

idæ^a EXCELENCIA
SEVERO
OCHOA

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS



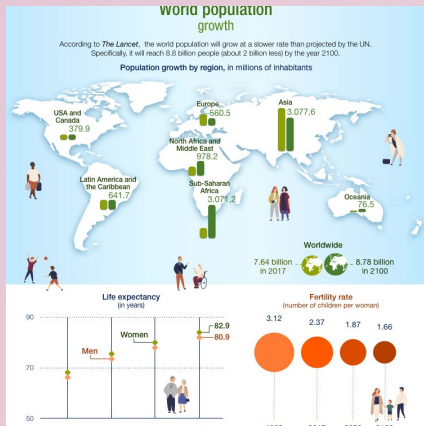
REMOVAL OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM WASTEWATER BY SOIL- AQUIFER TREATMENT: RISK ASSESSMENT RELATED TO DRINKING WATER PRODUCTION AND AGRICULTURAL USE

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CALDÚ, P. SEPÚLVEDA, G. QUINTANA, A. CONTRERAS,
L. MARTÍNEZ-LANDA, C. VALHONDO

Introduction

Population growth



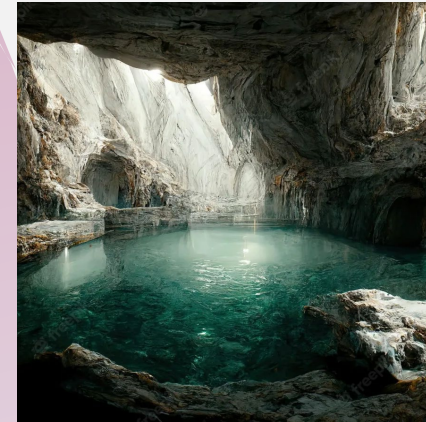
Increasing demand



Climate change



Aquifer



WWTP



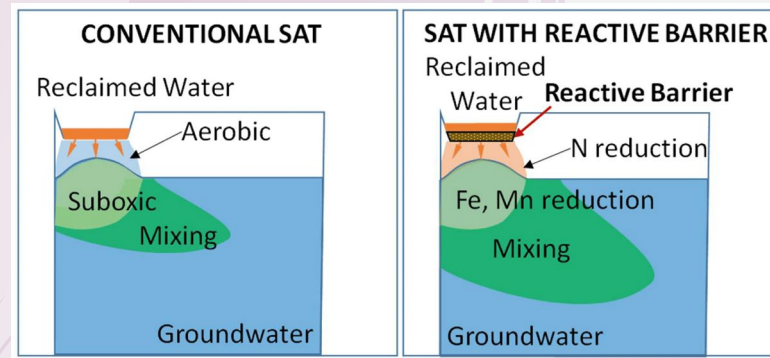
Groundwater recharge



CECs



CECs degradation



Treated wastewater for SAT



OBJECTIVES

Treated wastewater & SAT



Implement SAT with reactive barriers to enhance the natural attenuation of pollutants in soil-aquifer systems

Water reuse



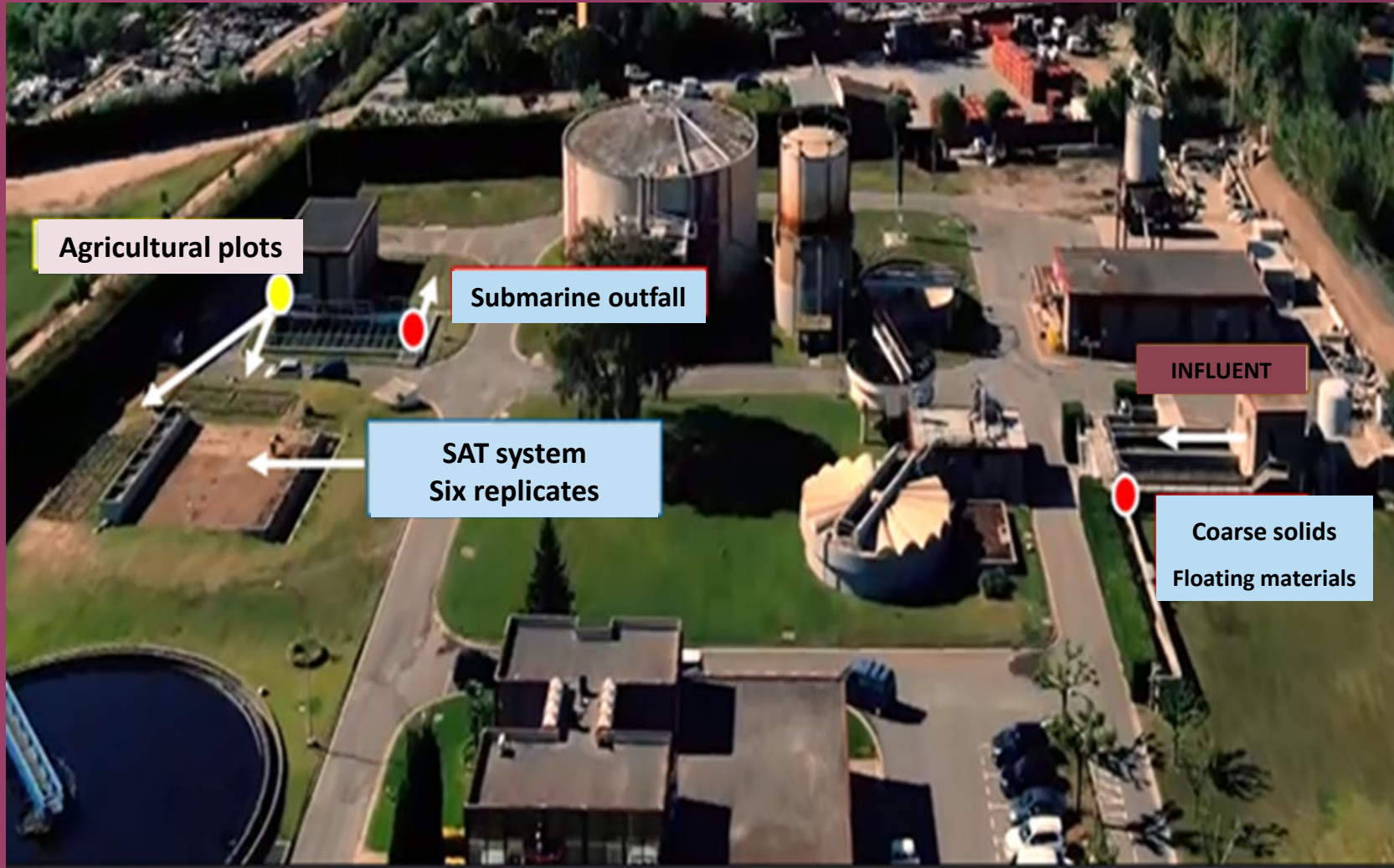
Increase of groundwater for drinking water production and agricultural irrigation

Human risk assessment



Consumption of drinking water and raw vegetables produced with the groundwater

EXPERIMENTAL SITE

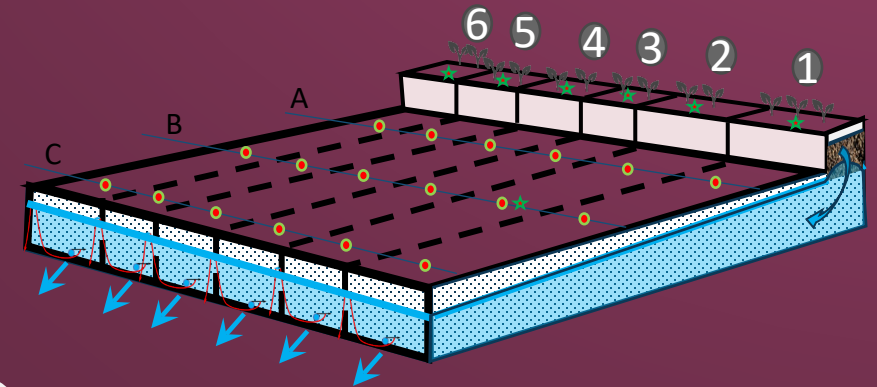
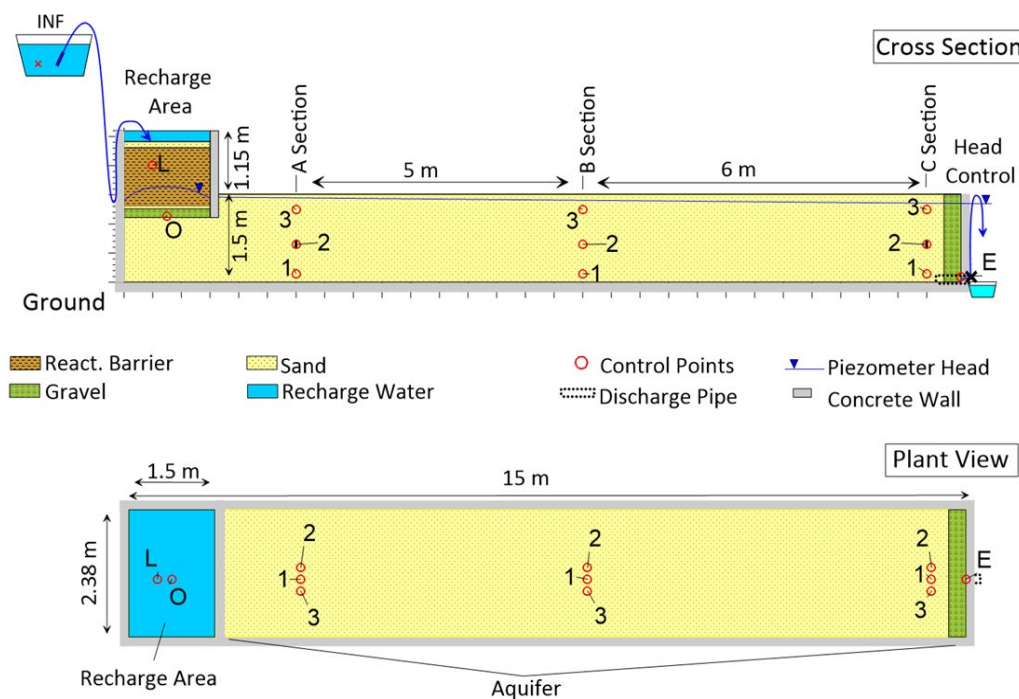


URBAN WASTEWATER TREATMENT PLANT
PALAMÓS, GIRONA (SPAIN)

STRUCTURE OF A REACTIVE BARRIER SYSTEM



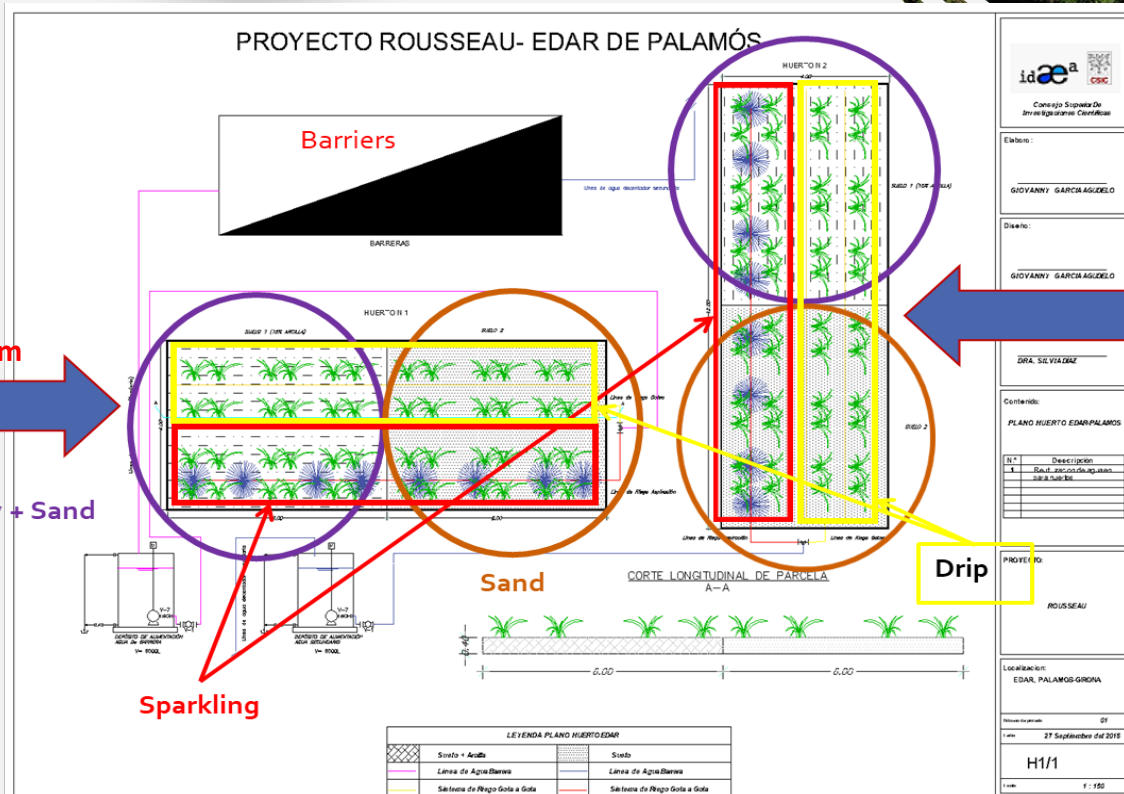
The pilot SAT system



AGRICULTURAL PLOTS DESIGN



The Agricultural plots



WWTP 2^o Effluent

Samples

Carrots



WWTP 2^o effluent



Lettuces



SAT system



Soil



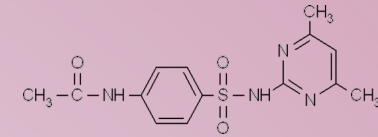
Tomatoes



Target CECs : PPCPs 57 compounds - 4 groups of substances

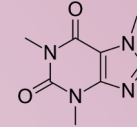


- **Pharmaceuticals**
- **35 Antibiotics, anti-inflammatories,...**



Sulfamethazine (SMZ)

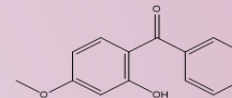
- **1 Stimulant: Caffeine**



Caffeine (CFF)

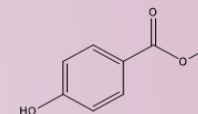
- **Personal care products**

- **15 UV filters /UV stabilizers**



Oxybenzone, benzophenone-3 (BP3)

- **4 Paraben preservatives**



Methylparaben (MePB)

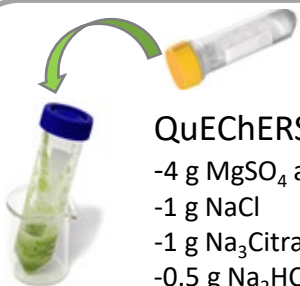
ANALYTICAL METHODOLOGY

SOILS AND VEGETABLES

QuEChERS[‡] & HPLC-QqLIT-MS/MS¹

WATERS

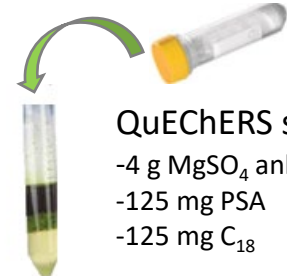
On-line SPE-HPLC-QqLIT-MS/MS²



QuEChERS salts 1:

- 4 g MgSO₄ anhidrous
- 1 g NaCl
- 1 g Na₃Citrate·2 H₂O
- 0.5 g Na₂HCitrate·1.5 H₂O

Centrifugation

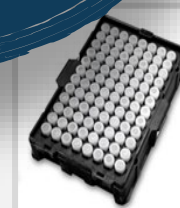


QuEChERS salts 2:

- 4 g MgSO₄ anhydrous
- 125 mg PSA
- 125 mg C₁₈

Centrifugation
pH adjustment

HPLC-MS/MS analysis



On-line SPE Cartridges
Oasis HLB (Waters)



Symbiosis™ Pico (Spark Holland) - 4000 Q TRAP
(Applied Biosystems-Sciex).

Samples	MLOD range*	MLOQ range*
Irrigation water	0.04-2.21 ng/L	0.15-7.36 ng/L
Soils	0.01-0.29 ng/g	0.0-0.97 ng/g
Lettuces	0.01-0.40 ng/g	0.05-1.34 ng/g
Tomatoes	0.01-1.46 ng/g	0.03-4.87 ng/g
Carrots	0.02-1.61 ng/g	0.08-5.35 ng/g

* all units in ng/g are expressed in dw

‡ Quick, Easy, Cheap, Effective, Rugged & Safe

1. Sunyer-Caldú, A and Diaz-Cruz M.S. ., Development of a QuEChERS-based method for the analysis of pharmaceuticals and personal care products in lettuces grown in field-scale agricultural plots irrigated with reclaimed water, Talanta, 2021, 230, 1–12.

2. Vassalle L., Sunyer-Caldú, Diaz-Cruz, M.S. et al., Bioremediation of emerging micropollutants in irrigation water. The alternative of microalgae-based treatments. J. Environ. Manage., vol. 274, 2020, 1-9.

**RECHARGED WATER
INTENDED FOR
DRINKING WATER
PRODUCTION?**



Human Health Risk Assessment

ADI (Acceptable Daily Intake)

$$ADI = \frac{NOAEL}{100}$$

NOAEL: no observed adverse effect level

DWEL (Drinking Water Equivalent Level)

$$DWEL = ADI \times BW \times 1000 / DWI$$

DWI: daily water ingestion rate
BW: body weight

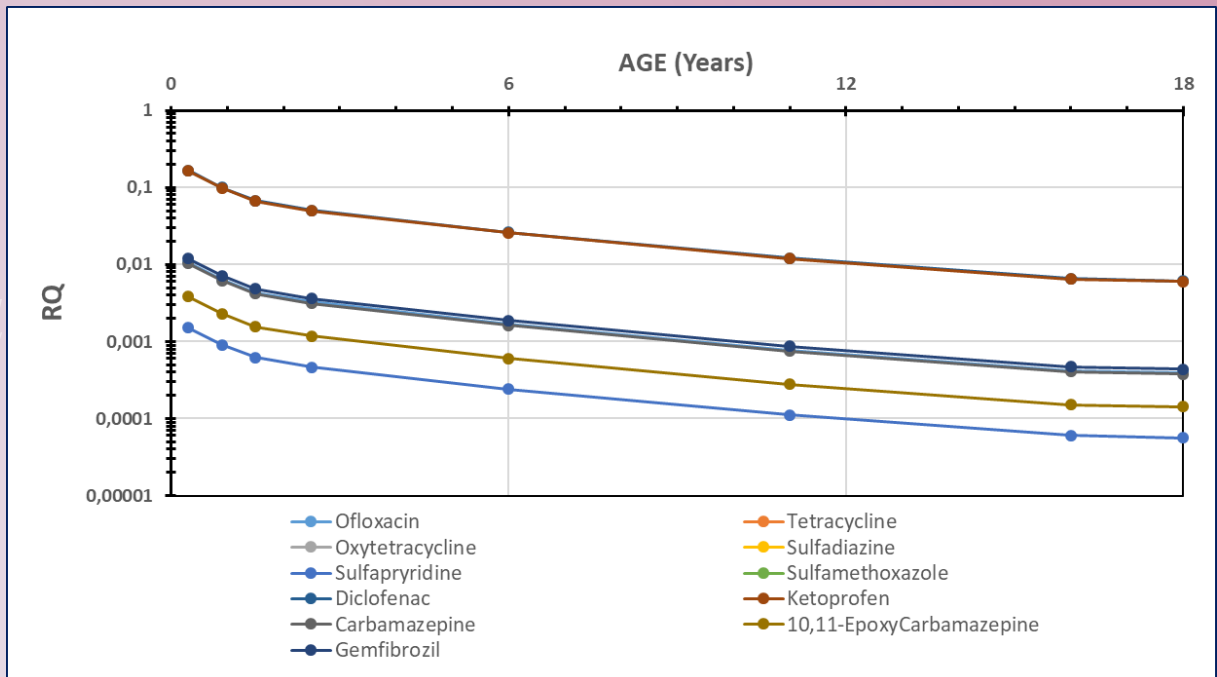
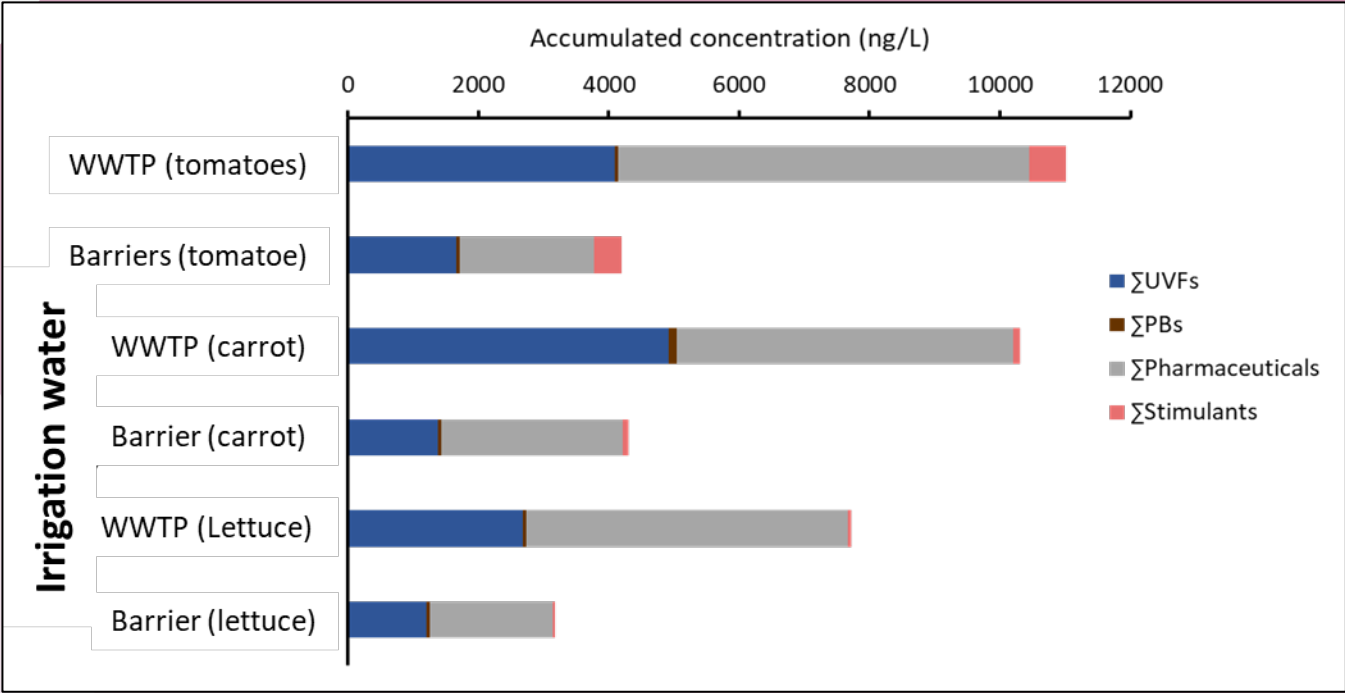
RQ (Risk Quotient)

$$RQ = C_{max} / DWEL$$

C_{max}: maximum CECs concentration

Age Groups	BW (kg)*	DWI (L/day)*
0-6 months	7.6	0.68
6-12 months	8.6	1
1-2 years	10.6	1.2
2-3 years	13	1.3
4-8 years	20.4	1.6
9-13 years	35.4	2
14-18 years	58	2.25
Adults	62	2.25

* Data on body weight was extracted from the WHO website and the DWI doses were those published by European Food Safety Authority (EFSA).



**RECHARGED WATER
FOR AGRICULTURAL
IRRIGATION OF
CROPS FOR HUMAN
CONSUMPTION**



Human Health Risk Assessment

HQ (Hazard Quotient)

$$HQ = \frac{ADI}{EDI}$$

HI (Hazard Index)

$$HI = \sum HQ$$

EDI (Estimate Daily Intake)

$$EDI = \frac{DI \cdot C_e}{BW}$$

DI: Daily Intake
 C_e: Average CECs concentration
 BW: Body Weight

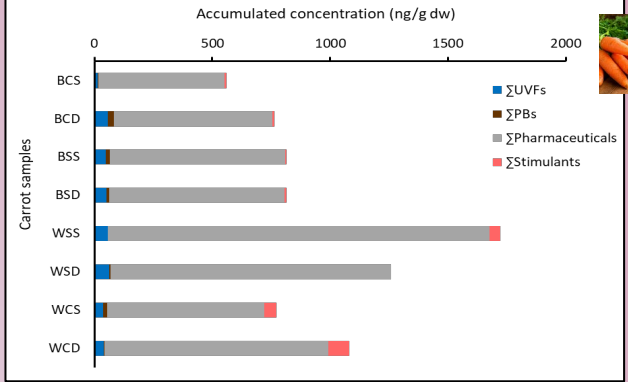
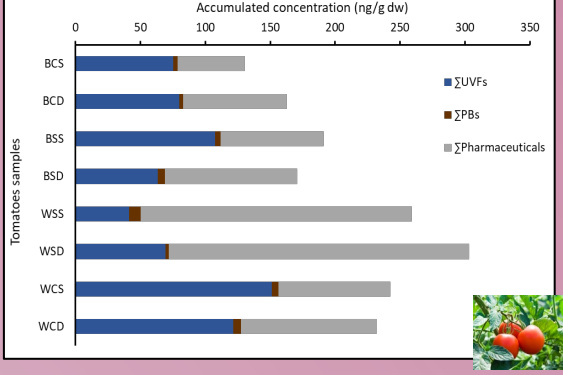
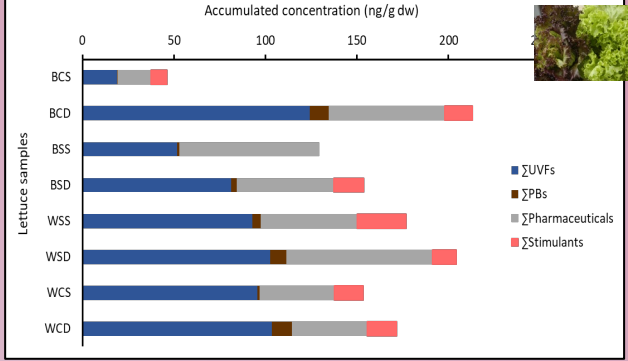
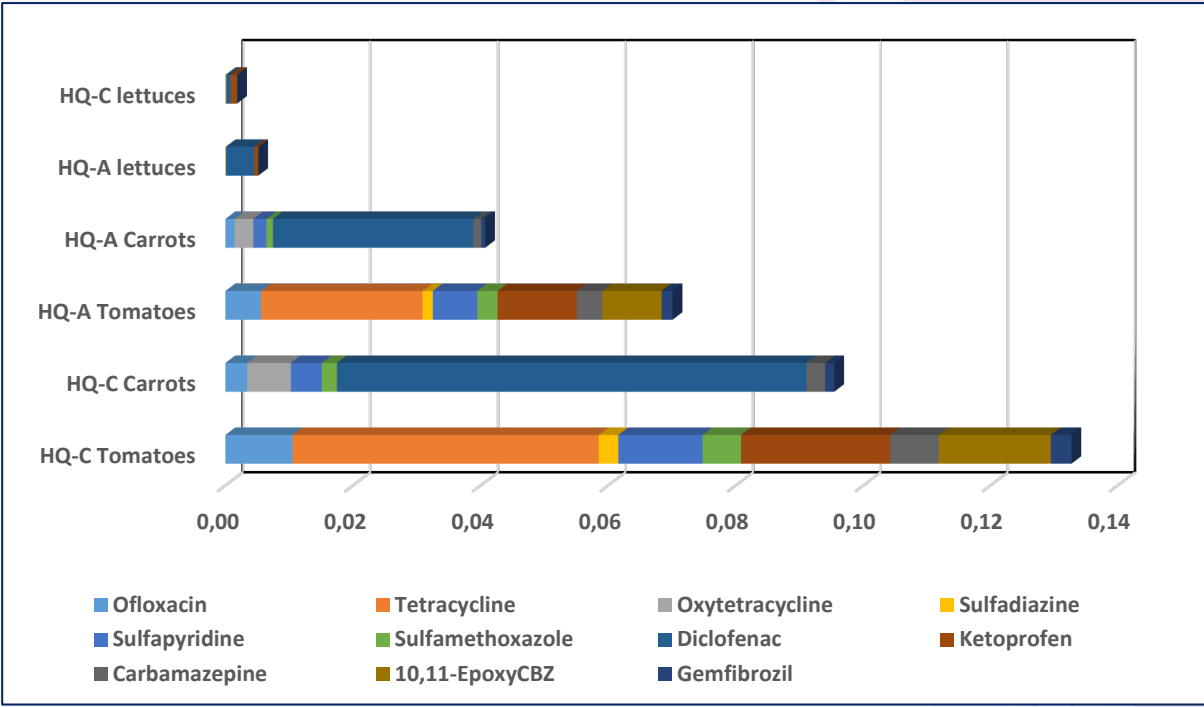
ADI (Acceptable Daily Intake)

$$ADI = \frac{NOAEL}{100}$$

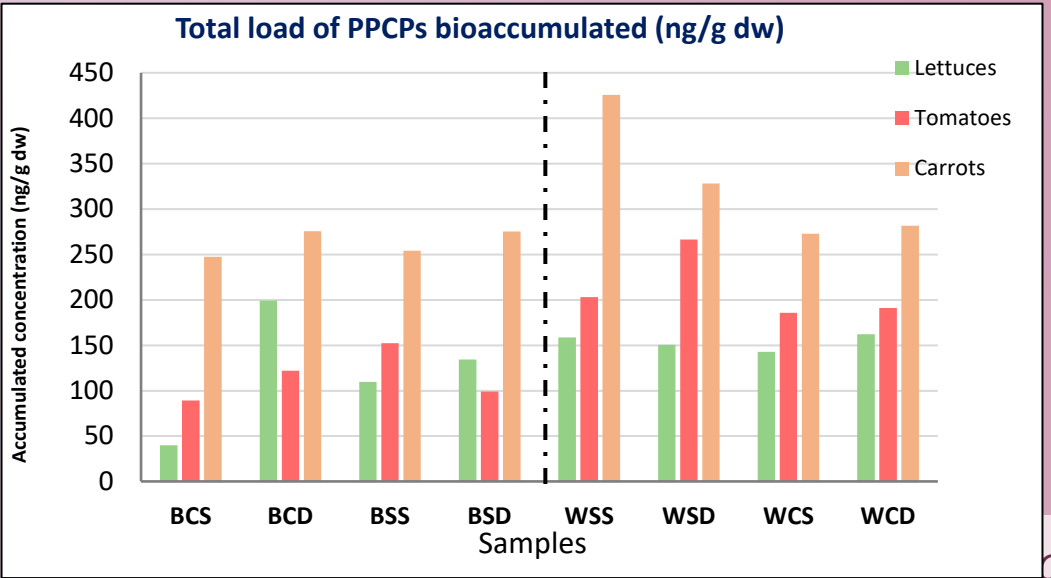
NOAEL: no observed adverse effect level

- DI, ENALIA and ENALIA2 Surveys from AECOSAN.
- BW, 70 Kg average Spanish male adult of 18-74 years, and 24 Kg average child of 3-9 y.

*ADI, from datasets compiled by Wang et al. 2017. ES&T, 51, 3518–3525 and Prosser et al., 2015. Environ. Int. 75, 223–233.



B: Barriers water, **W:** WWTP effluent water, **S:** sand (less clay) soil, **C:** clay soil, **S:** sprinkler irrigation system, **D:** drip irrigation system.



SAT + REACTIVE BARRIERS



**Significant attenuation
of CECs**



**Cost-effective, nature-
based approach**

SAT + REACTIVE BARRIERS WATER USE



**Improves water
quality**



**Safe for human health
No risk**

CONCLUSIONS

Sunyer-Caldú A., Sepúlveda-Ruiz P., Salgot M., Folch-Sánchez M., Barcelo D., Diaz-Cruz M.S. Reclaimed water in agriculture: a plot-scale study assessing crop uptake of emerging contaminants and pathogens. *J. Environ. Chem. Engin.* 2022, 10, 108831.

Sunyer-Caldú A., Quintana G., Diaz-Cruz M.S. Pharmaceuticals and personal care products uptake by crops irrigated with reclaimed water and human health implications. *Environ. Res.* 2023, 193, 116923.



Emerging risks of chemical and microbiological contamination in the reuse of wastewater for agricultural irrigation: integrated study. ROUSSEAU

<http://rousseauproject.es>



2018 JOINT CALL

MARadentro: Managed Aquifer Recharge:
Addressing the Risks of Recharging
Regenerated Water

<http://www.maradentro-jpi.eu>

THANK YOU

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