

**TERBUTHYLAZINE AND
DESETHYL-TERBUTHYLAZINE
IN GROUNDWATER:
MODELLING VERSUS MONITORING**

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Groundwater Daughter Directive (2006/118/EC) states that groundwater is a valuable natural resources and as such should be protected from deterioration and chemical pollution and sets groundwater quality standards (GQS) for pesticides, including relevant metabolites, as 0.1 µg/L for individual substances.

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our purpose was to

investigate the leaching of terbuthylazine (TBA) and desethyl-terbuthylazine (DES) in shallow groundwater in real conditions

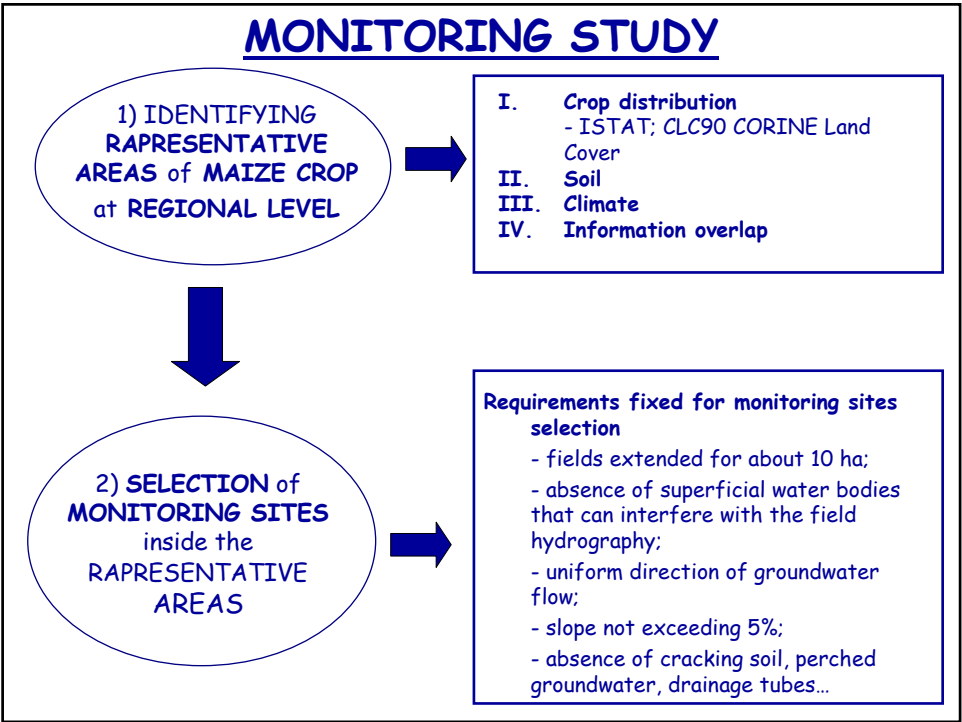
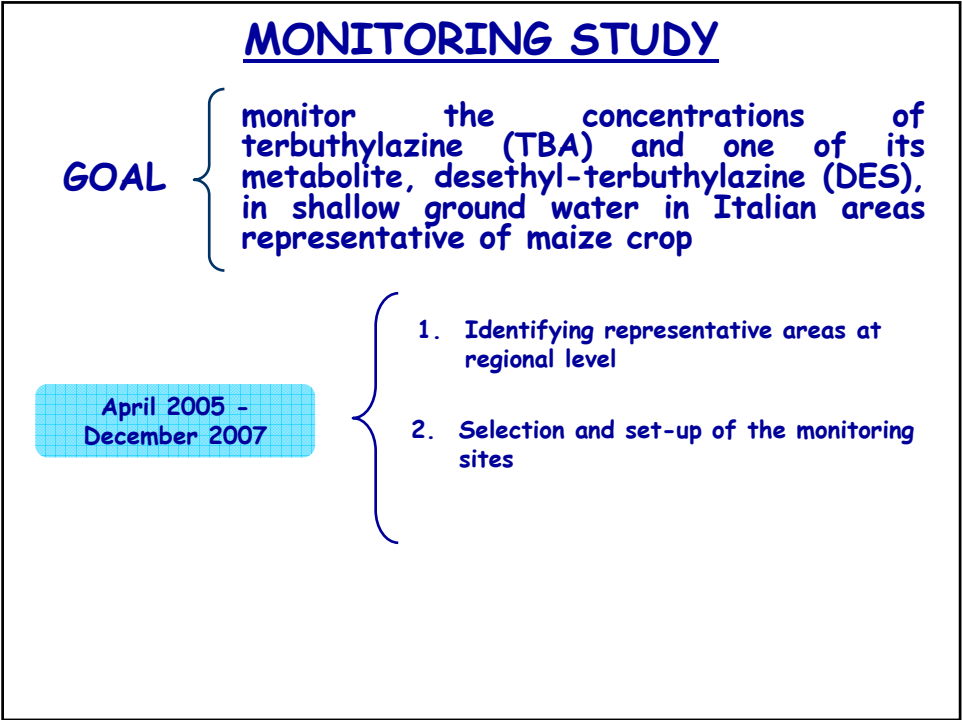
through

MONITORING

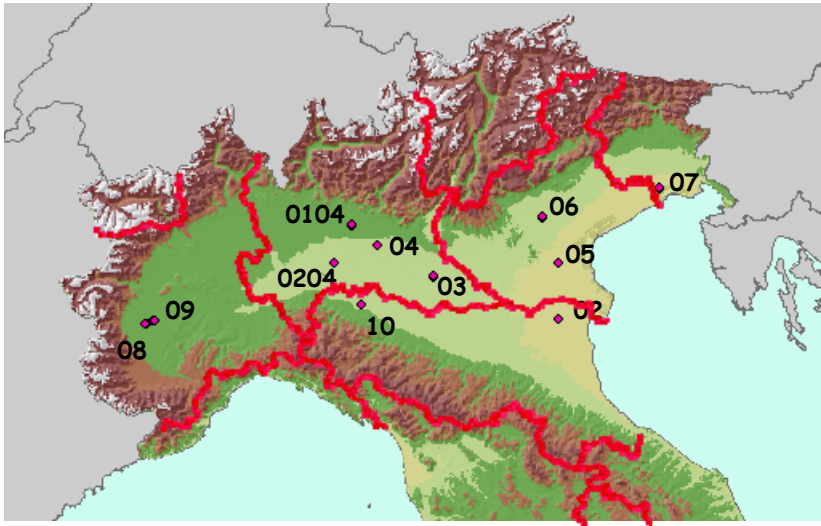
MODELLING

TBA→triazine herbicide, pre-emergent and early post-emergent selective weeds control in several crops, among which maize, its prominent dealkylation product is DES.

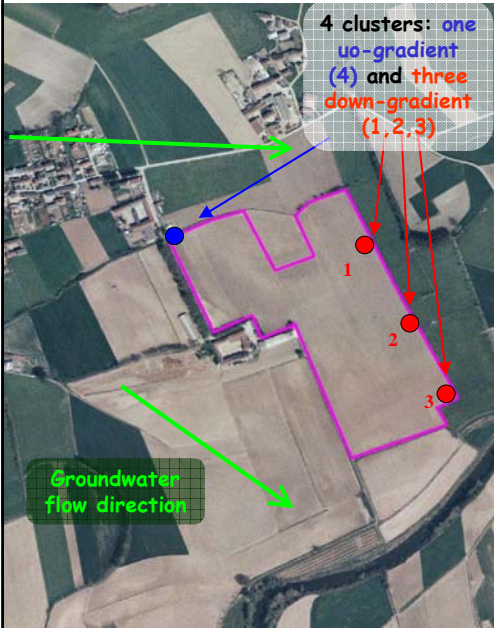
Dealkylated products are generally more persistent and water soluble → can represent a hazard to groundwater contamination



MONITORING SITES LOCALIZATION



MONITORING SITES SET-UP



- 1) **Hydrology study:** to place the piezometers according to the groundwater flow direction, and to calculate the piezometers depth so that they were deep enough to sample shallow groundwater
- 2) **Installation of 8 piezometers** grouped in four clusters
- 3) **Installation of field meteorological stations** to measure daily rainfall, temperatures, and groundwater table depth

MONITORING SITE CHARACTERISTICS

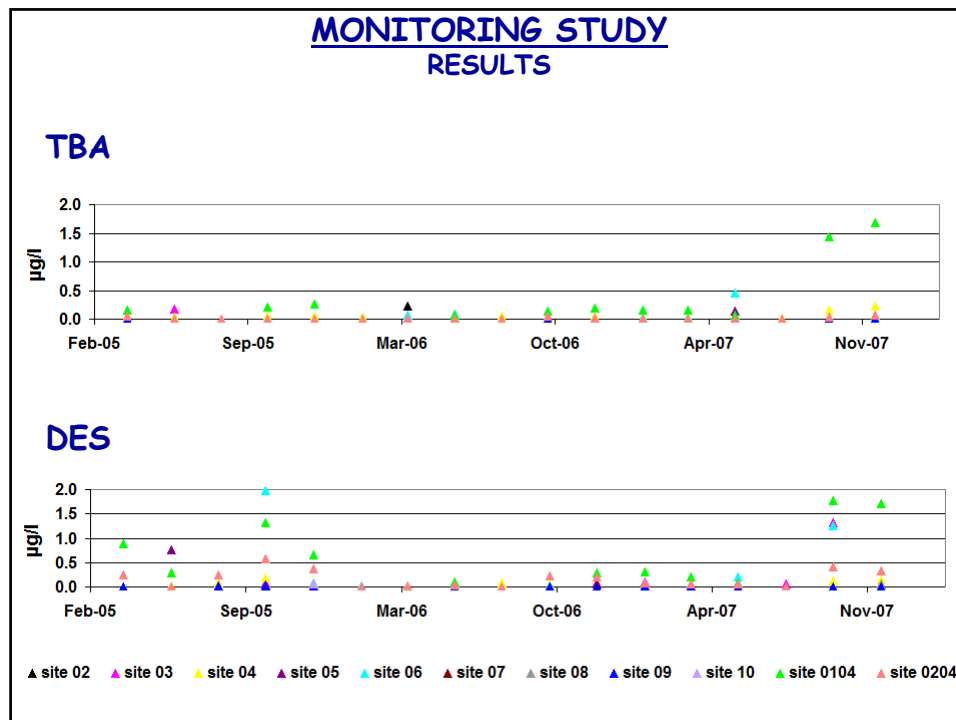
<i>Texture (USDA)</i>	<i>Organic carbon %</i>	<i>Irrigation System</i>	<i>Ground water table depth (m)</i>	<i>Average annual rainfall (mm)</i>
2 loam, 2 clay loam, 5 sandy loam, 1 silty clay loam, 1 sandy clay	0.8 - 1.7	no irrigation, sprinkling, border, basin	0.20 - 7.0	410 - 1073

MONITORING STUDY

GOAL { monitor the concentrations of
terbuthylazine (TBA) and one of its
metabolite, desethyl-terbuthylazine (DES),
in shallow ground water in Italian areas
representative of maize crop

April 2005 -
December 2007

- 1. Identifying representative areas at regional level
- 2. Selection and set-up of the monitoring sites
- 3. Samplings (every two months)



MONITORING STUDY
CONCLUSIONS

- low concentrations of TBA and DES in groundwater
- DES concentrations > TBA concentrations
- periods of low or undetectable concentrations, punctuated by periods of higher concentrations. These seasonal patterns identify the occurrence of the highest concentrations of pesticides and then when waters are potentially contaminated

However, some questions arose...

1. Did a "dilution effect" due to lateral recharge occur?
2. Was the sampling time appropriate?
3. Was the length of the monitoring adequate in order to investigate the metabolite leaching in time?



MODELLING STUDY

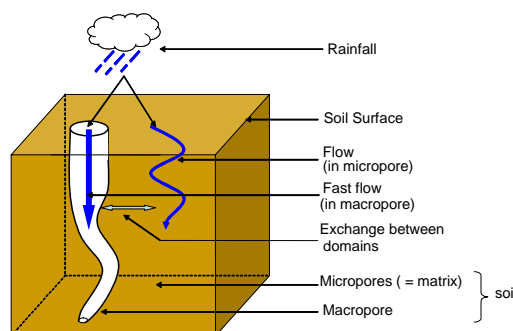
a scenario was set in each of the eleven sites monitored
from 2005 to 2007

- using:**
- ✓ pesticide fate model MACRO
 - ✓ data coming from the monitoring
 - ✓ soil core and reference profiles
 - ✓ different PTFs

THE MODEL: MACRO - Version 5.1

MACRO is a mechanistic one-dimensional model which considers preferential flow (i.e. 'micropores' and 'macropores') to describe the transport of water and solutes in soils

- Richard's equation → vertical movement of water in micropores
- a modified form of van Genuchten function → soil water retention in micropores
- Mualem model → hydraulic conductivity
- transport of solute in micropores → convection-dispersion equation; in macropores → dominated by convection
- Freundlich isotherm → partitioning of reactive solutes between liquid and solid phases
- first-order kinetics → degradation



MODELING STUDY STEPS

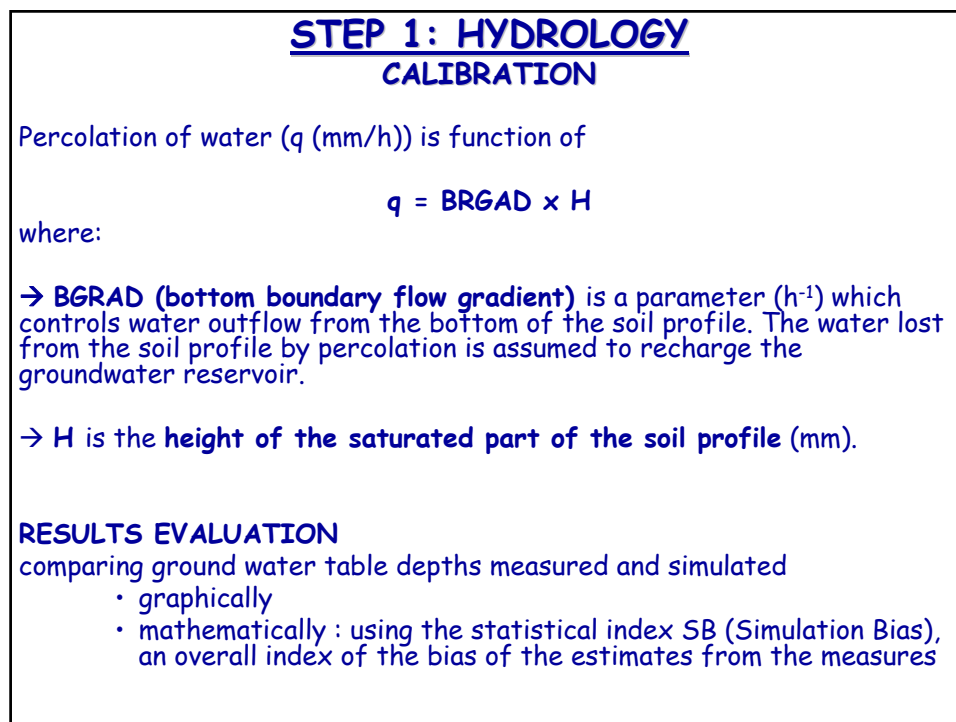
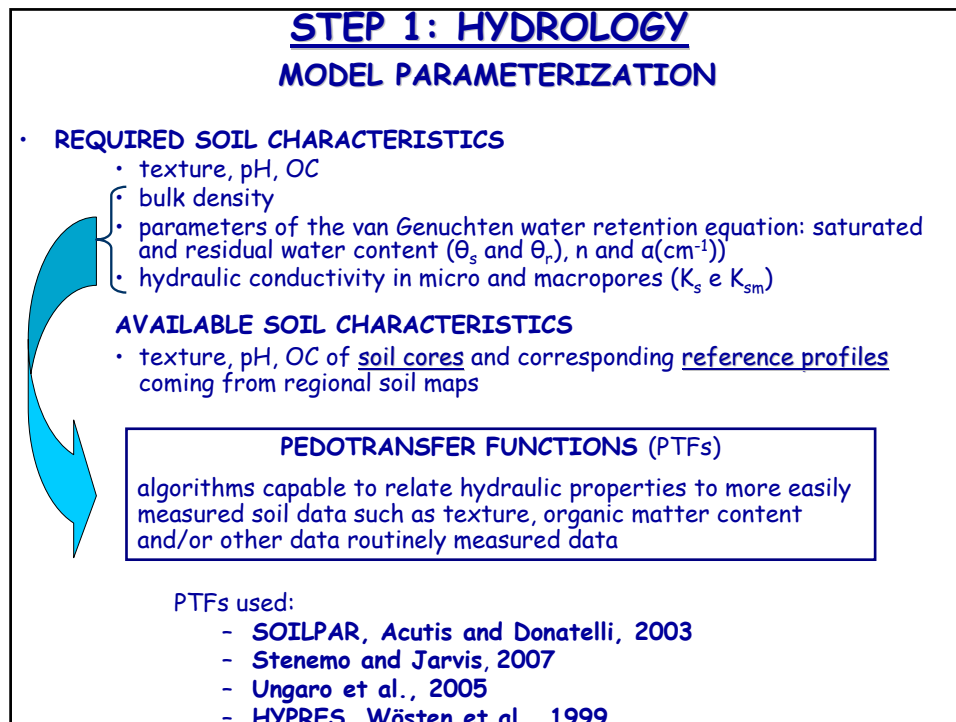
STEP 1. WATER MOVEMENT CALIBRATION

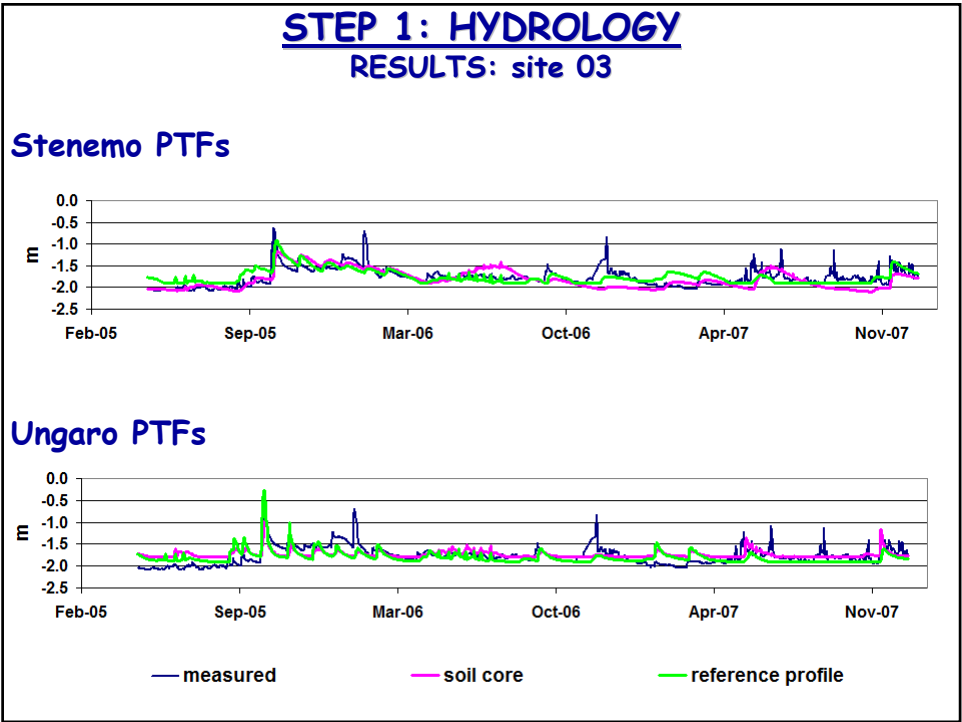
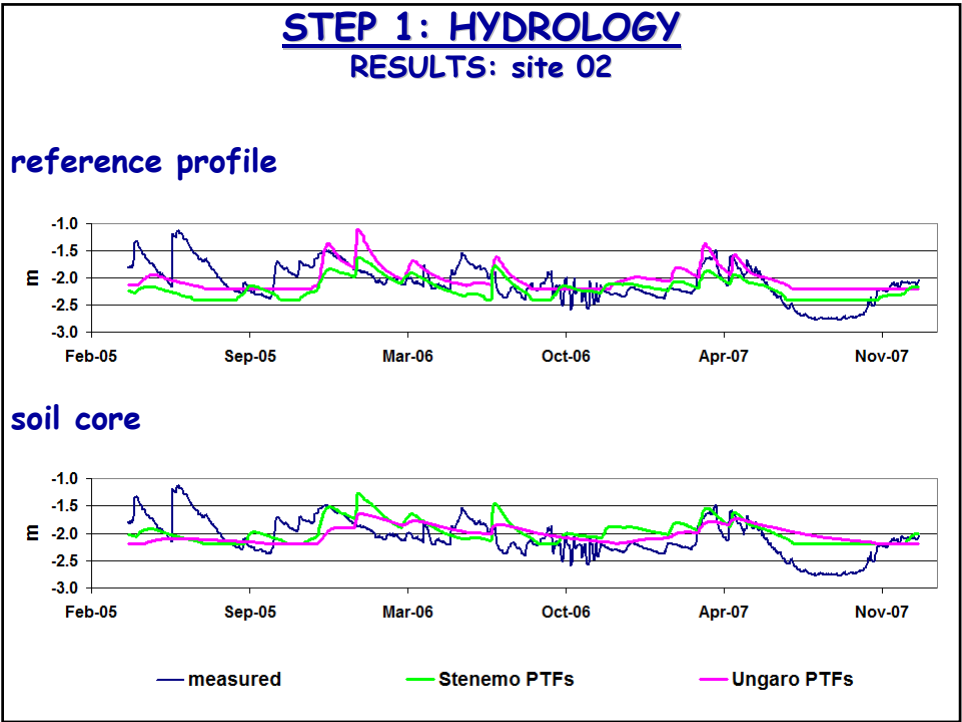
STEP 2. TERBUTHYLAZINE SIMULATION

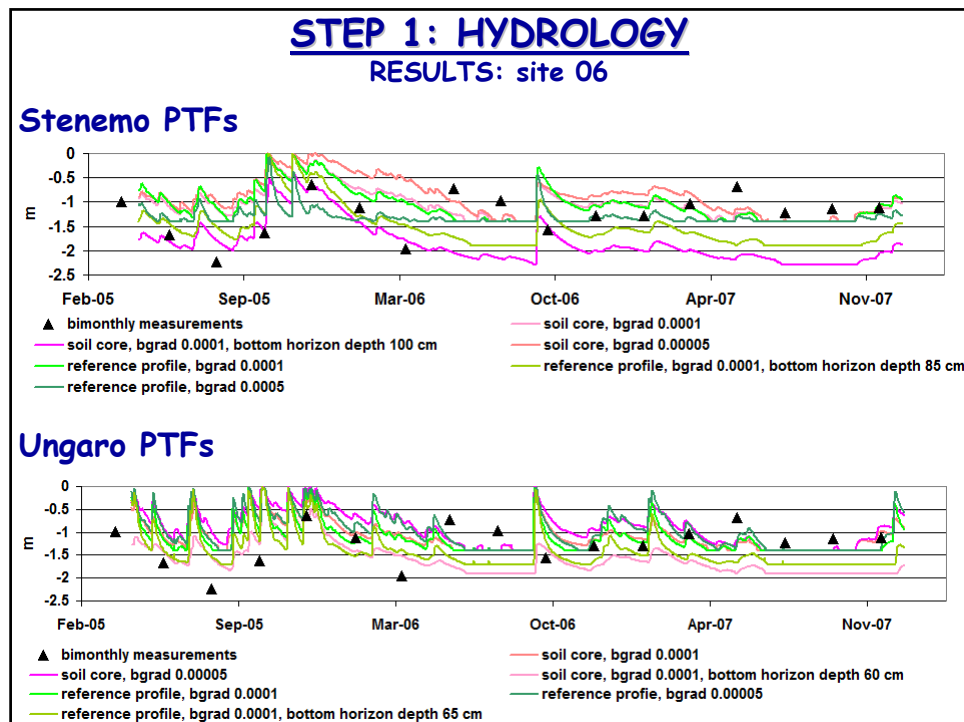
STEP 3. DESETHYL-TERBUTHYLAZINE SIMULATION

STEP 1: HYDROLOGY
MODEL PARAMETERIZATION

- **PERIOD:** 2005 - 2007
 - **CROP:** maize monoculture
 - **METEOROLOGICAL DATA**
 - rain, Tmin and Tmax
 - wind speed, relative humidity and solar radiation
 - vapour pressure
 - **GROUND WATER TABLE DEPTH**
 - **IRRIGATION**
- } potential evapotranspiration







STEP 1: HYDROLOGY

CONCLUSIONS

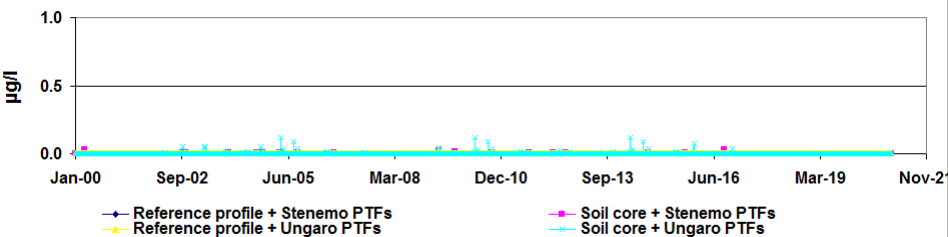
- simulation results fitted quite well with the measured data, then the groundwater level was function of time
- calibration not succeeded only for one site out of eleven. This case means that hydrological equilibrium is not given only by precipitation/irrigation and evapotranspiration, then lateral or bottom recharge and a consequent dilution effect can be assumed
- slight differences between Ungaro and Stenemo PTFs
- slight differences between soil cores and reference profiles

STEPS 2 and 3: TBA and DES SIMULATIONS
MODEL PARAMETERIZATION

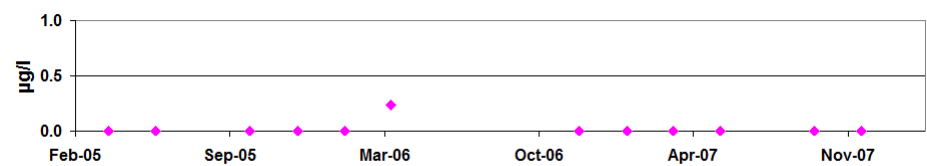
- **PERIOD:** 20 years → data randomized from available historical meteorological data
- **METEOROLOGICAL DATA:** regional stations
- **RESULTS**
 - water flow in macro and micropores
 - solutes flow in macro and microporesat 1m depth in order to calculate leacheate concentrations

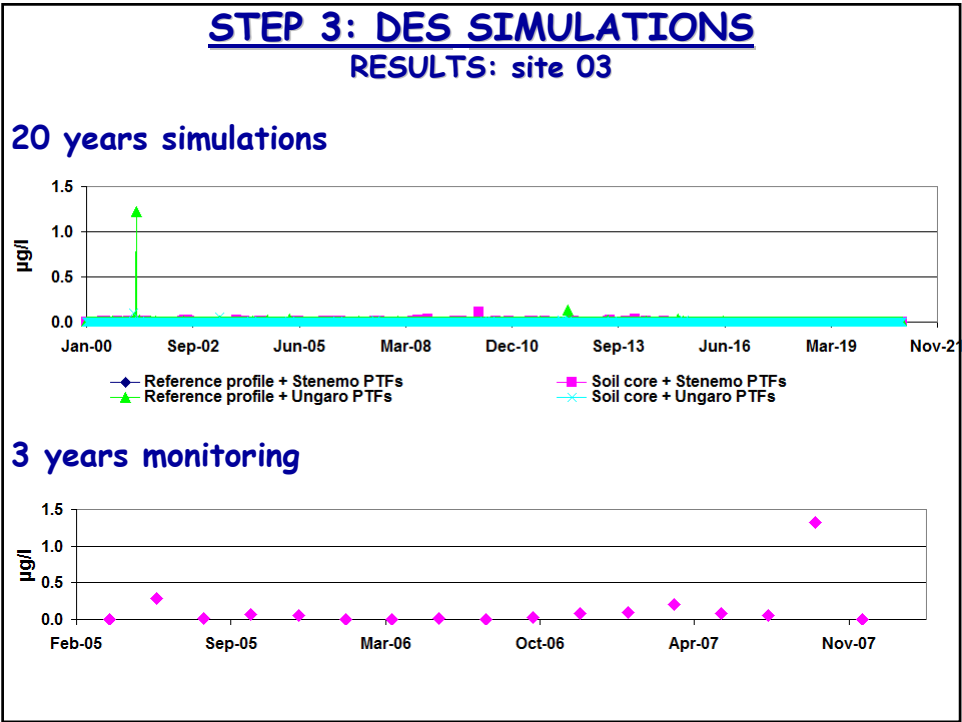
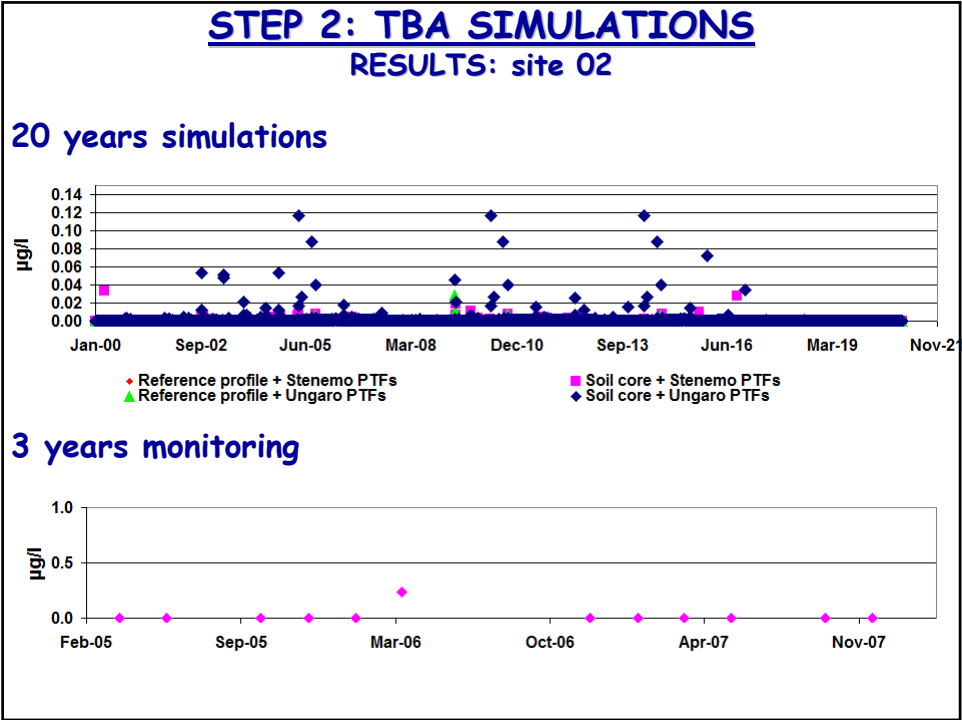
STEP 2: TBA SIMULATIONS
RESULTS: site 02

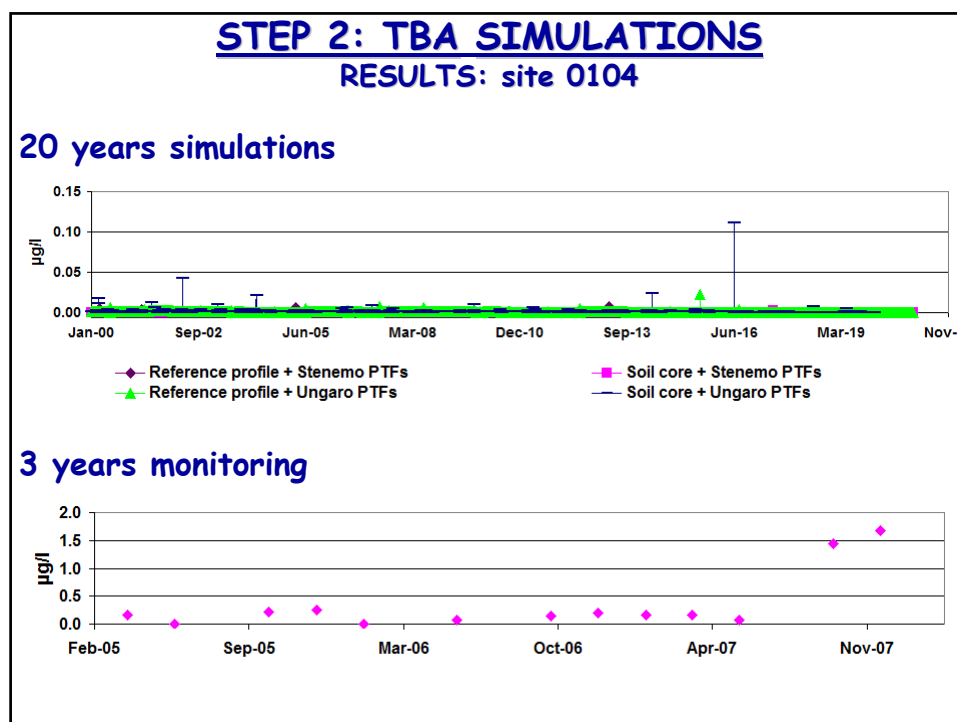
20 years simulations



3 years monitoring







STEPS 2 and 3: TBA and DES SIMULATIONS
CONCLUSIONS

- in general simulation results gave concentrations with the same order of magnitude of the measured concentrations, except for site 0104 where measured concentrations resulted to be always higher than the simulated ones (1 compared to 0.1 $\mu\text{g/l}$)
- the monitoring study resulted to be adequate in length and frequency of sampling
- simulations confirmed that DES is more mobile than TBA
- monitoring length was enough in order to individuate the peak of metabolite leaching

GENERAL CONCLUSIONS

- model resulted to be a useful tool to support a monitoring study in order to optimize the monitoring length and the sampling frequency
- reference profiles coming from the regional soil maps resulted to be representative of the reality, and then they can be also used in order to model wider areas (es FITOMARCHE)
- the model chosen was not able to simulate all the situations, and then in order to have a more complete study it could be better to use different models

Acknowledgments

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