Research centre
for toxic compounds
in the environment

Plant uptake and human health risks from dietary exposure

Organic non-ionised chemicals

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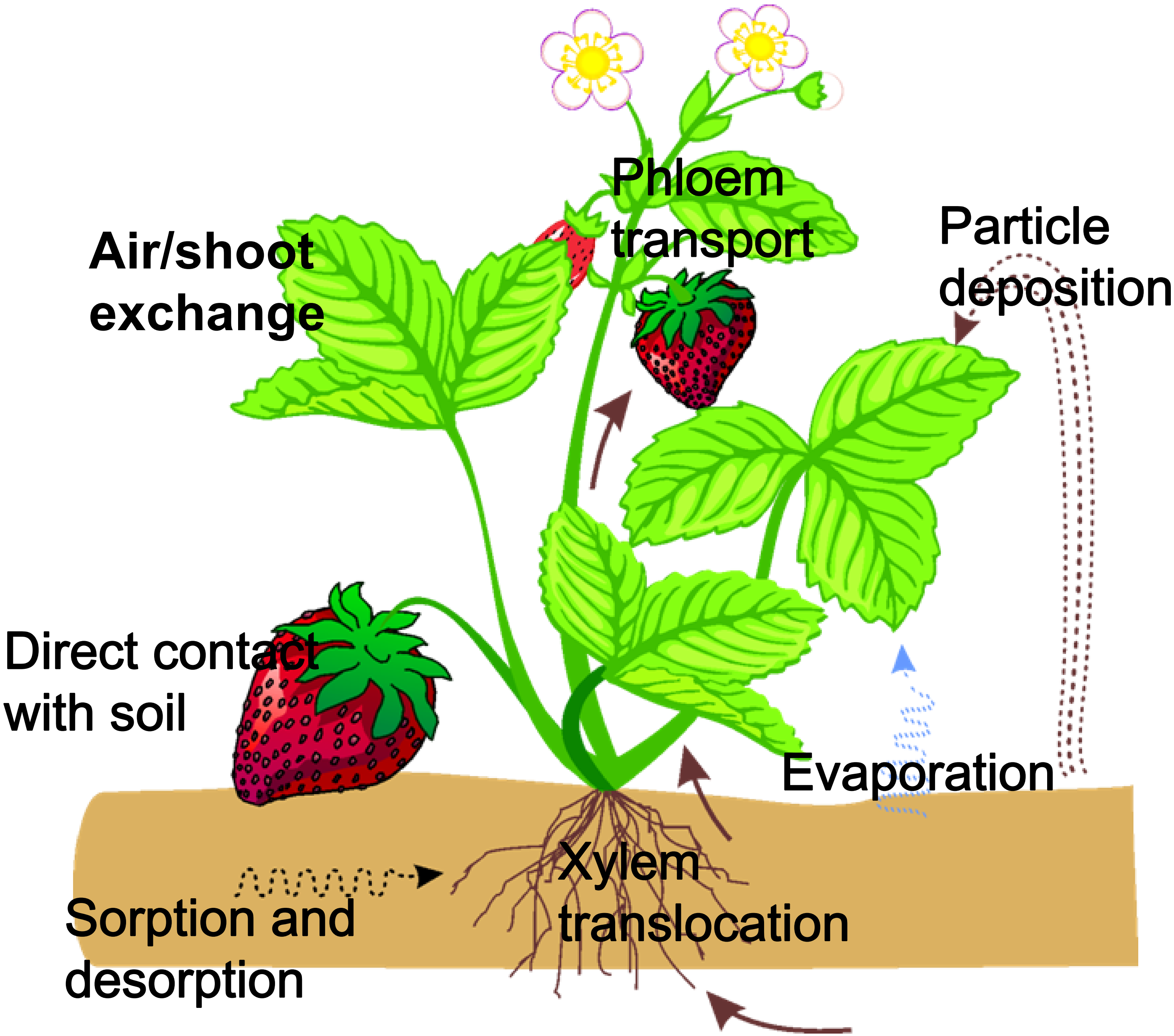
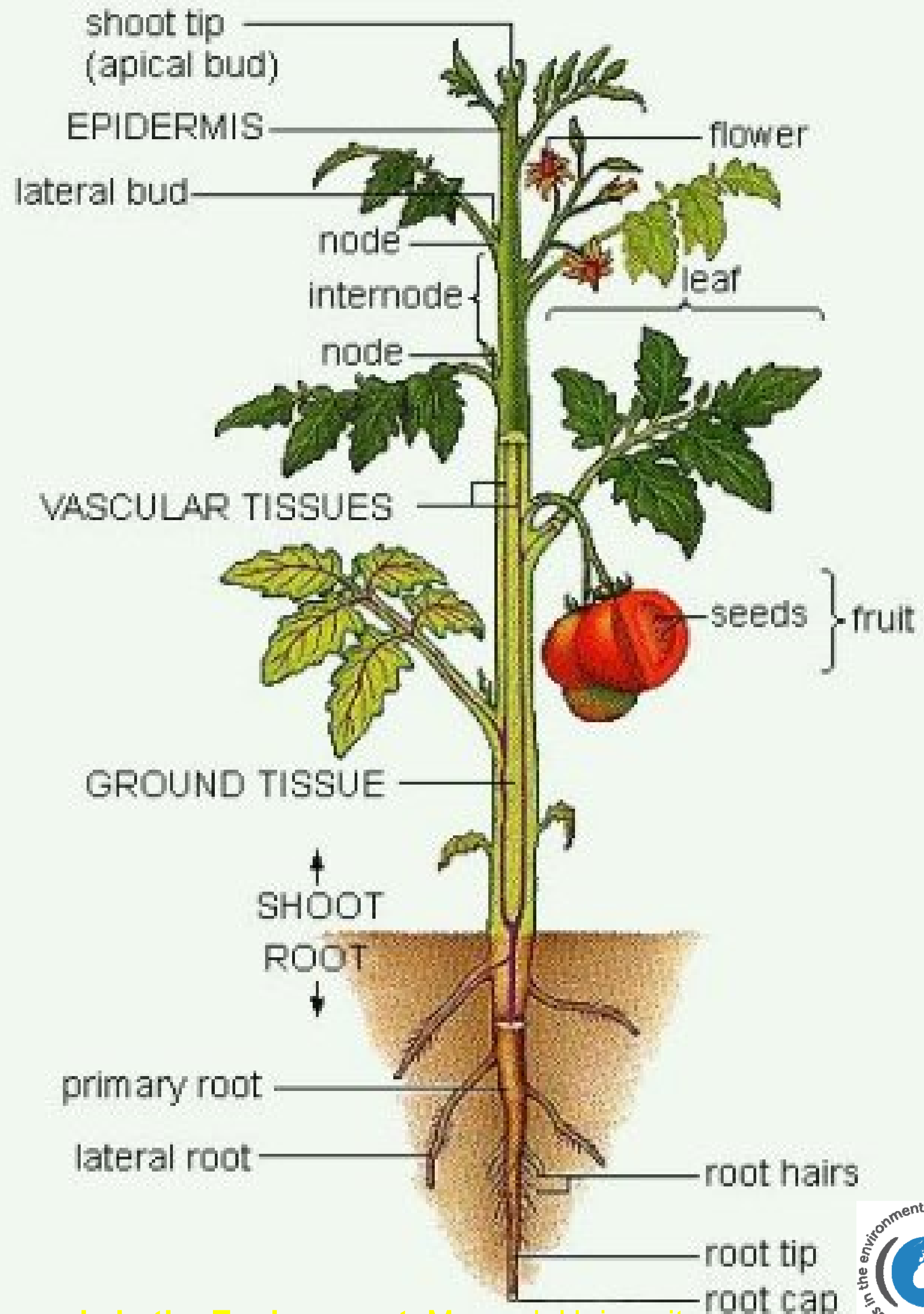
2007–13
OP Research and Development for Innovation

1. Pathways between soil/plant/air
2. Building model
3. Different crops
4. Chemicals
5. Dietary exposure



Trapp (with permission)

- **Roots = take up water and solutes**
- **Stems = transport water and solutes**
- **Xylem = dead water pipe**
- **Phloem = living sugar pipe**
- **Leaves = transpire water and take up gas**
- **Fruits = sink for phloem and xylem**



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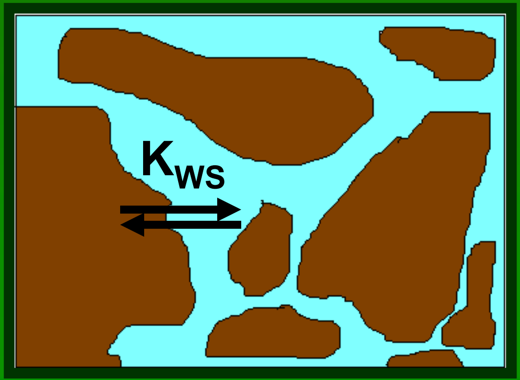
Soil pore water

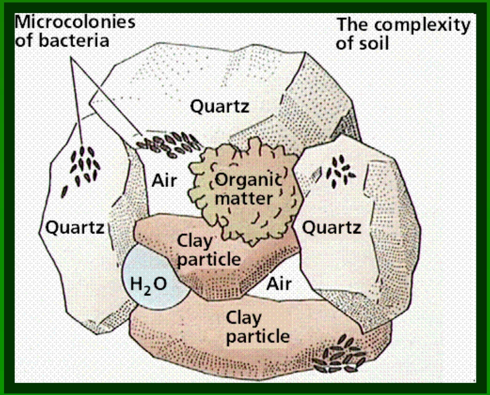
What is in the solution? Bioavailable

$C_W / C_{Soil} = K_{WS} = \rho_{wet} / (Kd \times \rho_{dry} + P_W)$

$Kd = K_{OC} x OC$ – sorption to soil (organic matter)

$LogK_{OC} = 0.81 \, logK_{OW} + 0.1$ (EU,1996) (Abdul, Piwoni, Karickhoff, Molecular connectivity…)

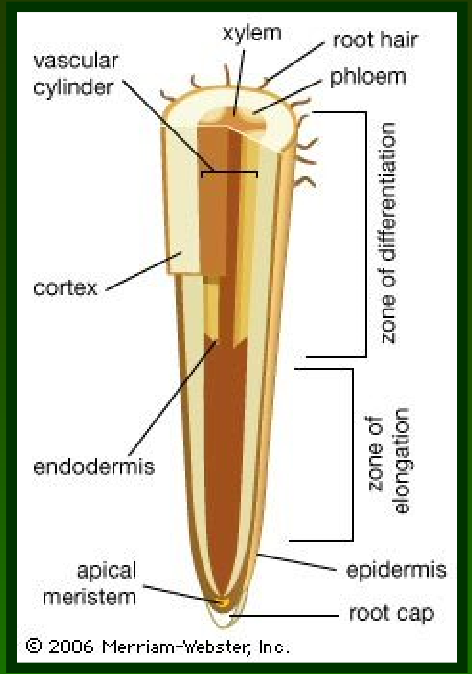


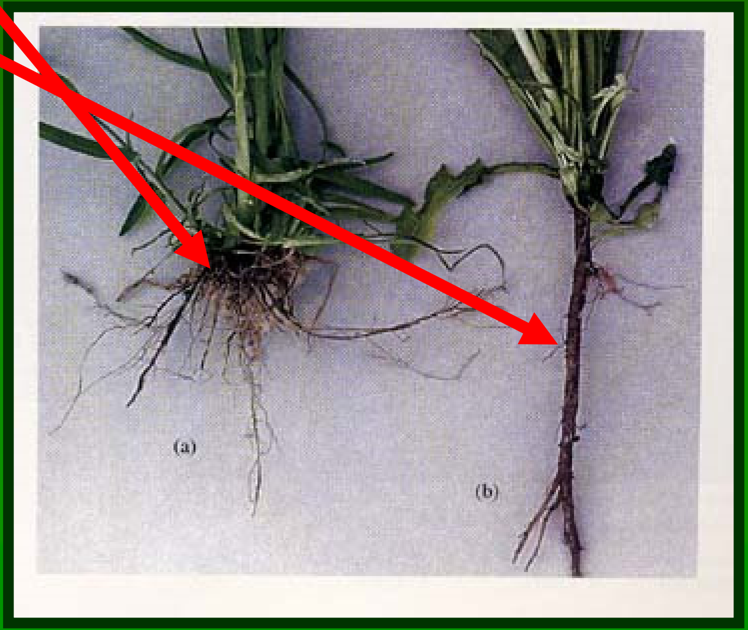


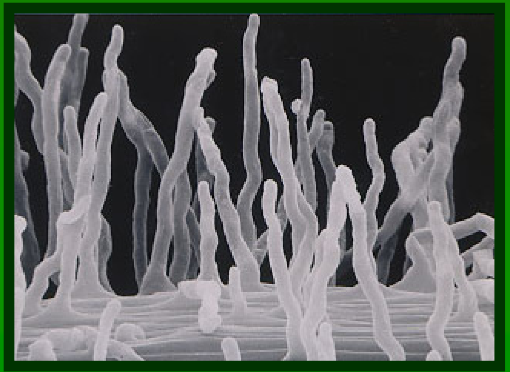
C_W-in mg/L, C_{Soil}-bulk mg/kg, OC-kg/kg, ρ-kg/L, Pw-pore water fraction in bulk soil

Roots

- Can‘t see them
- Livers of the Earth
- Monocotyledon –all cereals
- Dicotyledon- all root vegetables
- Root hairs
- Bioavailability



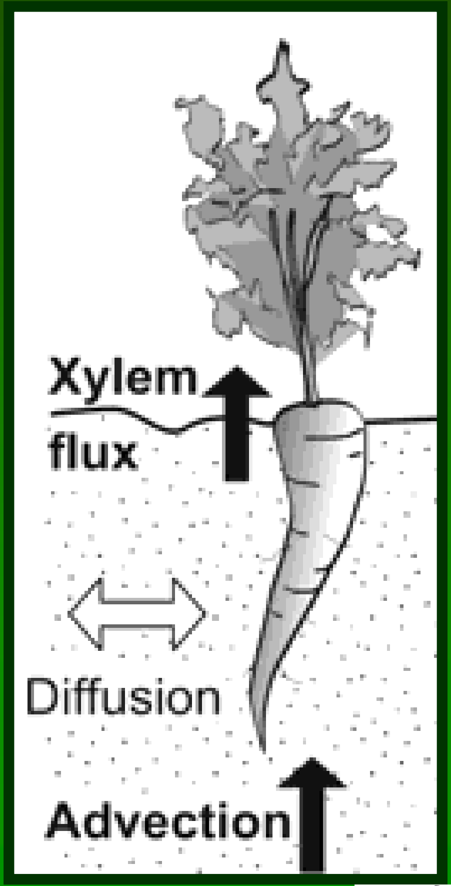




Diffusion and advection

- High surface – equilibrium assumption

$K_{RW}=W_R+L_R\ a\ K_{OW}^b$



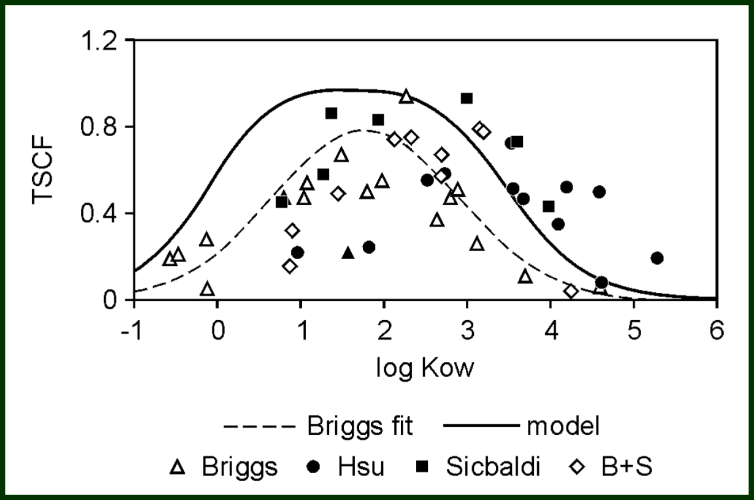
Change of concentration in roots =
+ uptake with water
– transport to shoots
– dilution by growth or metabolism (rate k)

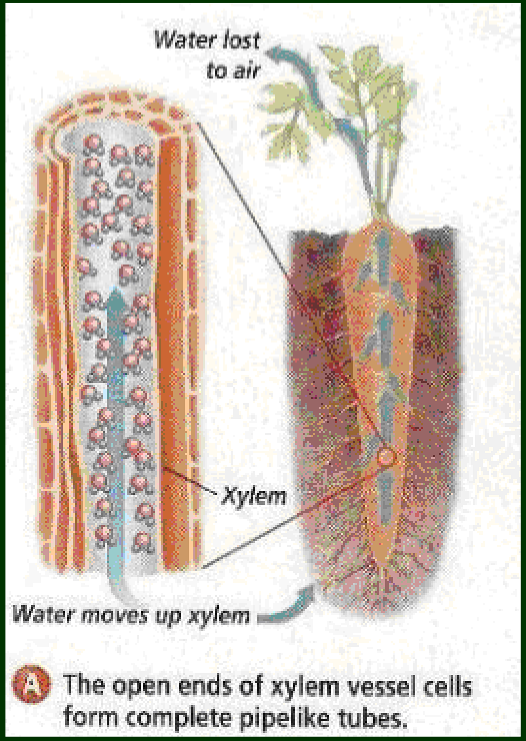
$$dC_R/dt = + C_W Q/M_R - C_{Xy} Q/M_R - kC_R$$

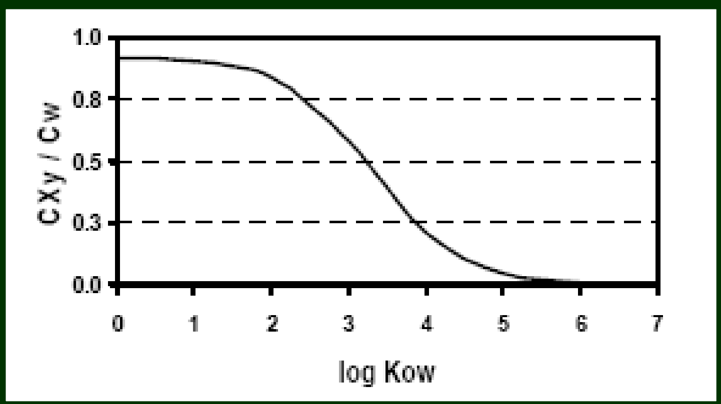
where
k - growth + metabolism rate [d^{-1}]
C_{Xy} - concentration in xylem = C_R/K_{RW}
C_W - concentration in soil pore water
Q - transpiration stream (L/d)
M - Mass of the roots (kg)

Translocation upwards

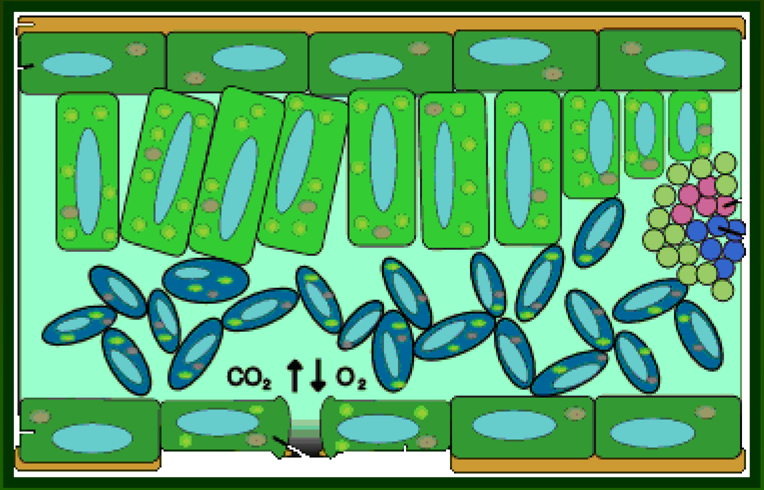
- TSCF = "Transpiration stream concentration factor"
- C_{Xy}/C_{W}, TSCF≤1
- C_{Xy}- outflux from roots = influx to stem or leaves







Leaves



Leaves are plant material, like roots. But they do not hang in soil nor in water. Leaves hang in air.

- Uptake from roots with transpiration water
- Uptake from air (conductance – m/s)
- Loss to air
- Degradation
- Particle deposition
- Soil attached
- Phloem transport

$K_{LW}=W_L+L_L\ a\ K_{OW}^{b}$ - leaf/water

$K_{LA}=K_{LW}/K_{AW}$ - leaf hang in the air

$$
\begin{aligned}
dC_L/dt= &+ C_R(Q/M_L x K_{RW}) \\
&+ C_A(A_L x g/M_L) \\
&- C_L(A_L x g x 1000 L m^{-3}/K_{LA} x M_L) \\
&- C_L(k_L)
\end{aligned}
$$

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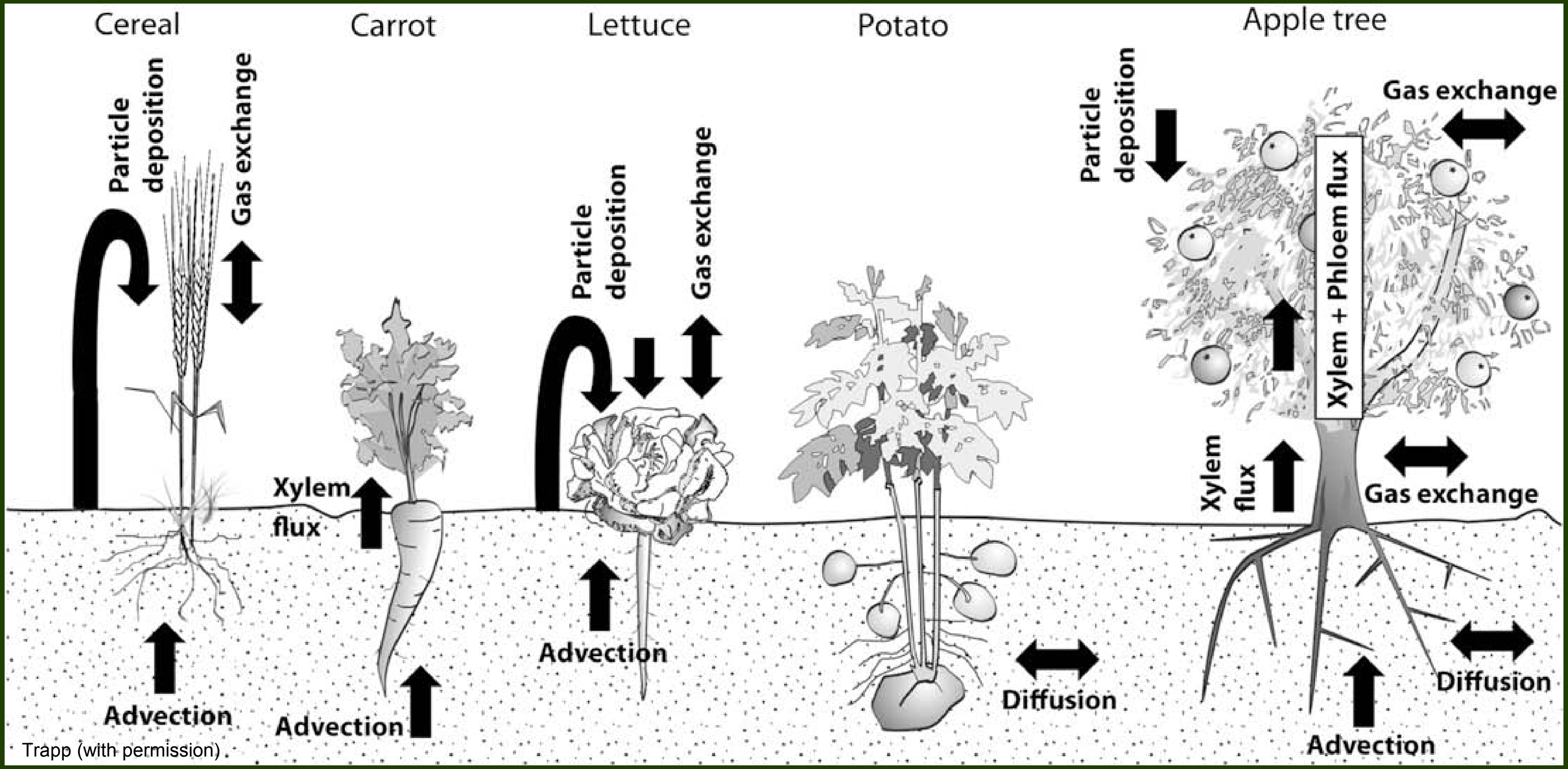


Different crops – phloem, influx to fruits, particles, turtuousity BUT similar model structure

For more information ask me or mail directly to Stefan Trapp stt@env.dtu.dk

http://homepage.env.dtu.dk/stt/

1. Pathways between soil/plant/air
2. Building model
3. Different crops
4. Chemicals and model
5. Dietary exposure

Standard Plant uptake model

Simple standard Plant Uptake Model stt 7 Apr 09

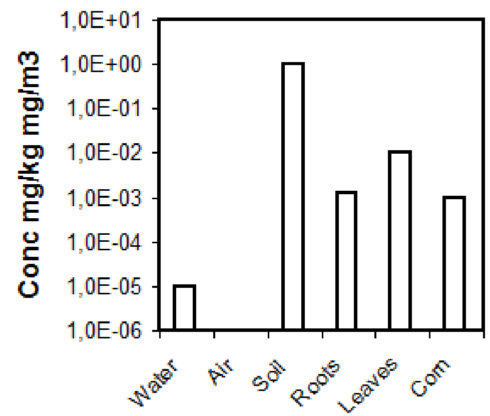
Chemical properties		
log Kow	7	(m3:m3)
Kaw	1,00E+01	(m3:m3)
Metab rate	0,00E+00	1/d
Concentrations in air and soil		
Air	1,00E-30	mg/m3
Soil (wet wt.)	1	mg/kg
Water	1,00E-05	mg/L
Equilibrium calculations		
K AS	**1,03E-03**	air-soil L/kg
KAS	**1,03E+00**	air-soil m3/kg
K WS	**1,03E-04**	water - soil
fP	**1,00E-04**	fraction particle
C air calc	**1,03E-03**	from soil
C W calc	**1,03E-04**	from soil

Results

Concentrations		
Water	1,00E-05	mg/L
Air	1,00E-30	mg/m3
Soil	1,00E+00	mg/kg
Roots	1,24E-03	mg/kg
Leaves	1,00E-02	mg/kg
Corn	1,00E-03	mg/kg

Soil data			Calculations soil		
Water cont.	0,35	L/kg	wet density	1,95	kg/L
orgC	0,02	g/g	Koc	5,89E+05	L/kg
dry density	1,6	kg/L	KWS	1,03E-04	L/kg
			C W soil	1,03E-04	mg/L
Root data	**for 1 m2**		**Calculations root**		
W Water content	0,89	L/kg	KRW	7,49E+03	L/kg
L Lipid content	0,025	kg/kg	KRS	7,75E-01	
M mass	1	kg	BCF root - water	1,20E+01	L/kg
Q Transpiration	1,2	L/d	BCF root - soil	1,24E-03	kg/kg
k rate root	0,1	1/d	**TSCF calc**	1,60E-03	L/L
			C root	1,24E-03	mg/kg
Leaves data	**for 1 m2**		**Calculations leaf**		
Shoot mass	1	kg	K*LW	54495,8	m3:m3
shoot density	500	kg/m3	KLA	5,45E+03	(-)
Leaf Area	5	m2	Uptake from soil	1,66E-07	mg/(kg d)
conductance g	1,00E-03	from Fruit tree mod	Uptake from air	4,32E-28	mg/(kg d)
Lipid content	0,02	g/g	Total uptake b	1,66E-07	mg/kg d)
Water content	0,8	g/g	Loss to air	3,96E+01	1/d
Transpiration	1	L/d	Total Loss	3,97E+01	1/d
Time to harvest	60	days	**C steady-state**	4,17E-09	mg/kg
Growth rate	0,035	1/d	**C (t)**	4,17E-09	mg/kg
Attached soil	0,01	g/g wet wt.	**C(t) plus soil**	1,00E-02	mg/kg
Corn data	**for 1 m2**		**Calculations corn**		units
mass	1	kg	K*LW	108990,9	m3:m3
density	1000	kg/m3	KLA	1,09E+04	(-)
Area	1	m2	Uptake from soil	3,31E-08	mg/(kg d)
conductance g	1,00E-03	from Fruit tree mod	Uptake from air	8,64E-29	mg/(kg d)
Lipid content	0,02	g/g	Total uptake b	3,31E-08	mg/(kg d)
Water content	0,15	g/g	Loss to air	7,93E+00	1/d
Transpiration	0,2	L/d	Total Loss	7,96E+00	1/d
Time to harvest	60	days	**C steady-state**	4,16E-09	mg/kg
Growth rate	0,035	1/d	**C (t)**	4,16E-09	mg/kg
Attached soil	0,001	kg/kg fw	**C(t) plus soil**	**1,00E-03**	mg/kg

Fraction in Air at Particles		
vapor pressure	1,00E+00	Pa
Melting point	200	K
Temperature	20	Celsius
Temperature	293,15	K
VP sub-colled	1,16E-01	Pa
VP used	1,00E+00	Pa
v dep	1,00E-03	m/s
fP	1,00E-04	(-)



Yellow-chemicals entry, blue-concentration, light brown-soil entry, light blue- root entry, dark green-leaves, orange- fruits, grey- calculation (don't touch), white-data entry and results

Exercise 1

Create 2 graphs for Croot, leaf, corn(steady-state) when:

Cair=1.10^{-6} mg/m^3 ,Csoil=1mg/kg,OC=0,02

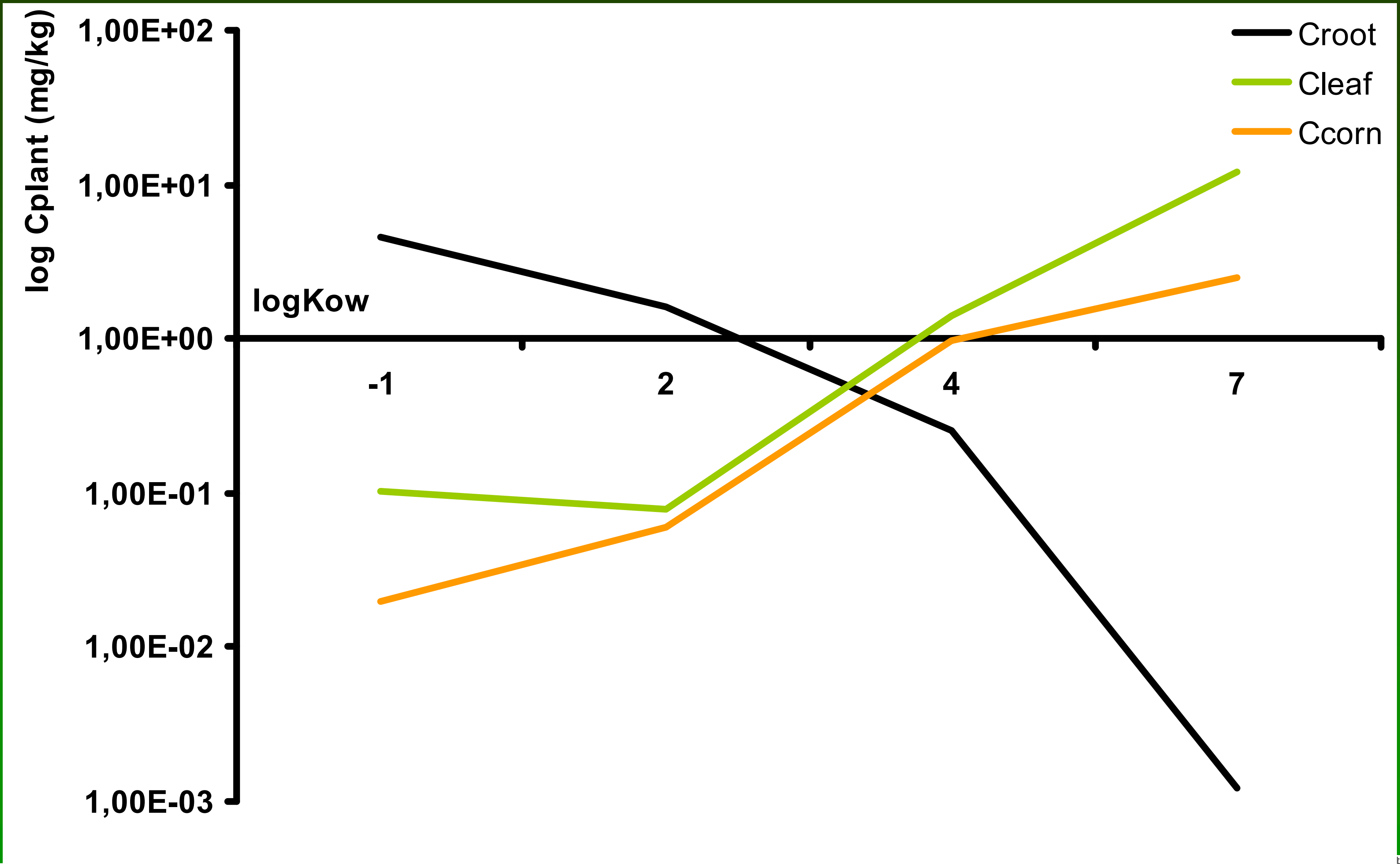
1^{st} – Kaw=1.10^{-4}, log Kow=-1,2,4,7

2^{nd}– log Kow=2, Kaw= 10^{-9},10^{-7},10^{-5},10^{-2},10^{1}

logKow	-1	2	4	7
Croot				
Cleaf				
Ccorn				

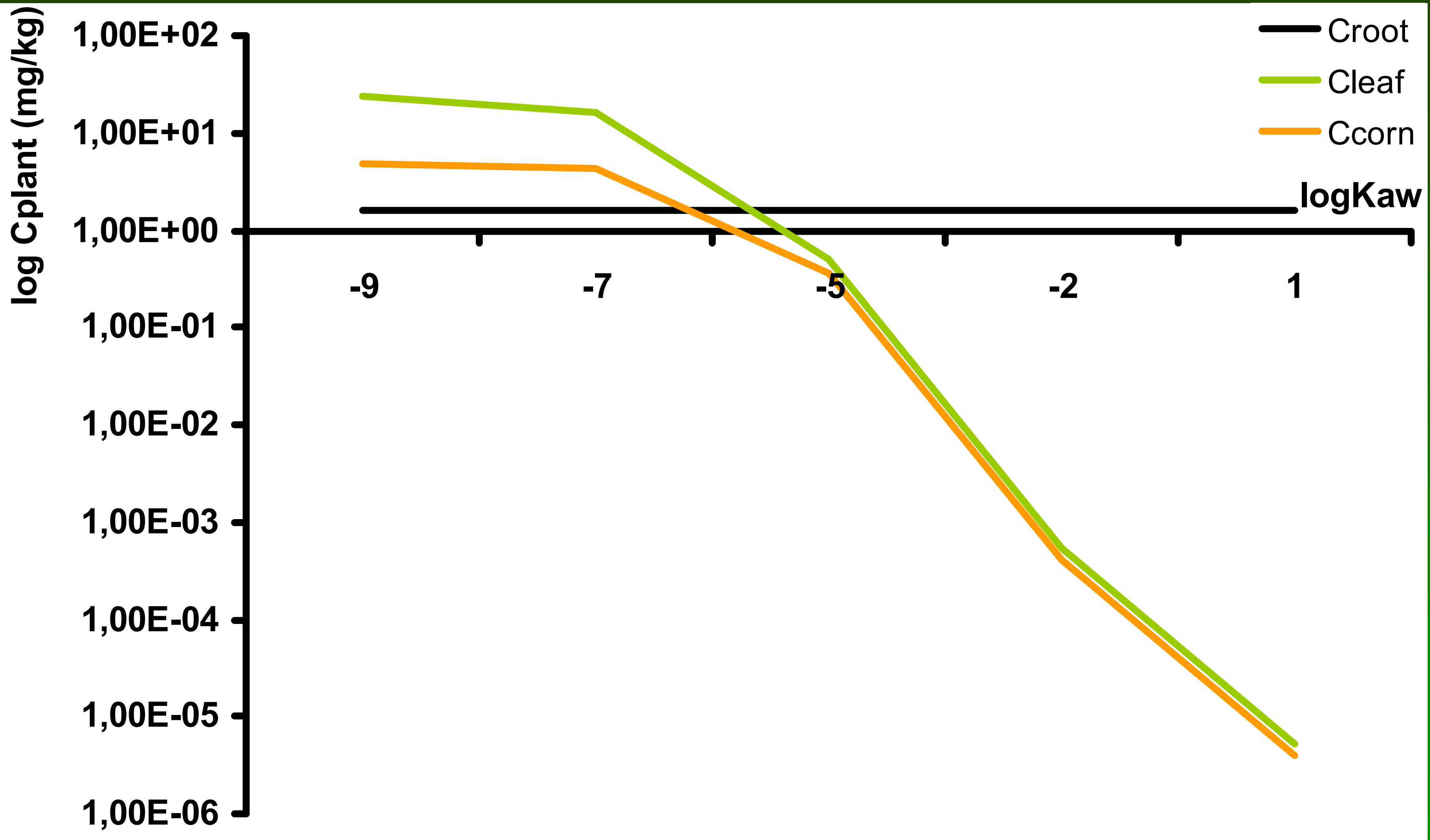
Kaw	1,00E-09	1,00E-07	1,00E-05	1,00E-02	1,00E+00
Croot					
Cleaf					
Ccorn					

Results

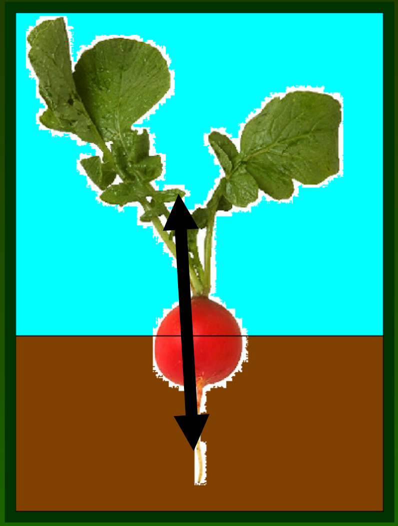


log Cplant (mg/kg)
1,00E+02
1,00E+01
1,00E+00
1,00E-01
1,00E-02
1,00E-03
logKow
-1
2
4
7
Croot
Cleaf
Ccorn

Results

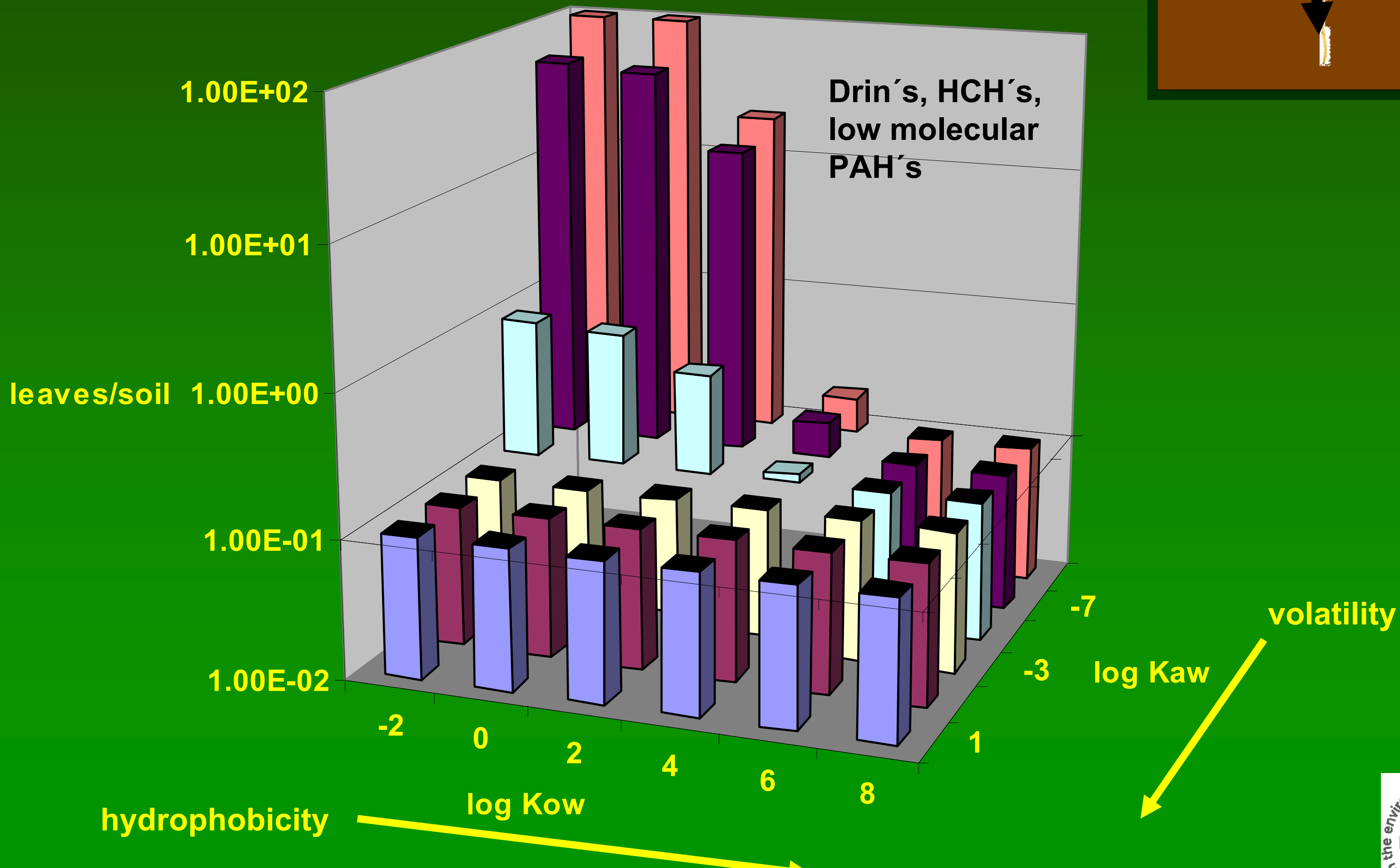

log Cplant (mg/kg)
1,00E+02
1,00E+01
1,00E+00
1,00E-01
1,00E-02
1,00E-03
1,00E-04
1,00E-05
1,00E-06
-9
-7
-5
-2
1
logKaw
Croot
Cleaf
Ccorn

Output from the model SOIL to LEAVES



Csoil=1 mg/kg
Cair = 0 mg/m^3
OC= 2%

Low to moderate Kow
Low to moderate Kaw



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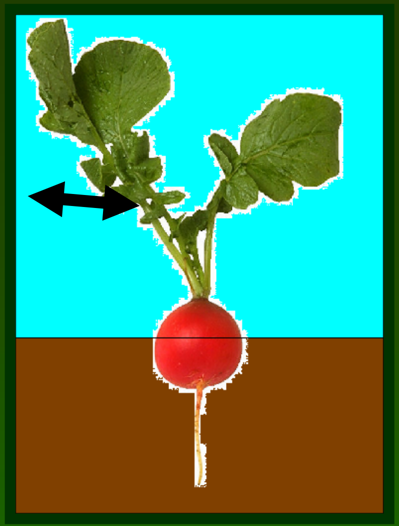
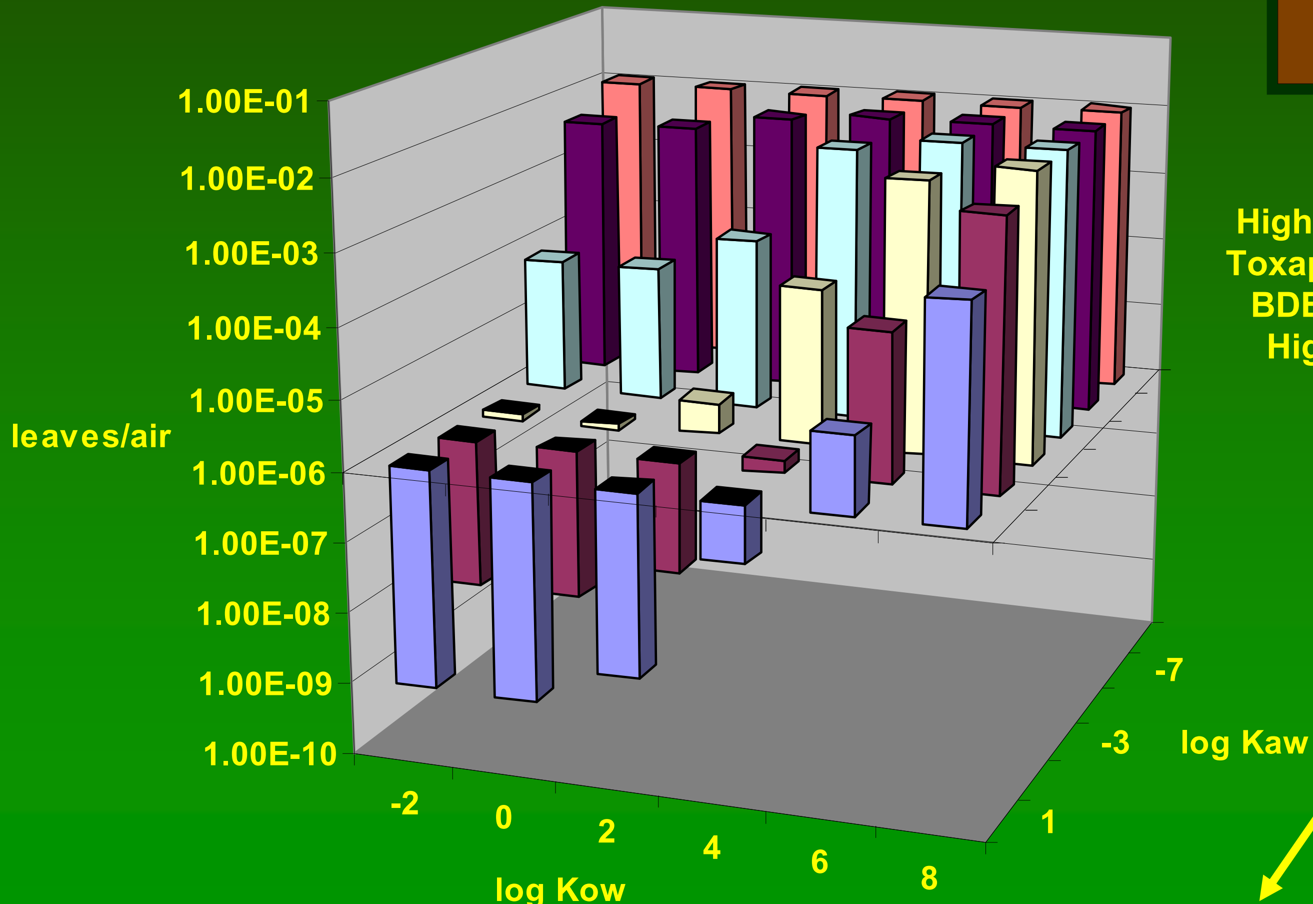
Output from the model AIR to LEAVES



Csoil=0 mg/kg
Cair = 1E-6 mg/m^3
OC= 2%

High to moderate Kow
Low to moderate Kaw



High molecular PAH´s
Toxaphene, Chlordane,
BDE-99, DDX, Mirex,
Highly chlorinated
PCB´s

volatility

hydrophobicity

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Health risk

"Dosis facit venumum"

Effect = Exposure x toxicity

Exposure – measured or modelled
Toxicity – usually measured NOEL/UF

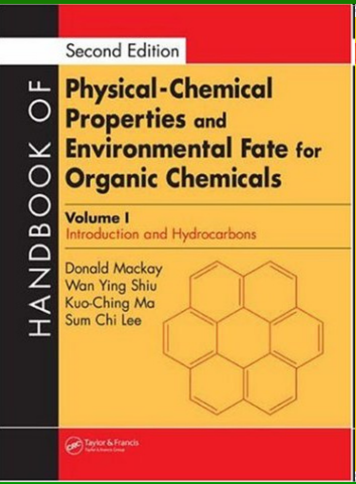
Oral exposure
Dermal exposure — **usually US-EPA guidelines**
Inhalation exposure
Dietary exposure — **measured food concentration needed**

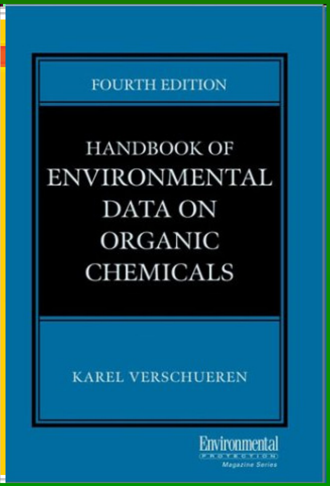
Data collection

Needed: log K_{OW}, K_{AW}, metabolism const., C_{SOIL}, C_{AIR}, C_{WATER}, OC (Env. Journals)

Phys-chem

- Databases: Mackay, Rippen, Verschueren…
- QSAR models : EPISuite, ACD/iLab, MOLPRO...





http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm

Exercise 2

Dietary risk for beta-HCH and BDE-99 :

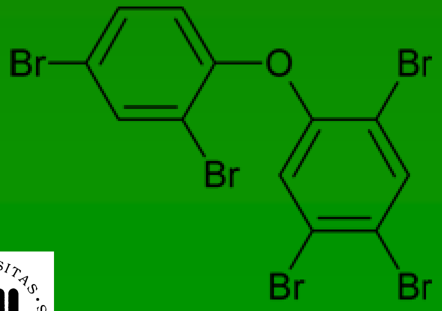
1st- phys-chem from EPI-Suite programme

2nd- environmental concentrations (lit.-given)

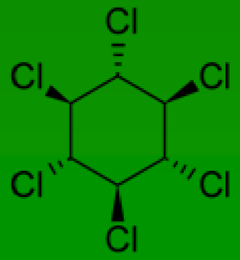
3rd- toxicology profiles US-EPA databases

4th- consumption data (national Czech survey)

5th- plant and risk calculation



CAS-60348-60-9



CAS-319-85-7

Input Data

	log K_{OW}	K_{AW}	Ref.	C_{SOIL}(WW) (mg/kg)	C_{AIR} (mg/m^3)	SF $(mg/kg\text{-}day)^{-1}$	RfD $(mg/kg\text{-}day)^{-1}$	Ref.
BDE-99								
β-HCH								

Women-adult (95%-percentile)	units
INroot	g/kg bw/day
INleaf	g/kg bw/day
INcorn	g/kg bw/day
Weight	kg

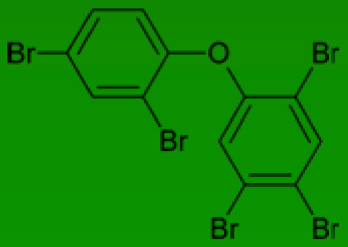
Corg=0,014 (average Czech soil)
(1,4%)

http://www.epa.gov/reg3hscd/risk/human/rb-concentration_table/Generic_Tables/index.htm

http://czvp.szu.cz/spotrebapotravin.htm

Risk calculation

	BDE-99 (mg/kg)	beta-HCH (mg/kg)	Food (kg/kg bw day)	BDE-99 consumption (mg/kg bw day)	β-HCH consumption (mg/kg bw day)
Croot	6,27E-09	9,97E-06	0,0014	8,78441E-12	1,39624E-08
Cleaf	2,37E-04	1,76E-03	0,00194	4,59799E-07	3,40977E-06
Ccorn	4,76E-05	1,35E-03	0,005	2,38041E-07	6,74114E-06
SUMA				6,97849E-07	1,01649E-05



BDE-99 (non-carc):

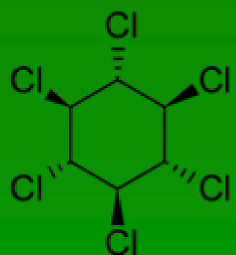
Risk=CDI/RfD

CDI=7E-7

RfD= 1E-4

Risk=7E-3

No risk, but!



β-HCH (carc):

Risk= 1- exp (-CDI * SF)

CDI= 1E-5

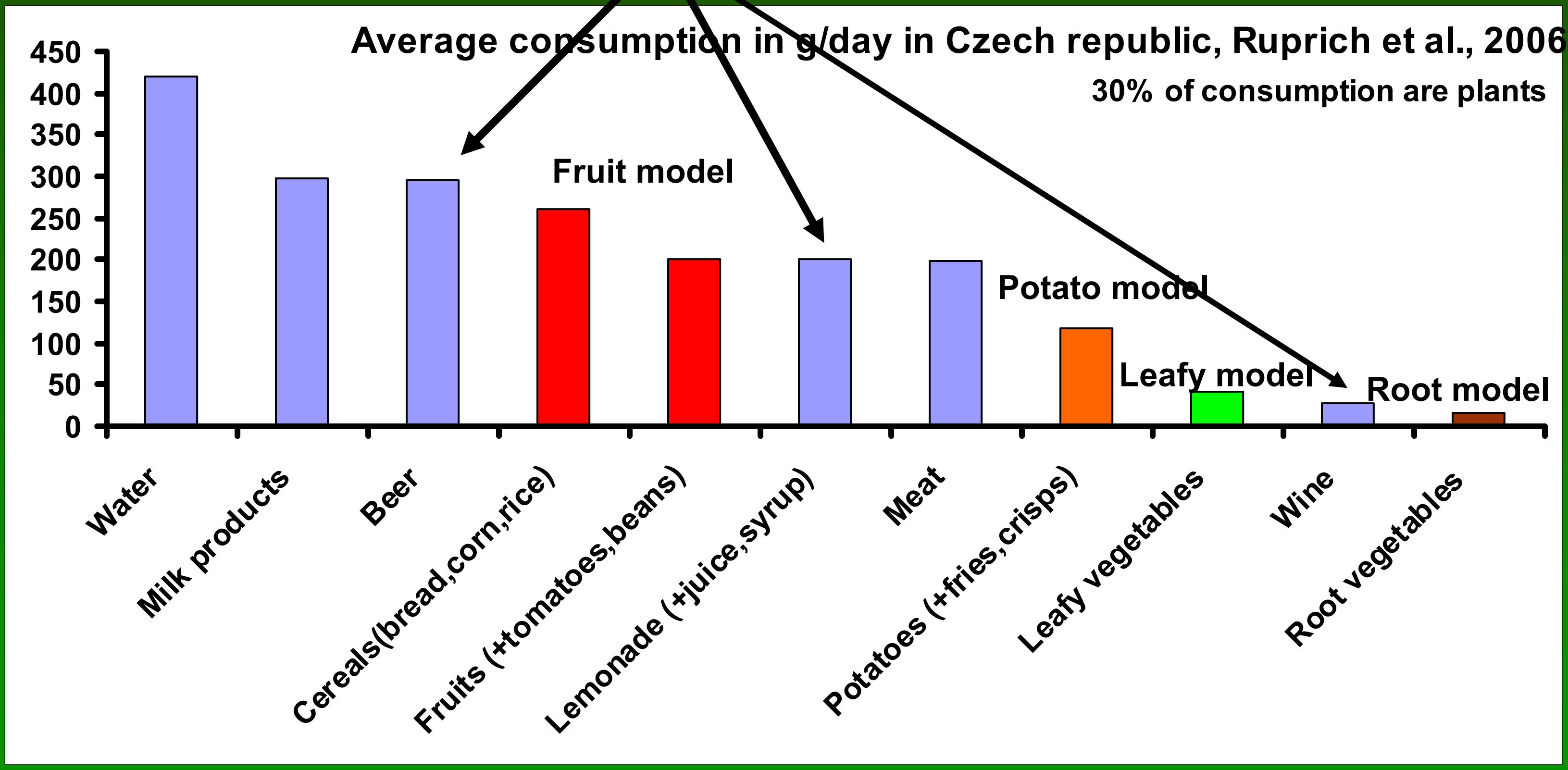
SF= 1,8

Risk=1,8E-5

Risky, but!

Czech dietary uptake

Potential fruit model + water concentration



Some limitations

1. Non-ionic – ionic diffusion follows Nernst-Planck equation
2. Metabolism (Michaelis-Menten kinetics usually more soluble compounds)
3. Growth is considered exponential
4. TSCF calculations
5. Easier approach? Travis and Arms (1988) log BV (dry wt) = 1.588 – 0.578 log KOW
6. On-spot measuring, exposure studies, worst case scenario
7. Always be careful with interpretation risk analysis results

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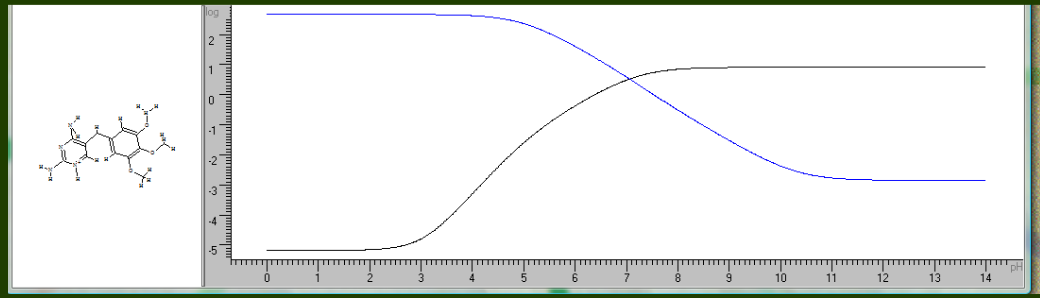
Other dietary/crop models?

- Paterson and Mackay(1994), Chiou(2001) Fantke(2011),
- Ionic chemicals (MAMI,Trapp, 2009)



- Heavy metals (CSOIL,CLEA,FIAM,Hough, 2001)
- Breast milk (US-EPA,2008, Trapp, 2009)

Knowledge to go

- Semi-volatile chemicals
- Low Kow (root uptake) High Kow (shoot uptake)
- Model is not predicting exact concentration – guide to insight and design experiments
- Modelling is easy
- Not only air is important
- Czech drinks a lots of beer

Question time