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The Environmental Fate of Pesticides

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Plant Protection Products (PPP): environmental issues

- **The main PPP environmental issues are due to:**
  - ✓ **DELIBERATELY RELEASED INTO THE ENVIRONMENT**
  - ✓ **HIGH INTRINSIC TOXICITY → Kill organisms "undesirable"**
  - ✓ **LIMITED SPECIES SELECTIVITY → Toxic for humans and environment**

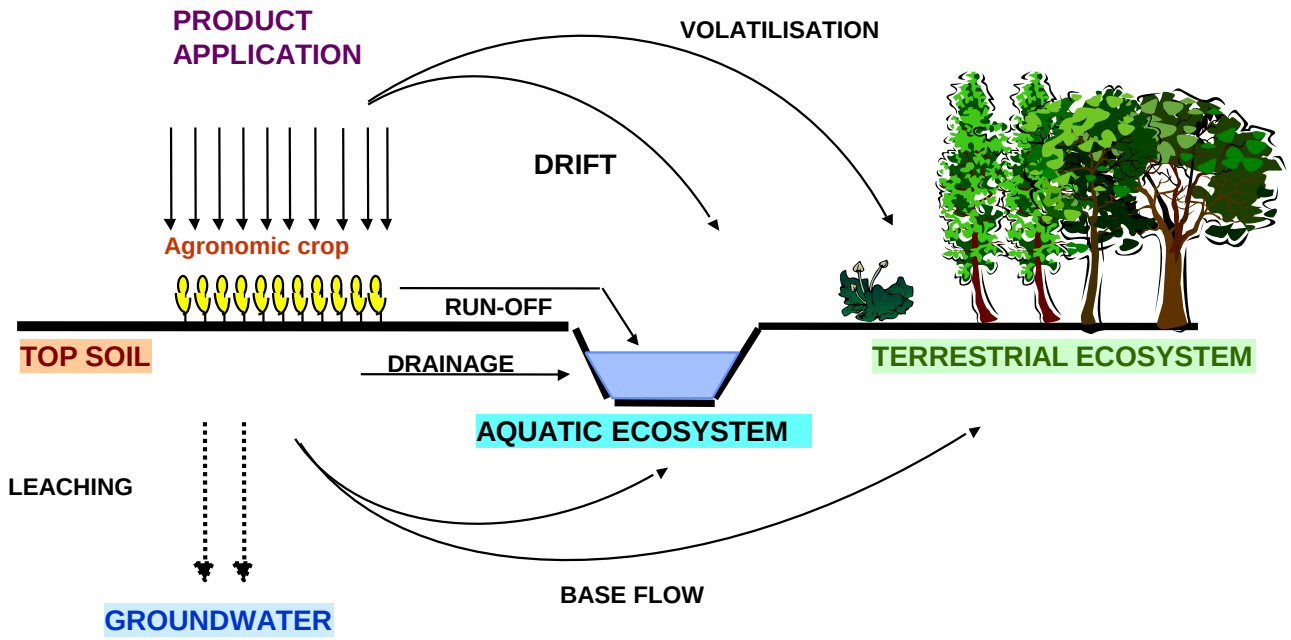
- **PPP move and transform into several environmental compartments before eventually disappear.**

- **PPP movements depend on:**

1. **The way chemicals are applied (several dozens of different spraying machines, soil incorporation, seed treatments, etc).**
2. **The chemical-physical characteristics of the active ingredient(s).**
3. **The chemical-physical characteristics of the formulation.**
4. **The meteorology conditions (rainfall abundance and distribution, temperature, sunlight, moisture, etc).**
5. **Some others compartment feature (e.g. for soil, amount of organic matter).**

ENVIRONMENTAL FATE AND BEHAVIOUR

E-FATE AND BEHAVIOUR OF A PESTICIDE



ENVIRONMENTAL EXPOSURE

Environmental compartments exposed to pesticide:

- soil
- groundwater
- surface water
- air

Species at risk of short and long terms effects:

non target organisms

PARAMETERS INFLUENCING CONTAMINATION

PESTICIDE FORMULATION
solvent used
particle size

MODE OF USE
spray volume
height of application

METEOROLOGICAL CONDITIONS
temperature
rainfall
relative humidity
wind velocity

E-Fate evaluation
Soil compartment

Soil

How do pesticides get there?

Soil is the main receptor of pesticides. Plant protection products are applied on crop canopy or directly to bare soil. Also when they are sprayed on the canopy, **plant intercept** only a fraction of what is applied (determined by the crop typology and by the phenological cycle → optical porosity). Most of the remaining fraction reaches the soil.

Moreover, pesticide residues on crops might be **washed off** during rainfall events and thus indirectly reach the soil. Washoff depends on:

- Solubility of the active ingredient in water
- Formulation (carrier)
- Rainfall intensity and timing (after application)

EXPOSURE: TOP SOIL

Pesticide may reach the top soil:

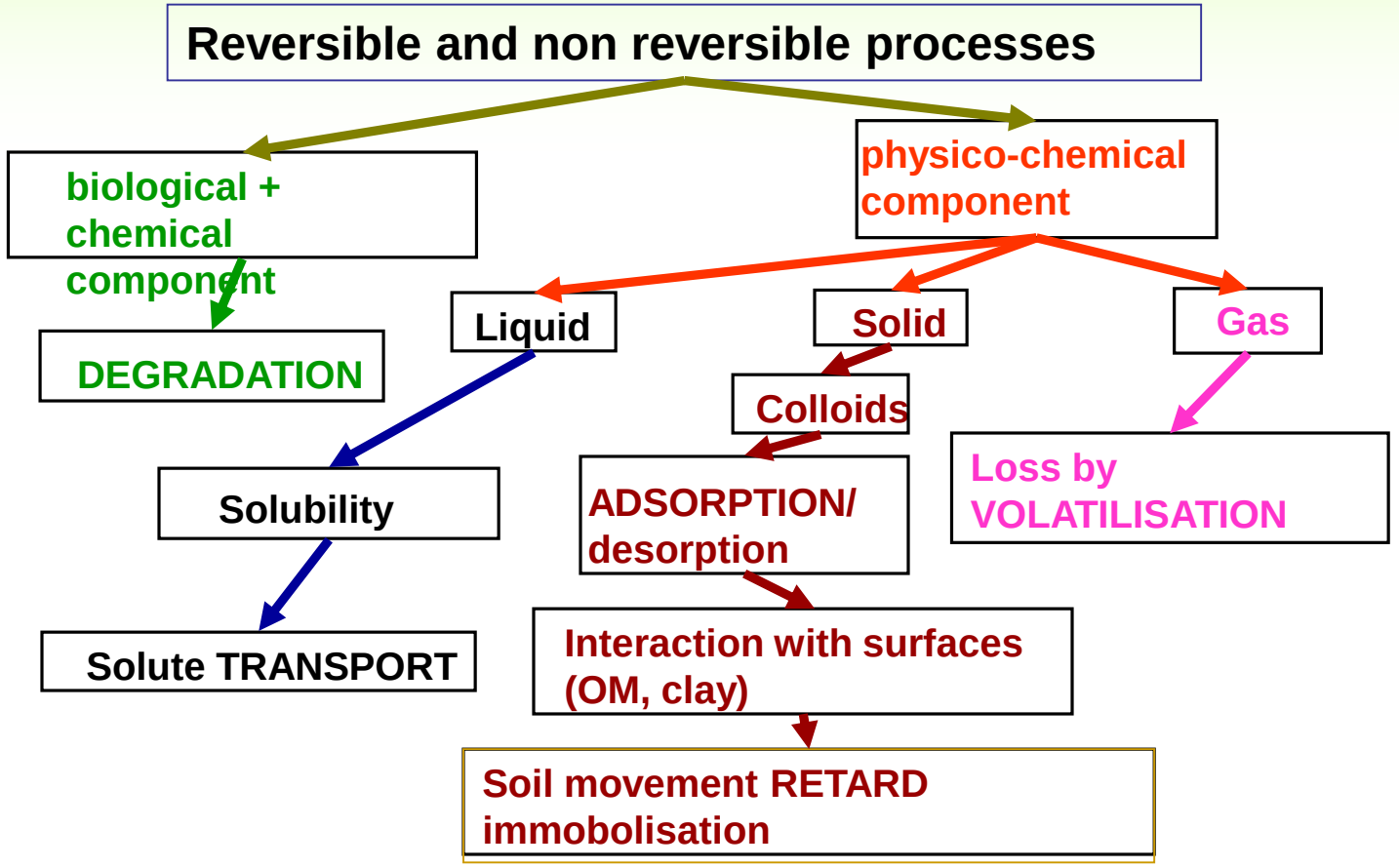
- after spraying
- by direct application into soil applying granules or treated seeds.

Spraydrift:
amount of pesticide on soil depends:

- application losses (evaporation)
- interception by plants.

Direct application
100 % of the nominal pesticide dose (kg/ha) will reach the soil

INTERACTION PESTICIDES - SOIL

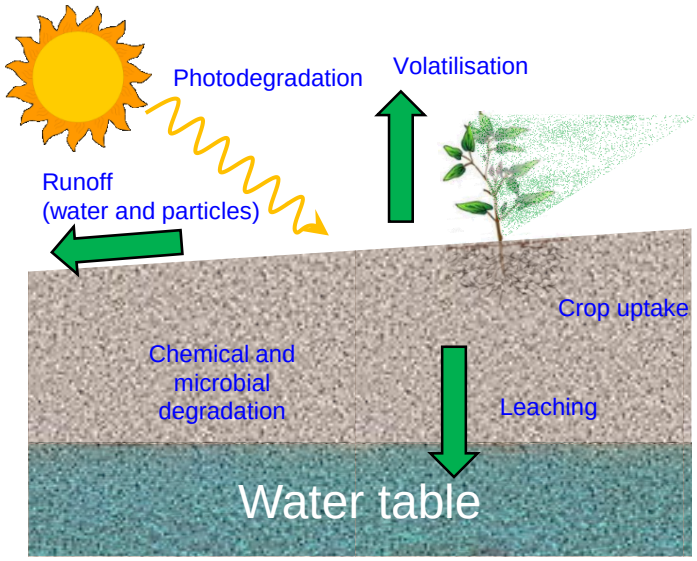


Soil

How do pesticides move?

Soil is a pretty static compartment. However, (soluble) pesticide may be transported by water toward deeper soil horizons (**leaching**) by gravity or following the slope of soil surface (**runoff**). Water moving on soil surface may also carry pesticides adsorbed on eroded soil particles.

Most of the processes are determined by chemical-physical characteristics of the compound (K_{oc}, water solubility, saturated vapour pressure, half-life) or by environmental factors (organic carbon content in soil, precipitation frequency and intensity, slope, soil moisture, temperature, etc).



BIOLOGICAL + CHEMICAL COMPONENT degradation

Degradation is the main phenomenon affecting pesticide persistence in soil.

Degradation: complete compound mineralization (O_2 + CO_2 + NH_3) or transformation in metabolites.

- Biotic degradation, due to bacteria living in soil
- Abiotic degradation due to physico-chemical phenomena (redox, hydrolysis)
- Fotodegradation (UV radiation)

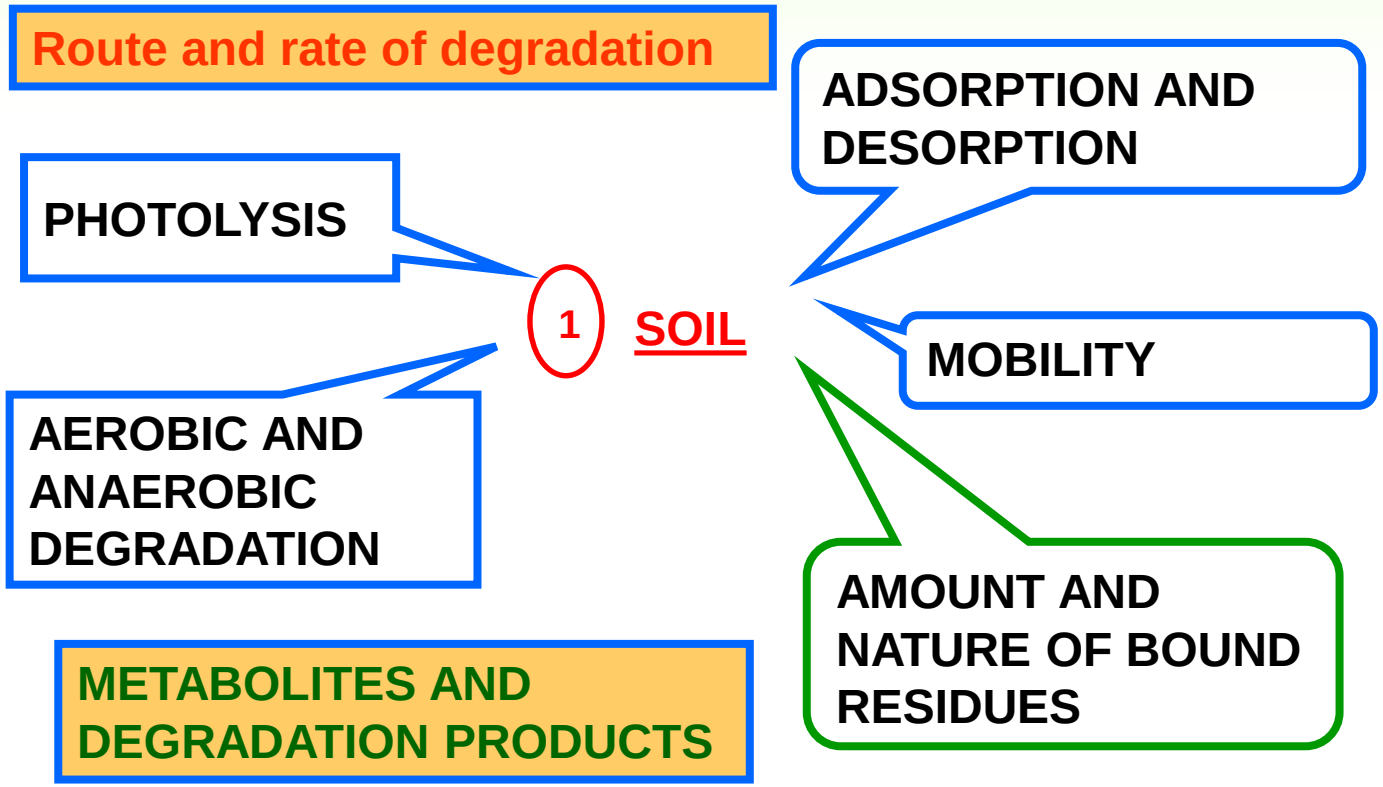
Physico-chemical component: solid state

Substance interaction with soil colloids; inorganic substances (clay) and organics (humic and fulvic substance):

- Increase with OM and clay
- Function of temperature (inversely proportional)
- Function of humidity
- pH

Mathematical modeling: adsorption isotherms which relates the amount adsorbed with the concentration.

FATE AND BEHAVIOUR IN SOIL



SOIL ENDPOINTS

- Amount and nature of bound residues
- Amount of mineralisation
- Amount and nature of metabolites

For a.i. and metabolites

- DT_{50} and DT_{90} aerobic at 20°C
- DT_{50} and DT_{90} anaerobic at 20°C
- DT_{50} aerobic at 10°C
- DT_{50} photo degradation
- DT_{50} and DT_{90} field
- K_d and K_{oc} at 20°C
- % of substance leached

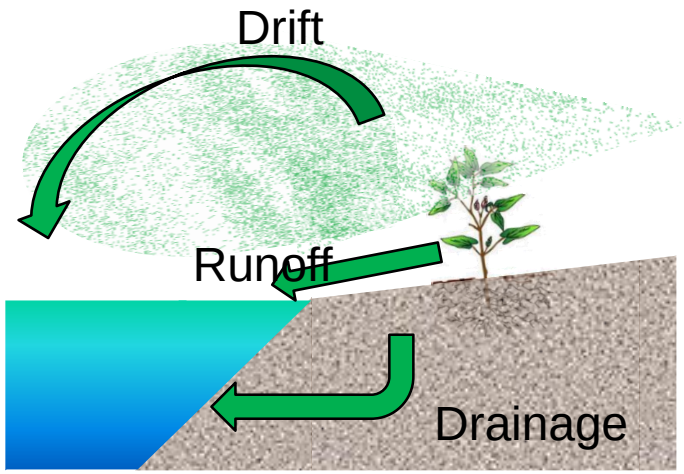
E-Fate evaluation Surface water compartment

Surface water

How do pesticides get there?

- **Pesticides enter surface water bodies through 3 main routes:**

1. Spray drift: during application droplets may be carried by the wind and deposit several meters away from the target field, sometimes reaching water bodies.
2. Drainage: pesticide may penetrate for some centimetres in the soil and than moving (sub)horizontally, entering in deep water layers.
3. Surface runoff: chemicals may move because of the transport action of rainfall water, following the slope of soil surface. Water moving on soil surface may carry pesticides in solution or adsorbed on eroded soil particles.



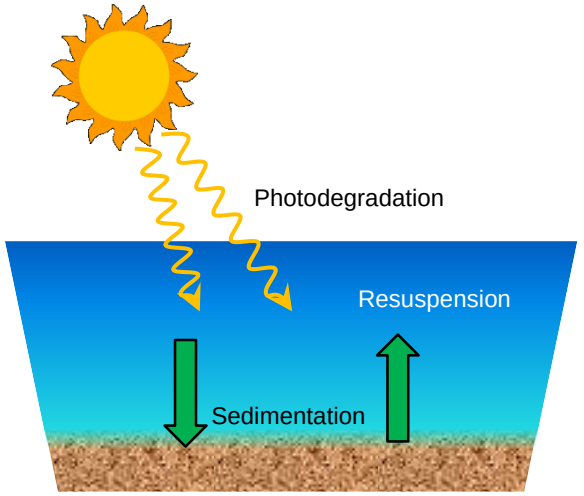
Surface water

How do pesticides move?

Once pesticides reach a water body, it may move following the flow (especially moving water bodies) and it may **partition** into the soil until reaching an equilibrium between water and sediment phase.

Partitioning (sedimentation and resuspension) is chiefly determined by **K_{oc}** and **sediment composition** (abundance of fine matter and organic content).

Degradation time of the compound may be different in water and sediment: this can cause further sedimentation and resuspension to maintain an equilibrium.



EXPOSURE: SURFACE WATER

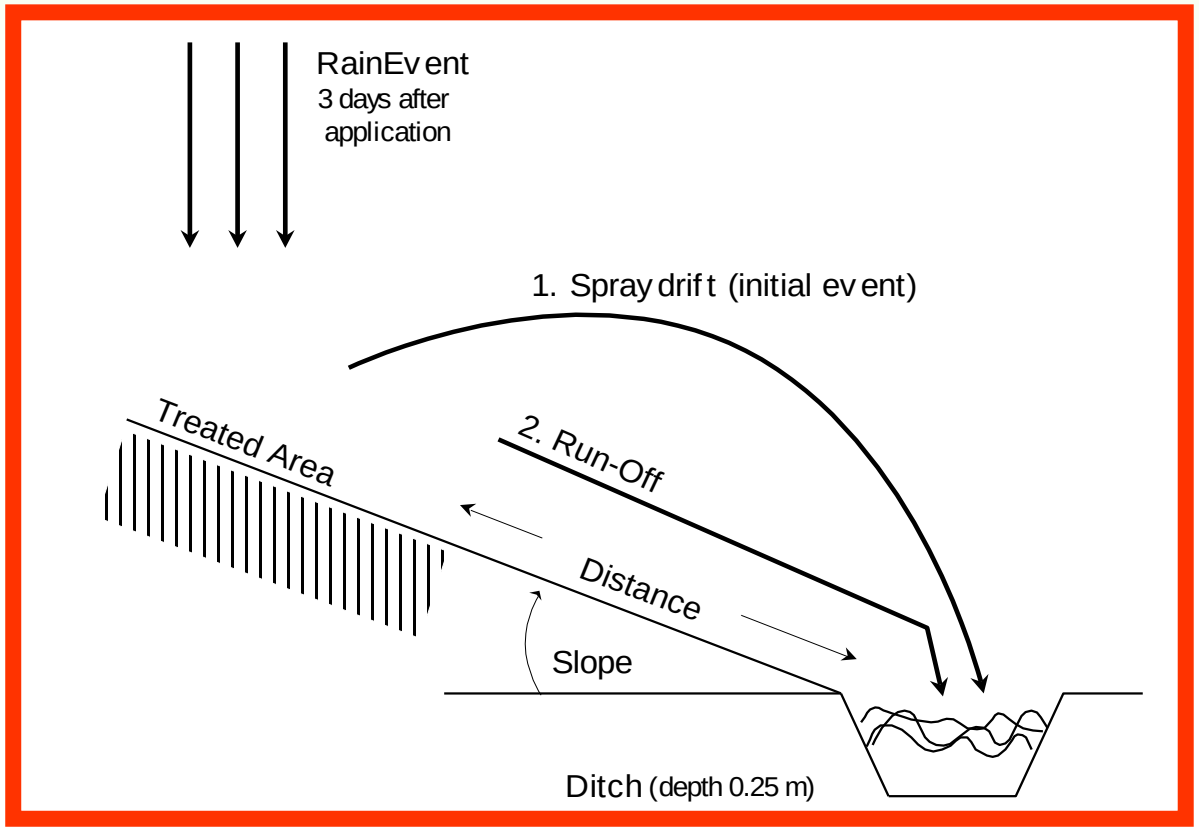
Major routes of exposure:

SPRAY DRIFT: water much far away from the application area

DRAINAGE: removal of surplus water from land, via within-field drains

RUNOFF: close to treated area. Dependent on the topography, the soil texture, the amount of rain

PESTICIDES
IN THE AQUATIC ENVIRONMENT



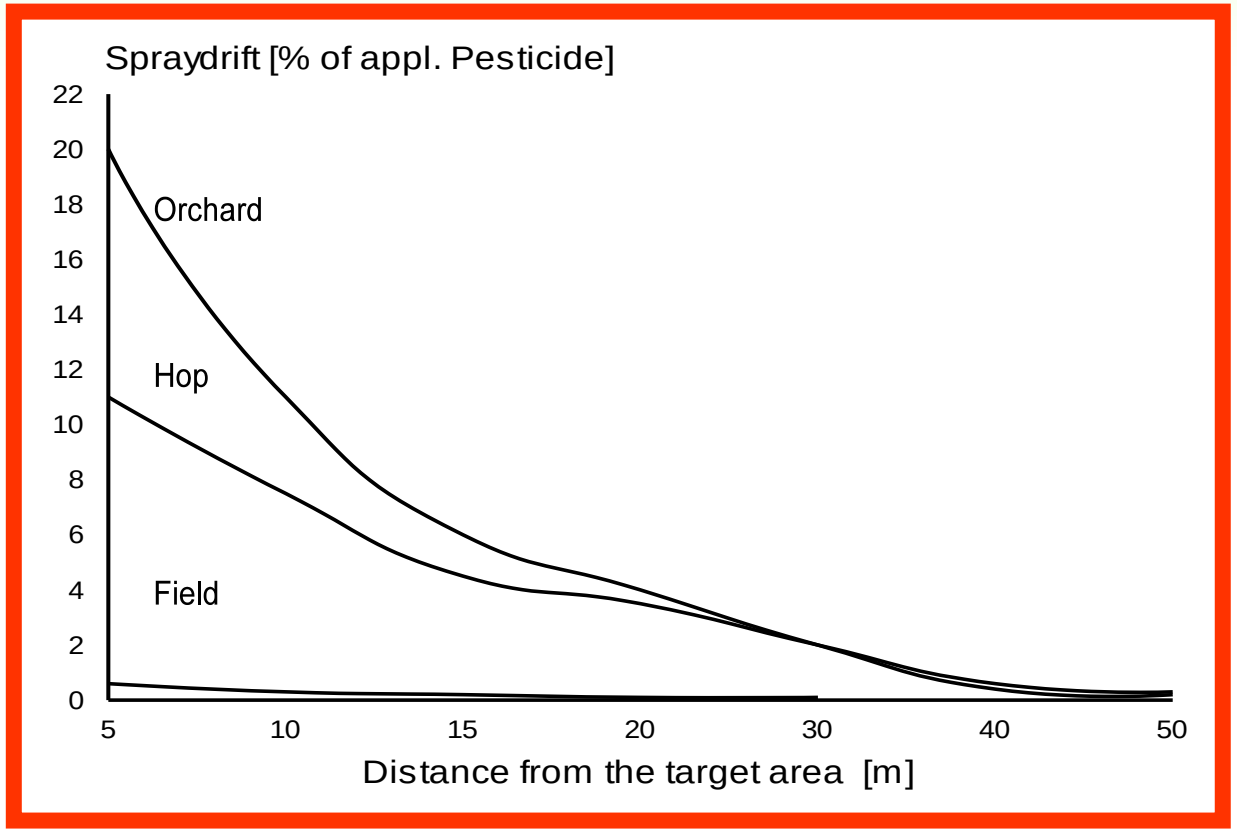
SPRAYDRIFT

The amount of spraydrift reaching non-target areas is dependent on:

- Distance from the area of application
- Mode of application (formulation, technical equipment)
- Crop (height, growth stage)
- Weather (e.g. wind speed)

Spraydrift deposition generally calculated as:
$DEPOSITION = DOSE_{nominal} \times f_{drift}$
f_{drift} = spraydrift fraction, dependent on crop, growth stage and distance from the target area

CONSIDERATION ON PESTICIDE SPRAYDRIFT

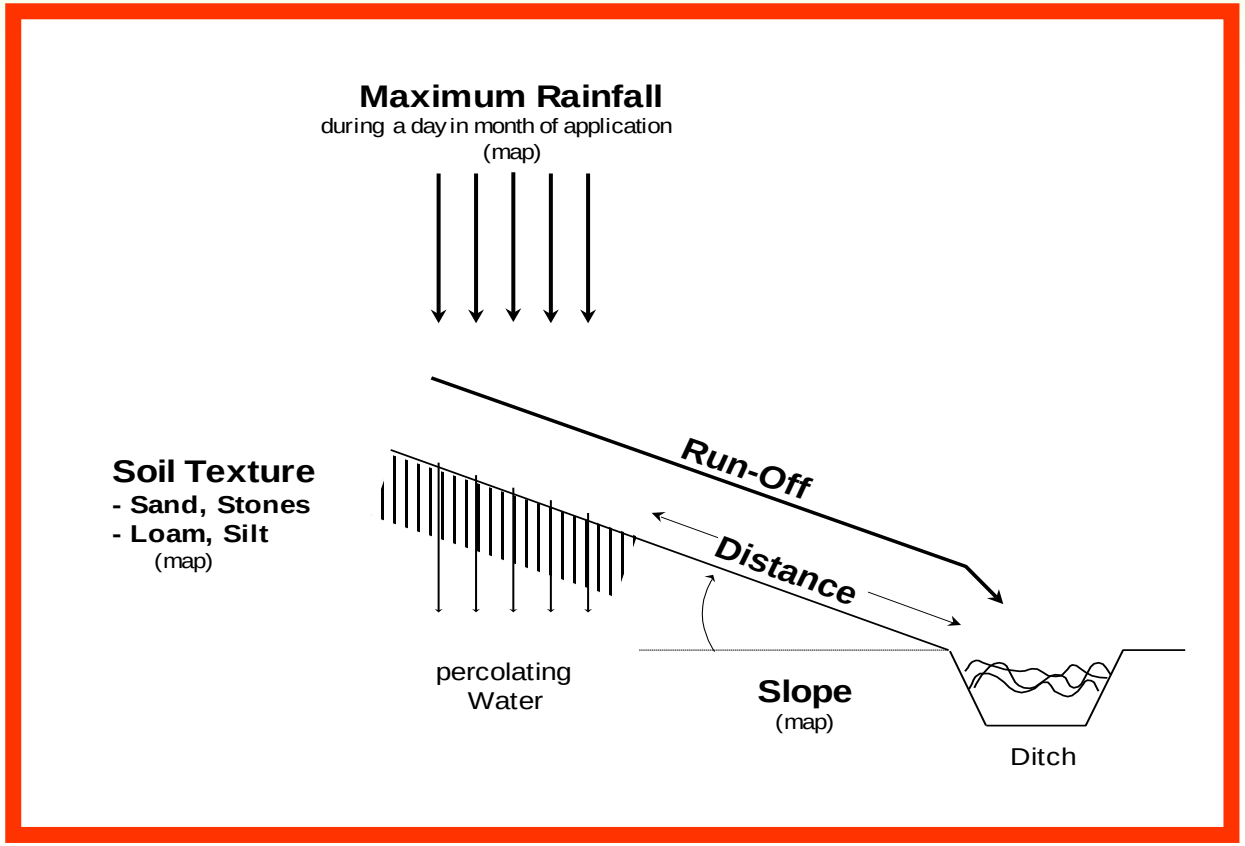


RUN-OFF

Occurrence and extent of run-off

- **topography** of the landscape (slope),
- **soil texture** (OC, presence/absence of sand and stone)
- **intensity** of the rain event
- **distance** between the treated area and the receiving ecosystem
- **elapsed time** between pesticide application and onset of rainfall.

CONSIDERATION ON PESTICIDE RUN-OFF



Degradation in surface water

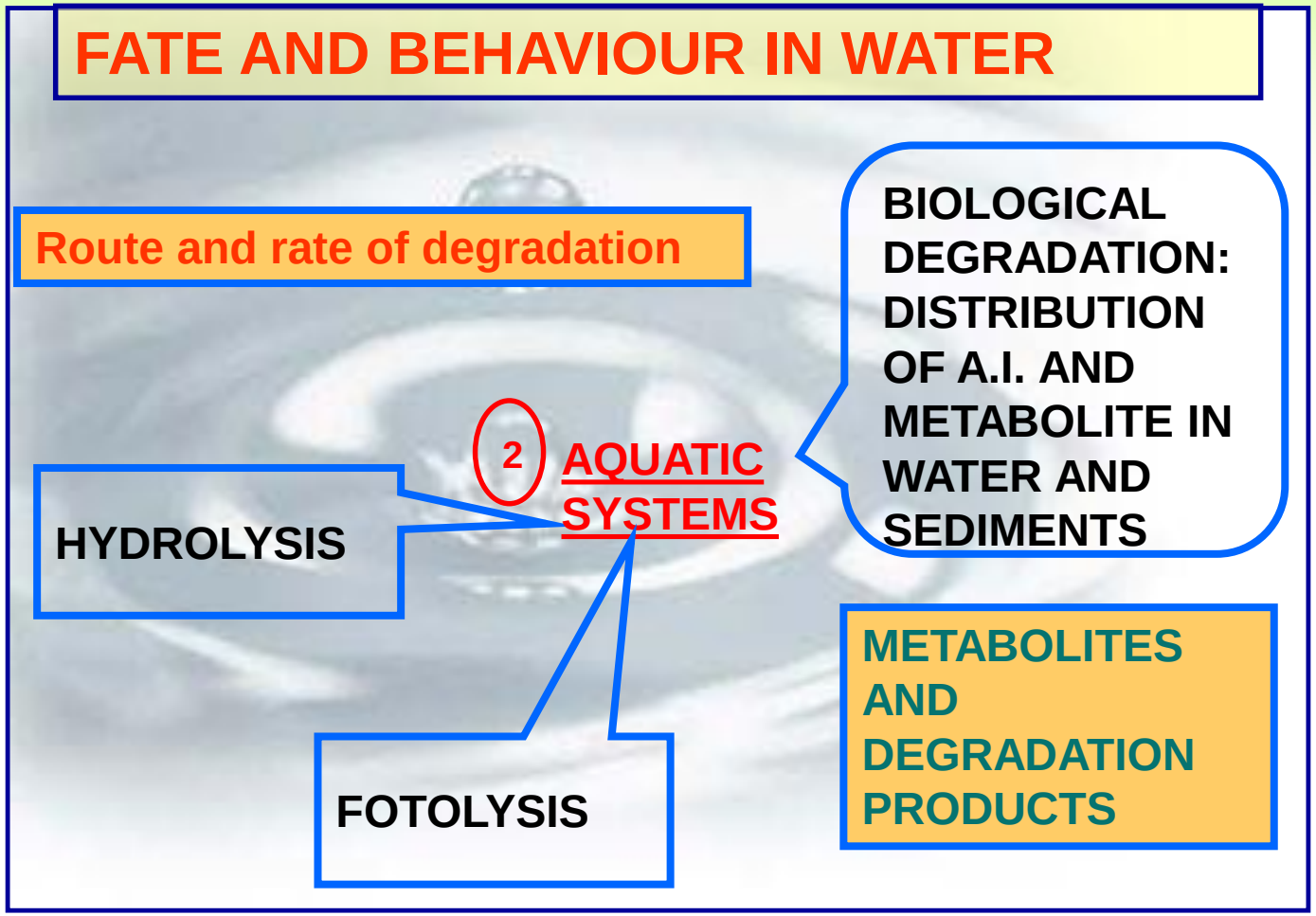
Physico chemical degradation of the substance in surface water: hydrolysys and photolysis phenomena

Biological degradation: repartition of the substance in a water/sediment system: could be pH and OM dependent

Water/sediment studies

- The only kinetics that can be straightforwardly derived from water/sediment studies are:
  - ✓ Whole system DegT50
  - ✓ Water column DT50
- This is due to the existence of an equilibrium interface of two compartments in which degradation happens at different velocities

FATE AND BEHAVIOUR IN WATER



WATER ENDPOINTS

For a.i. and metabolites

- DT_{50} hydrolysis at pH 4, 7, 9
- DT_{50} photolysis
- Biodegradability (Y/N)
- DT_{50} and DT_{90} water
- DT_{50} and DT_{90} sediment
- DT_{50} and DT_{90} water/sediment
- Repartition in water/sediment
- Mineralization

E-Fate evaluation Groundwater compartment

Groundwater

How do pesticides get there?

- Pesticide may reach groundwater by percolation only (unless some open well is accessible during application!!!). Gravity is the main force involved.

How do pesticides move?

- Pesticide movements are essentially the same as in soil. Pesticides are more likely to percolate if they have a **low affinity to organic matter** (low K_{oc}), **long half-life** (DT_{50}) in soil, **high water solubility**. In addition, a certain area is more vulnerable to pesticide leaching if it presents a low organic carbon content, conditions that facilitate water infiltration (low slope, high percentage in sand), low temperature (prevent degradation) and abundant rainfall.

What might be affected?

- Microorganisms and of course human being (use of groundwater as drinking water).

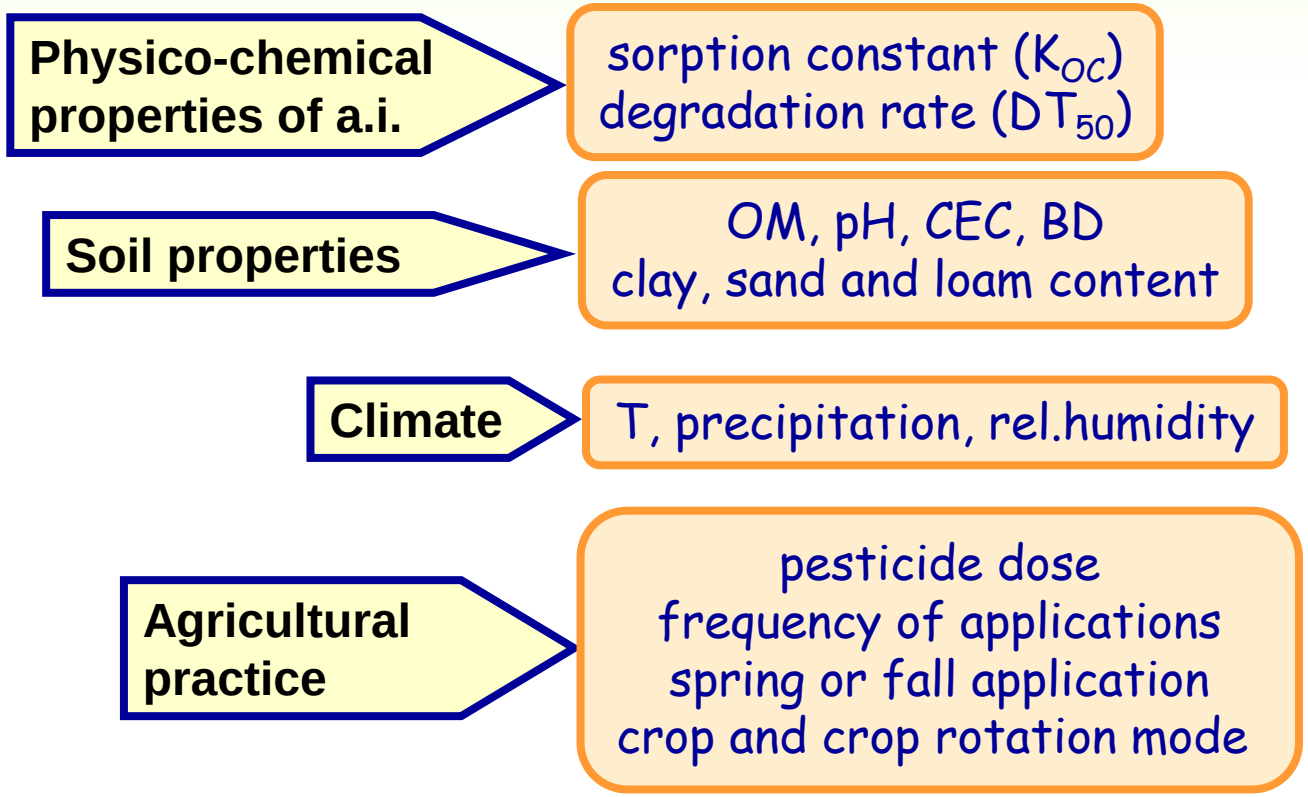
EXPOSURE: GROUNDWATER

DIRECT CONTAMINATION: wells and well borings
LEACHING: after rain events or irrigation practices

Crucial properties of pesticides with respect to groundwater

- biodegradability
- mobility
- water solubility

PARAMETERS INFLUENCING PESTICIDE LEACHING TO GROUNDWATER



…trigger values for groundwater

- **Active ingredient : 0.1 µg/L**

  refined assessment with prejudice is required, or monitoring programme of 5 y at least

- **NON-relevant metabolite : 0.75 µg/L**

  if 0.75 µg/L > NON-rel. metabolite > 10 µg/L → monitoring programme of 3 y is required (Italy)

  if NON-relevant metabolite is > 10 µg/L →no authorisation shall be granted

- **RELEVANT metabolite: 0.1 µg/L**

  refined assessment is required with prejudice

GUIDANCE DOCUMENT ON THE ASSESSMENT OF THE RELEVANCE OF METABOLITES IN GROUNDWATER

INDEX

- Uniform Principles
- Guidance document" relevant metabolites"
    1. Definitions
    2. When have metabolites to be considered?
    3. Stepwise approach: 5 Steps
- Case study

Uniform Principles

Annex VI, part B: evaluation

MS shall evaluate the possibility of PPP reaching the groundwater under the proposed conditions of use; if this possibility exists, they shall estimate, using a suitable calculation model validated at Community level, the concentration of the a.s. and of **relevant** metabolites, degradation and reaction products that could be expected in the groundwater ……

As long as there is no validated Community calculation model, Member States shall base their evaluation especially on the results of mobility and persistence in soil studies as provided for in Annexes II and III.

Uniform Principles

Annex VI, part C: decision making

No authorization shall be granted if the concentration of the active substance or of **relevant metabolites**, degradation or reaction products in groundwater, may be expected to exceed, as a result of use of the plant protection product under the proposed conditions of use, the lower of the following limit values:

1. the maximum permissible concentration laid down by the Drinking Water Directive (Council Directive 98/83/EC) regulating the quality of water intended for human consumption (0.1 μg/L)
2. including a.s. in Annex I, on the basis of appropriate data (toxicological data), otherwise, the concentration corresponding to 1/10 of the ADI laid down when the active substance was included in Annex

Pesticide and groundwater

European evalaution

FOCUS group modeling gw

FOCUS group standars scenarios

UE: possible authorization if exists at least one european scenario “safe”: PEC_{gw} < 0.1µg/L

MS: identification of vulnerable areas; limitation of use

Metabolites and groundwater

Directive 91/414/CEE: “relevant metabolites " (Annex VI, point C 2.5.1.2).

“Relevant metabolites” in Drinking Water Directive 98/83/EC: pesticides and relevant metabolites concentration in water for human consumption shall not exceed 0.1 µg/L.

“Relevant” metabolites: what are they?

Definition

Metabolite: for the purpose of this guidance document, the term is used for all reaction or breakdown products of an active substance of a plant protection product, which are formed in the environment after the application, be it by biotic (microbials, other taxa) or abiotic processes (hydrolysis, photolysis).

Definition

Relevant metabolite: a metabolite for which there is reason to assume that it has comparable intrinsic properties as the active substance in terms of its biological target activity, or that it has certain toxicological properties that are considered severe and unacceptable.

Relevant metabolite

Concentration > 0.1 µg/L

non inclusion EU
no national authorization

Definition

Metabolite of "no concern": A metabolite which meets the criteria outlined in Step 1 and is therefore deemed to be not relevant in the assessment

Non-relevant metabolite: a metabolite which does not meet the criteria provided for "relevant metabolites" and "metabolites of no concern". A non-relevant metabolite may be subject, on a case-by-case basis, to an individual groundwater limit concentration

General rule

All metabolites from soil degradation studies should be further assessed for their structure and e-fate

The same thing for metabolites in lysimeter studies

→ To quantitatively assess their ability to contaminate groundwater

it might not be possible to identify:

- metabolites which occurr transiently in soil, (< 10% of total applied on a molar basis)
- low amounts of metabolites (< 5 %) with no tendency to accumulate

When should metabolites be considered?

- Metabolites, which account for more than 10 % of the amount of active substance added in soil at any time during the studies ; or
- which account for more than 5 % of the amount of active substance added in soil in at least two sequential measurements during the studies; or
- for which at the end of soil degradation studies the maximum of formation is not yet reached.
- all metabolites found in lysimeter studies at annual average concentrations > 0.1 µg/L in the leachate

identification and evaluation

Metabolites: stepwise evaluation

Step 1: Exclusion of degradation products of no concern

Step 2: Quantification of potential groundwater contamination

Step 3: Hazard Assessment: Identification of relevant metabolites

- Stage 1: Screening for biological activity
- Stage 2: Screening for genotoxicity:
- Stage 3: Screening for toxicity

Step 4: Exposure assessment - threshold of concern approach

Step 5: Refined risk assessments for non-relevant relevant metabolites

Step 1 Exclusion of degradation products of no concern

This step applies to all metabolites

- it is CO_2 or an inorganic compound, not containing a heavy metal; or,
- it is an organic compound of aliphatic structure, with a chain length of 4 or less, which consists only of C, H, N or O atoms and which has no "alerting structures" such as epoxide, or other functional groups of known toxicological concern
- it is of no (eco)toxicological concern, and occurrs at much higher concentrations in the environment

yes

No concern
Stop evaluation

no

Step 2

Step 2 Quantification of potential groundwater contamination

Metabolites not excluded in Step 1 → characterisation and identification

PEC_{gw} needs to be estimated with the highest feasible accuracy and validity

FOCUS Models → Data on degradation and sorption are required. Experimental data should preferably be used

Step 2

Lysimeter studies

Metabolites in the leachate with annual average concentrations > 0.1 µg/L

Attemp to assess their leaching behaviour in other European regions

Monitoring studies

Existing substances
Data from regions with well-documented use of the a.s.

Useful instrument lor modelling and/or lysimeter studies

Step 2

representative use-scenarios identified as safe

no → **Step 3**

yes

Active substance is eligible for further consideration of inclusion in Annex I

if at least one Member State indicates an interest in granting an authorisation.

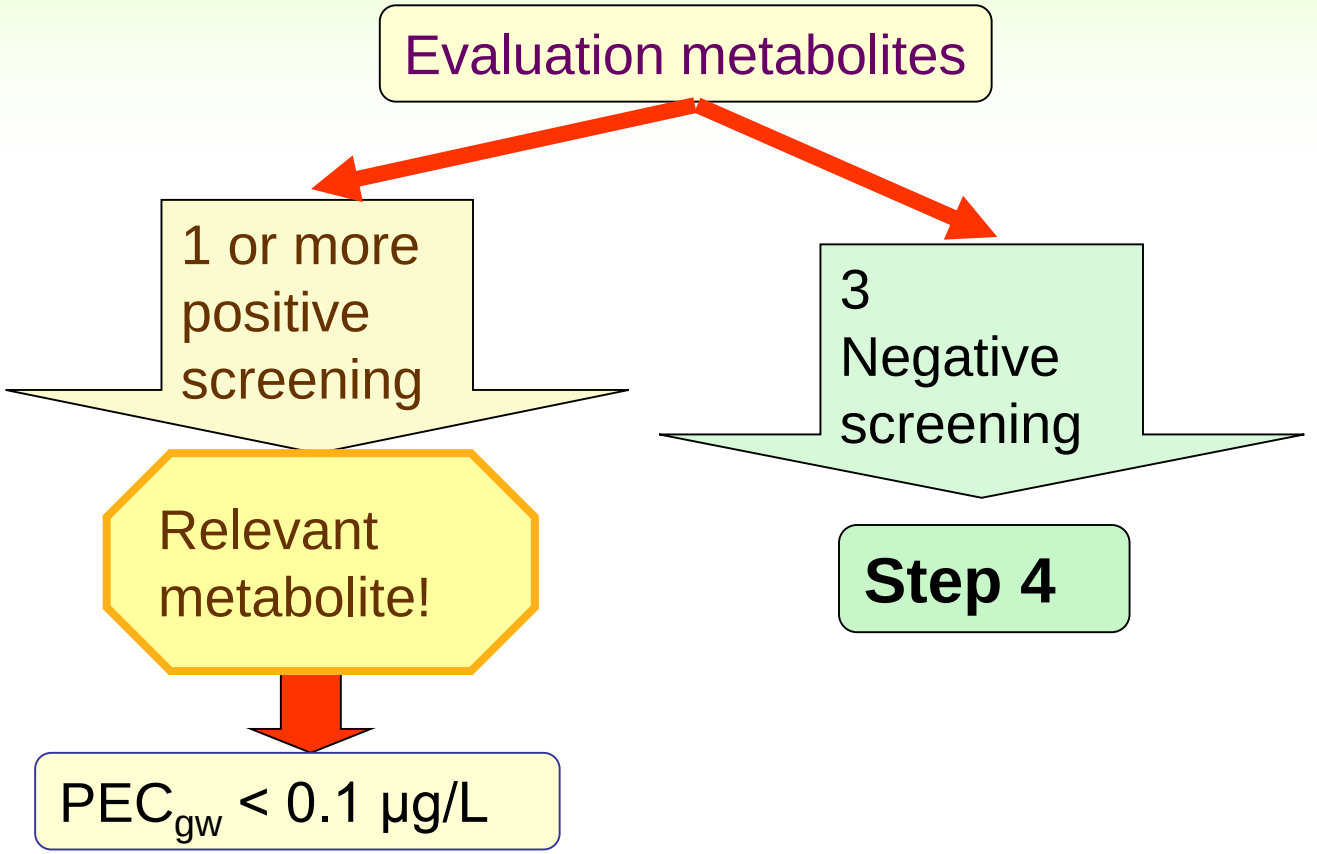
Possible "warning" to MS!!

The Review Reports for these substances will highlight this area of potential concern in such cases.

Step 3: Hazard Assessment: Identification of relevant metabolites

Stage 1:	Screening for biological activity
Stage 2:	Screening for genotoxicity
Stage 3:	Screening for toxicity

Step 3


Evaluation metabolites
1 or more positive screening
3 Negative screening
Relevant metabolite!
Step 4
PEC$_{gw}$ < 0.1 µg/L

Step 3 Stage 1: Screening for biological activity

To identify metabolites, which have a comparable target activity as the parent a.i.

In the absence of experimental data :
Structure-activity relationships
Behaviour chemical class

If no clear results: biological screening assays.
Refinement: maximum application rate based on a molar equivalent compared to the a.s..

Step 3 – Stage 1

Effect of metabolite against a range of target organisms. Comparison with a.i.

great precision not always possible in screening assays

Biological activity metabolite clearly < 50% a.i.

yes

Non biological active

Stage 2

n

relevant

Step 3 Stage 2: Screening for genotoxicity

in vitro screening studies

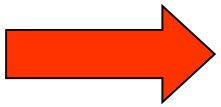
Ames test
Gene mutation test with mammalian cells
Chromosome aberration test

Equivocal results in *in vitro* → *in vivo* experiments

Mutagenic metabolites (any category) → Relevant!

Step 3 Stage 3: Screening per tossicità

A metabolite is considered “relevant” if its toxicological properties lead to a classification as toxic of very toxic (T o T^+)



the toxicity classification of the parent a.s. (Directive 67/548/EEC) is used for pragmatic reasons as a starting point to focus the screening activity.

Step 3 – Stage 3

Parent a.i. toxic or very toxic (acute and cronic):
T and R25, R24, R23, or R48;
$T^+$and R28, R27, R26 or R39

the acute or chronic toxicity of the metabolite must be determined

if metabolite T or T^+ → relevant!

Step 3 – Stage 3

Parent a.s., which are classified for reproductive toxicity (any category with R60, R61, R62, or R63)

appropriate test or convincing other evidence that the metabolite does not qualify for the same classification

metabolite with any classification + R60, R61, R62, o R63

relevant!

Step 3 – Stage 3

parent a.s. classified as category 1 or category 2 carcinogens (Carc Cat. 1 o Carc. Cat. 2 + R45)

all metabolites are considered to be “relevant !

parent a.s. classified as category 3 carcinogens (Carc. Cat. 3; R40)

convincing evidence must be provided that the metabolite will not lead to any risk of carcinogenicity

Step 3

independent of the classification of the parent a.s., if there is reason to expect that a metabolite may be toxic or highly toxic,

a targeted testing may be necessary

Metabolites “non relevant” according Step 3

Step 4

Step 4 Exposure assessment - threshold of concern approach

Non relevant metabolite ⇒ **Assessment of consumer exposure**

Pragmatical approach : threshold of concern

substances of unknown structure

Threshold of
1.5 μg/person/day
(0.02 μg/kg b.w./day)

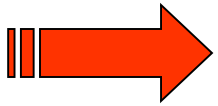
Step 4 Exposure assessment

Assuming a consumption of 2 liters of water (groundwater) per day

Evaluation of metabolite intake via other sources (e.g.: residues in diet)

Exposure < 0.02 μg/kg b.w./day

acceptable estimated upper limit for the concentration of a metabolite



0.75 μg/L
or less if there are other sources of exposure

Step 5 Refined risk assessments for non-relevant metabolites

Non relevant metabolites according step 1 to 3 with groundwater estimated concentration (Step 2) between 0.75 µg/L (Step 4) and 10 µg/L

require a refined assessment of their potential toxicological significance for consumers

must be fully identified and also synthesised by the notifier

Step 5

Appropriate strategy for the assessment to be developed on a case-by-case basis in collaboration between the notifier and the RMS

Possibly, open questions should be addressed with information already available (animal metabolism, consideration of molecular structure …)

Expert judgement to determine the necessity of requiring additional information.

Groundwater concentration > 10 µg/L → No guidelines

Summary

Metabolites: substances crucial in evaluation of acceptability of a.s. and in drinking water quality evaluation

Guidance document on relevant metabolites:

- definition of "relevant"
- proposal of a stepwise evaluation

It is not accepted by all European countries

It is used "at personal discretion" in Italy

E-Fate evaluation
Air compartment

Air

How do pesticides get there?

- Pesticide are normally sprayed and may remain suspended for some time. Furthermore, some chemicals may volatilize from soil or from crop canopy after deposition. The rate of pesticide volatilisation from plants mainly depends on its **vapour pressure**, but it is also influenced by the rate of the **competing processes** (washoff, penetration into the plants, degradation).

How do pesticides move?

- The main carrier of volatilised pesticide is, of course, wind.

What might be affected?

- Potentially every living organism in the area of the treated field might be affected. However, due to the rapid degradation of newer pesticides in air (as well as on plants) and considering that atmosphere is a very dynamic compartment, with great volume, concentrations in air are usually not considered a major harm for ecosystems.

EXPOSURE: AIR

Volatilisation: loss in atmosphere of pesticide residues during and after field application; losses can ranges from 10% to 90%.

Volatilisation depends on:

- Vapour pressure
- Concentration
- Adsorption
- Humidity
- Temperature
- Wind speed at the soil surface

Volatilasation may occur from:

- Soil
- Water
- Leaves

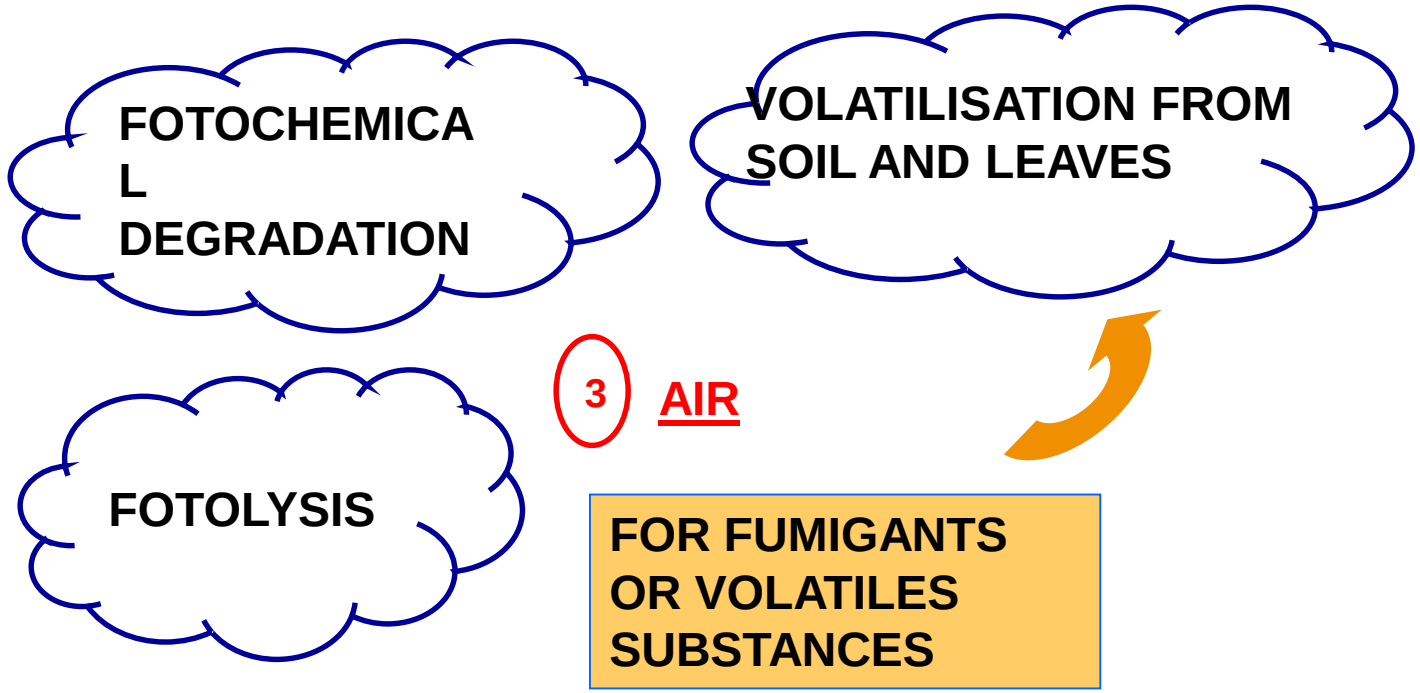
Ripartition coefficient water/air

$K_H = (V_p\ PM)/S$
K_H = Henry constant
V_p = solute partial pressure
PM = molecular weight
S = Solubility in water

- **Photochemical degradation**
- **Photolysis**

FATE AND BEHAVIOUR IN AIR

Route and rate of degradation



AIR ENDPOINTS

For a.i. and metabolites

- Direct photolysis in air
- Quantum yield of direct photo transformation
- Photochemical oxidative degradation in air
- Volatilisation