Implications and applications of clays colloids on pollutant transport in water cycle

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Journées Scientifiques du GDR Morphea
6-7 octobre 2020

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- Glaciation/déglaciation, niveau marin
- Mousson, ENSO, paléo-circulation océanique
- Cycle de l'eau, paléohydrologie
- Ecosystèmes, biodiversité, homme

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- Dynamique, cycle et traçage dans les écosystèmes
- Réactivité des phases nanométriques
- Innovations pour l'environnement (nanomatériaux, métaux, sols, eaux)

Terre, Planètes
Resp. Y. Quesnel & L. Siame
25 C/EC et 11 ITA

- Processus de surface, tectonique et géodynamique
- Fleuves, littoraux et deltas
- Magnétisme terrestre
- Planétologie
- Géochronomètres, paléo-environnements

Ressources, Réservoirs, Hydrosystèmes
Resp. P. Henry & C. Vallet-Coulomb
18 C/EC et 5 ITA

- Evolution des systèmes carbonatés de l'échelle globale à celle du réservoir
- Dynamique des bassins sédimentaires et couplage fluide/mécanique
- Ressources en eau, ressources énergétiques et stockages
- Traçage et quantification des flux aux interfaces

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C. Paillès & J.C.Mazur

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J. Labille

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K. Keddadouche & D. Bourlès

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Laboratoire Géomodélisation
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ANR — Agence Nationale de la Recherche

Programme FP7 ERA-NET SIINN
NANOHETER 2013-2016

Devenir des nanoparticules dans une eau de surface
Rôle de l'hétéroagrégation avec les colloïdes naturels

Une approche triple terrain – labo - modèle

échelle 100 km

APPROCHE HOLISTIQUE DE TERRAIN
- Rhône
- Lac de Cholet

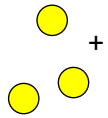
CARACTERISATION DE L'EAU

COCKTAIL

- matière en suspension
- matière organique
- pesticides

CHOIX D'ANALOGUES

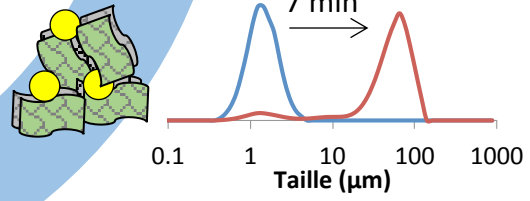
+ NP



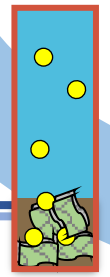
APPROCHE MÉCANISTIQUE DE LABORATOIRE
système synthétique expérimental

échelle nm

cinétique d'hétéroagrégation colloïdes - NP

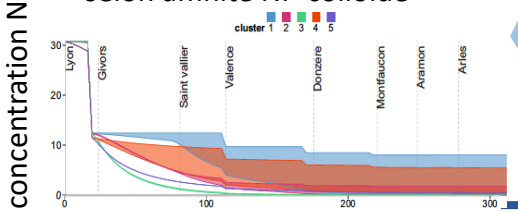


EFFICACITÉ DE COLLAGE NP - colloïde



MODÈLE DE DEVENIR
transport des NP dans le fleuve

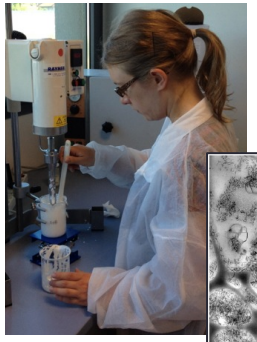
transport selon affinité NP-colloïde

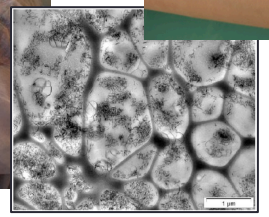


Eco-conception de crème solaire, vers une résilience pro-active

Risque consommateur
pénétration, prise de conscience

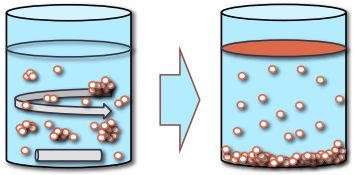
Formulation
caractérisation, optimisation

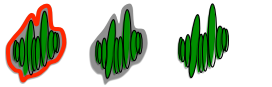


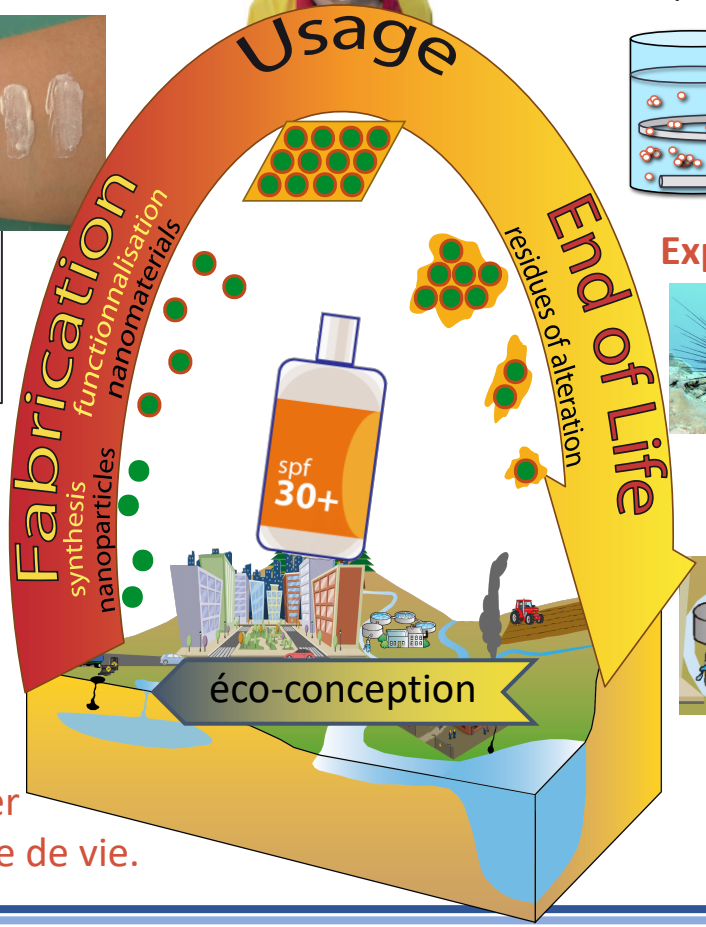


Vieillissement
quantification et caractérisation des sous-produits

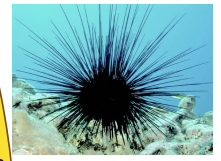
stabilité coating?







Exposition, Ecotoxicité



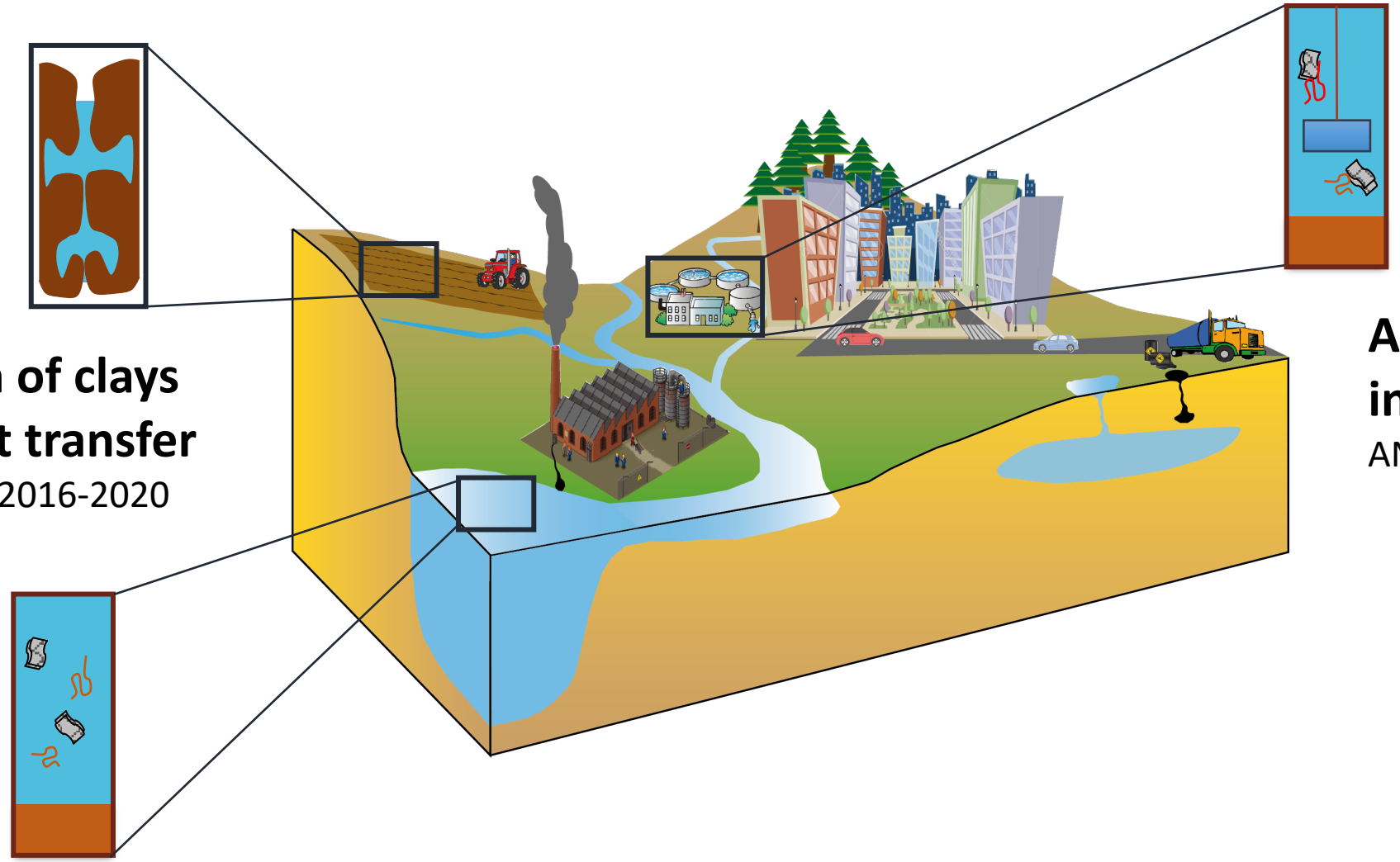
eau de mer
corail, oursin, méduse

nano-TiO_2
physico-chimie coating

Devenir dans les déchets
décharge, STEP

Enjeu :
Adapter la fabrication du produit pour minimiser son empreinte environnementale dans son cycle de vie.

Implications + applications of clays colloids
Nature-based solutions for water treatment



Implication of clays in pollutant transfer

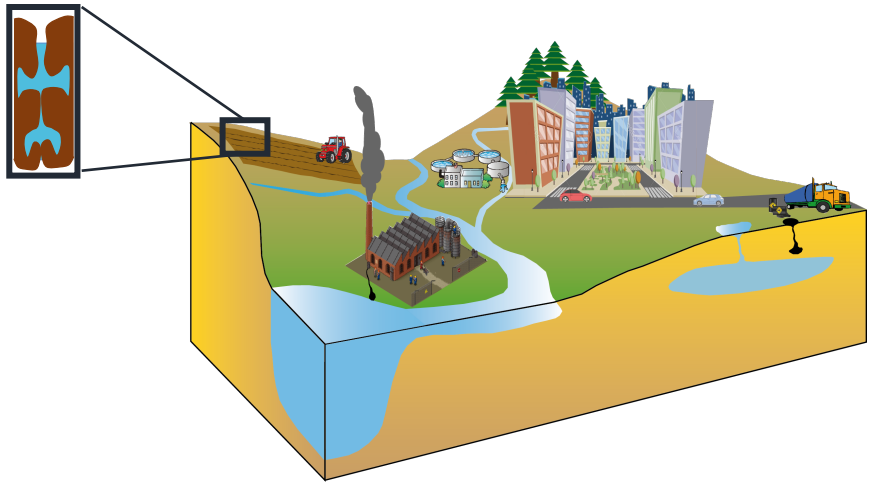
ANR Digestate 2016-2020

Application of clays in water treatment

ANR Polpharma 2016-2018

ANR Digestate

Diagnosis of wastes Treatments for contaminants fate in the Environment

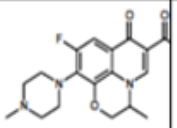
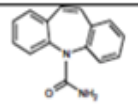
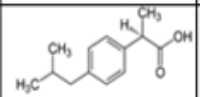


Soil characteristics

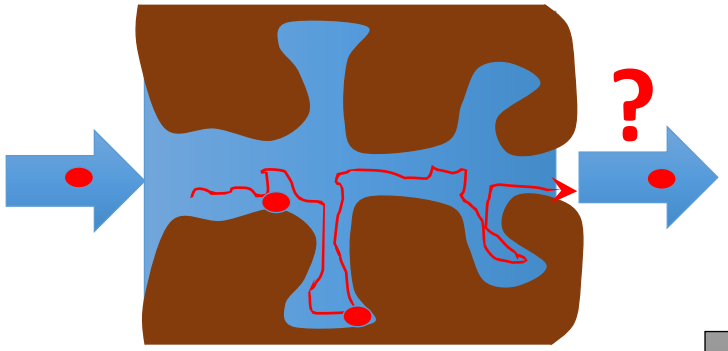
Colmar, France
(Bourdat-Deschamps et al., 2017)

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

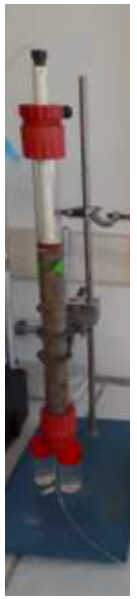
Pharmaceutical compounds

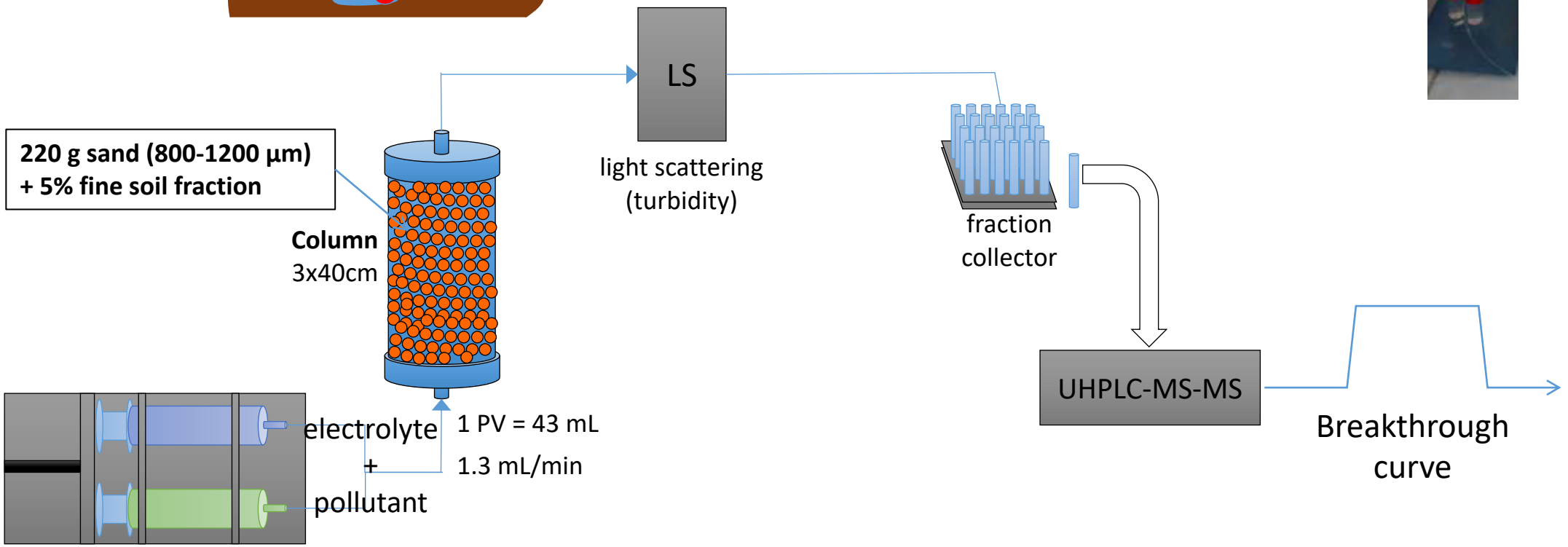
Product	Category	Chemical name (CAS)	Chemical structure	Water solubility mg L^{-1}	log K_{ow}	pKa	Kd l/kg	Koc l/kg
Ofloxacine OFL	Antibiotique, Fluoroquinolone	9-fluoro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-2.3-dihydro-7H-{1.4] oxazino-[2.3.4-ij]quinoline-6-carboxylic acid (82419-36-1)		3400	0,35[a]	5,97-8,98[a]	1000-3000	50000-300000
Carbamazépine CBZ	Antiepileptique	benzo[b][1] benzazepine-11-carboxamide (298-46-4)		18	2,45[a]	7[a]	0.5 - 37	130-500
Ibuprofène IBU	Anti-inflammatoire	acide alpha-méthyl-4-(2-méthylpropyl)phényl]propanoique (15687-27-1)		725.8 10^3	3,96-4,8	4,54	0.2-1	100-300[c]

Column experimental setup



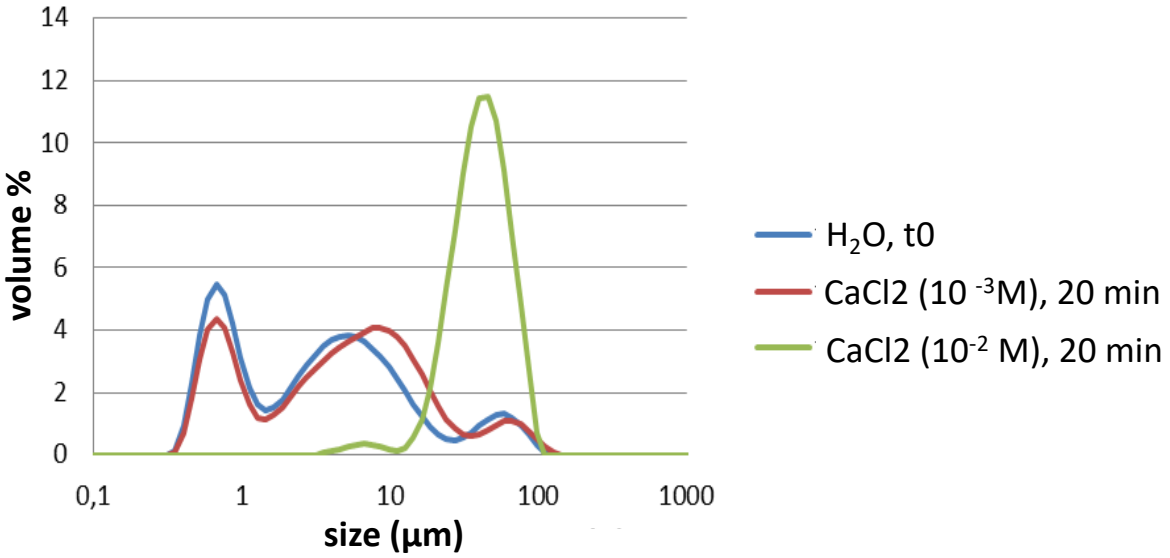
- breakthrough?
- deposition?
- colloidal vectorisation?

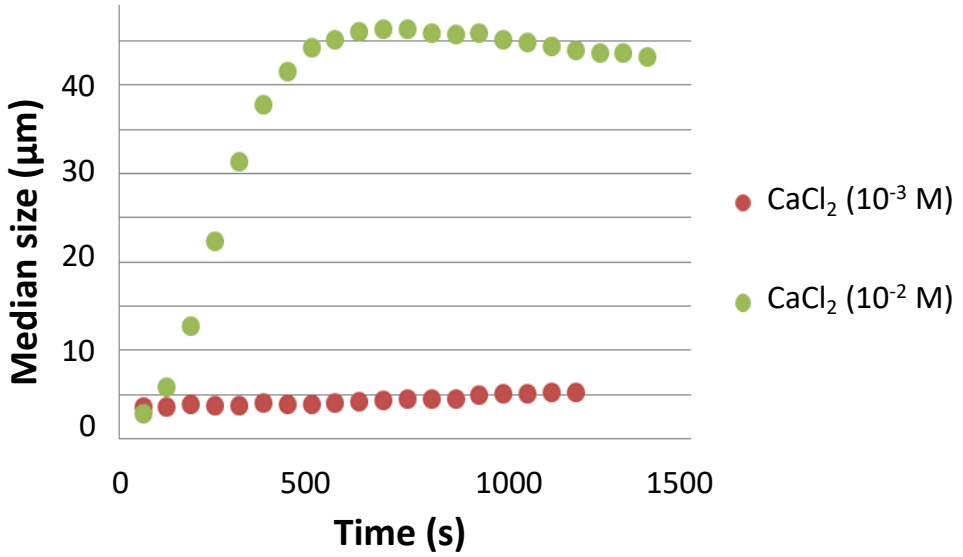




Colloidal dispersion of the soil fine particulate matter

colloids = 0.41 wt%





- $CaCl_2$ (10^{-2}M): rapid aggregation of soil colloids from 4 to 40 µm.

Hyp in column: favours stable soil aggregation, and no colloid mobilisation.

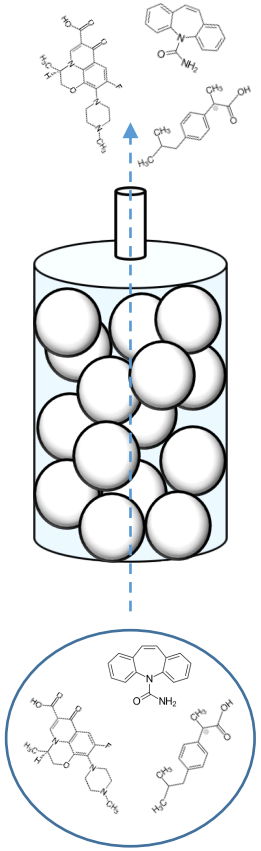
- $CaCl_2$ (10^{-3}M): stable dispersion of soil colloids.

Hyp in column: favours colloid mobilisation, and possible pollutant vectorisation.

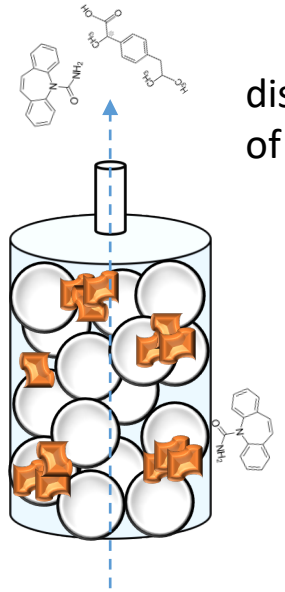
Working hypothesis and experimental approach

3 modalities to control the presence of colloidal vectors

Quartz sand only:
Reference free of colloids
$CaCl_2$ (10^{-3} mol / L)



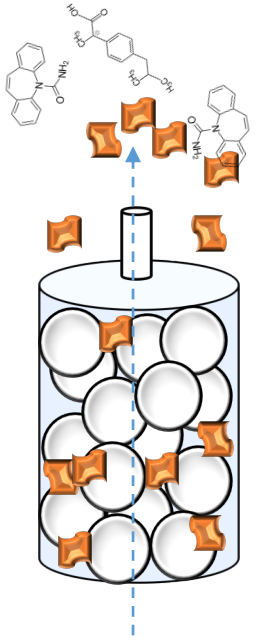
Quartz sand + soil (95/5)
favoring colloids **aggregation**
$CaCl_2$ (**10^{-2}** mol / L)



dissolved transport
of pollutant only?

+ attachment to soil or sand?

Quartz sand + soil (95/5)
favoring colloids **mobilization**
$CaCl_2$ (**10^{-3}** mol / L)

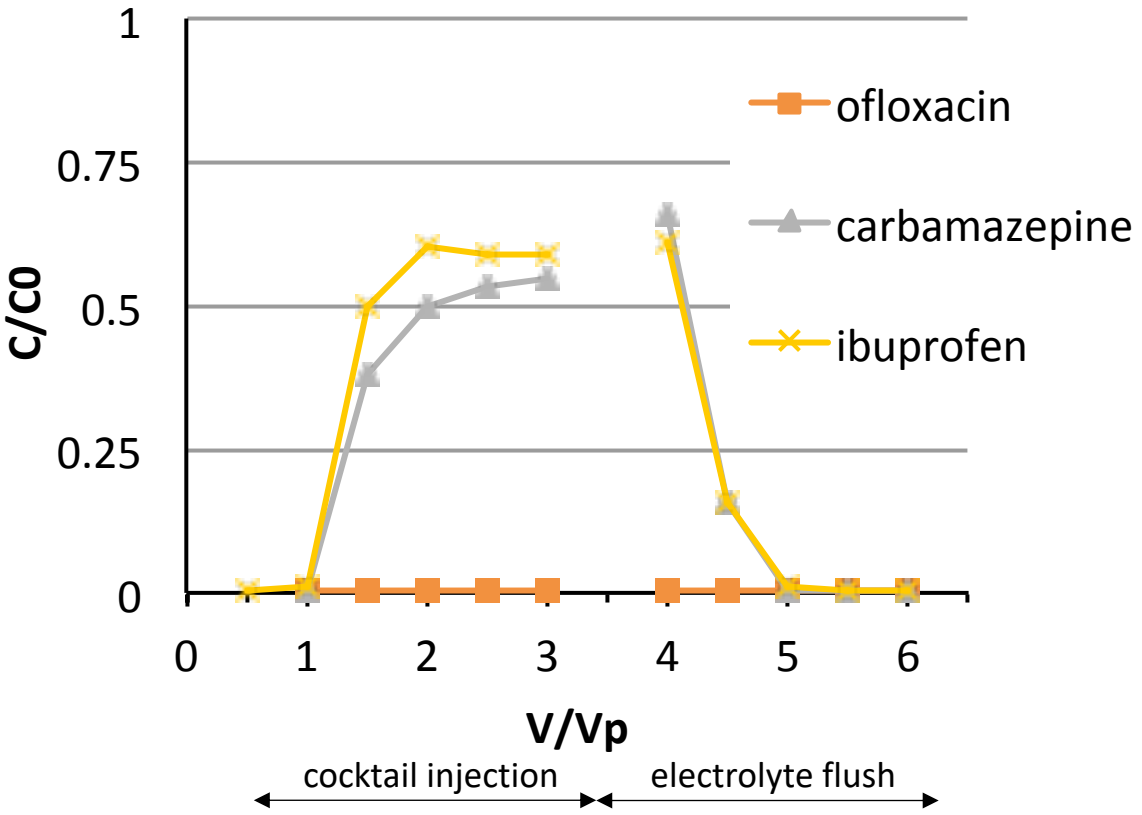


colloidal + dissolved
transport of pollutant?

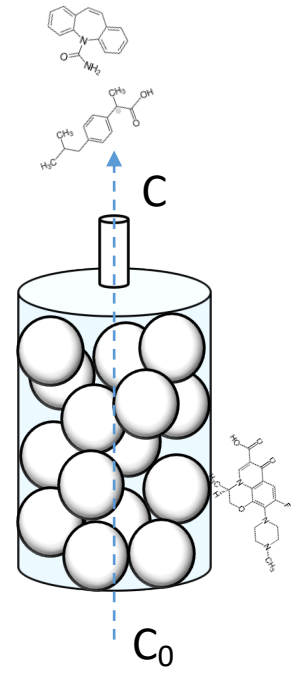
+ attachment to soil or sand?

Mobility of pharmaceutics in the reference quartz sand

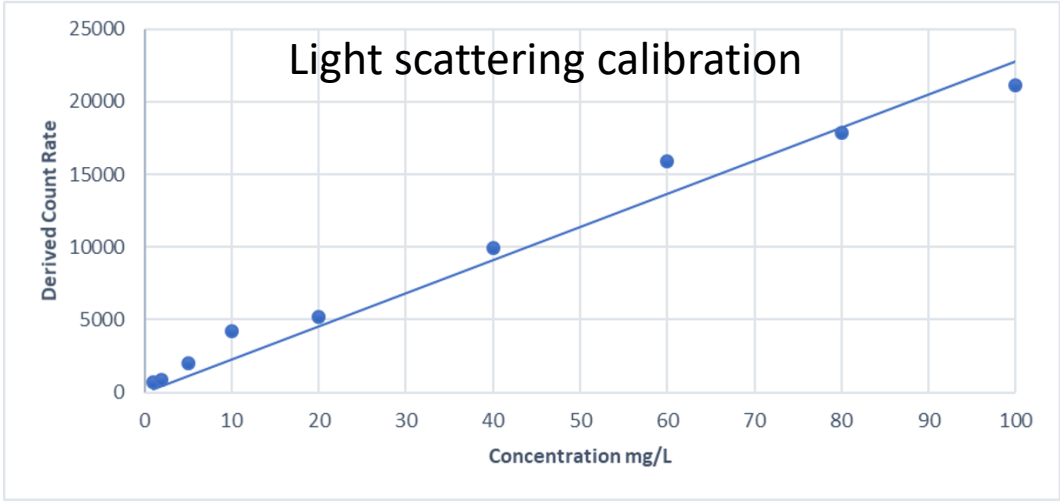
The breakthrough curve gives
the fraction of the pollutant mobile in the porous medium (C/C0),
as a function of the number of pore volumes (V/Vp) flowing at the column outlet.
A cocktail of the three pollutants was injected during 3 pore volumes.

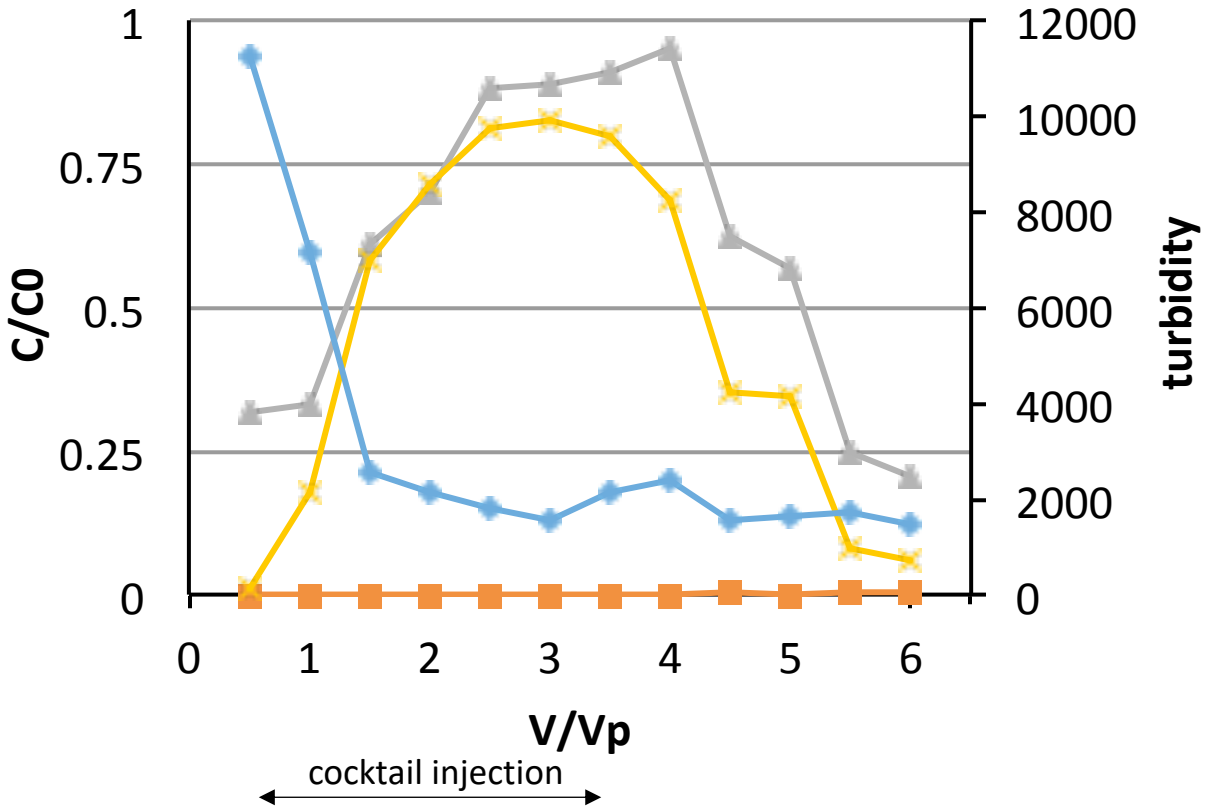


- Ofloxacin is not mobile.
  ← strong interactions with quartz
- Carba., ibu. mobile at 55-60%.



Mobility of pharmaceuticals in the sand + soil under dispersing condition ($CaCl_2$ 10^{-3}M)



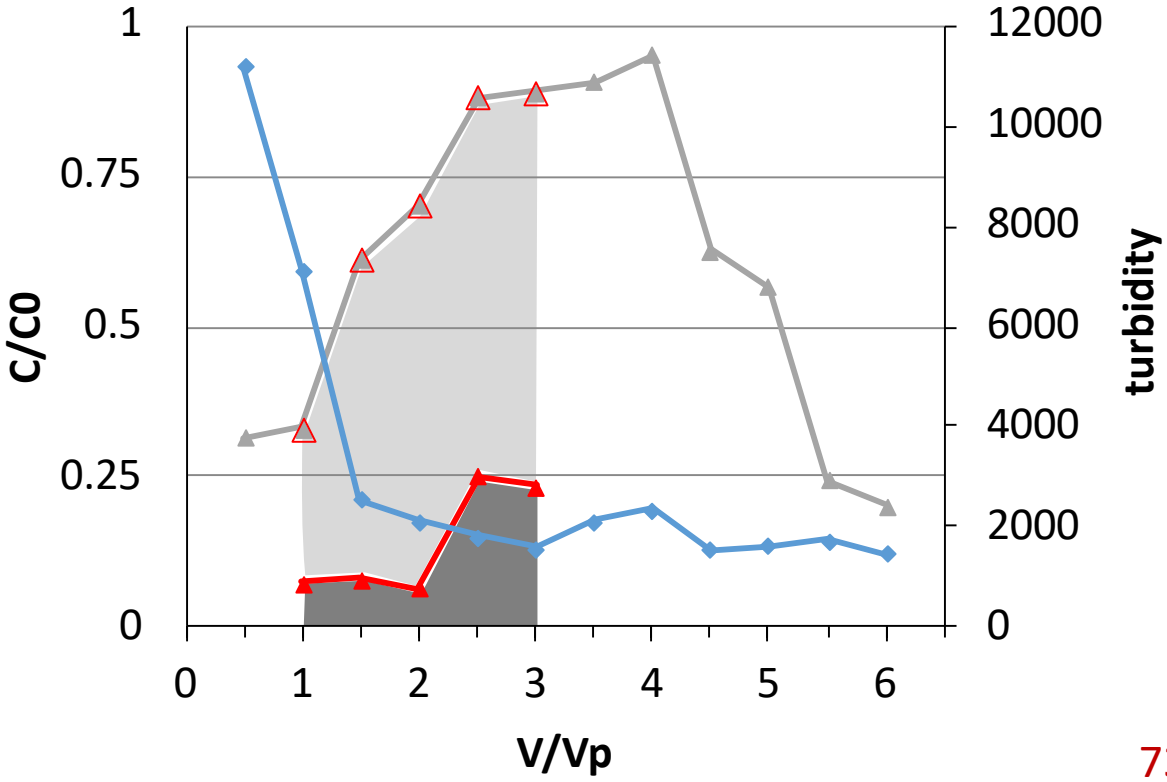


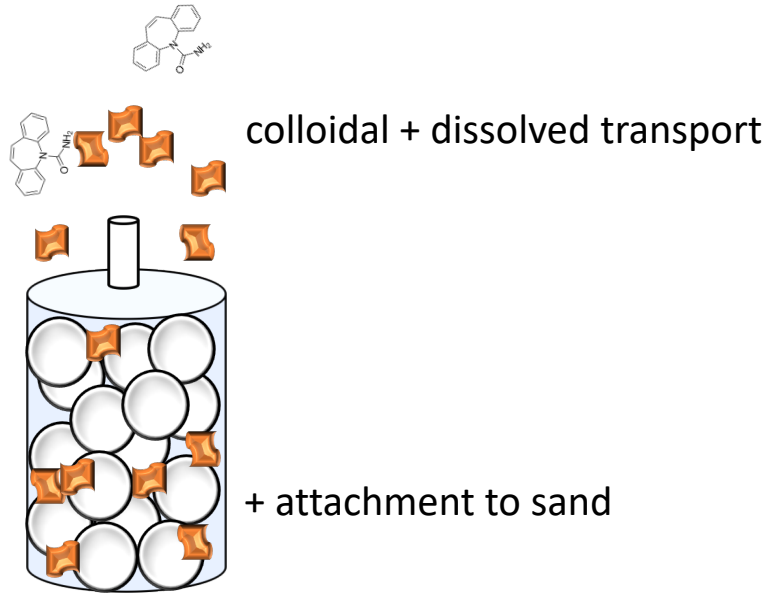
- Oflo still not mobile.
- carba + ibu mobile at 80-95% (25-35% more than in sand)
- colloids mobilisation (turbidity) stable after 1.5 V/Vp.

Hyp.: Colloidal vectorisation contributes to 25-35% of the compound mobility?

Carbamazepine colloidal vectorization in $CaCl_2$ 10^{-3}M

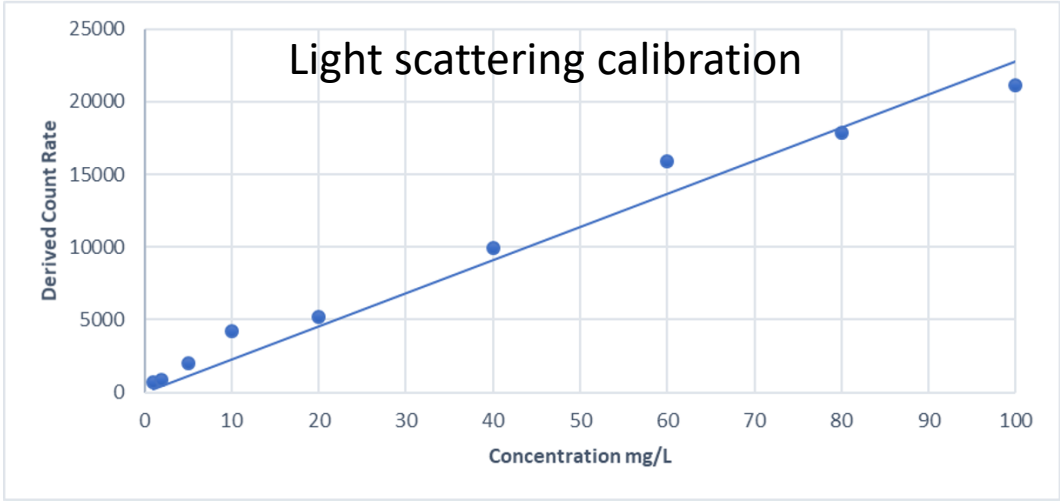
- 5 fractions (1 to 3 V/Vp) further treated by filtration at 0.2 µm
- Carba. analysed separately in the total and the filtrate
- Colloidal vectorization = total – filtrate < 0.2 µm

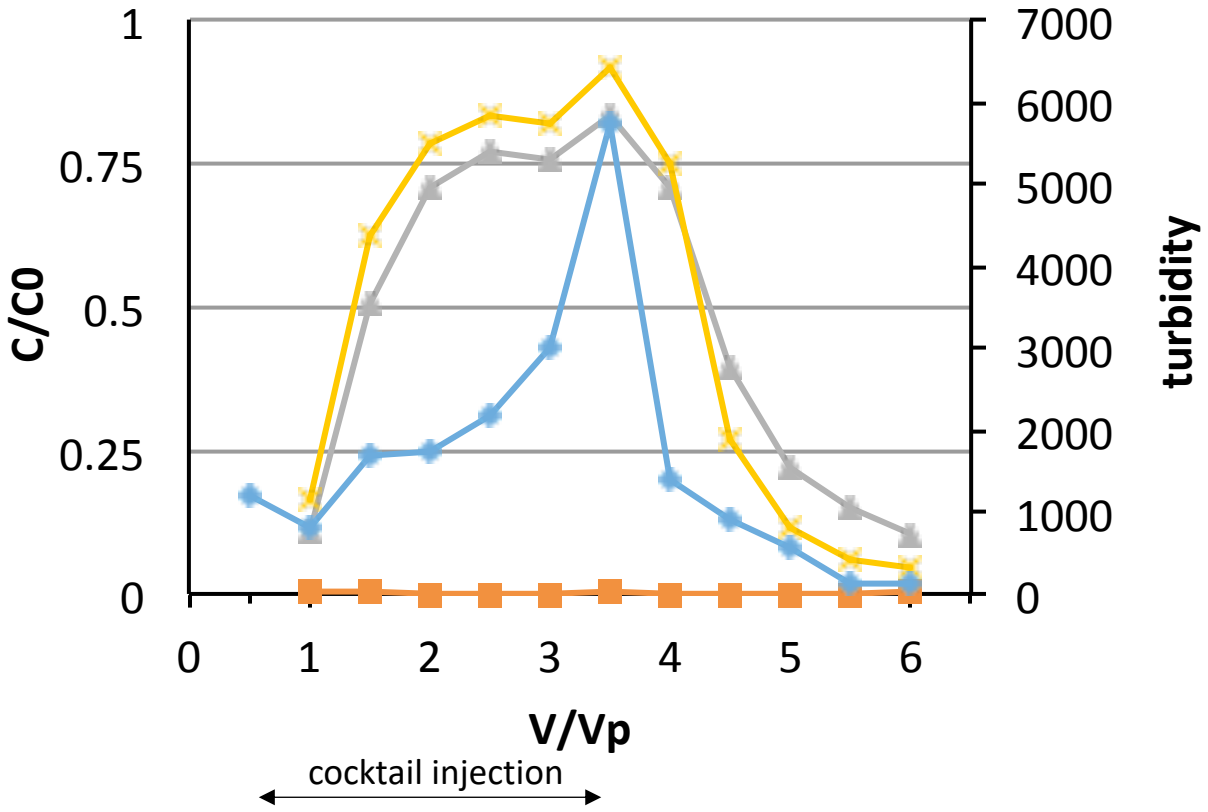




73% of the total breakthrough = breakthrough in quartz sand

Mobility of pharmaceutics in the sand + soil under aggregating condition ($CaCl_2$ 10^{-2}M)

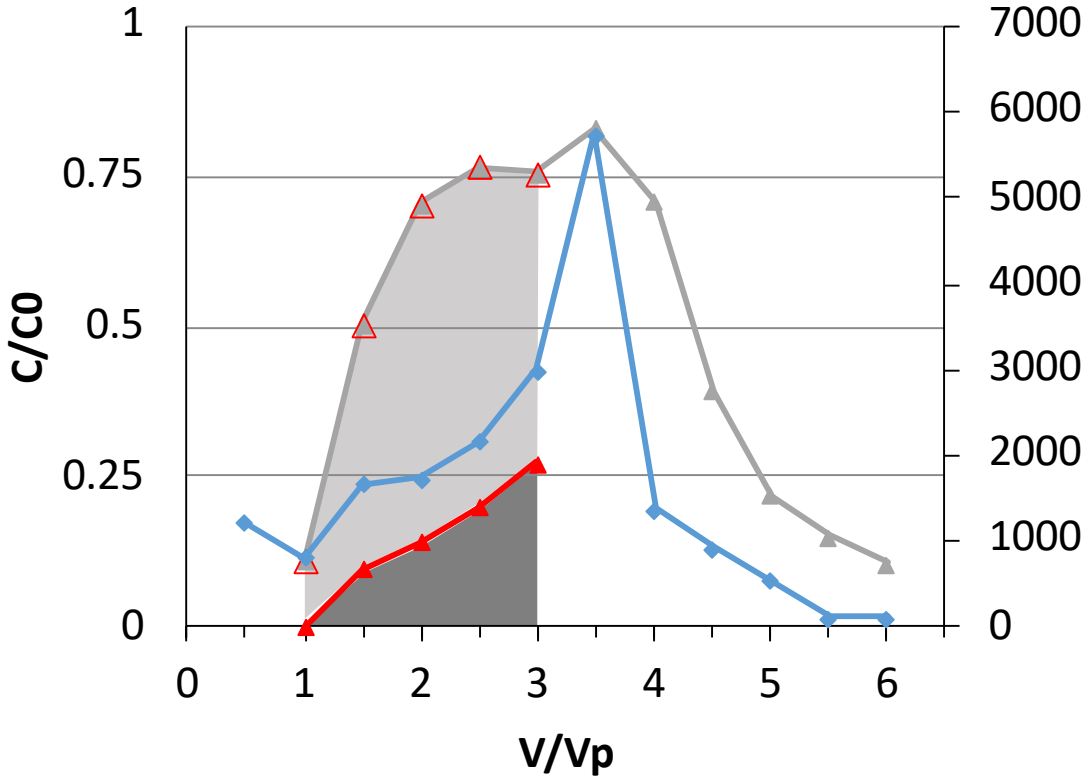


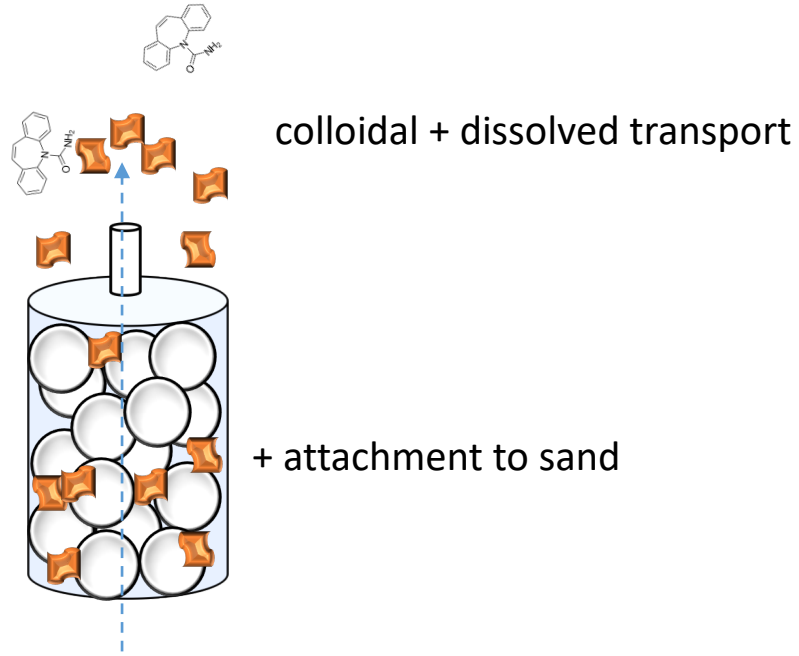


- Oflo still not mobile
- Carba, ibu mobile at 75-80% (20% more than in sand)
- Surprisingly, colloids mobilisation increases during pharmaceutical injection, from 1 to 3.5 V/Vp.

Carbamazepine colloidal vectorization in $CaCl_2$ 10^{-2}M

- 5 fractions (1 to 3 V/Vp) further treated by filtration at 0.2 µm
- Carba. analysed separately in the total and the filtrate
- Colloidal vectorization = total – filtrate < 0.2 µm





Colloidal vectorization reaches 36% and follows the turbidity.

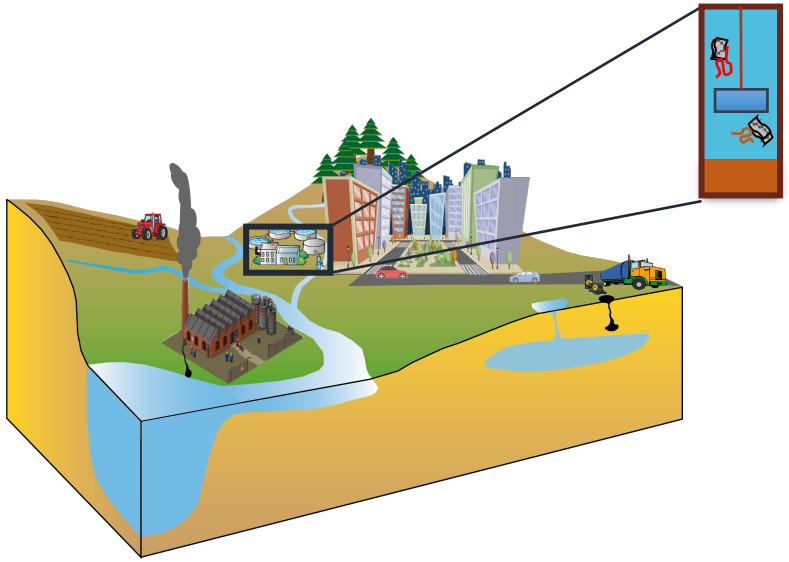
Summary of part 1

- Column setup adapted to evidence the role of colloidal transport in porous media
- Significant role of micrometric particulate matter constituting the soil in the mobility of pharmaceuticals.
- These colloids may cause either retention or vectorisation of the pharmaceuticals through the soil porous media, as a function of the physical-chemical conditions that determine dispersion conditions.

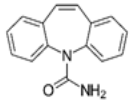
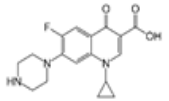
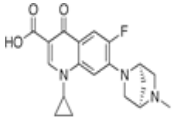
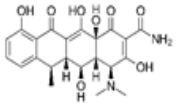
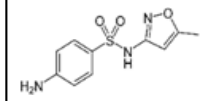
- Future work: assess the colloid characteristics (shape, surface area, reactivity)

ANR Polpharma

Innovative processes involving nanostructured materials for micropollutant removal in potable water treatment



Studied pharmaceutical compounds

Pharmaceutical class	Antiepileptic	Antibiotics			
Compounds	Carbamazepine	Ciprofloxacine	Danofloxacine	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

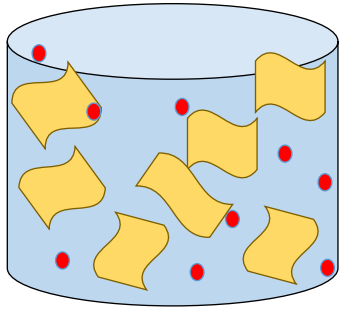
Objectives:

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

Approach

- Clay-based solution?

MMT/SiO_2 nanocomposite preparation



initial material:
Na/Ca/K-montmorillonite
Nador, North Morocco
+
Silica Klebosol 30R50 80 nm

agitation
in pure water

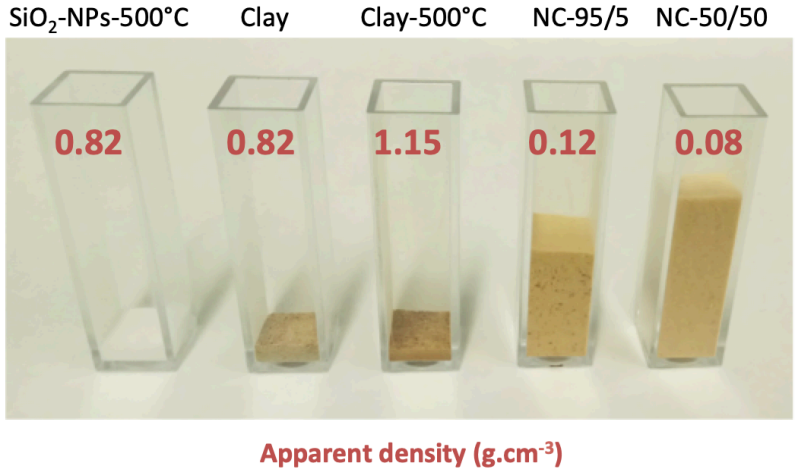
- get a homogeneous distribution

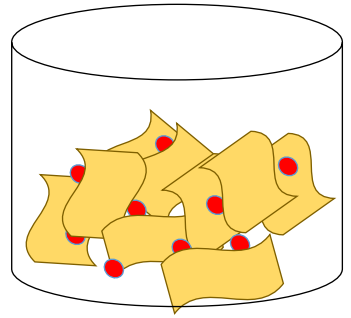
drying
flash freezing
+ freeze-drying

- avoid differencial settling or drying

calcination
oven 500 °C

- maintain the structure and make attachment irreversible

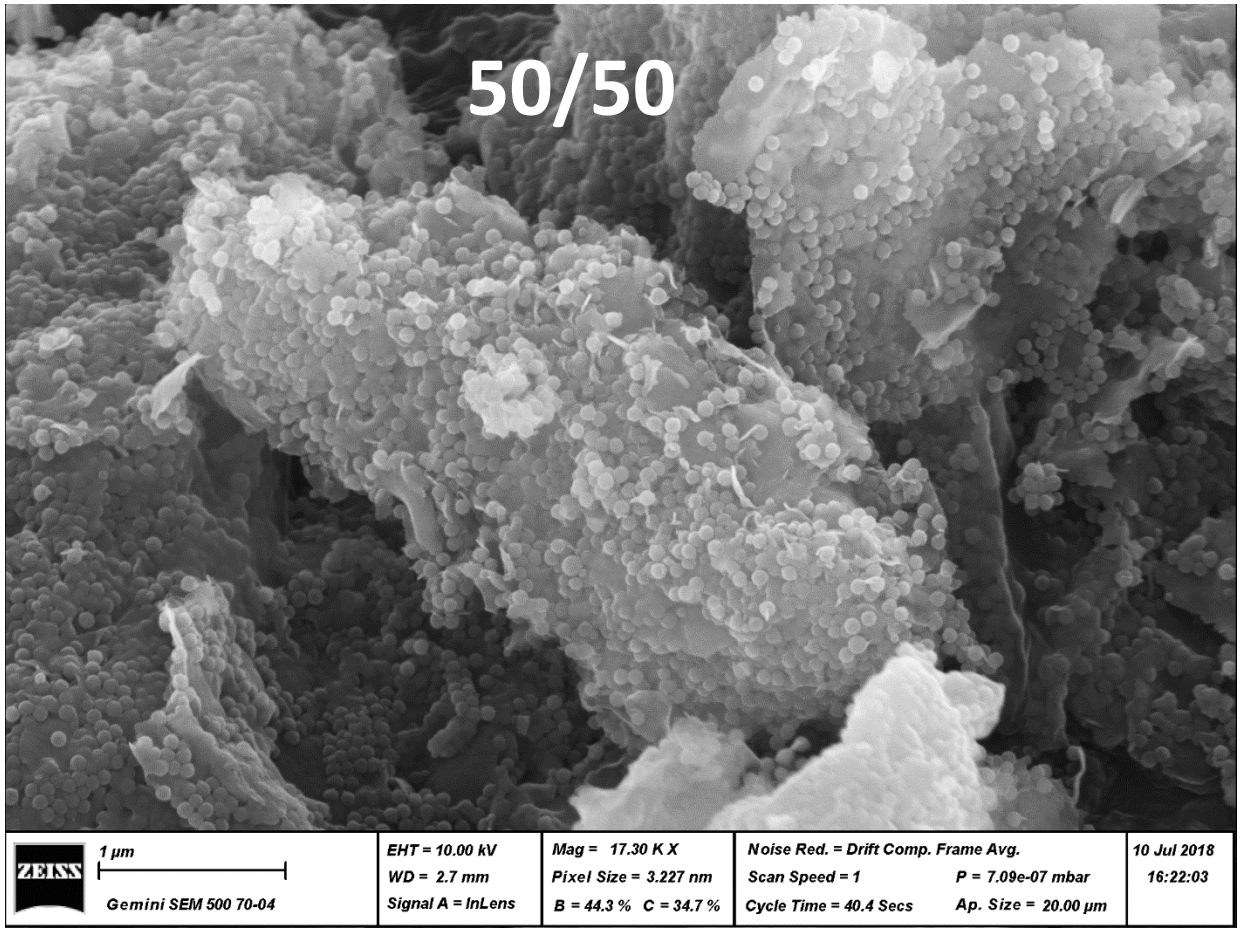


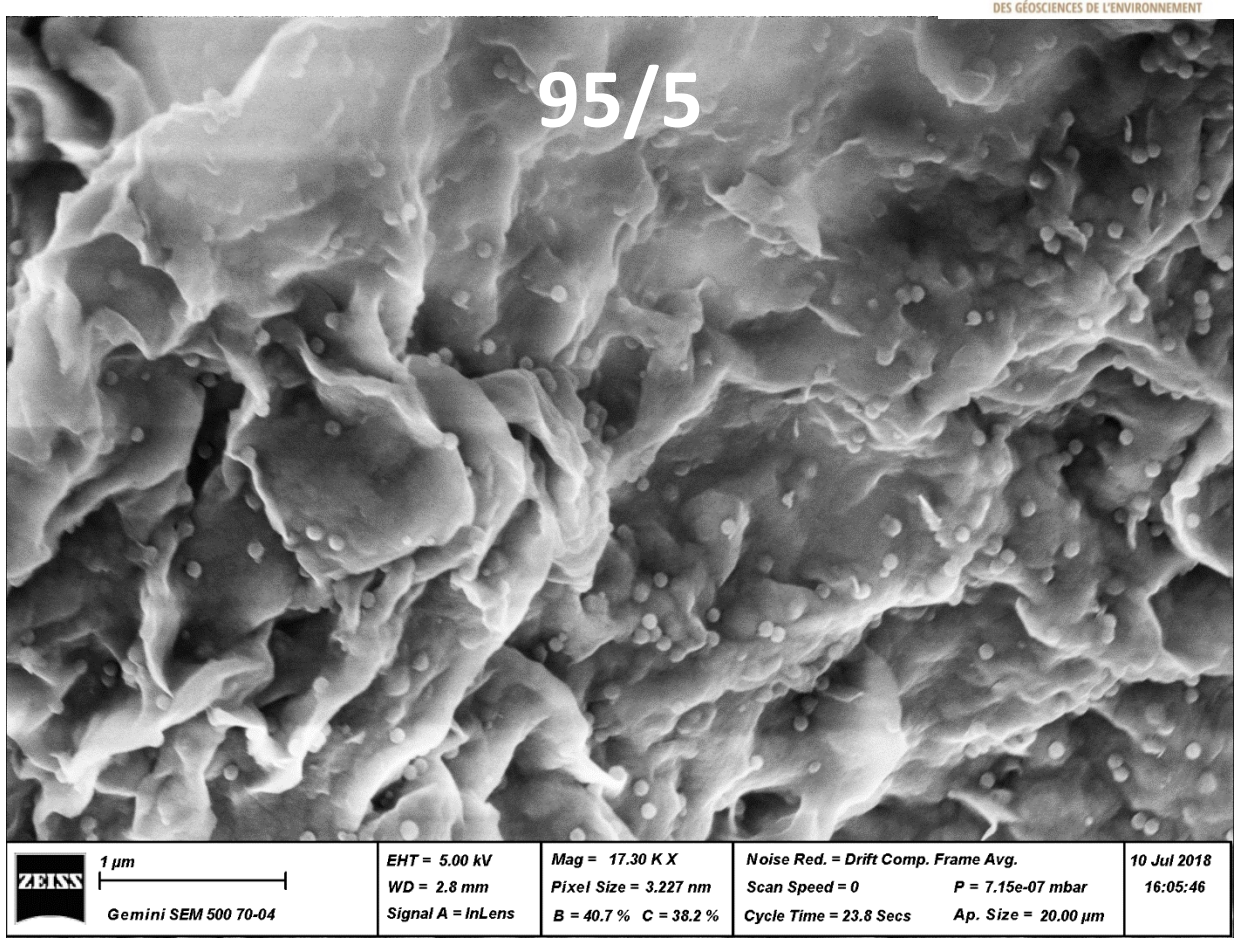


nanocomposite MMT/SiO_2

improved sorption capacity?

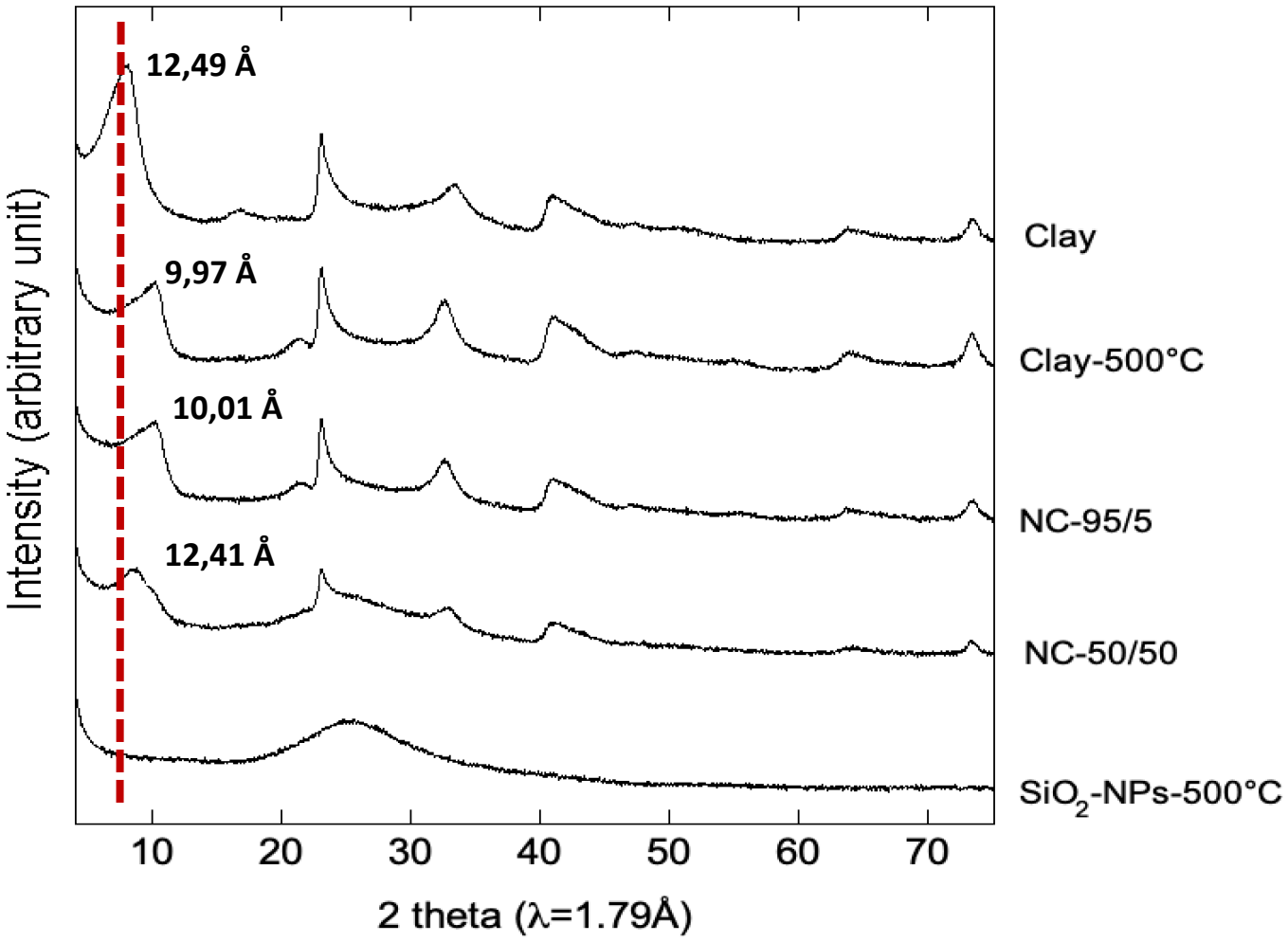
SEM observation of the MMT/SiO_2 nanocomposites





Levard et al., ESPR, 2020, in press

Characterisation of the MMT/SiO_2 nanocomposites – XRD

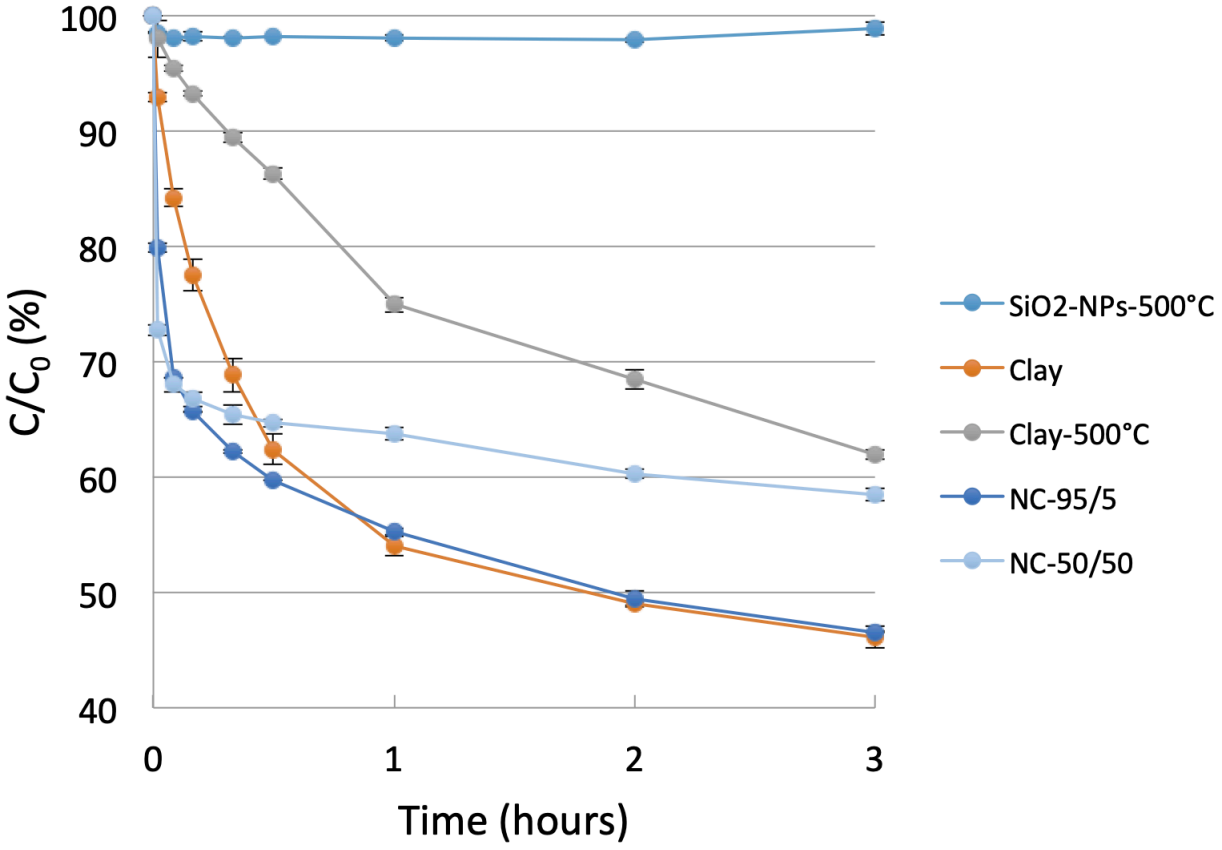


- MMT interlayer distance is affected by calcination due to dehydration
- No NP in interlayer space (80 nm)
- 50/50 composite displays hydrated interlayer space despite calcination

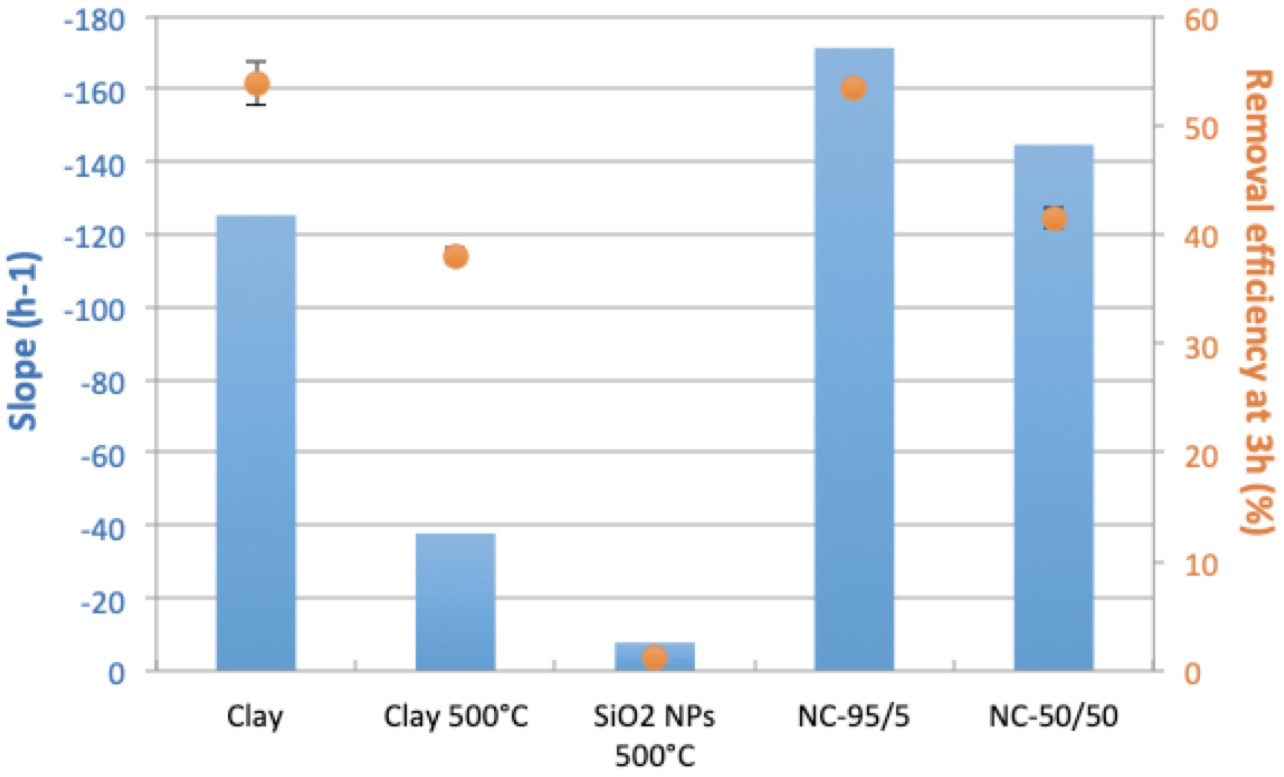
Levard et al., ESPR, 2020, in press

Optimisation of the MMT/SiO_2 ratio

Batch experiments
- aqueous medium: Evian water ; pH= 7,5-7,8
- sorbent concentration : 50 mg/L



Adsorption kinetics of ciprofloxacine on the composites.
Filtrates analysed with UV/vis abs.

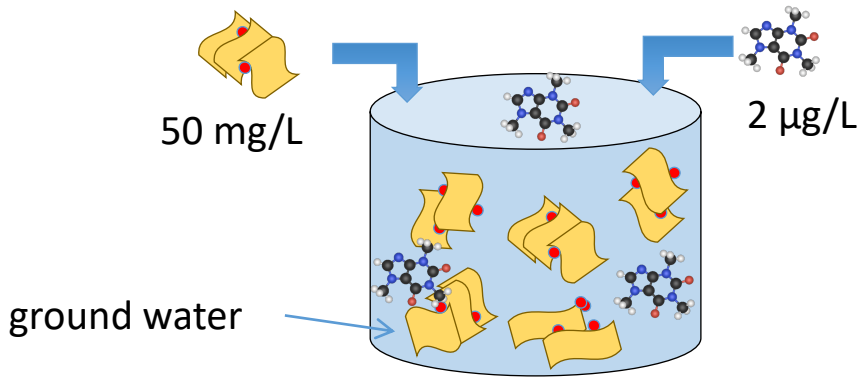


Levard et al., ESPR, 2020, in press

Micro-pollutant removal efficiency

Batch experiment

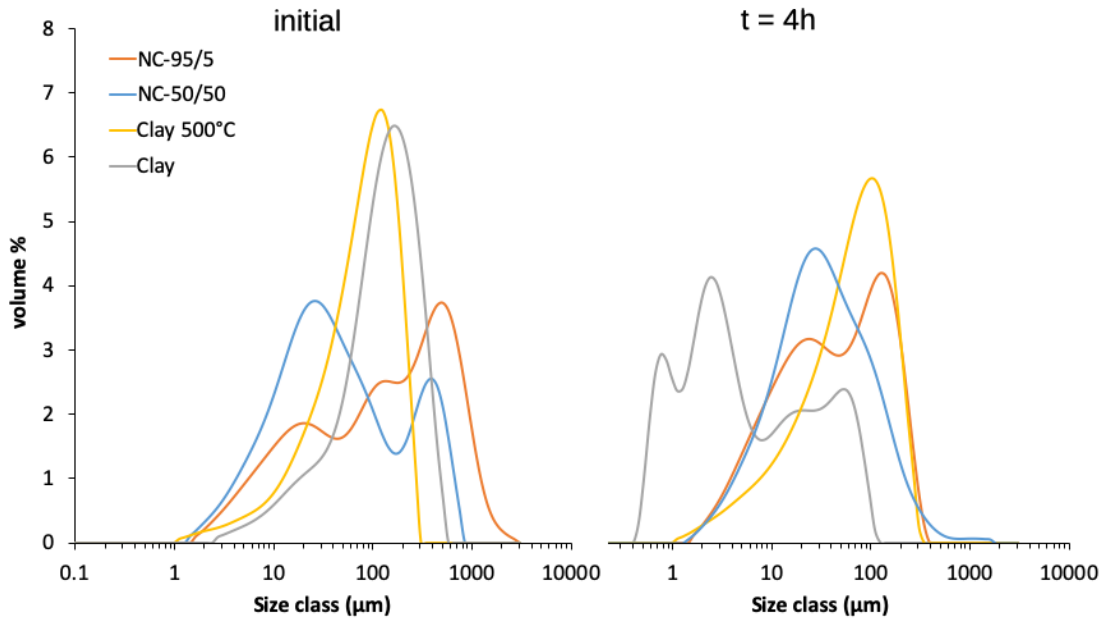
- µ-pollutant injection : **2 µg/L** each compound
- Sorbent concentration : **50 mg/L**
- Aqueous medium : **ground water**
- pH : **7.5**
- **Time : 48h**
- **Filtrates analysed with LC-MS/MS**

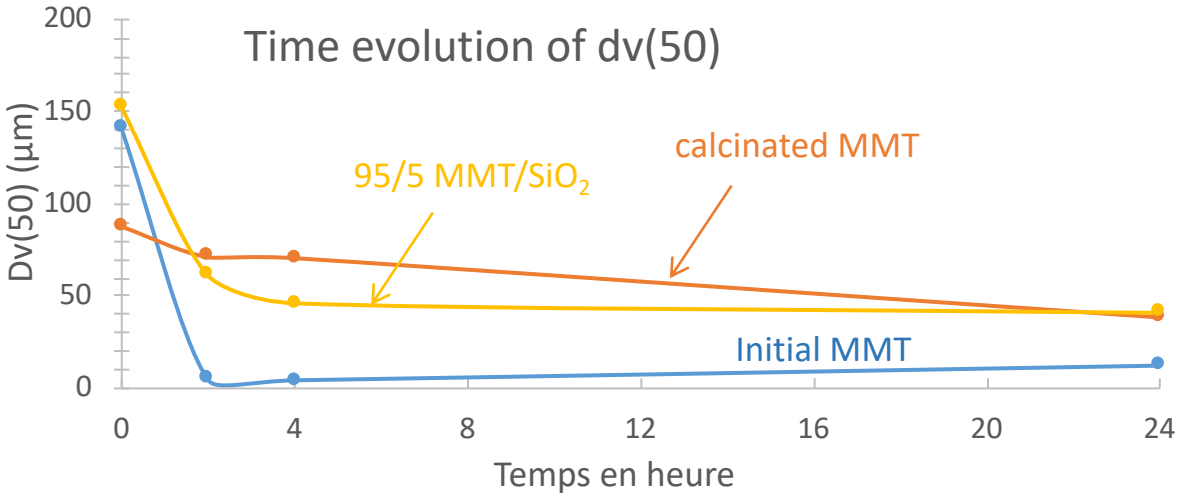


Sorbent (50mg/L)	Ciprofloxacine	Danofloxacine	Sulfamethoxazole	Doxycycline	Carbamazepine
Activated carbon	**100%**	**100%**	**100%**	**100%**	**100%**
MMT/Fe_2	39%	63%	0%	45%	3%
MMT/Fe_2/Fe_3	33%	69%	1%	74%	5%
MMT 20µm	60%	77%	0%	15%	3%
Fe_2 NP	1%	8%	0%	83%*	2%
MMT/SiO_2 (50/50)	99%	99%	0%	34%	3%
MMT/SiO_2 (95/5)	**100%**	**100%**	0%	**60%**	0%
MMT 2µm	**94%**	**95%**	0%	**41%**	0%
SiO_2 NP	0%	0%	0%	11%	0%

- no adsorption on NP alone
- **adsorption of some pollutants on pure clay with size effect**
- **Cipro, Dano, Doxy : similar structure**
- **most efficient sorbent : MMT/SiO_2 95/5**
- **Sulfa. and Carb. : not/weakly removed**

Aqueous dispersion of the composite



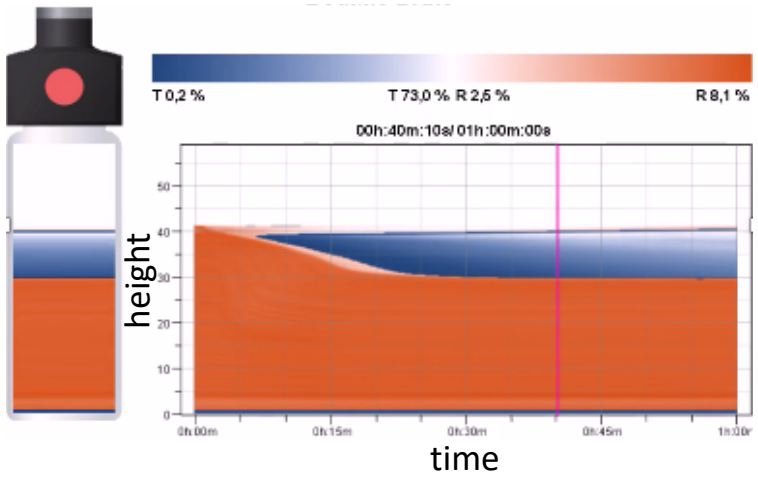


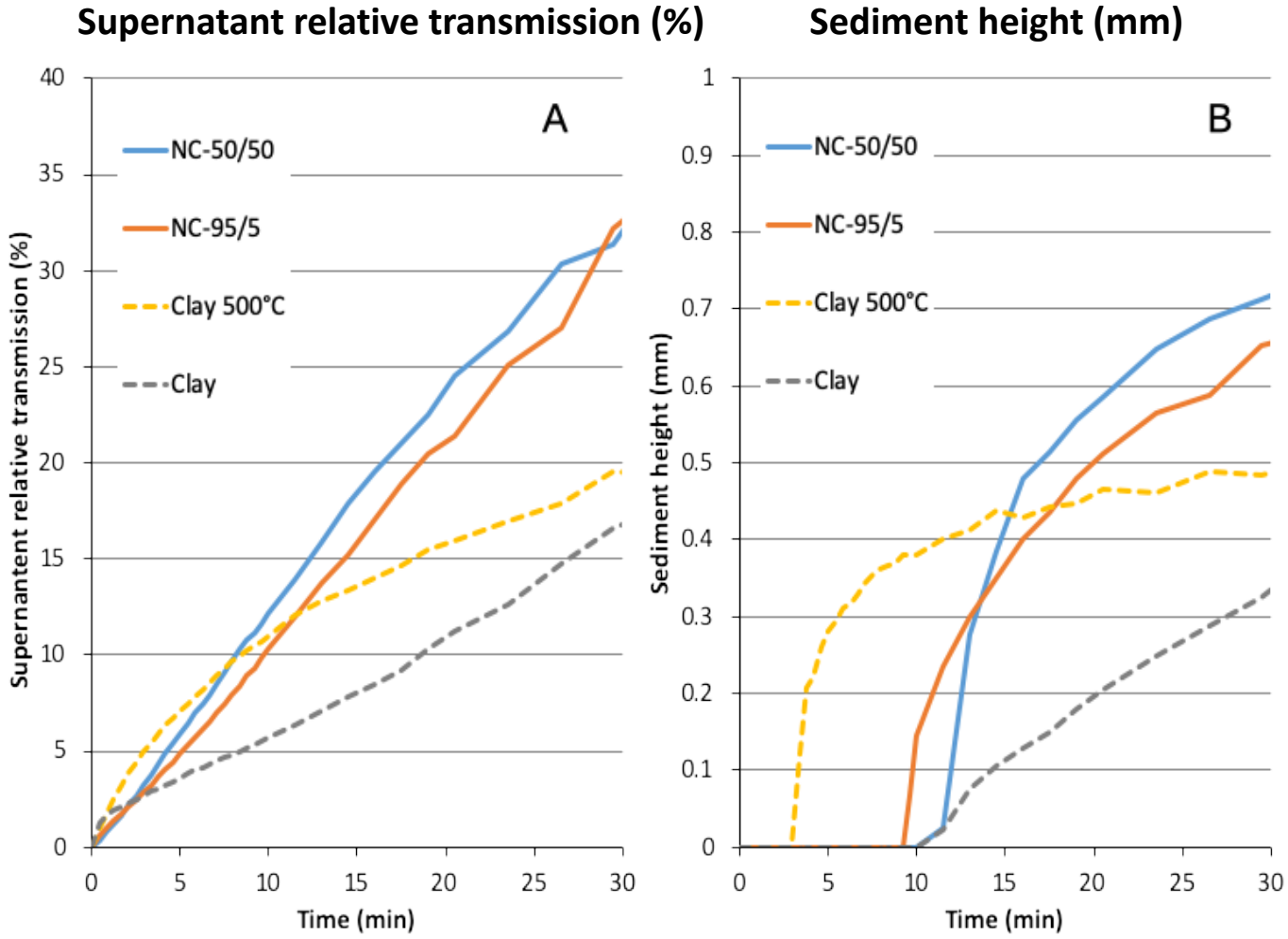
- Calcination at 500°C decreases dispersibility
- SiO_2/MMT composite behaves as 40 µm particles
- This should facilitate composite recovery by settling.

Levard et al., ESPR, 2020, in press

Settling velocity of the tested materials

Turbiscan Lab, Formulaction





Levard et al., ESPR, 2020, in press

Summary of part 2

- Modified clay was prepared as a candidate to eliminate pharmaceutical compounds in water treatment process
- MMT/nano-SiO_2 nanocomposites were synthesized that gave improved sorption capacity
  - 80 nm silica NP were used with Ca-montmorillonite
  - Aqueous dispersion followed by freeze drying and calcination was used
  - Optimal MMT/NP weight ratio was observed around 95/5
  - Irreversible hybrid aggregates are formed, that are easily recovered by settling.

Future works

- Recycle the material
- Test it in deep bed filtration

- Nature based solutions for wastewater reuse in irrigation
  - Treatment process?
  - Impact of pollutants, NOM and salts on soil?

Acknowledgements

Funding programs:
project **POLPHARMA** (ANR-15-CE04-0007)
Project **DIGESTATE** (ANR-15-CE34-0003)