Fate of pesticides in plant

Raphaël Charles

Swiss Federal Research Station for Plant Production, RAC - Changins, Nyon

Olivier Jolliet

Swiss Federal Institute of Technology, Laboratory of ecosystem management, Lausanne

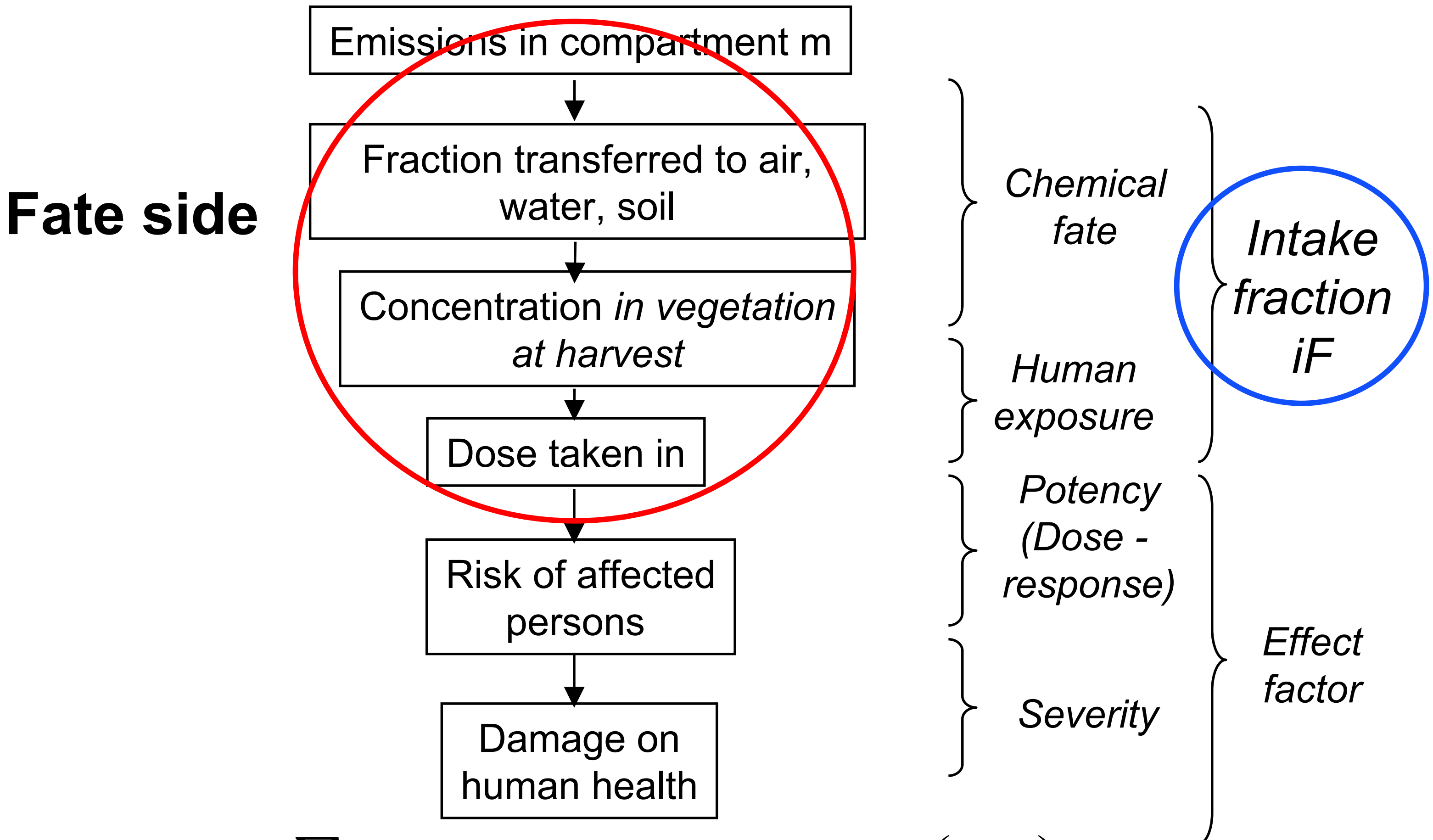
Fate of pesticides in plant

- Introduction
  - Fate of pesticides and assessment of toxicity on human health
- Objectives
  - Determine pesticides transfer fractions from environment to plant and toxicity to human health
- Methodology
  - Development of a model for pesticide fate in plant
- Results
  - Residue in harvest, transfer fractions
  - Human toxicity
- Conclusions

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
Laboratory of ecosystem management

Station recherche agronomique Changins

Emission to damage



$$iF = \frac{\sum_{\text{people, time}} \text{intake of pollutant by an individual } (\textit{mass})}{\text{mass released into the environment } (\text{mass})}$$

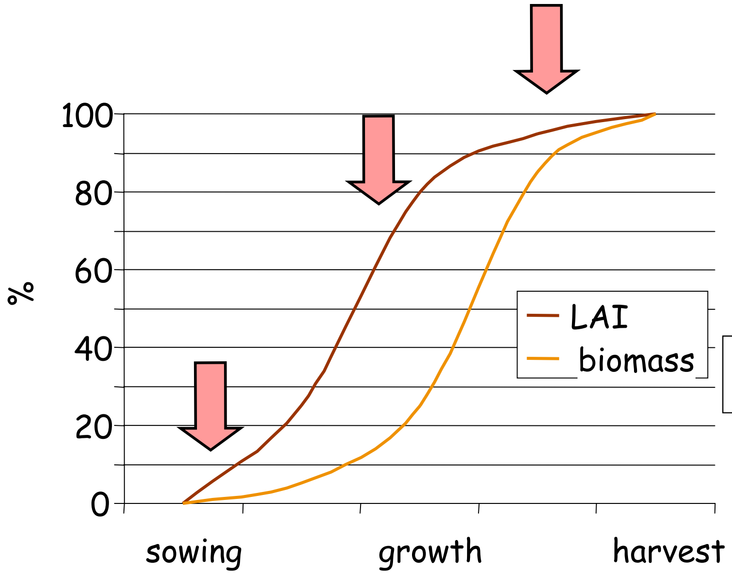
(ES&T, 2002)

Assessment of pesticides

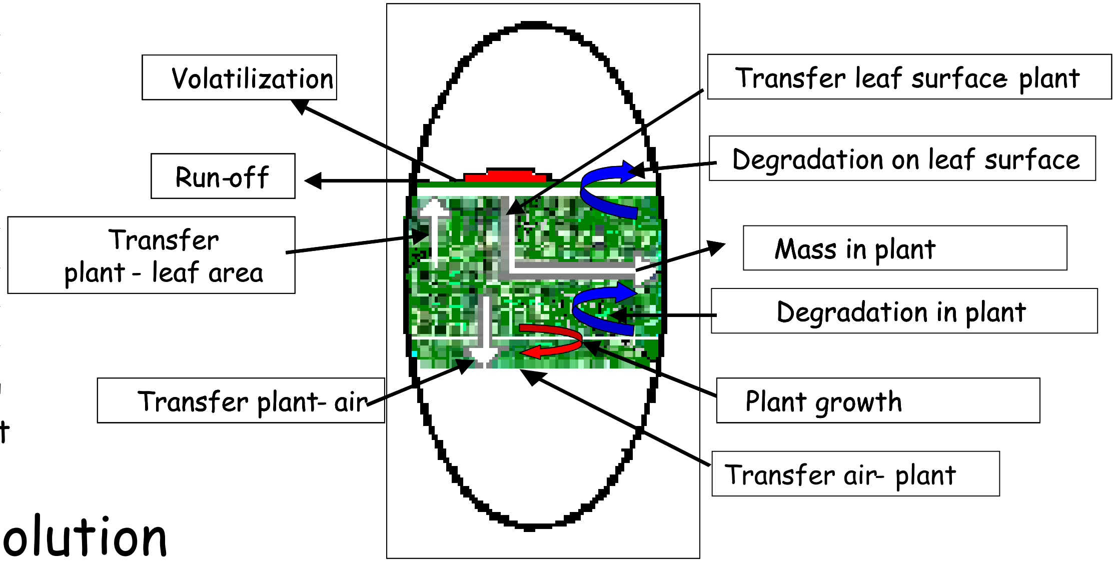
- Effects through residues in food are much higher than those generated by air inhalation and by drinking water
- Two types of methods to assess pesticides
  - Partial methods: applied quantity or toxicity
  - Comprehensive methods : fate, exposure and effect; diffuse multimedia transfers
- Specificity of agricultural emissions

Agricultural specificity

- Distribution of product between air soil and plant surface



- Direct application on vegetation and transfers to plant

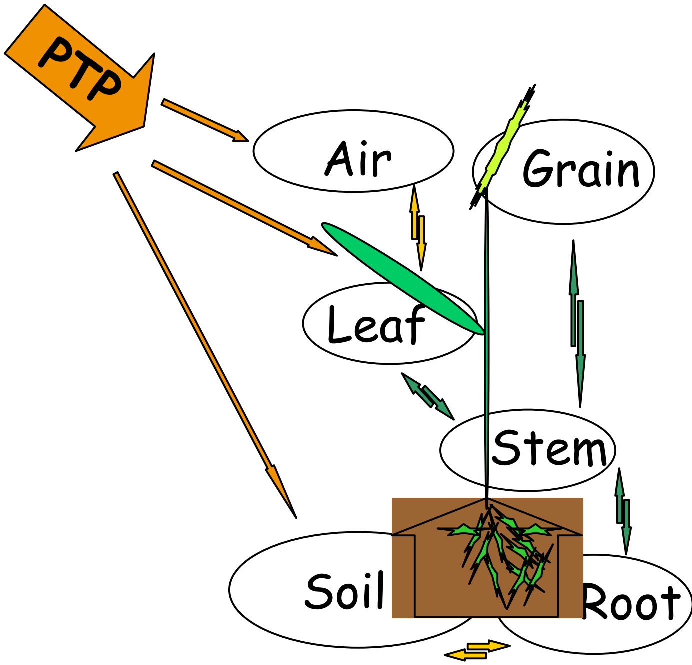


- Need for dynamic solution

Dynamic model for residues

- Date of application
  - interception of spray
  - degradation
  - dilution
- Phase of crop development
  - interception of spray
- Absorption of spray deposit on plant surface
  - recent models
- Calculation of residue at harvest

System and transfer rates



Transfer rates
- transport from the environment
- transport within the plant
- degradation

air	soil	formulation residue	fine roots	root stem	leaves
$-k_{out}$	0	0	0	0	$k_{leaves\text{-}air}$
0	$-k_{out}$	0	$k_{fine\ roots\text{-}soil}$	0	0
0	0	$-k_{out}$	0	0	$k_{leaves\text{-}form.res.}$
0	$k_{soil\text{-}fine\ roots}$	0	$-k_{out}$	0	0
0	$k_{soil\text{-}root\ stem}$	0	0	$-k_{out}$	$k_{leaves\text{-}root\ stem}$
$k_{air\text{-}leaves}$	0	$k_{form.res.\text{-}leaves}$	0	$k_{root\ stem\text{-}leaves}$	$-k_{out}$

$$M(t) = P \cdot diag(\exp \lambda_1 t, \ldots, \exp \lambda_n t) \cdot P^{-1} \cdot (M(0) + A^{-1}S) - A^{-1}S$$

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
Laboratory of ecosystem management

Transfer rate from spray deposit

Station recherche agronomique Changins

- Properties of the limiting skin and on the solute size (Schönherr and Baur, 1994; Schönherr and Baur, 1996, Buchholz et al., 1998)
  - Mobility rate k* (1/d):

$$k^* = k^{*0} \cdot e^{-2.3\beta' V_x}$$

  - k*0 (1/d) mobility of a hypothetical compound having zero molar volume, β' (mol/mL) size selectivity of the cuticular membrane, Vx molar volume of the substance (mol/mL)
- Transfer rate (1/d)

$$T_{fr,c} = k^* \cdot L_{ls} \cdot K_{cfr} \cdot A_c / V_{fr}$$

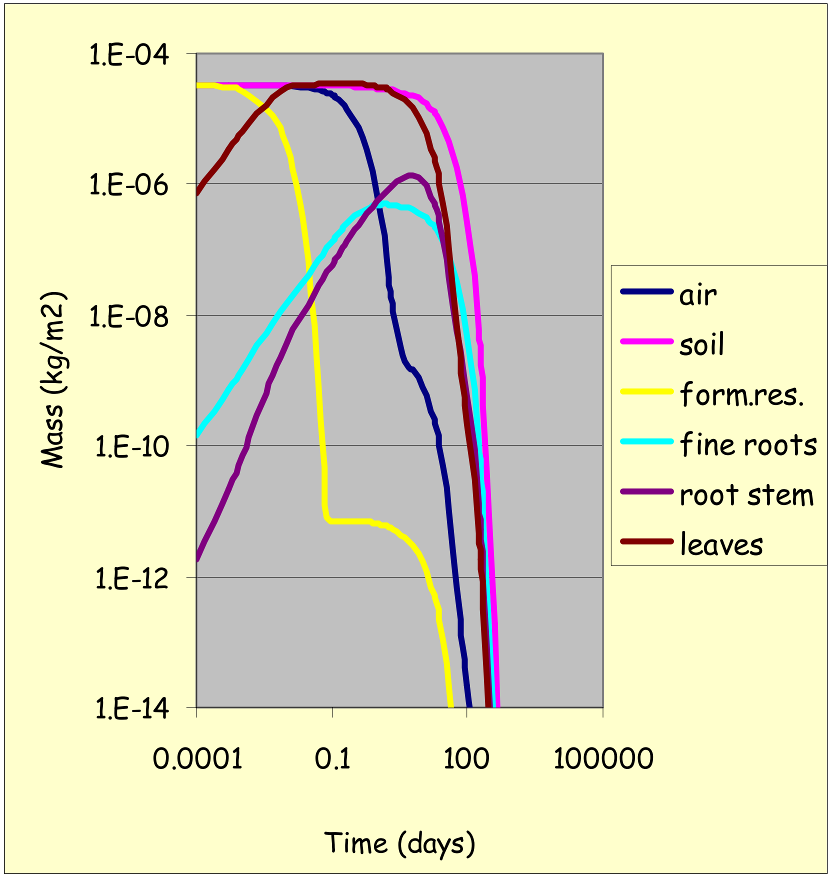
  - k^* (1/d) solute mobility, L_{ls} (m) diffusion path length, K_{cfr} (-) partition coefficient between cuticle and spray residue, surface of cuticle, volume of spray residue

Distribution of the substance in the system

- Distribution of the substance in the system according to 2 phases

    1° accumulation in the plant according to sources

    2° degradation of substance with equilibrium between the compartments

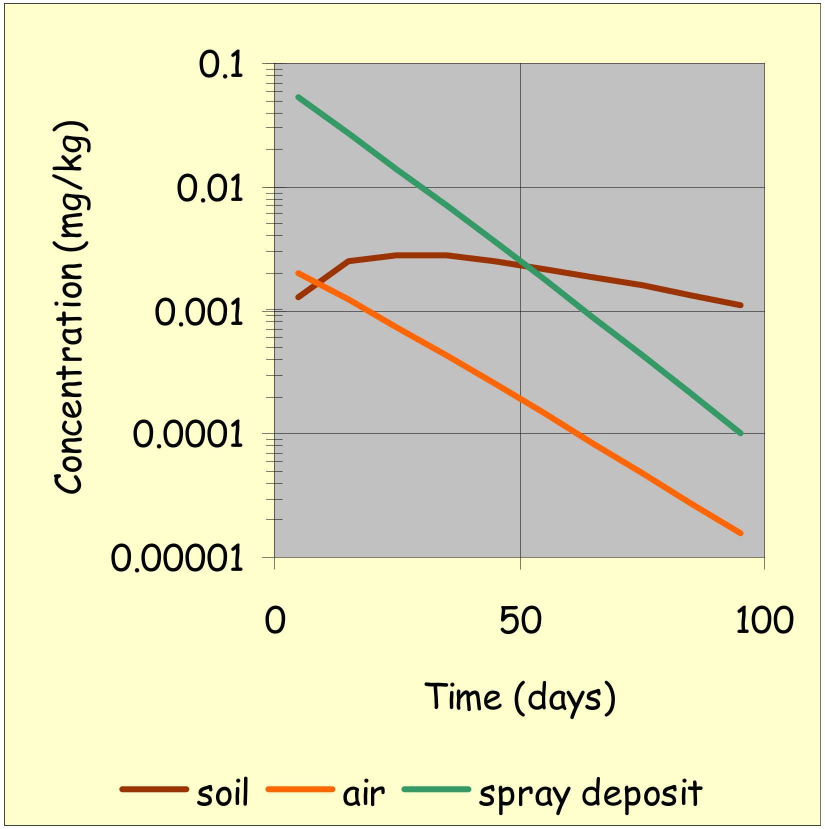


Laboratory of ecosystem management

Station recherche agronomique Changins

Sources

- What is the importance of absorption from spray residue ?
  - At spraying time, spray residue leads to the highest concentration. At long term, soil is the principal source



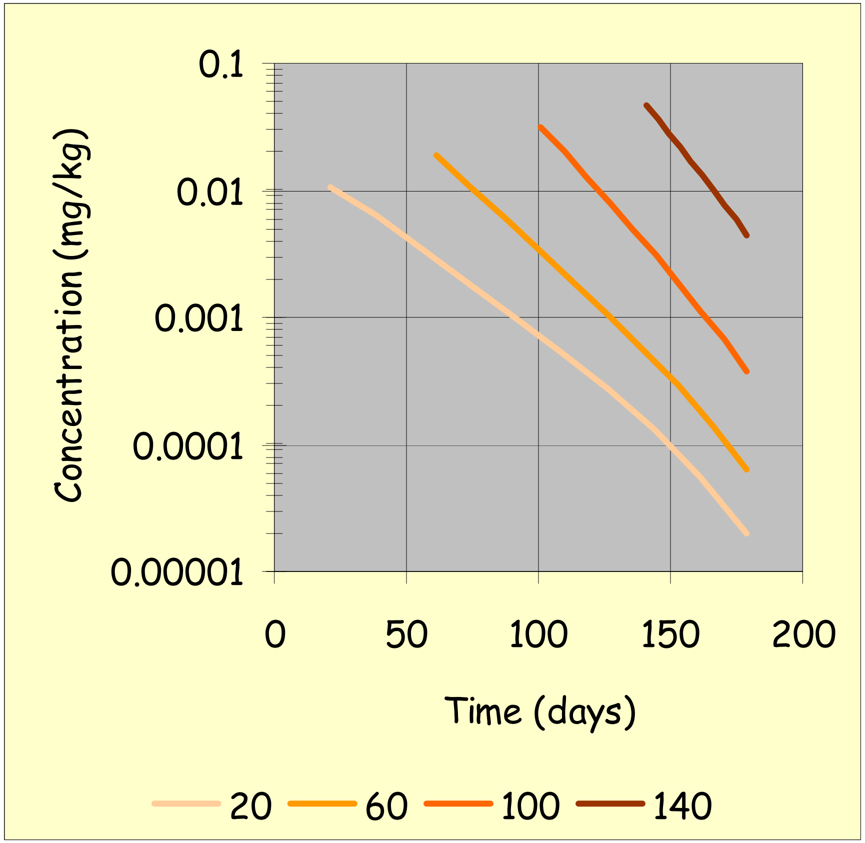
Evolution of the concentration in plant according to emissions in different media (per kg substance emitted in the medium)

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
Laboratory of ecosystem management

Station recherche agronomique Changins

Time of spraying

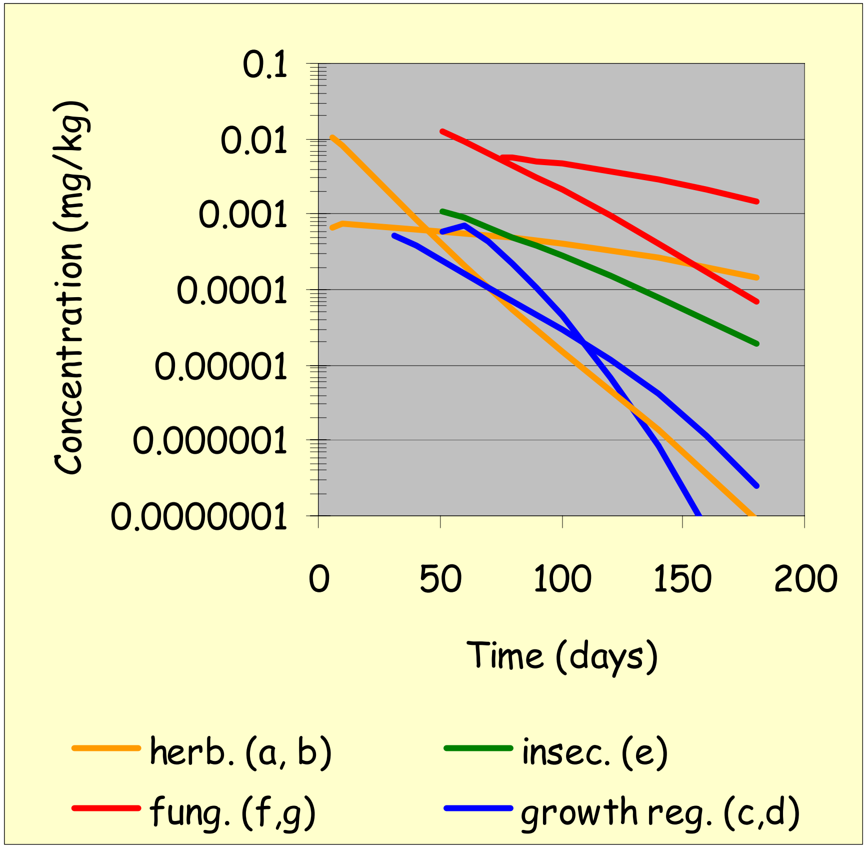
- What is the importance of the time lag between spraying and harvest ?
  - Initial concentration in plant increases with time
  - A variation factor of 7 of spraying time leads to a variation >200 of concentration at harvest (t1/2soil 40 days)



Evolution of the concentration in plant according to different periods of spraying

Time of spraying

- How does this affect the final residues in plants ?
  - Determinant variations are noticed according to the type of pesticide and to the properties of substances



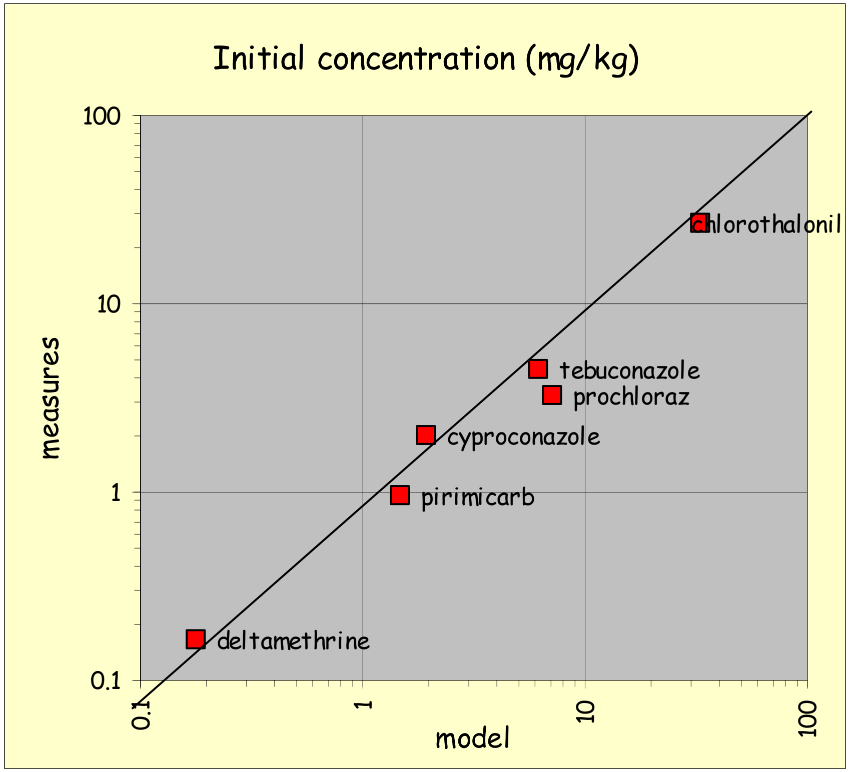
Evolution of the concentration in wheat for mostly used substances

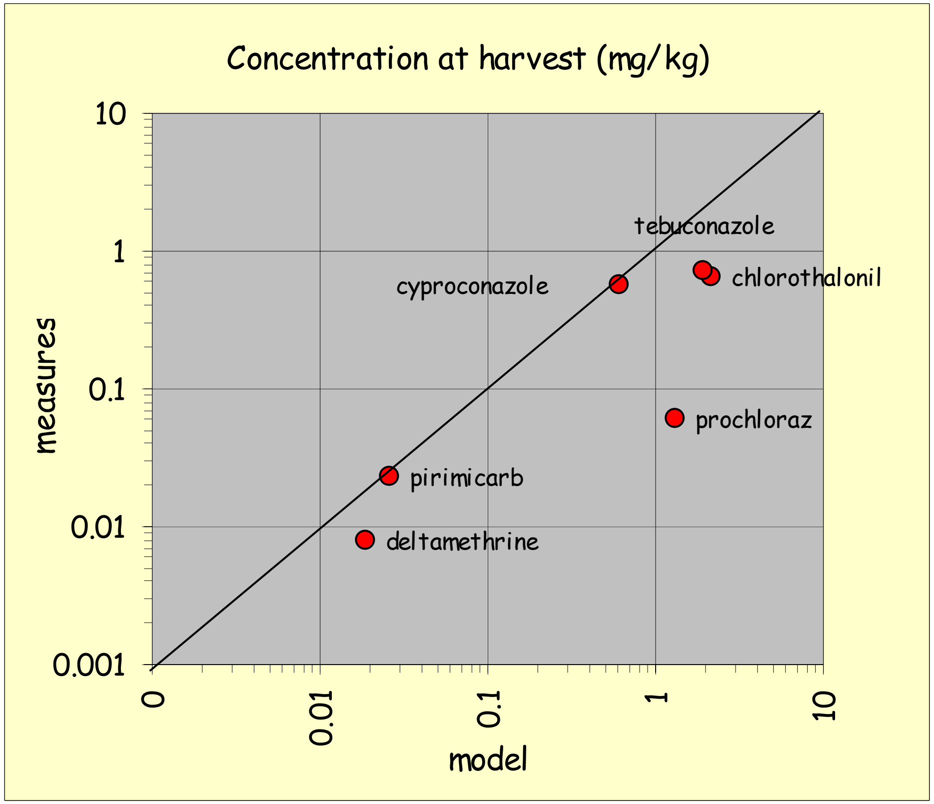
Laboratory of ecosystem management

Station recherche agronomique Changins

Measures and simulation results for wheat

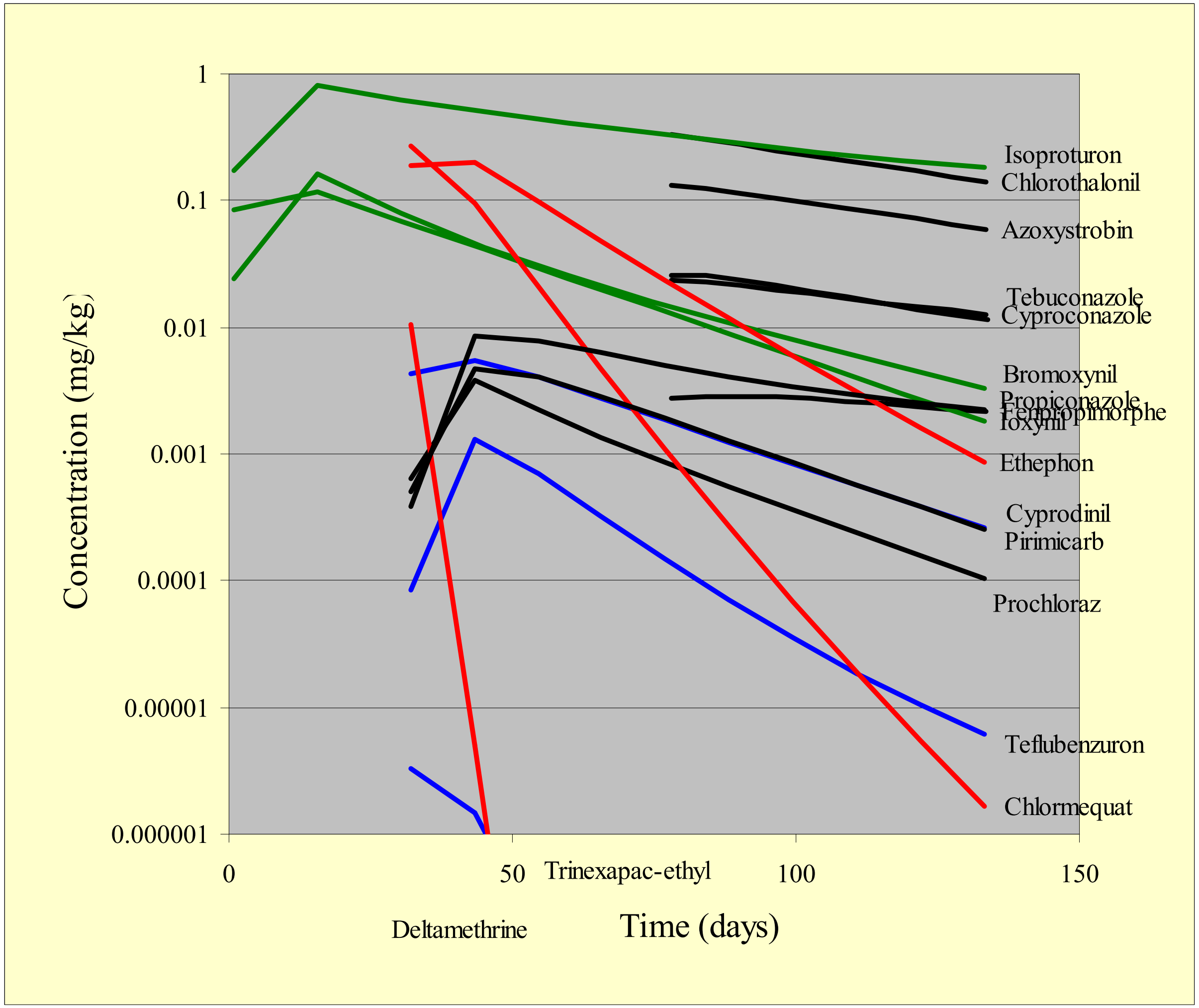
Compound	Mass sprayed (g/m2)	MW g/mol	log K_{aw} -	log K_{ow} -	$t_{1/2\ plant}$ days
Chlorothalonil	0.15	266	-4.9	1.9	11
Cyproconazole	0.008	292	-7.5	2.9	67
Prochloraz	0.03	377	-6.2	4.1	11
Tebuconazole	0.025	308	-8.2	3.7	53
Deltamethrin	0.00075	505	-4.9	5.4	14
Pirimicarb	0.0075	238	-7.5	-1.3	30





Phytosanitary measures in wheat

- Different treatments in wheat



Laboratory of ecosystem management

Station recherche agronomique Changins

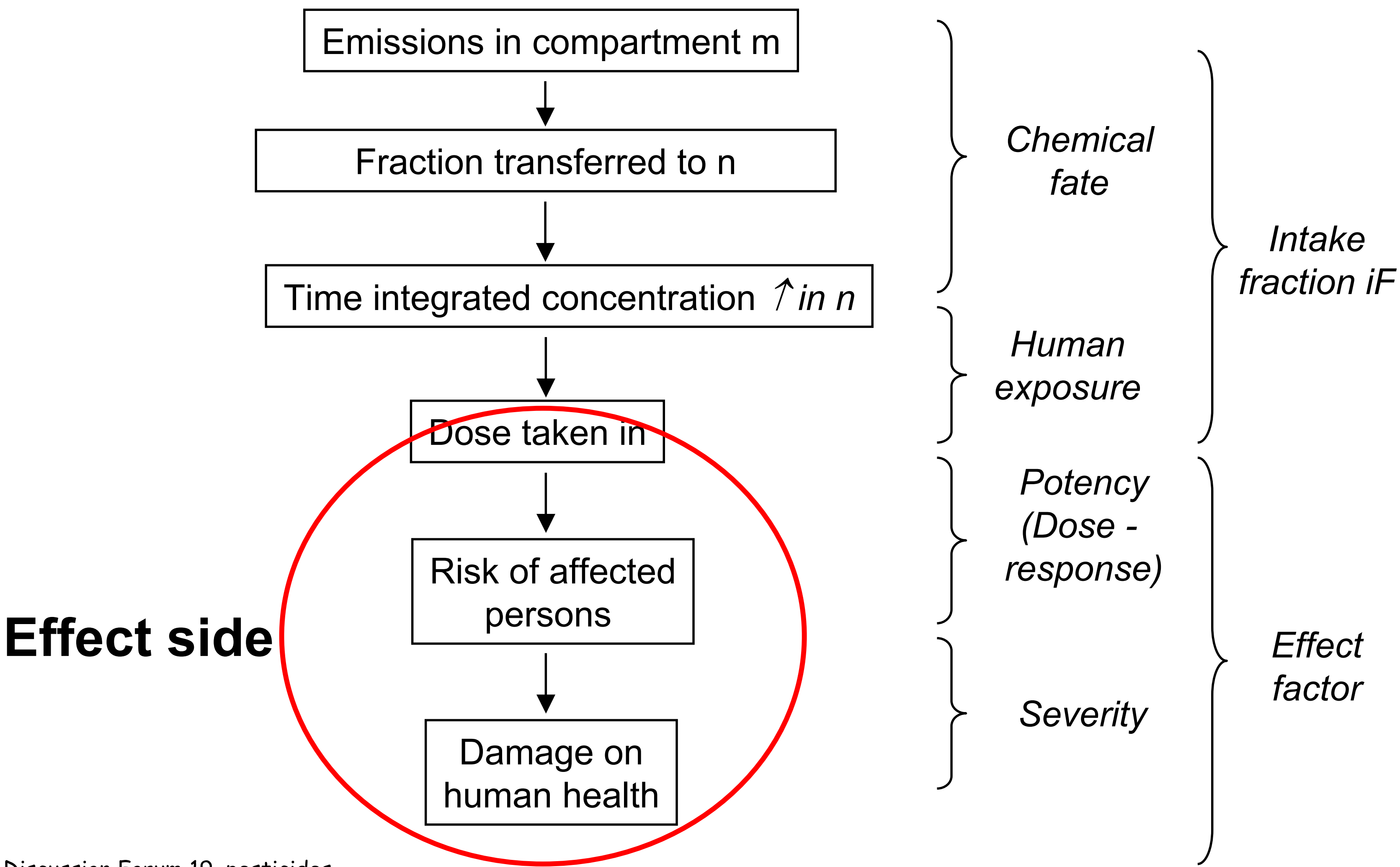
Transfer fractions

	Type	Time spray date	Rate kg/ha	Concentration mg/kg	Tol. val. mg/kg	Trans. frac. kg/kg
Bromoxynil	herbicide	20.3	0.48	0.00333	0.02	4.1E-05
Ioxynil	herbicide	20.3	0.355	0.00180	0.1	3.1E-05
Isoproturon	herbicide	20.3	1.5	0.18216	0.05	7.2E-04
Cyprodinil	fungicide	20.4	0.6	0.00026	0.3	2.6E-06
Prochloraz	fungicide	20.4	0.45	0.00010	0.2	1.4E-06
Propiconazole	fungicide	20.4	0.12475	0.00221	0.05	1.1E-04
Chlormequat	growth regulator	20.4	1.15	<0.00001	2	8.4E-09
Ethephon	growth regulator	20.4	0.72	0.00086	0.2	7.2E-06
Trinexapac-ethyl	growth regulator	20.4	0.15	<0.00001	0.2	5.9E-35
Deltamethrine	insecticide	20.4	0.0075	<0.00001	1	9.6E-12
Pirimicarb	insecticide	20.4	0.075	0.00026	0.01	2.1E-05
Teflubenzuron	insecticide	20.4	0.06	0.00001	0.05	6.0E-07
Azoxystrobin	fungicide	20.5	0.25	0.05990	0.3	1.4E-03
Chlorothalonil	fungicide	20.5	1.5	0.14025	0.2	5.6E-04
Cyproconazole	fungicide	20.5	0.08	0.01275	0.05	9.6E-04
Fenpropimorphe	fungicide	20.5	0.375	0.00214	0.1	3.4E-05
Tebuconazole	fungicide	20.5	0.25	0.01150	0.05	2.7E-04

Conclusions - perspectives

- Capacity to represent processes beyond analytical limits
- Identification of main processes
  - initial concentration
  - degradation
- Need for better pesticides description
  - half-life in plant
- Model versus experimental data
  - simplification in model

Emission to damage
a) Human health

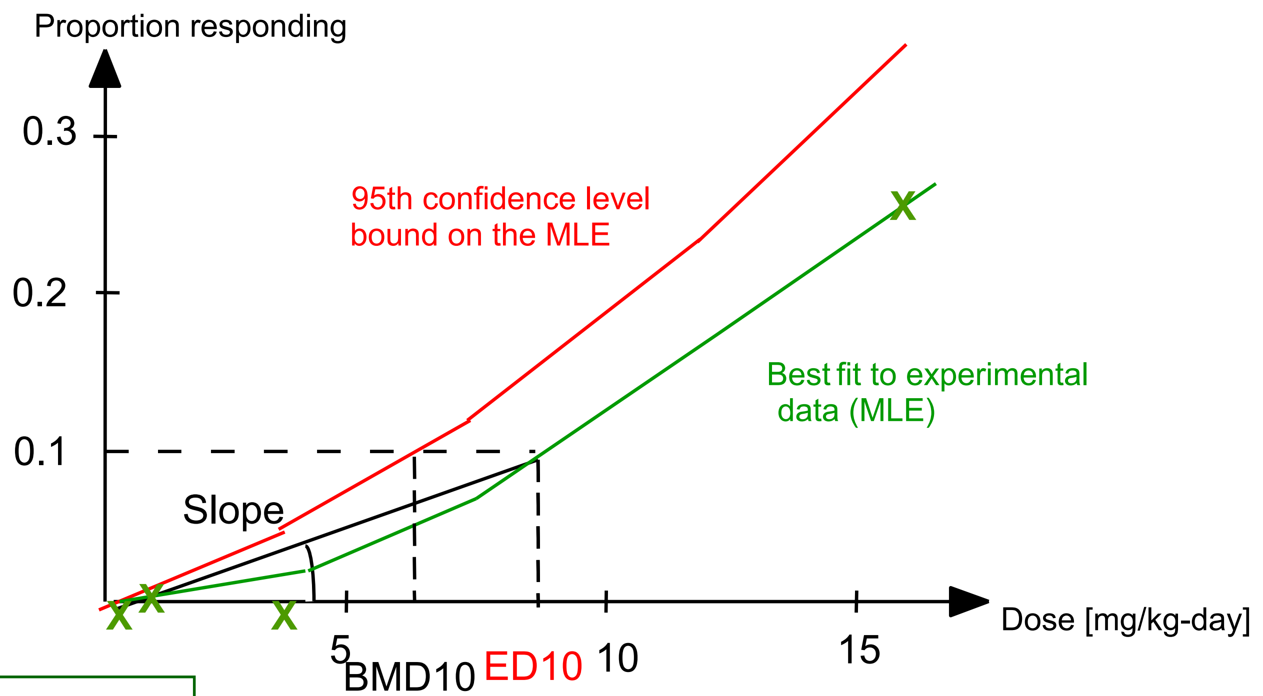


ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
Laboratory of ecosystem management

Carcinogens+non carcinogens The ED10 approach (EPFL&Harvard)

Station recherche agronomique Changins

Reference doses (RFD) or Acceptable Daly Intake (ADI): uncertainty factors of 10,100, 1000 are mixed with best estimate --> for comparative assessment: *Effect Dose 10%*

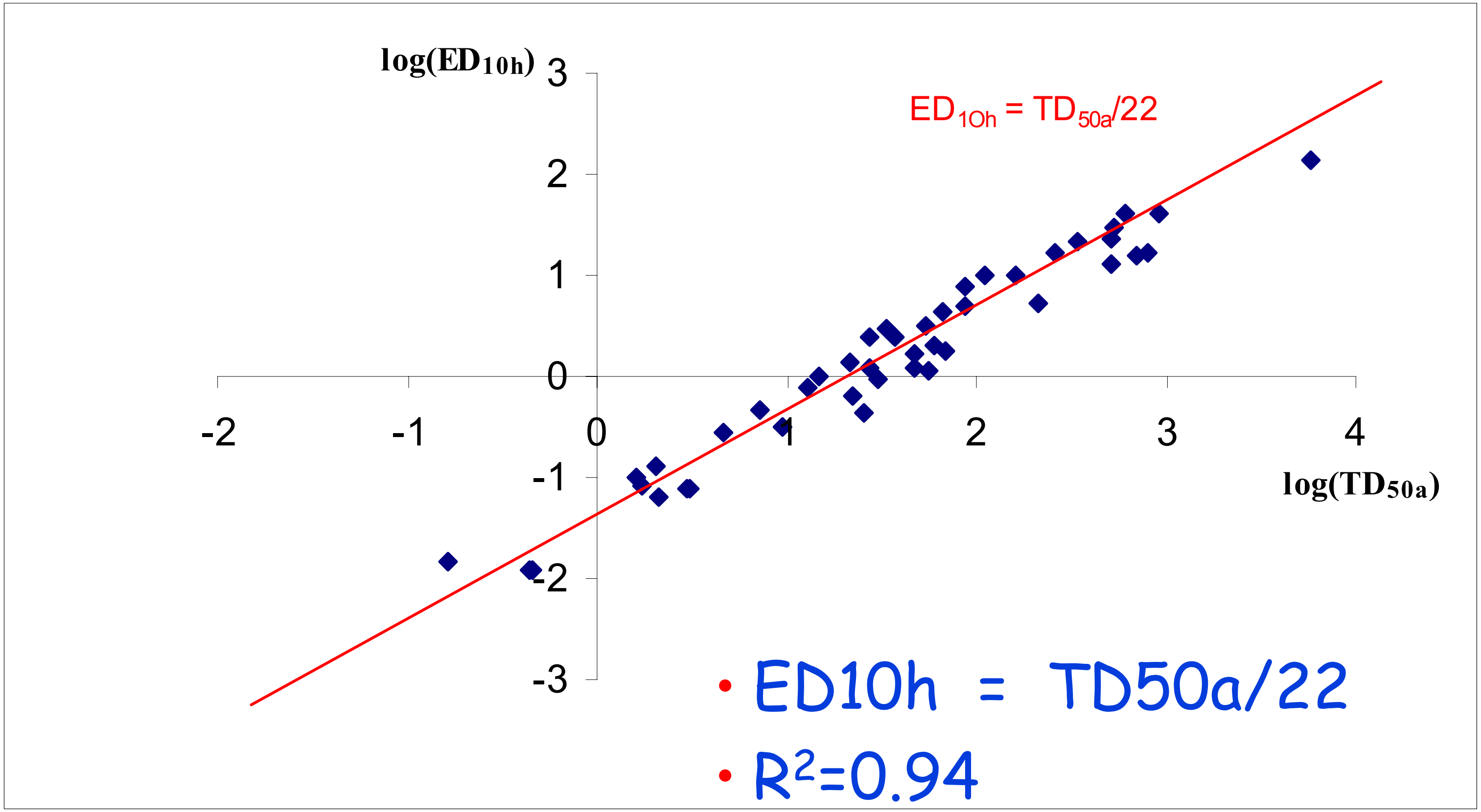


$$Slope = \frac{0.1}{ED10}$$

X = Values observed in a bioassay

____ Maximum likelihood estimate

Correlation ED10 - TD50 data provided for 300 carcinogens

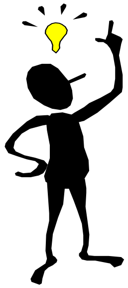


- ED10h = TD50a/22
- R^2=0.94

Similar approach for 600 non carcinogens + 10 substances with epidemiologic data

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
Laboratory of ecosystem management
Station recherche agronomique Changins

SEVERITY OF THE TUMORS



Disability Adjusted Life Years concept of Murray and Lopez [1996].

	Disability	Death	Disability and death
Types of cancer	$YLD_p = W*D$	$YLL_p = Li/N$	$DALY_p = YLD_p + YLL_p$
	[yr lost/pers]	[yr lost/pers]	[yr lost/pers]
mouth and oropharynx	0.62	2.9	3.5
prostate	0.47	1.6	2.1
Trachea, bronchis, lung	0.26	7.9	8.2
leukaemia	0.35	14.3	*14.6*
....			

Different cancers: more or less the same severity.

Average $DALY_p$ = 6.6 [yr lost/pers] => Default

Non carcinogens
Severity of the endpoints

DALYp: a simpler weighting is used

1	2	3
Irreversible/ life-shortening effects	May be irreversible/ life-shortening effects	Reversible / not life-shortening effects
Cancer Mutagenicity Teratogenic effects Reproductive effects	Immunotoxicity Neurotoxicity (*) Kidney damage Liver damage Heart disease Pulmonary disease	Irritation Sensitization
6 DALY/pers	**0.6 DALY/pers**	**0.06 DALY/pers**

DALYp and β_{ED10} => EF

[Burke et al, 1996]

Laboratory of ecosystem management

Station recherche agronomique Changins

Example chlorothalonil effect factor

Dose taken in

ED10 cancer 90 mg/kg-day

ED10 non cancer 1.5 mg/kg-day

Risk of affected persons

Damage on human health

	Cancer risk		Non cancer
Dose - response	0.0006	$\frac{\text{person affected}}{\text{kg ingested}}$	0.037
Severity	6.7	$\frac{\text{DALY}}{\text{person affected}}$	0.67
	0.0027	$\frac{\text{DALY}}{\text{kg ingested}}$	0.024

Application to Chlorothalonil

Emissions in compartment m
↓
Fraction transferred to air, water, soil
↓
Concentration *in vegetation at harvest*
↓
Dose taken in — Residue 0.2 mg/kg
↓
Risk of affected persons
↓
Damage on human health

Intake fraction iF: (Diffuse residues) (6E-06); Direct residues 6E-04

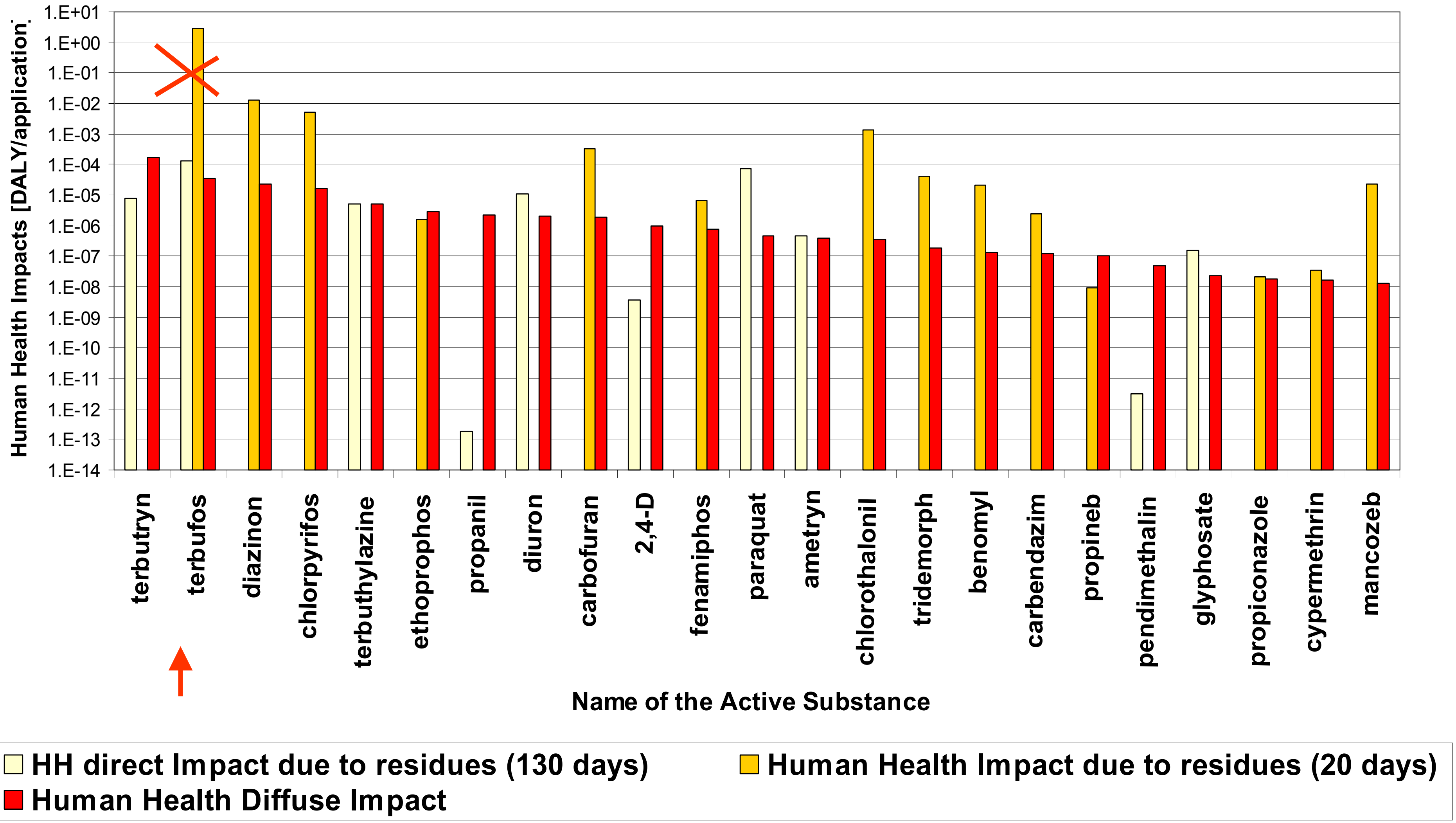
Dose - response: Non cancer 0.037 person/kg in

Severity: 0.67 DALY/person

1 kg applied
↓
0.0006 kg ingested (0.6 g)
↓
2E-6 person affected with non cancer
↓
1.4E-5 DALY non cancer
1.6E-6 DALY cancer

Characterisation factor: relative comparison

All Human Health Impacts per Application (per ha)



Laboratory of ecosystem management

Station recherche agronomique Changins

Conclusions
Impacts of pesticides on humans

- Central importance to model residues
- Only diffuse effects -> neglect variations of 10'000!

- Time between application and harvest need to be taken into account --> dynamic application !
- Crucial role of degradation constant in the plant

- Data availability on dose-response is rather good for pesticides compared to other chemicals

- --> Variations of 6 (pesticides) to 12 orders of magnitude down to 2 orders

Final formula

$$EF_i = \left[\beta_{ED10-i} \cdot \frac{1}{BW} \cdot \frac{1}{LT_h} \cdot \frac{1}{N_{365}} \right] \cdot DALY_p \qquad \left[\frac{risk}{mg} \cdot \frac{year}{person} \right]$$

Where $$\beta_{ED10} = \frac{0.1}{ED_{10h}}$$