National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

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A method for consumer exposure assessment

Report 320104011/2010

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Colophon

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This investigation has been performed by order and for the account of Food and Consumer Product Safety Authority (VWA), within the framework of project 320104 ‘Consumentenblootstelling’.

Abstract

Emission of chemical substances from solid matrices
A method for consumer exposure assessment

On request of the Food and Consumer Product Safety Authority RIVM has developed a method for assessing the human exposure to chemical substances emitted from solid products. This method is specifically intended for use in human exposure assessments of biocides emitted from treated articles. It can, however, be applied more broadly.

Data on model parameters, such as the coefficient of diffusion, the material air partition coefficient and the mass transfer rate, have to be available for the model to be applicable for practical exposure assessments. Data on model parameters is in many situations not available. The report presents data from literature. In cases in which representative data are not provided, default values and methods are suggested that can be used in exposure assessments. It should be noted that these default values will inevitably be of limited accuracy.

Next to application in risk assessment for substances and biocides, the model can be used to evaluate current exposure assessment methods, such as used in REACH. It can also be used to develop alternative methods to make quick evaluations of risks, such as need in REACH.

The model has been implemented in a computer program that is freely available to the general public (at www.consexpo.nl). To enhance the applicability of the method, the database on model parameters should be extended, preferably with measurement data on frequently occurring substances and materials.

Key words:
indoor air, exposure, chemicals, consumers, emission, products

Rapport in het kort

Emissie van chemische stoffen uit vaste materialen
Een methode voor blootstellingschatting uit consumentenproducten

Het RIVM heeft in opdracht van de nieuwe Voedsel en Waren Autoriteit (nVWA) een model ontwikkeld en beschreven waarmee de blootstellingschatting voor stoffen die uit vaste materialen vrijkomen, wordt verbeterd. Een dergelijke methode ontbreekt momenteel voor de blootstellingschatting van stoffen uit consumentenproducten. Het voorgestelde model beoogt vooral de blootstellingschatting voor biociden uit producten die met dergelijke ongediertebestrijdingsmiddelen zijn behandeld (‘treated articles’) te verbeteren, maar kan veel algemener worden toegepast.

Om het model te kunnen gebruiken, zijn gegevens over parameters nodig, zoals de snelheid waarmee de stof zich in het materiaal verplaatst (diffusiecoëfficiënt), de vluchtigheid van de stof uit het materiaal (materiaal lucht partitiecoëfficiënt) en hoe snel het van het oppervlak van het materiaal de lucht in wordt getransporteerd (massatransfercoëfficiënt). Voor deze parameters zijn in de literatuur waarden verzameld. Voor de gevallen waarin gegevens ontbreken, worden methoden voorgesteld om ze te schatten. Van deze methoden is de nauwkeurigheid overigens beperkt. Naast deze gegevens over parameters is een belangrijke voorwaarde voor bruikbaarheid van het model dat de beginconcentratie van de stof in de matrix bekend is.

Behalve voor toepassing in de risicobeoordeling voor stoffen en biociden kan het model ook worden gebruikt om gangbare methoden voor blootstellingschattingen, die bijvoorbeeld voor REACH worden gebruikt, te evalueren. Daarnaast kan het worden gebruikt om alternatieve methoden te ontwikkelen waarmee snelle inschattingen kunnen worden gemaakt, zoals die bijvoorbeeld nodig zijn voor REACH.

Het model is geïmplementeerd in een computerprogramma dat openbaar beschikbaar is (via www.consexpo.nl). Om de bruikbaarheid van de ontwikkelde methode te vergroten, wordt aanbevolen om de database met modelparametergegevens uit te breiden met gegevens over veelvoorkomende stoffen en producten.

Trefwoorden:
binnenlucht, blootstelling, chemische stoffen, consumenten, emissie, producten

Contents

Samenvatting

In dit rapport wordt een methode beschreven waarmee de emissie van chemische stoffen uit vaste materialen kan worden geschat. De methode is vooral bedoeld om de blootstelling van consumenten aan biociden die vrijkomen uit zogenaamde ‘treated articles’ te verbeteren. Ze kan echter ook veel algemener worden toegepast op emissies van stoffen uit diverse vaste materialen zoals vloerbedekking, behang, elektronische apparatuur et cetera.
De voorgestelde methode bestaat uit een mathematisch model dat de diffusie van de stof in het materiaal en de overdracht van materiaaloppervlak naar de binnenlucht beschrijft. Deze methode wordt beschreven in hoofdstuk 2. Ter ondersteuning van de methode is er een literatuuronderzoek gedaan naar gegevens voor cruciale modelparameters. Dit onderzoek is samengevat in hoofdstuk 3. Aangezien gegevens van dit soort schaars zijn, zijn er ook methodes voorgesteld waarmee schattingen voor de modelparameters te maken zijn. Deze methodes geven naar verwachting redelijke orde-van-grootte bepaling van de parameters, maar zijn van beperkte nauwkeurigheid en zouden alleen ruwe karakterisering van de blootstelling moeten worden gebruikt. In hoofdstuk 4 wordt beschreven hoe de methode kan worden gebruikt in ‘screening’ van de blootstelling. De methode is in hoofdstuk 5 getest voor een aantal toepassingen waarvoor emissiegegevens bekend zijn. Deze laten zien hoe de methode kan worden toegepast, en geven inzicht in de onzekerheid in de methode. Ook is in dit hoofdstuk een nauwkeuriger, experimenteel gevalideerd model voor de emissies van matige vluchtige organische stoffen (SVOCs) vergeleken met de methode die in dit rapport wordt voorgesteld. Dit model is, in samenwerking met de Deense Environmental Protection Agency (DEPA) toegepast in een realistische blootstellingschatting. Deze modelberekeningen geven belangrijke informatie over de beperkingen in nauwkeurigheid van de in dit rapport voorgestelde methode.
Het model dat is beschreven in hoofdstuk 2 is geïmplementeerd in een MS Windows computerprogramma dat openbaar beschikbaar gemaakt is via www.consexpo.nl. Ten slotte wordt dit programma in hoofdstuk 6 beschreven, zowel wat betreft het gebruik van het programma als wat betreft de beperkingen in zijn toepassing.

Summary

This report discusses a method that is developed to estimate the emission of chemical substances from solid matrices. The method aims in particular to improve the exposure estimation for biocides emitted from treated articles, but can be applied much more generally to emissions of substances from various materials and products such as flooring, wall covering and electronic equipment.

The proposed method consists of a mathematical model that describes diffusion of a substance in the material and the mass transfer of the substance into bulk indoor air. The method is described in chapter 2. In support of the model a literature search on values of crucial model parameters was conducted and summarised in chapter 3. However, data on these parameters is scarce. Therefore default methods to estimate these parameters are suggested. These methods will give reasonable order of magnitude estimates, but will be of limited accuracy and should only be used for screening assessments. Chapter 4 gives a description of how the method can be applied in screening assessments of exposure. In chapter 5 the model and the methods for parameter estimation are applied in a number of cases that demonstrate the applicability of the model and also give insight in the uncertainty associated with in the use of the methods. Also, a more accurate and experimentally verified version of the model for Semi-Volatile Organic Compounds has been implemented and applied to a practical exposure assessment for DEHP in collaboration with the Danish Environmental Protection Agency (DEPA). This model demonstrates the implications of the presence of absorption sinks in the indoor environment. The results give insight in the degree of inaccuracy of the more general model that neglects these sinks.

Finally, the model developed in chapter 2 has been implemented in a MS Windows program that is made publicly available via www.consexpo.nl. In chapter 6 the computer program is described both with respect to its use and to its limitations in application.

1 Introduction

The emission of chemical substances from consumer products may have a negative impact on the health of consumers exposed to these substances. To assess the safety of a product, the chemical exposure resulting from the use of products has to be determined. As representative measurements of exposure are mostly unavailable, prohibitively expensive or altogether impossible, the risk assessor has often to rely on the use of modelling.

Specifically, exposure to chemicals in articles (as defined in the Biocide Products Directive (BPD) Directive, REACH and EU-GHS) needs to be estimated. For such exposure assessments, little information on the release of a substance from the matrix is available. At present, standard consumer exposure modelling tools, such as the ConsExpo program (Delmaar et al., 2005) lack methods to model the release of substances from solid matrices. This hampers the applicability of these tools to important questions such as emissions of plasticisers and flame retardants from polymeric materials, and biocides from treated articles.

In current exposure assessment practice, emissions of substances from solid materials are (if at all) analysed with very crude estimation methods. Such as, for example, assuming that all the available substance will be emitted immediately or not at all, calculating the upper bound of the air concentration from the vapour pressure of the substance, et cetera. Such crude methods are only useful to quickly screen maximum exposure levels and potential risks. In cases where such crude methods are insufficient, more realistic modelling will enable the exposure assessor to acquire a higher level of realism and accuracy, but also to make more detailed scenario evaluations (including quantitative uncertainty analysis).

In this report a model to estimate emissions of substances from solid materials is described. This model is mainly based on published work in the field of volatile organic substance (VOC) and semi-volatile organic substance (SVOC) emissions from building materials.

For a model to be applicable in regulatory exposure assessments, data on model parameters have to be known, or at least methods to make reasonable estimates for these parameters have to be available. Fundamental parameters in the proposed emission model are the diffusion coefficient of the substance in the material, the material air partition coefficient and the mass transfer coefficient. It is anticipated that for these parameters data will mostly not be available in routine regulatory assessments, as these usually require separate experiments to be determined.

In support of the model and to enhance its applicability, a literature search was performed to collect available data and methods to estimate these fundamental model parameters. Collected data and methods can serve as a reference from which representative data may be derived in specific exposure assessments. For substances and products not represented in the database, a method is suggested to use the model in combination with default parameter values and parameter estimation methods.

The use of surrogate parameter values or estimation methods introduces a large degree of uncertainty in the modelled exposures. This generalised method is therefore only to be used as an order of magnitude estimator, and to be used in screening assessments only. If a higher degree of accuracy is needed, specific data have to be collected, or at least a quantitative analysis of the uncertainty has to be made.

The applicability of the model was tested in a number of ways:

1) By examining the changes in the results of the model to variations in the fundamental parameters, general tendencies of the model were studied. Such a sensitivity analysis provides insight in the importance of data quality and accuracy under various conditions. Also, the relative importance of input parameters can be studied.
2) By confronting the proposed method with emission experiments under controlled conditions. Using either representative data from the database or default data and

methods proposed in the generalised method, the emission of two substances from different product matrices was modelled and compared with emission experiments. These case studies, while not providing any conclusive validation, provide at least an indication of the error involved. In addition, the cases may serve as useful examples of the method.

3) For the case studies conducted in 2), the uncertainty in the method was analysed: as parameter values are not exactly known, but are subject to uncertainty, also the model outcomes will not be precise. Taking into account the imprecision in the input data, also the imprecision in the modelled exposures can be accounted for. This analysis of the uncertainty performed in 2):
4) gives insight in the overall inaccuracy of the default method;
5) serves as an example of a method that can be applied to analyse uncertainty in applications of the model in specific exposure assessments.

This report is produced for the Dutch Food and Consumer Safety Authority (VWA), which asked to develop methodology to estimate exposures of substances from articles, in particular articles treated with biocide products (treated articles). The methodology developed in this report can be used in exposure assessments of a subclass of these articles: articles of solid materials (such as wood and plastics et cetera) that have been impregnated with biocide products. For other classes of treated articles, such as textiles, other methods have to be developed.
In addition to treated articles, the methods developed in this work will be applicable to other product groups. They can be used, for example, to assess exposures of SVOCs such as plasticisers from vinyl flooring, and flame retardants from electronic devices, VOCs from solid furniture and building materials et cetera.
For the purpose of this report the proposed model was build in the mathematical simulation software Mathematica. In addition, a stand-alone software tool to be used in consumer exposure assessments was built. It is available at www.consexpo.nl.

In chapter 2 the mathematical model and simplifying assumptions that have been made are described. This chapter provides the technical and scientific background of the model. An analysis of the sensitivity of the model explores the general behaviour of the model and identifies different limiting cases in which data requirements to use the model may be reduced. In chapter 3 the results of the literature search on data and methods to estimate parameters are presented. The material in this chapter can serve as a reference for the risk assessor using the model, from which data may be obtained for specific exposure assessments. On the other hand, the collected information is used to make order of magnitude inferences on the numerical values of parameters. Chapter 4 proposes default methods and data to apply the model in screening exposure assessments where information is insufficient for making accurate exposure predictions. This chapter provides guidance for a risk assessor to apply the model in exposure assessments where data is scarce. In chapter 5, the default method given in chapter 4 is tested in two cases and compared with measured emissions. The uncertainty in the method is analysed in these two cases, which provides in indication of the degree of (in)accuracy of the method and provides examples of how to perform uncertainty analyses in regulatory exposure assessments. In section 5.3 another case study is described: the case of emission of bis(2-ethylhexyl) phthalate(DEHP) from various consumer products. This case was performed in close collaboration with the Danish Environmental Protection Agency (DEPA). In this case study the implications of including sinks such as adsorption to walls, floor and dust was investigated. Chapter 6 describes the computer program that implements the model developed in chapter 2. Chapter 7, finally, summarises and discusses the results and makes suggestions on future developments and research.

2 Modelling the emission of substances from solid matrices

Various models on the emission of substances from solid materials have been developed and used to simulate emission data. The majority of these models have been developed to estimate the emission of substances from building materials. The substance groups modelled included volatile organic substances (VOCs) such as solvents and semi-volatile organic substances (SVOCs) such as plasticisers, pesticides and flame retardants. Typically, the emission of a substance from solid materials is not only determined by volatisation of the substance and transfer from the product surface into bulk indoor air, but also by diffusional transport within the material. The latter process can usually be neglected in emission models describing the evaporation of a substance from a liquid, but may have an important effect on the emission from solid matrices.

From models as described in literature, a generalised emission model was derived. This model is described in detail in section 2.1. Section 2.2 describes the data requirements of the model. In section 2.3 a sensitivity analysis is conducted to investigate general tendencies of the model and investigate the relative importance of model parameters under different conditions.

2.1 Model description and formulation

The levels of indoor air concentrations that result from the emission of substances from materials are determined by various processes (see Figure 1). On one hand there is the emission of the substance from the material into the bulk air, on the other hand the removal of the substance from the indoor air. The first process is determined by diffusion of the substance to the surface of the material and subsequent mass transfer from surface into air. The removal of the substance from bulk indoor air is a resultant of different mechanisms such as ventilation, degradation and adsorption of the substance to indoor surfaces such as walls, furniture and dust. Adsorption is especially important for low-volatile substances such as phthalates and pesticides. When considering adsorption to indoor surfaces it should be noted that adsorbed substances may eventually desorb. This will lead to secondary emissions even after the primary source is removed.

Also, for low-volatile substances it may be that sorption to skin and clothing will give rise to dermal exposure which may be orders of magnitude higher than the exposure due to inhalation of the gas phase substance (in such cases, inhalation exposure via dust may be the most important inhalation pathway of exposure).

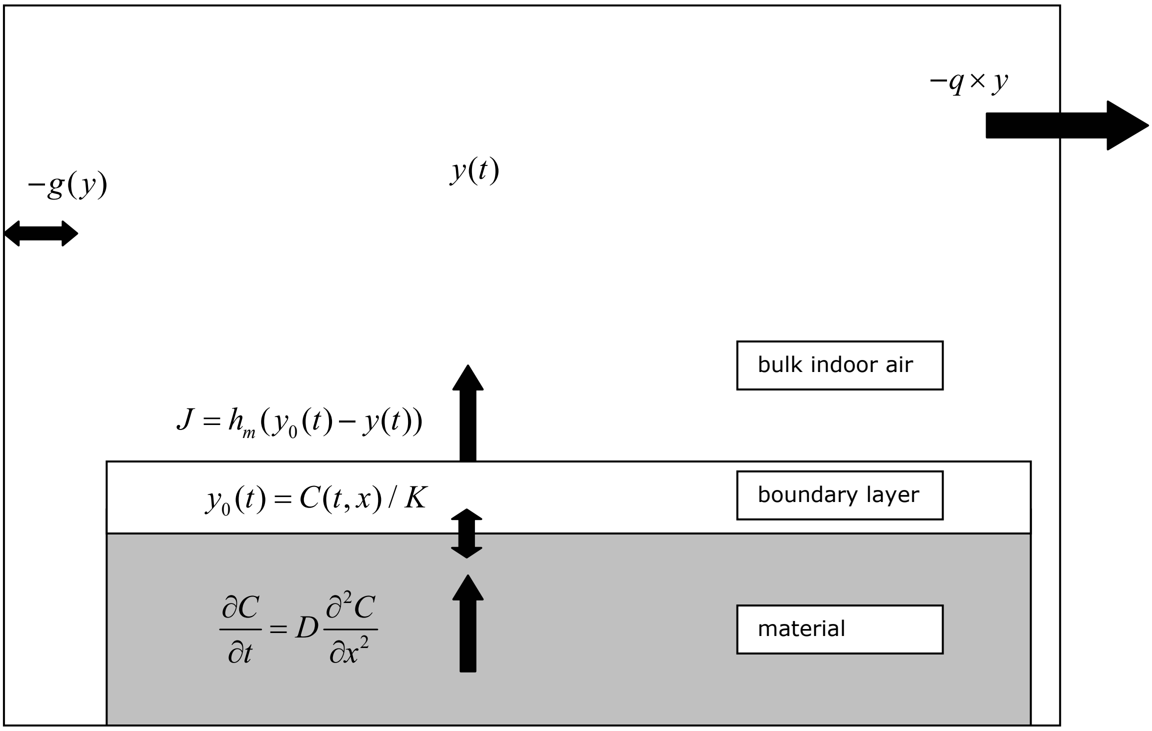


Figure 1. The generalised model describing the emission of (semi-)volatile substances from solid materials.

The emission of the substance is a result of diffusion in the product (characterised by the diffusion coefficient D) and mass transfer from the product surface area into bulk indoor air (characterised by the mass transfer coefficient h_m). The air concentration y(t) is determined by the emission from the material, the removal by ventilation q and additional, secondary sinks/sources g(y) such as sorption/re-emission to/from surfaces.

The model proposed in this work, is to be applied in exposure assessments for substances in articles and solid materials. Assessments of this type usually lack specificity in scenario definition and model input data. In order to keep the model applicable under general conditions, we make a number of simplifying assumptions.

1. The diffusion is usually assumed to be homogeneous and independent of the concentration of the substance in the material and can thus be described with a constant diffusion coefficient D.
2. Only the removal of material from the bulk (room) air by ventilation is considered. Other sinks, such as the adsorption to dust, indoor surfaces and degradation of the substance are discarded. This assumption will possibly lead to an overestimation of the air concentrations in the early stages of emission, but may underestimate the air concentrations due to secondary (re-)emissions, that may still occur when the emitting material has been removed or is depleted. This assumption is likely to be inaccurate for poorly evaporating (low vapour pressure) substances such as SVOCs. In section 5.3 the implications of neglecting sinks are studied in a specific example.
3. Emission of the substance is only from the top surface of the material. The other surfaces (i.e. the sides and bottom of the material) are supposed to be covered or to be so small as not to give a significant contribution to the emission.

It should be noted that these assumptions will limit the accuracy of the modelled emissions. To what extent the accuracy is hampered will depend on the specific application (e.g. type of substance, product material, time scale of the assessment, indoor environment). On the whole, the model should not be expected to accurately estimate realistic concentration levels under all circumstances, but rather serve as an estimation tool to screen order of magnitude exposure levels.

2.1.1 Model

In the model the material is modelled as a slab of thickness L. With the assumptions described above, the concentration C in the material is determined by a one-dimensional diffusion equation:

(1) $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Where t is the time, x is the depth in the material and D the diffusion coefficient. In our model formulation we further assume that emission takes place only at the surface of the material. Depending on the material the diffusion can be either the solid state diffusion or the gas phase diffusion. The latter is important for porous materials.

For materials with porosity ε, and assuming that gas phase diffusion dominates over solid state diffusion, equation 1) transforms to

(2) $$\varepsilon\frac{\partial C_{gas}}{\partial t} + (1-\varepsilon)\frac{\partial C_{ad}}{\partial t} = D_{gas}\frac{\partial^2 C_{gas}}{\partial x^2}$$

C_{ad} is the adsorbed concentration, which, under isothermal conditions is related to the gas phase concentration C_{gas} by $C_{ad} = K_s C_{gas}$ (with K_s the material surface air partition coefficient). Hence it follows that,

(3) $$\frac{\partial C_{gas}}{\partial t} = \frac{D_{gas}}{\varepsilon + (1-\varepsilon)K_s}\frac{\partial^2 C_{gas}}{\partial x^2} \equiv D^*\frac{\partial^2 C_{gas}}{\partial x^2}$$

Note that the mathematical form of this equation is completely identical to equation 1). In other words, the existence of a gas phase transport in addition to the solid state transport can be included by introducing a modified, 'effective' diffusion coefficient D^*.

To evaluate the concentration in the material, equation 1) or 3) should be solved with appropriate boundary conditions. In most practical applications the initial concentration C_0 can be assumed to be homogeneous. Its numerical value has to be known and specified in the model.

From assumption 3) above, it follows that at the bottom side (or at the sides) of the material there is no flux of substance out or into the material:

(4a) $$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0$$

At the material air surface (x=L) there is an out flux J of the substance:

(4b) $$J = -D\frac{\partial C}{\partial x}\bigg|_{x=L}$$

This flux of substance from the material surface equals the flux through the stagnant boundary layer in the air above the surface:

(4) $$-D\frac{\partial C}{\partial x}\bigg|_{x=L} = h_m(y_0(t) - y(t))$$

Under isothermal conditions, the air concentration y_0 directly above the surface is assumed to be proportional to the material concentration C(x=d):

(5) $$y_0 = C\big|_{x=L}\big/K$$

With K as the material air partition coefficient of the substance.

The mass transfer coefficient h_m describes the transport velocity of the substance from the material surface to the bulk indoor air y. The bulk air concentration is assumed to be homogeneous (well-mixed). It is determined by the emission from the material and the removal by ventilation:

(6) $$\frac{\partial y}{\partial t} = \frac{Sh_m}{V}(y_0 - y) - qy$$

With q the ventilation fold of the room, S the surface area of the material, and V the volume of the room.

The simplified diffusion model 1-7 with the given boundary conditions can either be solved analytically (as an infinite sum) or numerically (for example by finite difference methods).

2.2 Data requirements

In order to apply the emission model in practical exposure assessments, the following data are needed as input (units are specified in SI, but can be provided in any other consistent system of units):

Specifics of the material:

S: surface area of the material [m^2]
L: thickness of the material [m]
C_o: initial concentration in the material [kg/m^3]

Data on the indoor environment:

V: volume of the room [m^3]
q: ventilation fold of the room [s^{-1}]

Physical chemical data on the substance and/or material:

D: diffusion coefficient [m^2/s]
K: material air partition coefficient [-]
h_m: mass transfer coefficient [m/s]

In a typical case, data on material and the indoor environment will be known or chosen as part of a scenario when the model is used in an exposure assessment. The physical chemical data, on the other hand will mostly not be available.

To enhance the usability of the model, a literature search was performed to collect data on these physical chemical parameters, and estimation methods for these parameters. The resulting database and estimation methods can be used as a reference from which representative data may be selected in regulatory exposure assessments. The results of this literature survey are presented in chapter 3.

2.3 Sensitivity analysis of the model

Lack of accurate data on the physical chemical input data will be an issue in many situations in which the emission of substances from solid matrices has to be estimated. In this section, an analysis of the sensitivity of the model is made over the ranges of the parameter values that are expected to occur in practical applications. This analysis will identify general tendencies of the model and will identify situations in which the model is insensitive to variations in one or more of the model parameters. In these situations, the data requirements are effectively reduced.

The out flux of substance material is given by:

$$(7) \qquad \Phi = -D \left. \frac{\partial C}{\partial x} \right|_{x=L}$$

In steady state this out flux has to equal the transport flux over the boundary layer:

$$(8) \qquad -D \left. \frac{\partial C}{\partial x} \right|_{x=L} = h_m \left(\frac{C(L)}{K} - y \right)$$

If we approximate this by:

$$(9) \qquad -D \frac{C(L) - C(0)}{L} \approx h_m \left(\frac{C(L)}{K} - y \right)$$

and solve for the unknown material concentration at the surface C(L), we find:

$$(10) \qquad C(L) \approx \frac{Ky + \frac{DK}{Lh_m} C(0)}{1 + \frac{DK}{Lh_m}}$$

From this it is seen that for D/L >> h_m/K: $\frac{DK}{Lh_m} >> 1$ and $\frac{DK}{Lh_m} C(0) >> Ky$ (as $Ky \le C(0)$).

From this it follows that:

$$C(L) \approx C(0)$$

In other words, the concentration in the material is homogeneous: $C(x,t) = C(t)$, independent of x.

Then the emission into bulk indoor air (equation (6)) is given by:

$$\frac{dy}{dt} = \frac{h_m S}{V}\left(\frac{C(t)}{K} - y\right) - qy \tag{11}$$

And the change in concentration C in the material is reduced to:

$$\frac{dC}{dt} = \frac{h_m}{L}\left(\frac{C(t)}{K} - y\right) \tag{12}$$

Note that the diffusion coefficient D has been eliminated from these equations. The system is independent of the exact value of D (as long as D/L >> h_m/K). This situation is referred to as being mass transfer limited.

Conversely, if D/L << h_m/K:

$$C(L) \approx Ky$$

And from equations (4) and (6):

$$\frac{dy}{dt} = -\frac{S}{V} D \left.\frac{\partial C}{\partial x}\right|_{x=L} - qy \tag{13}$$

And the emission is independent of the exact value of h_m/K. The emission is diffusion limited.

The existence of two limiting cases, mass transfer and diffusion limited emission, has important implications for practical exposure evaluations: in the first case (diffusion limitation) it is not important to know the exact value of h_m/K. In the other case (mass transfer limitation) it is not important to know the diffusion coefficient D with high accuracy. In these situations the efforts in data collection may be reduced significantly.
However, it is important to keep in mind that the discussion above is only approximate. For example, in (9), the approximation $D\frac{\partial C}{\partial x} \approx D\frac{C(L) - C(0)}{L}$ is made. This can only be done if the diffusion length $L_{dif} = 2\sqrt{Dt}$ is of order L. For short times, this approximation may be inappropriate and the limiting situation (mass transfer or diffusion limitation) will only be in effect after the initial stages of emission.

2.3.1 *Example 1: emission of a volatile substance*

As an example, consider the emission of a volatile substance (vapour pressure > 10 Pa) from a (fictitious) product made of a material similar to vinyl. The product has a layer thickness of about 0.01 m. h_m depends on product shape and indoor conditions (airflow over the surface). As will be shown in chapter 3, h_m typically lies in a range of ~ 0.0005 – 0.005 m/s. Diffusion coefficients of substances in vinyl flooring are in a range of 10^{-10} – 10^{-13} m^2/s (see chapter 3), for this example a range of 10^{-10} – 10^{-12} m^2/s was assumed.

In the example, the following parameter values are used:

room volume	V	20	m^3
ventilation rate	q	1	hr^{-1}
product surface area	S	0.5	m^2
product thickness	L	0.01	m
product concentration	C_o	1	kg/m^3
exposure duration		50	hr
diffusion coefficient	D	10^{-10} – 10^{-12}	m/s^2

Typically, material air partition coefficients for volatile substances are between 1 – 1000 (discussed in chapter 3).

For this case, D/L was varied between 10^{-8} – 10^{-10} m/s, and h_m/K was varied between $5x10^{-3}$ – $5x10^{-7}$ m/s.

The air concentration resulting from the emission is simulated with the model for different values of D/L and h_m/K. For different simulations h_m/K was kept fixed at:

1) the lower extreme of its estimated range ($h_m/K = 5x10^{-3}$);
2) the higher extreme of its estimated range ($h_m/K = 5x10^{-7}$).

For both cases 1) and 2) D/L was varied in discrete steps over its entire range. The results are plotted in Figure 2 for case 1) and Figure 3 for case 2).

In these simulations it can be observed that:

- The estimated air concentrations depend strongly on the value of D/L: concentration levels vary approximately linearly with the value of D/L.
- The estimated air concentrations are insensitive to changes in the value of h_m/K.

That is, within the ranges of parameter values for this case the model is diffusion limited, as is expected based on the formal considerations above (equation (13)).

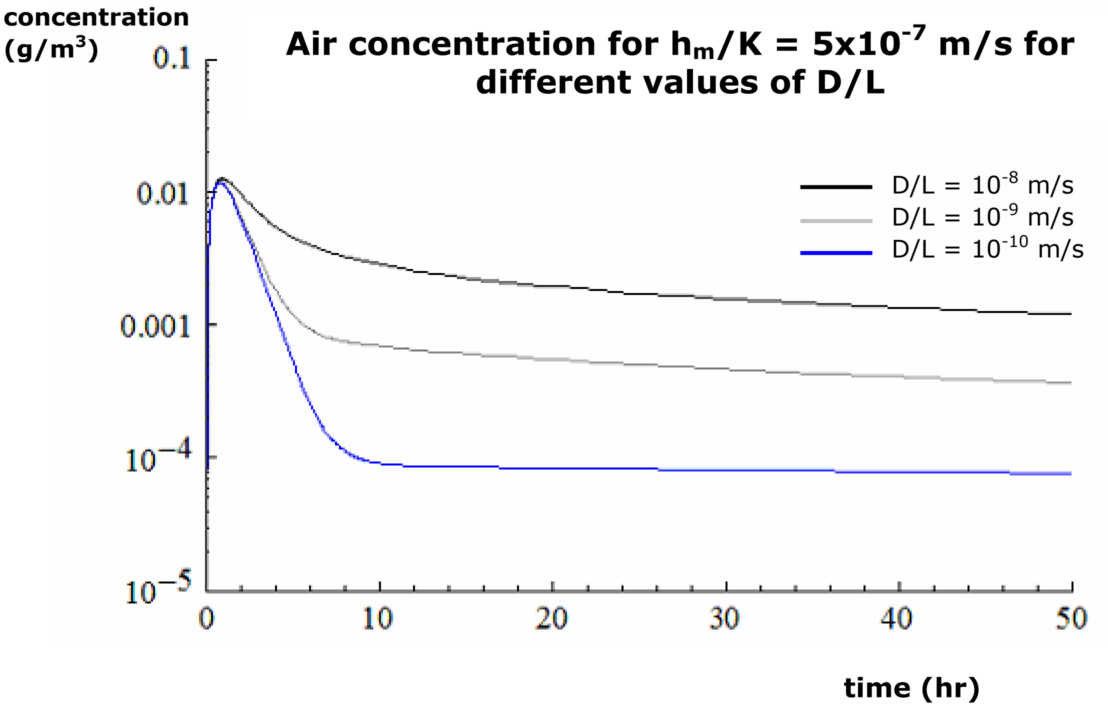


Figure 2. Log-linear plot of the variation of the air concentration with D/L for a fixed value of h_m/K of $5x10^{-7}$ m/s over the entire simulation duration (50 hrs).

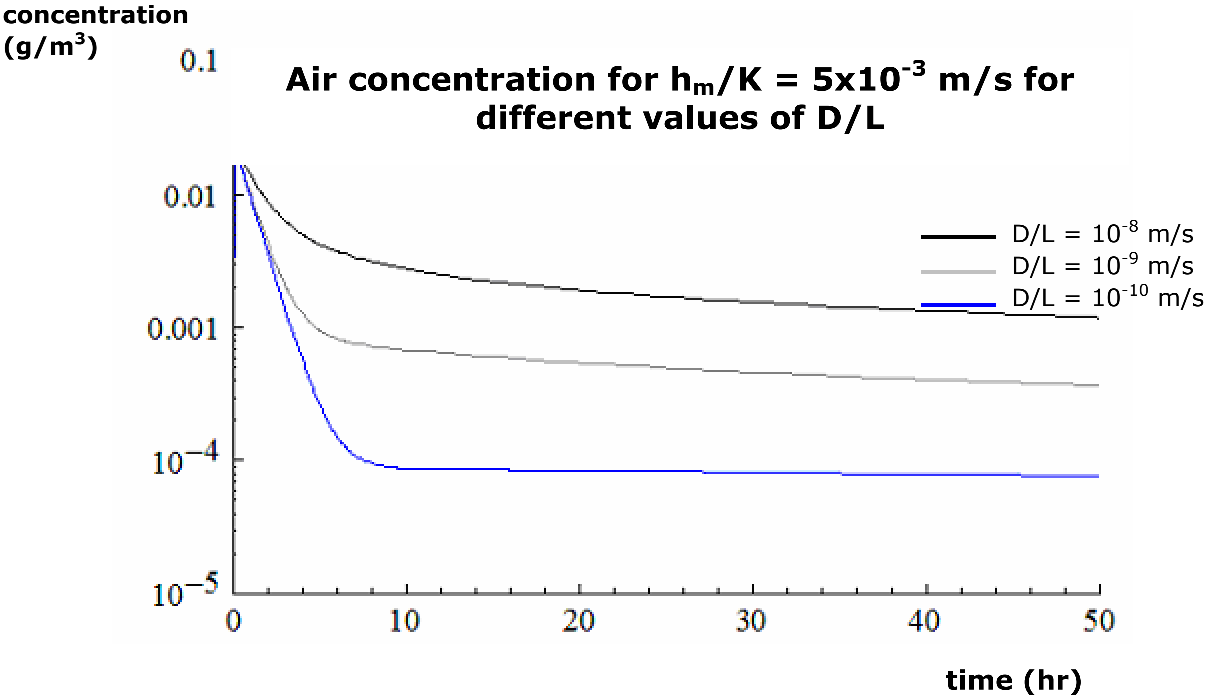


Figure 3. Log-linear plot of the variation of the air concentration with D/L for a value of h_m/K of $5x10^{-3}$ m/s over the entire simulation duration (50 hrs).

2.3.2 *Example 2: emission of a low-volatile substance*

As a second example, consider the emission of a semi-volatile substance (vapour pressure < 10 Pa) from a (fictitious) solid product. In this case the material air partition coefficient is typically larger than about 100,000 (see chapter 3, Table 3). Taking, as an example, a range of [1.0×10^{6} – 1.0×10^{8}] for the material air partition coefficient, and a typical value of 1×10^{-4} m/s for the mass transfer rate, we find a range of [1×10^{-10} – 1×10^{-12}] m/s for h_m/K.

Similar to the procedure followed in example 1, model simulations were conducted for the ranges of both D/L and h_m/K. In this case, D/L was kept at a fixed value during a single simulation and h_m/K was varied in discrete steps over its entire range. Two different simulations were performed, for D/L = 10^{-6} and 10^{-8} m/s respectively. The emission duration was chosen as 200 hours. All the other model input parameters were kept at fixed values (the same as in example 1).

In summary, the following parameter values were used in the simulation:

room volume	V	20	m^3
ventilation rate	q	1	hr^{-1}
product surface area	S	0.5	m^2
product thickness	L	0.01	m
product concentration	C_o	1	kg/m^3
exposure duration		200	hr

From the results of the simulations, shown in Figure 4a and Figure 4b, a clear dependence on h_m/K is observed. The air concentration levels vary roughly linearly with h_m/K. On the other hand, the concentration levels are independent of the exact value of D/L (within its range), as can be observed by comparing Figures 4a and 4b. The emission is mass transfer limited, as expected for these values of h_m/K and D/L.

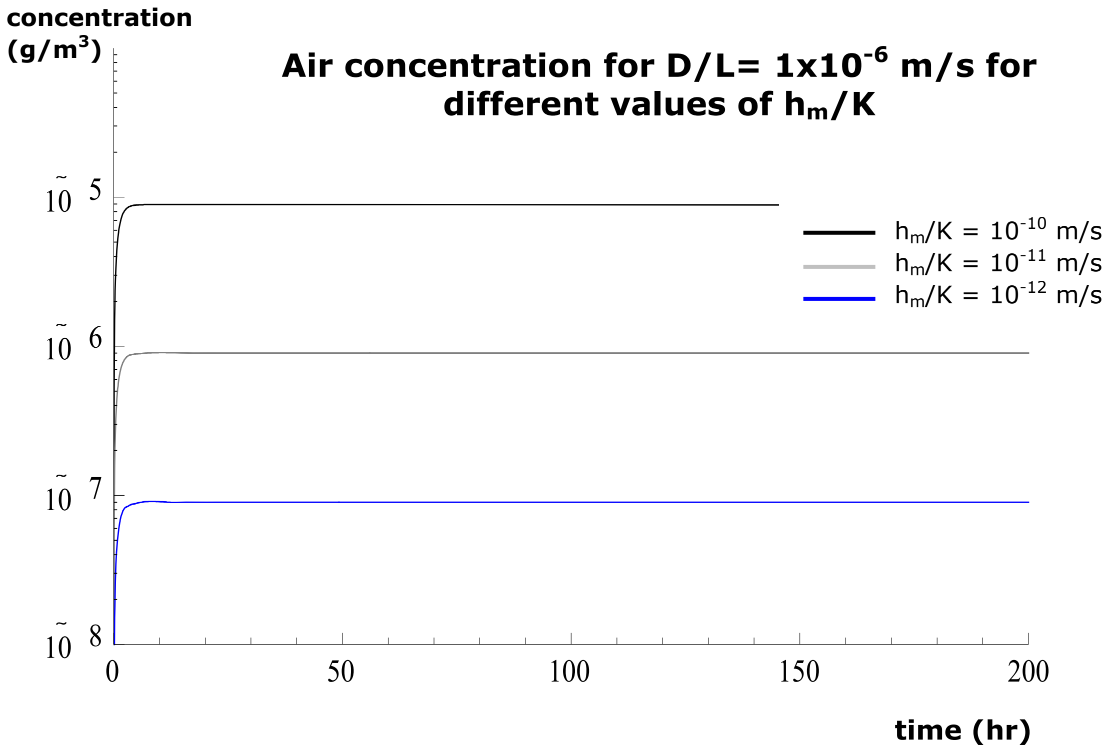


Figure 4a. Log-linear plot of the variation of the air concentration with h_m/K for a value of D/L of $1x10^{-6}$ m/s over the entire simulation duration.

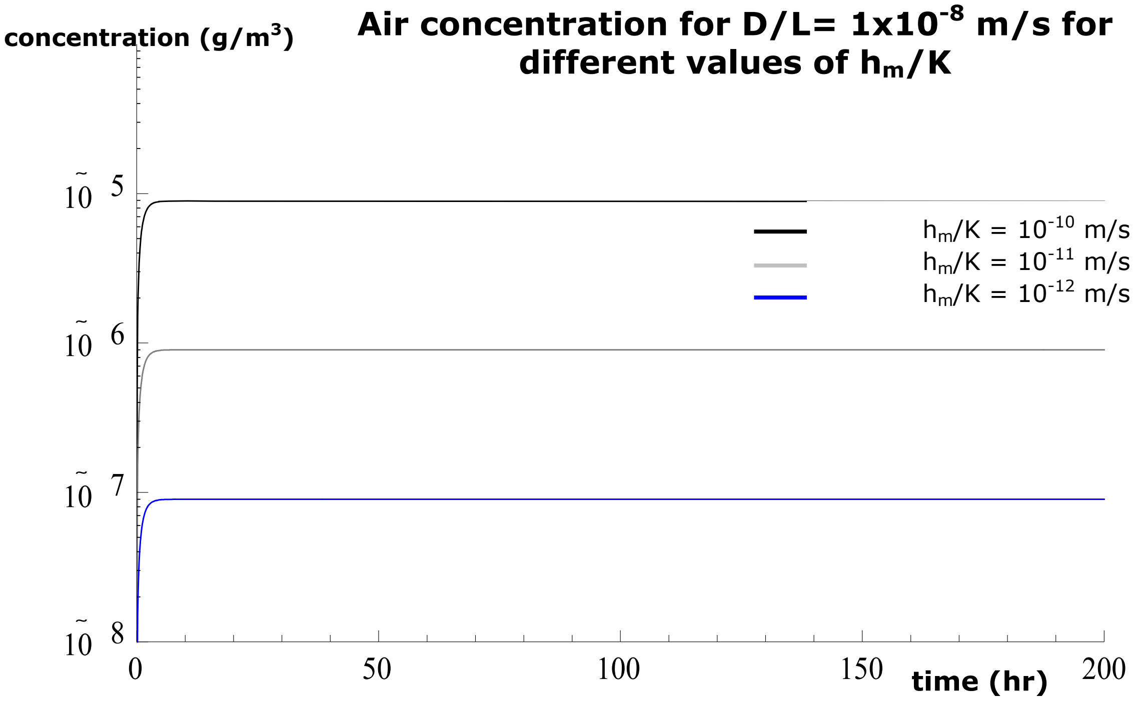


Figure 4b. Log-linear plot of the variation of the air concentration with h_m/K for a value of D/L of $1x10^{-8}$ m/s over the entire simulation duration.

2.4 Summary

This chapter describes the scientific formulation and background of a model that can be used to more realistically simulate the emission of substances from solid materials. The model takes into account the diffusion of the substance in the material, the transfer of the substance from the material surface into indoor air, and the removal of the substance from indoor air by ventilation. The model assumes that:

- the emission takes place indoor;
- the concentration of the substance in the material and the material itself are homogeneous;
- the emission is from one large surface area (the top side of a plate, thin slab of material or a thin layer of product) and not from the sides of the product. Emission of other product shapes are not adequately described by the model formulated above. However, the model can easily be adjusted to include other (simple) product geometries.

Additional removal processes, such as the addition of the substance to surfaces and dust and degradation of the substance are not included. These simplifications will limit the accuracy of the modelling results, especially in the case of the low-volatile substances (substances with vapour pressure of ~10 Pa and lower). The effect of neglecting additional sinks will be that during emission from the material, air concentrations will be overestimated, however air concentrations after depletion or removal of the material may be underestimated by the model. In section 5.3 the effects of neglecting sinks will be studied in a specific example.

A sensitivity analysis of the model demonstrates the existence of two limiting cases, determined by the quotient of D/L and h_m/K. In the case of mass transfer limitation (D/L >> h_m/K) the emission is mostly determined by the material air partition coefficient K and the mass transfer rate h_m. The exact value for D is not critical. This, in effect, reduces the need to collect precise numerical data on D. In the case of diffusion limitation (D/L << h_m/K), emission is mostly determined by D, and accurate determination of K and h_m are less critical under most conditions. This information is useful to simplify exposure assessments in many practical applications. As a rule of thumb, emissions of SVOC (and other low vapour pressure substances) from solid materials will be mass transfer limited and the emission of volatile substances will be diffusion limited. However, in any exposure assessment, it is recommended to verify the value of the quotient of D/L and h_m/K.

3 Data and estimation methods for the input parameters

3.1 Collecting data on fundamental model parameters

In order to be able to use the model described in chapter 2, numerical values of a number of fundamental model parameters has to be known. These are:

- the diffusion coefficient D of the substance in the material;
- the mass transfer coefficient h_m;
- the partition coefficient K of the substance between the material of the product and air.

Data on these parameters are scarce. The data that are available are mostly derived from research on VOC emissions from building materials. More recently, limited data on emissions of SVOCs from building materials have been published. Limited data on substances in polymeric matrices are also reported in literature.

In this section an overview is given of data and methods for parameter estimation published in literature. These data and methods may serve as a reference database to be used in consumer exposure assessments. It should be noted however, that the database is far from complete. Data and methods provided here, may serve as surrogate values in cases where adequate data is missing, but will not be a substitute for specific data on the substance and product. Extending the database with data on important substance/material combinations would greatly increase the applicability of the model.

Experimental data on model parameters are typically obtained in one of two ways:

1) from publications on a completely parameterised version of the model (or a similar version thereof), describing an experimental emission situation;
2) from direct measurements of the parameter.

The latter option often applies to either simultaneous measurement of the diffusion coefficient D and the partition coefficient K, or separate measurements of partition coefficients.

Data from publications that were found in literature are summarised in Tables 1-4, on diffusion coefficient and partition coefficient respectively.

Apart from reporting numerical values for model parameters, some authors also provide methods to estimate values for these parameters. Mostly, these methods are based on experimental observations of correlations between the parameter value and properties of the substance and the matrix, such as molecular weight or vapour pressure. Usually, these methods are derived in a specific domain, and have only been tested for a limited set of substances and materials.

Numerical values for the parameters and estimation methods are discussed in the next sections. Section 3.2 summarises data on diffusion coefficients, section 3.3 on the material air partition coefficient, and section 3.4 is on methods to estimate the mass transfer rate.

3.2 Diffusion coefficient

Diffusion coefficients of substances in solid materials will depend on many aspects, such as the size and shape of the molecules of the diffusing substance, on the molecular properties of the matrix and on the porosity of the product material.

Welty et al. (2007) report that, as a rough indication, diffusion coefficients of substances in (non-porous) materials typically lie in the range of 10^{-12} – 10^{-14} m^2/s.

Table 1 summarises experimental data on diffusion coefficients found in literature. Most of the data are obtained in the fields of VOC emissions from building materials and the migration of substances from polymeric matrices. The reported diffusion coefficients were determined at about room temperature (between 20-23 °C).

Table 1. Summary of diffusion coefficients published in literature.

Substance	Matrix/product	D [m^2/s] (x 10^{11})	Molecular weight[1] (g/mol)	Study
toluene	carpet backing	4.31	92.14	Bodalal et al., 2000
nonane	carpet backing	2.83	128.26	
	vinyl floor tile	1.48		
decane	carpet backing	0.54	142.29	
	plywood	1.28		
	vinyl floor tile	0.21		
undecane	carpet backing	0.28	156.31	
	vinyl floor tile	0.09		
cyclohexane	plywood	15.5	84	
ethylbenzene	plywood	4.04	116.25	
	vinyl floor tile	1.6		
water	vinyl flooring	0.36	18	Cox et al., 2001
n-butanol	"	0.067	74	
toluene	"	0.069	92	
phenol	"	0.012	94	
n-decane	"	0.045	142	
n-dodecane	"	0.034	170	
n-tetradecane	"	0.012	198	
n-pentadecane	"	0.0067	212	
hexanal	oriented strand board	0.18	100.16	Yuan et al., 2007
styrene	polysterene foam	0.62	104.15	
TVOC	particle board	7.7		Yang, 2001
Hexanal	"	7.7	100.16	
α-pinene	"	12	136.24	
ethyl acetate	brick	242	88.11	Zhang and Niu,

				2004
	concrete	4.33		
	gypsum board	1270		
	carpet	1030		
	wallpaper	0.28		
n-octane	brick	140	114.23	
	concrete	1.69		
	gypsum board	1200		
	carpet	3560		
	wallpaper	0.42		
styrene	carpet 1 (nylon fibre, polypropylene backing, styrene-butadiene rubber latex adhesive)	0.4	104.15	Little et al., 1994
	carpet 4 (polypropylene and nylon fibres, polypropylene backing, styrene-butadiene rubber latex adhesive)	0.31		
4-ethenylcyclohexane	carpet 1	0.52	110.2	
	carpet 4	0.21		
methane	low density polyethylene	1.9	16	Piringer, 2008
methane	‟	3.0	16	
ethane	‟	0.48	30	
ehtane	‟	0.54	30	
methanol	‟	0.48	32	
propane	‟	0.52	44	
n-pentane	‟	0.08	72	
benzene	‟	0.11	78	
benzene	‟	0.04	78	
n-hexane	‟	0.11	86	
n-hexane	‟	0.084	86	
phenole	‟	0.045	94	
heptanol	‟	0.053	116	
2,3-benzopyrole	‟	0.055	117	
2-phenyl-ethyl-alcohol	‟	0.043	122	
3-octene-2-one	‟	0.073	126	
n-octanal	‟	0.023	128	
4-isopropyl-toluene	‟	0.054	134	
limonene	‟	0.043	136	
3-phenyl-1-propanol	‟	0.028	136	
n-Nonanal	‟	0.018	142	

7-methyl-chinoline	“	0.043	143	
2,3,5,6 tetramethyl-phenol	“	0.016	150	
dimethyl-benzyl-carbinol	“	0.0075	150	
3,7-dimethyl-6-octene-1-al	“	0.01	154	
n-decanal	“	0.014	156	
3,7-dimethyl-octene-3-ol	“	0.013	158	
diphenyl-oxide	“	0.037	170	
n-dodecane	“	0.026	170	
dimethyl-phthalate	“	0.019	194	
n-tetradecane	“	0.019	198	
tetradecanol	“	0.0082	214	
2,6-di-tert-butyl-4-methyl-phenol	“	0.0048	220	
cedrylacetate	“	0.0041	264	
eicosane	“	0.0063	282	
docosane	“	0.0035	310	
timuvin 326	“	0.002	315.8	
2-hydroxy-4-ethandiol methyl-thioacetic acid ester	“	0.0009	346	
methyl-tricosanate	“	0.0015	368	
methyl-octacosanate	“	0.0003	438	
didodecyl-3-3-thio-dipropionate	“	0.0002	514	
3-(3,5—di-tert-butyl-4-hydroxy phenyl)-propionate	“	0.00011	531	

[1] If the molecular weight was not given in the cited reference, it was taken from the SRC Inc. PhysProp database (http://www.srcinc.com/).

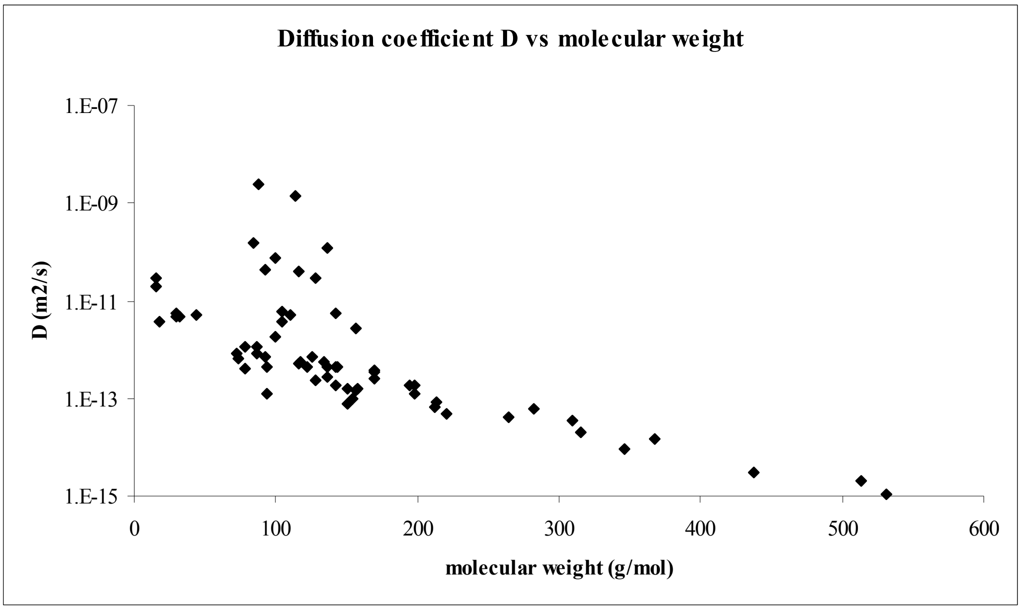


Figure 5. Plot of the diffusion coefficients D reported in Table 1 versus the molecular weight of the substance for all different matrices.

It is observed that the parameter values for the compound/material combinations reported here span a range from about 10^{-10} - 10^{-13} m^2/s. Diffusion in porous materials will consist of both gas and material phase diffusion and will usually be faster (as is seen, for example for ethyl acetate and n-octane in brick). Not many data on the diffusion in porous materials have been found. This lack of data constitutes an important data gap at present.

The diffusion coefficient is expected to correlate with both the molecular weight of the diffusing substance and the molecular weight of the matrix. The latter is not known for most matrices and products reported in Table 1. In Figure 5 the reported diffusion coefficients have been plot versus the molecular weight of the diffusing substance. A tendency of the diffusion coefficient to decrease with increasing molecular weight is observed. Given an extensive set of good quality data, it might be possible to make quantitative inferences on the diffusion coefficient based on only the molecular weight of the diffusing substance. However, the present database is too small to be used for this purpose.

Several empirical relations have been derived to estimate the diffusion coefficient for groups of substances and materials (summarised in Guo, 2002b).

The most general is the relation proposed in both (Bodalal et al., 2000) and (Cox et al., 2001):

$$D = \frac{A}{m_w^{\ n}} \tag{14}$$

in which D is the diffusion coefficient (m^2/s), m_w is the molecular weight (g/mol), and A and n are empirical parameters.

Values for A and n are given for different materials and compound groups (taken from Guo, 2002b):

Table 2. Parameters for the empirical model proposed by Guo, equation (14).

Material	Compound group	A	n
gypsum board	aromatics	4.481×10^{1}	5.99
oriented strand board	alkanes	1.450×10^{7}	8.36
particle board	aromatics	1.692×10^{7}	8.5
particle board	aldehydes	3.396×10^{8}	9.33
plywood	aromatics	1.337×10^{7}	8.56
plywood	aldehydes	7.900×10^{-4}	3.64
vinyl tile	alkanes	2.104×10^{1}	5.94
vinyl tile	aromatics	3.617×10^{2}	6.51
vinyl flooring	alkanes	5.006×10^{5}	7.45

From the data and estimation methods presented here representative values can be derived for similar product/material combinations. The question remains to what extent the materials and substances reported here are representative for other substances and materials. Also, porous materials are underrepresented in the database.

To enhance the models applicability, the database should be expanded to include reference values for materials and substances frequently encountered in regulatory assessments, such as wood, plastic et cetera.

3.3 Material air partition coefficient

Table 3 summarises experimental data on material air partition coefficients found in literature. Most of the data is obtained in the field of VOC emissions from building materials. In this document the partition coefficient is defined as the quotient of the (equilibrium) material concentration C_{mat} and the air concentration C_{air}. Another definition of the material air partition coefficient is defined as the ratio of the (equilibrium) material surface concentration and the air concentration. In this report we refer to this partition coefficient as the surface material air partition coefficient. This partition coefficient describes the adsorption to a surface rather than partition into a material. Whereas the former definition of the partition coefficient is a dimensionless number, the latter has dimensions of [length]. In this report we are mainly interested in the first, dimensionless partition coefficient, however, also adsorption partition coefficients are reported in a separate table. These surface partition coefficients will be useful when sorption to surfaces is included in the model. The surface air partition coefficients are reported in Table 4.

Table 3. Summary of material air partition coefficients for various material/substance combinations published in literature.

Substance	Matrix	K	Vapour pressure[1] (mmHg)[2]	Study
cyclohexane	ceiling tile: cellulose fibre and fibrous glass	6.8	77.54	Huang et al., 2006[3]
toluene		83.2	21.86	
ethyl acetate		239.3	76	
isopropyl alcohol		239.3	32.4	
methanol		678.6	97.48	‟
benzene	medium density board 1	190	94.8	Wang et al., 2008
benzene	medium density board 2	430		
toluene	medium density board 1	260	28.4	
toluene	medium density board 2	470		
xylene	medium density board 1	330	7.99	
xylene	medium density board 2	580		
toluene	carpet backing	6171	25.6 *(23°C)*	Bodalal et al., 2000
nonane		6216	3.93	
	vinyl floor tile	2142		
decane	carpet backing	14617	1.25	
	plywood	6948		
	vinyl floor tile	13045		
undecane	carpet backing	24255	0.35	
	vinyl floor tile	26647		
cyclohexane	plywood	348	35.6	
ethylbenzene		1636	8.58	
	vinyl floor tile	1920		
water	vinyl flooring	78	17	Cox et al., 2001
n-butanol	‟	810	4.1	
toluene	‟	980	22	
phenol	‟	1.2 x10^5	0.22	
n-decane	‟	3000	0.89	

n-dodecane	‶	1.7 x10^4	0.074	
n-Tetradecane	‶	1.2 x10^5	0.0071	
n-Pentadecane	‶	4.2 x10^5	0.0014	
hexanal	oriented strand board	6600	11.3	Yuan et al., 2007
styrene	polysterene foam	260	6.4	
TVOC	particle board	3300		Yang, 2001
Hexanal	‶	3300	11.3	
α-pinene	‶	5600	4.75	
ethyl acetate	brick	186.6	93.2	Zhang and Niu, 2004
‶	concrete	1186.4		
‶	gypsum board	88.68		
‶	carpet	43.91		
‶	wallpaper	3000		
n-octane	brick	23.14	14.1	
‶	concrete	61.4		
‶	gypsum board	70.02		
‶	carpet	98.42		
‶	wallpaper	2000		
DEHP	vinyl flooring	2.3x10^{11}	1.42x10^{-7}	Xu, 2006

[1] The reported vapour pressures are taken from the publication. If the study did not report a value for the vapour pressure, it was obtained from the SRC PhysProp database (http://www.srcinc.com/). Reported values are determined at about room temperature (20-23 °C).

[2] Units used in the model formulations in this document are in SI. To convert the vapour pressure to SI units (Pa), multiply by 133.32

[3] Calculated from [mg/kg solid]/[mg/ kg air] using ρsolid = 261 kg/m^3 and ρair = 1.2 kg/m^3.

The material air partition coefficient is expected to anti-correlate with the vapour pressure. Figure 6 plots K versus the vapour pressure on a double log scale for all materials and substances reported in Table 3. A negative correlation is observed. However, the database seems too small to make any general quantitative inferences. Especially, low-volatile materials are underrepresented.

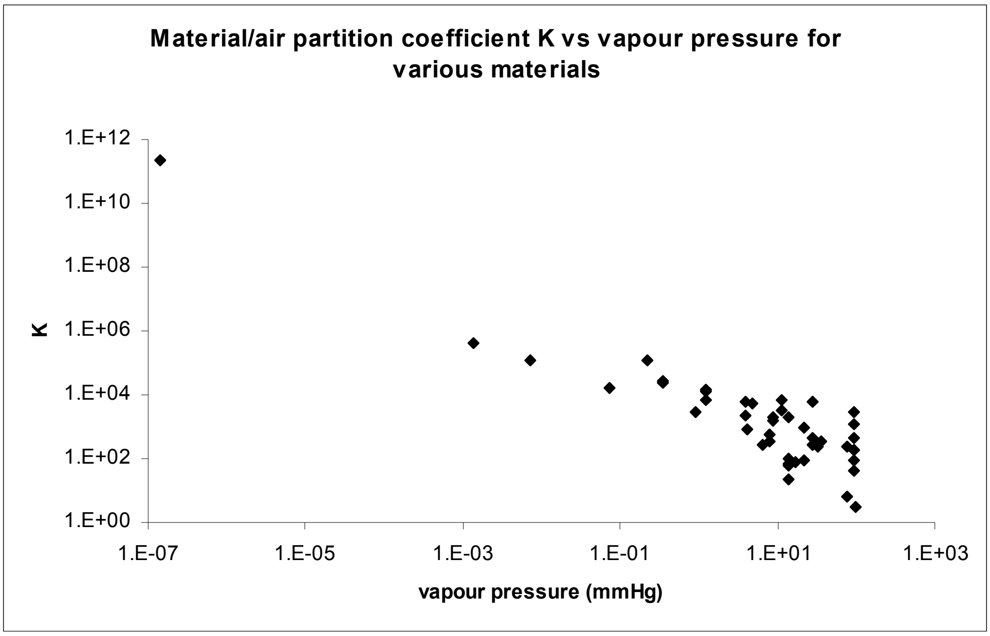


Figure 6. Material air partition coefficients from Table 3 plotted versus the vapour pressure of the substance.

No distinction is made between materials and the weight fraction of the substance in the material.

Table 4. Summary of surface air partition coefficients for various material/substance combinations published in literature.

Substance	Matrix	K (m)	Vapour pressure	Study
cyclohexane	carpet with pad	0.2	96.9	Won et al., 2001
"	pad	1.8		
"	painted gypsum board	0.05		
toluene	carpet with pad	1.7	25.64	
"	carpet pad	1.8		
"	virgin gypsum board	0.12		
"	painted gypsum board	0.17		
"	floor vinyl	0.14		
ethylbenzene	carpet with pad	3.2	9.6	
"	carpet pad	3.8		
"	virgin gypsum board	0.24		
"	painted gypsum board	2.7		
"	floor wood	0.63		
"	floor vinyl	0.28		
"				
nicotine	carpet	$4.6\text{x}10^4$	$1.5 \text{ x } 10^{-4}$	Van Loy et al., 2001
nicotine	painted wall board	$3.3\text{x}10^3$		
phenanthrene	carpet	28	0.02	
phenanthrene	painted wall board	18		

In addition to numerical values published for partition coefficients, a number of authors have developed empirical correlations that link material air concentrations to the vapour pressure of the compound for specific materials and substance groups (Zhao, 1999; Bodalal et al., 2000). Based on these, Guo (2002b) suggests a 'universal' relation:

$$\ln K = 8.76 - 0.785 \ln P \tag{15}$$

In this equation, the vapour pressure P is in mmHg.

This relation was developed using a set of 56 material/compound (exclusively building materials and VOCs) combinations and estimates the partition coefficients for the training set within 2 orders of magnitude. It should be kept in mind however, that this relation can most likely not be used for non-VOC substances and materials that are very different from the ones used in the training set.

Weschler and Nazaroff (2008) studied the fate of semi-volatile substances (SVOCs) such as plasticisers, pesticides and flame retardants in indoor environments. For the emissions from material into air they suggest, as an order of magnitude estimation method, to use Raoult's law for estimating a partial vapour pressure and its corresponding saturated air concentration. Raoult's law is formulated as:

$$P_{part} = xP_{vap} = \frac{n_{sub}}{n_{sub} + n_{rest}} \times P_{vap} \tag{16}$$

where x is the molar fraction of the SVOC in the product matrix, and n_{sub} and n_{rest} are particle number concentrations of the substance and the rest of the compounds in the matrix respectively.

Assuming that Raoult's law is a reasonable estimate of the driving pressure, we can derive for the air concentration at the surface C_{air}:

(17) $$C_{air} = \frac{m_{sub}}{RT} P_{part} = \frac{m_{sub}}{RT} \frac{n_{sub}}{n_{sub} + n_{rest}} P_{vap}$$

where use has been made of the ideal gas law.
R is the universal gas constant, T the absolute temperature, m_{sub} the molecular weight of the evaporating substance.

Now, making use of $n_i = \frac{w_i}{m_i} \rho$ for the particle number concentration n_i of component i in the material (ρ is the density of the product, m_i and w_i are is the mol weight and the weight fraction of component i in the matrix respectively):

(18) $$\frac{n_{sub}}{n_{sub} + n_{rest}} = \frac{\frac{w_{sub}}{m_{sub}}}{\frac{w_{sub}}{m_{sub}} + \sum_i \frac{w_i}{m_i}} = \frac{1}{\rho} \frac{C}{w_{sub} + m_{sub} \sum_i \frac{w_i}{m_i}}$$

If this is substituted this in (16), it is observed that this relation is not linear in w_{sub} (and thus C_{mat}), and the resulting expression can not be interpreted as linear partitioning. But in situations that w_{sub} in the denominator of (18) may be neglected, we may define a (linear) partition coefficient K as:

(19) $$K = \frac{C}{C_{air}} = \frac{RT}{P_{vap} m_{sub}} \rho [w_{sub} + m_{sub} \sum_i \frac{w_i}{m_i}] \approx \frac{RT}{P_{vap}} \rho \sum_i \frac{w_i}{m_i} \qquad (\sum \frac{w_i}{m_i} >> \frac{w_{sub}}{m_{sub}})$$

In this, use was made of $C = w_{sub} \rho$.

If experimental values for the vapour pressure are not available, the authors recommend the use of the 'SPARC' tool (http://ibmlc2.chem.uga.edu/sparc/), that was found to produce satisfactory results for a large number of substances, providing estimates usually within one order of magnitude deviation from measured values.

3.4 Mass transfer coefficient

Under typical indoor conditions, emission of a substance from a material into air is hampered by a layer of stagnant air (the so-called boundary layer) above the emitting surface. The mass transfer coefficient describes the diffusional transport over this layer (see, for example, Welty et al., 2007). The shape of the boundary layer (and thus the mass transfer coefficient) depends on the geometry of the emitting material, surface roughness of the material, and the airflow over the surface. Theoretical descriptions of various surface configurations have been developed. The method most commonly used in engineering applications is the one as described for example in (Kiil, 2006), which uses the theoretical correlation between Sherman, Reynolds and Schmidt numbers (Sh, Re, Sc) for a flat plate and laminar flow conditions over the material surface. From this relation it follows that:

(20) $$h_m = 0.664 \times D_{air} \times Re^{1/2} \times Sc^{1/3} / L_{sys}$$

Reynolds (Re) and Schmidt (Sc) numbers are given by:

$$Re = L_{sys} \times \frac{v}{\eta}$$

$$Sc = \frac{\eta}{D_{air}}$$

from which:

(21) $$h_m = 0.664 D_{air}{}^{2/3} \eta^{-1/6} (\frac{v}{L_{sys}})^{1/2}$$

In these equations, L_{sys} is a typical length of the system, v the velocity of the air over the surface, η the kinematic viscosity of air (1.5×10^{-5} m^2/s at 25 °C), D_{air} the diffusion coefficient of the substance in air.

Sparks et al. (1996) suggest that the theoretical correlation (20) for a flat plate is not appropriate as indoor air movement is not uni-directional. They determined the experimental correlation between Nusselt, Reynolds and Schmidt numbers (Nu, Re and Sc) for a cylindrical cup filled with pure p-dichlorobenzene. Schmidt, Reynolds and Nusselt numbers were determined for a range of representative indoor air velocities over the surface of 0.05 – > 0.6 m/s.

The authors suggest the following experimental correlation to predict the mass transfer coefficient:

$$h_m = 0.33 \times D_{air} \times Re^{0.67} / L_{sys}$$

In their work, it appears that 'Nusselt number' (which refers to convective heat transport) is used synonymously with Sherman number.

It should be noted that also in this case, in which the mass transfer correlation was determined by experiment, the adequacy of the proposed method depends on to what extend the experimental set up (emission from a cylindrical cup) is representative of the realistic emission conditions.

Below, in Figure 7, the predicted mass transfer coefficients for the two methods are plotted as a function of the air velocity over the surface. For the diffusion coefficient in air a typical value of 1.0×10^{-5} m^2/s was used. The emitting source was supposed to have a characteristic dimension of 1 m.

In this case the results of both methods differ by up to a factor of 3. The prediction by the flat plate method gives the higher estimates.

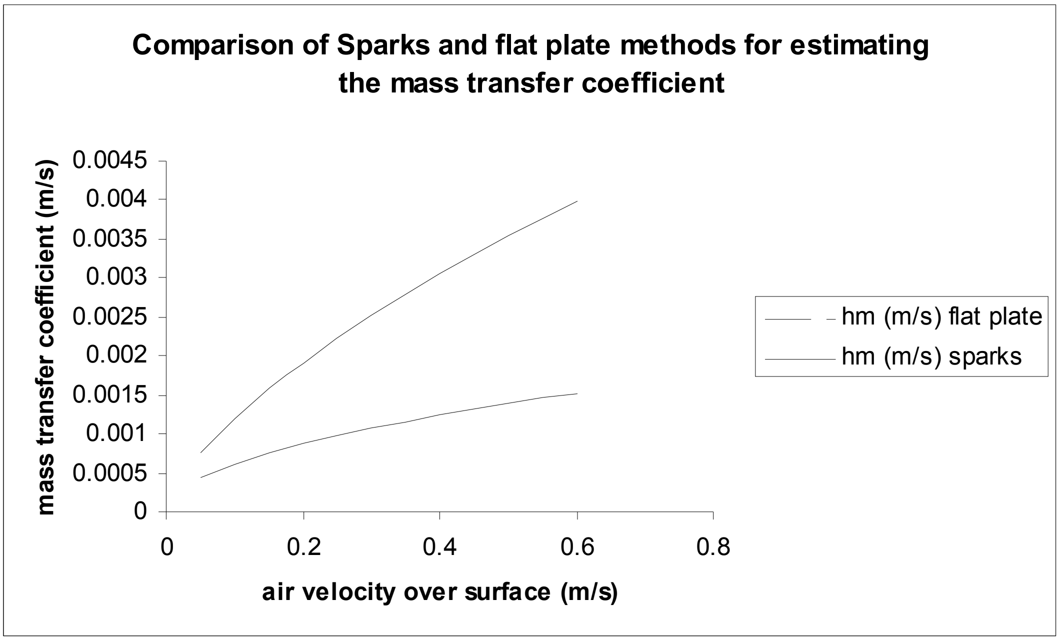


Figure 7. Example of mass transfer coefficients calculated by the flat plate correlation method and Sparks' method (Sparks et al., 1996) respectively.
For a typical air diffusivity D_{air} of 1.0 x 10^{-5} m^2/s and surface air velocities between 0.05 and 0.6 m/s. The flat plate method generally gives higher estimates of the mass transfer, leading to higher predictions of the emission rate.

3.5 Summary

Data on critical parameters D, K and h_m of the model are scarce. The available data is mostly for VOC and SVOC emissions from building materials. Also a reasonable amount of data on diffusion coefficients in polyethylene was found. The collected data may serve as a reference for exposure assessors. However, data for many important substances and products is not available. Ranges of values for the diffusion coefficient were derived from the collected data, for the mass transfer coefficient, reasonably accurate estimation models exist, for the material air partition coefficient K data is especially scarce. A very crude estimation method was suggested by Weschler and Nazaroff (2008) which may be useful as a first approximation. However, the inaccuracy of this method is unknown, but likely to be very high. The estimation methods and parameter value ranges are only approximate and can not be a substitute for case-specific data. Collection of more data on these fundamental model parameters (especially the partition coefficient K) will greatly enhance the usability of the model and the overall quality of the exposure assessment.

4 Applying the emission model in screening assessments

The model proposed in chapter 2 to simulate emissions of substances from a solid product matrix includes a detailed description of the transport of a substance within the material to the surface, and subsequent transport from the surface into bulk indoor air. As such, the model is a realistic representation of the actual emission process. In the case where adequate input values for the model parameters are given (most notably, the diffusion coefficient D, material air partition coefficient K and mass transfer rate h_m), the model is expected to give a reasonably accurate estimate of the emission of the substance into bulk indoor air.

The prediction of the resulting air concentrations in the model on the other hand, may be hampered by a number of simplifications made by the model as discussed in chapter 2. Most notably, not including the presence of other sinks, such as sorption onto surfaces and dust may lead to overprediction of the air concentration and therefore (as the emission is driven by the difference in saturated air concentration at the material surface and the air concentration in bulk air) to an underestimation of the actual emission. This error due to model simplification is expected to be most important for semi- and low-volatile substances (for example, substances with a vapour pressure of about 10 Pa and less).

In addition to this uncertainty due to model simplification, application of the model in actual exposure assessments will be hampered by the fact that in many situations adequate estimates of the fundamental model parameters are not available. However, the proposed model will have useful applications in these exposure assessments as well. In this chapter we propose a method to estimate exposure in these situations. In these cases, the results of an estimation have to be considered as an order of magnitude estimate of the air concentration that may arise due to emissions of substances from solid materials.

Based on the data and methods presented in chapter 3, default values or methods are suggested, to be used in situations where adequate data is not available. Because these defaults are intended to be used in a ‘screening’ type of assessment, the choice of the default value is chosen to be conservative, i.e. to be such that it will likely lead to a relative high level of exposure.

If the situation warrants (for example in cases of estimated exposures comparable to levels of concern), the user of the model is advised to include an analysis of the variation in the exposure as a result of parameter uncertainty. Such an analysis gives additional, crucial information on the magnitude of uncertainty in the assessment. Such information will lead to an increased robustness of the assessment. In addition to default parameter values and estimation methods, estimates for typical ranges of variation for the different model parameters will also be made. These may serve as a starting point of an uncertainty analysis, in applications of the model.

4.1 Default values and estimation methods for model parameters

4.1.1 Diffusion coefficient

From the overview of available data on diffusion coefficients given in section 3.2 it is observed that most diffusion coefficients are within the range of 10^{-10} – 10^{-13} m^2/s. It should be noted however that most of the reported materials are non-porous. Diffusion through porous materials may increase up to $1x10^{-8}$ m^2/s, as in the case of carpet and brick, for instance. The data set for porous materials is however too small to be representative. Ideally, the database should be expanded in this area to be able to draw better grounded conclusions.

Based on these considerations, it is suggested to:

1) use a default value of 1.0 x 10^{-10} m^2/s for a substance in a non-porous material;
2) include a range of at least 10^{-10} – 10^{-13} m^2/s in an uncertainty analysis.

Note that the precise value of the diffusion coefficient is less important when estimating emissions of semi- or low-volatile substances as the emission of these substances is mass transfer limited, rather than diffusion limited (see section 2.3).

As a rule of thumb, for low volatile substances (such as SVOCs, vapour pressures below ~10 Pa) the emission is mass transfer limited. For more volatile substances the emission will tend to be diffusion limited. However, it is advised to always check the ratio of D/L and h_m/K as described in section 2.3.

For porous materials, there is not enough data to even suggest an order of magnitude default value.

4.1.2 *Material air partition coefficient*

For the material air partition coefficient, most available data are for VOCs in building materials. For other material/substance combinations there is a severe lack of representative data. Thus, if for a specific application, a representative value is not given in the database, it is proposed as a default, to use the suggestion by Weschler and Nazaroff (2008) and to use Raoult’s law, as described in section 3.3, equation (19):

$$K = \frac{C}{C_{air}} = \frac{RT}{P_{vap} m_w} \rho [w_f + m_w \sum_i \frac{w_i}{m_i}] \approx \frac{RT}{P_{vap} m_w} \rho \sum_i w_i \frac{m_w}{m_i}$$

This method is only usable for relatively low concentrations of substance in the material. The degree of uncertainty in this method is unknown. The validity of the method and the margins of error in its results should be investigated further. Note that this approach is only applicable for relatively low concentrations of substance in the material.

4.1.3 *Mass transfer coefficient*

In section 3.4 two different methods were proposed to estimate the mass transfer coefficient. A general, theoretical method that calculated the mass transfer for the case of a flat plate with laminar airflow over it and the empirical method proposed by Sparks et al. (1996).

It should be remember that both methods are dependent on the presumed geometry in the modelled situation/experimental setup (i.e. flat plate vs. cylindrical emitter) and both methods lack generality. However, as a flat plate setup seems to be a situation that often represents emissions from a product, and on the other hand, this method seems to lead to higher estimates of the mass transfer and is thus more conservative, this method (equation (21)) is proposed here to use as a default:

$$h_m = 0.664 D_{air}{}^{2/3} \eta^{-1/6} (\frac{v}{L_{sys}})^{1/2}$$

The method requires the value of the airflow over the surface. Values for the diffusion coefficient in air D_{air} and system dimension L_{sys} can usually precisely be defined. If the exact value of D_{air} is unknown, it can be assumed, as a rule of thumb, that it is between $1x10^{-5}$ and $1x10^{-6}$ m^2/s (Welty et al., 2007). Mostly, the largest variation will be in the airflow. Typical values in indoor environments are 0.05 – 0.6 m/s (Sparks et al., 1996).

It is suggested that, by default, the mass transfer coefficient is estimated using an air velocity value of 0.6 m/s but that the entire range be considered in an analysis of the variation.

4.1.4 Limiting situations

As discussed in section 2.3, two limiting cases of mass transfer and diffusion limited emission respectively can be distinguished. Mass transfer limitation occurs when $D/L >> h_m/K$. In these cases, D has not to be accurately known, as results are insensitive to changes in the value of this parameter. On the other hand, when $D/L << h_m/K$ the emission is diffusion limited and h_m/K is not required to be specified with high accuracy.

4.2 Summary

This chapter suggests a method to use the emission model developed in chapter 2 in routine exposure assessments where data on model parameters is usually scarce. Based on the review in chapter 3 default ranges and estimation methods for the parameters D, K and h_m are suggested. These estimation methods for the parameters are very crude and values for D and K in particular will be very uncertainty (several orders of magnitude). Therefore an exposure estimate using the defaults values methods should always be combined with an analysis of the uncertainty, exploring the upper and lower limits of the possible exposure levels. Examples of such an uncertainty analysis can be found in chapter 5.

5 Verification of the model

In this chapter the general method proposed in chapters 2 and 4 is evaluated against two experiments on the emission of substances from materials. In the simulations the parameter values from the experiments were used. For parameter values that were not reported, the default methods suggested in chapter 4 were applied. Finally, for each case, a brief analysis of the uncertainty was performed to explore the margins of error in the modelled air concentrations.

The cases considered in this verification included the emission of phthalates from PVC and IPBC from treated wood.
Also, to investigate the implications of the presence of sinks on the emission of SVOCs, in collaboration with the Danish Environmental Protection Agency (DEPA) an exposure estimate was conducted on the emission of DEHP and other phthalates from various consumer products. Phthalate content of products and exposure scenarios were provided by DEPA. Exposure modelling was performed by National Institute for Public Health and the Environment (RIVM) in Berkley Madonna modelling software. It was shown in this case that the presence of sinks impacts the time it takes of the emission to reach (quasi-)stationary levels, but does not have an impact on the height of this ‘stationary’ level.

5.1 Case 1: emission of phthalates from PVC and other materials

Afshari et al. (2004) determined emissions from DEHP and DINP from various flooring materials (PVC, polyolefin, floor wax) in an emission chamber (Climpaq). Air concentrations in the Climpaq were monitored for 150 days. As a test of the proposed procedure, the model is applied for the case of DEHP emission from PVC flooring. Material and chamber data as reported in Afshari et al. (2004) are:

Parameter	Value	Units
area of test piece	1.6	m^2
weight fraction DEHP	0.17	-
volume chamber	0.051	m^3
ventilation rate	150	ml/s
air velocity over the material surface	0.12 – 0.18	m/s

The physical-chemical properties of DEHP are given by:

vapour pressure	8.3×10^{-6}	Pa
molecular weight	391	g/mol

Data not provided in the publication but needed in the model are the thickness of the flooring material and the density of the material (needed to arrive at an estimate of the initial concentration in the material). The thickness of the material was estimated to be between 1 and 5 mm. PVC density was assumed to be between 1.35 and 1.45 kg/l. From this, the initial DEHP concentration is estimated to be between about 0.230 and 0.245 kg/l. The material air partition coefficient K was obtained from Table 3. (Xu, 2006). For the diffusion coefficient of DEHP in PVC the range 10^{-10} – 10^{-13} m^2/s was used, as suggested in section 4.1. As the emission is expected to be mass transfer limited, the precise value of the diffusion is not expected to be critical. This was verified in the model simulations. An estimate of the air concentration was made using values from the estimated ranges of parameter values. These values where chosen in such a way that they tend to a high estimate of the exposure.

Parameter	Range	Point estimate	units
thickness flooring	0.001 – 0.005	0.001	m
initial DEHP concentration	230 – 245	245	kg/m^3
material air partition coefficient	1-5 x 10^{11}	2.3 x 10^{11}	
diffusion coefficient	10^{-10} – 10^{-13}	10^{-10}	m^2/s
mass transfer coefficient	0.0005 – 0.003	0.003	m/s

Using the data specified above, the air concentration profile given in Figure 8 was found.

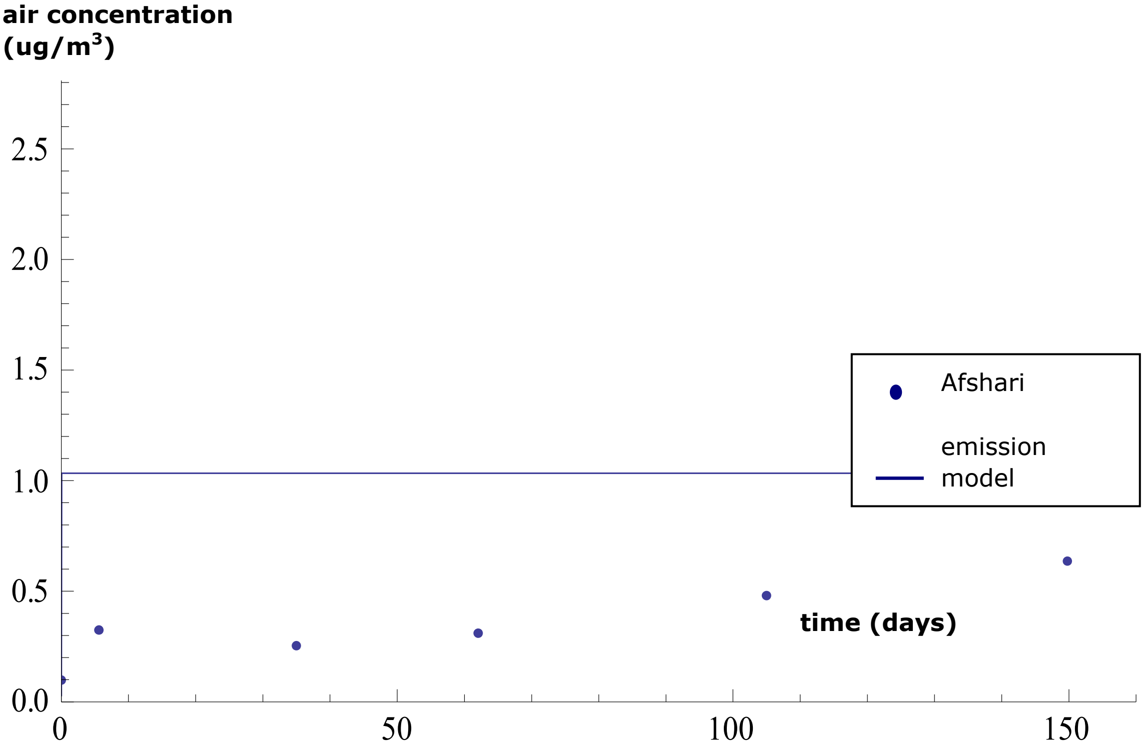


Figure 8. Comparison of the model estimate with experimentally determined air concentrations for the emission of phthalates from PVC (Afshari et al., 2004).

As is seen in Figure 8, the estimated air concentrations are about a factor of 2 higher than the actual air concentrations. This is in the right order of magnitude. Moreover, the model estimate is an overestimation of the actual air concentrations. This is acceptable for a screening model. For completeness, an analysis of the parameter uncertainty is made by means of a factorial design.

In a factorial design, the uncertainty in the precise value of the input parameters is taken into account by taking extreme values (i.e. highest and lowest values) of the parameters in their respective ranges and combining all these samples in repeated model evaluations. For simple, monotonic models, such as the emission model described here, the method yields an estimate of the range of possible model outcomes that result from uncertainty in parameter input values.

It was verified that the model is completely insensitive to changes in the diffusion coefficient, within the range of values that it may take on. Therefore, the uncertainty in the diffusion coefficient was not included in the analysis. To account for uncertainty in the experimentally determined K a variation in K of a factor 5 was included (varying K between $1x10^{11}$ and $5x10^{11}$). Also, the uncertainty in the mass transfer coefficient was accounted for by including the extreme values of the range [0.0005 – 0.003] m/s.

The results of the factorial design are plotted in Figure 9. The grey lines correspond to various evaluations in the factorial design. The entire range spanned (from minimal to maximal concentrations) is an estimate of the uncertainty in the assessment due to uncertainty in the parameter values. The 4 highest levels evaluated in the factorial design correspond to K = 5×10^{11}, the lowest 4 levels correspond to 1×10^{11}. For the parameters considered in the uncertainty analysis, the model is most sensitive to variations in this parameter (roughly linear dependence).

In this case, the model prediction, while in the right order of magnitude, still tends to overpredict the actually measured air concentrations. This may be due to the neglecting of sorption to surfaces. Although the latter is expected to be low in the experimental setup, it is not expected to be entirely negligible.

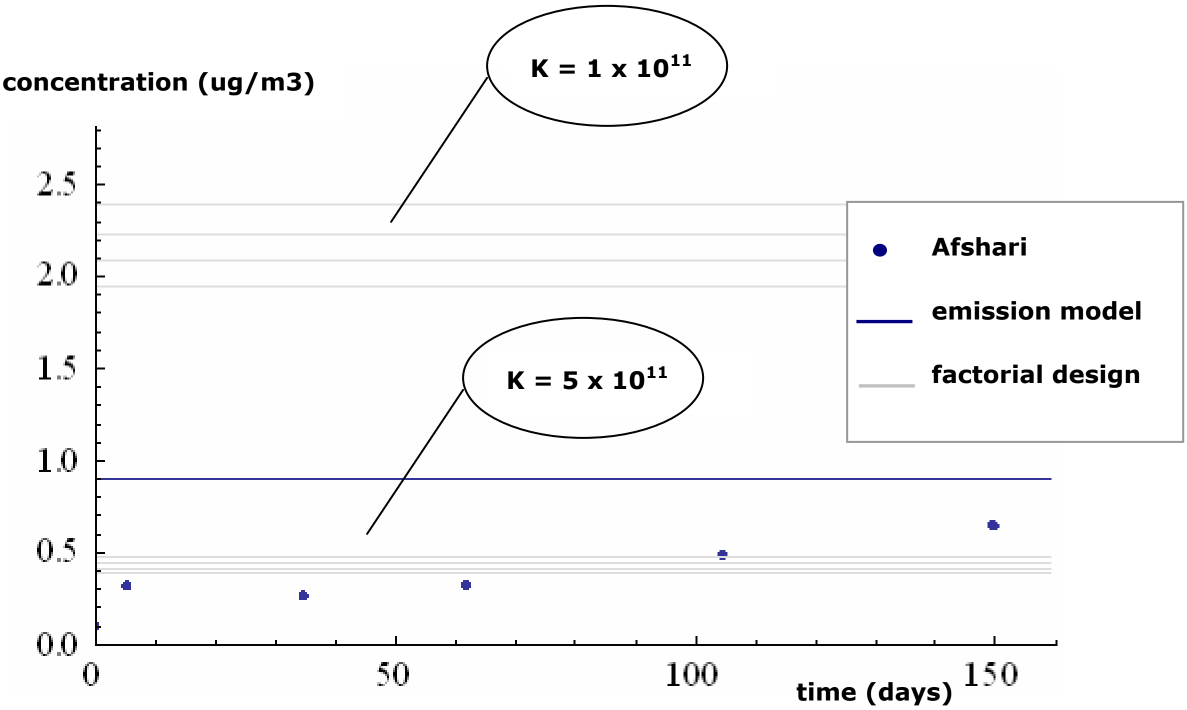


Figure 9. The modelled and measured air concentrations including an uncertainty analysis. The grey lines represent different evaluations in the uncertainty analysis. The four higher levels correspond to the minimal value of the material air partition coefficient, the four lower levels correspond to the maximal value of the material air partition coefficient. For the considered parameters in the uncertainty analysis, the material air partition coefficient is the most influential parameter.

5.2 Case 2: IPBC emission from treated wood

Horn et al. (2003) have measured emissions of several biocides from treated articles. As verification of the method proposed in chapter 4, the emission of Iodopropynyl Butylcarbamate (IPBC) from treated wood is estimated.

The experimental conditions in Horn et al. (2003) were as follows:

The material, a piece of wood was treated with a wood preservative that contained 0.3% IPBC. Application was according to prescriptions. In this case, the prescribed mass applied per surface area ΔA_{prod} was 88 g/m^2. The samples were stored for 24 hrs in an extractor hood to reduce solvent emissions during experiment. The treated wood was placed in a small, ventilated emission chamber (volume 20 l) and the air concentration was monitored by over a period up to 150 days.

The experimental conditions are given by:

material dimensions (width x length x thickness)	0.312 x 0.02 x 0.02 (x 5 samples)	m^3
quantity of IPBC applied	0.003 x 0.0312 x 88 = 8.23 x 10^{-3}	g
volume room	0.02	m^3
ventilation room	0.125	m^3/hr

The physical-chemical properties of IPBC are given by:

vapour pressure (25 ºC)	0.0023 – 0.0045	Pa
molecular weight	281	g/mol
CAS Nr	55406-53-6	

From these data the model parameters were estimated as follows:

Volume V_{mat}, surface area S and thickness L of the emitting material follow at once from the specification. To arrive at the initial concentration Co of IPBC in the wood it was assumed that the product permeated the entire slab of wood, so that the initial concentration in the material is homogeneous.

Now C_o is estimated using:

$$C_o = \frac{\Delta A_{prod} \times S \times w_f}{V_{mat}}$$

The diffusion coefficient of IPBC in wood is not known. It is assumed to be in the normal range of [10^{-10} – 10^{-13}] m^2/sand the default suggested in section 4.1 is used. The mass transfer coefficient is estimated using equation (21) and the typical ranges for the diffusion coefficient of IPBC in air and the air velocity over the surface, following the recommendations in section 4.1. In view of the rather high ventilation rate, the mass transfer should probably be in the high end of the normal range.

For the partition coefficient K representative experimental values are lacking. It is estimated here using equation (19). This is done as follows:

The density of wood was estimated to be between 0.4 (~red pine) and 1 (~ebony) kg/l. As a rough approximation for its mol weight the (number averaged) mol weight of wood lignin of *Pinus Taeda* was taken: 5147-7790 g/mol (Guerra et al., 2003).

Then, from equation (19), it follows (using kg, m and s as units):

$$K = \frac{RT}{P_{vap}} \rho \frac{w_i}{m_i} \approx \frac{RT}{P_{vap}} \frac{\rho}{m_i} := \frac{8.3 \times 299}{[2.3-4.5]\times 10^{-3}} \frac{[0.4-1.0]\times 10^{3}}{[5.1-7.8]} = [0.01-0.09]\times 2.5\times 10^{9} \approx [0.25-2.3]\times 10^{8}$$

where the square brackets indicate the estimated range.

From this a range of [10^7 – 10^8] for the material air partition coefficient K is adopted.

Summarising, we use for the model input:

Parameter	Range	Deterministic value	Units
V_{room}		2×10^{-2}	m^3
S		3.12×10^{-2}	m^2
V_{mat}		6.3×10^{-4}	m^3
C_o		0.0132	kg/m^3
q		6.25	hr^{-1}
K	1×10^7 – 1×10^8	1×10^7	
D		1×10^{-10}	m^2/s
h_m	0.0005-0.003	0.003	m/s

To compare the model simulations with the area specific emission rates (SER, in µg/m^2hr) reported in Horn et al. (2003), the modelled concentration data are converted using:

$$SER = C_{air} \frac{qV_{room}}{S}$$

The first thing to note is that D/L varies between ~5.0×10^{-7} and ~5×10^{-10} m/s. On the other hand, we expect h_m/K to be in the range of ~5×10^{-13} to ~5×10^{-11} m/s. That is, the emission is mass transfer limited and it is in all likelihood not critical to know the exact value of the diffusion coefficient.

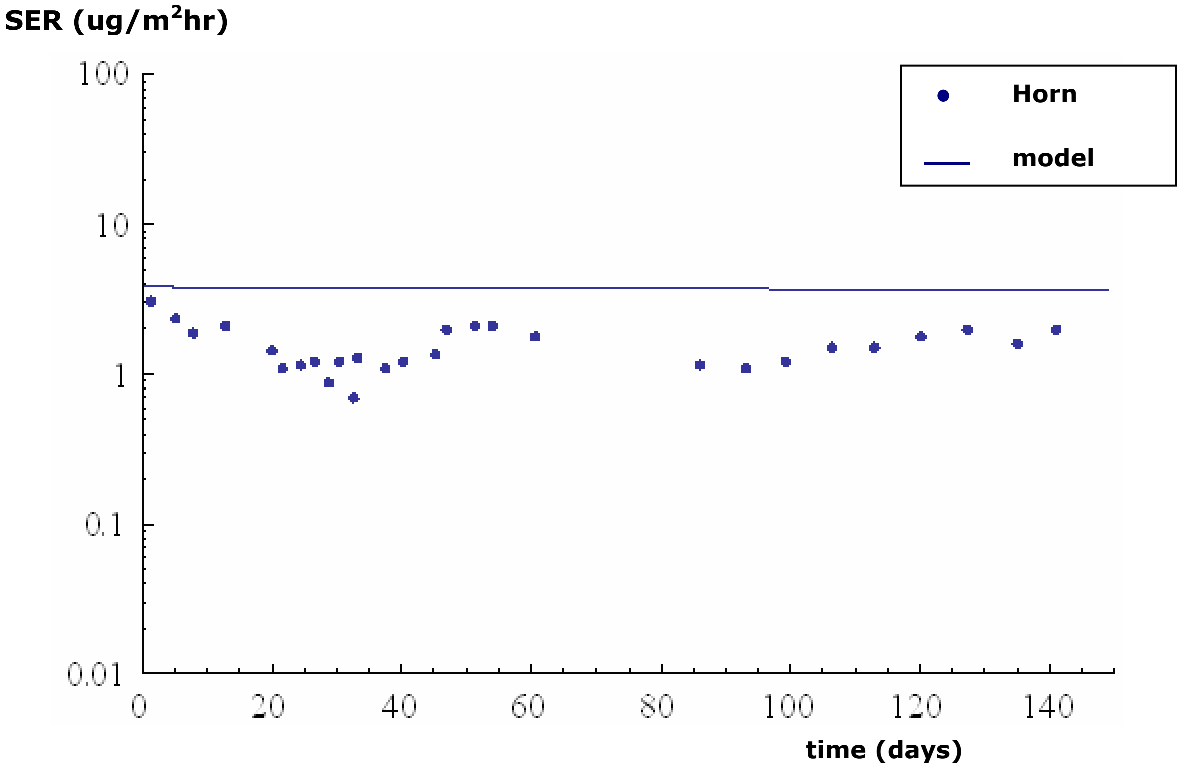


Figure 10. Area specific emission rates of IPBC from treated wood versus model simulation.

The estimated emission levels are close to measured values, however, it should be remarked that there is a number of (hard to quantify) uncertainties in the method used. These include:

- the assumption that the preservative is absorbed by the entire piece of wood, leading to a homogeneous concentration in the material at the onset of emission;
- the matrix (wood) is poorly defined and hard to characterise. The used values for molecular weight are derived from one specific study, for one type of wood. Variability in various wood types and inhomogeneities in the wood may lead to much higher uncertainty in the K than is accounted for in this case study.

An evaluation of the uncertainty was performed by means of a factorial design, analogous to the uncertainty analysis in case 1 (DEHP emission). The most sensitive and poorly characterised parameters K and h_m were included in the analysis with ranges as indicated in the table above. In addition, the effect of the assumption that the product permeates the entire piece of treated wood was modelled in the following way: in the one extreme case, the thickness of the layer was assumed to be the thickness of the material (20 mm). This corresponds with the default assumption that the product has permeated the entire material. In the other extreme it was assumed that the product only permeates into the product up to a depth of 2 mm. The corresponding initial concentration was adjusted so that the total applied mass remained the same. Both situations were included in the factorial design. The results are shown in Figure 11.

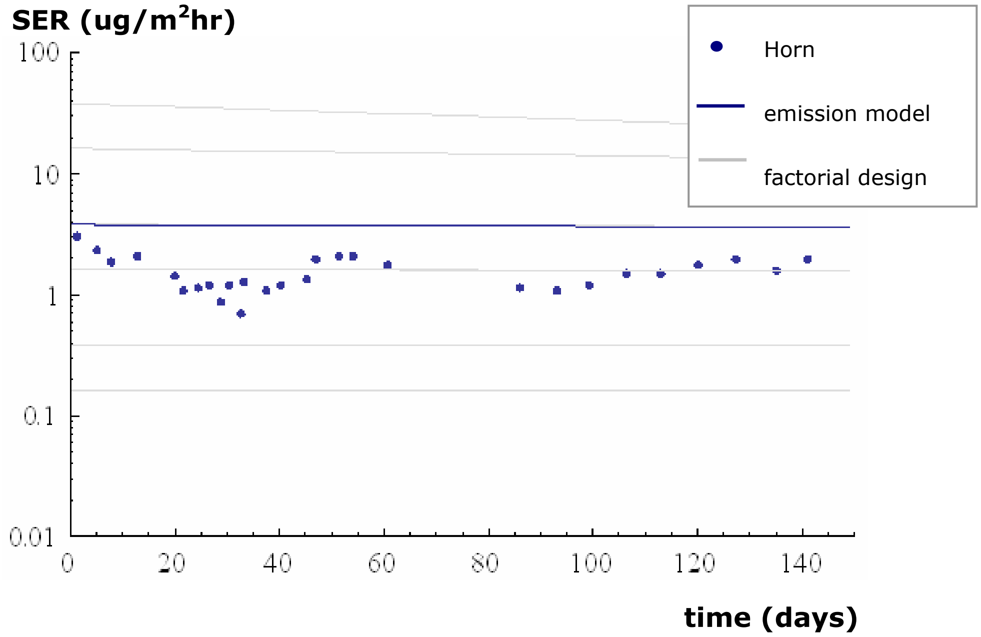


Figure 11. The modelled and measured air concentrations of IPBC emitted from treated wood.

The grey lines represent different evaluations in the uncertainty analysis. The uncertainty analysis includes uncertainties in the most critical parameters K and h_m and also includes uncertainty in the model assumption that the biocide product has permeated the entire piece of treated wood.

From this it can be seen that the overall uncertainty is rather large (over two orders of magnitude), underlining the observations made earlier. Nevertheless, the model with the proposed parameter defaults performs well. The modelled concentrations are in the right order of magnitude. Most of the uncertainties mentioned above could be reduced by the use of more specific and better quality data. The effect of model uncertainty is limited to about one order of magnitude (analysis not shown here).

5.3 Impact of sorbing surfaces: emission of DEHP from vinyl flooring

In the model proposed in this report a number of simplicifications has been made. Most notably, sorption of the chemical substance to indoor surfaces such as wall, rooms, furniture, dust and human skin are neglected. This simplification is appropriate for volatile substances, however for low volatile substances such as SVOCs it is inaccurate. To explore the implications and impact of this simplifying assumption, the results of the model developed in chapter 2 are confronted with the results of a more detailed indoor air model that includes the effects of sorption to and re-emission from indoor surfaces. A (mass transfer limited) version emission model including sorption to surfaces has been developed by Xu et al. (2009). This model was parametrised for DEHP emitting from vinyl flooring. In this section this parametrised model is applied to a realistic exposure assessment of DEHP that emits from vinyl sources. This work has been performed in collaboration with the Danish Environmental Protection Agency (DEPA), that provided measured data on the initial concentration of DEHP in a number of consumer products. DEPA also provided exposure scenarios.

5.3.1 *Complete model (Xu et al., 2009) parameter estimates for DEHP*

Sorption to surfaces will only be relevant for low volatile substances. For these substances emission will be mass transfer limited, as was discussed in section 2.3. Sorption and re-emission can, following Xu et al. (2009), under isothermal conditions be described by linear partitioning of the substance between the air layer adjacent to the surface and surface:

$$K_{surf} = C_{surf} / y_{0surf} \tag{22}$$

Here K_{surf} is the surface air partition coefficient, C_{surf} the concentration of substance sorbed on the surface, and y_{surf} the concentration in the air boundary layer. The units of C_{surf} are [mass/surface area], the units of y_{surf} are [mass/volume], from which it follows that K_{surf} has unit of [length].
Transport of the substance from the surface to bulk indoor air is described by mass transfer similar to right hand side of equation *(4)*. The change of the mass concentration on the surface $\frac{dC_{surf}}{dt}$ equals the material flux to the surface:

$$\frac{dC_{surf}}{dt} = h_m \times (y - y_{surf}) \tag{23}$$

For $y > y_{surf}$ this flux is positive and substance adsorbs from the air onto the surface, for $y_{surf} > y$ the flux is negative and substance re-emits into indoor air.
Terms of the form of (23) have to be included in the mass balance equations of the model for each sorbing surface. Xu et al. (2009) include ceilings/walls, glass, furniture and suspended particles. This leads to the following mass balance equation:

$$\frac{dy}{dt} = \frac{h_m S}{V}\left(\frac{C(t)}{K} - y\right) - \sum_{surfaces} \frac{S_i}{V}\frac{dC_i(t)}{dt} - \frac{dF(t)}{dt} - qF - qy \tag{24}$$

The terms in the summation over the surfaces in the equation are determined by a combination of (23) and (24).
The particle-phase air concentration $F(t)$ of the substance is again determined by assuming linear partitioning between suspended particles and air:

$$F = K_{particle} \times TSP \times y_{0p} \tag{25}$$

with TSP the total suspended particle concentration and y_{0p} the gas phase concentration at the particle surface. For the rate of change of the particle phase concentration a mass transfer term similar to (23) can be used:

$$\frac{dF}{dt} = h_{mp} \times (y - y_{op}) \times S_p \tag{26}$$

in which S_p is the surface area of the suspended particles (m^2/m^3 air) and h_{mp} the mass transfer coefficient for particles.

Xu et al. (2009) estimated surface air partition coefficients for DEHP for the included materials and surfaces from laboratory chamber experiments and residential field studies. In particular,

data from the children's total exposure to persistent pesticides and other persistent organic polutants (CTEPP) field study (US-EPA, 2005) were used. In this study, 48-hour integrated media samples were collected at children's homes and daycare centres in North Carolina and Ohio for a large number of SVOCs, including three phthalates. From mass concentrations in the media samples partitioning between various surfaces was inferred. From these data regression relations between vapour pressure and various partition coefficients were established that can be used to estimate surface air partition coefficients for other substances, not included in the CTEPP study.
Xu et al. (2009) give for DEHP the surface air partition coefficients for different materials/surfaces:

Surface	Partition coefficient
furniture, wall and ceiling	2500 (m)
carpet	1700 (m)
glass[1]	3800 $[(\mu g/m^2)/(\mu g/m^3)]^{1.5}$
skin	9500 (m)
airborne particle	0.25 ($m^3/\mu g$)
settled dust	21100 (m^3/g)

[1] For glass, the use of the Freundlich isotherm $C = K \times y^n$ with n = 1.5, rather than a linear partition coefficient was suggested.

The model equation (24) was used to simulate air concentrations of DEHP after emission from vinyl flooring. Initial concentration of DEHP in a specimen of vinyl flooring was determined by DEPA at 15% [w/w].
For this flooring air concentrations resulting from the emission of DEHP were determined for the scenario assumptions given below:

surface area vinyl flooring	10 (m^2)
room volume	27.5 (m^3)
ventilation rate	0.2 (ACH)
wall surface	40 m^2
window surface	1.5 m^2
vinyl air partition coefficient DEHP	2.3e11
mass transfer coefficient	0.0025 (m/s)
simulation duration	200 (days)

As sorbing surfaces only ceilings/walls windows were included as representative information on settled dust and airborne, particulates were not available.

In Figure 12 a graph of the air concentration for this scenario is shown (dashed line). For comparison, a plot of the air concentration for the model without the presence of sorbing surfaces is included (solid line). This situation corresponds to the simpler model derived in chapter 2. From this it can be observed that the steady state air concentrations in both cases are the same (0.9 $\mu g/m^3$). The consequence of the presence of sorbing surfaces impacts the time it takes to reach this (quasi-)steady state for the air concentration. In this case, with the sorbing surfaces present, air concentration reaches a steady state after about 250 days. Without the sorbing surfaces, the same air concentration level is reached almost instantaneously. For this example, it can be concluded that the long-term emissions can very well be estimated using the simplified model of chapter 2. This model will overpredict air concentrations in the initial stages of emission, but maximum (quasi-steady state) levels are not impacted by the presence of sinks.

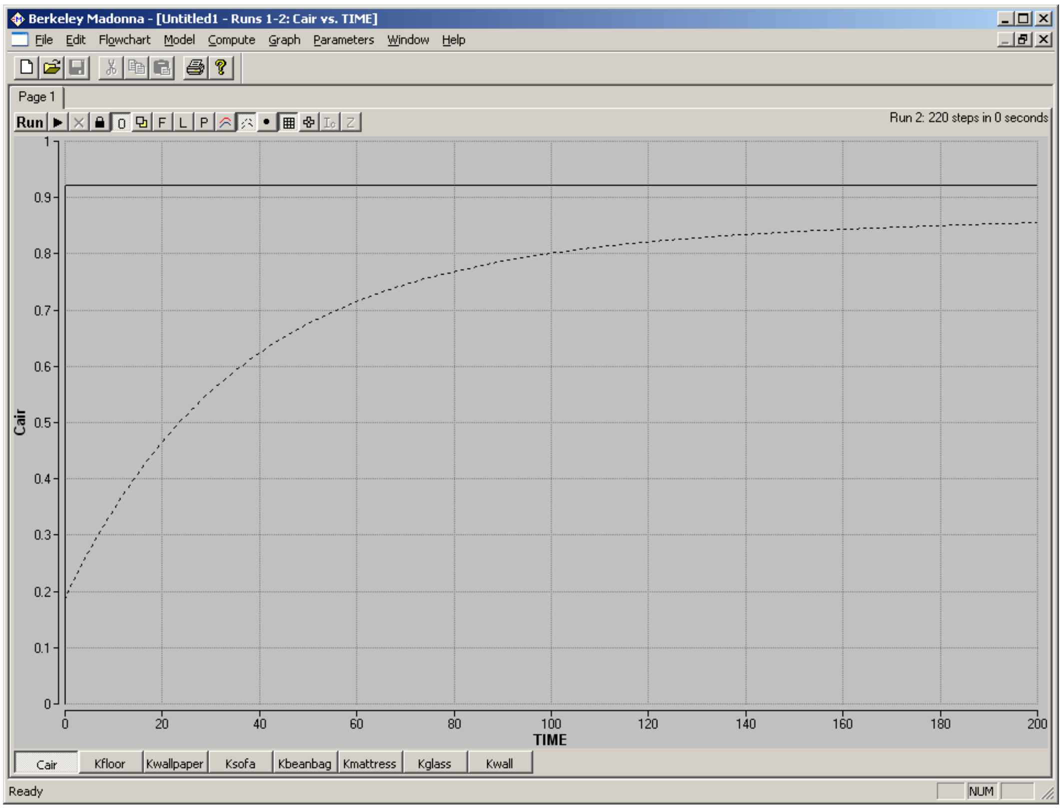


Figure 12. Evaluation of the effect of the presence of walls and glass as a sink on the air concentration of DEHP emitted from vinyl flooring.

The graph is a screenshot of the Berkley Madonna modelling software. The dashed line is the concentration time profile of the model including wall and glass windows as a sink. The solid line is the model without any additional sinks, other than ventilation. The air concentration is in µg/m^3. Time is in days.

5.4 Summary

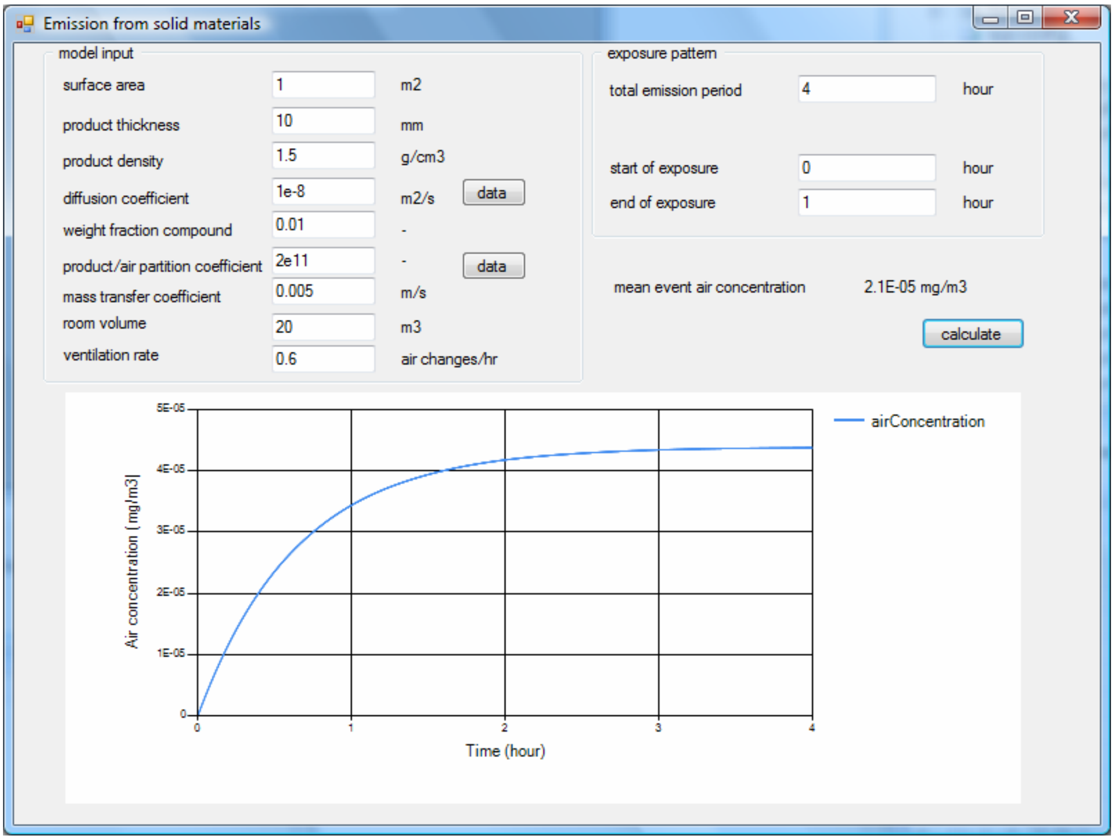
In this chapter the method recommended in chapter 4 is tested in two case studies. Emission of DEHP from vinyl and IPBC from treated wood were simulated and compared with emission experiments. Also, an analysis of the uncertainty in the modelled emissions was performed. The simulated results were in good agreement with the measurements. However, especially in the IPBC case, the estimated uncertainty in the simulated results was considerable. This was mostly due to lack of data on the matrix (wood) and on model uncertainty (i.e. whether the assumption that the concentration of IPBC in wood was uniform after treatment was justified). The considered cases studies consisted of fairly well-defined experiments, a situation that is not representative for typical exposure estimation situations. Testing the model in less defined situations should be performed. In these situations the uncertainty will usually be even larger.
A consideration of the simplification of the model by excluding sorption to surfaces such as walls, windows, dust et cetera, revealed that the maximum (quasi-)steady state air concentrations are hardly effected by the presence of other sinks, apart from ventilation. These sinks only have an impact on the time it takes to reach the maximum. This leads to the conclusion that the simplified model proposed in this report can be very well used as a screening method for assessing maximum air concentration levels. Only for detailed, time-dependent modelling, the simplifications of the model may hamper its accuracy.
In addition, the impact of a simplifying assumption of the model (namely, the neglecting of the presence of sinks) was tested in a case study for the emission of DEHP from various consumer

products. In the evaluated case, the presence of sinks only impacted the time the system took to reach (quasi-)steady state conditions, but not the steady state concentration level itself, suggesting that omission of sinks will result in a reasonable order of magnitude estimate for long term exposures, but may overestimate short-term emissions.

6 Emission modelling tool

The model described in chapter 2 has been implemented in a MS Windows program, to facilitate use of the model in exposure assessment.
In due time, the model is to be implemented in the consumer exposure modelling tool ConsExpo (Delmaar et al., 2005). The developed stand alone program described in this section is expected to be a temporary solution only.

The user interface of the program is shown in Figure 13.



model input		
surface area	1	m2
product thickness	10	mm
product density	1.5	g/cm3
diffusion coefficient	1e-8	m2/s
weight fraction compound	0.01	-
product/air partition coefficient	2e11	-
mass transfer coefficient	0.005	m/s
room volume	20	m3
ventilation rate	0.6	air changes/hr

exposure pattern		
total emission period	4	hour
start of exposure	0	hour
end of exposure	1	hour

mean event air concentration 2.1E-05 mg/m3

Figure 13. The user interface of the emission modelling tool.

In the ‘model input’ section in the upper left group box, model parameters describing substance, material and residential environment must be entered. In the ‘exposure pattern’ group box in the upper right, information on emission and exposure durations must be specified. The graph in the lower half shows the air concentration time profile over the entire emission period after the ‘calculate’ button is pressed.

The program simulates indoor air concentrations from basic information on the substance, material from which the substance emits, and information on the indoor environment.
The emission is assumed to start from time t=0 and to continue over the ‘total emission period’. The calculated air concentration for the entire emission duration is shown in a graph. Mean event air concentrations can be evaluated for a single exposure event by specifying ‘start of exposure’ (t_{start}) and ‘end of exposure’ (t_{end}) times respectively. This mean event air concentration $<y_{air}>$ is determined by averaging the modelled air concentration (obtained from equation ***(6)*** in chapter 2) over the exposure duration specified by the user:

(27) $$\langle y_{air} \rangle = \frac{1}{t_{end} - t_{begin}} \int_{t_{begin}}^{t_{end}} y_{air}(t)dt$$

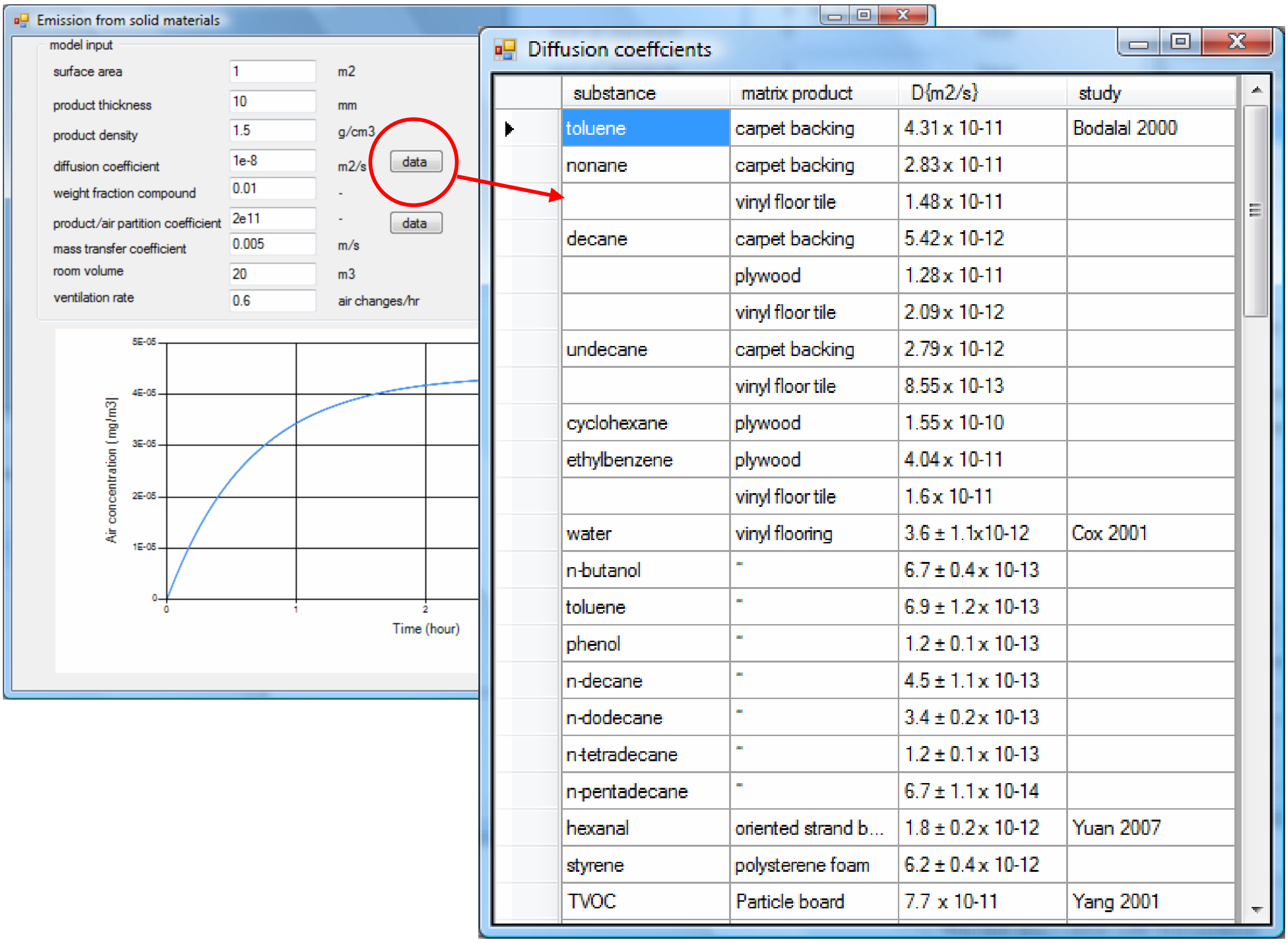
The input required by the program corresponds to the model input specified in section 2.3. In overview below the correspondence between model inputs in section 2.2 and the program input parameters is given.

Table 5. Correspondence of terminology between emission tool and text in report

Model Symbol	Description	Program input name	units
S	area of the emitting surface of the material	surface area	m^2
L	thickness of the material	product thickness	mm
C_o	initial concentration of the substance in the material	Combination (multiplying) of: 'weight fraction compound' and 'product density'	g/cm^3
V	volume of the room	room volume	m^3
q	ventilation fold of the room	ventilation rate	1/s
D	diffusion coefficient	diffusion coefficient	m^2/s
K	material air partition coefficient	product air partition coefficient	-
h_m	mass transfer coefficient	mass transfer coefficient	m/s

Simulations using the program are performed by specifying appropriate values for all input parameters in the required units and then pressing the 'calculate' button. As this program is anticipated to be only a temporary implementation, output options have been kept minimal. Program output is limited to the 'mean event air concentration'. In exposure and risk assessments, this output should be further processed outside this program (for example, to calculate inhaled doses et cetera).

For the parameters 'diffusion coefficient D' and the 'product air partition coefficient K' the databases with values collected from literature (Tables 1 and 2 in chapter 3) have been made available for reference in the program. Next to the parameter edit text boxes for these parameters, buttons with the text 'data' have been placed. Pressing these will open the database (see Figure 14 below for an example of the diffusion coefficient database).
As was reported in chapter 3, the diffusion coefficient of a substance in a solid material, not bound to the matrix is usually between 10^{-10} – 10^{-13} m^2/s, for solid matrices and up to 10^{-8} m^2/s for porous materials.
The material air partition coefficient K shows a wider variation, depending on the volatility (i.e. vapour pressure) of the substance. In chapter 3, data and estimation methods for K are given.
The mass transfer coefficient h_m is determined by air movement over the surface, surface shape and roughness and diffusivity of the substance in air. Methods for estimating this parameter are also given in chapter 3. In practice, its value will be in the range of 0.0005 – 0.003 m/s.



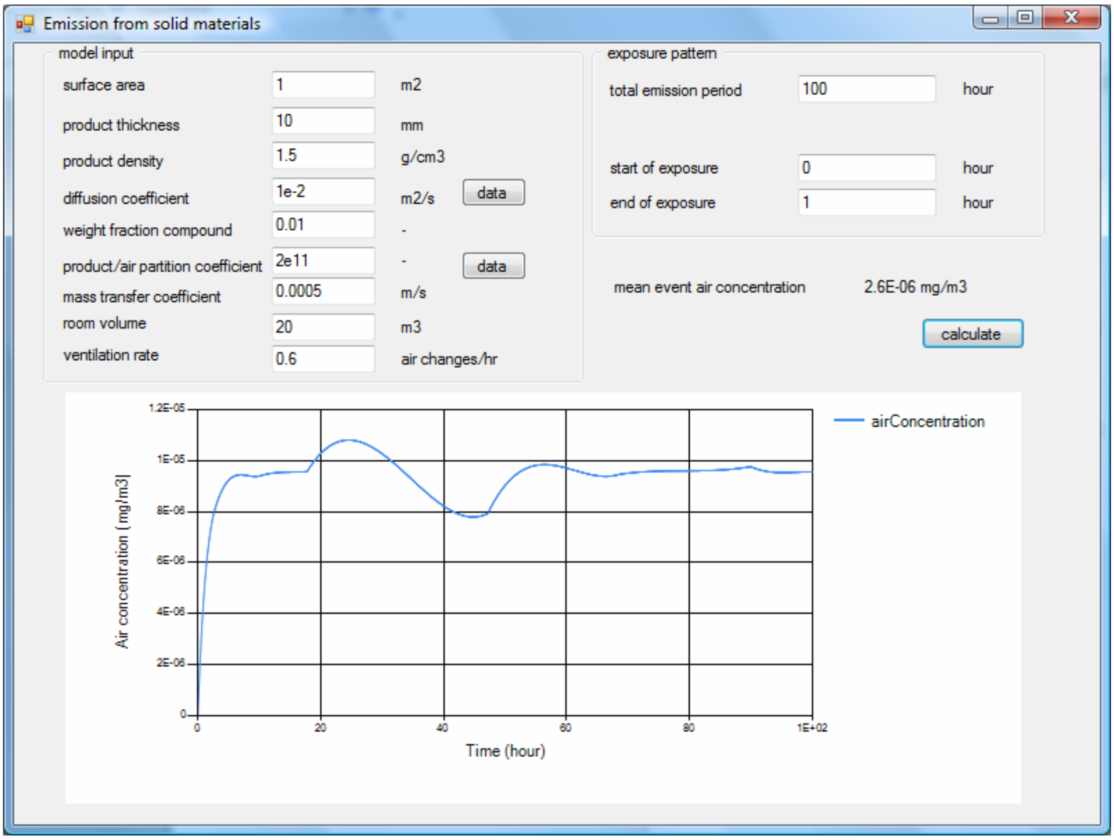
model input		
surface area	1	m2
product thickness	10	mm
product density	1.5	g/cm3
diffusion coefficient	1e-8	m2/s
weight fraction compound	0.01	-
product/air partition coefficient	2e11	-
mass transfer coefficient	0.005	m/s
room volume	20	m3
ventilation rate	0.6	air changes/hr

substance	matrix product	D{m2/s}	study
toluene	carpet backing	4.31 x 10-11	Bodalal 2000
nonane	carpet backing	2.83 x 10-11	
	vinyl floor tile	1.48 x 10-11	
decane	carpet backing	5.42 x 10-12	
	plywood	1.28 x 10-11	
	vinyl floor tile	2.09 x 10-12	
undecane	carpet backing	2.79 x 10-12	
	vinyl floor tile	8.55 x 10-13	
cyclohexane	plywood	1.55 x 10-10	
ethylbenzene	plywood	4.04 x 10-11	
	vinyl floor tile	1.6 x 10-11	
water	vinyl flooring	3.6 ± 1.1x10-12	Cox 2001
n-butanol	"	6.7 ± 0.4 x 10-13	
toluene	"	6.9 ± 1.2 x 10-13	
phenol	"	1.2 ± 0.1 x 10-13	
n-decane	"	4.5 ± 1.1 x 10-13	
n-dodecane	"	3.4 ± 0.2 x 10-13	
n-tetradecane	"	1.2 ± 0.1 x 10-13	
n-pentadecane	"	6.7 ± 1.1 x 10-14	
hexanal	oriented strand b...	1.8 ± 0.2 x 10-12	Yuan 2007
styrene	polysterene foam	6.2 ± 0.4 x 10-12	
TVOC	Particle board	7.7 x 10-11	Yang 2001

Figure 14. Model parameter database.

A database containing information on diffusion coefficients of various substances and materials can be consulted from within the program, pressing the 'data' button next to the diffusion coefficient input box. A similar database is included with information on the material air partition coefficient K.

The emission tool has been developed in MS Visual C# 2008 express edition. For numerical integration of the model equations, use has been made of the DotNumerics libraries for Visual Studio (DotNumerics, 2010). The integration method is 'Implicit 5 Point Runge Kutta'. While numerical integration with this method succeeds over a broad range of input parameter values, the method may break down for certain combinations of input parameters. Specific validity boundaries on parameters cannot be given, but problems can typically arise for relatively high values of the diffusion coefficient (in the order of ~0.01 m^2/s) combined with small product thickness (for example, < 1 mm) and/or low values of the mass transfer rate (for example, < 0.0005 m/s). Also, for very high values of the product air partition coefficient (e.g. > 1 x 10^6) integration may become problematic.
It is always advised to inspect the resulting air concentration graph for anomalies (such as for example shown in Figure 15).
Improvement of the tools performance may be obtained by implementing implicit numerical solvers such as the Gears BDF method available in the DotNumerics libraries (DotNumerics, 2010). Another possible improvement may be to implement the explicit mass transfer limited version of the model (see section 2.3) for high values of the diffusion coefficient and thin layers of product. However, it should be noted that stable numerical integration over the entire range of possible parameter inputs will probably not be achievable in practice.



model input

surface area	1	m2
product thickness	10	mm
product density	1.5	g/cm3
diffusion coefficient	1e-2	m2/s
weight fraction compound	0.01	-
product/air partition coefficient	2e11	-
mass transfer coefficient	0.0005	m/s
room volume	20	m3
ventilation rate	0.6	air changes/hr

exposure pattern

total emission period	100	hour
start of exposure	0	hour
end of exposure	1	hour

mean event air concentration 2.6E-06 mg/m3

Figure 15. Anomalic behaviour of the calculated air concentration.
It indicates a combination of input parameters that are outside the validity domain of the numerical integrator. These results should not be trusted.

7 Discussion and recommendations

7.1 Emission model for substances from solid materials

The purpose of this work was to develop a method for estimating the emission of substances from solid materials. Such a method is needed to evaluate the safety of articles, treated articles and other solid material consumer products that contain potentially harmful chemical substances. At present, such a method is not available and risk assessors have to revert to very inaccurate, conservative, low tier modelling approaches.

The method developed in this work is based on well-established and tested models in the field of chemical emissions from building materials. The proposed model describes the diffusion of a substance in the solid material to the surface of the material and subsequent emission into indoor air. The emitted substance is assumed to be removed by ventilation only. Degradation of the substance and other sinks are not considered. This limitation of the accuracy of the model may be especially important for low volatile substances that are known to adsorb to indoor surfaces, dust and humans, potentially leading to much lower air concentrations than predicted by the model. A limited test demonstrated that especially initial emissions are effected by this simplification. These initial emissions may take a long time (i.e. several months or years). Another limitation of the model as developed in this document is that it is strictly valid only for a specific geometry of the product: a product with a large surface area and small thickness. This geometry is expected to describe most products that have a large surface area, such as carpets, table tops et cetera. These types of products will constitute the most important products in view of their large emission potential due to their large emitting surfaces. But the model can also be easily extended to other product geometries as well.

In order to use the model, a number of model parameters have to be specified. The most critical parameters are the concentration of the substance in the product, the diffusion coefficient D of the substance in the product, the material air partition coefficient K of the substance in the product, and the mass transfer coefficient h_m of the substance. The initial concentration of the substance is assumed to be known in any exposure assessment. The other model parameters D, K and h_m are substance/material and scenario-specific. Ideally, these would all be accurately specified for any substance and product for which an assessment has to be made. However, in practice, appropriate data for these parameters will seldom be available.

To this end, a search in literature was conducted to collect numerical values for these parameters for different materials and substances, and for methods to estimate these parameters. From this search a database with reference values to be used in exposure assessments may be compiled. For the mass transfer coefficient scientifically well-founded theoretical estimation methods were found. For the diffusion coefficient D, and especially the partition coefficient K, only a limited amount of data was found. It is not to be expected that the database of these collected values will be sufficient to provide accurate data in routine exposure assessments. For realistic, accurate exposure assessment it is expected that separate (experimental) determination of D and K will be necessary.

7.2 Using the method in screening assessments

In spite of the fact that the use of the developed method will be hampered in routine exposure assessments, the method will still be useful as a screening tool. From the results of the data collection, general inferences on the approximate (range of) values of the model parameters can be made. From these inferences, default parameter values and methods for estimating the model parameters are recommended. These may be used to make an order of magnitude estimation of the air concentrations resulting from the emission of chemicals from solid products. It should be kept in mind, however that using the model in combination with the suggested defaults will lead to large uncertainties in the estimated exposure levels. The uncertainty ranges in the parameters span several orders of magnitude. An assessment using the defaults can also not be interpreted as an upper level of exposure. Exposure may be underestimated in particular cases. Using the model in screening assessments should always be accompanied with a consideration of the uncertainty. Rather than using only point estimates for the uncertain parameter values, the entire range of possible parameter values should be taken into account. This can be done with the relatively simple method of factorial design. This consideration of the uncertainty will give important insight in the quality and limitations of the assessment and may aid in increasing the robustness of the exposure assessment.
The default method was tested in two case studies. For two well-defined situations, in which case experimentally determined emission data were present, the model was used to simulate the resulting air concentrations. The results were satisfactory. In both cases the simulated results were of the same order of magnitude as the experimental data.

7.3 Recommendations

The model described in this report is believed to be appropriate to simulate the emissions for a wide variety of substances and materials. However, the applicability of the model in regulatory exposure assessments (REACH, regulation on biocides) could be greatly enhanced if more good quality data on the fundamental model parameters would be available. Also, additional testing and validation of the model would greatly provide invaluable insight in the limitations of the model and thereby improve confidence in its use.
Therefore the recommendations are as follows:

1) Firstly, the database on parameter values should be extended to include data on substances and materials that are more representative for products usually regarded in these assessments. For example, data on a number of pesticides for a set of relevant materials (such as wood, plastics et cetera) should be a very valuable addition to the database. As such data are only sparingly published in literature, it is recommended that experimental data collection efforts are actively encouraged. This should be preceded by an inventory of the most frequently evaluated substances and products. Data collection should focus on the determination of material air partition coefficients and diffusion coefficients. Different methods to directly determine these parameters exist. But these parameters could, in principle, also be determined from fitting the model to emission experiments. In this latter case, it is important to note that such an emission experiment is conducted in a relevant time interval. It is essential that a sufficient number of time samples be taken and also that the different phases of emission are adequately sampled (i.e. the onset of emission, the peak of the emission and the decay of concentration levels). The exact sampling strategy should be determined for each experiment separately as it depends critically on the substance, the material and the experimental conditions. In this respect the model and the proposed defaults will be a good starting point to establish this optimal sampling strategy. Such data collection effort could be promoted by setting up partnerships

between RIVM and other (experimental) institutes such as the Swiss Federal Institute of Technology (ETH) Zürich and the Virginia Tech University.

2) Secondly, the method developed in this document should be tested in a number of typical exposure assessments. In this document, the method was only tested in two, comparatively data rich, case studies. Testing the method for more representative (data poor) cases will:
   - help to evaluate the applicability of the method and develop casuistry that can serve as reference material for users of the method;
   - identify the most important data gaps, and in this way provide guidance on the type of data that should be collected in additional data collection efforts.
3) Thirdly, the model, which is explicitly developed for large surface area products with a relatively small thickness, should also be tested for other product shapes. This can be done by developing models for other shapes (e.g. cubical, spherical, cylindrical products) and comparing model assessments. It does not require experimenting. If large discrepancies between various product shapes are found, models for important product geometries should also be developed.
4) Finally, the model developed in this work, describes the emission of substances into air. From air, inhalation, dermal and oral exposure may occur. Dermal exposure by direct contact with the products surface may be an important exposure pathway for chemical substances as well. The model can, in principle, be extended to describe such exposures as well. It is recommended that the mechanisms of exposure by direct dermal contact be studied to evaluate whether and how this exposure pathway could be incorporated in the model.

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Appendices

Appendix I: Berkley Madonna code of emission model including sinks

```
METHOD stiff
STARTTIME = 0
STOPTIME = 1000 {1000 days ~ 3 years }
DT = 1000/500

{********************************************}
{ Implements the model developed and parametrised in :

Xu Y, Cohen Hubal A, Clausen PA, Little JC, 2009. Predicting Residential Exposure to Phthalate
Plasticizer Emitted From Vinyl Flooring: A Mechanistic Analysis. Environ. Sci. 43: 2374-2380.


Model and parameters for DEHP are used to model air concentrations on behalf and in
collaboration with Danish EPA.
Product samples were taken by DEPA, DEHP concentrations in vinyl flooring, vinyl wallpaper, a
leather sofa, a bean bag toy, and a mattress, were measured. The model was used to simulate
air concentrations for different combinations of products in a small, poorly ventilated room.

As possible sinks wall/ceiling, carpet, glass and total suspended particles were included. The
partition coefficients were obtained from Xu et al. 2009. The size (surface area) of these sinks
can be modified in the model.

}

{ *********************************** }
{       PARAMETERS                  }
{ *********************************** }

Cair=Ctot1

{ SOURCES }
Sfloor          = 10            {surface area vinyl flooring in m^2}
Swallpaper      = 0             {surface area wall paper in m^2}
Ssofa           = 0             {surface area sofa in m^2}
Sbeanbag        = 0             {surface area beanbag in m^2}
Smattress       = 0             {surface area mattress in m^2}

{ INITIAL CONCENTRATIONS SOURCES µg/m3 }
{ Data on sample concentrations provide by Danish EPA 2009 }
Cofloor         = 225*1e9
Cowallpaper     = 150*1e9
Cosofa          = 0
Cobeanbag       = 0
Comattress      = 225*1e9

{ ROOM CHARACTERISTICS}
{Scenario assumptions provided by Danish EPA, 2009}
Vr1     = 27.5          {room volume in m^3}
q1      = 0.2 * 24      {ventilation fold room in times/day}
```

```
{ SINKS ROOM}
{surface areas can be canged to adjust the size of the sink}

Sglass1         = 0     {surface area glass in m^2}
Swall1  = 41    {surface area wall in m^2}
Sparticle1      = 0     {particles surface area density m^2/m^3}
Scarpet1        = 0

{ SUBSTANCE PROPERTIES }
PvapDEHP        = 1.43e-7       { mmHg }
mwDEHP          = 391           { g/mol }


{ PARTITION COEFFICIENTS }
{ partition coefficients per plasticiser }
{DEHP}
{volume partition coefficients sources in [m] }
kfDEHP          = 2.3e11        {floor}
kwpDEHP         = 2.3e11        {wallpaper}
ksDEHP          = 2.3e11        {sofa}
kbbDEHP         = 2.3e11        {bean bag}
kmDEHP          = 2.3e11        {mattress}

{surface partition coefficients sinks, in [m]}
kwDEHP          = 2500          {wall}
kgDEHP          = 3800          {glass}
kcDEHP          = 1700          {carpet}
kpDEHP          = 0.25          {m^3/ug}  {particles}
kdDEH  P        = 21100         {m^3/g}


{GENERAL MODEL PARAMETERS}
hm      = 0.0025*3600*24        {m/day}
TSP     = 0                     {ug/m^3}
TDC     = 0                     { dust concentration in room g/m^3}
Nfr     = 1.5                   {non linear Freundlich isotherm coefficient glass}

{volume partitioning flooring air, dimensionless}
Kfloor          = kfDEHP
Kwallpaper      = kwpDEHP
Ksofa           = ksDEHP
Kbeanbag        = kbbDEHP
Kmattress       = kmDEHP

{surface partition coefficients, in m}
Kglass          = kgDEHP
Kwall           = kwDEHP
Kcarpet         = kcDEHP
Kpart           = kpDEHP
Kdust           = kdDEHP



{ ***********************************  }
{        initial conditions             }
{  ********************************** }
init Ctot1 = 0

init Cfl  = Cofloor
```

```
init Cwp = Cowallpaper
init Cs  = Cosofa
init Cbb = Cobeanbag
init Cm = Comattress

init Cgl1          = 0
init Cw1           = 0
init Cc1           = 0

{ ************************************}
{        MODEL EQUATIONS                }
{ ************************************}
{sources}
Gfloor             = Sfloor * hm/Vr1
Gwallpaper         = Swallpaper * hm/Vr1
Gsofa              = Ssofa * hm/Vr1
Gbeanbag           = Sbeanbag*hm/Vr1
Gmattress          = Smattress*hm/Vr1

{ MASS BALANCE EQUATIONS ROOM 1 }
ddtCfl             = Gfloor * (y1 - Cfl/Kfloor)
ddtCwp             = Gwallpaper * (y1 - Cwp/Kwallpaper)
ddtCs              = Gsofa * (y1 - Cs/Ksofa)
ddtCbb = Gbeanbag * (y1 - Cbb/Kbeanbag)
ddtCm  = Gmattress * (y1 - Cm/Kmattress)

{sinks}

Gglass1= Sglass1 * hm/Vr1
Gwall1             = Swall1*hm/Vr1
Gcarpet1           = Scarpet1 * hm/Vr1

ddtCgl1            = Gglass1 * (y1 - (Cgl1/Kglass)^(1/Nfr))
ddtCw1             = Gwall1 * (y1 - Cw1/Kwall)
ddtCc1             = Gcarpet1 * (y1-Cc1/Kcarpet)

{mass balance equations }

y1 =   Ctot1/ (1 + TSP/Kpart + TDC/Kdust)
d/dt (Ctot1 ) = - ddtCfl - q1 * Ctot1 - ddtCwp - ddtCs - ddtCbb - ddtCm -ddtCgl1 - ddtCw1 -
ddtCc1

d/dt (Cfl)         =  ddtCfl
d/dt (Cwp)         =  ddtCwp
d/dt (Cs)          =  ddtCs
d/dt (Cbb)         =  ddtCbb
d/dt (Cm)          =  ddtCm

d/dt (Cgl1)        =  ddtCgl1
d/dt (Cw1)         =  ddtCw1
d/dt (Cc1)         =  ddtCc1
```

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