DYNAMIC ROOT UPTAKE MODEL FOR NEUTRAL LIPOPHILIC ORGANICS

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Abstract—In current European risk assessment, an equilibrium approach is used to estimate chemical uptake from soil into root vegetables. Here a dynamic model for uptake of neutral lipophilic compounds from soil into roots is presented. Using experimental results, it is compared with the equilibrium approach. Very lipophilic compounds (e.g., DDT) diffuse very slowly into plant tissue, so they are likely to remain in the peel of root vegetables. In addition, a dynamic (steady-state) flux model for uptake with transpiration water into thick roots is presented. The model considers input from soil and output to stem with the transpiration stream plus first-order metabolism and dilution by exponential growth. For chemicals with low or intermediate lipophilicity (log $K_{ow} < 2$), there was no relevant difference between dynamic model and equilibrium approach. For lipophilic compounds, the dynamic model gave concentrations far below the thermodynamic equilibrium. The approach was tested against experimental uptake data of benzo[a]pyrene, polychlorinated biphenyls (PCBs), and chlorobenzenes from soil into carrots. Measured concentrations in carrot peels were up to 100 times higher than in the core. The equilibrium approach can predict concentrations in the peels, but for carrot cores and for the whole carrot, the flux model is superior and should be preferred for a more realistic risk assessment.

Keywords—Carrots Modeling Xenobiotics Risk assessment Roots

INTRODUCTION

For the purpose of chemical risk assessment, root concentrations have to be estimated in order to calculate human health risks from consumption of crops growing on polluted soils. In the European scheme of chemical risk assessment [1] and the German tool for risk assessment of contaminated sites UMS (Umwelt und Mensch mit Schadstoffen) [2], a generic one-compartment model has been implemented [3]. The model calculates aerial plant concentrations by a first-order linear equation, which includes sink processes such as dilution by growth, loss to atmosphere, and metabolism inside the plant. For roots, an estimate of the concentration is made from the chemical equilibrium to soil. In particular, for thicker roots and lipophilic chemicals, real concentrations can be far below chemical equilibrium. This means that, in the risk assessment process, risk from uptake of lipophilics into roots is probably overestimated.

MODEL DEVELOPMENT

Current model approach

In the Technical Guidance Documents (TGD) on chemical risk assessment (TGD Part I, Chapter 2, Appendix VII), the European Commission proposes estimating the concentration differences between water and $n$-octanol. Here a dynamic model for uptake with transpiration water into thick roots is presented. The model considers input from soil and output to stem with the transpiration stream plus first-order metabolism and dilution by exponential growth. For chemicals with low or intermediate lipophilicity (log $K_{ow} < 2$), there was no relevant difference between dynamic model and equilibrium approach. For lipophilic compounds, the dynamic model gave concentrations far below the thermodynamic equilibrium. The approach was tested against experimental uptake data of benzo[a]pyrene, polychlorinated biphenyls (PCBs), and chlorobenzenes from soil into carrots. Measured concentrations in carrot peels were up to 100 times higher than in the core. The equilibrium approach can predict concentrations in the peels, but for carrot cores and for the whole carrot, the flux model is superior and should be preferred for a more realistic risk assessment.

$K_{pw} = W_v + L_aK_{ow}$ (2a)

where $W_v$ and $L_a$ are the volumetric water and lipid content of the plant root and $b$ is an empirical factor found by Briggs et al. [4] (0.95 for leaves). The $K_{ow}$ is the equilibrium partition coefficient between $n$-octanol and water.

The value of $K_{pw}$ that is used subsequently in this work differs in units and parameterization and is

$K_{rw} = W + LaK_{ow}$ (2b)

where $W$ and $L$ have the unit mass per mass, $b$ is 0.77 (the value for roots [4]), and $a$ is a factor correcting density differences between water and $n$-octanol (1.22, [3] erratum). The $K_{rw}$ (L/kg) describes the equilibrium partitioning between root concentration $C_r$ (mg/kg fresh wt) and water $C_w$ (mg/L). Usually, the equilibrium partitioning gives a concentration ratio between root and bulk soil near one.

Diffusion into roots

Diffusion into roots has as its endpoint the thermodynamic equilibrium. The diffusive fluxes, which determine the time to reach near-equilibrium, are proportional to the surface area. The experiments of Briggs et al. were done with barley [4]. Grasses are monocotyledons, which usually do not make thick roots [5]. In the experiments, roots rapidly reached equilibrium. Root vegetables, such as carrots, are thick roots and have a smaller surface-to-volume ratio. The properties of soil, plant, and chemical affect the rate of diffusion and the time needed to reach chemical equilibrium.

The time scale of diffusion depends largely on the radius $R$ as [6]

*time scale* = $(R/2)^2/D_{root}$ (3)

where $D_{root}$ is the effective diffusion coefficient of a chemical in roots. Measured data are not available. The value is estimated with a method recently applied to wood [7]. The frac-
tions of chemical present in the water and the gas phase of the root, \( f_w \) and \( f_G \), are estimated from

\[
f_w = P_w/(K_{pw} + P_w + P_G K_{pwG})
\]

(4)

\[
f_G = P_G K_{pwG}/(K_{pw} + P_w + P_G K_{pwG})
\]

(5)

where \( K_{pw} \) is the equilibrium partition coefficient between air and water (also named dimensionless Henry’s Law constant), \( P_w \) and \( P_G \) are the volumetric water and gas fractions of roots, respectively. Values for water content of vegetables are well known, e.g., carrot has a water content around 0.89 g/g [8]. For physiological reasons, there must be some gaseous pore volume in root tissue, e.g., in the form of aerenchym [5], but data for carrots were not found, and \( P_G \) is set to 0.1 L/L. The effective diffusion coefficients in the water phase, \( D_{w,eff} \), and the gas phase, \( D_{G,eff} \), are calculated from

\[
D_{w,eff} = T f_w D_w
\]

(6)

\[
D_{G,eff} = T f_G D_G
\]

(7)

where \( T \) is a tortuosity factor reflecting physical hindrances. For wood, \( T = 0.01 \) was found [6], \( D_w \) and \( D_G \) are the diffusion coefficients of the chemical in water and gas phase (\( \approx 5 \times 10^{-3} \) and 1 m/d, respectively). The diffusion coefficient in the root, \( D_{roott} \), is the sum of \( D_{w,eff} \) and \( D_{G,eff} \). The results of Equation 3 for 10 chemicals (data from [9,10]) are shown in Table 1. Chemical equilibrium is reached rapidly for both fine and thick roots when the compounds are not strongly sorbing (log \( K_{pw} \) small) and have a potential to move in the gas phase (\( K_{pwG} \) high). Chemicals that are unlikely to reach equilibrium within one vegetation period (usually less than 150 d) are lindane, dieldrin, and DDT.

Table 1. Time scale for diffusion into root; chemical data from Rippen [9] except dieldrin and trichlorobenzene [10]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \log K_{ocw} )</th>
<th>( K_{ocw} )</th>
<th>Time scale (d) ( R = 0.1 ) cm</th>
<th>Time scale (d) ( R = 1 ) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.48</td>
<td>2.2 \times 10^{-3}</td>
<td>0.7</td>
<td>7.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.13</td>
<td>0.23</td>
<td>0.002</td>
<td>0.24</td>
</tr>
<tr>
<td>CB(^a)</td>
<td>2.78</td>
<td>0.15</td>
<td>0.008</td>
<td>0.84</td>
</tr>
<tr>
<td>( \omega )-Xylene</td>
<td>3.16</td>
<td>0.22</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>3.35</td>
<td>0.023</td>
<td>0.13</td>
<td>13.1</td>
</tr>
<tr>
<td>1,2-DiCB(^b)</td>
<td>3.4</td>
<td>0.1</td>
<td>0.03</td>
<td>3.3</td>
</tr>
<tr>
<td>Lindane</td>
<td>3.76</td>
<td>4.5 \times 10^{-3}</td>
<td>12.6</td>
<td>1,260</td>
</tr>
<tr>
<td>1,3,5-TrICB</td>
<td>4.02</td>
<td>0.15</td>
<td>0.06</td>
<td>6.3</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>5.14</td>
<td>0.00046</td>
<td>75.9</td>
<td>7,590</td>
</tr>
<tr>
<td>DDT</td>
<td>6.2</td>
<td>0.0011</td>
<td>290</td>
<td>2.9 \times 10^4</td>
</tr>
</tbody>
</table>

\( a \) CB = chlorobenzene.

Flux into roots

If only the peel of a root vegetable is in diffusive exchange with the surrounding soil, the core is loaded solely with the water taken up. Then, for this core, uptake is with the transpiration stream \( Q \) (L/d) and loss is by flux upward and metabolism \( k_m \) (d\(^{-1}\)).

\[
dm/dt = C_s Q - C_{XY} Q - k_m m_R
\]

(9)

where \( m_R \) is the mass of chemical in roots and \( C_{XY} \) is the concentration in the xylem (mg/L) at the outflow of the root. If the xylem sap is in equilibrium with the root, the concentration is \( C_{G}/K_{wG} \). The \( K_{wG} \), the partition coefficient between roots and water, is identical to \( K_{wG} \) in Equation 2b. The steady-state solution for the root core concentration is

\[
C_R = \frac{Q}{Q/K_{wG} + k v} C_S
\]

(10)

where \( k \) is the sum of an exponential growth rate and \( k_m \) and \( V \) is the root volume (L). The growth rate appears in the equation because, although the chemical mass may remain constant, the concentration may decrease by growth, which was assumed to be exponential. In the absence of metabolism or growth, the concentration ratio \( C_g/C_S \) equals the thermodynamic equilibrium \( K_{wG} \).

\( C_S \) is the concentration in soil solution (mg/L), related to that in soil matrix \( C_M (mg/kg) \) by the sorption coefficient \( K_d \) (L/kg), with \( C_S = C_g/K_d \). \( K_d \) of lipophilic organic compounds can be estimated from \( K_d = OC \times K_{ocw} \), where \( OC \) is the organic carbon content of the soil (g/g). The \( K_{ocw} \), the partition coefficient between organic carbon and water, can be estimated from the \( K_{ocw} \), e.g., with an equation applicable for predominantly hydrophobics [1], as

\[
\log K_{ocw} = 0.81 \log K_{ocw} + 0.1
\]

(11)

Then for the dynamic (steady-state) bioconcentration factor (BCF) between root core and soil matrix, \( Q/K_d \)

\[
BCF = C_R/C_M = \frac{Q/K_d}{Q/K_{wG} + k v}
\]

(12)

which gives, in the case of negligible \( k \), \( K_{wG}/K_d \) (equilibrium partitioning).

MODEL APPLICATION

Sensitivity analysis

The model (Eqs. 12 and 2b) has to be parameterized, and generic data were selected (Table 2). In Figure 2, the result of Equation 12 with varying loss rate \( k \) (0.1 and 0.01/d correspond to a half time of 6.9 and 69 d) and \( \log K_{ocw} \) of the chemical is.
shown. It can be seen that, for chemicals with low or intermediate lipophilicity (log $K_{ow} < 2$), the difference between equilibrium partitioning ($k = 0$) and the dynamic uptake equation is negligible. However, for the more lipophilic compounds, the difference is considerable, in particular for higher $k$ values.

**Limitations**

The model approach is strictly limited to nonionizing and lipophilic compounds. Polar compounds and weak acids undergo a phloem transport (from leaves to roots) that is not considered in the approach. Electrolytes have a completely differing partitioning behavior, which does not depend on lipophilic sorption but on the electrochemical gradient. Weak electrolytes may be subjected to the ion trap, which leads to additional accumulation [11,12].

The dynamic flux equation can be used for thick roots that are peeled before consumption. Potatoes, which are the major vegetables in Europe harvested from below the soil surface, are not roots but rather are storage organs of the stem. The transpiration stream does not cross the tubers, which are loaded from the phloem. Therefore, the dynamic flux approach (Eqn. 12) is not applicable for potatoes. However, the diffusion Equation 8 can be used (after proper parameterization). Another, easier approach is to assume the peel is in chemical equilibrium with the surrounding soil.

**Comparison with experimental data**

**Benzo[a]pyrene.** Benzo[a]pyrene (BaP) is a polycyclic aromatic hydrocarbon (PAH) with a log $K_{ow}$ of 6.04 [9]. Edwards [13] reviewed uptake of PAH into vegetation and gave data for peeled and nonpeeled root vegetables. Bioconcentration factors derived from his data are given for seven different experiments and for whole (washed) carrots in Figure 3. The highest measured BCF is 0.023, the mean is 0.008 (dry wt basis). The dynamic BCF is calculated to be 0.04 (dry wt), the thermodynamic equilibrium is at 5.8. This means the BaP concentrations in carrots are far from equilibrium and even lower than estimated by the dynamic approach with $k = 0.1/d$.

**Polychlorinated biphenyls (PCB).** Uptake into carrot peels and cores was determined separately in an outdoor lysimeter study with PCB (T. Delschen, http://www.lua.nrw.de/veroeffentlichungen/lieferbareveroeffentlichungen/vls1.html). The PCB had been applied in different dosages and forms. Bioconcentration factors were derived by curve fit (S. Trapp, http://www.usf.uni-osnabrueck.de/archive/~strapp/transfer.html) for the six PCBs Ballschmiter 28, 52, 101, 138, 153, and 180, with log $K_{ow}$ values from 5.71 to 7.21 [14]. Figure 4 shows the experimental results for carrot core and peel compared with the dynamic approach and the calculated chemical equilibrium. Measurements for PCB uptake into the carrot core were close to the dynamic BCF. Values for PCB 153 and 180 in carrot cores were below the detection limit, which is equal to a BCF of $<0.0005$. The PCB concentrations in peels were closer to thermodynamic equilibrium except concentrations of the very lipophilic PCB 180 (log $K_{ow}$ of 7.21) in carrot peels, which were almost a factor of 100 below equilibrium. This indicates that the chemical could only diffuse into a very thin layer of the carrots.

**Chlorobenzenes.** Uptake of chlorobenzenes into carrots from spiked and sewage-sludge amended soil was measured [8]. Di-, tri-, tetra-, penta-, and hexachlorobenzenes with log $K_{ow}$ values ranging from 3.44 to 5.76 were analyzed. Four sets of experiments were carried out, named control, spiked, low rate, and high rate (of sewage sludge application). The experiments differed in the type of chlorobenzene application. Plant growth

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**Table 2. Parameterization of Equations 12 and 2b**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root water content</td>
<td>2b</td>
<td>$W$</td>
<td>0.89</td>
<td>g/g</td>
<td>[8]</td>
</tr>
<tr>
<td>Root lipid content</td>
<td>2b</td>
<td>$L$</td>
<td>0.025</td>
<td>g/g</td>
<td>Generic</td>
</tr>
<tr>
<td>Root density</td>
<td>Neglected</td>
<td>$a$</td>
<td>1</td>
<td>kg/L</td>
<td>Generic</td>
</tr>
<tr>
<td>Density correction</td>
<td>2b</td>
<td>$b$</td>
<td>1.22</td>
<td>(--)</td>
<td>[3]</td>
</tr>
<tr>
<td>Empirical factor</td>
<td>2b</td>
<td></td>
<td>0.77</td>
<td>(--)</td>
<td>[4]</td>
</tr>
<tr>
<td>Transpiration stream</td>
<td>12</td>
<td>$Q$</td>
<td>1</td>
<td>L/d</td>
<td>Generic</td>
</tr>
<tr>
<td>Root volume</td>
<td>12</td>
<td>$V$</td>
<td>1</td>
<td>L</td>
<td>Generic</td>
</tr>
<tr>
<td>First-order rate</td>
<td>12</td>
<td>$k$</td>
<td>0.1</td>
<td>d$^{-1}$</td>
<td>Generic</td>
</tr>
<tr>
<td>Organic carbon in soil</td>
<td>For $K_d$</td>
<td>$OC$</td>
<td>0.02</td>
<td>g/g</td>
<td>Generic</td>
</tr>
</tbody>
</table>

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Fig. 2. Bioconcentration factor (BCF) for roots (fresh wt) to soil matrix simulated with the dynamic approach (Eqn. 12) versus log $K_{ow}$ for three values of $k$. Water fractions in root and soil neglected.

Fig. 3. Uptake of BaP into carrots, whole thick root, seven experiments [13] versus calculated steady-state concentration (Eqn. 12, $k = 0.1/d$).
was affected. Measured bioconcentrations differed largely for the experiments. The highest transfers into carrot cores were found for tri- and tetrachlorobenzenes (log $K_{oc}$ of 4.2 to 4.55; Fig. 5). Measured uptake of dichlorobenzenes (log $K_{oc}$ of 3.38 to 3.44) from soil into carrots was lower than for tri- and tetrachlorobenzenes and lower than expected by the dynamic model. Metabolism around or inside the carrots probably occurred. Only for dichlorobenzenes was uptake into cores higher than into peels (Fig. 6). For the lipophilic penta- and hexachlorobenzenes, concentrations in peel were up to two orders of magnitude higher than in the core. Generally, bioconcentration of cores was more accurately predicted with the dynamic model, but bioconcentration of peels was more accurately predicted with the equilibrium approach.

CONCLUSIONS

Experimental results and dynamic model simulations showed that the concentration of lipophilic organic chemicals in thick roots (root vegetables) is not accurately predicted by the equilibrium approach but rather is overestimated. This is contrary to the uptake of lipophobics into leaves, which is underestimated by the European Union’s risk assessment scheme because the process of particle deposition is missing [15]. Risk assessors may come to incorrect conclusions about risk management.

The dynamic approach does not need more chemical data than the chemical equilibrium approach except that knowledge about metabolism rates inside the plants can be used, if available. Plant values used above are generic but may be replaced by site- and plant-specific data.

The dynamic approach gives more realistic results for lipophilic compounds. Application of this approach is therefore proposed for a more realistic risk assessment of lipophilic compounds.

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REFERENCES