Emissions of organic compounds from technosphere articles

Measurement and modeling of mass transfer from consumer goods and building materials to air and water

Tomas Holmgren
Den mätta dagen, den är aldrig störst.  
Den bästa dagen är en dag av törst.  
Nog finns det mål och mening i vår färd men det är vägen, som är mödan värd.

(The sated day is never first.  
The best day is a day of thirst.  
Yes, there is goal and meaning in our path - but it's the way that is the labour's worth.)

Karin Boye, Härarna, 1927

"Mina målningar, sade Brokiga Blad, föreställer bara saker och ting. Föremålen som jag målar utgör så att säga ombud. Det är en ofantlig skillnad på att vara och att föreställa."

(“My paintings, said Brokiga Blad, is just an image of things. The objects that I paint are, so to say, representatives. There is a huge difference between an image and really being.”)

Torgny Lindgren, I Brokiga Blads vatten, 1999
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Abstract

This thesis describes the development of a generic model for predicting the emissions of organic compounds from materials used in the manufacture of various goods and products. Many products contain organic substances that are not bound to the matrix formed by their constituent materials and are thus able to dissociate from the material and become transferred into the surrounding environment. A wide range of materials and products are used in modern societies, and many compounds deriving from these materials are regarded as emerging pollutants in both indoor and outdoor environments.

The model uses three components to describe the transfer of compounds from materials to the surrounding environment: partitioning of the compound between the material and its surroundings based on linear free energy relationships, diffusion within the material based on the Piringer equation, and convective mass transfer in air or water based on an empirical flat surface model. The model’s predictive capacity was tested against three experimental case studies: emissions of plasticizers from vinyl flooring and triphenyl phosphate from LCD screens into the air, and leaching of organophosphates from concrete into water. The rates of emission from vinyl flooring were clearly affected by the number of layers comprising the material. Triphenyl phosphate was found in the front surface of all tested flat screens and its rates of emission were related to the nature of the screen and its operating temperature. The model accurately predicted emissions into the air and leaching from concrete into water once modified to include modules that describe dissolution from surfaces and diffusion in water-filled pores.

The model was then used to investigate emissions on the national scale. It was found that the rates of emission from vinyl flooring are not changing over time, and that the total mass of emitted material is dependent on annual sales volumes and the expected life span of the vinyl flooring. Moreover, the additive used has a large effect on the emitted mass. Emissions from flat screen displays depend strongly on their operating temperatures: displays with high working temperatures that are active for extended periods of time produce more emissions. The model was also used to study the release of organophosphates from the concrete used to make a bridge, which depended on the flow of water under the bridge, the temperature, the porosity of the concrete, and the additive’s water solubility. Data on annual sales volumes and the total surface area of sold goods are essential when studying emissions on a national scale. National retailers’ organizations are valuable sources of such information. When adequate data are not available, it is necessary to perform uncertainty analyses to determine the impact of uncertainty in the modeling of different stages of the emissions process in different scenarios.
List of papers

I. A generic emission model to predict release of organic substances from materials in consumer goods
   Tomas Holmgren, Leif Persson, Patrik L. Andersson, Peter Haglund

II. Measurement and modeling of organophosphates leaching from concrete to water
    Tomas Holmgren, Patrik L Andersson, Peter Haglund
    *Submitted manuscript*

III. Modeling and measurement of triphenyl phosphate emissions from flat screens
     Tomas Holmgren, Patrik L Andersson, Peter Haglund
     *Submitted manuscript*

IV. Emissions of two phthalate esters and BDE 209 to indoor air and their impact on urban air quality
    Anna Palm Cousins, Tomas Holmgren, Mikael Remberger
    *Manuscript*
### Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>System coefficient corresponding to hydrogen bond acidity</td>
</tr>
<tr>
<td>$A$</td>
<td>Hydrogen bond acidity</td>
</tr>
<tr>
<td>$A_S$</td>
<td>Surface area</td>
</tr>
<tr>
<td>$Ap$</td>
<td>Material specific coefficient with $\tau$</td>
</tr>
<tr>
<td>$Ap'$</td>
<td>Material specific coefficient</td>
</tr>
<tr>
<td>$b$</td>
<td>System coefficient corresponding to hydrogen bond basicity</td>
</tr>
<tr>
<td>$B$</td>
<td>Hydrogen bond basicity</td>
</tr>
<tr>
<td>$bo$</td>
<td>System coefficient corresponding to hydrogen bond basicity</td>
</tr>
<tr>
<td>$Bo$</td>
<td>Hydrogen bond basicity</td>
</tr>
<tr>
<td>$c$</td>
<td>System constant for partition prediction</td>
</tr>
<tr>
<td>$C^0$</td>
<td>Starting concentration</td>
</tr>
<tr>
<td>$C_A$</td>
<td>Concentration in air</td>
</tr>
<tr>
<td>$C_M$</td>
<td>Concentration in material</td>
</tr>
<tr>
<td>$C_S$</td>
<td>Surface concentration</td>
</tr>
<tr>
<td>$C_W$</td>
<td>Concentration in water</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$D_a$</td>
<td>Diffusion coefficient in air</td>
</tr>
<tr>
<td>DEHA</td>
<td>Diethyl hexyl adipate</td>
</tr>
<tr>
<td>DEHP</td>
<td>Di-(2-ethylhexyl) phthalate</td>
</tr>
<tr>
<td>DINCH</td>
<td>Diisononyl cyclohexane-1,2-dicarboxylate</td>
</tr>
<tr>
<td>DINP</td>
<td>Di-iso-nonyl phthalate</td>
</tr>
<tr>
<td>$D_p$</td>
<td>Diffusion coefficient in pores</td>
</tr>
<tr>
<td>$D_M$</td>
<td>Diffusion coefficient in micro-pores</td>
</tr>
<tr>
<td>$D_w$</td>
<td>Diffusion coefficient in water</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$e$</td>
<td>System coefficient corresponding to hydrogen bond acidity</td>
</tr>
<tr>
<td>$E$</td>
<td>Excess molar refraction</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>EF</td>
<td>Emission factor</td>
</tr>
<tr>
<td>FPD</td>
<td>Flame photometric detector</td>
</tr>
<tr>
<td>FLEC</td>
<td>Field and Laboratory Emission Cell</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>$h_m$</td>
<td>Convective mass transfer coefficient</td>
</tr>
<tr>
<td>isDEH</td>
<td>Diethyl hexylisoborate</td>
</tr>
<tr>
<td>$K$</td>
<td>Partition coefficient</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Coefficient of mass transfer</td>
</tr>
<tr>
<td>$K_{A/W}$</td>
<td>Air/water partition coefficient</td>
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<tr>
<td>$K_{M/A}$</td>
<td>Material/air partition coefficient</td>
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<tr>
<td>$K_{M/W}$</td>
<td>Material/water partition coefficient</td>
</tr>
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<td>$K_S$</td>
<td>Solubilization coefficient</td>
</tr>
<tr>
<td>$K_H$</td>
<td>Henry's law constant</td>
</tr>
<tr>
<td>$I$</td>
<td>System coefficient corresponding to Log (gas-hexadecane partition coefficient)</td>
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<tr>
<td>$L$</td>
<td>Logarithm of gas-hexadecane partition coefficient</td>
</tr>
<tr>
<td>LOQ</td>
<td>Limit of quantification</td>
</tr>
<tr>
<td>$L_D$</td>
<td>Diffusion length</td>
</tr>
<tr>
<td>$L_M$</td>
<td>Length of material</td>
</tr>
<tr>
<td>$M_0$</td>
<td>Total emittable mass per unit area of product surface</td>
</tr>
<tr>
<td>$m(t)$</td>
<td>Emitted mass per m² at time t</td>
</tr>
<tr>
<td>$m_{Dp}(t)$</td>
<td>Emitted mass from pores per m² at time t</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$m_{\text{DM}}(t)$</td>
<td>Emitted mass from micro pores per m$^2$ at time $t$</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>Mw</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PET</td>
<td>Poly ethylene terephthalate</td>
</tr>
<tr>
<td>PLE</td>
<td>Pressurized liquid extraction</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly methyl methacrylate</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>$p_a$</td>
<td>Vapor pressure of compound A</td>
</tr>
<tr>
<td>$p_a^*$</td>
<td>Partial pressure of compound A</td>
</tr>
<tr>
<td>$r$</td>
<td>Solute radius</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant: 8.31415 J mole$^{-1}$K$^{-1}$</td>
</tr>
<tr>
<td>REACH</td>
<td>Registration, Evaluation, Authorization and Restriction of Chemical substances</td>
</tr>
<tr>
<td>$s$</td>
<td>System coefficient corresponding to Polarizability /dipolarity</td>
</tr>
<tr>
<td>$s_{\text{dev}}$</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>S</td>
<td>Polarizability /dipolarity</td>
</tr>
<tr>
<td>$S_W$</td>
<td>Water solubility</td>
</tr>
<tr>
<td>$S_a$</td>
<td>Sorption or solubility of compound A</td>
</tr>
<tr>
<td>SER</td>
<td>Specific area emission rate (µg/m$^2$h)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>t</td>
<td>Time (s)</td>
</tr>
<tr>
<td>TBP</td>
<td>Tributyl phosphate</td>
</tr>
<tr>
<td>TiBP</td>
<td>Triisobutyl phosphate</td>
</tr>
<tr>
<td>TPP</td>
<td>Triphenyl phosphate</td>
</tr>
<tr>
<td>$u_m$</td>
<td>Recipient velocity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$\nu$</td>
<td>System coefficient corresponding to McGowan volume: van der Waals molecular volume/100</td>
</tr>
<tr>
<td>$V$</td>
<td>McGowan volume: van der Waals molecular volume/100</td>
</tr>
<tr>
<td>$V_A$</td>
<td>Molecular volume of the emitting additive</td>
</tr>
<tr>
<td>$V_B$</td>
<td>Molecular volume of air (20.1 cm$^3$/mol)</td>
</tr>
<tr>
<td>$x$</td>
<td>Material thickness</td>
</tr>
<tr>
<td>$x_a$</td>
<td>Mole fraction of compound A</td>
</tr>
<tr>
<td>$y$</td>
<td>Background concentration in recipient</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Partition coefficient x Diffusion coefficient / (convective mass transfer coefficient x material thickness)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Porosity in volume by volume</td>
</tr>
<tr>
<td>$\mu_a$</td>
<td>Viscosity of air</td>
</tr>
<tr>
<td>$\mu_W$</td>
<td>Viscosity of water</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of the medium</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>Density of air</td>
</tr>
<tr>
<td>$\rho_W$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\tau_M$</td>
<td>Temperature dependent material specific activation energy parameter</td>
</tr>
</tbody>
</table>
Enkel sammanfattning på svenska


Denna avhandling presenterar en generell modell som uppskattar utsläpp av organiska föreningar från material. Modellen består av tre moduler: den första bestämmer fördelningen i gränsskiktet mellan material och omgivning med hjälp av energiberäkningar, den andra beräknar hur ämnet rör sig i materialet från en del med högre koncentration till en med lägre och den sista beräknar hur utsläppet påverkas av omgivande mediums, tex luft eller vatten, temperatur och hastighet. Modellen har utvärderats med tre fallstudier.

För två av fallstudierna byggdes en emissionskammare i rostfri plåt med vilken utsläpp till luft kunde mätas. I det första studerades utsläpp av två mjukgörare (DINP och DINCH) från olika vinylgolv och dessa experiment visade att ytbehandling av materialet kan påverka utsläppen. I det andra placerades en LCD-TV i emissionskammaren och utsläppen av trifenylfosfat mättes då skärmens både var av- eller påslagen. Då fosfaten främst förekom i yttersta skiktet på skärmyn gjordes även separata mätningar på enbart skärm. Utsläppen visade sig vara tydligt kopplade till skärmens temperatur. Detta betyder att utsläppen var mycket högre för påslagen TV och att skärmar baserade på LCD eller LED teknik släpper ut mindre mängd additiv än skärmar med plamateknik då de senare har högre driftstemperatur. I den sista fallstudien mättes utsläppen av tributylfosfat från betong till vatten. Halten av emitterad substans mättes i vatten som cirkulerade runt gjutna betongcylindrar. Utsläppen var till att börja med mycket stora (10-tals %) och föll sedan till en lägre konstant nivå. Porositeten i betongen visade sig ha betydelse för utsläppen.
Modellerna visade generellt stor överensstämmelse med uppmätta emitterade halter. I fallet med betong krävdes ett tillägg av beräkningsdelar för upplösning från ytor och rörelser i vattenfyllda porer.

Modellerna tillämpades även på nationell skala och visade att utsläppshastigheten av ftalater från vinylgolv är relativt konstant under ett golvs livslängd. Totalt beräknades 250 kg ftalater släppas ut årligen. Modellen visade även att valet av mjukförare har en stor inverkan på den utsläppta mängden.

Utsläppsberäkningar för TV-apparater och datorer visade att dessa släpper ut ungefär lika mycket trifenylosfatt, ca. 2 kg per år. Slutligen tillämpades modellen på en järnvägsbro och utsläpp av organiska fosfater från betong skattades till 8 kg över 8 år vilket motsvarar ca 5% av den ursprungliga mängden.

För att beräkna hur mycket som släpps ut på en nationell nivå så är detaljerad information om sålda produkter eller material från försäljningsorganisationer mycket värdefulla. Vissa produkter har en stor variation i användning och innehåll. För många produkter saknas information om dess material-sammansättning och innehåll av additiv och hur dessa har förändrats över tiden.

Sammanfattningsvis visar denna avhandling att med bra data om användning, innehåll, materialegenskaper och kemikaliegenskaper så kan goda förutsägningar göras om utsläpp till luft och vatten.
1 Introduction

1.1 Background
Modern societies make use of a wide range of products and materials. Some, such as building materials, have long life spans and therefore tend to be stored in large quantities. Others, such as packaging materials, have shorter lifetimes but are used very extensively. New products that use new materials and contain new organic compounds are developed and brought onto the market on a regular basis, where they coexist with stocks of older products. As a result, more than 140000 substances have been pre-registered under the European Union REACH (Registration, Evaluation, Authorization, and Restriction of Chemical substances) regulations, many of which are used to produce materials and products [1]. It has been shown that a number of these registered compounds are emerging pollutants in the environment, including brominated flame retardants, organophosphorous compounds, phthalates and methyl siloxanes [2-8]. Some are found in indoor environments and some may affect human health [9-14].

Many materials and products contain organic compounds that are not bound to the material’s matrix. These compounds can be released into the environment during the product’s manufacturing, distribution, or usage, or as waste. They include residues from natural or manufacturing processes and additives added for some specific purpose. Additives are incorporated during product assembly or by treating the finished product and are used to confer desirable properties. A wide variety of additives are used, including compounds that prolong a product’s useful lifespan, air entraining agents, plasticizers, fillers, flame retardants, stabilizers, impregnating agents, pigments, release agents, blowing agents, etc. Organic compounds can be emitted from products and materials in several ways. These can be collectively grouped into five different routes [15]:

1) Release into and dilution within the surrounding air
2) Release into and dissolution within a surrounding liquid (usually water)
3) Release into and dissolution within a surrounding solid material (diffusion)
4) Release in the form of particles to various surroundings (due to wear)
5) Release as degradation products to various surroundings
The work presented in this thesis focused primarily on the first two routes. Compounds emitted as particles are expected to have the same composition as the original material and so the mechanisms studied should be applicable to the release of molecules from the particulate matter generated via the fourth route[15]. The initial emission routes to the environment are shown in figure 1.

A wide range of experimental setups have been developed for studying the emission of compounds from products and materials. These systems usually require that a sample of the material under investigation be placed into an emission chamber, whose air is then sampled in some way. Chambers with a volume of 1m³ are widely used [3;16-20]. Emissions data from material testing are normally reported in terms of Emission factors, which measure the amount of pollutant emitted from the material per unit area and time (µg/m²h)[21].

However, emission measurements conducted in this way are time consuming and costly, and can only be performed on a limited number of products and compounds. The laboratory setting can also affect the results obtained, which are then used to explain observations made in real-world environments. These problems can be addressed by using empirical and mechanistic mass transfer models, which have the advantage of being cost
effective, capable of predicting outcomes in multiple scenarios, and applicable to both historical and potential future situations [22].

If a material contains or is associated with organic compounds that are not covalently bound to the material’s matrix, these organic compounds may dissociate from the material and be transferred to the surrounding environment. Various methods for describing this process have been presented in the scientific literature.

One approach to describing the emission process is to use the empirical equation of first degree decay in the material, as shown in equation (1). Here, $EF$ is the emission factor (µg/m$^2$h), $k_1$ is the mass transfer coefficient, $M_0$ is the emittable mass per unit area, and $t$ is time [23].

$$EF = k_1 M_0 e^{-k_1 t}$$  \hspace{1cm} (1)

This model can be fitted to describe many different release scenarios but does not describe the underlying mechanism of release, and the estimated mass transfer coefficients are usually only applicable to specific scenarios and thus lack generality.

A more detailed way to describe the mass transfer is to divide the process up into a series of distinct steps. In this approach, one first considers a mass transfer between the material and its surroundings, then a mass transfer within the receiving media (e.g. the ambient air or surrounding water), and finally a mass transfer within the source material [24-29]. The mass transfer within the material is initiated by depletion of the emitted compound at the material’s surface, which generates a concentration gradient within the material (see the cover picture).

The ChEmiTecs research program financed by the Swedish Environmental Protection Agency was established to investigate the emission of organic substances from various goods and materials, and to determine the severity of these emissions within the context of a non-toxic environmental strategy. The research program was divided into eight different projects, as shown in figure 2.

The work presented within this thesis is related to the second project of the ChEmiTecs program. Its objective was to establish a method for identifying representative chemical-material-use combinations that could be used in case-studies. Five such combinations were identified: diisononyl phtalate in
vinyl flooring, perfluorinated compounds in textiles, benzothiazoles in car tires, triphenyl phosphate in electronics, and organophosphates in concrete.

The work presented herein is also related to the fourth project, which deals with the quantification of emissions. The aim of this project was provide fundamental improvements in our understanding of the processes that underpin the emission of organic compounds from materials and goods. This was to be achieved by compiling existing emission factors and generating new ones for specific combination of substances, materials and life cycle phases. These data would then be used to develop generic models capable of predicting the emissions from a broad range of materials and goods under various conditions. When used in conjunction with national statistics and survey data on the flows of goods and waste in society, these models could be used to obtain estimates of emissions on the national level and to predict how they can be expected to change over time.

**Figure 2.** The eight projects of the ChEmiTecs program.
1.2 Aim and hypothesis

The aim of this project was to develop models for calculating and predicting emission factors for organic substances emitted from materials and goods on a national scale. The model was to be developed and validated using data from various case-studies, including emissions of diisononyl phthalate from vinyl flooring into the air, triphenyl phosphate from liquid crystal display screens into the air, and tributyl phosphates from concrete into water.

The hypothesis was that by combining a fundamental understanding of the mechanisms responsible for emissions with existing and newly-measured emission factors, it should be possible to develop generic models capable of predicting the emissions of organic compounds from a wide range of materials used within the technosphere.
2 Experimental

Three experimental studies were performed to measure emissions from different materials. Two focused on emissions into the air – the first concerned emissions of plasticizers from vinyl flowing, while the second measured emissions of triphenyl phosphate from flat screens. The third study dealt with the leaching of organophosphates from concrete into water. Before conducting measurements, the recovery of the analytical methods used was tested. Moreover, blanks were sampled and analyzed in parallel with the experimental samples in all cases.

Measurements of leaching into water were performed by placing concrete samples in 1L jars filled with water for 16 weeks. The water was agitated throughout this period to maintain a surface velocity of 0.4 m/s. Sampling was performed after 4 days, 7 days, and then on a weekly basis for 16 weeks (see figure 3).

Figure 3. The experimental setup used to measure the leaching of tributyl phosphates from concrete into water.

Emissions to air were measured over periods of 10 days using an emission chamber made of stainless steel with an internal volume of 1m³. There was no exposed plastic or rubber within the chamber. The inlet air was filtered, and diffusers were used to generate a laminar airflow within the chamber. An exchange rate of 0.5 air changes per hour was maintained, which is similar to the typical level of indoor ventilation. The outlet air was sampled (every 24 h) via a cooled glass tube and then adsorbed on polyurethane filter plugs (PUFs); see figure 4.
Figure 4. The emission chamber with the PUF sampler and 1m cooling probe (top). The lower figure shows the dimensions of the apparatus.
2.1 Emissions from vinyl flooring to air

Information on the DINP content of vinyl flooring materials was collected from the product declarations for 62 different vinyl floorings provided by three Swedish manufacturers; the average value was $16 \pm 3.5\%$ (w/w). Using this information three representative vinyl samples were obtained from a local retailer. One sample had a multi-layered structure with an upper coating of polyurethane (floor 1), one consisted of a homogenous vinyl layer with an upper polyurethane coating (floor 4), and the third was a vinyl wall covering with no upper coating (wall cover 3). A fourth sample was obtained from a vinyl flooring producer (floor 2). This sample used a “new” type of plasticizer: diisononyl cyclohexane-1,2-dicarboxylate, DINCH, and was made up of a homogenous vinyl layer with an upper polyurethane coating. Details of the experimental protocol, the sampling and the chemical analysis are presented in figure 5.

![Diagram](image)

*Figure 5.* Analytical procedures used to measure the emissions of DINP and DINCH from vinyl flooring and wall cover samples.
2.2 Emissions from flat screen displays to air

The phosphorous contents of 61 LCD screens from 6 different manufacturers were measured. The screens were of different ages but were all manufactured between January 2001 and April 2012. The average triphenyl phosphate content of their front surfaces was estimated to be 25%.

In addition, a new 32 inch LCD television set was measured under four different sets of conditions: 1) with the LCD on standby 2) with the LCD displaying a looping video, 3) with the dismantled LCD-display (front surface) heated to 40°C, and 4) with the dismantled LCD-display heated to 60°C. The procedures used when acquiring these measurements are illustrated in figure 6.

Figure 6. Analytical procedures used to measure TPP emissions from flat panel displays.
2.3 Leaching from concrete to water

The concentration of organophosphate additives in concrete depends on decisions made by the constructor and the instructions provided by the manufacturers of the additives. In this work, two different additives, triisobutyl phosphate (TiBP) and tributyl phosphate (TBP), were added at concentrations recommended by a manufacturer of underwater cement and according to the Aberdeen Group’s recommendations on Air Entrainment and Concrete [30]. Concrete cylinders were molded from ready-mix concrete mixed with 0.002% TBP or 1.4% of underwater cement that contained 1.9% TiBP. Experiments on leaching were performed for samples containing both additives, and also using blank samples, as shown in figure 7. All experiments were performed in triplicate.

Figure 7. Analytical procedures used to measure the leaching of TBP and TiBP from concrete to water.
2.4 Quality assurance

The analyte recovery for the methods used to measure emissions into the air was determined by inserting a glass plate into the chamber, spiking the plate with the analyte, and then performing sampling and analysis as described. Under these conditions, the recoveries for DINP and TPP were 99±11% and 96±3%, respectively. The analyte recovery for the method used to measure emissions to water was tested by spiking water with the analyte and then analyzing the resulting solution as described in figure 7. The recovery of TBP and TiBP from water was 100±4%.

Before testing, the chamber was cleaned with a vacuum cleaner, wiped with water and ethanol, and then heated to 300°C for 72 hours. To reduce contamination, the PUFs were cleaned by extraction directly before the start of sampling. After sampling, the PUF plugs were extracted within 10 minutes.

Method blank samples were taken before and after sampling. The blanks were analyzed and the method’s limit-of-quantification (LOQ), $y_{\text{loq}}$, was calculated according to following equation:

$$y_{\text{loq}} = y_{\text{blank}} + 10s_{\text{dev}}$$

where $y_{\text{blank}}$ is the area measured for the method blanks and $s_{\text{dev}}$ is the standard deviation of the method blank area. The LOQ was then converted into units of mass based on $y_{\text{loq}}$ using a standard curve. The average levels of each analyte in the blank samples and the LOQs for the methods used are presented in table 1.

<table>
<thead>
<tr>
<th>Number of blank samples</th>
<th>Average blank level</th>
<th>Limit of quantification, LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DINP</td>
<td>12</td>
<td>0.12 µg</td>
</tr>
<tr>
<td>TPP</td>
<td>5</td>
<td>1.0 µg</td>
</tr>
<tr>
<td>TBP</td>
<td>6</td>
<td>1.2 pg</td>
</tr>
<tr>
<td>TiBP</td>
<td>6</td>
<td>25 ng</td>
</tr>
</tbody>
</table>
3 Modeling
To estimate the quantity of organic compounds released from a given material or products on the national level, it is necessary to determine the total surface area of the material or product in circulation and its rate of emission. The total area depends on the product’s design, sales and lifetime, while emission rates depend on the concentration and thickness of the source material and the molecular mechanisms of mass transfer from the material to the recipient. The usage of the product has to be considered because it affects both its lifetime and various environmental parameters that may affect its rates of emission. These include its operating temperatures, the media into which it may emit its organic compounds (e.g. air or water), and the flows of the receiving media. If the product’s rates of emission are initially high, they may be time-dependent as the material’s reserves of the organic compound are depleted. Conversely, materials that emit at relatively low rates may exhibit much less time-dependence.

A conceptual model was established to describe the mass transfer process. This was then used to establish a general and widely applicable generic model. The molecular model describes the emission of organic compounds in terms of a one-dimensional process of diffusion within the material, an equilibrium in the concentration of the organic compound at the boundary layer separating the bulk material from the receiving media, and the flow of the receiving media over the surface of the material (see figure 8). It was assumed that the organic compound was evenly distributed within the material and that its concentration in the receiving media was zero.

![Convection mass transfer coefficient](image)

Figure 8. Illustration of the mechanistic emissions model showing the three key processes: diffusion within the material, an equilibrium at the boundary layer, and convection mass transfer in the receiving media.
3.1 Equilibrium in the boundary layer

The boundary layer between the bulk material and its surroundings is the region in which organic compounds dissociate from the material via vaporization, desorption or dissolution. These processes can be described using Henry’s law, which states that the ratio of the solubility, \( S_{a'} \), of a gas in a solvent to its partial pressure above that solvent, \( P^*_{a'} \), is equal to a constant, \( K_H \) (see equation 3).

\[
K_H = \frac{S_{a'}}{P^*_{a'}}
\]  

If Henry’s law is combined with the ideal gas law, a dimensionless version of Henry’s constant can be obtained by dividing both sides of equation (3) by the product of the ideal gas constant, \( R \), and temperature, \( T \):

\[
K = \frac{S_{a'}}{P^*_{a'} / RT}
\]

The movement of organic compounds from the surface of the material to the receiving media can be described in terms of an attempt to achieve equilibrium in the concentrations of the organic compound within the two phases. This material/air partition coefficient for this equilibrium, \( K_{M/A} \), is defined by the concentration of the organic compound in the material, \( C_M \), and its concentration in the air, \( C_A \), as shown in equation 5.

\[
K_{M/A} = \frac{C_M}{C_A}
\]  

This expression can also be adapted to describe equilibria involving water rather than air as the receiving medium, in which case one must consider the air/water partition coefficient \( K_{A/W} \) as shown in equation 6.

\[
K_{M/W} = \frac{C_M}{C_W} = K_{M/A} \times K_{A/W} = \frac{C_M}{C_A} \times \frac{C_A}{C_W}
\]

Alternatively, these equilibria can be described in terms of solubility, as in equation 4. This assumes that there is an equilibrium (defined by the solubilisation coefficient, \( K_s \)) between the organic compound’s sorption or solubility in the material and that in water, \( S_W \) (equation 7).
This approach can be employed to estimate material/water partition coefficients based on material/air partition coefficients and equation 8.

\[ K_S = \frac{S_a}{S_w} \]  (7)

\[ K_S = K_{M/A} \times \frac{P_a / RT}{S_w} \]  (8)

At equilibrium the partition coefficient can be described in thermodynamic terms:

\[ \Delta G^0 = -RT \ln K = \Delta H^0 - T \Delta S^0 \]  (9)

where \( \Delta G^0 \) is the standard Gibbs free energy change associated with the transfer of the organic compound from one medium to the other, \( \Delta H^0 \) is the corresponding standard enthalpy change, and \( \Delta S^0 \) is the corresponding standard entropy change at equilibrium.

The temperature dependence of the equilibrium coefficient can be determined by using a solution of the Gibbs-Helmholtz equation:

\[ \ln K = -\frac{\Delta H^0}{RT} + \text{constant} \]  (10)

This free energy change depends on the molecular interactions between the organic compound and the material in the bulk material and at the boundary layer, and also on the interactions between the organic compound and the receiving media. Linear free energy relationships can be used to predict the strengths of these interactions, and can be established using the descriptors developed by Abraham for modeling a range of different solvation properties. These Abraham solvation parameters include hydrogen bond acidity (\( A \)), hydrogen bond basicity (\( B \)), excess molar refraction (\( E \)), polarizability/dipolarity (\( S \)) and the logarithm of the partition coefficient between hexadecane and air (\( L \)). The small letters describe the parameters of the system: \( c \) denotes a constant, while \( a,b,e,s, \) and \( l \) are coefficients corresponding to the capital letter descriptors. [31-35].
If these descriptors are used to describe the linear free energy changes associated with material/air partitioning, the following expression is obtained:

\[-\Delta G = RT \ln K_{M/A} = c + aA + bB + eE + sS + lL \quad (11)\]

The corresponding expression for material/water equilibrium is:

\[-\Delta G = RT \ln K_{M/W} = c + aA + bO_b + eE + sS + vV \quad (12)\]

Here, the hydrogen bond basicity (Bo) parameter for more polar systems is used in place of B because water is a polar solvent. The McGowan volume is used in place of L because molecular volume is an important parameter when describing solubility in liquids.

The Abraham solvation parameters for different substances can be estimated from their chemical structure (SMILES notation) using the Absolve package from version 5.0 of the ADME Suite (Advanced Chemistry Development, Inc., Canada). In the SMILES notation, the structure of DINP would be specified as follows:

\[\text{CC(C)CCCCCOC(=O)c1ccccc1C(=O)OCCCCCC(C)C}\]

where the letter C denotes a carbon atom, O denotes oxygens, = represents double bonds, c are aromatic carbons, and numbers indicate positions at which a ring closes. The two-dimensional structure obtained by decoding this sequence using the Absolve software is shown in figure 9.
Figure 9. The structure of DINP determined from its SMILES sequence using the Absolve software package. The predicted Abraham solvation parameters for this molecule are also shown. Atoms highlighted in blue in the structure are largely responsible for the molecule’s hydrogen bond basicity.

For systems undergoing equilibration, Abraham solvation coefficients (small letters) were obtained by multivariate regression using orthogonal partial least square (OPLS) models [36] that rely on calculated Abraham descriptors and partition coefficients taken from the scientific literature. The OPLS models were constructed using the Simca P+ 12.0 software package (Umetrics AB, Umeå, Sweden), with $RT\ln K_{M/A}$ as the dependent variable (Y-values) and the calculated Abrahams solvation parameters $(A,B,L,S,E)$ as the independent variables (X-values). OPLS was chosen because it allows the X-values to be orthogonally distributed and thus requires fewer principal components than alternative methods. $K_{M/A}$ values were obtained from the literature[37-44]. The resulting estimated system parameters are presented in table 2. The correlations between the predicted and modeled values of $\ln K_{M/A}$ are shown in figure 10.
Table 2. Parameters used in the material-air partition models (RTln \(K_{M/A} = c + aA + bB + sS + eE + lL\)) for the different polymers and groups of materials studied. [from PAPER 1]

<table>
<thead>
<tr>
<th>Material</th>
<th>c</th>
<th>a</th>
<th>b</th>
<th>s</th>
<th>e</th>
<th>L</th>
<th>Fit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper and glulam, cellulose and starch</td>
<td>-4700</td>
<td>36000</td>
<td>0</td>
<td>6200</td>
<td>610</td>
<td>2100</td>
<td>(N=153, PC=3, Q^2=0.70)</td>
</tr>
<tr>
<td>Nylon</td>
<td>6000</td>
<td>34000</td>
<td>23000</td>
<td>-27000</td>
<td>22000</td>
<td>3200</td>
<td>(N=29, PC=2, Q^2=0.85)</td>
</tr>
<tr>
<td>Polyethylene, PE</td>
<td>8900</td>
<td>0</td>
<td>0</td>
<td>-5900</td>
<td>18000</td>
<td>1700</td>
<td>(N=53, PC=2, Q^2=0.68)</td>
</tr>
<tr>
<td>Polyurethane, PU</td>
<td>-990</td>
<td>13000</td>
<td>0</td>
<td>4000</td>
<td>3000</td>
<td>1700</td>
<td>(N=269, PC=2, Q^2=0.75)</td>
</tr>
<tr>
<td>Polyethylene terephthalate, PET</td>
<td>5400</td>
<td>10000</td>
<td>0</td>
<td>2400</td>
<td>16000</td>
<td>420</td>
<td>(N=10, PC=2, Q^2=0.38)</td>
</tr>
<tr>
<td>Vinyl flooring</td>
<td>-3500</td>
<td>18000</td>
<td>-451</td>
<td>8500</td>
<td>3200</td>
<td>4800</td>
<td>(N=8, PC=4, Q^2=0.99)</td>
</tr>
</tbody>
</table>

R is the gas constant (J/K/mol), T is the temperature (K), c is a constant, and a, b, e, s and l are material coefficients corresponding to the following Abraham solvation parameter descriptors: the hydrogen bond acidity, A; the hydrogen bond basicity, B; the excess molar refraction, E; the polarizability/dipolarity, S; and the logarithm of the partition coefficient between hexadecane and air, L. N is the number of observations, PC is the number of significant principal components, and \(Q^2\) is the cumulative fraction of the total variation of values that can be predicted by the extracted components.
The equilibrium or partitioning of an organic compound between the source material and the recipient can be described as the difference between the compound’s solubility in the material and that in the recipient. In some cases, when the solubility in the material is lower than the amount of additive present, the added compound will accumulate on the material’s surface. If its solubility in the recipient is also low, the compound might
form a third phase between the material and recipient. In such cases, the process of mass transfer is governed by the rate of dissolution or vaporization of the neat compound. The phenomenon whereby an additive accumulates on the surface of the material is known as blooming. Blooming can be caused by changes in solubility due to changes in temperature, material composition (e.g. as a result of emissions or degradation), or material structure, among other things.

The dissolution of the additive from the surface can be estimated using the Nernst–Brunner equation

\[
\frac{dC}{dt} = A_s \frac{D_w}{L_D} \frac{C_s - C_w}{C_s}
\]  

(13)

where \( A_s \) is the surface area, \( D_w \) is the water diffusion coefficient, and \( C_s \) is the surface concentration.

### 3.2 Diffusion

The movements of molecules in the material are affected by the material’s structure and the other components present within it. Molecules within the matrix of the material can be considered to move randomly, colliding with other loosely-bound molecules and components of the matrix in a Brownian fashion. The speed at which the molecules move is determined by the energy of the system and their interactions with other molecules. While these processes can be described using molecular dynamics models, they require a lot of input data and are very complicated. The process as a whole can be regarded as a diffusion of molecules from areas of high concentration to regions of low concentration. If the flux of matter, \( F \), across a given plane is proportional to the concentration gradient across that plane and the \( x \) axis is parallel to the concentration gradient, the process can be described using a diffusion coefficient, \( D \), as shown in equation 14.

\[
F = -D \frac{\partial C}{\partial x}
\]  

(14)

This is called Fick’s first law and was established by Adolf Fick in 1855 [45]. \( F \) is the flux of matter in mass per unit area and time. \( C \) is the concentration at distance \( x \) and \( D \) is the diffusion coefficient (area/time). The diffusion coefficient is negative because the flux is directed from areas of high
concentration to areas of low concentration. If the concentration changes over time, the system is not in a steady state. This case is described by Fick’s second law (see equation 15), where $D$ is assumed to be a constant.

$$
\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} F = - \frac{\partial}{\partial x} \left( - D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}
$$

(15)

The diffusion coefficient is constant in a homogenous isotropic medium. The Einstein-Stokes equation can be used to obtain estimated diffusion coefficients in liquid media [46;47]:

$$
D_L = \frac{kT}{6\pi\eta r}
$$

(16)

Here, $k$ is the Boltzmann constant, $T$ is temperature, $\eta$ is viscosity, and $r$ is particle radius. This expression is widely used to estimate diffusion coefficients in liquids where the solute molecules are much larger than those of the solvent.

Diffusion within a solid material is sensitive to the material’s structure and to the chemical properties of the material itself as well as those of any additives it contains. In solids, the diffusion coefficient, $D_s$, can be determined by estimating the activation energy for the diffusion process, $E_a$, and using a function based on a pre-exponential athermal factor, $D_0$ [48]:

$$
D_s = D_0 \exp \left( - \frac{E_a}{RT} \right)
$$

(17)

In most rigid polymers and crystalline materials, the diffusion coefficient behaves as it does in solid materials such as metals. However, plasticized polymers and polymers that contain large quantities of unbound compounds have diffusion properties that are intermediate between those of liquids and more conventional solids.

The empirical Piringer equation was developed to estimate diffusion coefficients for the transfer of additives from polymeric food packaging materials into foods. It depends on the molecular weight of the additive of interest, a material specific parameter ($Ap$), and the temperature.
Some polymers have relatively crystalline structures and are less amorphous. The activation energy required for diffusion in such cases is relatively high, and a temperature dependent activation energy parameter, $\tau_M$, has been developed to account for this.

$$D = \exp \left( Ap - 0.1351(M_w)^{2/3} + 0.003M_w - \frac{10450}{T} \right)$$

(18)

$$Ap = A'p - \frac{\tau_M}{T}$$

(19)

The source material’s porosity also affects the rate of diffusion, which is highly sensitive to the size, shape, and occupation of the pores. The addition of fillers and other such additives can thus have a profound effect on rates of diffusion. These can be modeled by introducing an estimated empirical parameter, $A'p$, which is determined by comparison to other materials with similar internal properties. The rate of diffusion is also strongly affected by the presence of capillary pores that provide a direct connection from the bulk material to the receiving medium. In such cases, the rate at which compounds move from the material to the receiving medium is dominated by diffusion within the pores, which will typically be filled with the receiving medium (i.e. air or water in the cases considered herein), and by their interactions with the material forming the sides of the pores. A simplified equation can be used to calculate the diffusion coefficient in such cases, based on the diffusion coefficient in the pores, $D_p$, the porosity (v/v), $\varepsilon$, and an equilibrium coefficient, $K_S$.

$$D_p = \frac{D_w}{\varepsilon \left( 1 + \frac{1 - \varepsilon}{\varepsilon} K_S \right)}$$

(20)

The diffusion coefficient for water can be predicted using an empirical relationship based on the molecular volume, $V_a$, and the viscosity of water, $\mu_w$ (equation 21). [49]

$$D_w = \frac{13.26 \times 10^{-9}}{\mu_w^{1.14} \times V_a^{0.589}}$$

(21)
The same is true for the air diffusion coefficient:

\[ D_a = \frac{10^{-7} T^{1.75} \sqrt{M_r}}{p \left( \frac{V_A^{1/3}}{V_B^{1/3}} \right)^2} \tag{22} \]

where \( V_A \) is the molecular volume of the substance of interest, \( V_B \) is the molecular volume of air (20.1 cm\(^3\)/mol), \( p \) is the air pressure in atmospheres, and \( M_r \) is the relative mass, i.e., the sum of the molecular weights of air (28.97 g/mol) and the substance, divided by the product of the two molecular weights [49].

### 3.3 Convection mass transfer

Mass transfer within the receiving media can be described in two ways. In the first case, the medium is assumed to be immobile and mass transfer occurs by diffusion from the region of high concentration next to the material’s surface to more distant regions of low concentration. In the second case, a flow of the receiving medium is assumed. This means that mass transfer is achieved both by diffusion and by the momentum of the medium. The resulting flux, \( N \), is described in terms of the convective mass transfer coefficient (\( h_m \)) and the difference between the concentration of the substance next to the surface of a material (\( C_{A,S} \)) and that in regions that are further away from the source material (\( C_{A,\infty} \)):

\[ N = h_m \left| C_{A,S} - C_{A,\infty} \right| \tag{23} \]

As shown in figure 11, the flow of the receiving media over the surface causes the concentration of the substance to increase in the direction of the flow.
The formation of a concentration boundary layer due to a flow over the surface of the source material.

The convective mass transfer coefficient can be predicted using a boundary layer model for flows over a planar surface [28]:

\[
h_m = \frac{D_w}{x} 0.664 \left( \frac{u_m \rho_w x}{\mu_w} \right)^{1/2} \left( \frac{\mu_w}{D_w \rho_w} \right)^{1/3}
\]  

(24)

where \( D_w \) is the diffusion coefficient in water, \( x \) is the length over which the water flows, \( u_m \) is the velocity of the water current, and \( \rho_w \) is the density of water. The same equation can be used for air flow

\[
h_m = \frac{D_a}{x} 0.664 \left( \frac{u_m \rho_a x}{\mu_a} \right)^{1/2} \left( \frac{\mu_a}{D_a \rho_a} \right)^{1/3}
\]  

(25)

The viscosity of air can be estimated using Sutherland’s law (equation 26) and the density of air is obtained using the ideal gas law [50].

\[
\mu_a = 1.716 \times 10^{-5} \left( \frac{T}{273.15} \right)^{3/2} \left( \frac{273.15 + 110.4}{T + 110.4} \right)
\]  

(26)
Many empirical expressions for estimating $h_m$ have been developed, including one for describing flows in a field and laboratory emission cell (FLEC). In a FLEC, the receiving medium flow radially in towards the center of the cell. This produces an unusual concentration gradient, for which an appropriate value of $h_m$ can be calculated using equation 27:

$$
 h_m = 0.774 \left( \frac{u_m \rho_a x}{\mu_a} \right)^{0.86} \left( \frac{\mu_a}{D_a \rho_a} \right)^{0.68} \left( \frac{r_0 - r}{2\delta} \right)^{0.68} \frac{D_a}{2\delta}
$$

(27)

where $r_0$ and $r$ are the inner and outer diameters of the emission chamber, respectively, and $\delta$ is the distance between the surface of the source material and the FLEC cap at the central exit point [51]. For emissions from particles (consisting of the same material as the bulk source), the convective mass transfer coefficient could be calculated by using an empirical model for a different geometry (e.g. spheres).

### 3.4 Model calculations

The equations for mass transfer can be solved using different methods, including finite difference techniques and various numerical and analytical approaches. In this work, the partial differential equation developed by Xu and Little[52] were used (equations 28, 29 and 30).

$$
 m(t) = -D \times \left. \frac{\partial C(x,t)}{\partial x} \right|_{x=L_M} =
 D \times \sum_{m=1}^{n} \beta_m^2 \frac{L^2}{L_m} \beta_m^2 + H^2 + H \times \left[ C_M^0 - K_{M/A} C_A^0 e^{-D \beta_m^2 t} \right. \\
 + \left. \int e^{-D \beta_m^2 t-\tau} \times Kd\tau \right]
$$

(28)

$$
 \beta_m \times \tan \theta \beta_m L_M = H
$$

(29)

and

$$
 H = \frac{h_m}{K_{M/W} D_S}
$$

(30)
A numerical solution was supplied by Dr Leif Persson, Department of Mathematics and Mathematical Statistics, Umeå University, together with a user-friendly multiple-scenario batch mode calculation tool implemented in Maple 14 (Maplesoft, Waterloo Maple Inc, Canada).

It was found that when using the numerical approach, the use of the Maple software “Fsolve” command in cases where the $\alpha$-value was relatively high caused the Maple solver to break down because the eigenvalues generated were too close to the asymptotic value. These problems could be avoided by checking the $\alpha$-value before performing calculations:

$$\alpha = \frac{KD}{h_m L_M} \quad (31)$$

The $\alpha$-value should not be greater than $10^{15}$, depending on the starting concentration, time and the number of terms in the series expansion. The number of terms in the series expansion also influences the proximity of the estimated $\alpha$ to the asymptotic value. The use of more terms increases the precision of the calculation but also increases the time required for each batch calculation and the sensitivity of the solution to the $\alpha$-value.

In some cases, the emissions of additives from polymeric source materials were primarily limited by partitioning and convection. This was the case when the source material contained large quantities of an additive with low volatility that it did not readily deplete at the surface.

$$\dot{m}(t) = h_m \left( \frac{C_0}{K_{M/A}} - y \right) \quad (32)$$

Similarly dissolution from a surface into an aqueous solution can be calculated by assuming that substances on the surface diffuse into a semi-infinite medium, and that equation 16 follows Fick’s second law of diffusion by dissolution into water. The resulting equation was solved by Laplace transformation [28;53], giving:

$$m_{\Delta}(t) = C_S \cdot L_D \cdot erfc \left( \frac{L_D}{2\sqrt{D_w \cdot t}} \right) \quad (33)$$
3.5 Model uncertainties

Model uncertainties were calculated according to the EURACHEM/CITAC guidelines for each compound and emission scenario [54]. The main sources of uncertainties were identified and the combined uncertainties in each model parameter were calculated (see the Ishikawa diagram in Figure 12).

The overall combined model uncertainty \(u_c\) was then calculated as follows:

\[
  u_c(y(p,q,...)) = \sqrt{\left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(q)}{q}\right)^2 + ...}
\]

where \(p\) and \(q\) and \(u(p)\) and \(u(q)\) are the individual values and uncertainties, respectively.

![Ishikawa diagram](image1.png)

**Figure 12.** Ishikawa diagram showing the identified model uncertainties and their contributions to the overall model uncertainty

The process can be illustrated using an example from figure 12: the uncertainties in the calculated partition coefficient, “\(K\)”, were related to uncertainties in the linear-free-energy (OPLS) relationship, temperature (“\(temp\)”), type of material (“\(material\)”), and the uncertainty of the Absolve model (Partition model). The uncertainty in the partition coefficient was estimated as shown in equation 34. Similar calculations were performed for all of the other identified parameters and the resulting uncertainties were combined to estimate the overall uncertainty in the estimated emitted mass and rate of emission.
4 Experimental results and model evaluation

4.1 Emissions from vinyl materials to air

The measured rates of DINP emission were 0.37µg/m²h (floor 1), 0.62 µg/m²h (wall cover), and 0.52 µg/m²h (floor 3), as shown in the blue bars of figure 14. The measured rate of DINCH emission (floor 2) was 0.91 µg/m²h. Most (64%-86%) of the analyte that was lost from the source materials ended up adsorbed on the surfaces of the emission chamber, and so the emission rates in this case had to be calculated based on the sum of the recovered analyte masses divided by time (h). Consequently, in order to determine changes in the rate of emission over time, it was necessary to perform series of experiments that were halted at defined times to enable recovery and measurement of the emitted material that had been adsorbed on the chamber’s surfaces. Vinyl flooring materials that were made up of different layers had lower emission rates than the homogenous flooring. This is probably due to the uneven distribution of DINP in the different layers of floor 1 (see figure 13). The vinyl wall covering had no upper coating and therefore produced higher rates of emission. The different thicknesses of the source materials had no effect on the measured emission rates since the source materials were not appreciably depleted of the target compounds over the ten day experimental periods.

Figure 13. Microscopic picture showing floor 1 with different layers to the left and floor 2 with homogenous material to the right, both have an upper coating of polyurethane.

A model was developed for predicting the emissions from the investigated vinyl samples. The material/air partition coefficient for DINP was predicted to be 4.06 x 10¹¹ using equation 35 (from equation 11 and table 2), while the predicted partition coefficient for DINCH was 1.30 x 10¹¹ at 40°C. The
use of an $A'p$ value of 14.5 and a $\tau_M$ of 1577 gave predicted diffusion coefficients of $1.21 \times 10^{-13} \text{ m}^2/\text{s}$ for DINP and $1.07 \times 10^{-13} \text{ m}^2/\text{s}$ for DINCH.

$$RT\ln K_{M/A} = -3500 + 18000A - 451B + 8500S + 3200E + 4800L$$ (35)

The model’s output was in good agreement with the experimental data (see figure 14). The best fits were achieved for floors 2 and 3, which consisted of a homogenous material with a polyurethane top coating. This was probably because the model’s parameters were calibrated against products of this type. The predicted values for the vinyl wall cover were lower than the experimental values while those for the multi-layered floor 1 were greater than the experimental values (see figure 14). The predicted model uncertainty was 57% for DINP and 54% for DINCH. The factor that made the greatest contribution to the overall uncertainty of the model was the uncertainty in the estimated convective mass transfer coefficient, which accounted for 25% of the model’s overall uncertainty.

**Figure 14.** Modeled (blue) and measured (red) emissions of DINP and DINCH from four vinyl material samples.
4.2 Emissions from flat screens to the air

Triphenyl phosphate (TPP) was primarily found on the front surfaces of the tested screens. The estimated rates of TPP emission from the screens were 0.051 µg/m²h in standby mode (at an ambient temperature of 25°C) and 1.7 µg/m²h in operating mode (at a surface temperature of 50°C). In experiments where the screens were disassembled and only the front surfaces were placed in the chamber, the measured emissions were 0.66 µg/m²h at an ambient temperature of 40°C and 3.2 µg/m²h at 60°C (figure 15). This clearly shows that the emissions of TPP came almost exclusively from the screens' front surfaces and that they were strongly temperature-dependent.

The front surfaces were shown to be made of poly methyl methacrylate PMMA, but screens made using triacetyl cellulose surfaces are also known. Because it was not possible to determine which of these two materials is most widely used in the flat screens currently in circulation, a combined model was created using literature data on partition coefficients for 121 organic chemicals in different polymers[55]. The resulting Abraham solvation parameters for the system at equilibrium were:

\[
RT\ln K_{M/A} = -393 - 3590A - 35300B - 21000S + 13500E + 2940L
\]  
(36)

A three-component OPLS model was established for the compounds considered, with a regression coefficient of 0.83 (see figure 15).

![Figure 15](image-url)
The experimental rates of TPP emission were modeled in two different ways, using equations 28 and 32. The partition coefficient for TPP was estimated using equation 36, and the convection mass transfer coefficient was estimated with equation 27. It was assumed that diffusion was relatively unimportant in this system, since the surface material was thin (0.15 mm) and the concentration of the organic compound was high (20%). The diffusion coefficient was therefore not considered when performing calculations using equation 32. For comparative purposes, a second model that was based on equation 27 and incorporated a calculated diffusion coefficient was fitted using an $A'p$ value of 17 and a $\tau_M$ of 1577.

The modeled emission rates were found to agree well with the experimental data and were temperature dependent. The temperature dependence explains why the rate of emission was higher when the screen was turned on than when it was in standby mode (see figure 16). The measured amounts in the low temperature case were close to the limit of detection, and so the accuracy of the resulting experimental data is relatively uncertain. The estimated model uncertainty was 30%, which is within the range spanned by the measured results.

![Figure 16. Plot of measured emission rates (blue), rates calculated using the model that does not account for the diffusion coefficient (red), and rates calculated using the model that accounts for the diffusion coefficient (gray).](image)
4.3 Leaching from concrete to water

The initial rates at which organophosphates leached from the concrete samples into the water were relatively high: $2900 \pm 1060 \, \mu g/m^2 \, h$ for TBP and $8500 \pm 800 \, \mu g/m^2 \, h$ for TiBP. However, they decreased over time, reaching approximately $1 \, \mu g/ \, m^2 \, h$ for TBP and $10 \, \mu g/m^2 \, h$ for TiBP after 1000 hours. These results indicate that there are multiple mechanisms involved in the release process, all of which must be accounted for when constructing a predictive model.

Concrete is a complex material made of inorganic cement and aggregate filling (sand). It has both micropores and macropores (i.e. pores that allow for the direct transfer of additives from the bulk material to the receiving material). The model that was established for estimating the release of organophosphates accounted for diffusion via the micro pores and the macro pores, as well as dissolution from the surface.

A predictive model for estimating the equilibrium coefficients associated with the transfer of organophosphates from the concrete samples to the surrounding water was established by using equation 8 and literature data on concrete/air partition coefficients to generate Abraham solvation parameters for the system. The OPLS-model had 2 significant principal components and explained 91% ($R^2=0.91$) of the observed variation, with a crossvalidated explained variation of 90% ($Q^2=0.90$) (figure 17). The Abraham solvation parameters obtained for the equilibrium system were:

$$RT\ln(K_S) = 28100 - 8560A - 37500Bo - 19500S - 3860E + 15600V$$  \hspace{1cm} (37)$$

![Figure 17](image_url). Concrete-water equilibrium coefficients ($\ln K_S$) predicted using equation 37 plotted against literature values. [from PAPER 2]
The estimated equilibrium coefficients for TBP and TiBP were 1.4 and 0.46, respectively. The estimated diffusion coefficient was $5.2 \times 10^{-12}$ m$^2$/s with an $A'p$ value of 14.3 and a water diffusion coefficient of $5 \times 10^{-10}$ m$^2$/s. The rate of water flow in the experimental system was 0.4 m/s, giving a $h_m$ value of 6.6 x10$^{-7}$ m/s.

The output of the resulting three phase model (using equation 28 and 33) agreed well with the experimental data (figure 18) on the initial rate of organophosphate release (via dissolution) and on the long term rate (which is due to transfer via micropores).

**Figure 18.** Measured and modeled rates of tributyl phosphate (TBP) and triisobutyl phosphate (TiBP) emission from concrete samples to water during a 16 week leaching experiment. [from PAPER 2]
5 Application of the models

In order to use molecular models to estimate emissions on a local or national scale, it is necessary to acquire data on the nature and the total surface area of the source materials in circulation.

More specifically, one must determine the concentration of the compounds of interest within the prospective source material, the identity of the source material, and the thickness and shape of the items made from the source material. The concentration of the compound of interest and the identity of the source material may differ between products (even when dealing with items from the same brand) and the necessary information can be difficult to obtain. The total surface area of the source material in circulation is calculated from sales data (which provides a measure of the inflow to the region of interest) over the product’s life time. The duration of the product’s usage is also important if it becomes depleted of the compound of interest over time and so its rates of emission change. Some of this information can be obtained from sales organizations, producers, and bureaus of national statistics. The statistical data is normally obtained in terms of economic quantities or units of mass relevant to transportation (kg); data in the form of units sold or surface area is comparatively rare. It is therefore necessary to spend some time converting economic data or information on kilograms of material sold into surface areas; this increases the uncertainty of the resulting estimated emissions totals.

5.1 Plasticizer emissions from vinyl flooring in Sweden

The total area of vinyl flooring materials sold annually was obtained from the Swedish flooring trade association, and emissions factors were calculated for each year of a 20-year period; this was assumed to match the average lifetime of the studied flooring materials. Between 2001 and 2003, DEHP was gradually replaced by DINP in vinyl flooring materials sold in Sweden. Moreover, in 2012, one Swedish manufacturer of vinyl flooring replaced DINP with DINCH. An average air flow of 0.17 m/s over the surface of the vinyl flooring was assumed for indoor environments, and the ambient indoor temperature was assumed to be 23°C [56]. The thickness of the flooring material was assumed to be 2 mm, with a plasticizer concentration of 16% (w/w).

Given these assumptions, the predicted masses of plasticizers emitted from vinyl flooring in Sweden for 2012 were 210±95 kg for DEHP, 40±18 kg for DINP, and 3.6±1.5 kg for DINCH. The modeled changes in emission rates over 20 years were low, and so it was concluded that the overall rate of
emission is more sensitive to the quantity of material containing specific plasticizers that is sold in each year than to reductions in emissions from older materials that are already in circulation. The same calculation was performed for every year from 1990 to 2035, assuming that all plasticizers current in circulation were replaced with DINCH, isDEH or DEHA. It was found that the emissions of DINCH would be similar to those of DINP but much greater emissions of isDEH and DEHA would occur (figure 19).

Averages were used when making these calculations. However, in reality, there is considerable variation in the different products that are available (in terms of concentration, area, life time, material properties) and in terms of the properties of indoor environments. These factors all contribute to the uncertainty of the model’s estimates, which ranged from 57% for DEHA to 61% for DINP. The factor that made the greatest contribution (42%) to the overall uncertainty was the uncertainty in the individual diffusion coefficients, followed by the uncertainty for the convective mass transfer coefficient (16%).

![Figure 19. Calculated annual emissions to air in Sweden from vinyl flooring based on sales data and predicted sales for the near future, assuming an average plasticizer content of 16% (w/w) for di-iso-nonyl phthalate (DINP), di(2-ethylhexyl)phthalate (DEHP), di-iso-nonylphthalate diethyl hexyl-iso-sorbide (isDEH), di-iso-nonylphthalate diethyl hexyl-iso-sorbide (isDEH), di(2-ethylhexyl)adipate (DEHA), and di(2-ethylhexyl)adipate (DEHA). [from PAPER 1]]
The estimated overall mass of emitted plasticizers does not represent the total human exposure to plasticizers emitted from vinyl flooring. The total emitted mass will be spread out within the indoor environment and will thus be partitioned between surfaces and dust, some of which will be removed by ventilation. This means that the data on mass emissions should be coupled to a fate model. Because the rates of DEHP and DINP emission did not seem to change over time, equation 32 was used to calculate rates of emission together with cumulative area sales for 20 years. The emission rates were estimated using equation 10 and 32 based on experimental measurements and literature data [57;58]. The total emitted mass on the national scale was estimated based on the indoor environment described above and the results were then scaled down to obtain an estimate for the city of Stockholm (based on the fact that Stockholm is home to 9% of Sweden’s population). This emitted mass was then used in conjunction with the fate model created by Anna Palm-Cousins, Swedish Environmental Research Institute, and the resulting predicted concentration was compared to experimental data obtained by sampling in the Stockholm area.

The predicted concentrations obtained using the model based on data from emission experiments were slightly lower than those measured for indoor air (Paper 4 and Bergh et al[59;60]), see figure 20. This may be due to the presence of additional source materials that could contribute emissions in the real world, or may reflect the impact of the uncertainties in the experimental data and the model used. The difference between the predicted and experimental results was more pronounced for outdoor air, which could reflect the presence of additional source materials such as vinyl roofing tiles. Household dust will also contain particles formed by abrasion of flooring materials, which would contribute to the measured plasticizer concentrations but would not be accounted for by the emissions model.
Figure 20. Concentrations of DEHP, DINP, and BDE obtained by measurement and modelling for indoor and outdoor air and indoor dust in Stockholm. In some cases, data from other Swedish locations were also used. The error bars represent the boundaries determined by the median multiplied by 1/\( CF_0 \) and \( CF_0 \) respectively, and min and max values for the measured data. (\( CF_0 = 95\% \) confidence factor) [from PAPER 4]
5.2 Emissions of triphenyl phosphate from flat screen displays in Sweden

The total area of television screens sold in Sweden was obtained from the Swedish consumer electronics trade association (www.elektronikbranschen.se) and equivalent data for computer monitors were obtained from Statistics Sweden (www.scb.se). The number of screens sold was estimated from the tonnage sold by assuming the average unit to weigh 3 kg. The indoor environment was assumed to be identical to that used when making national emissions estimates for vinyl flooring. Television sets were assumed to be switched on for 4 hours per day and computer monitors for 8 hours a day. The assumed operating temperature for LCD screens was 30°C while that for plasma screens was 40 °C (see figure 21). Emissions from the back casings of the screens were not considered since not all of the rear casings studied contained triphenyl phosphate and the temperature of the back of the unit does not generally exceed 25°C when in operation. The estimated emissions were calculated using equation 32 (which does not account for diffusion coefficients).

Figure 21. Surface temperatures of flat panel displays after having been switched on for 90 minutes, measured using an IR-camera. a) LCD screen, front; b) LCD screen, rear; c) Plasma screen, front; d) LED screen, front.
The estimated current annual emissions of TPP from the screens of all flat panel displays in Sweden are 3.9 ± 1.7 kg. The estimated total surface area of LCD and plasma screens in circulation, rates of emission, and total emitted mass are presented in table 3. The emissions factors for active plasma screens are greater than those for active LCD screens due to their higher operating temperatures. For screens of the same size, the emissions factor for a plasma screen is twice that of an LCD screen. However, because the total surface area of LCD screens in circulation is considerably greater than that of plasma screens, the overall quantities of material emitted by both screen types are quite similar. It is apparent that the adoption of LCD screens with lower operating temperatures can be expected to reduce TPP emissions over time. Computer screens were found to account for around half of the total expected mass emissions. This is due to their high total surface area and relatively long operating times. The mass emissions from screens in standby mode are much lower than the uncertainty in the estimated values for active screens. This finding supports the decision to disregard emissions from the rear of the screens.

Table 3. Total display areas (based on sales data for years 2008-2012), emission factors in active (on) and standby (off) modes, and total annual emitted masses of triphenyl phosphate in Sweden for different LCD and plasma display types.

<table>
<thead>
<tr>
<th>Display Type</th>
<th>Total front surface area (m²)</th>
<th>Emission factor on (µg/m²h)</th>
<th>Emission factor off (µg/m²h)</th>
<th>Emitted mass on (g)</th>
<th>Emitted mass off (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TV set LCD - 23 inch</td>
<td>81500</td>
<td>0.39</td>
<td>0.17</td>
<td>46.7±19.7</td>
<td>0.102±0.036</td>
</tr>
<tr>
<td>TV set LCD 24-39 inch</td>
<td>755000</td>
<td>0.32</td>
<td>0.17</td>
<td>350±140</td>
<td>0.941±0.40</td>
</tr>
<tr>
<td>TV set LCD 40- inch</td>
<td>1330000</td>
<td>0.27</td>
<td>0.17</td>
<td>531±207</td>
<td>1.65±0.389</td>
</tr>
<tr>
<td>TV set Plasma</td>
<td>542000</td>
<td>0.68</td>
<td>0.17</td>
<td>535±207</td>
<td>0.676±0.387</td>
</tr>
<tr>
<td>Computer Monitors LCD</td>
<td>2120000</td>
<td>0.39</td>
<td>0.17</td>
<td>2430±1290</td>
<td>2.11±0.530</td>
</tr>
<tr>
<td>Sum</td>
<td>27100000</td>
<td>3890±1660</td>
<td>5.49±2.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>3900±1660</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The lowest combined uncertainties were achieved for the largest screens (40 inch and plasma: 39%) while the largest uncertainties were associated with emissions from computer monitors (53%). The uncertainty in the partition coefficient was similar in all cases. The estimated uncertainties reflect both the temperature variation within plasma screens and the variation between LCD screens with and without LED lights. Smaller screens are more sensitive to the airflow over their surfaces. Uncertainties in the estimated total surface areas stem from uncertainty regarding the actual size of the screens and uncertainty in the conversion of weight-based sales data to screen area for computer monitors. The latter factor accounts for the bulk of the uncertainty for computer monitors (figure 22).

Figure 22. Relative contributions (in %) to the overall uncertainty of the model from uncertainty regarding the screen area (sales data; A), the modeled parameters and partition coefficients (K), the convective mass transfer coefficient ($h_m$), and the concentration of triphenyl phosphate in the front screen material ($C_0$). [from PAPER 3]
5.3 Leaching of triisobutyl phosphate from bridge pillars in the Lögde River

When a bridge is built, the constructor selects the method of construction and decides whether underwater concrete should be used. The constructor normally only knows amount of underwater concrete that will be used and not the specific type of additive, which can only be determined by contacting the factory that actually mixed the concrete. Efforts to obtain this information were made for ten bridges built between 1990 and 2012. Of these bridges, three used mixtures containing TiBP, three used mixtures based on other compounds, two did not use underwater concrete, and no information was available for the remaining two bridges. A decision was made to focus on a single bridge because it would have been excessively demanding to estimate the total emissions of triisobutyl phosphate from every bridge in Sweden. Therefore, a local railroad bridge was considered in isolation.

The bridge’s basal pillars were constructed in January 2005. Their dimensions were 7 x 8 x 2m and the area facing water was 30m². The underwater concrete was mixed with 450 kg of TiBP. Various environmental parameters, such as water temperature and flow volumes were obtained from the Swedish University of Agricultural Sciences (info1.ma.slu.se) and the Swedish Metrological and Hydrological Institute (vattenweb.smhi.se).

The estimated total release was 8 kg emitted over 8 years (figure 23a and b). A simple estimate of the TiBP concentration in the water downstream of the bridge was made by assuming that the passing water is well mixed. The concentration of TiBP was predicted to vary between 1 µg/m³ and 9 µg/m³ depending on the temperature and the flow rate, with the highest concentrations occurring in the summer when the flow rate is low. The rate of release is predicted to decrease slowly over time, peaking during the summer when the water is warmer. The use of a thicker material, the lower ambient temperatures, and the longer time period considered meant that the results for leaching from the bridge differed noticeably from those obtained in the leaching experiments.
Figure 23. Release of triisobutyl phosphate from the foundations of a bridge over the Lögdeälven river: A) cumulative mass emissions as a percentage of total concrete content, B) leached mass per volume of water passing below the bridge in µg/m³, and C) emission rates in µg/m²² [from PAPER 2]

The contributions of different uncertainties to the overall uncertainty also differ. When modeling the results of the leaching experiments, uncertainties in the calculated convective mass transfer coefficient made the greatest initial contribution to the overall uncertainty of the model; as the experiment progressed, the contributions from the uncertainty in the two estimated diffusion coefficients became more significant (figure 24). In the bridge example, porosity made the greatest contribution to the overall uncertainty. The different outcomes in this case are due to both the sensitivity of the model and also to uncertainties in the input parameters, which were more severe in the bridge example.
Figure 24. Relative contributions to the model uncertainty from the equilibrium coefficient (Ks), micro-pore diffusion coefficient (Dm), water diffusion coefficient (Dw), convective mass transfer coefficient (hm), starting concentration (C0), material thickness (L), and relative porosity (volume/volume) (ε), after A) 4 days, B) 2 weeks, and C) in the case of data for a bridge pillar 8 years after its construction.
6 Conclusions and future perspectives

6.1 Conclusions

- The generic model works well at predicting emissions from various materials and can be used in multiple scenarios to test the impact of different environmental factors and for different chemicals.
- Environmental and human exposure can be estimated by coupling the model to a distribution model in order to estimate concentrations in the air or water.
- Detailed information on the sold area of products or materials from sales organizations are valuable for calculating mass emissions on a national scale.
- Compounds that have low rates of emission relative to their presence in source materials and are emitted steadily over long periods of time are not appreciably depleted. Therefore, older materials and products emit at similar rates to new ones and so sales data must be collected over the product’s life time.
- When measuring emissions of semi volatile substances from a material to air, most of the released material is adsorbed on the surfaces of the emission chamber. This fraction has to be recovered either by thermal desorption or in other ways to determine the overall emission rate.
- Material layers acts as barriers to diffusion and reduce emission rates. This is evident in vinyl flooring with different layers and polyurethane coatings.
- Triphenyl phosphate (TPP) was found in the front surfaces of all tested flat screens and its rate of emission is clearly temperature dependent. This means that screens with lower operating temperatures such as LED displays both save energy and reduce emission rates relative to hotter displays such as plasma screens.
- Underwater concrete and surface-treated concrete can be a source of organophosphates when used in construction.
- The distribution of organic compounds at the boundary layer can be described using linear free energy relationship based on the Abraham solvation parameters for many materials, provided that the model is calibrated against the material in question.
- Many products are used in a quite narrow temperature range. The temperature dependence of boundary layer coefficients could thus be calculated in a simplified way disregarding entropy effects.
Uncertainty analysis must be performed for different stages of the emission process as well as for different scenarios.

There are two important sources of uncertainty in predicted results: the sensitivity of the model as a whole and uncertainties in the input data. This sensitivity changes over time as different input parameters increase or decrease in importance. It is also affected by the relative magnitude of the input parameters.

### 6.2 Ideas for future model development

The development of the generic model generated some new ideas for future model development, as shown in figure 25.

![Figure 25. Ideas for improving the generic model.](image)

The first idea is that the model could be improved to predict emissions from multilayer materials. The partitioning between material layers could be estimated by using the predictive model to estimate the partitioning between material and air for each material and then calculating material/material coefficients by division. The emitted mass would then be obtained using a multilayer equation [61]. A multilayer model would also be useful for materials with a high degree of porosity such as textiles.

Secondly the method used for estimating total uncertainty involves changing one parameter at a time and then using the root – mean – square
method to add the different uncertainties. Some parameters might have a combined effect. This could be accounted for by developing a multivariate method for uncertainty analysis. For instance, one could use a full factorial design with response surface modeling similar to the methods used in experimental design. The model’s output could then be evaluated with multiple linear regression or partial least square methods.

A third improvement would be to predict the material descriptors required to describe the equilibrium in the boundary layer. The model as it currently stands requires empirical inputs from material studies to generate these descriptors. The interactions in the boundary layer between additive and material are described by intermolecular interactions such as hydrogen bonding, excess of molar refraction, polarity, and volatility or volume. Hydrogen bonds are formed between a hydrogen bond donor, a, and a hydrogen bond donator, b, which are described by the material descriptors A and B. Therefore, it should be possible to (for example) estimate the material parameter that corresponds to hydrogen-bonding acidity or basicity based on the bulk polymer’s hydrogen basicity (if no other additives are present). To illustrate this process, material a values were plotted against B’ values for oligomers of the studied polymers, and material b values were likewise plotted against oligomer A values. The excess of molar refraction was plotted in a similar way, with material e values plotted against polymer E values (figure 26). However, it seems more challenging to estimate the sizes of the cavities corresponding to the McGowan volume (v) and the hexadecane/gas partition coefficient (l). Volume is a three dimensional property, and the cavities formed in the material are different at different scales (e.g. in the primary, secondary and tertiary structures of the material). The material factor corresponding to the McGowan volume could be correlated to the density or three dimensional molecular descriptors, while the material factor corresponding to the logarithm of the hexadecane/gas partition coefficient could be determined by correlating differences in solubility in hexadecane and the material or by using another parameter to describe volatility e.g. vapor pressure.
Figure 26. Plotting estimated Abraham descriptors in terms of ‘a’ values for specific materials against B values for oligomers of selected polymers (top), material b values against A values for oligomers (middle), and material e values against E values for polymer monomers.

This ultimate goal would be to develop a model that could predict material properties without needing any empirical input. A model of this type may be more accurate at predicting the solubility-/sorption energies of the material with different additives. For example, it could be used to predict the effect of the blooming that occurs when an additive diffuses out of the bulk material and gathers on its surface, thereby changing the solubility properties of the bulk material.
Finally the estimation of diffusion coefficient could be improved by using data on molecular interactions. The same goes for micropores and other cavities. Increasing the accuracy of the predicted diffusion coefficient would significantly reduce the uncertainty in the estimated emissions.

6.3 Future challenges

A number of challenges remain to be addressed before it will be possible to predict the emissions of all compounds of interest from an arbitrarily chosen material or product. These include challenges relating to gathering data on a national level and areas where the molecular model needs to be improved (see figure 27).

Figure 27. Challenges associated with making a generic model that predicts emissions for all possible compounds and scenarios

On the national level, the major challenge is to obtain correct and reliable information for input into the model. For some products, there are precise product declarations and statistics on sales and waste data can be obtained from sales organizations. However, this is not universally true. The first and most important thing that must be determined is the content of the compound of interest in the sold material and the composition and structure of the sold material. Some products and materials vary widely in their composition because producers add additives with the aim of producing specific properties and do not generally record the precise quantity added. Similar issues arise when dealing with natural materials, whose composition and polymeric structure is not easily defined; this is the
case for cotton or wool in textiles, among other things. Many products also consist of different complex components with different compositions, and in such cases more detailed information is needed than for more homogenous products. The required data could be gathered by extensive screening of products or by requiring that manufacturers and retailers organizations provide detailed and reliable product declarations. However, this would need to be done on a global level since many products are produced in other countries. Both of these would be demanding and costly. While sales data are generally available, the challenge lies in converting it into a total surface area in circulation and relating it to the quantities of specific materials and their compositions. For some products, only economic or shipping data are available; the latter is usually in the form of mass and includes the weight of packaging materials. The uncertainties in estimated emissions would be greatly reduced if sales organizations were to collect information on the number of sold items, the total area sold, the composition of the sold materials, and their expected life spans.

Changes in usage patterns expose products and material to different environmental situations. Environmental information relating to usage patterns can be estimated but this is complicated by the fact that products may be used at different temperatures, exposed to different receiving media and flows, and may have different lifetimes. For example, consider textiles, which are use indoors and outdoors, worn next to the skin, washed, and tumble dried. The challenge in such cases is to develop methods for calculating the outcomes and emission rates in all these different uses and environments.

At the molecular level, the model cannot estimate the emissions of all types of compounds in all situations. The emissions of some compounds cannot be predicted by the generic model. Notably, the Absolve program cannot estimate Abraham solvation parameters for organometallic compounds and does not have descriptors for ionic interactions. To estimate emissions of such compounds, one would have to develop additional modules for the model. The same goes for compounds that are reactive or are degraded within the material or the boundary layer. For such compounds, the model estimates their emissions but will do so using an inaccurate concentration.

The most demanding challenge of molecular model development is to estimate the effects of washing and grinding. Many surfaces and materials are washed with surfactants, solvents and other washing agents. The presence of surfactants in water will change the solubility of the
compounds of interest. To estimate this, the compound’s micelle forming energy must be estimated as well as its solvation energy for the other solvents that are in the solution. Many different solvents and surfactants are in widespread use, and so an additional model is needed to perform these estimations. Some cleaning methods also grind the material’s surface, resulting in particle release. The effects of this could be estimated by estimating the wear of the product.

Finally simply estimating the mass of a compound that is emitted is not sufficient to determine whether or not its emissions are problematic. More research will be needed to identify emissions of particular concern. It will be necessary to compare to total emissions of each compound to those from other sources and to consider their effects on the environment, including their persistence, bioaccumulation, toxicology, and general effects on humans. Methods have to be developed to inform decision makers, producers and consumers without drowning them in floods of information, and this information must be presented together with practical strategies that will significantly reduce the severity of any identified problems.
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8 References


54. EURACHEM. Quantifying uncertainty in analytical measurement. 2. 2000. EURACHEM/CITAC. Ref Type: Report


9 Appendices

9.1 Estimated Abraham solvation parameters

<table>
<thead>
<tr>
<th>Substance</th>
<th>A</th>
<th>B</th>
<th>Bo</th>
<th>L</th>
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9.2 Two dimensional structures of compounds

DINP

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3
\end{array}
\]

\[
\text{O} \quad \text{O} \quad \text{O}
\]

\[
\text{H}_3\text{C} \quad \text{CH}_3
\]