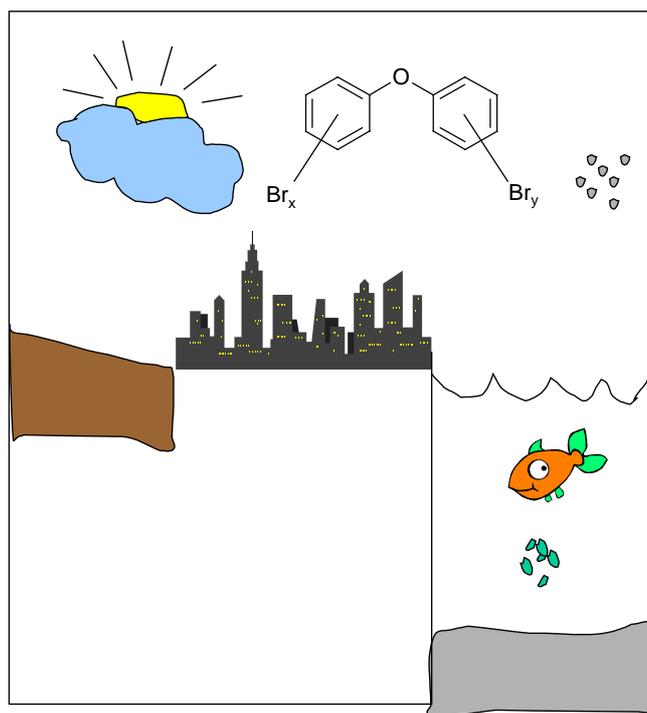




report

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The Environmental Fate of Polybrominated Diphenyl Ethers in the Centre of Stockholm - Assessment Using a Multimedia Fugacity Model



Master of Science Thesis in Engineering Biology

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Summary in Swedish

Bromerade flamskyddsmedel är ämnen som används bl a i elektronisk utrustning, textilier, plaster och byggmaterial för att förhindra att brand uppkommer. Under de senaste decennierna har ökande halter av en typ av flamskyddsmedel, nämligen de polybromerade difenyletrarna (PBDEer) påvisats i olika biologiska prover (Sellström 1999; de Wit 2000). Detta är oroväckande med tanke på att dessa ämnen till strukturen liknar välkända miljögifter såsom polyklorerade bifenyler (PCBer) och dioxiner, och därför misstänks liksom dessa ha potential för långväga transport, bioackumulation och biologiska effekter. För myndigheter och miljöansvariga är det av stort intresse att klarlägga hur flödet av dessa ämnen ser ut i miljön, för att kunna avgöra var resurser bör läggas in för mätningar eller eventuella utsläppsreduktioner. Innan detta görs på lokal nivå, är det dock viktigt att skaffa sig en allmän uppfattning om ämnets egenskaper, emissioner och beteende i miljön för att sedan stegvis arbeta sig fram till en detaljerad och platsspecifik beskrivning av det område man är särskilt intresserad av.

Mackay et al. (1996 a,b,c) har beskrivit en femstegsprocess där syftet är att med hjälp av sk multimedia fugacitetsmodeller utvärdera vad som sannolikt sker med ett ämne när det kommer ut i miljön. Ett sjätte riskbedömande steg lades till av MacLeod och Mackay (1999) där uppskattade koncentrationer jämfördes med aktuella gränsvärden, i den mån sådana fanns. Processen innebär:

- 1) Klassificering av ämnet samt bestämning av fysikalisk-kemiska egenskaper
- 2) Insamling av emissionsdata samt bakgrundsnivåer
- 3) Generell bedömning av kemikaliens uppträdan i miljön
- 4) Regional bedömning inklusive validering om möjligt
- 5) Lokal, platsspecifik bedömning inklusive validering om möjligt
- 6) Jämförelse mellan uppskattade koncentrationer med sk "predicted no effect concentrations (PNEC)"

Liksom för många andra ämnen som under senare år uppmätts i miljön, råder det stor brist på tillförlitliga uppgifter om PBDEers fysikalisk-kemiska egenskaper, men även om användning, flöden, emissioner samt förekomst i miljön. Genom att tillämpa denna fem- eller sexstegsprocess i ett inledande skede kan man få en första uppfattning om var de största kunskapsluckorna ligger och var resurser bör sättas in för vidare forskning. Palm et al. (manuskript) utförde de fyra första stegen för PBDEer, i syfte att identifiera de kunskapsluckor och databrister som föreligger för dessa ämnen. Resultaten från den studien visade att fysikalisk-kemiska egenskaper fortfarande är bristfälliga, att få mätningar har gjorts på förekomst i miljön samt att emissionsuppskattningar är osäkra.

Syftet med detta projekt har varit att komplettera ovan nämnda helhetsbedömning genom att utföra det femte steget i processen, dvs en lokal bedömning av fördelningen i

miljön av PBDEer. Tre kongener studeras närmare, nämligen 2,2',4,4'-tetraBDE (BDE 47), 2,2',4,4',5-pentaBDE (BDE 99) samt decaBDE (BDE 209). Urvalet gjordes med utgångspunkt från tillgänglighet av fysikalisk-kemiska data samt kongenernas förekomst i miljön och i kommersiella produkter. Det område som valts ut är centrala Stockholm, av den anledningen att det här relativt sett finns goda uppgifter på förekomsten i miljön av de aktuella kongenerna, samt att denna typ av ämnen förväntas förekomma i större mängder i tätbefolkad stadsmiljö, eftersom dess användning till stor del är populationsberoende.

För att kunna utföra studien har en multimedia fugacitetsmodell över centrala Stockholm utvecklats. I arbetet med modellen, som är programmerad i Excel och som vi kallar CeStoc, har ingått att bestämma specifika värden för centrala Stockholm på ett stort antal miljöparametrar, såsom exempelvis luftens residensid, halter av organiskt kol i jord, vattenvolymer och procentuell andel bebyggd mark. I vissa fall har specifika värden för Stockholm ej gått att få fram, varför schablonvärden antagits i dess ställe. Ekvationerna i modellen och nödvändiga miljöparametrar har baserats på existerande fugacitetsmodeller som beskrivits i ett flertal publikationer (t ex Mackay 1991; Mackay and Paterson 1991; Mackay et al. 1996a,b,c). CeStoc kalibrerades först mot en PAH (fluoranten) där data på halter i miljön och emissioner var relativt lättillgängliga. Resultaten från testkörningen visar att modellen förutsäger koncentrationer som generellt överensstämmer med uppmätta värden, och kan därför anses vara tillämpbar även på andra ämnen. Därefter kördes CeStoc för de tre PBDE-kongenerna. Validering med uppmätta halter gjordes även för dessa ämnen där det var möjligt, och överensstämmelsen mellan modellvärden och faktiska värden ansågs tillfredsställande.

Resultatet från CeStoc-modelleringen indikerar att majoriteten av de PBDEer som släpps ut i luft i centrala Stockholm transporteras ut ur området med luft, istället för att deponeras på mark och stadsytor. Det innebär att Stockholm sannolikt är en källa till föroreningar för andra områden. Följaktligen är möjligheten stor att inflöde via luft och vatten från andra områden kan påverka halterna i Stockholm, varför en undersökning av bakgrundshalter i inkommande luft och vatten vore av stort värde. Av de PBDEer som emitteras till jord och vatten stannar dock majoriteten kvar i området. Dessa emissioner bedöms vara lägre än emissioner till luft, men det finns stor osäkerhet i emissionsuppskattningarna, varför noggrannare studier över emissionsmedium rekommenderas.

Med de emissionsuppskattningar som gjorts i denna studie, är jord det medium där majoriteten av PBDE:erna hamnar, tätt följd av sediment. Dessa två medier står tillsammans för ca 98 % av den kvarvarande mängden PBDEer i systemet.

Bromeringsgraden tycks inte påverka halterna i Stockholm i någon större utsträckning, vilket delvis kan bero på det stora utflödet ur området. Palm et al. (manuskript) visade dock att det finns indikationer på att bromeringsgraden påverkar fördelningen i en

generell, mer storskalig miljö. Noggrannare uppgifter på fysikalisk-kemiska egenskaper krävs innan entydiga slutsatser kan dras om bromeringsgradens inverkan.

Predikterade halter av individuella PBDE-kongener i vatten och sediment ligger i samma storleksordning som uppmätta halter av individuella PCB-kongener i samma medier i Stockholm och Östersjön. Detta tyder på att PBDEer mycket väl skulle kunna vara ett nytt "PCB-problem", och att dess grad av miljöpåverkan är ungefär densamma som PCBernas.

CeStoc har visat sig tillämpbar på fluoranten samt tre PBDE-kongener. Modellen kan i framtiden med fördel användas även på andra organiska ämnen för att studera fördelning och transport i centrala Stockholm. Exempel på användningsområden är:

- Som en nödvändig länk mellan materialflödesanalyser (MFA) och miljöövervakning. Med MFA identifieras emissionskällor och storleken på dessa uppskattas. Dessa emissionsdata kan sedan användas i modellen och predikterade halter kan valideras med miljöövervakningsdata.
- Vid ett initialt screening-skede av nya organiska ämnen. Modellen kan hjälpa till att identifiera de kemikalier som är mest troliga att uppvisa lång persistens, samt kan ge en indikation på vilka medier som är de troligaste recipienterna.
- Som underlag vid utveckling av mätprogram, av samma anledning som ovan.

Det skall dock poängteras att CeStoc alltid bör ses som ett delverktyg i en större bedömningsprocess, där ovan nämnda fem- eller sexstegsprocess rekommenderas som utgångspunkt när ett nytt ämnes fördelning och persistens i miljön skall studeras.

Abstract

A local-scale assessment of the environmental fate of three congeners of polybrominated diphenyl ethers (PBDEs) has been performed for the centre of Stockholm. The partitioning properties and main transport processes of these congeners in Stockholm are identified using a site-specific multimedia fugacity model, called CeStoc, that was developed and parameterised for the area of interest. CeStoc was based on level III and IV fugacity models by Mackay (1991), Mackay and Paterson (1991) and Diamond et al. (manuscript). Five compartments were included: air, water, soil, sediment and an organic film covering the impervious surfaces in the city. The model was satisfactory calibrated with the PAH fluoranthene, before it was run for the compounds of interest. Validation with environmental levels of PBDEs was made where possible, showing reasonable agreement with model results. According to the CeStoc results, the majority of the PBDEs emitted are transported out of the region through air advection, implying that Stockholm may act as a source for chemical release to other regions. The largest sink for PBDEs in Stockholm is soil, closely followed by sediment, the two compartments together accounting for about 98 % of the total amount remaining in the system. The degree of bromination does not seem to have a large impact on the environmental distribution in this area, but further research on e.g. physical-chemical properties is necessary before this can be finally concluded. Predicted concentrations of individual PBDE congeners in sediment and water lie in the same range as measured levels of individual PCB-congeners, indicating that PBDEs could have an environmental impact of about the same size as the PCBs.

1 Introduction

Ever since humans first started to evolve they have been affecting the environment in one way or another. The fashions for this have varied over time and today we live in a “chemical society” where lots of known and unknown chemicals are being released to the environment. In several cases, chemicals believed to be harmless have later turned out to be just the opposite. Well-known examples of this are the polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDT). Recently, brominated flame retardants (BFRs), one type of these being polybrominated diphenyl ethers (PBDEs) (Fig 1) have raised the environmental concern. The main reasons for the interest in these compounds are the increasing levels in some biological samples (Sellström 1999) and the structural resemblance to well-known pollutants such as PCBs and polychlorinated dioxins.

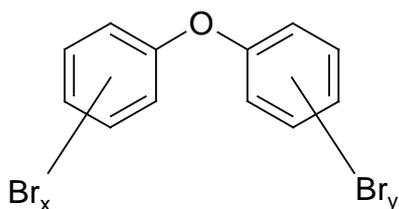


Figure 1. The general structure of a polybrominated diphenyl ether (PBDE).

An appropriate method for predicting environmental occurrence and distribution of chemicals in general and PBDEs in particular would be useful for legislative and voluntary control. Mackay et al. (1996 a,b,c) outlined a five-stage strategy for assessing the environmental fate of organic chemicals using multimedia fugacity models. This strategy involves classification of the chemical, estimation of emissions, evaluative assessment of fate, regional far-field evaluation and local near-field evaluation of fate. MacLeod and Mackay (1999) added a sixth stage of risk assessment to this procedure, including estimations of toxicity.

Palm et al. (manuscript) recently performed the first four stages evaluating the fate of PBDEs. The current study accounts for the fifth stage, with the centre of Stockholm being the area of interest. Stockholm was chosen because of the characteristics of the chemicals studied. PBDEs are mainly distributed through products, especially electronic devices and plastics, and due to the high population density the amounts in a large city are expected to be high compared to the levels in other environmental type regions.

An accurate fugacity model of the city of Stockholm would also be very useful for future assessments of the fate of chemicals in the area. The model could be applied to any organic chemical, with a few exceptions, given sufficient data on physical-chemical properties and emission rates. If environmental levels are well-known it could also be used to estimate emissions and perhaps background levels of a particular chemical in the region.

To environmental authorities, such a model would be useful, in that respect that it could act as a necessary link between material flow analysis (MFAs) and environmental monitoring, and thus reconcile emission estimates with observed environmental levels. Also, it could be used in initial screening-projects as a ranking method, that could help selecting those chemicals that are most likely to be environmentally persistent and thus have potential to cause harm. This would be valuable for the development of monitoring programmes of different chemicals.

1.1 Aim of project

The aim of this project was to develop a site-specific fugacity model for the centre of Stockholm and to study the environmental distribution of three selected PBDE congeners in this area, as well as the importance of the degree of bromination by using the diphenyl ether as a reference compound. The model is intended to be applicable also for evaluation of the environmental fate of other organic non-ionic chemicals in the region.

2 Background

2.1 Brominated flame retardants

During the last decade, the environmental concern about brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) has increased. This has been most apparent in Sweden, where the first signs of increasing environmental levels were detected, but also in the rest of Scandinavia. Lately the interest has spread to other parts of the world as well. The reasons for this concern are the suggested similarity of PBDEs to notorious environmental pollutants such as PCBs and chlorinated dioxins, their toxicological impact on exposed animals with endocrine disrupting effects (WHO 1994) and their rapidly increasing concentration in the environment (Sellström 1999). PBDEs are also believed to be so-called POPs, (persistent organic pollutants), subjected to long-range transport. There are presently several investigations going on, concerning the risk and fate of PBDEs. In the EU, a comprehensive risk assessment has been undertaken for these chemicals (EU 2000, EU 1998), resulting in a European ban of the pentabrominated compound (ECB 2000). PBDEs are also candidates to the UN-ECE convention on POPs (UN-ECE CLRTAP Expert group, 2000). A European ban need not necessarily imply that the release to the Swedish environment will cease. The compounds may still enter the country through imported flame retarded products and thus leach out during use.

There are two different kinds of flame retardants; those used as reactives and those used as additives. Reactive flame retardants are incorporated in the product, an application that is common in plastics, where flame retardants are chemically bound to the plastic polymer. These compounds are considered not easily removed from the product, but may leach out if not completely reacted. The percentage non-reacted chemical present in a product has been reported to be negligible (Larssen et al. 1999). Nevertheless, other studies have shown high environmental levels of tetrabromo-bisphenol A (TBBPA) (Sjödin 2000), a BFR which is exclusively used as reactive, and therefore contradicts the theory of non-mobility. Flame retardants that are used as additives are on the contrary only mixed into the product or applied onto the surface, and therefore these kinds of BFRs have a higher potential to leaching out into the surrounding environment. PBDEs are solely used as additives, which is one reason for the great environmental concern.

PBDEs are used as flame retardants mainly in plastics, electronic devices and textiles. There are three technical mixtures that are used, viz. PeBDE or penta-blend, OcBDE and DeBDE. Each mixture contains several different congeners, the compositions being shown in Table 1. There are 209 possible PBDE congeners, with the number of bromine atoms raising from one to ten. They are numbered after the same system as the PCBs.

Table 1. Composition of commercial PBDE flame retardants (de Wit 2000).

Technical mixture	Tetra-BDEs (%)	Penta-BDEs (%)	Hexa-BDEs (%)	Hepta-BDEs (%)	Octa-BDEs (%)	Nona-BDEs (%)	Deca-BDE (%)
PeBDE	24-38	50-60	4-8	-	-	-	-
OcBDE	-	-	10-12	44	31-35	10-11	<1
DeBDE						<3	97-98

During the last years the use of PBDEs as flame retardants has decreased in Sweden, and today the more harmful pentaBDE mixture has almost vanished from the market (B-O Lund pers. comm.). However, the more common deca-brominated compound is still in use and there is a possibility that this compound may be photolytically degradable to lower brominated and more harmful congeners, which was shown in a laboratory experiment by Sellström et al. (1998). PBDEs also enter the country through imported flame retarded products, and may due to this be released in the environment.

Despite the increasing environmental concern about these compounds, little is known about their properties and environmental behaviour. Until recently, only commercial products were available as analytical standards and therefore, analysis and characterisation of individual PBDE congeners has until now been very difficult. Still, there is a lack of reliable methods to analyse the most common compound, the decabrominated diphenyl ether.

The efficiency and cheapness of PBDEs have caused a widespread use and today they are found globally in the environment (Sellström 1999). They have even been found in sperm whales (de Boer et al. 1998) and pilot whales (Lindström et al. 1999) in the Atlantic, which reveals something about their distribution properties since sperm whales take their food deep down in the oceans.

2.2 The five-stage strategy

In order to evaluate the environmental fate of PBDEs, as well as other commercially emerging chemicals, an effective and structured strategy is needed. New restrictions concerning product choices and the substitution principle also require an instrument for industrial companies to evaluate the environmental fate of the chemicals used. Mackay et al. (1996 a,b,c) outlined a five-stage strategy for evaluating the environmental fate of chemicals and a sixth stage was added by MacLeod and Mackay (1999) (Fig 2).

This strategy involves classification of the chemical as a type I-V chemical, where type I chemicals are soluble in all media, type II are involatile compounds and type III are non-water soluble compounds. Type IV chemicals are insoluble in air and water and type V are chemicals that exist as several different species (for example ionising

compounds) (Mackay et al. 1996a). Different chemical types have different partitioning properties and thus, input data have to be modified for each type. Generally, type III, IV and V modelling is not performed since no convenient models for these chemical types currently exist, although there are ways to get around these problems. Stage 2 includes estimation of emissions and background concentration data, globally or in a particular region. This stage is important since emission data drive the model predictions of environmental concentrations. Stage 3 is an evaluative assessment of fate, where generic fugacity models (see section 2.3) such as the Equilibrium Criterion (EQC) model (Mackay et al. 1996b) may be used to assess the generic environmental fate of the chemical. The benefits of this stage are that it provides a foundation for comparison of different chemicals and that it is useful when it comes to international collaboration in the respect that it gives a common basis for discussion. Stage 4 is a regional far-field evaluation where a region of interest can be selected. The fifth stage is a local near-field evaluation of fate. This can be a city, a lake or some other area, where emissions or exposure are assumed to be high or where the environment is particularly sensitive. The sixth and last stage includes comparison of predicted environmental levels with observed effect levels. Palm et al. (manuscript) recently performed the first four stages evaluating the fate of PBDEs. The current study accounts for the fifth stage, with the centre of Stockholm being the area of interest.

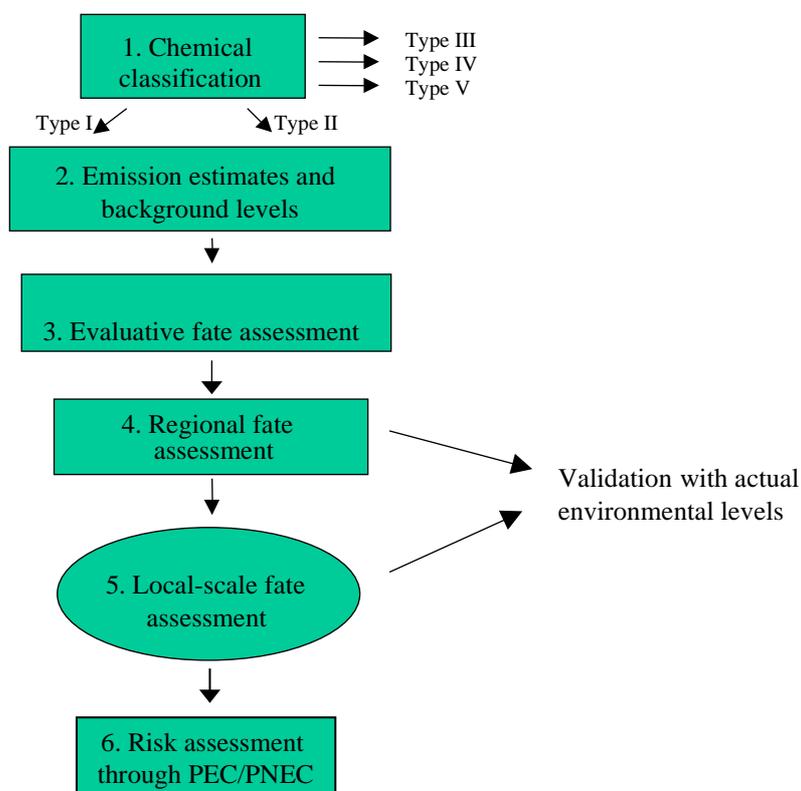


Figure 2. . The five-stage strategy (Mackay et al. 1996a) with the sixth stage of risk assessment (MacLeod and Mackay 1999).

2.3 Multimedia fugacity models

There are plenty of models concerning the fate of a compound in a particular medium, e.g. movement in air, soil or water. This is of course useful when the aim is to get an overview of a chemical's behaviour in a certain medium, but quite often the interest lies in understanding the overall environmental behaviour of the chemical. This is necessary for risk assessments of new and existing chemicals performed by environmental authorities and preceding legislative actions. As the responsibility for chemical politics shifts from government to producers, a method for evaluating overall behaviour of chemicals would be useful also for industrial companies, for product choices at the design and development stage. Multimedia fugacity models provide a useful tool for assessing this kind of environmental overall fate. The models have been described in several papers (Mackay 1991; Mackay and Paterson 1991; Mackay et al. 1996 a,b,c), and they are all based on the concept of fugacity (see section 2.3.1). In principle, any number of media can be included in the models, if transport processes are known. The four basic media are air, water, soil and sediment. The advantage of using the multimedia models is that they provide an overall picture of the environmental distribution of a chemical, and that they can be used for many different types of organic chemicals.

As with all models, it has to be kept in mind that the model predictions are not the actual truth, rather they show a likely picture of the truth. They help indicating where the main problems are, and can help focussing further research. However, the more environmental monitoring data there are, the more carefully the model can be validated, and the closer to the truth the model predictions will lie.

2.3.1 The concept of fugacity

Since the models here described are based on the concept of fugacity, an explanation of it is appropriate. The concept of fugacity was established in 1901 by the scientist G N Lewis (Mackay 1991). Fugacity is an equilibrium criterion that is logarithmically related to chemical potential and can be viewed in terms of pressure. In short, the fugacity of a chemical in a particular medium is the partial pressure that the chemical exerts when it tries to escape that medium, that is its 'escaping tendency'. Fugacity is also related to concentration through the equation

$$C = Z \times f, \quad (2.1)$$

where C = concentration (mol/m^3), Z = the fugacity capacity of the medium for the chemical of interest ($\text{mol}/\text{Pa} \times \text{m}^3$) and f is the fugacity of the chemical in that medium (Pa). The Z -value can be calculated for each medium and is dependent on the medium

itself and on the chemical of interest. The fugacity is the parameter that ultimately drives the transport of a chemical in a phase as well as between phases. Quite often, concentration gradients are denoted this property, but due to the relationship between concentration and fugacity it is realised that this is only possible inside a phase, not between phases (because of the different Z -values), where fugacity alone is the driving force. Equilibrium between two phases is reached when the fugacity of the chemical in one phase equals the fugacity in the other phase. The transport process can be described through the equation

$$N = D \times f, \quad (2.2)$$

where N (mol/h) is the flow of chemical and D (mol/Pa×h) is a transfer coefficient that can be calculated for each transport process, and that is dependent on the characteristics of the transport. By combining these parameters and writing up mass balance equations, where input equals output, the fugacities in each medium can be calculated and hence the concentrations and amounts present (Mackay 1991).

2.3.2 Four model levels

There are basically four different levels of the models. A short summary of each level will be given here. The four levels and their differences are depicted in Figure 3.

Level I is a steady state, equilibrium, closed system model, where emissions are fixed and instantaneous and no intermedia transport is considered. The required input data are simply the physical-chemical properties of the studied chemical, and the output data are media concentrations at equilibrium and distribution percentages. Level I gives a general implication about the chemical's tendency to partition into different media, and it can give useful insight about relative media concentrations and potential for e.g. long-range transport. Level II provides additional information about the main loss processes in the system and environmental persistence. At this level, degradation half-lives for each medium are required as additional input, properties that are normally quite difficult to find. Level II is a steady state, equilibrium, open system model where emissions are continuous but fixed and constant. At level III, equilibrium is no longer assumed, and emissions are media-specific and can be modified by the user. Level III gives information about intermedia transport processes, non-equilibrium concentration and environmental persistence at steady state. A level IV assessment can also be performed if unsteady state conditions are desired. For detailed descriptions of the models, the reader is referred to *Multimedia Environmental Models: the Fugacity Approach* (Mackay 1991).

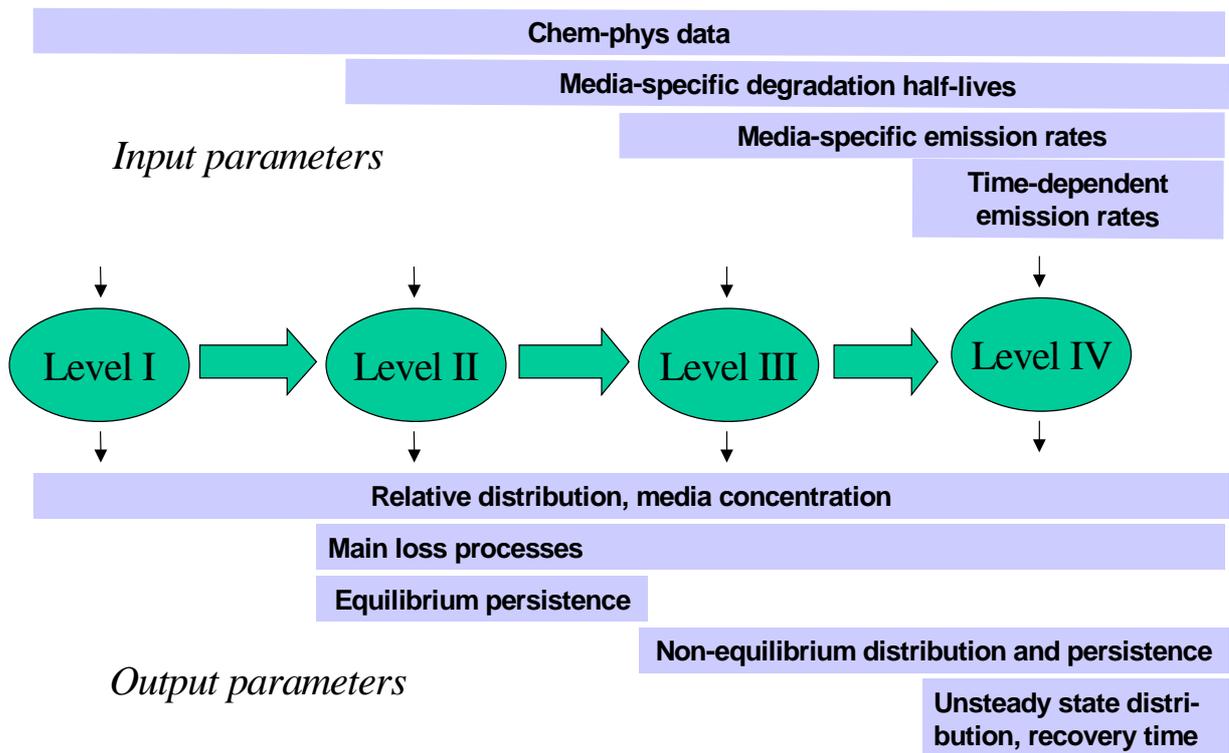


Figure 3. The four model levels. For each level additional input parameters are required, and additional output parameters are shown for each level.

3 Fugacity model of Stockholm

The objective of this section is to achieve a qualitative and quantitative but simplified description of the environment of the centre of Stockholm. The purpose is not to include all the details and complexities of the natural processes, rather it is to simplify them, so that the environment of interest can be treated as a somewhat homogenous area. The study concerns the area shown in Figure 4. Transport equations were obtained from existing fugacity models (Mackay 1991; Mackay and Paterson 1991; Diamond et al. manuscript) and site-specific input values for Stockholm were used where possible. Appendix 1 shows the selected environmental input parameters, used in the model developed. CeStoc is a level IV model, but since it was run until steady state was reached, only the steady state, i.e. level III situation was considered. Five different media were included: air, water, soil, sediment and urban surfaces. Vegetation was not included, due to lack of uptake data by this medium in Stockholm. Also, because of the cold climate and hence the seasonal absence of leaves, vegetation is assumed to have relatively low impact on the distribution of chemicals in Stockholm. Aquatic biota has also been excluded from the model. Algae and other particles have larger biomass than fish and therefore it is assumed that calculating the concentration in water particles and pure water will cover for the majority of the chemical amounts present in the Stockholm waters.

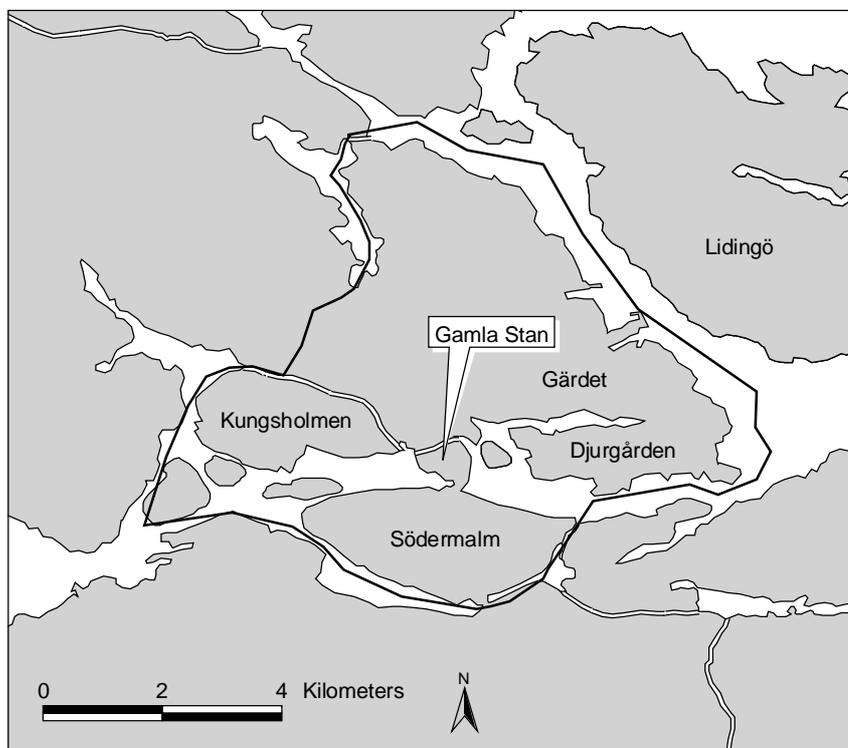


Figure 4. The line shows the studied area of Stockholm.

The area was selected with the purpose to include most of the urban areas in the centre of Stockholm. The centre of Stockholm, as defined in Fig 4, has an area of about 4700 ha, or 47 km² (A-M Hellsten pers. comm.), with a population of about 740 000 (USK 2001). The area mainly consists of islands, with Lake Mälaren crossing the centre of the city. The built-up areas or impervious surfaces contribute with about 50% (GFK 2000), and 25% of the surface area is water (A-M Hellsten pers. comm.). The remaining 25% is assumed to be soil. A description of each media and the parameters used in the CeStoc model is outlined in section 3.1. Figure 5 shows the volumes of environmental media in the selected region.

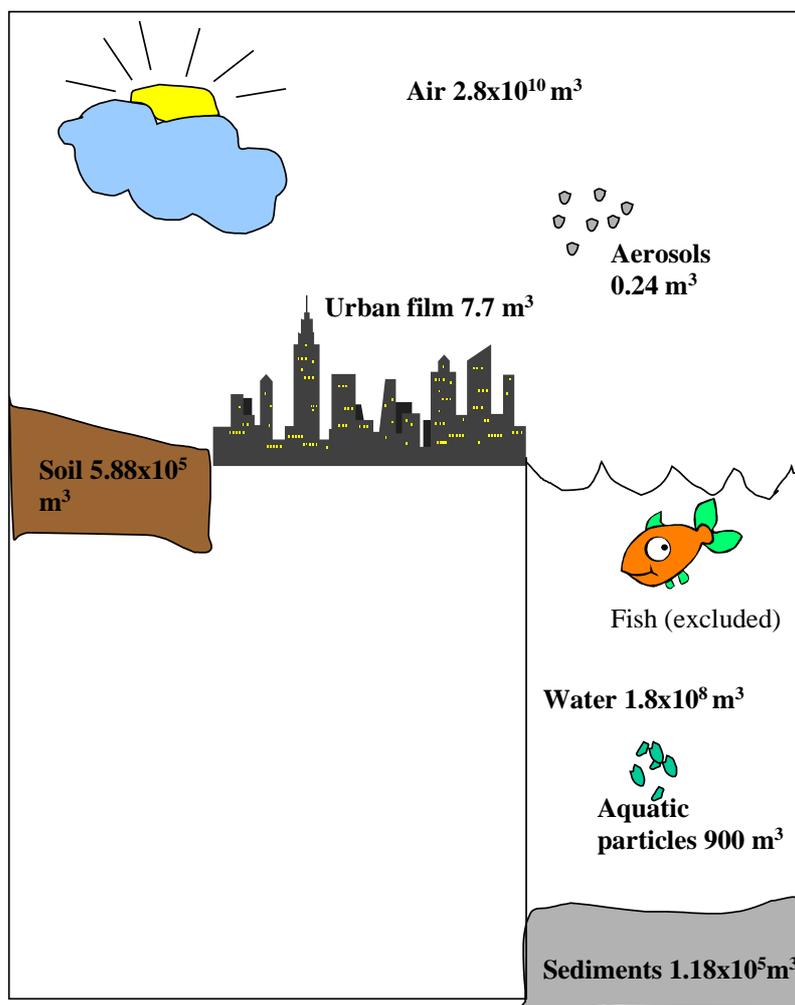


Figure 5. The environment of Stockholm, as defined in this project. For all the compartments, the bulk volumes are given.

3.1 Description of environmental media

3.1.1 Air

The atmosphere consists of different layers, among which the troposphere is the one in contact with the surface of the earth. The troposphere is about 10 km high, but properties change as height increases, and therefore we want to adopt a height that is available for chemicals released locally to the air, and also where temperature, density and other physical properties remain reasonably constant. The height of the air in Stockholm that has these properties varies over the year and the day between about 200 and 1000 m (C Johansson pers. comm.). Therefore, a mean value of 600 m or 0.6 km is adopted. Thus the air volume available for chemicals in the city of Stockholm is: $4.7 \times 10^6 \times 600 = 2.8 \times 10^{10} \text{ m}^3$. The expression for the Z-value for air is listed in Appendix 2.

3.1.2 Aerosols

The presence of aerosols in the atmosphere is important, since particles tend to attract substances with low vapour pressure. It is intuitively realised that the concentration of particles is higher in urban, polluted areas than for example at the countryside. PBDEs are assumed to be adsorbed or absorbed in a similar way as the polychlorinated dibenzodioxins (PCDDs), due to their structural resemblance, PCDDs being mainly attracted by smaller particles, with a diameter less than $1.35 \mu\text{m}$ (Harrad, 1998). Therefore, the concentration of particles of this size is of greatest interest when modelling PBDEs. The particle concentration of PM_{2.5} (less than $2.5 \mu\text{m}$) and PM₁₀ (less than $10 \mu\text{m}$) is regularly monitored by SLB-analysis in Stockholm, and the mean concentration of PM_{2.5} between October 1999 and October 2000 was $14.8 \mu\text{g}/\text{m}^3$ (Wallin, 1998). With an assumed particle density of $1.7 \text{ g}/\text{cm}^3$ this makes a total volume fraction of 8.7×10^{-12} . Since the air volume is $2.8 \times 10^{10} \text{ m}^3$ this gives a total particle volume of 0.24 m^3 . The measurements have been performed on Hornsgatan in Stockholm, which is a very busy street and thus relatively polluted compared to other areas in Stockholm. For comparison, it can be mentioned that Mackay (1991) suggested that a volume fraction of 2×10^{-11} would be convenient for a generic environment. Since urban areas are probably more polluted than the generic environments, the number for Stockholm should be somewhat higher. However, since only the PM_{2.5} particles are considered here, the number calculated for Stockholm is assumed to be appropriate. The Z-value expression for aerosols is listed in Appendix 2.

3.1.3 Water

The water of Stockholm covers about 25 % of the surface area, 1200 ha or 12 km^2 . The average depth of the lakes and streams in the inner city of Stockholm is about 15 m, considering Lake Mälaren, Riddarfjärden and Saltsjön contributing the most (GFK

2000). This yields a water volume of $15 \text{ m} \times 12 \times 10^6 \text{ m}^2 = 1.8 \times 10^8 \text{ m}^3$. The Z-value for water is simply $Z = 1/H$ (Mackay 1991) where H is the Henry's Law constant ($\text{Pa} \times \text{m}^3/\text{mol}$).

3.1.4 Aquatic particles

It is easily realised that the presence of particles in water affects the behaviour of a chemical, because chemicals can be absorbed or adsorbed to particles, often it is not clear which process that occurs. All the lakes of Stockholm are eutrophic, that is rich in organic material and hence in particles as well. However, to our knowledge, no studies have been performed concerning the concentration of particles in the Stockholm waters. Therefore, a general concentration of 12 mg/l (Mackay, 1991) was adopted, which yields a volume fraction of 5×10^{-6} , the density of the particles being about 2400 kg/m^3 . Thus, the total volume of water particles is $5 \times 10^{-6} \times 1.8 \times 10^8 = 900 \text{ m}^3$. The absorption or adsorption of hydrophobic chemicals to these particles is dependent on the content of organic carbon, that is, the Z-value for the particles is partly determined by this fraction. Broman et al. (1994) studied the organic carbon content in aquatic particles in Stockholm, yielding a mean percentage of 12%, that is a mass fraction of 0.12. The Z-value expression for water particles is listed in Appendix 2.

3.1.5 Sediment

Sediments are built up by depositing material from the water column, which can be algae, dead organisms, soil, airborne dust and leaf particles or other organic material. In the top layer of the sediment, organisms are commonly found that feed on organic material, which makes the upper layer more active, with bioturbation and currents stirring the solid material whereas the deeper layers are more inactive. Sediments can be regarded as a final storage compartment for a chemical. Once a chemical has been buried below the bioturbation layer in the bottom sediment, it has low mobility and can be viewed as removed from the system. However, there are many ways in which sediment material can be remobilized. Heavy storms and dredging can cause currents that stir the bottom layer so that buried material becomes available.

The property of sediments as a storage compartment is interesting because of its potential to also act as a source for chemical release. Many organic chemicals end up in the sediments due to their hydrophobic properties and thus, this compartment is of crucial importance in a multimedia model.

The surface area of the Stockholm sediments was assumed to be the same as the water surface area. The sediment area in Stockholm is thus $1.18 \times 10^7 \text{ m}^2$. The depth available to chemicals was assumed to be approximately 1 cm since the bioturbation layer in Stockholm has been shown to be minor (Rosenberg and Diaz 1993). This yields a total

sediment volume of $1.18 \times 10^5 \text{ m}^3$. Based on ca 60 sediment cores (Östlund et al. 1998), the average water content of the upper 2 cm of sediments was calculated and converted to a volume fraction of 0.91. The average organic carbon mass fraction of these sediment solids was measured to 0.046 (Östlund et al. 1998), the solid density being approximately 2400 kg/m^3 . The Z-value expression for sediment is listed in Appendix 2.

3.1.6 Soil

Due to its high organic content, soil acts as a major recipient of hydrophobic chemicals from wet and dry deposition. Chemicals that reside in soil can later be washed out through water and solids runoff, through leaching to groundwater or through erosion. Thus, it is of importance to include this compartment in the model. Because of the urbanisation in cities like Stockholm, much of the land has been replaced by buildings and hard surfaces. The percentage “soft surfaces” in the centre of Stockholm is approximately 25 % or 11.75 km^2 , mainly in the areas of Northern Djurgården and Gärdet. The depth available for chemicals was assumed to be about one half of that in a generic environment, since the residence time in air is shorter, and thus the time available for the chemical to partition to soil is also shorter. In practice this means that the soil depth available is smaller, due to the quick turn-over. Therefore, the soil depth was set to 5 cm. This yields a total soil volume of $11.75 \times 10^6 \times 5 \times 10^{-2} = 5.88 \times 10^5 \text{ m}^3$. The volume fractions of air, water and solids in soil used in the CeStoc model were the same as in the generic models (Mackay 1991), i.e. 0.2 for air, 0.3 for water and 0.5 for solids. The organic carbon content for soil solids was obtained from Linde et al. (2001) where it was reported to be 0.068 on the average. The Z-value expressions for soil are listed in Appendix 2.

3.1.7 Impervious surfaces

A city, or an urban area is quite different from the generic environments used in evaluative models such as the Equilibrium Criterion (EQC) model (Mackay et al. 1996b). One big difference is the presence of so-called “urban surfaces”, that is roadways, sidewalks, buildings, signs and so on. Diamond et al. (2000) showed that a thin organic layer covers these impervious surfaces in urban areas. The layer consists of semivolatile organic compounds and particles and may act as a secondary source for chemical release to e.g. surface waters. The thickness of the bulk phase of the urban film varied between 29 and 250 nm (Diamond et al. 2000). The samples were taken in Toronto, Canada. It is assumed that the thickness of the organic layer in Stockholm lies somewhere in the same range, and for illustrative purposes a mid-point value of 137 nm was selected. The urban film was analysed and characterised by Diamond et al. (2000) and a density equivalent to that of octanol was suggested (826 kg/m^3) due to the high organic content.

To estimate the total surface that is covered by this organic layer some kind of “impervious surface index” (ISI) was needed, that would describe the relationship between the total area of the impervious surfaces and the “ground surface”. In order to estimate the ISI it was assumed that 50% of the impervious area is two-dimensional (e.g. streets) with index 1, and that the remaining 50% consists of three-dimensional buildings. The average height (H_A) of buildings in Stockholm was assumed to be 18 m. The average width (W_A) of a building was assumed to be 100 m and the average length (L_A) 15 m. This yields a surface area of $(2 \times W_A \times H_A) + (2 \times L_A \times H_A) + (W_A \times L_A) = 5640 \text{ m}^2$. Dividing this number by the base area yields index 3.76 for three-dimensional buildings. The total ISI is therefore $0.5 \times 1 + 0.5 \times 3.76 = 2.4$. That is, the total volume of organic film in Stockholm is (percentage urban surface) \times ISI $\times A_{\text{tot}} \times T_F = 0.5 \times 2.4 \times 47 \times 10^6 \times 137 \times 10^{-9} = 7.7 \text{ m}^3$. Diamond et al. (manuscript) suggested that the same organic carbon content be used as for octanol (0.74), which is why this number was adopted. The Z-value for the organic film is listed in Appendix 2.

3.2 Transport processes

Each transport process can be described by a D-value which, combined with the fugacity of the transported chemical in the media from where it is being transported, yields the total flow N (mol/h). The D-values are depicted in Figure 6 and listed in Appendix 3. A description of the important parameters is given below.

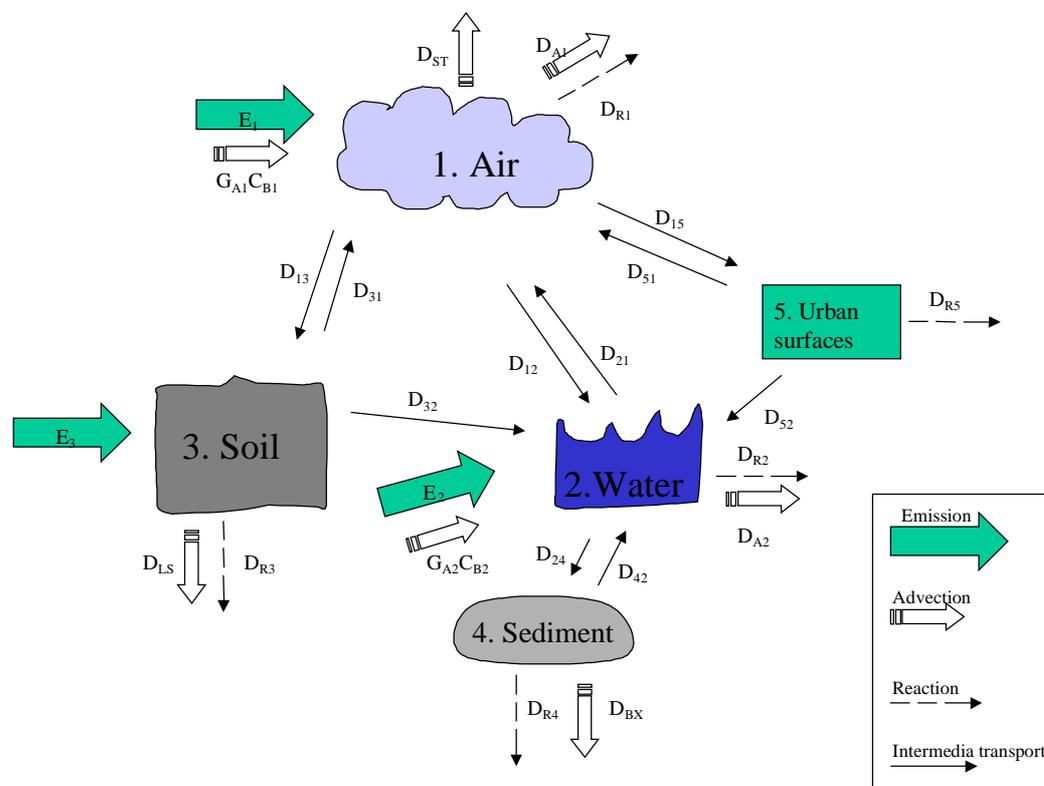


Figure 6. Transport processes in the Stockholm environment, as used in the CeStoc model.

3.2.1 Loss processes

The loss or removal processes for a chemical are the reaction or transport processes that make the chemical leave the system. In figure 6 the D-values for these processes are denoted by D_{Ri} and D_{Ai} . D_{Ri} stands for reaction D-value in medium i , and is the transfer coefficient that describes degradation or transformation of the chemical in that medium. Reaction D-values are calculated through the equation $D_{Ri} = k_{Ri} V_i Z_i$, where k_{Ri} is a first-order rate constant which is simply $\ln 2/t_{1/2}$, where $t_{1/2}$ is the degradation half-life in the medium. V_i is the bulk phase volume (m^3) and Z_i is the fugacity capacity of the medium ($mol/m^3 \times Pa$). Advection D-values are calculated through the equation $D_{Ai} = G_i Z_i$, where G_i is the flux (m^3/h) and Z_i is the fugacity capacity ($mol/m^3 \times Pa$). The advective outflow is also dependent on the residence time of air and water respectively, and hence those values were calculated. The residence time of air (τ_A) was calculated through

$$\tau_A = V_{tot}/(v \times A), \quad (3.1)$$

where V_{tot} = total air volume = $2.8 \times 10^{10} m^3$, v = wind speed = 3.5 m/s (SLB-analysis, 2001) and A is the cross-sectional area in the horizontal direction:

$$\sqrt{4.7 \times 10^7} \times 600 = 4.11 \times 10^6 m^2 \quad (3.2)$$

The residence time τ_A is therefore 1944.9 s or 0.022 days. The residence time in water, τ_W was calculated in the same way using the water flow through Saltsjön, which is $4.6 \times 10^9 m^3/year$ on the average (C Lennergren pers. comm.). Dividing the total volume ($1.76 \times 10^8 m^3$) by that number yields a residence time (τ_W) of 13.96 days.

Three advective D-values are treated separately since they are different from other advection processes in the sense that they can be viewed as removal processes without transport to the surrounding areas and thus the chemical is made unavailable to the environment studied. Therefore, these processes can also be treated as “semi-reactions”. The D-values refer to leaching from soil to groundwater (D_{LS}), sediment burial (D_{BX}) and transfer to stratosphere from air (D_{ST}), all being listed in Appendix 3.

3.2.2 Intermedia transport processes

3.2.2.1 Air-water exchange

Transfer of chemical between air and water occurs through i) bi-directional diffusion ii) dry and wet deposition from air to water and iii) transfer from air to water through rain dissolution, i.e. transfer of gaseous molecules dissolved in rain. For each of these processes a D-value can be calculated and these can then be summarised to the “total D-values” D_{12} and D_{21} . The expressions for the D-values are all listed in Appendix 3. The

diffusive processes are dependent on so-called mass transfer coefficients (MTCs), which are parameters that describe the velocity by which the chemical crosses the boundary layer between two phases. Both MTCs used were obtained from Mackay et al. (1991). The air-side MTC was set to 3 m/h and the water-side MTC to 0.03 m/h. Deposition and rain dissolution processes are dependent on dry deposition rate (U_P), rain rate (U_R) and scavenging ratio (Q), which is the relative volume that a raindrop falls through on its way down to the ground. The scavenging ratio is approximately 200,000 (Mackay 1991). The average rain rate in Stockholm is 0.54 m/year (A-M Holst pers. comm.). Caffrey et al. (1998) showed that the dry deposition velocity of particles of 2 μm in the vicinity of Chicago is 0.7 m/h. This is assumed to be applicable for urban areas in general and hence for Stockholm as well.

3.2.2.2 Air-soil exchange

Air-soil transfer processes were calculated as described in Mackay and Paterson (1991). This transport occurs through similar processes as air-water, D-values being listed in Appendix 3. The bi-directional diffusive process is dependent on an air-soil MTC (k_{SA}) which is approximately 5 m/h (Mackay 1991). Two other parameters that are necessary for the diffusion process as described in Mackay and Paterson (1991) are the effective diffusivities in air (B_A) and water (B_W) and the diffusion path length in soil (Y_S). The values for the diffusivities were adopted straight from Mackay and Paterson (1991) (Appendix 1) and the diffusion path length was set to half the soil depth as suggested by Mackay and Paterson (1991). The D-values for the deposition processes are derived in the same way as for air-water transport.

3.2.2.3 Air-urban surfaces exchange

Transport of chemical between air and the organic layer covering impervious surfaces in the city occurs through the same mechanisms as air to water and air to soil transport (Diamond et al. manuscript). The MTCs that drive the diffusive process are similar to air-water MTCs and they were derived as follows: The air-side MTC k_{AF} (m/h) is assumed to be of the same size as the air side air-water MTC and thus a value of 3 m/h was adopted. Diamond et al. (manuscript) suggested another calculation process for the derivation of k_{AF} but using that expression yielded a boundary layer thickness that was larger than the thickness of the urban film, which is why the k_{AW} value was used instead. The film-side MTC k_{FF} is calculated through the equation

$$\log [k_{FF}] = (0.704 \log K_{OW} - 11.2) / K_{AW} \text{ (Trapp, 1995).} \quad (3.3)$$

as suggested by Diamond et al. (manuscript). D-values for deposition processes are derived in the same way as air-water deposition, and listed in Appendix 3.

3.2.2.4 Water-sediment exchange

The chemical transport between water and sediment occurs through diffusion, deposition and resuspension processes. The diffusion D-value is derived in the same way as the air-soil transport, whereas the deposition and resuspension processes are dependent on deposition and resuspension rates. Broman et al. (1994) measured the flux of depositing aquatic particles in Stockholm. The rate was given in (g/m²/d) and refers to the weight of dry solids that deposits on a square surface during a period of time. Dividing this number by the density of the particles (2400 kg/m³) and the solid content of sediments yields an average “wet” deposition velocity of 1.7×10⁻⁶ m/h. Burial rates were measured using ²¹⁰Pb (Östlund et al. 1998). These rates referred to the bulk sediment, that is the velocity by which the sediment (water and solids) grows and was 1.6×10⁻⁶ m/h on the average in the upper sediments. The values for deposition and burial agree very well and suggest that resuspension is minor, perhaps in the order of 10⁻⁷ m/h.

3.2.2.5 Soil-water exchange

Chemicals may be transferred from soil to water through solids or water runoff. The D-values for these processes (Appendix 3) are dependent on a water and a solids runoff rate. No specific values for Stockholm could be derived, thus the values suggested by Mackay and Paterson (1991) were used, i.e. 3.9×10⁻⁵ m/h for water runoff and 2.3×10⁻⁸ m/h for solids runoff, as listed in Appendix 1.

3.2.2.6 Urban surfaces – water exchange

The transport between urban surfaces and water is assumed to occur mainly by washout through rain and wind to storm water, which follows the streams to lakes and rivers. In Stockholm, about 50% of the storm water actually goes to sewage treatment plants, but for simplicity, we have neglected this in the CeStoc model. It should however be kept in mind, that the real amount transported from urban film to water may be lower than the predicted amounts. Some of the chemical may also leach down into soil during transport between film and surface waters, but for illustrative purposes we assume this to be a negligible part of the total amount transported. The transport is assumed to be driven by a mass transfer coefficient k_{FW} , which was derived as suggested by Diamond et al. (manuscript) as $k_{FW} = T_F \times W$, where T_F is film thickness (m) and W is a wash-off rate constant (h⁻¹). The wash-off rate constant was calculated as follows: Assuming constant thickness of the film yields the relationship $F_1 = F_2$, i.e. steady state, where F_1 is the flow of depositing material on the film (g/m²×h) and F_2 is the flow of material that is being washed off by rain and wind (g/m²×h) (fig 7).

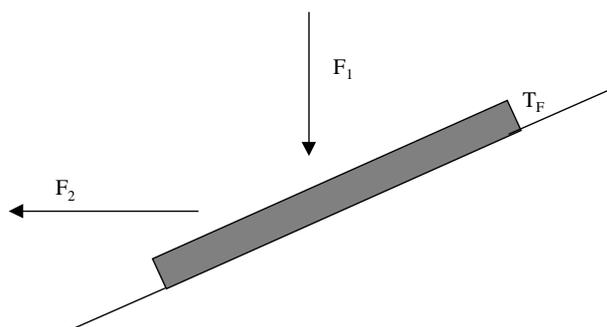


Figure 7. Illustration of urban film - water wash off.

Also, there is a relationship between film thickness and mass per area unit that can be described as:

$$M_A = \rho_{BF} \times T_F, \quad (3.4)$$

where M_A is the mass per area unit of the film (kg/m^2), ρ_{BF} is bulk film density (kg/m^3) and T_F is the thickness of the film (m). The density of the bulk film was calculated by converting mass fraction of particles and pure film to volume fraction through the formula $v_P = (\phi_P/\rho_P)/(\phi_P/\rho_P + \phi_F/\rho_F)$ (example for particle mass fraction), where ϕ_P is particle mass fraction (0.7) and ρ_P is particle density ($1700 \text{ kg}/\text{m}^3$) and then adding the products of volume fraction and density of particles and pure film respectively. M_A was calculated to $0.18 \text{ g}/\text{m}^2$ using a bulk film density of $1290 \text{ kg}/\text{m}^3$ and the thickness $1.37 \times 10^{-7} \text{ m}$. It was assumed that the PM10 concentration would correspond to the concentration of particles depositing on the urban surfaces. The PM10 concentration $5.1 \times 10^{-5} \text{ g}/\text{m}^3$ was obtained from Wallin (1998). The velocity of PM10 particles was derived by using a massmedian diameter of $5 \text{ }\mu\text{m}$ which yields a velocity of $0.09 \text{ cm}/\text{s}$ (Caffrey 1998) or $3.24 \text{ m}/\text{h}$. The flow of particles onto the urban surface is therefore $F_{1P} = 5.1 \times 10^{-5} \times 3.24 = 1.65 \times 10^{-4} \text{ g}/\text{m}^2 \times \text{h}$. The total flow was then obtained from the mass fraction of particles in film (0.7): $F_{1\text{tot}} = 1.65 \times 10^{-4} / 0.7 = 2.36 \times 10^{-4} \text{ g}/\text{m}^2 \times \text{h}$. The wash off rate constant was then calculated as $W = F_2/M_A = F_{1\text{tot}}/M_A = 2.36 \times 10^{-4} / 0.18 = 1.3 \times 10^{-3} \text{ h}^{-1}$. This gives a turnover time of 32 days.

4 Polybrominated diphenyl ethers

4.1 Physical-chemical properties

PBDEs are semivolatile compounds with low vapour pressure and low water solubility. In the air, they exist in the gaseous phase and in the particulate phase. Due to the low vapour pressure they tend to be strongly attracted to air particles, but the amount actually associated with particles is dependent on temperature, particle size and of course, particle concentration. Generally, a greater amount exist in the gaseous phase during warm periods than during cold periods (Bidleman 1988), because of the temperature dependence of the physical-chemical properties. In aquatic environments, PBDEs mainly become attracted by particles, because of the low water solubility.

The properties of chemicals that are necessary for multimedia modelling are essentially vapour pressure (P^S), water solubility (W_{SOL}) and the octanol-water partition coefficient (K_{OW}). On higher levels, media-specific degradation half-lives are also required. It is not unusual that reported values on physical-chemical properties for chemicals vary by several orders of magnitude (Mackay et al. 1991). Polybrominated diphenyl ethers are no exception from this rule. The reasons for this are probably partly the very low vapour pressure and low water solubility of PBDEs, which makes it difficult to measure these properties. Also, there is sometimes a confusion in the distinction between commercial products and individual congeners since they carry similar names. One example of this is that penta-BDE is sometimes referred to as a liquid at room temperature (EU 2000), while recent studies have shown that the melting points for pure penta-brominated congeners lie close to 100°C (Marsh et al. 1999; Örn et al. 1996). A closer look reveals that the commercial product, which is really a mixture of different congeners and probably some other compounds as well, is a liquid at room temperature (M Remberger pers. comm.). This is a well-known feature also for other groups of chemicals, e.g. the PCBs, where mixtures show very different properties than pure congeners (M Tysklind pers. comm.). Obtaining reliable values for physical-chemical properties is therefore one of the most demanding tasks when modelling PBDEs.

So far, only a few experimental studies of physical-chemical properties have been undertaken. In a recent study by Palm et al. (manuscript) the properties of PBDEs were correlated using the “three solubility” approach outlined by Cole and Mackay (2000). The results showed that estimated values of properties do not correlate well with the experimental values. Therefore, due to the limited amount of experimentally derived properties, reliable equations for the solubility of PBDEs in octanol, air and water as a function of bromination degree could not be achieved. Due to the high uncertainty in properties, the goal in the current study was to use experimental values as far as possible. Certain environmentally relevant congeners have been more studied than

others and therefore these congeners are used in this study. The physical-chemical properties of the compounds selected are listed in Table 2. In the following sections, we discuss only those parameters, for which conflicting results exist.

Table 2. Physical-chemical properties of PBDEs used in the Stockholm model. References not given in the table are given in sections 4.1.1-4.1.4.

	Diphenyl ether	BDE 47	BDE 99	BDE 209
M (g/mol)	170.2	485.8	564.7	959.2
Number of Br	0	4	5	10
MP (°C)	26.8	80.5	93.2 ¹⁾	300
W _{SOL} (mg/l)	18	1.1×10 ⁻²	2.4×10 ⁻³	2.8×10 ⁻¹¹
P ^S (Pa)	2.99	2.9×10 ⁻⁴	5.11×10 ⁻⁵	4.6×10 ⁻⁶
LogK _{OW}	4.21	6.0	6.7	9.97
<i>Half-lives (h)</i>				
Air	26.7	256	467	7620
Water	360	3600	3600	3600
Soil	360	3600	3600	3600
Sediment	1440	14400	14400	14400
Urban film	22.7	217.6	396.9	6477

1) Örn et al. (1996)

4.1.1 Diphenyl ether

Water solubility

The water solubility of diphenyl ether has been experimentally determined to 18 mg/l (SRC, 2001). Other reported values are the measured value 21 mg/l (EU, 2000) and an estimated value of 15.6 mg/l (EU, 2000). In this study, 18 mg/l was used.

Vapour pressure

The vapour pressure of diphenyl ether has been measured to 2.99 Pa (SRC, 2001). The measured value reported in EU risk assessment of pentaBDE is 2.7 Pa (EU, 2000) and an estimated value of the vapour pressure is 1.04 Pa (EU, 2000). In this study, the value 2.99 Pa was used.

Octanol-water partition coefficient

An experimental value of log K_{OW} of 4.21 was obtained from the SRC database (SRC 2001) An estimated value of 4.05 was reported in the EU risk assessment (EU 2000). The experimental value was used in this study.

Degradation half-lives

No experimental media-specific values could be found on the degradation rates of diphenyl ether. Therefore, estimated values from EPIWIN estimation software (2000) had to be used. These estimated values are for air, water, soil and sediment 26.7 h, 360 h, 360 h and 1440 h respectively. For urban film, the value for air was multiplied by 0.85, yielding a value of 22.7 h derived from the suggestion by Diamond et al. (manuscript) that reaction in the organic film would be about 15% faster than in air, due to the high organic carbon content.

4.1.2 BDE 47 (2,2',4,4'-tetrabromodiphenyl ether)

Melting point

Reported experimental values of the melting point of BDE 47 are 78.5-79°C (Marsh et al. 1999) and 82.0-82.5°C (Örn et al. 1996). In the current study a midpoint-value of these ranges was used, namely 80.5°C.

Water solubility

One experimental value of the water solubility of BDE 47 of 1.09×10^{-2} mg/l has been obtained. This has been referred to in the EU risk assessment (EU 2000) and by Hardy (2000). EPIWIN (2000) estimated the water solubility to 1.46×10^{-3} mg/l. Due to the uncertainties in estimated values as reported by Palm et al. (manuscript) the experimental value was used in this study.

Vapour pressure

Watanabe and Tatsukawa (1989) reported the vapour pressure of tetrabrominated compounds to lie in the range $(2.60-3.27) \times 10^{-4}$ Pa. EPIWIN (2000) estimated the vapour pressure of BDE 47 to 3.21×10^{-5} Pa. Tittlemier (2000) reported a value of the sub-cooled liquid vapour pressure of 1.45×10^{-5} Pa. In this study, a midpoint-value of the range given by Watanabe and Tatsukawa (1989) was used, which was 2.9×10^{-4} Pa.

Octanol-water partition coefficient

Watanabe and Tatsukawa (1989) derived a range of 5.87 –6.16 for the log K_{OW} of tetraBDEs. The mid-point value of this range is 6.0, whereas EPIWIN estimated the log K_{OW} to 6.77. In the study by Palm et al. (manuscript) it was shown that EPIWIN constantly predicted values of log K_{OW} that were higher than the experimental values reported. Therefore, the experimental value was used in the current study.

Degradation half-lives

No experimental values exist so far on the degradation rates of BDE 47. Therefore, estimated values from EPIWIN estimation software were used. These estimated values are for air, water, soil and sediment 256 h, 3600 h, 3600 h and 14400 h respectively. The value for urban film was obtained in the same way as for diphenyl ether, yielding a value of 217.6 h.

4.1.3 BDE 99 (2,2',4,4',5-pentabromodiphenyl ether)

Water solubility

The reported values of the water solubility of pentabrominated compounds vary by several orders of magnitude. WHO (1994) reported a water solubility of 9.0×10^{-7} mg/l. The original source of this value is not available, and neither is the method used known. Stenzel and Markley (1997) measured the water solubility of BDE 99 to 2.4×10^{-3} mg/l. EPIWIN (2000) estimated the water solubility of BDE 99 to 7.86×10^{-5} mg/l. When compared to the water solubility of 2,2',3,4,5-pentaPCB suggested by Lee and Mackay (1995), which is 4×10^{-3} mg/l, the value 2.4×10^{-3} mg/l seemed to be the one most reliable.

Vapour pressure

The vapour pressure of penta-BDE has been reported as $(2.9 - 7.3) \times 10^{-5}$ Pa (Watanabe and Tatsukawa 1989), 4.69×10^{-5} Pa for the commercial product (EU 2000) and an estimated value of 3.25×10^{-6} Pa (EPIWIN 2000). The sub-cooled vapour pressure was measured by Tittlemier et al. (2000) to 7.76×10^{-6} . In the current study, a mid-point value of the range obtained by Watanabe and Tatsukawa (1989) was used, since it was determined for pentabrominated congeners and not for the commercial product.

Octanol-water partition coefficient

The log K_{OW} was determined experimentally for penta-BDEs by Watanabe and Tatsukawa (1989). A mid-point value of the range (6.46-6.97) obtained in this study was 6.7. EPIWIN (2000) estimated the value to 7.66. The experimental value was considered most reliable and 6.7 was assumed to be applicable for BDE 99, as being one of the penta-brominated congeners.

Degradation half-lives

No experimental values exist so far on the degradation rates of BDE 99. Therefore, estimated values from EPIWIN estimation software were used. These estimated values are for air, water, soil and sediment 467 h, 3600 h, 3600 h and 14400 h respectively.

The value for urban film was obtained in the same way as for diphenyl ether and BDE 47 and was calculated to 396.9 h.

4.1.4 BDE 209 (Decabromodiphenyl ether)

Melting point

The melting point of decaBDE has been referred to as lying in the range 290-306°C (WHO 1994). In the EU risk assessment draft for the decabrominated compound (EU 1998.) the melting point was reported as 300-310°C. Therefore, we have used a midpoint-value of 300°C for the Stockholm assessment.

Water solubility

The water solubility of decaBDE is very low. The water solubility of decaPCB has been determined to 1×10^{-6} mg/l (Lee and Mackay 1995), and the similarity to PBDEs indicate that the solubility of decaBDE should be about the same order of magnitude. However, the low solubility also causes difficulties when measuring this property and this becomes evident when comparing different results. For example, one value of 2.5×10^{-2} mg/l has been reported (de Boer et al. 2000) In this case however, the method used is not known. In the EU risk assessment draft, an upper limit of the water solubility of the commercial decaBDE product was given as the experimentally obtained value 1×10^{-4} mg/l (EU 1998). An estimated value of the water solubility of decaBDE is 2.8×10^{-11} mg/l (EU 1998). According to Remberger (pers. comm.) the experimental value given in the EU draft is probably too high, and the real value should lie somewhere between the value for decaPCB and the estimated BDE 209 value. At present, the actual water solubility can hardly be obtained, but as the estimated value seemed to be the one most appropriate, this one was used.

Vapour pressure

Determining the vapour pressure of decaBDE faces similar problems as water solubility. Reported values are 1×10^{-5} Pa (de Boer et al. 2000), 4.6×10^{-6} Pa for the commercial DeBDE product, (EU 1998) and an estimated value of 5.8×10^{-11} Pa (EU 1998). According to Remberger (pers. comm.) the value for the commercial product should lie close to the truth since it contains about 97-98 % of the decabrominated congener (de Wit, 2000) and hence that number was used. However, the vapour pressure largely affects the aerosol-air partition coefficient, which in turn determines the amount that will partition to air particles and thus deposit on soil or water surfaces. As discussed in section 6, the value here used is probably too high, but since no other experimental data were available, it was used anyway.

Octanol-water partition coefficient

The log K_{OW} was measured to 9.97 by Watanabe and Tatsukawa (1989), which is the value used in the current study. Other reported values are 6.27, which was suggested as the lower limit for the commercial product in the EU risk assessment (EU 1998), 5.24 (EU 1998) and an estimated value of 12.11 (EU 1998).

Degradation half-lives

Sellström et al. (1998) studied the photolytic degradation rate of BDE 209 in soil, sand and sediment. The results showed half-lives that were considerably lower than the numbers estimated by EPIWIN, for example the half-life in sediment was measured to 81 h and in soil 200-600 h (M Tysklind pers. comm.), which is low compared to the EPIWIN estimation of 14400 h for sediments and 3600 h for soil. It is uncertain whether the laborative conditions used in that study are comparable to environmental conditions. Although experimental values are preferable, it is also important to use a common estimation method for the different congeners, otherwise comparison can be difficult. Thus, since no studies have been undertaken on degradation rates of other congeners, and the half-life for BDE 209 is believed to be longer than for lower brominated congeners, the estimated values were used, to avoid comparison problems. When more data on degradation rates exist, these numbers should be replaced by experimentally obtained values. The estimated values are for air, water, soil and sediment 7620 h, 3600 h, 3600 h and 14400 h respectively. For urban film, a value of 6477 h was used, based on the same estimation as for the other congeners.

4.2 Use and emissions in Stockholm

Brominated flame retardants are not produced or manufactured in Sweden. Hence, there are no obvious emission point sources in Stockholm. Estimations of environmental emissions must therefore be derived from use and probable emission routes. To the best of our knowledge, no measurements of emissions have been performed in Stockholm or in other similar areas, which is why estimates have to be used. Estimation of the amounts of PBDEs that are present in products in use in Stockholm is an extensive task, and would require a very long time of investigation and identification of possible sources and emission factors. However, Palm et al. (manuscript) estimated the yearly emissions per capita of decaBDE and pentaBDE based on a Danish material flow analysis (MFA) (Larssen et al. 1999). Since Denmark and Sweden are both Nordic countries with similar standards of living and consumption patterns, those estimations were assumed to be applicable for Sweden and Stockholm too. The total BFR emissions in Denmark 1999 estimated by DEPA (Larssen et al. 1999) were:

Air: 0.2 – 1.6 tonnes/year

Water: 0.005-0.07 tonnes/year

Soil: 0.03-0.3 tonnes/year

These numbers were divided by a factor of 5,357,000, the population of Denmark, yielding total BFR emissions per capita. Assuming that all the BFRs emitted are additive compounds, with PBDEs accounting for 24% of the additive use (Larssen et al. 1999), multiplying the per capita emissions obtained above by 0.24 yields the yearly emissions of total PBDEs as follows:

Air: 8.95-71.76 mg/capita×year

Water: 0.22-3.14 mg/capita×year

Soil: 1.34-13.4 mg/capita×year

75 % of the consumed PBDE technical mixtures is the commercial mixture DeBDE according to Larssen et al. (1999) of which about 97-98 % is BDE 209 (de Wit 2000). 10 % of the consumed products is PeBDE (Larssen et al. 1999), where tetra congeners stand for 24-38% and penta congeners for 50-60 % (de Wit 2000). For simplicity, we assume that all tetra congeners are BDE 47 and that all penta congeners are BDE 99. This is not necessarily the truth, but those two congeners are the ones most commonly found in environmental samples (Sellström, 1999), which is why we assume that they are in majority also in the commercial mixtures. Applied to the figures above, this yields yearly emissions of BDE 47, 99 and 209 as shown in Table 3. The highest values obtained were used for modelling purposes, assuming a worst-case scenario.

Table 3. Estimated emissions to the Stockholm environment in mg/capita×year. The total amount (kg/year) released based on the Stockholm population is given in parenthesis.

Compartment	BDE 47	BDE 99	BDE 209
Air	2.7 (2.0)	4.3 (3.18)	53.3 (39.4)
Water	0.12 (0.09)	0.19 (0.14)	2.31 (1.7)
Soil	0.51 (0.38)	0.8 (0.59)	9.8 (7.3)

4.3 Environmental occurrence in Stockholm

The polybrominated diphenyl ethers are subjected to at least one screening project in Stockholm at present. Stockholm Vatten is measuring the levels in storm water (C Wahlberg, pers. comm.). However, the analytical results will not be ready until the

summer 2001, and therefore, only a limited amount of data exists on the environmental concentrations in Stockholm so far. Some congeners have been detected in sewage sludge (Wahlberg, 1999) in Stockholm. A few measurements also exist from suburban air (Sjödín, 2000), but the detection limits in that study were very high compared to the concentrations actually detected in remote areas. BDE 47 and BDE 99 were detected in two observations from Ammarnäs in the north of Sweden and Hoburgen in the south (Bergander et al. 1995). To our knowledge, no measurements have been performed on the occurrence in bulk water in Stockholm. However, measurements in depositing aquatic particles in sediment traps have been performed (Broman unpubl.). Although the concentration in settling particles is not directly obtained from CeStoc, values should be roughly comparable to surface sediments and thus be comparable to the sediment concentrations predicted by the CeStoc model. Soil measurements are scarce, but there is one from a recycling plant in Taiwan (WHO 1994). Those levels are probably very different from the levels in Stockholm, but they have been included for illustrative purposes. Sediment observations exist from rivers close to a point source in Sweden (Sellström 1999), and from different European estuaries (Sellström 1999). No measurements have been performed in urban film in Stockholm. Table 4 lists the detected environmental concentration ranges in different environmental media.

Table 4. Reported concentrations of the selected PBDE congeners in the environment

Congener	Air (pg/m ³)	Water	Soil (ng/g dw)	Sediment (ng/g dw)
BDE 47	<100 ¹⁾	-	75-104 ³⁾	1.2-3.5 ⁴⁾
	6.3 ²⁾			<0.2-5.8 ⁵⁾
	0.7 ²⁾			0.24 - 4.81 ⁶⁾
BDE 99	<60 ¹⁾	-	41-84 ³⁾	1.7-3.7 ⁴⁾
	1.6 ²⁾			<0.2 - 6.9 ⁵⁾
	0.35 ²⁾			0.31-3.84 ⁶⁾
BDE 209	<40 ¹⁾	-	260-330 ³⁾	3.9-5.2 ⁴⁾
				<0.5 -1700 ⁵⁾
				2.4 -360 ⁶⁾

¹⁾ Suburban air, Stockholm (Sjödín 2000) ²⁾ Remote air (Bergander et al. 1995) ³⁾ Recycling plant Taiwan (WHO 1994) ⁴⁾ Sediment traps Stockholm (Broman pers. comm.) ⁵⁾ European estuaries (Sellström 1999) ⁶⁾ Swedish point source (Sellström 1999)

5 Model calibration with fluoranthene

Because of the poor data on physical-chemical properties of PBDEs and the uncertainty concerning emission rates and environmental concentrations, it was decided to calibrate the CeStoc model with another organic compound, for which emissions in Stockholm are easier to estimate and physical-chemical properties are well known. The compound selected for this purpose was the PAH fluoranthene. Table 5 lists the physical-chemical properties of fluoranthene.

Table 5. Physical-chemical properties of fluoranthene

Property	Fluoranthene
M (g/mol)	202.26
MP (°C)	107.8 ¹⁾
W _{SOL} (mg/l)	0.26 ¹⁾
P ^S (Pa)	1.22 × 10 ^{-3 1)}
LogK _{OW}	5.16 ¹⁾
<i>Half-lives (h)</i>	
Air	170 ²⁾
Water	1700 ²⁾
Soil	17000 ²⁾
Sediment	55000 ²⁾
Urban film	144 ³⁾

1) Experimental data obtained from SRC database (SRC 2001)

2) Mackay and Callcott (1998)

3) Assumption that reaction in film is 15% faster than reaction in air. (Diamond et al. manuscript)

5.1 Emissions and environmental occurrence of fluoranthene

The emission of PAH to air in Stockholm was estimated to 3250 kg/year by Holmgren (1999). The estimations concern the emissions of 16 PAH congeners where fluoranthene was one of them. The area studied was 187 km². The emission obtained was therefore scaled down on an area basis to yield an approximate emission value of the 16 PAHs for the selected region of 3250 × (47/187) = 816 kg/year. Assuming that fluoranthene accounts for exactly 1/16, i.e. 6.25 % of the total emissions of these 16 compounds would yield a yearly release of 51 kg to the air.

Larnesjö et al. (1999) calculated emission factors for 22 PAHs emitted from traffic, resulting in a percentage contribution for fluoranthene between 7.7 % and 28% depending on vehicle type, which indicates that fluoranthene accounts for more than 1/16 of the total emissions. A recent study of PAH emissions from road tunnels in Gothenburg, yielded an emission factor of fluoranthene of 50 µg/km (Wingfors pers. comm.), which was assumed to be applicable for Stockholm as well. The yearly distances driven by buses, vans and automobiles in Stockholm has been studied by SLB-analys (1998), and assuming that 50 % of the traffic occurs in the area studied here, yields a yearly distance of 1.5×10^9 km. Multiplied by the emission factor (50 µg/km) this gives a yearly emission of 75 kg of fluoranthene from traffic.

Based on these reports, the actual emission to air was assumed to be higher than 51 kg/year and is here estimated to 60 kg/year.

Holmgren (1999) also estimated the total yearly emission of PAH to the Stockholm waters. These were estimated to about 20 kg based on five PAHs including fluoranthene. In the current study the emission of fluoranthene to water was assumed to be slightly more than one fifth of that, based on the same discussion as above, which yielded an assumption of 5 kg/year. In absence of published data on emissions to soil, an equal emission as to water was assumed, based on the fact that elevated concentrations of such pollutants have been detected close to roads and highways, mostly due to emissions directly from wheels (Lindgren 1998).

Environmental levels of fluoranthene have been measured in air, water and sediment in or just outside Stockholm (Broman 1988; Broman et al. 1991; Axelman et al. 1997; Östlund et al. 1998). There are also air measurements from urban areas in the UK (AEA Technology website 2001) and background concentration measurements from air in Rörvik and Pallas in Scandinavia (Brorström-Lundén et al. 2000). Also, some measurements have been performed in soil in Sweden, most of them being close to point sources or in industrialised areas (Knulst et al. 1995). No measurements have been performed in urban film in Stockholm, but Diamond et al. (2000) measured the concentration of 20 PAHs in the urban film in Toronto, Canada, where fluoranthene was the major component, accounting for about 18 % of the 20 compounds analysed.

5.2 Observations versus model results

Figure 8 shows the modelled concentrations of fluoranthene in comparison to observed levels in Stockholm and some other areas. The model predicts levels that are generally in consistency with observed data.

For air, the model prediction lies about a factor of 70 below the observed values in Stockholm city. However, these observations were made close to a busy street

(Hornsgatan), where higher values than the average of a 600 m column might be expected. The fact that background levels were neglected in this study may also contribute to the low predicted value compared to the observed city levels of fluoranthene in air. The predicted value for water lies in the lower end of the observed range at the coast outside Stockholm. This is reasonable since the observations in water are from the late 80's to the early 90's. The environmental levels have probably decreased since then due to improved catalyst technology in cars and more environmental friendly fuels. A decreasing trend has been shown for concentration in air (Burman and Höglund 2000).

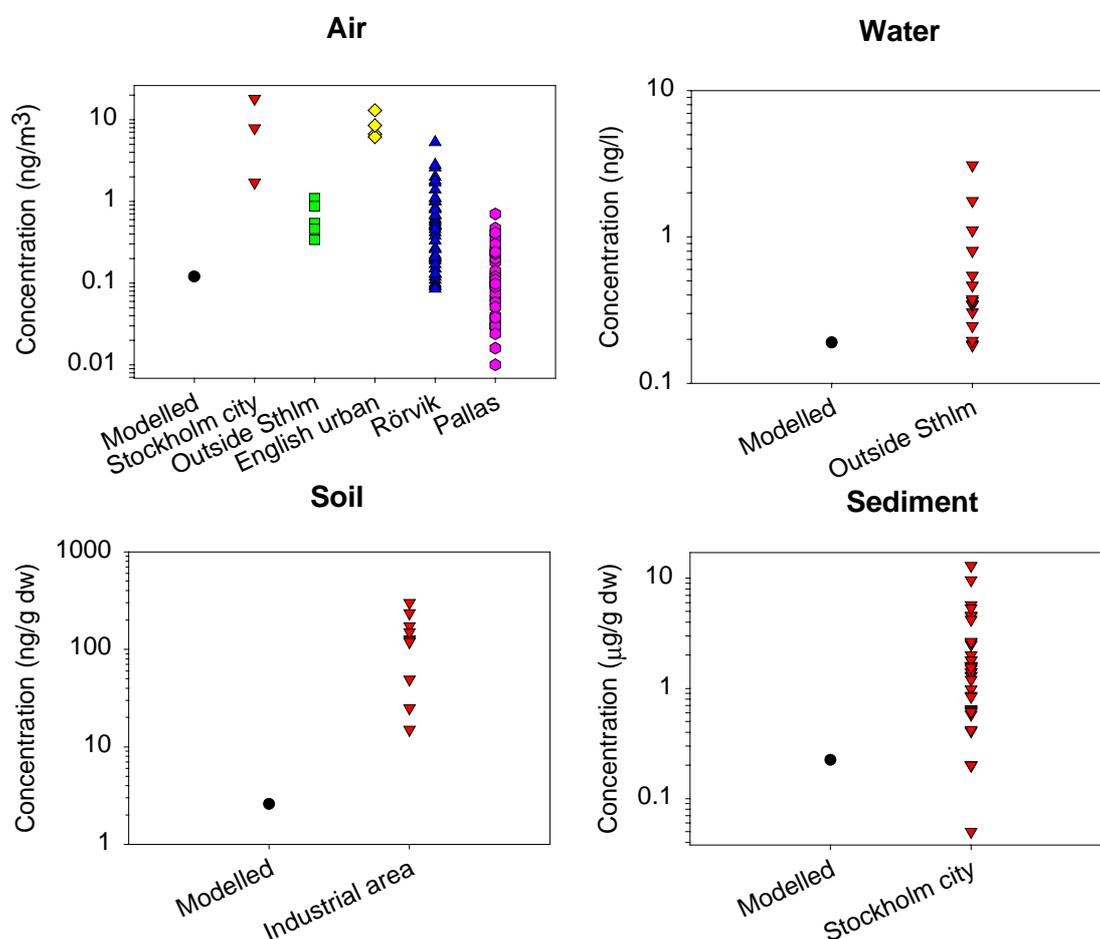


Figure 8. Predicted versus measured concentrations of fluoranthene in different compartments. Model predictions in soil and sediment have been converted to dry weight.

At a first glance, the model prediction for soil seems very low compared to observed values. It should be born in mind though, that the soil observations come from industrial areas, where concentrations are expected to be high, which partly can explain the

discrepancy. Observed soil levels of PAH in Stockholm are also likely to be heavily influenced by past emissions. Another reason could be that the direct emissions to soil (5 kg/year) are underestimated. For sediment, the predicted value lies in the observed range. On the whole, the model seems to predict values close to or in observed ranges for all environmental media, which brings us to the conclusion that it should be applicable also for the PBDEs.

6 Results and discussion

6.1 Model predictions versus environmental concentrations

The predicted environmental levels of the PBDE congeners in air, water, soil and sediment are shown in Figure 9. Comparison is made between model predictions and observed environmental levels where possible. At this point, urban film has not been included, due to lack of measured data for this compartment. The observed environmental concentrations shown in the diagrams were taken from Table 4.

Model predictions of concentrations in air lie close to, or in the observed range (Fig 9). The observations in air are from two remote sites (Ammarnäs and Hoburgen in Sweden) which can explain that the model predictions lie in the upper parts of or slightly above the observed ranges, since the levels in an urban area should be higher than in remote areas.

No measurements from water were found in the literature. The concentrations of some PBDE congeners in storm water in Stockholm are presently being measured (C Wahlberg, pers. comm.), but the results were not ready when this was published. At a first glance, it seems strange that the predicted water concentration for BDE 209 is a factor of ten higher than the other two congeners, considering the lower water solubility of the decabrominated congener, but this difference might be explained by the emission estimates, since emission of BDE 209 to water is about ten times higher than the emissions of the other two congeners.

As for soil, the model predictions lie about a factor of 100 or more below the measured values, but since the measurements were performed at a contaminated site in Taiwan, this difference might be expected. In general, data on POPs in Scandinavian soils are very rare.

The model predictions for sediment lie in the observed range (Fig 9). For BDE 47 and 99, they agree very well with the concentrations observed in depositing particles in sediment traps in Stockholm. For BDE 209, the model prediction lies above the observed range in Stockholm. This could be a sign of an overestimation of the emission to water of this compound. It could also mean that the concentrations in sediments are not directly comparable to the levels in depositing particles. Also, the decabrominated compound is known to be very difficult to analyse, so the observed levels might be different from the actual environmental concentrations of this compound in sediment.

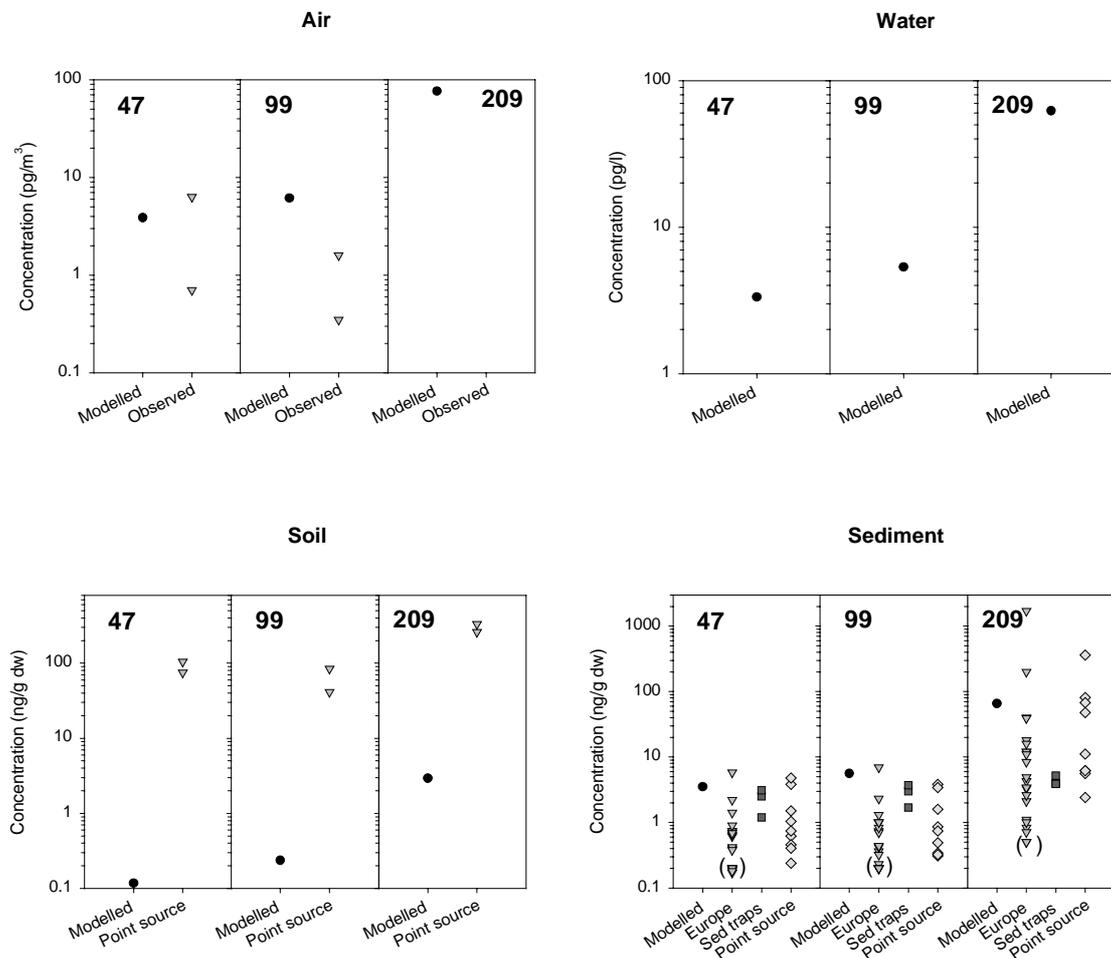


Figure 9. Predicted concentrations for the PBDE congeners versus measured concentrations. Model results for soil and sediment have been converted to dry weight. Parenthesis means that the concentration of the compound was below the detection limit.

6.2 Environmental distribution and transport processes

The flow charts in Figures 10-12 show the steady state amounts and concentrations in each compartment for the three PBDE congeners as well as the intermedia net transport processes, the advection and reaction processes out of the system and the environmental persistence.

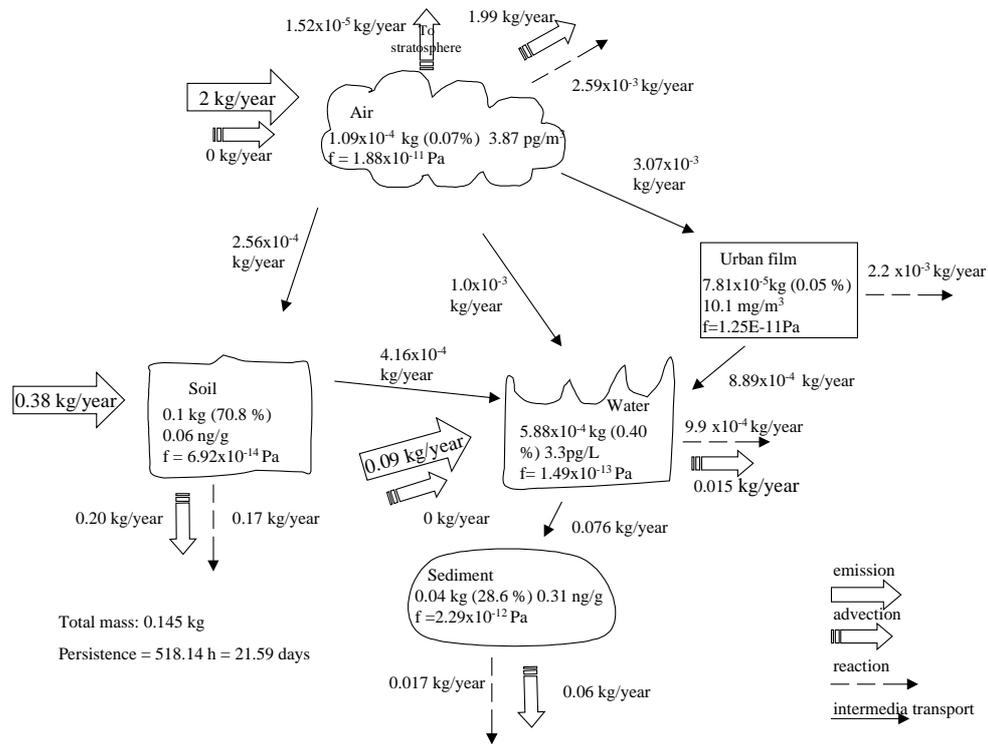


Figure 10. Environmental distribution and transport of BDE 47.

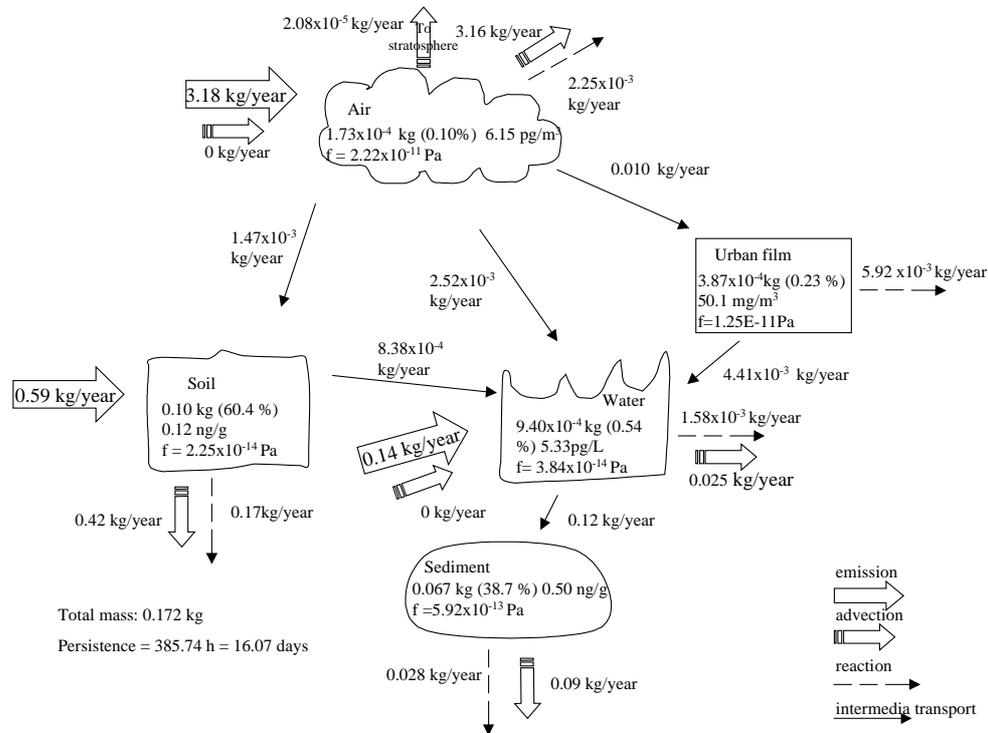


Figure 11. Environmental distribution and transport of BDE 99

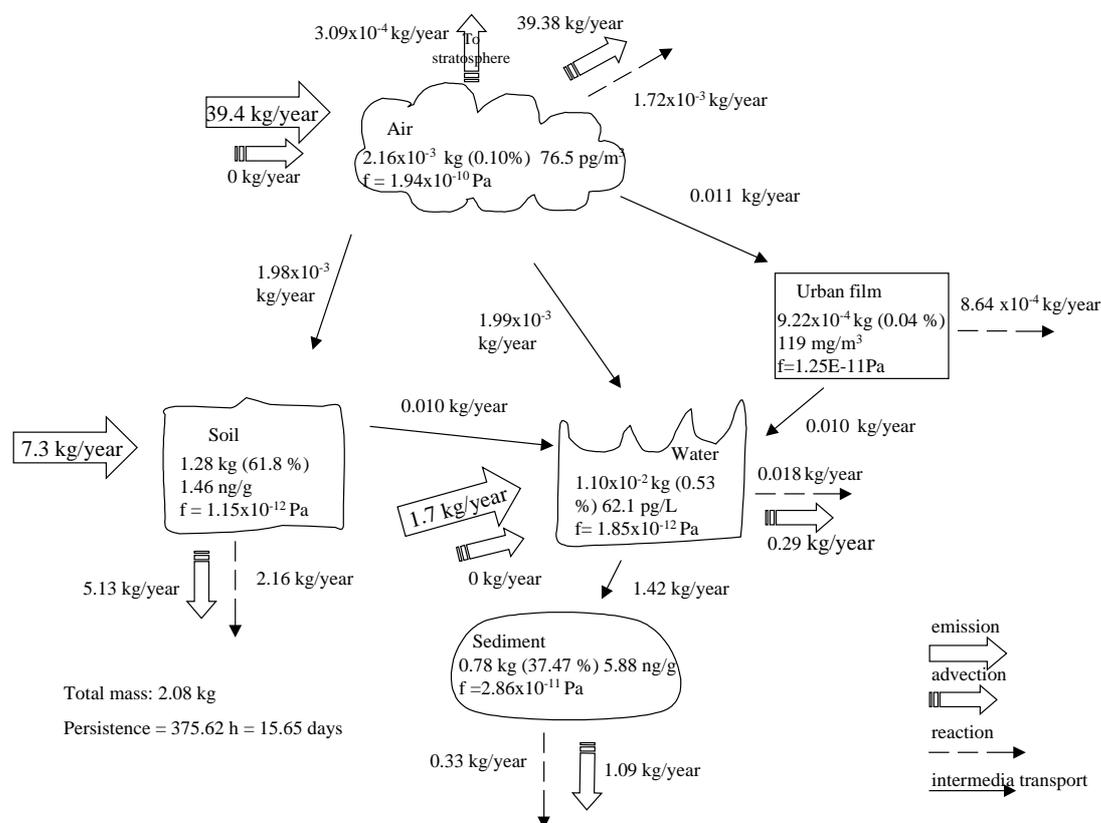


Figure 12. Environmental distribution and transport of BDE 209.

There is no clear difference in the relative distribution of the three congeners between the compartments. The majority of the chemical that stays in the system resides in soil (70.8 %, 60.4 % and 61.8 % for BDE 47, 99 and 209 respectively). Sediment acts as the second largest sink for the three PBDEs (28.6 %, 38.7 % and 37.5 % for 47, 99 and 209 respectively). The percentage residing in the urban film is slightly more for BDE 99 than for the other two compounds. It should be noted however, that due to the uncertainty in vapour pressure, the results obtained for BDE 209 possibly differ from the actual truth. Adopting a lower vapour pressure yields a higher amount partitioning to aerosols, which also increases the deposition of this chemical and thus the concentration in soil, urban film and sediment. Due to the large surface area of water, increased deposition also shifts the relative distribution from soil to sediment, resulting in a higher percentage residing in sediment and a lower in soil. Therefore, it is of importance to determine the vapour pressure of BDE 209 carefully in order to predict the environmental concentrations correctly.

The total concentrations in water predicted by the CeStoc model lie in the range 3-60 pg/l for individual congeners. This can be compared to total concentrations of 7 individual PCBs in the Baltic Sea (Stockholm levels are unavailable), which lie between 0.6-30 pg/l (Axelman et al.1997). The environmental concentrations of individual PCB

congeners in the Stockholm sediments have been well studied. Concentrations range from 3.6 to 84.4 ng/g dw in the surface sediments (Östlund et al. 1998), which is comparable to the model predictions of individual PBDE congeners, ranging from 3 to ca 65 ng/g dw.

The major removal process for all congeners is advection in air. It should be noted that removal here means removal out of the system, including both degradation and advection and does not necessarily imply that the problem is solved on a global scale. About 80 % of the chemicals emitted to the environment is transported out through air. This indicates that Stockholm may act as a source for chemical release to the surrounding areas. Also, it tells us that rather than being degraded, the chemicals are transported out and thus remain available to human exposure. This is in consistency with the findings by Palm et al. (manuscript) where air advection was shown to be the major removal process. The second largest removal process is leaching to groundwater, followed by reaction in soil and sediment burial. The rate of soil leaching to groundwater is possibly an overestimation by CeStoc. The transported amounts obtained would cause higher levels in the groundwater than has actually been detected, so probably a greater amount stays in soil than CeStoc predicts.

The difference between the three congeners is minor, although the actual amounts differ, due to the difference in emission estimates. Again, lowering the vapour pressure for BDE 209 would decrease the amount advected in air, since more would deposit on the ground, but air advection would probably still be the main removal process.

It should be noted that the emission medium has a great impact on the environmental distribution. As shown in Figs 10-12, a larger amount of the chemical emitted to air is transported out of the region, whereas the chemical emitted to soil to a much larger extent stays in the system or leaches to groundwater. The chemical emitted to water is mainly being transported to sediments, where it is being buried. Thus, identifying the emission media is of great importance when assessing the environmental fate of PBDEs. The importance of emission media is further discussed in section 6.4.

6.3 Impact of the degree of bromination

To study the impact of the degree of bromination on the environmental distribution in Stockholm more thoroughly, the CeStoc model was run for all three congeners and the diphenyl ether with identical emission scenarios. The emission scenario used was the upper limit of the range calculated in section 4.2 multiplied by the population of Stockholm which yielded the following emissions:

Air: 53.1 kg/year

Water: 2.3 kg/year

Soil: 9.9 kg/year

Estimated concentrations in each compartment were plotted for the four compounds (Fig 13).

For air, there is no obvious impact of the degree of bromination. The concentrations obtained hardly differ at all. This may be due to the quick outflow of the majority of the chemical released, with an air residence time of about 30 minutes. Thus, the amount remaining in air might be too small to show any big difference between the congeners. Also, the degree of bromination does probably not influence the concentration in bulk air, rather it affects the relative distribution between aerosols and air. A higher brominated compound has a lower vapour pressure, and thus more of the chemical is likely to partition to air particles. There is no monitoring data from Stockholm to confirm the air results.

For water and sediment, the predicted levels for diphenyl ether are lower than for the other congeners. However, there is no obvious relationship between degree of bromination and environmental concentration since all the brominated compounds show about the same levels. There is a vague trend that the concentrations in soil increase with increasing bromine number, which is not surprising since vapour pressure and water solubility decrease with increasing substitution. The concentration in urban film shows a quite different pattern. The penta-brominated compound achieves a high level in this compartment (800 mg/m^3), whereas the concentrations of the tetra- and decabrominated compounds are lower (200 mg/m^3), and the diphenyl ether shows a very low concentration.

Apart from the short residence times, another reason for the similarity between the results for BDE 99 and BDE 209 is likely to be the vapour pressure uncertainty of BDE 209. A lower vapour pressure would give higher concentrations in urban film, sediment and soil of this compound, and thus yield a bromination pattern that is perhaps more expected. Determination of the vapour pressure of BDE 209 is thus crucial in order to fully understand the influence of bromine number on environmental distribution.

Figure 14 shows the distribution percentages when assuming equal emissions of all congeners. The pattern is the same as shown in the flow charts (Figures 10-12) and no clear trend can be seen.

These results differ from the generic assessment performed by Palm et al. (manuscript), where increasing bromination in addition to increasing percentages in sediment and soil, also showed decreasing levels in air and water. Reasons to this discrepancy could be:

- The generic environments are larger, and have different environmental input parameters.
- Partly other values were used for the physical-chemical properties of the congeners in the study by Palm et al.(manuscript).
- The emissions to the generic world were much higher (1000 kg/h instead of 2-50 kg/year).
- Only penta- and decabrominated congeners were modelled with the generic models, which excludes the impact of the tetrabrominated congener to the bromination trend.

Apart from this, the generic models give a picture of the chemical's general behaviour, it does not tell us anything about the partitioning in a specific region, even though it helps giving an idea about likely partitioning pathways. The CeStoc model should not be expected to yield the same results as the generic models, since it is not a substitute, but a complement to generic models.

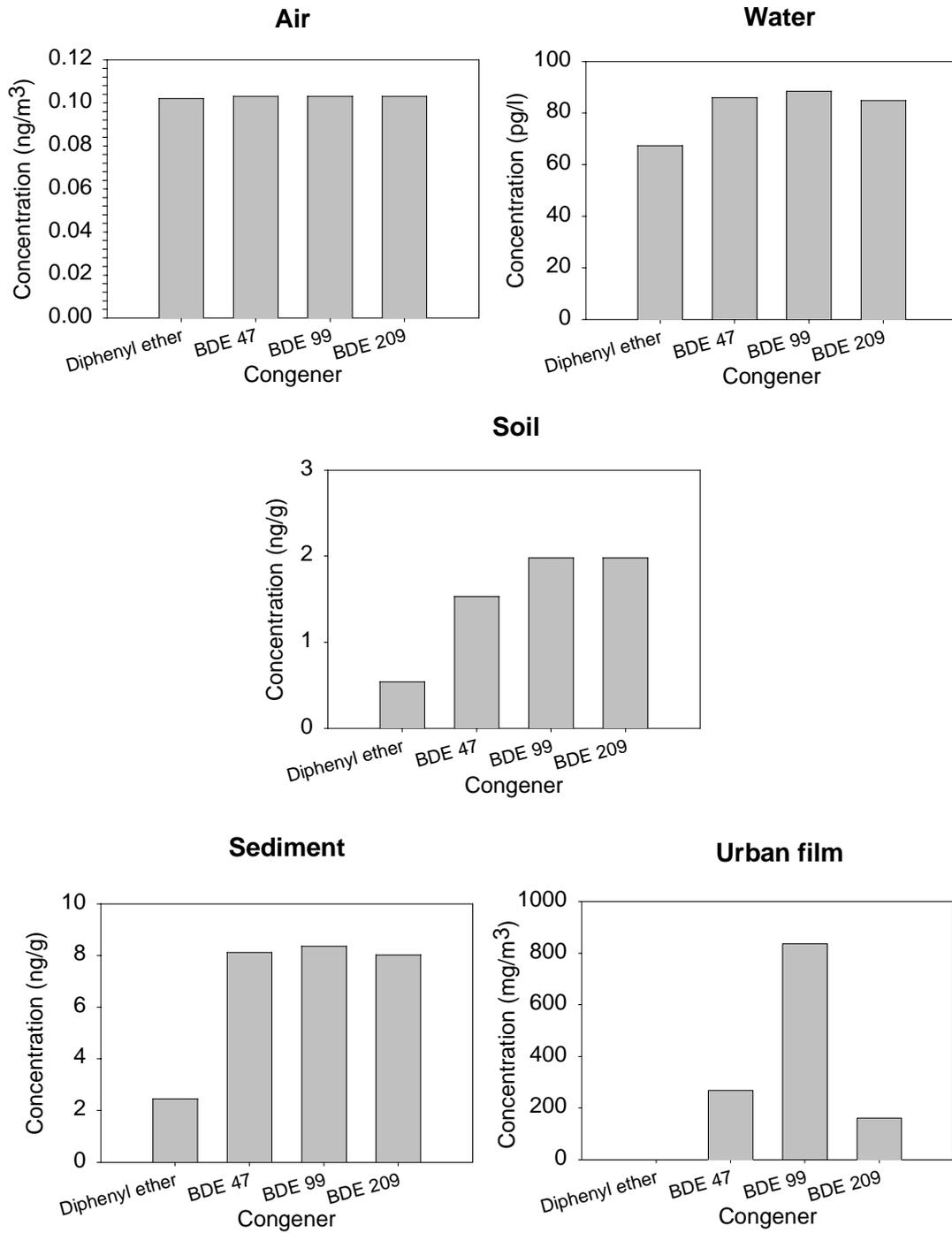


Figure 13. Influence of the degree of bromination on environmental concentrations.

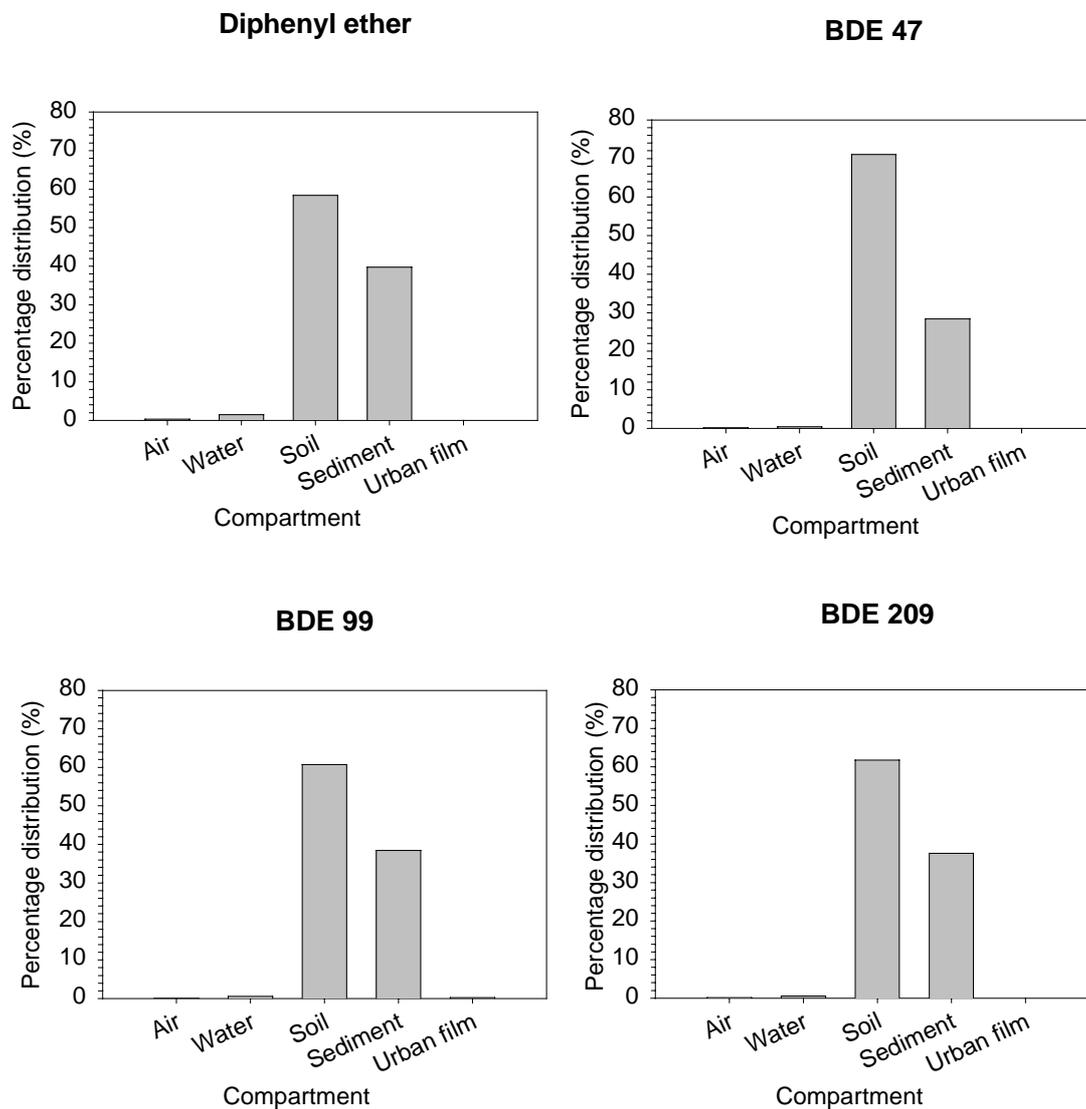


Figure 14. Percentage distribution in relation to the degree of bromination.

6.4 Emission dependence

In order to investigate the impact of the different absolute emission rates on the environmental distribution in the selected area, CeStoc was run for three different scenarios. The fractions of the total release emitted to each compartment were kept constant. Starting with the default emission, as estimated in section 4.2, the numbers obtained there were also divided by ten and multiplied by ten, to simulate high and low emissions. The results are shown in Fig 15.

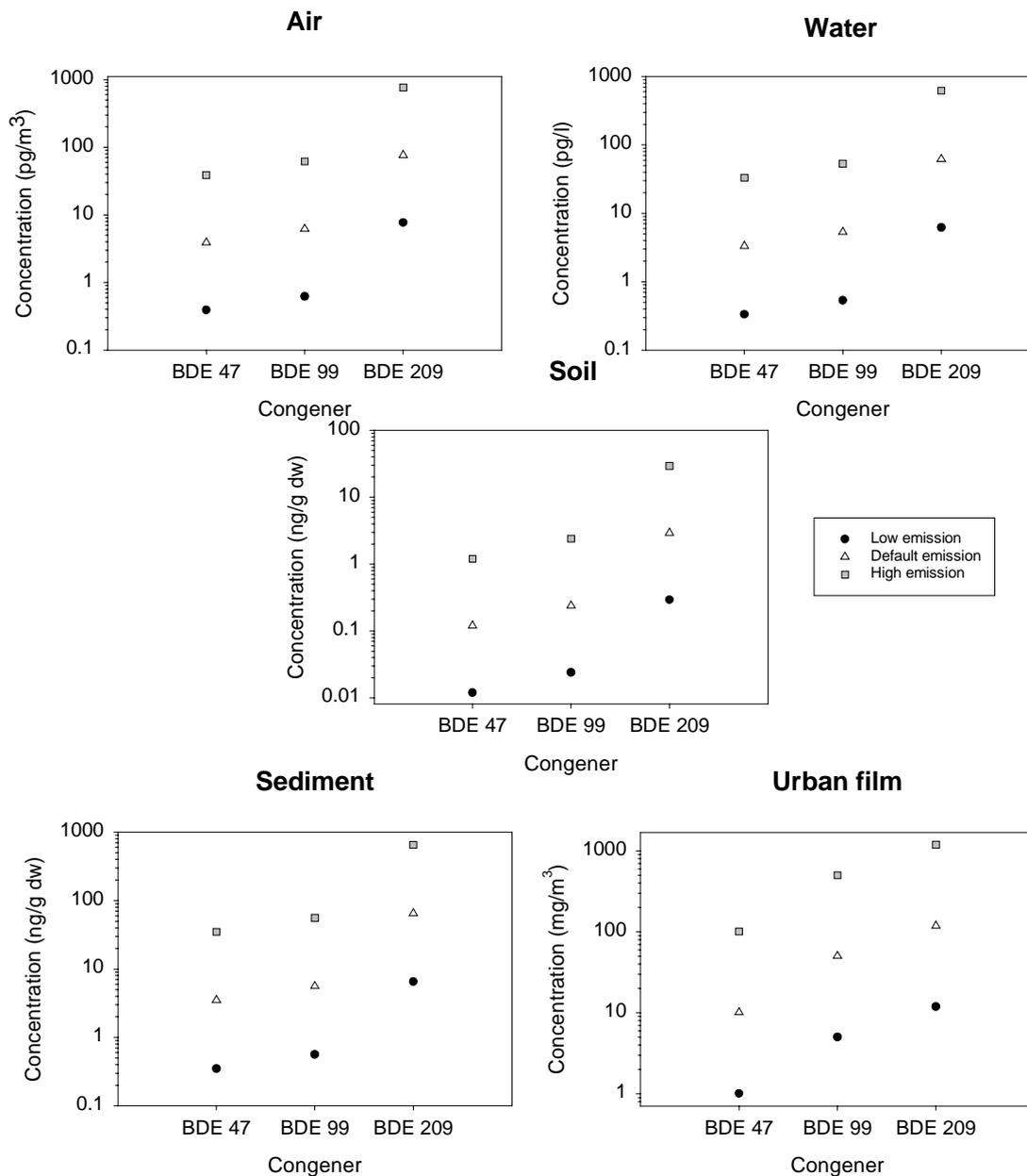


Figure 15. Influence of emission rates on the environmental concentrations.

Figure 15 shows that the environmental concentrations for all three congeners increase linearly with increasing emission. That is, for an emission increase by a factor of 10 to a certain compartment, the concentration in that compartment increases by a factor of 10.

As already mentioned, another thing that is crucial is emission medium. Figure 16 shows the amounts of BDE 47 that reside in each compartment assuming different emission media. Only the diagram of that congener is presented here, since they all

show similar patterns. The emission used is here 1000 kg/h, which is much more than the real PBDE emissions, but the aim is just to show the importance of emission media, and not to reconcile the obtained amounts with measured data.

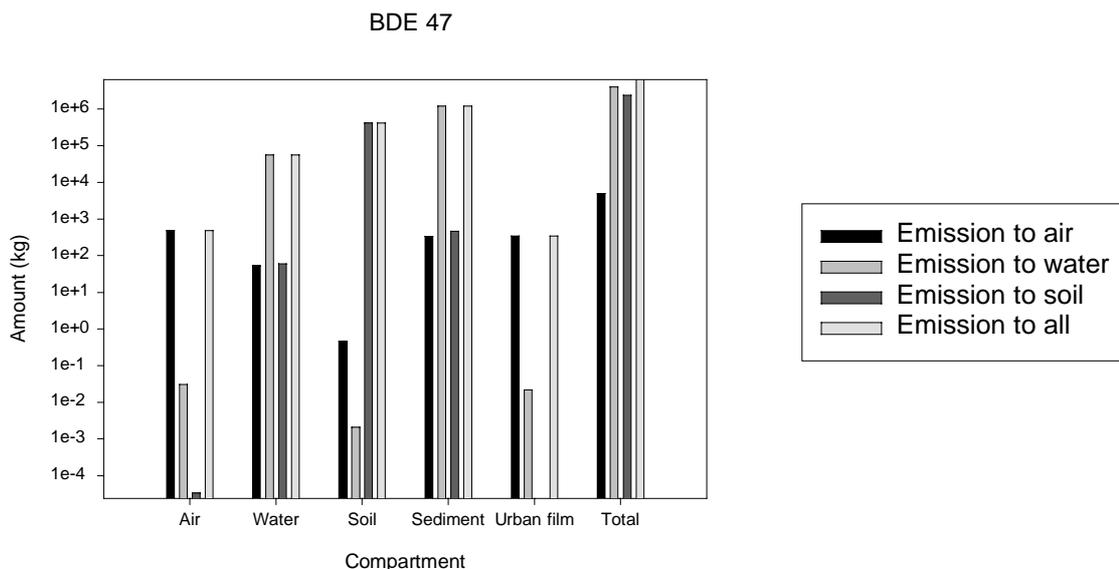


Figure 16. Amounts of BDE 47 in different compartments at different emission scenarios.

Figure 16 shows that the amounts in each compartment are highly influenced by the medium of release. For example, emission to air yields larger amounts in urban film, sediment and water than in soil, whereas emission to soil yields very small amounts both in air and urban film. Thus, identifying the media of release is very important when assessing the environmental fate of a chemical, in particular in small areas such as Stockholm city, with very short residence times of air and water.

7 Suggestions for further studies

7.1 PBDE assessment

For future assessments of the environmental fate of PBDEs, research should be focussed on:

- Experimental confirmation of the physical-chemical properties of individual congeners, with focus on BDE 209, since that compound is the one most commonly used. This involves development of analytical methods.
- Measuring environmental concentrations of individual PBDE congeners in Stockholm, with focus on air, soil and sediment.
- Identifying emission sources and rates more thoroughly, preferably through experimental studies, and thus also media of release.
- Estimating inflow concentrations, perhaps through development of a regional fugacity model of Sweden and prediction of national background levels.
- Studying the environmental distribution in the summer and in the winter, e.g. through using a fugacity model with temperature correction as discussed in section 7.2.

7.2 Improvement of the CeStoc model

In order to improve and develop the CeStoc model further, the following issues should be addressed:

- Validation or calibration with other organic compounds, for which properties, local emissions and environmental occurrence are well known, preferably in combination with the six-stage process described in this report.
- A multivariate sensitivity analysis should be performed, e.g. through using multivariate projection methods, such as principal component analysis (PCA) and/or partial least squares projection to latent structures (PLS). The input variables used in the CeStoc and other fugacity models contain many assumptions and it would be useful to identify the parameters that have the greatest impact on the output, i.e. environmental concentrations, persistence and so on. Due to the large amount of input data this identification is hard to perform just by looking at the results, and a multivariate approach is more convenient. With the help of multivariate analysis programs, e.g. the SIMCA program (Eriksson et al. 1999) the interactions between

various input parameters and response parameters can be identified, which in turn would indicate which input data that are crucial for the model results. This would be useful when there is a lack of data in e.g. physical-chemical properties, which often is the case with emerging chemicals, or when environmental parameters are uncertain. This kind of approach would be convenient for any multimedia fugacity model, and not only for the CeStoc model.

- A temperature correction should be included in the CeStoc, especially if modelling compounds where physical-chemical properties are well determined. The physical-chemical properties used in this study are all based on data at 25°C, which is not applicable as a mean temperature in Stockholm. Rather the mean temperature lies around 10°C (SLB website, 2001). This could cause an error in the calculations since many of the physical-chemical properties are temperature dependent, which in turn affects the partitioning properties.
- In order to make the CeStoc model user friendly, it should be converted to a more convenient programming language, e.g. Visual Basic, which is the one most commonly used for fugacity models.

8 Conclusions

A multimedia fugacity model (the CeStoc model) has been developed that is applicable for non-ionic organic chemicals in urban areas. It has been parameterised to the centre of Stockholm, but could be applied to other cities as well. It has been run for fluoranthene and three PBDE congeners, showing satisfactory agreement with observed environmental concentrations.

The CeStoc model indicates that soil is the largest sink for the PBDEs that stay in the area, and sediment the second largest. Therefore, these two media should be the focus of research and measurements of these compounds. According to the CeStoc results, the concentration of PBDEs in the urban film is very high (mg/m^3). However since this compartment has a very small volume compared to the others, the amounts residing here are minor. Still, the film has a potential to act as a storage compartment for PBDEs as well as other organic compounds, and therefore, the contribution of the film to the PBDE levels in e.g. surface waters may not be negligible.

Using the current emission estimates, the majority of the PBDEs emitted to the Stockholm environment is transported out of the system through air advection. This indicates potential for long-range transport, which is confirmed by other studies showing detectable levels of PBDEs in mammals from the Atlantic. However, media of release largely affects the fate of these compounds, since mainly the chemical emitted to air is being advected, whereas emission to other compartments mainly remains in the system.

The degree of bromination does not seem to influence the environmental distribution to any great extent. There is an indication that higher bromination levels cause larger amounts residing in soil. The uncertainty in vapour pressure of BDE 209 however seem to influence this pattern; lowering the value of this parameter yields a more significant dependence pattern of degree of bromination.

Except for the parameter just mentioned, physical-chemical properties do not affect the partitioning of PBDEs in the studied area to any great extent. When assuming equal emissions of all congeners, the distribution pattern looks quite much the same, even though parameters such as $\log K_{OW}$ and water solubility differ considerably. Thus, it is concluded that in such a small area as the centre of Stockholm, other parameters are crucial, such as residence time in air, and above all media of release. Greater fractionation would be expected for a larger area.

The predicted concentrations of individual PBDE congeners for water and sediment are well comparable to measured levels of individual PCB congeners in sediments in

Stockholm and water from the Baltic Sea. This indicates that the potential impact of PBDEs is of about the same size as the PCBs.

The CeStoc model provides a useful tool for environmental authorities in the region. Combined with generic models that gives a more complete picture of the environmental fate of a chemical the model could be used as:

- A necessary link between material flow analysis (MFA) and environmental monitoring, to reconcile emission estimates with observed environmental levels.
- A tool in initial screening-projects for new chemicals, in order to identify the chemicals most likely to be persistent and the most sensitive media.
- A basis for development of monitoring programmes, for the same reasons as mentioned above.

Finally, the CeStoc model is a level IV model. In this project, only the level III situation was considered, but it is possible to simulate time-changing emissions and thus study the change in environmental concentrations over time, which also would give an implication of recovery time for the environment of interest. In order to do this, historical emissions and background levels have to be known, but the model can also be used to show what would happen with the environmental concentrations of a substance if emissions decreased or ceased completely.

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Appendix 1

Environmental input parameters and their references

Parameter	Symbol	Value	Reference
Area		47 km ²	A-M Hellsten pers. comm.
Percentage water surface		25	A-M Hellsten pers. comm.
Air height		0.6 km	C Johansson pers. comm.
Water depth		15 m	GFK 2000
Soil depth		5 cm	Half the value of Mackay (1991)
Sediment depth		1 cm	Mackay (1991)
Percentage impervious surface		50	GFK 2000
ISI (impervious surface index)	ISI	2.4	Calculated
Thickness of urban film	T _F	137 nm	Mid-point value from Diamond et al. (2000)
Washoff rate constant	W	1.3 × 10 ⁻³ h ⁻¹	Calculated
Volume fraction particles in air PM2.5	v _Q	8.7 × 10 ⁻¹²	Calc. from Wallin (1998)
Volume fraction particles in water	v _P	5 × 10 ⁻⁶	Mackay (1991)
Volume fraction air in soil	v _{AS}	0.2	Mackay (1991)
Volume fraction water in soil	v _{WS}	0.3	Mackay (1991)
Volume fraction solids in soil	v _{SS}	0.5	Mackay (1991)
Volume fraction water in sediment	v _{WD}	0.91	Calc. from Östlund et al. (1998)
Volume fraction solids in sediment	v _{DD}	0.09	Calc. from Östlund et al. (1998)
Mass fraction particles in urban film	φ _{QF}	0.7	Diamond et al. (2000)
Mass fraction liquid in urban film	φ _{FF}	0.3	Diamond et al. (2000)
Air density	ρ _A	1.18	
Water density	ρ _W	1.0 kg/L	
Urban film density	ρ _F	0.83 kg/L	Diamond et al (2000)
Air particle density	ρ _Q	1.7 kg/L	Diamond et al. (2000)
Aquatic particle density	ρ _P	2.4 kg/L	Mackay (1991)
Soil solids density	ρ _S	2.4 kg/L	Mackay (1991)
Sediment solids density	ρ _D	2.4 kg/L	Mackay (1991)
Urban film particle density	ρ _Q	1.7 kg/L	Mackay (1991)
Fraction organic carbon in aquatic particles	x _{OC,P}	0.12	Broman et al. (1994)
Fraction organic carbon in soil solids	x _{OC,S}	0.068	Linde et al. (2001)

Appendix 1

Parameter	Symbol	Value	Reference
Fraction organic carbon in sediment solids	$x_{OC,D}$	0.046	Östlund et al. (1998)
Fraction organic carbon in urban film	$x_{OC,F}$	0.74	Diamond et al. (manuscript)
Air-side MTC over water	k_{AW}	3 m/h	Mackay & Paterson (1991)
Water-side MTC	k_{WW}	0.03 m/h	Mackay & Paterson (1991)
Diffusion to stratosphere	U_{ST}	0.01 m/h	Mackay & Paterson (1991)
Rain rate	U_R	0.54 m/år	A-M Holst pers. comm.
Scavenging ratio	Q	200,000	Mackay (1991)
Dry deposition velocity	U_P	0.7 m/h	Caffrey et al. (1998)
Air-side MTC over soil	k_{SA}	5 m/h	Mackay (1991)
Diffusion path length in soil	Y_S	2.5 cm	Mackay & Paterson (1991)
Molecular diffusivity in air	B_{MA}	0.04 m ² /h	Mackay & Paterson (1991)
Molecular diffusivity in water	B_{MW}	4×10 ⁻⁶ m ² /h	Mackay & Paterson (1991)
Water runoff rate from soil	U_{WW}	3.9×10 ⁻⁵ m/h	Mackay & Paterson (1991)
Solids runoff rate from soil	U_{SW}	2.3×10 ⁻⁸ m/h	Mackay & Paterson (1991)
Water-side MTC over sediment	k_{XW}	0.01 m/h	Mackay & Paterson (1991)
Diffusion path length in sediment	Y_D	0.5 cm	Mackay & Paterson (1991)
Sediment deposition rate	U_{DX}	1.7×10 ⁻⁶ m/h	Calc. from Broman et al. (1994)
Sediment resuspension rate	U_{RX}	1.0×10 ⁻⁷ m/h	$U_{DX} - U_{BX}$
Sediment burial rate	U_{BX}	1.6×10 ⁻⁶ m/h	Calc. from Östlund et al. (1998)
Air-side air-film MTC	k_{AF}	3 m/h	Assumption that $k_{AF} = k_{AW}$
Film-side air film MTC	k_{FF}	varies	Calc. according to Trapp (1995)
Film-water MTC	k_{FW}	1.8×10 ⁻¹⁰ m/h	$T_F \times W$ (Diamond et al. manuscript)
Leaching rate from soil to ground water	U_L	0.2 m/year	Keml (2000)

Appendix 2

Compartment	Z-value	Source
Air gas phase	$Z_A = 1/RT$	Mackay (1991)
Air particles	$Z_Q = 6 \times 10^6/P_L RT$	Mackay (1991)
Bulk air	$Z_{BA} = Z_A + (Z_Q \times v_Q)$	Mackay (1991)
Water dissolved	$Z_W = 1/H$	Mackay (1991)
Water particles	$Z_P = Z_W \times \rho_P \times K_{OC} \times x_{OC,P}$	Mackay (1991)
Bulk water	$Z_{BW} = Z_W + (Z_P \times v_P)$	Mackay (1991)
Soil solids	$Z_S = Z_W \times \rho_S \times K_{OC} \times x_{OC,S}$	Mackay (1991)
Air in soil	$Z_A = 1/RT$	Mackay (1991)
Water in soil	$Z_W = 1/H$	Mackay (1991)
Bulk soil	$Z_{BS} = (v_A \times Z_A) + (v_W \times Z_W) + (v_S \times Z_S)$	Mackay (1991)
Sediment solids	$Z_D = Z_W \times \rho_D \times K_{OC} \times x_{OC,D}$	Mackay (1991)
Sediment pore water	$Z_W = 1/H$	Mackay (1991)
Bulk sediment	$Z_{BD} = (v_W \times Z_W) + (v_D \times Z_D)$	Mackay (1991)
Pure urban film	$Z_F = Z_W \times K_{OW} \times x_{OC,F}$	Diamond et al. (ms)
Particles in film	$Z_Q = 6 \times 10^6/P_L RT$	Mackay (1991)
Bulk urban film	$Z_{BF} = (Z_F \times \phi_F) + (Z_Q \times \phi_Q)$	Diamond et al. (ms)

Appendix 3

D-values. The total D-values are denoted by numbers: Air = 1, Water = 2, Soil = 3, Sediment = 4, Urban film = 5

Compartment	Process	Process D	Total D
Air-water	Diffusion	$D_{VW} = 1/(1/k_{AW}A_{AW}Z_A + 1/k_{WW}A_{AW}Z_W)$	
	Rain dissolution	$D_{RW} = A_{AW}U_RZ_W$	
	Wet deposition	$D_{QW} = A_{AW}U_RQV_QZ_Q$	$D_{12} = D_{VW} + D_{RW} + D_{QW} + D_{DW}$
	Dry deposition	$D_{DW} = A_{AW}U_PV_QZ_Q$	$D_{21} = D_{VW}$
Air – soil	Diffusion	$D_{VS} = 1/(1/k_{SA}A_{AS}Z_A + Y_S/(A_{AS}(B_{AE}Z_A + B_{WE}Z_W)))$	
	Rain dissolution	$D_{RS} = A_{AS}U_RZ_W$	
	Wet deposition	$D_{QS} = A_{AS}U_RQV_QZ_Q$	$D_{13} = D_{VS} + D_{RS} + D_{QS} + D_{DS}$
	Dry deposition	$D_{DS} = A_{AS}U_PV_QZ_Q$	$D_{31} = D_{VS}$
Soil - water	Solids runoff	$D_{SW} = A_{AS}U_{SW}Z_S$	$D_{32} = D_{SW} + D_{WW}$
	Water runoff	$D_{WW} = A_{AS}U_{WW}Z_W$	$D_{23} = 0$
Sediment-water	Diffusion	$D_{TX} = 1/(1/k_{XW}A_{WD}Z_W + Y_D/A_{WD}B_{WX}Z_W)$	
	Deposition	$D_{DX} = A_{WD}U_{DX}Z_P$	$D_{24} = D_{TX} + D_{DX}$
	Resuspension	$D_{RX} = A_{WD}U_{RX}Z_X$	$D_{42} = D_{TX} + D_{RX}$
Luft – film	Diffusion	$D_{VF} = 1/(1/k_{AF}A_{AF}Z_A + 1/k_{FF}A_{AF}Z_F)$	
	Rain dissolution	$D_{RF} = A_{AF}U_RZ_W$	
	Wet deposition	$D_{QF} = A_{AF}U_RQV_QZ_Q$	$D_{15} = D_{VF} + D_{RF} + D_{QF} + D_{DF}$
	Dry deposition	$D_{DF} = A_{AF}U_PV_QZ_Q$	$D_{51} = D_{VF}$
Film – water	Film washoff	$D_{FW} = A_{AF}k_{FW}Z_{BF}$	$D_{52} = A_{AF}k_{FW}Z_{BF}$
Reaction		$D_{Ri} = k_{Ri}V_iZ_i$	
Advection		$D_{Ai} = G_iZ_i$	
Transfer to stratosphere		$D_{ST} = U_{ST}(A_{AW} + A_{AS})Z_A$	
Sediment burial		$D_{BX} = U_{BX}A_{WD}Z_X$	
Leaching from soil to groundwater		$D_{LS} = U_{LS}A_{AS}Z_W$	



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