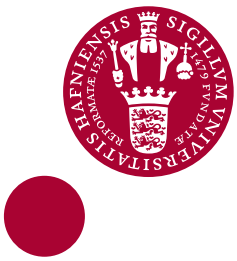

Uptake of organic chemicals in plants

human exposure assessment

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Human exposure assessment

PhD thesis

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Summary

This work gives an insight into the assessment of human exposure to xenobiotic compounds in food stuffs all the way from experiments to the use of model tools. In focus are neutral organic compounds, primarily from petroleum, and their uptake into plants.

A new analytical method was developed for the determination of chemical activity of volatile compounds in plant tissue and soil. Chemical activity is a valuable concept. Chemical activity is related to the chemical potential and is a measure of how active a substance is in a given state compared to its reference state. It is the difference in chemical activity that drives diffusion. The analytical method employs SPME (solid-phase microextraction), is automated, fast, reliable, uses almost no solvents compared to traditional methods and reduces the contact between sample and the person handling it. The method was applied for the determination of BTEX (benzene, toluene, ethylbenzene, o-, m- and p-xylene) and naphthalene in willows from a growth chamber experiment and birch from a fuel oil polluted area.

The uptake of xenobiotic compounds in plants is described. In spite of the large differences between plants and the vast amount of organic chemicals in use, general uptake pathways to plants have been described. Also, process oriented model tools exist for the calculation of uptake into plants.

Model tools are needed to answer the following question: Do chemicals in our daily diet pose a risk to human health? Here crop-specific models were used to estimate the daily exposure to selected chemicals with the diet for both adults and children. The exposure of children was calculated separately, because children have a higher consumption than adults considering their bodyweight. Also, a model for the uptake of xenobiotic compounds in breast milk allows for the assessment of exposure to chemicals for babies in the applied model framework.

The daily exposure to BaP (benzo(a)pyrene) and TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) was estimated with the new model framework. It was found to be in the range of results reported from studies based on the analysis of food stuffs. We expect the new model framework to be capable of estimating the daily exposure with diet for other neutral organic chemicals as well. This holds, as long as the calculations are based on a thorough knowledge of both models and chemicals. The behaviour of the chemicals in the environment, such as their degradation in soil, air and biological matrices like plant and animal, should receive special attention.

Sammendrag

Her gives et indblik i vurdering af human eksponering for miljøfremmede stoffer i fødevarer helt fra den eksperimentelle analyse til anvendelsen af modelværktøjer. Fokus er rettet mod neutrale organiske stoffer, primært fra råolie, og deres optag i planter.

En ny analysemetode til bestemmelse af den kemiske aktivitet af flygtige forbindelser i plantemateriale og jord er udviklet. Kemisk aktivitet er et værdifuldt koncept. Kemisk aktivitet er relateret til det kemiske potentiale og er et mål for, hvor aktivt et stof er i en given tilstand i forhold til dets referencetilstand. Det er forskelle i kemisk aktivitet, der driver diffusion. Analysemetoden anvender SPME (fast-fase mikroekstraktion), er automatiseret, hurtig, pålidelig, bruger næsten ingen solventer i forhold til traditionelle metoder og reducerer kontakten mellem prøve og laboratoriepersonel. Metoden blev anvendt til analyse af BTEX (benzene, toluene, ethylbenzene, o-, m- og p-xylene) og naphthalen i pil fra et vækstkammerforsøg og birk fra et olieforurenet område.

Optaget af miljøfremmede stoffer i planter er beskrevet. På trods af store forskelle fra plante til plante og den enorme mængde organiske kemikalier i brug, er generelle optagsveje ind i planter blevet beskrevet. Procesorienterede modelværktøjer eksisterer også til beregning af optaget i planter.

Modelværktøjer er nødvendige for at besvare følgende spørgsmål: Udgør kemikalier i vores daglige kost en sundhedsrisiko? Her er afgrødespecifikke modeller blevet anvendt til at estimere indtaget af udvalgte kemikalier via føden for både børn og voksne. Børns eksponering blev bestemt separat, da disse har et større fødeindtag end voksne set i forhold til deres kropsvægt. En model for optaget af miljøfremmede stoffer i brystmælk muliggør også estimeringen af eksponeringen til kemikalier for babyer i den anvendte modelstruktur.

Indtaget af BaP (benzo(a)pyrene) og TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) blev ved hjælp af modelstrukturen estimeret inden for den samme størrelsesorden, som tidligere rapporteret af studier, hvor indtaget blev estimeret ud fra eksperimentelle analyser af fødevarer. Vi forventer, at den nye modelstruktur også vil kunne estimere indtaget med føden for andre neutrale organiske kemikalier. Så længe beregningerne er baseret på et indgående kendskab til kemikalierne og modellerne. Speciel fokus skal rettes mod kemikaliernes egenskaber i miljøet, deres nedbrydning i jord, luft og biologiske matricer såsom planter og dyr.

Preface

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Contents

Paper I. Charlotte N. Legind, Ulrich Karlson, Joel G. Burken, Fredrik Reichenberg, and Philipp Mayer, 2007. Determining chemical activity of (semi)volatile compounds by headspace solid-phase microextraction. Analytical Chemistry 79, 2869-2876.

Paper II. Stefan Trapp and Charlotte N. Legind, 2008. Uptake of organic contaminants from soil into vegetables. Chapter 9 in Dealing with Contaminated Sites: From Theory towards Practical Application, accepted.

Paper III. Charlotte N. Legind and Stefan Trapp, 2008. Modeling the exposure of children and adults via diet to chemicals in the environment with crop-specific models. Environmental Pollution, in print. DOI: 10.1016/j.envpol.2008.11.021

Paper IV. Stefan Trapp, Li Ma Bomholtz, and Charlotte N. Legind, 2008. Coupled mother-child model for bioaccumulation of POPs in nursing infants, Environmental Pollution 156, 90-98.

Introduction

Chemicals are indispensable for our society today; they form the basis of many important processes and valuable applications. However, some of these chemicals cause problems when they distribute into environmental media, and currently human exposure to toxic chemicals is suspected or known to be responsible for promoting or causing a range of diseases such as cancer, birth defects, and learning disabilities. This exposure can to some extent be attributed to contamination of food.

Exposure to environmental contaminants is linked to their bioavailability in environmental matrices. This determines their potential for uptake into food crops and thereby ultimately their content in the human diet. Bioavailability of compounds in soil has been defined in a multitude of ways, but recent advances suggest using chemical activity of compounds in soil as a well defined measure. Chemical activity or the related measures, fugacity and freely dissolved concentration, have widespread use, also in plant uptake modeling.

Models are important tools for exposure assessments. They can be used for an initial screening, to determine whether the compounds in question can be found in crops from their sources in soil and air. However versatile they are, models should be used together with measurements, since models rely on measurements. Models can help design experiments. This saves time and other resources spent for unnecessary sampling and laboratory work.

Human exposure assessment of organic compounds is the topic of the presented work. The context is uptake of neutral organic compounds in plants determined by both model calculations and measurements. Model compounds were chosen from environmental contaminants present in petroleum.

The thesis comprises an introductory part and four papers. The first paper was published and describes a method that was developed for determining chemical activity of (semi)volatile organic compounds using solid-phase microextraction. The second paper is a book chapter, which is accepted and gives a review on uptake of organic soil contaminants in plants. The third paper is submitted and deals with dietary exposures to environmental pollutants. This was estimated for children and adults using crop-specific models. The fourth paper was published and presents a model for estimating contaminant concentrations in breast milk, and the body load of contaminant in both mother and child.

The overall objective is to gain insight into exposure assessment all the way from measurement to application of models.

New analytical methodology

Paper I focuses on the analysis of volatile and semi-volatile non-polar compounds in different sample matrices like plant tissue and soil. The context was uptake in plants, so the primary goal was to follow the compounds from the source, e.g. soil to the plant, and within the plant. This demanded a method that could analyse the compounds in different matrices and preferably provide a measure of the compounds that could be compared directly among the different matrices. In addition, the general requirements for analytical methods in terms of accuracy, precision, and speed and ease of operation needed to be fulfilled. So the objective was to develop a method that fulfils these demands. This led to a new measurement methodology for determining chemical activity of volatile and semi-volatile non-polar organic compounds (Paper I).

Method description

The new analytical method is based on the principle, that it is the chemical activity of analytes in a sample that determines the equilibrium concentration of the analytes in a solid-phase microextraction (SPME) fibre. In short, the method comprises four steps: 1) a sample is transferred to a gastight vial, ensuring that the headspace air does not decrease the chemical activity of analytes in the sample, 2) a SPME fibre is inserted into the vial headspace air and equilibrium between sample and fibre is obtained, again without reducing the chemical activity of analytes in the sample, 3) the SPME fibre is transferred to a gas chromatograph inlet for thermal desorption and analysis, and 4) calibration is performed with external standards in either methanol or liquid polydimethylsiloxane (PDMS) by repeating steps 1-3, so-called partitioning standards.

Model substances for the method development were chosen among the non-polar and volatile or semi-volatile constituents of gasoline and lighter fuel oils. Structures and selected properties are given in Figure 1 and Table 1. They were chosen from the aromatic constituents (benzene, toluene, ethylbenzene, o-, m- and p-xylene (BTEX) and naphthalene) and from the aliphatic constituents (linear alkanes C_9, C_{10}, C_{12}, C_{14}, C_{16}) of petroleum.

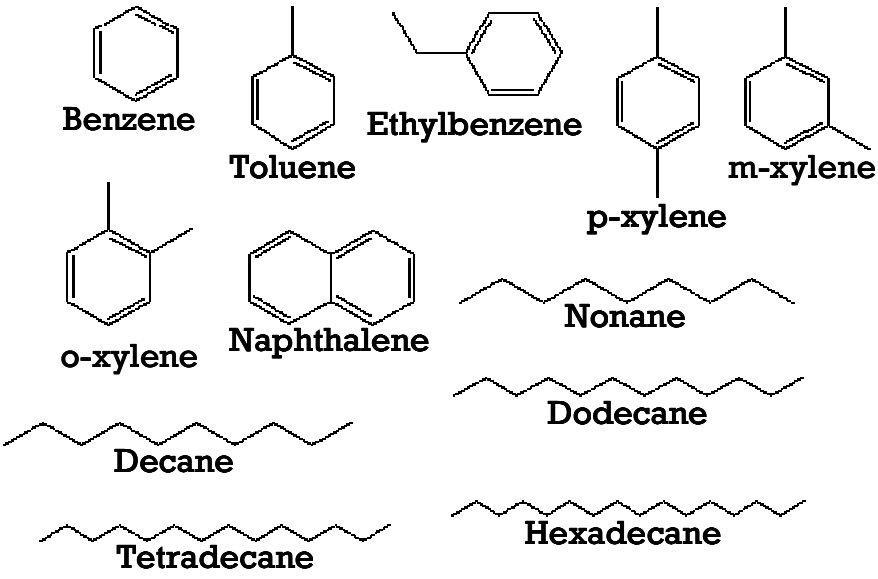

Figure 1. Structure of model substances used for the method development (CambridgeSoft Corporation, 2008).

BTEX form 20 – 35% (v/v) of gasoline (Alberici et al., 2002), and they belong to the more water-soluble compounds present in petroleum. They have high vapour pressures, so they are very volatile and they all boil below 180 °C, which means they are distilled off in the gasoline fraction, and only minor amounts are present in the lighter fuel oils like diesel (Hansen et al., 2001). Due to their high water solubility, their K_{OW} (octanol-water distribution constant) is in the lower end of petroleum compounds. This also holds for their K_{OA} (octanol-air distribution constant), so they only slightly prefer staying in the organic phase as opposed to air.

Table 1. Selected properties of the model substances.

Compound	M_W (g/mol)	V_p (Pa)	T_b (°C)	S_W (mg/L)	Log K_{OW}	Log K_{OA}
Benzene	78	13 700	78	2300	1.9	2.8
Toluene	92	4200	118	725	2.4	3.3
Ethylbenzene	106	1540	143	250	2.9	3.7
p-xylene	106	1150	140	233	3.0	3.9
m-xylene	106	1260	138	252	2.9	3.8
o-xylene	106	1100	141	304	2.8	3.9
Naphthalene	128	14	208	39	3.2	5.2
Nonane	128	641	154	0.17	5.7	3.8
Decane	142	194	178	0.040	6.3	4.3
Dodecane	170	16	222	0.011	7.5	5.2
Tetradecane	198	1.4	259	$6.1 \cdot 10^{-3}$	8.7	6.2
Hexadecane	226	0.13	292	$3.7 \cdot 10^{-3}$	9.9	7.1

M_W: Molar weight, V_p: Vapour pressure, T_b: Boiling temperature, S_W: Solubility in water, K_{OW}: Octanol-water distribution constant, K_{OA}: Octanol-air distribution constant. Compound properties were found with the SPARC online calculator (Hilal et al., 2003, Hilal et al., 2004, SPARC, 2007).

Naphthalene is the smallest of the PAH's (polycyclic aromatic hydrocarbons), it contains only two fused aromatic rings. It has a low vapour pressure compared to BTEX, and it is a semi volatile compound. It boils above 180 °C, which means that it is mainly found in the lighter fuel oils. Its K_{OW} is comparable to the ones of BTEX, but it has a lower vapour pressure leading to a higher K_{OA}, giving it a higher preference to an organic phase as opposed to air than BTEX.

The linear alkanes selected as model substances belong predominantly to the gasoline fraction (C_9-C_{10}) and to the lighter fuel oil fraction of the oil (C_{12}-C_{16}), when setting the boundary at a boiling point of 180 °C. So some of them are volatile and some are semi volatile. Their vapour pressures and water solubility are lower than the ones of BTEX and decrease with increasing molecular size. They have high K_{OW}, and also high K_{OA}, although lower than their K_{OW}, reflecting a low water solubility and strong affinity for organic matter.

The measurement endpoint most typically used for reporting contents of organic compounds in soil and plant samples is total analyte concentration in the sample. This can be in terms of mass of analyte per kilogram wet weight (ww) or dry weight (dw) of material for soil and plant samples. Whether the given concentration is really the total concentration in the sample depends on the compounds, the extraction procedure, the sample matrix, and the calibration of the method.

Currently, no accepted standard methods exist for the determination of VOCs (volatile organic compounds) in plant tissues (Alvarado and Rose, 2004). And no guidance for collection and handling of vegetation is provided, so this is performed in a multitude of ways. It is important to take representative samples of the plants under study. This can cause some difficulties, because between plants there is biological variability, and in the plant, the distribution of chemical is not uniform, e.g. there may be a difference with height. Determination of VOCs can be performed by headspace analysis followed by chromatographic analysis, which require very little sample preparation (Zygmunt and Namiesnik, 2003, Ma and Burken, 2002, Larsen et al., 2008). But this approach requires thorough calibration based on partitioning between plant tissue and headspace, which has to be investigated for each study. The method developed in Paper I circumvents this problem.

Chemical activity and the related measures fugacity and freely dissolved concentration employed in Paper I have advantages as measurement endpoints compared to total concentration. One is the simplicity of the calibration demonstrated in Paper I. Another is the direct link to exposure when uptake into organisms is diffusive, whereas total concentrations of contaminants in e.g. soil give little information on the exposure to these contaminants. It is not always so that the presence of a contaminant constitutes a risk. For example, if the contaminant is adsorbed to the soil organic matter, the risk for diffusion into soil pore water and subsequent transport in the xylem flux of crops will be negligible. Soils are very complex matrices, so in addition to determining total concentrations of contaminants in soil, numerous parameters in the soil need to be known like texture, organic carbon content and microbial activity, as these tend to affect the bioavailability of contaminants in soil. Bioavailability has been determined in several ways, but recently chemical activity has been proposed as a well defined measure of bioavailability (Reichenberg and Mayer, 2006).

Disadvantages of using chemical activity and related measures to describe exposure to pollutants are that advective processes are less elegantly described. It is the gradient in chemical activity that drives diffusion; whereas advection is performed by the motion of the fluid (e.g. xylem water in plants) itself (Schwarzenbach et al., 1993). Another problem is the convention and tradition of using concentrations to describe pollutants in the environment. Up to now, chemical activities of pollutants in the environment have hardly been measured. Therefore, much information is naturally specified in concentrations, e.g. soil quality standards.

Chemical activity was introduced by G. N. Lewis. The activity of a substance is defined by (Lewis and Randall, 1961, Alberty and Silbey, 1997):

$$\mu = \mu^{o} + RT \ln a \quad (1)$$

where μ (J mol^{-1}) is the chemical potential of the substance, μ^o (J mol^{-1}) is the standard state chemical potential, R (J K^{-1} mol^{-1}) is the gas constant, T (K) is the temperature and a is the chemical activity. Chemical activity is dimensionless and at $a = 1$, the chemical is in its reference state, where $\mu = \mu^o$ (Alberty and Silbey, 1997). Chemical activity is a measure of how active a substance is in a given state compared to its reference state (Schwarzenbach et al., 1993). For real gases (Alberty and Silbey, 1997):

$$a = f / P^o \quad (2)$$

where f (Pa) is the fugacity of the substance and P^o (Pa) is the standard state pressure. However for solutions, chemical activity of a substance can be expressed in the following way (Alberty and Silbey, 1997):

$$a = \gamma C \quad (3)$$

where γ (L mol^{-1}) is the activity coefficient of the substance divided by the standard value of the molar concentration (1 mol L^{-1}). This is the approach applied in Paper I, where the reference state is the subcooled liquid solubility of the substance in methanol.

Chemical activity is applied in almost every field of chemistry. Examples are the proton ion activity (pH) (McNaught and Wilkinson, 1997), water activity used in food science (Lewicki, 2004) and the equilibrium partitioning theory used in environmental toxicology (Ditoro et al., 1991). Diffusion processes can be studied by measuring chemical activity, since chemical activity is defined in terms of chemical potential (Eq. 1). Diffusion occurs as a result of a gradient in the chemical potential. At phase equilibrium there is no net diffusion ($\mu_{phase1} = \mu_{phase2}$, so $d\mu/dx = 0$) at the same temperature and pressure (Alberty and Silbey, 1997, Schwarzenbach et al., 1993).

Despite of the potentials, only a few analytical methods have been applied to measure chemical activity of organic compounds in environmental matrices. These methods employ equilibrium sampling devices for the measurement: Headspace SPME (Paper I), direct immersion SPME (Ossiander et al., 2008) and polymer-coated vials (Reichenberg et al., 2008).

Fugacity was like chemical activity defined by G. N. Lewis:

$$\overline{G} = \overline{G^o} + RT \ln \frac{f}{P^o} \quad (4)$$

where G (J/mol) is the molar Gibbs energy (Lewis and Randall, 1961, Alberty and Silbey, 1997). So, fugacity is a measure of the molar free Gibbs energy of a real gas. It can be understood as the escaping tendency of a substance from a phase into an ideal gas. The fugacity is at most environmental conditions equivalent to partial pressure. This requires that the substance is present in the gaseous form, i.e. not bound to particles. Then the gas law applies and fugacity can be determined in the following manner (Mackay and Paterson, 1981):

$$f = R\,T\,C \tag{5}$$

where C (mol L^{-1}) is the concentration of the substance in air. This approach was used in Paper I.

In environmental sciences, fugacity is widely used to quantify toxics transport and bioaccumulation in air, water and sediment. Like chemical activity, equal fugacities of analytes in different matrices form the basis for thermodynamic equilibrium, and diffusion will always be directed from high to low fugacity. So, fugacity can also be used for comparing different matrices directly. Bioaccumulation of compounds in e.g. fish has been described with the concept of fugacity. Mackay pioneered using the fugacity approach for creating a multimedia modeling framework (Mackay, 1979). Others have followed in using fugacity, one of the latest models developed for bioaccumulation of organic contaminants in the food chain, ACC Human, uses fugacity (Czub and McLachlan, 2004). However, for nonvolatile compounds, the fugacity approach makes little sense. Here, chemical activity is more appropriate.

Many techniques have been applied for measuring fugacities of organic compounds, but only the method in Paper I uses SPME. Most methods applied use gas chromatography coupled to a detector for the ultimate quantification, but the sample preparation varies. The techniques include: Closed air water systems with headspace analysis for determination of fugacity in aqueous samples (Resendes et al., 1992, Yin and Hassett, 1986), thin film solid phase extraction (SPE) followed by liquid extraction or thermal desorption for measuring fugacity in fish (Wilcockson and Gobas, 2001), a fugacity-meter for measuring fugacity in spruce needles (Horstmann and McLachlan, 1992), and static headspace analysis for fugacity in fish food and fecal samples from fish (Gobas et al., 1993).

Freely dissolved concentration is perhaps the most successful of the three measures: Chemical activity, fugacity and freely dissolved concentration. It is easily understood as the effective (unbound) concentration of analytes in a sample (Mayer et al., 2000b). Like chemical activity and fugacity, the freely dissolved concentration controls bioconcentration and toxicity (Ditoro et al.,

1991, Kraaij et al., 2003). However, the freely dissolved concentration is less suited to describe systems with little or no water, like e.g. air.

Freely dissolved concentration has been measured and applied in numerous studies. It is well suited for determining distribution constants between environmental media and water, and for the determination of protein-binding affinities (Heringa and Hermens, 2003). In addition to SPME, several techniques exist for the determination of freely dissolved concentrations of organic compounds.

SPME (solid-phase microextraction) was introduced in the early 1990's as a simple and solvent-free technique (Arthur and Pawliszyn, 1990). It is now a well-accepted and frequently applied method that can integrate sampling and sample introduction for gas chromatography. The possibility for automation also exists now, so in addition to saving solvents, the method also saves time previously used for sampling.

The method uses a small SPME fiber, coated with a sampling phase with a large surface area to volume ratio. By exposing the fiber to a sample, analytes from the sample either adsorb onto or diffuse into the sampling phase depending on the type of fiber used. After sampling, the fiber is injected into the inlet of a gas chromatograph for thermal desorption and determination of analytes.

SPME can be used for almost any compound; the only limitation in that respect is the type of coating available for use. The analyte has to move onto or into the fiber coating. With regards to sample types, SPME has two major applications: direct immersion SPME and headspace SPME. Direct immersion SPME means inserting the SPME fiber into a sample exposing it to the whole matrix, whereas headspace SPME is performed by sampling above a sample. Direct immersion SPME has been applied to e.g. water, soil, and sediment samples (Mayer et al., 2000b). For VOCs, headspace SPME is preferable, because it avoids problems related to the sample matrix – e.g., surface fouling of the fiber.

PDMS (polydimethylsiloxane) is the SPME fiber coating, which is used for the analytical method described in Paper I. This coating can be used for equilibrium sampling, where the sample is brought into thermodynamic equilibrium with the fiber coating without reducing the chemical activity of the analytes in the sample (Mayer et al., 2003). In Paper I, a coating thickness of 100 µm was chosen, because this gives a larger amount of analyte in the coating, than for the thinner fibers. This reduces detection limits. The thinner, 7 µm or 30 µm, coatings of PDMS can

be used when the analytes require longer equilibrium times, because the thinner coating will achieve equilibrium faster than the thicker ones.

Distribution constants between PDMS fiber and air were determined using liquid PDMS with a viscosity of 50 centistokes (Sigma Aldrich) in Paper I. Comparing these values to distribution constants determined for the PDMS phase of the SPME fiber and PDMS used in columns for gas chromatography indicates that the phases show similar behavior in the absorption of the investigated compounds in Paper I. So measurements with liquid PDMS can be used to predict the behavior of the PDMS SPME fiber.

The PDMS fiber is an absorbent fiber (Mayer et al., 2000a). Absorbent fiber coatings are liquid and retain analytes by partitioning, whereas adsorbent fiber coatings trap the analytes physically in their porous structures, which contain a high surface area. Besides PDMS, PA (polyacrylate) is used as an absorbent fiber coating. PA is a polar fiber and shows better performance than PDMS for polar analytes. The adsorbent fiber coatings are mixed. In addition to PDMS or PA they contain carbowax, carboxen or divinylbenzene. They can be used for analyses that require low detection limits (Valor et al., 2001).

Calibration of SPME can be directed at the initial total concentration of analyte in the sample, or the freely dissolved concentration (C_{free}), fugacity or chemical activity of analyte in the sample (Paper I). The initial total concentration of analyte in the sample, C_0, is found from the amount of analyte retained by the fiber, n, in the equilibrium sampling mode (Louch et al., 1992):

$$n = \frac{K_{fs} V_f V_s C_0}{K_{fs} V_f + V_s} \tag{6}$$

where K_{fs} is the distribution constant between fiber coating and sample, V_f is the volume of fiber coating and V_s is the volume of sample. The amount on the fiber, n, can be found from external calibration with either liquid injection of solvent standards or SPME extraction of aqueous standards (Zeng and Noblet, 2002).

In addition to equilibrium sampling conditions, determination of the freely dissolved concentration, fugacity and chemical activity of analytes in samples requires negligible depletion of the mass of analyte in the sample. The freely dissolved concentration of analyte in the sample can be found from external calibration with either liquid injection of solvent standards or SPME extraction of aqueous standards, but the principle differs from Eq. 6. From liquid injections C_{free} is found from the distribution constant between fibre and water (Mayer et al., 2000b), and aqueous standards give the measure directly (Heringa and Hermens, 2003). Paper I introduces partitioning

standards of liquid PDMS or methanol from which C_{free} can be obtained by either the distribution constant between liquid PDMS and water or the activity coefficient of the analytes in methanol together with their liquid solubilities. For naphthalene the subcooled liquid solubility is used.

Fugacity or chemical activity of analytes can also be determined using the partitioning standards in methanol introduced in Paper I (Eqs. 3 and 5). SPME has not previously been used for the determination of chemical activity or fugacity of analytes in environmental samples, even though it is the chemical activity of the analytes in the sample rather than the total concentration that drives and determines the uptake into the fibre. SPME was never intended for exhaustive extractions.

Negligible depletion during sampling is required, because it ensures that the chemical activity of analyte in the sample is not disturbed during sampling. For headspace SPME this means that 1) the SPME fiber and 2) the headspace must not deplete the sample by more than 5% of its chemical mass (Figure 2). Due to the minute mass of PDMS on the fiber, the first requirement is always fulfilled for samples containing organic matter, so e.g. water samples can not be analyzed in this manner. The second requirement depends on the volume ratio of air to sample, and the sample to air distribution coefficient of the analyte:

$$\frac{m_{air}}{m_{sample}} < 0.05 \quad => \quad \frac{V_{air}}{V_{sample}} \times 20 < K_{sample,air} \tag{7}$$

where m_{air} is mass of analyte in headspace air, m_{sample} is mass of analyte in sample, V_{air} is volume of headspace air and V_{sample} is the volume of sample. This requirement is most restrictive for rather volatile analytes with low sample-air distribution constants ($K_{sample,air}$). Decreasing the volume ratio of air to sample by using larger sample masses in larger vials may extend the applicability range. The mass required for achieving negligible depletion is found and given in terms of organic matter content (Paper I) because this ultimately determines depletion.

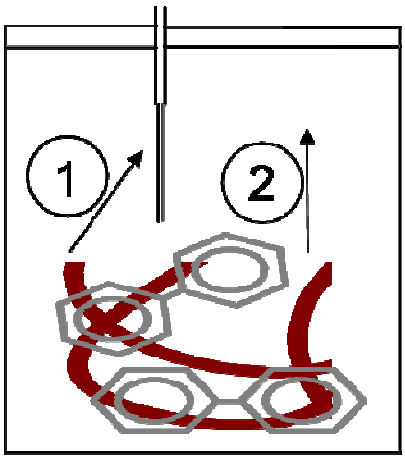

Figure 2. Schematic of the closed sampling system. The SPME fiber (1) and the headspace air (2) may not deplete the mass of analyte in the sample with more than 5%.

Negligible depletion SPME was introduced in the 1990's (Kopinke et al., 1995, Vaes et al., 1996) for measuring the freely dissolved concentration of analytes in complex samples.

Kinetics is linked to depletion. If the fiber depletes the headspace of mass of analytes by more than 5% during sampling this is not a problem as long as the resupply of analyte from sample to headspace is fast enough to keep up with the removal of analyte from the headspace. In this case, the headspace is actually not depleted. This was the case for some analytes in Paper I, where the eventual quantity that partitioned into the fiber was larger than the quantity present in the headspace at any time. However, there may be other sample types, where the surface provides too little desorption from sample into headspace. In this case, care should be taken not to deplete the headspace of analytes.

The applicability of the method requires that the kinetics of different sample matrices are rather similar. This was checked in Paper I. One major finding was that diffusion through the headspace air was rate limiting for the overall mass transfer from sample into fiber for compounds with the ratio of the $K_{PDMS,air}$ to the diffusion coefficient in air (D_a) above 10^4 cm^2/s. This gave the method a fairly high precision. For compounds with a $K_{PDMS,air}/D_a$ below 10^4 s/cm^2, diffusion in the PDMS coating seems to be rate limiting for the overall mass transfer. Previous systems with water have shown the same trend where increasing hydrophobicity of the analytes changed the rate limiting step from membrane controlled to aqueous diffusion layer controlled (Flynn and Yalkowsky, 1972 as cited in (Heringa and Hermens, 2003)).

Activity coefficients of the model compounds in methanol used in Paper I have been estimated with the SPARC online calculator (Hilal et al., 2004, SPARC, 2007). The activity coefficients have been checked by comparing standard pressures (P^o) and liquid solubilities in water ($S_{W,L}$) of the compounds calculated from the method detection limits (Paper I) to literature values (Table 2) (Reichenberg, 2007). The literature values are not more than factor 1.4 higher than the values determined from the method (except for dodecane, where the literature value is factor 2.3 lower).

These calculations are performed according to the fact, that each parameter (chemical activity, fugacity and freely dissolved concentration) can be estimated from one of the other two parameters. The principle is that at a chemical activity of 1, the fugacity equals the standard pressure of the substance (Eq. 2) and the freely dissolved concentration (C_{free} (mol L^{-1}) equals the subcooled liquid solubility of the substance in water ($S_{W,L}$ (mol L^{-1})) (Reichenberg and Mayer, 2006).

$$P^o = f/a \qquad S_{W,L} = C_{free}/a \tag{8}$$

Table 2. Liquid solubilities in water and standard pressures calculated from the detection limits in Paper I and compared to literature values (Schwarzenbach et al., 1993). Adapted from (Reichenberg, 2007)

Compound	- log ($S_{W,L}$ (M))		- log (P^o (atm))	
	$S_{W,L} = C_{free} / a$	Lit.	$V_P = f / a$	Lit.
Benzene	1.55	1.64	0.86	0.90
Toluene	2.12	2.25	1.38	1.42
ethylbenzene	2.64	2.80	1.80	1.90
p-xylene	2.70	2.77	1.94	1.93
m-xylene	2.63	-	1.91	-
o-xylene	2.57	2.76	1.95	2.05
Naphthalene	3.02	3.06	3.33	3.43
Nonane	5.85	5.94	2.20	2.24
Decane	6.51	6.57	2.72	2.76
Dodecane	7.88	7.52	3.73	3.80

Application of the method

In a growth chamber experiment (data not shown) chemical activity measurements were applied to study the transport and distribution of contaminants inside a soil-plant system. The results with o-xylene from one soil-plant system are shown in Figure 3. It is seen from the graph to the right that the plant has a higher chemical activity of o-xylene than the soil. This implies that

measurements taken from the same layers determine the direction of diffusion of o-xylene in that layer, which is shown with horizontal arrows from plant to soil in the diagram in the left part of the figure. This information about extent and direction of diffusion is difficult if not impossible to obtain via measurements of total concentrations. The vertical arrows in the diagram show the advective transport of o-xylene with the xylem water flow inside the plant.

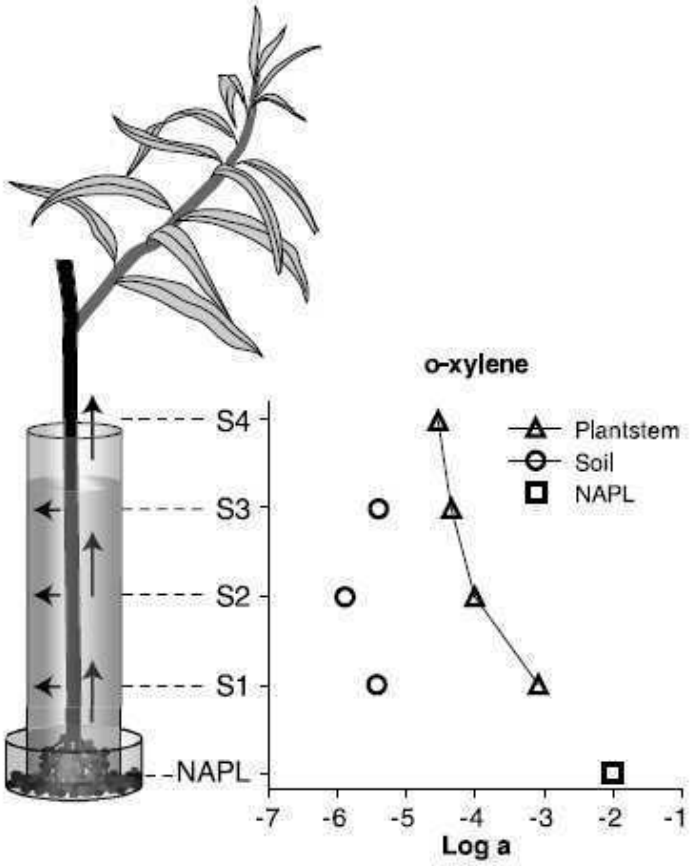

Figure 3. Practical application of the new method to study the transport and distribution of o-xylene in a soil-plant system. Two o-xylene gradients dominate this system: 1) advection vertically in the plant and 2) diffusion horizontally from plant to soil. (NAPL (non-aqueous phase liquid))

Chemical activity of the model substances were also determined in tree samples taken at a fuel-oil polluted site, Hradcany (Machackova et al., 2008), in the Czech Republic (data not shown). The results from the tree cores taken at the fuel oil polluted site show no difference in chemical activity of o-xylene with height of the tree (Figure 4). This indicates that o-xylene is taken up from air instead of soil. So trees might not be suitable as biomonitors for soil contamination,

when the contaminant is degraded in soil. Another possibility that should be excluded is that plants produce and emit o-xylene.

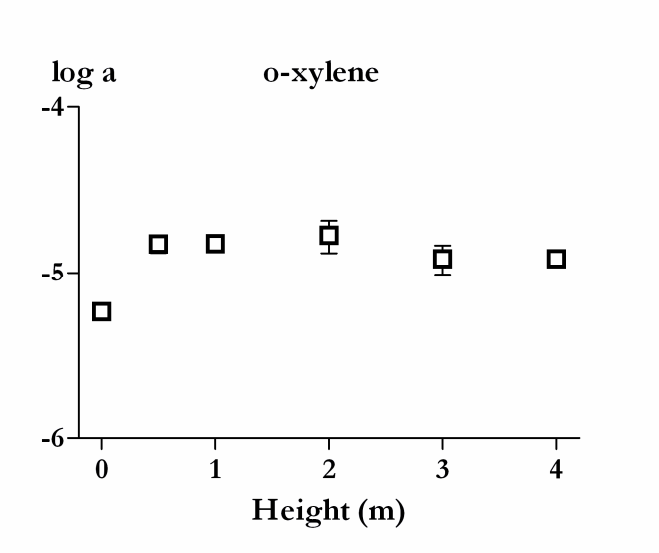

Figure 4. Chemical activity of o-xylene in a birch tree growing at a fuel oil polluted site. 14 tree core samples were taken at 6 different heights.

In conclusion, the method developed in Paper I works for volatile and semi-volatile non-polar organic compounds, and it provides a measurement endpoint that can be directly compared between dissimilar matrices. This helps in the prediction of equilibrium partitioning phenomena and the study of diffusion processes. The method is automated, fast, reliable, almost solvent free compared to traditional analytical methods, and reduces the risks of working with hazardous chemicals, because of the reduced contact between sample and the person handling it.

However, the question of bioavailability or chemical activity is more relevant for the less volatile compounds like PAHs with more than 2 rings and compound groups like the dioxins. These are persistent, bioaccumulative, toxic (PBT) and of great concern to humans and the environment when it comes to e.g. soil and air pollution. Further development of the method to encompass the analysis of these compounds is a challenge, and might not be feasible due to detection limits and equilibration times. Another recently developed technique exists that is more appropriate for analysis of these compounds than the one above (Reichenberg et al., 2008). Another limitation of the method in Paper I, is caused by the demand of a certain amount of

organic matter in the sample, this precludes the analysis of water and air samples in the current set up.

The method was applied for a growth chamber experiment and to analyse field samples of tree cores (data not shown). Future experiments in growth chambers would benefit from more replicates, clear hypotheses, and a fully working analytical method before onset of plant tests. Possible biodegradation should also be covered when working with these compounds, but preferably other compounds should be chosen, when the objective is biomonitoring with trees.

Exposure modeling

To cover the vast amount of chemicals present ubiquitously, predictive tools are needed to indicate compounds of possible concern for exposure via diet. One pressing question is: Do the environmental contaminants present in our daily diet pose a risk to the human population, i.e. are there any health risks? The first step in answering this question is to determine the exposure to chemicals from diet. This can be done by modelling contaminant accumulation in food crops from their presence in environmental matrices like soil and air as well as by performing measurements. So the overall objective of this part was to compare estimated results based on both model calculations and measurements.

Paper II covers the topic of uptake of organic contaminants from soil by plants. The goal was to gain insight into both experimental data and predictive methods. Knowledge of uptake of contaminants in plants is relevant for several areas. Here, two will be mentioned: 1) for a limited range of compounds, trees can be used as biomonitors for pollution of soil and groundwater, and 2) generally, the uptake of contaminants in crops is of great significance, because ultimately, this leads to consumer exposure to a wide range of environmental contaminants. So, the objective was to study the uptake of neutral organic compounds into plants via experiments, and a literature study.

Paper III aims at estimating dietary exposures to selected environmental contaminants through the terrestrial food chain. Crop-specific models were used for assessing the exposure via diet for children and women with a new model framework (NMF). The framework was tested on three compounds: Dodecyl benzenesulfonic acid (a linear alkylbenzene sulfonate, LAS), 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and benzo(a)pyrene (BaP). The latter two are relatively well-investigated and allows for the comparison of model predictions to measured values. A second goal was to elucidate the need for separate exposure assessments for children, since children are not miniature versions of adults.

Uptake of organic chemicals in plants

Paper II aims at determining the potential for accumulation of organic chemicals from soil in food crops. Many studies have been performed with uptake of organic contaminants in plants. However, the number is small compared to the number of plant species and organic compounds present worldwide. So in this context, we have only limited knowledge of plant uptake of organic

contaminants. Nonetheless, general patterns are known and process-oriented models have been established (Paper II).

Limitations and uncertainties are issues for both model and experiment. The key for both approaches lies in the design and interpretation. Even well performed and documented experiments with uptake of organic chemicals in plants may produce unexplainable results. An example is the root to shoot transfer of dioxins in cucumber and zucchini (Hulster et al., 1994). Plants are living organisms and therefore highly variable. This introduces a high degree of uncertainty to the experiments. This, of course, does not make modelling the uptake of organic compounds into plants any easier. However, combining models and experiments gain a lot of insight into the topic, and models can be used to help design and interpret experimental results.

Uptake pathways for organic contaminants into plants are several. Known passive transport and uptake processes are shown in Figure 5 (Paper II). They are all ultimately driven by the activity of the compounds in soil and air, and main processes comprise the following:

- Uptake with soil water
- Diffusion from soil into roots
- Diffusive (gaseous) exchange with air
- Particle deposition from soil and air followed by diffusion into plant tissue

After entering the plant, the contaminants may distribute with the xylem and phloem flux depending on plant type (e.g. roots or fruits) and chemical properties of the contaminant.

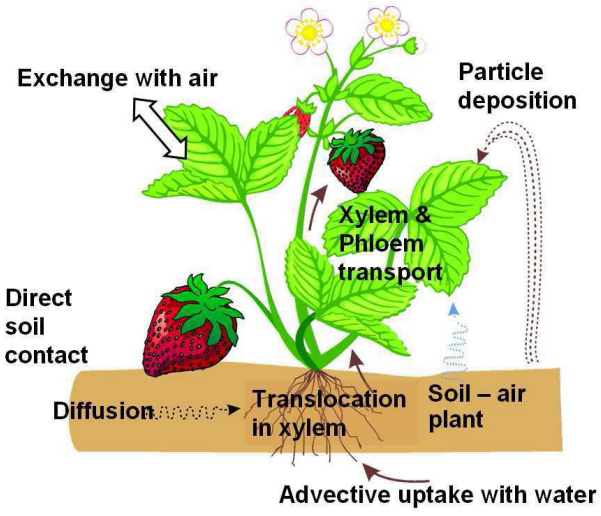

Figure 5. Transport and uptake processes in the soil-air-plant system (Paper II).

Predictive methods for uptake of contaminants into plants have been developed. Both empirical methods (Travis and Arms, 1988, Briggs et al., 1982) and mechanistic models, pioneering models were developed by Trapp et al. (1990), Paterson et al. (1994), and Hung and Mackay (1997). In Paper II a standard model for plant uptake of organic chemicals was introduced. This was based on processes previously described for uptake into roots (Trapp, 2002), lettuce (Trapp and Matthies, 1995) and tree fruits (Trapp, 2007). The model calculates the steady-state concentration of contaminants in roots and leaves from their concentrations in soil and air. The concentration in roots, C_R (mg kg ww^{-1}), is found from the concentration in soil pore water, $C_{W,S}$ (mg L^{-1}) (Paper II):

$$C_R = \frac{Q}{Q/K_{RW} + k\,M_R} C_{W,S} \tag{9}$$

where Q (L d^{-1}) is the xylem flux, K_{RW} (L kg ww^{-1}) is the root water distribution constant, k is a first order loss rate including dilution by growth and metabolism, and M_R (kg ww) is the mass of roots. The concentration in leaves, C_L (mg kg ww^{-1}), is found from the concentration in roots and total (gas and particulate) concentration in air, $C_{A,t}$ (mg m^{-3}). Input, I (mg kg ww^{-1} d^{-1}) to leaves:

$$I = \frac{Q}{M_L\,K_{RW}} C_R + \frac{A}{M_L} C_{A,t} \left(g_L\,(1-f_P) + \frac{v_{dep}}{2} f_P\right) \tag{10}$$

where M_L (kg ww) is the mass of leaves, A (m^2) is the area of leaves, g_L (m d^{-1}) is the conductance of leaves, f_P is the fraction associated with particles in air and v_{dep} (m d^{-1}) is the deposition velocity of particles in air. Loss, a_L (d^{-1}), from leaves:

$$a_L = \frac{A\,g_L}{M_L\,K_{LA}} + k \tag{11}$$

Where K_{LA} (m^3 kg^{-1}) is the air-leave distribution constant. Dividing input by loss gives the steady-state concentration in leaves:

$$C_L = \frac{I}{a_L} \tag{12}$$

In addition, a new dynamic solution was introduced for this standard model (Paper II). This allows for pulse and constant input of chemicals to soil, air, roots, and leaves as well as determination of metabolite formation.

Biomonitoring of soil pollution has been performed with success doing coring of trees growing at polluted sites (Vroblesky et al., 1999, Gopalakrishnan et al., 2007, Larsen et al., 2008,

Sorek et al., 2008). However, this is currently limited to the analysis of volatile chlorinated hydrocarbons. Other compounds, like e.g. BTEX (Sorek et al., 2008), have not been detected in high amounts in trees growing above a plume of soil contamination containing BTEX. This can be explained by the high biodegradability of BTEX in soil and especially rhizosphere. So instead of moving into the roots of the trees like the chlorinated solvents do, the BTEX are degraded in the rhizosphere. Still for chlorinated solvents, tree coring is not a precise tool for determining soil or groundwater concentrations; the method provides merely an indication of the presence or not of the compounds in the subsurface. However, this approach saves time and money when placing wells to monitor the contaminants more precisely.

Dietary exposures to environmental contaminants

Dietary exposures to pollutants can be estimated in different ways. However, two factors should be covered: 1) The concentration of pollutant in food stuffs and 2) The quantity of consumption of food stuff. The first can be found with both model and measurement, and the second by food surveys. The World Health Organisation recommends doing Total Diet Studies (TDS). For TDS the food is bought, prepared, homogenized and then the contaminant level is measured. This mimics the real world, but is time consuming, so most often contaminant levels are measured in retail food directly. Processing can then be neglected or accounted for by processing factors. Nevertheless, analysing all contaminants is not possible, so model schemes like the new model framework (NMF) (Paper III) are needed. Other approaches exist, e.g. a food chain model developed by (Czub and McLachlan, 2004), the technical guidance document (TGD) for assessing indirect exposure (EC, 2003), CSOIL (Brand et al., 2007) and CLEA (DEFRA, 2002). The latter two includes uptake from soil only into food.

The NMF consists of 4 crop specific models: Potato (Trapp et al., 2007), root (Trapp, 2002), lettuce (Trapp and Matthies, 1995) and tree fruit (Trapp, 2007). In addition, the lettuce model is modified to account for uptake of contaminants in cereals and the Travis and Arms (1988) regressions are used for milk and meat. All models and regressions include uptake from soil into food. The lettuce and tree fruit models also include uptake from air. Background levels of the contaminants in soil and air are input to the models. The daily dietary exposure is then found from the modelled concentrations in food together with the consumption of each food item. Inhalation and soil ingestion are also included.

The crop specific model predictions were compared to the root and leaf model from the TGD (technical guidance document) as well as to measured values. This is shown for BaP in Figure 5. A major conclusion from this is that the equilibrium approach for roots used in the TGD grossly overestimates the exposure from roots for lipophilic compounds. Whereas, the dynamic root model used in the NMF (new model framework) is acceptable.

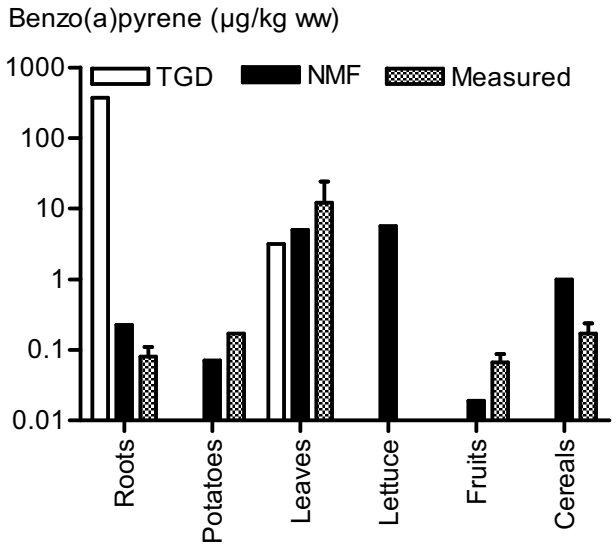

Figure 5. A Comparison of model predictions (NMF (new model framework) and TGD (technical guidance document)) with measured values (Kazerouni et al., 2001, Samsøe-Petersen et al., 2002, FSA, 2002) for benzo(a)pyrene (BaP).

Children age 4-5 are included in the NMF with their own consumption pattern and bodyweight. Children eat almost the same amount of fruits, vegetables, cereal products and meat as adults, even though they are much smaller. They drink more milk per day than adults. So naturally, they are approximately exposed to twice the amount of contaminant per kg bodyweight than adults (Paper III). Considering this and their vulnerability (Landrigan et al., 2004) it is very important to account for their specific behaviour in exposure assessments.

Babies could also be included in the NMF by adding the mother-child model described in Paper IV. The consumption pattern of babies is very straightforward. During their first 4-6 months they only consume formula or breast milk. The mother child model calculates the concentration of environmental pollutants in breast milk from the dose taking in by the mother via diet and inhalation, so this could be added directly. The rapidly increasing bodyweight of

babies is also included in the mother child model offering the possibility of following the body burden of pollutants with time.

Risk management can be aided by model outputs. The NMF offers details on important exposure routes, e.g. it can determine whether the dominant entry of pollutant into crops is from soil or air. It also tells you the most significant food stuffs for exposure via diet for a certain contaminant, so that exposure can be minimised by eating less roots or fruits. The best choice is of course always to stop the source that emits the contaminant into the environment, but this takes time.

In conclusion, Paper II provides a thorough review on the topic of plant uptake of organic chemicals from soil. Already, the literature provides some experimental data for plant uptake of organic compounds, and models exist for predicting their uptake. A combination of models and experiments, using the models to help design and interpret experiments would be advantageous.

The applied model framework predicted the dietary exposures to BaP and TCDD within reasonable error margins (Paper III). This is judged from comparing the results with results from diet studies using measured concentrations of the pollutants in food items. We anticipate, that the NMF can predict the dietary exposure to other neutral organic compounds also. However, this should be based on a thorough knowledge of the compounds together with the models. The compound behaviour, especially degradation in soil, air, plant and animal matrices should be studied.

Approaches for modelling the uptake of ionisable compounds in plants have been developed (e.g. Trapp, 2000, Trapp, 2004) and future work could focus on the adaptation and applicability of the NMF towards ionisable compounds. These can be present in their neutral or ionic form in environmental matrices. This results in different uptake processes in plants, currently not accounted for in the NMF. A process that may cause high accumulation in plants of ionisable compounds is the ion trap (Paper II).

Conclusion

Chemical activity is a valuable concept. It describes the chemical itself, instead of the sample matrix, so it gives more information on exposure to the chemical than total concentrations do. Chemical activity is easily measured for a range of semi volatile and volatile compounds in environmental matrices containing organic matter (Paper I). However, total concentrations are currently the standard choice for reporting contaminant concentrations in environmental matrices. So legislation up to now uses total concentrations for e.g. soil quality standards.

Uptake of environmental organic contaminants into plants can be described by both measurement and model for many neutral organic compounds. However, there are numerous plant species and environmental conditions vary, so uncertainties are large and care should be taken when translating result from uptake studies to other crop types or other climates (Paper II). In this context we use models describing uptake of contaminants into plants to predict the dietary exposure and to determine whether soil or air is the main entry into the terrestrial food chain of the compounds (Paper III). This is done separately for adults and children, and the possibility to include babies in the framework exists (Paper IV).

The NMF has been applied to study fairly 'old' and well-studied chemicals, so knowledge of their behaviour in environmental matrices could be used. We anticipate that the model framework can be applied to 'new' less intensely-studied chemicals as well. But a higher degree of uncertainty can then be anticipated. Nonetheless, for screening purposes this will prove valuable, and possible processes of concern can be identified and subsequently monitored by measurements. However, measurements are not flawless and should also be judged with care.

REACH (registration, evaluation, authorisation and restriction of chemicals) is a new chemical legislation in the EU and has the goal of securing a high protection level for the environment and humans. It lays down regulation for the immense number of chemicals presently being used in our society and for introduction of new chemicals. This requires an enormous amount of knowledge of the chemicals and their behaviour in the environment – also in the food chain.

The NMF could be one of the tools applied for identification of substances of very high concern (SVHCs) under REACH. These substances will be subject to authorisation or restriction, and one parameter for their identification is indirect exposure via the food chain (ECHA, 2008).

References

Alberici, R.M., Zampronio, C.G., Poppi, R.J., Eberlin, M.N., 2002. Water solubilization of ethanol and BTEX from gasoline: on-line monitoring by membrane introduction mass spectrometry. Analyst 127, 230-234.

Alberty, R. A., Silbey, R. J., 1997. Physical Chemistry. Second edition ed. John Wiley & Sons, Inc., New York.

Alvarado, J.S., Rose, C., 2004. Static headspace analysis of volatile organic compounds in soil and vegetation samples for site characterization. Talanta 62, 17-23.

Arthur, C.L., Pawliszyn, J., 1990. Solid-phase microextraction with thermal-desorption using fused-silica optical fibers. Analytical Chemistry 62, 2145-2148.

Brand, E., Otte, P.F., Lijzen, J.P.A., 2007. CSOIL 2000: an exposure model for human risk assessment of soil contamination. RIVM Report 711701054/2007, National Institute of Public Health and the Environment (http://rivm.openrepository.com/rivm/bitstream/10029/13385/1/711701054.pdf)

Briggs, G.G., Bromilow, R.H., Evans, A.A., 1982. Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. Pesticide Science 13, 495-504.

CambridgeSoft Corporation, ChemBioFinder.com (http://chembiofinderbeta.cambridgesoft.com/) (September 2007)

Czub, G., McLachlan, M.S., 2004. A food chain model to predict the levels of lipophilic organic contaminants in humans. Environmental Toxicology and Chemistry 23, 2356-2366.

DEFRA (Department for Environment Food and Rural Affairs), 2002. The Contaminated Land Exposure Assessment Model (CLEA): Technical basis and algorithms. R & D Publications CLR 10, Environment Agency (http://publications.environment-agency.gov.uk/pdf/SCLR10-e-p.pdf?lang=_e)

Ditoro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., Paquin, P.R., 1991. Technical basis for establishing sediment quality criteria for nonionic organic-chemicals using equilibrium partitioning. Environmental Toxicology and Chemistry 10, 1541-1583.

EC (European Commission), 2003. Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market., European Communities, Italy (http://ecb.jrc.it/documents/TECHNICAL_GUIDANCE_DOCUMENT/EDITION_2/)

ECHA (European Chemicals Agency), 2008. Guidance on inclusion of substances in Annex XIV (list of Substances subject to Authorisation). European Chemicals Agency (http://reach.jrc.it/docs/guidance_document/annex_xiv_en.pdf?vers=12_08_08)

FSA (Food Standards Agency), 2002. PAHs in the UK diet: 2000 total diet study samples. Food Survey Information Sheet Number 31/02 (http://www.food.gov.uk/multimedia/pdfs/31pah.pdf)

Gobas, F.A.P.C., Zhang, X., Wells, R., 1993. Gastrointestinal Magnification - the Mechanism of Biomagnification and Food-Chain Accumulation of Organic-Chemicals. Environmental Science & Technology 27, 2855-2863.

Gopalakrishnan, G., Negri, M.C., Minsker, B.S., Werth, C.J., 2007. Monitoring subsurface contamination using tree branches. Ground Water Monitoring and Remediation 27, 65-74.

Hansen, O.C., Pommer, K., Lassen, P., 2001. Sporstoffer til benzin, diesel og fyringsolie - indledende screening. Miljøprojekt 612, Miljøstyrelsen

Heringa, M.B., Hermens, J.L.M., 2003. Measurement of free concentrations using negligible depletion-solid phase microextraction (nd-SPME). Trac-Trends in Analytical Chemistry 22, 575-587.

Hilal, S.H., Karickhoff, S.W., Carreira, L.A., 2003. Prediction of the vapor pressure boiling point, heat of vaporization and diffusion coefficient of organic compounds. Qsar & Combinatorial Science 22, 565-574.

Hilal, S.H., Karickhoff, S.W., Carreira, L.A., 2004. Prediction of the solubility, activity coefficient and liquid/liquid partition coefficient of organic compounds. Qsar & Combinatorial Science 23, 709-720.

Horstmann, M., McLachlan, M.S., 1992. Initial development of a solid-phase fugacity meter for semivolatile organic compounds. Environmental Science & Technology 26, 1643-1649.

Hulster, A., Muller, J.F., Marschner, H., 1994. Soil-plant transfer of polychlorinated dibenzo-p-dioxins and dibenzofurans to vegetables of the cucumber family (Cucurbitaceae). Environmental Science & Technology 28, 1110-1115.

Hung, H., Mackay, D., 1997. A novel and simple model of the uptake of organic chemicals by vegetation from air and soil. Chemosphere 35, 959-977.

Kazerouni, N., Sinha, R., Hsu, C.H., Greenberg, A., Rothman, N., 2001. Analysis of 200 food items for benzo[a]pyrene and estimation of its intake in an epidemiologic study. Food and Chemical Toxicology 39, 423-436.

Kopinke, F.D., Porschmann, J., Remmler, M., 1995. Sorption behavior of anthropogenic humic matter. Naturwissenschaften 82, 28-30.

Kraaij, R., Mayer, P., Busser, F.J.M., Bolscher, M.V., Seinen, W., Tolls, J., 2003. Measured porewater concentrations make equilibrium partitioning work - A data analysis. Environmental Science & Technology 37, 268-274.

Landrigan, P.J., Kimmel, C.A., Correa, A., Eskenazi, B., 2004. Children's health and the environment: Public health issues and challenges for risk assessment. Environmental Health Perspectives 112, 257-265.

Larsen, M., Burken, J., Machackova, J., Karlson, U.G., Trapp, S., 2008. Using tree core samples to monitor natural attenuation and plume distribution after a PCE spill. Environmental Science & Technology 42, 1711-1717.

Lewicki, P.P., 2004. Water as the determinant of food engineering properties. A review. Journal of Food Engineering 61, 483-495.

Lewis, G. N., Randall, M., 1961. Thermodynamics. Second Edition ed. McGraw-Hill Book Company, Inc., New York.

Louch, D., Motlagh, S., Pawliszyn, J., 1992. Dynamics of organic-compound extraction from water using liquid-coated fused-silica fibers. Analytical Chemistry 64, 1187-1199.

Ma, X.M., Burken, J.G., 2002. VOCs fate and partitioning in vegetation: Use of tree cores in groundwater analysis. Environmental Science & Technology 36, 4663-4668.

Machackova, J., Wittlingerova, Z., Vlk, K., Zima, J., Linka, A., 2008. Comparison of two methods for assessment of in situ jet-fuel remediation efficiency. Water Air and Soil Pollution 187, 181-194.

Mackay, D., 1979. Finding fugacity feasible. Environmental Science & Technology 13, 1218-1223.

Mackay, D., Paterson, S., 1981. Calculating Fugacity. Environmental Science & Technology 15, 1006-1014.

Mayer, P., Tolls, J., Hermens, L., Mackay, D., 2003. Equilibrium sampling devices. Environmental Science & Technology 37, 184A-191A.

Mayer, P., Vaes, W.H.J., Hermens, J.L.M., 2000a. Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: High partition coefficients and fluorescence microscopy images. Analytical Chemistry 72, 459-464.

Mayer, P., Vaes, W.H.J., Wijnker, F., Legierse, K.C.H.M., Kraaij, R.H., Tolls, J., Hermens, J.L.M., 2000b. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. Environmental Science & Technology 34, 5177-5183.

McNaught, A. D., Wilkinson, A., 1997. IUPAC Compendium of Chemical Terminology. Blackwell Science, Oxford, United Kingdom.

Ossiander, L., Reichenberg, F., McLachlan, M.S., Mayer, P., 2008. Immersed solid phase microextraction to measure chemical activity of lipophilic organic contaminants in fatty tissue samples. Chemosphere 71, 1502-1510.

Paterson, S., Mackay, D., Mcfarlane, C., 1994. A model of organic-chemical uptake by plants from soil and the atmosphere. Environmental Science & Technology 28, 2259-2266.

Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. Environmental Toxicology and Chemistry 25, 1239-1245.

Reichenberg, F., 2007. The accessibility and chemical activity of polycyclic aromatic hydrocarbons in soil. Ph.D thesis, Analytical Chemistry, Lund. (http://www.receto.dk/People/~/media/Receto/docs/pdf/Thesis/Reichenberg_thesis_2007.ashx)

Reichenberg, F., Smedes, F., Jönsson, J.-Å., Mayer, P., 2008. Determining the chemical activity of hydrophobic organic compounds in soil using polymer coated vials. Chemistry Central Journal 2.

Resendes, J., Shiu, W.Y., Mackay, D., 1992. Sensing the fugacity of hydrophobic organic chemicals in aqueous systems. Environmental Science & Technology 26, 2381-2387.

Samsøe-Petersen, L., Larsen, E.H., Larsen, P.B., Bruun, P., 2002. Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. Environmental Science & Technology 36, 3057-3063.

Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M., 1993. Environmental organic chemistry. John Wiley & Sons, Inc..

Sorek, A., Atzmon, N., Dahan, O., Gerstl, Z., Kushisin, L., Laor, Y., Mingelgrin, U., Nasser, A., Ronen, D., Tsechansky, L., Weisbrod, N., Graber, E.R., 2008. "Phytoscreening": The use of trees for discovering subsurface contamination by VOCs. Environmental Science & Technology 42, 536-542.

SPARC, on line calculator, (http://ibmlc2.chem.uga.edu/sparc/index.cfm) (September 2007)

Trapp, S., 2000. Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. Pest Management Science 56, 767-778.

Trapp, S., 2002. Dynamic root uptake model for neutral lipophilic organics. Environmental Toxicology and Chemistry 21, 203-206.

Trapp, S., 2004. Plant uptake and transport models for neutral and ionic chemicals. Environmental Science and Pollution Research 11, 33-39.

Trapp, S., 2007. Fruit tree model for uptake of organic compounds from soil and air. Sar and Qsar in Environmental Research 18, 367-387.

Trapp, S., Cammarano, A., Capri, E., Reichenberg, F., Mayer, P., 2007. Diffusion of PAH in potato and carrot slices and application for a potato model. Environmental Science & Technology 41, 3103-3108.

Trapp, S., Matthies, M., 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environmental Science & Technology 29, 2333-2338.

Trapp, S., Matthies, M., Scheunert, I., Topp, E.M., 1990. Modeling the bioconcentration of organic chemicals in plants. Environmental Science & Technology 24, 1246-1252.

Travis, C.C., Arms, A.D., 1988. Bioconcentration of organics in beef, milk, and vegetation. Environmental Science & Technology 22, 271-274.

Vaes, W.H.J., Ramos, E.U., Verhaar, H.J.M., Seinen, W., Hermens, J.L.M., 1996. Measurement of the free concentration using solid-phase microextraction: Binding to protein. Analytical Chemistry 68, 4463-4467.

Valor, I., Perez, M., Cortada, C., Apraiz, D., Molto, J.C., Font, G., 2001. SPME of 52 pesticides and polychlorinated biphenyls: Extraction efficiencies of the SPME coatings poly(dimethylsiloxane), polyacrylate, poly(dimethylsiloxane)-divinylbenzene, carboxen-poly(dimethylsiloxane), and carbowax-divinylbenzene. Journal of Separation Science 24, 39-48.

Vroblesky, D.A., Nietch, C.T., Morris, J.T., 1999. Chlorinated ethenes from groundwater in tree trunks. Environmental Science & Technology 33, 510-515.

Wilcockson, J.B., Gobas, F.A.P.C., 2001. Thin-film solid-phase extraction to measure fugacities of organic chemicals with low volatility in biological samples. Environmental Science & Technology 35, 1425-1431.

Yin, C.Q., Hassett, J.P., 1986. Gas-partitioning approach for laboratory and field studies of mirex fugacity in water. Environmental Science & Technology 20, 1213-1217.

Zeng, E.Y., Noblet, J.A., 2002. Theoretical considerations on the use of solid-phase microextraction with complex environmental samples. Environmental Science & Technology 36, 3385-3392.

Zygmunt, B., Namiesnik, J., 2003. Preparation of samples of plant material for chromatographic analysis. Journal of Chromatographic Science 41, 109-116.

Paper I

Determining chemical activity of (semi)volatile compounds by headspace solid-phase microextraction

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Determining Chemical Activity of (Semi)volatile Compounds by Headspace Solid-Phase Microextraction

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This research introduces a new analytical methodology for measuring chemical activity of nonpolar (semi)volatile organic compounds in different sample matrices using automated solid-phase microextraction (SPME). The chemical activity of an analyte is known to determine its equilibrium concentration in the SPME fiber coating. On this basis, SPME was utilized for the analytical determination of chemical activity, fugacity, and freely dissolved concentration using these steps: (1) a sample is brought into a vial, (2) the SPME fiber is introduced into the headspace and equilibrated with the sample, (3) the SPME fiber is injected into the GC for thermal desorption and analysis, and (4) the method is calibrated by SPME above partitioning standards in methanol. Model substances were BTEX, naphthalene, and alkanes, which were measured in a variety of sample types: liquid polydimethylsiloxane (PDMS), wood, soil, and nonaqueous phase liquid (NAPL). Variable sample types (i.e., matrices) had no influence on sampling kinetics because diffusion through the headspace was rate limiting for the overall sampling process. Sampling time was 30 min, and relative standard deviations were generally below 5% for homogeneous solutions and somewhat higher for soil and NAPL. This type of activity measurement is fast, reliable, almost solvent free, and applicable for mixed-media sampling.

Solid-phase microextraction (SPME) was introduced in the early 1990s by Arthur and Pawliszyn as a simple and solvent-free sampling technique.[1] Since then it has been applied in many analytical, primarily gas chromatographic (GC), methods, to a wide range of sample matrices, and to an even wider range of analytes. Many of the developed methods are very successful due to high analytical performance, minimized solvent use and sample handling, small sample size needed, and reduced demand for valuable technician time. During the last 15 years SPME has evolved into a well-accepted and frequently applied technique that integrates sampling and sample introduction, which can be fully automated.

Limits to further SPME application include problems with matrix effects, because the SPME method is less sensitive to bound forms of the analytes than free forms. Another limitation is the difficulty of applying conventional calibration approaches that were developed for exhaustive extractions. The fundamental problem is the mismatch between the traditional, accepted measurement endpoint of "total analyte concentration in the sample" and the "chemical activity of analyte in the sample", because it is the chemical activity, rather than the absolute concentration, that drives and determines the uptake into the fiber coating. The most common approach to deal with this problem is thorough calibration, which has to be based on an understanding of the analyte partitioning inside the sample and between sample, headspace, and SPME fiber.[2,3] In this paper we suggest another approach to circumvent the problem by making chemical activity the actual measurement endpoint of the presented SPME technique.

Chemical activity is an established concept with extensive applications in almost every field of chemistry. Examples include the water activity used in food science,[4] the proton ion activity[5] better known as pH, and the equilibrium partitioning theory used in environmental toxicology and chemistry.[6] To use chemical activity as a practical term, appropriate measurement techniques are required. Methods to measure water activity and pH are well established, widely available, and frequently applied. However, the chemical activity of organic chemicals is rarely measured due to lack of accepted methods. The working hypothesis of the research presented here is that chemical activity is the inherent measurement endpoint of SPME and that conventional SPME devices can be easily applied for the measurement of chemical activity. The aim of this paper is therefore to introduce and report a new measurement methodology for the determination of chemical

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† University of Aarhus.

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(1) Arthur, C. L.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145−2148.

(2) Pawliszyn, J. *Solid Phase Microextraction: Theory and Practice*; Wiley-VCH: New York, 1997.

(3) Ouyang, G.; Pawliszyn, J. *Trends Anal. Chem.* **2006**, *25*, 692−703.

(4) Lewicki, P. P. *J. Food Eng.* **2004**, *61*, 483−495.

(5) McNaught, A. D.; Wilkinson, A. *IUPAC Compendium of Chemical Terminology*; Blackwell Science: Oxford, United Kingdom, 1997.

(6) Ditoro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R. *Environ. Toxicol. Chem.* **1991**, *10*, 1541−1583.

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activity of nonpolar and semivolatile organics including the application of partitioning standards for the calibration of the method toward chemical activity.

Working Principle. The SPME method is based on the diffusive transfer of chemical activity from sample to fiber coating and requires that the coating is brought into a thermodynamic equilibrium with the sample while ensuring that the chemical activity of the analytes in the sample remains unaffected. The SPME method to measure chemical activity can be divided into four steps:

1. The sample is brought into a gastight vial, while ensuring that the sorption capacity of the sample dominates the chemical activity in the entire vial including the headspace.

2. The SPME fiber is introduced into the vial headspace until thermodynamic equilibrium between fiber coating and sample is reached, again without reducing the chemical activity (a) in the sample, meaning $a_{PDMS,fiber}$ is equal to a_{sample}.

3. The SPME fiber is then transferred into the GC injection port for thermal desorption and analysis.

4. External calibration is accomplished with partitioning standards.

Calibration. A new calibration principle is presented that applies organic solvent standards for the control of chemical activity in the headspace above the solvent, called partitioning standards. Such external standard solutions are prepared in either methanol or liquid polydimethylsiloxane (PDMS), and these external standards are sampled as described above (steps 1−3). The concept of chemical activity is closely related to both fugacity and freely dissolved concentration (C_{free}),[7] and all three measures are currently applied to quantify, study, and understand the environmental fate, exposure, and effects of organic chemicals. The new calibration principle is, for that reason, directed at each of these three measurement endpoints.

Chemical Activity. The chemical activity of an analyte in a sample is determined by external activity standards in methanol:

$$a_{MeOH} = \gamma_{MeOH} C_{MeOH} \quad (1)$$

where a_{MeOH} is the chemical activity of the analyte, γ_{MeOH} is its activity coefficient (L/kg), and C_{MeOH} is its concentration (kg/L). The subscript MeOH denotes methanol. The activity coefficients in methanol can be estimated by the SPARC on-line calculator, which only requires the molecular structure as user input. The computational approach is a blend of conventional linear free energy relationships, structure−activity relationships, and perturbed molecular orbital theory.[8,9] A systematic and practical guide to other estimation models (e.g., UNIFAC) has been written by Prausnitz et al.[10] Earlier, SPME has been applied for the determination of activity coefficients in liquid polymer coatings.[11]

Fugacity. The fugacity of an analyte can be determined from the air concentration (C_{air} (kg/L)) of the analyte above the sample. External partitioning standards in methanol can be used for calibration to fugacity:

$$f_{MeOH} = \frac{RTC_{air}}{M_w} = \frac{RTC_{MeOH}}{M_w K_{MeOH,air}} \quad (2)$$

where f_{MeOH} is the fugacity of the analyte (Pa), R is the gas constant (8.315×10^3 Pa·L/mol·K), T is the absolute temperature (K), $K_{MeOH,air}$ is the distribution constant of the analyte between methanol and air, and M_w is the molar weight of the analyte (kg/mol). Previously published work used techniques other than SPME for measuring fugacity in aqueous[12,13] and biological samples.[14−16]

Freely Dissolved Concentration. The freely dissolved concentration of an analyte can be determined with external partitioning standards in liquid PDMS (eq 3) or methanol (eq 4):

$$C_{free} = \frac{C_{PDMS}}{K_{PDMS,w}} \quad (3)$$

$$C_{free} = \gamma_{MeOH} C_{MeOH} S_{L,w} \quad (4)$$

where $K_{PDMS,w}$ is the distribution constant of the analyte between liquid PDMS and water, C_{PDMS} is the analyte concentration in liquid PDMS (kg/L), and $S_{L,w}$ is the (subcooled) liquid solubility in water (kg/L). Other already published methods also apply SPME for the measurement of freely dissolved analyte concentrations in, for instance, in vitro test systems,[17] aquatic environments,[18,19] field sediment,[20] and samples containing protein.[21] However, these methods were calibrated differently using either aqueous standard solutions or liquid injections of solvent standards.

The analyte concentration in the PDMS coating of the fiber ($C_{PDMS,fiber}$ (kg/L)) can also be estimated with this new calibration principle. Assuming that the PDMS coating of the SPME fiber has the same sorptive properties as the liquid PDMS, $C_{PDMS,fiber}$ can be determined with external standards in liquid PDMS, C_{PDMS} (kg/L), according to

$$C_{PDMS,fiber} = C_{PDMS} \quad (5)$$

EXPERIMENTAL SECTION

Materials. Analytes used were benzene (>99.5%, Fluka), toluene (≥99.5%, Fluka), ethylbenzene (≥99%, Fluka), *p*-xylene

(7) Reichenberg, F.; Mayer, P. *Environ. Toxicol. Chem.* **2006**, *25*, 1239−1245.
(8) SPARC on line calculator. http://ibmlc2.chem.uga.edu/sparc/index.cfm (accessed June 14, 2006).
(9) Hilal, S. H.; Karickhoff, S. W.; Carreira, L. A. *QSAR Comb. Sci.* **2004**, *23*, 709−720.
(10) Prausnitz, J.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall: Englewood Cliffs, NJ, 1999.
(11) Zhang, Z. Y.; Pawliszyn, J. *J. Phys. Chem.* **1996**, *100*, 17648−17654.
(12) Resendes, J.; Shiu, W. Y.; Mackay, D. *Environ. Sci. Technol.* **1992**, *26*, 2381−2387.
(13) Yin, C. Q.; Hassett, J. P. *Environ. Sci. Technol.* **1986**, *20*, 1213−1217.
(14) Wilcockson, J. B.; Gobas, F. A. P. C. *Environ. Sci. Technol.* **2001**, *35*, 1425−1431.
(15) Horstmann, M.; McLachlan, M. S. *Environ. Sci. Technol.* **1992**, *26*, 1643−1649.
(16) Gobas, F. A. P. C.; Zhang, X.; Wells, R. *Environ. Sci. Technol.* **1993**, *27*, 2855−2863.
(17) Vaes, W. H. J.; Ramos, E. U.; Hamwijk, C.; vanHolsteijn, I.; Blaauboer, B. J.; Seinen, W.; Verhaar, H. J. M.; Hermens, J. L. M. *Chem. Res. Toxicol.* **1997**, *10*, 1067−1072.
(18) Ramos, E. U.; Meijer, S. N.; Vaes, W. H. J.; Verhaar, H. J. M.; Hermens, J. L. M. *Environ. Sci. Technol.* **1998**, *32*, 3430−3435.
(19) Poerschmann, J.; Zhang, Z. Y.; Kopinke, F. D.; Pawliszyn, J. *Anal. Chem.* **1997**, *69*, 597−600.
(20) Mayer, P.; Vaes, W. H. J.; Wijnker, F.; Legierse, K. C. H. M.; Kraaij, R. H.; Tolls, J.; Hermens, J. L. M. *Environ. Sci. Technol.* **2000**, *34*, 5177−5183.
(21) Vaes, W. H. J.; Ramos, E. U.; Verhaar, H. J. M.; Seinen, W.; Hermens, J. L. M. *Anal. Chem.* **1996**, *68*, 4463−4467.

(≥95%, BDH Chemicals), *m*-xylene (≥99%, Fluka), *o*-xylene (≥99%, Fluka), naphthalene (>99%, Sigma Aldrich), nonane (>99%, Fluka), decane (≥98%, Fluka), dodecane (≥99%, BDH Chemicals), tetradecane (99%, Acros), and hexadecane (>99%, Merck−Schuchardt). Used as solvents were acetone (glass-distilled grade, Rathburn), methanol (≥99.9%, Merck), and liquid PDMS with a viscosity of 50 centistokes (cSt) (Sigma Aldrich). The soil contaminated with BTEX and naphthalene had an organic matter content of 3.9% dry weight (dw). Sodium azide (>99%, Merck) was used to inhibit microbial degradation of analytes in the soil. Match sticks used were of dry aspen wood and had a length of 4.7 cm (Tordenskjold, Sweden). Nonaqueous phase liquid (NAPL) was obtained from a fuel oil polluted area in the Czech Republic. Gastight glass vials with Teflon (PTFE)-lined screw caps were from Supelco.

SPME Sampling. The measurement principle was headspace SPME operated in the negligible depletion and equilibrium mode. Equilibrium was ensured for all analytes. A 100 μm PDMS fiber (Supelco, Bellefonte PA) was used for the sampling, which was fully automated using a Combi PAL autosampler (CTC Analytics, Switzerland). Transfer of the SPME fiber from vial to GC injector took less than 5 s. Static samplings were performed at 25−28 °C and shaken samplings at 35 °C with 250 rpm (orbital shaking of the entire vial).

GC Analysis. Separation and detection of analytes were conducted using an HP5890 Series II GC with a flame ionization detector (FID). The column was a 30 m Supelcowax10 with an i.d. of 0.53 mm and a film thickness of 1.0 μm (Supelco, Bellefonte PA). The temperature program was 40 °C (10 min), 6 °C/min to 110 °C, 12 °C/min to 190 °C (8 min), and 70 °C/min to 250 °C (2 min). The injector temperature was set at 250 °C and the FID temperature at 270 °C. Head of column pressure was set to 10 kPa hydrogen (measured as 2.7 mL/min) and kept in the splitless mode for 10 min.

***K*$_{PDMS,air}$ Determination.** $K_{PDMS,air}$ distribution constants were determined with a modification of previously reported methods.[22,23] Liquid PDMS was spiked with solvent stock solutions or neat analytes, and a range of air to PDMS volume ratios was established in gastight vials. The values for $K_{PDMS,air}$ were then deduced from the decrease in air concentration as a function of volume ratio.

Three spiking levels were made: PDMS solution no. 1 contained approximately 9 mg/L per compound of all analytes, solution no. 2 approximately 18 mg/L per compound of BTEX and naphthalene, and solution no. 3 approximately 1 g/L per compound of naphthalene and the alkanes. Solvent contents were not exceeding 1% (in one case 3%). Different volumes of these PDMS solutions were transferred to 20 mL vials to generate three series of increasing volume ratios of air to PDMS. After at least 2 h of equilibration all vials were sampled 1 min for solution no. 1, and 0.5 min for solution nos. 2 and 3, which was sufficiently short to ensure negligible depletion SPME at a headspace sampling rate ($kK_{PDMS,air}V_{fiber}$) not exceeding 2.5 mL/min. The obtained peak areas were proportional to headspace concentrations and were applied for determining $K_{PDMS,air}$ as described by[22]

$$PA = PA_0\left(1 - \frac{VR}{VR + K_{PDMS,air}}\right) \quad (6)$$

where VR is the volume ratio of air to PDMS and PA_0 is the peak area at VR = 0. The two parameters PA_0 and $K_{PDMS,air}$ including their respective confidence intervals were determined by fitting peak areas and volume ratios to eq 6 using GraphPad Prism.[24] The minimum acceptable r^2 for these regressions was set to 0.9. The obtained $K_{PDMS,air}$ values were plotted against their respective octanol air distribution constants (K_{oa}), which were estimated with SPARC.[8,9]

Determining SPME Sampling Kinetics. The SPME sampling kinetics were studied for a number of sample types in order to (1) determine the sampling time needed to ensure equilibrium sampling, (2) select the best mode of sampling (static or shaken), (3) test whether the sample matrix affects the kinetics, and (4) if possible identify the rate-limiting step for the SPME sampling process.

SPME sampling experiments in 10 mL vials were carried out for samples of liquid PDMS, dry wood (aspen), and soil. Liquid PDMS was spiked with a methanol stock solution keeping the methanol concentration in the PDMS below 1%. Two milliliters of liquid PDMS was used as sample volume. An amount of 50 g of dry wood was first spiked by soaking it in an acetone solution and afterward rinsing twice with distilled water. The mass of wood was approximately 0.5 g dw per sample. The contaminated soil was suspended in MilliQ water containing 600 mg of sodium azide/L, and each vial contained approximately 7 g dw.

Series were obtained in both static and shaken sampling modes. The sampling times ranged from 0.25 to 100 min, and each vial was only sampled once. Peak area (PA) as a function of sampling time (t (min)) was fitted, using GraphPad Prism,[24] to a first-order one-compartment model:

$$PA(t) = PA_{eq}(1 - e^{-kt}) \quad (7)$$

where k is a sampling rate constant (min^{-1}) and PA_{eq} is peak area at equilibrium. The sampling time to reach 90% of the equilibrium concentration ($t_{90\%}$) was estimated from

$$t_{90\%} = \frac{\ln 10}{k} \quad (8)$$

Diffusion coefficients of the analytes in air were estimated by SPARC.[8,25]

Determining the Required Sample Mass. The required sample mass to ensure negligible depletion was determined for dry wood and soil. Series were obtained with 0.06−2 g of spiked dry wood and with 0.04−8.9 g dw of soil. Each vial was sampled statically for 30 min and only once.

(22) Ter Laak, T. L.; Mayer, P.; Busser, F. J. M.; Klamer, H. J. C.; Hermens, J. L. M. *Environ. Sci. Technol.* **2005**, *39*, 4220−4225.
(23) Mayer, P.; Vaes, W. H. J.; Hermens, J. L. M. *Anal. Chem.* **2000**, *72*, 459−464.
(24) *GraphPad Prism. Prism 4 for Windows*, version 4.03; GraphPad Software, Inc.: San Diego, CA, 2005.
(25) Hilal, S. H.; Karickhoff, S. W.; Carreira, L. A. *QSAR Comb. Sci.* **2003**, *22*, 565−574.

Peak area (PA) as a function of sample mass (m (g dw)) was, in analogy with eq 7, described by

$$\mathrm{PA}(m) = \mathrm{PA}_{m\infty}\,(1 - \mathrm{e}^{-k_m m}) \qquad (9)$$

where k_m is a mass rate constant (g dw^{-1}) and $\mathrm{PA}_{m\infty}$ is the peak area at infinite sample mass. The two parameters were found by plotting peak area as a function of sample mass using GraphPad Prism.[24] Negligible depletion was achieved when the reduction of peak area due to losses to headspace, inner vial surfaces, and the SPME was less than 5%.[21] The sample mass needed to ascertain this was deduced from eq 9:

$$m_{95\%} = \frac{\ln 20}{k_m} \qquad (10)$$

where $m_{95\%}$ (g dw) is the sample mass required to ensure negligible depletion sampling.

New Calibration Principle. The method was calibrated by equilibrating the SPME fiber above solvent standards with known chemical activities. Preliminary experiments demonstrated methanol to be a suitable solvent because (1) it provides sufficiently high solubility for the target analytes and (2) the uptake of methanol into the PDMS coating of the fiber is limited compared to that of other less polar solvents. The uptake of methanol and other solvents into PDMS was determined gravimetrically by placing a medical grade PDMS tubing (A-M Systems Inc., Carlsborg, WA) into the appropriate solvent. The tubing absorbed only 1.5 wt % methanol, an amount that does not affect the sorptive properties of the PDMS.[26] For comparison, the PDMS tubing absorbed 5.5 wt % of octanol, 136 wt % of toluene, and 129 wt % of pentane.

A six-point calibration series was prepared by diluting appropriate methanol stock solutions to achieve final chemical activities in the range from 10^{-6} to 10^{-1} per analyte. Volumes of 2 mL of standard solutions were transferred to 10 mL vials and sampled statically for 30 min. Activity coefficients were determined with SPARC[8] and then converted from $n_{\mathrm{MeOH}}/n_{\mathrm{analyte}}$ (mol/mol) to $V_{\mathrm{MeOH}}/m_{\mathrm{analyte}}$ (L/kg).

Determining Method Detection Limits and Precision. Method detection limits (MDLs) were determined in order to find the lower applicability range for measurements of chemical activity, fugacity, and freely dissolved concentration. Seven replicates of the two lowest standard solutions were analyzed for MDL determinations.[27]

Relative standard deviations (RSDs) for a number of sample types were determined in order to find the method precision for both kinetic and equilibrium sampling. For this purpose 10 mL vials containing samples of liquid PDMS (2 mL), soil (7 g dw), and NAPL (2 mL) were used. The RSDs were determined from seven replicates and, for liquid PDMS, during two different weeks. Liquid PDMS was spiked with a methanol stock solution keeping the methanol concentration in the PDMS below 1%. Each vial was sampled statically for 30 min and only once. Additionally, two sets of seven vials containing a liquid PDMS solution were sampled statically for 1 min.

(26) Gill, K.; Brown, W. A. *Anal. Chem.* **2002**, *74*, 1031−1037.

(27) U.S. Environmental Protection Agency. Part 136, Appendix B, Revision 1.11, 40 CFR, Definition and procedure for the determination of the method detection limit. http://www.setonresourcecenter.com/CFR/40CFR/P136_008.HTM (accessed May 1, 2006).

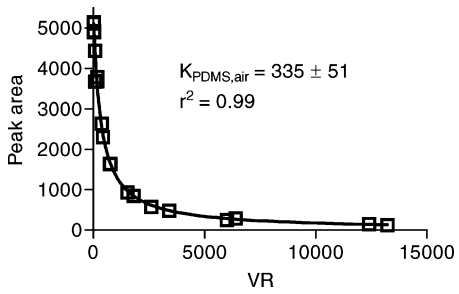

Figure 1. $K_{\mathrm{PDMS,air}}$ ((95% CI) determination data. The peak area is plotted against the volume ratio for benzene including nonlinear regression (eq 6).

Table 1. $K_{\mathrm{PDMS,air}}$ Determined from Three Different PDMS Solutions[a]

	$K_{\mathrm{PDMS,air}}$ (±95% CI)		
compd	PDMS 1	PDMS 2	PDMS 3
benzene	356 (±35)	335 (±51)	ND
toluene	969 (±127)	974 (±71)	
ethylbenzene	2114 (±246)	2307 (±145)	
p-xylene	2348 (±273)	2533 (±143)	
m-xylene	2398 (±254)	2663 (±142)	
o-xylene	2717 (±240)	3245 (±224)	
naphthalene	ND	24 923 (±3857)	16 762 (±2283)
nonane	3792 (±487)	ND	3475 (±293)
decane	7742 (±1455)		7913 (±735)
dodecane	ND		33 508 (±6006)
tetradecane	ND		104 689 (±38 248)
hexadecane	ND		ND

[a] Generally PDMS 2 and 3 gave the best precision, so these values were used for further method analysis. ND: not determined. All values from regressions with $r^2 > 0.9$, r^2_{average} (±95% CI) = 0.99 (±0.01).

RESULTS AND DISCUSSION

$K_{\mathrm{PDMS,air}}$ Determination. PDMS to air distribution constants ($K_{\mathrm{PDMS,air}}$) were determined in order to understand the analyte partitioning inside the vial. The distribution constants were found as described above by fitting SPME measurements of a series of increasing air to PDMS volume ratios to eq 6, which is exemplified for benzene in Figure 1. This was repeated with three different solutions of liquid PDMS; the results are shown in Table 1. $K_{\mathrm{PDMS,air}}$ values obtained from PDMS solution nos. 2 and 3 were more precise than those obtained from PDMS solution no. 1, so they were used for further method analysis. The $K_{\mathrm{PDMS,air}}$ estimate for naphthalene was markedly lower at the spiking level of 1 g/L (PDMS solution no. 3) compared to the spiking level of 18 mg/L (PDMS solution no. 2). The obtained $K_{\mathrm{PDMS,air}}$ value of naphthalene will be applied at analyte levels that are markedly lower than for solution no. 3, so we selected the value obtained from solution no. 2 for further method analysis.

The obtained $K_{\mathrm{PDMS,air}}$ values were plotted against log K_{oa} values in Figure 2, which also includes $K_{\mathrm{PDMS,air}}$ values from previous studies.[28−30] The experimental $K_{\mathrm{PDMS,air}}$ values (log $K_{\mathrm{PDMS,air}} = 0.73$ log $K_{\mathrm{oa}} + 0.63$) agreed well with the reported values that were obtained with PDMS-coated SPME fibers and GC columns (all

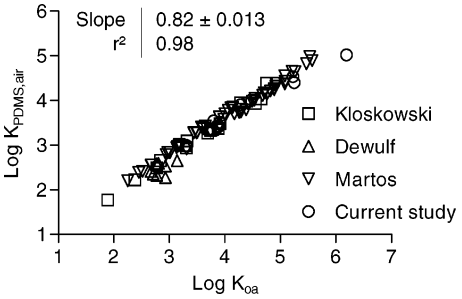

Figure 2. $K_{PDMS,air}$ value comparison with literature values: log $K_{PDMS,air}$ from three different studies (refs 28−30) and the current one versus log K_{oa} (refs 8 and 9).

data combined: log $K_{PDMS,air}$ = 0.82 log K_{oa} + 0.32). The results indicate that $K_{PDMS,air}$ values determined with liquid PDMS can also be applied to describe the partitioning behavior of the SPME fiber coating.

SPME Sampling Kinetics. SPME sampling kinetics were determined for different sample matrices in both static and shaken mode (Table 2). The sampling rates were on average 36% higher in the shaken compared to the static mode. This can be explained by the higher temperature in the shaken mode, which leads to an increase in both diffusion coefficients and headspace concentrations of the analytes. Static sampling was chosen for all further analyses because it is considered more robust with regards to evaporative losses and because it offers more flexibility for sampling at environmentally relevant temperatures. A sampling time of 30 min was, from SPME uptake curves, found to be sufficient to reach equilibrium for all analytes (examples are shown in Figure 3a). The application of sampling rate constants from Table 2 in eq 8 confirms this for all tested analytes except for tetradecane and hexadecane. Consequently, the sampling time was set to 30 min, and tetradecane and hexadecane were omitted from all further analysis.

The applicability of the described method to a broad range of sample types requires that the SPME sampling kinetics are relatively similar for different sample matrices. Fortunately, no significant effect of sample matrix on the sampling rate constants (Table 2) was observed, which is evidenced in Figure 4a. The analyte quantity that eventually partitions into the fiber coating exceeds for some analytes the quantity that is present in the headspace. This implies that a portion of such analytes actually originates from the sample rather than the headspace. Still, this

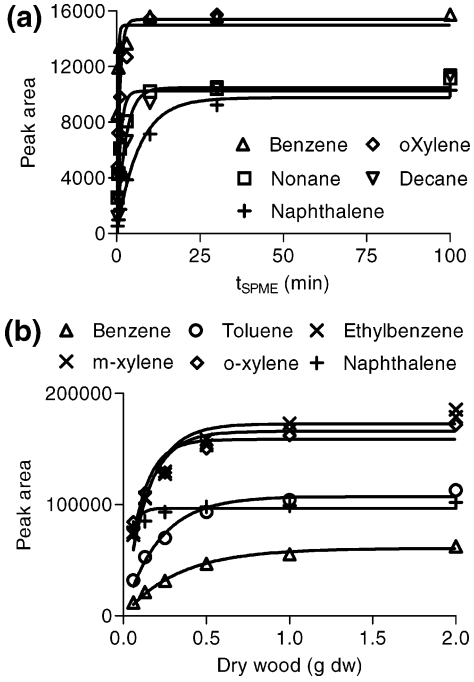

Figure 3. (a) SPME sampling kinetics from liquid PDMS samples under static conditions. The peak area is plotted against the SPME sampling time and fitted to eq 7. (b) Determination of required sample mass. The peak area is plotted against the mass of dry wood and fitted to eq 9.

did not affect the sampling kinetics (Figure 4a) because of the large surface between sample and headspace, which provides efficient mass transfer conditions for supply from sample to headspace. However, there might be sample types that provide insufficient desorption to headspace, and the system should then be carefully designed to ensure that the headspace to fiber coating volume ratio is sufficient to ensure negligible depletion, < 5%, of the headspace during equilibration.

The decrease of sampling rate constants with increasing $K_{PDMS,air}$ values in Figure 4a suggests that diffusion through air is rate limiting for the overall mass transfer into the SPME fiber coating. The rate-limiting step can either be the headspace between fiber and sample or an unstirred boundary layer (UBL) next to the fiber coating. The UBL has been found rate limiting in similar aqueous systems,[29,31] but care should be taken to extrapolate this finding to headspace sampling due to the much higher diffusion coefficients in air compared to those in water.

Table 2. Values of the Rate Constant *k* for Different Matrices, Static and Shaken SPME Samplings

	k_{static} (min^{-1}) (±95% CI)			k_{shaken} (min^{-1}) (±95% CI)	
compd	PDMS	dry wood	soil	PDMS	dry wood
benzene	3.20 (±1.14)	2.84 (±1.71)	4.26 (±2.48)	4.45 (±1.82)	3.36 (±1.26)
toluene	2.53 (±1.04)	2.33 (±1.02)	3.03 (±1.15)	3.23 (±1.31)	2.78 (±1.22)
ethylbenzene	1.50 (±0.62)	1.51 (±0.51)	2.06 (±0.65)	1.98 (±0.62)	1.94 (±1.01)
p-xylene	1.57 (±0.71)	ND	2.25 (±0.61)	2.14 (±0.69)	ND
m-xylene	1.42 (±0.65)	1.44 (±0.47)	1.92 (±0.52)	1.92 (±0.61)	1.87 (±1.02)
o-xylene	1.11 (±0.51)	1.20 (±0.37)	1.59 (±0.43)	1.53 (±0.46)	1.56 (±0.83)
naphthalene	0.15 (±0.05)	0.17 (±0.05)	0.08 (±0.05)	0.28 (±0.09)	0.19 (±0.08)
nonane	0.90 (±0.41)	ND	ND	1.30 (±0.36)	ND
decane	0.39 (±0.16)	ND	ND	0.65 (±0.20)	ND
dodecane	0.063 (±0.023)	ND	ND	0.11 (±0.06)	ND
tetradecane	0.018 (±0.002)	ND	ND	0.016 (±0.007)	ND
hexadecane	ND	ND	ND	ND	ND

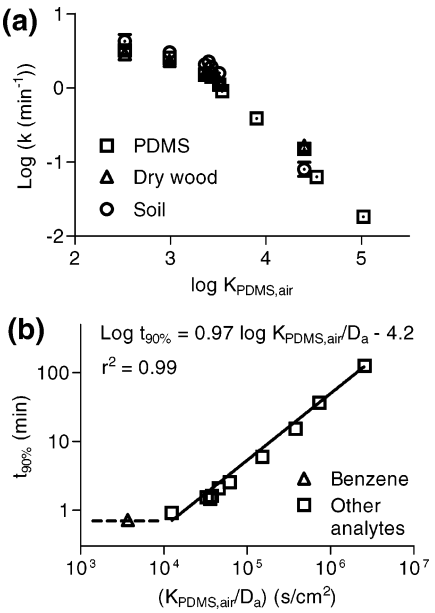

Figure 4. SPME sampling kinetics for 11 different analytes. (a) Sampling rate constants (log *k*) for analytes in liquid PDMS, dry wood, and soil are plotted against log $K_{PDMS,air}$. The bars denote the SE. (b) Proportionality between sampling time to reach 90% of equilibrium, $t_{90\%}$, and $K_{PDMS,air}/D_a$. Analytes included in the regression are toluene, ethylbenzene, *p*-, *m*-, and *o*-xylene, naphthalene, nonane, decane, dodecane, and tetradecane. The dotted line is tentative for analytes with $K_{PDMS,air}/D_a < 10^4$.

Equilibration times (log $t_{90\%}$) were plotted against the ratio between $K_{PDMS,air}$ and the diffusion coefficient in air (log($K_{PDMS,air}/D_a$)) in Figure 4b. Proportionality, indicated by a slope of 1 in a double-logarithmic plot, confirms that the uptake kinetics are directly related to the volume of air to be sampled (proportional to $K_{PDMS,air}$) relative to the diffusion velocity of the analytes through air (D_a (cm^2/s)). For analytes with a log($K_{PDMS,air}/D_a$) above 4, $t_{90\%}$ and $K_{PDMS,air}/D_a$ are indeed proportional (log($t_{90\%}$ (min)) = log(($K_{PDMS,air}/D_a$) (s/cm^2)) − 4.2), and so diffusion through air is the rate-limiting step for mass transfer into the fiber coating. The linear regression can now be used to predict $t_{90\%}$ of other potential analytes in order to determine the applicability domain of the method. One way to accelerate the uptake kinetics and in that way extend the application range to less volatile analytes would be to use an SPME fiber with a thinner polymer coating.[14,32]

For benzene with a log($K_{PDMS,air}/D_a$) below 4 diffusion in the PDMS coating seems to be rate limiting for the overall mass transfer, and the equilibration time for such substances can be expected to be of the order of 1 min.

Determining the Required Sample Mass. The sample mass needs to be sufficiently large to ensure that the sample is not depleted by (1) the fiber or (2) the headspace. The first criterion will always be fulfilled for samples with a certain organic matter content, due to the minute PDMS mass of only 0.6 mg on the SPME fiber. The second criterion will depend on the analyte and will be most restrictive for rather volatile analytes with a low sample to air distribution constant ($K_{sample,air}$) giving the criterion $K_{sample,air} > 20V_{headspace}/V_{sample}$. Benzene is expected to have the lowest $K_{sample,air}$ value (see Table 1), and so it is the most critical analyte with regards to criterion 2. Both criteria are fulfilled when analyte peak area is independent of sample mass (i.e., above $m_{95\%}$). Peak area as a function of sample mass is seen in Figure 3b. Values for $m_{95\%}$ were determined using eq 10 for both dry wood and soil (Table 3), and they were very similar for different sample types when normalized to organic matter content. The $m_{95\%}$ value for benzene was determined to be 1.0 g of organic matter, and $m_{95\%}$ values for all other analytes were, as expected, below this value. Samples with an organic matter content ≥1 g will thus satisfy both criteria for all tested analytes. This guideline can be utilized to simplify sample handling. It will generally be sufficient to mark the level of $1.2m_{95\%}$ on the side of a sample vial and to use this mark for the other samples. Such a procedure not only saves time but also reduces the contact between sample and laboratory, which in turn might improve blanks and will reduce potential occupational exposure to harmful constituents (e.g., pathogenic bacteria or toxic chemicals) of the sample. Simplified sample handling should also improve reproducibility in analyses of field samples.

Table 3. Organic Matter Content Needed to Ensure Negligible Depletion of Soil and Wood Samples (Eq 10) Depends on the Analyte

	$m_{95\%}$ (g dw) (95% CI)	
compd	dry wood	soil org matter
benzene	0.99 (0.82−1.3)	1.03 (0.72−1.8)
toluene	0.64 (0.49−0.93)	0.72 (0.44−1.9)
ethylbenzene	0.43 (0.3−0.76)	0.37 (0.24−0.83)
p-xylene	ND	0.32 (0.21−0.71)
m-xylene	0.39 (0.27−0.74)	0.33 (0.21−0.75)
o-xylene	0.31 (0.2−0.66)	0.29 (0.18−0.67)
naphthalene	0.11 (0.08−0.24)	0.15 (0.06−0.32)

MDL Determination. Method detection limits (MDLs) were determined using the standard deviation of the lowest standards, except for naphthalene which in the absence of sufficient peak areas at the lowest level was based on the second lowest standards. MDLs expressed in chemical activity, freely dissolved concentration, and fugacity are presented in Table 4. MDLs expressed in chemical activity were in a narrow range around 10^{-6} and the six-point calibration yielded linear regressions for all analytes with r^2 values exceeding 0.996. This means that the method can determine chemical activity from 0.1 down to about 6 orders of magnitude below liquid saturation ($a = 1$) and 4 orders of magnitude below baseline toxicity ($a = 0.01-0.1$).[7] MDLs expressed as freely dissolved concentration (C_{free}) decreased with increasing hydrophobicity and ranged from 6 μg/L for benzene to 36 pg/L for dodecane. MDLs expressed as fugacity increased with increasing volatility in the range of 0.3−38 mPa. All MDLs correspond to 0.2−0.7 ng of analyte reaching the detector, and the detection limits can as a result be markedly reduced when using a more sensitive detector.

Method Precision. Method precision was determined as RSDs between SPME samplings of replicate samples. Conse-

(28) Kloskowski, A.; Chrzanowski, W.; Pilarczyk, M.; Namiesnik, J. *J. Chem. Thermodyn.* **2005**, *37*, 21−29.
(29) Dewulf, J.; VanLangenhove, H.; Everaert, M. *J. Chromatogr., A* **1997**, *761*, 205−217.
(30) Martos, P. A.; Saraullo, A.; Pawliszyn, J. *Anal. Chem.* **1997**, *69*, 402−408.
(31) Louch, D.; Motlagh, S.; Pawliszyn, J. *Anal. Chem.* **1992**, *64*, 1187−1199.
(32) Mayer, P.; Tolls, J.; Hermens, L.; Mackay, D. *Environ. Sci. Technol.* **2003**, *37*, 184A−191A.

Table 4. Method Detection Limits from Calibration with Partitioning Standards in Methanol According to Eqs 1−3

	MDL		
compd	activity (10^{-6})	C_{free}	f (mPa)
benzene	2.7	5.9 μg/L	38
toluene	1.7	1.2 μg/L	7.2
ethylbenzene	3.3	0.8 μg/L	5.3
p-xylene	3.3	0.7 μg/L	3.8
m-xylene	2.8	0.7 μg/L	3.5
o-xylene	2.8	0.8 μg/L	3.2
naphthalene	21	2.6 μg/L	1.0
nonane	2.2	0.4 ng/L	1.4
decane	6.8	0.3 ng/L	1.3
dodecane	16	36 pg/L	0.3

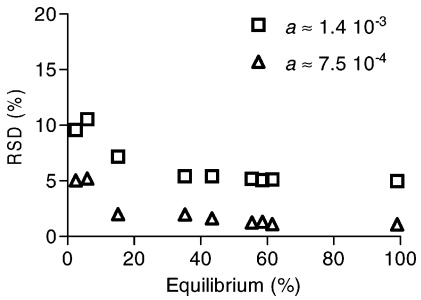

Figure 5. Method precision at an SPME sampling time of 1 min. The relative standard deviation is plotted as a function of percent of equilibrium reached for benzene, toluene, ethylbenzene, *p*-, *m*-, and *o*-xylene, naphthalene, nonane, decane, and dodecane in two PDMS solutions.

quently, these RSDs include error sources related to differences between subsamples, between SPME samplings, and between GC runs. RSDs were generally below 5% for equilibrium sampling of liquid PDMS, and measurement averages of the 2 weeks differed generally less than 9% from each other. This demonstrates the high precision of automated SPME that has been achieved through the control and automation of the sampling process.

The RSDs for NAPL and polluted soil were significantly higher, which might be attributed to sample heterogeneity leading to differences in subsamples. RSDs were below 20% for NAPL and below 25% for soil. In soil it was lowest for *o*-xylene with 16% and highest for benzene with 24%. These RSDs are slightly higher or comparable to other studies of BTEX determinations of spiked soil. Voice and Kolb[33] found RSDs between 5% and 36% with headspace analysis, Ezquerro et al.[34] noted values of around 15% with headspace SPME using a carboxen−PDMS fiber, and Llompart et al.[35] reported values between 4% and 10% with headspace SPME using a PDMS fiber. The higher RSDs in this study might be explained by the higher heterogeneity of the analyzed soil. The soil samples used here were not spiked but had been polluted with a NAPL source in a previous study, and except for adding an aqueous solution of sodium azide and rolling the soil suspension for a few hours, no additional steps to homogenize the soil were taken.

RSDs were also determined in the kinetic regime at a sampling time of only 1 min, where most of the analytes did not reach their equilibrium. RSDs for each analyte were then plotted against its progress of equilibration (in percent of equilibrium) as reported earlier[20] (Figure 5). The RSDs in the kinetic sampling regime was generally below or around 5% and somewhat higher for analytes which reached less than 20% of their equilibrium during sampling. This result is in contrast to reported RSDs for manual matrix−SPME measurements of sediment, which provided good precision only under equilibrium conditions.[20] The improved precision in the kinetic regime can be attributed to the fully automated and highly controlled SPME operation in combination with diffusion through air being the rate-limiting step. This combination has the significant implication that chemical activity also should be measurable in the kinetic sampling regime. This finding can increase the applicability range to less volatile analytes such as PAHs, PCBs, and dioxins, which have equilibrium times that are too long to be suited for automated equilibrium sampling. This deserves further research.

Extension to Other Analytes. The current method is based on 30 min of SPME sampling with a 100 μm PDMS fiber in a 10 mL vial containing at least 1 g of organic matter as the sample matrix. This sets, in terms of distribution constants for analytes, a lower limit determined by negligible sample depletion and a higher limit determined by sampling time. The criterion for negligible sample depletion by headspace requires a sample to air partitioning ($K_{sample,air}$) equal to or higher than the one for benzene. To give an estimate of this lower applicability limit set by negligible sample depletion, we have here used the $K_{PDMS,air}$ value (Table 1) as a rough estimate for $K_{sample,air}$. The higher limit set by the equilibration criterion (100 μm PDMS fiber, 30 min) requires a $K_{PDMS,air}/D_a$ below 585 000 s/cm^2 (Figure 4b).

Based on these two criteria, we expect the method to be applicable to, e.g., alkylated benzenes up to C11, paraffins from C7 to C11, chlorinated solvents like PCE and TCE, and some minor oil constituents like thiophene, pyridine, pyrimidine, pyrrole, benzofuran, indene, indane, and tetraline. The method should further be applicable to a number of chemical warfare agents. These include the nerve agents tabun, sarin, and soman, the blister agents sulfur and nitrogen mustard, and the choking agents diphosgene and chloropicrin. The proposed analytical technique seems very suited for such highly hazardous chemicals due to the reduced contact between sample and laboratory personnel.

Conclusions and Perspectives. This study demonstrates that automated headspace SPME can be applied to measure the chemical activity of semivolatile organic chemicals. We expect that this new analytical methodology will facilitate (1) risk assessment and risk management of organic pollutants, (2) reduction of solvent usage in the analytical laboratory, (3) prediction of equilibrium partitioning phenomena, and (4) the study of diffusion processes that always are directed from high to low chemical activity.

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(33) Voice, T. C.; Kolb, B. *Environ. Sci. Technol.* **1993**, *27*, 709−713.
(34) Ezquerro, O.; Ortiz, G.; Pons, B.; Tena, M. T. *J. Chromatogr., A* **2004**, *1035*, 17−22.
(35) Llompart, M.; Li, K.; Fingas, M. *Talanta* **1999**, *48*, 451−459.

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Paper II

Uptake of organic contaminants from soil into vegetables

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Chapter 9 in Dealing with Contaminated Sites: From Theory towards Practical Application, accepted.

9 UPTAKE OF ORGANIC CONTAMINANTS FROM SOIL INTO VEGETABLES

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ABSTRACT.

Contaminants may enter vegetables by several pathways: by uptake with pore water, by diffusion from soil or air, by deposition of soil or airborne particles, or by direct application. The contaminant-specific and plant-specific properties that determine the importance of the pathways are described in this Chapter. A variety of models have been developed, specific for crop types and with steady state or dynamic solutions. Model simulations can identify sensitive properties and relevant processes. Plant uptake predictions are uncertain, due to the variability of environmental and plant physiological conditions. Persistent, polar and non-volatile contaminants have the highest potential for accumulation from soil, and concentrations in leaves may be several hundred times higher than in soil. However, for most contaminants the accumulation in vegetables is much lower. Lipophilic contaminants are mainly transported to leaves by attached soil particles, or from air. Volatile contaminants have a low potential for accumulation because they quickly escape to air. Experimental data are listed that support model predictions but underline also the high variability of accumulation under field conditions. Uptake of organic contaminants into vegetables leads to human health risks, but it may also be used to delineate subsurface plumes and monitor natural attenuation. Most models mentioned in this Chapter are freely available from the authors.

9.1 Introduction

Residues of contaminants in fruits and vegetables are a major concern of European citizens (EFSA 2006). In fact, uptake via diet is often a major contribution to human exposure to contaminants (Travis and Hattemer-Frey 1991, SCF 2002a). Contaminants released to the soil environment may distribute between soil pore water, soil air and soil. From there, they may be taken up into vegetables and subsequently accumulate in the human food chain (Czub and McLachlan 2004) and affect the health of humans. Consequently, uptake of contaminants into vegetables is an essential part of many exposure models, for example CSOIL (Brand et al. 2007), CLEA (DEFRA 2002) and EUSES (EC 2003).

About 20,000 plant species are used by the human race, and about 600 species are cultivated (Franke 1987). Additionally, about 250,000 wild plants grow on earth (Sitte et al. 1991). Thus, there is a large variability in plant properties. Also the growth conditions vary, depending on soil type, soil properties, climatic conditions and agricultural practice. Similar, the number of organic contaminants is very high. More than 5 million compounds have been synthesized. Around 30,000 compounds are marketed in Europe, and contaminants released to the environment may also be metabolized. Thus, from a researcher's point of view, the number of possible combinations of plant species and contaminants is close to infinite. And even though many studies have been done on plant uptake of organic contaminants, this number is small compared to the total number of plant species and contaminant combinations. Therefore, we have only limited knowledge of the transfer of contaminants into vegetables, even though general patterns are known and process-oriented models have been established.

This Chapter will give an overview of uptake processes of organic contaminants from soil into plants, on prediction methods and on experimental results. Model simulations will be carried out to identify the chemical properties that control the accumulation in food crops. These predictions will be confronted with experimental results, in order to determine the potential of soil contaminants for accumulation in food crops.

9.2 Uptake and transport processes

Contaminants in the environment can enter plants by various ways (Fig. 9.1). Main passive transport and uptake processes from soil are:

- uptake with transpiration water;
- diffusion from soil into roots;
- attachment of soil particles, eventually followed by diffusion into plant tissue;

However, contaminants can also be present in air. Main uptake processes from air are:

- diffusive (gaseous) exchange with air;
- particle deposition from air on plant surfaces followed by diffusion into plant tissue.

Inside the plant, the phloem and xylem flux may distribute the contaminants. The xylem flows from the roots into the stem to the leaves and, to some extent, to fruits. The phloem flows from the leaves to all growing parts of the plant and to fruits and storage organs,

such as tubers. The relative importance of these processes varies with plant type, environmental conditions and properties of contaminants. Active uptake processes, which involve energy or enzymes of the plant, may also play a role, but have not yet been shown to be of relevance for environmental organic contaminants.

<Figure 9.1>

9.3 Interpretation of measured results

Laboratory and field experiments are conducted to determine the uptake of contaminants from soil into plants. Measurements of the concentrations in plants and the concentrations in soil will often (but not always) yield a relationship, such as the "bioconcentration factor" *BCF*, which is defined as

$$BCF = \frac{C_{Plant}}{C_{Soil}} \qquad \text{(Eq. 9.1)}$$

where C_{Plant} is the concentration in plants and C_{Soil} is the concentration in soil.

Care must be taken when this *BCF* definition is applied to cases where a measurable background concentration in plants is present. Because then, for low soil concentration ($C_{Soil} \rightarrow 0$), the concentration ratio *BCF* can be very high ($C_{Plant}/C_{Soil} \rightarrow \infty$). For higher soil concentrations, however, the *BCF* decreases and approaches a constant value. This pattern was occasionally interpreted as a variable *BCF* with soil concentration, i.e. a decreasing *BCF* with increasing soil concentration. A "real-world" example, the ratio between the measured concentration of p,p'-DDT in radishes and in soil, is shown in Fig. 9.2. The concentration ratio is much higher at low soil concentrations, and decreases more than a factor of 5 for higher soil concentrations. A plausible explanation for this pattern is that plants have a limited sorption capacity for organic contaminants, which becomes saturated at higher soil concentrations. However, a more likely interpretation is that the uptake into plants is from two different and independent sources, namely from soil and from air. When soil concentrations are very low there still is a background contamination of the plant tissue originating from air.

Instead of simply calculating the concentration ratio plant to soil, the relationship between concentrations in plant and soil can be quantified by a linear regression between both (if measurements at different concentration levels are available). The slope of the regression between soil concentration as predictor variable and plant concentration as estimated variable can be interpreted as the *BCF* plant to soil (in case of roots as root concentration factor, *RCF*), while the y-axis-intercept can be interpreted as the background concentration due to uptake from air. In mathematical notation the regression equation is as follows:

$$y = a\,x + b \qquad \text{(Eq. 9.2)}$$

where slope *a* and intercept *b* is interpreted as follows:

$$C_{Plant} = BCF \text{ x } C_{Soil} + C_{Background} \quad \text{(Eq. 9.3)}$$

Where $C_{Background}$ is the background concentration due to uptake from air

This method has several advantages:

- all measured values contribute to the calculated *BCF*;
- variations in the measured concentrations are adequately considered;
- the y-axis gives the concentration in plant due to the (constant) concentration in air;
- the square of the correlation coefficient (R^2) describes how much of the variance in the measured concentration in plants is explained by the variance of the concentrations in soil.

In case of an insignificant correlation, the concentration in plant is not dependent on the concentration in soil.

An example is shown in Fig. 9.3. It shows the same situation as Fig. 9.2. But in Fig. 9.2, the "*BCF*" was derived from the concentration ratio (Eq. 9.1), which decrease from 0.94 to 0.17 (mg kg_{dw}^{-1} : mg kg_{dw}^{-1}) with increasing soil concentration. In Fig. 9.3, the slope of the regression curve, i.e. the value 0.17, is the *BCF* derived from all measured values minus the background concentration in air. The *BCF* is statistically highly significant. R^2 is 98%, which means that the increase of the concentrations in plant can be explained almost completely by the increase of the concentration in soil.

<Figure 9.2> <Figure 9.3>

9.4 Prediction methods for uptake of contaminants into vegetables

This section describes prediction methods for the uptake of contaminants into vegetables.

9.4.1 Empirical methods

A common way to predict complex processes is to use empirical models. Regressions were established for the prediction of the uptake of organic contaminants from soil into plants.

9.4.1.1 The regression of Travis and Arms

A frequently applied regression for the uptake of organic contaminants from soil into above-ground plants stems from Travis and Arms (1988):

$$\log B_v = 1.588 - 0.578 \times \log K_{OW} \quad \text{(Eq.4)}$$

where B_v is the bioconcentration factor vegetation to soil (kg kg_{dw}^{-1}) and K_{OW} is the partition coefficient between n-octanol and water (L L^{-1}). The curve was fitted with 29 data in the range $1.15 \leq \log K_{OW} \leq 9.35$. A limitation of the regression is that only uptake from soil is considered, and the impact of air remains unknown.

9.4.1.2 Equilibrium partitioning to soil and root

The concentration ratio between root and aqueous solution in phase equilibrium was named *root concentration factor RCF* (Shone et al. 1974):

$$RCF = \frac{Concentration\ in\ root\ (\text{mg g}^{-1})}{Concentration\ in\ solution\ (\text{mg mL}^{-1})} \qquad \text{(Eq.5)}$$

The most widely applied regression for the *RCF* is from Briggs et al. (1982). It has been fitted to data derived from experiments with macerated barley roots and mainly *phenylureas*. For neutral organic chemicals, the relation between lipophilicity (expressed as log K_{OW}) and sorption to roots was:

$$\log (RCF - 0.82) = 0.77 \log K_{OW} - 1.52 \qquad (n = 7, r = 0.981) \qquad \text{(Eq.6)}$$

The dependency on the log K_{OW} is explained by lipophilic sorption of the contaminants to plant lipids. The value of 0.82 was interpreted as water content of the roots. A similar result was obtained for cut pieces of bean roots and stems for *N-methyl-arylcarbamates* (Trapp and Pussemier 1991):

$$\log (RCF - 0.85) = 0.557 \log K_{OW} - 1.34 \qquad (n=12, r = 0.96) \qquad \text{(Eq.7)}$$

This equation gives lower root concentration factors for lipophilic contaminants (Fig. 9.4). Both *RCF*-regressions describe partitioning to water. But roots typically grow in soil. The sorption of organic contaminants to soil is related to the organic carbon content, *OC*. Many regressions for the sorption to soil organic carbon, K_{OC} (L kg^{-1}), were established, for example (EC 2003)

$$\log K_{OC} = 0.81 \log K_{OW} + 0.1 \qquad \text{(Eq.8)}$$

For the concentration ratio between soil pore water and bulk soil, K_{WS} (kg L^{-1}) follows

$$K_{WS} = \frac{C_W}{C_{Soil}} = \frac{\rho_{wet}}{OC \times K_{OC} \times \rho_{dry} +} W \qquad \text{(Eq.9)}$$

where OC is the fraction of organic carbon in soil (kg kg^{-1}) and W is the soil pore water content (L kg^{-1}). Multiplication of RCF with K_{WS} gives the equilibrium concentration ratio roots to soil.

Both RCF-regressions (Eqs. 9.6 and 9.7), the experimental data of Briggs et al. (1982) and the concentration ratio between bulk soil and soil pore water, K_{SW} (=1/K_{WS}), for a typical soil (OC = 0.025 kg/kg and W = 0.2 L/kg) are plotted in Fig. 9.4. For low K_{OW} values RCF is higher than K_{SW}, due to the higher water content of roots. For higher K_{OW} values Briggs' RCF regression and the K_{SW} equation yield very similar results. This suggests that the sorption capacity of roots equals that of soil. This makes sense, because the content of organic carbon in soil (in this case 2.5%) is similar to the lipid content of roots (about 2 to 3%, including waxes and lignin), and the slope of the log K_{OW} in the regressions is similar (0.81 for K_{OC} in Eq. 9.8 and 0.77 for RCF in Eq. 9.6).

<Figure 9.4>

9.4.1.3 Sorption to stems and leaves

Briggs et al. (1983) also measured the sorption to macerated barley stems, $SXCF$, and again found a relation with the log K_{OW} of the contaminants, as follows:

$$\log (SXCF - 0.82) = 0.95 \log K_{OW} - 2.05 \qquad (n = 8, r = 0.98) \qquad \text{(Eq.10)}$$

Trapp et al. (1994) interpreted the data as equilibrium partition coefficients between plant tissue and water, K_{PW}, and introduced the general equation:

$$K_{PW} = W + L\ a\ K_{OW}^{\ b} \qquad \text{(Eq.11)}$$

where W and L are water and lipid content of the plant, 'b' is a correction factor for differences between solubility in octanol and sorption to plant lipids (in the regressions of Briggs et al. 'b' was 0.77 for roots and 0.95 for leaves), and 'a' is a factor correcting density differences between water and n-octanol ($1/\rho$ of octanol = 1.22 L kg^{-1}). When parameterized accordingly this equilibrium approach gives the same results for roots as the Briggs RCF-regression. Stems and leaves are in contact with air. The sorption equilibrium of contaminants between leaves and air can be described as follows:

$$K_{LA} = C_L / C_A = K_{LW} / K_{AW} \qquad \text{(Eq.12)}$$

where K_{LA} is the partition coefficient between leaves and air (L kg^{-1}) and K_{AW} (L L^{-1}) is the partition coefficient between air and water (also known as the dimensionless Henry's Law constant). Instead of dividing by K_{AW}, K_{LA} was often directly fitted to K_{OA}, i.e. the partition coefficient between octanol and air (e.g., Kömp and McLachlan 1997).

9.4.1.4 Translocation from roots into stem and leaves

Translocation of contaminants from roots into stems in the xylem is often described by the transpiration stream concentration factor *TSCF* (Shone et al. 1974):

$$TSCF = \frac{\textit{Concentration in xylem sap} \text{ (kg m}^{-3}\text{)}}{\textit{Concentration in solution} \text{ (kg m}^{-3}\text{)}} \qquad \text{(Eq.13)}$$

Briggs et al. (1982) fitted a Gaussian optimum curve to their data:

$$TSCF = 0.784 \exp[-(\log K_{OW}-1.78)^2/2.44] \qquad \text{(Eq.14)}$$

Later experiments by other research groups yielded similar results (Sicbaldi et al. 1997, Hsu et al. 1990), Burken and Schnoor 1998), e.g.:

$$TSCF = 0.756 \exp [-(\log K_{OW} - 2.50)^2 / 2.58] \qquad \text{(Eq.15)}$$

9.4.2 Mechanistic models

Donald Mackay was the driving force behind the development of plant uptake models. The first author of this Chapter met him at the University of Bayreuth in 1986, where Mackay encouraged his audience to develop models for the plant uptake of organic contaminants. Indeed, this resulted in a plant uptake model for organic contaminants (Trapp et al. 1990). Mackay and his team also developed some of the early models for this purpose, formulated in the fugacity approach (Paterson et al. 1994). The models were later simplified by Hung and Mackay (1997) to three mass balance equations and solved numerically. At about the same time, the numerical model PlantX was developed (Trapp et al. 1994). Later, crop-specific models were derived, i.e. specific models for roots (Trapp 2002), potatoes (Trapp et al. 2007a), leaves (Trapp and Matthies 1995) and fruits (Trapp 2007). These models are based on the same physico-chemical principles and describe the same basic processes, such as advective uptake into plants, diffusive uptake, chemical equilibrium, transport in xylem and phloem, dilution by growth, and particle deposition from soil and air. The actually occurring processes and their parameterization depend on the type of crop (Fig. 9.5). For electrolytes, such as acids and bases, very different approaches were developed. Examples of such models are the phloem transport model by Kleier (1988), the model relating to pesticide spray application by Satchivi (2000 ab) and the "cell model" by Trapp (2000, 2004).

<Figure 9.5>

9.4.3 A "simple standard model"

A plant uptake model should consider both uptake from soil and air into plants. A relatively simple model includes the compartments soil, roots and leaves (or fruits) and the processes:

- continuous and pulse input to all compartments (soil, roots and leaves);
- degradation, leaching, run-off and plant uptake, resulting in loss from soil;
- uptake into roots with the transpiration water;
- growth dilution, degradation and metabolism in roots;
- translocation from roots to leaves (or fruits) with the transpiration water;
- loss from leaves to air;
- deposition from air to leaves;
- transport to leaves with attached soil;
- growth dilution, degradation and metabolism in leaves.

9.4.3.1 Mass balance

The mass balance for soil can be described as follows:
Change of contaminant mass in soil is deposition from air minus leaching minus run-off minus uptake into roots.

The mass balance for roots (thick roots, such as carrots) can be described as follows:
Change of contaminant mass in roots is influx with water minus outflux with water. Diffusive uptake is not considered, since it usually only makes a small change in the concentration in roots. Also, it is assumed that the root (e.g., a carrot) is peeled before consumption. Hydrophobic contaminants only reach the peel of the root by diffusion. This results in the following equation:

$$\frac{dm_R}{dt} = Q \times C_W - Q \times C_{Xy} \qquad \text{(Eq.16)}$$

where m_R is the mass of contaminant in roots (mg), Q is the transpiration stream (L d^{-1}), C_W is the concentration in soil pore water (mg L^{-1}) and C_{Xy} is the concentration in the xylem at the outflow of the root (mg L^{-1}). If the xylem sap is in equilibrium with the root, the concentration $C_{Xy} = C_R/K_{RW}$. The concentration in soil pore water, C_W, is K_{WS} x C_S. Substituting these expressions in Eq.16 gives the following equation:

$$\frac{d(C_R \times M)}{dt} = \frac{dm_R}{dt} = Q \times K_{WS} \times C_S - \frac{Q}{K_{RW}} \times C_R \qquad \text{(Eq.17)}$$

If plant mass growth is exponential, and the ratio Q/M (transpiration stream to plant mass) is constant, the growth by exponential dilution can be considered by a first-order growth rate k (d^{-1}). If degradation or metabolism (first order) occurs, the rate k is the sum

of the loss processes and the growth dilution. The concentration in roots results by dividing with the mass of the root *M*:

$$\frac{dC_R}{dt} = \frac{Q}{M} \times K_{WS} \times C_S - \frac{Q}{M \times K_{RW}} \times C_R - k \times C_R \qquad \text{(Eq.18)}$$

The mass balance for leaves (or, better: for above-ground plant parts) is:
Change of contaminant mass in leaves is influx with transpiration water plus gaseous and particulate deposition from air minus diffusion to air. This results in the following equation:

$$\frac{dm_L}{dt} = \frac{Q}{K_{RW}} C_R + A \times g \times (1 - f_P) \times C_A + \frac{A \times v_{dep}}{2} \times f_P \times C_A - \frac{A \times g \times \rho}{K_{LA}} \times C_L \qquad \text{(Eq.19)}$$

where A is leaf area (m^2), g is the conductance of leaves (m s^{-1}), ρ is leaf density (kg m^{-3}), and K_{LA} is the partition coefficient between leaves and air (L L^{-1}). C_A is the total concentration in air (mg m^{-3}) and f_P is the fraction of the total concentration in air that is adsorbed on particles. Uptake from air can either be by diffusive exchange in the gas phase with conductance g (m d^{-1}), or by deposition of particles on the surface of the leaves (A/2) with velocity v_{dep} (m d^{-1}). For the concentration in leaves follows:

$$\frac{dC_L}{dt} = \frac{Q}{M_L \times K_{RW}} \times C_R + \frac{A \times g}{M_L} \times (1 - f_P) \times C_A + \frac{A \times v_{dep}}{2 \times M_L} \times f_P \times C_A - \frac{A \times g \times \rho}{K_{LA} \times M_L} \times C_L - k \times C_L \qquad \text{(Eq.20)}$$

where k (d^{-1}) again includes growth dilution and biotic and abiotic (photolysis) degradation processes. The first term of the equation quantifies translocation from roots to leaves and replaces the *TSCF* in earlier model versions (Trapp and Matthies 1995). The advantages of this new formulation are as follows:

- There is a relation between concentrations in roots and in leaves. This allows, for example, to calculate the fate of metabolites formed in roots.
- The *TSCF* is related to plant physiological parameters, such as transpiration Q, growth rate k and partitioning K_{RW}.

The calculated concentration ratio between the xylem and the external solution is close to the calculated concentration resulting from the empirical *TSCF*-regressions (Trapp 2007), except for polar contaminants. Trapp (2007) speculates, based on this equation, that plants growing in soil outdoors would have a different *TSCF*-curve than plants grown in hydroponic solutions. This is due to the formation of root hairs in soil, which leads to

better diffusive uptake of polar contaminants and subsequently higher *TSCF*-values (The *TSCF* remains high (i.e. near 1) for contaminants with a log $K_{OW} < 1$).

An additional process not considered in Eq. 9.20 is the contamination of leaves with attached soil, R (kg soil kg plant^{-1} (wet weight)). A convenient way of calculation is to add the concentration due to attachment of particles from soil with subsequent deposition on leaves to the calculated C_L, as follows:

$$C_{L,Final} = C_{L,Calc} + R \times C_{Soil} \qquad \text{(Eq. 21)}$$

Default values for R range from 0.001 kg kg^{-1} to 0.01 kg kg^{-1} (see Section 9.5.2.3).

9.4.3.2 Steady state solution

The steady state ($t \rightarrow \infty$) concentration in roots, C_R, with constant concentration in soil, C_{Soil}, is as follows:

$$C_R = \frac{Q}{\frac{Q}{K_{RW}} + kM} \times K_{WS} \times C_{Soil} \qquad \text{(Eq.22)}$$

For leaves, the steady state concentration is:

$$C_L = \frac{I}{a} \qquad \text{(Eq.23)}$$

where I is the sum of all input terms (mg kg^{-1} d^{-1}):

$$I = \frac{Q}{M_L \times K_{RW}} \times C_R + \frac{A \times g}{M_L} \times (1 - f_P) \times C_A + \frac{A \times v_{dep}}{2M_L} \times f_P \times C_A \qquad \text{(Eq.24)}$$

and a is the sum of all loss processes (d^{-1}):

$$a = \frac{A \times g \times \rho}{K_{LA} \times M_L} + k \qquad \text{(Eq.25)}$$

9.4.4 General solution scheme for pulse and constant inputs

Frequently, a pulse input to the system occurs. Examples are inputs from accidents, pesticide spray application and application of manure or compost. For dynamic simulations, the differential equation scheme can be solved numerically or analytically. Analytical solutions are always possible when the differential equations are linear (1st order), as shown in Trapp and Matthies (1998).

9.4.4.1 Matrix formulation

The differential equations for the contaminant concentration in soil, root and leaves can be treated as a diagonal matrix, so that:

$$\frac{dC_1}{dt} = -k_1 C_1 + I_1 / M_1 \qquad \text{(Eq.26)}$$

$$\frac{dC_2}{dt} = +k_{12} C_1 - k_2 C_2 + I_2 / M_2 \qquad \text{(Eq.27)}$$

$$\frac{dC_3}{dt} = +k_{23} C_2 - k_3 C_3 + I_3 / M_3 \qquad \text{(Eq.28)}$$

where indices 1 to 3 refer to soil, roots and leaves, respectively; C (mg kg^{-1}) is concentration; k_1, k_2 and k_3 are the sum of all first-order loss processes in compartment 1, 2 and 3, and k_{12} and k_{23} are the transfer rates from compartment 1 to 2 and 2 to 3, respectively. I (mg d^{-1}) describes the constant input to the compartments, e.g., from air, and M (kg) is the mass of compartment (kg). The matrix elements can be derived from the differential equations above.

9.4.4.2 General solution for the steady state

Linear differential equations approach steady state for $t \rightarrow \infty$, i.e. the change of concentration with time is zero, $dC/dt = 0$. The steady-state solutions for matrix equations 1 (soil), 2 (roots) and 3 (leaves) are as follows:

$$C_1(t=\infty) = \frac{I_1}{k_1 M_1} \qquad \text{(Eq.29)}$$

$$C_2(t=\infty) = \frac{I_2}{k_2 M_2} + \frac{k_{12}}{k_2} C_1 \qquad \text{(Eq.30)}$$

$$C_3(t=\infty) = \frac{I_3}{k_3 M_3} + \frac{k_{23}}{k_3} C_2 \qquad \text{(Eq.31)}$$

The steady-state solution follows the general scheme:

$$C_n(t=\infty) = \frac{I_n}{k_n M_n} + \frac{k_{n-1,n}}{k_n} \times C_{n-1}(t=\infty) \quad \text{(Eq.32)}$$

9.4.4.3 General solution for pulse input

The analytical solutions for the matrix equations 1 (soil), 2 (roots) and 3 (leaves) and for initial concentrations $C(0) \neq 0$ are

$$C_1(t) = C_1(0) \times e^{-k_1 t} \quad \text{(Eq.33)}$$

$$C_2(t) = k_{12} C_1(0) \times \left(\frac{e^{-k_1 t}}{(k_2 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)} \right) + C_2(0) \times e^{-k_2 t} \quad \text{(Eq.34)}$$

$$\begin{aligned} C_3(t) = {} & k_{12} k_{23} C_1(0) \left\{ \frac{e^{-k_1 t}}{(k_1 - k_2)(k_1 - k_3)} + \frac{e^{-k_2 t}}{(k_2 - k_1)(k_2 - k_3)} + \frac{e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)} \right\} \\ & + k_{23} C_2(0) \times \left(\frac{e^{-k_2 t}}{(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_2 - k_3)} \right) \\ & + C_3(0) \times e^{-k_3 t} \end{aligned} \quad \text{(Eq.35)}$$

The general solution scheme for pulse input to soil only, i.e. $C_1(0) \neq 0$ and $C_n(0) = 0$ with $n = 2,\ldots,n$ is as follows:

$$C_n(t) = \prod_{i=1}^{n-1} k_{i,i+1} C_1(0) \times \left\{ \sum_{j=1}^{n} \frac{e^{-k_j t}}{\prod_{k=1,k\neq j}^{n} (k_k - k_j)} \right\} \quad \text{(Eq.36)}$$

and for pulse input into all compartments, i.e. $C_n(0) \neq 0$ with $n = 1,\ldots,n$:

$$C_n(t) = \sum_{a=1}^{n-1} \left(C_a(0) \times \prod_{i=a}^{n-1} k_{i,i+1} \times \sum_{j=a}^{n} \frac{e^{-k_j t}}{\prod_{k=a,k\neq j} (k_k - k_j)} \right) + C_n(0) \times e^{-k_n t} \quad \text{(Eq.37)}$$

This solution scheme can offer solutions for several soil-plant-air system variations. For example, in analogy with this example, matrix element 1 could be soil, element 2 roots, and element 3 leaves. Or, alternatively, element 1 could be parent contaminant in soil,

element 2 metabolite in soil, element 3 metabolite in root, element 4 metabolite in leaves, and element 5 metabolite of metabolite in leaves.

9.4.4.4 Solution by superposition

The principle of superposition is that concentrations are added. It may happen that a contaminant is present in the soil-plant-air system at the background concentration, and the steady state solution applies. Imagine a situation in which one, two or more subsequent pulse inputs occur. In that case, the resulting concentration can be calculated by adding the concentrations resulting from steady state and one, two or more pulse inputs. To this purpose, the simulation is split up into several periods. The concentration vector $\boldsymbol{C}(t)$ at the end of a specific period serves as initial concentration vector $\boldsymbol{C}(0)$ for the next period. This refers to concentrations in any compartment (i.e. soil, roots and leaves).

9.4.4.5 Input data

Input data are the same for the steady state and the dynamic model version and were mostly taken from the carrot model (Trapp 2002) and the leafy vegetables model (Trapp and Matthies 1995) (Tab. 9.1).

< Table 9.1>

9.5 Sensitive parameters that determine uptake of contaminants into vegetables

Which contaminants are taken up into vegetables and the variation in the affinity for uptake, and hence accumulation, depends on the combination of contaminant-specific, environmental and plant-specific parameters. The importance of some of these parameters is investigated in this section by using the models described before.

9.5.1 Impact of contaminant-specific parameters

9.5.1.1 Impact of log K_{OW} on accumulation in roots and potatoes

Fig. 9.6 shows the calculated concentration in roots (steady-state solution provided above) and potatoes (Trapp et al. 2007a) for a constant soil concentration of 1 mg kg^{-1} (wet weight). The most relevant contaminant-specific parameter in the root and potato model is the log K_{OW}, which is varied from 0 (polar contaminants) to 8 (super-lipophilic contaminants). The concentrations are compared to the concentrations resulting from the equilibrium partition coefficient approach (*RCF*, Eqs. 9.6 and 9.11) and to the Travis and Arms-regression ("T&A"). For very polar contaminants, the concentration in roots is predicted to be higher than the concentration in soil. This is because very polar contaminants are mainly found in aqueous phases, and roots contain usually more water (up to 95%) than soil (about 30%). For more lipophilic contaminants, the *RCF* (here related to soil, i.e. RCF/K_{SW}) approaches a value of 1, due to the similar sorption capacity of roots and soil.

For polar contaminants, the regression of T&A and the two dynamic models give results close to the equilibrium (*RCF*). With increasing lipophilicity, the predicted concentration decreases and the deviation from equilibrium increases. The root and the potato model include growth dilution, and the effect of this growth dilution increases with increasing log K_{OW}. The *BCF* predicted by the root model at log K_{OW} 7 is more than a factor 1000 below chemical equilibrium. Chemical equilibrium may be found in the peel or close to the peel. But the inner of roots and potatoes will have much lower concentrations (Trapp 2002, 2007).

Interestingly, the T&A regression was originally established for above-ground crops. But Fig. 9.6 shows that the predicted bioconcentration in plants is very close to that predicted by the root model (advective uptake) and the potato model (diffusive uptake).

In current chemical risk assessment (EC 2003) and in some risk assessment tools for contaminated soils, predictions of concentrations in root vegetables are based on the equilibrium approach. This will lead to an overestimation of the concentration in roots and, hence, of human exposure (Legind and Trapp 2008). Recent studies showed that uptake into root vegetables (radishes) may also be from air (Mikes et al. 2008). This is yet not considered in any available root uptake model.

<Figure 9.6>

9.5.1.2 Impact of log K_{OW} and K_{AW} on accumulation of contaminants in leaves

Simulations were done with the leaf model described in the previous section. A value of 0.1% attached soil was chosen as default. This gives a minimum *BCF* of 0.01 kg kg^{-1} (wet weight) for all contaminants.

Fig. 9.7a shows the calculated concentration in leaves for a concentration in soil of 1 mg kg^{-1}, and in air of 0 mg m^{-3}. Log K_{OW} (x-axis) is varied for volatile (K_{AW}: 0.2 L L^{-1}), semi-volatile (K_{AW}: 0.001 L L^{-1}) and non-volatile contaminants (K_{AW}: is 10^{-6} L L^{-1}). For all volatile contaminants, the concentration in leaves is low (0.001 mg kg^{-1}) over the whole range of log K_{OW}. This means that their accumulation due to translocation to leaves is low; the plotted concentration is due to attachment of soil particles only (default 0.1%).

The semi-volatile contaminants show some accumulation, up to a *BCF* of 0.01 kg kg^{-1} for the most polar contaminants. With increasing lipophilicity of the contaminants the accumulation decreases. The largest accumulation is seen for non-volatile contaminants, in particular for the polar ones (low log K_{OW}). These contaminants are readily soluble in soil pore water, taken up by plants with the soil pore water and translocated to the leaves. From the leaves, the water evaporates, but the contaminants remain. For lower K_{AW}-values, the accumulation is even higher and may reach values above 100 kg kg^{-1}.

9.5.1.3 Uptake from air versus uptake from soil

A frequent experimental result is that contaminants are found in moderate or even high concentrations in plants even though concentrations in soil are low (Mikes et al. 2008, Delschen et al. 1996, 1999). This is typically the case when uptake is mainly from air (compare section 9.3). The simulations displayed in Fig. 9.7b were done for identical conditions as for Fig. 9.7a, except that the concentration in air was set to phase equilibrium to soil (i.e. $C_{Air} = K_{AW} \times K_{WS} \times C_{Soil}$, with concentration in soil equal to 1 mg kg^{-1}). The development of the concentration in plants is completely different as in Fig.

9.7a (note that the figure was rotated and the z-axis crosses now at C_{Leaf} equal to 1 mg kg^{-1}). The concentration in leaves is higher than in Fig. 9.7a where there was no contaminant present in the air, in particular for volatile contaminants (K_{AW}: 0.2 L L^{-1}). Also, the concentration was less variable, with most values between 1 and 10 mg kg^{-1}. This is because for most contaminants the system is close to equilibrium in regard to soil with air and air with leaves. An exception are the non-volatile contaminants, their predicted concentration does not change substantially. For the polar and non-volatile contaminants, the calculated concentration in leaves is particularly high.

The pattern of uptake of contaminants from soil into fruits is very similar (not shown), although the level of concentrations is typically about a factor of 10 lower (Trapp 2007). This means that also in fruits polar and non-volatile contaminants have the highest potential for accumulation from soil.

What do these results tell us? A major conclusion is that the partition coefficient between air and water (also known as the dimensionless Henry's Law constant) is a very important parameter for the calculation of the accumulation in leaves, because K_{OA} (the ratio of K_{OW} and K_{AW}) determines partitioning into leaves. Leaves have a very high exchange with air (that is their role in plant physiology), and any *volatile* contaminant (with high K_{AW}) will escape from leaves into air and will not accumulate. A second conclusion is that the *polar* contaminants are preferably translocated from soil and accumulate in leaves. Lipophilic contaminants will be retained in soil, roots and the lower stem and will not reach the leaves. Thus, *polar and non-volatile* contaminants, i.e. contaminants with low log K_{OW} and low K_{AW}, have the highest accumulation potential from soil into leaves. This is in conflict with the usual concept of bioaccumulation, where high bioaccumulation is assumed to occur for highly lipophilic contaminants (EC 2003, Mackay and Fraser 2000). Furthermore, under background conditions, all except the polar and non-volatile contaminants will preferably be taken up from air and the concentration in soil does not have much impact on the concentration in vegetables, unless it is far above chemical equilibrium.

<Figure 9.7 ab>

9.5.1.4 Impact of degradation

The simulations above were done for the steady-state situation, with constant concentration in soil. However, the contaminants can be rapidly dissipated from soil by several removal processes, such as degradation, leaching, plant uptake and volatilization.

An example is shown in Fig. 9.8. Ortho-xylene is a moderately lipophilic contaminant which is rapidly degraded in soil. Søvik et al. (2002) give a degradation rate constant of 0.11 d^{-1}, i.e. a half-life of about 1 week. After a few weeks, the concentration in soil has approached zero. The simulated concentration in roots closely follows this pattern: About four days after the pulse input, the calculated concentration in root is already close to equilibrium to soil, and parallel with the concentration in soil, concentration in roots falls to very low values within a few weeks, in any case before the harvest. A steady state simulation with constant soil concentration would overpredict concentrations in the harvest product by several orders of magnitude.

The degradation rate (or, more generally, the loss rate from soil) is a key variable. To some extent, elimination in soil is related to physico-chemical properties. Volatilization

to air depends on K_{AW} (or K_{OA}). Leaching and plant uptake are more important for soluble contaminants with low K_{OW}. Also bacterial degradation depends on the bioavailable fraction of the contaminants (Alexander 2000, Reichenberg and Mayer 2006), which is typically higher at low sorption. Therefore, polar and volatile contaminants (low K_{OW}, high K_{AW}) show shorter residence time in soil. The actual loss rate, however, cannot be predicted from physico-chemical properties alone but is an input data.

<Figure 9.8>

9.5.1.5 Impact of pKa and pH on uptake of ionisable contaminants

Ionisable contaminants, i.e. acids, bases, zwitterions or amphoters, may be present in soils as neutral or ionic molecules. The neutral and the ionic molecules have completely different physico-chemical properties. The ion is usually much more polar and water soluble and has a very low vapor pressure compared to the neutral species. Thus, the ion is a polar and non-volatile contaminant, and as such has a high potential for accumulation in vegetables. On the other hand, cations have a strong tendency to adsorb to soil organic matter and/or clay (Franco and Trapp 2008). Besides, charged contaminants cross biomembranes slowly (Trapp 2004), which limits their uptake.

A process that may lead to high accumulation of ionisable contaminants is the "ion trap". This principle is described in Fig. 9.9, for an acid. If the pH outside in the soil pore water is low, a weak acid is at least partly neutral. The uptake into the cell is rapid (provided that the contaminant is not too hydrophilic). The pH in cell sap (cytosol) is about 7 to 7.5, in xylem about 5.5, and in phloem about 8. In particular in cytosol and phloem, weak acids dissociate and form the anion. The membrane permeability of the anion is very low, and reverse diffusion is slow. As a consequence, the anion is trapped inside the cytosol or the phloem. The same process occurs for a base, when the cell sap is acid, compared to the outside soil pore water, for example in the vacuoles of plant cells and in the xylem (pH is 5.5).

Summarizing, the ion trap requires a gradient in pH between outside and inside of the plant, so that the outside pH is lower (for bases: higher) than the inside pH. Second, a pKa at or somewhat below (for bases: above) the outside pH is necessary, so that a relevant fraction of contaminants is neutral outside, but most of it is ionic inside. This means that weak acids may accumulate in the alkaline phloem (and are in consequence transported to fruits), while weak bases tend to accumulate in the acidic xylem (and are translocated to leaves).

<Figure 9.9>

9.5.2 Impact of plant-specific parameters

As pointed out in the introduction, there is a very high number of plant-contaminant combinations, and the simulations done for a generic plant are not necessarily valid for the whole plant empire and all contaminants. In this section, some properties of plants are discussed, which vary and may lead to different accumulation of contaminants.

9.5.2.1 Crop types and uptake pathways

673 The crop type has a very large impact on uptake processes. Clearly, roots and potatoes are
674 in close contact to soil, while apples are not. As a consequence, accumulation of
675 contaminants in apples, like in other tree fruits, is much lower, but fruits have a higher
676 uptake from air. It is obvious that crop-specific models will give more realistic
677 predictions of concentrations.
678
679 *9.5.2.2 Physiological parameters*
680 The importance of physiological plant-specific parameters, such as transpiration rate, leaf
681 area, conductance, water and lipid contents and growth rate, depends largely on the type
682 of contaminant. For water soluble contaminants, which are rapidly translocated from soil
683 to leaves, the transpiration rate is among the most important parameters, since the
684 accumulation in leaves is almost directly dependent on the transpiration.
685 This is illustrated by the calculated carbofuran concentration as an example, in Fig. 9.10.
686 The log K_{OW} of this contaminant is 1.6 to 2.07 (Trapp and Pussemier 1991). Two
687 calculations were done, one with the standard transpiration of 1 L d^{-1}, the other with an
688 increased transpiration of 5 L d^{-1}. The simulated concentration in roots remains
689 practically constant with increasing transpiration, only the time period until steady state is
690 reached in a shorter time period. However, the breakthrough of contaminant into leaves is
691 faster and the calculated concentration is a factor of 5 higher for a factor of 5 increase in
692 transpiration rate. The translocation of carbofuran in bean plants was determined
693 experimentally, and the concentration pattern as well as the close relation between
694 transpiration and concentration in leaves was confirmed (Trapp and Pussemier 1991).
695 In turn, the amount of transpired water depends on temperature, humidity, leaf area and
696 stomata permeability. However, the transpiration depends also on the availability of
697 water. Students in a field course at the Technical University of Denmark noticed that
698 concentrations of chlorinated solvents (PCE and TCE) measured in wood cores taken
699 from trees growing at the Glostrup site (Denmark) were much lower in the very dry June
700 2008 than in the very wet June 2007. A plausible explanation is a reduced transpiration
701 due to water stress in 2008 (Mette Broholm, personal communication).
702
703 **<Figure 9.10>**
704
705 *9.5.2.3 Plant morphology and collection efficiency for particles*
706 The transport with particles from soil to plant surfaces is a very important transport
707 mechanism for lipophilic contaminants. This transfer pathway was well studied using
708 insoluble radionuclides, and large variations were found in soil attachment among plant
709 species. Soil particles may reach leaf surfaces mainly by three mechanisms, namely rain
710 splash, wind erosion and erosion due to agricultural practice (ploughing, harvesting et
711 cetera). Tab. 9.2 shows measured values for the transfer of radionuclides (Li et al. 1994).
712 The transfer range varies from 1.1 mg soil g_{plant}^{-1} (dry weight) to 260 mg g^{-1}, i.e with a
713 variation of a factor of 236. Also the interspecies variation was considerable, as can be
714 seen from the confidence interval. The highest value was found for lettuce, with 26% (dry
715 weight), probably due to the small size of the plant (< 40 cm), the leaf morphology where
716 leaves are collecting particles to the interior of the plant, and the surface structure. Note
717 that the transfer values were determined after washing of the vegetables. It was also
718 demonstrated that particle-bound organic contaminants migrate from the leaf surface to

719 the interior of the leaf (i.e. are overgrown by surface waxes), from where they can not be
720 washed off (Kaupp 1996). A BCF for radish leaves to soil of 0.08 kg kg_{dw}^{-1} was recently
721 measured at a Czech site for persistent lipophilic contaminants and was contributed to
722 soil particle attachment (Mikes et al. 2008).
723 A default value of 1% (based on wet weight; this corresponds to about 20% dry weight)
724 for transfer of attached soil was chosen for lettuce in the New Model Framework for
725 dietary exposure of children and adults (Legind and Trapp 2008). For cereals, 0.1%
726 transfer with attached soil particles was assumed, due to pollution at harvest. In models
727 predicting the exposure to radio-nuclides, the default value for the transfer of attached
728 soil is 0.5% wet weight (2.5% dry weight) for pasture grass, and 0.1% wet weight for
729 other plants (Paretzke and Garland 1990).
730 Note that the ingestion of soil attached to the daily vegetable diet may be higher than the
731 direct ingestion. The direct ingestion of soil is 50 mg/day for adults and 100 mg/d for
732 children (ECETOC 2001). The mean lettuce consumption in Denmark is 6 g/d for
733 children and 9 g/d for an adult woman. A transfer of 1% due to attached soil corresponds
734 to 60 mg/d and 90 mg/d soil ingestion with lettuce only. Other vegetables and fruits are
735 consumed at 389 g/d (children) and 475 g/d (mother). If on average 0.1% soil were
736 attached, this corresponds to 389 mg/d and 475 mg/d soil, which is much more than the
737 value of direct ingestion of soil and deserves consideration in human exposure
738 assessment.
739
740 **<Table 9.2>**
741
742 *9.5.2.4 Variation of partition coefficients*
743 The different regressions for *RCF* of barley and bean plants have been plotted in Fig. 9.4.
744 The partition coefficients between plant lipids and air, K_{PA}, also vary with plant species.
745 The K_{PA} depends both on plant-specific parameters (such as plant lipid content, empirical
746 exponent '*b*') and contaminant-specific parameters (K_{OW} and K_{AW} or K_{OA}). Kömp and
747 McLachlan (1997) found differences in the uptake of PCB between five different plant
748 species of up to a factor of 20. There was a linear relationship between log K_{PA} and log
749 K_{OA} values (octanol/air partition coefficients) within each plant species, but the slopes of
750 the regressions ranged from 0.57 to 1.15. The "standard value" for leaves (slope is 0.95,
751 Eq. 9.11) was determined by Briggs et al. (1982) and lies in this range.
752
753 *9.5.2.5 Permeability*
754 The velocity of diffusive uptake from air and loss to air is controlled by the permeability
755 of leaves (exchange velocity, conductance or transfer velocity). Three major resistances
756 control the exchange: air boundary layer resistance, stomata resistance and cuticle
757 resistance (Riederer 1995). Their importance depends on the chemical properties but
758 varies for each leaf. Volatile and gaseous contaminants will prefer stomata for the entry
759 to (or escape from) plants, while lipophilic contaminants will preferably diffuse through
760 cuticles. The stomata resistance for water and contaminants can be calculated from the
761 transpiration rate, leaf area, temperature and humidity (Trapp 1995, Trapp 2007). The
762 cuticle resistance depends on thickness and diffusivity inside the cuticle (Schönherr and
763 Riederer 1989). The latter is highly variable with species and temperature (Buchholz et
764 al. 1998): at high temperatures, the surface waxes liquidize and get more permeable.

765 A method for estimation of conductance g (m s^{-1}, related to gas phase) is given by Trapp
766 (1995, 2007). The g estimated with this method ranges from 9×10^{-3} m s^{-1} for non-volatile,
767 lipophilic contaminants to 0.2×10^{-3} m s^{-1} for volatile or polar contaminants. A default
768 value of 10^{-3} m s^{-1} was suggested, to avoid lenghty calculations (Trapp and Matthies
769 1995).
770
771 *9.5.2.6 Particle deposition*
772 A similar variability can be observed for the particle deposition rate. Particle deposition
773 depends on both the fraction of contaminant adsorbed to particles as well as the
774 deposition velocity of particles, but also on characteristics of the leaves. Bakker et al.
775 (1999) studied the deposition of polycyclic aromatic hydrocarbons (PAHs) on leaves
776 from three closely related *Plantago* species and found variations up to a factor of five,
777 which could be explained solely by plant morphology and surface structure. The fraction
778 adsorbed to particles is often calculated from the *Junge* equation, using vapor pressure as
779 input data. Newer methods are based on the K_{OA} (Cousins and Mackay 2001).
780 The particle deposition rate, v_{dep}, changes with the diameter of the particles. Default
781 values are given in the German TA-Luft and are listed in Tab. 9.3. Generally, diameters
782 (and thus deposition velocities) are higher close to the source of emission. At larger
783 distance the coarse particles have settled, and finer particles remain. The deposition rate
784 of fine particles is similar to the deposition rate of gases (conductance g), and the default
785 value of v_{dep} (10^{-3} m s^{-1}) is the same as for conductance g. Thus, uncertainties in f_P and
786 v_{dep} are not crucial for the calculated result.
787
788 **<Table 9.3>**
789
790 *9.5.2.7 Metabolism in vegetables*
791 Rapid metabolism in vegetables will significantly decrease the contaminant concentration
792 in vegetables. Transformation of contaminants may occur in the rhizosphere, inside the
793 vegetable and on the leaf surface (photolysis). Often, it is difficult to differentiate
794 between metabolism by fungi or bacteria living on and in plants and metabolism by plant
795 cells. Stimulation of bacterial degradation in the root zone has been observed frequently
796 and is a key process in phytoremediation projects (Trapp and Karlson 2001). Therefore, it
797 may happen that non-persistent contaminants do not reach the roots but are degraded by
798 bacteria living on or in the vicinity of roots.
799 Different from bacteria, plants do not grow on the contaminants. The role of their enzyme
800 system is detoxification, and there is an upper limit, beyond which plants suffer from
801 toxic effects and probably die (Trapp et al. 2007b). This may limit, besides contamination
802 of plants, gardening, agriculture and forests on contaminated sites.
803 Metabolism by plants has been described by the "green liver concept", because plant
804 metabolism rather resembles the processes in the animal liver than the bacterial
805 metabolism (Sandermann 1994). The first step (phase I reaction) is typically an
806 oxygenation with cytochrome P-450, followed by conjugation reactions (phase II) with
807 glutathione-S-transferases (GST) (Pflugmacher and Schröder 1995, Barret 1995). Unlike
808 animals, plants are not able to excrete conjugates via the urine. Instead, phase III of plant
809 xenobiotic metabolism involves storage of soluble conjugates in the vacuole and of
810 insoluble conjugates in the cell wall (Komossa et al. 1995). This may lead to so-called

"bound residues". These bound unextractable residues resist solubilization in common laboratory solvents and are therefore not accessible to standard residue analysis. It was found that bound residues can be present in larger amounts than the parent contaminant and could therefore represent a source of significant consumer exposure (Sandermann 1994).

Little is known about metabolism rates of contaminants by vegetation. Cyanide (HCN) was used as model contaminant to study the variation of rates among plant species. The removal of free cyanide followed Michael-Menten kinetics (Larsen et al. 2004). Adding Michaelis-Menten kinetics to the mass balance equation for roots leads to the following non-linear equation:

$$\frac{dC_R}{dt} = \frac{Q}{M_R} \times C_W - \left(\frac{Q}{M_R \times K_{RW}} + k_R \right) \times C_R - \frac{v_{\max} \times C_R}{K_M + C_R} \qquad \text{(Eq.38)}$$

where v_{max} (mg kg^{-1} d^{-1}) is the maximal metabolism velocity of the contaminant per kg plant mass with concentration C (mg L^{-1}), K_M (mg L^{-1}) is the half-saturation constant and M (kg) is the mass of the plant.

At a low external concentration in soil pore water, all contaminants that are taken up are metabolized (Fig. 9.11). At higher concentrations, however, the enzyme system is overloaded. Then, uptake is linearly related to the external concentration. This was shown experimentally for free cyanide (HCN) by Larsen et al. (2005). A non-linear *BCF* relation indicating enzymatic activity of plants was found repeatedly, e.g. for phenol (Ucisik and Trapp 2006) and salt, NaCl (Trapp et al. 2008a). Subsequently, the *BCF* is low at a low external concentration in soil pore water, but increases at higher external concentrations.

The Michaelis-Menten parameters K_M and v_{max} varied with plant species, but less than expected. Values of v_{max} of 12 species from nine families were found in a relatively narrow range between 6.7 and 21.9 mg CN kg^{-1} h^{-1} and were normally distributed with a mean of 13 mg CN kg plant^{-1} h^{-1} (Yu et al. 2004). The authors concluded that the variation of metabolism rates between plant species was small, and that it is likely that all investigated plants used the same enzyme for detoxification. Another sign for common pathways and rates of metabolism in plant species is the difficulty to find selectively acting herbicides: it is rare that a contaminant hits weeds but not crops (Börner 1995).

<Figure 9.11>

9.5.3 Environmental variables

9.5.3.1 Climate

Principally, the models can be adapted to all climatic conditions at which plants grow. In particular temperature influences uptake and fate of xenobiotics in various ways. At higher temperatures plant physiological processes such as transpiration, growth and metabolism are stimulated. According to *Claudius-Clapeyron*'s law, the vapor pressure increases exponentially with temperature, so the vapor pressure of water in air is 872 Pa at 5°C but 5635 Pa at 35°C, i.e. a factor of 6.5 higher. The potential transpiration is directly proportional to the vapor pressure of water. Similarly, metabolic reactions are stimulated at higher temperatures. For example, the removal rate of cyanide was 3 to 5

times higher at 30°C than at 11°C (Yu et al. 2005a, 2007). Also, contaminant properties change with temperature. Like the vapor pressure, the partition coefficient air to water, K_{AW} also increases exponentially with temperature. For chlorinated solvents, such as TCE, the K_{AW} at 5°C is about a factor of 3 below that at 35°C (Kühne et al. 2005). This means less transport into leaves and more volatilization to air at higher temperatures.

9.5.3.2 Bioavailability

The concentration in the soil pore water is calculated from the K_{OC}. Reduced bioavailability, for example due to aging, can be considered by an increase in K_{OC} . At contaminated sites the soil pore water concentrations can be much lower and sorption coefficients can be much higher than equilibrium partitioning models predict (Ter Laak et al. 2006). Also, a depletion of contaminants in the soil due to uptake into vegetables is usually not taken into consideration. On the other hand, some plants can solubilize lipophilic contaminants in soil (Hülstner and Marschner 1995). In Hodson and Peijnenburg (2009; Chapter 16 in this book) an extended description of bioavailability is given.

9.5.3.3 Soil pH

Soil pH directly affects the speciation of acids and bases, as described by the *Henderson-Hasselbalch* law. Uptake of anions is generally lower than of neutral molecules, due to electrical repulsion and slow transfer across membranes. Cations are attracted by the electrical potential of living cells, but also adsorb to soil organic carbon and to negatively charged clay particles. This reduces their bioavailability and, hence, uptake. Both weak acids and bases can undergo the ion trap process (section 9.5.1.4). This will lead to an accumulation of weak acids from acidic soils, and of bases from alkaline soils. This conclusion is based on a model prediction and has not yet been confirmed by experiments. The pH also has an indirect effect on uptake: many vegetables do not grow well outside their optimum pH range. Extreme pH (high or low), will lead to reduced growth, and this may be accompanied by reduced uptake of contaminants.

9.5.4 Variations and uncertainties

The previous section listed parameters and variables that impact the uptake of contaminants into vegetables. Most likely, this list is far from complete. This may explain why under some conditions, in some experiments, a high uptake of a contaminant into a crop may be found, while this may not be the case in the next investigation, under other conditions. It also explains why data from experiments with plants often suffer from large scatter. Besides, care must be taken when results obtained from uptake studies are translated to other crop types, other climates, and other agricultural practices.

Models may help to design and interpret uptake experiments, in indicating relevant processes and pathways, and hence in translating results to other conditions. But due to the large number of parameters and their high variability in space and time, these models can not be expected to give exact results. Some studies tested the validity of model approaches (Rikken et al. 2001, Fryer and Collins 2003, Trapp and Schwartz 2000, McKone and Maddalena 2007, Legind and Trapp 2008). Often, the results were

ambiguous, because the influence of concentrations in air could not be quantified (compare section 9.3), but also due to large uncertainties in measured as well as predicted concentrations in plants (McKone and Maddalena 2007). The primary role of models is to indicate relevant processes and the potential for accumulation of contaminants in crops. Good decision making needs to consider both model predictions and experimental data.

9.6 Experimental results

This section reports results from several studies, not only with the intention to give a review, but also in order to confirm (or to falsify) the processes and the principal outcomes of the model simulations described above. Many experimental studies on plant uptake of organic contaminants are available, but most of them are from laboratory or greenhouse experiments, and the results may not always be applicable to field conditions. Results from field studies, however, are less often published. This may be due to high expenses, analytical difficulties or other research priorities. But a reason may also be that the results of uptake studies from outdoors often show a very large variation and are difficult to interpret.

9.6.1.1 Uptake of the polar and non-volatile compound sulfolane into plants

Sulfolane (synonym: tetramethylene sulfone) is an organo-sulfur contaminant used as solvent. Sulfolane is neutral, polar (log K_{OW} of -0.77) and non-volatile (K_{AW} of 2.14×10^{-4}). The uptake of sulfolane into wetland vegetation was measured in field and greenhouse studies (Doucette et al. 2005). The measured *RCF* was between 0.3 and 1.4 L kg^{-1} (related to the initial concentration in solution). High translocation to leaves was found. The *BCF* values for shoots were up to 160. Another experiment with sulfolane was done for apples (W. Doucette, personal communication). The concentration ratio fruit to soil was 2.8. For leaves, a *BCF* of 652 was found. As far as the authors are aware, this is the highest *BCF* plant to soil that was ever measured, and confirms model predictions in which polar, non-volatile contaminants are best translocated to and accumulated in leaves.

9.6.1.2 Uptake of trichloroethene

Trichloroethene is a volatile chlorinated solvent (K_{AW}: 0.5 L L^{-1}). A study on trichloroethylene uptake by apple and peach trees and transfer to fruit was performed by Chard et al. (2006). No TCE could be detected in fruits, but ^{14}C from unidentified metabolites was found. In leaves, the metabolites dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) could be detected. The article cites a field study were TCE could be detected in several fruits, but only in traces. Overall, the findings confirm the model prediction (Fig. 9.7a) that volatile contaminants do not show high accumulation in above-ground plant parts.

9.6.1.3 Transfer of PCDD/F from contaminated sites into field crops

The transfer of PCDD/F from contaminated sites into field crops has been intensively studied. Müller et al. (1994) found an increase of PCDD/F concentrations in the peel of carrots, when grown at a PCDD/F-contaminated site. No increase of the concentration in lettuce and peas was found. In a similar study, it could be shown that the transfer of

PCDD/F into apples and pears is exclusively from air (Müller et al. 1993). The results from these studies confirm the model predictions in which uptake of lipophilic contaminants into above-ground plant parts is primarily from air. However, there are exceptions. Hülster et al. could proof a transfer of PCCD/F into zucchini and pumpkins in field experiments, which was much higher than for other fruits (Hülster et al 1994).
For zucchini and pumpkin (*Cucurbita pepo*), both members of the plant family *Cucurbitaceae* and the genus *Cucurbita*, root uptake and subsequent translocation to shoots and fruits was the main uptake route of PCDD/F, probably due to root exudates which mobilize lipophilic contaminants (Hülster and Marschner 1995). Fruits and leaves from other plant species, even for the closely related cucumber plant (*Cucumis sativus*), were mainly contaminated by airborne PCDD/F (Hülster et al. 1994, Hülster and Marschner 1994). The exact reason for the ability of cucurbita plants to extract lipophilic contaminants from soil is yet unknown, but it was observed repeatedly, and for a number of lipophilic organic contaminants, such as p,p'-DDE (White 2002), DDT (Lunney et al. 2004), PCB (Whitfield Åslund et al. 2007) and PBDE (Mueller et al. 2006). For phenanthrene, unusual high adsorption to a range of plant species was observed (Zhu et al. 2007).

9.6.1.4 Uptake of polycyclic aromatic hydrocarbons into vegetables and uptake pathways
In systematic experiments, Delschen et al. (1996, 1999) investigated the uptake and the uptake pathways of PAHs (polycyclic aromatic hydrocarbons) into vegetables and crops. They found that uptake of PAHs can both be from contaminated sites and from the atmosphere. In some experiments, the soil was covered with fine sand or a gas-permeable foliage. This avoided soil particle attachment, but allowed for volatilization with subsequent adsorption to leaves. In fact, this coverage reduced the uptake of 15 PAHs from soil almost completely, indicating soil particle attachment to leaves as major transfer pathway of PAHs (in particular benzo(a)pyrene and dibenz(a,h)-anthracene) from soil to vegetables. Thus, crops with harvested parts close to the soil surface have the highest affinity for accumulation, because soil particle attachment by rain splashing rarely affects plants with a height above 40 cm (Dreicer et al. 1984, Li et al. 1994). No systemic uptake of PAHs via plant roots was found. Concentrations of PAHs in peels of potato and carrots from organic farming were generally higher than in the core of potato and carrots (Zohair et al. 2006). The *BCF* for individual PAHs ranged from 0.0002 to 0.3 kg kg^{-1} and decreased with log K_{OW} (Zohair et al. 2006, Trapp et al. 2007a). The results from the experiments are in very good accordance with the model predictions in section 9.5.2.
The range of measured concentrations of BaP in food crops was quite large, from 0.01 to 48 µg kg^{-1}. Generally, leafy vegetables and lettuce had the highest concentrations, followed by cereals, potato and root vegetables (Kazerouni et al. 2001, Samsøe-Petersen et al. 2002, SCF 2002). This indicates air as primary source for the contamination of vegetables with PAHs.

9.6.1.5 Uptake of POPs into radishes
An uptake of organochlorine pesticides and polychlorinated biphenyls (PCBs) from soil and air into radishes was measured at a contaminated field site in the Czech Republic (Mikes et al. 2008). Root concentration factors (*RCF*) and above-ground bioconcentration

factors (*BCF*) were determined by linear regression. The transfer from soil into leaves (average *BCF* 0.08 kg kg_{dw}^{-1}) was rather constant for all contaminants and could best be explained by soil particle attachment. A negative correlation between *RCF* and log K_{OW} was found for edible radish bulbs. Generally, uptake from air was higher than uptake from soil. Uptake from air into radish roots and bulbs was observed. The example in Section 9.3 was taken from this study.

9.6.1.6 Uptake of the explosive RDX into vegetables

In a critical review of uncertainties related to plant-to-soil bioconcentration factors by McKone and Maddalena (2007), *BCF*-values for the explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) are listed. RDX is a quite persistent, relatively polar (log K_{OW}: 0.87) and non-volatile contaminant (K_{AW}: 6.3 x 10^{-8} atm m^3 mol^{-1}). *BCF*-values range from 0.06 (mg $kg_{ww\ plant}^{-1}$: mg $kg_{dw\ soil}^{-1}$) in bean pods and 0.07 (mg $kg_{ww\ plant}^{-1}$: mg L $water^{-1}$) in bean fruits at the lower end to 19.2 (mg $kg_{ww\ plant}^{-1}$: mg L_{water}^{-1}) in bean leaves and 28.6 (mg $kg_{dw\ plant}^{-1}$: mg $kg_{dw\ soil}^{-1}$) in carrot shoots at the upper end. Overall, fruits tend to have lower *BCF* values than roots, and leaves have the highest accumulation, but there is a very large variation in the data. The *BCF* values for fruits range from 0.07 to 5.50, for roots from 0.08 to 4.50 and for leaves from 0.30 to 28.6, i.e. the maximum *BCF* is 79 fold, 56 fold or 93 fold larger than the minimum *BCF*. Even though the units are not uniform (i.e. a mix of wet weight and dry weight, soil and water), this variation is quite impressive for one single contaminant and similar crop type. Overall, it can be concluded that:

- The model prediction that polar, non-volatile contaminants tend to accumulate in particular in leaves is correct.
- The uncertainties in the model predictions are very high, and very large variations may be expected in experimental data.
- The variations of contaminant-specific, physiological and environmental parameters listed in section 9.5 do lead to high variations in uptake.

9.6.1.7 Uptake of acids and bases

Briggs et al. (1987) determined the *RCF* and *TSCF* of weak organic acids with log K_{OW} between 0.06 and 4.51 and pKa-values near 3. At pH 7 in external solution, *RCF*-values were low, between 0.5 and 4.5 L kg^{-1}. At pH 4, the *RCF*-values were higher and ranged from 2.6 to 72 L kg^{-1}. Similar, the *TSCF*-values of weak acids at pH 7 was low, 0.04 to 0.05 L L^{-1}, while at pH 4 *TSCF*-values up to 4.2 L L^{-1} were found. Briggs et al. used the ion trap process to interpret their results. Chamberlain et al. (1998) studied the uptake into roots and translocation to shoots of two weak bases, i.e. dodemorph (pKa 7.8) and tridemorph (pKa 7.4). At pH 5, *RCF*-values of dodemorph were < 10 L kg^{-1}, and of tridemorph about 20 L kg^{-1}. With increasing pH, *RCF* increased to 49 L kg^{-1} for dodemorph and 183 L kg^{-1} for tridemorph at pH 8. In parallel, the *TSCF* increased from < 1 L L^{-1} for both bases at pH 5 to 24 L L^{-1} for dodemorph and slightly below 10 L L^{-1} for tridemorph at pH 8. To the knowledge of the authors of this Chapter, the *TSCF* of dodemorph in this experiment was the highest *TSCF* ever determined. A similar study was done by Inoue et al. (1998), who also found a large increase of uptake and translocation of weak bases in plants with increasing pH. The results from these studies

underline the importance of pH in the soil pore water for uptake and translocation of weak electrolytes. However, the results have not yet been confirmed by field studies.

9.7 Classification of contaminants with respect to uptake into vegetables

This section gives a short classification of several frequently found soil and groundwater contaminants with respect to their uptake into vegetables. It is based on the model simulations, measured data and the process review above, but also on the experience of the authors.

9.7.1.1 Chlorinated solvents (PCE, TCE and others)

Chlorinated solvents such as perchloroethene (PCE) and trichloroethene (TCE) are probably the most frequently found groundwater contaminants world-wide. They are water-soluble, relatively persistent and very volatile. Uptake of chlorinated solvents into tree trunks has been reported frequently (Sorek et al. 2008, Vroblesky et al. 1999, Larsen et al. 2008, Chard et al. 2006). However, these contaminants are highly volatile and escape rapidly from branches, small stems and leaves into the air (Baduru et al. 2008). Thus, in fruits, only metabolites of chlorinated solvents could be detected (Chard et al. 2006). Accumulation in root crops and potatoes is likely, though not described yet. During storage and cooking, chlorinated solvents could be eliminated from food stuff, due to their high volatility. Moreover, these contaminants are not expected to be present in high concentrations in top soil, i.e. the root zone, due to volatilization to the air and leaching to the groundwater.

9.7.1.2 Gasoline contaminants

Gasoline is a mixture of light petroleum products (for example alkanes such as hexane, and aromates such as benzene and toluene) plus additives like ethanol and MTBE. They frequently occur in the groundwater due to leaching storage tanks. Gasoline contaminants are volatile and usually rapidly degraded. Thus, concentrations in aerated soil are generally low (Fig. 9.8). Accumulation in crops from soil has not been described, except in laboratory experiments. An exception is MTBE, which is less volatile and more persistent. MTBE was not metabolized in any of 24 plant species tested (Trapp et al. 2003). Uptake of benzene from air is rapid but levels are low, due to a low K_{OA}, and insignificant for human exposure (Collins et al. 2000).

9.7.1.3 Heavy petroleum products

The heavy fraction of petroleum products consists of long-chain alkanes and some polycyclic aromatic hydrocarbons. These contaminants are lipophilic, volatile and degradable under aerobic conditions. Significant uptake into vegetables has not been observed and is not expected.

9.7.1.4 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) is a group of contaminants with two (naphthalene) to seven or more condensed aromatic rings with wide-spread occurrence in the environment from incomplete combustion. Most of these contaminants are very

lipophilic (log K_{OW} 5 to 7) and have a very low water-solubility. Uptake into plants with transpiration water is therefore unlikely. Contamination of plants is mainly via attached soil particles or from air (Delschen et al. 1999). Uptake from soil into the peel of carrots or potatoes may occur. Solubilization by cucurbita species (pumpkin and zucchini) is likely.

9.7.1.5 Persistent organic pollutants POPs

Persistent Organic Pollutants (POPs) are chlorinated compounds like the pesticides DDT, dieldrin and lindane, but also polychlorinated biphenyls (PCB) and polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F). POPs are persistent, semi-volatile and lipophilic. Similar to PAHs, the uptake with transpiration water into vegetables is very unlikely, while attached soil particles can lead to contamination of crops. Solubilization with subsequent translocation by cucurbita species (pumpkin and zucchini) has been observed repeatedly.

9.7.1.6 Explosives

Explosives such as trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are relatively polar contaminants with low vapor pressure. High uptake into plants has been observed (McKone and Maddalena 2007, Thompson et al. 1998). Inside plants, a reduction of the nitro groups to amino groups is likely and would lead to an increase of the toxic potential. Furthermore, bound residues may be formed.

9.7.1.7 Phenols

"Phenols" is the common name for a class of contaminants with a phenolic ring. A variety of chemical groups may be attached to the ring and leads to contaminants with a large variety of properties (nitrophenols, anilines, chlorinated phenols). Phenols are less volatile than the aromatics benzene, toluene, ethylbenzene and xylene (BTEX). The contaminant phenol as well as monochlorophenol were degraded rapidly in the root zone (Ucisik and Trapp 2006, 2008), while 2,4-dichlorophenol was taken up into roots and translocated to stem, and to some extent also to leaves (Ucisik et al. 2007).

9.7.1.8 Cyanides

"Cyanides" are contaminants with a CN-group found at (abandoned) gasworks sites and gold mines. Free cyanides (HCN, CN^-) are rapidly taken up into roots and are rapidly metabolized. An accumulation in healthy plants was not observed, because free CN is highly toxic (Larsen et al. 2004, 2005, Yu et al. 2004, 2005b). Iron-complexed cyanide (ferri- and ferrocyanide) is taken up by plants and translocated upwards, while slow metabolism was observed (Ebbs et al. 2003, Samiotakis and Ebbs 2003, Larsen and Trapp 2006). Field measurements at a former gas works site showed no accumulation of total cyanide (sum of free and complexed CN) in leaves (Trapp and Christiansen 2003, and own results, unpublished). Surface contamination of crops by solid iron cyanide (such as Prussian blue) is possible and has been observed ("blue strawberries").

9.8 Monitoring of contaminants in soils and shallow aquifers with vegetation

The uptake of soil and groundwater contaminants into vegetation has also positive aspects: contaminants such as chlorinated solvents in soils and shallow aquifers can be monitored using vegetation samples. In principle, every tree could be considered as a well, a pump and a passive sampler, all in one. Vegetation samples can be taken from stems of trees (Fig. 9.12) and analyzed to identify and map subsurface contamination. The method is rapid and cheap. Screening an area suspect of contamination in the upper aquifer with the tree core method prior to boring observation wells can support the determination of optimal location of these wells, instead of arbitrary placing wells. This reduces the number of wells necessary for the investigation and thus reduces overall costs. Besides, tree cores can be sampled at sites which are difficult to access with heavy equipment, for example gardens in residential areas or dense forests. Even better, the effect on trees of the contaminants in a plume is reflected by the size of tree rings, and dendrochronology can be used to determine when a plume passed below the tree (Balouet et al. 2007).

The potential of this monitoring procedure is large. Tree core sampling as monitoring method was successfully applied for chloroethenes (Vroblesky et al. 1999, Gopalakrishnan et al. 2007). Larsen et al. (2008) found a good agreement between the plume delineation by traditional well drilling and by tree core sampling, but only monotone (and not linear) relations. The authors could also use the method to monitor natural attenuation of a PCE spill. Sorek et al. (2008) even detected several before unknown spills in Tel Aviv by a random sampling of trees in the city. But there are also limitations. Tree core sampling should rather be used for assessing the presence of contaminants than for determining exact subsurface concentrations. Because from tree core measurements alone, precise evaluation of subsurface contamination will not be possible, due to varying concentrations in wood (Larsen et al. 2008, Sorek et al. 2008).

The method could also be successful for some heavy metals such as cadmium and copper, and it may also work for MTBE, perchlorate and dichlorophenol. For a number of contaminants the method was not successful, to mention are BTEX, PAHs (except naphthalene), free and iron complexed cyanide, long-chain alkanes (generally petroleum products), phenol, monochlorophenol, iron and lead.

A free guide to vegetation sampling for screening of subsurface pollution is available from the web (Trapp et al. 2008b).

<Figure 9.12>

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Model availability

Most models mentioned in this Chapter are freely available via the authors. Please send an email if you are interested.

References

Alexander M. 2000. *Aging, bioavailability, and overestimation of risk from environmental pollutants*. Environ Sci Technol 34:4259–4265

Baduru KK, Trapp S, Burken JG. 2008. *Direct measurement of VOC diffusivities in tree tissues: impacts on tree-based phytoremediation*. Environ Sci Technol 42:1268-1275

Bakker M, Vorenhout M, Sijm DTHM, Kollöffel C. 1999. *Dry deposition of atmospheric polycyclic aromatic hydrocarbons in three plantago species*. Environ Toxicol Chem 18, 2289-2294

Balouet J-C, Oudijk G, Smith KT, Petrisor I, Grudd H, Stocklassa B. 2007. *Applied dendroecology and environmental forensics. Characterizing and age dating environmental releases: Fundamentals and case studies*. Environ Forensics 8:1–17

Barret M. 1995. *Metabolism of herbicides by cytochrome P 450 in corn. Drug Metabolism and Drug Interactions* 12:299-315

Börner H. 1995. *Unkrautbekämpfung*. Gustav Fischer, Jena, D.

Brand, E., Otte, P.F., Lijzen, J.P.A. 2007. *CSOIL 2000: an exposure model for human risk assessment of soil contamination*. RIVM Report 711701054/2007, National Institute of Public Health and the Environment (http://rivm.openrepository.com/rivm/bitstream/10029/13385/1/711701054.pdf)

Briggs GG, Bromilow RH, Evans AA.1982. *Relationship between lipophilicity and root uptake and translocation of non-ionised chemicals by barley*. Pestic Sci 13:495-504

Briggs GG, Bromilow RH, Evans AA, Williams M. 1983. *Relationships between lipophilicity and the distribution of non-ionised chemicals in barley shoots following uptake by the roots*. Pestic Sci 14:492-500

Briggs, G.G., Rigitano, R.L.O., Bromilow, R.H. 1987. *Physicochemical factors affecting uptake by roots and translocation to shoots of weak acids in barley*. Pestic Sci 19:101-112.

Buchholz, A., Baur, P., Schönherr, J. 1998. *Differences among plane species in cuticular permeabilities and solute mobilities are not caused by differential size selectivities*. Planta 206:322-328.

Burken JG, Schnoor JL. 1998. *Predictive relationships for uptake of organic contaminants by hybrid poplar trees*. Environ Sci Technol 32:3379-3385

Chamberlain, K., Patel, S., Bromilow, R.H. 1998. *Uptake by roots and translocation to shoots of two morpholine fungicides in barley*. Pestic Sci 54:1-7.

Chard BK, Doucette WJ, Chard JK, Bugbee B, Gorder K. 2006. *Trichloroethylene uptake by apple and peach trees: greenhouse study*. Environ Sci Technol 40:4788-4793

Collins CD, Bell JNB, Crews C. 2000. *Benzene accumulation in horticultural crops*. Chemosphere 40:109-114

Cousins I, Mackay D. 2001. *Gas-particle partitioning of organic compounds and its interpretation using relative solubilities*. Environ Sci Technol 35:643-647

1219 Czub, G., McLachlan, M.S. 2004. *A food chain model to predict the levels of lipophilic organic*
1220 *contaminants in humans*. Environ Toxicol Chem 23:2356-2366.
1221 DEFRA (Department for Environment Food and Rural Affairs) 2002. *The Contaminated Land Exposure*
1222 *Assessment Model (CLEA): Technical basis and algorithms*. R & D Publications CLR 10,
1223 Environment Agency (http://publications.environment-agency.gov.uk/pdf/SCLR10-e-
1224 p.pdf?lang=_e)
1225 Delschen T, Hembrock-Heger A, Necker U. 1996. *Systematische Untersuchungen zum Verhalten von PAK*
1226 *und PCB im System Boden/Pflanze auf der Lysimeter-Anlage Waldfeucht (1989-1994)*. In
1227 Landesumweltamt NRW, eds, Materialien zur Ermittlung und Sanierung von Altlasten, LUA
1228 Essen, Germany, pp 1-214.
1229 Delschen T, Hembrock-Heger A, Leisner-Saaber J, Sopczak D. 1999. *Bedeutung verschiedener*
1230 *Belastungsursachen für den PAK-Gehalt von Kulturpflanzen*. Umweltwissenschaften und
1231 Schadstoff-Forschung, UWSF – Z Umweltchem Ökotox 11:79- 87
1232 Doucette WJ, Chard TJK, Moore BJ, Staudt WJ, Headley JV. 2005. *Uptake of sulfolane and*
1233 *diisopropanolamine (DIPA) by cattails (Typha latifolia)*. Microchem J 81:41– 49.
1234 Dreicer M, Hakonson TE, White GC, Whicker FW. 1984. *Rainsplash as a mechanism for soil*
1235 *contamination of plant surfaces*. Health Physics 46:177-187
1236 Ebbs S, Bushey J, Poston S, Kosma D, Samiotakis M, Dzombak D. 2003. *Transport and metabolism of free*
1237 *cyanide and iron cyanide complexes by willow*. Plant Cell Environ 26:1467-1478
1238 EC (European Commission). 2003. *Technical Guidance Document on Risk Assessment in support of*
1239 *Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission*
1240 *Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of*
1241 *the European Parliament and of the Council concerning the placing of biocidal products on the*
1242 *market*, European Communities, Italy (http://ecb.jrc.it/documents/)
1243 ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals). 2001. *Exposure Factors*
1244 *Sourcebook for European Populations (with Focus on UK Data)*. Technical Report No. 79,
1245 Brussels, Belgium
1246 EFSA (European Food Safety Authority) 2006. *Pesticides are EU citizens' top food-related health concern*.
1247 Available online at http://www.euractiv.com (accessed 17 March 2006).
1248 Franco A, Trapp S. 2008. *Estimation of the soil-water partition coefficient normalized to organic carbon*
1249 *for ionizable organic chemicals*. Environ Toxicol Chem 27 No 8, in print. DOI:10.1897/07-583.1
1250 Franke W. 1987. *Nutzpflanzenkunde*. Thieme Verlag, Stuttgart, Germany.
1251 Fryer ME, Collins CD. 2003. *Model intercomparison for the uptake of organic chemicals by plants*.
1252 Environ Sci Technol 37:1617 -1624
1253 Gopalakrishnan G, Negri MC, Minsker BS, Werth CJ. 2007. *Monitoring subsurface contamination using*
1254 *tree branches*. Ground Wat Monit Rem 27: 65-74
1255 Hsu FC, Marxmiller RL, Yang AYS. 1990. *Study on root uptake and xylem translocation of cinmethylin*
1256 *and related compounds in detopped soybean roots using a pressure chamber technique*. Plant
1257 Physiol 93:1573-1578
1258 Hülster A, Marschner H. 1994. PCDD/PCDF-Transfer in Zucchini und Tomaten. Veröff PAÖ 8:579-589
1259 Hülster A, Marschner H. 1995. Identifizierung PCDD/PCDF-mobilisierender Verbindungen in
1260 Wurzelexudaten von Zucchini. Veröff PAÖ 12:359-369
1261 Hülster, A., Müller, J.F., Marschner, H. 1994. *Soil-plant transfer of polychlorinated dibenzo-p-dioxins and*
1262 *dibenzofurans to vegetables of the cucumber family (Cucurbitaceae)*. Environ Sci Technol
1263 28:1110-1115.
1264 Hung, H., Mackay, D. 1997. *A novel and simple model of the uptake of organic chemicals by vegetation*
1265 *from air and soil*. Chemosphere 35:959-977.
1266 Inoue, J., Chamberlain, K., Bromilow, R.H. 1998. *Physicochemical factors affecting the uptake by roots*
1267 *and translocation to shoots of amine bases in barley*. Pestic Sci 54:8-21.
1268 Kaupp H. 1996. *Atmosphärische Eintragswege und Verhalten von polychlorierten Dibenzo-p-dioxinen und*
1269 *-furanen sowie polyzyklischen Aromaten in einem Maisbestand*. PhD thesis, faculty of biology,
1270 chemistry and earth science, University of Osnabrück
1271 Kazerouni N, Sinha R, Hsu CH, Greenberg A, Rothman N. 2001. *Analysis of 200 food items for*
1272 *benzo[a]pyrene and estimation of its intake in an epidemiologic study*. Food Chem Toxicol
1273 39:423-436
1274 Kleier DA. 1988. *Phloem mobility of xenobiotics*. Plant Physiol. 86:803-810

1275 Komossa D, Langebartels C, Sandermann jr H. 1995. *Metabolic processes for organic chemicals in plants*.
1276 In: Trapp S, Mc Farlane C (eds), 'Plant Contamination - Modeling and Simulation of Organic
1277 Chemical Processes'. Lewis Pub., Boca Raton, Florida, USA, 69-103
1278 Kömp P, McLachlan M. 1997. *Interspecies variability of the plant/air partitioning of polychlorinated*
1279 *biphenyls*. Environ Sci Technol 31:2944-2948
1280 Kühne R, Ebert RU, Schüürmann G. 2005. *Prediction of the temperature dependency of Henry's Law*
1281 *constant from chemical structure*. Environ Sci Technol 2005, 39:6705-6711
1282 Larsen, M., Trapp, S. 2006. *Uptake of iron cyanide complexes into willow trees*. Environ Sci Technol
1283 40:1956-1961.
1284 Larsen, M., Trapp, S., Pirandello, A. 2004. *Removal of cyanide by woody plants*. Chemosphere 54, 325-
1285 333.
1286 Larsen M, Ucisik A, Trapp S. 2005. *Uptake, metabolism, accumulation and toxicity of cyanide in willow*
1287 *trees*. Environ Sci Technol 39:2135-2142
1288 Larsen M, Burken J, Machackova J, Karlson UG, Trapp S. 2008. *Using tree core samples to monitor*
1289 *natural attenuation and plume distribution after a PCE spill*. Environ Sci Technol 42:1711–1717
1290 Legind CN, Trapp S. 2008. *Modeling the exposure of children and adults via diet to chemicals in the*
1291 *environment with crop-specific models*. Submitted to Environ Pollut July 2008.
1292 Li JG, Gerzabek MH, Mück K. 1994. *An experimental study on mass loading of soil particles on plant*
1293 *surfaces*. Bodenkultur 45:15-24
1294 Lunney AI, Zeeb BA, Reimer K. 2004. *Uptake of weathered DDT in vascular plants: Potential for*
1295 *phytoremediation*. Environ Sci Technol 38:6147-6154
1296 Mackay D, Fraser A. 2000. *Bioaccumulation of persistent organic chemicals: mechanisms and models*.
1297 Environ Pollut 110:375-391
1298 McLachlan MS. 1999. *Framework for the interpretation of measurements of SOCs in plants*. Environ Sci
1299 Technol 33:1799-1804
1300 McKone TE, Maddalena RL. 2007. *Plant uptake of organic pollutants from soil: bioconcentration*
1301 *estimates based on models and experiments*. Environ Toxicol Chem 26:2494-2504
1302 Mikes O, Cupr P, Trapp S, Klanova J. 2008. *Uptake of polychlorinated biphenyls and organochlorine*
1303 *pesticides from soil and air into radishes (Raphanus sativus)*. Accepted by Environ Pollut 12 Sep
1304 2008.
1305 Müller JF, Hülstner A, Päpke O, Ball M, Marschner H. 1993. *Transfer pathways of PCDD/F into fruits*.
1306 Chemosphere 27:195-201
1307 Müller JF, Hülstner A, Päpke O, Ball M, Marschner H. 1994. *Transfer of PCDD/F from contaminated sites*
1308 *into carrots, lettuce and peas*. Chemosphere 29:2175-2181
1309 Mueller KE, Mueller-Spitz SR, Henry HF, Vonderheide AP, Soman RS, Kinkle BK, Shann JR. 2006. *Fate*
1310 *of pentabrominated diphenyl ethers in soil: Abiotic sorption, plant uptake, and the impact of*
1311 *interspecific plant interactions*. Environ Sci Technol 40:6662-6667
1312 Paretzke HG, Garland JA. 1990. *Assessment of the radiological significance of surface contamination in*
1313 *entrained radioactivity*. Final Report, EC-contract No 90-ET-015
1314 Paterson, S., Mackay, D., McFarlane, C. 1994. *A model of organic-chemical uptake by plants from soil and*
1315 *the atmosphere*. Environ Sci Technol 28:2259-2266.
1316 Pflugmacher S, Schröder P. 1995. *Glutathione S-transferases in trees: inducibility by various organic*
1317 *xenobiotics*. Z Pflanzenernähr Bodenk 158:71-73
1318 Reichenberg F, Mayer P. 2006. *Two complementary sides of bioavailability: accessibility and chemical*
1319 *activity of organic chemicals in sediments and soils*. Environ Toxicol Chem 25:1239-1245
1320 Riederer M. 1995. *Partitioning and transport of organic chemicals between the atmospheric environment*
1321 *and leaves*. In: Trapp S, Mc Farlane JC (eds.): Plant contamination. Modeling and simulation of
1322 organic chemical processes. Boca Raton, FL, Lewis Pub, 153-190
1323 Rikken MGJ, Lijzen JPA, Cornelese AA.2001. *Evaluation of model concepts on human exposure.*
1324 *Proposals for updating the most relevant exposure routes of CSOIL*. RIVM report 711 701 022,
1325 Bilthoven, NL.
1326 Samiotakis M, Ebbs SD. 2003. *Possible evidence for transport of an iron cyanide complex by plants*.
1327 Environ Pollut 127:169-173
1328 Samsøe-Petersen L, Larsen EH, Larsen PB, Bruun P. 2002. *Uptake of trace elements and PAHs by fruit and*
1329 *vegetables from contaminated soils*. Environ Sci Technol 36:3057-3063

1330 Sandermann H. 1994. *Higher plant metabolism of xenobiotics: the 'green liver' concept*. Pharmacogenetics
1331 4:225-241
1332 Satchivi NM, Stoller EW, Wax LM, Briskin DP. 2000a. *A nonlinear dynamic simulation model for*
1333 *xenobiotic transport and whole plant allocation following foliar application I. Conceptual*
1334 *foundation for model development*. Pestic Biochem Phys 68:67-84
1335 Satchivi NM, Stoller EW, Wax LM, Briskin DP. 2000b. *A nonlinear dynamic simulation model for*
1336 *xenobiotic transport and whole plant allocation following foliar application II. Model validation*.
1337 Pestic Biochem Phys 68:85-95
1338 SCF (Scientific Committee on Food) 2002. *Annex: Background document to the opinion of the Scientific*
1339 *Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food.*
1340 *Polycyclic Aromatic Hydrocarbons – Occurrence in foods, dietary exposure and health effects.*
1341 (http://ec.europa.eu/food/fs/sc/scf/out154_en.pdf)
1342 Schönherr, J., Riederer, M., 1989. *Foliar penetration and accumulation of organic-chemicals in plant*
1343 *cuticles*. Rev Environ Contam Toxicol 108:1-70.
1344 Shone MGT, Bartlett OB, Wood AV. 1974. *A comparison of the uptake and translocation of some organic*
1345 *herbicides and a systemic fungicide by barley. II. Relationship between uptake by roots and*
1346 *translocation to shoots*. J Exp Botany 25:401-409
1347 Sicbaldi F, Sacchi GA, Trevisan M, Del Re AAM. 1997. *Root uptake and xylem translocation of pesticides*
1348 *from different chemical classes*. Pestic Sci 50:111-119
1349 Sitte P, Ziegler H, Ehrendorfer F, Bresinsky A. 1991. *Lehrbuch der Botanik für Hochschulen*. Stuttgart:
1350 Gustav Fischer, 33rd ed.
1351 Sorek A, Atzmon N, Dahan O, Gerstl, Z, Kushisin, L, Laor Y, Mingelgrin U, Nasser A, Ronen D,
1352 Tschachansky L, Weisbrod N, Graber ER (2008) *"Phytoscreening": The use of trees for*
1353 *discovering subsurface contamination by VOCs*. Environ Sci Technol 42:536–542
1354 Søvik AK, Alfnes E, Breedveld GD, French HK, Pedersen TS, Aagaard P. 2002. *Transport and*
1355 *degradation of toluene and o-xylene in an unsaturated soil with dipping sedimentary layers*. J
1356 Environ Qual 31:1809–1823
1357 TA-Luft (Technische Anleitung zur Reinhaltung der Luft). 1986. In: *Handbuch des Umweltschutzes*, Vol.
1358 II-2, appendix 3.1. ecomed, Landsberg aL, D.
1359 Ter Laak TL, Barendregt A, Hermens JLM. 2006. *Freely dissolved pore water concentrations and sorption*
1360 *coefficients of PAHs in spiked, aged, and field-contaminated soils*. Environ Sci Technol 40:2184-
1361 2190
1362 Thompson PL, Ramer LA, Guffey AP, Schnoor JL. 1998. *Decreased transpiration in poplar trees exposed*
1363 *to 2,4,6-trinitrotoluene*. Environ Toxicol Chem 17:902-906
1364 Trapp S. 1995. *Model for uptake of xenobiotics into plants*. In: Trapp S, Mc Farlane JC (eds.): Plant
1365 contamination. Modeling and simulation of organic chemical processes. Boca Raton, FL, Lewis
1366 Pub, 107-152
1367 Trapp S. 2000. *Modeling uptake into roots and subsequent translocation of neutral and ionisable organic*
1368 *compounds*. Pest Manage Sci 56:767-778
1369 Trapp S. 2002. *Dynamic root uptake model for neutral lipophilic organics*. Environ Toxicol Chem 21:203-
1370 206
1371 Trapp S. 2004. *Plant uptake and transport models for neutral and ionic chemicals*. Environ Sci Pollut Res
1372 11:33-39
1373 Trapp S. 2007. *Fruit Tree model for uptake of organic compounds from soil and air*. SAR QSAR Environ
1374 Res 18:367-387
1375 Trapp S, Christiansen H. 2003. *Phytoremediation of cyanide-polluted soils*. In: McCutcheon SC, Schnoor
1376 JL (Eds.). Phytoremediation: Transformation and Control of Contaminants. John Wiley & Sons,
1377 Hoboken, New Jersey, USA, pp. 829-862
1378 Trapp S, Karlson U. 2001. *Aspects of phytoremediation of organic compounds*. J Soils Sed 1:37-43
1379 Trapp S, Matthies M. 1995. *Generic one-compartment model for uptake of organic chemicals by foliar*
1380 *vegetation*. Environ Sci Technol 29:2333-2338; erratum 30, 360
1381 Trapp S, Matthies M. 1998. *Chemodynamics and Environmental Modeling*. Springer, Berlin, D.
1382 Trapp S, Pussemier L. 1991. *Model calculations and measurements of uptake and translocation of*
1383 *carbamates by bean plants*. Chemosphere 22:327-339
1384 Trapp S, Schwartz S. 2000. *Proposals to overcome limitations in the EU chemical risk assessment scheme*.
1385 Chemosphere 41:965-971

1386 Trapp S, Matthies M, Scheunert I, Topp EM. 1990. *Modeling the bioconcentration of organic chemicals in*
1387 *plants*. Environ Sci Technol 24:1246-1252
1388 Trapp S, Matthies M, Mc Farlane C, 1994. *Model for uptake of xenobiotics into plants: Validation with*
1389 *bromacil experiments*. Environ Toxicol Chem 13:413-422
1390 Trapp S, Yu X, Mosbæk H. 2003. *Persistence of methyl tertiary butyl ether (MTBE) against metabolism by*
1391 *Danish vegetation*. Environ Sci Pollut Res 10:357-360
1392 Trapp S, Cammarano A, Capri E, Reichenberg F, Mayer P. 2007a. *Diffusion of PAH in potato and carrot*
1393 *slices and application for a potato model*. Environ Sci Technol 41:3103-3108
1394 Trapp S, Ucisik AS, DelChicca Romano P, Larsen M. 2007b. *The role of plants and bacteria in*
1395 *phytoremediation - kinetic aspects*. In: Heipieper HJ (Ed.) Bioremediation of Soils Contaminated
1396 with Aromatic Compounds. NATO Science Series, IV. Earth and Environmental Sciences – Vol.
1397 76. Springer, Dordrecht, NL, 41-49
1398 Trapp S, Feificova D, Rasmussen NF, Bauer-Gottwein P. 2008a. *Plant uptake of NaCl in relation to*
1399 *enzyme kinetics and toxic effects*. Environ Exp Bot 10.1016/j.envexpbot.2008.05.001 in press
1400 Trapp S, Larsen M, Legind CN, Burken J, Machackova J, Karlson UG. 2008b. *A Guide to Vegetation*
1401 *Sampling for Screening of Subsurface Pollution*. Freely available at
1402 http://www2.er.dtu.dk/homepages/stt/GuidetoVegetationSampling.pdf
1403 Travis CC, Arms AD. 1988. *Bioconcentration of organics in beef, milk, and vegetation*. Environ Sci
1404 Technol 22:271-274
1405 Travis CC, Hattemer-Frey HA. 1991. *Human exposure to dioxin*. Sci Total Environ 104:97-127
1406 Ucisik AS, Trapp S. 2006. *Uptake, removal, accumulation, and phytotoxicity of phenol in willow trees*
1407 *(Salix viminalis)*. Environ Toxicol Chem 25:2455-2460
1408 Ucisik AS, Trapp S. 2008. *Uptake, accumulation, phytotoxicity and removal of 4-chlorophenol in willow*
1409 *trees*. Arch Environ Contam Toxicol 54:619–627
1410 Ucisik AS, Trapp S, Kusk KO. 2007. *Uptake, accumulation, phytotoxicity and removal of 2,4-*
1411 *dichlorophenol in willow trees*. Environ Toxicol Chem 26:1165-1171
1412 Vroblesky DA, Nietch CT, Morris JT. 1999. *Chlorinated ethenes from groundwater in tree trunks*. Environ
1413 Sci Technol 33:510-515
1414 Whitfield Åslund ML, Zeeb BA, Rutter A, Reimer KJ. 2007. *In situ phytoextraction of polychlorinated*
1415 *biphenyl - (PCB) contaminated soil*. Sci Total Environ 374:1-12
1416 White JC. 2002. *Differential bioavailability of field-weathered p,p'-DDE to plants of the Cucurbita and*
1417 *Cucumis genera*. Chemosphere 49:143–152
1418 Yu X, Trapp S, Puhua Z, Chang W, Xishi Z. 2004. *Metabolism of cyanide by Chinese vegetation*.
1419 Chemosphere 56:121-126
1420 Yu X, Trapp S, Zhou P, Hu H. 2005a. *The effect of temperature on the rate of cyanide metabolism of two*
1421 *woody plants*. Chemosphere 59:1099-1104
1422 Yu XZ, Trapp S, Zhou P. 2005b. *Phytotoxicity of cyanide to weeping willow trees*. Environ Sci & Pollut
1423 Res 12:109-113
1424 Yu, X.Z., Trapp, S., Zhou, P.H., Chen, L. 2007. *Effect of temperature on the uptake and metabolism of*
1425 *cyanide by weeping willows*. Int J Phytorem 9:243-255.
1426 Zhu Y, Zhang S, Zhu Y-G, Christie P, Shan X. 2007. *Improved approaches for modeling the sorption of*
1427 *phenanthrene by a range of plant species*. Environ Sci Technol 41:7818-7823
1428 Zohair A, Salim A-B, Soyibo AA, Beck AJ. 2006. *Residues of polycyclic aromatic hydrocarbons (PAHs),*
1429 *polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed*
1430 *vegetables*. Chemosphere 63:541-553

Tables

Table 9.1: Input data set for the standard model for the calculation of plant uptake (1 m^2 of soil).

Parameter	Symbol	Value	Unit
Soil			
Soil wet density	ρ_{wet}	1.95	kg L^{-1}
Organic carbon content	OC	0.02	kg kg^{-1}
Soil pore water content	P_W	0.35	L L^{-1}
Soil dry density	ρ_{dry}	= ρ_{wet} - P_W	kg L^{-1}
Mass of soil	M_S	1000	Kg
Roots			
Water content of roots	W_R	0.89	L kg^{-1}
Lipid content of roots	L_R	0.025	kg kg^{-1}
Transpiration stream	Q	1	L d^{-1}
Root mass	M	1	Kg
1^{st} order growth rate	K	0.1	d^{-1}
Leaves			
Shoot mass	M_L	1	Kg
Leaf area	A	5	m^2
Shoot density	ρ	1000	kg m^{-3}
Lipid content leaves	L	0.02	kg kg^{-1}
Water content leaves	W	0.8	L kg^{-1}
Conductance leaves	G	10^{-3}	m s^{-1}
Deposition velocity from air	v_{dep}	10^{-3}	m s^{-1}
Growth rate leaves	k_L	0.035	d^{-1}
Transfer with attached soil	R	0.01 - 0.001	kg kg^{-1}
Time to harvest	T	60	D

1436 **Table 2**. Transfer of attached soil particles to leaf surfaces (Li et al. 1994); expressed as
1437 mg soil $g_{plant\ dw}^{-1}$ ± 95% confidence interval.

Plant species	**Amount of soil** (mg soil $g_{plant\ dw}^{-1}$)
Lettuce	260 ± 100
Turnip	32 ± 11
Grass	18 ± 48
Tomato	17
Broccoli	10 ± 8.1
Bean leaves	9.5
Grass (Lolium)	5.8
Wheat	4.8
Sun flowers	2.6 ± 0.9
Tobacco	2.1 ± 0.6
Soy bean	2.1
Maize	1.4
Cabbage	1.1 ± 1.1
Average	28.2
Average fresh weight *	1.4

1438 * based on 95% water content of plants
1439
1440
1441
1442 **Table 3**. Deposition velocities of particles (TA-Luft 1986).

Diameter (µm)	v_{dep} (mm s^{-1})
< 5	1
5 to 10	10
10 to 50	50
> 50	100
unknown	70

1443
1444

Figure Captions

Figure 9.1: Transport and uptake processes in the soil-air-plant system.

Figure 9.2: Measured concentration ratio of p,p'-DDT in radish plant versus concentrations in soil, at a Czech site (from Mikes et al. 2008).

Figure 9.3: Calculation of *BCF* from the slope of the regression between concentrations in soil and plant; calculation of background concentration due to uptake from air from the y-axis intercept of the regression. Example from Mikes et al. (2008), p,p'-DDT in roots and soil.

Figure 9.4: Measured data and root concentration factor (*RCF)*-regression lines of Briggs et al. (1982) and Trapp and Pussemier (1991), compared to the concentration ratio bulk soil to water (K_{SW}).

Figure 9.5: Overview of crop-specific plant uptake models and processes considered (Legind and Trapp 2008).

Figure 9.6: Concentration in root (fresh weight) with varying log K_{OW}, predicted with the regression of Travis and Arms (T&A), the root concentration factor (RCF), the root model and the potato model. Concentration in soil is equal to 1 mg kg^{-1} (wet weight).

Figure 9.7: Simulated concentration in leaves for compounds with varying log K_{OW} and varying partition coefficient air-water (K_{AW}), for a concentration in soil equal to 1 mg kg^{-1} (wet weight). Concentration in air is **a)** 0 and **b)** in phase equilibrium with soil.

Figure 9.8: Simulated concentration of o-xylene in soil and roots as a function of time, with a degradation rate of 0.11 d^{-1}.

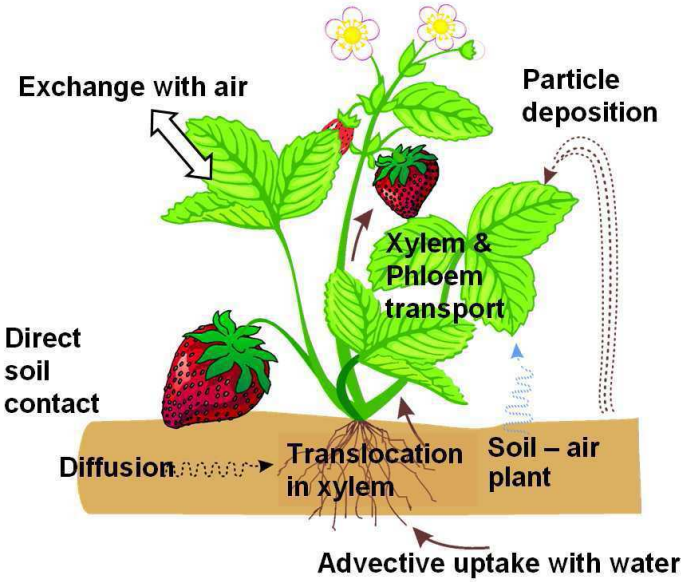
Figure 9.9: Principle of the ion trap. AH is the neutral contaminant (here an acid), and A^- is the ion (here an anion)

Figure 9.10: Simulation of the concentration of carbofuran in plants as a function of time, with low transpiration (Q is 1 L d^{-1}) and high transpiration (Q is 5 L d^{-1}). Dynamic model version, data Tab. 1.

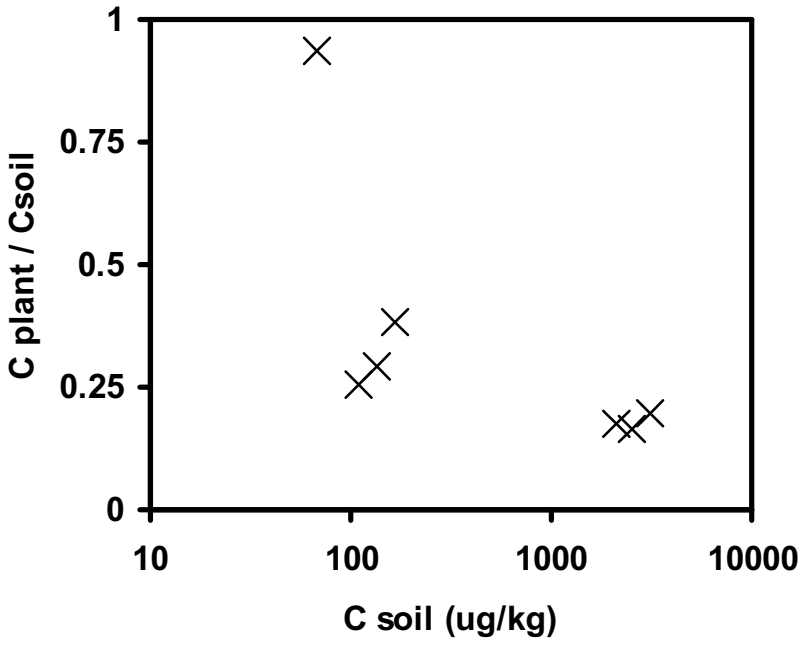
Figure 9.11: Calculation of concentration in roots of cyanide as a function of the concentration in external aqueous solution (C_W), using Michaelis-Menten kinetics for metabolism; v_{max} is 6.9 mg kg^{-1} h^{-1}; K_M is 0.44 mg L^{-1} (Larsen et al. 2005).

Figure 9.12: Demonstration of the tree core method by Morten Larsen.

1491 **Figures**
1492



1493
1494 Trapp Figure 1



1495
1496 Trapp Figure 2
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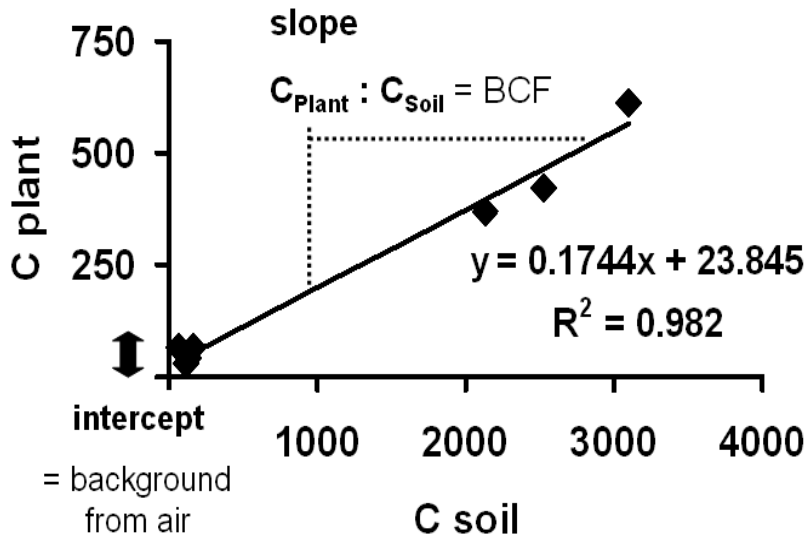

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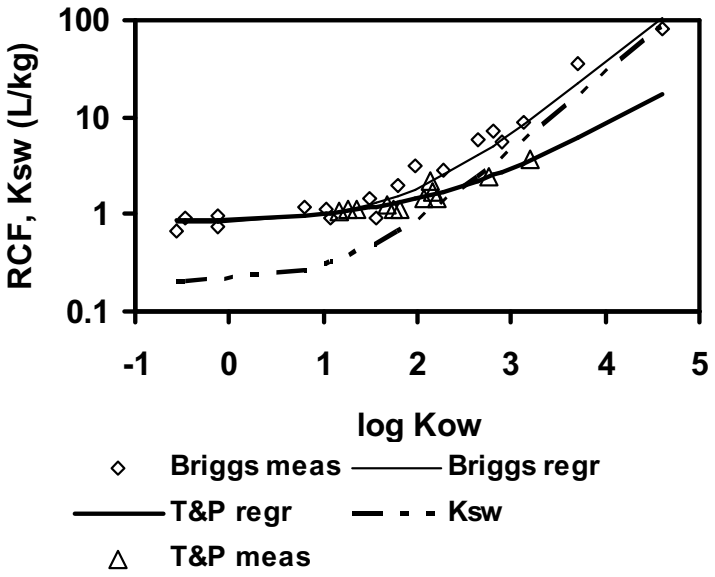

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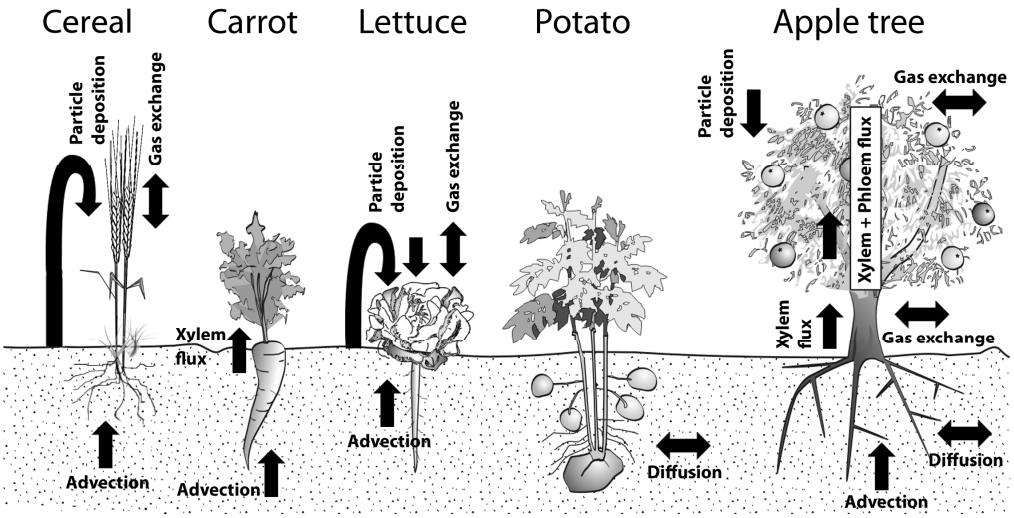

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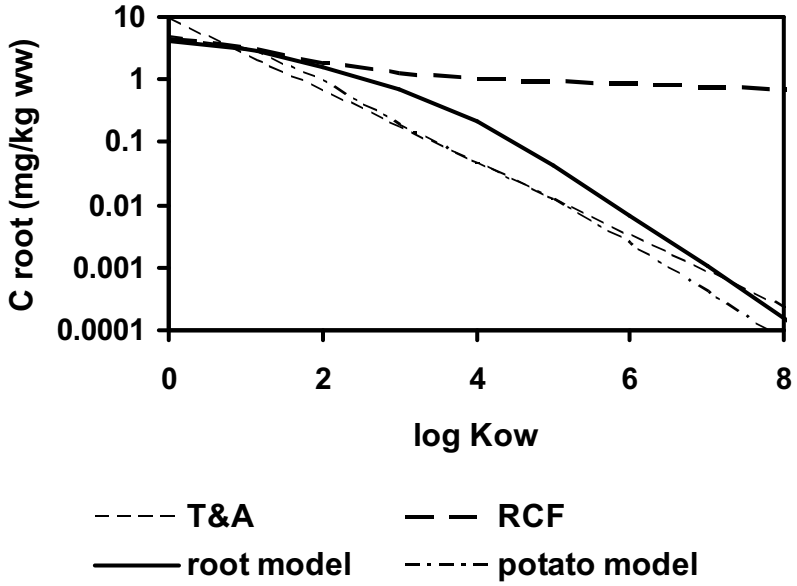

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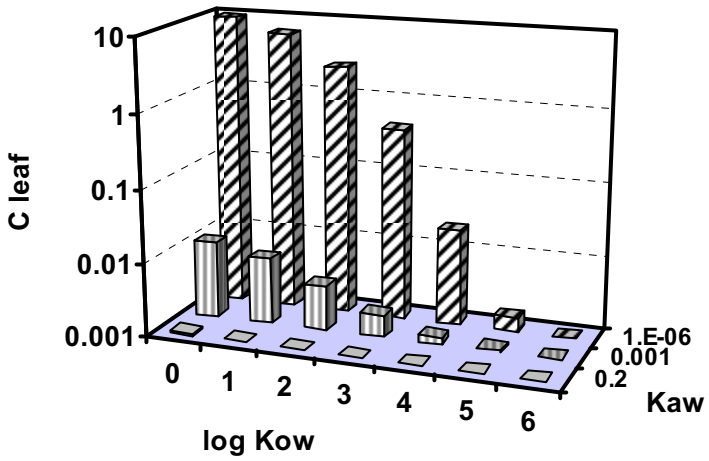

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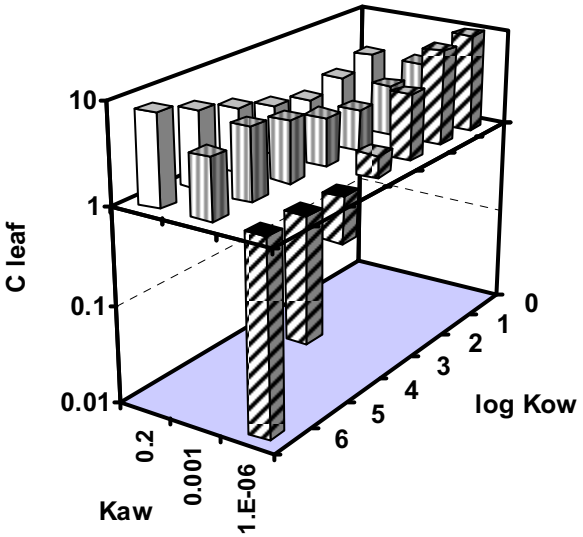

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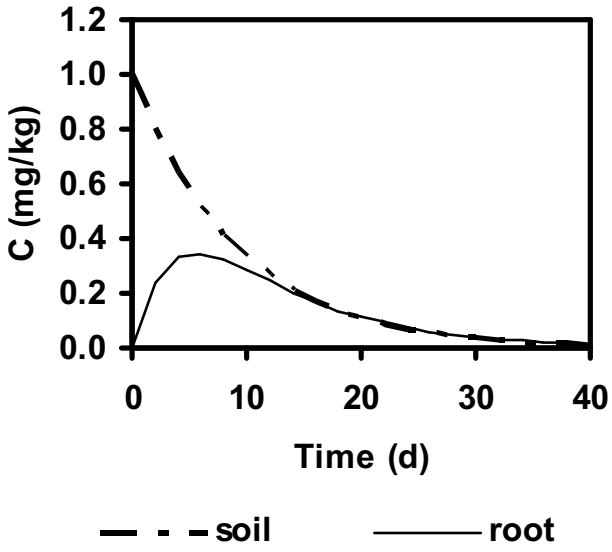

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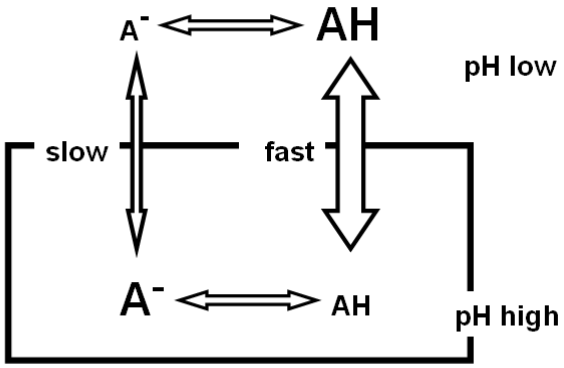

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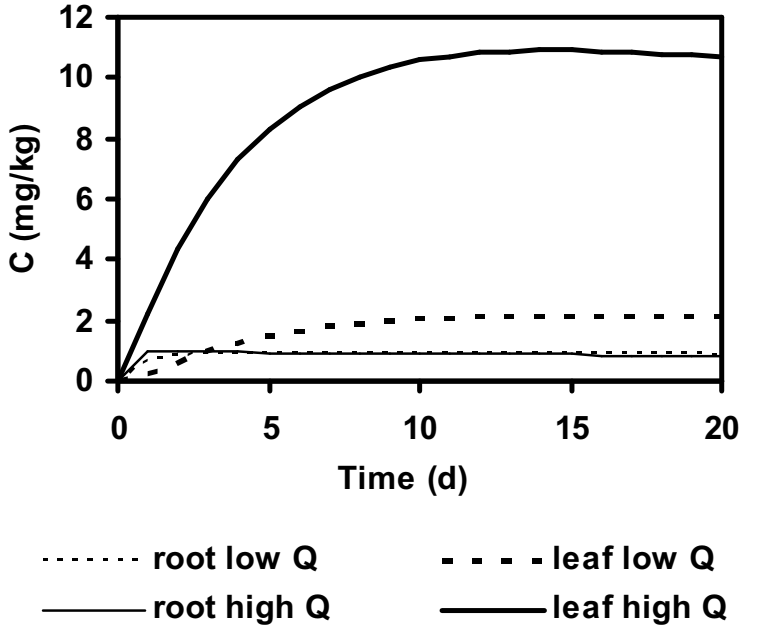

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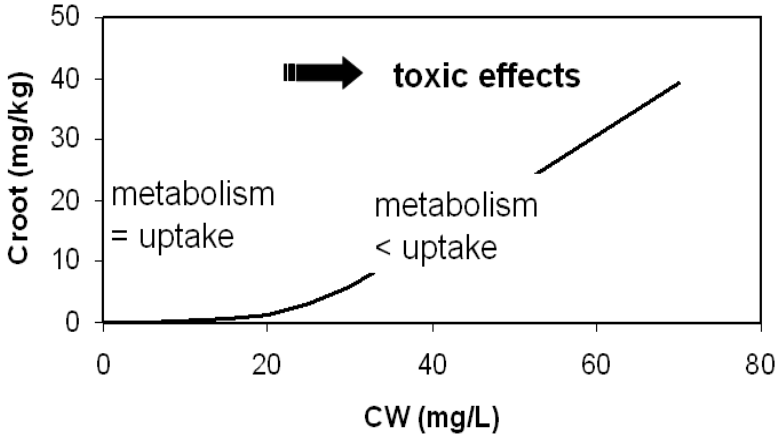

Trapp Figure 11

Trapp Figure 12

Paper III

Modeling the Exposure of Children and Adults via Diet to Chemicals in the Environment with Crop-Specific Models

Charlotte N. Legind and Stefan Trapp

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Modeling the exposure of children and adults via diet to chemicals in the environment with crop-specific models

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This paper addresses exposure of children and adults to environmental chemicals via the terrestrial food chain using crop-specific plant uptake models.

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ABSTRACT

Exposure to chemicals via diet is a major uptake pathway for many compounds but is often estimated in a rather generic way. We use a new model framework (NMF) with crop-specific models to predict the dietary intake by 4–5-year-old children and 14–75-year-old women of three environmental compounds from their background concentrations in soil and air. Calculated daily intakes of benzo(a)pyrene and 2,3,7,8-TCDD are in good agreement with measured results from diet studies. The major source of both compounds in human diet is deposition from air. Inhalation of air and ingestion of soil play a minor role. Children take up more than twice the amount than adults per kg bodyweight, due to higher consumption per kg bodyweight. Contrary, the methods for indirect human exposure suggested in the Technical Guidance Document (TGD) for chemical risk assessment in the EU lead to overprediction, due to unrealistic consumption data and a false root model.

1. Introduction

Chemicals released to the environment may distribute in water, air and soil. From there, they may be taken up into plants, accumulate in the human food chain (Czub and McLachlan, 2004) and affect the health of humans, and in particular of children (WHO, 2007). The exposure to the large number of these chemicals cannot be assessed by field tests or monitoring studies entirely, but relies mostly on predictive methods, such as mathematical models or quantitative structure-activity relationship (QSAR) methods. Consequently, a number of modeling tools for human exposure assessment were developed, for example CLEA (DEFRA, 2002), CSOIL (Brand et al., 2007), VLIER-HUMAAN (Nouwen et al., 2001) or ACC-Human (Czub and McLachlan, 2004).

New and existing chemicals in the European Union are regulated by the new legislation REACH (Registration, Evaluation, Authorisation and restriction of CHemicals) (EC, 2006). The procedure for risk assessment was laid down in the Technical Guidance Document (TGD) (EC, 2003) and implemented in the computer program EUSES (European Uniform System for the Evaluation of Substances). The TGD describes in detail how to perform a risk assessment for chemicals. It includes methods to predict the indirect exposure of humans by uptake of chemicals from environment (air, water and soil) into diet. The consumption data suggested in the TGD for dietary intake calculations are supposed to represent a "reasonable worst case", but the exposure assessment is done for adults with a bodyweight of 70 kg.

The behavior of children can expose them in other ways and also at higher levels to chemicals than adults. Children eat more, drink more and breathe more than adults in proportion to their body mass (WHO, 2007) – "… their food, water, and air must therefore be especially safe" (U.S. EPA, 2006). Summarized, the exposure of children to environmental chemicals is greater than that of adults, and in terms of risk assessment, children should be regarded as a particularly vulnerable group (Landrigan et al., 2004).

One objective of our study is therefore to develop a tool for the prediction of the indirect exposure of children to chemicals in the environment, and to compare their exposure to that of adults. Therefore, the exposure estimations distinguish between adults and children, by using realistic dietary consumption data for two age groups (4–5 and 14–75 years of age) to estimate the intake of chemicals via the daily diet.

A second objective of our study is to refine the method for indirect human exposure assessment. The existing method, described in the TGD (EC, 2003), considers only one generic plant

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type consisting of roots and leaves. We present a new model framework (NMF) that includes crop-specific plant models, which predict the concentrations of chemicals in roots, potatoes, leafy vegetables, lettuce, fruits and cereal separately. The focus is on the terrestrial food chain (i.e. crops, meat and milk), so fish is excluded from the study. The exposure of nursing infants to chemicals via breast milk is also included in the NMF but was handled earlier (Trapp et al., 2008). The outcome of the new, crop-specific models (NMF) is compared to the results of the current method (TGD) for relatively well-investigated compounds. By comparison to results from diet studies, the validity of the approaches and the level of improvement can be tested.

Briefly, the goal of our study is to refine chemical risk assessment under REACH by improving the assessment of human exposure to chemicals in the environment (air, water and soil) through consideration of children and crop-specific dietary uptake.

2. Materials and methods

Model compounds chosen for the study were: benzo[a]pyrene (BaP), 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), and dodecyl benzenesulfonic acid (a linear alkylbenzene sulfonate, LAS). Their properties and tolerable daily intakes (TDI) are given in Table 1. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) has not established a TDI for BaP because of lack of data (JECFA, 1991). However, several studies have been estimating TDI values for BaP ranging from 0.6 to 5 ng kg^{-1} d^{-1} (SCF, 2002b). We have chosen the value of 5 ng kg^{-1} d^{-1} from Kroese et al. (2001) giving $1:10^6$ excess lifetime cancer risk for oral exposure. No TDI was found for LAS.

Input concentrations in soil and air for the calculations with TGD and NMF are Danish data and shown in Table 1. Measured background concentrations in arable soil were found for BaP (Samsøe-Petersen et al., 2000) and TCDD (Vikelsøe, 2004). For LAS the input concentration was a former Danish soil quality criterion concerning sewage sludge application. Concentrations in air (sum of gaseous and particulate) were either measured (TCDD (Vikelsøe et al., 2006) and BaP (LAI, 1991)) or neglected (LAS). The background concentration of BaP in air was measured in Germany and is equal to the current European target value (EC, 2005).

Metabolism of the compounds in both plant and animal matrices was included where evidence for this process was found. For BaP, metabolism in animals is rapid (SCF, 2002b; Ciganek and Neca, 2006). Consequently, dietary exposure to BaP from meat and milk was neglected (i.e., a BaP concentration of 0 in meat and milk was assumed; BaP may have high concentrations in grilled meat, but this is not from environmental sources (SCF, 2002a)). For TCDD, a photolysis rate constant of 0.3744 d^{-1} (McCrady and Maggard, 1993) during sunlight (30 % of the time) was used in the lettuce, leaf, cereal and fruit tree models.

TGD methods. Current EU risk assessment considers consumption of root and leaf crops, fish, meat and dairy products in the assessment of indirect human exposure (EC, 2003). Concentrations in meat and dairy products are calculated with the regression equations of Travis and Arms (1988) for beef and milk, but with modified consumption rates. Concentrations in plants are calculated with the steady-state version of the model by Trapp and Matthies (1995). Concentrations in roots are calculated from phase equilibrium to soil. Uptake into leaves may be from soil with the transpiration stream and from air by gaseous deposition. Cattle feed on the leaves, but do also take up chemicals via ingestion of soil and inhalation of air. Concentrations in air and soil were not calculated, but are input data.

The basic equations are listed in Table 2 and in the Supporting Information (SI). For the complete set of equations we refer to the Technical Guidance Document (TGD) for risk assessment in the EU (EC, 2003). For our study, the TGD equations were implemented as a spreadsheet version.

The new model framework (NMF) consists both of models from the TGD and new crop-specific models. Since the establishment of the TGD guidelines, new crop-specific models were developed, namely a root model (“carrot model”) (Trapp, 2002), a fruit tree model (“apple model”) (Trapp, 2007), and a potato model (Trapp et al., 2007). All plant models are based on the same physicochemical principles and describe the same basic processes, such as advective uptake into plants, diffusive uptake, partitioning to plant tissue, fluxes inside the plants with xylem and phloem, dilution by growth, and particle deposition from soil and air. However, the actually occurring processes and the parameterization vary with the crop type (Fig. 1).

For lettuce and other leafy vegetables, the plant model developed by Trapp and Matthies (1995) was applied, which is also suggested in the TGD, but with modifications, in order to eliminate short-comings identified earlier (Trapp and Schwartz, 2000). Particle deposition from air to leaves was added ($v_{dep} \neq 0$ in Table 2) assuming 100% transfer of the contaminants from particle to plant. A soil resuspension to leaf surfaces of 1% attached soil (ww) was assumed for lettuce (Li et al., 1994). The transpiration stream concentration factor (TSCF) was estimated using the regression of Burken and Schnoor (1998) instead of that of Hsu et al. (1990), besides the regression of Briggs et al. (1982). The conductance of leaves was calculated as in the fruit tree model. The TGD equilibrium approach for roots was replaced by a dynamic root model (Trapp, 2002) that considers growth dilution. Uptake of chemicals into tree fruits was calculated with an eight-compartment-model parameterized for apples (Trapp, 2007). Uptake of chemicals into potatoes was calculated with a model for diffusion into a growing sphere (Trapp et al., 2007). No special model for uptake into grains has been developed yet, and uptake into cereal was estimated with the lettuce model adapted to cereal with parameters from wheat. Birak et al. (2001) re-evaluated the data in Travis and Arms (1988) on bioaccumulation in beef and milk and suggested different regressions, which were tested but later not used in the NMF approach. Air inhalation rates were adapted to Danish conditions. Soil ingestion as uptake pathway was considered additionally.

The basic equations are listed in Table 2. The models are briefly described in the SI. Besides, all models are published, and the reader is encouraged to consult the primary literature for more details, validation studies, application examples, and further explanations. The equations were implemented as a user-friendly spreadsheet version, which is freely available from the authors.

Consumption data for children and women were taken from the Danish national survey of dietary habits and physical activity (Lyhne et al., 2005) and the pesticide monitoring report (Poulsen et al., 2005). The data are shown in Table 3 together with the consumption data suggested in the TGD. More details on their derivation can be found in the SI.

The daily dietary intake (*DDI*) of each chemical per kilogram bodyweight (μg kg^{-1} d^{-1}) was calculated by multiplying the consumption of each food item ($Consumption_i$ (kg/d)) with the calculated concentration in it (C_i (μg/kg)), and dividing by the bodyweight (kg):

$$\mathrm{DDI} = \frac{\sum_i (C_i \,\mathrm{Consumption}_i)}{\mathrm{Bodyweight}} \tag{2}$$

Table 1
Compound properties, TDI, and input concentrations for Denmark.

Parameter	Symbol (unit)	BaP	TCDD	LAS
log octanol–water partition coefficient	Log K_{OW} (L/L)	6.38	6.84	1.96 [g]
Air–water partition coefficient	K_{AW} (L/L)	1.78×10^{-4}	4.90×10^{-4}	3.55×10^{-4}
Melting point	T_m (°C)	177	295	10
Vapor pressure	V_p (Pa)	1.7×10^{-6}	6.0×10^{-8}	2.1×10^{-13}
Molar mass	M_m (g/mol)	252.32	321.97	326.5
Tolerable daily intake	TDI (μg kg bw^{-1} d^{-1})	0.005 [a]	2×10^{-6} [d]	–
Average concentration in soil	C_S (mg/kg ww)	0.069 [b]	4.02×10^{-8} [e]	4.1 [h]
Average concentration in air	C_A (μg/m^3)	0.001 [c]	6.6×10^{-10} [f]	0

$T = 20$ °C (average growing season). If not mentioned otherwise compound properties were found with the SPARC online calculator (SPARC, 2007; Hilal et al., 2003).
[a] Kroese et al. (2001); divide by factor 10 when BaP is used as an indicator for other dietary PAH.
[b] Samsøe-Petersen et al. (2000).
[c] German value (LAI, 1991).
[d] EFSA (2004).
[e] Vikelsøe (2004).
[f] Vikelsøe et al. (2006).
[g] Hand and Williams (1987).
[h] Former Danish soil quality criterion. Concentrations in soil given in mg/kg dry weight (dw) were converted to mg/kg wet weight (ww) using a soil dry density of 1.6 kg dw/L and a soil wet density of 1.95 kg ww/L.

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Table 2
Equations for the estimation of indirect human exposure via the environment.

Pathway	Equation	Ref.
All leaf crops (TGD) leafy vegetables and cereals (NMF)	$C_L = \frac{b}{a}a = \frac{Ag}{K_{LA}M_L} + k$ $b = \frac{Q}{M_L}TSCFC_SK_{WS} + (1-f_p)\frac{C_A g A}{M_L} + f_p\frac{C_A v_{dep} A/2}{M_L}$	[a]
Root vegetables	TGD: $C_R = K_{RW}K_{WS}$ NMF: $C_R = \frac{Q}{\frac{Q}{K_{RW}} + kM}K_{WS}C_S$	[a,b]
Meat [d]	TGD: $\log BTF_{meat} = \log K_{OW} - 7.6$ NMF: $\log BTF_{meat} = 1.033 \log K_{OW} - 7.735$	[c]
Milk [d]	TGD: $\log BTF_{milk} = \log K_{OW} - 8.1$ NMF: $\log BTF_{milk} = 0.992 \log K_{OW} - 8.056$	[c]
Potato (NMF)	$BCF = \frac{k_{uptake}}{k_{loss} + k_{growth}}$	[e]
Fruits (NMF)	$C_F = \frac{Q_F C_X + (1-f_P)A_F P_F C_A/K_{AW} + f_p v_{dep} C_A A_F/2}{1000 A_F P_F/K_{FW} + kM_F}$	[f]

[a] Trapp and Matthies (1995).
[b] Trapp (2002).
[c] Travis and Arms (1988).
[d] the regression of Birak et al. (2001) was tested in the NMF, but not used later.
[e] Trapp et al. (2007).
[f] Trapp (2007). C is concentration, Q is water flow, TSCF is transpiration stream concentration factor, g is conductance, A is surface area, v_{dep} is deposition velocity of particles (0 in TGD and cereal model), k is loss rate, K is partition coefficient; M is mass; P is permeability; f_P is the fraction of particles in air; BTF is the biotransfer factor (C_{meat}/intake, C_{milk}/intake), BCF is the bioconcentration factor (C_{potato}/C_{soil}). Indices: L leaf; W soil water, R root, S bulk soil; A air; F fruit; X xylem.

Similarly, daily intake of chemicals by ingestion of soil and inhalation of air were calculated and added to give the total daily intake of chemical.

Recent reports of monitoring studies of the daily oral intake of dioxin-like compounds express the exposure in WHO-TEQ (toxic equivalents). The TEQ is summing up the results for several PCDD/F and PCB. To come to an exposure to (2,3,7,8-)TCDD from these studies, we assume that about 50% of the TEQ are dioxin-like PCB (DFVF, 2005), and of the remaining PCDD/F-TEQ about 8% of TEQ are TCDD (Focant et al., 2002). This means that 4% of the WHO-TEQ are contributed to TCDD. Results from food monitoring studies may include fish, which we excluded. The intake of TCDD with fish was taken as 46% (Fromberg et al., 2005). For comparison purposes, this was deducted from estimates of exposures including fish.

3. Results

Total daily intakes of BaP and TCDD by children (4–5 years) and women (14–75 years) predicted with the new crop-specific model framework (NMF) and the TGD methods are shown in Fig. 2 a, b. The predicted intake is more than 100 times higher with the TGD than with the NMF. This is even true when the 95th percentile consumption data is used as input data for the NMF. Note that none of the models accounted for the processing of food, which could influence the intake, e.g., BaP is formed by smoking of fish and grilling of meat (SCF, 2002a).

For BaP, the predicted daily intake by the NMF is 4.9 ng kg bw^{-1} d^{-1} (average adult woman), 9.1 ng kg bw^{-1} d^{-1} (95% consumption data, adult woman), 12.8 and 21 ng kg bw^{-1} d^{-1} (child, average and 95%). With the TGD method, an intake of BaP of 2100 ng kg bw^{-1} d^{-1} was predicted for adults.

There are also differences in the predicted daily intake of TCDD. The NMF predicts 0.009 pg kg bw^{-1} d^{-1} and 0.021 pg kg bw^{-1} d^{-1} for the average adult and the 95%-consumption adult, and 0.035 and 0.063 pg kg bw^{-1} d^{-1} for the average and 95%-consumption child. The predicted daily intake with TGD is 1.4 pg kg bw^{-1} d^{-1} for adults.

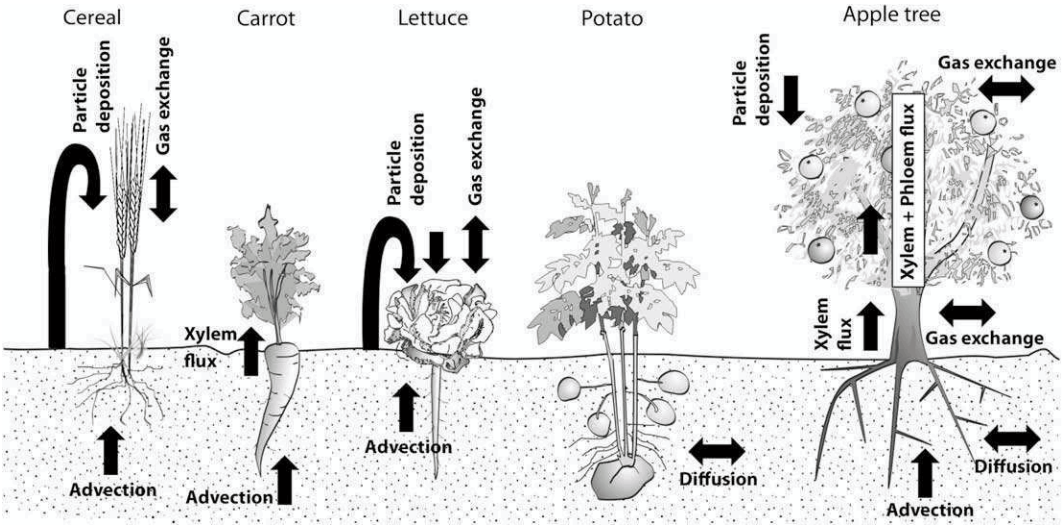

Fig. 1. Overview of crop-specific uptake models and processes considered.

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Table 3
Daily consumption data for Danish consumers of the age 4-5 years and 14-75 years (females), mean and 95th percentile for both groups, and consumption data suggested in the TGD.

Food type	4–5		14–75 (♀)		TGD
	Mean	95th	Mean	95th	
Root vegetables (g/d)	30	54	43	89	384[c]
Potatoes (g/d)	56	137	90	198	
Lettuce (g/d)	6	11	9	18	1200[d]
Other leafy veg. (g/d)	7	13	10	21	
Tree fruits (g/d)	111	235	137	318	
Cereal products (g/d)	185	269	195	309	
Milk (g/d)	448	796	303	754	561
Meat (non-poultry) (g/d)	76	138	89	166	301
Inhalation (m^3/d)	8.3	28.8[a]	11.3	38.4[a]	20×0.75[e]
Soil ingestion (mg/d)	100	200[b]	50	300[b]	0
Bodyweight (kg)	22	22	67.3	67.3	70

[a] Moderate activity.
[b] ECETOC (2001).
[c] Only one below-ground crop type in TGD.
[d] Only one above-ground crop type in TGD.
[e] Inhalation rate is 20 m^3/d, hereof 75% is bioavailable.

For LAS, the numbers differ much less (not shown). The predicted daily intake by NMF of an average adult woman is 88 μg kg bw^{-1} d^{-1}, of an average child is 228 μg kg bw^{-1} d^{-1}. The respective numbers using the 95%-consumption data are 160 and 376 μg kg bw^{-1} d^{-1} for woman and child, respectively. The TGD predicts a daily intake of LAS of 1024 μg kg bw^{-1} d^{-1} for adults.

Concentrations in food items predicted with the NMF and the TGD are shown in Table 4. The TGD models predict high concentrations of BaP in roots, namely 373 μg/kg (fresh weight), but about a factor of 100 lower concentrations in leaves (3.1 μg/kg). The NMF models predict very similar concentrations of BaP in leaves and lettuce, 5.0 and 5.7 μg/kg. The predicted concentrations in roots with the NMF are much lower than with TGD, at 0.23 μg/kg. Predicted concentrations in potatoes (NMF) are about factor three lower than those in roots (0.07 μg/kg). Predicted concentrations in fruits (NMF) are the lowest of all crop types, 0.02 μg/kg. Predicted concentrations in cereals (NMF) are 1 μg/kg.

For TCDD, the pattern is similar. The value obtained with the TGD for leaves (0.13 pg/kg) is within the range of values predicted with the NMF for the various crops (0.006–1 pg/kg). The value of the TGD for roots is orders of magnitudes higher (252 pg/kg). This is due to the assumption of phase equilibrium between root and soil in the TGD, while the new root model is dynamic and considers growth dilution. For leaves, the NMF predicts higher concentrations than does TGD for both BaP and TCDD. The reason is the consideration of particle deposition, which lacks in the TGD. However, gaseous uptake is the more important route, and the difference is small. Concentrations of TCDD in meat and milk were calculated with the same regressions in both model systems. Still, there is a small difference, due to differences in input concentrations (leaves) and consumption data of cows.

From the predicted concentrations can be seen that the large difference between TGD and NMF in the prediction of the total daily intake of BaP and TCDD can be contributed mainly to the difference in the root model.

For LAS, both model systems predict relatively similar concentrations in food items. This is to be expected, since the dynamic root model and the equilibrium approach give similar BCF for less lipophilic compounds, and there is also only a small difference between NMF and TGD in the results of the leaf model. Intake of LAS via meat and milk is of low relevance for the total daily intake. Due to the low log *K*ow, this compound does not accumulate in the food chain.

4. Discussion

4.1. Studies on total daily exposure via diet

The total daily exposure found in diet studies is also shown in Fig. 2 a, b.

For the average daily exposure of adults in Denmark to BaP, 3.7 ng kg bw^{-1} d^{-1} was found (Larsen, 1993). Children from the UK of 4–6 years were on average exposed to 3.3 ng kg bw^{-1} d^{-1}, the 97.5%-exposure was at 5.0 ng kg bw^{-1} d^{-1}, and the exposure of adults in the UK was determined to 1.6 ng kg bw^{-1} d^{-1} (mean) and 2.7 ng kg bw^{-1} d^{-1} (maximum) (FSA, 2002). For the US, a range between 0.60 and 0.89 ng kg bw^{-1} d^{-1} was estimated (Kazerouni et al., 2001). Adults in the Netherlands had a daily exposure to BaP of 1.8 (mean) to 6.2 (maximum) ng kg bw^{-1} d^{-1} (De Vos et al., 1990). The numbers include smoked fish and grilled meat. However, the contribution is small (approximately 10%, De Vos et al. (1990)), except for the US data, where grilled and barbecued meat accounted for 21% of the daily exposure to BaP (Kazerouni et al., 2001). As can be seen, these values are close to the predicted daily exposure to BaP using the NMF (Fig. 2a), whereas the TGD estimate is three orders of magnitude higher than the measured data.

The same trend in prediction accuracy is seen for TCDD (Fig. 2b). The daily exposure to WHO-TEQ from diet excluding fish of children age 4–6 in the period 1998–2003 was 1.5 (average) and 2.4 (95th percentile) pg kg^{-1} d^{-1}, Danish adults were exposed to 0.51 (average) and 0.91 (95th percentile) pg kg^{-1} d^{-1} (Fromberg et al.,

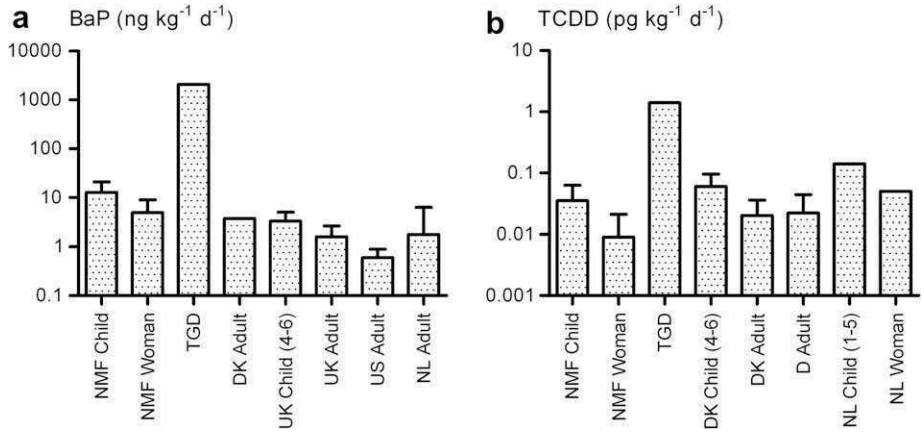

Fig. 2. a, b. Daily dietary intake estimates based on calculations compared to measured intake. Error bars give the 95th percentile (NMF and DK data) or maximum values (US, NL, D). BaP: DK Adult (Larsen, 1993), UK Child 4–6 and UK Adult (FSA, 2002), US Adult (Kazerouni et al., 2001), NL Adult (De Vos et al., 1990). TCDD: DK Child (4–6) and DK Adult (Fromberg et al., 2005), D Adult (BfR, 2006), NL Child (1–5) and NL Woman (Patandin et al., 1999). Measured TCDD-data given as WHO-TEQ in the original references.

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Table 4
Calculated concentrations in food items compared to experimental data.

Food type	BaP (μg/kg fw)			TCDD (pg/kg fw)			LAS (mg/kg fw)	
	NMF	TGD	Measured	NMF	TGD	Measured	NMF	TGD
Root vegetables	0.23	373	0.15 [a] 0.01–0.1 [b] 0.06 [c]	0.056	252	–	6.6	8.2
Potatoes	0.07		0.17 [a]	0.016		–	2.8	
Lettuce	5.7		0.6–5.6 [l]	1.0		0.03 [d]	63	
Other leafy veg.	5.0	3.1	0.10–0.12 [a] 0.2–48 [b] 3.0–4.2 [l]	0.62	0.13	0.02 [d] 20 [e,f]	63	57
Tree fruits	0.02		0.10 [a] 0.03 [b] 0.07 [c] 1.5 [l]	0.006		–	6.0	
Cereal products	1.0		0.02–0.25 [a] 0.09–0.32 [c] 0.04–5.4 [l]	0.12		–	17	
Plants average	2.0 [m]	188 [m]	3.0 [m]	0.3 [m]	126 [m]	0.4 [g,h]	26 [m]	33 [m]
Milk	–	–	0.02 [a] 0.01 [c]	1.2	0.68	2.9 [i,j] 0.74 [g,h,j]	0.004	0.031
Meat (non-poultry)	–	–	0.05 [c]	2.4	2.2	2.5–22 [i,k] 25 [e,k] 2.0–6.0 [g,h,k]	0.005	0.009

[a] Kazerouni et al. (2001).
[b] Samsøe-Petersen et al. (2002).
[c] FSA (2002).
[d] Tsutsumi et al. (2002).
[e] Domingo et al. (1999).
[f] Assuming $\rho_{dry} = 0.1$ kg dw/L and $\rho_{wet} = 0.5$ kg ww/L.
[g] Based on TCDD being 4% of WHO-TEQ.
[h] BfR (2003).
[i] Focant et al. (2002).
[j] Assuming a fat content of 0.0368 (Birak et al., 2001).
[k] Assuming a fat content of 0.25 (Birak et al., 2001).
[l] SCF (2002a); some values are from industrial areas.
[m] Average of values in the Table.

2005). Assuming 4% of TEQ is TCDD (see Section 2), the daily exposure of adults was between 0.02 (average) and 0.036 (95th percentile) pg TCDD kg^{-1} d^{-1}, for children age 4–6 it was 0.06 (average) and 0.096 (95th percentile) pg TCDD kg^{-1} d^{-1}. The average daily exposure to WHO-TEQ in Germany was between 1 and 2 pg kg^{-1} d^{-1}, including fish (BfR, 2006). This corresponds to about 0.02 to 0.04 pg kg^{-1} d^{-1} of TCDD without fish. From the Netherlands, a daily exposure to WHO-TEQ of 6.3 (adult woman) and 6.5 pg kg^{-1} d^{-1} (child aged 1–5 years) was reported (Patandin et al., 1999), i.e. 0.136 and 0.140 pg kg^{-1} d^{-1} of TCDD in diet excluding fish. As can be seen from Fig. 2b, the daily exposure to TCDD by an average adult woman using NMF is slightly underestimated, but the estimate for the intake by children is quite close to estimates based on measured values. The TGD, however, clearly overpredicts the dietary exposure to TCDD.

According to the NMF calculations, children are exposed approximately 2–4 times as much as adults per kg bodyweight (Fig. 2 a, b). This is in agreement with previous measured results for BaP in vegetables (Boyd et al., 1999), dioxins in the Danish diet (Fromberg et al., 2005), and dioxins in vegetables and meat in an impacted area (Nouwen et al., 2001).

No data on the daily exposure to LAS with food was found.

4.2. Tolerable Daily Intake (TDI)

Diet is the major source of human exposure to BaP in non-smokers (SCF, 2002b; Phillips, 1999), similar for dioxins (Pohl et al., 1995; Päpke, 1998). It was estimated that 90% of the background exposure to dioxins in Denmark stems from food (Jensen, 2003). By assuming that the exposure through other routes than those considered in this study (diet, soil ingestion and inhalation) is small, the calculated exposures can be compared to the TDI for TCDD and BaP (Table 1). The TDI for TCDD was not exceeded. On the other hand, the estimated exposure to BaP with diet was close to or above the virtually safe dose of BaP (Kroese et al., 2001), in particular by children. This underlines that it is important to consider children in exposure assessments of environmental compounds.

4.3. Measured concentrations in food items

Table 4 shows also measured concentrations in various food items and from several sources.

The range of measured concentrations of BaP in food crops is quite large, from 0.01 to 48 μg/kg. Generally, leafy vegetables and lettuce have the highest concentrations, followed by cereals, potato and root vegetables. The average concentration of the crop-specific models in NMF is 2.0 μg/kg, while the average of the measured concentrations is 3.0 μg/kg. All predicted concentrations are in the range of measured data, except the prediction of the TGD for roots which is far too high. It can be concluded that the method, i.e. the assumption of equilibrium concentration in roots, does overestimate the concentration of lipophilic compounds.

Based on 7200 samples, a German study (BfR, 2003) reports the average contamination of food with dioxins and dioxin-like compounds. The average concentration in fruits and vegetables is 10 pg WHO-TEQ/kg, corresponding to an approximate TCDD concentration of 0.4 pg/kg. The TGD estimate for concentration of TCDD is 0.13 pg/kg for leaves, and much higher for roots (252 pg/kg), giving an average of 126 pg/kg for plants. The NMF-predictions

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Table 5
The contribution (%) of input sources (soil versus air), and soil ingestion, inhalation, drinking water and food stuffs to the daily intake of contaminant.

%	BaP			TCDD			LAS		
	TGD	NMF 4–5	NMF 14–75	TGD	NMF 4–5	NMF 14–75	TGD	NMF 4–5	NMF 14–75
Soil source	97	12	12	99	16	18	100	100	100
Air source	3	88	88	1	84	82	–	–	–
Soil ingestion	–	2	1	–	–	–	–	–	–
Inhalation	–	3	3	–	1	1	–	–	–
Roots	97	2	3	99	–	–	4	4	5
Potatoes	–	1	2	–	–	–	–	3	4
Leafy veg.	3	12	15	–	1	1	95	9	11
Lettuce	–	12	19	–	1	1	–	8	9
Fruits	–	1	1	–	–	–	–	13	14
Milk	–	–	–	–	66	54	–	–	–
Meat	–	–	–	1	28	39	–	–	–
Cereal	–	66	59	–	3	3	–	63	57

– : below 1%

for TCDD in crops vary from 0.006 pg/kg (tree fruits) to 1.0 pg/kg (lettuce), with 0.3 pg/kg in average.

The predicted concentrations in meat and milk are close to or in the range of measured concentrations. Birak et al. (2001) revised the regressions of Travis and Arms (1988) for bioaccumulation in meat and milk. We tested the new regressions in this study. The bioaccumulation factors obtained for TCDD were about factor 10 lower than those obtained from Travis and Arms' regressions, but from the comparison to measured data we could not conclude that the new BTF regressions would improve the predictions.

No measured data were found for the concentrations of LAS in foodstuff. A BCF ray grass leaf to soil of 0.15 (kg_{ww} soil kg_{ww} $plant^{-1}$) was given by Tørsløv et al. (1997). This value is lower than the calculated value (BCF leaves is 15), probably due to degradation.

The sources of environmental compounds in the diet (without fish) can be identified by two calculations, one with soil as sole input source of the chemicals and one with air (Table 5). According to the TGD, the most relevant source of all compounds in the diet is soil (97% of BaP and 99% of TCDD). For LAS, the uptake into the terrestrial food chain is 100 percent from soil (because air concentration was set to zero). According to the NMF, soil is less relevant as source of contamination of the diet with BaP (12%, child and adult) and TCDD (16% (child) and 18% (adult)). This is in accordance with results from experimental studies, which showed that the most important source of BaP in food is from air via gas and particle deposition onto and uptake into crops (JECFA, 1991; Phillips, 1999). Likewise, for TCDD it has been shown that uptake from air into vegetation is the dominant uptake pathway (Schuhmacher et al., 2006).

Furthermore, the most important food stuffs contributing to daily exposures (excluding fish) can be identified (Table 5). According to the TGD, roots are the dominant source of BaP and TCDD in the diet (97–99%). According to the NMF, the major contribution to BaP in the diet is from cereals and also by leafy vegetables and lettuce. BaP enters these crops mainly from air. Indeed, previous studies have shown that major dietary sources of BaP are cereals, vegetables, oils and fats (SCF, 2002b; Phillips, 1999). The TGD gives roots as the major uptake pathway also for TCDD, while the NMF gives milk and meat. A Danish diet study (Fromberg et al., 2005) has previously identified fish (not considered here), followed by milk and meat as the most important sources of dioxins in the diet. According to Travis and Hattemerfrey (1991), food contributes with 98.8% to the human intake of TCDD, inhalation of air contributes 1.1% and ingestion of soil 0.05%. Beef is the most important foodstuff, followed by milk and dairy products and fish. Crops contribute with 3.4% to the total uptake of TCDD. According to the NMF, cereals and fruits are the most important sources of LAS in the diet. This result is questionable, because the calculations do not include a possible degradation of LAS. Inhalation and soil ingestion play a minor role for all three compounds.

In a study by Swartjes (2007), the exposure of adults to soil contaminants was calculated with 7 European exposure models. Different from the results of our study, soil ingestion was the most important exposure pathway for BaP (average 49%), consumption of crops was less important (34% in average) and inhalation of air (only indoor air) was not relevant (0%). This difference in uptake pathways can largely be explained by the difference in scenarios. In the study of Swartjes, a highly contaminated soil was considered, with 40 mg/kg of BaP, and the contribution from air was negligible. This was opposite in our background contamination scenario (Tables 1 and 5). Second, uptake of BaP with soil attached to leaves was counted to the crop consumption pathway in our study. By default, 1% soil is attached to lettuce in the NMF. Female adults consume 9 g lettuce per day; this corresponds to 90 mg attached soil per day and is higher than the 50 mg direct soil ingestion of adults (Table 3).

The study by Swartjes (2007) also showed that model estimations of human exposure can show large variations, depending on model and scenario. The variation of the predicted exposure via the crop consumption pathway was "substantial" (up to factor 10), using seven different European exposure assessment tools.

4.4. Limitations

The models and estimation methods have limitations, which are listed in the references for the models. The limitations of the model system are the sum of the limitations of the single elements. This was investigated by Trapp and Schwartz (2000). For example, the common regression range of all regressions (and thus the applicability domain) suggested in the TGD for indirect human exposure assessment is only from log *K*ow 3–4.7. Strictly seen, none of the three compounds studied here, LAS, BaP and TCDD, falls in this range.

The TGD was designed as a "reasonable worst-case" (EC, 2003). As shown in this study, it really overestimates the exposure to the lipophilic compounds BaP and TCDD. The largest deviation was seen for roots. A second reason for the overestimation with TGD are the high consumption rates, which represent the highest average consumption rates in the EU member states for each food item. The resulting food basket is unrealistic. A more controlled approach would be to use 95%-probability consumption data, as was suggested by the WHO (2007). The daily dietary exposure calculated for the reasonable worst-case using the TGD methods was higher than the exposure calculated by the NMF for the child and the 95%-consumption data. It may be concluded that the TGD is (over-) protective also for children, except for some scenarios where the TGD could tend to underestimate (e.g. main input to food crops via particle deposition from air).

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5. Conclusions

Exposure of children to chemicals in the environment via food, inhalation and soil ingestion was found to be higher than the exposure of adults. It is recommended that the risk assessment procedure for chemicals in the environment in the future should consider children explicitly as a relevant and particularly vulnerable target group. Generally, the new crop-specific model framework was more realistic in predicting the dietary exposure to environmental compounds for both children and adults, compared to the TGD. The major reason is the more realistic root uptake model. But the NMF also gives a more detailed and accurate picture of the dietary exposure and the sources of contamination. This is valuable information for risk management and can help to decide which risk reduction efforts should be prioritized.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2008.11.021.

References

BfR (Bundesinstitut für Risikobewertung), 2003. Mittlere Dioxinkonzentrationen in Lebensmitteln in Deutschland von 2000 bis 2003. Available from: http://www.pop-dioxindb.de/d/stat_datenuebersicht-lebensmittel.html.

BfR (Bundesinstitut für Risikobewertung), 2006. EU-Höchstgehalte für Dioxine und dioxinähnliche PCB in Fisch schützen Vielverzehrer von fetthaltigem Fisch nicht immer ausreichend. Gesundheitliche Bewertung Nr Available from: http://www.bfr.bund.de/cm/208/eu_hoechstgehalte_fuer_dioxine_und_dioxinaehnliche_pcb_in_fisch.pdf 041/2006 des BfR.

Birak, P., Yurk, J., Adeshina, F., Lorber, M., Pollard, K., Choudhury, H., Kroner, S., 2001. Travis and arms revisited: a second look at a widely used bioconcentration algorithm. Toxicology and Industrial Health 17, 163–175.

Boyd, H.B., Pedersen, F., Cohr, K.H., Damborg, A., Jakobsen, B.M., Kristensen, P., Samsoe-Petersen, L., 1999. Exposure scenarios and guidance values for urban soil pollutants. Regulatory Toxicology and Pharmacology 30, 197–208.

Brand, E., Otte, P.F., Lijzen, J.P.A., 2007. CSOIL 2000: an Exposure Model for Human Risk Assessment of Soil Contamination. RIVM Report 711701054/2007. National Institute of Public Health and the Environment. Available from:. http://rivm.openrepository.com/rivm/bitstream/10029/13385/1/711701054.pdf.

Briggs, G.G., Bromilow, R.H., Evans, A.A., 1982. Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. Pesticide Science 13, 495–504.

Burken, J.G., Schnoor, J.L., 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environmental Science and Technology 32, 3379–3385.

Ciganek, M., Neca, J., 2006. Polycyclic aromatic hydrocarbons in porcine and bovine organs and tissues. Veterinarni Medicina 51, 239–247.

Czub, G., McLachlan, M.S., 2004. A food chain model to predict the levels of lipophilic organic contaminants in humans. Environmental Toxicology and Chemistry 23, 2356–2366.

De Vos, R.H., Vandokkum, W., Schouten, A., Dejongberkhout, P., 1990. Polycyclic aromatic-hydrocarbons in Dutch total diet samples (1984–1986. Food and Chemical Toxicology 28, 263–268.

DEFRA(Department for Environment Food and Rural Affairs), 2002. The Contaminated Land Exposure Assessment Model (CLEA): Technical Basis and Algorithms, vol. 10. R&D Publications CLR Environment Agency. Available from: http://publications.environment-agency.gov.uk/pdf/SCLR10-e-p.pdf.

DFVF (Danmarks Fødevareforskning), 2005. Dioxinhandlingsplan 2000–2004. Slutrapport. Available from: http://www.dfvf.dk/Admin/Public/DWSDownload.aspx?File=Files%2FFiler%2FF%C3%B8devaresikkerhed%2FOrganiske+forureninger%2Fdioxin-DFVFrapport2005.pdf.

Domingo, J.L., Schuhmacher, M., Granero, S., Llobet, J.M., 1999. PCDDs and PCDFs in food samples from Catalonia, Spain. An assessment of dietary intake. Chemosphere 38, 3517–3528.

EC (European Commission), 2003. Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, European Communities, Italy. Available from:http://ecb.jrc.it/documents/TECHNICAL_GUIDANCE_DOCUMENT/EDITION_2/

EC (European Commission), 2005. Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in air. Official Journal of the European Union L 23/3 Available from: http://eur-lex.europa.eu/LexUriServ/site/en/oj/2005/l_023/l_02320050126en00030016.pdf.

EC (European Commission), 2006. European Parliament and the Council of the European Union (2006): Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals), 2001. Exposure Factors Sourcebook for European Populations (with Focus on UK Data). Technical Report No. 79, Brussels, Belgium.

EFSA (European Food Safety Authority), 2004. Dioxins. Methodologies and principles for setting tolerable intake levels for dioxins, furans, and dioxinlike PCBs.EFSA Scientific Colloquium Summary Report, Brussels, Belgium. Available from: http://www.efsa.europa.eu/etc/medialib/efsa/press_room/publications/scientific/1497.Par.0003.File.dat/efsa_dioxins1.pdf.

Focant, J.F., Eppe, G., Pirard, C., Massart, A.C., Andre, J.E., De Pauw, E., 2002. Levels and congener distributions of PCDDs, PCDFs and non-ortho PCBs in Belgian foodstuffs – assessment of dietary intake. Chemosphere 48, 167–179.

Fromberg, A., Larsen, E.H., Hartkopp, H., Larsen, J.C., Granby, K., Jørgensen, K., Rasmussen, P.H., Cederberg, T., Christensen, T., 2005. Chemical contaminants. Food monitoring, 1998–2003. Part I. FødevareRapport 2005:01. Danish Veterinary and Food Administration. Available from: http://gl.foedevarestyrelsen.dk/FDir/Publications/2005001/rapport.PDF.

FSA (Food Standards Agency), 2002. PAHs in the UK diet: 2000 total diet study samples. Food Survey Information Sheet Number 31/02. Available from: http://www.food.gov.uk/multimedia/pdfs/31pah.pdf.

Hand, V.C., Williams, G.K., 1987. Structure-activity relationships for sorption of linear alkylbenzenesulfonates. Environmental Science & Technology 21, 370–373.

Hilal, S.H., Karickhoff, S.W., Carreira, L.A., 2003. Prediction of the vapor pressure boiling point, heat of vaporization and diffusion coefficient of organic compounds. Qsar & Combinatorial Science 22, 565–574.

Hsu, F.C., Marxmiller, R.L., Yang, A.Y.S., 1990. Study of root uptake and xylem translocation of cinmethylin and related compounds in detopped soybean roots using a pressure cham-ber technique. Plant Physiology 93, 1573–1578.

JECFA (Joint FAO/WHO Expert Committee on Food Additives), 1991. Benzo(a)pyrene. WHO Food Additives Series No. 28. World Health Organization. Available from: http://www.inchem.org/documents/jecfa/jecmono/v28je18.htm.

Jensen, A.A., 2003. Kortlægning af dioxinforurening samt kilder til dioxinforurening i Østersøen. Miljøprojekt Nr 796 Available from: http://www2.mst.dk/udgiv/publikationer/2003/87-7972-570-8/pdf/87-7972-571-6.pdf Miljøstyrelsen.

Kazerouni, N., Sinha, R., Hsu, C.H., Greenberg, A., Rothman, N., 2001. Analysis of 200 food items for benzo[a]pyrene and estimation of its intake in an epidemiologic study. Food and Chemical Toxicology 39, 423–436.

Kroese, E.D., Muller, J.J.A., Mohn, G.R., Dortant, P.M., Wester, P.W., 2001. Tumorigenic effects in Wistar rats orally administered benzo[a]pyrene for two years (gavage studies). Implications for human cancer risks associated with oral exposure to polycycylic aromatic hydrocarbons. Rivm report no. 658603 010. National Institute for Public Health and the Environment. http://rivm.openrepository.com/rivm/bitstream/10029/9641/1/658603010.pdf.

LAI (Länderausschuss für Immissionsschutz), 1991. III. "Beurteilungsmassstäbe zur Begrenzung des Krebsrisikos durch Luftverunreinigung" in, Krebsrisiko durch Luftverunreinigungen, Ministerium für Umwelt, Raumordnung und Landwirtschaft des Landes Nordrhein-Westfalen.

Landrigan, P.J., Kimmel, C.A., Correa, A., Eskenazi, B., 2004. Children's health and the environment: public health issues and challenges for risk assessment. Environmental Health Perspectives 112, 257–265.

Larsen, P.B., 1993. Benzin- og dieselforurenede grunde. Toksikologisk vurdering. Environmental Project No. 223. Danish Environmental Protection Agency. Available from: http://www2.mst.dk/Udgiv/publikationer/1993/87-7810-063-1/pdf/87-7810-063-1.pdf.

Li, J.G., Gerzabek, M.H., Muck, K., 1994. An experimental study on mass loading of soil particles on plant surfaces. Bodenkultur 45, 15–24.

Lyhne, N., Christensen, T., Groth, M.V., Fagt, S., Biltoft-Jensen, A., Hartkopp, H., Hinsch, H.-J., Matthiessen, J., Møller, A., Saxholt, E., Trolle, E., 2005. Danskernes kostvaner 2000–2002. Hovedresultater, Danmarks Fødevareforskning. Available from: http://www.dfvf.dk/Files/Filer/Ern%C3%A6ring/kostunders%C3%B8gelser/DKV2002.pdf.

McCrady, J.K., Maggard, S.P., 1993. Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Environmental Science & Technology 27, 343–350.

Please cite this article in press as: Charlotte N. Legind, Trapp, S., Modeling the exposure of children and adults via diet to chemicals in the environment with crop-specific models, Environ. Pollut. (2009), doi:10.1016/j.envpol.2008.11.021

Nouwen, J., Cornelis, C., De Fre, R., Wevers, M., Viaene, P., Mensink, C., Patyn, J., Verschaeve, L., Hooghe, R., Maes, A., Collier, M., Schoeters, G., Van Cleuvenbergen, R., Geuzens, P., 2001. Health risk assessment of dioxin emissions from municipal waste incinerators: the Neerlandquarter (Wilrijk, Belgium). Chemosphere 43, 909–923.

Päpke, O., 1998. PCDD/PCDF: Human background data for Germany, a 10-year experience. Environmental Health Perspectives 106, 723–731.

Patandin, S., Dagnelie, P.C., Mulder, P.G.H., de Coul, E.O., van der Veen, J.E., Weisglas-Kuperus, N., Sauer, P.J.J., 1999. Dietary exposure to polychlorinated biphenyls and dioxins from infancy until adulthood: a comparison between breast-feeding, toddler, and longterm exposure. Environmental Health Perspectives 107, 45–51.

Phillips, D.H., 1999. Polycyclic aromatic hydrocarbons in the diet. Mutation Research-Genetic Toxicology and Environmental Mutagenesis 443, 139–147.

Pohl, H., Derosa, C., Holler, J., 1995. Public health assessment for dioxins exposure from soil. Chemosphere 31, 2437–2454.

Poulsen, M.E., Andersen, J.H., Petersen, A., Hartkopp, H., 2005. Pesticides. Food Monitoring, 1998–2003. Part 2. FødevareRapport 2005:2. Danish Veterinary and Food Administration. Available from: http://gl.foedevarestyrelsen.dk/FDir/Publications/2005002/Rapport.pdf.

Samsøe-Petersen, L., Larsen, E.H., Andersen, N.L., 2000. Optagelse af metaller og PAH-forbindelser i grøntsager og frugt. Environmental Project No. 571. Danish Environmental Protection Agency. Available from: http://www2.mst.dk/Udgiv/publikationer/2000/87-7944-304-4/pdf/87-7944-305-2.pdf.

Samsøe-Petersen, L., Larsen, E.H., Larsen, P.B., Bruun, P., 2002. Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. Environmental Science & Technology 36, 3057–3063.

SCF (Scientific Committee on Food), 2002a. Annex: background document to the opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food. Polycyclic Aromatic Hydrocarbons – Occurrence in foods, dietary exposure and health effects. Available from: http://ec.europa.eu/food/fs/sc/scf/out154_en.pdf.

SCF (Scientific Committee on Food), 2002b. Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food., Brussels, Belgium. Available from: http://ec.europa.eu/food/fs/sc/scf/out153_en.pdf.

Schuhmacher, M., Jones, K.C., Domingo, J.L., 2006. Air-vegetation transfer of PCDD/PCDFs: an assessment of field data and implications for modeling. Environmental Pollution 142, 143–150. SPARC, on line calculator 2007. Available from: http://ibmlc2.chem.uga.edu/sparc/index.cfm.

Swartjes, F.A., 2007. Insight into the variation in calculated human exposure to soil contaminants using seven different european models. Integrated Environmental Assessment and Management 3, 322–332.

Tørsløv, J., Samsøe-Petersen, L., Rasmussen, J.O., Kristensen, P., 1997. Use of Waste Products in Agriculture. Environmental Project No. 366. Danish Environmental Protection Agency. Available from:. http://www2.mst.dk/Udgiv/publications/1997/87-7810-843-8/pdf/87-7810-843-8.pdf.

Trapp, S., Matthies, M., 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environmental Science & Technology 29, 2333–2338.

Trapp, S., Schwartz, S., 2000. Proposals to overcome limitations in the EU chemical risk assessment scheme. Chemosphere 41, 965–971.

Trapp, S., 2002. Dynamic root uptake model for neutral lipophilic organics. Environmental Toxicology and Chemistry 21, 203–206.

Trapp, S., 2007. Fruit tree model for uptake of organic compounds from soil and air. Sar and Qsar in Environmental Research 18, 367–387.

Trapp, S., Cammarano, A., Capri, E., Reichenberg, F., Mayer, P., 2007. Diffusion of PAH in potato and carrot slices and application for a potato model. Environmental Science and Technology 41, 3103–3108.

Trapp, S., Ma, L., Legind, C.N., 2008. Coupled mother-child model for bioaccumulation of POPs in nursing infants. Environmental Pollution 156, 90–98.

Travis, C.C., Arms, A.D., 1988. Bioconcentration of organics in beef, milk, and vegetation. Environmental Science & Technology 22, 271–274.

Travis, C.C., Hattemerfrey, H.A., 1991. Human Exposure to Dioxin. Science of the Total Environment 104, 97–127.

Tsutsumi, T., Iida, T., Hori, T., Nakagawa, P., Tobiishi, K., Yanagi, T., Kono, Y., Uchibe, H., Matsuda, R., Sasaki, K., Toyoda, M., 2002. Recent survey and effects of cooking processes on levels of PCDDs, PCDFs and co-PCBs in leafy vegetables in Japan. Chemosphere 46, 1443–1449.

U.S. EPA (U.S. Environmental Protection Agency), 2006. Children's Environmental Health: 2006 Report. Environment, Health, and a Focus on Children. EPA 100-F-06-011 Available from: http://yosemite.epa.gov/ochp/ochpweb.nsf/content/CEH06_Final.htm/$file/CEH06_Final.pdf.

Vikelsøe, J., 2004. Dioxin in Danish Soil. A Field Study of Selected Urban and Rural Locations. NERI Technical Report, No. 486. National Environmental Research Institute. Available from:. http://www2.dmu.dk/1_viden/2_Publikationer/3_fagrapporter/rapporter/FR486.PDF.

Vikelsøe, J., Andersen, H.V., Bossi, R., Johansen, E., Chrillesen, M.-A., 2006. Dioxin in the Atmosphere of Denmark. A Field Study at Selected Locations. NERI Technical Report No. 565. National Environmental Research Institute. Available from:. http://www2.dmu.dk/1_viden/2_Publikationer/3_fagrapporter/rapporter/FR565.PDF.

WHO (World Health Organisation), 2007. Principles for evaluating health risks in children associated with exposure to chemicals. IPCS. Unedited draft. Restricted. Available from: http://www.who.int/ipcs/features/ehc_children.pdf.

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Supporting Information

Modeling the exposure of children and adults to chemicals in the environment

Complete set of equations for crop- and food specific human exposure assessment

Charlotte N. Legind and Stefan Trapp 2008

Table of Contents

33 pages including 9 tables

1 Introduction

This document lists the equations and the input data for the new model system used in this study.

The models are implemented in Excel and fully parameterized. All models are published in the scientific literature. If modifications were made, this is mentioned.

Crop-specific models, overview. Crop-specific models were developed for most major crop types, to mention are root vegetables, leafy vegetables, cereal, potato and fruits (apples). All models are based on the same physico-chemical principles and describe the same basic processes, such as advective uptake into plants, diffusive uptake, partitioning to plant tissue, fluxes inside the plants with xylem and phloem, dilution by growth, and particle deposition from soil and air. This mechanistic principle of building is similar for all crop-specific models. However, the actually occurring processes and the parameterization depend on the type of crop (Figure 1). All model equations are given in this document. Nonetheless, the reader is encouraged to consult the primary literature for more details, validation studies, application examples and further explanations.

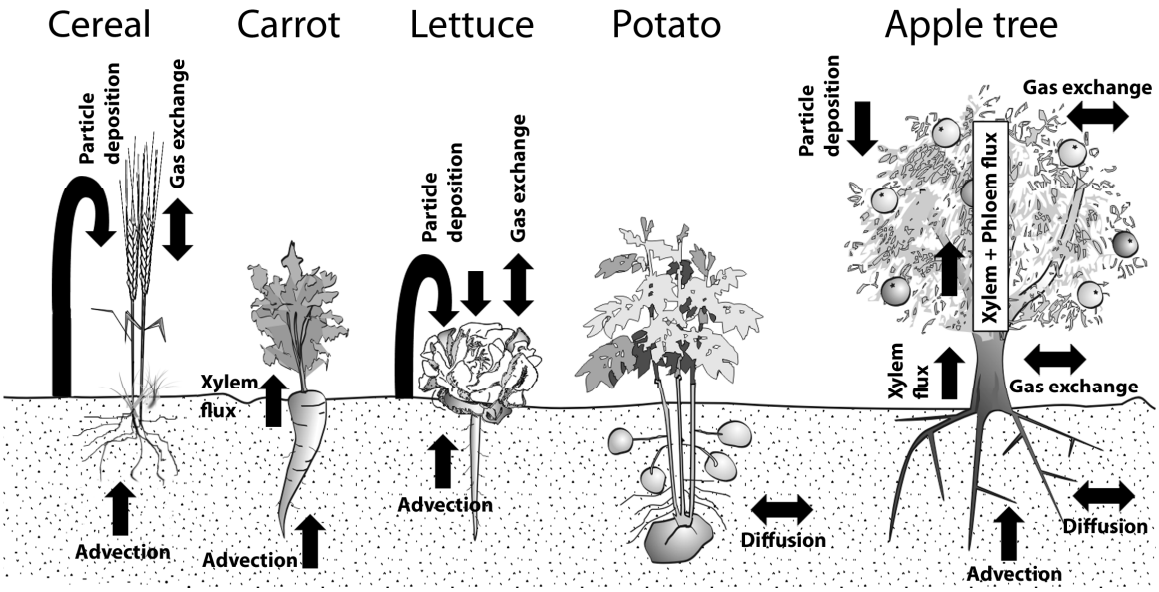

Figure 1. Overview of crop-specific uptake models and processes considered

2 Root Model

A separate root model was developed by Trapp (2002), considering uptake and loss in roots by advective processes plus dilution by growth. Diffusion into and across the peel is not considered, with the argument that the root vegetables, such as carrots, are usually peeled. And the chemicals do not reach the bulk of a thick root by diffusion because chemical equilibrium is not reached for more lipophilic compounds.

2.1 Chemical equilibrium between fine roots and soil. The natural bulk soil consists of soil matrix, soil solution and soil gas. This is considered in the calculation of the chemical equilibrium between soil water and wet bulk soil K_{WS}.

$$\frac{C_W}{C_S} = K_{WS} = \frac{\rho_{wet}}{OC \times K_{OC} \times \rho_{dry} + W_S + G_S \times K_{AW}} \quad (\text{kg L}^{-1})$$

where C_W (mg L^{-1}) is the concentration of the chemical in soil water and C_S (mg kg^{-1}) in wet bulk soil; ρ_{wet} is the density of wet soil (kg L^{-1}), OC is the fraction of organic carbon (kg kg^{-1}), ρ_{dry} (kg L^{-1}) is the density of the dry soil, and W_S and G_S are the volume fractions of water and gas in soil (L L^{-1}). K_{AW} is the partition coefficient between air and water. The air phase can usually be neglected, except for very high K_{AW}. K_{OC} (L kg^{-1}) is the partition coefficient between organic carbon and water and can be estimated from the octanol-water partition coefficient K_{OW} (EC, 2003):

$$\log K_{OC} = 0.81 \times \log K_{OW} + 0.1$$

The phase equilibrium between roots and water, K_{RW} (L kg^{-1}), considers sorption to root lipids and dissolution into the aqueous solution of root cells:

$$K_{RW} = \frac{C_R}{C_W} = W_R + L_R \times a \times {K_{OW}}^{b} + G_R \times K_{AW}$$

where C_R is concentration in root (mg kg fresh $weight^{-1}$), C_W (mg L^{-1}) is concentration in water, W_R (L kg^{-1}), L_R (kg kg^{-1}), and G_R (L kg^{-1}) are water, lipid, and air contents of the root, '*b*' for roots

is 0.77 and 'a' = $1/\rho_{Octanol}$ = 1.22 L kg^{-1}. The concentration in fine roots in phase equilibrium is thus

$$C_{R,eq} = C_S \times K_{RS} = C_S \times K_{RW} \times K_{WS}$$

2.2 Dynamic uptake model for thick roots ("Carrot model")

The "carrot model" calculates uptake into roots with the transpiration water.
Change of chemical mass in roots = +flux in with water – flux out with water

$$\frac{dm_R}{dt} = C_W \times Q - C_{Xy} \times Q$$

m_R is the mass of chemical in roots (mg), Q is the transpiration stream (L/d), C_{XY} is the concentration in the xylem (mg/L) at the outflow of the root. Diffusive uptake is not considered (the carrot is peeled!). From mass, the concentration is derived by dividing through the mass of the root M:

$$\frac{dC_R}{dt} = C_W \times Q/M - C_{Xy} \times Q/M$$

If growth is exponential, and the ratio Q/M (transpiration to plant mass) is constant, the growth by exponential dilution can be considered by a first-order growth rate k (d^{-1}):

$$\frac{dC_R}{dt} = C_W \times Q/M - C_{Xy} \times Q/M - k \times C_R$$

If the xylem sap is in equilibrium with the root, the concentration $C_{Xy} = C_R/K_{RW}$. Then,

$$\frac{dC_R}{dt} = C_W \times Q/M - C_R/K_{RW} \times Q/M - k \times C_R$$

Setting this to steady-state ($dC_R/dt = 0$) gives for the concentration in the root C_R:

$$C_R = \frac{Q}{\frac{Q}{K_{RW}} + kM} C_W$$

The ratio of the concentration in soil water C_W to that in bulk soil C_{Soil} is K_{WS}, and for the bioconcentration factor *BCF* between root vegetable and bulk soil follows:

$$BCF = \frac{C_R}{C_{Soil}} = \frac{C_R}{C_W} \times K_{WS} = \frac{Q}{\frac{Q}{K_{RW}} + kM} \times K_{WS}$$

In a similar model approach, the root part of the Fruit Tree model (Trapp, 2007), diffusion into roots was also considered. The difference in the result is minimal, but the effort for calculation of diffusion is considerable. Therefore, we neglect this process here.

2.3 Parameterization of the root model

Soil data correspond to a Danish standard soil (Table S1). The parameterization of the root model is for 1 m^2 soil, with 1 kg roots, a transpiration of 1 L d^{-1} and a root growth rate of 0.1 d^{-1}. The data corresponds to those in the original reference (Trapp, 2002) (Table S2).

Table S1. Soil data.

Parameter	Symbol	Value	Unit
Soil wet density	ρ_{wet}	1.95	kg L^{-1}
Organic carbon content	OC	0.02	g g^{-1}
Soil pore water	W_S	0.35	L L^{-1}
Soil gas pores	G_S	0.1	L L^{-1}
Soil dry density	ρ_{dry}	ρ_{wet} - W_S	kg L^{-1}

Table S2. Parameters of the root.

Parameter	Symbol	Value	Unit	Value TGD	Unit
Root water content	W_R	0.89	L kg^{-1}	0.65	m^3 m^{-3}
Root lipid content	L_R	0.025 (*)	kg kg^{-1}	0.01	m^3 m^{-3}
Root air content	G_R	0.1	L kg^{-1}		
Growth rate root	k_R	0.1	d^{-1}		
Transpiration	Q	1	L d^{-1}		
Mass of thick roots	M_R	1	kg		
Density of plant	RHO_{plant}			700	kg m^{-3}

(*) This lipid content includes all lipid-like compounds, not only fat and oil, but also waxes like suberin and cutin.

2.4 TGD root model

The TGD root model uses the equilibrium approach for fine roots with the concentration in soil water as input and slightly different parameters. K_{RW} (m^3 m^{-3}) is calculated with b = 0.95:

$$K_{RW} = \frac{C_R}{C_W} = W_R + L_R \times K_{OW}{}^{b}$$

The concentration in roots is found by dividing with the plant density, RHO_{plant} (kg m^{-3}):

$$C_{R,eq} = \frac{C_W \times K_{RW}}{RHO_{plant}}$$

3 Potato Model

3.1 Equations

The potato model (Trapp et al., 2007) considers as processes diffusion from soil into spherical potatoes, dilution by growth and eventually 1st order metabolism. The equation for the steady-state is

$$\frac{C_P}{C_S} = \frac{k_1}{k_2 + k_G} \qquad \left[\frac{kg}{kg}\right]$$

where C_P (mg kg^{-1} fresh weight) and C_S (mg kg^{-1} wet weight) are the chemical concentrations in potato and soil; k (d^{-1}) are uptake rate (1), loss rate (2) and growth rate (G). The growth rate is an input data. The loss rate k_2 is deduced from a radial diffusion model

$$k_2 = \frac{23 \times D_P}{R^2}$$

where D_P (m^2 d^{-1}) is the diffusion coefficient of the chemical in potato, and R is the radius of the potato (m). The uptake rate k_1 is calculated from phase equilibrium

$$k_1 = k_2 \times \frac{K_{PW}}{K_{SW}}$$

The equilibrium between soil and water K_{SW} is $1/K_{WS}$ and is calculated as described in section 2.1. The phase equilibrium between potato and water, K_{PW}, is calculated from

$$K_{PW} = \frac{C_P}{C_W} = W + f_{CH} \times K_{CH} + L \times a \times K_{OW}{}^{b} + G_P \times K_{AW}$$

where C_W (mg L^{-1}) is the chemical concentrations in water; W is the water content of potato (L kg^{-1}); f_{CH} is the fraction of carbohydrates (L kg^{-1}); L is the lipid content (including waxes and lignin) (kg kg^{-1}); b is an empirical value describing differences between root lipids and n-octanol

and is 0.77 (Huber, 1956), $a = 1/\rho_{Octanol} = 1.22$ L kg^{-1}, G_P is the air content of the potato (L kg^{-1}), and K_{CH} is the partition coefficient of carbohydrates to water. Chiou et al. (2001) give values for $K_{CH} = 0.1$ for log $K_{OW} < 0$ to $K_{CH} = 3$ for log $K_{OW} > 3$. The carbohydrate fraction usually plays a minor role.

The diffusion coefficient in potato, D_P, is calculated with the same method as the diffusion coefficient in roots D_R (described in (Trapp, 2007)), but with potato-specific data:

$$D_P = D_{W,eff} + D_{G,eff}$$

Diffusion coefficient in potato (based on Trapp et al. (2007) and Supporting Information)

Let D_W (m^2 d^{-1}) be the diffusion coefficient of the chemical in pure water and D_G (m^2 d^{-1}) the diffusion coefficient in pure gas phase. The diffusion coefficients of chemicals can be related to the square root of the molar mass M (g mol^{-1}). The diffusion coefficient of the chemical in pure water D_W (Trapp and Matthies, 1998):

$$D_W = D_{O2} \times \frac{\sqrt{32}}{\sqrt{M}}$$

where D_{O2} is the diffusion coefficient of oxygen O_2 (M = 32 g mol^{-1}) in water (1.728 x 10^{-4} m^2 d^{-1}). For the estimation of D_G, the diffusion coefficient of water vapor D_{H2O} in air is used, with $D_{H2O} = 2.22$ m^2 d^{-1} (Trapp and Matthies, 1998)

$$D_G = D_{H2O} \times \frac{\sqrt{18}}{\sqrt{M}}$$

In porous solids (such as plant tissue), the diffusion is hampered by a "labyrinth factor", named tortuosity T. This tortuosity is estimated by the method of Millington and Quirk (cited in (Jury et al., 1983)). T_W is the tortuosity in the water pores of the plant tissue, and T_G is the tortuosity of the gas-filled pores. The expressions are not unit-true.

$$T_W = \frac{W_P^{10/3}}{(W_P + G_P)^2}$$

$$T_G = \frac{G_P^{10/3}}{(W_P + G_P)^2}$$

The fraction of chemical f_W (mg L^{-1} : mg kg^{-1}) dissolved in the water W_P (L kg^{-1}) of the plant (the ratio between concentration in water phase of the plant tissue to total concentration) is

$$f_W = \frac{C_{W,P}}{C_P} = \frac{W_P}{K_{PW}}$$

The fraction of chemical f_G (mg L^{-1} : mg kg^{-1}) present in gas pores G_P (L kg^{-1}) of the plant (the ratio between concentration in gas phase of the plant tissue to total concentration) is

$$f_G = \frac{G_P \times K_{AW}}{K_{PW}}$$

We can now define effective diffusion coefficients D_{eff} related to the total concentration. For diffusion in the water pores of the plant $D_{W,eff}$

$$D_{W,eff} = D_W \times f_W \times T_W$$

and for diffusion in the gas pores $D_{G,eff}$

$$D_{G,eff} = D_G \times f_G \times T_G$$

The sum of $D_{W,eff}$ and $D_{G,eff}$ gives the diffusion coefficient of the chemical in plant tissue D_P (m^2 d^{-1})

$$D_P = D_{W,eff} + D_{G,eff}$$

2.2 Default input data

The properties of soil are identical to those of the root model (Table S1). Table S3 lists the properties of the potato, which were taken from the original reference (Trapp et al., 2007).

Table S3. Properties of potatoes.

Parameter	Symbol	Value	Unit
Water content	W_P	0.778	L kg^{-1}
Lipid content (*)	L_P	0.001	g g^{-1}
Gas pores	G_P	0.04	L kg^{-1}
Carbohydrate fraction	f_{CH}	0.086	L kg^{-1}
Growth rate	k_G	0.139	d^{-1}
Radius	R	0.04	m

(*) This lipid content includes all lipid-like compounds, not only fat and oil, but also waxes like suberin and cutin.

The TGD uses the model for fine roots for potatoes.

4 a Leafy Vegetables Model

This model calculates the uptake of neutral organic substances into leafy vegetable or green fodder. The model was adopted in the Technical Guidance Documents (TGD) of the European Union System for the Evaluation of Substances (EUSES) (EC, 2003).

4.1 Basic Equations

For leafy vegetables, there is uptake from soil via the xylem and exchange with air (as in (Trapp and Matthies, 1995)). The change of mass in leaves = + translocation from stem + uptake from air by gaseous diffusion + uptake from air by particle deposition - loss to air by gaseous diffusion

$$\frac{dm_L}{dt} = +Q_L \times TSCF \times C_W + g \times A_L \times (1 - f_p) \times C_A + \frac{v_{dep} \times A_L}{2} \times f_P \times C_A$$
$$- \frac{g \times A_L}{K_{LA}} \times C_L - k_m \times m_L$$

where L is the index for leaves, W for soil water and A for air; Q is the transpiration stream (L d^{-1}), $TSCF$ is the transpiration stream concentration factor (L L^{-1}), C_W is the concentration of chemical in soil water (mg L^{-1}), g is the conductance for diffusive transfer between leaves and air (m d^{-1}), C_A is the concentration in air (mg m^{-3}), K_{LA} is the partition coefficient between leaves and air (m^3 kg^{-1}), ρ is the density of leaves (kg m^{-3}), k_m is a first-order rate for degradation (d^{-1}) and m_L (mg) is the mass of chemical in leaves. f_P is the fraction adsorbed on particles and v_{dep} is the deposition velocity (m d^{-1}) of particles on leaves. The deposition is only to the upper side of the leaf (A_L/2); v_{dep} is the deposition velocity of particles and is 3 m h^{-1} = 0.833 mm s^{-1} = 8.33 x 10^{-4} m s^{-1} = 72 m d^{-1} divided by 2.5 for correction from canopy to leaves (Czub and McLachlan, 2004). f_P is calculated from the vapor pressure (*Junge* equation):

$$f_P = \frac{10^{-4}}{p_S + 10^{-4}}$$

where 10^{-4} is the product of Junge constant and particle surface area (EC, 2003), and p_S is the saturation vapor pressure (Pa). For solids ($T_M > T$), the sub-cooled liquid vapor pressure $p_{S,l}$ should be used, with

$$p_{s,l} = \frac{p_s}{e^{6.79\times(1-\frac{T_m}{T})}}$$

where T_M is the melting point (K) and T is the temperature (K). The phase equilibrium between leaves and air, K_{LA} (m^3 kg^{-1}), is calculated from:

$$K_{LA} = \frac{C_L}{C_A} = \frac{W_L + L_L \times a \times K_{OW}{}^{b} + G_L \times K_{AW}}{K_{AW} \times 1000}$$

where C_L is concentration in leaves (mg kg^{-1} fresh weight), C_A (mg m^{-3}) is concentration in air, W_L (L kg^{-1}), L_L (kg kg^{-1}), and G_L (L kg^{-1}) are water, lipid, and air contents of the leaves, '*b*' for leaves is 0.95 and '*a*' = $1/\rho_{Octanol}$ = 1.22 L kg^{-1}.

For the concentration follows:

$$\frac{dC_L}{dt} = + \frac{Q_L}{M_L} \times TSCF \times C_W + \frac{g \times A_L}{M_L} \times (1 - f_P) \times C_A + \frac{v_{dep} \times A_L}{2 \times M_L} \times f_P \times C_A$$
$$- \frac{g \times A_L}{K_{LA} \times M_L} \times C_L - k \times C_L$$

where k (d^{-1}) is the sum of growth rate and degradation rate, $k = k_G + k_m$.

The equation can be rewritten and gives the standard linear differential equation

$$\frac{dC_L}{dt} = b - aC_L \quad \text{with the standard solution}$$

$$C_L(t) = C_L(0) \times e^{-at} + \frac{b}{a}(1 - e^{-at})$$

where

$$a = \frac{A \times g}{K_{LA} \times M_L} + k$$

and

$$b = C_W \times TSCF \times Q / M_L + (1 - f_P) \times C_A \times g \times \frac{A_L}{M_L} + f_P \times C_A \times v_{dep} \times \frac{A_L}{2 \times M_L}$$

The steady-state solution is $C_L(t = \infty) = \frac{b}{a}$ or

$$C_L = \frac{Q_L \times TSCF \times C_W + A_L \times g \times (1 - f_P) \times C_A + \frac{v_{dep} \times A_L \times f_P \times C_A}{2}}{\frac{A_L \times g}{K_{LA}} + k \times M_L}$$

For the exposure assessment the analytical solution with a growth period of 60 days is applied (t = 60 d).

Attached soil. Many green vegetables are contaminated by attached soil (e.g., lettuce). For a part of the vegetables, a default soil-to-plant transfer with particles of 1% attached soil was assumed, which means a minimum BCF plant/soil of 0.01 (wet wt. based), when M_L = 1 kg:

BCF with soil = BCF model + 0.01

4.3 Calculation of input parameters

Transpiration Stream Concentration Factor. The 'Transpiration Stream Concentration Factor (*TSCF*)' is defined as the concentration ratio between xylem sap and external solution (soil water).

$TSCF = C_{Xy}/C_W$

The *TSCF* according to Briggs et al. (1982) is a bell-shaped (Gaussian) curve

$$TSCF = 0.784 \times \exp\left\{\frac{-(\log K_{OW} - 1.78)^2}{2.44}\right\}$$

For poplar trees, Burken and Schnoor (1998) found a similar relation

$$TSCF = 0.756 \times \exp\left\{\frac{-(\log K_{OW} - 2.50)^2}{2.58}\right\}$$

It is recommended to use Briggs' equation for herbal plants (experiments were done with the grass barley), and Burken & Schnoors equation for woody plants (experiments were done on poplars). We use the higher value of the two *TSCF* estimates. In the original model version (Trapp and Matthies, 1995), the *TSCF* regression by Hsu et al. (1990) was used as second equation. It is not recommended to use this regression anymore, because it is based on pressure chamber experiments. The use of the pressure chamber technique may lead to artificial results (Ciucani et al., 2002). For the chemicals considered in this study, the traditional TSCF does not lead to relevant differences compared to the modern version, where the concentration in xylem is calculated from the concentration in root (Trapp, 2007).

Conductance of leaves. The relation between conductance, g (m d^{-1}), and permeability, P (m d^{-1}), is

$$g = P / K_{AW}$$

The difference is that P is related to concentrations in water, while g is related to concentrations in the gas phase. Input to the leafy vegetables model is g.

Stomata. If the water loss Q (L d^{-1}) by transpiration and the leaf surface area A (m^2) of the plant are known, the resistance of the stomatal pathway can be calculated (Trapp, 2007)

$$g_{H2O} = \frac{Q}{A \times (C_{H2O,Leaf} - C_{H2O,Air})}$$

where g (m d^{-1}) is the conductance of the stomatal pathway for water, A is the leaf area (m^2), and C_{H2O} is the concentration of water (kg m^{-3}) in the inner leaf or in air. The saturation vapour pressure of water, $p_{H2O,sat}$ (Pa), at given temperature, *Temp* (°C), may be calculated by the empirical Magnus-equation:

$$p_{H2O,sat} = 610.7 \times 10^{\frac{7.5 \times Temp}{237 + Temp}}$$ (note: it is really 237 and not 273).

The (gas-phase) concentration of water inside the leaves, $C_{H2O,Leaf}$ (kg m^{-3}), is

$$C_{H2O,sat} = \frac{p_{H2O}}{461.9 \times T}$$

where T is the absolute temperature (K), $T = Temp\ (°C) + 273.15$, 461.9 is R/M_{H2O}, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and M_{H2O} is 1 mol H_2O = 0.018 kg. The concentration of water vapour in air is the saturation water concentration C_{H2O} times the relative humidity, *rh* (-).We receive the equation

$$g_{H2O} = \frac{Q}{A \times (C_{H2O,sat} - rh \times C_{H2O,sat})}$$

To come from the conductance of water to that of the chemical, we use the fact that

$$g = \frac{D_G}{\Delta x}$$

The diffusion pathway does not change with the chemical, while the diffusion coefficient does, and so

$$g_S = g_{H2O} \times \frac{\sqrt{18}}{\sqrt{M}}$$

where g_S (m d^{-1}) is the conductance for the stomatal exchange between leaves and air for a chemical with molar mass M (g mol^{-1}). The permeability P_S (m d^{-1}) of the stomatal pathway, related to water, is then the conductance multiplied by the partition coefficient air-water K_{AW}:

$$P_S = g_S \times K_{AW}$$

Cuticles. A regression equation derived for the permeability P_C of citrus cuticles is (Kerler and Schonherr, 1988)

$$P_C = 10^{0.704 \times \log Kow - 11.2} \quad (\text{m s}^{-1})$$

Air boundary layer. After the chemical has crossed the cuticle, the next resistance is provided by the air boundary layer around the leaf. A resistance of 200 m s^{-1} was estimated as typical for a chemical with molar weight, M = 300 g mol^{-1} (Thompson, 1983). The conductance of the air boundary layer, g_{Air}, for a chemical with molar mass M is thus

$$g_{Air} = \frac{1}{200} \times \frac{\sqrt{300}}{\sqrt{M}} \quad (\text{m s}^{-1})$$

The total permeability of the cuticle pathway (m d^{-1}) is

$$P_{C,total} = \frac{1}{\frac{1}{P_C} + \frac{1}{g_{Air} \times K_{AW}}} \times 86400$$

The exchanges of the chemical through cuticle and stomata occur in parallel, and thus the permeabilities are added to derive the total permeability for the exchange between leaf and air, P_L (m d^{-1}):

$$P_L = P_S + P_{C.total}$$

Finally, the conductance (m d^{-1}) is

$$g = P_L / K_{AW}$$

4.3 Input parameters for the leafy vegetables / TGD model

The parameterization is taken from the original reference and is given in Table S4 along with the TGD parameterization.

Table S4. Parameterization of the leafy vegetables model, normalized to 1 m^2 (data taken from the original publication (Trapp and Matthies, 1995) except particle deposition velocity).

Parameter	Symbol	Value	Unit	TGD Value	Unit
Shoot mass	M_L	1	kg	0.002	m^3
Leaf area	A	5	m^2	5	m^2
Shoot density	ρ	500	kg m^{-3}	700	kg m^{-3}
Transpiration	Q	1	L d^{-1}	1	L d^{-1}
Lipid content	L_L	0.02	kg kg^{-1}	0.01	m^3 m^{-3}
Water content	W_L	0.8	L kg^{-1}	0.65	m^3 m^{-3}
Air content	G_L	0.1	L kg^{-1}		
Conductance	g	Calculated	m d^{-1}	86.4	m d^{-1}
Deposition velocity of particles	v_{dep}	28.8	m d^{-1}		
Growth rate	k_L	0.035	d^{-1}	0.035	d^{-1}
Time to harvest	t	60	d	∞	d

4.2 Differences between new leafy-vegetation-model and model formulation in the TGD

In the implementation of the TGD, no deposition of particles is foreseen. The equations for the leafy vegetables model remain the same, but $v_{dep} = 0$. Furthermore, soil attachment is not included in the TGD. A third difference is that the conductance g (deposition velocity of gaseous compounds) is set at the default value g = 86.4 m d^{-1}, while in the new version it is calculated from stomata and cuticle resistance. One more difference is the choice of the *TSCF* regression equation. The model formulation in the TGD is in accordance with the original reference (Trapp and Matthies, 1995), except for the *TSCF* regression by Hsu et al. (1990) and slightly different parameter values. Our current implementation has been updated according to the short-comings identified in (Trapp and Schwartz, 2000).

4 b Cereal Model

No specific model for uptake of organic contaminants into cereal was developed so far. Therefore, we use a modified leafy vegetables model to calculate uptake into cereal. The mass balance equation remains unchanged, but the physiological parameters, such as surface area, volume and fluxes were adapted. Particle deposition was disregarded.

4.1 Model description

Wheat flour consists of 0.15 L kg^{-1} of water, 0.02 kg kg^{-1} of lipids and 0.602 kg kg^{-1} of carbohydrates. So the major fraction is carbohydrates (Elmadfa et al., 1991).

The phase equilibrium between cereal and air is calculated from

$$K_{CA} = \frac{C_C}{C_A} = \frac{W_C + L_C \times a \times K_{OW}{}^{b} + G_C \times K_{AW} + CH_C \times K_{CH} \times \rho_{CH}}{K_{AW} \times 1000}$$

where C_C is concentration in cereal (mg kg^{-1} fresh weight), C_A (mg m^{-3}) is concentration in air, W_C (L kg^{-1}), L_C (kg kg^{-1}), G_C (L kg^{-1}), and CH_C (kg kg^{-1}) are water, lipid, air, and carbohydrate contents of cereal, '*b*' for cereal is the same as for leaves, 0.95, and 'a' = $1/\rho_{Octanol}$ = 1.22 L kg^{-1}. K_{CH} is the partition coefficient of carbohydrates to water. Chiou et al. (2001) give values for $K_{CH} = 0.1$ for log $K_{OW} < 0$ to $K_{CH} = 3$ for log $K_{OW} > 3$. The carbohydrate fraction usually plays a minor role.

The mass balance equation is

Change of mass in corn = + translocation from stem + uptake from air by gaseous diffusion - loss to air by gaseous diffusion

$$\frac{dm_C}{dt} = +Q_C \times TSCF \times C_W + g \times A_C \times (1 - f_p) \times C_A - \frac{g \times A_C}{K_{CA}} \times C_C - k_m \times m_C$$

where C is the index for cereal, W for soil water and A for air; Q_C is the water flux to corn (L d^{-1}). All other parameters are described in the section for the leafy vegetables model.

The solution of the differential equation is as before

$$\frac{dC_C}{dt} = b - aC_C$$ with the standard solution

$$C_C(t) = C_C(0) \times e^{-at} + \frac{b}{a}(1 - e^{-at})$$

where

$$a = \frac{A_C \times g}{K_{CA} \times M_C} + k$$

and

$$b = C_W \times TSCF \times Q / M_C + (1 - f_P) \times C_A \times g \times \frac{A_C}{M_C}$$

The steady-state solution is $$C_C(t = \infty) = \frac{b}{a}$$

For the exposure assessment, steady-state is assumed.

Attached soil. Cereal is, whenever possible, harvested at dry weather, and the modern machines used for this produce dust. This leads to a small, but noticeable pollution of the harvest product with soil particles. Paretzke and Garland (1992) report that milled wheat and barley corn contains 0.001 kg soil per kg dry weight. Based on this, we use a default value of 0.001 kg soil per kg cereal (wet weight) for the BCF soil to corn via soil resuspension:

BCF with soil = *BCF model* + 0.001

4.2 Input parameters for the cereal model

The parameterization is similar to the leafy vegetables model, but with adaptions. Table S5 shows the input parameters which are different from the leafy vegetables model.

Table S5. Parameterization of the cereal model, normalized to 1 m^2. Parameters not listed see Table S4.

Parameter	Symbol	Value	Unit
Cereal mass	M_L	1	kg
Cereal surface area	A_C	1	m^2
Cereal density	ρ_C	1000	kg m^{-3}
Water flux to cereal*	Q_C	0.2	L d^{-1}
Lipid content	L_C	0.02	kg kg^{-1}
Water content	W_C	0.15	L kg^{-1}
Air content**	G_L	0	L kg^{-1}
Carbohydrate content	CH_C	0.602	kg kg^{-1}
Carbohydrate density	ρ_{CH}	2	kg L^{-1}
Deposition velocity of particles**	v_{dep}	0	m d^{-1}

* sum of xylem and phloem flux

** not considered

5 Fruit Tree Model

The model consists of eight compartments (soil 1, soil 2, fine roots, thick roots, stem, leaves, fruit, air). For four compartments (thick roots, stem, leaves, fruits), the mass balances were formulated as differential equations. The equations for roots are identical to the equations given in section 2 for the root model, but with diffusion. The compartment leaves of the fruit tree model is not required for human exposure assessment and is not shown here. The harvested product are fruits, which can be contaminated via xylem and phloem flux from the stem and by gaseous and particle deposition from air. The model is based on the recent version of the Fruit Tree model (Trapp, 2007) and not on the earlier version (Trapp et al., 2003).

5.1 Stem. The transpiration water is translocated upwards in the xylem. Dissolved chemicals can flow with the water in the stem, and can undergo elimination processes. The basic equation is

$$\frac{dC}{dt} = -kt$$

with the common solution

$$C(t) = C(0) \times e^{-kt}$$

The time coordinate t (d) is transferred to stem height z (m) via $t = z/u$, where u is the flow velocity (m d^{-1}). The initial concentration in xylem, when it enters the stem, is identical to the outflow concentration from thick root C_{Xy2} (see root model, section 2). The concentration in stem at height $z = 0$ is assumed to be in chemical equilibrium with xylem

$$C_{Stem}(0) = C_{Xy2} \times K_{StemWater}$$

where K is the partition coefficient. The concentration at height z is

$$C_{Stem}(z) = C_{Stem}(0) \times e^{-kz/u_c}$$

where u_c is the flow velocity of the chemical, and k is the sum of the loss rates (metabolism and volatilization) plus the rate of growth dilution. The concentration of the chemical in the xylem, when it leaves stem at height h, C_{Xy3}, is

$$C_{Xy3} = \frac{C_{stem}(h)}{K_{StemWater}}$$

The loss rate via volatilization from stem is

$$k_V = \frac{A_{St}}{M_{Stem}} \times P \times \rho_{Stem}$$

or, easier, because for a cylinder of height h and radius r, volume $V = M/\rho = \rho\, r^2\, h$ and outside area $A = 2\, \rho\, r\, h$:

$$k_V = \frac{2P}{r}$$

The flow velocity of the chemical u_C is the flow velocity of water u_W multiplied with the fraction of chemical present in water, $u_C = u_W\, x\, f_{W,}$ where $f_W = W_{Stem} / K_{StemWater}$.

Partition coefficient. The concentration ratio in chemical equilibrium between stem (wood + water + air) and water (such as xylem sap) is

$$K_{StemWater} = \frac{\rho_{dry}}{\rho_{wet}} \times K_{wood} + W_{St} + G_{St} \times K_{AW}$$

where W and G are the fractions of water and gas in the stem (L kg^{-1}). The ratio between a chemical's concentration in wood and its concentration in the water, K_{Wood} (mg chemical g^{-1} dry wood to mg chemical mL^{-1} water), is

$$\log K_{Wood} = -0.27 + 0.632 \times \log K_{OW} \qquad \text{(Oak)}$$

Input from air. While the xylem flow moves upwards, chemicals from air can enter the stem and the xylem. This is treated in the differential equation as a constant input I (mg kg^{-1} d^{-1})

$$I = \frac{A \times P}{V \times K_{AW} \times 1000} \times K_{StemWater} \times C_{Air}$$

where 1000 is a conversion factor for C_{Air} from mg m^{-3} (the usual unit for air) to mg L^{-1} (the usual unit for water) ; or, easier, replacing A/V

$$I = \frac{2 \times P}{r \times K_{AW} \times 1000} \times K_{Stem} \times C_{Air}$$

Final solution stem. Adding input from air to the mass balance yields

$$\frac{dC}{dt} = -kC + I$$

with the common solution

$$C(z) = C(0) \times e^{-kz/u} + \frac{I}{k} \times (1 - e^{-kz/u})$$

This means that due to input from air, the concentration can increase along the stem from $z = 0$ to $z = h$ (height).

Sapwood and flow velocity. Measured flow velocities of water in trees range from 0.4 m h^{-1} to 44 m h^{-1} (Huber, 1956). This is above the filter velocity (transpired water Q (L d^{-1}) divided by stem cross-area A_{cross}), because the water flows only in the sapwood. The volume of the sapwood can thus be calculated by comparing the measured water flow velocity u_W with the filter velocity.

Filter velocity = $u_F = \frac{Q}{A_{cross} \times W_{St} \times \rho_{stem} \times 1000}$

The cross area of the sapwood ring is

$$A_{Ring} = \pi \times (R^2 - r^2)$$

where R is the outer stem radius and r the inner radius of the sapwood. For $A_{Ring}/A_{cross} = u_{meas} / u_F$ follows:

$$r = \sqrt{R^2 - R^2 \times \frac{u_F}{u_{meas}}}$$

and R - r is the thickness of the sapwood.

Permeability for exchange between stem and air. The permeability of the stem is calculated by a two-sides-resistance model, with one resistance being the wood and bark of the tree, the other being a stagnant air layer around the bark. The resistance inside the stem is calculated analogously to the potato. $K_{StemWater}$ is used instead of K_{PW}, W_{St} and G_{St} replace W_P and G_P. The diffusion path-length is taken as R - r + d_{Bark}, where d_{Bark} is the thickness of the bark (default 0.01 m). The permeability of the air layer is calculated as

$P_{Air} = \frac{D_G}{dx}$ where dx is the thickness of the stagnant air layer, by default 0.01 m.

The total permeability follows from Kirchhoff's Law:

$$P_{total} = \frac{1}{\frac{1}{P_{Stem}} + \frac{1}{P_{Air} \times K_{AW}}}$$

5.2 Fruits. The mass balance for chemicals in fruits considers transport from stem via phloem and xylem and uptake from air via gaseous and particulate deposition, loss is by metabolism and to air. The concentration in fruits is

$$\frac{dC_F}{dt} = + \frac{Q_F}{M_F} \times C_{Xy3} + \frac{A_F \times P_F}{K_{AW} \times M_F} \times (1 - f_P) \times C_A + \frac{v_{dep} \times A_F}{2 \times M_F} \times f_P \times C_A$$
$$- \frac{1000 \times A_F \times P_F}{K_{FW} \times M_F} \times C_F - k_F \times C_F$$

In steady-state:

$$C_F = \frac{Q_F \times C_{Xy3} + A_F \times P_F \times \frac{(1 - f_P) \times C_A}{K_{AW}} + \frac{v_{dep} \times A_F \times f_p \times C_A}{2}}{\frac{1000 \times A_F \times P_F}{K_{FW}} + k \times M_F}$$

where F is the index for fruits. Q_F is the sum of phloem and xylem flow (L d^{-1}), K_{FW} (L kg^{-1}) is the partition coefficient between fruits and water, calculated as for leaves but with other water and lipid content. P_F is the permeability for exchange between fruits and air (m d^{-1}).

Phloem and xylem transport. The xylem flow to leaves Q_L (L d^{-1}) and fruits Q_{FX} (L d^{-1}) is calculated from the total xylem flow out of the stem Q_{St} by averaging with the respective surface areas:

$$Q_{FX} = \frac{A_F}{A_F + A_L} \times Q_{St}$$

and $Q_L + Q_{FX} = Q_{St}$

The phloem flux into fruits is calculated from dry matter content (10%). It may be assumed that the total phloem flow into fruits, *Sum* Q_{FP} (L) is about 10 times the dry matter content:

Sum $Q_{FP} = (1 - W_F) \times M_F \times 10$

where $(1 - W_F) \times M_F$ is the dry mass of the fruit. The daily phloem sap flow into fruits, Q_{FP} (L d^{-1}), is calculated by dividing *Sum* Q_{FP} with 60 days, Q_{FP} = *Sum* Q_{FP} / 60 d. The total water flux into fruits Q_F is the sum of xylem and phloem flux:

$$Q_F = Q_{FX} + Q_{FP}$$

Permeability. Loss from fruits to air via stomata and cuticles is considered, as before, by P_S and P_C. P_S is calculated from Q_{FX} (xylem flow) and A_F. For $P_{C,\,total}$ of the fruit, the same value as for leaves is used. The resistance of the fruit tissue P_{tissue} is added, calculated in the same way as for roots (described in (Trapp, 2007)), but with water and gas fraction of the fruit and with a default diffusion length of 1 cm. The total permeability for the exchange between fruits and air is then

$$P_F = \frac{1}{\frac{1}{P_{C,total} + P_S} + \frac{1}{P_{tissue}}}$$

5.3 Input data

The input data for the Fruit Tree model were taken unchanged from the original reference (Trapp, 2007). Data for soil and roots were listed in section 2, Tables S1 and S2. The data for the stem and fruit compartment are listed in Table S6.

Table S6. Parameters for the Fruit Tree model.

Parameter	Symbol	Value	Unit
Growth rate stem	k_{St}	2.74 x 10^{-5}	d^{-1}
Stem water fraction	W_{St}	0.38	L kg^{-1}
Stem gas pores	G_{St}	0.2	L kg^{-1}
Density of stem (wet)	ρ_{stem}	1	kg L^{-1}
Relative humidity	Rh	0.5	(-)
Temperature	$Temp$	20	°C
Apple fruit water content	W_F	0.844	L kg^{-1}
Apple fruit air pores	G_F	0.25	L kg^{-1}
Apple fruit lipid content (*)	L_F	0.006	g g^{-1}
Growth rate fruits	k_F	0.035	d^{-1}
Diffusion length fruits	X	0.01	m
Transpiration	Q	0.822	L d^{-1}
Sap flow to fruits	Q_F	0.023	L d^{-1}
Water flow velocity	u_W	40	m d^{-1}
Stem height	Z	5	m
Stem radius	R_{St}	0.1	m
Fruit radius	R_F	0.04	m
Fruit mass	M_F	0.4	kg
Bark thickness	d_{Bark}	0.01	m
Deposition velocity of particles	v_{dep}	28.8	m d^{-1}

(*) This lipid content includes all lipid-like compounds, not only fat and oil, but also waxes like suberin and cutin.

The TGD uses the model for leafy vegetables for fruits.

6 The Regressions for beef and milk

The TGD uses the constrained regressions of Travis and Arms (1988) for estimating concentrations in meat and milk, and include soil (V_S), air (V_A) and water (V_W) intake rates as well as grass for the cow ($Intake = V_{grass}\ x\ C_{grass} + V_S\ x\ C_S + V_A\ x\ C_A + V_W\ x\ C_W$).

$$\log BTF_{meat} = \log K_{OW} - 7.6$$

$$\log BTF_{milk} = \log K_{OW} - 8.1$$

The TGD use these regressions for compounds with a log K_{OW} in the range 1.5 – 6.5 for meat, and 3 – 6.5 for milk, outside these ranges the minimum or maximum log K_{OW} values are used. The grass concentration is estimated with the TGD model for leaves. Input parameters are shown in Table S7.

Different from this, the original regressions were applied in the NMF:

$$\log BTF_{meat} = 1.033 \times \log K_{OW} - 7.735$$

$$\log BTF_{milk} = 0.992 \times \log K_{OW} - 8.056$$

As can be seen, the differences are very small. The same regression range was chosen, but different consumption rates of the cow, namely those given in the original reference (Travis and Arms, 1988).

Alternative Equations. The regressions proposed by Birak et al. (2001) for beef and milk were tested (but later not used) for meat and milk. The biotransfer factor for meat, $BTF_{meat} = C_{meat}/intake$ (d kg^{-1} ww), is calculated according to the following regression:

$$\log BTF_{meat} = 0.53 \times \log K_{OW} - 5.8$$

where *intake* is equal to the grass consumption rate for nonlactating cows V_{grass} (kg ww d^{-1}) multiplied with the concentration in grass C_{grass} added to the cow inhalation rate multiplied with the air concentration. The biotransfer factor for milk, $BTF_{milk} = C_{milk}/intake$ (d kg^{-1} ww), is calculated in a similar fashion:

$$\log BTF_{milk} = 0.44 \times \log K_{OW} - 5.7$$

where *intake* is equal to the grass consumption rate for lactating cows (kg ww d^{-1}) multiplied with C_{grass} added to the cow inhalation rate multiplied with the air concentration. For both regressions the grass concentration is estimated with the model for leafy vegetables.

Table S7. Input parameters for the Travis and Arms regressions.

Parameter	**Symbol**	**Value NMF**	**Value TGD**	**Unit**
Grass consumption rate, nonlactating cow	V_{grass}	40	67.6	kg ww d^{-1}
Grass consumption rate, lactating cow	V_{grass}	80	67.6	kg ww d^{-1}
Soil intake rate, cow	V_S		0.46	kg ww d^{-1}
Air intake rate, cow	V_A	150	122	m^3 d^{-1}
Water intake rate, cow	V_W		55	L d^{-1}
Water content of grass	W_{grass}	0.8		L $kg\ ww^{-1}$

7 Consumption Data and Daily Dietary Intake

Consumption data Denmark. Consumption data for children and women were taken from the Danish national survey of dietary habits and physical activity (Table S8). Only products that can be produced in Denmark were included, previously it has been estimated that 86% of the consumption in Denmark are Danish products (Jensen and Dengsøe, 2004). The products were categorized into root vegetables, leafy vegetables with (lettuce) and without (others) attached soil, fruits (including fruit juice), cereal and potatoes, according to the crop-specific model types used in this study. For fruits, the fraction of tree fruits, and for vegetables, the fractions of lettuce, other leafy vegetables, and root vegetables were taken from a pesticide monitoring report (Poulsen et al., 2005) (see Table S9 for products included in these categories). These fractions were then multiplied with the total amounts of fruits and vegetables taken from the Danish national survey (Lyhne et al., 2005) to get the consumption data. Data for potato, cereal, milk, and meat (without poultry) were taken directly from the Danish national survey (Lyhne et al., 2005). Not included is the consumption of exotic fruits and vegetables, cheese products, eggs, poultry, fish and fats. Soil and air intake estimates for the two groups, children age 4-5 and women age 14-75, were taken from the Exposure Factors Handbook (U.S.EPA, 1997), except soil ingestion 95th percentiles (ECETOC, 2001).

Table S8 lists also the consumption data suggested in the TGD for indirect human exposure assessment. There is only one data for roots, and one data for leaves, since other crops are not considered. Soil ingestion is also neglected in the TGD. As can be seen, the suggested consumption values are rather generous. The consumption of roots in the TGD is a factor 2.9 the mean consumption of the sum of roots and potatoes of females in Denmark. For the sum of above-surface crops, the TGD is factor 3.4 higher; for milk, factor 1.9; and for meat factor 1.8. The reason is that to "account for the fact that intake rates vary between countries, for each food product, the highest country-average consumption rate of all member states" was used. It was recognized that the resulting food basket is unrealistic, but this was justified as worst-case approach to indicate possible concern (EC, 2003).

The daily dietary intake (*DDI*) of each chemical pollutant per kilo bodyweight (µg kg^{-1} d^{-1}) is calculated by multiplying the consumption of each food item ($Consumption_i$ (kg d^{-1})) with the calculated concentration in it (C_i (µg kg^{-1})), and dividing by the *Bodyweight* (kg):

$$DDI = \frac{\sum_i (C_i \cdot Consumption_i)}{Bodyweight}$$

Similarly, daily intake with soil and air was calculated and added to give the total daily intake.

Table S8. Daily consumption data for Danish consumers of the age 4-5 years and 14-75 years (females), mean and 95th percentile for both groups, and consumption data suggested in the TGD. Data given as fresh weight.

Food type	4-5		14-75 (♀)		TGD
	Mean	95th	Mean	95th	
Root vegetables (g/d)	30	54	43	89	384[c]
Potatoes (g/d)	56	137	90	198	
Lettuce (g/d)	6	11	9	18	
Other leafy veg. (g/d)	7	13	10	21	1200[d]
Tree fruits (g/d)	111	235	137	318	
Cereal products (g/d)	185	269	195	309	
Milk (g/d)	448	796	303	754	561
Meat (non-poultry) (g/d)	76	138	89	166	301
Inhalation (m^3/d)	8.3	28.8[a]	11.3	38.4[a]	20 x 0.75[e]
Soil ingestion(mg/d)	100	200[b]	50	300[b]	0
Bodyweight (kg)	22		67.3		70

[a]: Moderate activity, [b]: ECETOC (2001), [c]: Only one below-ground crop type in TGD, [d]: Only one above-ground crop type in TGD, [e]: Inhalation rate is 20 m^3 d^{-1}, hereof 75% is bioavailable.

Table S9. Danish products included in the vegetable and fruit categories.

Category	Lettuce	Other leafy vegetables	Roots	Tree fruits
Products included	Lettuce	Asparagus, celery, chinese cabbage, chives, dill, head cabbages, herbs, kale, leeks, parsley, spinach, spring onions, rhubarbs	Beetroot, carrots, celeriac, parsnips, radish	Apple juice, apples, fruit juice (other than orange and apple), peaches and nectarines, pears, plums

References

Birak, P., Yurk, J., Adeshina, F., Lorber, M., Pollard, K., Choudhury, H., Kroner, S., 2001. Travis and Arms revisited: a second look at a widely used bioconcentration algorithm. Toxicology and Industrial Health 17, 163-175.

Briggs, G.G., Bromilow, R.H., Evans, A.A., 1982. Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. Pesticide Science 13, 495-504.

Burken, J.G., Schnoor, J.L., 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environmental Science & Technology 32, 3379-3385.

Chiou, C.T., Sheng, G.Y., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environmental Science & Technology 35, 1437-1444.

Ciucani, G., Trevisan, M., Sacchi, G.A., Trapp, S., 2002. Measurement of xylem translocation of weak electrolytes with the pressure chamber technique. Pest Management Science 58, 467-473.

Czub, G., McLachlan, M.S., 2004. A food chain model to predict the levels of lipophilic organic contaminants in humans. Environmental Toxicology and Chemistry 23, 2356-2366.

EC (European Commission), 2003. Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market., European Communities, Italy (http://ecb.jrc.it/documents/TECHNICAL_GUIDANCE_DOCUMENT/EDITION_2/)

ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals), 2001. Exposure Factors Sourcebook for European Populations (with Focus on UK Data). Technical Report No. 79, Brussels, Belgium

Elmadfa, I., Aign, W., Muskat, D., Fritsche, D., Cremer, H. D., 1991. Die grosse GU Nährwert Tabelle. Gräfe und Unzer, Giessen, Germany.

Hsu, F.C., Marxmiller, R.L., Yang, A.Y.S., 1990. Study of root uptake and xylem translocation of cinmethylin and related compounds in detopped soybean roots using a pressure chamber technique. Plant Physiology 93, 1573-1578.

Huber, B., 1956. Die Saftströme der Pflanzen, p. 42. Springer, Berlin, Germany.

Jensen, D.B., Dengsøe, N., 2004. Værdisætning af skadesomkostninger ved affaldsforbrænding. TemaNord 2004:518, Nordisk Ministerråd, København, Denmark (http://www.norden.org/pub/miljo/miljo/sk/TN2004518.pdf)

Jury, W.A., Spencer, W.F., Farmer, W.J., 1983. Behavior assessment model for trace organics in soil 1. Model description. Journal of Environmental Quality 12, 558-564.

Kerler, F. , Schonherr, J. 1988. Permeation of lipophilic chemicals across plant cuticles - prediction from partition-coefficients and molar volumes. Archives of Environvental Contamination and Toxicology 17, 7-12.

Lyhne, N., Christensen, T., Groth, M.V., Fagt, S., Biltoft-Jensen, A., Hartkopp, H., Hinsch, H.-J., Matthiessen, J., Møller, A., Saxholt, E., Trolle, E., 2005. Danskernes kostvaner 2000-2002. Hovedresultater., Danmarks Fødevareforskning (http://www.dfvf.dk/Files/Filer/Ern%C3%A6ring/kostunders%C3%B8gelser/DKV2002.pdf)

Paretzke, H.G., Garland, J.A., 1992. Assessment of the radiological significance of surface contamination in entrained radioactivity. Final Report, EC-contract No. 90-ET-015

Poulsen, M.E., Andersen, J.H., Petersen, A., Hartkopp, H., 2005. Pesticides. Food monitoring, 1998-2003. Part 2. FødevareRapport 2005:2, Danish Veterinary and Food Administration (http://www.foedevarestyrelsen.dk/FDir/Publications/2005002/Rapport.pdf)

Thompson, N. 1983. Diffusion and uptake of chemical vapor volatilizing from a sprayed target area. Pesticide Science 14, 33-39.

Trapp, S., Matthies, M., 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environmental Science & Technology 29, 2333-2338.

Trapp, S., Matthies, M., 1998. Chemodynamics and Environmental Modeling. An Introduction. Springer, Berlin, Germany

Trapp, S., Schwartz, S., 2000. Proposals to overcome limitations in the EU chemical risk assessment scheme. Chemosphere 41, 965-971.

Trapp, S., 2002. Dynamic root uptake model for neutral lipophilic organics. Environmental Toxicology and Chemistry 21, 203-206.

Trapp, S., Rasmussen, D., Samsoe-Petersen, L., 2003. Fruit tree model for uptake of organic compounds from soil. Sar and Qsar in Environmental Research 14, 17-26.

Trapp, S., 2007. Fruit tree model for uptake of organic compounds from soil and air. Sar and Qsar in Environmental Research 18, 367-387.

Trapp, S., Cammarano, A., Capri, E., Reichenberg, F., Mayer, P., 2007. Diffusion of PAH in potato and carrot slices and application for a potato model. Environmental Science & Technology 41, 3103-3108.

Travis, C.C., Arms, A.D., 1988. Bioconcentration of organics in beef, milk, and vegetation. Environmental Science & Technology 22, 271-274.

U.S. EPA (U.S.Environmental Protection Agency), 1997. Exposure Factors Handbook. (http://www.epa.gov/nceawww1/pdfs/efh/front.pdf)

Paper IV

Coupled mother-child model for bioaccumulation of POPs in nursing infants

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Coupled mother–child model for bioaccumulation of POPs in nursing infants

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This paper addresses a model for accumulation of organic compounds by mother and breast-fed infant, applicable for exposure assessment within larger frameworks.

Abstract

Bioaccumulation of persistent organic pollutants (POPs) leads to high levels in human milk and high doses of POPs for nursing infants. This is currently not considered in chemical risk assessment. A coupled model for bioaccumulation of organic chemicals in breast-feeding mother and nursing infant was developed and tested for a series of organic compounds. The bioaccumulation factors (BAFs) in mother, breast milk and child were predicted to vary with log K_{OW} and, for volatile compounds, with K_{AW} and concentration in air. The concentrations of POPs in the infant body increase the first half year to about factor 3 above mother and decline thereafter to lower levels. The predicted results are close to empirical data and to an empirical regression. The new mother–child model is compact due to its easy structure and the analytical matrix solution. It could be added to existing exposure and risk assessment systems, such as EUSES.

Keywords: Accumulation; Breast milk; Human exposure; Infant; Model; POP

1. Introduction

Persistent organic pollutants (POPs) are ''chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms, and are toxic to humans and wildlife'' (UNEP, 2007). POPs, such as polychlorinated dibenzodioxins and dibenzofurans (PCDD/F), polychlorinated biphenyls (PCB) and chloroorganic pesticides, have been detected in human milk samples all over the world (Rogan et al., 1986; Schecter et al., 1996; Filser et al., 1997; Raab et al., 2007; Shen et al., 2007; Wittsiepe et al., 2007; Tanabe and Kunisue, 2007). This raised considerable concern about adverse health effects on nursing infants (Harrison, 2001; CEHAPE, 2004; US EPA, 2006).

The uptake of POPs, such as PCDD/F, by adults is mainly via food ingestion (Travis and Hattemeyer-Frey, 1991). The uptake by nursing infants via breast milk has been reported to be higher than by adults via diet, for some POPs at levels above the acceptable daily intake (Dahl et al., 1995; Kreuzer et al., 1997; Schade and Heinzow, 1998; BgVV, 2000; Tanabe and Kunisue, 2007). POPs may accumulate for a longer period in the body of the mother and then be transferred to the nursing infant via mother's milk. Travis et al. (1988) developed empirical relations for the accumulation of chemicals in human adipose tissue and human milk. The regressions are based on 12 (tissue) or six (milk) organic chemicals with a log K_{OW} between 1.32 and 6.50 (tissue) or 5.16–6.50 (milk). The bioaccumulation factors B_f (tissue) and B_m (milk) were defined as

$$B_f = \frac{\text{concentration of organic in adipose tissue } \left(\text{mg kg}^{-1} \text{ lipid}\right)}{\text{average daily intake of organic } \left(\text{mg d}^{-1}\right)}$$

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$$B_{\mathrm{m}} = \frac{\text{concentration of organic is breast milk } \left(\mathrm{mg\,kg^{-1}\ lipid}\right)}{\text{average daily intake of organic } \left(\mathrm{mg\,d^{-1}}\right)}$$

Travis et al. (1988) related these bioaccumulation factors to the log K_{OW} of the substances.

$$B_{\mathrm{f}} = 2.0 \times 10^{-4} K_{\mathrm{OW}}^{1.05} \quad \left[\frac{\mathrm{d}}{\mathrm{kg}}\right] \quad (n = 12, r = 0.98)$$

$$B_{\mathrm{m}} = 9.8 \times 10^{-5} K_{\mathrm{OW}}^{1.14} \quad \left[\frac{\mathrm{d}}{\mathrm{kg}}\right] \quad (n = 6, r = 0.97)$$

Besides this empirical approach, several mathematical model approaches exist to predict human tissue concentrations after uptake, e.g., the models prepared by Kreuzer et al. (1997) or Filser et al. (1997) and Maruyama et al. (2003) for PCDD/F. Accumulation in the food chain with subsequent accumulation in humans was addressed by Czub and McLachlan (2004a,b). To summarize, compound-specific models, comprehensive numerical models and also easy empirical models for the prediction of the accumulation of POPs in humans are available.

However, what lacks is a model predicting accumulation of POPs or other compounds in breast-feeding mother and nursing infant after uptake of chemicals via diet or other relevant sources by mother, which is compact enough to be combined with other models and estimation routines, e.g., for chemical safety assessment tools such as EUSES (EC, 1996).

"Traditional risk assessment approaches and environmental health policies have focused mainly on adults and adult exposure patterns, utilizing data from adult humans or adult animals" (CEHAPE, 2004). Indeed, current chemical risk assessment in the EU (EC, 2003) considers only grown-ups (70 kg bodyweight). An additional focus on children and in particular nursing infants, which are one trophic level higher and are eventually also more sensitive to chemicals, requires a compact exposure estimation method that can run with a minimum data set.

This paper addresses the development, parameterization, sensitivity analysis, validation and application of a coupled model for accumulation of organic compounds by nursing mother and child. The coupled differential equations were solved analytically. The model was tested with 2,3,7,8-TCDD and compared to empirical data for 11 other compounds collected by Travis et al. (1988).

2. Methods

2.1. Model development

Fig. 1 gives an overview of the system considered by the model. The human body is considered as a flux-through system. The input of chemical occurs via diet (mother) or milk (child) and inhalation (both). Inside the body, phase equilibrium is assumed. The compound is eliminated from the body by exhalation and excretion (both together are named "outflux"), by metabolism and, in case of the nursing mother, with breast milk.

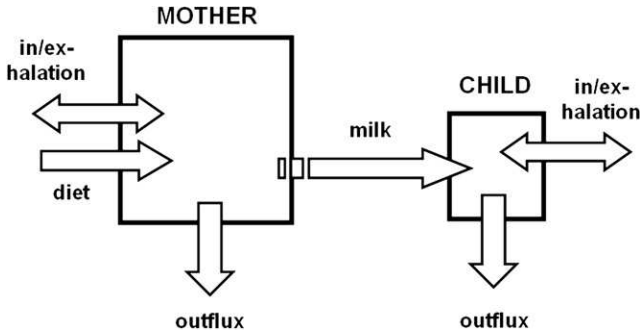

Fig. 1. System overview.

2.1.1. Mother before birth of the child

The input of chemical into the mother is independent of the concentration in her body, C_{H}, while the output is proportionally related to it. This yields a linear differential equation for the mass balance of the form

$$\frac{\mathrm{d}m}{\mathrm{d}t} = I - km \tag{1}$$

where m [mg] is the mass of chemical in the human body, I [mg d^{-1}] is the sum of daily uptake of chemical and k [d^{-1}] is the loss rate constant.

The input I can be derived from measurements or exposure assessments. The loss rate constant k is calculated from the flux of chemical out of the body.

The human body is considered as composed of lipids and water phases. Lipids were assumed to have properties similar to octanol. The phase equilibrium between concentration in human body, C_{H} [mg kg^{-1}], and concentration in water, C_{W} [mg L^{-1}], is

$$K_{\mathrm{HW}} = \frac{C_{\mathrm{H}}}{C_{\mathrm{W}}} = W_{\mathrm{H}} + \frac{L_{\mathrm{H}}}{\rho_{\mathrm{L}}} K_{\mathrm{OW}} \quad \left[\frac{\mathrm{L}}{\mathrm{kg}}\right] \tag{2}$$

where K_{HW} is the partition coefficient human body to water [L kg^{-1}], W_{H} is the water content [L kg^{-1}] and L_{H} is the lipid content of the human body [kg kg^{-1}], ρ_{L} is the density of lipids [kg L^{-1}] and K_{OW} [L L^{-1}] is the partition coefficient between octanol and water.

The change of chemical mass in time due to outflux of chemical from the body $\mathrm{d}m_{\mathrm{F}}/\mathrm{d}t$ [mg d^{-1}] is the sum of outflux with water, lipid and air

$$\frac{\mathrm{d}m_{\mathrm{F}}}{\mathrm{d}t} = F_{\mathrm{W}} C_{\mathrm{F,W}} + F_{\mathrm{L}} C_{\mathrm{F,L}} + F_{\mathrm{A}} C_{\mathrm{F,A}} = F C_{\mathrm{F}} \quad \left[\frac{\mathrm{mg}}{\mathrm{d}}\right] \tag{3}$$

where F_{W} is the outflux of water [L d^{-1}], F_{L} is the outflux of lipids [kg d^{-1}] (with feces) and F_{A} is the outflux of air [L d^{-1}] (exhalation). $C_{\mathrm{F,W}}$ [mg L^{-1}], $C_{\mathrm{F,L}}$ [mg kg^{-1}] and $C_{\mathrm{F,A}}$ [mg L^{-1}] are the concentrations in the water, lipid and gas fraction of the outflux; C_{F} [mg kg^{-1}] is the weighted average concentration in the outflux. The total material outflux, F [kg d^{-1}], is the sum of the outfluxes of water, lipids and air,

$$F = F_{\mathrm{W}} \rho_{\mathrm{W}} + F_{\mathrm{L}} + F_{\mathrm{A}} \rho_{\mathrm{A}} \quad \left[\frac{\mathrm{kg}}{\mathrm{d}}\right] \tag{4}$$

Using the assumption of phase equilibrium we can rewrite to

$$F C_{\mathrm{F}} = F f_{\mathrm{W}} C_{\mathrm{F,W}} + F f_{\mathrm{L}} K_{\mathrm{OW}} C_{\mathrm{F,W}} + F f_{\mathrm{A}} K_{\mathrm{AW}} C_{\mathrm{F,W}} \tag{5}$$

where K_{AW} is the partition coefficient [L L^{-1}] between air and water (also known as dimensionless Henry's Law constant), and f are the flux fractions [L d^{-1}:kg d^{-1}] of water (W), lipids (L) and air (A) of the total flux F,

$$f_{\mathrm{W}} = \frac{F_{\mathrm{W}}}{F}, f_{\mathrm{L}} = \frac{F_{\mathrm{L}}/\rho_{\mathrm{L}}}{F}, f_{\mathrm{A}} = \frac{F_{\mathrm{A}}}{F} \quad \left[\frac{\mathrm{L}}{\mathrm{kg}}\right] \tag{6}$$

The average concentration of chemical in the outflux, C_{F}, is then

$$C_{\mathrm{F}} = f_{\mathrm{W}} C_{\mathrm{F,W}} + f_{\mathrm{L}} K_{\mathrm{OW}} C_{\mathrm{F,W}} + f_{\mathrm{A}} K_{\mathrm{AW}} C_{\mathrm{F,W}} \tag{7}$$

Note that for phase equilibrium, $C_{F,W}$ (concentration in aqueous phase of outflux) equals C_W (concentration in aqueous phase of human body), and thus we derive

$$K_{FW} = \frac{C_F}{C_W} = f_W + f_L K_{OW} + f_A K_{AW} \quad \left[\frac{L}{kg}\right] \tag{8}$$

where K_{FW} [L kg^{-1}] is the partition coefficient between outflux [kg d^{-1}] and water [L d^{-1}]. Then, the partition coefficient between human body and outflux, K_{HF} [kg kg^{-1}], is

$$K_{HF} = \frac{C_H}{C_F} = \frac{K_{HW}}{K_{FW}} \quad \left[\frac{kg}{kg}\right] \tag{9}$$

where C_H and C_F are the concentrations [mg kg^{-1}] in human body and outflux in phase equilibrium. It follows for the loss rate constant k [d^{-1}] in Eq. (1), which is the sum of the losses by outflux and by metabolism or degradation with first-order k_{deg} [d^{-1}]

$$k = \frac{F}{M_H K_{HF}} + k_{deg} \quad \left[\frac{1}{d}\right] \tag{10}$$

where M_H [kg] is the bodyweight. The analytical solution of Eq. (1) for the chemical mass m [mg] in human body at time t is

$$m(t) = m_0\, e^{-kt} + \frac{I}{k}\left(1 - e^{-kt}\right) \tag{11}$$

which gives in steady-state ($t \to \infty$)

$$m(\infty) = \frac{I}{k} \tag{12}$$

Concentrations C_H [mg kg^{-1}] in the human body were derived from $C_H = m/M_H$, assuming a constant bodyweight M_H

$$C_H(\infty) = \frac{m(\infty)}{M_H} = \frac{I}{kM_H} \quad \left[\frac{mg}{kg}\right] \tag{13}$$

This solution was used to calculate the concentration of chemical in the woman before birth of the child (and before pregnancy, the bodyweight is constant at 60 kg).

2.1.2. Nursing mother with child

In this scenario, the mother gives birth to a child and nurses the infant. Equations for the mother were modified, and new equations for breast milk and nursing child were introduced.

2.1.2.1. Mother. Nursing changes the outflux from the mother. Milk consists in the model of water and lipids. The flux of milk F_M [kg d^{-1}] was added to the outflux F in Eq. (4)

$$F = F_W \rho_W + F_L + F_A \rho_A + W_M \rho_M F_M + L_M F_M \quad \left[\frac{kg}{d}\right] \tag{14}$$

where W_M [L kg^{-1}] is the water content and L_M [kg kg^{-1}] is the lipid content of human milk. Fractions of outflux [L kg^{-1}] f_W, f_L and f_A were recalculated for the case of nursing.

$$f_W = \frac{F_W + W_M F_M}{F}, f_L = \frac{F_L + L_M F_M}{F \rho_L} \text{ and } f_A = \frac{F_A}{F} \quad \left[\frac{L}{kg}\right] \tag{15}$$

The other equations (Eqs. (1), (2), (8)–(13)) were applied without changes, but the new values of F and f were entered.

2.1.2.2. Milk. With breast milk, chemical is lost from the mother and transferred to the baby (Schecter et al., 1996). To calculate the concentration of chemical in milk, phase equilibrium between milk and mother was assumed. The concentration in milk C_M [mg kg^{-1}] is

$$C_M = K_{MH} C_H \quad \left[\frac{mg}{kg}\right] \tag{16}$$

where K_{MH} [kg kg^{-1}] is the partition coefficient between milk and human. The partition coefficient milk to water K_{MW} [L kg^{-1}] is

$$K_{MW} = \frac{C_M}{C_W} = W_M + \frac{L_M}{\rho_L} K_{OW} \quad \left[\frac{L}{kg}\right] \tag{17}$$

The partition coefficient between milk and human body K_{MH} [kg kg^{-1}] is then

$$K_{MH} = \frac{C_M}{C_H} = \frac{K_{MW}}{K_{HW}} \quad \left[\frac{kg}{kg}\right] \tag{18}$$

2.1.2.3. Child. The breast-fed infant can take up chemicals by breast milk and by inhalation. Breathing is external input to the child, $I_C = F_A C_A$, where F_A [here: m^3 d^{-1}] is the flux of inhaled air and C_A [mg m^{-3}] is the concentration of chemical in air. Loss of chemical occurs via outflux and by metabolic elimination with first-order rate constant k_{deg} [d^{-1}]. The mass balance for the child is

$$\frac{dm_C}{dt} = I_C + C_M F_M - C_F F_C - k_{deg} m_C \tag{19}$$

where C_M [mg kg^{-1}] denotes the concentration in breast milk, F_M [kg d^{-1}] is the flux of milk from mother to child, C_F [mg kg^{-1}] is the concentration in the outflux of the child and F_C [kg d^{-1}] is the outflux from the child.

Using the partition coefficients, the equation can be rewritten to

$$\frac{dm_C}{dt} = I_C + K_{MH}\frac{F_M}{M_H} m_H - \frac{F_C}{K_{CF} M_C} m_C - k_{deg} m_C \quad \left[\frac{mg}{d}\right] \tag{20}$$

where m_H [mg] is the chemical mass in mother (human H), m_C [mg] is the chemical mass in the child, K_{CF} [kg kg^{-1}] is the partition coefficient between child and outflux and M_C [kg] is the body mass of the child. The phase equilibrium between child body (index C) and water (index W) is

$$K_{CW} = \frac{C_C}{C_W} = W_C + \frac{L_C}{\rho_L} K_{OW} \quad \left[\frac{L}{kg}\right] \tag{21}$$

where K_{CW} [L kg^{-1}] is the partition coefficient child body to water, C is the equilibrium concentration in child, index C [mg kg^{-1}], or water, index W [mg L^{-1}], W_C [L kg^{-1}] is the water content and L_C [kg kg^{-1}] is the lipid content of the child body. The initial concentration in the child C_C (0) [mg kg^{-1}] was calculated from phase equilibrium to mother

$$C_C(0) = \frac{K_{CW}}{K_{HW}} C_H \tag{22}$$

The outflux F_C [kg d^{-1}] from the child was summed up, as was done for the outflux from the mother:

$$F_C = F_W \rho_W + F_L + F_A \rho_A \tag{23}$$

where indices W, L and A indicate water, lipid and air. Again, the flux fractions were used to calculate the phase equilibrium between outflux and water, K_{FW}:

$$K_{FW} = \frac{C_F}{C_W} = f_W + f_L K_{OW} + f_A K_{AW} \quad \left[\frac{L}{kg}\right] \tag{24}$$

The partition coefficient between child body and outflux, K_{CF} [kg kg^{-1}], is

$$K_{CF} = \frac{C_C}{C_F} = \frac{K_{CW}}{K_{FW}} \quad \left[\frac{kg}{kg}\right] \tag{25}$$

2.2. Matrix solution

The differential equations of mother and child are coupled and were treated as a linear 2 × 2 matrix system of the form

$$\frac{dm_1}{dt} = a_{11} m_1 + a_{12} m_2 + I_1 \tag{26}$$

$$\frac{dm_2}{dt} = a_{21} m_1 + a_{22} m_2 + I_2 \tag{27}$$

Matrix element 1 is the mother. The matrix constant a_{11} [d^{-1}] is the sum of all loss processes from the mother and is identical with the negative loss rate k

(Eq. (10)). The matrix constant a_{12} [d^{-1}] is what mother receives from the child and is zero (therefore, the equation for chemical mass in mother can be solved independently of that for the child, Eqs. (1) and (11)). Input I_1 [mg d^{-1}] is the sum of all input to mother.

Matrix element 2 is the nursed child. The matrix constant a_{21} [d^{-1}] describes the transfer via milk from mother to child, $a_{21} = K_{MH} \times F_M/M_H$. The matrix constant a_{22} [d^{-1}] describes all losses of chemical from the child, $a_{22} = -F_C/(K_{CF} \times M_C) - k_{deg}$. Input I_2 includes all chemical input independent from the mother, i.e. via inhalation, $I_2 = F_A \times C_A$. A standard solution for this system of differential equations exists for the case of constant rates and inputs (Nazaroff and Alvarez-Cohen, 2001). Concentrations [mg kg^{-1}] were derived by dividing the chemical mass [mg] by the bodyweight [kg].

2.3. Parameterization of the model

Input data (Table 1) were selected from several sources, preferably from existing models (Kreuzer et al., 1997; Czub and McLachlan, 2004b), in order to allow a comparison of the results. The application of the steady-state solution (Eqs. (12) and (13)) for the mother before the birth of her child avoids the need to choose an appropriate initial mass m_0 for the first generation. The 95% steady-state is reached for latest $t = 18$ years for all chemicals with the default parameterization.

The total daily uptake I [mg d^{-1}] was calculated as the sum of uptake via diet i_D [mg d^{-1}] and inhalation of air:

$$I = i_D + F_A C_A \quad \left[\frac{mg}{d}\right] \tag{28}$$

For the breast-fed baby, i_D is 0.

Table 1
Default input data for the mother–child model

Parameter	Symbol	Value	Unit	Reference
Mother				
Age	t	25	a	Kreuzer et al. (1997)
Body mass	M_H	60	kg	Maruyama et al. (2003)
Body water fraction	W	0.71	L kg^{-1}	Czub and McLachlan (2004b)
Body lipid fraction	L	0.284	kg kg^{-1}	Deurenberg et al. (1991)
Outflux of water	F_W	1.24	L d^{-1}	Maruyama et al. (2003)
Outflux of lipid	F_L	0.007	kg d^{-1}	10% of lipids in diet
In/exhalation of air	F_A	11	m^3 d^{-1}	Layton (1993)
Breast milk data				
Milk flux	F_M	1	kg d^{-1}	Kreuzer et al. (1997)
Milk water content	W_M	0.87	L kg^{-1}	Czub and McLachlan (2004b)
Milk lipid content	L_M	0.045	kg kg^{-1}	Kreuzer et al. (1997)
Child				
Age	t	0–3	a	
Body mass	M_b	3.5–7.25	kg	Hesse et al. (1997)
Body water fraction	W	0.71	L kg^{-1}	Czub and McLachlan (2004b)
Body lipid fraction	L	0.233	kg kg^{-1}	Deurenberg et al. (1991)
Outflux of water	F_W	0.87	L d^{-1}	water content of 1 kg milk
Outflux of lipid	F_L	0.0045	kg d^{-1}	10% of influx
Outflux of air	F_A	4.5	m^3 d^{-1}	Layton (1993)
Other data				
Density of water	ρ_W	1	kg L^{-1}	
Density of lipids	ρ_L	0.82	kg L^{-1}	
Density of air	ρ_A	1.3×10^{-3}	kg L^{-1}	

Outflux of lipids was assumed to be 10% of lipids in the diet. With 70 g d^{-1} as average lipid ingestion, 0.007 kg d^{-1} outflux of lipids results. For the baby, 0.0045 kg d^{-1} (1/10 of influx of lipids with milk) was used. Table 1 lists the input data chosen as default for the model and used in the following simulations.

To calculate concentrations in the body of the child during the simulation period, the respective bodyweight was used, to account for growth effects. The bodyweight of the child with age (in years) was approximated by a second-order polynom fitted to growth data for girls in Germany (Hesse et al., 1997) (Eq. (29))

$$\text{bw} = -0.053 \times \text{age}^2 + 3.76 \times \text{age} + 3.54 \quad (n = 36, R^2 = 0.98) \tag{29}$$

3. Results

3.1. Example simulation TCDD

To illustrate the general behaviour of the model, an example simulation with 2,3,7,8-tetrachlordibenzo-*p*-dioxin (TCDD) was performed. TCDD is a highly toxic, persistent lipophilic (log K_{OW} 6.76) and semivolatile (K_{AW} 0.0015) compound (Rippen, 1990–2007). The concentration of TCDD in air was set to 4 fg m^{-3} (background concentration in Southern Germany, McLachlan, 1992). Ingestion of TCDD by the mother with diet was 25 pg d^{-1} (Kreuzer et al., 1997). Fig. 2 shows the simulated concentration of TCDD in lipids for mother and child over a 3-year period. The starting concentration of the mother [3.6 ng kg^{-1} lipid] is the steady-state concentration (Eq. (13)). For $t > 0$, the matrix solution was applied. For $t > 0$, the concentration of TCDD in mother decreases exponentially and falls to 63% of the initial concentration after 0.5 year and to 42% after 1 year of nursing. The initial concentration in the infant [3.6 ng kg^{-1} lipid] is in equilibrium to mother. It steeply increases to 12.3 ng kg^{-1} lipids after 0.5 year. Hereafter, it falls, due to depletion of the mother's body burden and growth dilution, to 8.8 ng kg^{-1} lipids after 1 year and to 1.73 ng kg^{-1} lipid after 3 years (of course, 3 years of nursing is rare). The concentration in lipids of milk is identical to that in lipids of the mother's body and was not plotted.

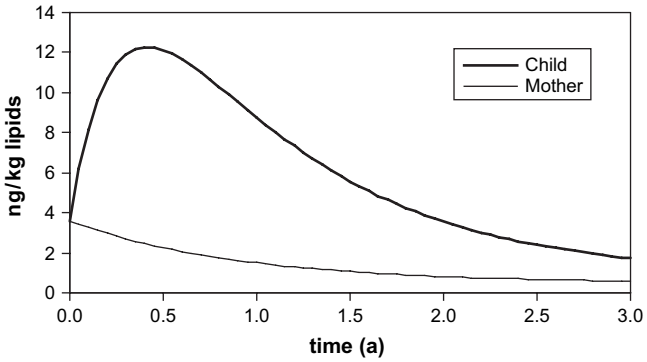

Fig. 2. Concentrations in nursing mother and child (ng kg^{-1} lipids) after uptake of 25 pg TCDD per day with diet by the mother.

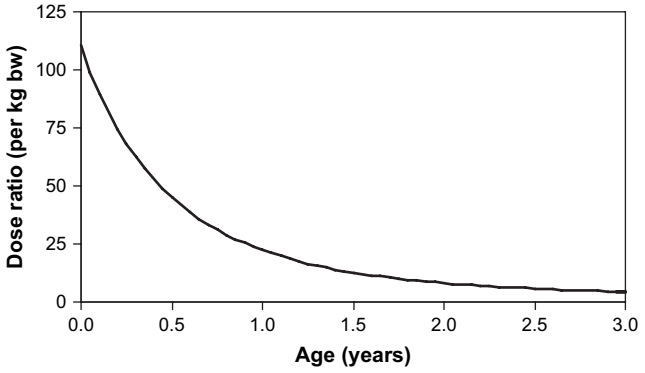

Fig. 3. Ratio of the TCDD-dose taken up by the nursing infant (per kg bw) to the dose taken up by the mother (25 pg d^{-1} = 0.42 pg kg^{-1} bw d^{-1}).

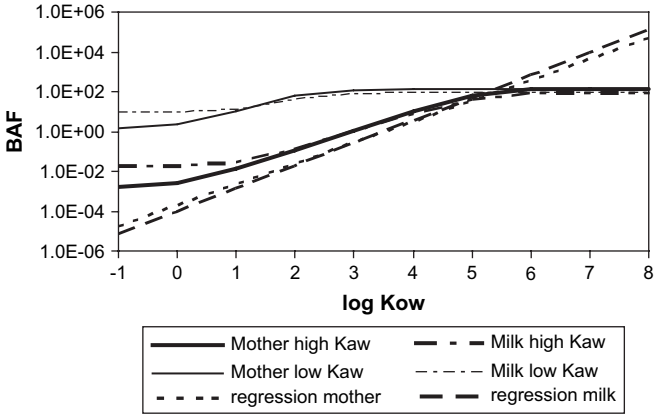

Fig. 4. Calculated bioaccumulation factor (BAF) mother ($t = 0$) and milk ($t = 0.5$ a) with varying log K_{OW} for low K_{AW} ($K_{AW} = 10^{-9}$ L L^{-1}) and high K_{AW} ($K_{AW} = 0.1$ L L^{-1}) compared to the result derived with the regression of Travis et al. (1988).

During the period of nursing, the loss of TCDD from mother with milk is higher than the daily intake, which is the reason for the depletion of TCDD from the body of the mother.

Fig. 3 shows the ratio of the TCDD-dose taken up by the infant (per kg bw) divided by the dose taken up by the mother (25 pg d^{-1} = 0.42 pg kg^{-1} bw d^{-1}). The ratio is initially 110 and falls later to 45 ($t = 0.5$ a), 22 ($t = 1$ a) and 4.5 ($t = 3$ a). The dose ratio is much higher than the concentration ratio (Fig. 2). Uptake of TCDD with air is neither for mother (inhalation 11 m^3 per day, uptake 44 fg TCDD per day) nor infant (inhalation 4.5 m3 per day, uptake 18 fg TCDD per day) of relevance. The maximum concentration ratio child to mother is reached after $t = 0.5$ a. The concentration in the child is maximally 3.4 times that in mother before birth and falls to 2.5 times ($t = 1$ a) and to 0.48 times ($t = 3$ a), due to rapid elimination and growth dilution. The calculated elimination half-time (ln 2 divide by rate constant k) of TCDD from the body is 4.6 years for the mother before birth, 0.6 years for the nursing mother and only 0.34 years for the infant.

These simulation results can be confronted to empirical data (Kreuzer et al., 1997; Filser et al., 1997). Measured concentrations of TCDD in lipids of adipose tissue and blood for adults in Germany in early 1990s range from <0.1 ng kg^{-1} lipids to 16 ng kg^{-1} lipids, with an average background level of 3 ng kg^{-1} lipids (Filser et al., 1997). Concentrations in breast milk vary between 1 and 3.9 ng kg^{-1} lipids, decreasing during the period of nursing, with an average of about 2 ng kg^{-1} lipids. TCDD concentrations in stillborn range from 1.3 to 2.1 ng kg^{-1} lipids. Concentrations of TCDD in lipids of adipose tissue, faeces and blood of infants did not differ much and ranged from <0.2 to 7.3 ng kg^{-1} lipids. TCDD levels in adipose tissue of 20 breast-fed infants aged between 0 and 44 weeks ranged from 0.16 to 4.1 ng kg^{-1} tissue and were higher than that of non-breast-fed children (0.16–0.76 ng kg^{-1} lipids) (Kreuzer et al., 1997). Predicted half-life of TCDD in infants was short (0.42 years), and increased to about 10 years for adults between 40 and 60 years of age. These results are throughout close to the outcome of the simulations with the mother–child model, without any conflicting results.

4. Discussion

4.1. Comparison of regression and mother–child model

The regression of Travis et al. (1988) uses only one physico-chemical parameter, the K_{OW}, while the mother–child model requires K_{OW} and K_{AW}. The bioaccumulation factors (BAFs), related to concentration in lipids, derived from model and regression were compared. The concentration in air was set to 0. The steady-state BAF of mother at birth of the child ($t = 0$) and the BAF milk after $t = 0.5$ year were plotted in Fig. 4. The BAFs for mother and milk are practically identical, except for very hydrophilic compounds (the relation to lipids gives artificially higher concentrations for milk if compounds do not partition into lipids). The model BAFs differ more than two orders of amount with low (10^{-9}) or high (0.1) K_{AW} except for high log K_{OW}, because volatile compounds are rapidly lost from the body via exhalation. Within its regression range (log K_{OW} 1.32–6.50), the regression gives similar results as the model with high K_{AW}, probably because the less lipophilic compounds in the training set of the regression were all solvents with high K_{AW} (Table 2). With increasing lipophilicity, the BAFs predicted by the mother–child model reach a plateau (mother at $t = 0$: BAF is 143 [d kg^{-1} lipid], milk at $t = 0.5$ years: BAF is 90 [d kg^{-1} lipid]), while the BAFs derived by the regression increase unlimited with K_{OW}. This is unrealistic, except for short time-periods, as the loss of super-lipophilic compounds via milk would be several orders of amount higher than the daily intake. The daily intake (1 mg d^{-1}) is balanced at a BAF milk (4.5% lipids) of 22 [d kg^{-1} lipid]. The regression gives a BAF = 22 [d kg^{-1} lipid] with log $K_{OW} = 4.7$, but higher BAF for all log K_{OW} above that value. On the contrary, the steady-state ($t = \infty$) BAF milk predicted by the mother–child model for compounds with log $K_{OW} > 4.7$ is constant at 19 [d kg^{-1} lipid]. In the initial period of nursing, the BAF milk is above steady-state, therefore, mother is depleted from POPs by nursing (Fig. 2).

Table 2
Names and physico-chemical data of the compounds in Travis et al. (1988)

Abbreviation	Compound	log K_{OW}[a]	K_{AW}[b]
Benzene	Benzene	2.13	0.23
DDE	1,1-Bis(4-chlorphenyl)-2,2-dichloroethene	5.83	0.05
DDT	1,1-Bis(4-chlorphenyl)-2,2,2-trichlorethan	5.76	0.0016
DCM	Dichlormethane	1.32	0.087
Dieldrin	Dieldrin	5.16	0.0044
HE	Heptachlor epoxide	5.40	0.01
HCB	Hexachlorbenzene	5.45	0.028
PCE	Perchlorethene	2.53	0.54
PCB	Polychlorinated biphenyls	6.50	0.001[c]
TCE	Trichlorethene	2.33	0.35
MC	Methylchloroform	2.47	0.715
TCDD	2,3,7,8-Tetrachlordibenzo-*p*-dioxin	6.76[b]	0.0015

[a] Travis et al. (1988) if not given otherwise.
[b] Rippen (1990–2007) if not given otherwise.
[c] Estimate; PCB is a mix of 209 compounds.

4.2. Uptake via inhalation compared to uptake via food

The impact of exhalation on BAF of hydrophilic to medium lipophilic compounds ($\log K_{OW} < 5$) is evident from Fig. 4: fugitive compounds with high K_{AW} show much lower bioaccumulation, due to this process. On the other hand, the K_{AW} may also impact the uptake by inhalation. Basically, this uptake is calculated from the product of concentration in air and inhalation (Eq. (28)). Under certain conditions, such as ubiquitous background distribution of persistent compounds, we may assume that the concentrations in diet and air are near phase equilibrium. Using the formalism of Section 2.1, the equilibrium ratio K_{DA} [L kg^{-1}] between concentration in diet C_D [mg kg^{-1}] and in air C_A [mg L^{-1}] is

$$\frac{C_D}{C_A} = K_{DA} = \frac{W_D + L_D K_{OW}}{K_{AW}} \quad \left[\frac{L}{kg}\right] \tag{30}$$

where W_D is the water content [kg kg^{-1}] and L_D is the lipid content [kg kg^{-1}] of the diet.

The relation between the input data i_D (uptake of chemical with diet, mg d^{-1}) and C_D is

$$i_D = C_D F_D \tag{31}$$

where F_D is the daily dietary consumption [kg d^{-1}]. Thus, the equilibrium concentration in air $C_{A,eq}$ [mg L^{-1}] is

$$C_{A,eq} = \frac{i_D}{K_{DA} F_D} \tag{32}$$

The dose via inhalation i_A [mg d^{-1}] is subsequently

$$i_A = F_A C_{A,eq} \tag{33}$$

where F_A is the inhalation of air [mother 11 m^3 d^{-1} and child 4.5 m^3 d^{-1}].

A typical diet of an adult Danish female (F_D) contains 60 g lipids and 2 L water, hereof 1.4 L drinking water. Using these numbers, the ratio of uptake via air to uptake via diet, assuming phase equilibrium between air and food (including water), was calculated.

Fig. 5 shows that the relevance of inhalation as uptake pathway for chemicals into the human body depends much on the value of the partition coefficient air to water, K_{AW}. For non-volatile compounds (low K_{AW}, 10^{-6} L L^{-1}), inhalation is not relevant at all. With very low K_{AW} (10^{-9} L L^{-1}), the ratio of uptake with inhalation versus uptake with diet is never above 1:100,000 (not shown). On the other hand, inhalation is the dominant way of entry into the body for volatile compounds (high K_{AW}, 0.1 L L^{-1}) with up to log K_{OW} of 4. With moderate K_{AW} (10^{-3} L L^{-1} in Fig. 5), the relative importance of inhalation for the body burden decreases, but it is still higher than uptake by diet for the less lipophilic compounds ($\log K_{OW} \leq 2$). For lipophilic compounds ($\log K_{OW} > 5$), which have the highest bioaccumulation, uptake by inhalation is generally not of much relevance. Compared to the mother, uptake via inhalation has similar (hydrophilic compounds) or lower importance (lipophilic compounds) for the child.

Note that these calculations were done for the rare case of near-equilibrium conditions. In real life, many individuals live in urban centers, while the agricultural production is in remote rural areas. It may be expected that the air pollution is higher in the cities, in particular when additional indoor sources of pollutants are present. Furthermore, lipophilic compounds may be strongly adsorbed to particles, which are inhaled simultaneously with air. Thus, these conclusions are surely not of general validity, and the relative importance of inhalation for the uptake of pollutants may be higher in real life than expected from the calculations displayed in Fig. 5.

4.3. Validation against empirical data

To derive their regressions for bioaccumulation in adipose tissue and breast milk, Travis et al. (1988) collected 12 bioaccumulation factors (BAFs) for human adipose tissue and six BAFs for breast milk from literature and pharmacokinetic

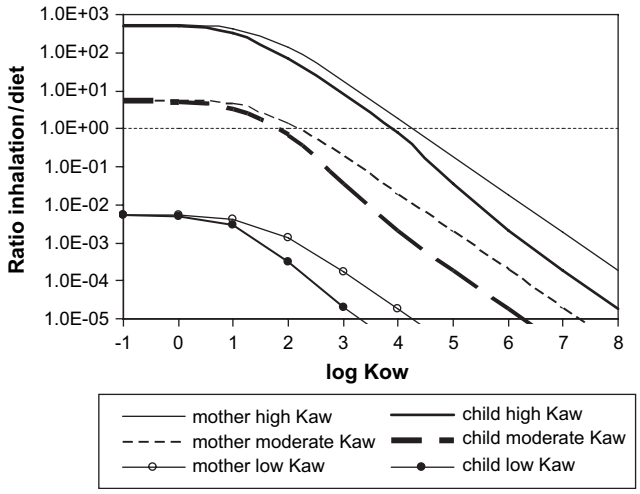

Fig. 5. Calculated ratio of uptake via inhalation to uptake via diet for the assumption of phase equilibrium for mother and child ($t = 0.5$ a) with varying log K_{OW} for high K_{AW} (0.1 L L^{-1}), moderate K_{AW} (0.001 L L^{-1}) and low K_{AW} (10^{-6} L L^{-1}). Dotted line shows ratio 1:1.

models. The model was tested against these data. Additionally, BAFs for TCDD were calculated from data in Kreuzer et al. (1997). The concentrations are related to lipid content. The log K_{OW}-values given in the original reference (Travis et al., 1988) were used, except for TCDD (Rippen, 1990–2007) (Table 2). One compound, pentachlorophenol, had to be excluded from the analysis because it is not a neutral compound but a weak acid (Rippen, 1990–2007). The uptake of weak electrolytes into living cells follows principles that are not covered by the model (Trapp, 2004).

In order to reproduce the experimental conditions under which empirical BAFs were derived, concentration in air was set to zero. Fig. 6 shows the measured BAF for human adipose tissue of the 12 organic compounds, the results from the regression by Travis et al. (1988) and the model outcome for mother before birth at steady-state. The measured BAFs range from 0.013 (TCE) to 724 (DDE) and are lowest for the volatile compounds with low log K_{OW}. Naturally, the regression predicts this range, and its results are generally less than factor 5 from the measurements, except for TCDD (over-predicted factor 21), which is out of the regression range. The model simulations are also close to the measured data and differ maximally factor 7 (dieldrin). The averaged ratio between predicted and measured BAF is 1.54 for the regression (3.15, including TCDD) and 2.0 for the model (including TCDD).

Fig. 7 shows the measured BAF for human milk of seven organic compounds. The measured BAFs range from 43 (dieldrin) to 1660 (PCB). The regression results are quite close to the measured BAF, except for TCDD. To derive the BAF, averaged values from milk samples in the period between birth and up to 18 month after birth have been used (Rogan et al., 1986). Therefore, the measured BAF were compared to the model result at birth ($t = 0$) and for $t = 1$ year. The calculated BAF milk are higher for $t = 0$ and do not vary much, as all compounds are lipophilic with log $K_{OW} > 4.7$. The predicted BAFs are somewhat too low, except for dieldrin and TCDD. The largest deviation is seen for PCB, which is not a single compound but a mix of 209 congeners. The averaged ratio between regression result and measured BAF is 2.02 (1.09 without TCDD). The ratio between model prediction and measurements is 0.99 (0.87 without TCDD) for $t = 0$ and 0.42 (0.37 without TCDD) for $t = 1$ year.

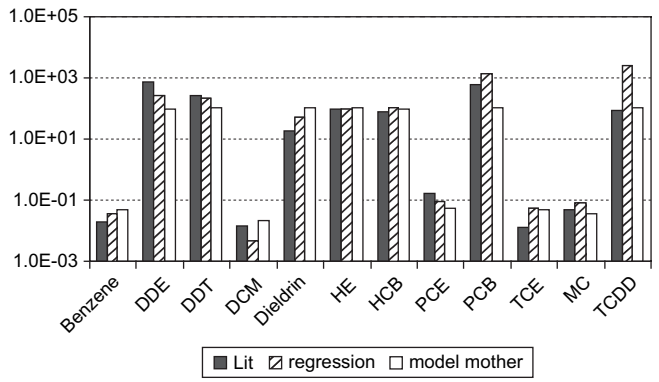

Fig. 6. Bioaccumulation factors (related to lipid content) for human adipose tissue for 12 neutral organic compounds collected from literature (Lit) compared to the regression by Travis et al. (1988) and the model outcome for mother before birth at steady-state.

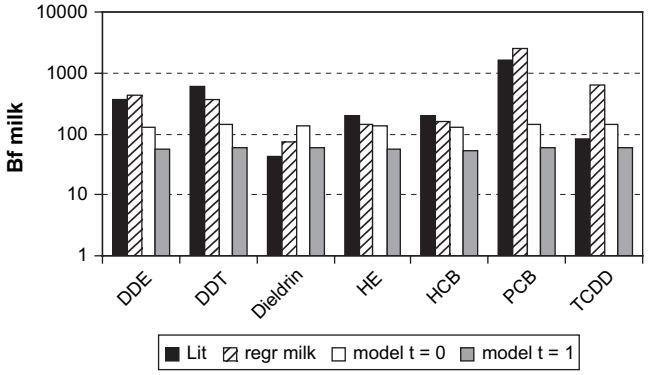

Fig. 7. Bioaccumulation factors (related to lipid content) for human milk for seven neutral organic compounds collected from literature (Lit) compared to the regression by Travis et al. (1988) and the model outcome for $t = 0$ (model $t = 0$, at birth) and $t = 1$ year (model $t = 1$).

4.4. Comment on nursing

The question is often raised whether nursing may have an adverse impact on the health of the child (BgVV, 2000). While the high dose of POPs (here: TCDD) that the infant receives with breast milk suggests so, the moderate increase of infant body concentration gives less reasons to be concerned. There is evidence that after a few life-years, the difference between breast-fed and formula-fed infants in their body burden with POPs, such as TCDD, vanishes (Kreuzer et al., 1997). If the mother nurses more than one child without longer periods in between, the model predicts lower body-burdens for the later children, i.e., for the second child after 1-year nursing, the body concentration is about the same as in the mother, if she never had breast-fed. Empirical studies confirm that the first born child is at higher risk to be exposed to POPs that have accumulated in mother and are transferred via mother milk (Tanabe and Kunisue, 2007), and that levels of POPs decrease during lactation (Harris et al., 2001). An argument pro nursing may also be that the mother reduces her POP pool (Schecter et al., 1996). Metabolism in the body of the mother reduces the dose transferred to the nursing infant. With metabolism half-times below 14 days, the model predicts that the dose the nursing infant receives is always below the dose for the mother. According to the model, the mother has a "filter effect" for less lipophilic and volatile compounds: for those, the dose for the infant via breast milk is lower than the dose mother takes up (per kg bw) (Fig. 4).

4.5. Limitations and application range of the new model

The new mother–child model is, due to the underlying equations for phase equilibrium, not valid for inorganic

(Wuenschmann et al., 2008) and electrolytic organic compounds (Trapp, 2004; Trapp and Horobin, 2005). The assumption of phase equilibrium within the body for neutral lipophilic organic compounds is supported by the results of Kreuzer et al. (1997), who found comparable levels of TCDD in lipids of adipose tissue, feces, blood, liver, breast milk and newborns. Deviations from equilibrium could in particular occur for compounds with rapid metabolism. However, for those the model predicts low transfer into infants anyhow, thus, a ''false alarm'' due to over-prediction would not occur, if accurate metabolism rate constants were at hand.

The new mother–child model is more complex than the regression of Travis et al. (1988), but still, the struture is easily understood, and the analytical solution of the differential equations keeps the calculations compact and robust. The model requires five chemical input parameters (i_D, K_{OW}, C_A, K_{AW} and k_{deg}). It may be more troublesome to acquire these data, but the differences in the accumulation behavior of persistent and reactive compounds can be considered, and uptake via diet and inhalation can be calculated simultaneously or separately. Therefore, results from diet studies can be used as input data, and bioaccumulation factors as defined by Travis et al. (1988) can be calculated, using $i_D = 1\ \mathrm{mg\,d^{-1}}$ and $C_A = 0$. The regression necessarily will fail if uptake from air plays a major role.

Another advantage of the deterministic approach, compared to empirical relations, is that the relevant processes behind the BAF can be identified. The variation of physiological parameters (for the human body) allows to determine the influence of age, diet, bodyweight, growth, metabolism, etc. Furthermore, the regression violates the mass balance for more lipophilic compounds with high $\log K_{OW}$ and gives unrealistically high BAF, as was shown before.

In comparison to more sophisticated models for bioaccumulation (Kreuzer et al., 1997; Van Der Molen et al., 1996; Maruyama et al., 2003), the new mother–child model is more compact and easier adapted to new compounds (i.e., it does not require the measurement of any chemical-specific data, besides the minimum data set, and it needs no calibration steps). Compared to the human bioaccumulation model ACC (Czub and McLachlan, 2004b), which calculates the body concentration of a single human over the whole life-time, the mother–child model is less complex and more flexible, due to the analytical solution. If, for the purpose of risk assessment, only the dose for the infant is required, the differential equation system is decoupled, and the solution for the breast-feeding mother alone can be solved (Eq. (11)).

The development of the new mother–child model was driven by the need to predict the exposure of nursing children within the framework of chemical risk assessment and/or risk assessment of polluted sites. Model systems for these purposes exist (EC, 1996; Rikken et al., 2001; Kulhanek et al., 2005) but none of them considers nursing infants (in fact, children are not considered at all in most of them). The new model could be added with small effort to existing exposure assessment tools, in order to fill this gap.

4.5.1. Model availability

The new mother–child model is available as unprotected excel-spreadsheet version from the first author. Please mail to stt@env.dtu.dk.

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References

BgVV (Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin), 2000. Trends der Rückstandsgehalte in Frauenmilch der Bundesrepublik Deutschland – Aufbau der Frauenmilch- und Dioxin-Humandatenbank am BgVV. http://www.bfr.bund.de/cd/432 (accessed 12.03.06).

CEHAPE Children's Environment and Health Action Plan for Europe, 2004. Fourth Ministerial Conference on Environment and Health, Budapest, Hungary, 23–25 June 2004. Working paper. http://www.euro.who.int/document/che/edoc07.pdf (accessed 04.07.07).

Czub, G., McLachlan, M.S., 2004a. Bioaccumulation potential of persistent organic chemicals in humans. Environ. Sci. Technol. 38, 2406–2412.

Czub, G., McLachlan, M.S., 2004b. A food chain model to predict the levels of lipophilic organic contaminants in humans. Environ. Toxicol. Chem. 23, 2356–2366.

Dahl, P., Lindström, G., Wiberg, K., Rappe, C., 1995. Absorption of polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans by breast-fed infants. Chemosphere 30, 2297–2306.

Deurenberg, P., Weststrate, J.A., Seidell, J.C., 1991. Body mass index as a measure of body fatness: age- and sex-specific prediction formulas. Br. J. Nutr. 65, 105–114.

EC (European Commission), 1996. EUSES, the European Union System for the Evaluation of Substances. National Institute of Public Health and the Environment (RIVM), The Netherlands. Available from the European Chemicals Bureau (EC/DG XI), Ispra, Italy.

EC (European Commission), 2003. Technical Guidance Document on Risk Assessment in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances, and Directive 98/8/EC of the European Parliament and of the Council Concerning the Placing of Biocidal Products on the Market. Available from: http://ecb.jrc.it/documents/.

Filser, J.G., Baur, C., Csanády, G., Kessler, W., Kreuzer, P.E., 1997. Toxicokinetic modeling as a tool for risk estimation: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Int. J. Toxicol. 16, 433–448.

Harris, C.A., Woolridge, M.W., Hay, A.W.M., 2001. Factors affecting the transfer of organochlorine pesticide residues to breastmilk. Chemosphere 43, 243–256.

Harrison, K., 2001. Too close to home: dioxin contamination of breast milk and political agenda. Policy Sci. 34, 35–62.

Hesse, V., Jaeger, U., Vogel, H., Kromeyer, K., Zellner, K., Bernhardt, I., et al., 1997. Wachstumsdaten deutscher Kinder von Geburt bis zu 18 Jahren. Sozialpädiatrie 19, 20–22.

Kreuzer, P.E., Csanády, G., Baur, C., Kessler, W., Päpke, O., Greim, H., Filser, J.G., 1997. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and congeners in infants. A toxicokinetic model of human lifetime body burden

by TCDD with special emphasis on its uptake by nutrition. Arch. Toxicol. 71, 383–400.

Kulhanek, A., Trapp, S., Sismilich, M., Janků, J., Zimová, M., 2005. Crop-specific human exposure assessment for polycyclic aromatic hydrocarbons in Czech soils. Sci. Total Environ. 339, 71–80.

Layton, D.W., 1993. Metabolically consistent breathing rates for use in dose assessments. Health Phys. 64, 23–26.

Maruyama, W., Yoshida, K., Tanaka, T., Nakanishi, J., 2003. Simulation of dioxin accumulation in human tissues and analysis of reproductive risk. Chemosphere 53, 301–313.

McLachlan, M.S., 1992. Das Verhalten hydrophober chlororganischer Verbindungen in laktierenden Rindern [doctoral thesis]. University of Bayreuth, Germany.

Nazaroff, W.N., Alvarez-Cohen, L., 2001. Environmental Engineering Science. John Wiley & Sons, New York. 624–625.

Raab, U., Schwegler, U., Preiss, U., Albrecht, M., Fromme, H., 2007. Bavarian breast milk survey – pilot study and future developments. Int. J. Hyg. Environ. Health 210, 341–344.

Rikken, M.G.J., Lijzen, J.P.A., Cornelese, A.A., 2001. Evaluation of Model Concepts on Human Exposure. Proposals for Updating the Most Relevant Exposure Routes of CSOIL. RIVM Report 711 701 022. Bilthoven, The Netherlands.

Rippen, G., 1990–2007. Handbuch Umweltchemikalien (permanently updated). ecomed, Landsberg am Lech, D.

Rogan, W.J., Gladen, B.C., McKinney, J.D., Carreras, N., Hardy, P., Thullen, J., et al., 1986. Polychlorinated biphenyls (PCB) and dichlorophenyl dichloroethane (DDE) in human milk: effects of maternal factors and previous lactation. Am. J. Public Health 76, 172–177.

Schade, G., Heinzow, B., 1998. Organochlorine pesticides and polychlorinated biphenyls in human milk of mothers living in northern Germany: current extent of contamination, time trend from 1986 to 1997 and factors that influence the levels of contamination. Sci. Total Environ. 215, 31–39.

Schecter, A., Päpke, O., Lis, A., Ball, M., Ryan, J.J., Olson, J.R., et al., 1996. Decrease in milk and blood dioxin levels over two years in a mother nursing twins: estimates of decreased maternal and increased infant dioxin body burden from nursing. Chemosphere 32, 543–549.

Shen, H., Main, K.H., Virtanen, H.E., Damggard, I.N., Haavisto, A.-M., Kaleva, M., Boisen, K.A., Schmidt, I.M., Chellakooty, M., Skakebaek, N.E., Toppari, J., Schramm, K.-W., 2007. From mother to child: investigation of the prenatal and postnatal exposure to persistent bioaccumulating toxicants using breast milk and placenta biomonitoring. Chemosphere 67, S256–S262.

Tanabe, S., Kunisue, T., 2007. Persistent organic pollutants in human breast milk from Asian countries. Environ. Pollut. 146, 400–413.

Trapp, S., 2004. Plant uptake and transport models for neutral and ionic chemicals. Environ. Sci. Pollut. Res. 11, 33–39.

Trapp, S., Horobin, R.W., 2005. A predictive model for the selective accumulation of chemicals in tumor cells. Eur. Biophys. J. 34, 959–966.

Travis, C.C., Hattemer-Frey, H.A., Arms, A.A., 1988. Relationship between dietary intake of organic chemicals and their concentrations in human adipose tissue and breast milk. Arch. Environ. Contam. Toxicol. 17, 473–478.

Travis, C.C., Hattemeyer-Frey, H.A., 1991. Human exposure to dioxin. Sci. Total Environ. 104, 97–127.

UNEP (United Nations Environmental Program), 2007. Stockholm Convention on Persistent Organic Pollutants (POPs). http://www.pops.int/ (accessed 04.06.07).

US EPA (U.S. Environmental Protection Agency), 2006. Children's Environmental Health: 2006 Report. Environment, Health, and a Focus on Children. http://yosemite.epa.gov/ochp/ochpweb.nsf/content/homepage.htm (accessed 04.07.07).

Van Der Molen, G.W., Kooijman, S.A.L.M., Slob, W., 1996. A generic toxicokinetic model for persistent lipophilic compounds in humans: an application to TCDD. Fundam. Appl. Toxicol. 31, 83–94.

Wittsiepe, J., Fürst, P., Schrey, P., Lemm, F., Kraft, M., Eberwein, G., et al., 2007. PCDD/F and dioxin-like PCB in human blood and milk from German mothers. Chemosphere 67, S286–S294.

Wuenschmann, S., Fraenzle, S., Markert, B., Zechmeister, H., 2008. Input and transfer of trace metals from food via mothermilk to the child – bioindicative aspects to human health. In: Prasad, M.N.V. (Ed.), Trace Elements: Nutritional Benefits, Environmental Contamination, and Health Implications. John Wiley and Sons, New York.