



# XIV Symposium in Pesticide Chemistry

Pesticides in the environment: fate, modelling and risk mitigation

## PESTICIDE TRANSFER IN THE UNSATURATED ZONE: SORPTION AND DEGRADATION PROCESSES EXPERIMENTATION

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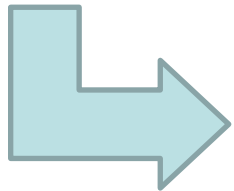
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# Introduction

- Models need to describe transfer processes of pesticides in all compartments
- Lots of studies in soils, water
- The unsaturated zone considered as passive transfer
- However, unknown stock of pesticides in catchments



**Need to better describe the unsaturated zone :**

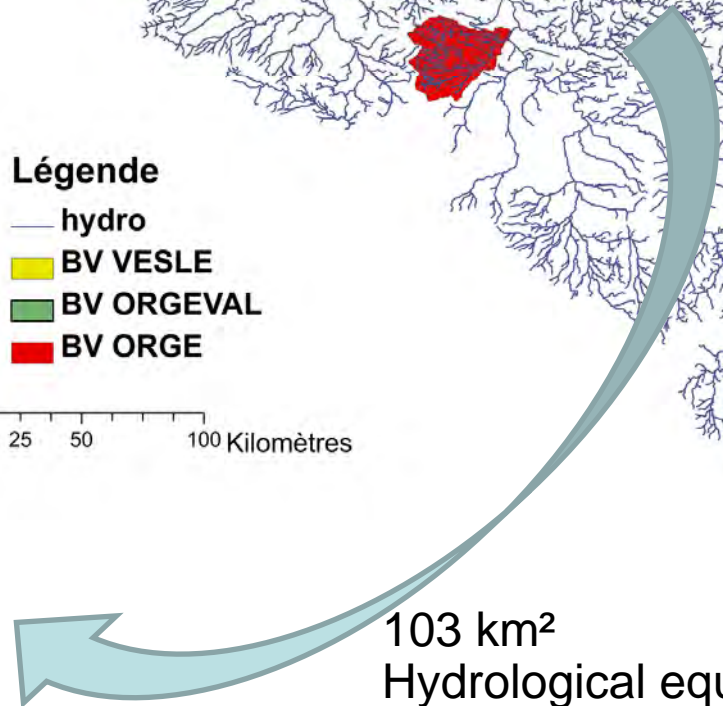
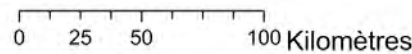
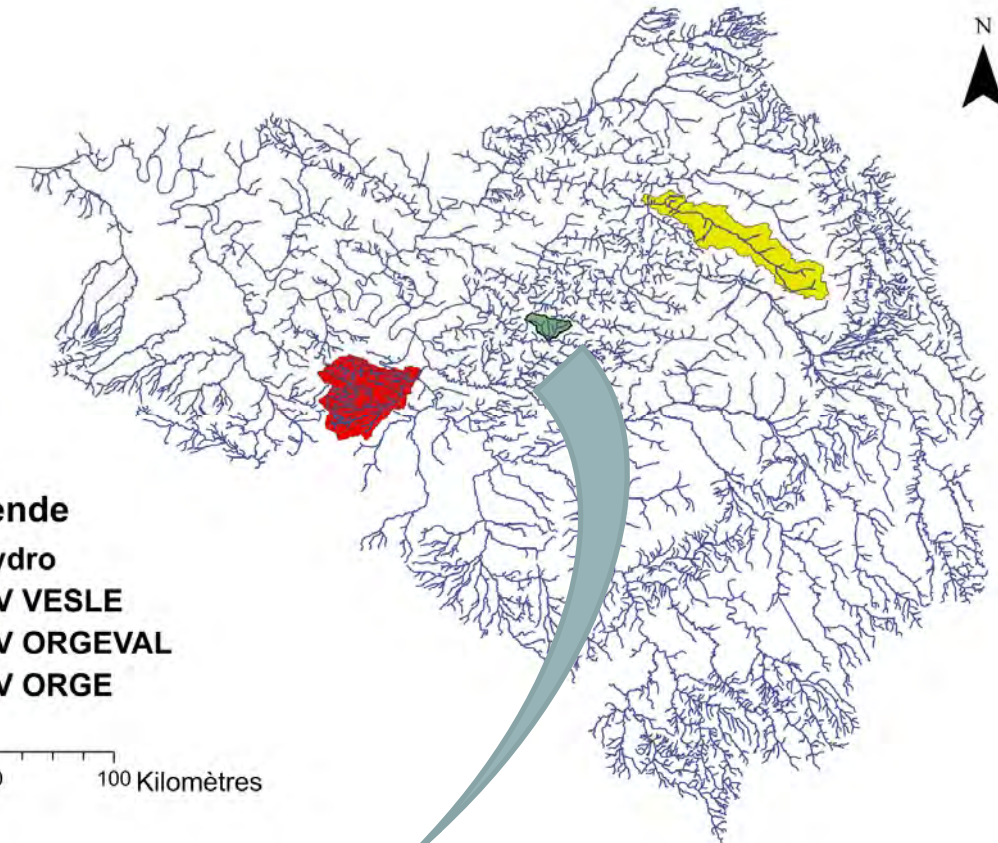
**Sorption processes of pesticides**

**Degradation processes**

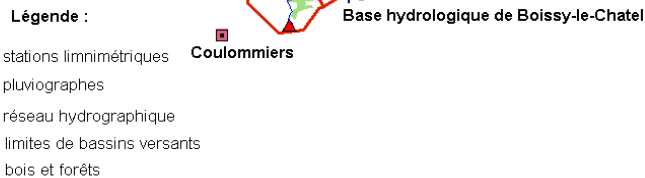
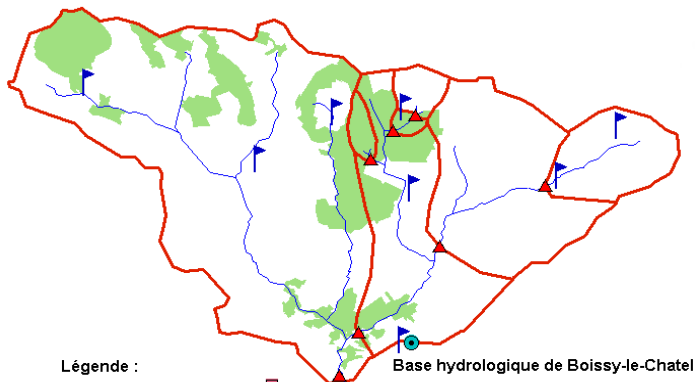
# The Orgeval catchment

The PIREN Seine Program:  
3 sites for pesticides studies

The Orgeval catchment  
for the soil-groundwater-  
river system studies

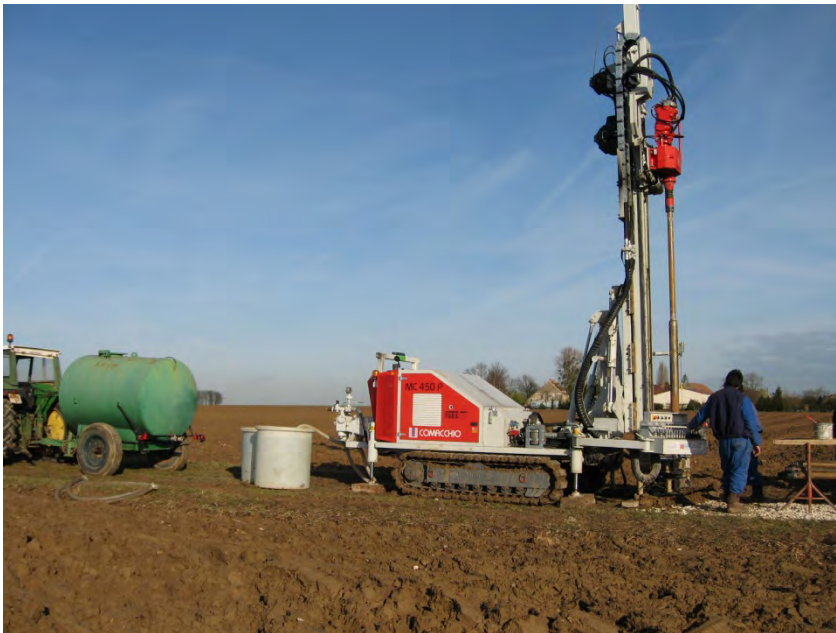


103 km<sup>2</sup>  
Hydrological equipment since 1962  
Mainly agricole  
81% culture  
18% forest  
1% urban area



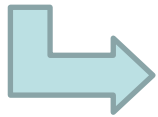
# The Orgeval catchment

- New studies: The Phyt'Oracle Project (CNRS funding)
- Pesticide uses description and crop studies
- Core sample until groundwater (FIRE 3020 funding)
- Long term observation of contamination of groundwater and river by pesticides
- Modeling chain development : The Eaudyssée Platform

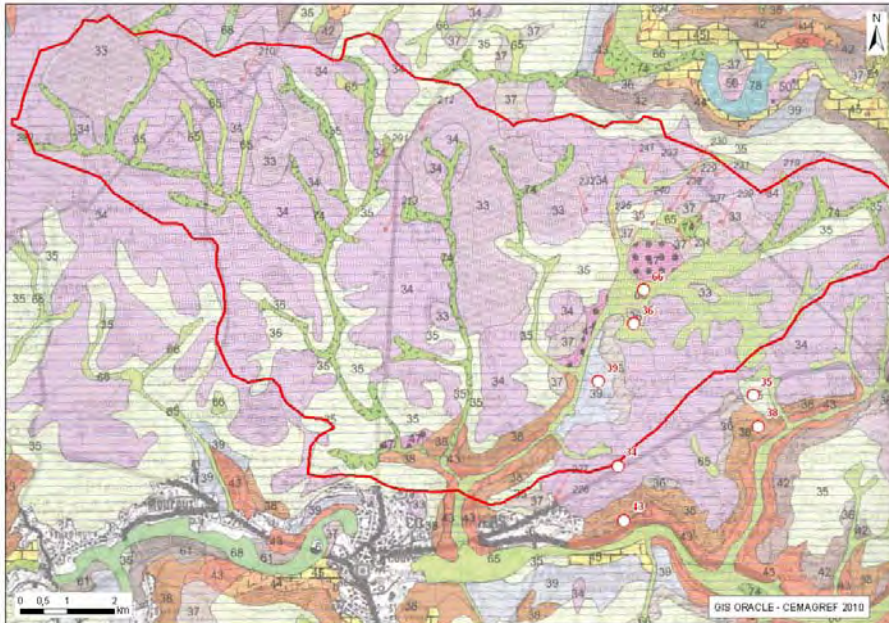


# Sampling procedure

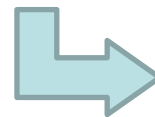
- Core samples over 40m depth in 2008
- Layer characteristics
- Measure of adsorption
- Measure of degradation kinetics : mineralisation and by products formation
- Bacterial community profiling (second core sampling in 2011)



**Description of pesticide behaviour in the unsaturated zone**



- Sorption and degradation in soils (2009)
- Monthly pesticide contamination in river and piezometers (since 2008)



**Data collection for modeling and comparison with the unsaturated zone**

- Adsorption procedure

- $^{14}\text{C}$  U-ring labelled atrazine and isoproturon (only isoproturon for surface soils)
- Triplicate 10ml water (with 2mg pesticide) to 2g of dried soils (about 10mg/kg)
- 24h shaking (dark and room temperature)
- Centrifugation (10 min.)
- Supernatant sample for radioactivity measure (compteur Tri-Carb 2100TR Packard)

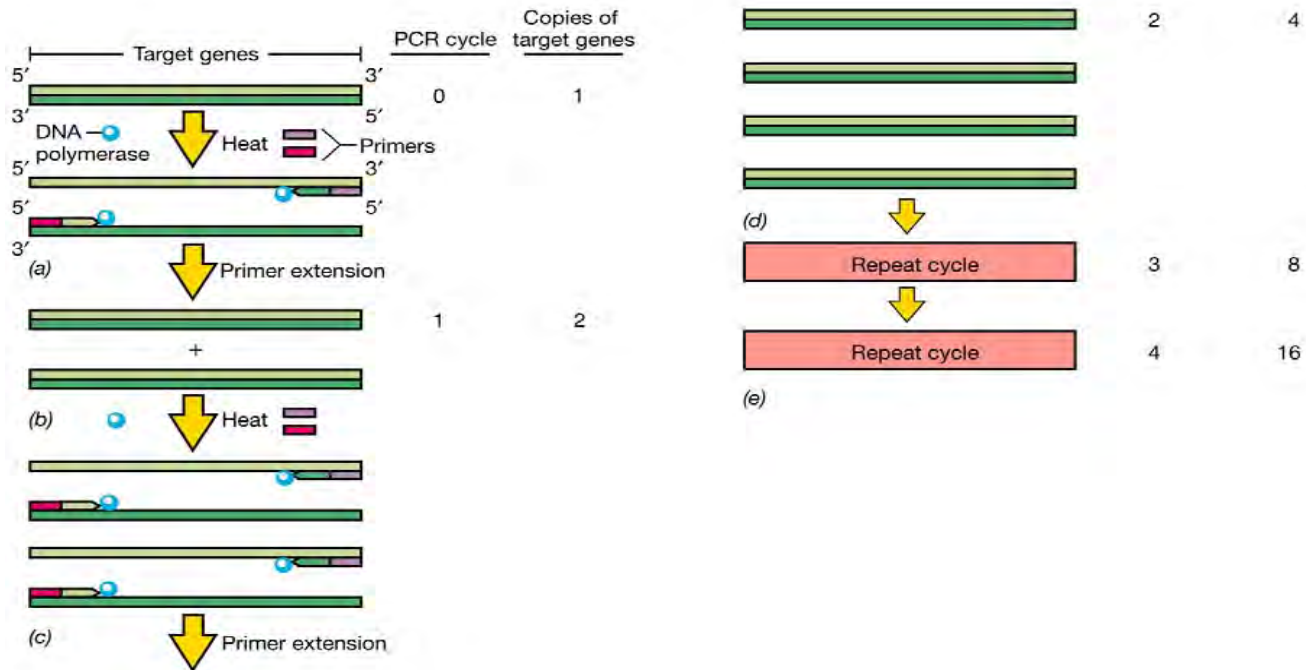


- Degradation procedure

- $\text{C}^{14}$  U-ring labelled atrazine and isoproturon (only isoproturon for surface soils)
- Triplicate 10g of dried soils for each pesticide and each date of incubation
- Add 1ml water containing about 11mg/L of each pesticide
- Put in a 500ml hermetic jar with 1 beaker of water (humidity control) and 1 with 3 ml of  $\text{NaOH}$  2N ( $^{14}\text{CO}_2$  capture) in dark at  $28^\circ\text{C}$  during incubation times: 7, 14, 28 & 70 days
- Triplicates sacrificed for each incubation date and extracted 1 time with water containing  $\text{CaCl}_2$   $10^{-2}$  mole/L and 3 times with methanol for radioactivity measure (compteur Tri-Carb 2100TR Packard) and residues analyses (HPLC: diode array detector, Waters)

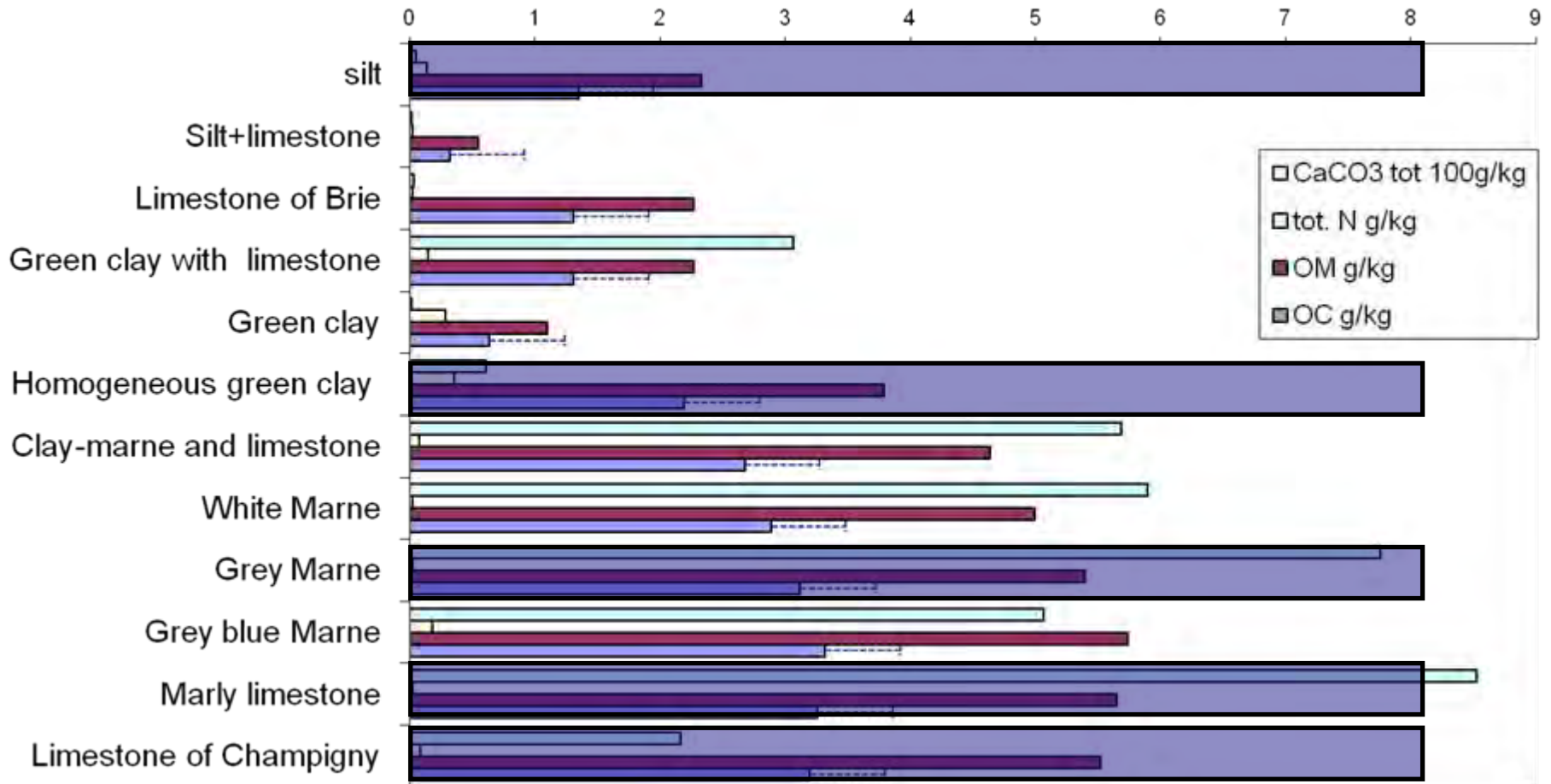
# Materials and method

- Bacterial community profiling by PCR (Polymerase Chain Reaction)



- Samples were collected in another core sampled in 2011
- DNA extractions were done in duplicate, consequently 2 profiles of each depth
- PCR with 16S RDNA targeting primers (3 different trials to get enough PCR product)

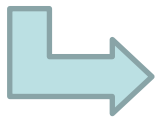
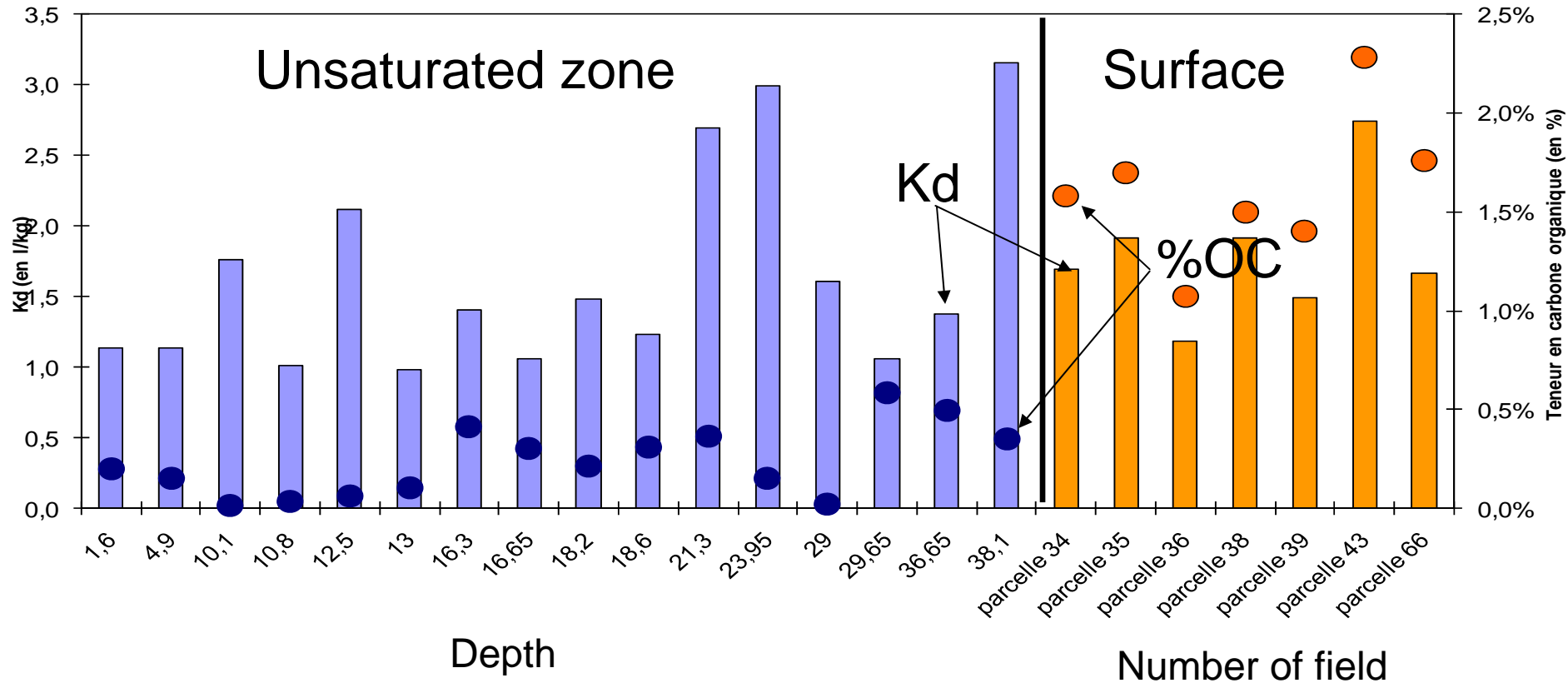
# Layers composition



Adsorption in each layer (16 samples)  
 Degradation until 70 days (5 samples)



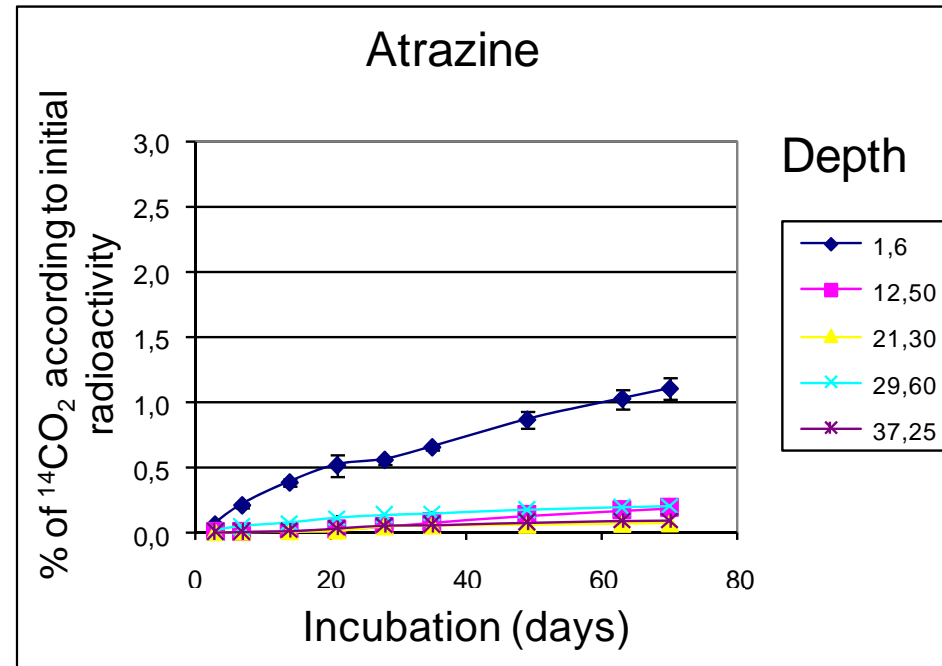
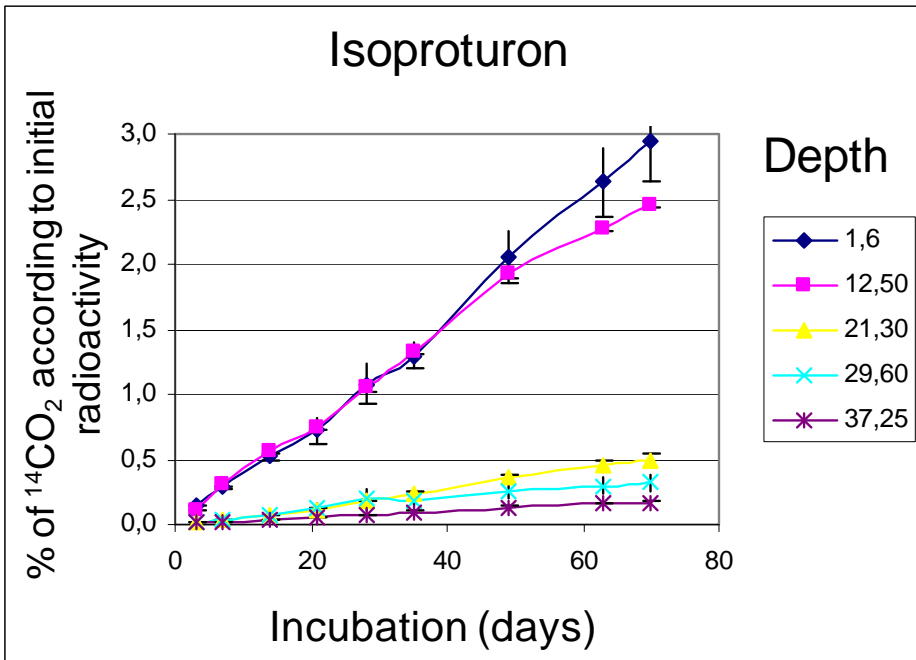
# Results : Isoproturon Sorption



Low % of organic carbon in the unsaturated zone (ZNS)  
Same  $K_d$  for isoproturon in soils and the unsaturated zone

# Results : Mineralisation rate

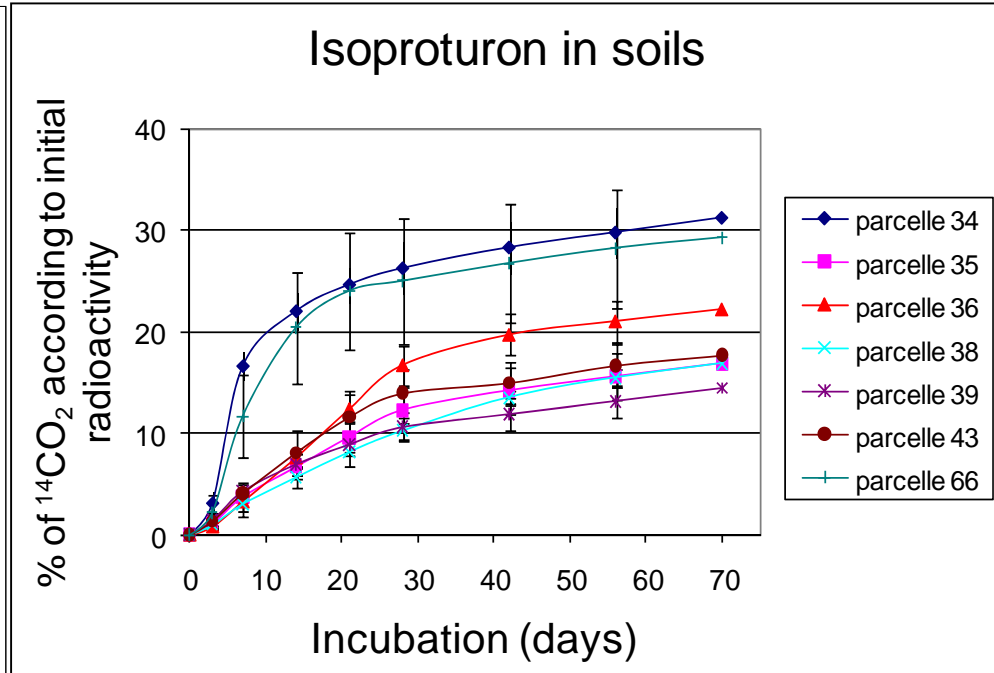
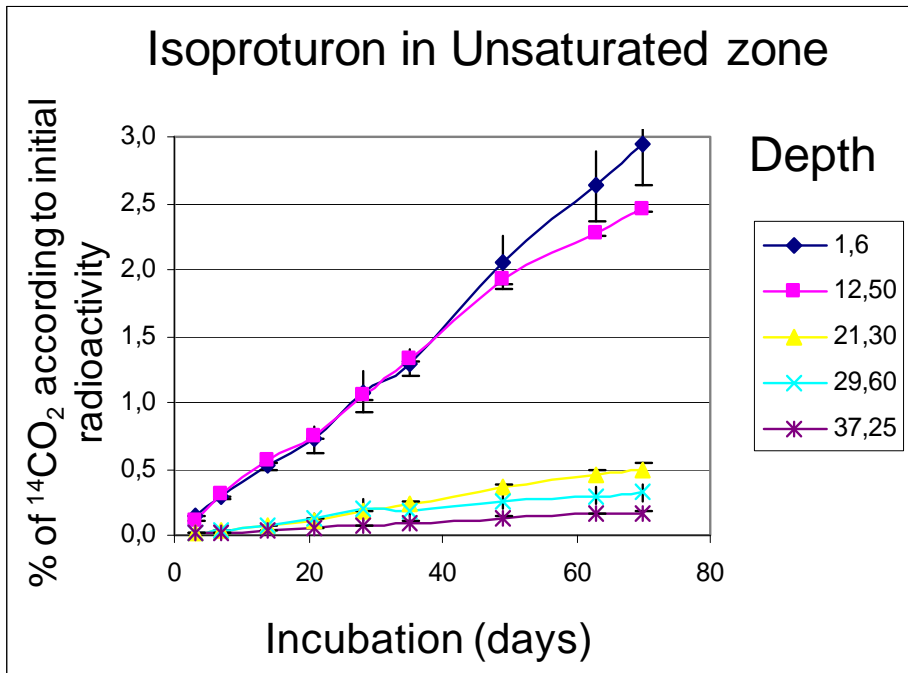
In the unsaturated zone :



Low mineralisation after 70 days :  
1% for atrazine, 3% for isoproturon in upper layers,  
Less than 0,5% in deeper layers

# Results : Mineralisation rate

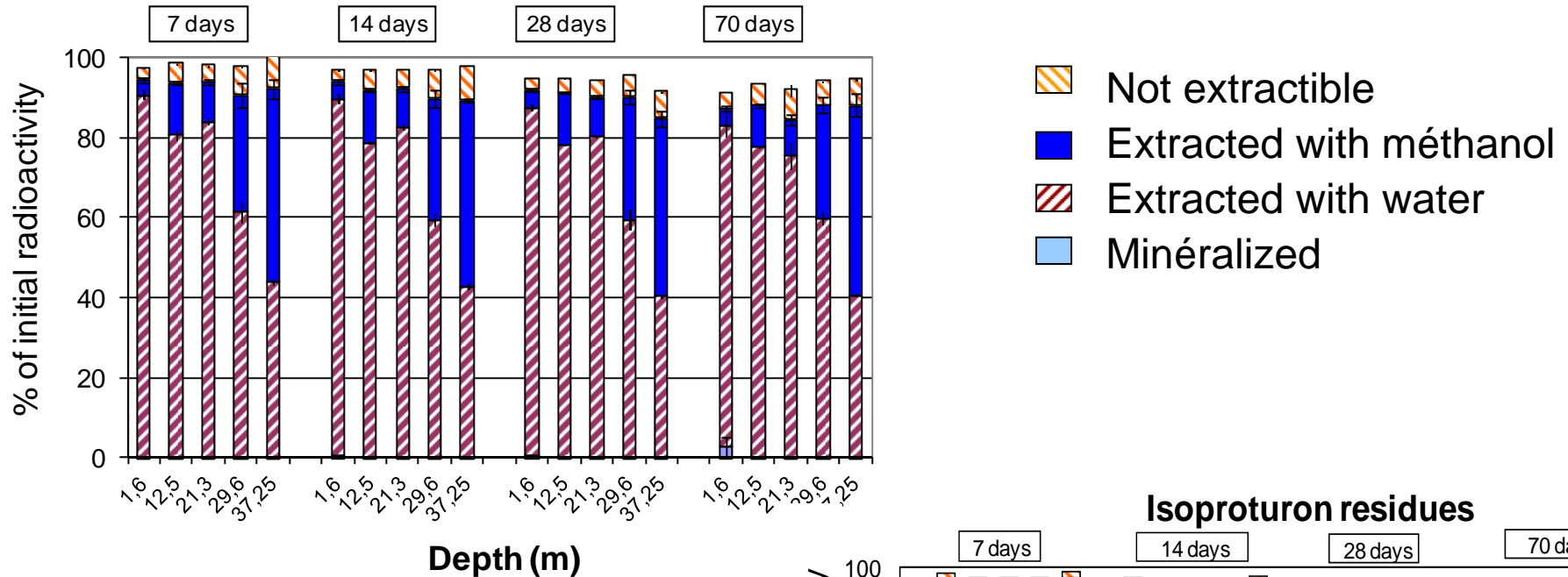
Comparison between the unsaturated zone and soil surface :



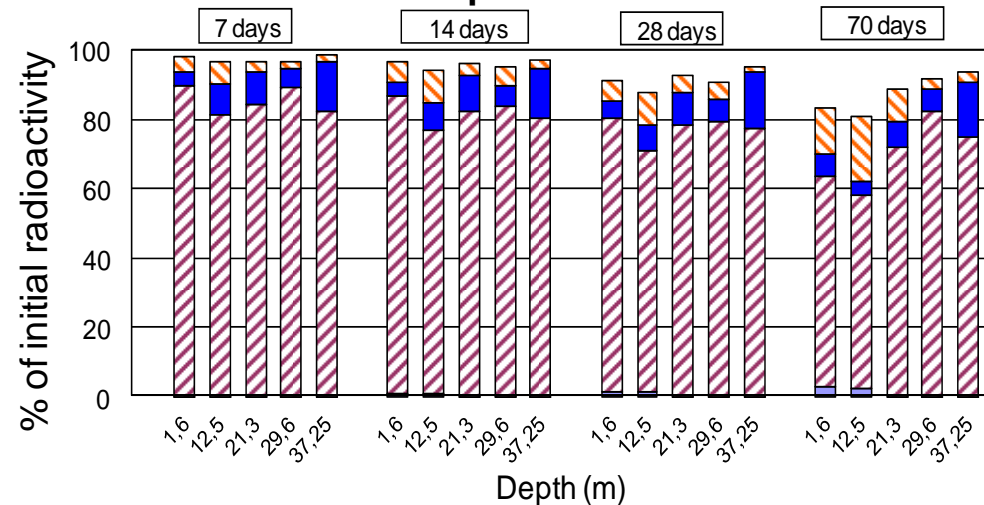
Low mineralisation in the unsaturated zone compared with soils  
Soil mineralisation between 15 and 30% of initial quantities

# Results: Disponibility of residues

## Atrazine residues



## Isoproturon residues

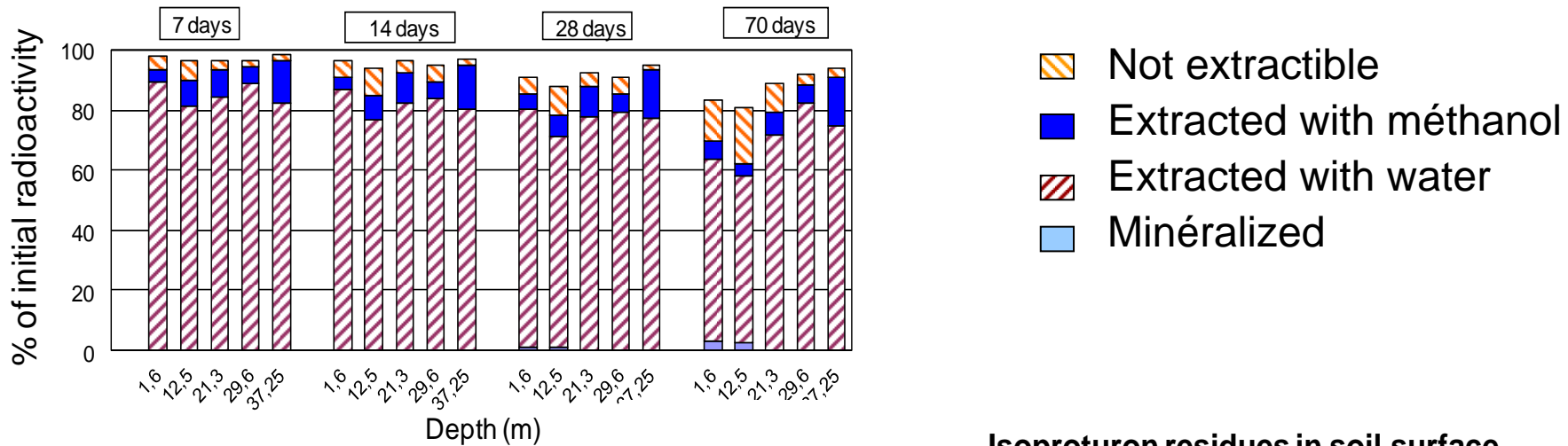


➡ No change of the disponibility during incubation  
Residues are mainly extracted with water  
**No bound residues in the unsaturated zone**

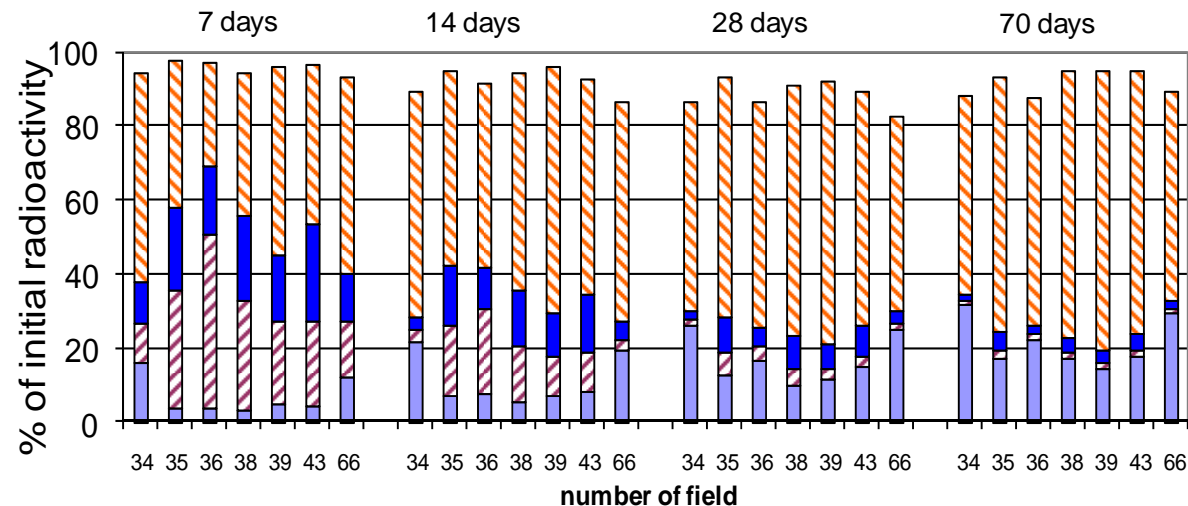
# Results: Disponibility of residues

Comparison between the unsaturated zone and soil surface :

Isoproturon residues in the unsaturated zone



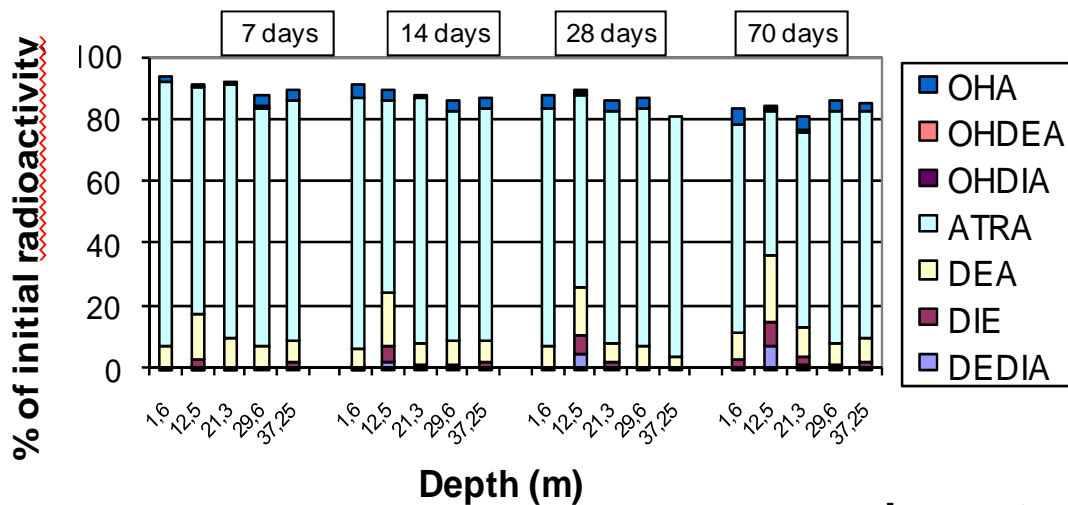
Isoproturon residues in soil surface



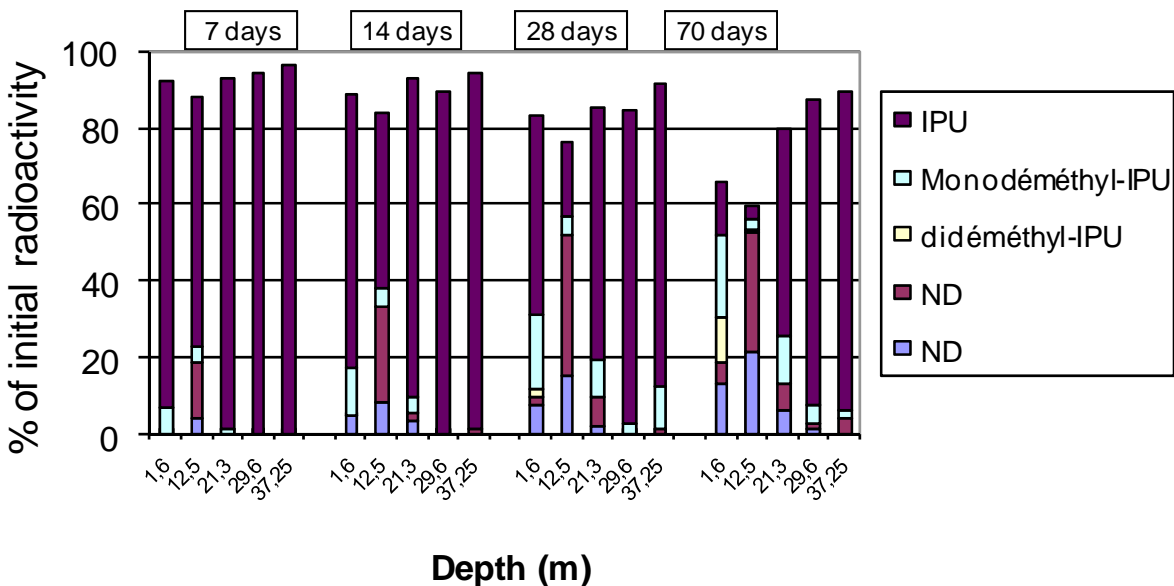
➔ Larger bound residues in soils  
Extracted residues decrease from 7 to 28 days in soils

# Results: Identification of extracted residues

## Atrazine residues



## Isoproturon residues



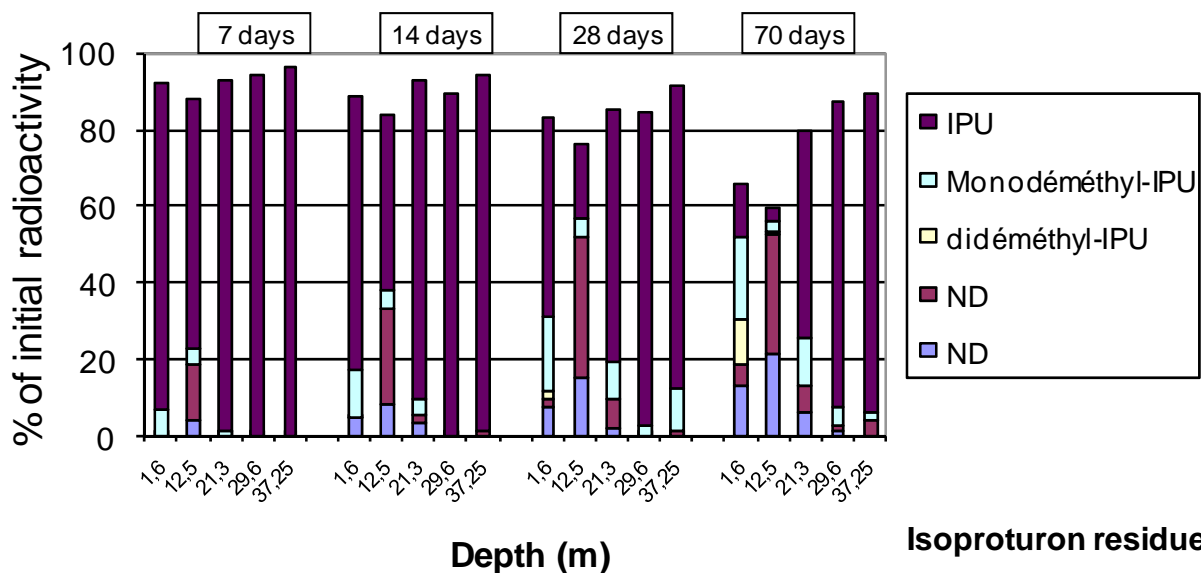
Mainly the active substances, mainly in deeper layers  
More by-products in the upper layer



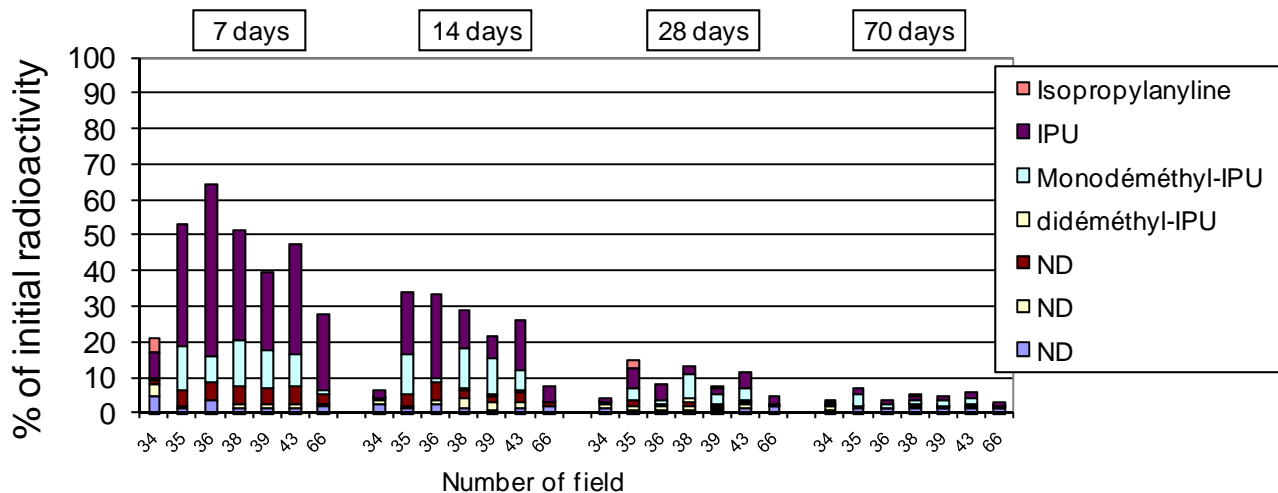
# Results: Identification of extracted residues

Comparison between the unsaturated zone and soil surface :

### Isoproturon residues in unsaturated zone

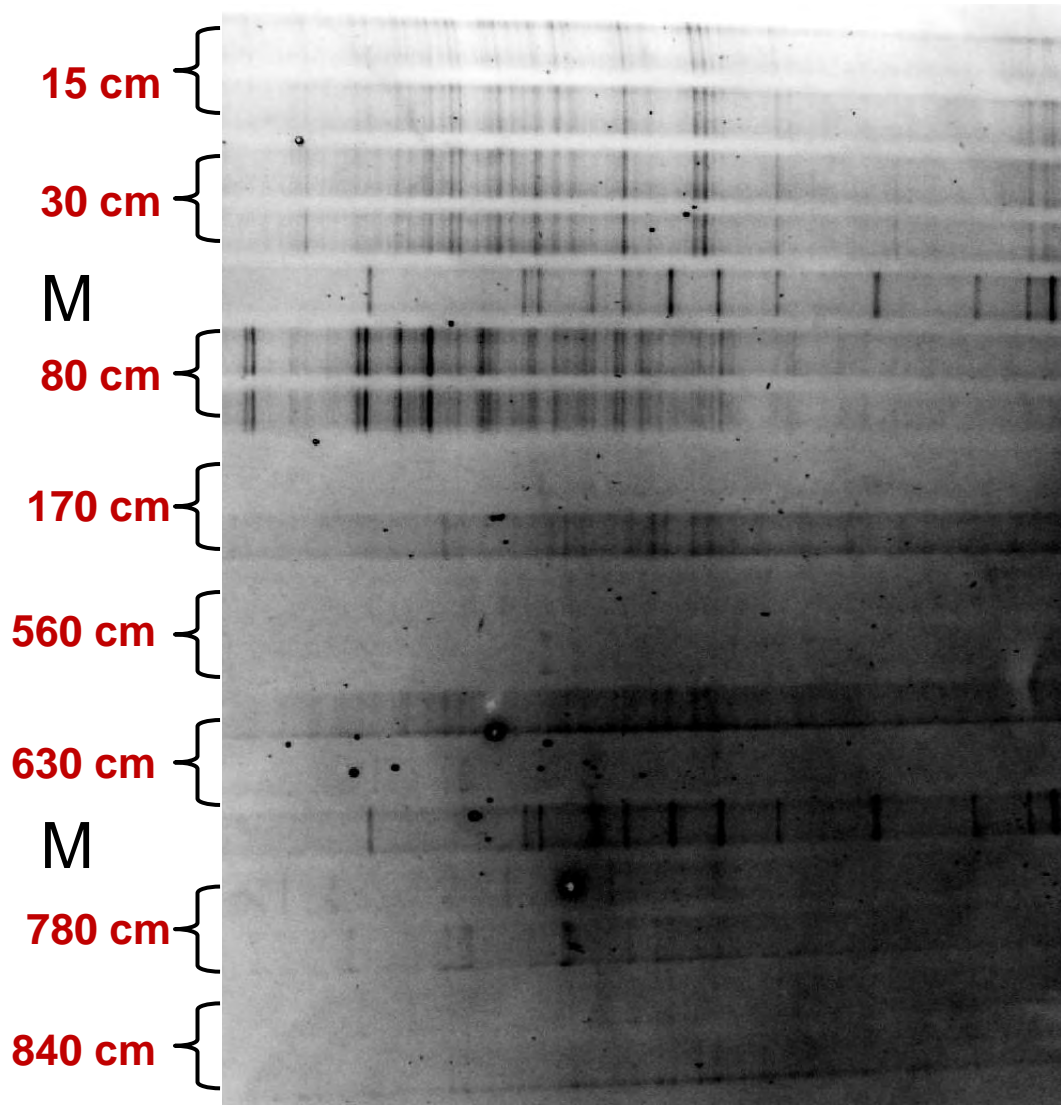


### Isoproturon residues in surface soils



Larger quantities of bound residues and mineralisation  
More by-products in surface soils

# Results : Bacterial community profiling



- High bacterial diversity in the top layers: 15 and 30 cm depth
  - Highly variable bacterial community structure at 80 cm, very different from the upper layers
  - Deeper layers containing less DNA ; difficult to obtain PCR products
  - At deeper depth a less diverse bacterial community structure
- Further analysis of the profiles to be done (image analysis of the profiles)



# Discussion: experimental data

- Adsorption : low OC in the unsaturated zone but adsorption occurs

Unsaturated zone	Kd Atrazine (mL/kg)	Koc atrazine	Kd isoproturon (mL/kg)	Koc isoproturon
Min-max	0.1 – 13.8	44 – 4200	1.0 – 3.1	180 - 3475
Mean	1.64	1480	1.61	2050
Surface soils			Kd isoproturon (mL/kg)	Koc isoproturon
Min-max			1.2 – 2.7	9.4 – 12.8
Mean			1.80	11.1

- This adsorption is reversible
- Degradation: faster in upper than in lower layers related to bacterial activity, but low compared with surface soils

Depth (m)	DT50 atrazine	DT50 isoproturon
1,6	127	26
12,50	57	12
21,30	106	74
29,60	219	220
37,25	186	259
Surface Soils		DT50 isoproturon
Mean of fields	-	4-6 days

# Conclusion

- Transfer of pesticides in the unsaturated zone (Atrazine and Isoproturon)
  - Only few mineralisation in deepest zones:  $< 0,5\%$ , due to low bacterial activity
  - Disponibility of the active substance: extractible with water: 40% after 70 days of incubation
- Processes for modeling the unsaturated zone
  - Adsorption-desorption processes can be considered in the unsaturated zone
  - $K_d$  is a better descriptor of sorption than  $K_{oc}$  in the unsaturated zone
  - Adsorption is mainly reversible
  - Mineralisation can be neglected (for atrazine and isoproturon)
- Next step : modeling approach (cf poster)

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## **XIV Symposium in Pesticide Chemistry**

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Auditorium Mazzocchi • Università Cattolica del Sacro Cuore

**Thank you for your attention!**