Impacts of sludge stabilization processes and sludge origin on the mobility of pharmaceuticals following sludge land-spreading

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Who are we ????

Magali CASELLAS-Français
Associate Professor

Maryline SOUBRAND
Associate Professor

Topics :

PROCESS ENGINEERING : Wastewater and waste biological treatment.

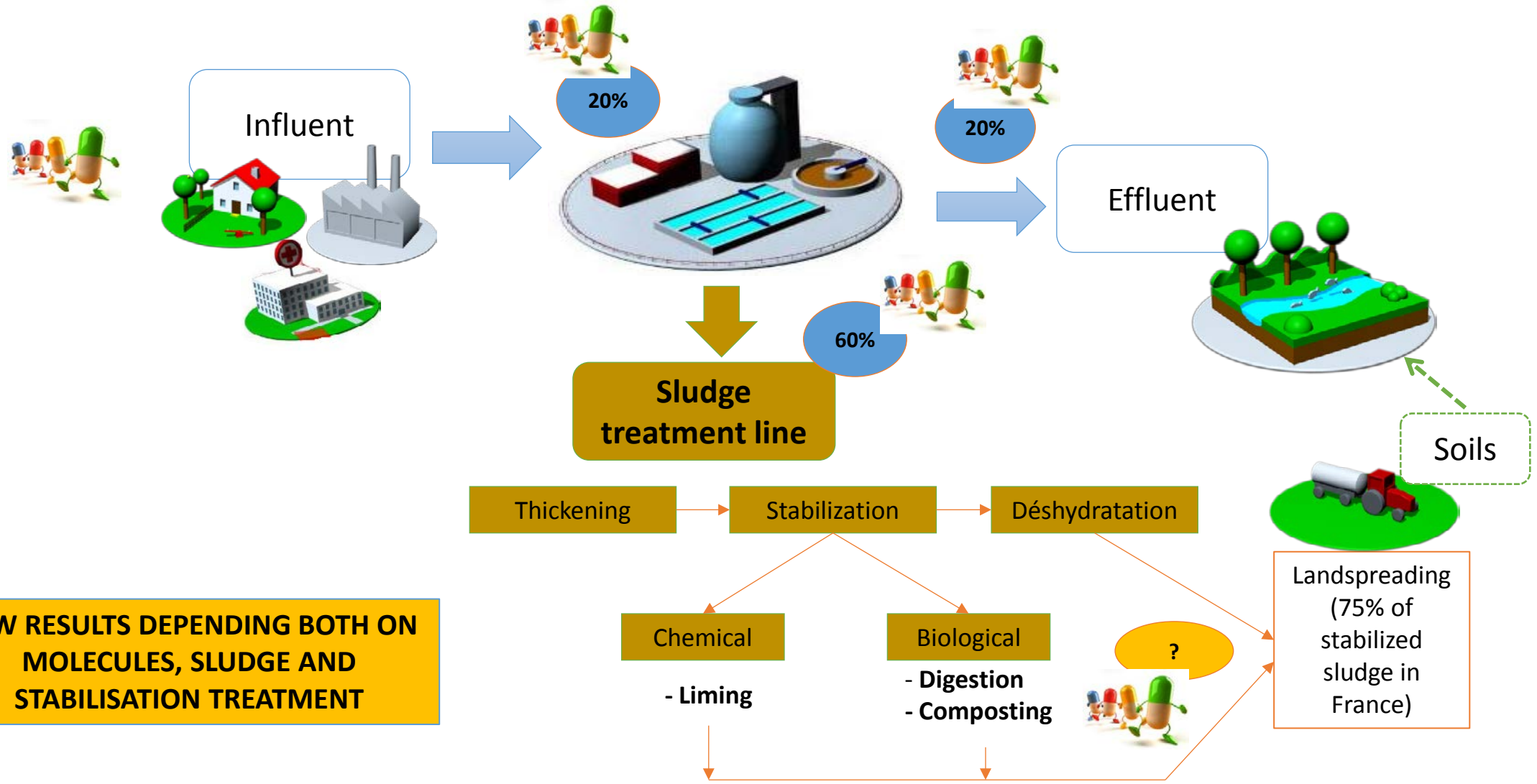
MICROPOLLUTANTS : Fate during biological processes implementation and impact on process design.

LIMOGES TECHNOPOLE

Topics :

SOIL GEOCHEMISTRY : fate of pharmaceutical compounds in soils

PHARMACEUTICAL COMPOUNDS : AN IMPORTANT ISSUE FOR SLUDGE LANDSPREADING



FEW RESULTS DEPENDING BOTH ON MOLECULES, SLUDGE AND STABILISATION TREATMENT

Impacts of sludge stabilization processes and sludge origin on the mobility of pharmaceuticals following sludge land-spreading

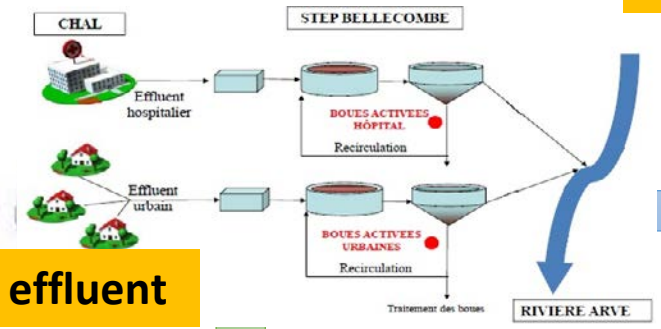
SOME KEY RESULTS FROM PREVIOUS STUDIES

TWO SLUDGE ORIGIN : WWTP with **2 separate lines of treatment (urban effluent and hospital effluent)**

hospital effluent

SIPIBEL Site Pilote de Bellecombe

Influent



Effluent

urban effluent

SIPIBEL PROGRAM (Pilot Site of Bellecombe, Haute-Savoie, France, near boarder with Switzerland)

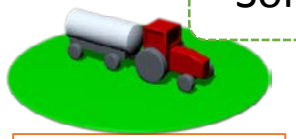
Sludge treatment line

Thickening → Stabilization → Déshydratation

Chemical — Biological

Liming — **Anaerobic Digestion**

Soils



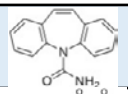
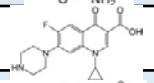
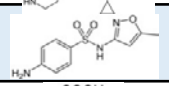
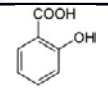
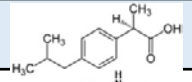
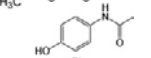
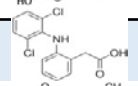
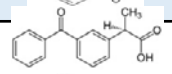
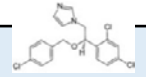
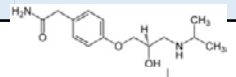
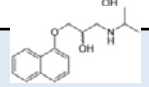
Landspreading (75% of stabilized sludge in France)

TWO STABILIZATION PROCESSES

SIPIBEL program 11 pharmaceutical compounds : Choosen considering their consumption and occurrence

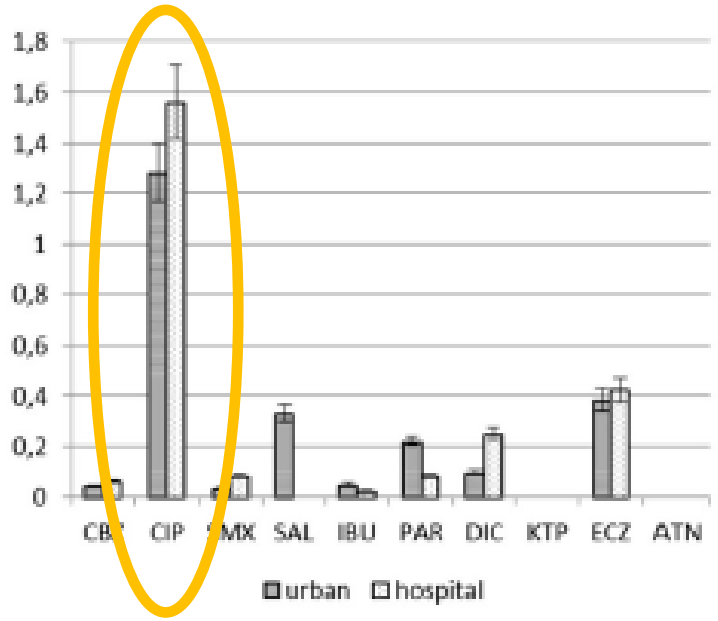
SIPIBEL Site Pilote de Bellecombe

Volatilisation excluded (H<100)

Familly	CompoUND	Structure	Molecular weight (g/mol)	Solubility in water (mg/L)	pKa	logKow	Henry constant ($Pa.m^3/mol$)	Hydrophobicity et charge at pH=7
Antiépileptic	Carbamazépine (**CBZ**)		236,27	17,7	13,9	2,25	$1,09.10^{-5}$	Hydrophobic, charged +
Antibiotiques	Ciprofloxacin (**CIP**)		331,34	30000	5,9 – 8,89	0,4	$5,16.10^{-14}$	Zwitterion, neutral
	Sulfaméthoxazole (**SMX**)		253,3	610	1,85 – 5,6	0,89	$6,50.10^{-8}$	Charged –
Anti-inflammatories /analgésics/ antalgics	Salicylique Acide (**SAL**)		138,12	2240	2,98 – 13,6	2,26	$7,39.10^{-4}$	Charged –
	Ibuprofène (**IBU**)		206,28	21	4,91	3,97	$1,52.10^{-2}$	Charged –
	Paracétamol (**PAR**)		151,16	14000	9,38	0,46	$6,50.10^{-8}$	Zwitterion, neutral
	Diclofénac (**DIC**)		296,15	2,37	4,15	4,51	$4,79.10^{-7}$	Hydrophobic, charged –
	Kétoprofène (**KTP**)		254,28	51	4,45	3,12	$2,15.10^{-6}$	Hydrophobic, charged –
Antifungal	Econazole (**ECZ**)		381,68	$6,46.10^{-2}$	6,77	5,61	$3,34.10^{-4}$	neutral
Bétablockers	Aténolol (**ATN**)		266,34	13300	9,6	0,16	$1,39.10^{-13}$	Hydrophilic, charged +
	Propranolol (**PRP**)		259,34	61,7	9,58	3,48	$8,08.10^{-8}$	Hydrophilic, charged +

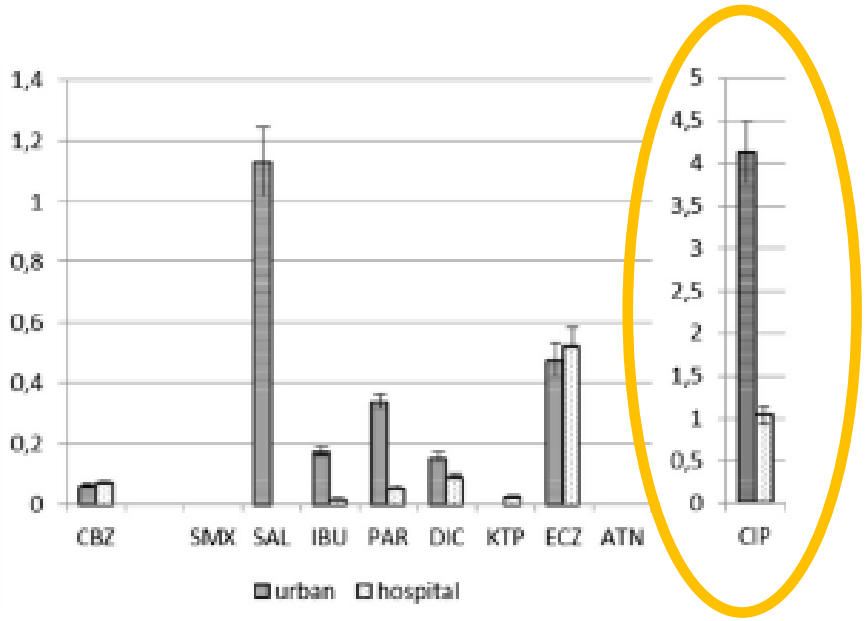
Impact of sludge stabilization process on the concentration of 11 pharmaceutical compounds in urban and hospital sludge

Total concentration (µg/gTS)



a (Limed sludge)

Total concentration (µg/gTS)



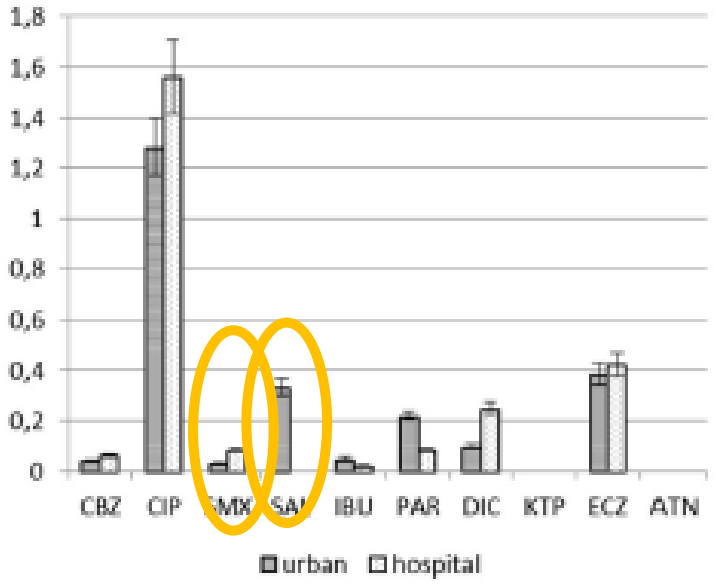
B (Digested sludge)

Lachassagne et al., 2015, DOI 10.1007/s11356-015-4918-4, ESPR

The antibiotic ciprofloxacin exhibited the highest concentration in sludge, whatever the treatment and origin of the sludge.

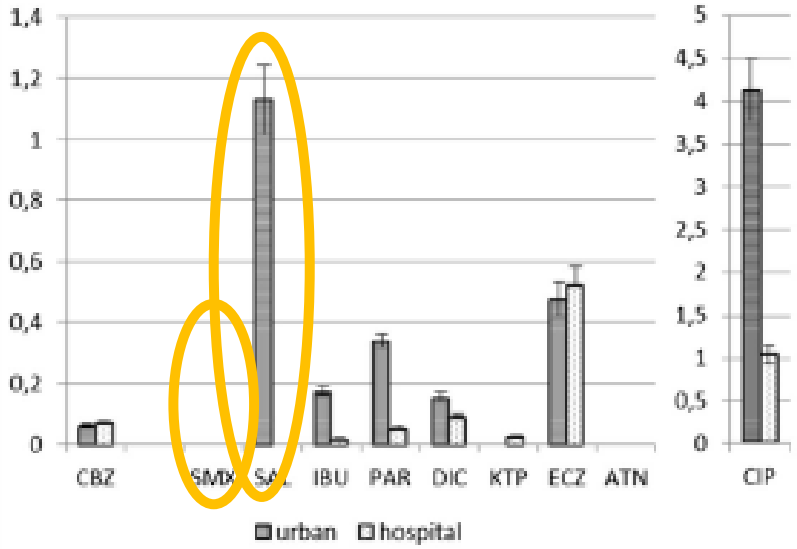
Impact of sludge stabilization process on the concentration of pharmaceutical compounds in urban and hospital sludge

Total concentration (µg/gTS)



a (Limed sludge)

Total concentration (µg/gTS)



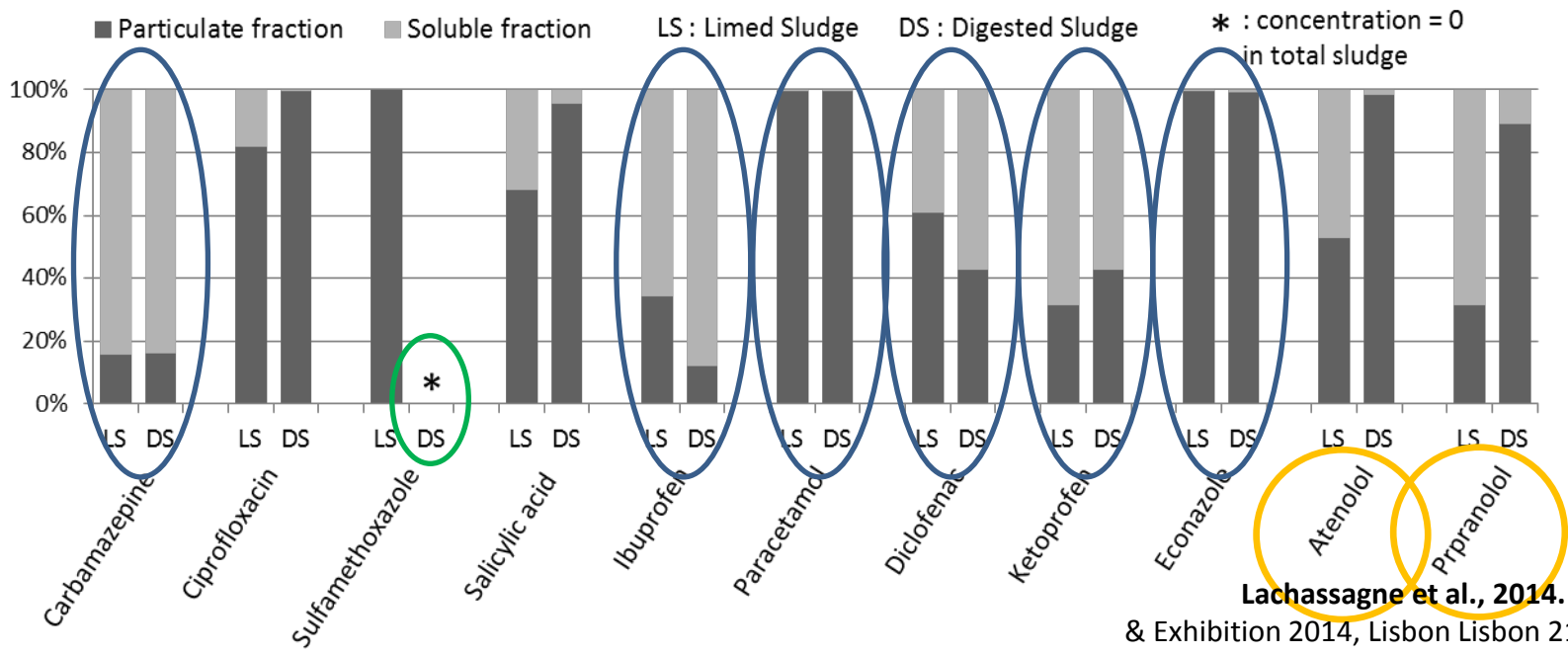
B (Digested sludge)

Lachassagne et al., 2015, DOI 10.1007/s11356-015-4918-4, ESPR

Some discrepancies in the concentration values of micropollutants with respect to the stabilization process used (ie Salicylic acid, SMX)

Impact of sludge stabilization steps on the phase distribution of pharmaceutical compounds

Case of urban sludge



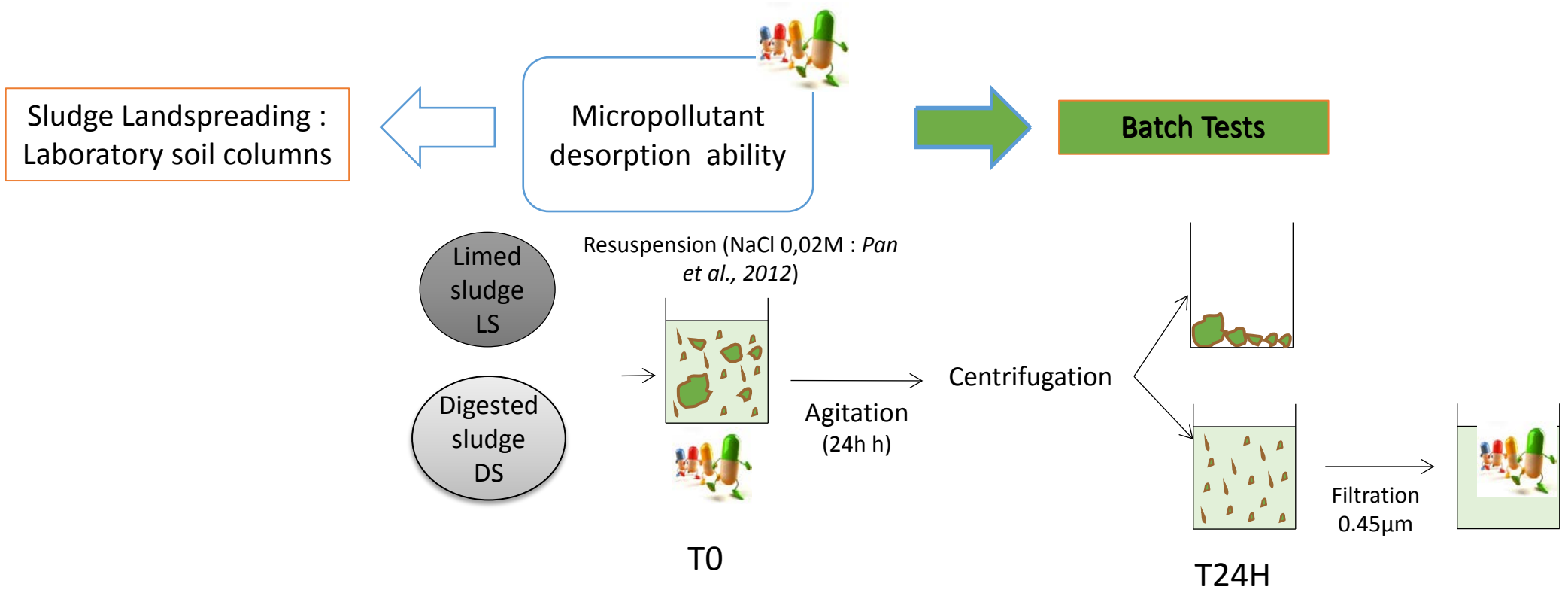
Lachassagne et al., 2014. World Water Congress & Exhibition 2014, Lisbon Lisbon 21 – 26 September 2014

Some compounds : no or only slight effect of sludge treatment (carbamazepine, paracetamol, ketoprofene, econazole)

Other compounds : noticeable effect of sludge treatment

- Concentrated in particulate fraction of digested sludge
- Biodegradation : Sulfamethoxazole is the only MP completely removed during anaerobic digestion (Carballa *et al.*, 2007 ; Narumiya *et al.*, 2013)

Availability of micropollutants in sludge before landspreading



$$K_{désorption} = \frac{[MP\ soluble\ concentration\ t24h]}{[MP\ particulate\ Concentration\ t0]}$$

Availability of micropollutants in sludge before landspreading

Micropollutant desorption ability

→ Batch Tests

$$K_{désorption} = \frac{[MP\ soluble\ concentration\ t24h]}{[MP\ particulate\ Concentration\ t0]}$$

Results highly dependent upon sludge origin, stabilization process, kind of molecule…..

Table 4 Desorption constant values for stabilized sludge

$K_{desorption}$	Limed sludge		Digested sludge	
	LS-U	LS-H	DS-U	DS-H
Carbamazepine	$742.6.10^{-3}$	0	0	0
Ciprofloxacin	$76.7.10^{-3}$	$341.6.10^{-3}$	$1.59.10^{-3}$	$12.7.10^{-3}$
Sulfamethoxazole	0	0	N.d.	N.d.
Salicylic acid	$516.6.10^{-3}$	N.d.	$7.32.10^{-3}$	N.d.
Ibuprofen	$240.8.10^{-3}$	$193.3.10^{-3}$	$158.5.10^{-3}$	107.10^{-3}
Paracetamol	0	0	0	0
Diclofenac	$48.2.10^{-3}$	$11.5.10^{-3}$	$83.9.10^{-3}$	$78.3.10^{-3}$
Ketoprofen	N.d.	N.d.	N.d.	0
Econazole	$5.28.10^{-3}$	$4.14.10^{-3}$	0	0
Atenolol	N.d.	N.d.	N.d.	N.d.

N.d. not detected in the total sludge

Lachassagne et al. 2015 Environmental Science and Pollution Research 22 (21), pp. 17135-17150

Availability of micropollutants in sludge before landspreading

Micropollutant desorption ability

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$$K_{désorption} = \frac{[MP\ soluble\ concentration\ t24h]}{[MP\ particulate\ Concentration\ t0]}$$

Results highly dependent upon sludge origin, stabilization process, kind of molecule…..

Difficult to establish simple prediction of desorption ability

$$K_{désorption} = \mathrm{f}[MP\ soluble\ concentration\ t24h]???????$$

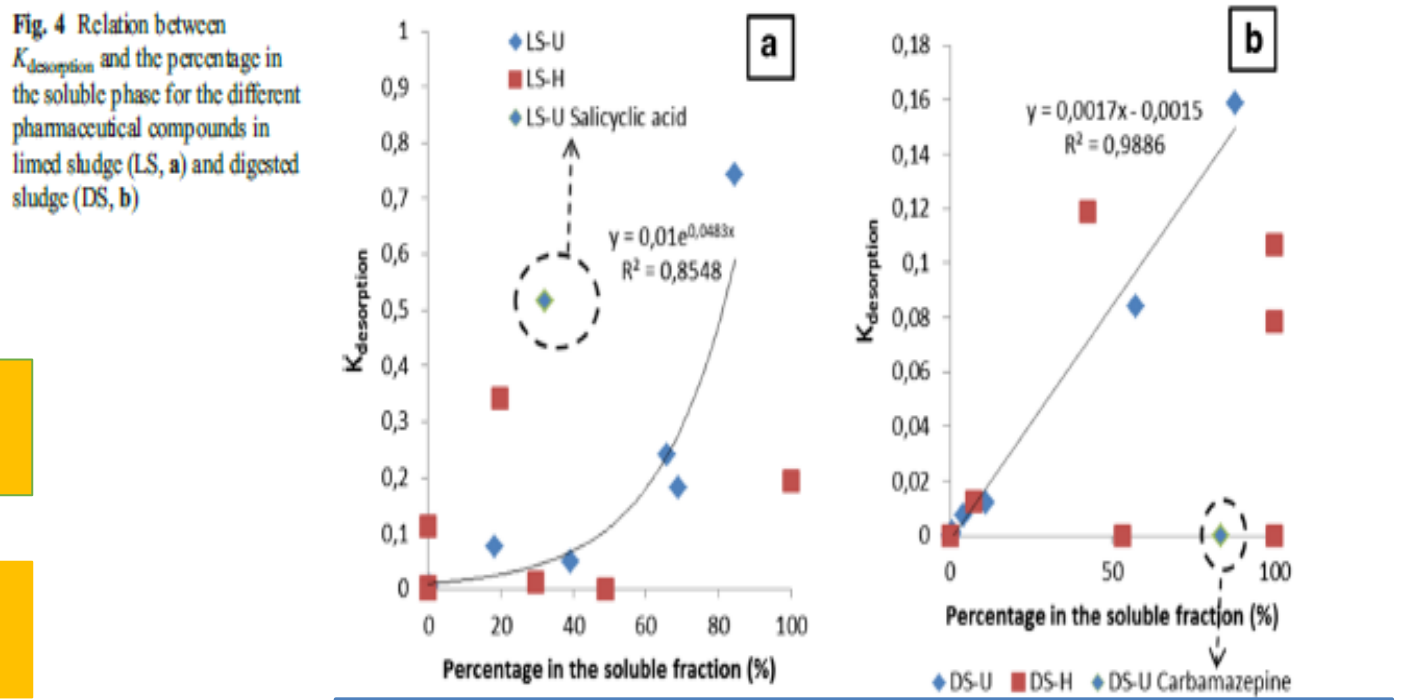


Fig. 4 Relation between $K_{désorption}$ and the percentage in the soluble phase for the different pharmaceutical compounds in limed sludge (LS, **a**) and digested sludge (DS, **b**)

No direct link

Lachassagne et al. 2015 Environmental Science and Pollution Research 22 (21), pp. 17135-17150

Availability of micropollutants in soil during landspreading

Sludge Landspreading :
Laboratory soil columns
Leaching tests
(Lachassagne et al. 2015)

Micropollutant desorption ability

Direct sludge landspreading
Control = (soil alone)

Control | Limed sludge | Digested sludge

Simulation of a one year precipitation in Limousin (France), Artificial rain $CaCl_2$ 0,01M

Soil

The topsoil sample of grassland (A horizon 0–10 cm, Cambisol, pH=5,6, clay 24%, OM 6%)

?

Leachate

Pharmaceutical concentration
Toxicity :Tests microtox and Daphnies

Availability of micropollutants in soil during landspreading

Sludge Landspreading : Laboratory soil columns **Leaching tests** (*Lachassagne et al. 2015*)

Micropollutant desorption ability

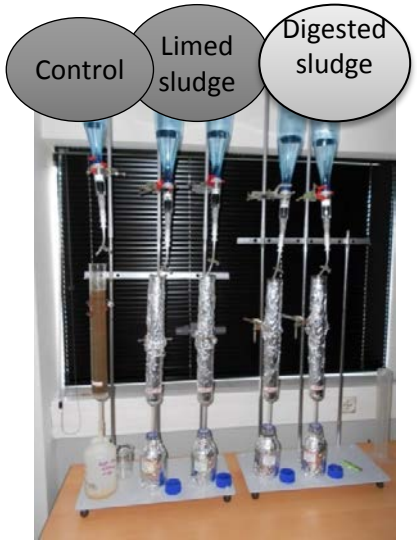


Table 6 Concentrations of pharmaceutical compounds in the composite leachate samples after the simulated rainfall (1020 mm for a year corresponding to 2358 mL during 30 days)

Compound	Concentration (µg/L)			
	LS-U	LS-H	DS-U	DS-H
CBZ	n.d.	n.d.	n.d.	n.d.
CIP	n.d.	n.d.	n.d.	n.d.
SMX	n.d.	n.d.	n.d.	n.d.
SAL	n.d.	0.045±0.009	n.d.	0.104±0.014
IBU	0.055±0.0045	n.d.	0.515±0.004	n.d.
PAR	n.d.	$2.5.10^{-4}$±0.0006	n.d.	n.d.
DIC	n.d.	n.d.	0.102±0.008	n.d.
KTP	n.d.	n.d.	n.d.	n.d.
ECZ	n.d.	n.d.	n.d.	n.d.
ATN	n.d.	n.d.	n.d.	n.d.

n.d. not detected in the total sludge

Leachate concentration ?

Leachate toxicity? X

Very low

Impacts of sludge stabilization processes and sludge origin on the mobility of pharmaceuticals following sludge land-spreading

- **SOME KEY RESULTS FROM PREVIOUS STUDIES**

Availability of micropollutants in sludge before landspreading ?

Difficult to establish simple prediction of desorption ability

Results highly dependent upon sludge origin, stabilization process, kind of molecule…..

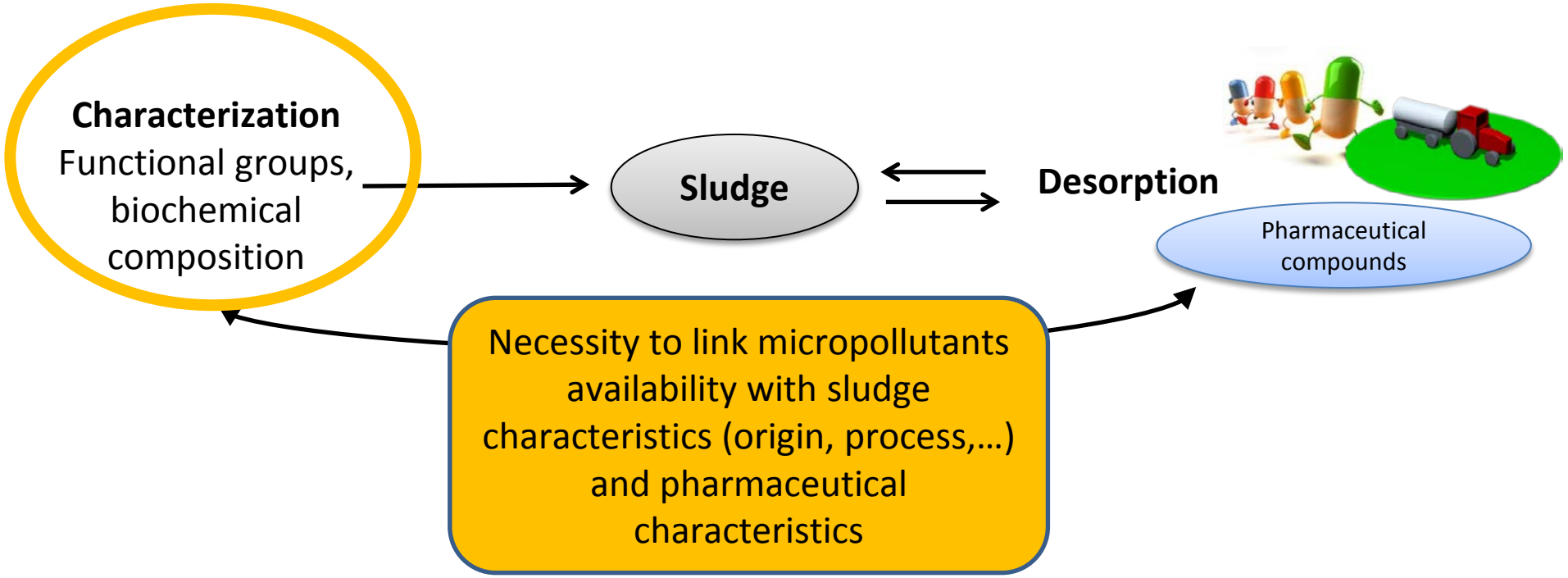
Availability of micropollutants in soil during landspreading ?

Most of the pharmaceuticals : not detected in leachate

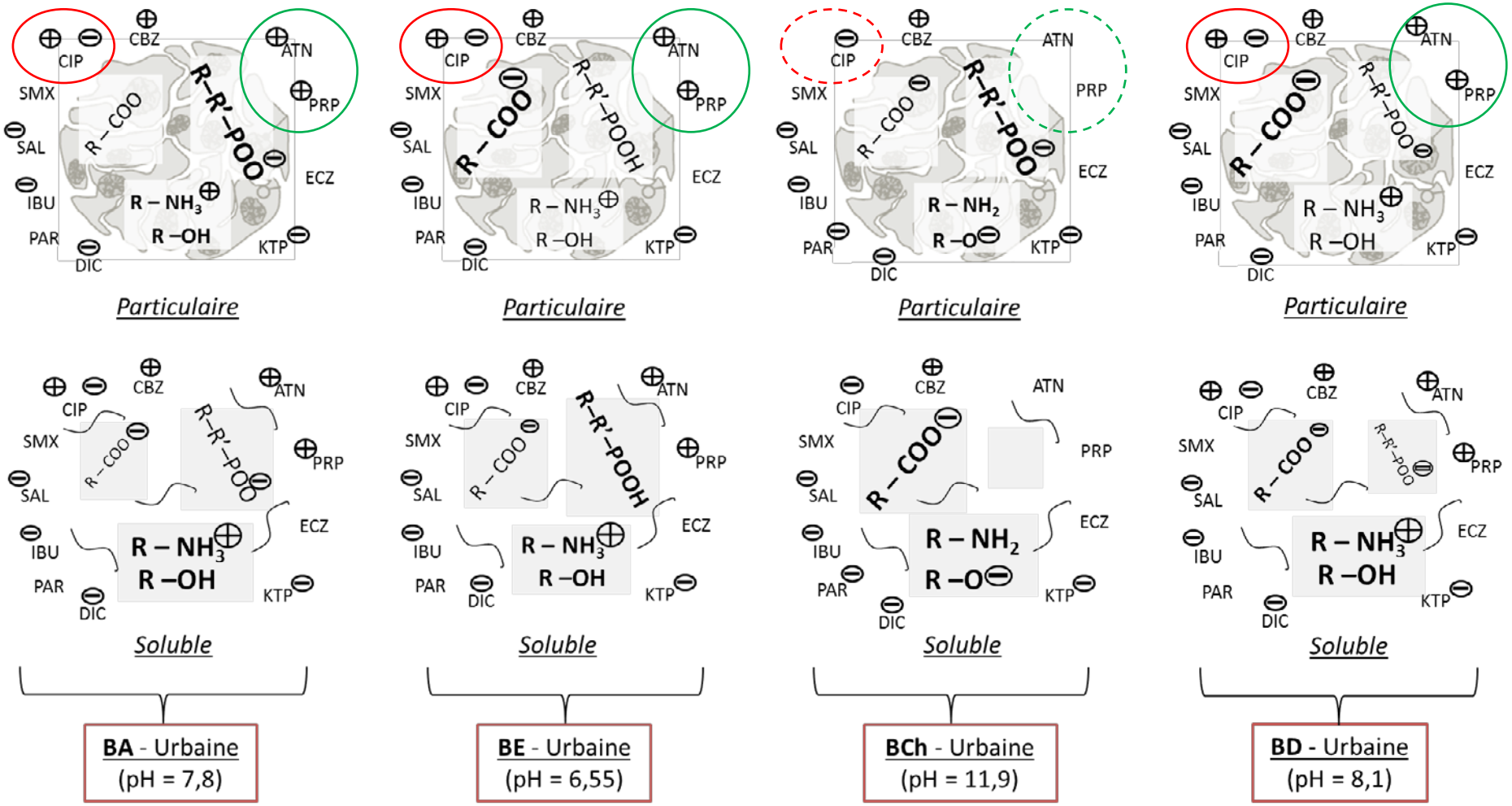
NO ECOTOXICITY OF THE LEACHATE

Impacts of sludge stabilization processes and sludge origin on the mobility of pharmaceuticals following sludge land-spreading

- TOWARDS A METHODOLOGY



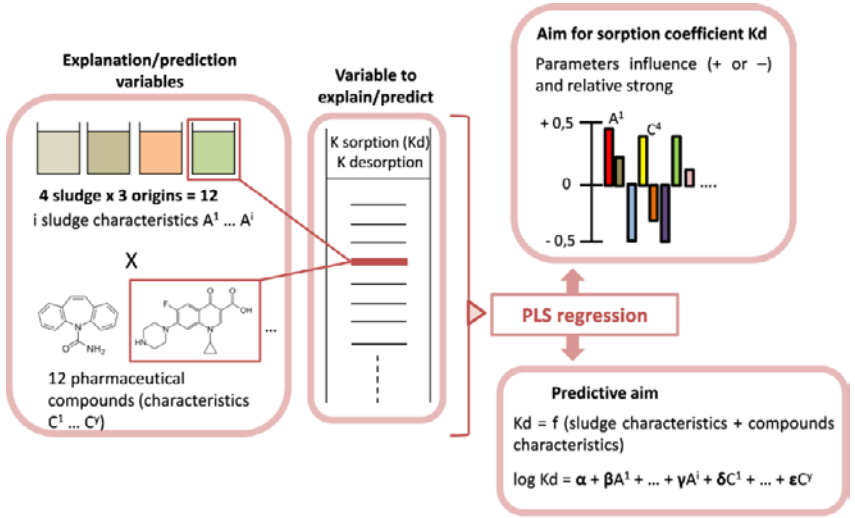
Ex : urban sludge



SLUDGE : SOLUBLE AND PARTICULATE CHEMICAL FUNCTIONAL GROUPS
PHARMACEUTICAL COMPOUND : CHARGE= f(pH)

Impacts of sludge stabilization processes and sludge origin on the mobility of pharmaceuticals following sludge land-spreading

• TOWARDS A METHODOLOGY



Necessity to link desorption parameter with sludge characteristics during treatment

Pharmaceutical compounds

Characterization
Functional groups, biochemical composition

Sludge

Sorption + Desorption

Fate and **behaviour of micropollutants** in regard to **sludge characteristics**

Statistical analysis to rely all the parameters (sludge, MP, Kd) : predictive aim (e.g.: influence of a parameter to another on desorption)

Example of PLS regression :

$$\text{Log } K_{\text{désorption}} = \text{cste} - 0{,}0042 \times (\text{molecular weight})_{\text{micropol.}} - 0{,}11 \times \log(\text{solubility})_{\text{micropol.}} + 0{,}12 \times pH_{\text{boue}} - 0{,}013 \times (\%\ \text{carboxylic groups in particulate phase})_{\text{sludge}}$$

Impacts of sludge stabilization processes and sludge origin on the mobility of pharmaceuticals following sludge land-spreading

- TO GO ON

Influence of soil characteristics ? Other organic micropollutants? Other stabilization processes ? Other fertilizing matter?

ESCO MAFOR (France, 2014)

IMOPOLDYN PROJECT (2015-2018

Interactions micropollutants / organic matrices in the fertilizer materials of waste origin: influence on the dynamics of micropollutants during landspreading.

THANKS FOR YOUR ATTENTION

LIMOUSIN
NEW
SENSATION