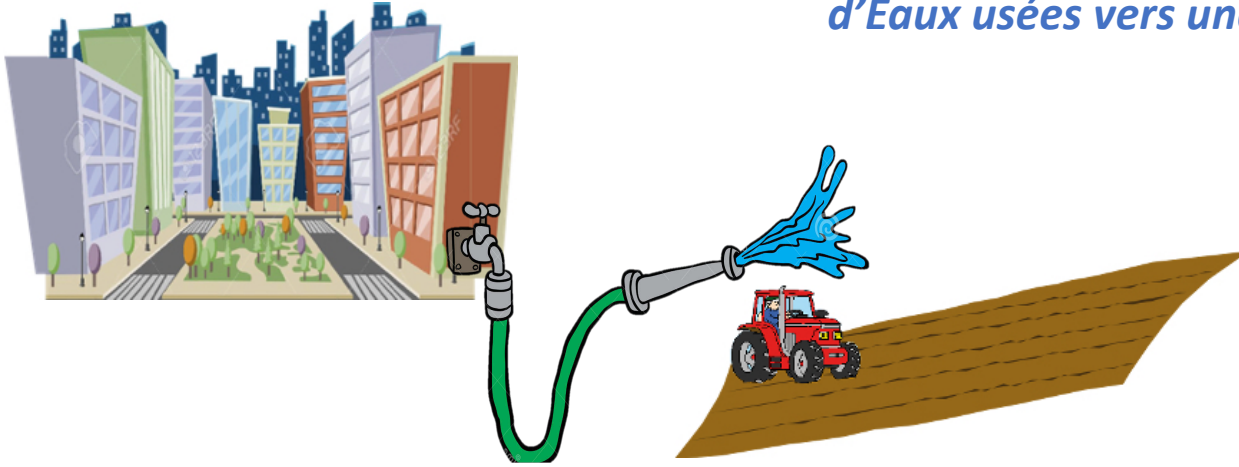


## NEREIDE - Solutions basées sur la Nature pour l'Épuration et la Réutilisation d'Eaux usées vers une Irrigation Durable



3 cofinancements acquis

- 2020, projet EUR interne **CEREGE**
- 2020-2023, projet NEREIDE, **Institut Carnot Eau et Environnement**
- 2020-2023 Thèse **CampusFrance**, M. Fatahizadeh, CEREGE

3 partenaires

- CEREGE: J. Labille, M. Fatahizadeh, N. Roche
- INRAE ECOSYS: M. Deschamps, P. Benoit
- HSM: G. Duporte, P. Montfort, E. Gomez

*Une approche expérimentale, en labo,  
de l'échelle nm (interface) à m (semi-pilote)*

### 1. Nouveaux traitements d'affinage des eaux usées

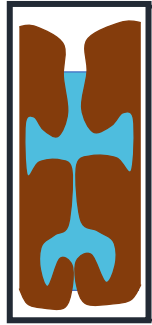
Peut-on obtenir une eau de qualité avec un procédé de traitement sobre et économique ?

### 2. Transfert et impacts de la qualité de l'eau traitée sur le système sol - plante

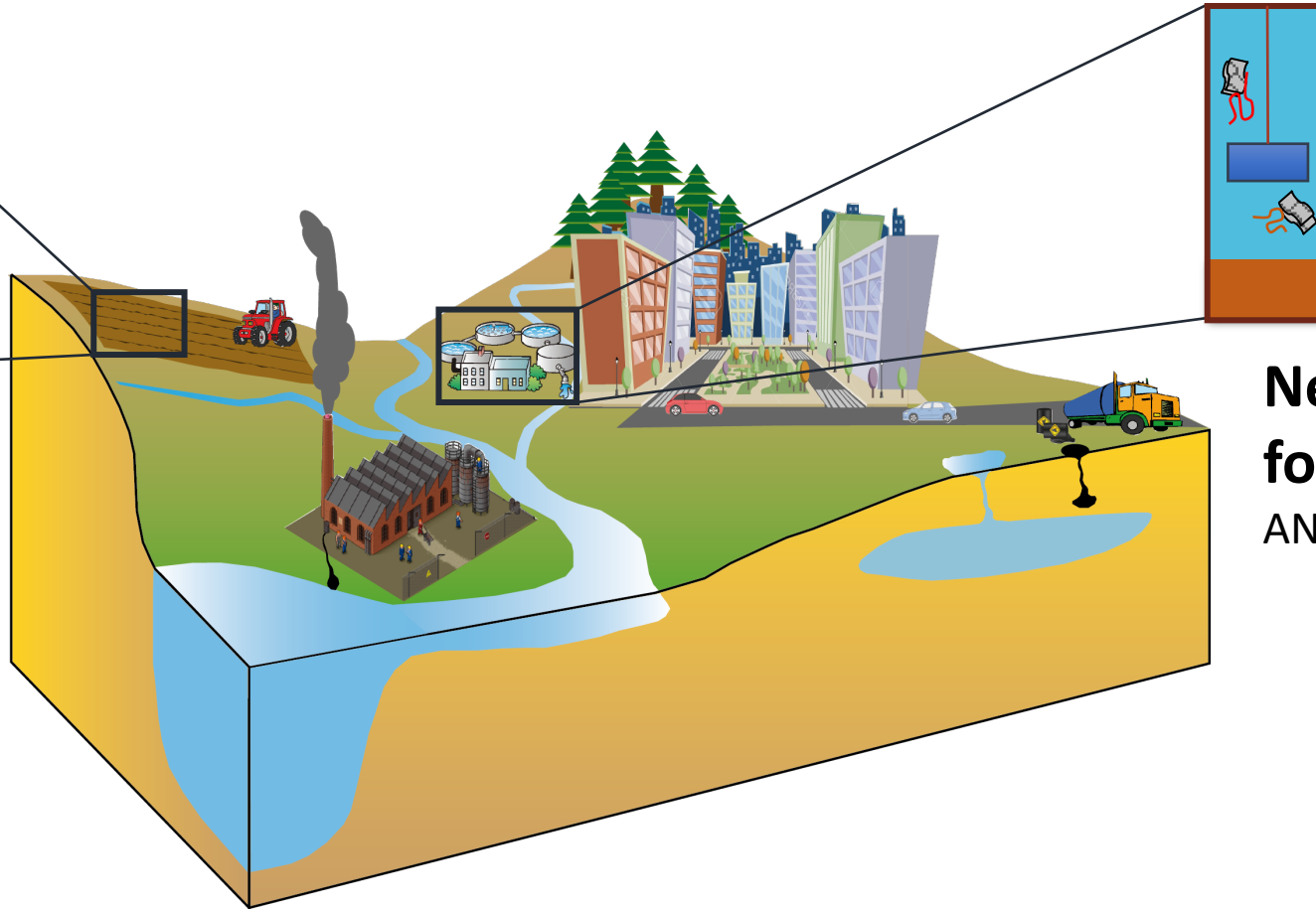
Quelle qualité d'eau d'irrigation requise?

L'effet auto-épuration du sol est-il un procédé durable en REUT ?

### 3. Quelle approche analytique développer pour suivre les micropolluants?



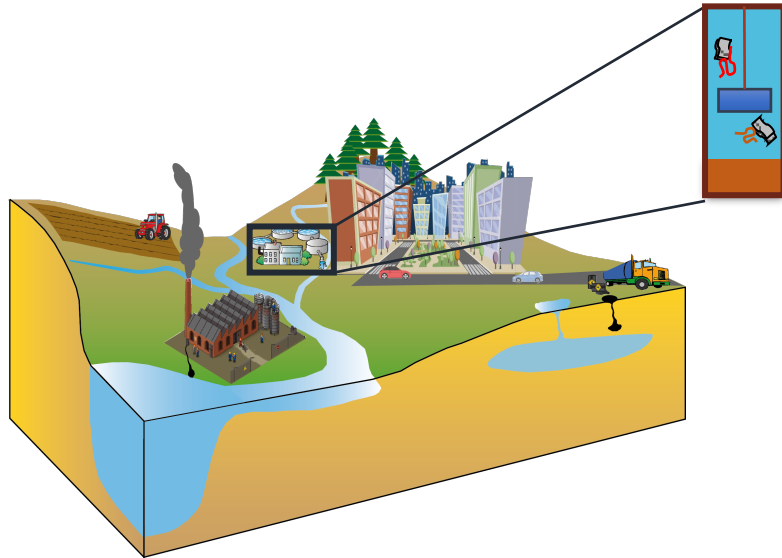
**pollutant transfer  
in soil**  
ANR Digestate 2016-2020



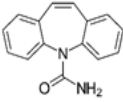
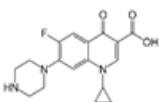
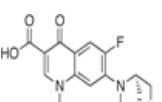
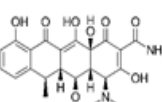
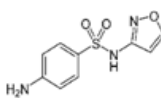
**New sorbent material  
for water treatment**  
ANR Polpharma 2016-2018

# Project ANR Polpharma

## Modified clay as a nature-based solutions for water treatment



## Studied pharmaceutical compounds

| Pharmaceutical class   | Antiepileptic   | Antibiotics   |   |   |   |
|------------------------|---|---|---|---|---|
| Compounds              | Carbamazepine   | Ciprofloxacin   | Danofloxacin  | Doxycycline   | Sulfamethoxazole  |
| Chemical formula       | $C_{15}H_{12}N_2O$  | $C_{17}H_{18}FN_3O_3$   | $C_{19}H_{20}FN_3O_3$   | $C_{22}H_{24}N_2O_8$  | $C_{10}H_{11}N_3O_3S$   |
| Chemical structure     |  |  |  |  |  |
| Molecular mass (g/mol) | 236.27  | 331.34  | 357.38  | 444.43  | 253.28  |
| pKa                    | 13.9  | 5.86 ; 8.24   | 6.07 ; 8.56   | 3.09 ; 8 ; 9.2  | 1.83 ; 5.57   |
| Solubility (mg/L)      | 18  | 30 000  | 20 000  | 630   | 610   |
| Log Kow                | 2.45  | 0.28  | -0.3  | -0.02   | 0.89  |
| Type of use            | Human use   | Human use   | Veterinary use  | Human and veterinary use  | Human and veterinary use  |

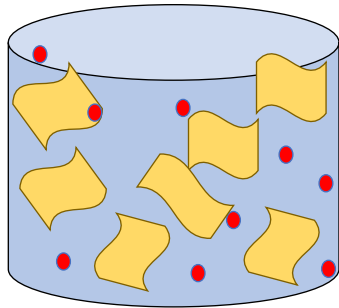
### Objectives:

- To develop a sorbent material as efficient and cheaper than activated carbon to eliminate micropollutants;
- To test in lab the material efficiency

### Approach:

- Montmorillonite hybridized with silica nanoparticles

# MMT/SiO<sub>2</sub> nanocomposite preparation



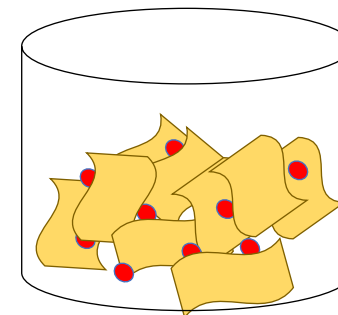
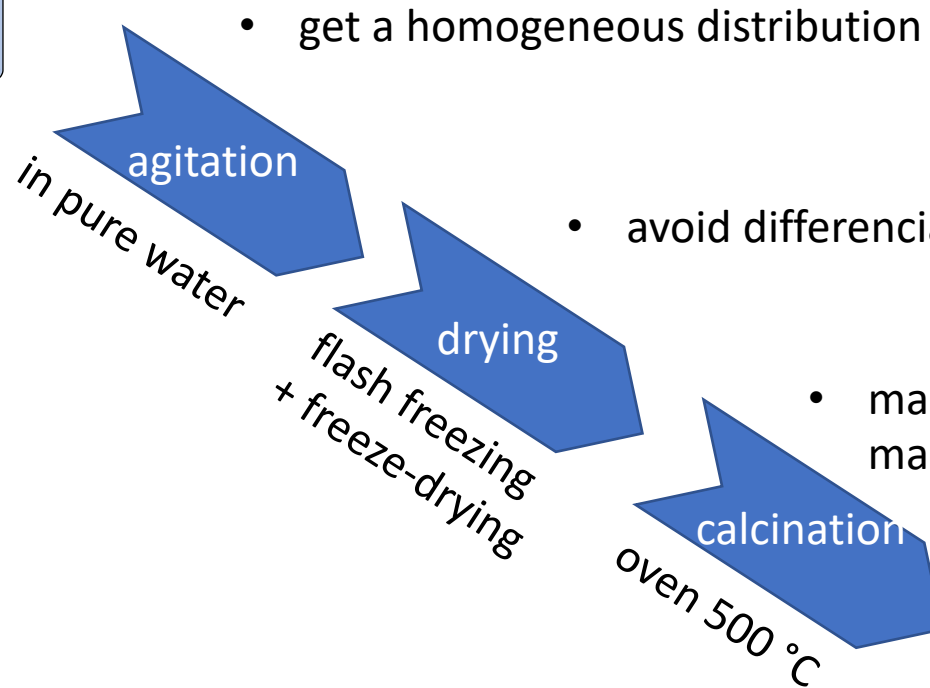
initial material:

**Na/Ca/K-montmorillonite**

Nador, North Morocco

+

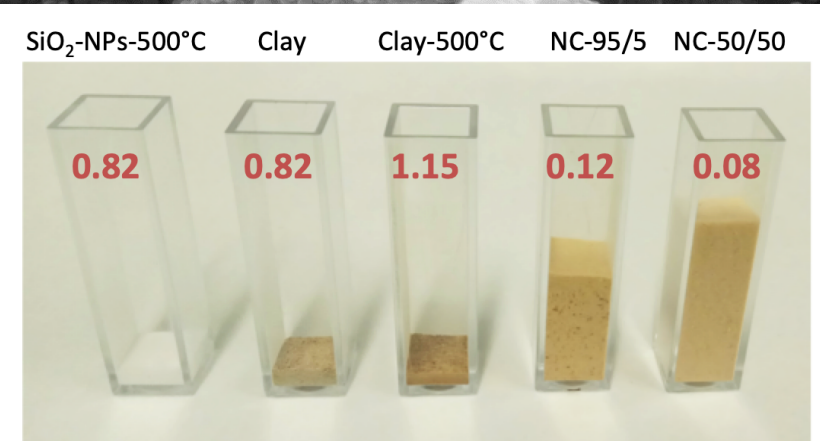
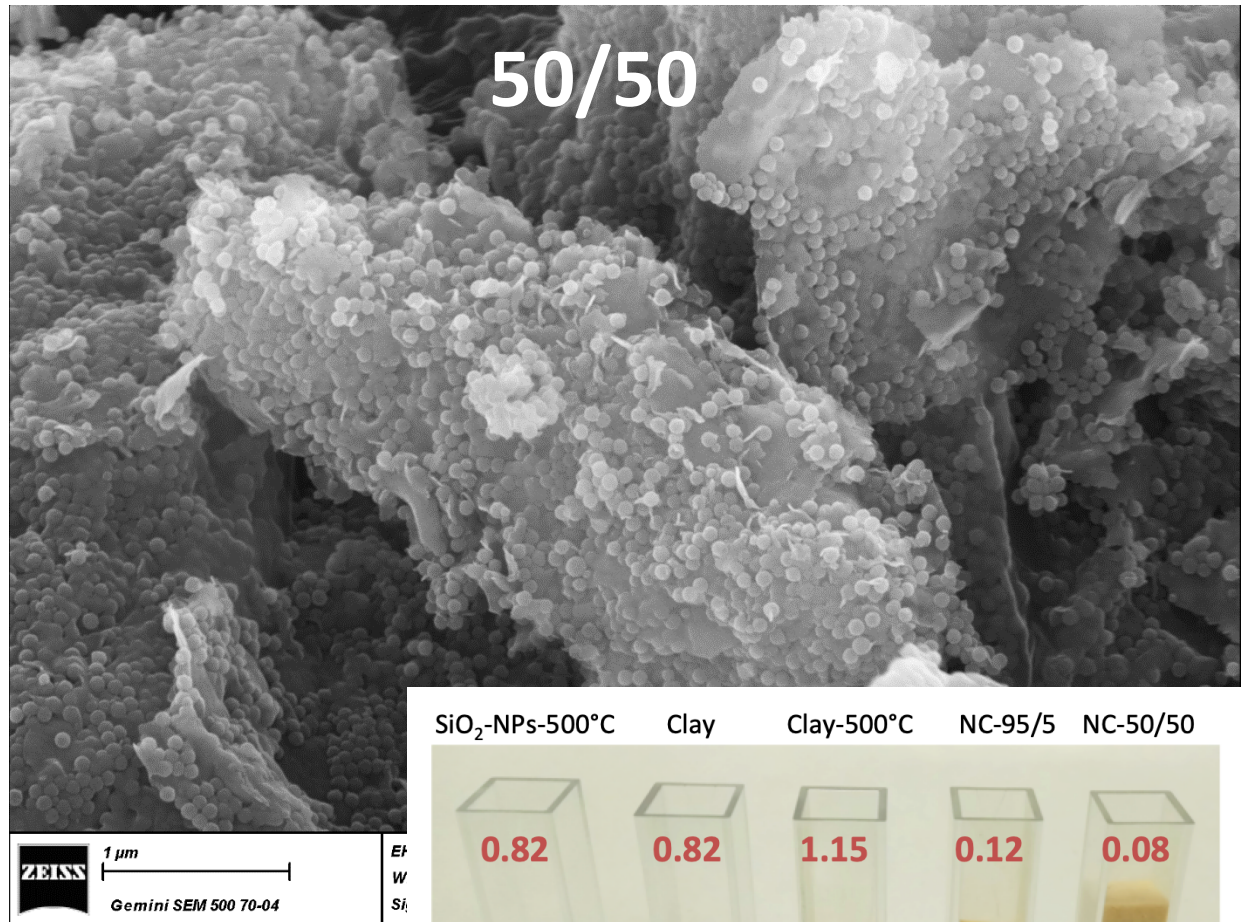
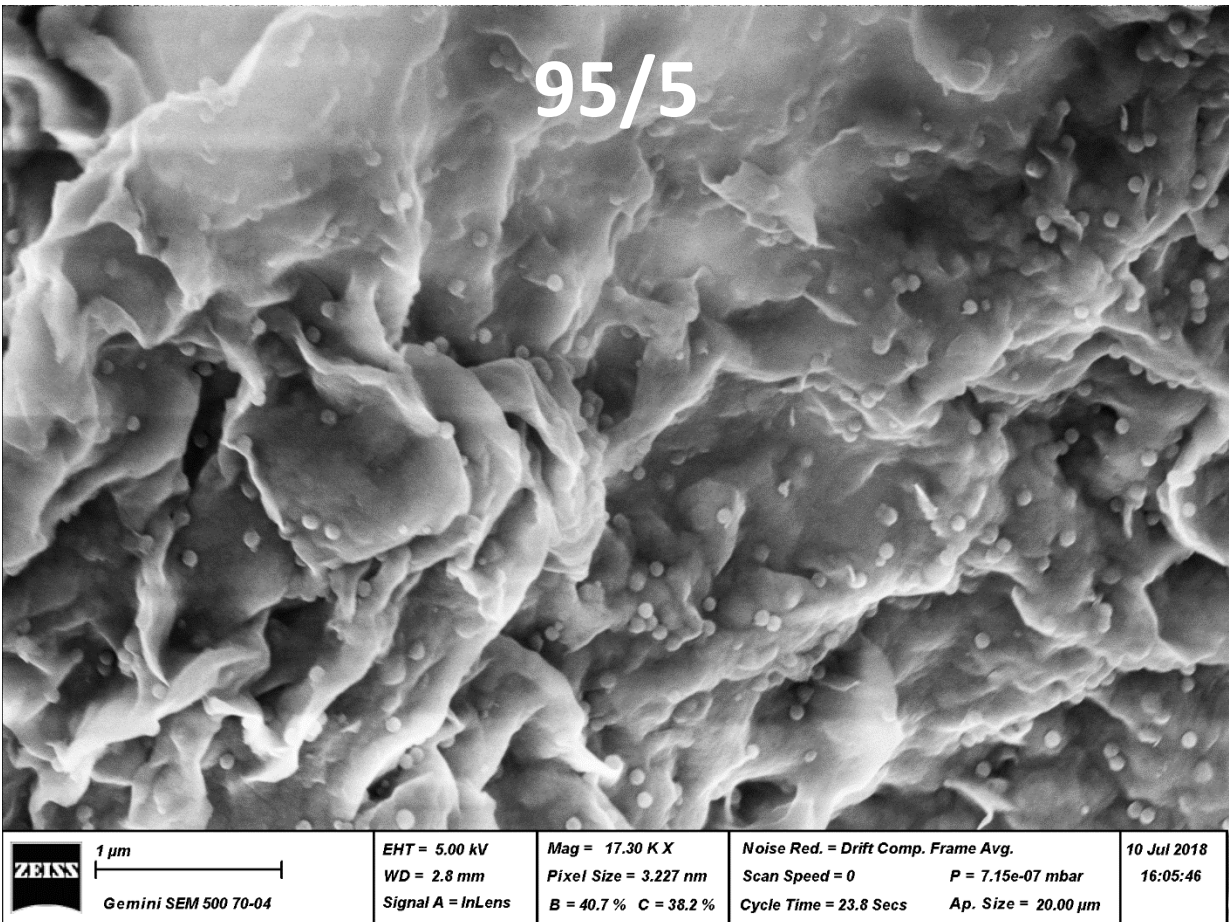
Silica Klebosol 30R50 80 nm



**nanocomposite  
MMT/SiO<sub>2</sub>**

**improved  
sorption capacity?**

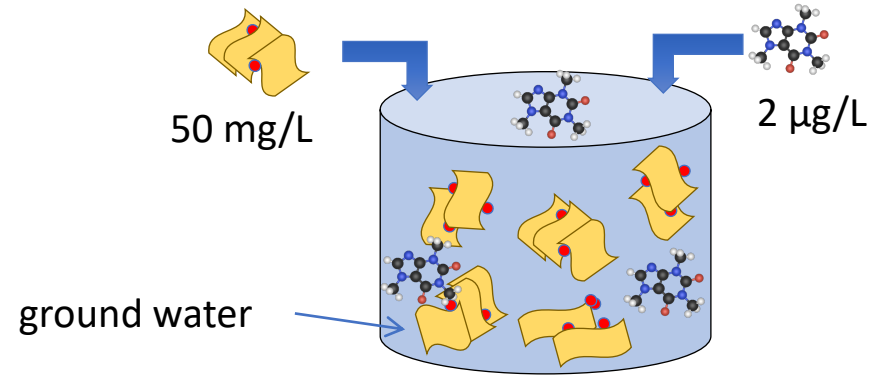
# SEM observation of the MMT/SiO<sub>2</sub> nanocomposites



Apparent density (g.cm<sup>-3</sup>)

**Batch experiment**

- $\mu$ -pollutant injection : **2  $\mu\text{g/L}$**  each compound
- Sorbent concentration : **50 mg/L**
- Aqueous medium : **ground water**
- pH : **7.5**
- **Time : 48h**
- **Filtrates analysed with LC-MS/MS**



| Sorbent (50mg/L)                  | Ciprofloxacin | Danofloxacin | Sulfamethoxazole | Doxycycline | Carbamazepine |
|-----------------------------------|---------------|--------------|------------------|-------------|---------------|
| Activated carbon                  | <b>100%</b>   | <b>100%</b>  | <b>100%</b>      | <b>100%</b> | <b>100%</b>   |
| MMT/SiO <sub>2</sub> (50/50)      | 99%           | 99%          | 0%               | 34%         | 3%            |
| <b>MMT/SiO<sub>2</sub> (95/5)</b> | <b>100%</b>   | <b>100%</b>  | 0%               | <b>60%</b>  | 0%            |
| MMT 2 $\mu\text{m}$               | <b>94%</b>    | <b>95%</b>   | 0%               | <b>41%</b>  | 0%            |
| SiO <sub>2</sub> NP               | 0%            | 0%           | 0%               | 11%         | 0%            |

- **no adsorption on NP alone**
- **Cipro, Dano, Doxy : similar structure**
- **Sulfa. and Carb. : not/weakly removed**
- **most efficient sorbent : MMT/SiO<sub>2</sub> 95/5**

# Tâche 1 NEREIDE - Nouveaux traitements de finition des eaux usées domestiques

Tester de nouveaux procédés pour l'élimination de polluants récalcitrants en étape d'affinage du traitement

- Matériaux adsorbants en colonne de filtration : Argile modifiée, résidus de bauxite modifiés, compost, charbon...
- Filtre planté
- Combinaison hybride

## Sélection des polluants apportés par dopage de l'eau synthétique

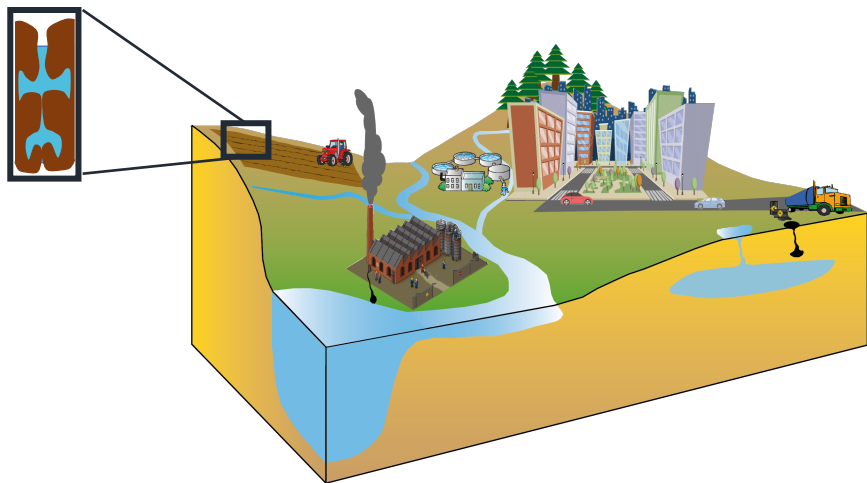
- 10 **pharma** en cocktail (1 représentant par famille de molécule)  
carbamazepine (neuroleptique), cafeine, sulfamethoxazole (antibio), sulfonamide ofloxacine (antibiotique fluoroquinolone), gemfibrozil, (lipid regulator), atenolol (beta bloquant), triclocarban (bactericide), tetracycline (antibiotique), diclofenac  
analyse INRAE ECOSYS

Mise au point d'une méthode non ciblée pour l'analyse des polluants organiques dans l'eau (HSM)

- **Filtres UV**
  - Minéraux  
nano-TiO<sub>2</sub>, nano-ZnO (postdoc MOPGA F. Loosli)
  - Organiques (2 molécules)
- Complexes de **Gd**  
inorganique, agent de contraste IRM, bon marqueur anthropique
- ARN phage f, comme analogue de **pathogène**  
P. Montfort (HSM)

## ANR Digestate

Diagnosis of wastes Treatments for contaminants fate in the Environment



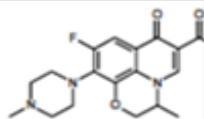
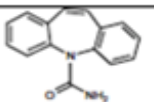
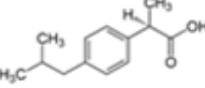
## Soil characteristics

Colmar, France  
(Bourdat-Deschamps et al., 2017)



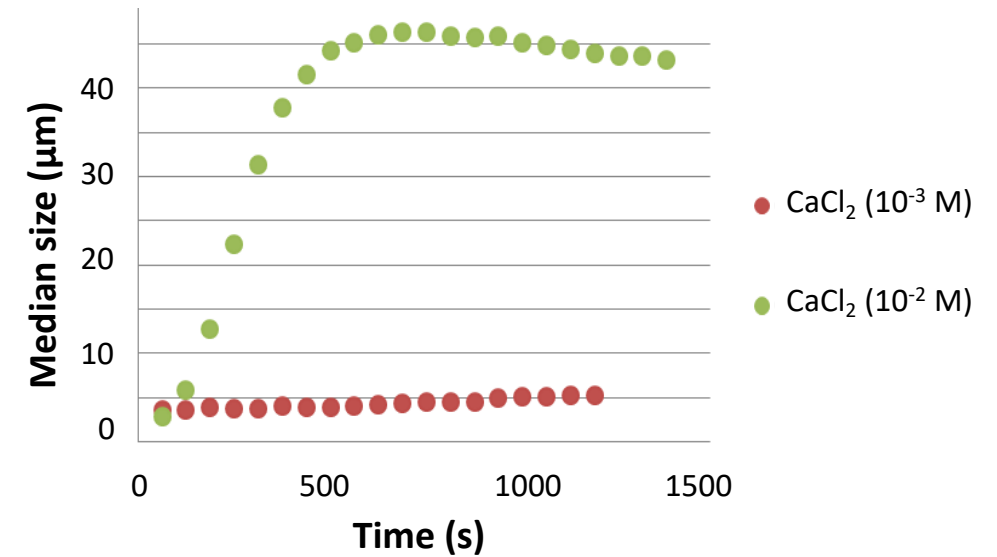
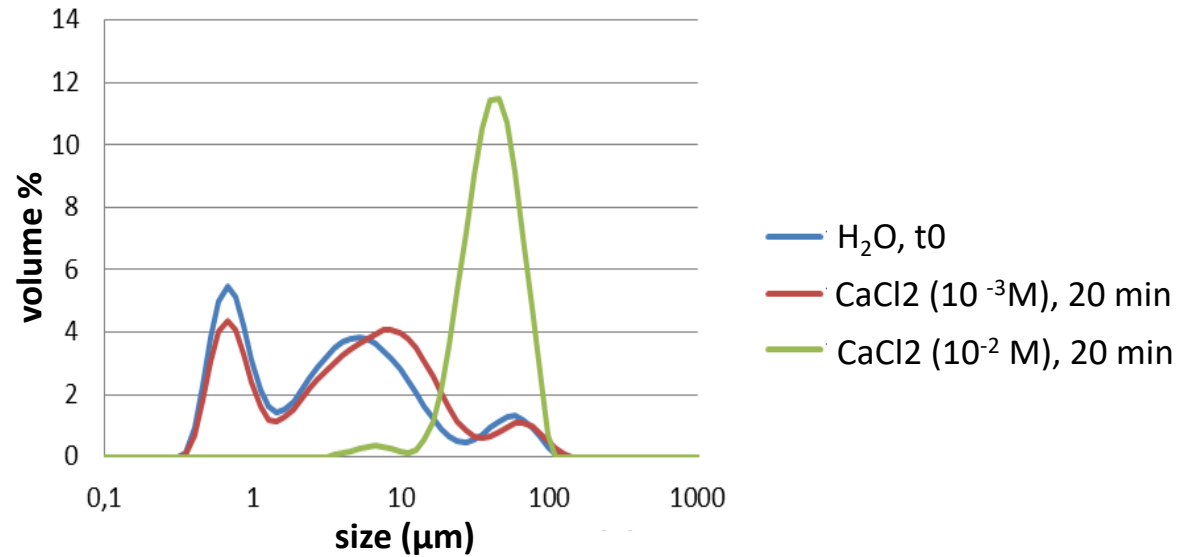
|                           |          |   |
|---------------------------|----------|---|
| <b>Size class</b>         | loam     | 69%                                     |
|                           | clay     | 24%                                     |
|                           | sand     | 7%                                      |
| <b>Organic matter</b>     |          | 2.6%                                    |
| <b>TOC</b>                |          | 15.1 ppm                                |
| <b>pH</b>                 |          | 8.5                                     |
| <b>Mineralogy</b>         |          | calcite, quartz, dolomite, albite, clay |
| <b>Colloidal fraction</b> |          | 0.41 %                                  |
| <b>Clay minerals</b>      | smectite | 34.8                                    |
|                           | chlorite | 12.4                                    |
|                           | illite   | 34.3                                    |

## Pharmaceutical compounds

| Product           | Category                         | Chemical structure  | Water solubility<br>mg L <sup>-1</sup> | log K <sub>ow</sub> | pKa                    | K <sub>d</sub><br>l/kg | K <sub>oc</sub><br>l/kg |
|-------------------|----------------------------------|---|--|---------------------|------------------------|------------------------|-------------------------|
| Ofloxacin OFL     | Antibiotique,<br>Fluoroquinolone |   | 3400                                   | 0,35 <sup>a</sup>   | 5,97-8,98 <sup>a</sup> | 1000-3000              | 50000-300000            |
| Carbamazépine CBZ | Antiepileptique                  |  | 18                                     | 2,45 <sup>a</sup>   | 7 <sup>a</sup>         | 0.5 - 37               | 130-500                 |
| Ibuprofène IBU    | Anti-inflammatoire               |  | 725.8<br>10 <sup>3</sup>               | 3,96-4,8            | 4,54                   | 0.2-1                  | 100-300 <sup>c</sup>    |



# Colloidal dispersion of the soil fine particulate matter

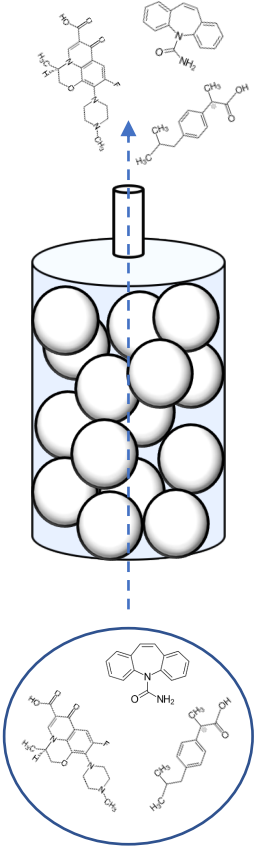


- CaCl<sub>2</sub> (10<sup>-2</sup>M): rapid aggregation of soil colloids from 4 to 40 μm.  
Hyp in column: favours stable soil aggregation, and no colloid mobilisation.
- CaCl<sub>2</sub> (10<sup>-3</sup>M): stable dispersion of soil colloids.  
Hyp in column: favours colloid mobilisation, and possible pollutant vectorisation.

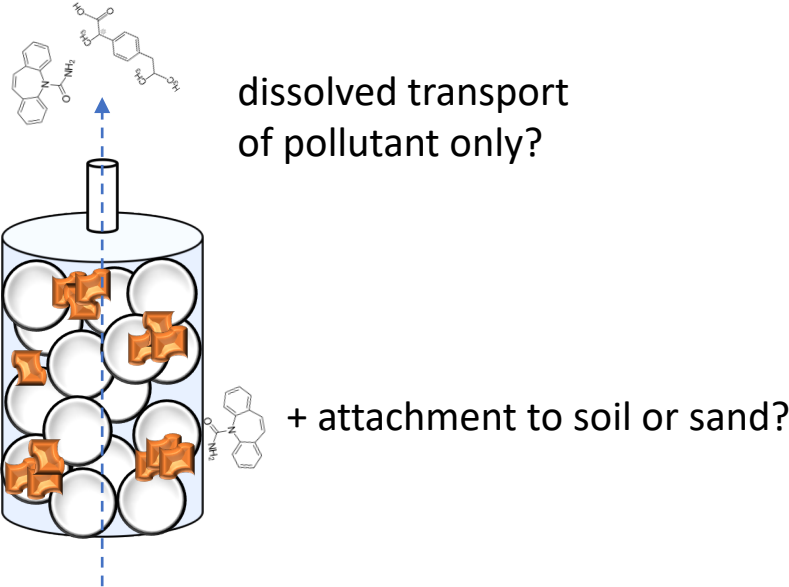
# Working hypothesis and experimental approach

## 3 modalities to control the presence of colloidal vectors

**Quartz sand only:**  
**Reference free of colloids**  
 $\text{CaCl}_2$  ( $10^{-3}$  mol / L)



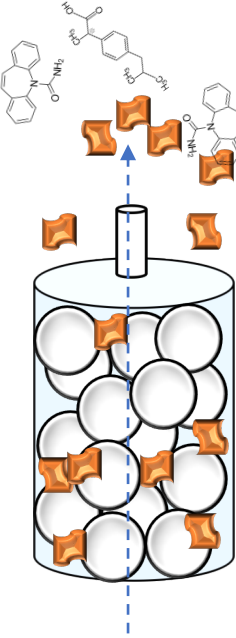
**Quartz sand + soil (95/5)**  
favoring colloids **aggregation**  
 $\text{CaCl}_2$  ( $10^{-2}$  mol / L)



dissolved transport  
of pollutant only?

+ attachment to soil or sand?

**Quartz sand + soil (95/5)**  
favoring colloids **mobilization**  
 $\text{CaCl}_2$  ( $10^{-3}$  mol / L)

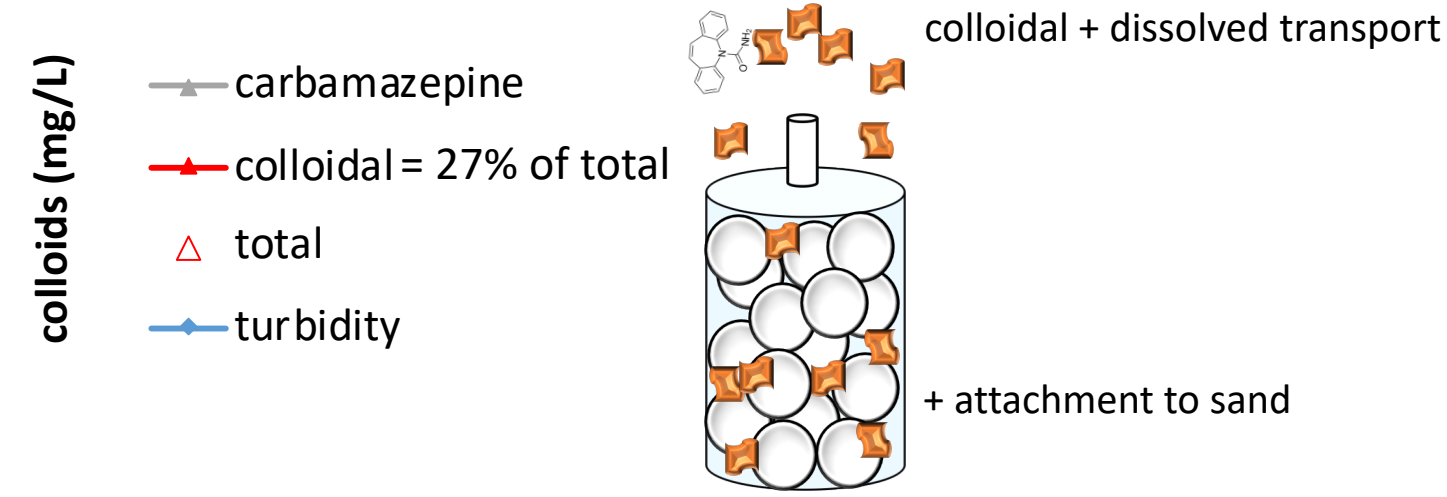
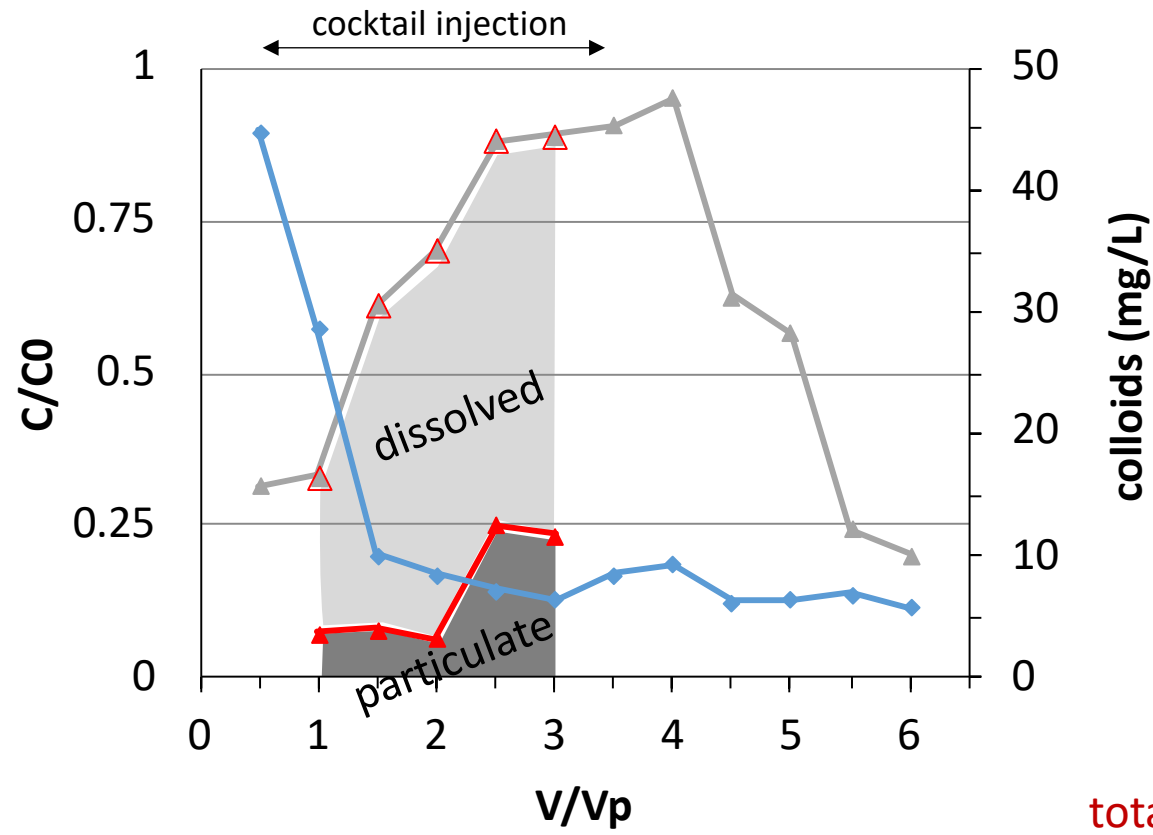


colloidal + dissolved  
transport of pollutant?

+ attachment to soil or sand?

# Carbamazepine colloid facilitated transport in $\text{CaCl}_2$ ( $10^{-3}\text{M}$ )

- Carba. was analysed in the total and the filtrate
- Colloidal vectorization = total – filtrate <  $0.2 \mu\text{m}$



total breakthrough – colloidal transport = breakthrough in quartz sand

## Tâche 2 NEREIDE - Tolérance des sols recevant des eaux dégradées

Etudier le transfert et l'impact des polluants, pathogènes, sels et nutriments à travers deux compartiments :  
Système sol – plante

Mise en place de lysimètres de laboratoire (x4)

- Cultures en **lysimètre** : scénario d'une **agriculture urbaine**, parc de culture pérenne de graminées irrigué avec des eaux usées traitées.

**Durée longue** : 2 ans sans remaniement du sol pour étudier les effets de la qualité de l'eau, l'accumulation des contaminants et leurs effets sur le sol et la plante.

4 lysimètres : 1 référence sol sans plante – 1 référence sol avec plante – 1 sol avec plante irrigué par une eau dégradée - 1 sol sans plante irrigué par une eau dégradée

- Cultures en **pots** : scénario de jardins ou **jardins collectifs**, en utilisant des cultures de maraichage (salade, tomate, etc)

**Durée courte** : varier les paramètres : caractéristique du sol, de l'eau...

# Lysimètre de laboratoire Ecotech

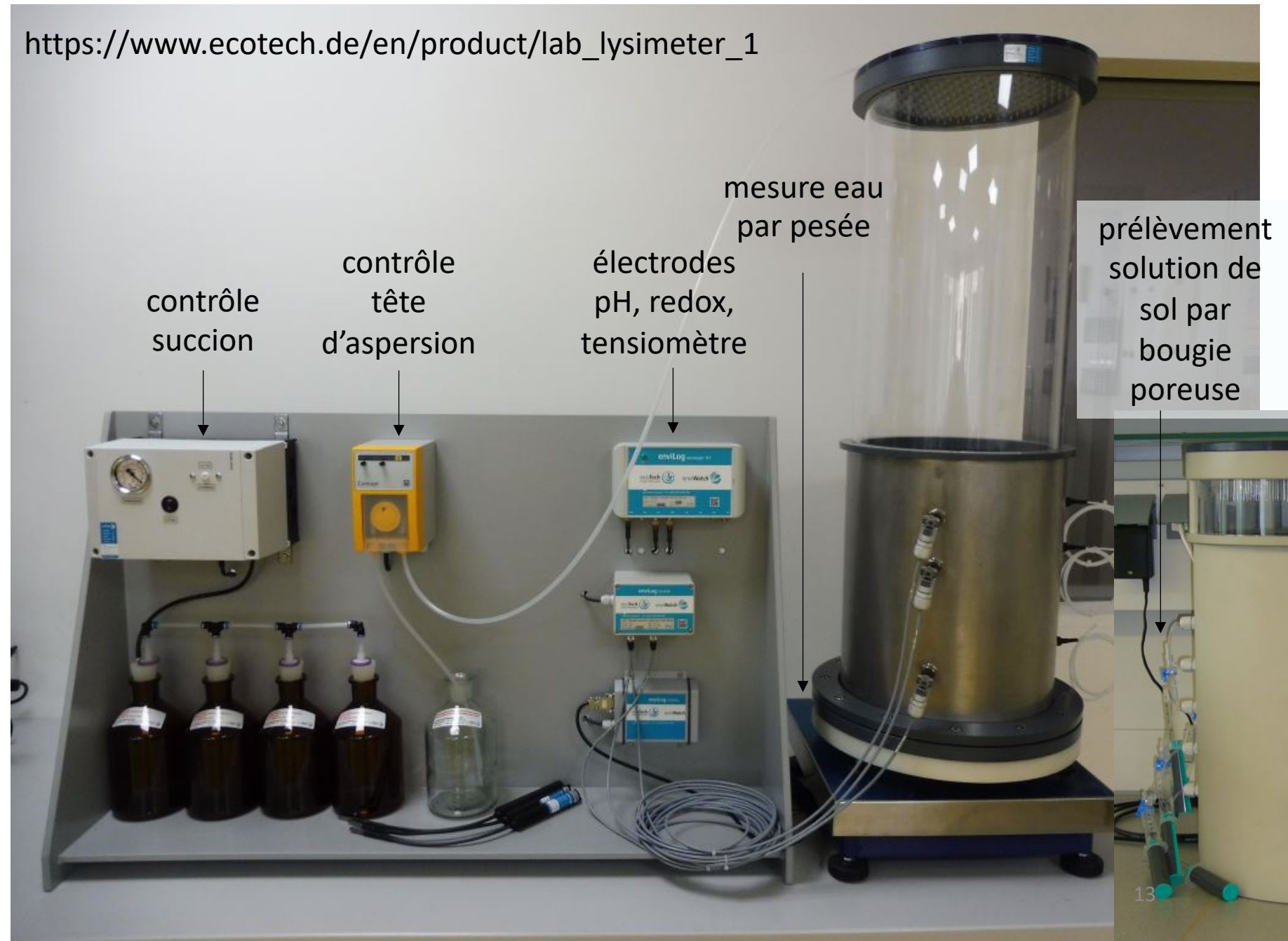
Diamètre 30 cm  
Hauteur 50 cm

Quantité :  
2 en cours de livraison  
2 à commander

Prélèvement de solution  
à 3 hauteurs + en  
percolation

Mesure de l'humidité par  
pesée

[https://www.ecotech.de/en/product/lab\\_lysimeter\\_1](https://www.ecotech.de/en/product/lab_lysimeter_1)



# Tâche 2 – Sol de l'étude

Impact of long-term irrigation with municipal reclaimed wastewater on the uptake and degradation of organic contaminants in lettuce and leek.

Rayana Manasfi<sup>a</sup>, Monica Brienza<sup>a</sup>, Nassim Ait-Mouheb<sup>b</sup>, Nicola Montemurro<sup>c</sup>, Sandra Perez<sup>c</sup>, Serge Chiron<sup>a\*</sup>

<sup>a</sup>UMR HydroSciences Montpellier, Montpellier University, IRD, 15 Ave Charles Flahault 34093 Montpellier cedex 5, France

<sup>b</sup>UMR G-eau, Montpellier University, INRAE, 361, rue Jean-François Breton, 34196 Montpellier cedex 5, France

<sup>c</sup>ENFOCHEM, IDAEA-CSIC, c/Jordi Girona 18-26, 08034 Barcelona, Spain

## Caractéristiques du sol de Lavallette (site Murviel)

| Depth (cm)         | 0 – 20 cm | 50 – 60 cm |
|--------------------|-----------|------------|
| Clay (%)           | 24.0      | 14.9       |
| Silt (%)           | 25.6      | 4.2        |
| Very fine sand (%) | 19.5      | 7.4        |
| Fine sand (%)      | 16.4      | 23.0       |
| Coarse sand (%)    | 14.4      | 50.5       |
| Organic matter (%) | 2.70      | 0.43       |
| CEC (m.e. / 100 g) | 11.11     | 4.84       |
| pH (KCl)           | 7.6       | 7.9        |

## A B S T R A C T

A two years drip irrigation of lettuce and leek crops with treated municipal wastewater without and with spiking with fourteen wastewater relevant contaminants at 10 µg/L concentration level was conducted under greenhouse cultivation conditions to investigate their potential accumulation in soil and leaves and to assess human health related risks. Lettuce and leek crops were selected as a worse-case scenario since leafy green vegetable has a high potential for organic contaminants uptake. The results revealed limited accumulation of contaminants in soil and plant leaves, their concentration levels being in the range of 1–30 ng/g and 1–660 ng/g range in soil and leaves, respectively. This was likely related to abiotic and biotic transformation or simply binding processes in soil, which limited contaminants plant uptake. This assumption was underpinned by studies of the enantiomeric fractionation of chiral compounds (e.g. clmbazole and metoprolol) in soil as pieces of evidence of biodegradation and by the identification of transformation products or metabolites in leaves by means of liquid chromatography - high resolution - mass spectrometry using a suspect screening workflow. The high bioconcentration factors were not limited to compounds with intermediate  $D_{ow}$  (100 to 1000) such as carbamazepine but also observed for hydrophilic compounds such as clarithromycin, hydrochlorothiazide and the food additives acesulfame and sucralose. This result assumed that accumulation was not only driven by passive processes (e.g. lipoidal diffusion through lipid bilayer cell membranes or Casparian strip) but might be supported by carrier-mediated transporters. As a whole, this study confirmed earlier reports on the *a de minimis* human

Questions levées:

Mécanismes d'interaction entre polluant et constituants du sol?

L'approche lysimètre doit permettre d'aborder cette échelle.