

# Gas-phase exposure history derived from material-phase concentration profiles

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## Abstract

Non-reactive gas-phase pollutants such as benzene diffuse into indoor furnishings and leave behind a unique material-phase concentration profile that serves as a record of the past gas-phase indoor concentrations. The inverse problem to be solved is the diffusion equation in a slab such as vinyl flooring. Using knowledge of the present material-phase concentration profile in the slab, we seek to determine the historical material-phase concentration at the surface exposed to indoor air, and hence the historical gas-phase concentration, which can be used directly to determine exposure. The problem as posed has a unique solution that may be solved using a variety of approaches. We use a trained artificial neural network (ANN) to derive solutions for hypothetical exposure scenarios. The ANN results show that it is possible to estimate the intensity and timing of past exposures from the material-phase concentration profile in a building material. The overall method is limited by (1) the resolution of techniques for measuring spatial material-phase concentration profiles, (2) how far back in time we seek to determine exposure and (3) the representational power of the ANN solution. For example, we estimate that this technique can estimate exposure to phenol up to 0.5 y in the past from analyses of vinyl flooring.

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## 1. Introduction

“If the walls could talk, what stories they would tell.” This popular phrase expresses the hope that information about past events is stored in the building materials that witness the event. If the walls could indeed surrender that information, a

great deal could be learned about recent exposure. Metaphysics aside, we know that building materials *do* store information about chemical exposure in indoor environments. When a person walks into a room where cigarette smoking has recently occurred, they *know* that someone in the recent past was smoking; they do not need any sophisticated tools other than their nose. We propose that the past history of chemical exposure in buildings can be ascertained with surprising temporal detail. The ability to more accurately characterize exposure

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history will substantially enhance the power of epidemiology and risk assessment.

Recent reviews of environmental epidemiology and risk assessment recognize that new exposure assessment methods are needed. Gibb et al. (2002) report that “erroneous exposure assessment is a pervasive shortcoming of epidemiologic research.” Their *Epidemiology Work Group* at the *Workshop on Future Research for Improving Risk Assessment Methods* recommended that existing exposure assessment methods be improved and that new methods be developed. Transient exposure is also of concern because the traditional focus on a single measure of exposure (average concentration  $\times$  time exposed) fails to correlate with observed outcomes. For example, the carcinogenic effect of 1,3-butadiene (Melnick et al., 1990) appears to be related more to exposure intensity than to exposure duration. Both Gibb et al. (2002) and Toraason et al. (2002) explain that the intensity and timing of exposure are commonly unavailable but vital in assessing risk.

This need for new exposure assessment methods is reinforced by a growing body of evidence linking indoor exposures to a variety of organic compounds and the incidence of childhood asthma and other respiratory problems. Recent epidemiological studies have identified these associations with commonly occurring compounds such as formaldehyde, aromatics, phthalates and aliphatic compounds. For example, Rumchev et al. (2002) found that increased levels of indoor formaldehyde were correlated with increased asthma in young children, with a statistically significant odds ratio of 1.4. Allergies are also enhanced even at relatively low formaldehyde levels. Garrett et al. (1999) showed that sensitization increased when children were exposed to concentrations above  $20 \mu\text{g m}^{-3}$ . Phthalate plasticizers emitted by PVC flooring are associated with enhanced asthma diagnosis in children (Bornehag et al., 2004) and a decrease in pulmonary function in adults (Hoppin et al., 2004). For children, knowing the exposure from conception to birth and onward is critical for identifying causative agents. Exposure soon after birth may be most critical because newborns are particularly sensitive. Yet information about exposure during the early years can only be gleaned from questionnaires and retroactive indoor modeling. Knowledge of early exposures would greatly strengthen epidemiological conclusions.

Given the recognized risks of indoor air pollution and the inadequacy of existing exposure informa-

tion, we require more than just spot measurements; we need a comprehensive past history of indoor concentrations. Unless we have a history of all indoor modeling parameters (e.g., emission rates and air exchange rates) or we have the forethought to set up monitoring equipment (e.g., passive samplers), estimates of past exposure are highly uncertain. Fortunately, materials already present indoors, such as vinyl flooring, are continuously storing valuable information about indoor pollutant dynamics. Contaminants leave a unique signature by diffusing into furnishings, allowing us to mine concentration profiles to determine exposure. However, unlike sedimentary processes, e.g., seafloor layering of microorganism shells used for determination of the past temperature history, diffusion is reversible and does not leave a permanent record of past events.

By measuring the concentration profile within a building material, as achieved in practice with vinyl flooring by Cox et al. (2002), the dynamics of the episode itself will be evident through a “back-calculation” of the diffusion equations governing the system.

In this paper, we demonstrate proof-of-principle for determining the past history of indoor gas-phase concentrations using information extracted from furnishings. Specific objectives to meet this goal are:

- (1) Develop approximate, artificial neural network (ANN) solutions of the inverse-diffusion problem for hypothetical exposure scenarios. ANNs are rapid, reliable and have recently been used to solve similar problems.
- (2) Evaluate the quality, limitations and usability of the method.

## 2. Methods

### 2.1. Inverse diffusion analysis

Inverse diffusion problems are most well developed in the geophysical and heat-transfer literature. For example, it is valuable to ascertain the source location and strength of a spill based on subsurface concentration measurements years after the event. The most common heat-transfer problem that requires an inverse-diffusion solution is determining heat flux at a surface from a history of internal temperature measurements at a single location within a slab (e.g., re-entry vehicle heat shielding

tiles) (Özsisik and Orlande, 2000). Li and Niu (2005) apply a mathematically similar treatment to determine the initial internal concentration profile of volatile organic compounds in dry building materials. The literature on inverse-diffusion problems dates back over 100 years, beginning with Fourier and Kelvin (see Carslaw and Jaeger, 1959). Yet the problem we will pose here has not to our knowledge been posed or solved. The closest manifestation of this problem was treated most recently by Skaggs and Kabala (1994, 1995), but was only solved for a slab of infinite dimensions. While the difference may appear subtle, a slab of finite dimensions (e.g., vinyl flooring) is dramatically different, mathematically, from the infinite case. There may be some indoor materials for which the Skaggs and Kabala semi-infinite slab solution are applicable, but finite slab geometry better mimics indoor materials.

The following is a description of the constant-temperature *forward diffusion* problem with boundary and initial conditions specific to an indoor material such as vinyl flooring (please refer to Table 1 and Fig. 1). The physical system to be modeled is a one-dimensional ( $x$ , the depth into the solid) slab of finite extent which is subject to internal diffusion of a contaminant; diffusion within the slab is therefore described by Fick's second law (row 1), where  $D$  is the diffusion coefficient and  $C$  is the concentration of the pollutant within the material. At the surface ( $x = L$ ), the gas-phase contaminant partitions to the slab material by a linear equilibrium partition function (row 2), where  $K$  is the partition coefficient. The base is adjacent to an impermeable material, resulting in a contaminant flux equal to zero (row 3). The initial condition assumes that the material is initially free of the contaminant (row 4). The objective of the forward diffusion problem is to find the concentration profile within the slab at a time in the future,  $t = \tau$  (row 5).

A note on row 3, the no-flux boundary condition. This boundary condition is chosen because there are at least two instances in which the no-flux condition is meaningful for an indoor material. In the first instance, the slab material is adjacent to an impermeable or near-impermeable material. A high density plastic adjacent to a wood panel may act in this manner. In the second instance, the no-flux condition actually occurs at the center of a slab subjected to identical gas-phase concentrations from each side. A table top meets this requirement. As a compound diffuses into the table top from both upper and lower surfaces, there exists a point halfway between where no-net flux occurs due to symmetry. Thus, the model as posed in Table 1 corresponds to half the table top, either upper or lower.

The forward problem has been solved by others (Cox et al., 2002; Carslaw and Jaeger, 1959). Instead, our objective is to determine the *past* history of the gas-phase room concentration by quantifying the internal material-phase concentration profile of the contaminant within the slab at the present time,  $t = \tau$  (row 5). This is equivalent to finding the past history of the slab concentration at  $x = L$  (row 2). For simplicity, we again assume that

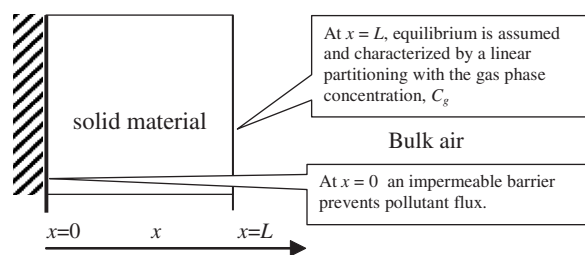


Fig. 1. Geometry of finite slab model of indoor material. A gas-phase pollutant partitions to the exposed surface ( $x = L$ ) and diffuses into the material. The no-flux condition at  $x = 0$  corresponds to either an impermeable barrier or to the center of a slab exposed to identical concentrations on both sides.

Table 1  
Forward and inverse forms of the diffusion problem

	The forward diffusion problem	The inverse diffusion problem
(1) Governing equation (Fick's second law)	$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$	$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$
(2) Boundary condition at surface	$C(L, t) = KC_g(t)$	$C(L, t) = \text{objective}$
(3) No flux boundary at base	$\frac{\partial C}{\partial x}(0, t) = 0$	$\frac{\partial C}{\partial x}(0, t) = 0$
(4) Initial condition: material phase concentration = 0	$C(x, 0) = 0$	$C(x, 0) = 0$
(5) Concentration profile within the material	$C(x, \tau) = \text{objective}$	$C(x, \tau) = f(x) = \text{measured}$

the initial concentration of the contaminant within the slab is zero (row 4). This turns out to be a reasonable assumption for long exposure times because the initial condition has little influence on the solution for large  $\tau$ . The *inverse diffusion* problem to be solved is then similar to the forward problem with the same governing equation (row 1), same initial condition (row 4) and the same no-flux boundary condition at  $x = 0$  (row 3).

A new condition is now applied. We *measure* the spatial concentration at time  $t = \tau$  (present time) within the slab and that concentration profile is denoted by  $f(x)$ . Our goal then is to determine the functional form of the time dependent boundary concentration at the surface of the slab ( $x = L$ ). Table 2 illustrates how this problem differs from similar problems posed and solved in the heat transfer and geophysical literature. The difference between the heat transfer problem and our problem is in what is measured; others measure temperature at a single location for all time,  $T(x_i, t)$ , while we must measure the concentration for all locations at the final time,  $C(x, \tau)$ . While these reflect only a few specific problems, they are indicative of the types of questions posed. To derive an approximate solution to this inverse diffusion problem, we use ANNs. To generalize the technique we make the problem dimensionless by defining the following dimensionless terms:  $C' = C/C_0$ ,  $x' = x/L$  and  $t' = tD/L^2$ , where  $C_0$  is a characteristic concentration.

## 2.2. Solution to inverse diffusion problem

We have demonstrated (Morrison et al., 2005) that this inverse-diffusion problem has a unique solution. However, despite this existence proof, the method of solution remains unclear. A mathe-

matical method to determine past history of exposure from physical material-phase concentration measurements is critical to the success of this method. Fortunately, there are many examples of solution methods for inverse problems. For example, Özisik and Orlande (2000) cataloged 14 different methods to treat the standard formulation of the inverse heat transfer problem, including ANNs. While most of these methods do not require training, they have been developed for a different formulation of the inverse diffusion problem and may not be suitable for our problem. ANNs can be used to generate approximate solutions regardless of problem formulation, as long as unique solutions exist, and appropriate historical training data are available. An early approximation of the inverse solution will guide the design of laboratory experiments including identification of conditions, exposure dynamics, and analytical targets. The advantages of using the ANN method are that (1) ANNs have been successfully used to solve inverse problems (Kindermann and Linden, 1990; Li et al., 2005), (2) they are reliable and allow for generalization (Baum and Haussler, 1990; Pineda, 1987), and (3) they can be trained to generate a solution within a reasonable period of time. A key disadvantage is that the representational power of ANN solutions is limited by the training inputs.

### 2.2.1. Artificial neural network approach

In this approach we create a variety of hypothetical exposure scenarios. From these scenarios, we use the well-established solution to the *forward diffusion* problem,  $Y = C(x, \tau)$ , to compute material-phase concentration profiles. We then use these scenarios (hundreds) to train an ANN, as shown in Fig. 2. Instead of using the exposure scenario data

Table 2  
Comparison of selected inverse diffusion problems

	Seeking historical exposure in finite slab	Seeking heat flux at surface	Seeking historical subsurface concentration profiles
Transport type	Mass in slab	Heat in slab	Mass in infinite subsurface
Governing 1-D equation	$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$	$\frac{\partial T}{\partial t} = \left(\frac{\rho c}{k}\right) \frac{\partial^2 C}{\partial x^2}$	$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}$
Boundary condition 1	$C(L, t) = \text{objective}$	$T(L, t) = \text{objective}$	$C(0, t) = \text{objective}$
Boundary condition 2	$\frac{\partial C}{\partial x}(0, t) = 0$	$\frac{\partial T}{\partial x}(0, t) = 0$	$C(\infty, t) = 0$
Initial condition	$C(x, 0) = 0$	$T(x, 0) = T_0(x)$	$C(x, 0) = 0$
Measurement	$C(x, \tau) = \text{measured}$	$T(x_i, t) = \text{measured}$	$C(x, \tau) = \text{measured}$
Solutions	None known	Many, see Özisik and Orlande (2000)	Skaggs and Kabala (1995)

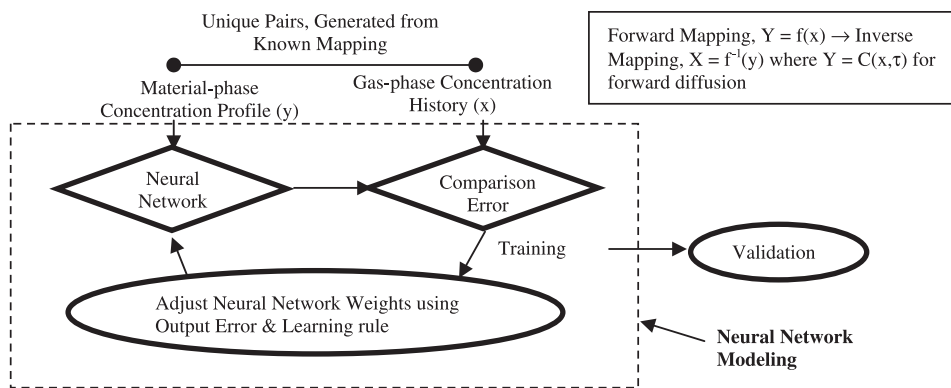


Fig. 2. Training, testing and artificial neural network (ANN) for finding the inverse function.

( $x$ ) as an input to map the corresponding material-phase concentration profiles ( $y$ ), the profiles generated from the solution methodology are provided as input to the ANN, with the resulting outputs representing the gas-phase concentration history. The functional mapping of the trained ANN then inverts the forward diffusion problem to generate a temporal gas-phase concentration history from a given material-phase concentration profile. Unique material-phase concentration profiles are used to validate the trained ANN by comparing outputs with known gas-phase concentration histories.

The ANN is characterized by the pattern of connections and associated weights among the various network layers, the numbers of neurons in each layer, the learning algorithm, and the neuron activation functions (Haykin, 1999). During a training phase, the network learns by adjusting the weights so as to be able to correctly predict or classify the output target of a given set of input samples, thereby generating a function mapping. For this research, a feed-forward ANN was used such that an input data set was functionally mapped to a corresponding output data set. Feed-forward ANNs are often used to map and predict the dependent variable (Vellido et al., 1999).

Although realistic exposure scenarios can be rather complex, we considered two simple types of exposure scenarios for training: constant exposure and square-wave exposure. Constant exposure is the simplest possible exposure scenario. Square-wave exposure is the simplest exposure scenario that also allows for evaluation of timing and intensity of exposure. For the constant exposure, a constant concentration is applied for a dimensionless time period  $t' = 1$  and the forward diffusion problem is

solved to arrive at a unique solution. A set of 100 constant concentration scenarios were created, where  $C'$  ranges from 0 to 0.1. Similarly, a set of 200 pairs of square-wave exposure scenarios and diffusion profiles were created. The number, magnitude and duration of square waves for each scenario were randomized. Thus, an exposure scenario may have two or more overlapping, single-cycle, square waves of different magnitudes. Half of the pairs from each set, constant or square wave, were used for training while the remaining half were sampled randomly to validate the quality of ANN predictions as shown in Fig. 3.

The Levenberg–Marquardt back-propagation training algorithm was used to train the network. For the case with constant exposure, a two-layered ANN was used with five neurons in the first layer and one neuron in the second layer. A hyperbolic tangent sigmoid function was used in the first layer and a linear transfer function was used in the second layer. For the square-wave exposure case, the targets were sampled to reduce the number of neurons at the output layer in order to attain computational efficiency. The targets were reduced from 1000 to 20 entities. Once again, a two-layered ANN was used with 21 neurons in the first layer and 20 neurons in the second layer. The log sigmoid function was used in the first layer and a linear transfer function was used in the second layer.

### 2.2.2. Temporal and physical limitations

It is well known that solutions to inverse diffusion problems tend to amplify uncertainty (Beck et al., 1985; Özisik and Orlande, 2000), significantly limiting the precision and temporal reach of these methods. Therefore, an important task is to assess

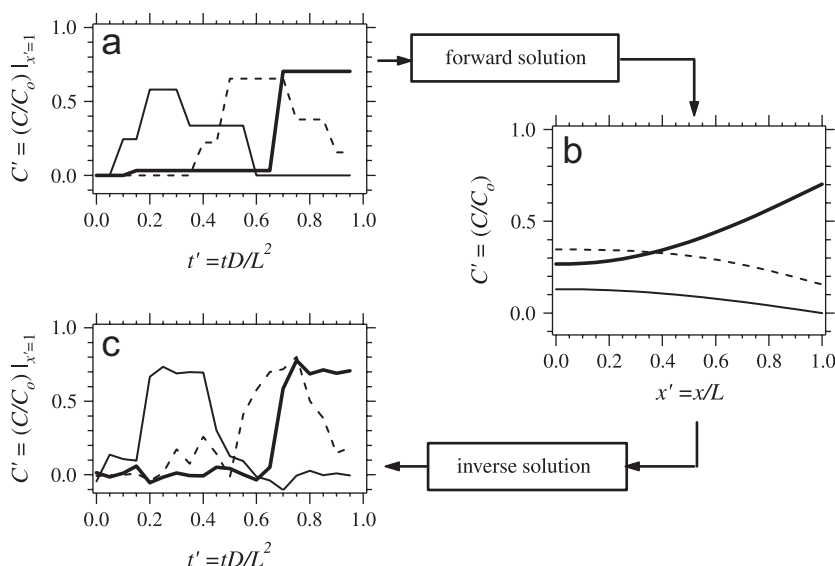


Fig. 3. Forward and inverse solutions for three sets of exposure scenarios. (a) dynamic exposure scenarios over a time interval  $0 < t' < 1$ , represented by the dimensionless concentration  $C'$  at the surface of the solid material,  $x' = 1$ ; (b) forward solutions of the material-phase concentration for the three scenarios shown in (a); (c) historical exposure estimates based on ANN inverse solutions of material-phase concentration profiles in (b).

limitations inherent in the mathematical formulation and sensitivity to the inputs (e.g., material-phase concentration profiles).

We anticipate that there is a limit to how far back in time we can make predictions about past exposure. For example, if the material-phase concentration profile is analytically indistinguishable from a uniform concentration, then we know that the gas-phase concentration has been roughly constant for a relatively long, but unknown, period of time. This is because there is no way to predict historical exposures further than some finite time into the past. Einstein (1905) showed that the characteristic time,  $\tau_c$ , for a species with a diffusion coefficient,  $D$ , to diffuse a distance  $L$  in a homogeneous medium is  $\tau_c = L^2/2D$ . If we attempt to estimate exposure significantly further back in time than  $\tau_c$ , a pollutant molecule would have had sufficient time to have traveled to the base of the slab, and then returned towards the surface of the slab or even to have departed the slab altogether. Thus the function  $C(L, t)$  (Table 1, inverse problem) is analogous to a photograph in which the foreground is clearly in focus, but the background becomes more and more out of focus as the distance from the camera increases.

We also expect that there exist combinations of materials and VOCs for which this method will not

be usable. For example, if the gas-phase concentration of benzene is so low that the material-phase concentration is below the analytical limit of detection, then there is no way to generate a past history. Alternatively, the material may be thin or have a large diffusion coefficient so that the effective temporal range is too short to be useful. Also, some indoor materials may not be sufficiently uniform in structure for the assumptions inherent in the inverse diffusion problem to be valid.

Therefore, using Einstein's diffusion equation as a guide, we estimate the temporal and practical limits of this method for a variety of pollutant/material pairs, based on published values of  $D$ ,  $L$  and  $K$  and the analytical limitations for measuring material-phase concentrations. Specifically, using the mean uncertainty of  $\sim 4 \text{ g VOC m}^{-3}$  (for vinyl flooring) from Cox et al. (2001a) as a lower detection limit, we estimate the lower detection limit for the gas-phase concentration as  $C_{\text{gas}} = (4 \text{ g VOC m}^{-3})/K$ .

### 3. Results

#### 3.1. Approximate solution

The trained ANN solutions for the "constant" scenario prove very accurate, though trivial. Given

a constant concentration over a dimensionless time-interval equal to 1, the method is able to use material-phase concentration profiles to predict what that gas-phase concentration was to better than 0.01%.

The predictions for square-wave exposure are more useful as they demonstrate that the method is able to roughly quantify the exposure intensity and identify the time intervals over which the exposure has occurred. In Fig. 3a are shown three exposure scenarios, plotted as the dimensionless concentration at the exposed surface of the building material (at  $x' = 1$ ). The thin-line plot is an exposure that occurs long ago; the dotted line is an exposure that occurred an intermediate time in the past; the thick-line plot is an exposure that began a short time ago and continues into the present. Three material-phase concentration profiles that result from applying the “forward solution” to the three exposure scenarios are shown in Fig. 3b. From each of these material-phase concentration profiles, an inverse solution was generated using the trained ANN. Note that each solution from the trained ANN uniquely corresponds to one material-phase concentration profile and that the ANN was not trained on these pairs. The inverse solutions follow the actual exposure scenarios, roughly matching the magnitude and period of the exposure.

The method appears to lose some accuracy for exposures that occur further back in time. Shown in Fig. 4 are the root-mean-square uncertainties for 100 scenarios (from untrained sets) as a function of  $t'$ . As anticipated, error increases as we attempt to look further back in time. Although we anticipated error to be greatest at  $t' = 0$ , we observed that the error was consistently lower here than for mid-range periods. This may be an artifact of the fact that  $C'(t' = 0) = 0$  for most scenarios used for training and testing.

The method reasonably captures the dynamics of most, but not all, exposure scenarios. In Fig. 5a, we plot the RMS error for all 100 untrained sets sorted from best to worst. For 60 sets, the RMS error is 0.1 or less. A comparison of each ANN solution concentration as a function of the actual concentration for the 60 “best” data sets is shown in Fig. 5b. With a slope of 0.96, and little spread around the mean, most ANN solutions closely match the actual solution. Fig. 5c is identical to Fig. 5b, but includes all 100 solutions. The poor correspondence is due primarily to the worst 10% of the solutions.

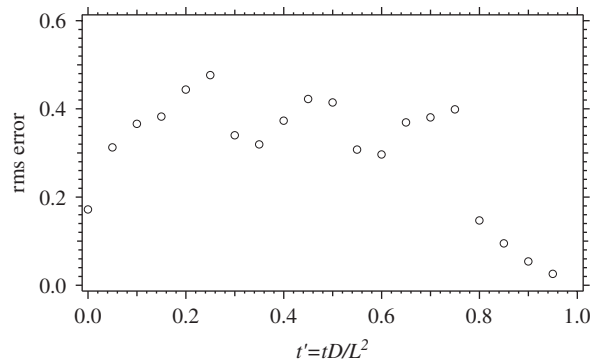


Fig. 4. Evaluation of solution quality: error as a function of dimensionless time,  $t'$ . Greater error occurs for the smaller dimensionless time, in other words, further in the past.

Since actual pollutant exposure corresponds to the time-integral of each exposure scenario, a key metric of solution quality is to compare the time-integral of concentration for actual scenarios against ANN solutions (Fig. 6). Strikingly, 80% of ANN solutions predicted integrated exposures within 40% of actual values, and 50% of ANN solutions within 15% of the actual integrated exposures.

### 3.2. Temporal and physical limitations

Table 3 illustrates predicted results, based on the hypothesis that the historic time-limit of the method is determined primarily by Einstein's equation, and also based on instrumental limits of detection (Cox et al., 2001a,b, 2002; Corsi, 2006; Zhang et al., 2006). For example, given a typical vinyl flooring thickness of 2 mm, the furthest back in time that the method can adequately make predictions is roughly 0.5 y. Manufactured wood products (e.g., plywood and medium density board) may be good candidates for this analysis since they are relatively thick. Due to high diffusion coefficients, drywall appears to be a poor material for past exposure analysis, with  $t'$  ranging from hours to days.

Key also is the minimum historical concentration detectable by the method. For example, we anticipate being able to determine gas-phase phenol concentrations roughly 0.5 y back in time, but the gas phase concentration must be greater than  $100 \mu\text{g m}^{-3}$  for the vinyl flooring sample mass used in Cox et al. (2001a). Toluene has a higher diffusion coefficient and only allows us to determine gas-phase concentrations about 0.1 y in the past. In

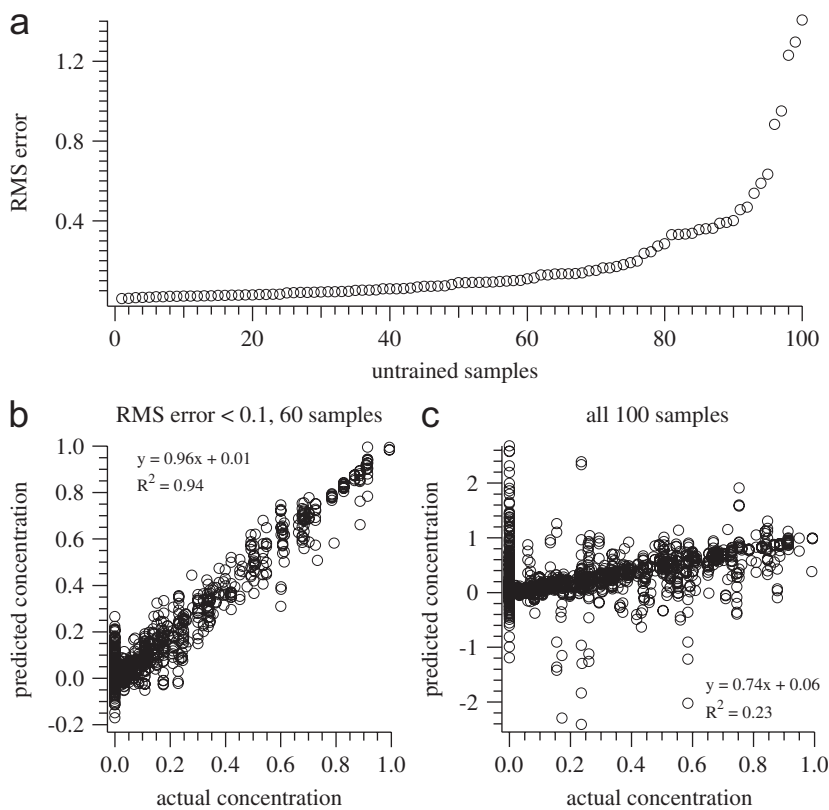


Fig. 5. Evaluation of solution quality: (a) RMS error for each sample, organized from best to worst; (b) correspondence of the approximate ANN solution to the exact solution for the 60 best samples; (c) correspondence of the approximate ANN solution to the exact solution for all 100 samples.

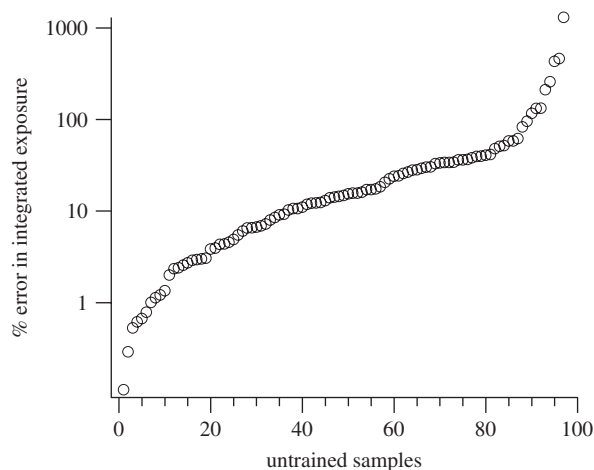


Fig. 6. Evaluation of solution quality: the absolute value of the % error in the integrated exposure for ANN solutions.

addition, the exposure event in the past must have had much higher concentrations than were needed for phenol because the partition coefficient is

smaller. However, this concentration corresponds to levels ( $\sim 0.4$  ppm) that are relevant to occupational exposures. Larger core samples will allow lower gas-phase concentrations to be evaluated.

#### 4. Discussion

The results show that it is possible to estimate the intensity and timing of past exposures from the solid phase concentration profiles in building materials. Beyond the use of existing indoor materials, diffusive samplers composed of engineered polymers can be envisioned. A low-cost, simple-to-deploy sampler could be deployed for months to years, providing temporal information that is otherwise only available using a sequence of many passive samplers or more costly real-time methods.

As illustrated, ANNs provide a relatively quick and reliable solution methodology for this inverse diffusion problem. This is because ANNs have the ability to learn patterns and non-linear functions (and inverses) without a prior knowledge of the

Table 3  
Estimated temporal and concentration limits for several material/contaminant pairs

Material	VOC	$D$ (cm <sup>2</sup> s <sup>-1</sup> )	$K$	$L$ (cm)	min $C_{\text{gas}}$ (μg m <sup>-3</sup> )	$\tau_c$ (y)
<sup>a</sup> Vinyl floor (25.6 °C)	Phenol	$1.2 \times 10^{-9}$	$1.2 \times 10^5$		30	0.5
	<i>n</i> -butanol	$6.7 \times 10^{-8}$	810		3000	0.01
	Toluene	$7.0 \times 10^{-9}$	980		4000	0.1
	<i>n</i> -decane	$4.5 \times 10^{-9}$	3000	0.2	1300	0.14
	<i>n</i> -dodecane	$3.4 \times 10^{-9}$	$1.7 \times 10^4$		230	0.18
	<i>n</i> -tetradecane	$1.2 \times 10^{-9}$	$1.2 \times 10^5$		30	0.53
	<i>n</i> -pentadecane	$6.7 \times 10^{-10}$	$4.2 \times 10^5$		10	0.95
<sup>b</sup> Vinyl floor (30 °C)	Formaldehyde	$2.5 \times 10^{-9}$	4800	0.08	<sup>c</sup>	0.08
<sup>b</sup> Particle board (30 °C)	Formaldehyde	$6.1 \times 10^{-8}$	$1.6 \times 10^4$	1.6	<sup>c</sup>	0.67
<sup>b</sup> Medium density board (30 °C)	Formaldehyde	$2.2 \times 10^{-8}$	$1.0 \times 10^5$	0.8	<sup>c</sup>	0.46
<sup>b</sup> High density board (30 °C)	Formaldehyde	$7.0 \times 10^{-8}$	$2.6 \times 10^4$	0.3	<sup>c</sup>	0.04
<sup>d</sup> Plywood	Ethyl acetate	$2 \times 10^{-7}$	170	1.6	<sup>c</sup>	0.2
	Butanol	$3 \times 10^{-8}$	1500	1.6	<sup>c</sup>	1.5
	Methyl ethyl ketone	$2 \times 10^{-7}$	240	1.6	<sup>c</sup>	0.3
<sup>d</sup> Drywall	Ethyl acetate	$2 \times 10^{-4}$	45	1.3	<sup>c</sup>	0.0002
	Butanol	$1 \times 10^{-5}$	780	1.3	<sup>c</sup>	0.003
	Methyl ethyl ketone	$2 \times 10^{-4}$	36	1.3	<sup>c</sup>	0.0001

<sup>a</sup>Cox et al. (2001b).

<sup>b</sup>Zhang et al. (2006).

<sup>c</sup>No material-phase detection limit available.

<sup>d</sup>Corsi (2006).

functional mapping. All that is needed is a relevant architecture and appropriately sized input–output data sets. Unfortunately, neural network modeling is somewhat of an art than a science since it is still necessary to choose the proper type of architecture, and settle on the proper number of neurons and layers. Too many neurons and layers will result in a functional mapping that memorizes that data, thereby reducing its ability to generalize. Training time also increases rapidly with an increased number of neurons and layers. Conversely, too few neurons results in an improper functional mapping. Trial-and-error and skill are still necessary to arrive at the proper architecture and size. Furthermore, generalization is ultimately limited, such that although the magnitude of the errors may be reduced through more rigorous training, the ANN solutions are affected by the type of training sets (input–output pairs) used and may not provide good estimates of past exposures that do not match the patterns use for training. Therefore, we are now pursuing a more comprehensive analytical or numerical solution.

The assumptions used in the development of the model restrict the range of usefulness. For example, many new materials are placed in a child's room just

before birth. The assumption that the initial concentration within the material is zero may not be appropriate here as embodied contaminants are still off-gassing. However, the presence of contaminants does not necessary preclude the material's use, if it does not initially contain the species of interest. Also, since we assume that compound transport is limited by internal diffusion, phthalates and other semi-volatile compounds are precluded from this analysis because their transport is limited by external mass transfer (Xu and Little, 2006). Any modifications to the existing model, to incorporate more complicated phenomena such as mass-transfer limitations of coatings or reactive species, are likely to increase uncertainty. The characteristic time analysis indicates that the exposure history of certain key species will not be available, simply because insufficient mass builds up in the material. However, passive samplers based on this concept may be designed to target those compounds.

Uncertainty in the model parameters themselves will limit the reach of this method. From Table 3, we see that reducing the method quantification limits for material-phase concentration measurements will allow us to reach further back in time. In

addition, uncertainty in the diffusion coefficient,  $D$ , and partition coefficient,  $K$ , reduces our certainty in the estimates of past exposure. Note that indoor temperatures in conditioned homes tend to vary over a range of  $\sim 15$ – $25$  °C. The parameters,  $D$  and  $K$ , can vary by as much as a factor of two in building materials over this same range (Zhang et al., 2006).

## 5. Conclusions

The proposed exposure assessment method meets immediate needs and delivers a product able to answer a broad range of environmental questions. Specifically, it meets the immediate need (Gibb et al., 2002) for more precise methods of deriving temporal details of human exposure. The method broadens the reach of traditional exposure analysis and epidemiology by generating *real* exposure information otherwise available only through models. This is especially important for correlating children's symptoms with past contaminant exposure. The validated method will be transferable to many environmental systems where diffusion records historic exposures in solid materials. The neural network approach is presently limited by the fact that the neuron framework, and resulting architecture and connection weights, depends on the solution. We now need to generalize this method so that the method of solution is not dependent on the solution itself.

The methods and solutions developed in this project can be used by epidemiologists to quantify dose–response relationships for indoor contaminants. Additionally, health professionals can better understand symptoms by identifying causative agents, on a case-by-case basis. The proposed method may be generalized beyond indoor environments, and expanded beyond the limitations of pure diffusive and non-reactive species. For example, the past history of contamination in an aquatic system may be extracted from core samples of concrete dock supports. We focus here on indoor settings for several reasons: this is the primary environment for human inhalation exposure to most VOCs, a wide variety of solid materials are available for analysis, and indoor environmental conditions, such as temperature, tend to be stable. Additionally, incorporating reaction kinetics, advection or other phenomena is mathematically tractable once the basic methodology is in place.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at [10.1016/j.atmosenv.2006.07.055](http://dx.doi.org/10.1016/j.atmosenv.2006.07.055).

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