be shown to be physically consistent under some restrictive assumptions, they do not approach linear behaviour at low air-phase concentrations as expected theoretically – the other models above do – and, for this reason, should be used with caution for indoor air applications where air-phase concentrations tend to be low.

In spite of recent progress in this area (Seifert and Schmahl 1987; Borrazzo and Davidson 1990; Borrazzo and Davidson 1990; Liu 1990) there is a paucity of equilibrium data for the sorption of indoor air pollutants, at the low concentrations commonly found in buildings, on building materials or sorption filtration media. It will be seen that an understanding of sorption transport in buildings and building filtration systems depends critically on such data – additional fundamental measurements of this data is urgently needed to proceed.

Multi-component Sorption

The discussion above has been limited to *single-component* sorption. In practical situations building materials and sorption filtration media will be exposed to multi-component mixtures of compounds that will tend to compete for available active sites, consequently, *multi-component sorption* equilibirum will have to be accounted for. A variety of multi-component equilibrium relations have been developed and their efficacy for industrial separation applications (Yang 1987; Trogen 1992) and for air cleaning applications in chemical and industrial environments (Yu 1987; Noll et al. 1992) has been investigated. Liu has

successfully demonstrated the application of a multi-component approach based on Polanyi's potential theory and a technique known as *component grouping* to the sorption of low-concentration VOC mixtures (i.e., corresponding to conditions found in buildings) on activated carbon (Liu 1991).

In general, for multi-component mixtures (under isothermal conditions at atmospheric pressure) the equilibrium sorbed concentration for component i, $C_{se,i}$, will depend upon not only on the air-pahse concentration of component i, $C_{e,i}$, but the air-phase concentrations of all other components due to *competition* among the adsorbates for available active sites, as:

$$C_{se,i} = g(C_{e,1}, C_{e,2}, \dots C_{e,i}, \dots C_{e,n}) \qquad (8)$$

The *Extended Langmuir Equation* developed by Markham and Benton for component molecules that do not influence each other provides the simplest example of a multi-component model:

$$C_{se,i} = \dfrac{C_{so,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{n} K_{L,j} C_{e,j}} \qquad (9)$$

The model parameters are defined for each component as presented above in Table 1. For very low air-phase concentrations (i.e., such that $1 \gg \sum K_{L,j} C_{e,j}$) this multi-component model simplifies to a series of n *uncoupled* single-component Linear isotherms and, therefore, under these conditions multicomponent competition may be ignored.

Chemical Transformation

While a variety of chemical transformations could be considered, the elemental unimolecular reaction

of the sorbed species to yield product species and, possibly, the recovery of active sites provides the simplest example:

$$A \cdot S - * \xrightarrow{k} products + S - * \tag{10}$$
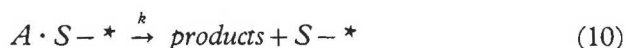
where k is a first order rate constant for this reaction $(1/s)$. The rate of removal of the sorbed species may be expected to be proportional to the amount adsorbed – the product of C_s and the mass of sorbent present M_s (Satterfield 1991) thereby defining a scalar equation for a *first order chemical transformation element*:

$$\{R^e\} = kM_s[1]\{C_s^e\} \tag{11}$$

External Diffusion

Diffusion through the air-phase boundary layer surrounding an adsorbent or adsorbent particle, sometimes called *external diffusion*, is intimately related to the details of airflow near the sorbent surface – details that must remain largely indeterminate due to the computational challenge demanded to predict them. Nevertheless, mass transport through this boundary layer may be estimated using the discrete approximation from boundary layer theory to yield the following *boundary layer transport element equation*:

$$\begin{Bmatrix} w_i^e \\ w_j^e \end{Bmatrix} = \rho A_s \bar{h} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} C_i^e \\ C_j^e \end{Bmatrix} \tag{12}$$

where w_i^e and w_j^e are the species mass flow rates to and from the sorbent surface, C_i^e and C_j^e are the air-phase concentrations of the bulk and near-surface locations respectively, A_s is the exposed surface area of the sorbent (m²), ρ is the density of the air-phase (g-air/m³), and $\bar{h}$ is the surface-average mass transfer coefficient (m/s). Correlations are available to estimate the surface average mass transfer coefficient for airflow past flat surfaces (White 1988) and for airflow through fixed beds of particles (Yang 1987; Noll et al. 1992).

Internal Diffusion

Transport within the pores of effective adsorbents – *internal diffusion* – is invariably complex involving molecular and Knudsen diffusion within the gas-

phase, surface diffusion along the surfaces enclosing the pores, and possibly, Poiseuille flow driven by pressure gradients. These diffusion processes may reasonably be modeled analogously to Fick's Law through the introduction of an *effective diffusion coefficient* D_e (m²/s) (Yang 1987), although more accurate results may be obtained for microporous sorbents such as activated carbon by accounting separately for the gas-phase diffusion and the surface diffusion using a so-called *combined diffusion* model (Yu 1987; Noll et al. 1992). Unlike simple diffusion, however, diffusion of adsorbates in adsorbents is constrained by the equilibrium sorption conditions discussed above. By assuming the sorbed-phase concentration remains in equilibrium with the porous air-phase concentration one may obtain partial differential equations that describe this equilibrium-constrained diffusion process.

Planar Sorbents

For one-dimensional diffusion into sheet-like adsorbents, a reasonable geometric idealization for many building materials, the resulting partial differential equation assumes the form of the classic 1D diffusion equation (Axley and Lorenzetti 1992). A solution to this partial differential equation may be approximated using Finite Element procedures by discretizing the adsorbent sheet into a number of layers. In so doing, element equations are obtained that describe the species mass transport rate from adjacent nodes, i, j, into the element in terms of air-phase concentrations as:

$$\begin{Bmatrix} w_i^e \\ w_j^e \end{Bmatrix} = \frac{\rho A_s D_e}{\delta x^e} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} C_i^e \\ C_j^e \end{Bmatrix} + M_{eff} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\times \begin{Bmatrix} \dfrac{dC_i^e}{dt} \\[2mm] \dfrac{dC_j^e}{dt} \end{Bmatrix} \; ; \; M_{eff} = \frac{A_s \delta x^e}{2} \left(\rho \varepsilon + \rho_s \frac{\partial f}{\partial C} \right) \tag{13}$$

where δx^e is the element (discrete layer) thickness, ε is the porosity of the sorbent, ρ_S is the bulk density of the sorbent and all other terms are as defined above. The effective capacity M_{eff} is seen to be dependent on the mass of air and sorbent in the layer and the tangent slope of the sorption isotherm used.

Granular sorbents

Porous diffusion within the granules of sorption filtration media may, in a similar manner, be modeled

using partial differential equations describing radially symmetric diffusion within spherical sorbent particles. Again, Finite Element procedures (or the closely related orthogonal collocation procedure) may be used to transform these partial differential equations into ordinary differential equations of the desired form of Equation 2 (Hossain and Yonge 1992; Noll et al. 1992). The *Linear Driving Force (LDF)* model provides, however, a computationally simpler, albeit less accurate, alternative (Weber Jr. and Smith 1987; Yang 1987). The LDF approximation leads directly to an element equation expressed in terms of an air-phase concentration at the exposed surface of the sorption granules C_i^e, a mean sorbed-phase concentration of the granules, $\overline{C}_{sj}^e$, and the sorbent granule radius, R_p, as:

$$\begin{Bmatrix} w_i^e \\ w_j^e \end{Bmatrix} = \frac{15\, M_s D_e}{R_p^2} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} f(C_i^e) \\ \overline{C}_{sj}^e \end{Bmatrix}$$

$$+ M_s \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \begin{Bmatrix} \dfrac{df(C_i^e)}{dt} \\ \dfrac{d\overline{C}_{sj}^e}{dt} \end{Bmatrix} \qquad (14)$$

Note, here, the *driving force* is the difference between the sorbed-phase concentration at the granules' exposed surface that is in equilibrium with the near-surface air-phase concentration $C_{si}^e = f(C_i^e)$ and the mean sorbed-phase concentration of the granule $\overline{C}_{sj}^e$.

Application

The element equations presented above may be directly assembled to form systems of equations that govern the dispersal of air pollutants in rooms containing adsorbent materials and in HVAC sorption filtration devices. These room and HVAC sorption filtration models may, in turn, be directly assembled with other element, room and component models to form systems of equations that describe the dispersal of air pollutants in larger, more complex building/HVAC systems.

Room Sorption Dynamics

An idealization of a single, well-mixed room containing a volume of air of mass M_a and an adsorbent sheet-like material of mass M_s – discretized into n layers – is shown in Figure 1.
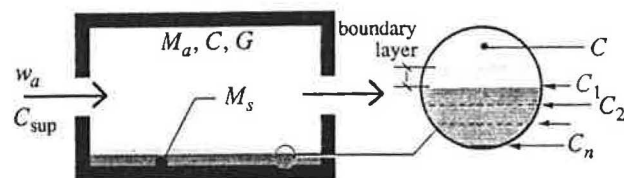

Fig. 1 idealization of a single, well-mixed room containing an adsorbent sheet.

Given the mass flow rate of air flowing into the compartment, w_a, the supply air concentration, C_{sup}, and an internal contaminant generation rate, G, equations governing the behavior of this system may be directly assembled from the element equations presented above:

$$\begin{bmatrix} (w_a + K_h) & -K_h & 0 & \cdots & 0 \\ -K_h & (K_h + K_D) & -K_D & \cdots & 0 \\ 0 & -K_D & 2K_D & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & K_D \end{bmatrix}$$

$$\times \begin{Bmatrix} C \\ C_1 \\ C_2 \\ \vdots \\ C_n \end{Bmatrix} + \begin{bmatrix} M_a & 0 & 0 & \cdots & 0 \\ 0 & M_{eff} & 0 & \cdots & 0 \\ 0 & 0 & 2M_{eff} & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & M_{eff} \end{bmatrix}$$

$$\times \frac{d}{dt} \begin{Bmatrix} C \\ C_1 \\ C_2 \\ \vdots \\ C_n \end{Bmatrix} = \begin{Bmatrix} w_a C_{sup} + G \\ 0 \\ 0 \\ \vdots \\ 0 \end{Bmatrix} \qquad (15)$$

where $K_h = \rho A_s \overline{h}$ and $K_D = \rho A_s (D_e / \delta x^e)$. Equation 15 represents a family of models with individual members distinguished by the specific adsorption isotherm used in formulating M_{eff}.

This $n+1$ degree of freedom (DOF) model accounts for both boundary layer and porous diffusion transport and, as such, will be identified as the *BLPD model*. Three limiting cases may be derived directly from this general model by imposing appropriate algebraic constraints.

EA Model: If the mass transport due to advection is slow relative to both the external and internal diffusion rates (i.e., $w_a \ll K_h$ and $w_a \ll K_D$) then the air-phase concentrations will tend to remain equal and the sorbed phase concentration will, therefore,

remain in equilibrium with the bulk air-phase concentration. This *equilibrium adsorption* model may be derived directly from Equation 15 by imposing the algebraic condition that $C = C_1 = C_2\ldots = C_n$ to produce a single DOF model expressed in terms of the bulk air-phase concentration C:

$$w_a C + \left(M_a + \left(\frac{\rho\varepsilon}{\rho_s} + \frac{\partial f}{\partial C} \right) M_s \right) \frac{dC}{dt} = (w_a C_{\text{sup}} + G) \tag{16}$$

The sorbent is seen to impact the capacity of the zone. Without the sorbent, the room's capacity would simply be equal M_a. With the sorbent, the capacity is increased by the mass of air contained in the sorbent pores $\rho\varepsilon M_s / \rho_s$, – an insignificant contribution – and the mass of sorbent scaled by the tangent slope of the sorption isotherm for the current state of concentration – a contribution that may far exceed M_a.

BLDC Model: If it is assumed that boundary layer transport is rate limiting (i.e., $w_a > K_h < K_D$) then the air-phase concentrations within the porous sorbent will tend to be equal. This *boundary layer diffusion controlled* model may be derived directly from Equation 15 by imposing the algebraic condition that $C_1 = C_2\ldots = C_n$ to produce a two DOF model expressed in terms of the bulk air-phase concentration C and the external surface concentration C_1:

$$\begin{bmatrix} (w_a + K_h) & -K_h \\ -K_h & K_h \end{bmatrix} \begin{Bmatrix} C \\ C_1 \end{Bmatrix} \tag{17}$$

$$+ \begin{bmatrix} M_a & 0 \\ 0 & \left(\frac{\rho\varepsilon}{\rho_s} + \frac{\partial f}{\partial C} \right) M_s \end{bmatrix} \frac{d}{dt} \begin{Bmatrix} C \\ C_1 \end{Bmatrix} = \begin{Bmatrix} w_a C_{\text{sup}} + G \\ 0 \end{Bmatrix}$$

Again, the sorbent impacts the capacitance matrix, this time providing a second capacitance identical to the increase seen in the single DOF model.

PDC Model: If it is assumed that porous diffusion transport is rate limiting and the boundary layer transport is rapid (i.e., $w_a < K_h \gg K_D$) then the bulk air-phase concentration will tend to be equal to the external surface concentration. This *porous diffusion controlled* model may be derived directly from Equation 15 by imposing the algebraic condition that $C = C_1$ to produce a n DOF model expressed in terms of the bulk air-phase concentration C and the internal concentrations $C_2, C_3, \ldots C_n$:

$$\begin{bmatrix} (w_a + K_D) & -K_D & \ldots & 0 \\ -K_D & 2K_D & \ldots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \ldots & K_D \end{bmatrix} \begin{Bmatrix} C \\ C_2 \\ \vdots \\ C_n \end{Bmatrix}$$

$$+ \begin{bmatrix} (M_a + M_{\text{eff}}) & 0 & \ldots & 0 \\ 0 & 2M_{\text{eff}} & \ldots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \ldots & M_{\text{eff}} \end{bmatrix}$$

$$\times \frac{d}{dt} \begin{Bmatrix} C \\ C_2 \\ \ldots \\ C_n \end{Bmatrix} = \begin{Bmatrix} w_a C_{\text{supp}} + G \\ 0 \\ \vdots \\ 0 \end{Bmatrix} \tag{18}$$

In contrast to the EA and BLDC models, this model offers little computational savings over the full BLPD model and, for this reason, has not been applied

Comparisons have been made between measured and predicted behavior using these models and the results are encouraging (Axley 1991; Axley 1991; Axley and Lorenzetti 1992). Given the limited amount of data, however, the accuracy provided by these models has yet to be fully characterized. Figure 2, taken from these earlier studies, compares measured and predicted results for a NIST chamber study of the sorption of formaldehyde on gypsum board. The EA, BLDC, and BLPD models were used, each employing a linear adsorption isotherm model. From the results it is clear that the effective time constant of this dynamic system was on the order of days, yet the fresh air exchange rate was approximately 1 ACH – the impact of sorption, in this case, overwhelmed the dilution dynamics. This particular system was sensitive to boundary
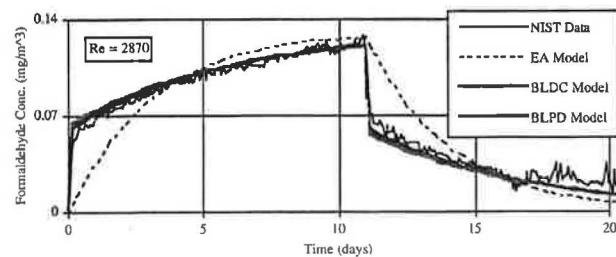

Fig. 2 Comparison of results for the sorption of formaldehyde on gypsum. Results were sensitive to boundary layer transport which may be correlated to the boundary layer Reynolds number, Re, here, estimated to be 2870.

layer transport, consequently the BLDC model performed significantly better than the EA model yet provided practically the same results as that obtained with the BLPD model (without the additional computational expense).

Chemical Transformation

To account for the possibility of the unimolecular chemisorption processes discussed above, we may assemble first order chemical transformation element equations, Equation 11, at each of sorbent nodes (i.e., C_1, C_2, ... C_n) with the BLPD model above, being careful to properly account for the mass of sorbent participating at each node. This assembly operation will alter only the system transport matrix to produce:

$$
\left|
\begin{array}{ccc}
(w_a + K_h) & -K_h & \\
-K_h & (K_h + K_D + k(\rho_s A_s \delta x^e/2)f\bullet) & \\
0 & -K_D & \\
\vdots & \vdots & \\
0 & 0 &
\end{array}
\right.
$$

$$
\left.
\begin{array}{ccc}
0 & \cdots & 0 \\
-K_D & \cdots & 0 \\
2K_D + k(\rho_s A_s \delta x^e)f\bullet & \cdots & 0 \\
\vdots & & \vdots \\
0 & \cdots & K_D + k(\rho_s A_s \delta x^e/2)f\bullet
\end{array}
\right| \quad (19)
$$

where the somewhat unorthodox notation $f \bullet C \equiv f(C)$ is used to maintain a similar equation form.

This theoretical representation of chemisorption is quite different from that contained in the conventional *deposition velocity* formulation. Here, chemical reaction occurs throughout the interior of the (assumed) porous solid at rates consistent with the local (porous) gas-phase concentration, while the *deposition velocity* formulation is implicitly based on the notion that the sorbed species reacts at the external surface. It is interesting to consider the equilibrium adsorption (EA) variant of this chemisorption model that may be derived in the same manner as Equation (16):

$$
(w_a + kM_s f\bullet)C + \left(M_a + \left(\rho\varepsilon + \frac{\partial f}{\partial C}\right)M_s\right)\frac{dC}{dt} \quad (20)
$$

$$
= (w_a C_{sup} + G)
$$

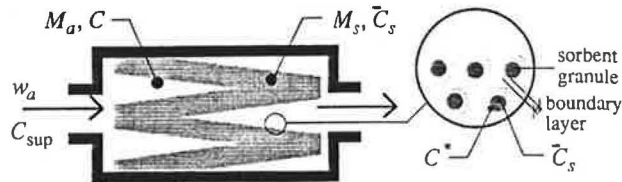The *deposition velocity* formulation of this problem would be equivalent to this equation when

Fig. 3 Idealization of a uniform-concentration sorption filtration cell.

$kM_s f(C) = \rho v_d A_d C$, where v_d is the deposition velocity and A_d is the area available for deposition (most often taken as the external surface area of the chemi-sorbent). This equality will only be realized when equilibrium is governed by a linear isotherm model.

The *deposition velocity* model has become an accepted approach, yet the theory presented above places this conventional approach into question. Specifically, from this theory we should not only expect boundary and/or porous diffusion transport to influence chemisorption in some cases, but may expect a nonlinear dependency on (local) gas-phase concentration, rather than linear, for all equilibrium relations except the linear model. Furthermore, for more complex chemical kinetics (e.g., bimolecular transformations), we may expect chemisorption rates to depend on more than one species. Recent research support these hypotheses (Nazaroff et al. 1992; Ryan and Koutrakis 1993).

Sorption Filtration Dynamics

An idealization of a sorption filtration chamber containing a volume of air of mass M_a and a quantity of sorbent of mass M_s with (assumed) uniform distributions of bulk air-phase concentration, C, near-surface air-phase concentration, $C^\star$, and mean sorbed-phase concentration, $\bar{C}_s$, is shown in Figure 3.

Given the supply air flow rate, w_a, and concentration, C_{sup}, a system of equations governing the behavior of this *filter cell* may be directly assembled from the element equations presented above to obtain:

$$
\begin{bmatrix}
(w_a + K_h) & -K_h & 0 \\
-K_h & (K_h + K_D' f\bullet) & -K_D' \\
0 & -K_D' f\bullet & (K_D' + kM_s)
\end{bmatrix}
\begin{Bmatrix}
C \\
C^\star \\
\bar{C}_s
\end{Bmatrix}
$$

$$
+ \begin{bmatrix}
M_a & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & M_s
\end{bmatrix}
\frac{d}{dt}
\begin{Bmatrix}
C \\
C^\star \\
\bar{C}_s
\end{Bmatrix}
=
\begin{Bmatrix}
w_a C_{sup} \\
0 \\
0
\end{Bmatrix} \quad (21)
$$

where $K'_D = (15\,M_r D_e / R_p^2)$ and $f \bullet C^* \equiv f(C^*)$. Equation 21 represents a *family* of models with individual members distinguished by the specific adsorption isotherm used for f.

This 3 DOF model accounts for first order chemical transformation as well as boundary layer and porous diffusion transport and, as such, will be identified as the *FOBLPD filter cell*. When chemical transformation does not play a role (i.e., $k = 0$) this model will be identified as the *BLPD filter cell*. As above, both a 2 DOF model, which will be identified as the *BLDC filter cell*, and a single DOF model, identified as the *EA filter cell*, may be formulated.

A variety of techniques are available to better account for actual nonuniform concentrations in the filtration chamber. For fixed bed adsorbers, Finite Element and orthogonal collocation approximations have proven reliable for industrial applications (Yu 1987; Hossain and Yonge 1992; Hossain and Yonge 1992; Noll et al., 1992). In buildings, however, packed bed filters are not usually employed, instead filter chambers consist of plenums containing relatively thin filter panels spaced apart from each other. The author has chosen to model these chambers using a linked-series of *filter cells* with each cell accounting for a fraction of the sorbent and air capacities contained in the chamber as a whole, as illustrated in Figure 4.

This linked-cell model was used to predict the performance of an activated carbon filtration system studied by Liu (Liu 1990; Axley and Lorenzetti 1992). Figure 5 compares the measured and predicted breakthrough – the ratio of exhaust to supply concentration C_{exh}/C_{sup} – of heptane using a 10-cell BLDC and a 5-cell EA models with a Polyani D-R adsorption isotherm.
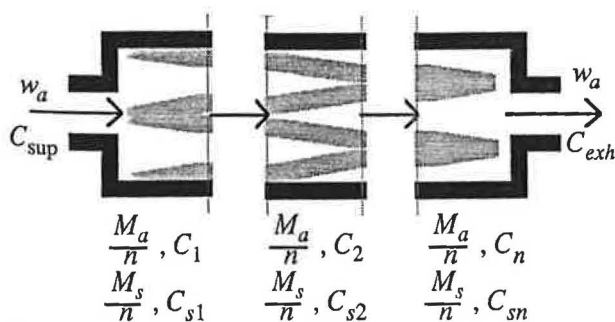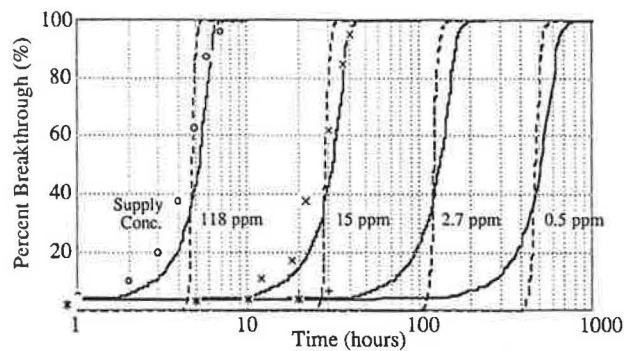
Fig. 5 Comparison of 10-cell BLDC model (solid line), 5-cell EA model (dashed line) predictions of heptane breakthrough on activated carbon with measured data (markers) for a range of supply concentrations.

Chemisorption

A study is presently underway to investigate the application of these sorption filtration models, including the chemical transformation term, to the problem of modeling ozone filtration on activated carbon. To date, both linear and Langmuir isotherm models have been considered and model prediction show, qualitatively, behavior that has been observed experimentally (e.g., recuperation after rest and saturation effects at high supply concentrations). Ironically, however, the activated carbon filtration systems being investigated are so efficient that they are effectively exhibiting quasi steady-state behavior and have not, therefore, provided data that reveals their dynamic character.

Discussion

This paper has presented a fundamental approach to the modeling of sorption and chemisorption dynamics in rooms and sorption filtration devices based on an elemental consideration of the diffusion, sorption, and chemical transport steps involved. For room sorption dynamics, a general model is presented that, in principle, accounts for all relevant transport processes involving planar porous adsorbents and simplified cases are derived from this general model. For sorption filtration systems, a lumped parameter model is presented and, again, simplified models are derived. Strategies that may be used to more accurately account for nonuniform sorption in filtration devices are also outlined. Finally, first comparisons of measured data and predicted results are presented.

As presented, the theory is limited to single-component sorption and first order, unimolecular chemical kinetics. Indoor air contains, invariably, a

Fig. 4 A linked-series of filter cells to account for nonuniform concentrations is building sorption filtration chambers.

complex mix of contaminants that may be expected to result in competition for sorption sites in those cases where one or more species exists in significant concentration. Water is likely to be most important in this regard. Consequently, available multicomponent theory should be cast into *element equation* form and investigated for practical indoor air quality analysis. The surface chemistry in rooms and filtration devices has received very little attention – it is likely that additional mechanism beyond unimolecular removal will have be considered.

In spite of these fundamental limitations, the approach appears to have the potential to provide accurate results when the sorption and chemical characteristics of the sorbate-sorbent system being considered are well understood and the external and internal diffusion processes are well characterized. Regrettably, trace-level sorption isotherms and sorbate diffusivity for common building materials and sorption filtration media have not yet been well-characterized, the relevant surface chemistry has yet to be studied, and the details of airflow in rooms, that determine the magnitude of external diffusion, remain uncertain. Consequently, much of the data needed to apply these models is either unavailable or uncertain at this time. Research should, therefore, be directed toward building an understanding of these processes through fundamental experimental determination – at the trace concentration levels found in buildings – of a) sorption equilibrium relations (e.g., isotherms), b) porous diffusion coefficients and their dependency on species concentration, c) the mechanisms of relevant surface chemistry and their rate relations, and d) surface average mass transfer rates found in common building settings. Inasmuch as the elemental transport processes considered are likely to be important in contaminant source dynamics, source modeling efforts may benefit from a similar fundamental approach.

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