

EXCELENCIA

Improvement of the chemical quality of water in MAR operations implemented with nature-based reactive layers



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The livelihood of millions of people depends on groundwater that is overexploited and polluted or at risk. To prevent groundwater (GW) depletion, MAR can be applied using effluents from wastewater treatment plants (WWTPs) as a recharge source. However, in this practice, there is a risk of contaminating the aquifers with chemical substances carried by the water. Contaminants of emerging concern (CECs) represent a major threat since most of them do not degrade efficiently.



Among the CECs, pharmaceuticals are of particular concern, since they exhibit biological activity, especially antibiotics that can spread antibiotic resistance, and personal care compounds, many of which are endocrine disruptors and have been banned in some countries.

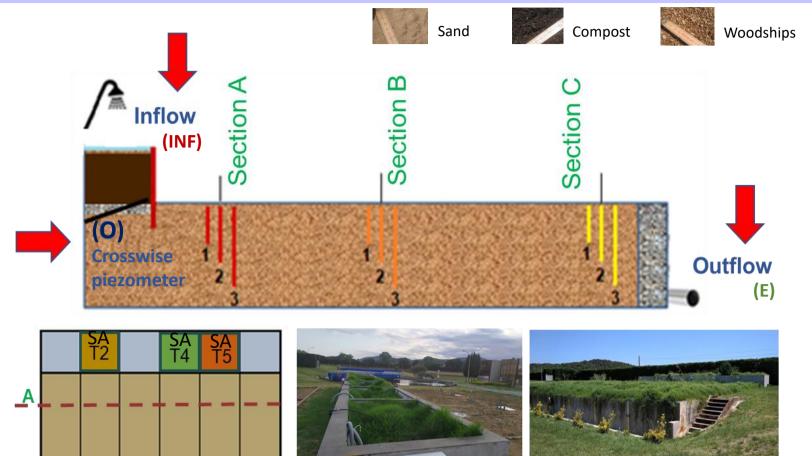
Analytes studied and the pilot MAR system

A total of 58 analytes and their metabolites were investigated in the inflow water of the MAR system.

The results presented here correspond to those substances whose frequency of detection in the inflow water was >50%. The selected 23 compounds were grouped to facilitate the presentation of the results.

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Subgroup	Compound	Acronym	Subgroup	Compound	Acronym
UVF	Benzophenone 3	BP3	Fluoroquinolone	Ofloxacin	OFX
	Benzophenone1	BP1	antibiotics	Ciprofloxacin	CFX
UVF (TPs)	2,2'-Dihydroxy-4-	DHMB,		Sulfadiazine	SDZ
	methoxybenzophenone	BP8	Sulfonamide and	Sulfamethoxazole	SMX
			Trimetoprim	Sulfapyridine	SPY
	Ethyl-PABA, Benzocaine	EtPABA	antibiotics	N ⁴ -Acetylsulfapyridine	acSPY
UVF	1,2,3-Benzotriazole	BZT		Trins at la surviva	
	1-Methyl-1H-benzotriazole	e MeBZT		Trimethoprim	ТМР
				Mefenamic acid	MFA
Lipid regulator	Gemfibrozil	GFZ	Anti-	Naproxeno	NPX
Stimulants	Caffeine	CFF	inflammatories	Ketoprofen	KTF
Antidepressants	s N-Desmetilvenlafaxina	N-desVFX		Ibuprofen	IBU
ß-blockers	Atenolol	ATL	Anti-epileptics	Carbamazepine	CBZ



Background

Aim

Evaluate the removal of contaminants of emerging (CECs), including pharmaceuticals and concern personal care products (PPCPs), in managed aquifer recharge (MAR) operations by implementing a reactive layer/barrier to increase the natural capacity of the soil to remove pollutants.

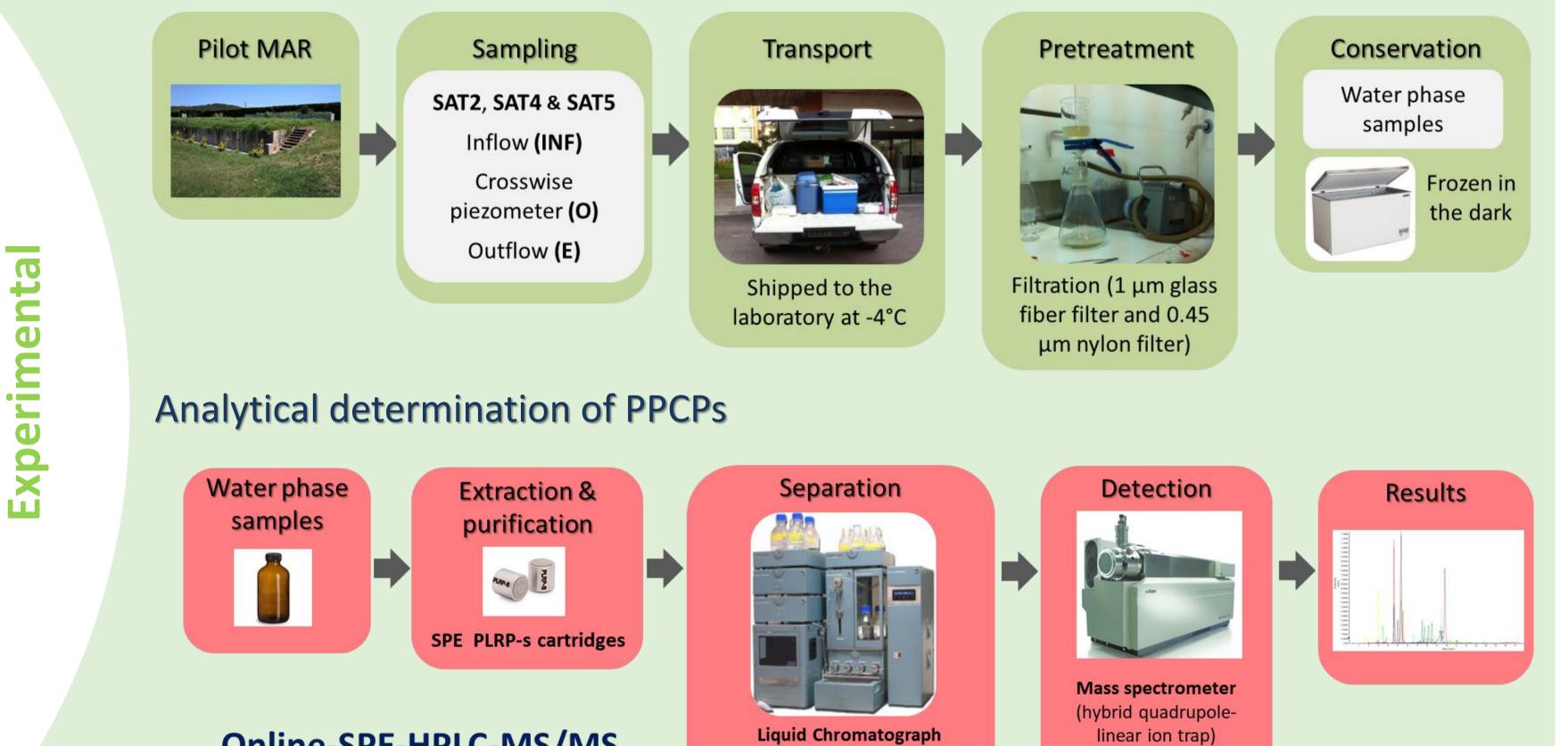
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Study

Objectives

- Estimate the goodness of the removal of PPCPs from the secondary effluents of an urban WWTP using MAR in a pilot system with and without a reactive barrier.
- Compare the removal rate obtained in the systems with a reactive barrier composed of

Sampling, sample pretreatment and Analysis



different natural materials and without a barrier.

Online-SPE-HPLC-MS/MS

Symbiosis Pico (Spark Holland) LC-column Purospher STAR RP-18 (125 mm x 2.0 mm, 5 μm) (Merk)

/b 40000

4000 QTRAP (Electrospray ionization source, ESI) (Applied Biosystems-Sciex)

Conclusions

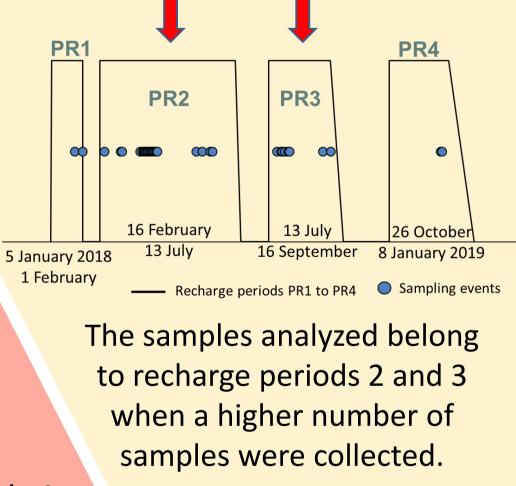
High variability in the concentration of target CECs in the inflow water feeding the MAR systems, is a consequence of season and tourism.

Recharge periods can provide different removal rates for the same CECs, likely due to population increase and season, but we cannot rule out potential exhaustion of the barrier and the microbial communities grown.

Most of the target CECs are removed more efficiently in the systems SAT4 and SAT5 than in T2. Removal rates in SAT4 and SAT5 are different for some compounds, but overall, there are no notorious differences between the removal provided by SAT4 and SAT5.

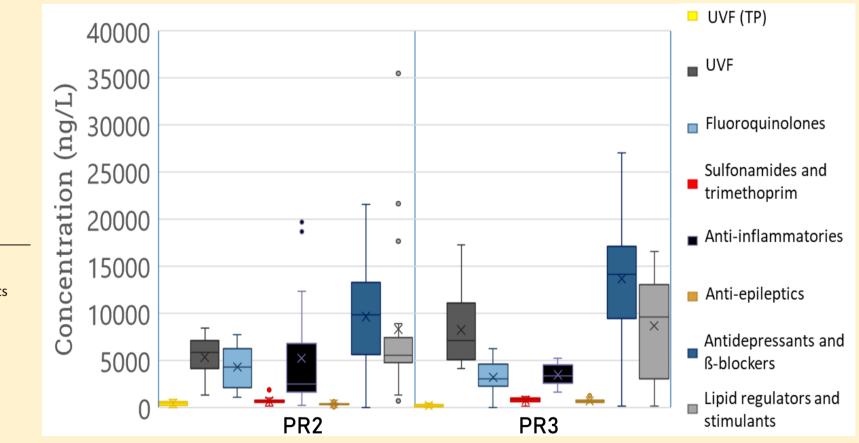
In general, the concentrations of CECs decrease during MAR, producing a significant removal along the unsaturated zone, followed by a more attenuated decrease along the saturated zone, when flowing through the aquifer. This shows that barriers accelerate the natural degradation of CECs.

Recharge periods and samples

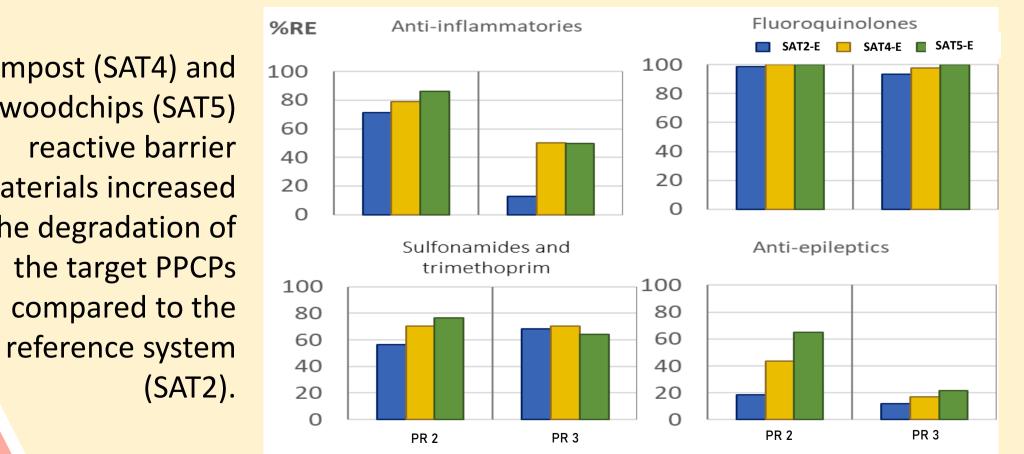


Compost (SAT4) and woodchips (SAT5) reactive barrier materials increased the degradation of the target PPCPs compared to the

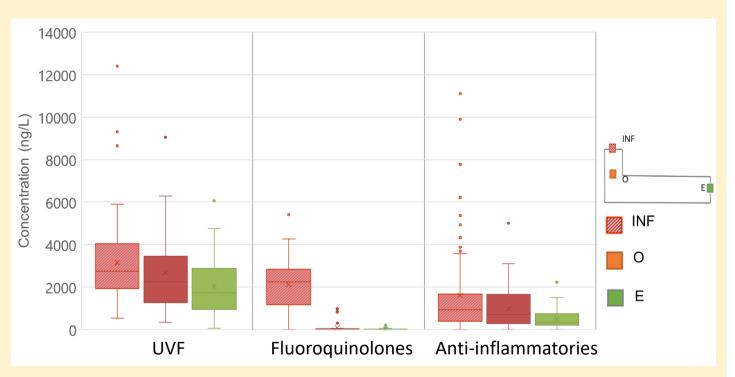
CECs concentration profile Inflow water

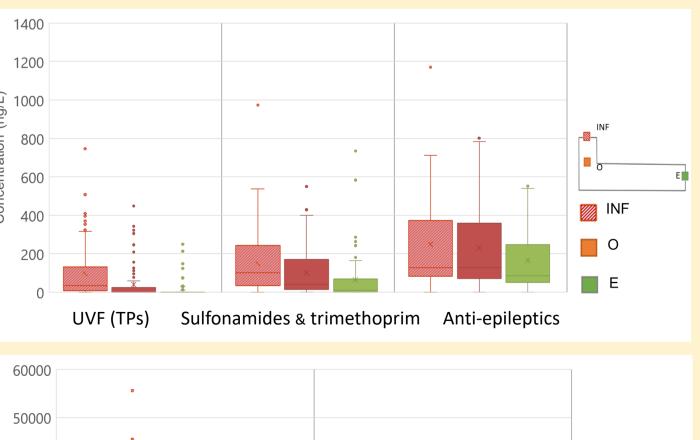


CECs Removal comparison, examples



CECs concentration evolution in MAR PR2 system SAT4





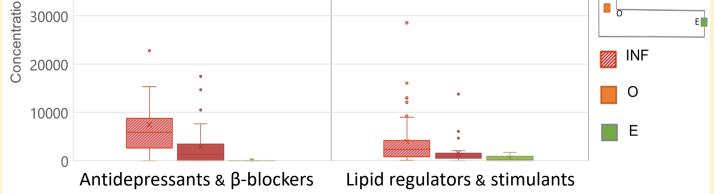
SAT4 and SAT5 are especially effective in the elimination/transformation of the fluoroquinolones, antidepressants and β -blockers studied, for which elimination rates of over 99% in both systems have been obtained. In contrast, the antiepileptic drugs studied appeared to be more persistent and exhibited elimination rates of 64% in PR2 and 21% in PR3.

References: [1] VALHONDO, C., MARTINEZ-LANDA, L., CARRERA, J., DIAZ-CRUZ, M.S., AMALFITANO, S., LEVANTESI, C., 2020. Six Artificial Recharge Pilot Replicates to gain Insight into Water Quality Enhancement Processes. Chemosphere 240. doi 10.1016/j.chemosphere.2019.124826. [2] VALHONDO, C., CARRERA, J., MARTINEZ-LANDA, L., WANG, J., AMALFITANO, S., LEVANTESI, C., DIAZ-CRUZ, S, 2020. Reactive Barriers for renaturalization of reclaimed water during soil aquifer treatment. Water, 12(4), 1012. doi: 10.3390/w12041012.

The removal of the target CECs oscillated in a wide range based on their physicochemical properties; water solubility, dissociation constant, lipophilicity, and adsorption potential.







The different removal extent of CECs depends on the recharge period and season.

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