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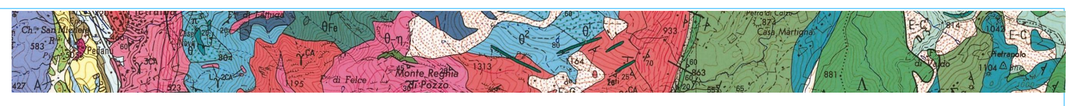

Geoscience for a sustainable Earth

Établissement public du ministère chargé du développement durable

Pesticide and metabolites transport and storage in vadose zone: time bomb or not?

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Diffuse pollution by pesticides and their metabolites is a major concern for groundwater management policies, especially given the constraints imposed by the European Water Framework Directive. Effects of past and present land-use practices may take decades to become apparent in groundwater. Albeit some knowledge has been gained in pedological soil, only scarce data are available on pesticides and metabolites transfer in the unsaturated zone. It is still a challenge to link the current pesticides pressure and the observed impacts on groundwater quality.

Objectives

The project aims to improve our understanding of the transfer of pesticides and their metabolites in contrasted geological materials issued from unsaturated zone in order to estimate their transfer time.

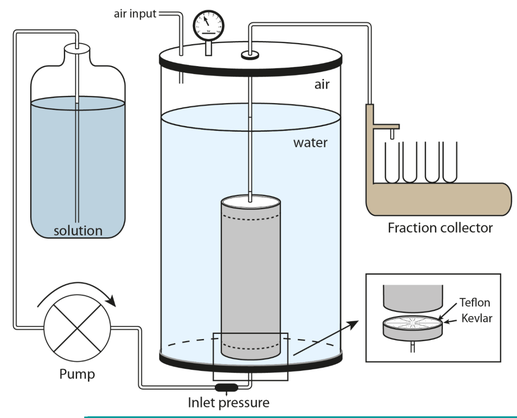
Materials and methods

Geological materials

- limestone (Bajocian; 7.3 m b.s.l)
- altered amphibolite (basement – Brioverian; 2.6 m b.s.l)

Studied molecules:

- Selection of molecules based on their occurrence in French groundwaters and their characteristics.
- Injected as a mixture (individual concentration ~10 µg/L) and bromide.
- *Active substances:* Dimethenamid-P, Metazachlor, S-Metolachlor, Atrazine, Chlortoluron
- *Metabolites:* ESA-Dimethenamid, OXA-Dimethenamid, ESA-Metazachlor, OXA-Metazachlor, ESA- Metolachlor, OXA-Metolachlor, Deethylatrazine

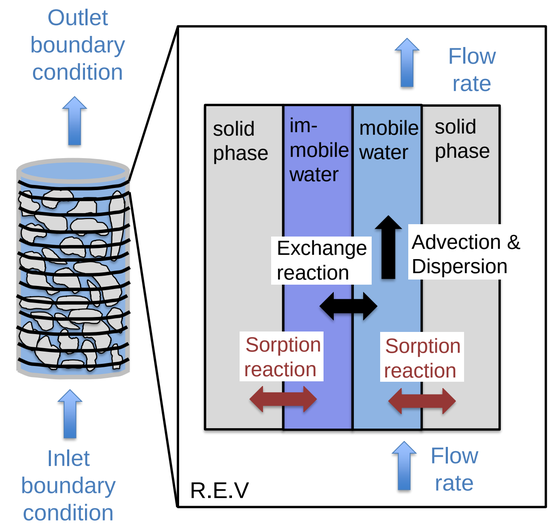


Column experiments design:

- One drill core of rock (without any fluid), ~8 cm long and 4 cm in diameter
- A sealed pressurized to maintain pressure was used
- Solutions were introduced upward using piston pump
- Column was pre-equilibrated by circulating background solution (> 1 PV)
- Flow rate was set at 0.01mL/min

Modeling Strategies

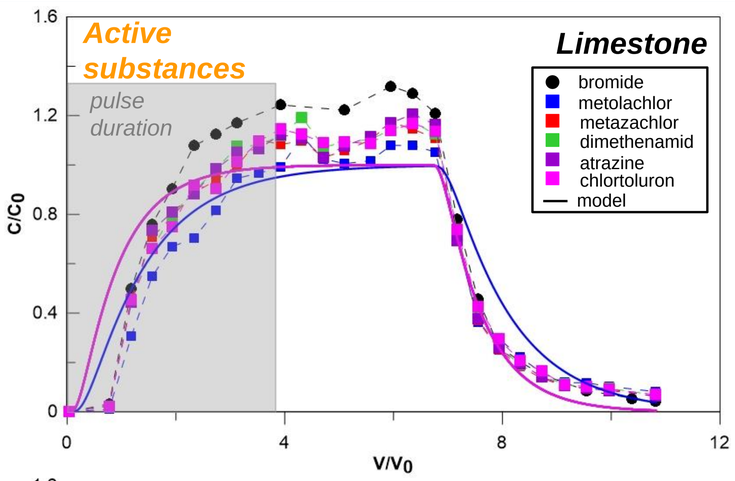
- Column were divided in 30 cells (R.E.V. approach)
- Inlet boundary condition was fixed while outlet boundary condition was dynamic
- Transport was simulated accounting for advective and dispersive processes.
- For altered amphibolite, a dual-porosity transport model was used
- Sorption reactions were simulated using a linear sorption isotherm
- Models were build using PHREEQC software

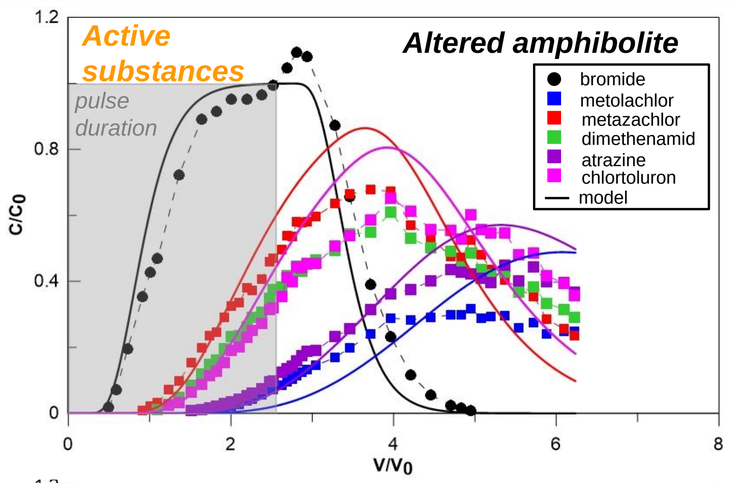


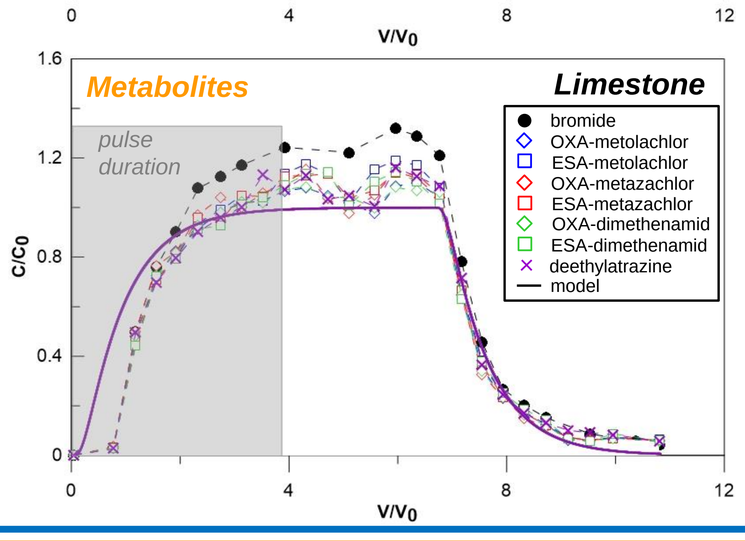
Results

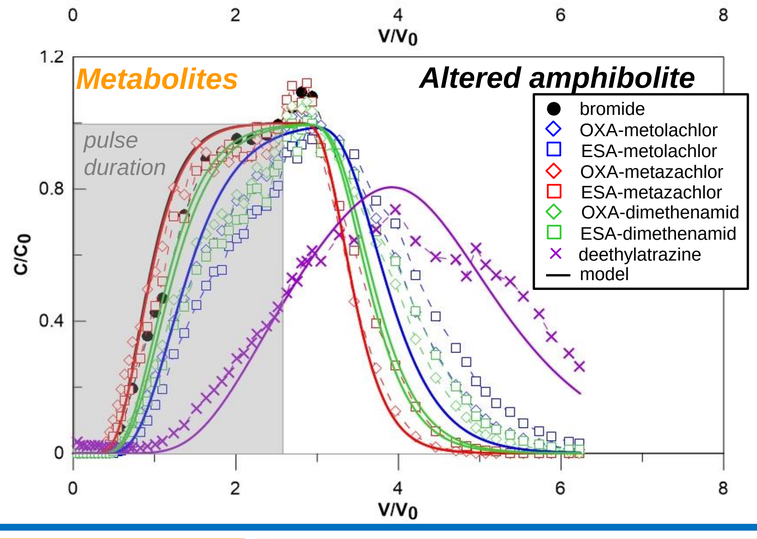
- Effective porosities are equal to 0.15 and 0.51 for limestone and altered amphibolite, respectively
- Longitudinal dispersivities are equal to 0.04 m^{-1} and 0.005 m^{-1} for limestone and altered amphibolite, respectively
- Model predicts quite accurately fate of active substances and metabolites
- The transfer of the studied molecules in the vadose zone is not or little controlled by the limestone.
- Interactions between some metabolites and active substances and the altered amphibolite are likely to occur in the vadose zone during infiltration.
- Delayed transfer in altered amphibolite :

  bromide ~ ESA metazachlor ~ OXA metazachlor < ESA-dimethenamid ~ OXA-dimethenamid ~ OXA-metolachlor < ESA-metolachlor << deethylatrazine ~ metazachlor < dimethenamid ~ chlortoluron < atrazine < S-metolachlor









Take-home messages

- For a given molecule, the time lag observed compared to the non reactive tracer is geological material dependent.
- Interactions between the organic molecules and matrix are more important for the altered amphibolite than for limestone.
- Retardation factors are lower for metabolites compared to their parent molecules in the altered amphibolite.
- Metabolites of chloroacetanilides revealed lower interactions than deethylatrazine (metabolite of atrazine, a triazine) for the altered amphibolite.

⇨ For substances that have migrated beyond the pedological soil, the transfer time to saturated zone can be strongly delayed compared to water

⇨ The interactions between the studied molecules and the geological materials in the vadose zone must be taken into account to establish a relationship between use of pesticides and impact on groundwater quality

Next – In progress

- Mineralogical characterization of the geological materials to identify the potential sites of interaction (key role of clays? surface charges of material?)
- Assessment of preferential flow and transport in altered amphibolite

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