Uptake of Organic Chemicals into Plants

Models, equations and exercises

Second edition, Stefan Trapp 2009, version 28 May 09

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References
Introduction

The need for models predicting the uptake and transport of chemicals in plants occurs in many
disciplines, to mention some:

- Pesticide design. Pesticide uptake and fate inside of plants are of large economical and ecological
  interest.
- Risk assessment. The uptake of chemicals (pesticides or environmental contaminants) into plants
  may lead to residues that are a hazard to human health and ecosystems. There is a large interest in
  the prediction of the amount and type of these residues.
- Ecotoxicology. The toxicity of chemicals depends on the doses at the target. Therefore, the uptake
  and transport of chemicals in plants are a pre-requisite for a toxic effect, e.g. of non-target plants
  near pesticide spray applications.
- Environmental biotechnology. Environmental biotechnology, e.g. the cleaning of polluted
  wastewater and soils using plants and associated microbes, is an emerging area called
  phytoremediation. Knowledge about transport and fate of pollutants is needed to define the best
  clean-up strategy.
- Plant physiology. The physiological processes inside plants and the primary and secondary
  metabolism involve chemicals, which are transported across membranes and by the vascular system
  of the plants. These plant-born chemicals follow the same physico-chemical laws as xenobiotics.
  However, plants have developed special transport systems for chemicals essential in their
  metabolism, whereas this is not likely for xenobiotic compounds.

The above and other relevant applications make it worth developing and using mathematical models
for the prediction of chemical uptake into plants, and the resulting effects. This script for PhD
courses summarizes processes, models and equations, gives example data sets, example
calculations, and contains the EXERCISES you can do to improve your predictive skills. Solutions
are handed out separately. The most important equations are marked by red numbers.

What can be done by hand calculations can also be done with excel in a spread-sheet. During the
course we will exercises with computers, where the models are applied. Course participants and all
that ask for will receive the models as files in a open (and hopefully error-free) version.

All what you receive is free for your use. Please do not duplicate in high numbers without asking,
ok? If you find mistakes or if something is unclear, please tell me or mail to me: stt@env.dtu.dk

Good luck and have fun,

Lyngby May 2009
Most of our plants have the three organs roots, stems, and leaves. From time to time, flowers and fruits occur. The role of roots is to anchor the plant in the soil and to take up water and nutrients. The role the of stems is to transport the water upwards, and to bring the leaves to the light. The role of the leaves is to take up sunlight and CO₂, and to make photosynthesis. When the plant takes up carbon dioxide from atmosphere, water is evaporating. Only a very small fraction (<2%) of the water taken up by roots is actually taken up into plant cells.

Most plants we know are “vascular plants”, which means they have two transport systems inside: the xylem and the phloem. The xylem is a dead pipe system. Water is drawn upwards by physical forces. The phloem is composed of living cells, the sieve tubes. Flux in phloem occurs from the leaves to all growing points of the plant, and to the fruits. In the phloem, sugar and other essential substances are transported, e.g., to the fruits.

The structure that enables plants to extract water and nutrients from soil and to exchange gases with the air allows chemicals to enter the plant and to be transported inside.

Several uptake processes are known and occur simultaneously (Figure):

- Uptake with soil water and translocation upwards in the xylem; diffusion in gas or water phase into roots; direct soil contact; particle deposition from soil or air; phloem transport; gas flux out of the soil and into the aerial tissue; direct exchange with air.

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**Figure**: Uptake and transport processes in plants.

**Uptake pathways of chemicals into plants**

**Figure**: Uptake pathways of chemicals into plants.
Data

The models presented below are based on the physiology of plants, and therefore they need real data. Within twenty years of model evolution, the models developed towards easy and available data input. Still, retrieving the input data from literature or measuring these data in experiments can be a tough business, therefore some basic rules here.

As outlined in the previous section, most plants, but in any case most cash-crops, are rather similar in their basic architecture: roots, stems, leaves, and eventually fruits or grains. Besides, most plants are also quite similar in their performance, when it comes to extraction of CO2 from atmosphere and water from soil. Therefore, there are ranges of data or combinations of data which are "typical", and which are helpful to estimate data for the models.

Rules of thumb

a) Mass, leaf area, growth rates

- 50% of plant mass (excluding wood) is below surface - i.e. root mass is similar to shoot mass.

- an excellent harvest is 100 dezitons (100 * 100 kg = 10 000 kg) per hektar, a good harvest is 50 dezitons per hektar (5 000 kg/ha). One hektar is 10 000 m², thus 0.5 to 1 kg corn per m² is harvested. Corn is about 50% of the above-ground plant mass (the other 50% is straw). This means that 1 - 2 kg/m² is a usual crop yield and plant mass.

- The most effective leaf area (area of leaves divided by soil surface area) is 4 (i.e. 4 m² of leaves per m² of soil). Below, light is not used efficiently, above, leaf area is higher than required to use light efficiently. Some plants, for example trees, will nonetheless produce a higher leaf area - just in case nasty insect will start to eat them. Thus, the realistic range of leaf area is 0 to 8.

1 g of leaf is 100 cm² area (measured for willow leaves), with 50% of shoot mass is leaves this gives a leaf area of 5 m² per kg shoot.

- Common plants need between 200 and 1000 L of water, in average 500 L, to produce 1 kg of dry plant matter.

- Green plants have about 90% water content (corn: 15%)

- 1 kg plant mass (fresh weigh) requires thus 50 L transpired water.

- 1 kg plant mass requires 50 to 60 days for growth

- a meadow doubles its biomass in 3 weeks, a maize field in (minimum) 3 days - average is 1 week.

- 2/3rd of precipitation is evapotranspired (means: evaporating from soil and transpired from plants). Let's say 75% is transpiration, 2 L precipitation per day (730 L/m² and year), hereof 2/3rd and 75% = 1 L/d transpiration in average.

OK; we've got it. From this we can deduce the numbers
Plant mass per m$^2$
roots 1 kg
leaves 1 kg
fruits 0.5 kg

Transpiration
1 L d$^{-1}$ m$^{-2}$

Growth rate
0.1 d$^{-1}$ (doubling in 1 week) for field crops
0.035 d$^{-1}$ (doubling in 3 weeks) for meadows

In steady-state modeling, the data need to fit together, i.e. they should be taken from the same point in time. A possibility is the harvest, but it may also be another time-point, e.g., the end of exponential growth. It is in all models the ratios (area to mass, transpiration to mass) that count, rarely the absolute values. If you enter values for individual plants - please take large care that the RATIOS between mass, transpiration and leaf area are within or near the given values - otherwise, they are most likely non-realistic or not representative!

Good luck in searching for data. It is a hard job.

**Crop-specific models, overview**

Not all crops are grown at the same time in an area, and processes relevant for the crops vary. Crop-specific models have been developed by describing the basic processes of convective or diffusive uptake, chemical equilibrium between plant tissue (roots, wood, leaves, tubers) and surrounding soil or air, as well as fluxes inside the plants. This mechanistic principle of building is similar for all crop-specific models. However, the processes and the parameterization depend on the type of crop (Figure). The models are briefly described below but for more detailed descriptions, validation studies and the limits of applicability we refer the reader to published original work (Trapp and Matthies 1995; Trapp 2002; Trapp 2007, Trapp et al. 2007; Legind and Trapp 2009).

**Figure:** Crop types and processes of the plant uptake models. "Not considered" is outdated: in the meanwhile we added most of these processes.
The Chemicals

About 5 million different chemicals are known. About 100 000 are used in European economy. About 20 000 of them are available on the Danish market. More than 1000 chemicals have a production volume of > 1000 tons per year.

We selected 3 chemicals for the exercises. Data are listed in Table 1.

**MTBE** Methyl tertiary butyl ether is a gasoline additive. It is the second most produced chemical in the US (probably world-wide). MTBE is quite persistent and provides problems in groundwater. The chemical is water soluble and has a high vapour pressure.

**TBA** Terbutylazine is a herbicide of the triazine type (like atrazine). Triazines are taken up via roots and disturb photosynthesis. TBA is not very water soluble and therefore relatively “lipophilic”. The vapour pressure is low. It is highly toxic to most plants (herbicide).

**BaP** Benzo(a)pyrene is a polycyclic aromatic hydrocarbon. It is the longest known and one of the strongest carcinogens. Its sources are incomplete burning processes from heating, traffic, industry, and smoking. It occurs practically everywhere in the environment. It is very lipophilic and has a relatively low vapour pressure.

![Chemical structures](Image)

Methyl tertiary butyl ether MTBE Terbutylazine TBA Benzo(a)pyrene BaP

**Table 1**: Partition coefficient between octanol and water $K_{OW}$, and between air and water $K_{AW}$.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$K_{OW}$</th>
<th>log $K_{OW}$</th>
<th>$K_{AW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>13.8</td>
<td>1.14</td>
<td>0.0175</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>1622</td>
<td>3.21</td>
<td>$1.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>1348 963</td>
<td>6.13</td>
<td>$1.39 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
CHAPTER 1: Chemical Equilibrium


1A About Equilibrium

Air, water and hydrophobic phases (not mixable with water) are found in the biotic and abiotic environment. The calculation of equilibrium partition coefficients allows the estimation of the diffusion tendency of a chemical. The equilibrium is the condition with the highest entropy, a condition, which is only approximately reached within finite time periods. Diffusion processes always go towards higher entropy, i.e. to equilibrium. The smaller the scale, the closer are the concentrations to equilibrium (local equilibrium).

Partitioning between lipid phases and water

The equilibrium partitioning between a hydrophobic phase (lipids, oils, etc.) and water is described by the n-octanol-water partition coefficient $K_{OW}$ ($m^3: m^3$).

$$K_{OW} = C_O/C_W$$

$C_O$ is the equilibrium concentration of a substance in n-octanol ($kg m^{-3}$), and $C_W$ is that in water ($kg m^{-3}$). The $K_{OW}$ is used as a predictor for the partitioning between lipid phases in the environment and water. Measured values are available for many compounds.

Partitioning between air (gas phase) and water

The partitioning of a liquid between air and water describes the Henry's law constant $H$. It can be calculated from solubility in water $S$ and saturation vapour pressure $p_S$:

$$H = p_S/S$$

$H$ is the Henry's law constant ($Pa m^3 mol^{-1}$), $p_S$ is the saturation vapor pressure (Pa) and $S$ the solubility in water (mol m$^{-3}$). The partition coefficient air to water $K_{AW}$ (= non-dimensional Henry's Law Constant) is then:

$$K_{AW} = H/(R T) = C_A/C_W$$

$C_A$ is the equilibrium concentration in air ($kg m^{-3}$), $C_W$ is the equilibrium concentration in water ($kg m^{-3}$), $R$ is the universal gas constant ($8.314 J mol^{-1} K^{-1}$) and $T$ is the temperature (K). Values of $K_{AW}$ can vary by many orders of magnitude (Table 1).
Multimedia partitioning

If the equilibrium concentration ratio between lipid and water is \( C_{\text{Lipid}} / C_{\text{Water}} = K_{\text{OW}} \) and that between air and water is \( C_{\text{Air}} / C_{\text{Water}} = K_{\text{AW}} \) and if furthermore the concentration of MTBE in air is 1 mg m\(^{-3}\), what is the equilibrium concentration in air, water and in a lipid droplet?

Example calculation for MTBE

\[
C_{\text{Air}} = 1 \text{ mg m}^{-3}
\]

\[
C_{\text{Air}} / C_{\text{Water}} = K_{\text{AW}} \rightarrow C_{\text{Water}} = C_{\text{Air}} / K_{\text{AW}} = 1 \text{ mg m}^{-3} / 0.0175 = 57 \text{ mg/m}^3 = 0.057 \text{ mg/L}
\]

\[
C_{\text{Lipid}} / C_{\text{Water}} = K_{\text{OW}} \rightarrow C_{\text{Lipid}} = C_{\text{Water}} \times K_{\text{OW}} = 0.057 \text{ mg/L} \times 13.8 = 0.788 \text{ mg/L}
\]

Exercise 1A

If the concentrations of in air of terbutylazine and of benzo(a)pyrene are 1 ng m\(^{-3}\), what are the equilibrium concentrations in air, water and in a lipid droplet?

1B Partitioning in soil

Soil is composed of water, the “soil matrix”, and gas pores – a typical multimedia system. Uptake into plants is often related to the concentration of a chemical in soil water. This makes sense, when the chemicals are taken up with the transpired water. However, what is the concentration in the soil pore water, related to the total, “bulk soil” concentration?

Sorption to soil matrix.

Sorption to solids is described by the empirical Freundlich relation:

\[
x/m_M = K \times C_W^{1/n}
\]

\( x \) is the adsorbed amount of chemical (mg), \( m_M \) is the mass of sorbent, here the soil matrix \( M \) (kg), \( K \) is the proportionality factor (Freundlich constant) (L water / kg soil), \( C_W \) is the equilibrium concentration in the aqueous solution (mg/L water) and \( n \) is a measure of non-linearity of the relation. For small concentrations, values of \( n \) are close to one. The Freundlich constant can then be seen as the slope of the linear adsorption/desorption isotherm. It is often called the distribution coefficient \( K_d \) between soil matrix and water.

\[
x/m_M = C_M = K_d \times C_W
\]

\( C_M \) is the concentration sorbed to the soil matrix (mg/kg).

The \( K_d \) of organic chemicals is related to the fraction of organic carbon in soil \( OC \):

\[
K_d = OC \times K_{OC}
\]

\( K_{OC} \) see below
**Bulk soil.** The natural bulk soil consists of soil matrix, soil solution and soil gas. We need to consider that.

The concentration ratio of dry soil (= soil matrix, index M) to water is as before:

\[ C_M / C_W = K_d \quad \text{[mg/kg : mg/L = L/kg]} \]

For a liter of dry soil (index Mvol), we multiply with the dry soil density \( \rho_{dry} \) [kg/L]

\[ C_{M\text{Vol}} [\text{mg/L}] / C_W [\text{mg/L}] = K_d \times \rho_{dry} \quad \text{[mg/L : mg/L = L/L]} \]

For wet soil (C_{SoilVol}), we add the pore water fraction \( P_W \) [L/L] and gas pore fraction \( P_A \) [L/L]:

\[ C_{SoilVol} / C_W = K_d \times \rho_{dry} + P_W + P_A \times K_{AW} \quad \text{[mg/L : mg/L = L/L]} \]

Now we go back to the unit mg/kg for the soil concentration (C_{Soil}). We achieve that by dividing by the wet soil density \( \rho_{wet} (= \rho_{dry} + P_W) \), unit kg/L:

\[ C_{Soil} / C_W = (K_d \times \rho_{dry} + P_W + P_A \times K_{AW}) / \rho_{wet} \quad \text{[mg/kg : mg/L = L/kg]} \]

When we turn this around, we finally have the concentration ratio between water (mg/L) and wet soil (mg/kg) \( K_{WS} \):

\[ C_W / C_{Soil} = K_{WS} = \rho_{wet} / (K_d \times \rho_{dry} + P_W + P_A \times K_{AW}) \quad \text{[mg/L : mg/kg = kg/L]} \]

for chemical equilibrium. The relation describes the concentration ratio between bulk soil (wet soil) and soil water. Replacing the \( K_d \) by \( OC \times K_{OC} \) gives us the expression we can use to calculate the dissolved concentration of a chemical in soil (mg/L) from the total concentration in soil (mg/kg, wet weight):

\[
\frac{C_W}{C_{Soil}} = \frac{\rho_{wet}}{OC \times K_{OC} \times \rho_{dry} + P_W + K_{AW} \times P_A} = K_{WS} = \frac{1}{K_{SW}}
\]

Equation 1

As defined, \( C_W \) (mg L\(^{-1}\)) is the concentration of the chemical in soil water and \( C_{Soil} \) (mg kg\(^{-1}\)) is the concentration of the chemical in bulk (total) soil. \( \rho_{wet} \) is the density of the wet soil (kg/L), \( OC \) (also named \( f_{OC} \)) is the fraction of organic carbon (kg/kg), \( \rho_{dry} \) is the density of the dry soil, and \( P_W \) and \( P_A \) are the volume fractions of water and air in the soil (L/L). \( K_{AW} \) is the partition coefficient between air and water (also named dimensionless Henry's Law constant) and \( K_{OC} \) is the partition coefficient between organic carbon and water and can be estimated from:

\[
\log K_{OC} = 0.81 \log K_{OW} + 0.1
\]
Example calculation MTBE

The concentration of MTBE in wet soil is 1 mg/kg. The log $K_{OW}$ is 1.14. What is the concentration in soil solution (data Table 2)?

$$K_{OC} = 10^{0.81 \log K_{OW} + 0.1} = 10^{0.81 \times 1.14 + 0.1} = 10.55$$

$$C_w = \frac{\rho_{wet}}{OC \times K_{OC} \times \rho_{dry} + P_W + K_{AW} \times P_A} \times C_{soil}$$

$$= \frac{1.95 \text{ kg/L}}{0.02 \text{ kg/kg} \times 10.5 \text{ L/kg} \times 1.6 \text{ kg/L} + 0.35 \text{ L/L} + 0.1 \text{ L/L} \times 0.0175 \text{ L/L}} \times 1 \text{ mg/kg}$$

$$= 2.8 \text{ mg/L}$$

This is higher than in bulk soil! Can that be? Of course: MTBE is quite water soluble, and most of it is found in the soil water. But this soil has only 0.35 L water per L soil. Therefore, the concentration in 1 kg soil is lower than in 1 L of pure water.

**Table 2**: Soil data, Danish standard soil.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil wet density</td>
<td>$\rho_{wet}$</td>
<td>1.95</td>
<td>kg/L</td>
</tr>
<tr>
<td>Organic carbon content</td>
<td>OC</td>
<td>0.02</td>
<td>kg/kg</td>
</tr>
<tr>
<td>Soil pore water</td>
<td>$P_W$</td>
<td>0.35</td>
<td>L/L</td>
</tr>
<tr>
<td>Soil gas pores</td>
<td>$P_A$</td>
<td>0.1</td>
<td>L/L</td>
</tr>
<tr>
<td>Soil dry density</td>
<td>$\rho_{dry}$ = $\rho_{wet} - P_W$</td>
<td></td>
<td>kg/L</td>
</tr>
</tbody>
</table>

**Exercise 1B Soil concentrations**

The concentration of BaP and TBA in wet soil is 1 mg/kg.

a) What is the concentration in soil solution? (Eq. 1)

b) What is the concentration in dry soil?

**Don't get confused**

An alternative formulation for $K_{SW}$ is often used, e.g. by Don Mackay in his fugacity models, where the density of solids is given as 2.5 kg/L (or 2500 kg m$^{-3}$). This is the density of the pure solid - i.e. without pores. This is different from the dry soil density above, which is the density with pores. We use this second density because it is much easier to measure. If the density of the pure solid is multiplied with the volume fraction of the solid, the values are quite similar (0.6 L/L x 2.5 kg/L = 1.5 kg/L).
Briggs et al. (1982) pulverized (“mazerated”) barley roots and made shaking experiments in water with chemicals of different $K_{OW}$. They expressed the result as “root concentration factor” RCF:

$$RCF = \frac{\text{concentration in roots (mg/kg)}}{\text{concentration in water (mg/L)}}$$

The RCF increased with $K_{OW}$ (Figure). The fit curve between RCF and $K_{OW}$ is

$$\log (RCF - 0.82) = 0.77 \log K_{OW} - 1.52$$

or

$$RCF = 0.82 + 0.03 K_{OW}^{0.77}$$

Figure: log RCF vs log $K_{OW}$ →

Equilibrium between concentration in roots $C_R$ (mg kg$^{-1}$) and water $C_W$ (mg L$^{-1}$) = $K_{RW}$

The RCF can be rewritten as $K_{RW}$ (L/kg), which describes the equilibrium partitioning between root concentration $C_R$ (mg/kg fresh weight) and water $C_W$ (mg/L). The partitioning occurs into the water, the lipid and the gas phase of the root:

$$K_{RW} = W_R + L_R a K_{OW}^b + P_A(\text{root}) K_{AW}$$

Equation 2

$K_{OW}$ is the equilibrium partition coefficient between n-octanol and water, $W$ and $L$ are water and lipid content of the plant root, 'b' for roots is 0.77, ‘a’ = $1/\rho_{\text{Octanol}} = 1.22$ L/kg. Partitioning into the gas phase of the root, $P_A(\text{root})$, is usually negligible.

**Table 3:** Water and lipid content of carrots.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrot water content</td>
<td>$W_R$</td>
<td>0.89</td>
<td>L/kg</td>
</tr>
<tr>
<td>Carrot lipid content (*)</td>
<td>$L_R$</td>
<td>0.025</td>
<td>kg/kg</td>
</tr>
<tr>
<td>Carrot air pores</td>
<td>$P_A(\text{carrot})$</td>
<td>0.05</td>
<td>L/kg</td>
</tr>
</tbody>
</table>

(*) This lipid content includes all lipid-like compounds, not only fat and oil, but also waxes like suberin and cutin.
Example 1C Root concentration factor of MTBE

By Briggs’ equation

\[
\log (RCF - 0.82) = 0.77 \log K_{OW} - 1.52
\]

\[
\log(RCF - 0.82) = 0.77 \times 1.14 - 1.52 = -0.6422
\]

\[
RCF - 0.82 = 10^{-0.6422} = 0.22
\]

\[
RCF = 0.82 + 0.22 = 1.04 \text{ mg kg}^{-1} / \text{mg L}^{-1}
\]

or \(RCF = 0.82 + 0.03 \times K_{OW}^{0.77} = 0.82 + 0.03 \times 13.8^{0.77} = 1.04 \text{ mg kg}^{-1} / \text{mg L}^{-1}\) (identical)

By Trapp’s equation (Eq 2)

\[
K_{RW} = W_R + L_R a K_{OW}^b + P_a(\text{root}) K_{AW}
\]

\[
K_{RW} = 0.89 \text{ L kg}^{-1} + 0.025 \text{ kg kg}^{-1} \times 1.22 \text{ L kg}^{-1} \times 13.8^{0.77} + (0.05 \text{ L kg}^{-1} \times 0.0175) = 1.12 \text{ L kg}^{-1}
\]

(marginal differences, due to the higher water content)

Exercise 1C

1Ca) Calculate the RCF and the \(K_{RW}\) of BaP and TBA for carrots with the data given in Tables 1 and 3.

1Cb) Which root phase is the most important (water, lipids or gas) for the sorption of BaP?

1Cc) Calculate the chemical equilibrium between carrots and soil for MTBE, TBA and BaP with the data in Table 1, 2, 3.
**Before Chapter 2: Linear differential equations**

To establish a mass balance is easy:

*Change of mass = input - loss*

For a constant input and a loss proportional to the chemical's mass:

\[ \frac{dm}{dt} = I - km \]

where \( m \) is the mass (mg), \( t \) is time (d), \( I \) is the input (mg/d) and \( k \) is the loss rate (d\(^{-1}\)).

The solution of this linear differential equation is always (!)

\[ m(t) = m(0) \times e^{-kt} + \frac{I}{k} \left( 1 - e^{-kt} \right) \]

For \( t \rightarrow \infty \), the solution always (!) reaches steady state (\( \frac{dm}{dt} = 0 \)), which is \( I/k \).

**Example**

m1: \( m(0) = 100, \ k = 0.2, \ I = 0, \ I/k = 0 \)

m2: \( m(0) = 100, \ k = 0.2, \ I = 2, \ I/k = 10 \)

m3: \( m(0) = 0, \ k = 0.2, \ I = 2, \ I/k = 10 \)

m4: \( m(0) = 50, \ k = 0.2, \ I = 2, \ I/k = 10 \)

**From mass to concentration**

From the chemical's mass, we get the chemical's concentration \( C \) by dividing through the mass of the sample \( M \) (kg, for solids) or the volume \( V \) (L) for liquids and gases:

\[ C = \frac{m}{M} \text{ or } C = \frac{m}{V} \]

It follows that \( \frac{d(C \times M)}{dt} = \frac{dm}{dt} = I - km \)

For constant \( M \), we can write \( M \times \frac{dC}{dt} = I - km \) and

\[ \frac{dC}{dt} = \frac{I}{M} - km/M = \frac{I}{M} - kC \]

with the known common solution

\[ C(t) = C(0) \times e^{-kt} + \frac{I}{k \times M} \left( 1 - e^{-kt} \right) \]
From mass to concentration for growing plants

Plants either grow (and transpire) or they die. But how to solve

\[ d(C \times M)/dt = dm/dt = I - k \, m \]

for a non-constant plant mass \( M \)? The equation needs to be integrated for both \( C \) and \( M \). Not easy. But there is a "trick":

The figure shows the typical growth of an annual plant. Directly after germination of the seed, the growth is quite limited (lag phase). It follows a phase of exponential growth. This phase lasts until ripening of the seeds. At this stage, growth stops, and there may even be a loss of plant mass (mainly due to drying and leaf fall). Soon after, the plant dies.

If we plot now concentration (\( C = m/M \)) of a chemical with an initial mass, we can see the dilution by growth:

\[
m = \text{const.} \]

\[
M(t) = M(0) \times e^{kt} \text{ where } k \text{ is the growth rate}
\]

\[
C = m/M = C(0) \times e^{-kt}
\]

The dilution follows an exponential decay.

In the differential equation, we can consider this by a first order rate.

Example

\[ d(C \times M)/dt = I \]

\[ dC/dt = I/M - k \, C \]

where \( k \) is the growth rate. If two first order rates appear, e.g., a metabolism rate \( k_M \) and a growth rate \( k_G \), the rates can be added:

\[ k = k_M + k_G \]

Typical half-times for doubling in summer are about 1 week, corresponding to a growth rate of about 0.1 \( \text{d}^{-1} \). In our models, this trick is only valid when the ratio of plant mass to plant transpiration is approximately constant. This is often fulfilled during the exponential growth phase (i.e. for plants before ripening).
CHAPTER 2 Dynamic Root Uptake Model for Neutral Lipophilic Organics


The “carrot model” calculates uptake into root 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, \(Q\) 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, we get the concentration as before by dividing through the mass of the root \(M\):

\[
\frac{d(C_R \times M)}{dt} = \frac{dm_R}{dt} = C_w \times Q - C_{xy} \times Q
\]

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 us

\[
C_w \times Q / M = C_R \times (\frac{Q}{K_{RW} \times M} + k)
\]

And we solve for the concentration in the root \(C_R\):

\[
C_R = \frac{Q}{K_{RW} + kM} C_w
\]
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 carrot and bulk soil follows:

$$BCF = \frac{C_{R}}{C_{Soil}} = \frac{C_{R}}{C_{W}} \times K_{WS} = \frac{Q}{Q + kM} \times K_{WS}$$  \hspace{1cm} \text{Equation 3}

**Limitations:** The model approach is limited to non-ionising compounds.

The parameterization of the model is for 1 m$^2$ soil, with 1 kg roots, a transpiration of 1 L d$^{-1}$ (or 1.2 L/d, when grains and fruits are considered) and a root growth rate of 0.1 d$^{-1}$. This parameterization seems idealized, but the values are within what is realistic.

**Table 4:** More data for carrots, for an area of 1 m$^2$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transpiration stream</td>
<td>$Q$</td>
<td>1 or 1.2</td>
<td>L/d</td>
</tr>
<tr>
<td>Root mass</td>
<td>$M$</td>
<td>1</td>
<td>kg</td>
</tr>
<tr>
<td>1st order growth rate</td>
<td>$k$</td>
<td>0.1</td>
<td>d$^{-1}$</td>
</tr>
</tbody>
</table>

Example calculation for MTBE

$$BCF = \frac{C_{R}}{C_{Soil}} = \frac{C_{R}}{C_{W}} \times K_{WS} = \frac{Q}{Q + kM} \times K_{WS}$$

What we have from before: $K_{WS} = 2.8$ kg/L; $K_{RW} = 1.12$ L/kg

$$BCF = \frac{Q}{Q + kM} \times K_{WS} = \frac{1L/d}{1L/d/1.12L/kg + 0.1d^{-1} \times 1kg} \times K_{WS} = 1.0L/kg \times 2.8kg/L = 2.8kg/kg$$

and $C_{R} = C_{Soil} \times BCF$

**Exercise 2**

2.1 Calculate $C_{R}$ with the carrot model for the chemicals BaP and TBA for $C_{Soil} = 1$ mg/kg wet wt.

2.2 What is $C_{R} / C_{W}$ if the growth rate of root $k = 0$ d$^{-1}$?

2.3 Why is $C_{R}$ with the carrot model (ex. 2.1) close to $K_{RW} \times K_{WS}$ (ex. 1C) for MTBE, but not for BaP? (or: why is MTBE in the carrot model close to equilibrium, but not BaP?)

2.4 How can the BCF root-to-soil be converted from fresh / wet weight to dry / dry weight?
CHAPTER 3 Translocation upwards

On the way from soil to xylem, where the water is translocated upwards, the water (and any solutes) must pass either one cell (and therefore one biomembrane), or the “Casparian strip”. This strip, which separates the outer root (“cortex”) from the inner root, is a waxy layer. Only very lipophilic compounds pass it.

The biomembranes have “aquaporines”, which are special “doors” through which the water, but only water, can quickly pass (= facilitated diffusion). Chemicals need to diffuse across the biomembranes. Biomembranes are lipid bilayers, and lipophilic chemicals can pass faster.

The water, which is taken up by the roots, does not stay there but is translocated in the xylem to the leaves and evaporates there. Only 1-2% is taken up into the plant cells. Chemicals, which are dissolved in the “transpiration stream” (= the xylem sap), can be moved upwards, too.

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

\[ TSCF = \frac{C_{xy}}{C_W} \]  

Equation 4

The most recent TSCF-estimation equation stems is a sigmoid curve from Dettenmaier et al. (2009)

\[ TSCF = \frac{11}{11 + 2.6 \log K_{ow}} \]  

Eq. 4a

Older TSCF-estimates give bell-shaped relation to log K_{ow}, Briggs et al. (1982) for barley

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

Eq. 4b

and Burken and Schnoor (1998) for poplar trees

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

Eq. 4c

The TSCF can also be calculated from the root model (next section). This gives a sigmoid curve similar to eq. 4a.
Modeling of “TSCF”

The TSCF can also be calculated with the root model. Remember: \( C_{XY} = C_R / K_{RW} \) and

\[
C_R = \frac{Q}{Q + kM}
\]

and therefore

\[
\frac{C_{XY}}{C_W} = \frac{Q / K_{RW}}{Q / K_{RW} + kM} \quad \text{Eq. 4d}
\]

\[
\text{or } C_{XY} = \frac{Q}{Q + k \times M \times K_{RW}}
\]

(in this form of the equation it can be seen immediately that the concentration in xylem goes down when the \( K_{RW} \) (log \( K_{OW} \)) is high)

and related to bulk soil

\[
\frac{C_{XY}}{C_{Soil}} = \frac{C_R \times K_{WS} / K_{RW}}{Q / K_{RW} + kM} = \frac{Q}{Q + kM} \times K_{WS} / K_{RW}
\]

This “calculated TSCF” (eq. 4d) is sigmoid, as Dettenmaier's TSCF-curve. For high log \( K_{OW} \), it is also similar equivalent to the empirical curves of Briggs et al. (4b) and Burken and Schnoor (4c) (Figure).

Note that the calculated TSCF changes with plant parameters (\( Q \), \( k \), \( K_{RW} \) and \( M \)).

**Figure**: Comparison of empirical and calculated TSCF; ‘Briggs fit’ is eq. 4b; ‘B+S fit’ is Burken and Schnoor (1998); ‘\( C_{XY} \)’ is calculated with eq. 4d; Dettenmaier is eq. 4a.
Example calculation: TSCF of MTBE

Dettenmaier’s equation (eq. 4a):

\[
\text{TSCF} = \frac{11}{11 + 2.6^{\log_{10}K_{ow}}} = \frac{11}{11 + 2.6^{1.14}} = \frac{11}{11 + 2.97} = 0.79 \text{ L/L}
\]

Briggs’ equation (eq. 4b):

\[
\text{TSCF} = 0.784 \times \exp\left(\frac{-(\log K_{ow} - 1.78)^2}{2.44}\right) = 0.784 \times \exp\left(\frac{-(1.14 - 1.78)^2}{2.44}\right) = 0.784 \times \exp\left(-\frac{0.41}{2.44}\right) = 0.784 \times 0.85 = 0.66 \text{ L/L}
\]

Burken & Schnoor’s equation (eq. 4 c)

\[
\text{TSCF} = 0.756 \times \exp\left(\frac{-(\log K_{ow} - 2.50)^2}{2.58}\right) = 0.756 \times \exp\left(\frac{-(1.14 - 2.50)^2}{2.58}\right) = 0.37 \text{ L/L}
\]

Trapp’s equation (4d) with Q = 1 L/d:

\[
\frac{C_{xy}}{C_w} = \frac{Q / K_{RW}}{Q / K_{RW} + kM} = \frac{1 \text{ L/d} / 1.12 \text{ L/kg}}{1 \text{ L/d} / 1.12 \text{ L/kg} + 0.1 \text{ d}^{-1} \times 1 \text{ kg}} = 0.90 \text{ L/L}
\]

All three models would predict good translocation of MTBE.

Exercise 3

3.1 What is the TSCF (C_{xy}/C_w) using Briggs equation and the root model for TBA and BaP?

3.2 What is the concentration ratio between xylem sap and bulk soil for these two compounds?
The function of the leaves is gas exchange with air. Therefore, leaves have a high surface to volume ratio. Chemicals in air come onto/into the leaves by various ways: Gaseous deposition through the cuticle; gaseous exchange through the stomata; dry particulate deposition; wet particulate deposition. Inside the leaves, several more resistances exist (epidermis, intercellular water and air, deeper cells). The Figure depicts these resistances. The deposition velocities for all this uptake pathways depend crucially on chemical and environmental properties.

A rough estimate (which is used as default for gases and particles) is that the deposition velocity from leaves to air, the conductance \( g \), is about \( 10^{-3} \) m s\(^{-1} \) for gaseous and particulate deposition. For details see Riederer in Trapp & McFarlane 1995.

\[ \frac{C_L}{C_{Air}} = K_{LA}/\rho \]

\( K_{LA} \) is the partition coefficient leaves to air (in the unit mg/m\(^3\) leaves to mg/m\(^3\) air), and \( \rho \) is the density of the leaves (kg/m\(^3\)). \( C_L \) has the unit mg/kg, and \( C_{Air} \) has the unit mg/m\(^3\).

Furthermore, \( K_{LA} = K_{LW}/K_{AW} \)

The units have to be considered. Similar to the root-water partition coefficient, we can define a partition coefficient leaves to water [L kg\(^{-1}\)]:

\[ K_{LW} = W + L a K_{OW} b \]

with \( a = 1.22 \) L/kg and \( b = 0.95 \) for leaves.

However, \( K_{AW} \) is in the unit [m\(^3\) m\(^{-3}\)]. We require a unit correction

\[ K_{LW}^{*} [L L^{-1} = m^{3} m^{-3}] = K_{LW} [L kg^{-1}] \times \rho_L [kg L^{-1}] \]

where \( \rho_L \) is the density here in the unit kg L\(^{-1}\).

The diffusive flux between leaves and air is calculated with the 1\(^{st}\) Law of Fick

\[ \text{change of mass in leaves} = + \text{uptake from air} - \text{loss to air} \]
\[
\frac{dm_L}{dt} = \left( A \times g \times C_{air} - A \times g \times \frac{C_L \times \rho}{K_{LA}} \right) \text{ [mg d}^{-1}] \\
\]

where A is the leaf area (m²).

Example calculation: Equilibrium leaf-air for benzo(a)pyrene

A = 5 m², ρ = 500 kg m⁻³, W = 0.8 L/kg, L = 0.02 kg/kg

Chemical BaP → log K_{OW} = 6.13, K_{AW} = 1.35 \times 10^{-5}

If C_{Air} = 2 ng m⁻³ and the concentration in leaf is 1 mg/kg – is there uptake or loss of BaP?

\[
(K_{LA} = K_{LW}/K_{AW} = 8 \times 125 / 1.35 \times 10^{-5} = 6.0 \times 10^{8} \text{ (mg/m}^3 \text{ leaf : mg/m}^3 \text{ air)}
\]

K_{LA}/\rho = 6 \times 10^{8} \text{ (mg/m}^3 \text{ leaf : mg/m}^3 \text{ air) / 500 kg/m}^3 \text{ leaf = 1.2} \times 10^{6} \text{ (m}^3 \text{ air / kg leaf)}

(as can be seen, the density is there for formal reasons; the value is divided out; only factor 1000 remains, for m³ \rightarrow \text{L}; yes, it's confusing. An alternative is to calculate with SI units kg and m³ from the beginning).

Exercise Chapter 4:

Calculate the equilibrium leaves to air for MTBE and TBA, please.
CHAPTER 5 Model for uptake into leaves


5.1 Mass Balance

This model is for the uptake of neutral organic substances into leafy vegetable or green fodder. The main objective of the model was the integration into multi-media fate models, which are used in risk assessment of new and existing chemicals. The model was adopted in the Technical Guidance Documents (TGD) of the European Union System for the Evaluation of Substances (EUSES) (EC 1996, 2003). Here, we reformulated transport from roots to leaves, which was originally calculated using the TSCF.

For leafy vegetables, there is uptake from soil via the xylem and exchange with air (as before).

The change of mass in leaves = + translocation from roots + uptake from air - loss to air

\[
\frac{dm_L}{dt} = +Q \times C_{xy} + C_{Air} \times g \times A - \frac{C_L \times g \times A \times \rho}{K_{LA}}
\]

where \( m_L \) (mg) is the mass of chemical in leaves, \( Q \) (L/d) is the transpiration stream to leaves, \( C_{xy} \) (mg/L) is the concentration in xylem, \( C_{Air} \) (mg m\(^{-3}\)) is the concentration in air (here, no difference is made between particulate and gas form), \( g \) is the conductivity of leaves (m/d, = permeability), \( A \) is the leaf area (m\(^2\), up and downside), \( C_L \) is the concentration in leaves (mg/kg), \( \rho \) is the leaf density (kg m\(^{-3}\)) and \( K_{LA} \) is the partition coefficient leaves to air (m\(^3\)/kg), as described in teh previous section.

The differential equation for the concentration in leaves considers again additionally the dilution by exponential growth with the rate \( k_{Growth} \) (d\(^{-1}\)):

\[
\frac{dC_L}{dt} = + \frac{Q}{M_L} \times C_{xy} + \frac{C_{Air} \times g \times A}{M_L} - k_{Growth} \times C_L - \frac{C_L \times g \times A \times \rho}{K_{LA} \times M_L}
\]

Equation 5

where \( L \) is the index for leaves. The chemical concentration in the xylem sap, \( C_{xy} \), can be calculated by two ways: using the root model (see Chapter 3, Modeling of TSCF) or using the TSCF, see there.

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

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

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

and the steady-state solution

\[
C_L(t = \infty) = \frac{b}{a}
\]
where

\[ a = \frac{A \times g \times \rho}{K_{La} \times M_L} + k_{Growth} \]

and

\[ b = C_{w} \times TSCF \times \frac{Q}{M_L} + C_{Air} \times g \times \frac{A}{M_L} \]

5.2 Input data

**Table.** Parameterization of the leafy vegetables model, normalized to 1 m² (data taken from the original publication, Trapp & Matthies 1995).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoot mass</td>
<td>M_L</td>
<td>1</td>
<td>kg</td>
</tr>
<tr>
<td>Leaf area</td>
<td>A</td>
<td>5</td>
<td>m²</td>
</tr>
<tr>
<td>Shoot density</td>
<td>( \rho )</td>
<td>500</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Transpiration</td>
<td>Q</td>
<td>1</td>
<td>L/d</td>
</tr>
<tr>
<td>Lipid content</td>
<td>L</td>
<td>0.02</td>
<td>kg/kg</td>
</tr>
<tr>
<td>Water content</td>
<td>W</td>
<td>0.8</td>
<td>L/kg</td>
</tr>
<tr>
<td>Conductance</td>
<td>g</td>
<td>(10^{-3})</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>Growth rate</td>
<td>k_L</td>
<td>0.035</td>
<td>d⁻¹</td>
</tr>
<tr>
<td>Time to harvest</td>
<td>t</td>
<td>60</td>
<td>d</td>
</tr>
</tbody>
</table>

5.3 Example calculation

Benzo(a)pyrene again. \( C_{Soil} \) is 1 mg/kg and \( C_{Air} \) is 1 ng m⁻³. What is the concentration in leaves?

**Step 1: Concentration in xylem sap \( C_{Xy} \)**

\( C_W \) is \( 0.5 \times 10^{-3} \) mg/L (from exercise 1); TSCF (Briggs) = 0.00036 (from exercise 3)

\[ C_{Xy} = TSCF \times C_W = 1.8 \times 10^{-7} \text{ mg/L} \]

**or** \( C_{Xy} \) from root model, exercise 3.1 (preferred): (BCF with \( Q = 1.2 \) L/d)

\[ C_{Xy} = C_W \times \frac{BCF_{Root-Water}}{K_{RW}} = 0.5 \times 10^{-3} \text{ mg/L} \times 9.94 \text{ L/kg} / 1600 \text{ L/kg} = 0.5 \times 10^{-3} \text{ mg/L} \times 6.2 \times 10^{-5} \text{ L/L} = 3.1 \times 10^{-6} \text{ mg/L} \]

Both methods give similar (i.e very low) concentrations in xylem sap.

**Step 2: Loss term**

\[ a = \frac{A \times g \times \rho}{K_{La} \times M_L} + k_{Growth} \]

\[ = 5 \text{ m}^2 \times 10^{-3} \times 86400 \text{ m}^3 \times 500 \text{ kg m}^{-3}/(0.6 \times 10^9 \text{ m}^3 : \text{m}^3 \times 1 \text{ kg}) + 0.035 \text{ d}^{-1} =0.035 \text{ d}^{-1} \]

Loss is mainly due to growth dilution.
Step 3: Input term

\[ b = C_{xy} \times Q / M_L + C_A \times g \times - \frac{A}{M_L} \]
\[ = 3.1 \times 10^{-6} \text{ mg/L x 1 L/d / 1kg} + 10^{-6} \text{ mg m}^{-3} \times 10^{-3} \times 86400 \text{ m d}^{-1} \times 5 \text{ m}^{2} / 1 \text{ kg} \]
\[ = 3.1 \times 10^{-6} \text{ mg kg}^{-1} \text{ d}^{-1} + 0.000432 \text{ mg kg}^{-1} \text{ d}^{-1} = 0.000432 \text{ mg kg}^{-1} \text{ d}^{-1} \]

Question in between: Is the uptake of BaP into this plant from soil or from air?

From an inspection of this last line it can be seen that uptake into leaves from air is more than 100 times faster than from soil water: 4.32 \times 10^{-4} / 3.1 \times 10^{-6} = 133

Step 4: Concentration at harvest

Finally, the concentration in leaves at \( t = 60 \) days is

\[ C_L(t) = C_L(0) \times e^{-at} + \frac{b}{a} (1 - e^{-at}) = 0 + \frac{0.00043 \text{ mg kg}^{-1} \text{ d}^{-1}}{0.035 \text{ d}^{-1}} (1 - e^{-0.035 \times 60}) = 0.012 \times (1 - 0.12) = 0.011 \text{ mg/kg} \]

And steady-state: \( b/a = 0.00043 \text{ mg kg}^{-1} \text{ d}^{-1} / 0.035 \text{ d}^{-1} = 0.012 \text{ mg/kg} \).

(That means that after 60 days, steady-state is almost reached. This will be the same for all compounds, because the loss rate is determined by growth of plants, and that is independent of the chemical.)

5.4 Uptake by soil resuspension

That model lacks one important pathway: deposition of soil on leaves. Many green vegetables are contaminated by attached soil (e.g., lettuce). To consider this, there is always a default soil-to-plant transfer with particles of 1% attached soil assumed, which means a minimum BCF plant/soil of 0.01 (wet wt. based):

\[ BCF \text{ with soil} = BCF \text{ model} + 0.01 \text{ kg/kg} \]

For cereals, such as wheat and corn, we use a lower value, namely 0.001 kg/kg. This small amount of soil particles is usually mixed in at harvest (a very dusty thing for corn).

Exercise 5

5.1 Calculate the concentration of BaP in leafy vegetable for a concentration in air = 0 ng m\(^{-3}\).
5.2 Calculate the steady-state concentration of TBA and MTBE in leafy vegetable for a concentration in air = 0 ng m\(^{-3}\) and a concentration in soil of 1 mg/kg (wet wt.).
5.3 Calculate the concentration of TBA and MTBE in leafy vegetable for a concentration in air = 1 ng m\(^{-3}\) and a concentration in soil of 1 mg/kg (wet wt.).
5.4 If 1% soil is attached – what is then the BCF?
CHAPTER 6 The Standard Plant Uptake Model

Since the year 2008, we (at DTU) use a "simple standard model" that combines the models for roots and leaves. The standard plant uptake model considers uptake from soil and air into plants and includes the compartments soil, roots and leaves (or fruits or grains) and the processes:

- continuous and/or 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 stream (for fruits: also phloem);
- loss from leaves (fruits) to air;
- deposition from air to leaves (fruits) and soil;
- growth dilution, degradation and metabolism in leaves (fruits);
- optionally: transport to leaves (fruits) with attached soil.

6.1 Mass balances

6.1.1 Soil

The mass balance for soil is

Change of contaminant mass in soil is deposition from air minus leaching, run-off, volatilization, degradation and uptake into roots. Division by soil mass, $M_s$, results in the concentration in soil (compartment 1):

\[
\frac{dC_s^1}{dt} = \frac{I_1}{M_s} - k_1 \times C_s^1
\]

Eq. 6a

where $I_1$ (mg d$^{-1}$) is input to soil (including deposition from air), and $k_1$ (d$^{-1}$) is the sum of all first-order loss rates from soil.

6.1.2 Roots

The mass balance for advective uptake into thick roots is

Change of contaminant mass in roots is influx with water minus outflux with xylem sap. The root is described with the following equation:

\[
\frac{dm_R}{dt} = Q \times C_w - Q \times C_{Xy} - k_{met} \times m_R
\]

where $m_R$ is the mass of contaminant in roots (mg), $Q$ is the transpiration stream (L d$^{-1}$), $k_{met}$ is the first-order rate constant for metabolism of compound (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 is $C_{Xy} = C_R/K_{RW}$. $K_{RW}$ (L kg$^{-1}$) is the partition coefficient between root and water. The concentration in soil pore water, $C_w$, is $C_s \times K_{WS}$. Substituting these expressions into the above equation gives
\[
\frac{d(C_R \times M_R)}{dt} = \frac{dm_R}{dt} = Q \times K_{WS} \times C_s - \frac{Q}{K_{RW}} \times C_R - k_{met} \times C_R \times M_R
\]

If plant growth is exponential, and the ratio \( Q/M_R \) (transpiration stream \( Q \) to root mass \( M_R \)) is constant, the growth by exponential dilution can be considered by a first-order growth rate \( k_R \) \((d^{-1})\). The rate \( k_R \) is the sum of the loss processes and the growth dilution. The concentration in roots results by dividing with the mass of the root:

\[
\frac{dC_R}{dt} = \frac{Q}{M_R} \times K_{WS} \times C_s - \frac{Q}{M_R \times K_{RW}} \times C_R - k_R \times C_R
\]

with the "classical" steady-state solution (Trapp 2002) being

\[
C_R = \frac{Q}{\sqrt{K_{RW} + k_R M_R}} \times K_{WS} \times C_s
\]

The dynamic analytical solution is

\[
C_R(t) = C_R(0) \times e^{-k t} + \frac{I}{k} \times (1 - e^{-k t}) \quad \text{Eq. 6b}
\]

where \( C_R(0) \) is the initial concentration in root, \( I \) is the sum of all constant input terms to roots (advective flux from soil), and \( k \) is the sum of all loss terms (advective flux to shoots, metabolism and growth dilution).

How to find I and k?

All terms in the differential independent of \( C_R \) are summarized to I; all terms dependent on \( C_R \) are summarized to k.

\[
I = Q \times K_{WS} \times C_s \quad \text{plus input into roots (if this occurs)}
\]

\[
k = \frac{Q}{M_R \times K_{RW}} + k_R
\]

6.1.3 Leaves

The mass balance for leaves 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:

\[
\frac{dm_L}{dt} = \frac{Q}{K_{RW}} C_R + A_L \times g_L \times (1 - f_p) \times C_A + \frac{A_L \times v_{dep}}{2} \times f_p \times C_A
\]

\[- A_L \times g_L \times 1000 \frac{L}{m^3} \times C_L - k_{met,L} \times m_L\]
where \( A_L \) is leaf area (m\(^2\)), \( K_{\text{LA}} \) is the partition coefficient between leaves and air (L kg\(^{-1}\)), \( C_A \) 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 \( g_L \) (m d\(^{-1}\)), or by deposition of particles on the surface of the leaves (A/2) with velocity \( v_{\text{dep}} \) (m d\(^{-1}\)). For the sake of simplicity, we may set \( g \) to \( 10^3 \) m/s and \( v_{\text{dep}} \) to \( 2 \times 10^3 \) m/s, so that gaseous and particle deposition have the same value. The factor 1000 stems from the conversion of m\(^3\) to L.

For constant conditions, the concentration in leaves is

\[
\frac{dC_L}{dt} = \frac{Q}{M_L \times K_{RW}} \times C_R + \frac{A_L \times g}{M_L} \times (1 - f_P) \times C_A + \frac{A_L \times v_{\text{dep}}}{2 \times M_L} \times f_P \times C_A
\]

\[
- \frac{A_L \times g_L \times 1000 \times L^{-1} \times K_{LA} \times M_L}{M_L} \times C_L - k_L \times C_L
\]

where \( k_L \) (d\(^{-1}\)) again is the first-order rate that includes growth dilution and biotic and abiotic (photolysis) degradation processes.

The steady-state solution (only applicable if concentrations in soil, root and air are constant) is

\[
C_L = \frac{I}{k \times M_L}
\]

where \( C_L \) is the steady-state concentration in leaves, \( I \) is the sum of all constant input terms (flux from roots, diffusion and deposition from air), and \( k \) is the sum of all loss terms (diffusive loss to air, metabolism and growth dilution).

The dynamic analytical solution (in case of constant concentrations in soil, root and air) is

\[
C_L(t) = C_L(0) \times e^{-kt} + \frac{I}{k \times M_L} (1 - e^{-kt}) \quad \text{Eq. 6c}
\]

where \( C_L(0) \) is the initial concentration in leaves. If concentrations in soil and roots are not constant, a coupled differential equation system has to be solved, see below.

### 6.1.4 Fruits or grains

Mass balances for fruit and grain can be set up analogous to leaves. However, the processes and parameters differ. For the uptake into fruits and grains, the following balances are used (Trapp 2007):

\[
\frac{dm_F}{dt} = \frac{Q_F}{K_{RW}} \times C_R + \frac{A_F \times P_F}{K_{AW \times \text{air}}} \times C_{\text{air}} - 1000 \times \frac{A_F \times P_F}{K_{FW}} \times C_F - k_{\text{met,F}} \times m_F
\]

where \( F \) is the index for fruits. The solution is analog to leaves:

\[
C_F(t) = C_F(0) \times e^{-kt} + \frac{I}{k \times M_F} (1 - e^{-kt}) \quad \text{Eq. 6d}
\]
6.2 Input data

Input data are the same for the steady state and the dynamic model version and are mostly taken from the carrot model (Trapp 2002) and the leafy vegetables model (Trapp and Matthies 1995) (Table 1).

**Table 1.** Input data set for the standard model for the calculation of plant uptake (normalised to 1 m² of soil).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil wet density</td>
<td>$\rho_{\text{wet}}$</td>
<td>1.95</td>
<td>kg$_{\text{ww}}$ L$^{-1}$</td>
</tr>
<tr>
<td>Organic carbon content</td>
<td>$OC$</td>
<td>0.02</td>
<td>kg kg$_{\text{sw}}$ $^{-1}$</td>
</tr>
<tr>
<td>Soil water content</td>
<td>$\theta$</td>
<td>0.35</td>
<td>L L$^{-1}$</td>
</tr>
<tr>
<td>Soil dry density ($\rho_{\text{wet}} - \theta$)</td>
<td>$\rho_{\text{dry}}$</td>
<td>1.6</td>
<td>kg$_{\text{dw}}$ L$^{-1}$</td>
</tr>
<tr>
<td>Mass of soil</td>
<td>$M_S$</td>
<td>1000</td>
<td>kg$_{\text{sw}}$</td>
</tr>
<tr>
<td>Roots</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water content of roots</td>
<td>$W_R$</td>
<td>0.89</td>
<td>L kg$^{-1}$</td>
</tr>
<tr>
<td>Lipid content of roots</td>
<td>$L_R$</td>
<td>0.025</td>
<td>kg kg$_{\text{sw}}$ $^{-1}$</td>
</tr>
<tr>
<td>Transpiration stream</td>
<td>$Q$</td>
<td>1.2</td>
<td>L d$^{-1}$</td>
</tr>
<tr>
<td>Root mass</td>
<td>$M_R$</td>
<td>1</td>
<td>kg$_{\text{sw}}$</td>
</tr>
<tr>
<td>1st order growth rate</td>
<td>$k_R$</td>
<td>0.1</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>Leaves</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leaf mass</td>
<td>$M_L$</td>
<td>1</td>
<td>kg$_{\text{sw}}$</td>
</tr>
<tr>
<td>Leaf area</td>
<td>$A_L$</td>
<td>5</td>
<td>m²</td>
</tr>
<tr>
<td>Shoot density</td>
<td>$\rho_L$</td>
<td>1000</td>
<td>kg$_{\text{sw}}$ m$^{-3}$</td>
</tr>
<tr>
<td>Transpiration stream</td>
<td>$Q_L$</td>
<td>1.0</td>
<td>L d$^{-1}$</td>
</tr>
<tr>
<td>Lipid content leaves</td>
<td>$L_L$</td>
<td>0.02</td>
<td>kg kg$_{\text{sw}}$ $^{-1}$</td>
</tr>
<tr>
<td>Water content leaves</td>
<td>$W_L$</td>
<td>0.8</td>
<td>L kg$^{-1}$</td>
</tr>
<tr>
<td>Conductance leaves</td>
<td>$g_L$</td>
<td>86.4</td>
<td>m d$^{-1}$</td>
</tr>
<tr>
<td>Deposition velocity from air</td>
<td>$v_{\text{dep}}$</td>
<td>86.4</td>
<td>m d$^{-1}$</td>
</tr>
<tr>
<td>Growth rate leaves</td>
<td>$k_L$</td>
<td>0.035</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>Time to harvest</td>
<td>$t_L$</td>
<td>60</td>
<td>d</td>
</tr>
<tr>
<td>Attached soil</td>
<td>$R$</td>
<td>0.01</td>
<td>kg/kg</td>
</tr>
<tr>
<td>Grains or fruits</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fruit mass</td>
<td>$M_F$</td>
<td>1</td>
<td>kg$_{\text{sw}}$</td>
</tr>
<tr>
<td>Fruit area</td>
<td>$A_F$</td>
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<td>m²</td>
</tr>
<tr>
<td>Fruit density</td>
<td>$\rho_F$</td>
<td>1000</td>
<td>kg$_{\text{sw}}$ m$^{-3}$</td>
</tr>
<tr>
<td>Phloem and Transpiration stream to fruits</td>
<td>$Q_F$</td>
<td>0.2</td>
<td>L d$^{-1}$</td>
</tr>
<tr>
<td>Lipid content fruits</td>
<td>$L_F$</td>
<td>0.02</td>
<td>kg kg$_{\text{sw}}$ $^{-1}$</td>
</tr>
<tr>
<td>Water content fruits</td>
<td>$W_F$</td>
<td>0.15</td>
<td>L kg$^{-1}$</td>
</tr>
<tr>
<td>Conductance fruits</td>
<td>$g_F$</td>
<td>86.4</td>
<td>m d$^{-1}$</td>
</tr>
<tr>
<td>Deposition velocity from air</td>
<td>$v_{\text{dep}}$</td>
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<td>$k_F$</td>
<td>0.035</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>Time to harvest</td>
<td>$t_F$</td>
<td>60</td>
<td>d</td>
</tr>
<tr>
<td>Attached soil</td>
<td>$R$</td>
<td>0.001</td>
<td>kg/kg</td>
</tr>
</tbody>
</table>
6.3 Solution of the differential equations

The standard model is implemented in three versions: Once as steady-state solution. The results will be more or less those obtained by the root model and the leaf model (except the difference in TSCF and particle deposition). And once as dynamic model with analytical solutions ("cascade model"). These solutions are somewhat complex and are described in the next chapter. Third, there is also a numerical model that allows free input function and non-exponential growth.

Exercises to Chapter 6.

Sensitivity Analysis

A sensitivity analysis shows which input parameters have an effect on the result. "Sensitive" parameters should be selected with care, while the others ... well, they don't count and can be roughly estimated. Thus, a sensitivity analysis can save a lot of time and money. But the sensitivity of the models depends also largely on the chemical that is simulated.

1) Take the "Standard model", enter the data for benzo(a)pyrene, with concentration in air is 1 ng/m³ (10⁻⁶ mg/m³) and in soil is 1 mg/kg.

Now change all plant related parameters - first of roots, then of leaves - plus 10%. Write down how much the initial result changes. Set back the parameter to default and continue with the next.

Which plant parameters are the most relevant?

2) Take the "Standard model", enter the data for TBA, with concentration in air is 100 ng/m³ (10⁻⁴ mg/m³) and in soil is 1 mg/kg.

Now change all plant related parameters - first of roots, then of leaves - + - 10%. Write down how much the initial result changes. Set back the parameter to default and continue with the next.

Which plant parameters are the most relevant?

3) Stay with TBA. Double Transpiration Q, root mass Mᵣ, leaf mass Mₗ, and leaf area Aₗ at the same time. What happens?

4) Back to benzo(a)pyrene and the default scenario, with concentration in air is 1 ng/m³ (10⁻⁶ mg/m³) and in soil is 1 mg/kg. Set soil resuspension to zero (cell E25). How much of BaP is taken up from soil, and how much from air? How can you find out (there are two possibilities)?
Whether or not the steady-state approach is applicable depends also on the type of input function. Only for constant input, steady-state may be used. For non-constant input, the analytical solution of the differential equation system succeeds for pulse input and constant-over-time input function (Figure a and b). If the input is irregular (Figure c) and cannot be described by a pulse input of by a rectangular input function, the numerical integration of the equations is the only method of solution.

The differential equations for soil, root, leaves and metabolites formed in leaves are a coupled differential equation system. Several analytical solutions for various input functions exist. This section will deal with analytical solutions

\[ \frac{dC}{dt} = -kC + b \]

for a given compartment, where \( C \) (mg kg\(^{-1}\)) is concentration, \( k \) (d\(^{-1}\)) is a first-order loss rate constant and \( b \) (mg d\(^{-1}\) kg\(^{-1}\)) is constant input from external sources into the compartment, with \( b = I/M \), i.e. input \( I \) (mg d\(^{-1}\)) divided by compartment mass \( M \) (kg). If two or more compartments are linearly related, this leads to a matrix of the general form

\[ \frac{d\vec{C}}{dt} = A\vec{C} + \vec{b} \]

For 4 matrix elements, i.e. 4 compartments, the respective diagonal matrix is given by:

\[ \frac{d\vec{C}}{dt} = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ k_{12} & -k_2 & 0 & 0 \\ 0 & k_{23} & -k_3 & 0 \\ 0 & 0 & k_{34} & -k_4 \end{bmatrix} \vec{C} + \vec{b} \]

with vector of concentration \( \vec{C} \) (mg kg\(^{-1}\)), transfer rate constants \( k_{ij} \) (d\(^{-1}\)) are the transfer rates from compartment \( i \) to \( j \), loss rate constants \( k_i \) (d\(^{-1}\)) are the sum of all first-order loss processes in compartment \( i \) and \( b \) is the input vector (mg kg\(^{-1}\) d\(^{-1}\)). The matrix elements \( k \) and \( b \) can be derived from the differential equations (for concentrations) above.
The formulation as matrix is mathematically identical to

\[
\frac{dC_1}{dt} = -k_1C_1 + b_1 \\
\frac{dC_2}{dt} = +k_{12}C_1 - k_2C_2 + b_2 \\
\frac{dC_3}{dt} = +k_{23}C_2 - k_3C_3 + b_3 \\
\frac{dC_4}{dt} = +k_{34}C_3 - k_4C_4 + b_4
\]

**Eq. 7a**

**Eq. 7b**

**Eq. 7c**

Such diagonal matrices can be solved analytically, depending on the initial conditions and the input function (Trapp and Matthies 1998). Compartment 1 is soil, 2 is root, 3 is leaves (or fruits) and 4 is metabolite in leaves (or fruits). Other combinations are possible.

7.2 Steady-state solution

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

\[
C_1(t \to \infty) = \frac{I_1}{k_1M_1} = \frac{b_1}{k_1}
\]

\[
C_2(t \to \infty) = \frac{I_2}{k_2M_2} + \frac{k_{12}}{k_2}C_1(t \to \infty)
\]

\[
C_3(t \to \infty) = \frac{I_3}{k_3M_3} + \frac{k_{23}}{k_3}C_2(t \to \infty)
\]

etc.

The steady-state solution follows the general scheme:

\[
C_n(t \to \infty) = \frac{I_n}{k_nM_n} + \frac{k_{n-1,n}}{k_n} \times C_{n-1}(t \to \infty)
\]

where \( n \) is the compartment number.
7.3 Pulse input

The analytical solutions for the differential equations 1 (soil), 2 (roots) and 3 (leaves) for a pulse input is the same as for initial concentrations \( C(0) \neq 0 \):

\[
C_1(t) = C_1(0) \times e^{-k_1 t}
\]

Eq. 8a

\[
C_2(t) = k_{12} C_1(0) \times \left( \frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right) + C_2(0) \times e^{-k_2 t}
\]

Eq. 8b

\[
C_3(t) = k_{12} k_{23} C_1(0) \left\{ \frac{e^{-k_1 t}}{(k_1 - k_2)(k_1 - k_3)} + \frac{e^{-k_2 t}}{(k_2 - k_1)(k_2 - k_3)} + \frac{e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)} \right\}
\]

\[
+ k_{23} C_2(0) \times \left( \frac{e^{-k_2 t}}{k_3 - k_2} + \frac{e^{-k_3 t}}{k_2 - k_3} \right) + C_3(0) \times e^{-k_3 t}
\]

Eq. 8c

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

\[
C_n(t) = C_1(0) \times \prod_{j=1}^{n-1} k_{i,j+1} \sum_{j=1}^{n} \frac{e^{-k_j t}}{\prod_{k=1,k\neq j}^{n} (k_k - k_j)}
\]

Eq. 8d

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

\[
C_n(t) = \sum_{a=1}^{n-1} C_a(0) \times \prod_{i=a}^{n-1} k_{i,j+1} \times \sum_{j=a}^{n} \frac{e^{-k_j t}}{\prod_{k=a,k\neq j}^{n} (k_k - k_j)} + C_n(0) \times e^{-k_n t}
\]

Eq. 8e

7.4 Constant input for some time

The common analytical solution for one compartment with constant input \( b \) and initial condition \( C(0) = C_0 \), is:

\[
C(t) = C_0 \times e^{-k t} + \frac{b}{k} \left( 1 - e^{-k t} \right)
\]

Eq. 9

The analytical solutions for \( C(t) \) in the 4 compartments, with initial condition \( C_n(0) \neq 0 \) (compartment i) are:
\[ C_1(t) = \frac{b_1}{k_1} \left(1 - e^{-k_1 t} \right) + C_1(0) \times e^{-k_1 t} \quad \text{Eq. 9a} \]

\[ C_2(t) = A \times \left( e^{-k_2 t} - e^{-k_1 t} \right) + B \times \left(1 - e^{-k_2 t} \right) + C_2(0) \times e^{-k_2 t} \quad \text{Eq. 9b} \]

\[ C_3(t) = D \times \left( e^{-k_3 t} - e^{-k_2 t} \right) + E \times \left( e^{-k_3 t} - e^{-k_1 t} \right) + F \times \left(1 - e^{-k_3 t} \right) + C_3(0) \times e^{-k_3 t} \quad \text{Eq. 9c} \]

\[ C_4(t) = G \times \left( e^{-k_4 t} - e^{-k_3 t} \right) + H \times \left( e^{-k_4 t} - e^{-k_2 t} \right) + I \times \left( e^{-k_4 t} - e^{-k_1 t} \right) + J \times \left(1 - e^{-k_4 t} \right) + C_4(0) \times e^{-k_4 t} \quad \text{Eq. 9d} \]

with:

\[ A = \frac{C_1(0)k_{12} - k_{12}b_1}{(k_2 - k_1)k_1} \]

\[ B = \frac{k_{12}b_1 + k_1b_2}{k_1k_2} \]

\[ D = A \cdot \frac{k_{23}}{k_3 - k_1} \]

\[ E = \frac{k_{23}(C_2(0) - A - B)}{k_3 - k_2} \]

\[ F = \frac{k_{34}b_3}{k_3} \]

\[ G = \frac{k_{34}}{k_4 - k_1} \]

\[ I = \frac{k_{34}(C_3(0) - D - E - F)}{k_4 - k_3} \]

\[ J = \frac{k_{34}F + b_4}{k_4} \]

Looks difficult, but is not. This is the solution programmed in the "Cascade" model.

7.5 General solution

The equations were obtained by integration. Further compartments can be added by further integration, or by applying the general scheme. The analytical matrix solution with initial concentrations \( C_n(0) \neq 0 \) and constant input terms \( b_n \), for \( n \geq 2 \) and \( t_0 = 0 \), follows the scheme:

\[ C_n(t) = \sum_{a=1}^{n-1} \left[ C_a(0) \cdot \sum_{j=a}^{n} \frac{e^{-k_j t}}{\prod_{i=a}^{n} (k_i - k_j)} + b_a \cdot \frac{1 - e^{-k_a t}}{\prod_{i=a}^{n} k_i} - \sum_{m=a}^{n-1} \left( \sum_{s=1}^{n} \frac{e^{-k_s t}}{\prod_{i=s}^{n} (k_i - k_s)} \right) \right] \]

\[ + C_n(0) \cdot e^{-k_n t} + \frac{b_n}{k_n} \left(1 - e^{-k_n t} \right) \quad \text{Equation 10} \]

Even though complex, this solution allows the direct calculation of concentrations in all compartments at any time \( t \) and for pulse- and/or constant input.
Combination of all solutions and superposition

Also for repeated applications there is a solution. This is 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 $C(t)$ at the end of a specific period serves as initial concentration vector $C(0)$ for the next period. This refers to concentrations in any compartment (i.e. soil, roots and leaves).

Concentrations are additive. This means, concentrations resulting from constant background contamination (e.g., from air) add to those concentrations from pulse- or constant input. Constant input can also be used to simulate "rectangular" input functions, by splitting the simulation up into several periods with different constant input. During each period, the conditions and parameters need to be constant, but they may differ from one to the other period. This allows to simulate seasonal changes, or day/night conditions, or other non-constant conditions.

7.6 Example simulation

The application of the cascade model allows to combine steady-state input, pulse input and input constant over time. Several periods can be combined. The figure shows a simulation result for pulse input to soil and constant input from air. The concentrations in roots follow closely those in soil. But in leaves, the pulse in soil and roots leads to a very small response, because in this scenario the compound enters the leaves from air.

![Figure](image)

**Figure.** Dynamic simulation of repeated application of a medium lipophilic, low volatile compound with pulse input plus constant background from air.

7.7 Exercises

1) Find $k$ and $b$ for leaves (compartment 3) from this differential equation:

$$\frac{dC_L}{dt} = \frac{Q}{M_L \times K_{RW}} \times C_R + \frac{A_L \times g}{M_L} \times (1 - f_p) \times C_A + \frac{A_L \times v_{dep}}{2 \times M_L} \times f_p \times C_A - \frac{A_L \times g_L \times 1000 \times m^{-3}}{K_{LA} \times M_L} \times C_L - k_L \times C_L$$

More exercises with computer ("Cascade model").
CHAPTER 8 The Potato Model

The potato model was described in Trapp et al. (2007). It is based on a solution for diffusion into a sphere. Diffusion coefficients in potatoes are estimated from partitioning to potato tissue and tortuosity.

8.1 Diffusion coefficient in potato tissue

Under the assumption that diffusion only takes place in the water-filled pores (this implies that transport in solids and in air filled pores is negligible, which is the case due to small air pore space of potatoes), the effective diffusion coefficient in the potato tissue, $D_p$, is

$$D_p = D_w \times T_w \times f_w$$

where $T_w$ is a tortuosity coefficient to account for the porosity of the medium, and $f_w$ (kg L$^{-1}$) is the fraction of chemical dissolved in the water phase of plant tissue, calculated as

$$f_w = \frac{C_{W,p}}{C_p} = \frac{W}{K_{pw}}$$

where $C_{W,p}$ (mg/L) is the concentration of the chemical in the water phase of the potato tissue, $C_p$ is the total concentration in potato tissue (mg/kg) and $W$ is the pore water fraction of the potato tissue (L kg$^{-1}$). The tortuosity factor is calculated using the method of Millington and Quirk:

$$T = \frac{W^{10/3}}{(W + G)^{2/3}} = W^{4/3}$$

where $G$ is the gas pore volume fraction (L kg$^{-1}$), which is small and neglectable. It should be noted that this expression is not unit-true (it probably originates from a regression), which is ignored here. Summarized,

$$D_p = \frac{D_w \times W^{7/3}}{K_{pw}}$$

$K_{pw}$ is the partition coefficient potato to water. Potato is composed of water, carbohydrates and traces of lipids. The phase equilibrium to water (the partition coefficient potato to water), $K_{pw}$ (L kg$^{-1}$), can be estimated from

$$K_{pw} = \frac{C_p}{C_w} = W + f_{CH} \times K_{CH} + L \times a \times K_{OW}^b$$

where $C_p$ (mg kg$^{-1}$ fresh weight) and $C_w$ (mg L$^{-1}$) are the chemical concentrations in potato and water; $W$ is the water content of potato (L kg$^{-1}$); $f_{CH}$ is the fraction of carbohydrates; $L$ 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 (as in the root model), $a = 1/\rho_{octanol} = 1.22$ 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.
8.2 Uptake model for potato

The diffusion coefficients in potatoes can be used to estimate the accumulation of pollutants in this foodstuff. We consider the potato to be a sphere and assume a purely diffusive uptake from soil through the peel.

Generally, the uptake of chemicals from a surrounding medium into an organism can be described by a compartment system:

\[
\frac{dC}{dt} = k_1 C_1 - k_2 C_2
\]

where \(k_1\) is an uptake rate and \(k_2\) is a depuration rate. In our case, compartment 1 is the soil, and compartment 2 is the potato. In steady-state \((dC/dt = 0)\), this leads to the equation for the bioconcentration factor \(BCF\)

\[
BCF = \frac{C_2}{C_1} = \frac{k_1}{k_2}
\]

This \(BCF\) describes the situation when forward- and back-diffusion are balanced; the situation is equivalent to phase equilibrium.

The equilibrium \(BCF\) of potatoes (kg kg\(^{-1}\)) in soil can be calculated from

\[
BCF = \frac{C_p}{C_s} = \frac{K_{pw}}{K_{sw}}
\]

From the radial diffusion model, an estimate for \(k_2\) can be deduced

\[
k_2 = \frac{23 \times D_p}{R^2}
\]

\(R\) is the radius of the potato (m). Now follows for \(k_1\)

\[
k_1 = k_2 \times BCF
\]

These equations describe the equilibrium between uptake and depuration of a compound, which is here identical to the equilibrium between potato and soil. Additional processes, i.e. \(1^{st}\) order degradation, may be added. For potatoes, dilution by growth is relevant. For exponential growth, the growth rate \(k_G\) can be added to the depuration rate, and the steady-state concentration ratio (bioaccumulation with growth) \(BCF^*\), is

\[
BCF^* = \frac{k_1}{k_2 + k_G}
\]

Equation 11

This \(BCF^*\) is used as "potato model" and considers diffusive in- and outflux plus dilution by growth. It is thus similar to the root model, which considers advective in- and outflux plus dilution by growth.
Table. Data for BCF calculation for potato

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato water content</td>
<td>W</td>
<td>0.778</td>
<td>L kg⁻¹</td>
</tr>
<tr>
<td>Potato lipid content</td>
<td>L</td>
<td>0.001</td>
<td>kg kg⁻¹</td>
</tr>
<tr>
<td>Potato fraction of carbohydrates</td>
<td>f_{CH}</td>
<td>0.154</td>
<td>kg kg⁻¹</td>
</tr>
<tr>
<td>Potato growth rate *</td>
<td>k_{growth}</td>
<td>0.139</td>
<td>d⁻¹</td>
</tr>
<tr>
<td>Potato radius</td>
<td>R</td>
<td>0.04</td>
<td>m</td>
</tr>
<tr>
<td>Soil organic carbon content</td>
<td>f_{OC}</td>
<td>0.02</td>
<td>kg kg⁻¹</td>
</tr>
<tr>
<td>Soil pore water</td>
<td>W_{S}</td>
<td>0.35</td>
<td>L L⁻¹</td>
</tr>
<tr>
<td>Soil wet density</td>
<td>\rho_{wet}</td>
<td>1.95</td>
<td>kg L⁻¹</td>
</tr>
<tr>
<td>Soil dry density</td>
<td>\rho_{dry}</td>
<td>1.6</td>
<td>kg L⁻¹</td>
</tr>
</tbody>
</table>

* calculated from a potato doubling time of 5 days.

The Figure shows a calculation of the BCF and BCF* potato to soil versus log \( K_{OW} \) using the data given in the Table. For very polar compounds, the calculated BCF is > 1, due to the higher water content of potatoes, compared to soil. For more lipophilic compounds, the BCF decreases. This is due to the low lipid content of potatoes (0.1%), relative to the organic carbon OC of soil (2%). For log \( K_{OW} > 4 \) there is an increasing difference between BCF (equilibrium) and BCF* (with growth). This is because the depuration rate \( k_2 \) (calculated from the diffusion coefficient in potatoes) decreases with increasing log \( K_{OW} \) (increasing \( K_{PW} \)), while the growth rate is independent of chemical properties.

![Figure](image.png)

Figure. Calculated BCF potato to soil with growth ("potato model") and without growth (chemical equilibrium).

Exercises to Chapter 8

Sensitive parameters

Open the potato model (it's part of "Plant uptake models 12.xls”).

1) What is the BCF* for BaP, TBA and MTBE?

2) What is the difference of BCF (equilibrium) and BCF* (dynamic solution) for BaP and MTBE? Why is the ratio BCF/BCF* not constant?

3) BaP. Which of the four plant parameters radius R, water content W, lipid content L and carbohydrate content f_{CH} is least important?
CHAPTER 9 The "Fruit Tree model"

There are two versions of the fruit tree model: the first version (Trapp et al. 2003) considers solely uptake from soil into fruits. The second version (Trapp 2007) considers additionally exchange to air. This second Fruit Tree model uses a new approach (units, processes, implementation), which is the basis for all subsequent models from our team.

Fruit trees are complex organisms, and the Fruit Tree model is also quite complex. It is composed of eight compartments (see Figure). We refer therefore to the reference (Trapp 2007) and apologize for not describing the model here in this script. It would take about 30 pages - i.e. half of the script.

**Figure.** Structure of the Fruit Tree model.

An important outcome of the Fruit Tree model is that polar, non-volatile compounds accumulate in fruits from soil; if uptake is from air, it is non-polar (lipophilic) non-volatile compounds (see Figure).

**Figure.** Result of the Fruit Tree model for (left side) concentration in soil is 1 mg/kg, air is zero and (right side) concentration in soil is zero and concentration in air is 1 µg/m³.
CHAPTER 10 The regression of Travis and Arms (T&A).

After all these equations, the reader might wish for an easier method. Well, there is one. Travis and Arms (1988) established a regression that estimates uptake of neutral organic chemicals into above-ground plants. The regression has been obtained from a range of empirical data acquired by the authors from literature. Mainly data from uptake of pesticides with a log $K_{OW}$ ranging from 1.15 to 9.35 were used but no particular type of vegetation was targeted in the original study. The form of the regression is:

$$\log BV (\text{dry wt}) = 1.588 - 0.578 \log K_{OW}$$

Equation 12

where BV is the bioconcentration factor vegetation and is the concentration ratio between plants (dry wt) and soil (dry wt). The BV can be converted into wet weight bioconcentration factors (BCF) using

$$BCF (\text{wet}) = BV (\text{dry}) \times (1 - W) \times \frac{\rho_{wet}}{\rho_{dry}}$$

where $W$ is the water content of the plants, and $\rho$ is the density of the soil.

The regression of Travis and Arms needs little efforts to calculate BCFs. Therefore, it might serve as an "early warning". A real disadvantage of the T&A regression is that it can not consider any contribution from air! It should only be used when the contamination clearly is soil born.

The regression of Travis & Arms was established for above-ground plants. Therefore, it may surprise that the result of this regression (if translated to fresh weight) is very similar to the result of the potato model, and close to the root model (see Figure).

![Figure: Calculated BCF fresh weight using the regression of Travis & Arms (T&A), the root model and the potato model, in comparison to the RCF (equilibrium).](image)

Example: BCF of MTBE with the Travis and Arms regression

$$\log BV (\text{dry wt}) = 1.588 - 0.578 \times 1.14 = 0.92 \quad \rightarrow BV (\text{dry}) = 10^{0.92} = 8.32$$

Now which plant do we chose to calculate wet weight? OK, carrots; $W = 0.89$

$$BCF (\text{wet}) = BV (\text{dry}) \times (1 - 0.89) \times \frac{1.95}{1.6} = 1.11$$

Compare: Carrot model BCF was 2.8.

Exercise 8: What are dry and wet weight BCF with the regression of Travis and Arms for carrots and for TBA and BaP?
The concept of crop-specific human exposure assessment for soil pollutants allows adapting to different food habits, different life-styles, different regions and different accepted risks. Models for transfer into major food crops are combined with regional food baskets to give the exposure of the population, which can be compared to tolerable risks based on health considerations. Backwards, tolerable concentrations of pollutants in soil for the agricultural production and gardening can be derived. The approach might therefore be used to derive rational soil quality standards for a large variety of chemicals with reasonable effort (Figure).

**Figure**: Risk Assessment of Transfer into food RATfood.

### 11.1 Daily Dietary Intake (DDI)

For the calculation of the daily dietary intake (DDI), the consumption of vegetable is multiplied with the calculated concentration in the crop types, i.e. root vegetable, fruits, potatoes and leafy vegetable. The daily dietary intake DDI is then

\[
\text{DDI} [\text{mg/d}] = \sum_i \text{concentration in crop}(i) [\text{mg kg}^{-1}] \times \text{amount of crop}(i) \text{ consumed} [\text{kg d}^{-1}]
\]

The consumption data for most European countries are known, and often available. Below, find data for Denmark and Czech republic.

**Table**: Average consumption and 90% percentile for a child (4-13 years) and a woman (14-75 years) from Denmark. Data from Legind & Trapp 2009.

<table>
<thead>
<tr>
<th></th>
<th>Child mean</th>
<th>Child 90%</th>
<th>Woman mean</th>
<th>Woman 90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root vegetables (kg d⁻¹)</td>
<td>0.033</td>
<td>0.058</td>
<td>0.043</td>
<td>0.074</td>
</tr>
<tr>
<td>Potatoes (kg d⁻¹)</td>
<td>0.073</td>
<td>0.141</td>
<td>0.09</td>
<td>0.168</td>
</tr>
<tr>
<td>Lettuce w. soil (kg d⁻¹)</td>
<td>0.007</td>
<td>0.012</td>
<td>0.009</td>
<td>0.015</td>
</tr>
<tr>
<td>Other leafy veget. (kg d⁻¹)</td>
<td>0.008</td>
<td>0.013</td>
<td>0.01</td>
<td>0.017</td>
</tr>
<tr>
<td>Tree fruits (kg d⁻¹)</td>
<td>0.127</td>
<td>0.229</td>
<td>0.137</td>
<td>0.262</td>
</tr>
<tr>
<td>Cereal products (kg d⁻¹)</td>
<td>0.205</td>
<td>0.282</td>
<td>0.195</td>
<td>0.284</td>
</tr>
<tr>
<td>Milk (kg d⁻¹)</td>
<td>0.500</td>
<td>0.823</td>
<td>0.303</td>
<td>0.612</td>
</tr>
<tr>
<td>Meat (kg d⁻¹)</td>
<td>0.109</td>
<td>0.187</td>
<td>0.113</td>
<td>0.199</td>
</tr>
<tr>
<td>Fish (kg d⁻¹)</td>
<td>0.012</td>
<td>0.028</td>
<td>0.017</td>
<td>0.038</td>
</tr>
<tr>
<td>Air (m³ d⁻¹)</td>
<td>10.700</td>
<td>28.8</td>
<td>11.3</td>
<td>38.4</td>
</tr>
<tr>
<td>Soil (kg d⁻¹)</td>
<td>0.0001</td>
<td>0.0002</td>
<td>0.00005</td>
<td>0.0003</td>
</tr>
<tr>
<td>Water (L d⁻¹)</td>
<td>0.900</td>
<td>1.5</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Bodyweight (kg)</td>
<td>35.1</td>
<td>67.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table: Average consumption \([\text{g person}^{-1} \text{d}^{-1}]\) of vegetables and fruits in CZ (Ruprich et al. 2000).

<table>
<thead>
<tr>
<th>Type of crop</th>
<th>Typical species</th>
<th>Consumption</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beans</td>
<td>pea, beans, lens</td>
<td>3.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Leafy vegetable</td>
<td>lettuce, spinach, rhubarb</td>
<td>2.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Root vegetable</td>
<td>carrot, celery, parsley</td>
<td>13.5</td>
<td>7.1</td>
</tr>
<tr>
<td>Potatoes</td>
<td>potatoes and potato products</td>
<td>97.4</td>
<td>51.5</td>
</tr>
<tr>
<td>Tree fruit</td>
<td>apples, pears</td>
<td>62.7</td>
<td>33.1</td>
</tr>
<tr>
<td>Other fruit</td>
<td>berries</td>
<td>6.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Nuts</td>
<td>hazelnuts</td>
<td>3.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Sum all</td>
<td></td>
<td>189.3</td>
<td>100</td>
</tr>
</tbody>
</table>

**11.2 Acceptable Daily Intake (ADI).** “Dosis facit venenum (Paracelsus, 16\textsuperscript{th} century) – everything is toxic, it is only the dose that makes a thing a poison or a remedy. An acceptable daily intake of the chemical under investigation has to be defined by human toxicologists:

A "virtually safe dose of BaP as a marker of the mixture of carcinogenic PAH in food would be in the range 0.06 to 0.5 ng BaP kg\textsuperscript{-1} bw d\textsuperscript{-1}" (EC 2002). If we chose the lowest value of this virtually safe dose as acceptable, the acceptable daily intake of BaP via food for an adult weighing 70 kg would be 4.2 ng d\textsuperscript{-1}. If the upper limit of the virtually safe dose is used, the ADI of BaP would be 35 ng d\textsuperscript{-1}. (The unit “ng BaP kg\textsuperscript{-1} bw d\textsuperscript{-1}” means nanogram benzo(a)pyrene per kilogram bodyweight and day)

**11.3 Acceptable Soil Concentration (ASC).** To derive the acceptable soil concentration, we expect that the life-long consumption of food produced from this soil does not lead to oral intake above the virtually safe dose. Using the linearity of BCF to concentration in soil, the acceptable soil concentration (ASC) can be estimated from DDI (calculated for a concentration in soil of 1 mg/kg):

\[
\text{ASC [mg kg}^{-1} \text{ wet wt]} = \left\{ \frac{\text{ADI [mg d}^{-1}]}{\text{DDI [mg d}^{-1}]} \right\} \times 1 \text{ mg kg}^{-1} \text{ wet wt}
\]

**Example 11. Calculation Risk Assessment Benzo(a)pyrene - Danish Woman**

The average Danish woman has a bodyweight of 67 kg. She consumes 1.4 L water, inhales 11.3 m\textsuperscript{3} air, and ingests 50 mg soil per day. The consumption of plant food (vegetables, cereals, fruits and roots) by a typical Danish woman is 0.484 kg /day.

Benzo(a)pyrene (BaP) is a strong carcinogen (makes cancer). The legal standards in Denmark are: Water 10 ng/L (sum of PAH); Air 1 ng/m\textsuperscript{3} (target value EU); Soil 0.3 mg/kg (since 2006; dry weight, but ignore).

The BCF soil-to-plant of BaP is in average 0.005 mg/kg plant : mg/kg soil (freshweight). The BCF air-to-plant is in average 3000 mg/kg plant : mg/m\textsuperscript{3} air. The resulting concentrations in plant are:
- from soil 0.005 mg/kg; from air 0.003 mg/kg
- total concentration in plant (concentrations add) 0.0045 mg/kg

These values shall be used in the following calculations.

**Consumption data**

<table>
<thead>
<tr>
<th></th>
<th>Woman</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.4</td>
<td>L/d</td>
</tr>
<tr>
<td>Air</td>
<td>11.3</td>
<td>m3/d</td>
</tr>
<tr>
<td>Soil</td>
<td>5.05</td>
<td>kg/d</td>
</tr>
<tr>
<td>Plants</td>
<td>0.484</td>
<td>kg/d</td>
</tr>
</tbody>
</table>

bodyweight 67 kg
Results calculated by Stefan Trapp

1 a) How much BaP takes the Danish woman up per day, oral pathway (via water, soil, plants, sum oral)?

\[\text{uptake} = \text{concentration} \times \text{consumption}\]

1 b) What is the oral uptake per kg bodyweight and day for the woman?

\text{divide calculated uptake by bodyweight}

1 c) How much BaP takes the Danish woman up due to inhalation of air?

<table>
<thead>
<tr>
<th></th>
<th>unit</th>
<th>per kg bodyweight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>14 ng/d</td>
<td>0.209 ng/kg bw /d</td>
</tr>
<tr>
<td>Soil</td>
<td>15.0 ng/d</td>
<td>0.22 ng/kg bw /d</td>
</tr>
<tr>
<td>Plant</td>
<td>2178 ng/d</td>
<td>32.5 ng/kg bw /d</td>
</tr>
<tr>
<td>total oral</td>
<td>2207 ng/d</td>
<td>32.9 ng/kg bw /d</td>
</tr>
<tr>
<td>Air</td>
<td>11.3 ng/d</td>
<td></td>
</tr>
</tbody>
</table>

The uptake with food is much higher than the uptake with water or by soil ingestion. This is due to a high consumption, and also rather high concentrations in plants.

2 Cancer risk

The cancer risk for benzo(a)pyrene is, for life-long exposed persons,

\text{via inhalation: at an air concentration of 0.012 ng/m}^3 \text{ 1 additional disease case out of 1 million exposed persons (at 10fold concentration, 10 cases per million etc.)}

\text{via oral exposure : for an uptake of 0.06 ng per kg bodyweight and day, 1 additional cancer case occurs (then at 0.6 ng/kg bw and day, 10 additional cases occur etc)}

a) What is the cancer risk at legal standard for the woman (oral uptake; inhalation; total) ?

\text{to calculate the oral risk, divide uptake per kg bodyweight and day by 0.06 ng/kg bw /d}

<table>
<thead>
<tr>
<th></th>
<th>risk</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>3.5</td>
<td>per million</td>
</tr>
<tr>
<td>Soil</td>
<td>3.7</td>
<td>per million</td>
</tr>
<tr>
<td>Plant</td>
<td>541.8</td>
<td>per million</td>
</tr>
<tr>
<td>total oral</td>
<td>549.0</td>
<td>per million</td>
</tr>
</tbody>
</table>

The oral risk is 549 cancer diseases per million exposed persons. High! Most of this risk is due to consumption of plants.

\text{inhalation: divide concentration in air by 0.012 ng/m}^3

\[1 \text{ ng/m}^3 / 0.012 \text{ ng/m}^3 = 83.3 \text{ cases per million} \]

b) What is the total cancer risk due to benzo(a)pyrene in Denmark (5.1 mio inhabitants) for an average women (cases per million)?

\[549 + 83.3 = 632.3 \text{ cancer cases per million - or more than 3000 disease cases for all Denmark (lifelong).} \]
Some frequently asked questions

Is this real? Probably. In fact, about 30% of all death cases in DK are cancer.

Why was this calculation made for women? Why not?

Is the risk the same for men? Almost. But for children, the risk is twice as high, due to their smaller bodyweight (but similar consumption). But we are not lifelong children.

What is a safe legal standard for soil and air? Well - what means “safe”? If we say, safe is 1 case per 100 000 exposed persons (is this acceptable?), then air had to be 8.3 times lower than now (now: 83 cases per million = 8.3 cases per 100 000), i.e. 1/8.3 = 0.12 ng/m3. For soil, such a “safe” concentration would be (under consideration of all sources) about 0.012 ng/kg.

Does the government know this? It seems so. This here is from Miljøstyrelsen (Danish EPA). I translate: "By usage of the latest knowledge, and if health-based criteria would be used, then the value [for the legal standard of benzo(a)pyrene in soil] would be 0.013 mg/kg [soil]."

De nuværende jordkvalitetskriterier er for bly 40 mg/kg og for PAH-indikatorstoffet benzo(a)pyren 0.1 mg/kg. En opdatering med den nyeste viden for bly og PAH viser, at hvis principperne for fastsættelse af de sundhedsbaserede kriterier anvendes, vil værdierne for benzo(a)pyren blive på 0.013 mg/kg og for bly under 5 mg/kg. Disse værdier er lavere end de nuværende jordkvalitetskriterier, og er på niveau med eller under baggrunds niveauerne i Danmark.


Why is the legal standard in soil then so high? A “safe” legal standard for soil would be near or below the background concentrations of benzo(a)pyrene (i.e. what you find in remote areas). Thus, the whole country would be declared "poisnened". This doesn't help.

What can I do to reduce my risk? Wash your vegetables carefully (lettuce etc.). Peel them, if possible (carrots etc.). Do not buy when the fruits were all day long exposed at dirty streets.

Exercise 11. Risk Assessment Benzo(a)pyrene - Danish Child

The average Danish child (age 4 to 13) has a bodyweight of 35 kg. It consumes 0.9 L water, inhales 10.7 m3 air, and ingests 200 mg soil per day.

Benzo(a)pyrene is a strong carcinogen (makes cancer). The legal standards in Denmark are:

Water 10 ng/L (sum of PAH)
Air 1 ng/m³ (target value EU)
soil 0.3 mg/kg (since 2006).

1 a) How much BaP takes the Danish child up per day (sum, water, soil, air)?

1b) What is the uptake per kg bodyweight and day for the child?

2) The cancer risk for benzo(a)pyrene is:

inhalation: at an air concentration of 0.012 ng/m3,
oral: 0.06 ng/kg bw and day

for 1 additional disease case out of 1 million life-long exposed persons
What is the cancer risk for BaP-concentrations at legal standard for the child (oral and inhalation and sum)?

3) The BCF soil-to-plant of BaP is in average 0.005 kg/kg. The BCF air-to-plant is in average 3000 mg/kg plant : mg/m3 air

a) For the soil concentration at legal standard, what is the concentration in plant via uptake from soil ?

b) For the air concentration at legal standard, what is the concentration in plant via uptake from soil ?

4) The consumption of plant food (vegetables, cereals, fruits and roots) by a typical Danish child is 0.453 kg/day.

What is the additional oral uptake with plant food for the child

a) due to uptake from soil?
b) due to uptake from air?
c) sum of both?

5) What is the additional cancer risk due to plant food consumption for the child ?
(assume life-long childhood)

a) due to uptake from soil?
b) due to uptake from air?
c) sum of both?

d) What is the total cancer risk due to benzo(a)pyrene in Denmark for a child?

6) To have a cancer risk of 1 : 100 000, which concentration in soil would be maximal allowable

if a) the only oral exposure pathway is soil ingestion by child
and b) oral exposure is by ingestion of soil plus plant food (uptake into plant only from soil) ?

CHAPTER 12 Ionic Compounds

(based on the Trapp (2004) and several manuscripts, which appear probably 2010)

Some compounds, if dissolved in water, increase the electric conductivity and were named "electrolytes". Electrolytes comprise acids, bases, ampholytes and salts. A further separation is possible into weak and strong electrolytes, the former being partly dissociated in aqueous solution under normal pH conditions, while the latter dissociate (almost) completely.

Between 20% and 50% of all organic compounds on the market are electrolytes. Some product classes are typically ionizable compounds. For example, systemic herbicides are typically weak acids (Hsu and Kleier 1996) and systemic fungicides are weak bases (Chamberlain et al. 1998). Many pharmaceuticals are weak bases (in particular those derived from alkaloids) or ampholytes (Newton and Kluza 1978). Detergents are often of a cationic or anionic type.

Only a few plant uptake models are applicable to ionic or ionizable organic compounds (Trapp 2004). To mention are the model of Kleier (1988) for phloem transport, the Satchivi model for pesticide spray application (Satchivi et al. 2000 ab) and the Fick-Nernst-Planck model ("Cell model") by Trapp (2000, 2004).

The organic ionics have unique properties and undergo processes which are different from those of neutral compounds:
ionizable compounds occur in (at least) two species, namely the neutral and the ionic molecule
- the concentration ratios of these two or more species change with pH
- ions are attracted or repelled by electrical fields, while neutral compounds are unaffected
- different permeabilities of neutral and ionic molecules may lead to accumulation of electrolytes inside living cells, which is known as ion trap effect.
- ions, and in particular multivalent ions, are subject to larger changes in their "active concentration" (the activity) with ionic strength (in sea water or in body fluids) than neutral compounds
- ions are much more polar than the corresponding neutral molecules
- ions have no measurable vapor pressure and thus do not tend to volatilize. If formed in atmosphere they thus partition irreversibly to aerosol particles, fog, rain or snow.

To describe their transport, we use an approach based on the activity of ions. The basics is the so-called "cell model".

12.1 Basic concept

The following equations relate to monovalent ions. For bivalent ions see Trapp, Rosania et al. (2008).

Dissociation

The activity ratio between ionic (index d) and neutral molecule (index n) is calculated by the Henderson-Hasselbalch equation:

\[
\log \frac{a_d}{a_n} = i(pH - pK_a)
\]

where \(a\) is the activity, \(d\) is the index for dissociated (synonym ionic), \(n\) for neutral, \(i\) is +1 for acids and -1 for bases; \(pK_a\) is the negative logarithm (\(\log_{10}\)) of the dissociation constant. It follows for the fraction of neutral molecules \(F_n\) that

\[
F_n = \frac{1}{1 + 10^{pH - pK_a}}
\]

In pure water, the fraction of dissociated molecules \(F_d\) is \(1 - F_n\). Else, the Henderson-Hasselbalch equation applies: \(\frac{F_d}{F_n} = 10^{pH - pK_a}\)

From concentration to activity

For solutes, it is convenient to use activity in the unit \(\text{mol} \ L^{-1}\) or \(\text{mol} \ m^{-3}\). In non-dilute solutions, molecules interact with each other. The chemical potential is reduced, due to these interactions, and, for ions, the activity \(a\) is lower than the concentration \(C\):

\[a = \gamma \times C\]

where \(\gamma\) is the activity coefficient (-). The activity coefficient of the ion, \(\gamma_d\), can be calculated with the modified Debye-Hückel equation. Several approximations exist, among them the Davies approximation:
\[
\log \gamma_d = -A \times z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \times I \right) \quad \text{for } I \leq 0.5 \text{ M}
\]

where \(A\) depends on ambient pressure and temperature, \(A = 0.5\) for 15 to 20° and 1 atm. With an ionic strength \(I\) of 0.3 M, \(\gamma_d\) is 0.74 for a monovalent and 0.30 for a bivalent ion.

For neutral compounds, too, the activity differs from the dissolved concentration at high ionic strength. The activity coefficient of the neutral compound, \(\gamma_n\), is found by the \textit{Setchenov} equation:

\[
\gamma_n = 10^{kI}
\]

where \(k\) is the \textit{Setchenov}-coefficient, that increases with the size of the molecule. For smaller molecules, \(k = 0.2\) (taken as default), and \(\gamma_n\) in plant saps with \(I = 0.3\) M is 1.23. This means, in water with high ionic strength, the activity of neutral molecules is higher than in salt-free water. This is the reason for the well-known "out-salt"-effect of neutral organic chemicals in salt water.

**Activity and adsorption**

Not only in pure water, but in all phases, activity is related to the truly dissolved concentration. If, for example in soil or in plant cells, the molecule is partly adsorbed, the activity can still be calculated. The relation between the activity \(a\) (kg m\(^{-3}\)) of free (truly dissolved) molecules and the total concentration \(C_t\) (kg m\(^{-3}\)) can generally be defined by fractions \(f\), which consider dissociation, ionic strength and sorption to lipids, so that \(a = f \times C_t\).

The total (measurable) concentration \(C_t\) of the compound is comprised of the neutral (n) and dissociated (d) molecules, both kinds can be free (\(C_{\text{free}}\)) in solution or sorbed (\(C_{\text{ads}}\)):

\[
C_t = W \times C_{\text{free,n}} + L \times C_{\text{ads,n}} + W \times C_{\text{free,d}} + L \times C_{\text{ads,d}}
\]

where \(W\) and \(L\) are the volumetric fractions of water and lipids (L L\(^{-1}\)).

With \(L \times C_{\text{ads}} = K \times C_{\text{free}}\) we can write

\[
C_t = W \times C_{\text{free,n}} + K_n \times C_{\text{free,n}} + W \times C_{\text{free,d}} + K_d \times C_{\text{free,d}}
\]

Furthermore, using Henderson-Hasselbalch's equation and \(a = \gamma \times C_{\text{free}}\), we receive for the relation between the activity \(a_n\) of the neutral molecules and the total concentration the "activity capacity" \(f\):

\[
f_n = \frac{a_n}{C_t} = \frac{1}{W / \gamma_n + K_n / \gamma_n + 10^{(pH-pK_a)} \times (W + K_d) / \gamma_d}
\]

The respective relation for the ions, with \(a_i = a_n \times 10^{(pH-pK_a)}\) is \(f_i = a_i / C_t = f_n \times 10^{(pH-pK_a)}\).

The values of \(K_n\) and \(K_d\) are calculated from lipid content using the log Kow:

\[
K_n = L \times K_{\text{OW,n}}
\]
\[
K_d = L \times K_{\text{OW,d}}
\]

Note that the \(K_d\) here describes the adsorption of the dissociated molecules and is not related to the \(K_d\) (distribution coefficient in soil).
Diffusive exchange of electrolytes across membranes

The diffusive flux of neutral molecules (index n) across membranes, $J_n$, is described by Fick’s 1st Law of Diffusion:

$$J_n = P_n (a_{n,o} - a_{n,i})$$

where $J$ is the unit net flux of the neutral molecules n from outside (o) to inside (i) of the membrane (kg m$^{-2}$ s$^{-1}$), $P_n$ is the permeability of the membrane (m s$^{-1}$) for neutral molecules, and $a$ is the activity of the compound (kg m$^{-3}$).

The unit net flux of the ions (index d, for dissociated) across electrically charged membranes, $J_d$, is described by the Nernst-Planck equation. An analytical solution for constant electrical fields is (Goldman 1943, Hodgkin and Katz 1949, Briggs et al. 1961)

$$J_d = P_d \frac{N}{e^N - 1} (a_{d,o} - a_{d,i} e^N)$$

where $P_d$ is the permeability of the membrane (m s$^{-1}$) for dissociated molecules, $N = z E F / (R T)$; $z$ is the electric charge (synonym valency, for acids -, for bases +), $F$ is the Faraday constant (96484.4 C mol$^{-1}$), $E$ is the membrane potential (V), $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature (K).

The total flux $J$ of the compound across the membrane is the sum of the fluxes of the neutral molecule and the ion, $J_n$ and $J_d$:

$$J = P_n (a_{n,o} - a_{n,i}) + P_d \frac{N}{e^N - 1} (a_{d,o} - a_{d,i} e^N)$$

Diffusive equilibrium for ionisable compounds

Let us generally define the endpoint of diffusion as the equilibrium between compartments (i.e. the state with the highest entropy). The driving force for diffusive exchange is the activity gradient. It follows that diffusive exchange stops when $a_o = a_i$.

For neutral compounds

$$J_n = P_n (a_{n,o} - a_{n,i}) = 0 \rightarrow a_{n,o} = a_{n,i}$$

where o denotes outside and i inside the compartment. For concentrations, using $a = f \times C$

$$C_{t,o}, f_{n,o} = C_{t,i}, f_{n,i}$$

It follows that the equilibrium partition coefficient $K_{Eq,n}^{n}$ of neutral compounds is the inverse ratio of the activity capacity values $f$:

$$\frac{C_{t,i}}{C_{t,o}} = \frac{f_{n,o}}{f_{n,i}} = K_{Eq,n}^{n}$$

For ions, too, the flux stops when equilibrium is reached. But diffusion is calculated with the Nernst-Plank-equation, thus
\[ J_d = P_n \frac{N}{e^N - 1} (a_{i,o} - a_{d,i} e^N) \]

The endpoint of diffusion is reached, with \( N = z E F / (R T) \), when

\[ \frac{a_{i,d}}{a_{o,d}} = e^{-zEF/R} \]

This is the well-known Nernst ratio (Nernst, 1889). Due to the exponential relation, the theoretical accumulation can be quite high, in particular for high electrical potentials, and for polyvalent bases \((z \geq +2)\). For example, with a field of -120 mV (-0.12 V), the equilibrium activity ratio is 115 for \( z = +1 \), but 13 373 for \( z = +2 \).

Thus, if only ions are present, for the concentration ratio follows

\[ \frac{C_{t,i}}{C_{t,o}} = \frac{f_{d,o}}{f_{d,i}} e^{-zEF/R} = K_{lo}^{Eq,i} \]

Equilibrium in binary systems

Diffusion of both neutral compound and ion is calculated with the above equation. With \( a = f \times C \), the flux into the compartment is

\[ J_i = P_n f_{n,o} C_o + P_d \frac{N}{e^N - 1} f_{d,o} C_o \]

and the flux out is

\[ J_o = P_n f_{n,i} C_i + P_d \frac{N}{e^N - 1} f_{d,i} e^N C_i \]

In equilibrium, influx and outflux are equal, and therefore

\[ K_{lo}^{Eq} = \frac{C_i}{C_o} = \frac{f_{n,o} \times P_n + f_{d,o} \times P_d \times N / (e^N - 1)}{f_{n,i} \times P_n + f_{d,i} \times P_d \times e^N \times N / (e^N - 1)} \quad \text{Equation 13: Equilibrium electrolytes} \]

For dissociating compounds, the equilibrium concentration ratio is a complex function of the fractions in solution, \( f \), the permeabilities for diffusive exchange, \( P \), and of valency \( z \) and charge \( E \) (because \( N = \frac{zEF}{RT} \)).
12.2 Cell Model

The cell model describes distribution within a cell. This may be a plant cell (cytosol, lipids, vacuole, mitochondria, nucleus) or an animal cell (cytosol, lipids, lysosome, mitochondria, nucleus). The major difference is that the acidic vacuole of plants covers about 50% to 90% of the cell volume, while the similar organelle in animals, the acidic lysosome, only covers 0.5% - 1%.

Steady-state solution

In the absence of degradative processes, the steady-state concentration ratio between cytoplasm and outside is identical to the flux equilibrium, $K_{i:o}$ Eq, where $o$ is outside the cell and $i$ is the cytoplasm. For the partitioning between cytosol and soil, $K_{cs}$, soil is $o$ outside and cytosol is $i$ inside. For the partition coefficient between vacuole and cytosol, $K_{vc}$, cytosol is $o$ outside and vacuole is $i$ inside. Similarly, for xylem and phloem, cytosol is the outside compartment.

To derive the overall partition coefficient between xylem (and phloem; and vacuole) and soil solution, the partition coefficient xylem to cytosol is multiplied with the partition coefficient cytosol to soil solution:

$$K_{cs} = \frac{C_{c}}{C_{s}}$$ Cytosol to soil

$$K_{yc} = K_{yc} \times K_{cs} = \frac{C_{v}}{C_{s}}$$ Vacuole to soil

$$K_{xy} = K_{xy} \times K_{cs} = \frac{C_{xy}}{C_{s}}$$ Xylem to soil

$$K_{ph} = K_{ph} \times K_{cs} = \frac{C_{ph}}{C_{s}}$$ Phloem to soil

Dynamic solution

If $o$ denotes the outside of the cell, $c$ the inside, $m$ the mitochondria (or any other organelle), and $J$ the corresponding unit fluxes across surface area $A$, then the

change of mass in the cytoplasm $m_{c} =$

+ flux from outside – flux to outside – flux to mitochondria + flux from mitochondria

$$\frac{dm_{c}}{dt} = A_{c} \times J_{o,c} - A_{c} \times J_{c,o} - A_{m} \times J_{c,m} + A_{m} \times J_{m,c}$$ Eq. 14a cytoplasm

change of mass in the mitochondria $m_{m} = +$ flux to mitochondria – flux to cytoplasm

$$\frac{dm_{m}}{dt} = A_{m} \times J_{c,m} - A_{m} \times J_{m,c}$$ Eq. 14b mitochondria

Concentration $C = m/V$, where $V$ is the volume, and therefore

$$\frac{dC_{c}}{dt} = A_{c} \times J_{o,c} / V_{c} - A_{c} \times J_{c,o} / V_{c} - A_{m} \times J_{c,m} / V_{c} + A_{m} \times J_{m,c} / V_{c}$$ Eq. 14c

$$\frac{dC_{m}}{dt} = A_{m} \times J_{c,m} / V_{m} - A_{m} \times J_{m,c} / V_{m}$$ Eq. 14d
In the cell model, this coupled linear differential equation system is solved analytically. All equations are implemented as a spread-sheet version.

Figure. Molecule species and model processes in the soil - solution - cell system shown for a weak acid. AH is the neutral molecule, A⁻ is the dissociated anion, f( ) means "function of". Source: Trapp (2004)

12.3 Electrolytes in soil

The soil pH varies usually between 4 and 10, with most soils being slightly acidic (pH 6 to 7). The ratio between neutral and dissociated compound is calculated as described by the Henderson-Hasselbalch equation.

The Koc of electrolytes is calculated using special regressions (Franco and Trapp 2008), namely

\[ \log K_{OC} = 0.54 \log K_{OW} + 1.11 \]  
for the acid, neutral molecule \hspace{1cm} \text{Eq. 15a}

\[ \log K_{OC} = 0.33 \log K_{OW} + 1.82 \]  
for the base, neutral molecule \hspace{1cm} \text{Eq. 15b}

\[ \log K_{OC} = 0.11 \log K_{OW} + 1.54 \]  
for the anion \hspace{1cm} \text{Eq. 15c}

\[ \log K_{OC} = 0.47 \log K_{OW} + 1.95 \]  
for the cation \hspace{1cm} \text{Eq. 15d}

\[ \log K_{OC} = pK_a^{0.65} \times f^{0.14} \]  
for the cation or \hspace{1cm} \text{Eq. 15e}

where \( \log K_{OW} \) is the octanol-water partition coefficient of the neutral molecule, and \( f \) is calculated from the apparent \( K_{OW} \) at pH 7 (the \( D_{pH=7} \)): \( f = D/(D + 1) \).

From the regressions follows that anions sorb only weakly. Cations show the strongest sorption, for a given \( K_{OW} \). The first regression for cations considers the lipophilic interactions, while the second does more consider the electrical attraction to organic matter.

The log D is composed of the contribution of the neutral molecule, \( K_{OW,n} \), and the contribution of the ionic molecule, \( K_{OW,d} \)

\[ D = F_n \times K_{OW,n} + F_d \times K_{OW,d} \]

From experimental values, the average relation between log \( K_{OW,n} \) and log \( K_{OW,d} \) was found to be

\[ \log K_{OW,d} = \log K_{OW,n} - 3.5 \]
Concentration in soil pore water of ionizable compounds

For a liter of dry soil (index Mvol), we had (in section 1)

\[
C_{\text{Mvol}} / C_W = K_{OC} \times OC \times \rho_{\text{dry}}
\]

where concentration in soil matrix, \(C_{\text{Mvol}}\) and in soil pore water, \(C_W\) were in the unit [mg/L]. This changes for weak electrolytes to

\[
C_{\text{Mvol}} / C_W = (f_n \times K_{OC,a} + f_d \times K_{OC,d}) \times OC \times \rho_{\text{dry}}
\]

Consequently follows for the concentration ratio between water (mg/L water) and wet soil (mg/kg) \(K_{\text{WS}}\) of weak electrolytes:

\[
\frac{C_W}{C_{\text{Soil}}} = K_{\text{WS}} = (f_n \times K_{OC,a} + f_d \times K_{OC,d}) \times OC \times \rho_{\text{dry}} + \rho_{\text{wet}}
\]

Equation 16 a

Advective fluxes (namely: the uptake of water by roots) are related to the dissolved concentration \(C_W\). Diffusive exchange, however, will be related to the activity \(a\) of a compound. We can write for the relation \(f_n\) between activity \(a_n\) [mg/L] and total concentration in bulk soil \(C_{\text{soil}}\) [mg/kg]

\[
f_n = \frac{a_n}{C_{\text{Soil}}} = \frac{\rho_{\text{wet}}}{P_w / \gamma_n + K_{OC,a} \times OC \times \rho_{\text{dry}} / \gamma_n + 10^{(pH-pK_a)} \times P_w / \gamma_d + 10^{(pH-pK_a)} \times K_{OC,d} \times OC \times \rho_{\text{dry}} / \gamma_d}
\]

Equation 16 b

Again holds for \(f_d\) (fraction of freely dissolving ions)

\[
f_d = \frac{a_d}{C_i} = f_n 10^{(pH-pK_a)}
\]

12.3 Data for a plant cell

The major compartments of plant cells are cytosol (< 10% to 50% of volume) and vacuoles (50% to 90% of volume), and both consist of an aqueous and a lipid fraction and are surrounded by a biomembrane (see Figure). Plant cells are additionally surrounded by a cell wall and a biomembrane called plasmalemma. The charge at the outside biomembrane of plant cells is about -120 mV. The cell sap (cytosol) has neutral pH (pH 7 to 7.4). Vacuoles are acidic (pH 4 to 5.5) and surrounded by a membrane called tonoplast. The tonoplast is positively charged, relative to the cytosol, with +20 mV in average. The ionic strength inside plant cells is 0.3 mol/L. Note that the phloem sap is alkaline (pH 8) and the xylem sap is acidic (pH 5.5). Instead a mitochondrium and a vacuole, also phloem and xylem can be calculated with the standard cell model (but I do not know about the electrical charges at the respective biomembranes).

Permeabilities

Important parameters in the cell model are the permeabilities of neutral compound and ion. Before a chemical can enter the cytoplasm, it must cross the cell wall and the plasmalemma, both are in series. The cell wall may be considered as an unstirred aqueous layer with polysaccharides providing additional resistance. A permeability value of 0.25 mm s\(^{-1}\) was calculated earlier (Trapp 2000).
The permeability of biomembranes $P_n$ (m s$^{-1}$) for neutral organic compounds is calculated from the compound lipophilicity. From diffusion velocities and membrane thickness, the following equation was derived (Trapp 2004):

$$\log P_n = \log K_{OW,n} - 6.7$$
$$\log P_d = \log K_{OW,d} - 6.7 = \log K_{OW,n} - 10.2$$

Similar regressions have been suggested by Kleier et aliii (Hsu and Kleier 1996).

For the permeability of the neutral molecule, $P_n$, the log $K_{OW}$ of the neutral molecule is used, and for the permeability of the dissociated molecules, $P_d$, the log $K_{OW}$ of the ion (which is 3.5 log units lowered). Therefore, the membrane permeability of ions $P_d$ is always factor 3162 times lower than the corresponding $P_n$.

The data used in the "Cell Model Plant" are shown in the Table below.

**Table.** Data set for Cytosol and vacuole (xylem) of a plant cell used in the standard cell model for plants.

<table>
<thead>
<tr>
<th>Cytosol</th>
<th>Vacuole (=Xylem)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>5.00E-06 m</td>
</tr>
<tr>
<td>Volume</td>
<td>6.54E-17 m$^3$</td>
</tr>
<tr>
<td>area</td>
<td>7.85E-11 m$^2$</td>
</tr>
<tr>
<td>% volume</td>
<td>11.09 %</td>
</tr>
<tr>
<td>pH inside</td>
<td>7.4</td>
</tr>
<tr>
<td>pH outside</td>
<td>variable</td>
</tr>
<tr>
<td>lipid</td>
<td>0.05 g/g</td>
</tr>
<tr>
<td>water</td>
<td>0.95 g/g</td>
</tr>
<tr>
<td>Ion strength</td>
<td>0.3 mol</td>
</tr>
<tr>
<td>$E$</td>
<td>-1.20E-01 V</td>
</tr>
</tbody>
</table>

**Table.** Data set for mitochondria (phloem) and nucleus of a plant cell used in the standard cell model for plants.

<table>
<thead>
<tr>
<th>Mitochondria (Phloem)</th>
<th>Nucleus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>1.0E-06 m</td>
</tr>
<tr>
<td>Volume</td>
<td>5.2E-19 m$^3$</td>
</tr>
<tr>
<td>area</td>
<td>3.1E-12 m$^2$</td>
</tr>
<tr>
<td>%volume</td>
<td>0.09 %</td>
</tr>
<tr>
<td>pH inside</td>
<td>8</td>
</tr>
<tr>
<td>pH outside</td>
<td>7.4</td>
</tr>
<tr>
<td>lipid</td>
<td>0.05 g/g</td>
</tr>
<tr>
<td>water</td>
<td>0.95 g/g</td>
</tr>
<tr>
<td>Ion strength</td>
<td>0.3 mol</td>
</tr>
<tr>
<td>$E$</td>
<td>-1.60E-01 V</td>
</tr>
</tbody>
</table>

### 12.4 Plant uptake models for electrolytes

In order to derive a dynamic model for plant uptake of electrolytes, the cell model was coupled to the simple standard model described in Chapter 6. The cell model calculates the partition coefficients, i.e. root to water $K_{RW}$, leaves to water $K_{LW}$, leaves to air $K_{LA}$, Xylem to root $K_{XyR}$, Phloem to root $K_{PhloR}$ etc. These partition coefficients are then entered into the simple standard model - and that's it.

The model gives some very interesting results, which we are about to publish. In order to further develop the model to a really good robust and valid tool, we would need some research money. Let's see …
Exercises

1 Ion trap
a) Use the "Standard cell model" for plants. Enter data for the veterinary antibiotics trimethoprim (log Kow 0.70, pKa 7.2, z 1, i 1). Set the pH outside (cell B32) to 5, 7 and 9. What happens to concentrations in the cell and BCF?

b) Use the "Standard cell model" for plants. Enter data for the pesticide 2,4-D (log Kow 3, pKa 3, z -1, i -1). Set the pH outside (cell B32) to 5, 7 and 9. What happens to concentrations in the cell and BCF?

2 Kinetics of uptake
Enter data for a base: log Kow 2, 0 -2, -4; pKa 12; z 1; i 1. Outside pH is 7. What are concentrations at t = oo ? How fast is the uptake at the various log Kow-values?

3 Dissociation of bivalent ionics
A bivalent electrolyte, acid or base, has two dissociation processes (shown for the base):

\[
K_1 = \left[ \frac{H^+ \cdot HB^-}{H_2B} \right]
\]
\[
K_2 = \left[ \frac{H^+ \cdot B^{2-}}{HB^-} \right]
\]
with two corresponding pK_a-values, pK_{a1} and pK_{a2}, giving the activity ratios

\[
\frac{a_{d2}}{a_u} = 10^{\frac{\text{pH} - \text{pK_{a2}}}{a}}
\]
\[
\frac{a_{d1}}{a_{d2}} = 10^{\frac{\text{pH} - \text{pK_{a1}}}{a}}
\]

(the parameter a here is the opposite of i above, i.e. a is +1 for bases and -1 for acids; this doesn't matter much).

What is the fraction of neutral compound, the fraction of the mono-dissociated compound and the fraction of the completely (bi-)dissociated compound?
CHAPTER 13 Addition of metabolism and biodegradation

*(based on Larsen et al. 2005 and Trapp, Feificova et al. 2008, salt paper)*

So far we considered only first-order decay rates (in form of a rate $k$ that sums up metabolism and growth dilution). However, enzyme reactions typically follow the *Michaelis-Menten* kinetics, which is only in some cases first order.

### 13.1 Michaelis-Menten kinetics

Let us assume that solutes dissolved in water are taken up into plants passively with the water, unless there is a mechanism to discriminate (or concentrate) the solutes. The plant may either metabolise or actively (by use of energy and enzymes) "pump out" undesired solutes from root cells. The kinetics of enzymatic processes can be described by the *Michaelis-Menten* equation:

$$v = \frac{v_{\text{max}} C}{K_M + C} \times M$$

where $v$ (g/d) is the removal rate of the substrate of concentration $C$ (g/L), $v_{\text{max}}$ (g d⁻¹ kg⁻¹) is the maximal removal rate per plant mass, $K_M$ (g/L) is the half-saturation constant and $M$ is the mass of the plant (kg). This equation (the *Michaelis-Menten kinetics*) will lead to a first-order (exponential decay) curve when $C < K_M$; but it will lead to a linear decay when $C > K_M$ (see Figure).

$$\frac{dC}{dt} = -\frac{v_{\text{max}} C}{K_M + C}$$

where $C << K_M \rightarrow \frac{dC}{dt} = -\frac{v_{\text{max}}}{K_M} \times C$

"first order", exponential

$C >> K_M \rightarrow \frac{dC}{dt} = -v_{\text{max}}$

"zero order", linear

**Figure.** Michaelis-Menten kinetics can be exponential (for $C < K_M$) or linear (for $C > K_M$).

### 13.2 Michaelis-Menten in the mass balance

In the absence of metabolic removal by the plants, and if the uptake occurs exclusively with the transpiration stream, the change of chemical mass $m$ in the roots with time is inflow minus outflow (root model, section 2, equation 3):

$$\frac{dm}{dt} = C_w \times Q - C_{xy} \times Q$$

where $C_w$ and $C_{xy}$ (g/L) are the concentrations of the chemical in the external solution and in the xylem sap, and $Q$ (L/d) is the flow of water with the transpiration stream. We assume furthermore,
that the concentration in the root, \( C_R \), is related to the concentration in the xylem \( C_{xy} \) by a constant factor \( K_{RW} \). Thus, the mass balance is:

\[
\frac{dm_R}{dt} = C_W \times Q - C_R \times \frac{Q}{K_{RW}}
\]

where \( K_{RW} \) (L/kg) is the concentration ratio between root tissue and transpiration stream. Substituting chemical mass \( m_R \) in the roots by \( C_R/M_R \), where \( M_R \) (mg/kg) is the mass of roots (kg), results in the differential equation for the chemical concentration in roots without metabolism, as we had it in the Chapter 2 (root model):

\[
\frac{dC_R}{dt} = C_W \times \frac{Q}{M_R} - C_R \times \frac{Q}{M_R \times K_{RW}} - k_R \times C_R
\]

where \( k_R \) is the growth rate of the roots (1/d).

Adding the term for enzymatic removal yields for the mass of chemical

\[
\frac{dm}{dt} = C_W \times Q - C_R \times \frac{Q}{K_{RW}} - v_{\text{max}} \times C_R \times M_R
\]

and for the concentration

\[
\frac{dC_R}{dt} = C_W \times \frac{Q}{M_R} - C_R \times \frac{Q}{M_R \times K_{RW}} - v_{\text{max}} \times C_R \times M_R - k_R \times C_R
\]

This is a non-linear equation, which describes uptake and metabolism of chemicals by plants.

In steady-state \((dC_R/dt = 0)\), we obtain

\[
0 = \frac{K_M \times Q \times C_W}{M_R} + \frac{Q \times C_W \times C_R}{M_R} - \frac{K_M \times Q \times C_R}{M_R \times K_{RW}} - \frac{C_R^2 \times Q}{M_R \times K_{RW}} - K_M \times k_R \times C_R - k_R \times C_R^2 - v_{\text{max}} \times C_R
\]

which leads to a quadratic equation of the general form \( aC^2 + bC + c = 0 \) with the two real solutions

\[
C_1 = \frac{-b - \sqrt{b^2 - 4ac}}{2a}
\]

\[
C_2 = \frac{-b + \sqrt{b^2 - 4ac}}{2a}
\]

where

\[
a = -k_R - \frac{Q}{M_R \times K_{RW}}
\]

\[
b = \frac{C_W \times Q}{M_R} - \frac{K_M \times Q}{M_R \times K_{RW}} - k_R \times K_M - v_{\text{max}}
\]
\[ c = C_R \times K_M \times Q \div M_R \]

Only the first solution \( C_1 \), gives realistic (i.e. positive) values. The concentration in the roots \( C_R \) (mg kg\(^{-1}\)) is proportional to the concentration in the xylem \( C_{xy} \) (mg L\(^{-1}\))

\[ C_{xy} = \frac{C_R}{K_{RW}} \]

where \( K_{RW} \) is the partition coefficient root to water (L kg\(^{-1}\)).

### 13.3 Application

This equation was successfully used to describe uptake and metabolism of cyanide (Larsen et al. 2005), and uptake and "pumping-out" of NaCl (Trapp, Feificova et al. 2008).

In the study by Larsen et al., the Michaelis-Menten parameter (\( v_{max}, K_M \)) were determined for willow trees by using a closed-bottle test with plant material inside. The parameters could be used to predict accumulation and toxicity of cyanide in living willow trees (see Figures).

In our study, the concentration of salt in solutions with trees (NaCl) and the toxicity to trees were determined simultaneously. At low external salt concentrations, the external concentrations increased when the plants transpired water. At high doses, the concentration remained almost constant. The explanation was that the trees are able to pump low amounts of salt out of their root cells, back into solution. At higher dose, this defense system collapses, and salt accumulates inside trees. This was correlated to toxic effects (Figures). The Michaelis-Menten parameters (\( v_{max}, K_M \)) were determined by model fit ("inverse modeling").

Figure. Relation between external concentration of free cyanide and concentration in roots of exposed willow trees. At low concentrations, all CN taken up by the trees is metabolized. Above a certain external concentration, the enzyme system is overloaded, CN breaks through, and the plants die. Left side: theoretical prediction using the model and measured Michaelis-Menten parameters (\( v_{max}, K_M \)); right side: comparison to experimental results. From Larsen et al. (2005).
13.4 How to find the breakthrough-point and the enzyme capacity

Inverse modeling to determine Michaelis-Menten parameters is actually a very elegant method: Different to experiments with single cells or isolated enzymes, the real in vivo metabolic capacity of the plants is determined.

For salt, we did like this: We have defined the breakthrough-point as the external concentration above which the plant cannot exclude salt. The breakthrough-point must therefore be connected to the maximal enzyme capacity $v_{\text{max}}$. Under the assumption that $C_{\text{w}} >> K_M$ (as obtained by the fit) and that $K_{RW} = 1$ (salt does not adsorb to lipids in the cell), the mass balance simplifies to a linear differential equation:

$$\frac{dm}{dt} = C_{\text{w}} \times Q - C_R \times Q - v_{\text{max}} \times M_R$$

In steady-state holds

$$C_R = C_{\text{w}} - v_{\text{max}} \frac{M_R}{Q}$$

We could thus calculate $v_{\text{max}}$ from this linearized solution by entering $C_{\text{w}0}$ for the point where $C_R = 0$ (the regression crosses the x-axis, $C_{\text{w}0}$ is the x-axis intercept) and find

$$v_{\text{max}} = C_{\text{w}0} \times \frac{Q}{M_R}$$

The values for $v_{\text{max}}$ calculated by this approach, were an average $v_{\text{max}}$ for all experiments of 18.9 g kg$^{-1}$ d$^{-1}$, which is quite close to the value fitted using the model directly (best fit), 20 g kg$^{-1}$ d$^{-1}$. It has to be noted that the removal $v$ (g d$^{-1}$) is the product of $v_{\text{max}}$ and root mass $M$, so the values may differ for individual trees.
We must admit that, despite intense search, we haven't seen often a good Michaelis-Menten kinetics. The more usual case is that bacteria degrade compounds, or a combination of plants and bacteria. Very often, the bacteria sit on roots (root zone degradation) or even inside the plants ("endophytic bacteria"), and it seems as if plants would degrade the compound. But from the kinetics it can be seen which organism class "does the job", because bacterial degradation follows the **Monod** kinetics.

### 13.5 Kinetics of bacterial degradation - Monod kinetics

Most bacteria are heterotrophic organisms, that means, they need an organic substrate to feed on. This substrate can be xenobiotics, which are then used as nutrient source by degrader bacteria. Bacteria have developed a wide range of enzymes that can chemically alter xenobiotics. Xenobiotics can hereby be used as electron acceptor, electron donator, as energy source or as precursor for other molecules.

The growth of bacteria depends on the availability of substrate. The bacterial growth or decay is described by the **Monod** kinetics plus a decay term:

\[
\frac{dB}{dt} = \frac{\mu_{max} \times C \times B}{K_s + C} - k_{death} \times B
\]

where \( B \) is the bacterial mass (kg), \( \mu_{max} \) is the maximal growth rate of the bacteria, \( C \) is the substrate concentration (mg/L), \( K_s \) is the half-growth concentration (i.e., the concentration where the growth is half of the maximum) and \( k_{death} \) is a first order rate describing the death of bacterial cells by arbitrary events, e.g., by grazing protozoa.

During growth, the bacteria metabolize the substrate. The kinetics of the enzymatic reaction can again be described by the *Michaelis-Menten* kinetics.

The mass balance equation for the substrate mass \( m \) (mg) is then

\[
\frac{dm}{dt} = \frac{v_{max} \times C}{K_m + C} \times B
\]

where \( v_{max} \) has the unit mg (kg bacteria)\(^{-1}\) d\(^{-1}\). As for plants, this enzymatic reaction velocity has an upper limit. The relation between bacterial mass produced and chemical mass consumed is known as growth yield \( Y \) [here: kg bacteria / mg chemical], and \( v_{max} \) can be expressed as

\[
v_{max} = \frac{\mu_{max}}{Y}
\]

This introduced into the latter equation gives

\[
\frac{dm}{dt} = \frac{\mu_{max} \times C}{K_m + C} \times \frac{B}{Y}
\]

This last equation shows that the loss of mass by bacterial metabolism has no upper limit, because the number of bacteria \( B \) can increase, as long as substrate mass \( m \) of concentration \( C \) is available (and some other resources, such as nutrients etc.). Therefore, the reaction velocity of the bacterial degradation has (mathematically) no upper limit. In reality, there might be an inhibition of the bacterial growth at higher xenobiotics' concentrations.
However, from an inspection of the bacterial growth equation it can be seen that the degradation by bacteria has a *lower* limit: If the substrate concentration is from the beginning too low to allow a growth of degrader bacteria, the number of bacteria will decline, and thus also the bacterial degrader capacity. Therefore, higher xenobiotics pollution might be degraded faster and more complete, than low contamination (see Figure).

![Graph showing bacterial population and substrate concentration](image)

**Figure.** Bacterial population $B$ and substrate concentration $C$ at low (left) and high (right) initial $C$.

### 13.6 Comparison of Mass Balances of Plants and Bacteria

It is an interesting exercise to compare the degradation of a xenobiotic, which can be metabolized by both bacteria and plants. The conclusions from this area:

- It is not only the presence of degrader pathways in plants or bacteria, that decides about the role the organisms play in biodegradation. Kinetic aspects need to be considered, too.

- Even if plants are able to detoxify a xenobiotic substrate, plants always have an *upper limit* for their detoxification capacity.

- Bacteria, which depend on the availability of substrate for their growth, have a *lower limit* for their degradation capacity. Below this limit, a growth on that substrate is no more possible under environmental conditions.

- Plants are not suited to treat "hot spots" of pollution: First, because toxic effects are to be expected; second, because their metabolism is limited and slow at high pollution levels.

- Bacteria are well-suited to treat "hot spots". However, at low substrate concentrations, e.g., pesticides in the nanogram/L level in groundwater, bacteria may fail to degrade to "null"-levels.

- Plants might be favorable for low contamination levels (e.g., after initial clean-up of a site, as final polishing step), because their metabolic capacity does not decrease with the pollution level.

- A combination of bacteria and plants might be most useful in bioremediation.
Final words

This is a very condensed guide to plant uptake modeling of chemicals. If you are interested in the topic, or wish to go deeper, have a look at the original literature. You may contact me (stt@env.dtu.dk) to get copies of papers, excel files and help of any kind. Usually free of charge.

Thanks for your interest

Stefan

References


**Further reading**

