

# Micropollutants in wastewater treatment plants of rural areas

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**SMALLWAT11 – S evilla (Spain)**

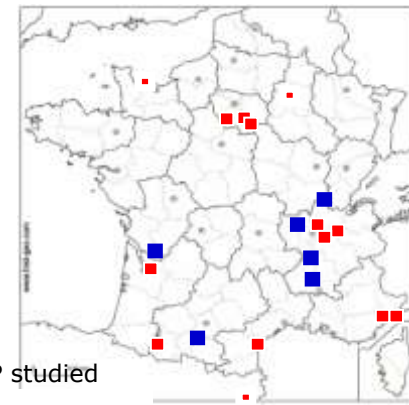
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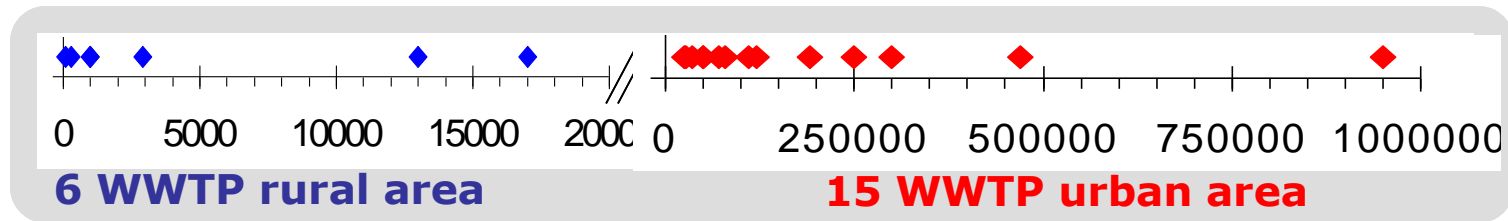


# Objectives of the study

Assess the fate of micropollutants through treatment processes adapted for rural areas



AMPERES project: 21 WWTP studied



- **Stabilization pond** (3000 m<sup>2</sup>) + vertical reed-bed filter (100 m<sup>2</sup>/filter), 300 P.E.
- **Rotating biological contactor** (8647 m<sup>2</sup> discs) + vertical reed-bed filter, 1,000 P.E.
- **Trickling filter** + vertical reed-bed filter, 1,000 P.E.
- **Vertical** (3\*30 m<sup>2</sup>/filter) + **Horizontal** (2\*60 m<sup>2</sup>/filter) reed-bed filters, 100 P.E.
- **2 activated sludge plants**, 3,000 P.E., Nitrifying/Denitrifying



# 13 analytical techniques

127 substances

41 priority substances [WFD] + substances potentially harmful + 43 pharmaceuticals

**Dissolved/Particulate phases of WW (except VOC) + Sludge**



Methods	Extraction	Separation technique	LoQ water (ng/L)	LoQ sludge (µg/kg)
Multiresidus (organic semi-volatils)	Liquid-liquid + Florisil	GC-MS-MS	20 – 1000 (DEHP)*	20 – 1000 (DEHP)*
VOCs (ISO 15680:2003)	Purge & trap	GC-MS	100	Not analyzed
Chlorophenols	SPME	GC-MS	50 – 150*	Not analyzed
Pesticids-antibiotics	SPE	HPLC-MS-MS	1 – 2*	4
Glyphosate/AMPA	SPE	HPLC-MS-MS	100	Not analyzed
Chloroalcanes	SBSE	TD-GC-EDC	500	1000
PBDEs / Bisphénol A	SBSE	TD-GC-MS	1 – 100*	4 – 50*
Alkylphenols + ethoxylates	SPE	LC-ESI-MS	10	100
Analgésics, antidepressors, broncho-dilatants, hypolipemiants	SPE	LC-MS-MS, UPLC-MS-MS	0.5 – 2	1 - 5
Betablockers	SPE	LC-ESI(+)-MS/MS	1 – 5*	0.2 - 1*
Hormones	SPE + Florisil	LC-ESI(-)-MS/MS	1	3 - 10*
Mercury	-	ASF	0,5	10
Metals and métalloïds	-	ICP-MS	10 – 5000	300 - 3000

# Sampling / Conditionning / Shipping

Refrigerated automatic sampler  
 Teflon pipe, glass container  
 Cleaning (acid, acetone), Field blank



Buhler 5010



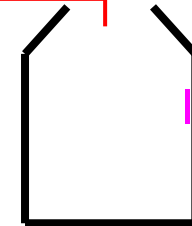
Isco 4230



24 glass container, cooled @4°C



Composite sample  
 (20L-glass container)

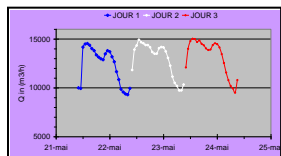


Influent  
 Effluent  
 intermédiaire



Shipping

Flow  
 (m<sup>3</sup>/h)



day D@9h → D+1@9h

day D+1@9h → D+1@12h





## More about practical aspects

- **Measurements on the influent and the effluent during 2 successive 24h-periods @ dry weather conditions**
- **About thirty samples of liquid and ten samples of sludge**
- **Accurate calculation rules were applied to secure the data calculated for the removal yields of micro-pollutants**
- **Mass balance were carried out with data on WW and sludge**



# PLAN

Introduction

Method

**Results**

concentrations in treated effluents  
removal rates  
released fluxes

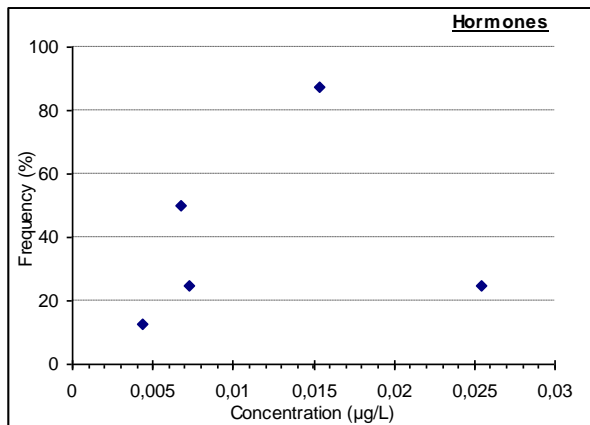
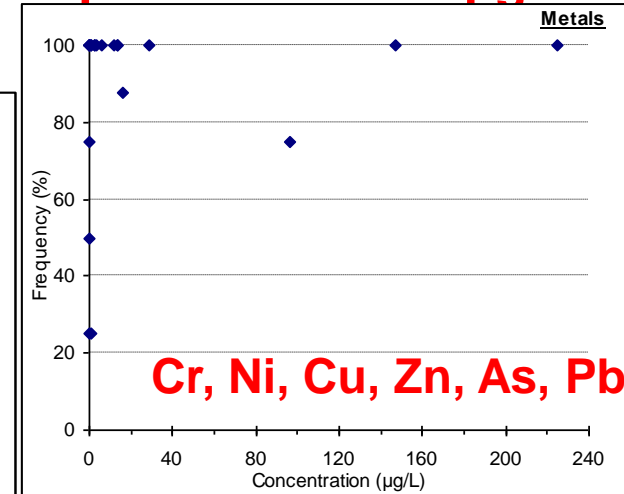
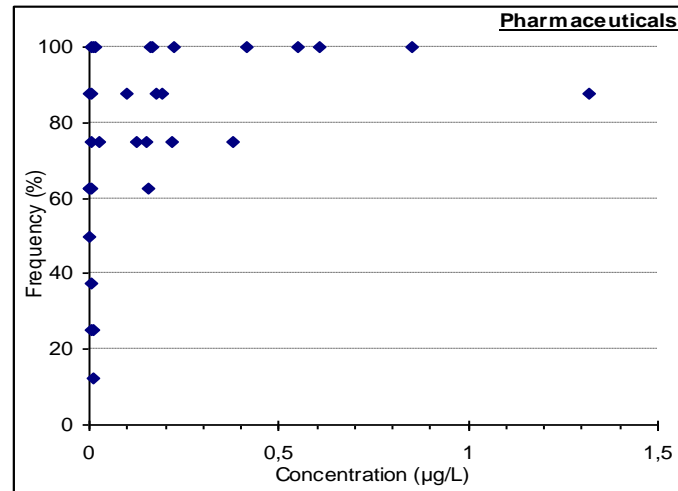
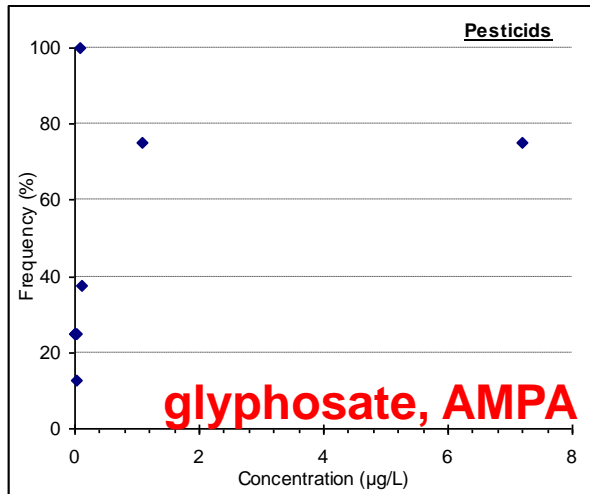
Conclusion



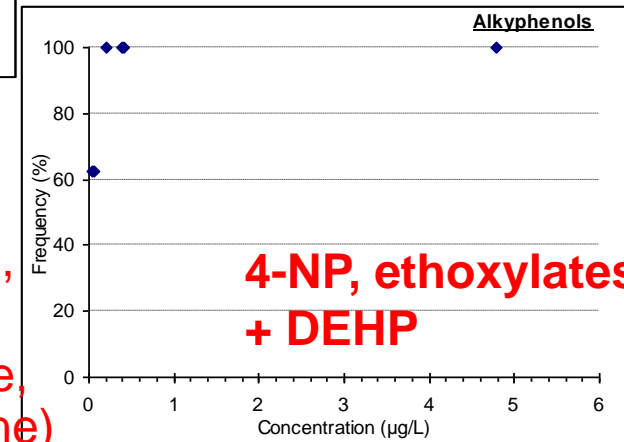
# 1- Concentrations in treated effluents of WWTP (rural areas)

**Raw WW:** 100 micropollutants quantified, 44 always quantified > 0.1 µg/L

**Treated effluents:** 48 substances quantified, **32 with quantified > 0.1 µg/L**



**betablockers** (propranolol, acebutolol, atenolol, sotalol),  
**antibiotics** (sulfamethoxazole, roxithromycine)  
**other** (ketoprofene, naproxene, diclofenac, cafeine, theophylline)

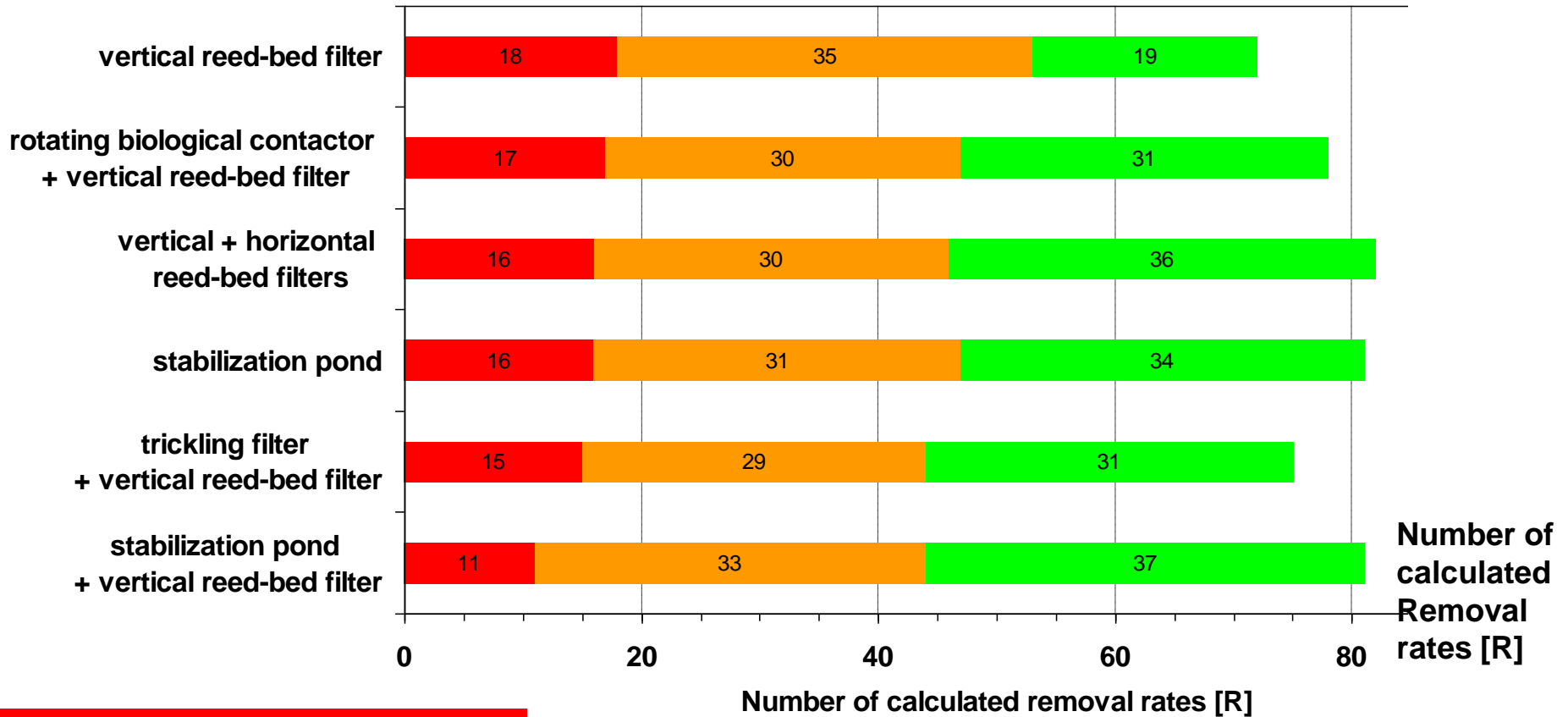


# 2- Removal rates

■ R <30%

■ R in [30-70%]

■ R >70%



**Metals** (Cd, Ni, Sb, Co, As, Ti)  
**Pesticides** (atrazine, simazine, diuron, glyphosate and AMPA )  
**Other** (trichlorobenzène, benzothiazole, tributyl phosphate, acide nonylphenoxyacetique)  
**Betablockers** (sotalol, propranolol, metoprolol)  
**Other** sulfamethoxazole, carbamazepine, nordiazepam, diclofenac

**Alkylphenols** (4-tert-butyl-, nonyl-, octyl-phenol and ethoxylates)  
**Metals** (Hg, Pb, Zn, Cu, Cr)  
**Other** (trichloromethane, DEHP, dichlorophenols, triclosan, mono di-butyltin)  
**Hormones** (estrone, 17 $\alpha$  and 17 $\beta$ -estradiol, estriol)  
**Pharmaceuticals** (fluoxetine, doxepine, atenolol, nadolol, acebutolol, amitriptyline, ketoprofene, naproxene, ibuprofene, aspirine, paracetamol)

## Mass balance

### Partially transformed in sludge

DEHP, triclosan  
 AKP [4-NP]  
 Hormones  
 Pharmaceuticals

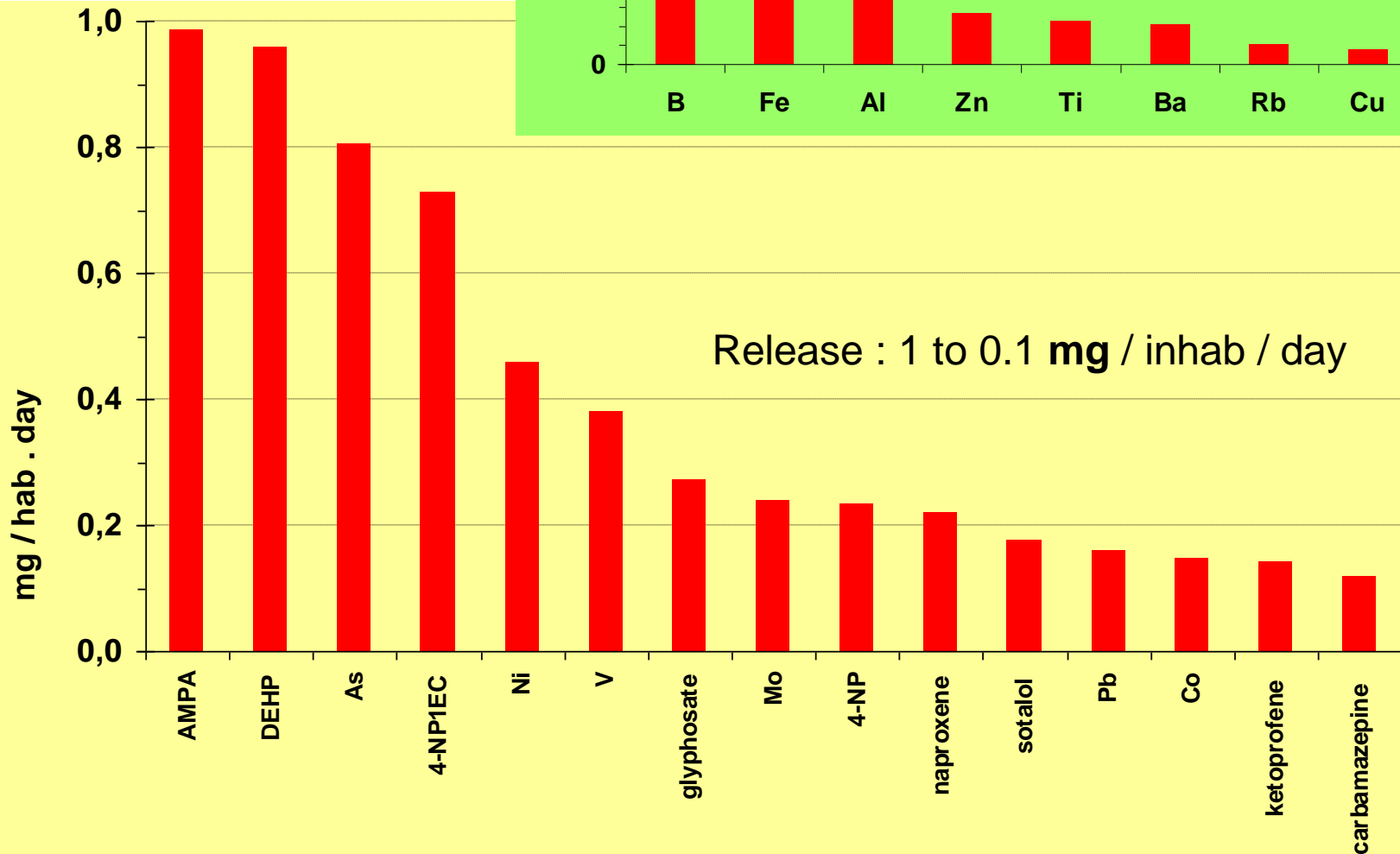
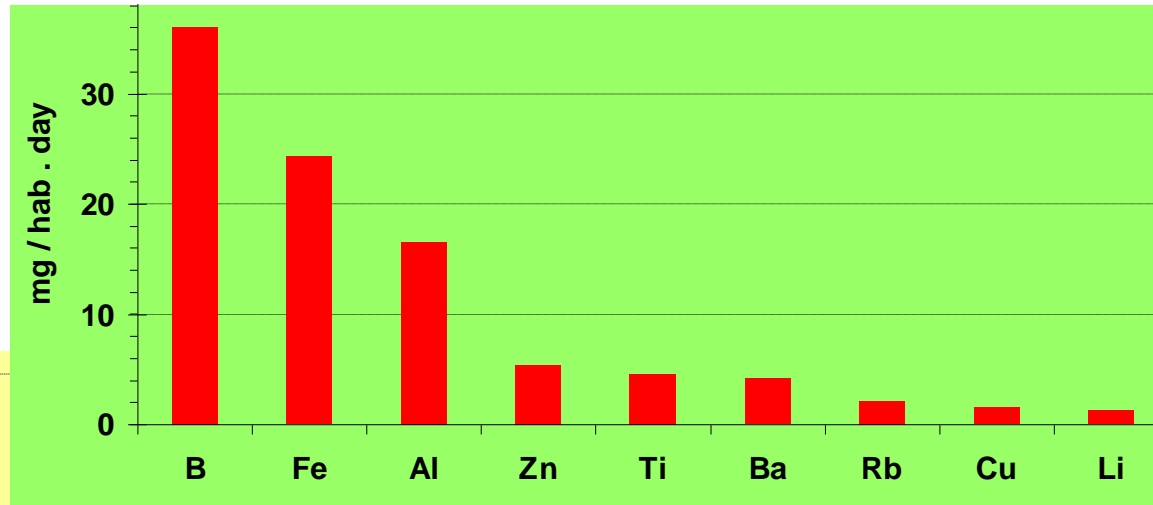
### Stored in sludge

AKP [4-t-OP, 4-NP1EC]  
 Metals (Hg, Pb, Zn, Cu, Cr)

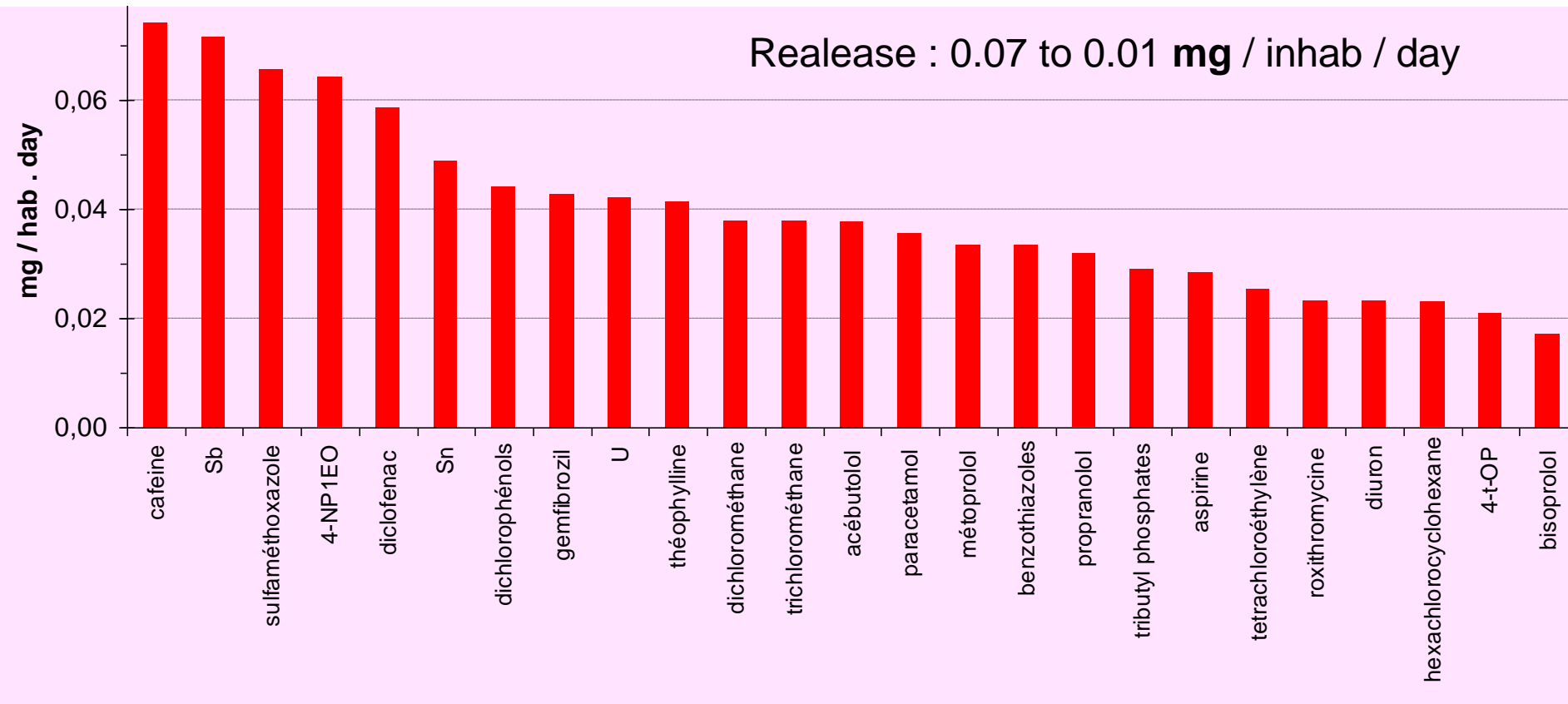
# 3- Fluxes released after treatment rural)

1 inhabitant of rural area release 30 g BOD<sub>5</sub>/day

Release : 36 to 1 mg / inhab / day



# Pharmaceuticals ?





# CONCLUSIONS

- From on-site mass balance applied to more than 100 micro-pollutants at wastewater treatment plant of rural areas (6 process types), the removal rates were assessed.
- In treated water, more than half of substances are not detected, or quantified at low concentrations.
- Assessed biological processes of rural areas have shown comparable removal rates, with more than 30% removal for 85% of the substances quantified.
- They perform a significant reduction of pollution loads of micropollutants, but complementary treatments are required for refractory substances and also to bring concentration levels of accessible micro-pollutants close to their limits of quantification.

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Funding support



More about AMPERES project

<https://projetamperes.cemagref.fr/>  
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Continuation: ARMISTIQ project

Choubert *et al.* (2011). *Water Science and Technology* 63(1), 57-65.

Martin Ruel *et al.* (2010). *Water Science and Technology* 62(12), 2970-2972

Recherche institut pour Engineering of Agriculture and Environment