SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 21, No. 1, pp. 203–206, 2002

Printed in the USA
0730-7268/02 $9.00 + .00

DYNAMIC ROOT UPTAKE MODEL FOR NEUTRAL LIPOPHILIC ORGANICS

STEFAN TRAPP*
Environment and Resources, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

(*Received* 12 *February* 2001; *Accepted* 21 *June* 2001)

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 in roots using an equilibrium approach [1]. It is argued that the upper boundary for concentrations in roots (fresh wt) is chemical equilibrium to soil. The equations in the TGD are based on the model proposed by Trapp and Matthies [3] but are not identical to it, i.e.,

$$C_R = K_{PW} C_S / \rho_P \quad (1)$$

where C_R and C_S are the concentrations in roots (mg/kg) and in soil pore water (mg/m^3), ρ_P is the bulk density of the root (kg/m^3), and K_{PW} is the partition coefficient between plant material and water (m^3/m^3). In the TGD,

$$K_{PW} = W_v + L_v K_{ow}^b \quad (2a)$$

where W_v and L_v 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_{RW} that is used subsequently in this work differs in units and parameterization and is

$$K_{RW} = W + LaK_{ow}^b \quad (2b)$$

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]

$$\textit{time scale} \approx (R/2)^2 / D_{root} \quad (3)$$

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-

* stt@er.dtu.dk.

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

Compound	Log K_{ow}	K_{AW}	Time scale (d) $R = 0.1$ cm	Time scale (d) $R = 1$ cm
Phenol	1.48	2.2×10^{-5}	0.7	7.0
Benzene	2.13	0.23	0.002	0.24
CB[a]	2.78	0.15	0.008	0.84
o-Xylene	3.16	0.22	0.01	1.0
Naphthalene	3.35	0.023	0.13	13.1
1,2-DiCB[a]	3.4	0.1	0.03	3.3
Lindane	3.76	4.5×10^{-5}	12.6	1,260
1,3,5-TriCB	4.02	0.15	0.06	6.3
Dieldrin	5.14	0.00046	75.9	7,590
DDT	6.2	0.0011	290	2.9×10^4

[a] CB = chlorobenzene.

tions of chemical present in the water and the gas phase of the root, f_W and f_G, are estimated from

$$f_W = P_W/(K_{PW} + P_W + P_G K_{AW}) \quad (4)$$

$$f_G = P_G K_{AW}/(K_{PW} + P_W + P_G K_{AW}) \quad (5)$$

where K_{AW} 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

$$D_{W,eff} = T f_W D_W \quad (6)$$

$$D_{G,eff} = T f_G D_G \quad (7)$$

where T is a tortuosity factor reflecting physical hindrances. For wood, $T \approx 0.01$ was found [6]. D_W and D_G are the diffusion coefficients of the chemical in water and gas phase ($\sim 5 \times 10^{-5}$ and 1 m^2/d, respectively). The diffusion coefficient in the root, D_{root}, 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_{ow} small) and have a potential to move in the gas phase (K_{AW} high). Chemicals that are unlikely to reach equilibrium within one vegetation period (usually less than 150 d) are lindane, dieldrin, and DDT.

The analytical solution for diffusion in the z-direction into a plane sheet without advection, growth, or reaction and with constant concentration C_0 at the surface $z = 0$ is

$$C(z, t) = C_0 \mathrm{erfc}[z/\sqrt{(4Dt)}] \quad (8)$$

where D is the diffusion coefficient. For diffusion into root tissue, D is D_{root} (Eqns. 6 and 7). The resulting concentrations after 150 d of diffusion of DDT, dieldrin, and lindane into carrot tissue are shown in Figure 1. Lindane can be found up to 5 mm deep in the carrot, whereas dieldrin and in particular DDT remain almost completely in the peel. In normal kitchen preparation, carrots (and other root vegetables) are peeled (1 mm) and the majority of lipophilic chemicals would be removed. Some people eat carrots just washed but not peeled (e.g., the author).

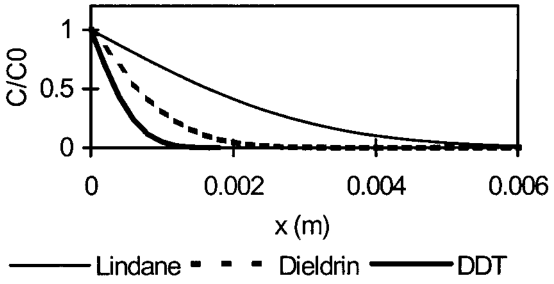

Fig. 1. Concentration versus distance for diffusion of lindane, dieldrin, and DDT into a carrot after $t = 150$ d.

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}),

$$dm_R/dt = C_S Q - C_{XY} Q - k_m m_R \quad (9)$$

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_R/K_{RW}. The K_{RW}, the partition coefficient between roots and water, is identical to K_{RW} in Equation 2b. The steady-state solution for the root core concentration is

$$C_R = \frac{Q}{Q/K_{RW} + kV} C_S \quad (10)$$

where k is the sum of an exponential growth rate and k_m and where 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_R/C_S equals the thermodynamic equilibrium K_{RW}.

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 $C_S = C_M/K_d$. K_d of lipophilic organic compounds can be estimated from $K_d = OC \cdot K_{oc}$, where OC is the organic carbon content of the soil (g/g). The K_{oc}, the partition coefficient between organic carbon and water, can be estimated from the K_{ow}, e.g., with an equation applicable for predominantly hydrophobics [1], as

$$\log K_{oc} = 0.81 \log K_{ow} + 0.1 \quad (11)$$

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

$$BCF = C_R/C_M = \frac{Q/K_d}{Q/K_{RW} + kV} \quad (12)$$

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

MODEL APPLICATION

Sensitivity analysis

The model (Eqns. 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_{ow} of the chemical is

Table 2. Parameterization of Equations 12 and 2b

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

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 (B*a*P) 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 B*a*P 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

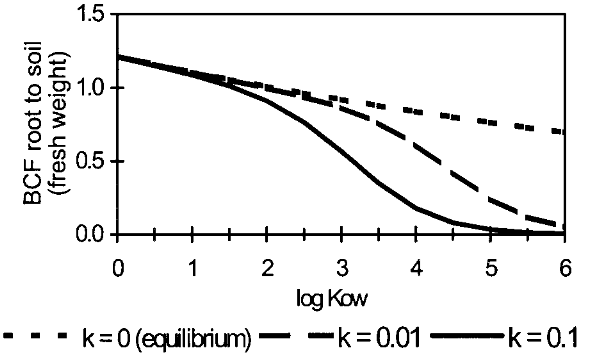

Fig. 2. Bioconcentration factor (BCF) for roots (fresh wt) to soil matrix simulated with the dynamic approach (Eqn. 12) versus log K_{ow} for three values of k. Water fractions in root and soil neglected.

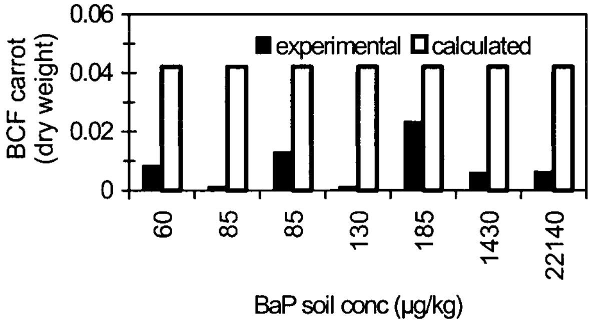

Fig. 3. Uptake of B*a*P into carrots, whole thick root, seven experiments [13] versus calculated steady-state concentration (Eqn. 12, $k = 0.1$/d).

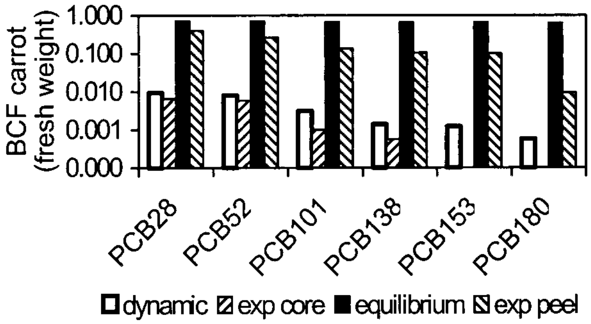

Fig. 4. Bioconcentration factors (BCFs) of polychlorinated biphenyl (PCB) from soil into core and peel of carrots; comparison of experimental results to the dynamic and the equilibrium model calculation.

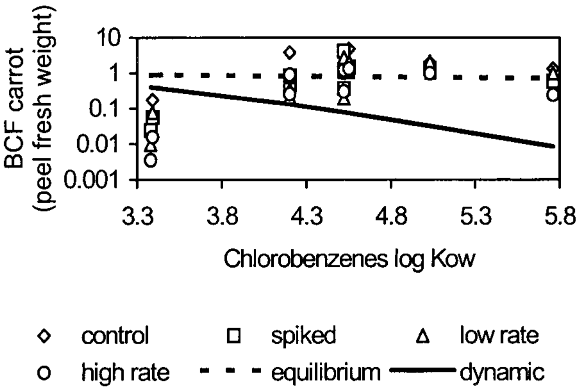

Fig. 6. Uptake of chlorobenzenes from soil into carrot peels compared with the model calculations. BCF = bioconcentration factor.

was affected. Measured bioconcentrations differed largely for the experiments. The highest transfers into carrot cores were found for tri- and tetrachlorobenzenes (log K_{ow} of 4.2 to 4.55; Fig. 5). Measured uptake of dichlorobenzenes (log K_{ow} 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 hexachlorbenzenes, 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 lipophilics 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.

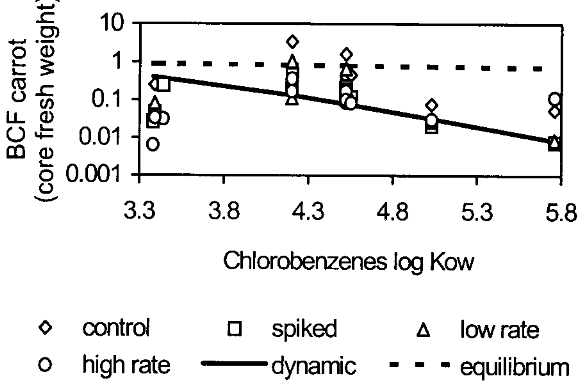

Fig. 5. Uptake of chlorobenzenes from soil into carrot cores compared with the model calculations.

Acknowledgement—This work was supported by the European Commission, program Quality of Life, grant QLK3-CT2000-00164.

REFERENCES

1. EC European Commission. 1996. Technical guidance document in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) no. 1488/94 on risk assessment for existing substances. Office for Official Publications of the European Communities, Luxembourg, Luxembourg.
2. Fresenius Umwelt-Consult. 1997. *Umwelt und Mensch mit Schadstoffen.* Taunusstein, Germany.
3. Trapp S, Matthies M. 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. *Environ Sci Technol* 29:2333–2338; Erratum 30:360.
4. Briggs GG, Bromilow RH, Evans AA. 1982. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pestic Sci* 13:495–504.
5. Sitte P, Ziegler H, Ehrendorfer F, Bresinsky A. 1991. *Lehrbuch der Botanik für Hochschulen,* 33rd ed. Gustav Fischer, Stuttgart, Germany.
6. Mackay AA, Gschwend PM. 2000. Sorption of monoaromatic hydrocarbons to wood. *Environ Sci Technol* 34:839–845.
7. Trapp S, Miglioranza KSB, Mosbæk H. 2001. Sorption of lipophilic organic compounds to wood and implications for their environmental fate. *Environ Sci Technol* 25:1561–1566.
8. Wang M-J, Jones K. 1994. Uptake of chlorobenzenes by carrots from spiked and sewage-sludge amended soil. *Environ Sci Technol* 28:1260–1267.
9. Rippen G. 2000. *Handbuch Umweltchemikalien.* Ecomed, Landsberg am Lech, Germany.
10. Mackay D, Shiu WY, Ma KC. 1992. *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals,* Vol. 1-5. Lewis, Boca Raton, FL, USA.
11. Bromilow RH, Chamberlain K. 1995. Principles governing uptake and transport of chemicals. In Trapp S, McFarlane C, eds, *Plant Contamination: Modeling and Simulation of Organic Chemical Processes.* Lewis, Boca Raton, FL, USA, pp 37–68.
12. Trapp S. 2000. Modeling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. *Pestic Manag Sci* 56:767–778.
13. Edwards NT. 1983. Polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment—A review. *J Environ Qual* 12:427–441.
14. Brodsky J. 1986. Zusammenhang von Molekülstruktur und Retention in ''reversed-phase''-HPLC-Systemen bei Chlorbenzolen und Polychlorbiphenylen. PhD thesis. Faculty for Natural Science and Mathematics at the University of Ulm, Ulm, Germany.
15. Trapp S, Schwartz S. 2000. Proposals to overcome limitations in the EU chemical risk assessment scheme. *Chemosphere* 41:965–971.