ESPP General Assembly : **use on farmland of sewage biosolids**

Anaerobic digester

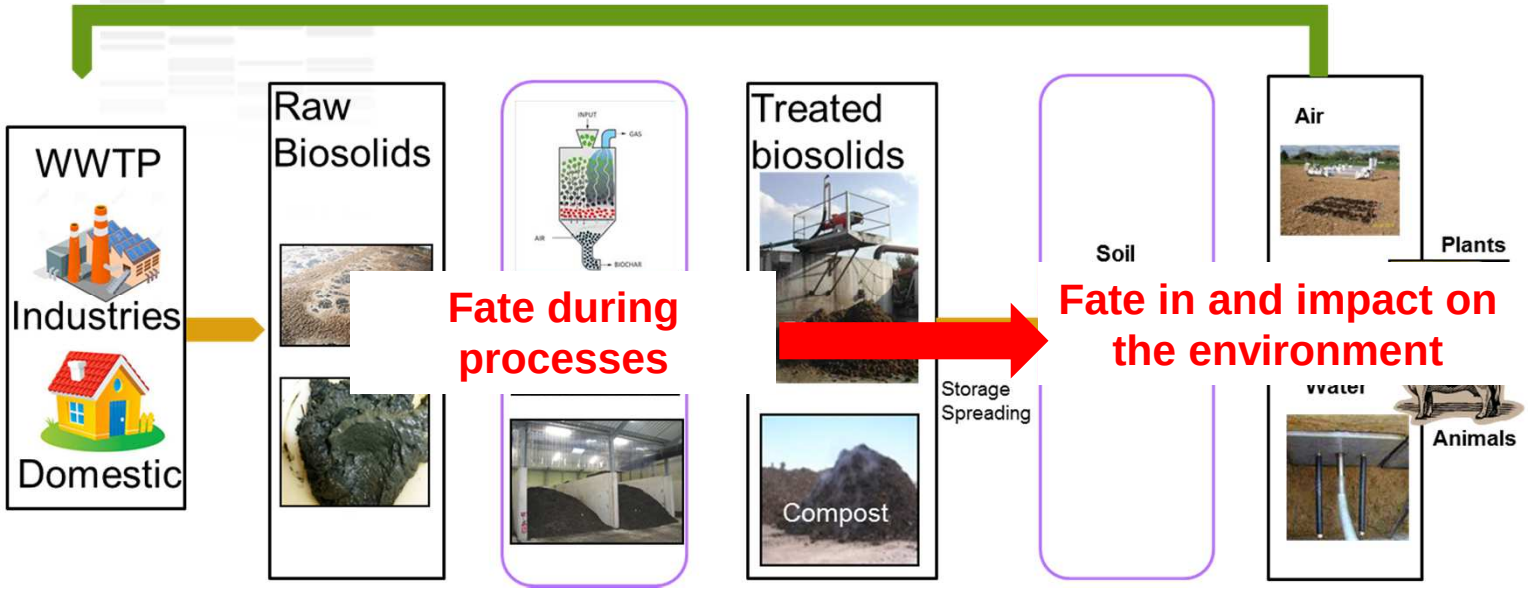
Composting process

Soil spreading

Fate of pharmaceuticals during biosolids processing and after soil spreading

D. Patureau, P. Benoit, M. Bourdat-Deschamps, S. Nélieu, S. Nazaret, S. Houot.

Since 20 years, our playground is :



Integration of :

- Diversity of organic contaminants (OC) : pesticides, endocrine disruptors, persistents, pharmaceuticals
- Diversity of organic wastes (OW)
- Diversity of interactions OW-contaminants
- Multi-scale : from lab to field scale (SOERE long term field assay)
- Chemical and biological contamination (genes and bacteria)

Since 20 years, researches are devoted to :

Scientific goals

- Quantify the contaminants fluxes from IN to OUT– in situ mass balance
- Optimise the contaminants removal during processing (toxicity, transformation products)
- Assess the transfers of contaminants and their transformation products into environment
- Quantify the potential impacts onto the quality of the food production, the soil/water/air resources and onto the functions realised by organisms
- Develop and test models and scenarii on the long term
- Class the compounds according to their behaviour and their molecular descriptor (TyPol tool)

Operationnal goals

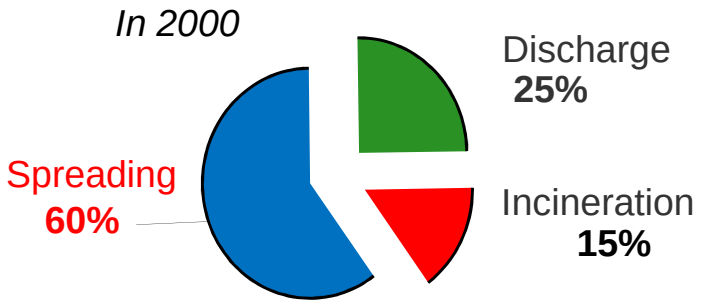
- Sustain the OW recycling
- Reduce the contaminant load towards environment
- Reduce the impacts

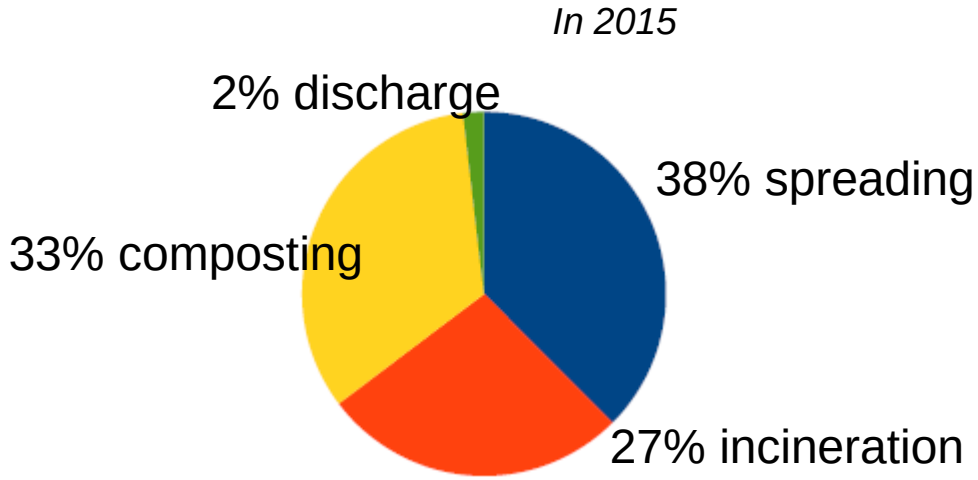
Sludge production and use in France

Production from 2000 to 2015

Year	2001	2002	2009	2013	2014	2015
Production (T DM/y)	893 252	910 255	1 180 000	1 122 194	1 142 939	1 374 161

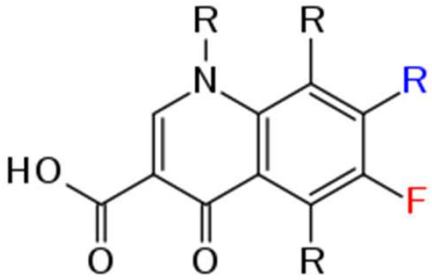
Use



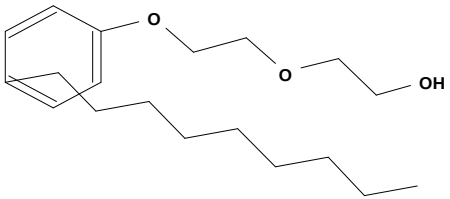


Less than 6% of the spread organic fertilizers
To be compared to 94% for manure (300 M tons)

? Occurrence

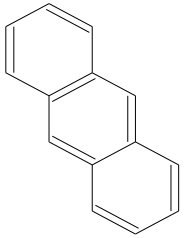


fluoroquinolone

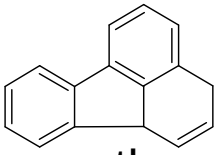


Nonylphenol ethoxylates

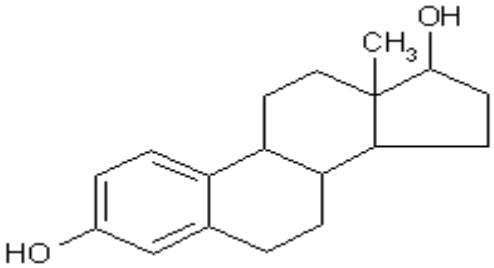
PAHs



anthracene



fluoranthene



Oestradiol (E2)

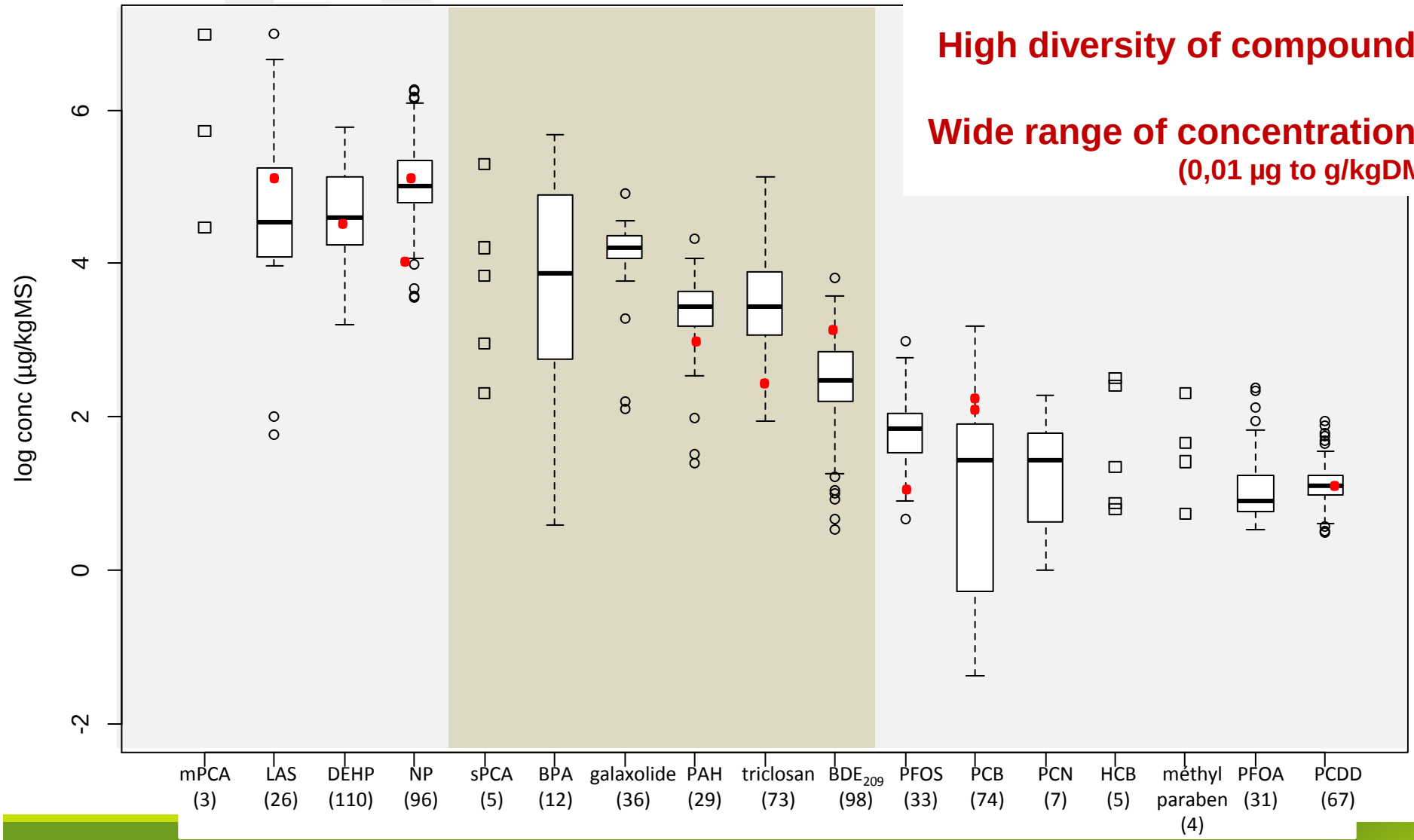
Organic contaminants in raw/treated sludge

- French data

Sludge : more studied OW

High diversity of compounds

Wide range of concentrations
(0,01 µg to g/kgDM)



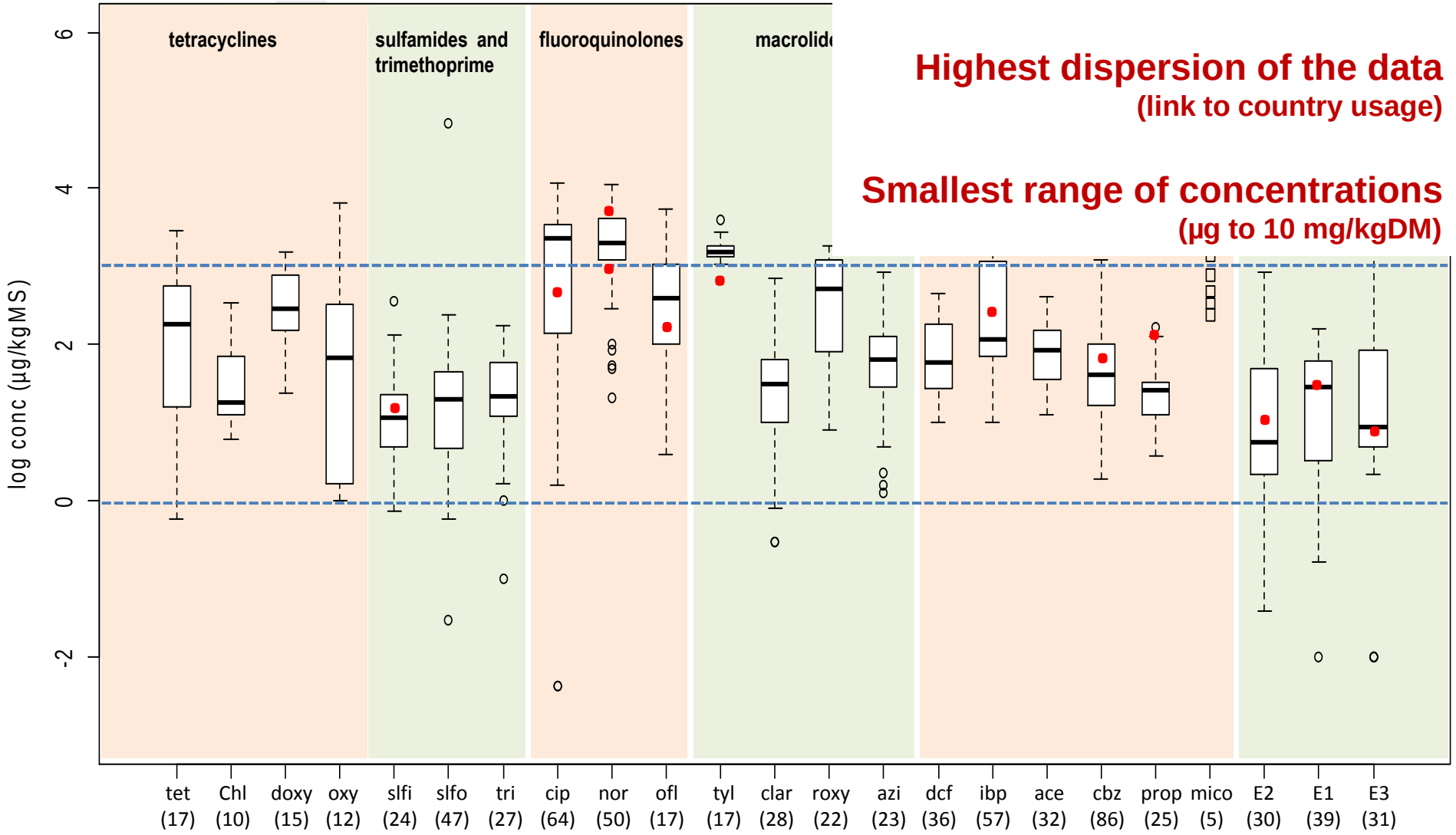
Pharmaceuticals and PPCPs in sludge

- French data

High diversity of pharmaceuticals

Highest dispersion of the data
(link to country usage)

Smallest range of concentrations
(µg to 10 mg/kgDM)

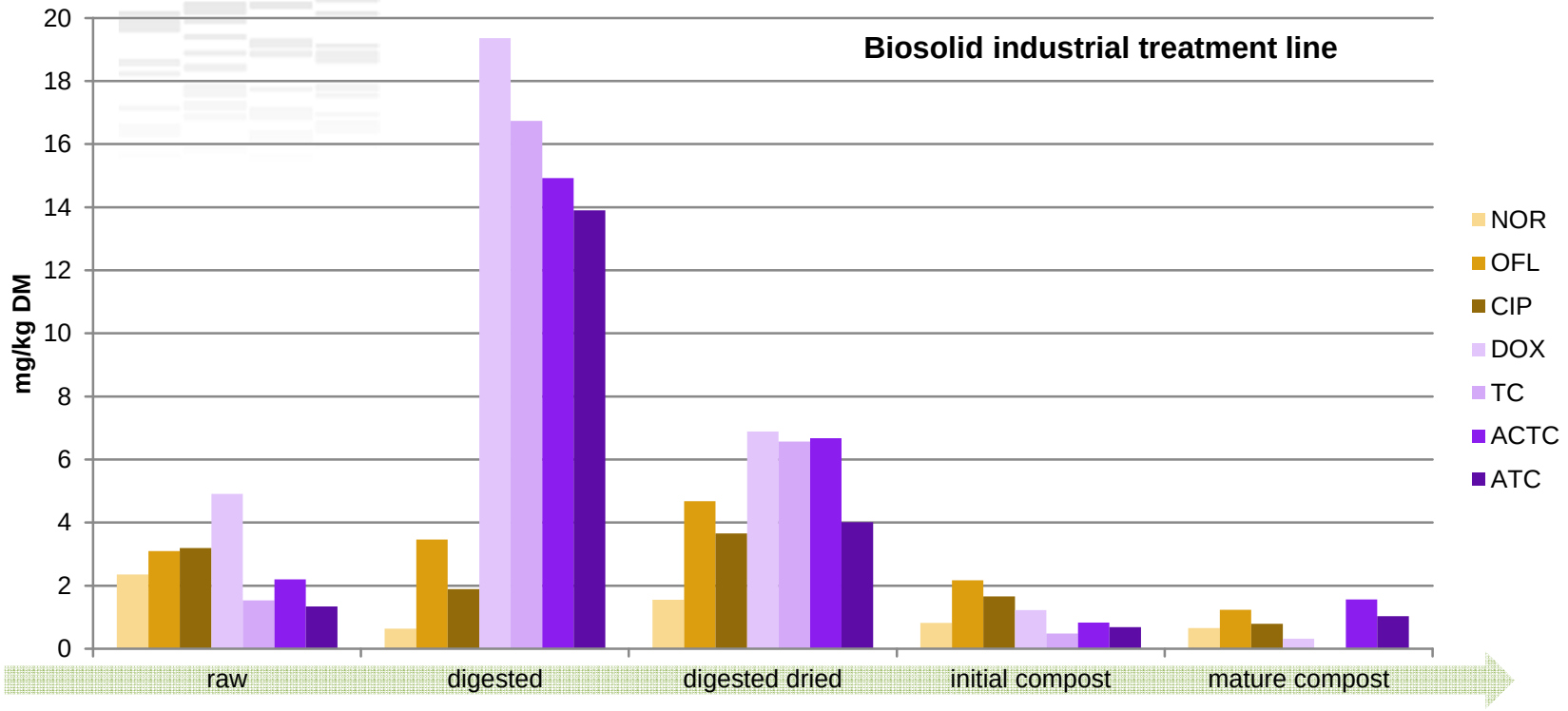


Industrial scale

Lab-scale

Fate during treatment

Concentration of OC in raw and treated sludge/industrial

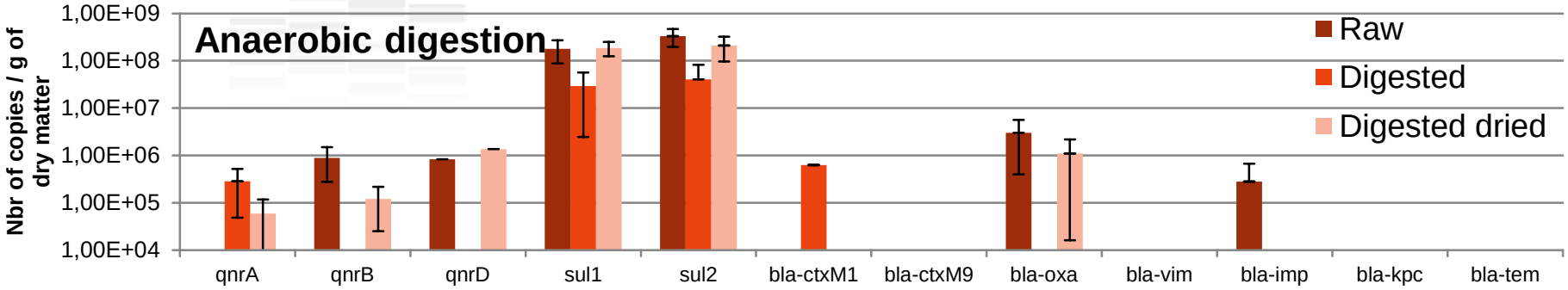


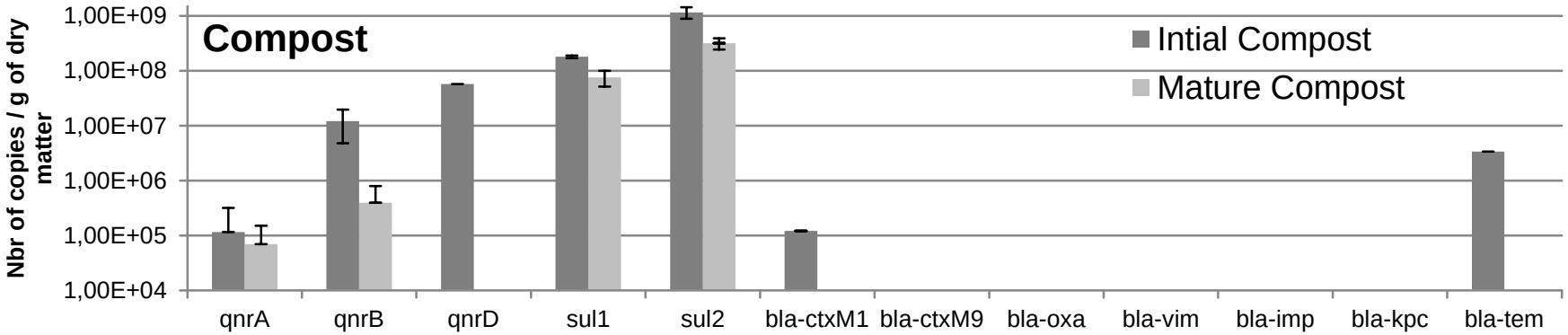
- 11/24 compounds >LoD. 8>LoQ. mostly quinolones and tetracyclines, no sulfonamides
- **Digestion** : Drop in concentration (exept for tetracycline: extractability ?same day sampling?)
- **Drying** : No effect (except tetracycline), same levels as digested
- Dilution by the green waste
- **Composting** : Drop in concentration

⇨ General drop along the line

For funding the DIGESTATE project, PhD N. Sertillanges (2016-2019)

Concentration of antibiotic resistance genes in raw and treated sludge





- Detection of mostly Fluoroquinolone and sulfonamide ARGs (sul in all samples)
- **Digestion and drying** : Lack of data, no trends. No changes on sul (mass loss)
- **Composting** : Sul abondance higher than digested dried (GW addition). Trends : droping to 0 or decreasing. (thermophilic phase)

⇒ Along the line : absolute abondance equal or lower = drop (mass loss)

For funding the DIGESTATE project, S. Nazaret from

Removal of OC during anaerobic digestion

Removal class	X < 30	30 < X < 70	X > 70
Sludge[1]	para, cbz, dcf, ibp, acid salicyclic, gem, ofl, nor, cip, LAS, NP, NP2EO, PAH, PCB, E1, E3, T, αEE2, αE2, βE2, DEHP, BBP, DEP, BPA, ahtn, hhcb, triclosan, triclocarban, diuron, benzotriazole, clozapine, benzophenone, iopromide, bisoprolol	pfoa, pfos, para, cbz, propra, smx, cefo, esci, lido, vera, citalopram, keto, ibp, dcf, diazepam, roxi, ctc, ofl, nor, cip, LAS, NP2EO, PCB, E1, E3, T, αEE2, αE2, βE2, DEHP, BBP, DEP, DnBP, BPA, ahtn, hhcb, triclosan, triclocarban	pfos, para, cbz, propra, smx, azi, cefo, esci, lido, lora, mico, trama, vera, domp, dcf, ibp, ate, caf, trim, nap, oxybenzone, roxi, otc, flx, citalopram, furosemide, clofibric acid, keto, nor, cip, NP2EO, NP1EO, E2, E1, αEE2, DEP, DnBP, BPA, ahtn, hhcb, triclosan
Manure[2]	sulfathiazole, sulfamethazine, sulfadiazine, sulfaguanidine, sulfamerazine, sulfapyridine monensine, doxycycline, tetracycline	oxytetracycline, sulfachloropyridazine, sulfathiazole	smx, sulfamerazine, sulfadiazine, sulfadimethoxine, sulfamethoxypyridazine, trimethoprim, tylosine, florfenicol, ampicillin, chlortetracycline

[1] Trably, 2002; De Mes, 2008; Carballa, 2007; Malmborg and Magner, 2015; Paterakis, 2012; Samaras, 2014; Barret, 2010; Narumiya, 2013; Gonzales-Gil, 2016; Muller, 2010; Phan, 2018; Ezzariai, 2018

[2] Mohring, 2009; Arikan, 2006, 2008; Alvarez, 2010; Varel, 2012; Mitchel, 2013; Angenent, 2008; Akyol, 2016; Spielmeyer, 2015, 2017

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Manure[2]	sulfadiazine, sulfaguanidine, sulfamerazine, sulfapyridine monensine, doxycycline, tetracycline	sulfachloropyridazine, sulfathiazole	ne, sulfadimethoxine, sulfame thoxypyridazine, trimethoprim, tylosine, florfenicol, ampicillin, chlortetracycline

- Mass balance is needed BUT is a real challenge
- AD removal depends on the OC
- Anaerobic transformation is linked to the presence of functional group able to give electrons

[1] Trably, 2002; De Mes, 2008; Carballa, 2007; Malmborg and Magner, 2015; Paterakis, 2012; Samaras, 2014; Barret, 2010; Narumiya, 2013; Gonzales-Gil, 2016; Muller, 2010; Phan, 2018; Ezzariai, 2018

[2] Mohring, 2009; Arikan, 2006, 2008; Alvarez, 2010; Varel, 2012; Mitchel, 2013; Angenent, 2008; Akyol, 2016; Spielmeyer, 2015, 2017

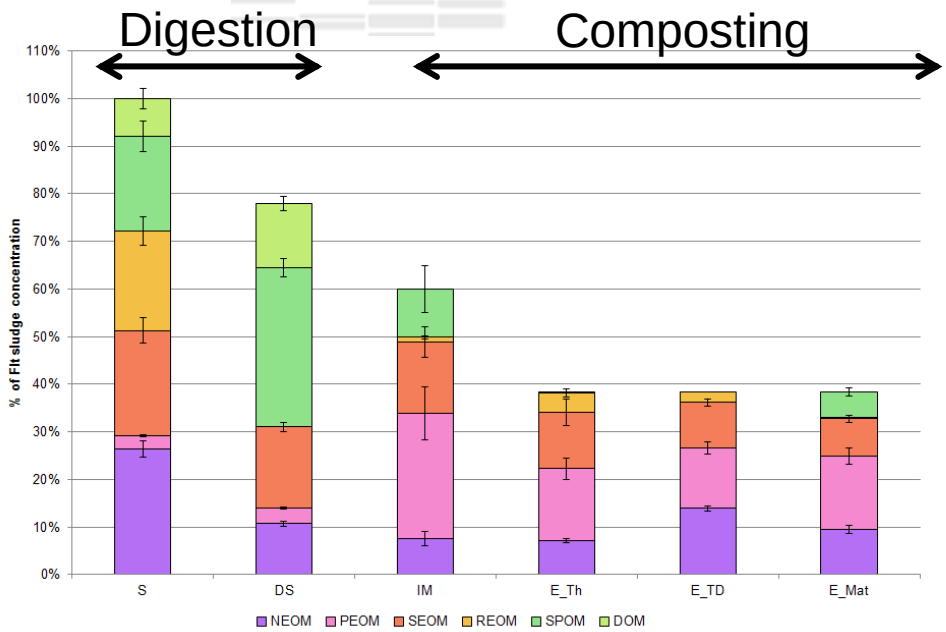
Removal of OC during composting

Removal class	X < 30	30 < X < 70	X > 70
Sludge[1]	cip, citaprolame	cip, roxi, ahtn, triclosan, fluoxetine, sertraline	ctc, otc, roxi, hhcb, triclosan, DEHP, fluvoxamine
Manure[2]	sulfamethazine, E2	monensine et tylosin	tet, otc, ctc, trim, tilmicosine, tyl, ery, enro, flum, nor, sulfadiazine, doxi, progesterone, salinomycine

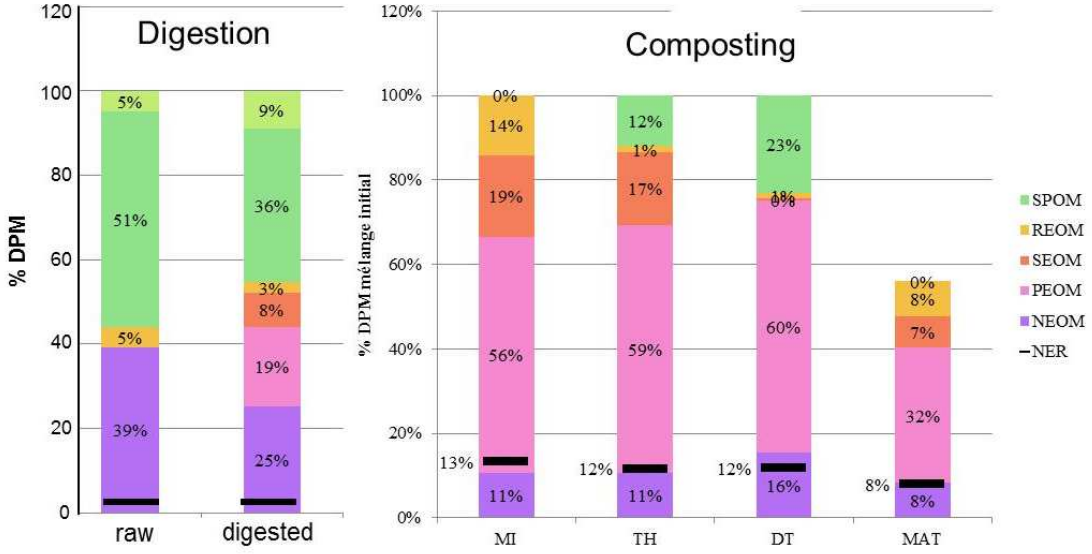
[1] Ezzariai, 2018; Poulsen and Bester, 2010; Sadef et al., 2014; Vasskog et al., 2009

[2] Dolliver, 2008; Hakk and Sikora, 2011; Ho et al., 2013; Hu et al., 2011; Ramaswamy et al., 2010

What's behind removal ?

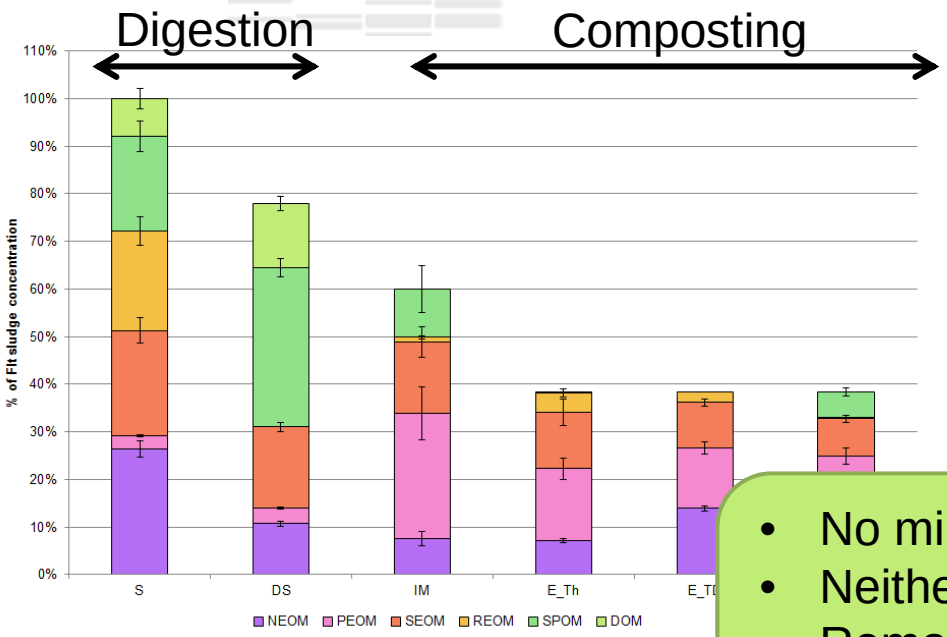


Fluoranthene



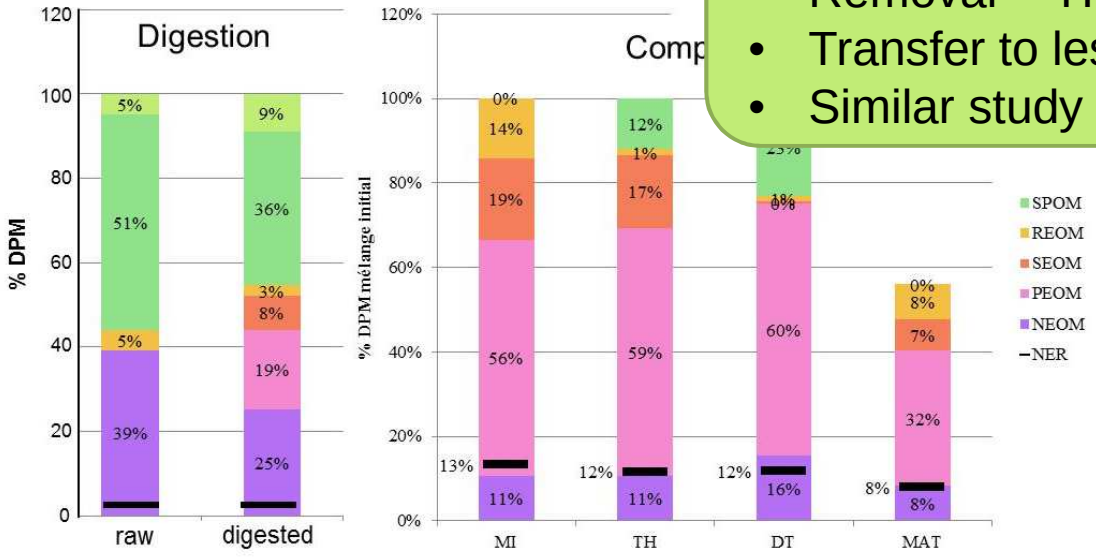
^{14}C-Fluoranthene

What's behind removal ?



Fluoranthene

- No mineralization
- Neither bound residues formation
- Removal = TP formation, to be identified
- Transfer to less accessible fraction
- Similar study with pharma



^{14}C-Fluoranthene

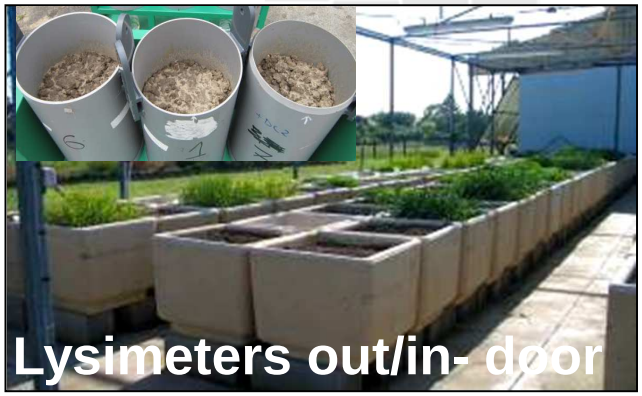
Aemig et al., PhD, 2014, 2016

??

? Fate AFTER treatment

Persistence (stock)
Transformation (TP)
Water transfer
Plant transfer

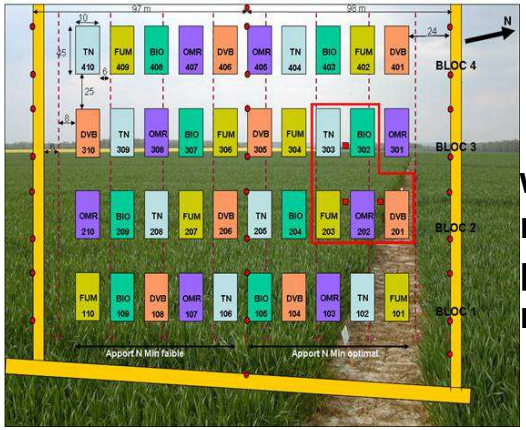
The various scales of studies



with/without radiolabelled molecules (transformation/mineralization)

PROCESSUS / PARAMETERS

- Sorption/bound residues formation : Kd, Koc, Kfoc
- Transformation (biotic and abiotic) : half-lives, kinetic constants (k)
- Transfer to plant : BCF, BCR
- Transfer to water : leaching coefficient and θ (probability to reach groundwater)

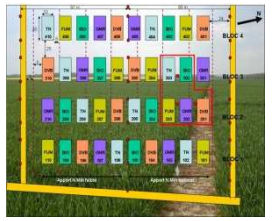


wheat
maize
potatoes
rape

French long-term experimental site - SOERE-PRO + INERIS Study (2011-2014) E/SRA

Deschamps et al. (2017) Fate and impacts of pharmaceuticals and personal care products after repeated applications of organic waste products in long-term field experiments Science of the Total Environment 607–608 (2017) 271–280

Contaminants in soil : French case study



$\mu g/kgDM_{biosolid} \times$ kg DM/ha = LOAD $\rightarrow$ PEC

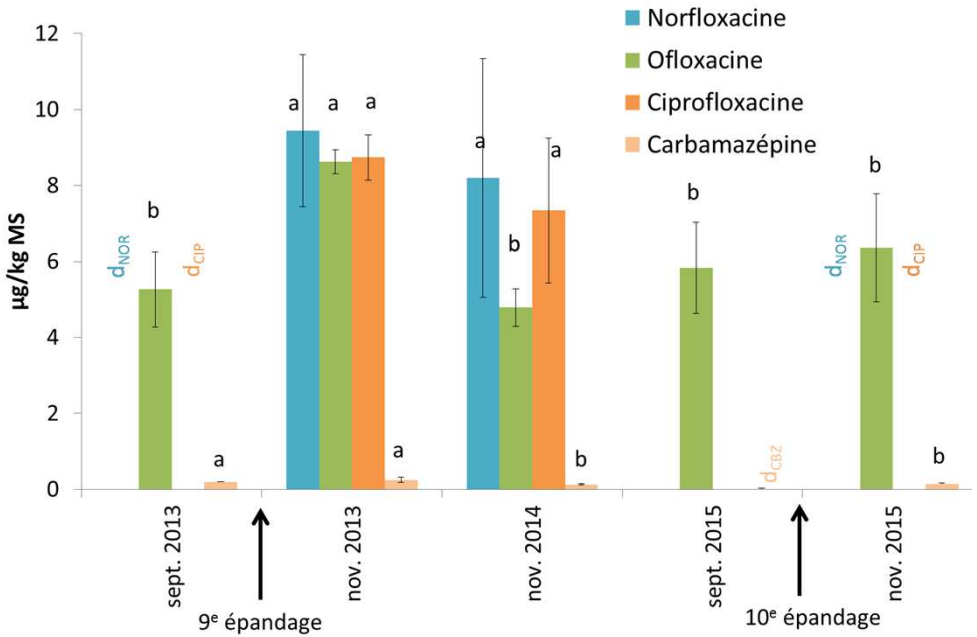
Dose of biosolid

$\updownarrow$ PNEC ERA/RQ

$\mu g/kgDM_{soil} \times$ kg DM/ha = STOCK MEC

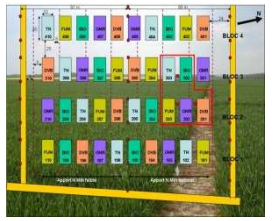
Surface mass of soil

Soil + sludge compost



- No detection in the non amended soils
- Mainly compounds found in the soils, also present in the compost BUT it doesn't correspond to the highest fluxes
- Increase of conc just after spreading then decrease
- Compounds detected in soils : flux corresponds to 10-50% of the initial stock level

Contaminants in soil : French case study



PEC >> MEC

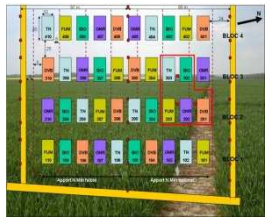
→ dissipation (transformation, lixiviation, irreversible adsorption…)

$$MEC_{soil,n} = \sum_{i=1}^{n} \frac{[PPCP]_{OWP} * APP_{OWP}}{DEPTH_{soil} * RHO_{soil} * 10{,}000} * e^{\frac{-\ln(2) * t_i}{DT_{50}}}$$

Compound	Field half life estimation
fluoroquinolones doxycycline	1500 - 2500 d
Carbamazepine	900 d
diclofenac ibuprofene	150 - 1000 d 190 - 300 d

Medium to High persistence

Contaminants in soil : impact ??



- Calcul of the risk factor RF

After n spreadings,

$$RF = \frac{MEC}{predictive\ non\ effect\ concentration\ (PNEC)}$$

literature

$$PNEC = \frac{data\ ecotox\ (EC_{50}, NOEC)}{factor}$$

EMEA book 2006

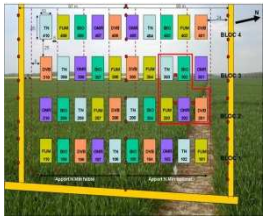
RF < 0,1 : low risk 0,1 < RF < 1 : medium RF > 1 : high

- Literature review on ecotoxicological date on terresterial organisms:
  E. fetida, worm; soil microorganisms ; plants
  low data; Selection of the lowest *PNEC* (**worse case**)

	MEC max	EC50, NOEC	PNEC	RF	
	µg/kg DM	mg/kg	µg / kg		
Norfloxacine	9,4				
Olfoxacine	8,6				
Ciprofloxacine	8,7	0,54	10,8	0,806	lettuce root elongation *(Chetram, 1996)*
Doxycycline	<5	1,6	160	<0,031	microbial activity *(Szatmari, 2014)*
Fluoxetine	<1				
Carbamazepine	0,5	12,5	125	0,004	springtail reproduction *(Jensen, 2012)*
Diclofenac	<5	65,7	657	<0,008	springtail reproduction *(Jensen, 2012)*
Ibuprofen	<1	64,8	648	<0,002	earthworm survival *(Pino, 2015)*

measured
<LOQ

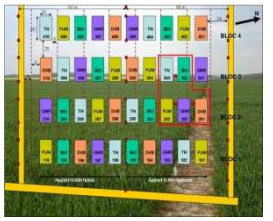
Contaminants in the soil water



	Nb determinations (nb sample)	Detection frequency	quantification frequency	Concentration	Treatment	Main compounds
Soil + biosolid compost	3684 (276)	7 %	0.5 %	~ 0,02 µg/L 0,27 µg/L (4 times)	all	carbamazepine Ibuprofene

- Very low frequencies of detection and quantification (Topp 2008, Edwards 2009, Sabourin 2009)
- Very low concentration – No comparison between treatments
- Carbamazepine, Ibuprofene – mobile compounds (Chabauty 2016, Topp 2008)

Contaminants in the soil water



- Calcul of the risk factor RF

  RF < 0,1 : low risk 0,1 < RF < 1 : medium RF > 1 : high

- Data from literature on terresterial organisms / soil water :
  V. fischeri, model organism exposed to soil pore water
  More data but with huge variability;
  Selection of *PNEC* with the longest contact time

	MEC max	EC50	PNEC	**RF**	
	µg/L	mg/L	µg/L		
Ofloxacine	<0,013	0,014	0,01	<0,928	*(Backhaus, 2000)*
Sulfamethoxazole	<0,005	1,77	1,77	<0,003	*(Majewski, 2014)*
Carbamazepine	0,011	94	94,00	0,000	*(Di Nica, 2017)*
Ibuprofen	0,27	18,3	18,30	0,015	*(Di Nica, 2017)*

measured

<LOQ

Conclusions

Occurrence

- Huge diversity of organic contaminants (OC) present in raw and treated organic wastes

sludge	>	manures	>	Biowaste/greenwaste
All OC		Mainly pharma		Persistant C + pesticides

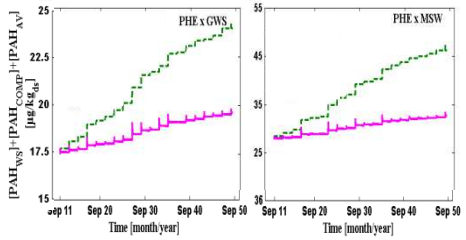
Fate during processes

- Becareful of the removal assessment (mass balance)
- Low to high efficiencies depending of the OC
- Aerobic removal more studied, more efficient than anaerobic)
- Biovailability as the main limiting factor
- Difficult to decipher between transformation and bound residues formation
- Importance of the bearing phases (aqueous/particulates) to understand, optimize and model their fate
- Metabolites ????

Conclusions

Fate in soils/water/plant system

- Various scales/conditions of studies with various conclusions
- Persistence and mobility of OC condition their fate (behaviour class)
- Ecotoxicological assays : no effect at conventional dose
- Low soil accumulation of persistent compounds (PAH, fluoroquinolone, triclosan) (Models, PAH, Brimo et al., 2018)
- Low transfer to plant[1] (existing model)
- Very low transfer to water (importance of DOM/POM)
- Transformation products (change of behaviour class)



[1]Sabourin et al., 2012, Sci Tot Env, Uptake of pharmaceuticals, hormones and parabens into vegetables grown in soil fertilized with municipal biosolids

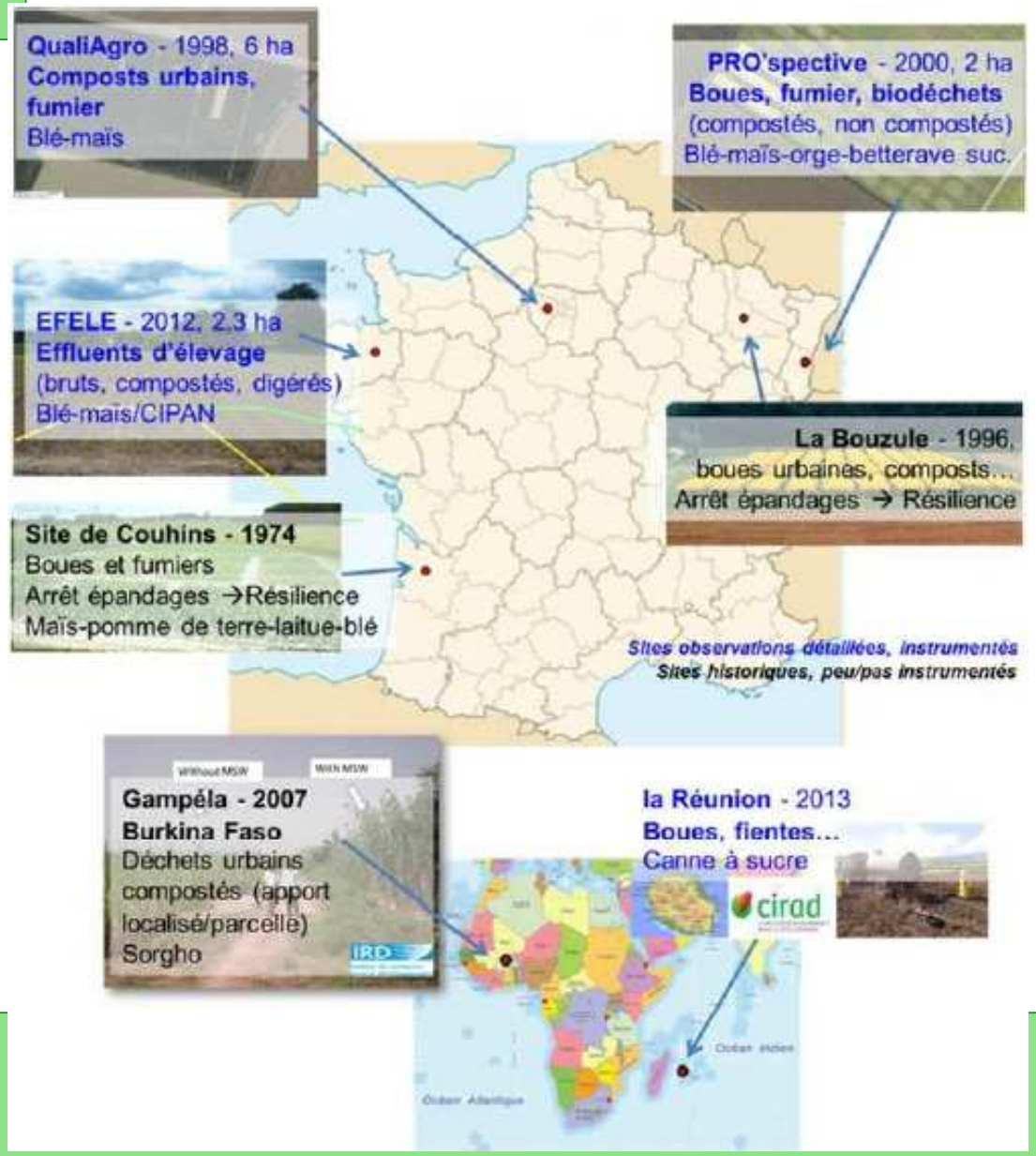
Prosser, R.S., Lissemore, L., Topp, E., Sibley, P.K., 2014a. Bioaccumulation of triclosan and triclocarban in plants grown in soils amended with municipal dewatered biosolids. Environmental Toxicology and Chemistry 33(5), 975–984.

Prosser, R.S., Sibley, P.K., 2015. Human health risk assessment of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, and wastewater irrigation. Environment International 75, 223–233.

Thank you for your attention

At the INRA website, look at the summary in english of the national expertise !

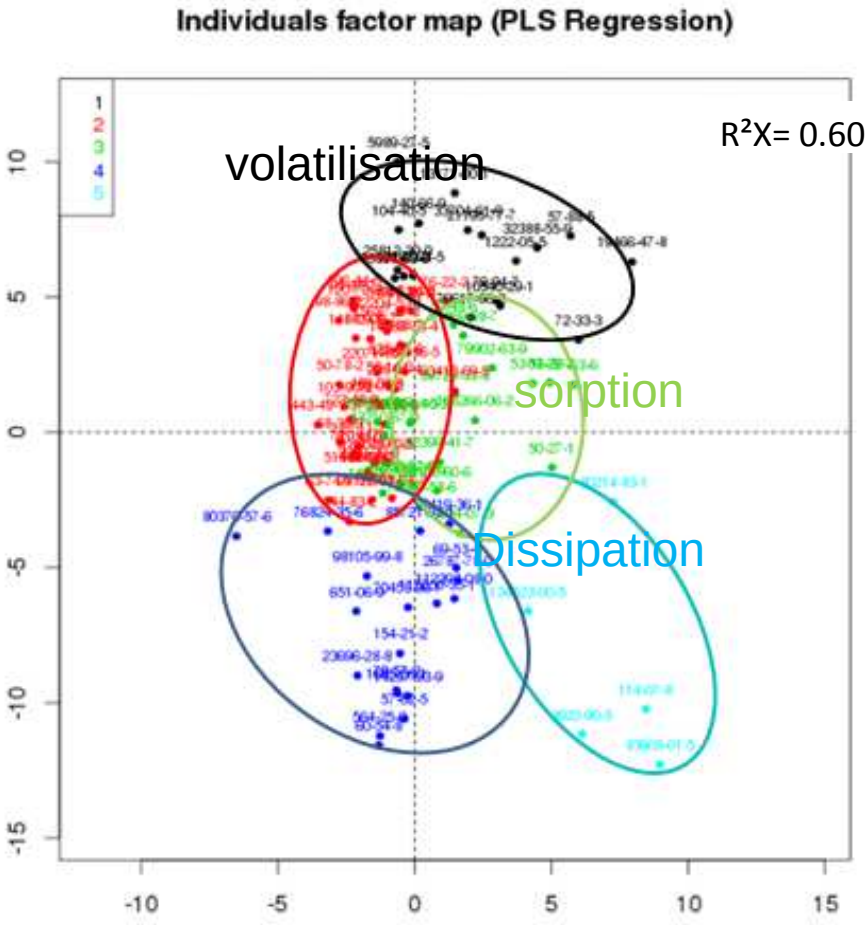
French long-term experimental site



330 Mt of OW
Manures : 300 Mt,
Sludge, composts and digestates : 7 Mt
Sludge from industries : 23 Mt.

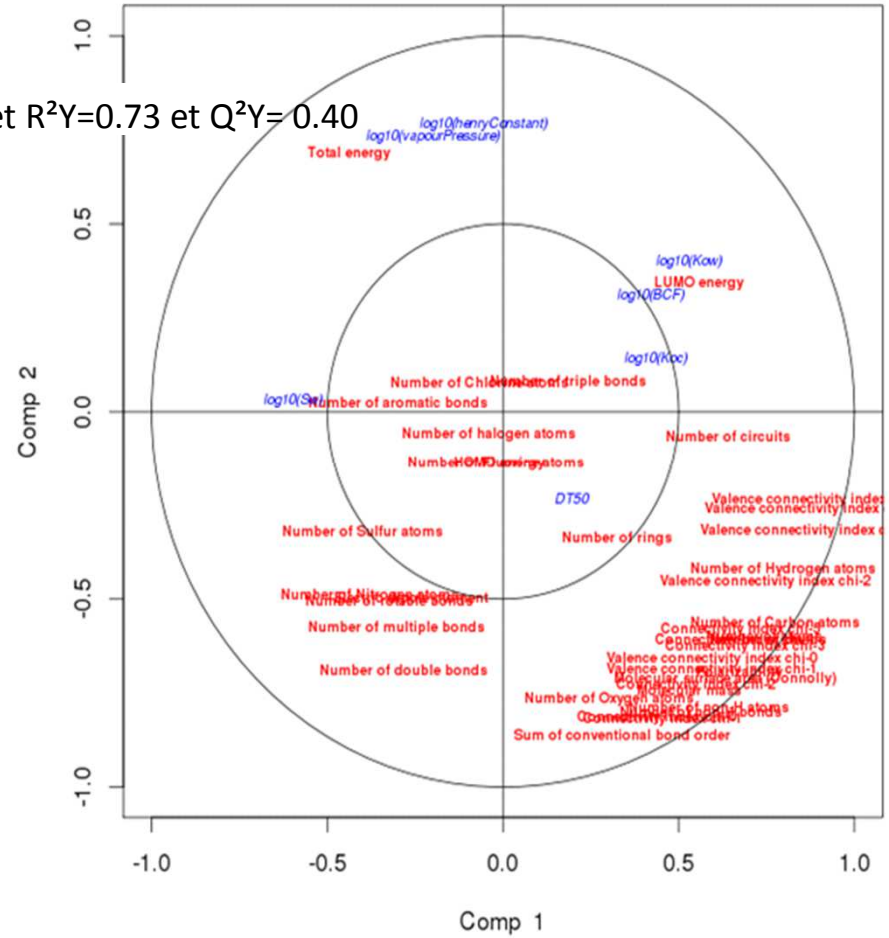
Classification of pharmaceuticals - TyPol

105 molecules « pharma » - molecular descriptors and environmental parameters



PLS data for the group « Pharma »

R^2X= 0.60 et R^2Y=0.73 et Q^2Y= 0.40



Correlation circle for the group « Pharma »

Zayet (2017)

Classification of pharmaceuticals

Cluster	Nombre de composés	Principale famille chimique	Caractéristique moléculaire	Devenir environnemental et effet écoxotoxicologique
Cluster 1	18	Stérol, Alkyl phénol	Faible moment dipolaire, E_{HOMO} faible, nombre réduit de liaison multiple	Forte bioaccumulation (BCF élevé), Forte volatilisation (Kh et Pvap maxi), Forte adsorption (Koc le plus élevé)
Cluster 2	41	Sulfonamide, Imidazole, Oxypropanolamine, Méthylphénol	Indices de connectivité et de valences les plus faibles, nombre d'atome le plus faible, polarisabilité plus faible, énergie totale la plus élevée	Faible dégradation, forte dissolution
Cluster 3	22	Quinolone, Stéroïde	Indice de connectivité d'ordre 1 le plus élevé	Forte dégradation
Cluster 4	19	Fluoroquinolone, Tétracycline	Indices de connectivité les plus élevés, E_{LUMO} la plus faible	Faible bioaccumulation, faible adsorption
Cluster 5	5	Macrolide, Mevinolimic	Moment dipolaire élevé, masse molaire élevée, surface, nb atomes élevés (en général), énergie totale la plus faible	Faible volatilisation, faible solubilisation

Zayet (2017)

Class of persistence (P) / dissipation

5 classes:

TPP : very low P
PP : low P
MP : median P
P : P
TP : high P

Composés	DT 50 (jours/mois/ans)	Persistance	Références
HAP	[2-10 ans]	P à TP	Barriuso *et al.*, 1996
PCB	[4-6 ans]	TP	Barriuso *et al.*, 1996
PCDD/PCDF	[1-10 ans]	TP	Barriuso *et al.*, 1996
PFC, Composés fluorés	[1-3 ans pour C6 à C11 et + pour chaine alkyle longue]	P à TP	Washington *et al.*, 2010
PBDE, Composés polybromés	[4-20 ans]	P à TP	Clarke et Smith, 2011
LAS	[jours]	TPP	Smith, 2009
Nonylphénol	[jours-mois]	PP à MP	Mao *et al.*, 2012
Bisphenol A	[jours]	PP	Xu *et al.*, 2009b
Phthalates	[jours-mois - < an]	PP à MP	Staples *et al.*, 1997
Pesticides	[jours-mois-an]	PP à TP	PPDB, 2014
Hormones			
17α-Oestradiol	[jours]	TPP	Colucci et Topp, 2001
17β-Oestradiol	[jours]	TPP	
Estrone	[jours]	TPP	
Antibiotiques			
Ciprofloxacine	[jours - mois]	PP à MP	Girardi *et al.*, 2011
Enrofloxacine	[jours - mois]	PP à MP	Thiele-Bruhn, 2003
Oxytétracycline	[mois]	MP	Li *et al.*, 2010
Sulfamethoxazole	[jours - mois]	PP à MP	Lin et Gan, 2011 ; Wu *et al.*, 2012c
Sulfaméthazine	[jours]	PP	Accinelli *et al.*, 2007
Triméthoprim	[jours - mois]	PP à MP	Wu *et al.*, 2012c
Tylosine	[jours]	PP	Thiele-Bruhn, 2003
Produits de Soins			
Galaxolide	[mois-ans]	MP à P	Litz *et al.*, 2007
Tonalide	[mois-ans]	MP à P	Litz *et al.*, 2007
			009b
			, 2011
			et al., 2009
Carbamazépine	[mois-ans]	MP à P	Lam *et al.*, 2004 ; Monteiro et Boxall, 2009
Diclofenac	[jours]	PP	Xu *et al.*, 2009b ; Al Rajab *et al.*, 2010a
Fluoxétine	[mois-ans]	MP à P	Walters *et al.*, 2010 ; Monteiro et Boxall, 2009
Gemfibrozil	[jours-mois]	PP	Walters *et al.*, 2010 ; Fang *et al.*, 2012
Ibuprofen	[jours-mois]	PP à MP	Xu *et al.*, 2009a ; Lin et Gan, 2011
Naproxen	[jours]	PP	Xu *et al.*, 2009a ; Lin et Gan, 2011

Dissipation….degradation/mineralization OR bound residues formation
Ex : NP

Class of mobility

4 classes:

TM : high mobility
MM : median mobility
PM : low mobility
TPM : very low mobility

Composés	Kd (L/kg) Ordres de grandeur	Mobilité	Références
HAP	[1 - 10 000]	PM à TPM	Schwarzenbach *et al.*, 2003
PCB	[1 -5 000]	PM à TPM	Schwarzenbach *et al.*, 2003
PCDD/PCDF	[500 -100 000]	TPM	Bamuso *et al.*, 1996
Composés fluorés	1-300 et ++	Mobilité plus élevées des molécules à chaine alkyle courte	Higgins et Luthy, 2006 (sédiment) Ahrens *et al.*, 2011 (sédiment) 9 à 250 l/kg logKd : 2-35 sol Zareitalabad *et al.*, 2013
PBDE, Composés polybromés	[100 - 100 000]	PM - TPM	Wang *et al.*, 2011 (sédiment)
LAS	[1-20]	TM à MM	Jensen, 1999
Nonylphénol	[10 - 2000]	MM à TPM	Murillo-Torres *et al.*, 2012 ; Langdon *et al.*, 2010 ; During *et al.*, 2002
Phthalates	[1 - 90 000]	TM à PM	Staples *et al.*, 1997
Bisphénol A	[10 - 50]	MM à PM	Xu *et al.*, 2009b
Pesticides	[0,1- 500]	TM à PM	PPDB, 2014
Hormones			
17α-Oestradiol	[1 - 100]	MM à PM	Mashtare *et al.*, 2011
17β-Oestradiol	[4 - 100]	MM à PM	Casey *et al.*, 2005 ; Caron *et al.*, 2010
Estrone	[0,5 - 50]	TM à MM	Caron *et al.*, 2010 ; Mashtare *et al.*, 2011
Antibiotiques			
Ciprofloxacin	[400-5000]	PM à TPM	Nowara et., 1997
Doxycycline	[0,5-5]	TM	Langdon *et al.*, 2010
Enrofloxacine	[200-5000]	PM à TPM	Nowara et., 1997
Norfloxacin	[0,1-1]	TM	Langdon *et al.*, 2010
Oxytetracycline	[400- 1000]	PM	Rabolle et Spliid, 2000
Sulfamethoxazole	[1 - 20]	TM à MM	Yu *et al.*, 2009 ; Lin et Gan, 2011
Trimethoprim	[1 - 10]	MM	Langdon *et al.*, 2010 ; Lin et Gan, 2011
Tylosine	[5 - 150]	MM à PM	Rabolle et Spliid, 2000
Produits de Soins			
Acetophenone	[2 - 10]	PM	Langdon *et al.*, 2010
Galaxolide	[500 - 5000]	PM à TPM	Langdon *et al.*, 2010
Tonalide	[500 - 5000]	PM à TPM	Langdon *et al.*, 2010
Triclocarban	[100 - 500]	PM	Langdon *et al.*, 2010
Triclosan	[1- 500]	PM	Xu *et al.*, 2009b ; Karnjanapiboonwong *et al.*, 2010
Pharmaceutiques			
Acetaminophen	[1- 50]	TM	Langdon *et al.*, 2010
Carbamazepine	[0,2 - 50]	MM à PM	Drillia *et al.*, 2005 ; Williams *et al.*, 2006
Diclofenac	[1- 20]	MM à PM	Xu *et al.*, 2009a; Lin et Gan, 2011
Fluoxetine	[10 -100]	PM	Langdon *et al.*, 2010
Gemfibrozil	[0,1 - 150]	TM à PM	Fang *et al.*, 2012, Langdon *et al.*, 2010
Ibuprofen	[0,5 - 60]	TM à PM	Xu *et al.*, 2009a; Lin et Gan, 2011
Naproxen	[1- 20]	TM à PM	Xu *et al.*, 2009a ; Langdon *et al.*, 2010