4th INTERNATIONAL CONFERENCE ON RISK ASSESSMENT OF PHARMACEUTICALS IN THE ENVIRONMENT

Barcelona, 9 - 10 October 2023

RISK ASSESSMENT OF PHARMACEUTICALS AND MICROPLASTICS IN IRRIGATED CROPS WITH RECLAIMED WATER IN ALMERIA, SOUTH EAST OF SPAIN

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European Commission

EURL-FV

OUTLINE

-Agricultural use of regenerated water

-Chemicals present, crop uptake, and risk associated

-Soil contamination

-Presence of MPs. Standardization?

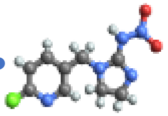
-Effect of MPS in crops

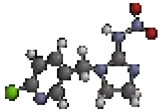
-Are MPs a Troy Horse?

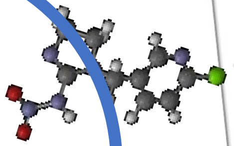
Introduction

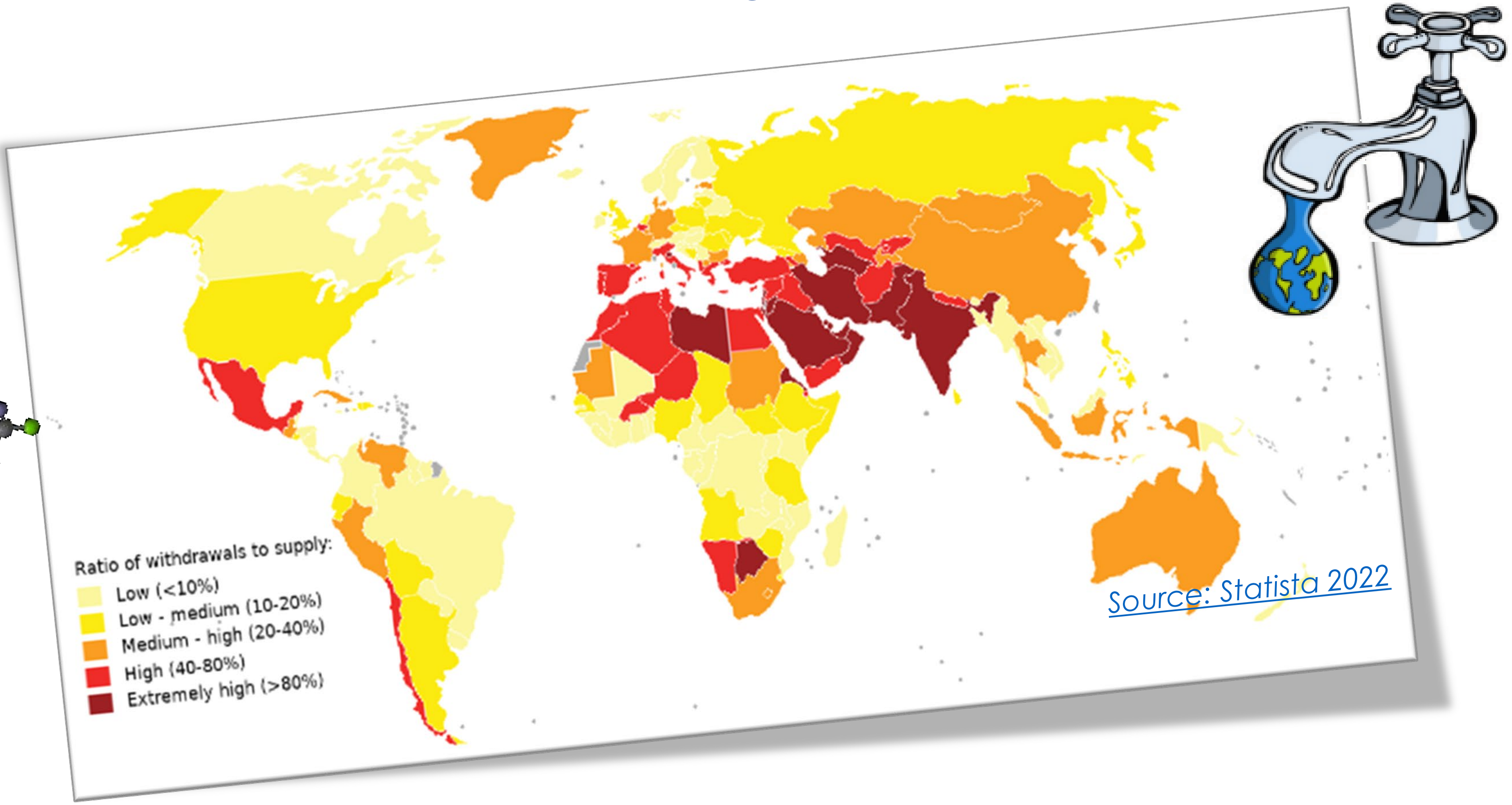
Water is a limited resource in the world

A quarter of the world's population experiencing water stress



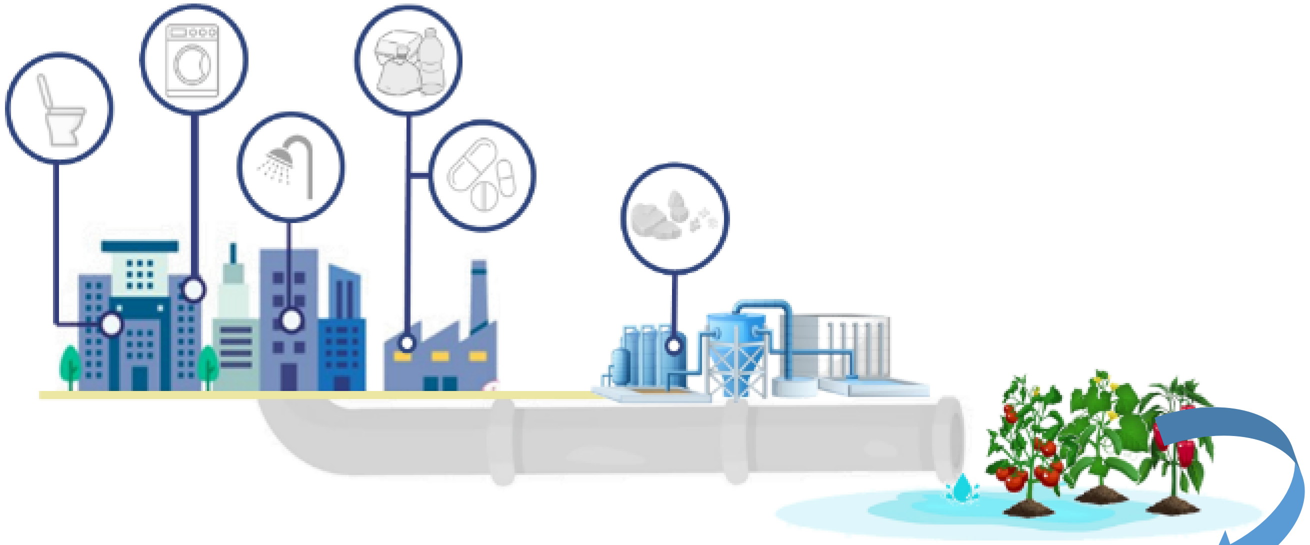


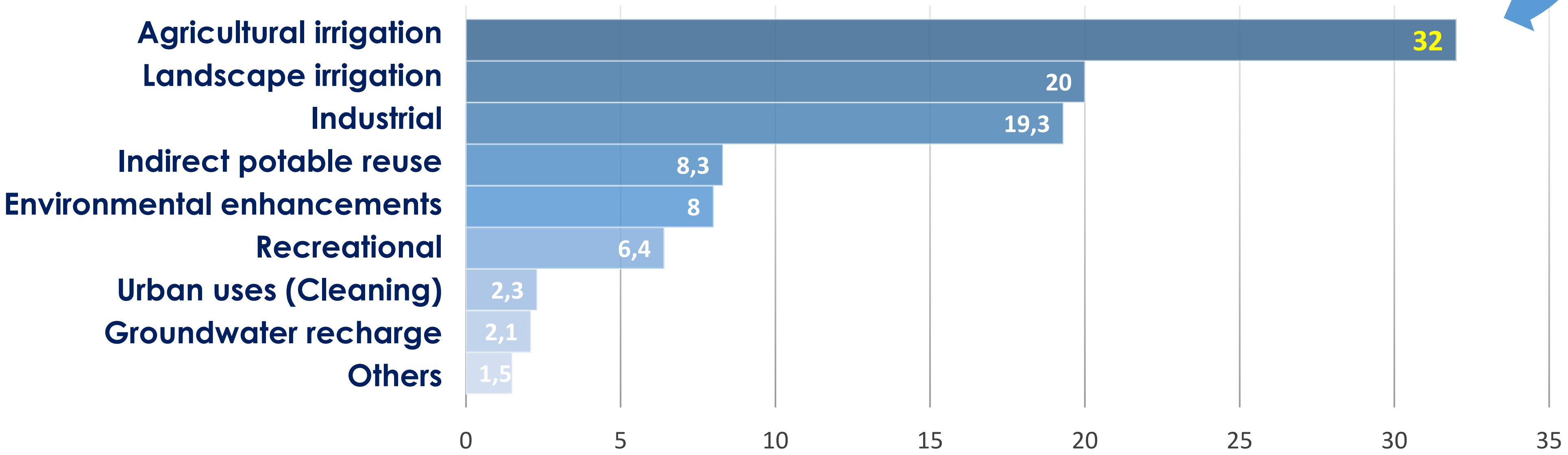




- Low Environmental Impact
- Environmental, economic and social benefits

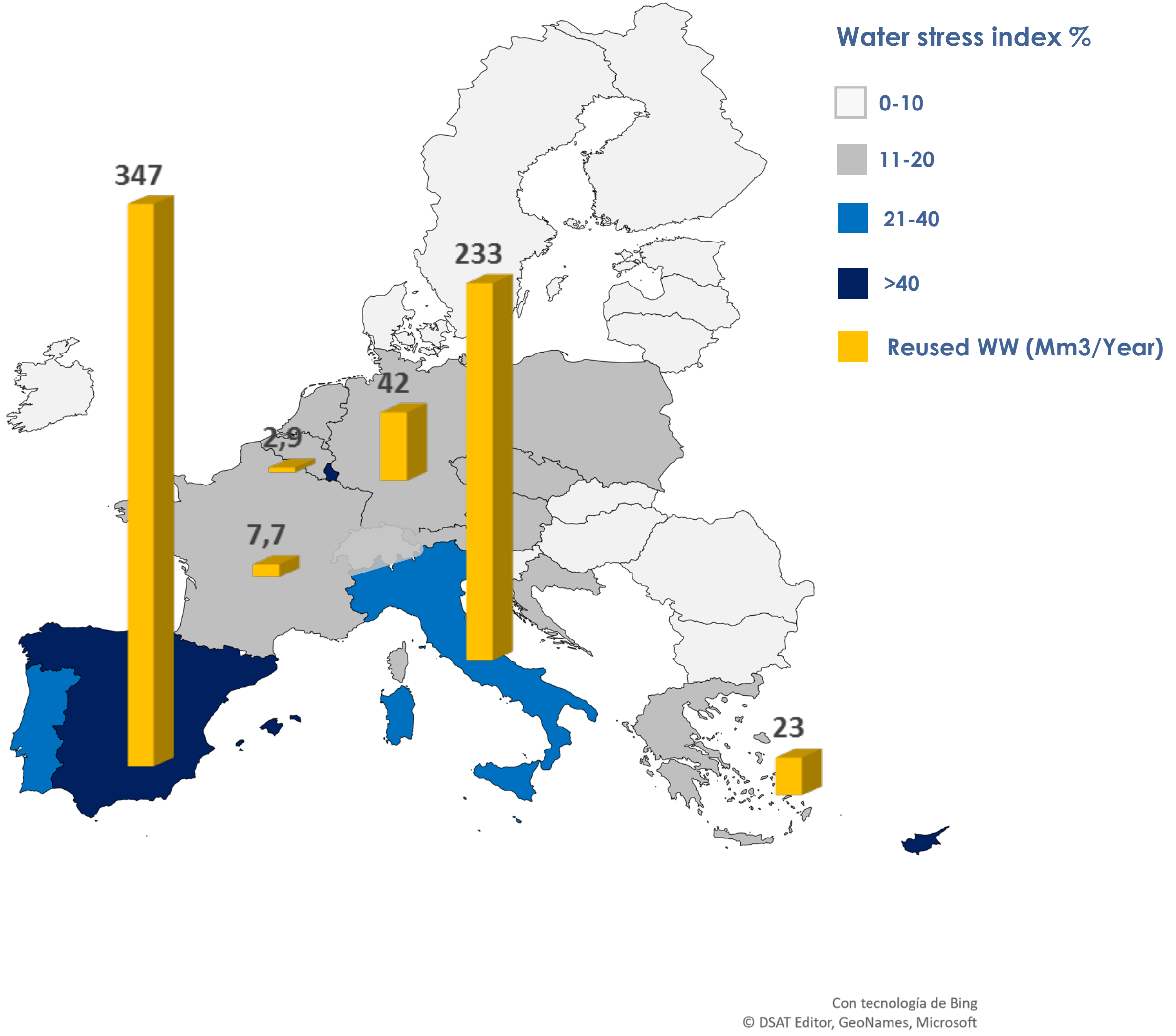
Reclaimed water from WWTPs in %





Source: The United Nations World Water Development Report 2017

Spatial distribution of water stress/water reuse in Europe

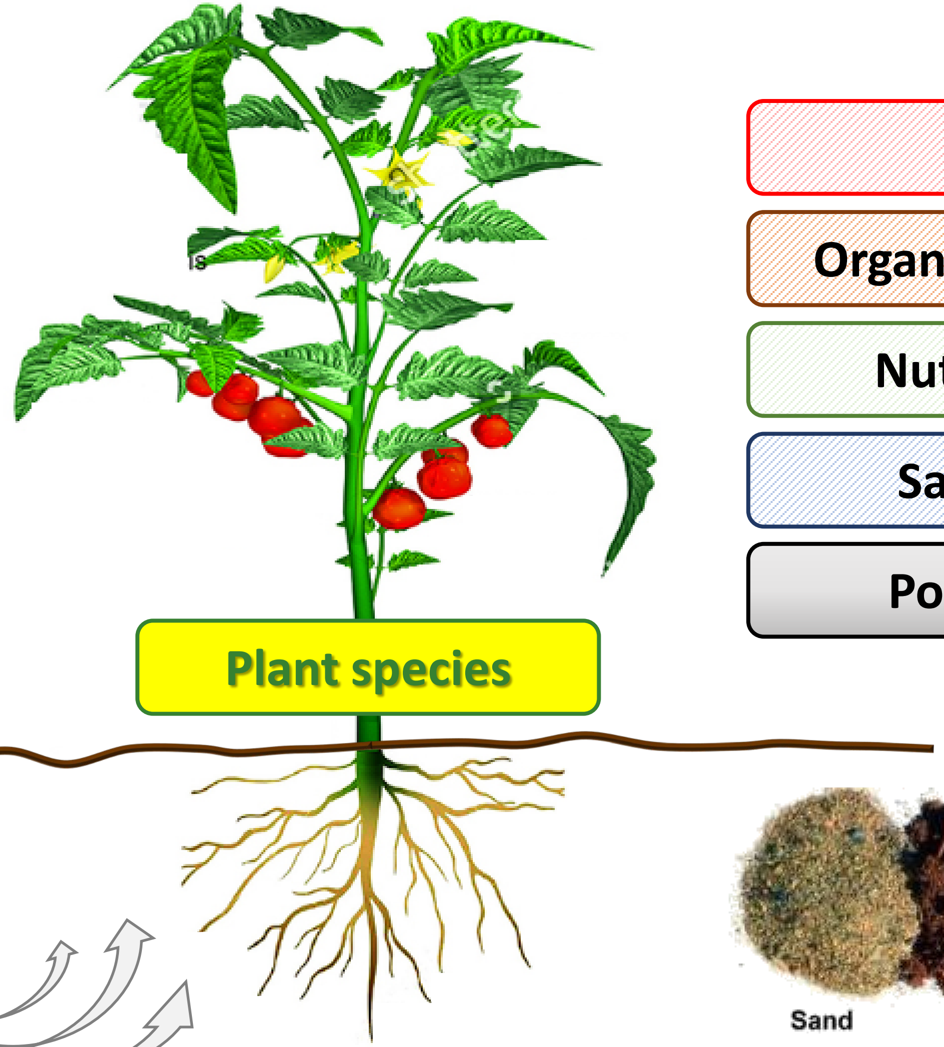


In Europe, water reuse is a top priority area in the Strategic Implementation Plan of the European Innovation Partnership on Water.

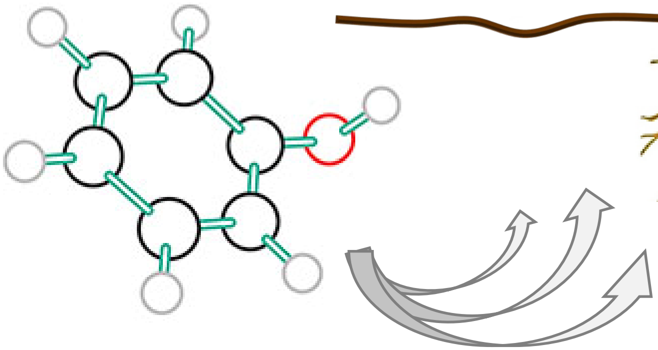
Uptake & Bioaccumulation

- Kow
- pKa
- Solubility
- Koc

- pH
- Organic matter
- Nutrients
- Salinity
- Porosity



Plant species



Jaramillo, M. F.; Restrepo, I. Wastewater reuse in agriculture: a review about its limitations and benefits. Sustainability ***2017****, 9, 1734.*

EU Regulation on minimum requirements for water reuse

- Water Framework Directive (WFD) - Directive 20... ...plementation Decision (EU) 2018/840
- ...Wastewater Treatment Directive – *91/271/EEC*

Not specify conditions for water reuse

…..creating commercial difficulties


L 177/32 EN Official Journal of the European Union 5.6.2020

REGULATION (EU) 2020/741 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 25 May 2020

on minimum requirements for water reuse

(Text with EEA relevance)

After transmission of the draft legislative act to the national parliaments,

Having regard to the opinion of the European Economic and Social Committee (1),

Having regard to the opinion of the Committee of the Regions (2),

Acting in accordance with the ordinary legislative procedure (3),

Regulation (EU) 2020/741
Minimum requirements for treated urban water reuse for agricultural irrigation

(a) heavy metals;
(b) pesticides;
(c) disinfection by-products;
(d) pharmaceuticals;
(e) other substances of emerging concern;
(f) anti-microbial resistance.

Type	Crop category						
A	All food crops, including root crops consumed raw and food crops where the edible part is in direct contact with reclaimed water		disinfection				
B	Food crops consumed raw where the edible part is produced above ground and is not in direct contact with reclaimed water, processed food crops and non-food crops including crops to feed milk- or meat-producing animals	All irrigation methods	Secondary treatment, and disinfection	≤100	According to Council Directive 91/271/EEC1	According to Council Directive 91/271/EEC 1	-
C		Drip irrigation only		≤1,000			-
D	Industrial, energy, and seeded crops	All irrigation methods		≤10,000			-

Bibliographic data research & OBJECTIVE

Scopus Analyze search results

Search documents *
emerging cont

The long-term impact on crops permanently irrigated with reclaimed water under real agronomic conditions evaluating the plant uptake & soil accumulation of CECs

Uptake of pharmaceuticals by plants grown under hydroponic conditions and natural occurring plant species: A review

To date, most of them have been carried out in the laboratory (unrealistic agricultural conditions), or in field trials at concentration levels higher than those expected in reclaimed water

Pilot studies under real agronomic conditions

The reclaimed water were provided from the General Community of Users of Waters of Almería (CGUAL)

- Regulation (EU) 2020/741
- Directive 2013/39/EU
- Directive 91/271/EEC

Crops grown in greenhouses managed by CGUAL´s farmers of Almeria

From September 2021 to May 2022

- 22 irrigation water samples (taken weekly)
- 8 vegetables (cucumber, tomato, pepper and zucchini)
- 8 soil samples

Extraction methods

10 g of sample

+ 5 mL MiliQ-H_2O

10 mL AcN (0.5% v/v, formic acid) + 10 µL IS

Shake automatically 6 min

4 g $MgSO_4$ anh. + 1 g $NaCl_4$ + 1 g $Na_3Citrate \cdot 2H_2O$ + 0,5 g Na2HCitrate·1,5H2O

Shake automatically 6 min

Centrifuge 5 min 3500 r.p.m.

Take 5 mL aliquot

750 mg $MgSO_4$ anh. +125 mg C18

Shake 30 second/Vortex

Centrifuge 5 min 3500 r.p.m.

Centrifuge 5 min 3500 r.p.m.

LC-QqQ-MS/MS Analysis

*García Valverde et al. **2021**. Sci. Total Environ. 782, 146759; Martinez Bueno, et al. **2022**. Sci. Total Environ. 806, 150909.*

Analytical workflow

Sciex Exion HPLC

Chromatographic separation

Zorbax Eclipse Plus C8 *(1.8 µm × 2.1 mm × 100 mm)*

Mobile phases

(A) H_2O + 0.1% formic acid
(B) AcN

Gradient program

Flow rate: 0,3 mL/min

- 0 – 0,5 min, 10 % (B) isocrático
- 0,5 – 11,5 min, 10 % to 100 % (B)
- 11,5 – 15,5 min, 100 % (B)

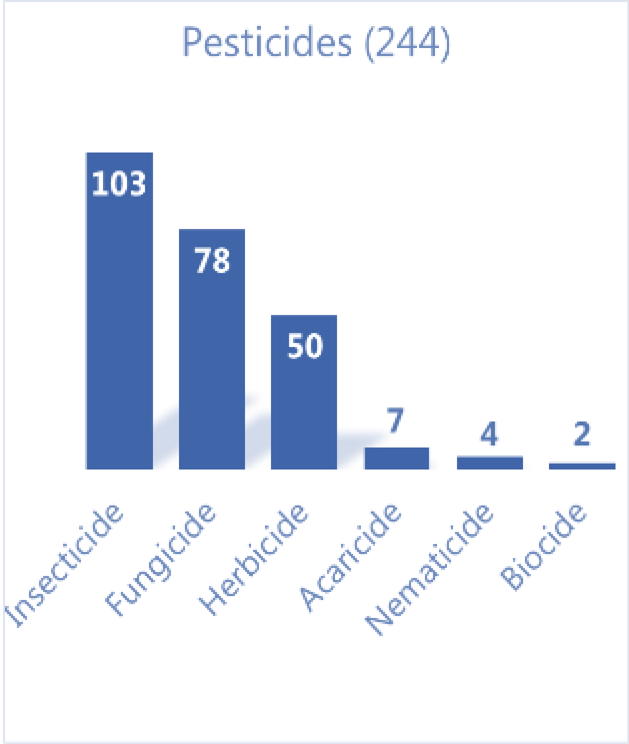
MS & ionization settings

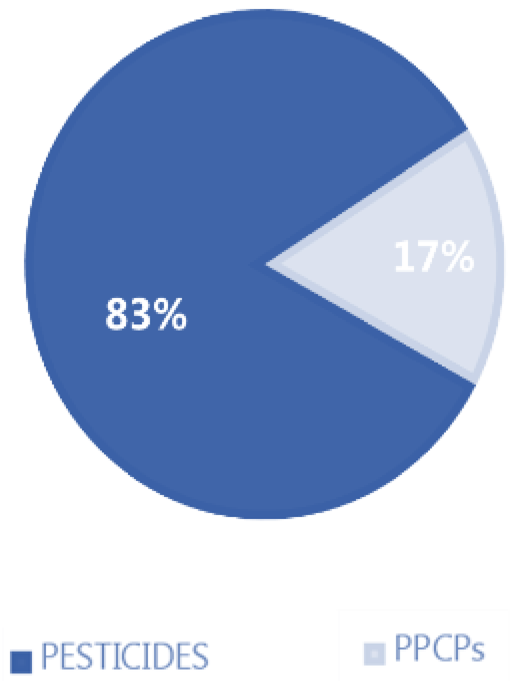
- MRM in mode ESI (+/-)
- Ionspray voltages: 5000 (+) / −4500 (-)
- Injection volume: 5 µL
- Curtain gas: 20 (arbitrary units)
- GS1: 50 psi
- GS2: 40 psi
- Tª: 500 °C

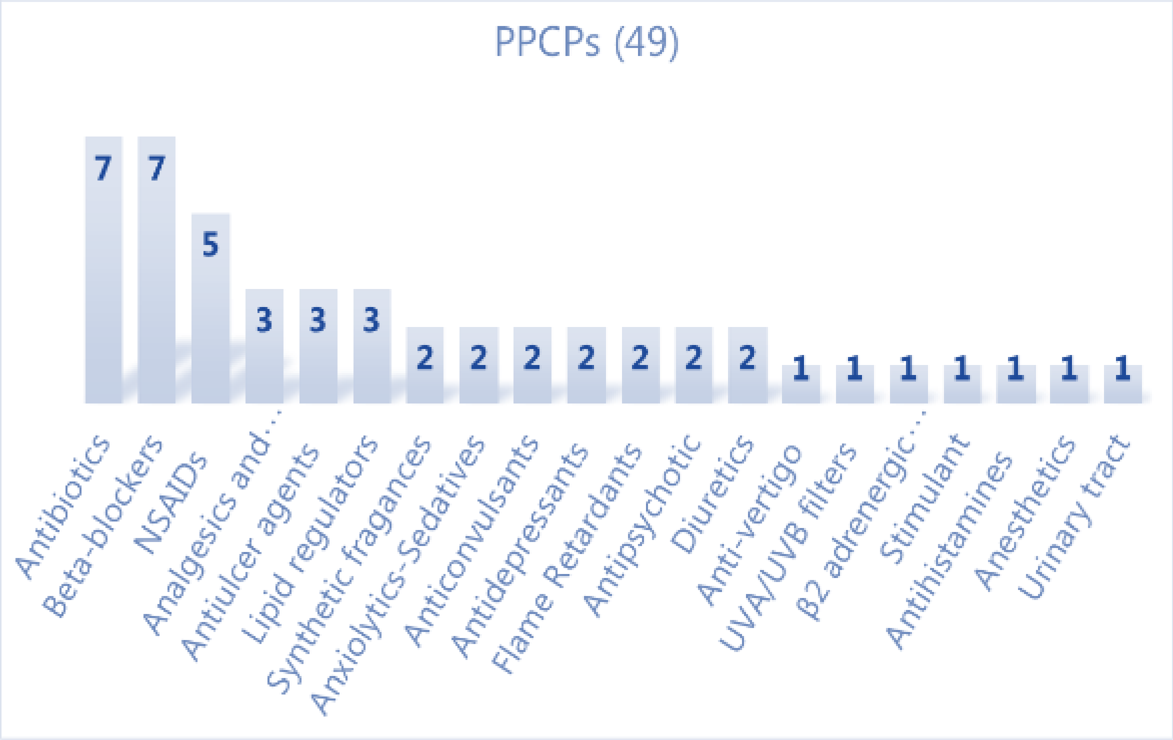
Sciex 6500+ TripleQuand-LC-MS/MS

Target compound

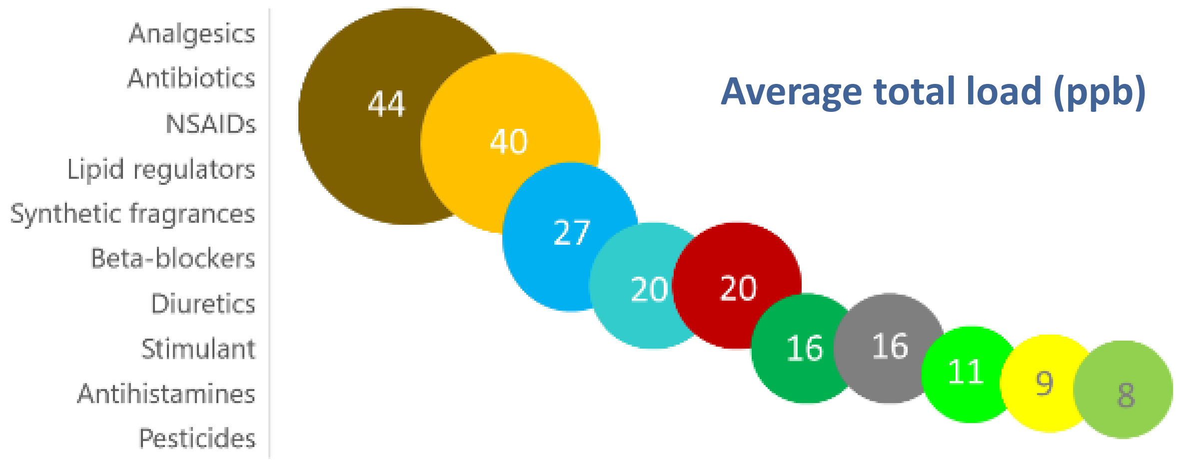
Target compounds (293)

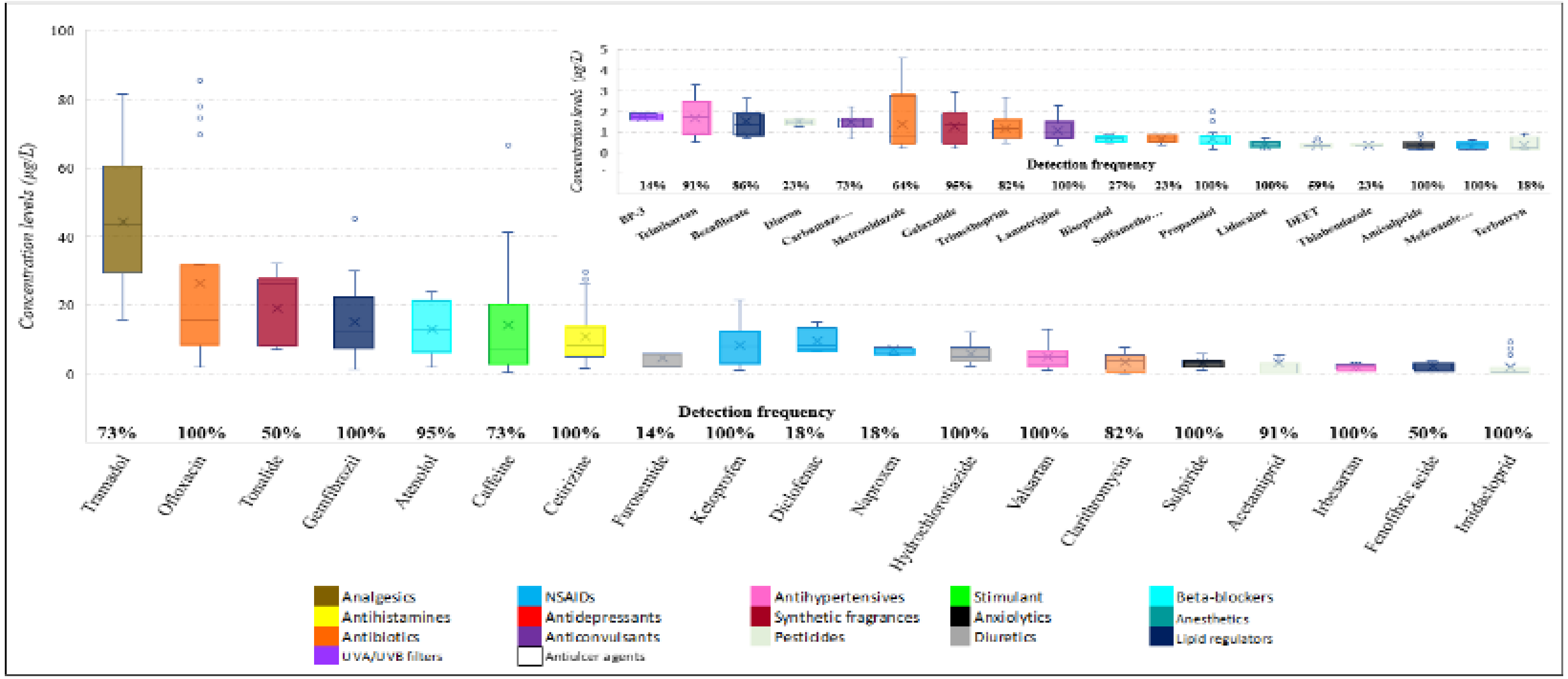




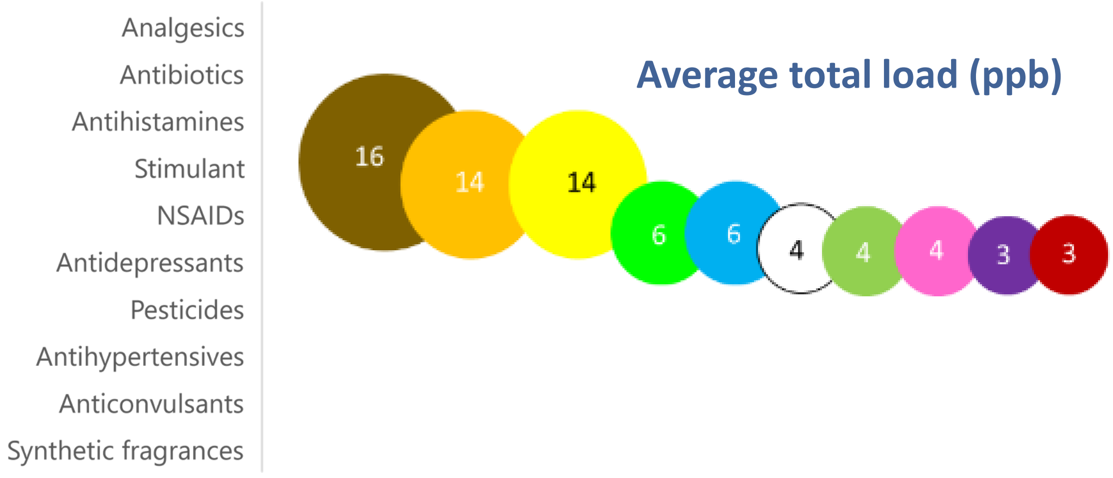


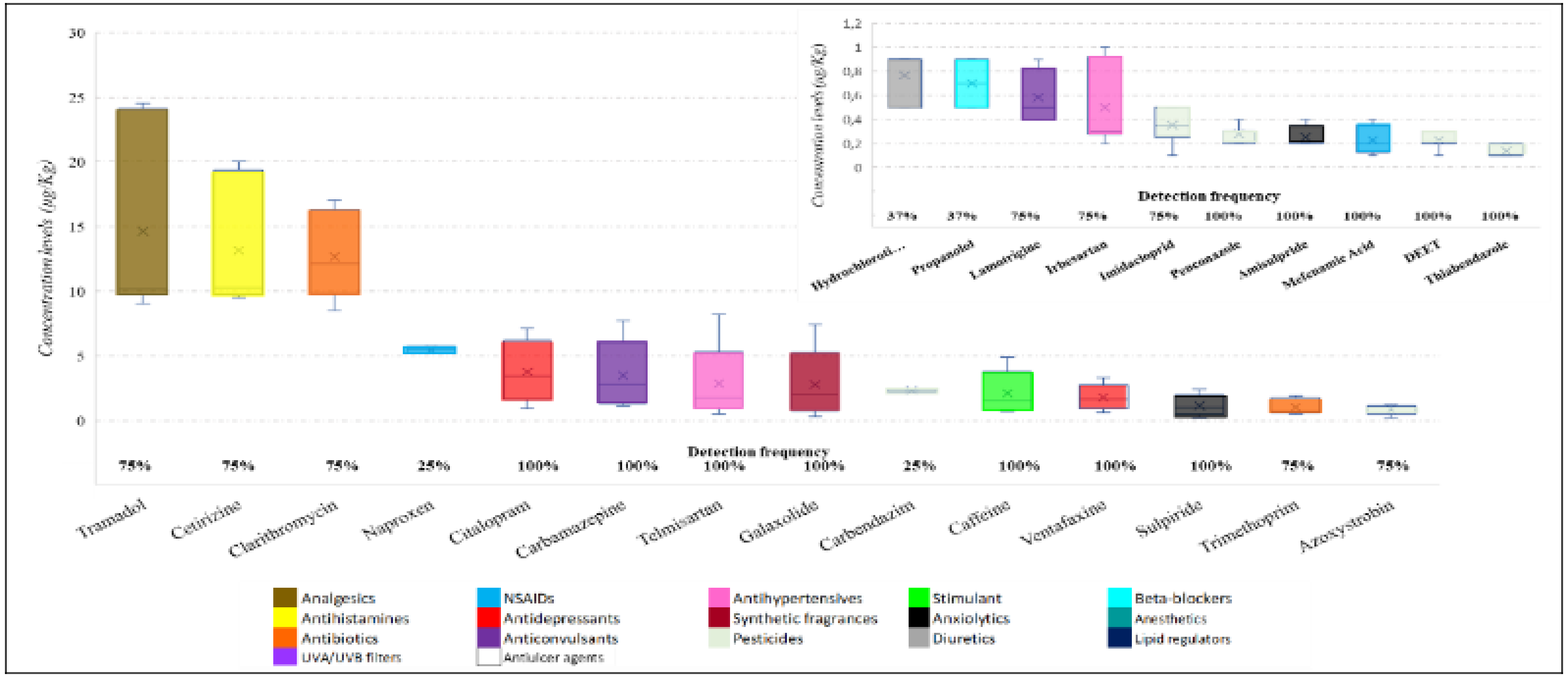
Results CECs in reclaimed water



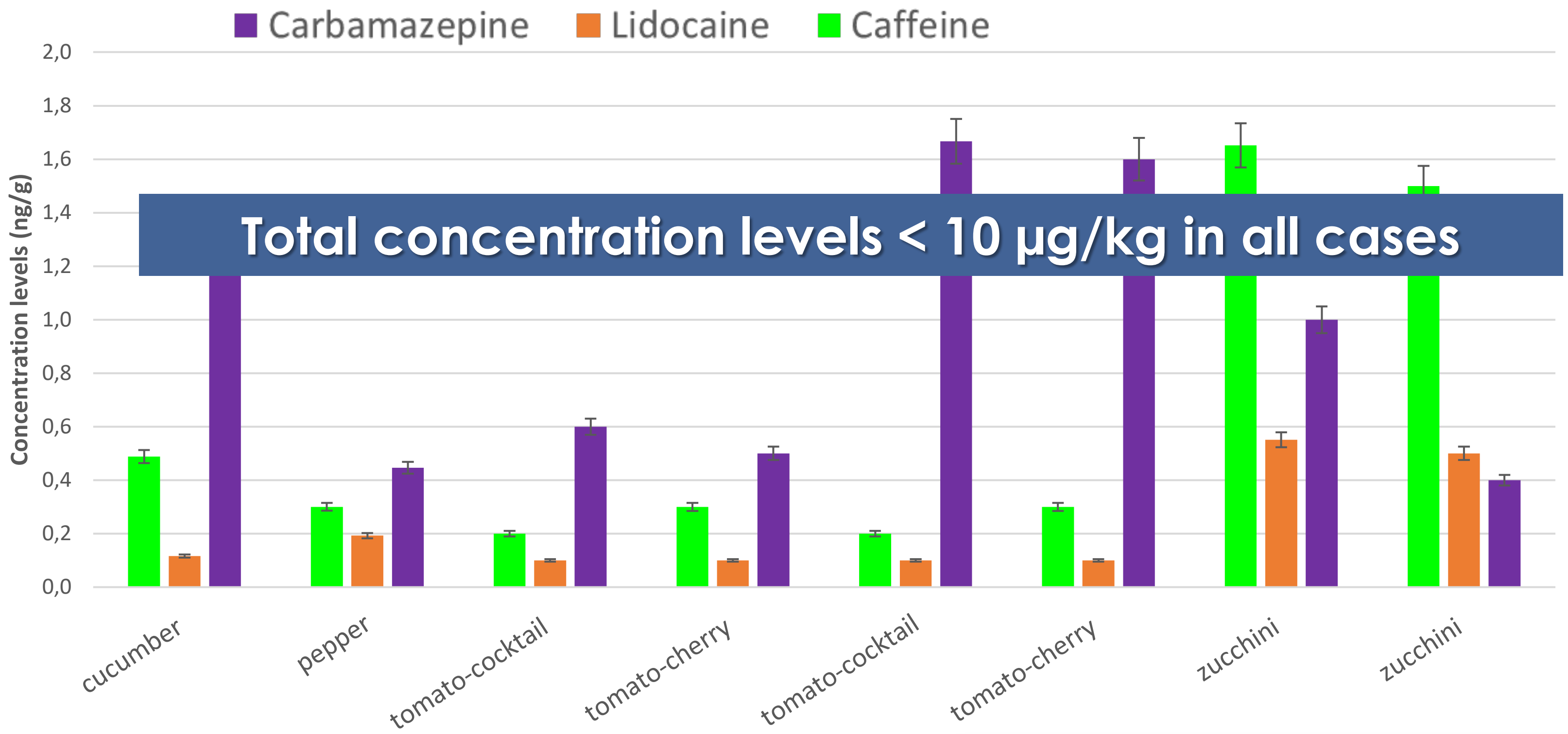


Results CECs in soil samples



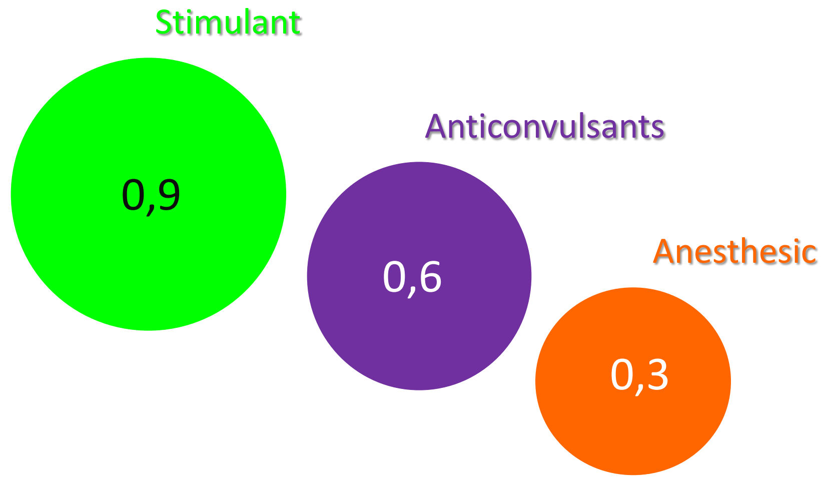


Results – CECs in vegetables samples



Total concentration levels < 10 µg/kg in all cases

Average Total Load (ppb)



$$BCF\ (L/kg) = \frac{\text{concentration in edible part of plant } (\mu g/kg)}{\text{concentration in irrigation water } (\mu g/L)}$$

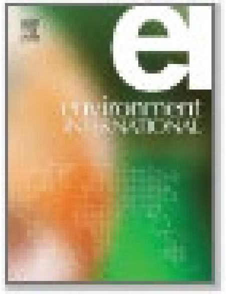
	Caffeine	Carbamazepine	Lidocaine
Bioconcentration factor (BCF)	0,06	0,44	0,73
Human Exposure (µg) - Daily Consumption	0,16	0,17	0,05

The daily human intake was estimated by multiplying the concentration measured in the edible part of the crop (ug/Kg in f.w.) and the daily consumption per capita of fresh vegetables (Kg f.w/day). Considering the worst cases: the highest detected concentration and a daily consumption of 100 g f.w

Environment International

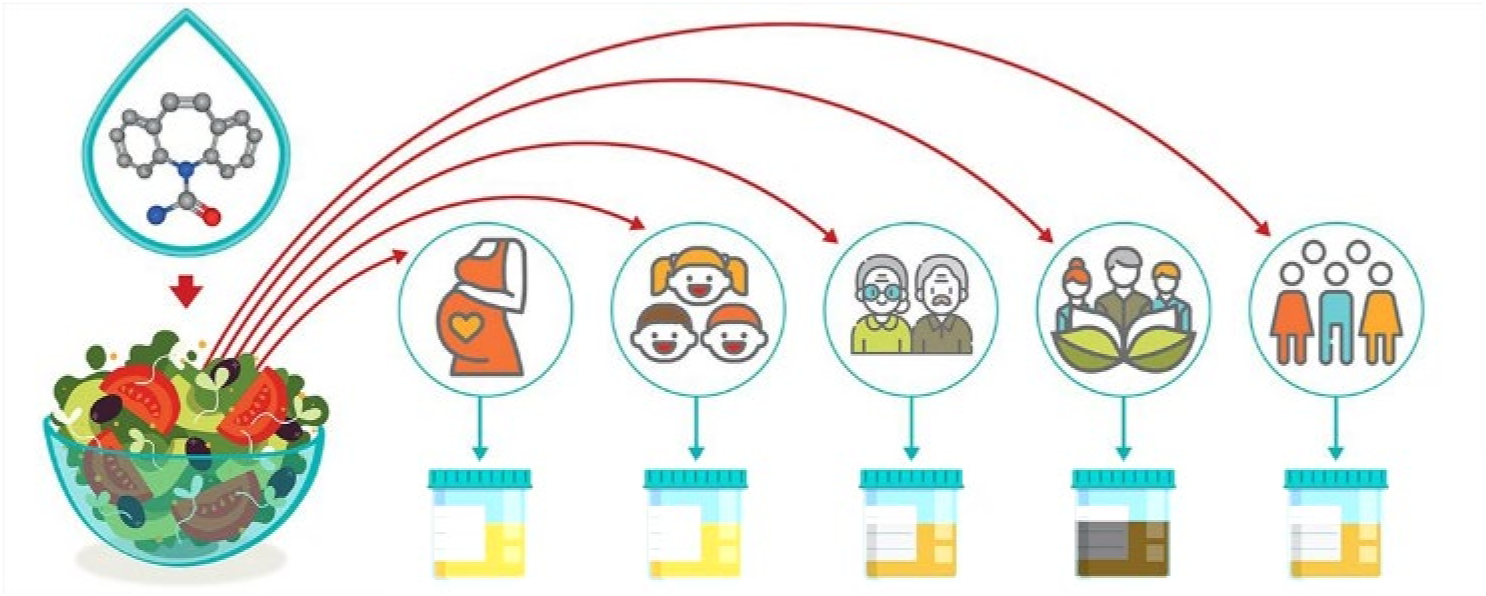
Volume 143, October 2020, 105951

ELSEVIER

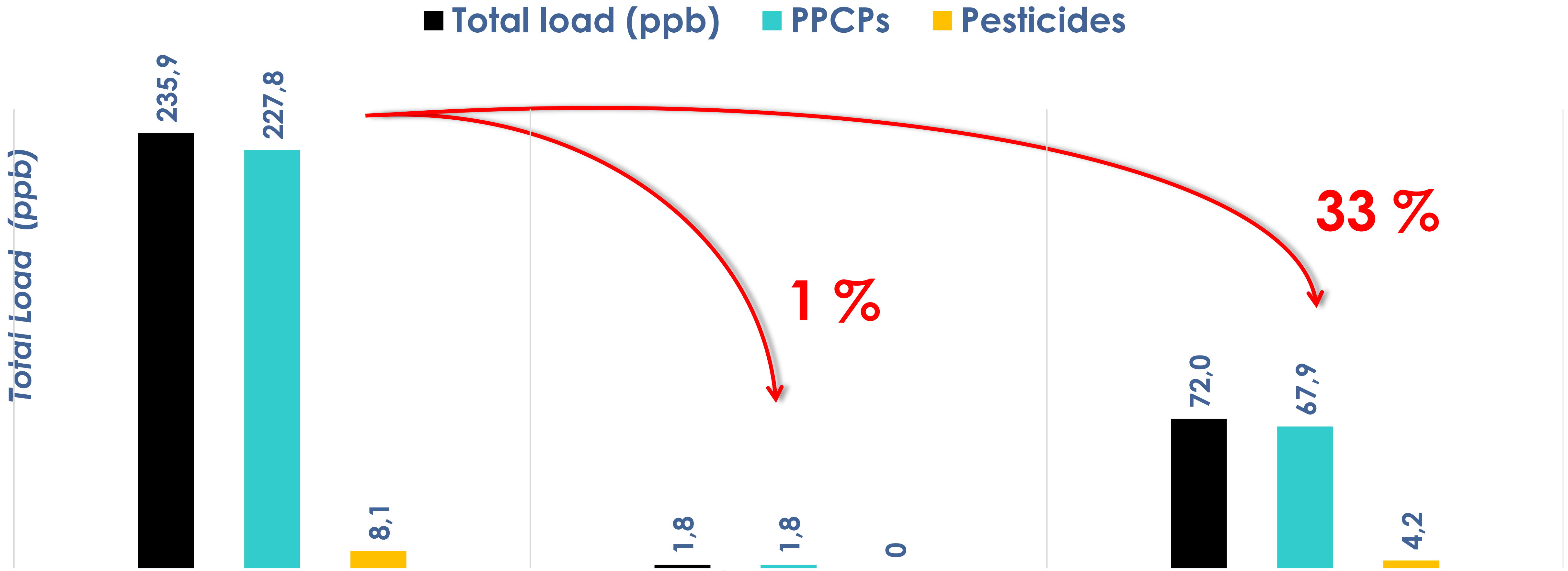


Involuntary human exposure to carbamazepine: A cross-sectional study of correlates across the lifespan and dietary spectrum

Michael Schapira [a], Orly Manor [a], Naama Golan [b], Dorit Kalo [c], Vered Mordehay [b], Noam Kirshenbaum [b], Rebecca Goldsmith [a, d], Benny Chefetz [b, 1], Ora Paltiel [a, 1]



Results – CECs SUMMARY



One macrolide antibiotic included in the Commission Implementing Decision (EU) 2018/840 (clarithromycin) and two of the pesticides (diuron and terbutryn) included in the list of priority substances covered by the Water Framework Directive (Directive 2013/39/EU)

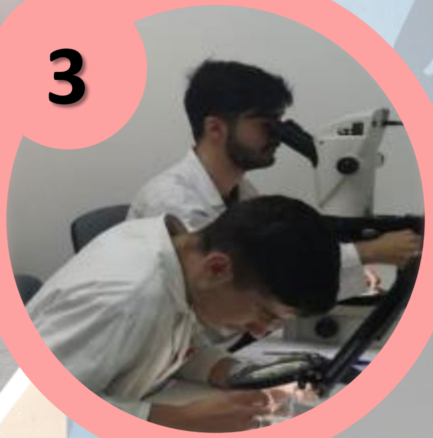
- None of them was detected in the vegetables irrigated with that water

- Clarithromycin was accumulated in agricultural soil.

1

2

3



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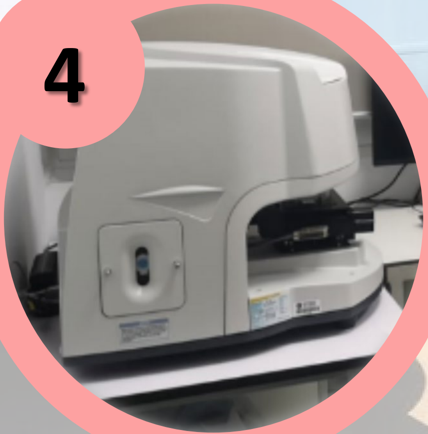


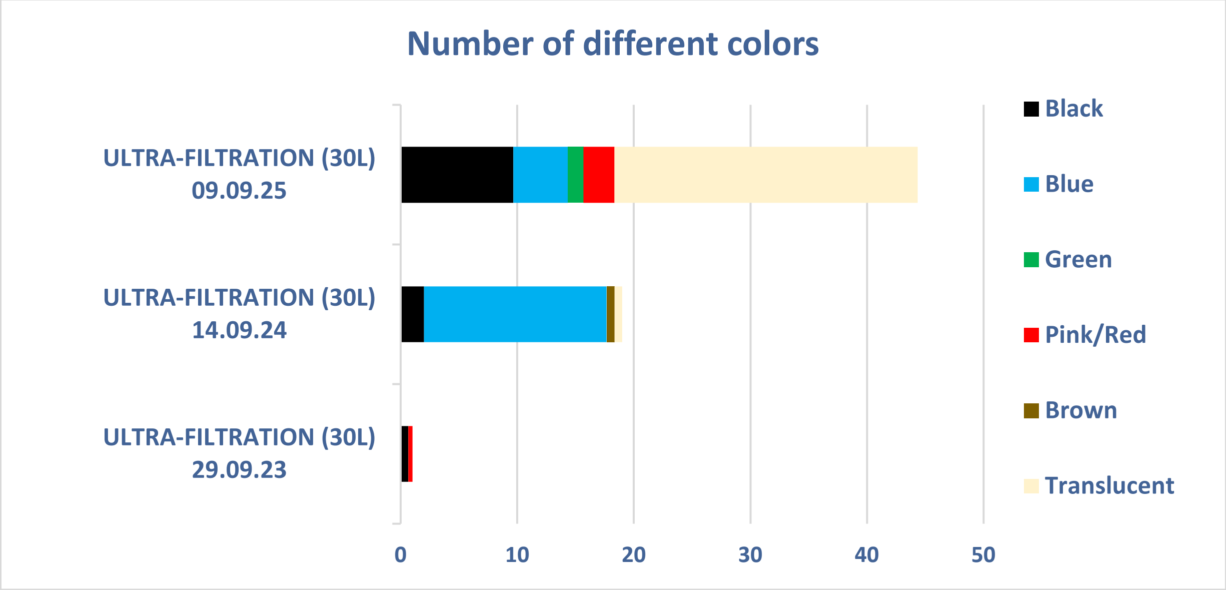
MPs

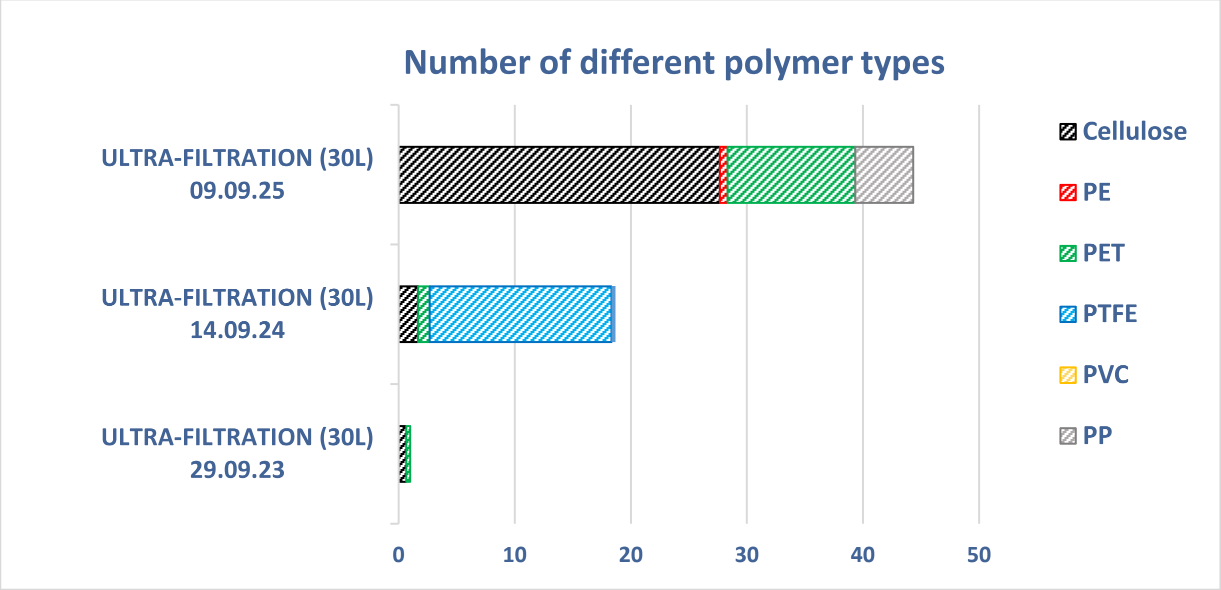
Sample collection & extraction

Microscopy & FT-IR Analysis

Total Flow = 30 L reclaimed water by triplicate

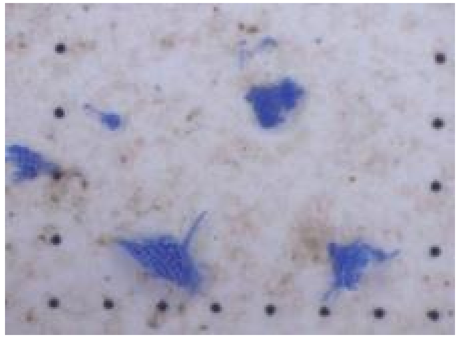
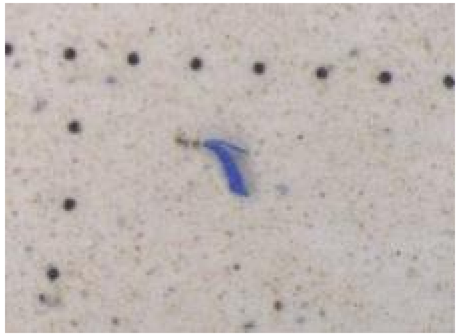
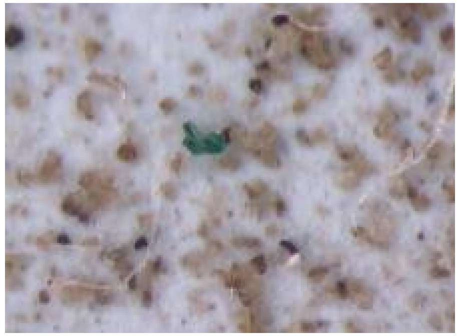
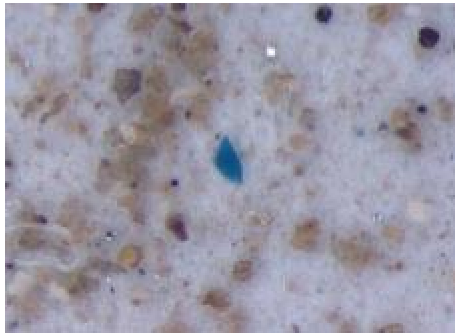
Results – FIBRES in reclaimed water used to crop irrigation

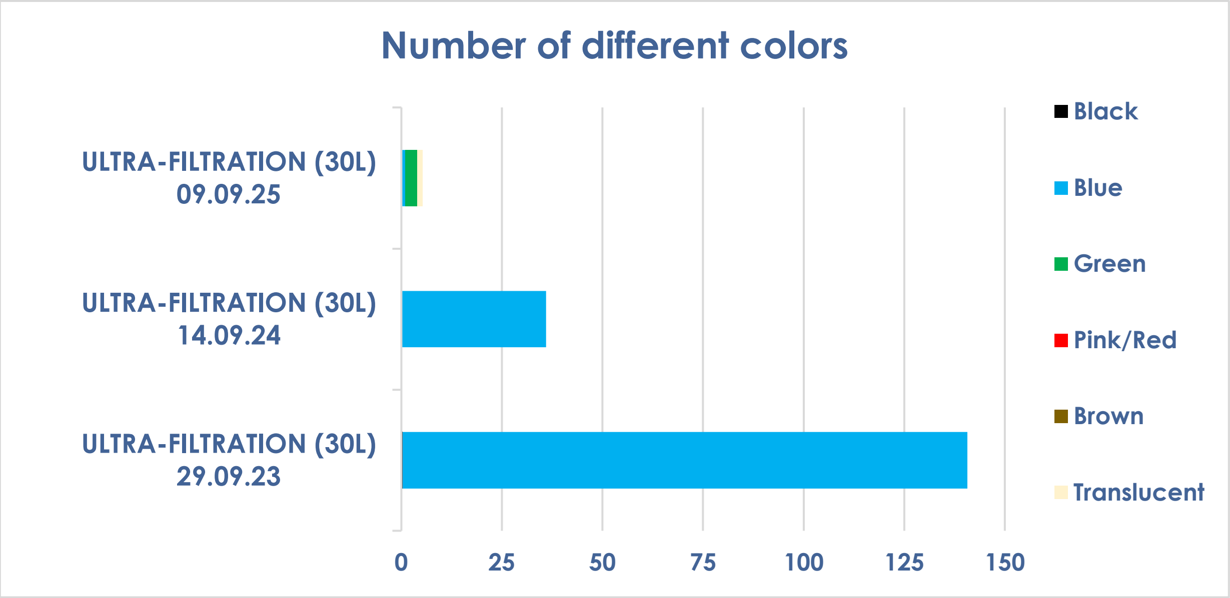


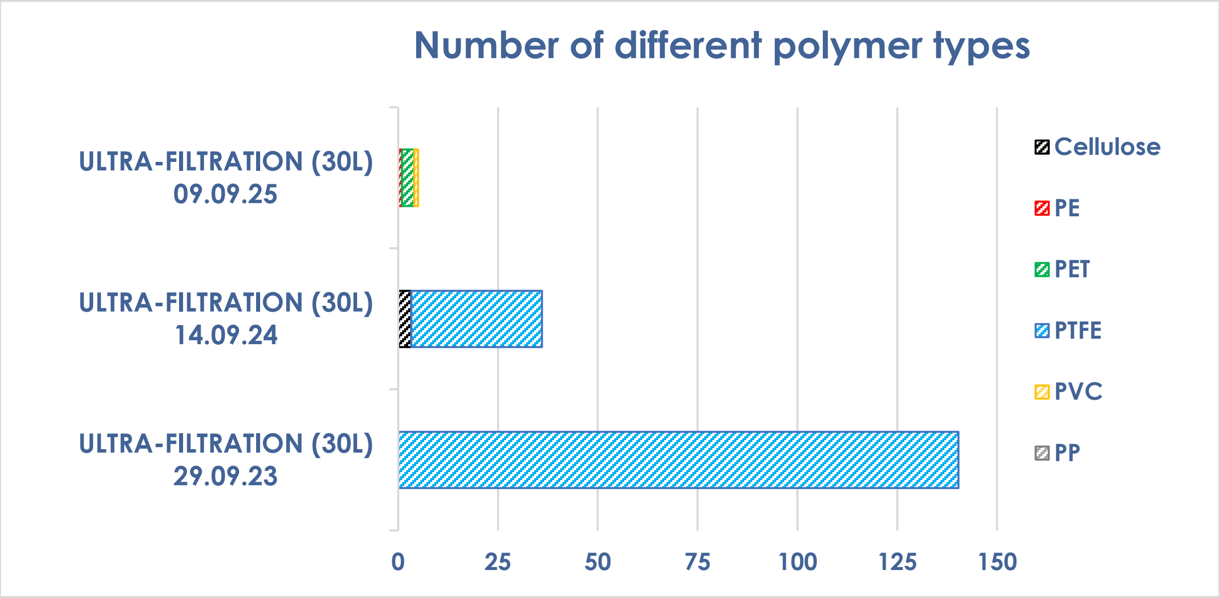


PE: Polyethylene; PET: Polyethylene terephthalate; PTEF: Polytetrafluoroethylene; PVC: Polyvinyl chloride; PP: Polypropylene;

Results – FRAGMENTS in reclaimed water used to crop irrigation

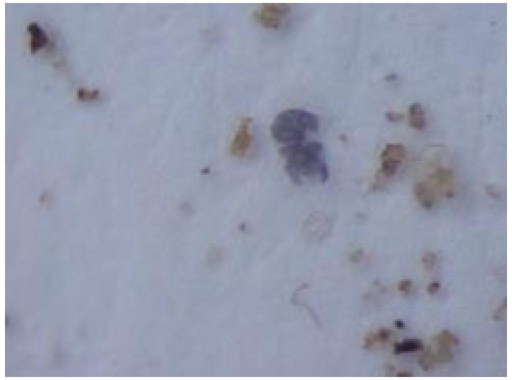



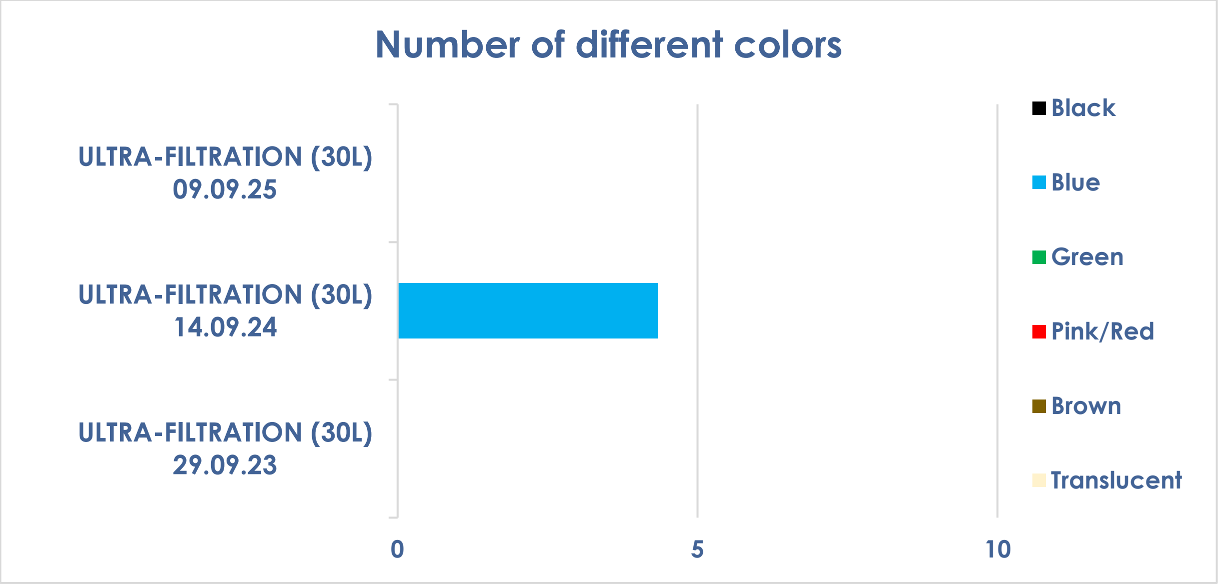


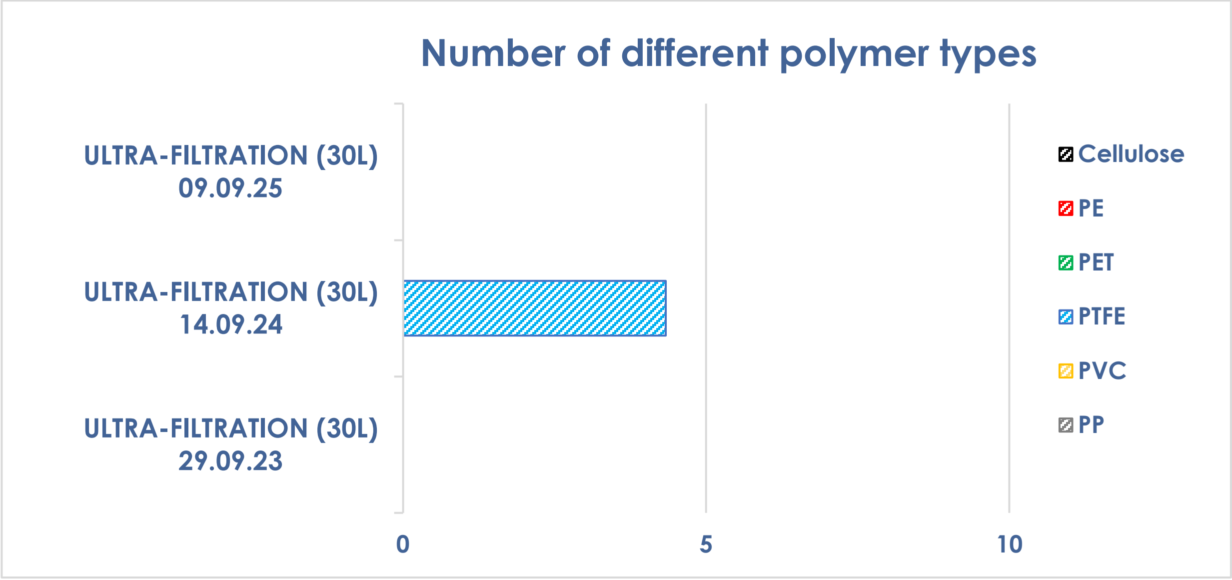
PE: Polyethylene; PET: Polyethylene terephthalate; PTEF: Polytetrafluoroethylene; PVC: Polyvinyl chloride; PP: Polypropylene;

Results – FILMS in reclaimed water used to crop irrigation







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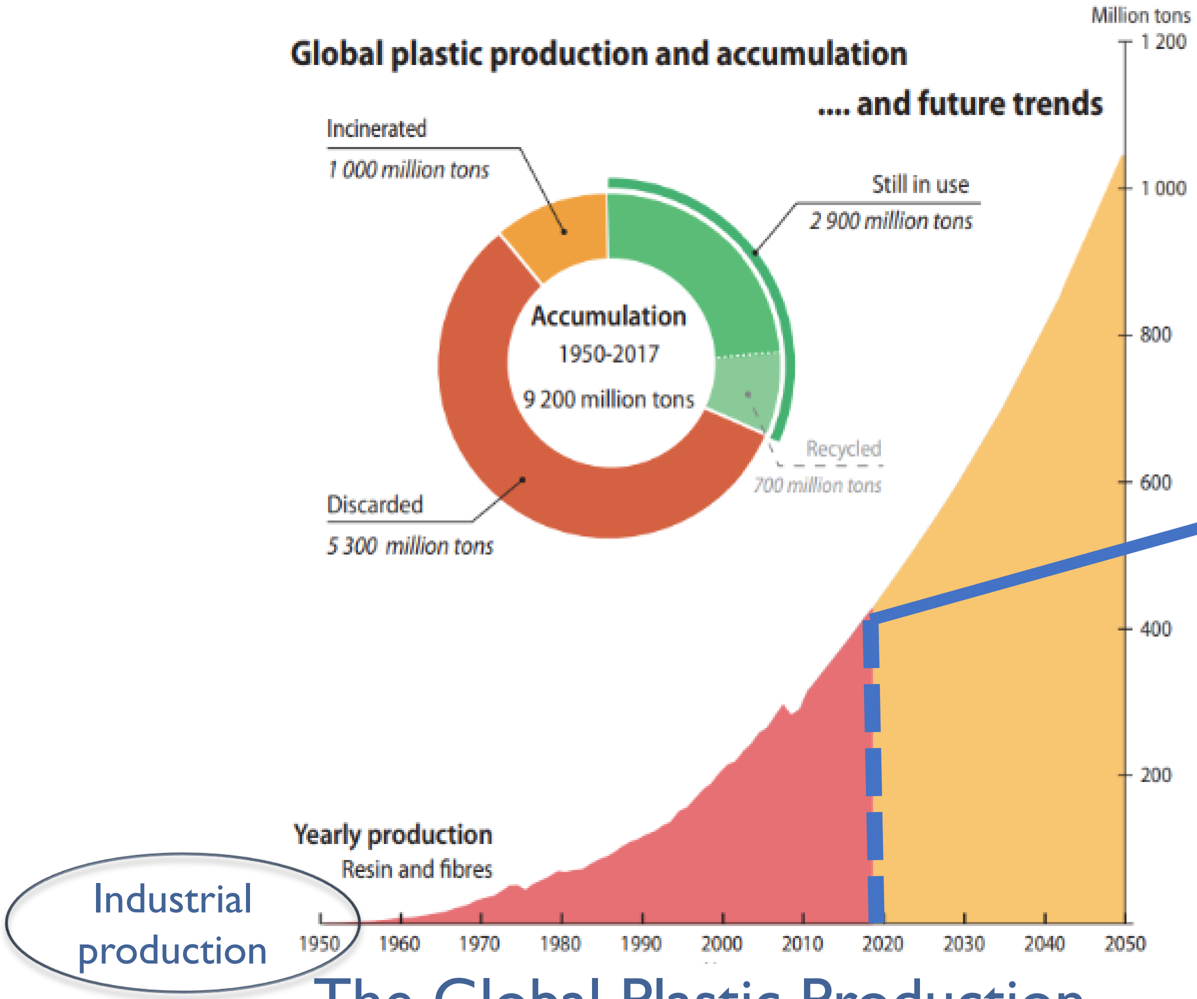
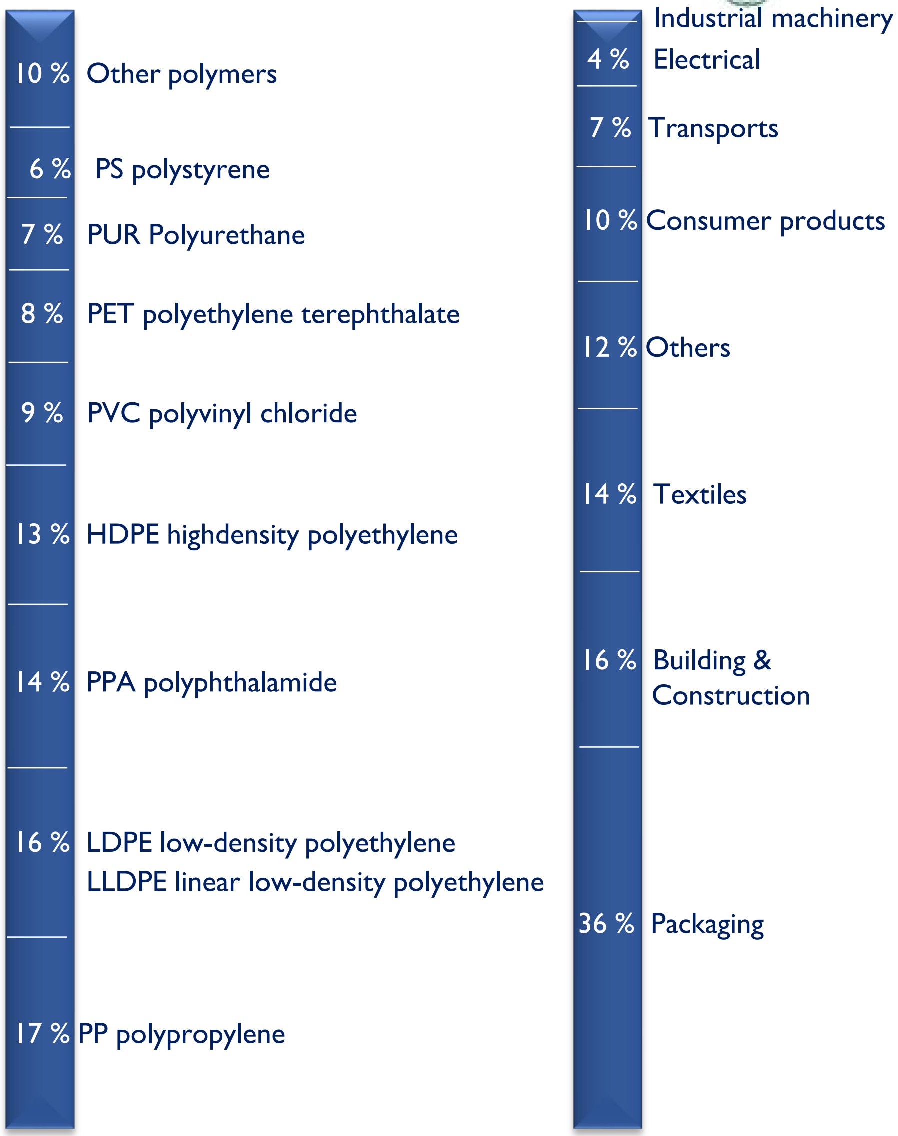


The Global Plastic Production



By polymer type

By sector

Sources: UNEP 2021, adpated from Jambeck et al. 2018, Plastics Europe 2019; Geyer 2020

Results – Area, Roundness & Total amount

Ultra-filtration Reclaimed water

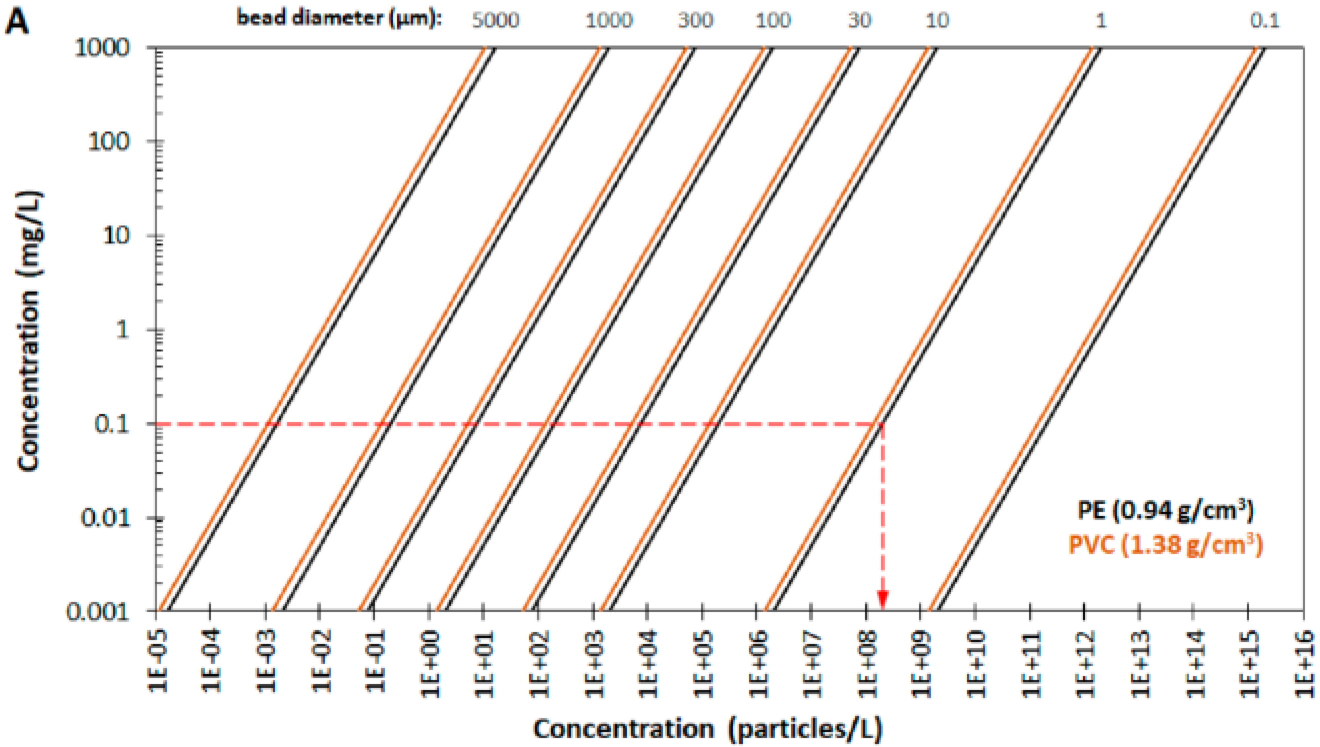
Total Flow = 30 L reclaimed water by triplicate

		Sample 1			Sample 2			Sample 3		
		Fibres	Fragments	Films	Fibres	Fragments	Films	Fibres	Fragments	Films
Average área (µm²)	29.09.23	4,51E+03	6,94E+03	-	6,48E+03	2,64E+04	-	1,33E+04	1,32E+04	-
	14.09.23	7,03E+03	1,94E+04	6,59E+04	5,05E+03	2,70E+04	2,07E+04	6,50E+03	2,82E+04	-
Roundness (µm)	29.09.23	<0,1	0,2	-	<0,1	0,1	-	<0,1	0,1	-
	14.09.23	0,1	0,2	<0,1	0,1	0,3	<0,1	0,1	0,2	-
Total amount (µm²/Litre)	29.09.23	**26.154**			**12.518**			**130.725**		
	14.09.23	**62.158**			**165.446**			**19.591**		
Concentration (mg/L - ppt)	29.09.23	**2,1E-03 (< 1 ppt)**			**2,0E-03 (< 1 ppt)**			**1,5E-02 (< 1 ppt)**		
	14.09.23	**1,9E-03 (< 1 ppt)**			**1,3E-02 (< 1 ppt)**			**1,1E-03 (< 1 ppt)**		

Environmental Science & Technology
pubs.acs.org/est Viewpoint

Converting mg/L to Particles/L: Reconciling the Occurrence and Toxicity Literature on Microplastics

Frederic D.L. Leusch* and Shima Ziajahromi

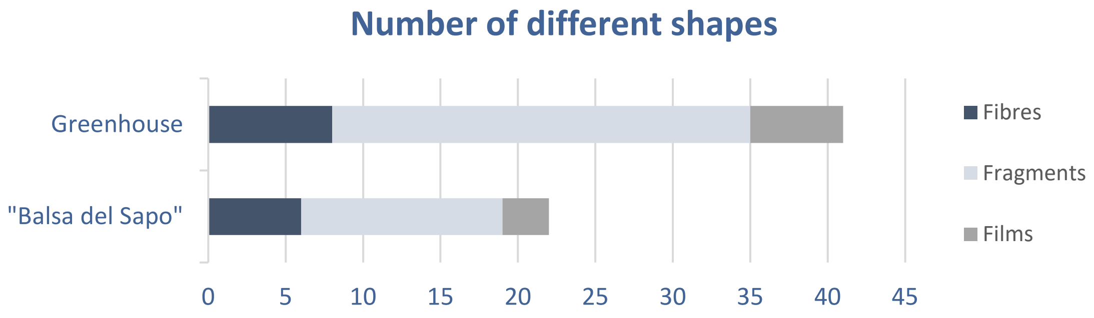


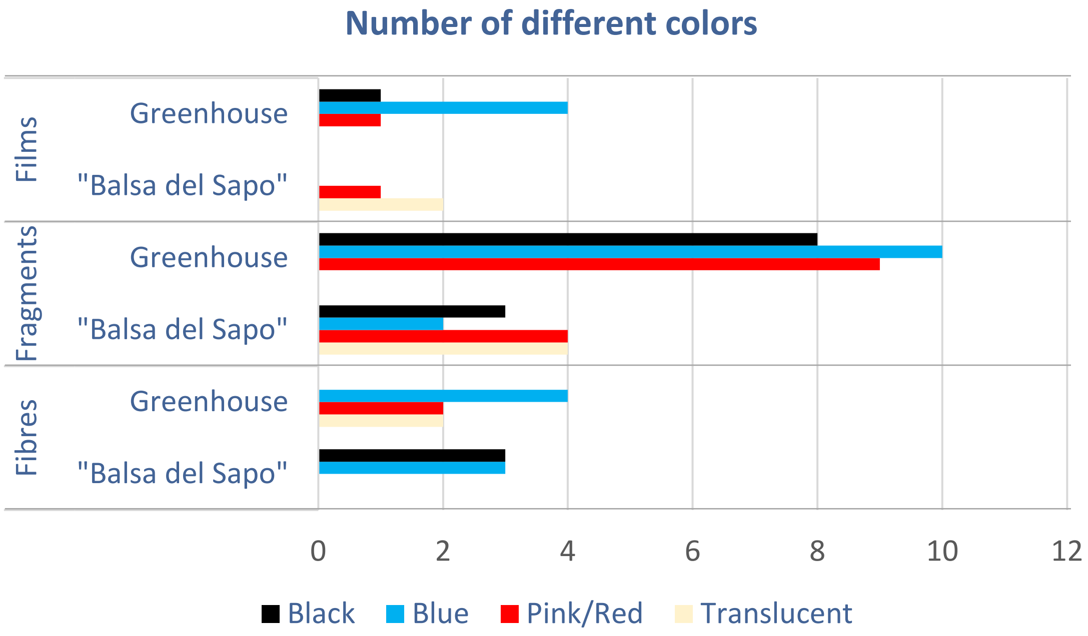
$$y\ (\text{mg/L}) = \frac{(\Pi / 6) \times \text{density (g/cm}^3) \times x\ (\text{particles/L}) \times [\text{diameter } (\mu\text{m})]^3}{10^9\ (\text{unit conversion factor})}$$

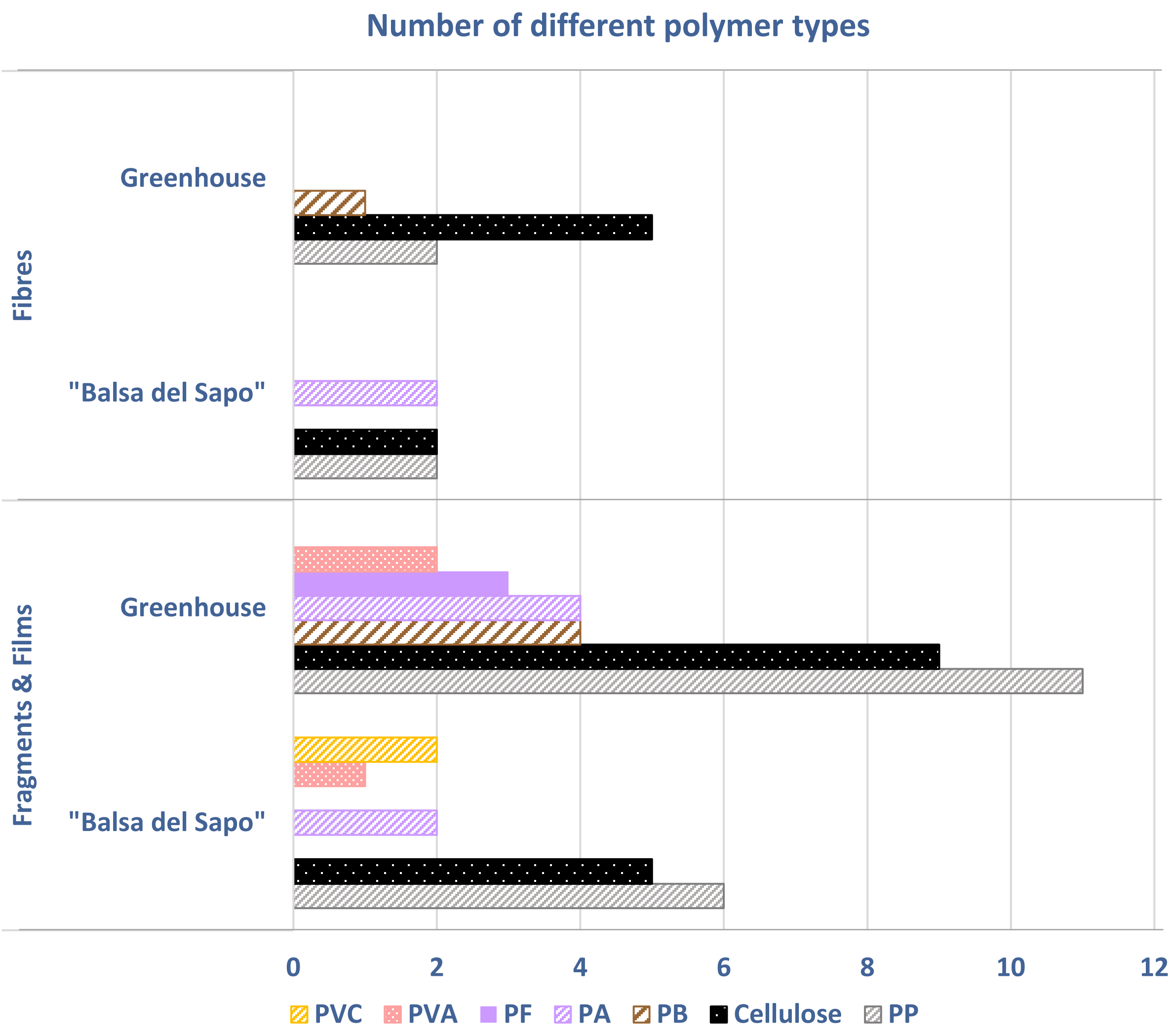

Total Flow = 900 L / 25 min


"Balsa del Sapo"

Results
DRONE SAMPLER for atmosphere (100 m)







PP: Polypropylene; PE: Polyethylene; PET: Polyester; PA: Polyamide; PVC: Polyvinyl chloride; PVA: Polyvinyl alcohol; PF: Phenolic polymer; PO: Polyvinyl chloride; PB: Polybutene;

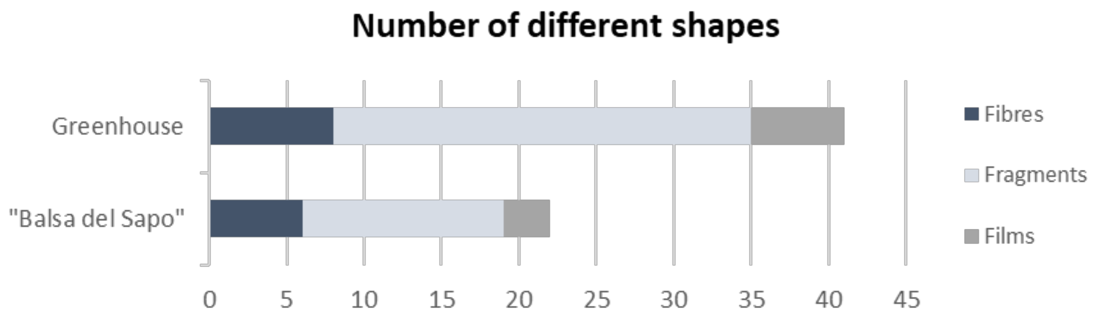
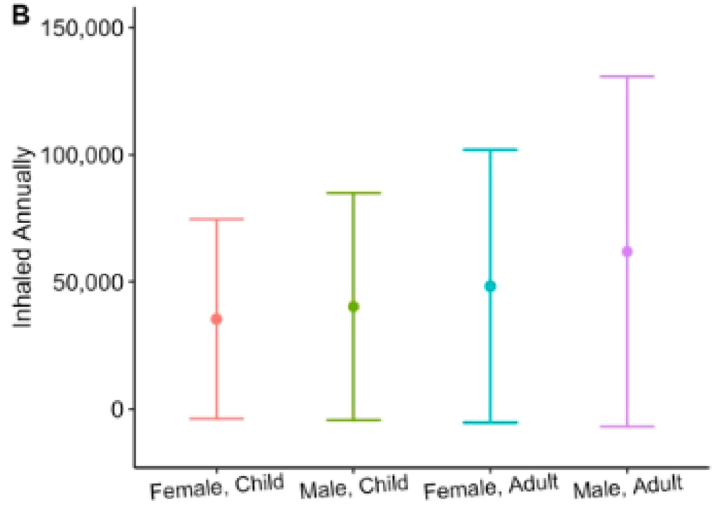


Table 1. Daily and Annual Consumption and Inhalation of Microplastic Particles for Female and Male, Children and Adults[a]

	Daily		Annual		Total	
	Consumed	Inhaled	Consumed	Inhaled	Daily	Annually
Male Children	113	110	41106 ± 7124	40225 ± 44730	223	81331
Male Adults	142	170	51814 ± 8172	61928 ± 68865	312	121664
Female Children	106	97	38722 ± 6977	35338 ± 39296	203	74060
Female Adults	126	132	46013 ± 7755	48270 ± 53676	258	98305



Environmental Science & Technology
Article
Cite This: Environ. Sci. Technol. 2019, 53, 7068−7074
pubs.acs.org/est

Human Consumption of Microplastics

Kieran D. Cox,[*,†,‡] Garth A. Covernton,[†] Hailey L. Davies,[†] John F. Dower,[†] Francis Juanes,[†] and Sarah E. Dudas[†,‡,§]

Results
DRONE SAMPLER for atmosphere (100 m)

"Balsa del Sapo"

Total Flow = 900 L / 25 min

Greenhouse

Total Flow = 900 L / 25 min

	Balsa del Sapo: Fibres	Balsa del Sapo: Fragments	Balsa del Sapo: Films	Greenhouse: Fibres	Greenhouse: Fragments	Greenhouse: Films
Average área (μm^2)	**4,76E+03**	**2,42E+03**	**2,45E+04**	**5,29E+03**	**2,73E+03**	**3,90E+03**
Roundness (μm)	0,2	0,4	<0,1	0,1	0,5	0,1
Total amount ($\mu m^2/m^3$)	**1,5E+05 (2,4E+04)**			**1,6E+05 (4,5E+04)**		

Total amount of MPs ($\mu m^2/m^3$)

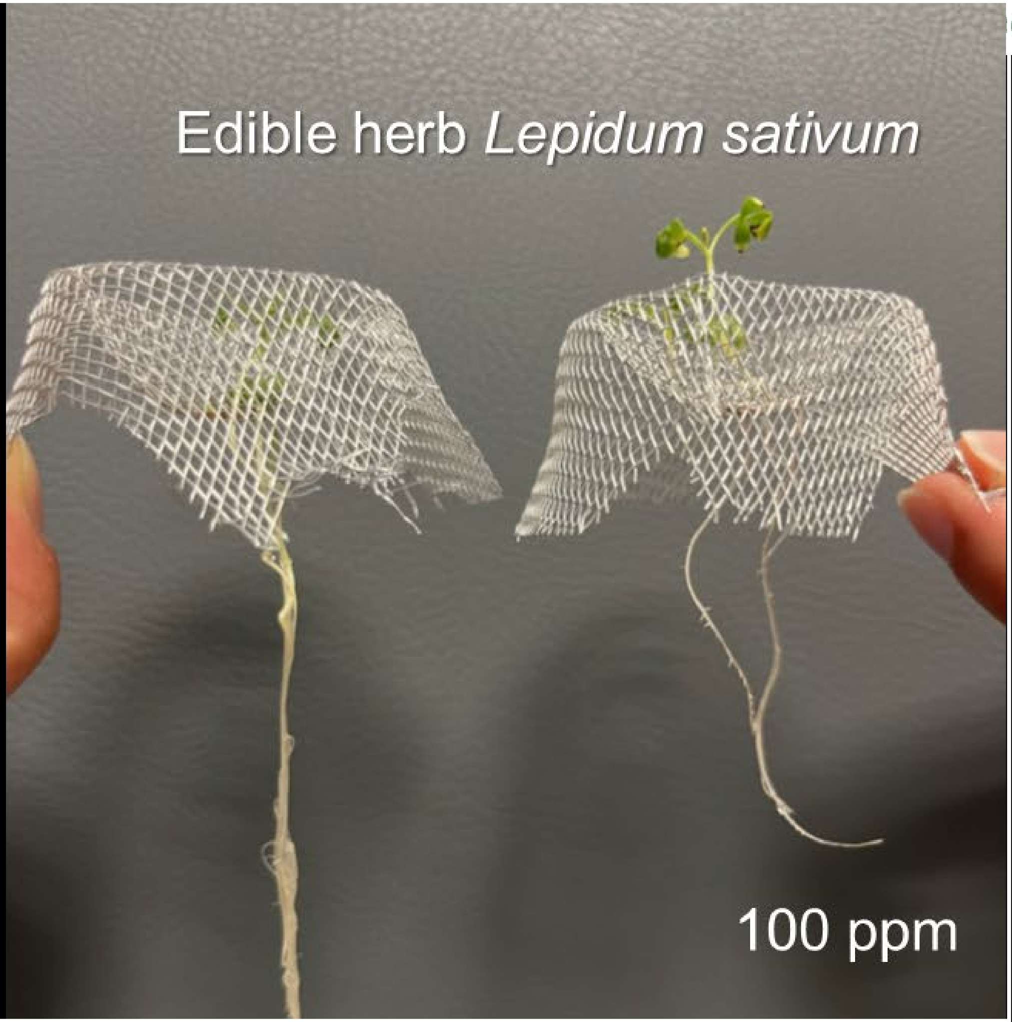
Σ=1,5E+05

Σ=1,7E+05

Σ=1,6E+05

Σ=1,7E+05

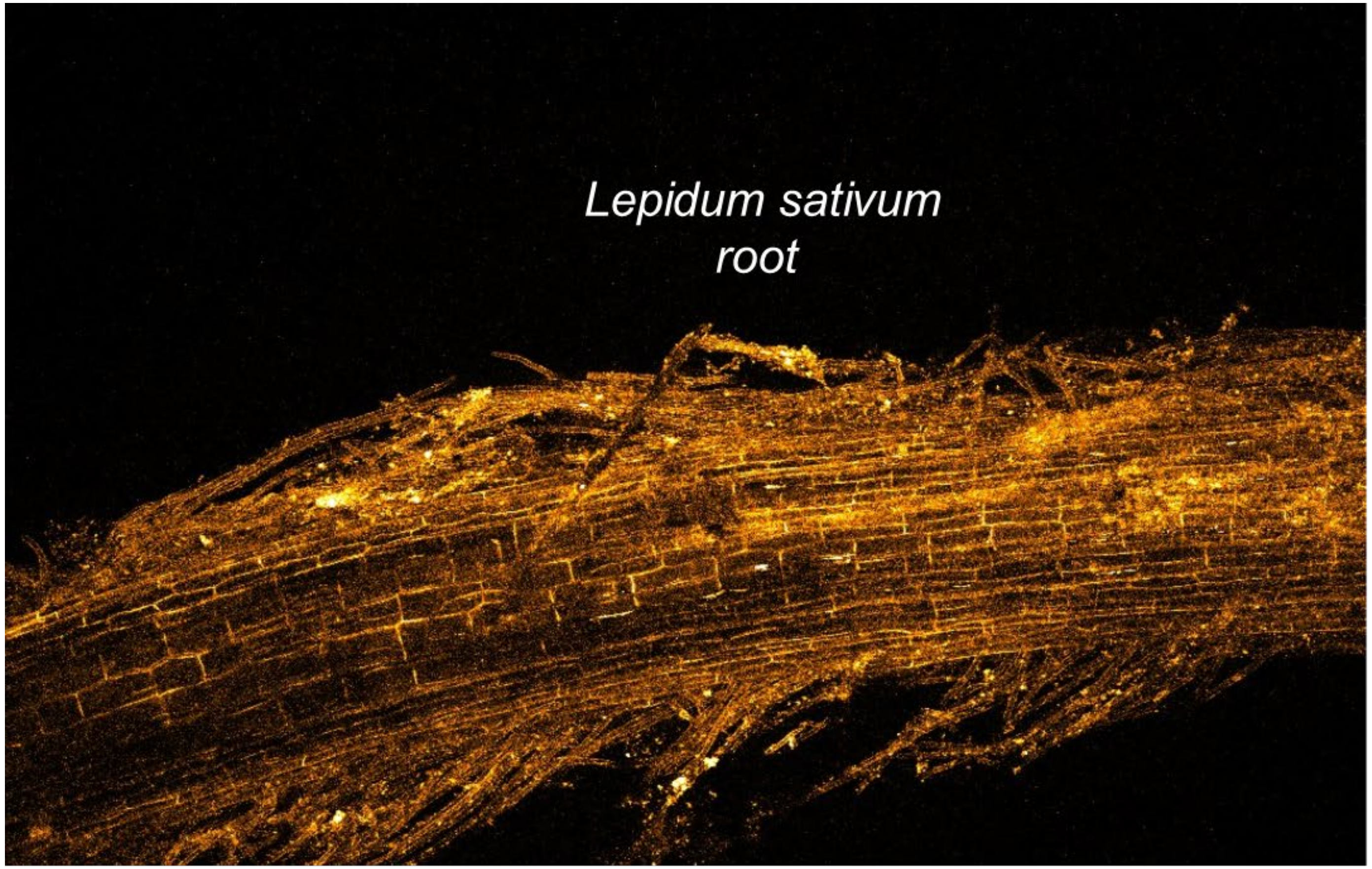
STUDY OF THE EFFECTS

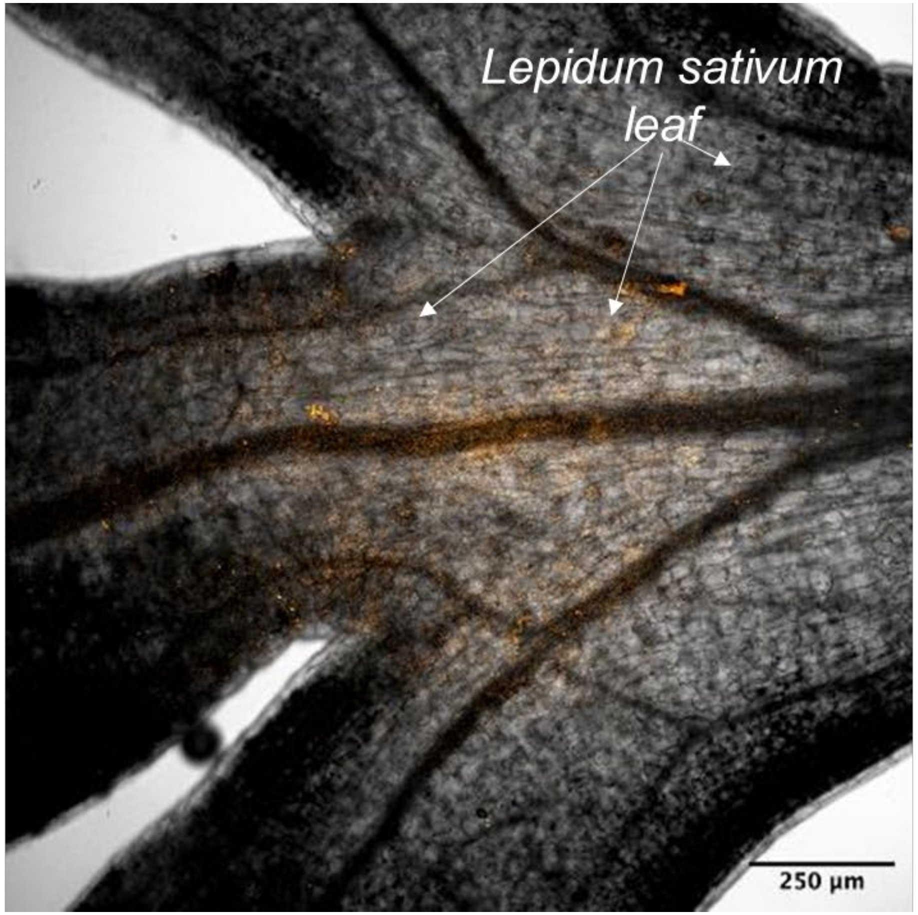


Uptake of PS Nanoplastics by plants

Uptake of PS nanoplastics by plants

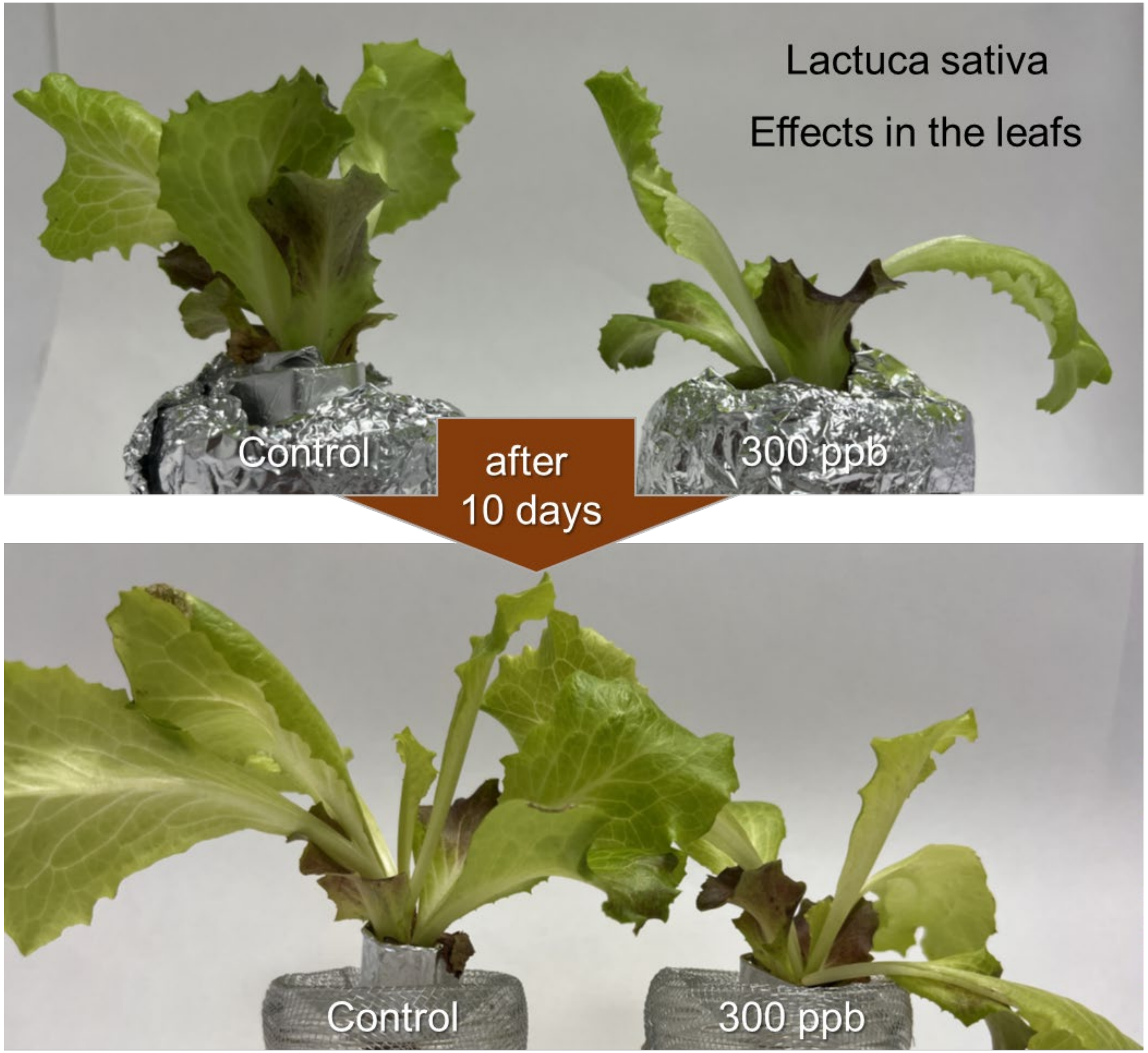
Confocal fluorescence microscopy





Uptake of PS nanoplastics by plants

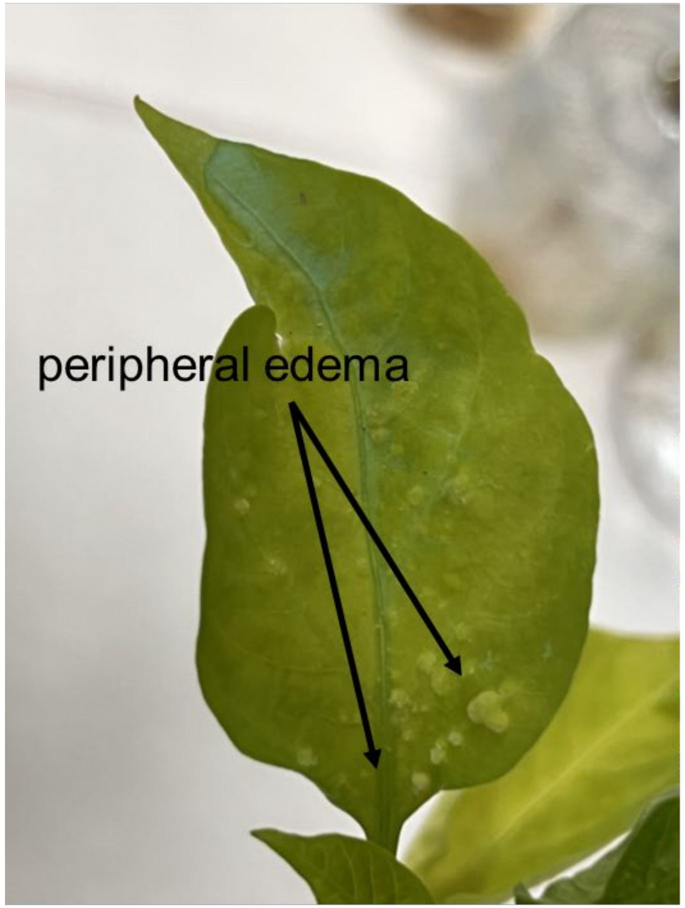
Exposure:
polystyrene nanospheres
particle size 100 nm

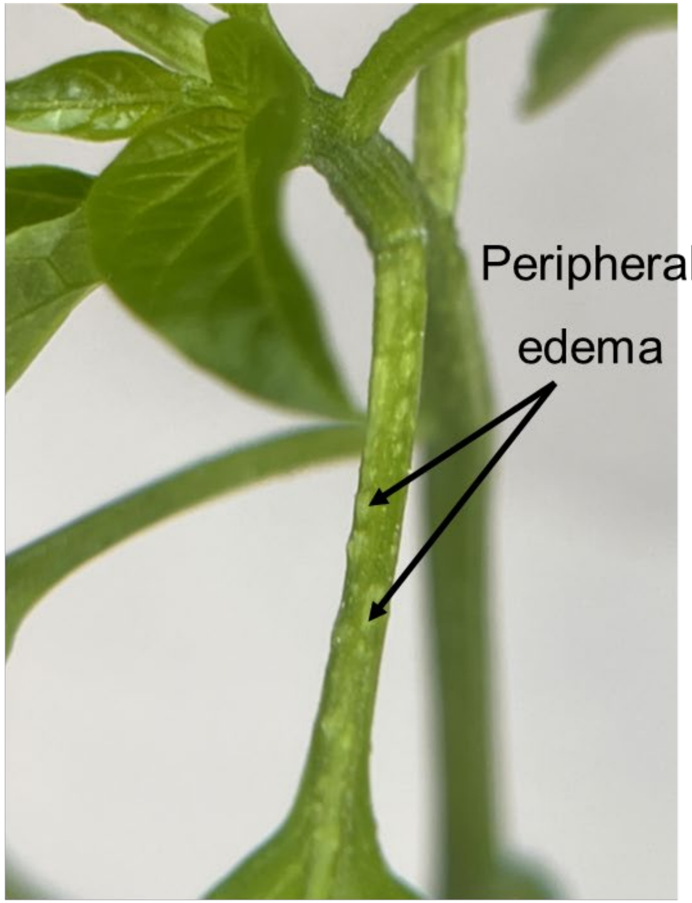


Uptake of PS nanoplastics by plants

15 days exposure

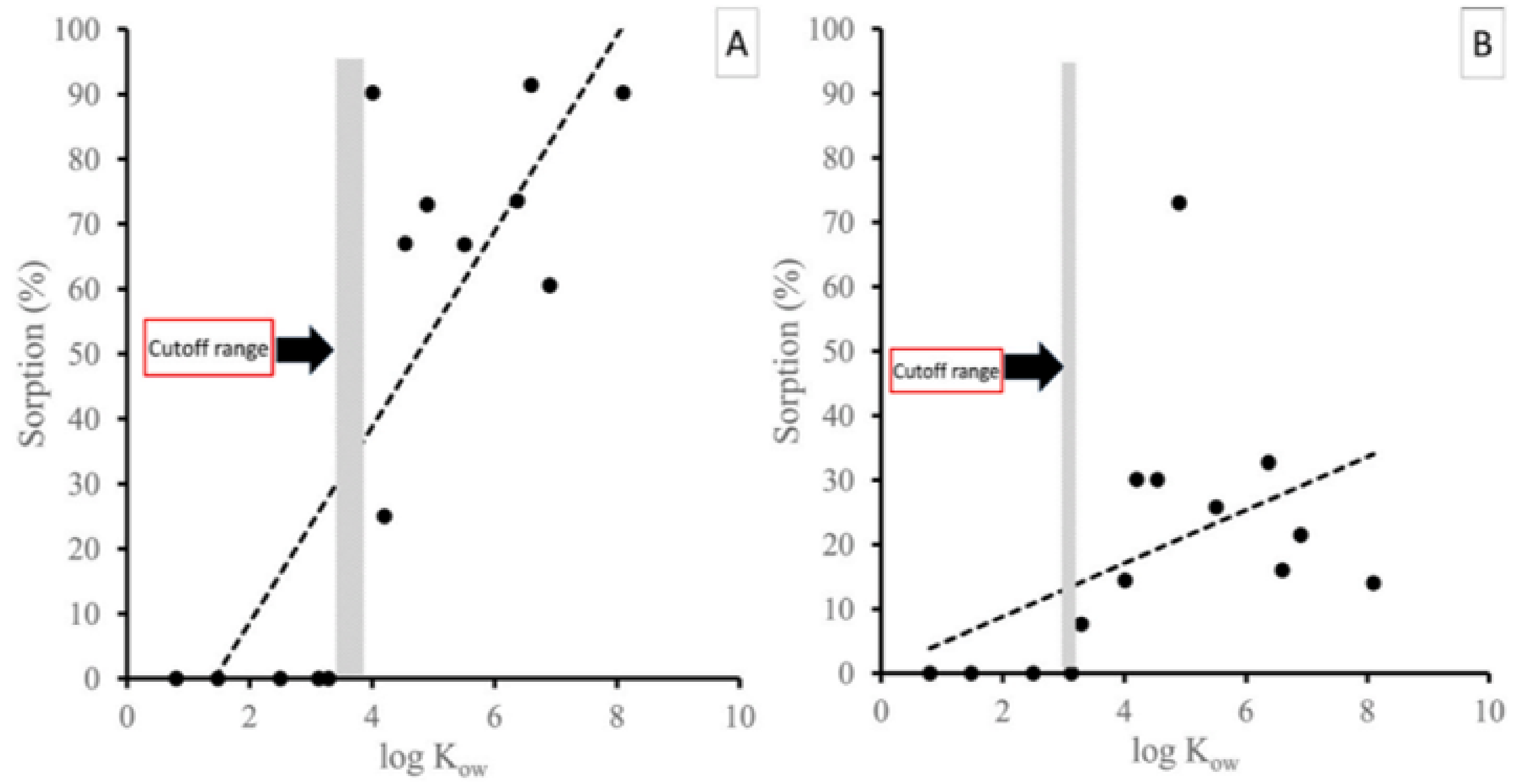
Capsicum annuum



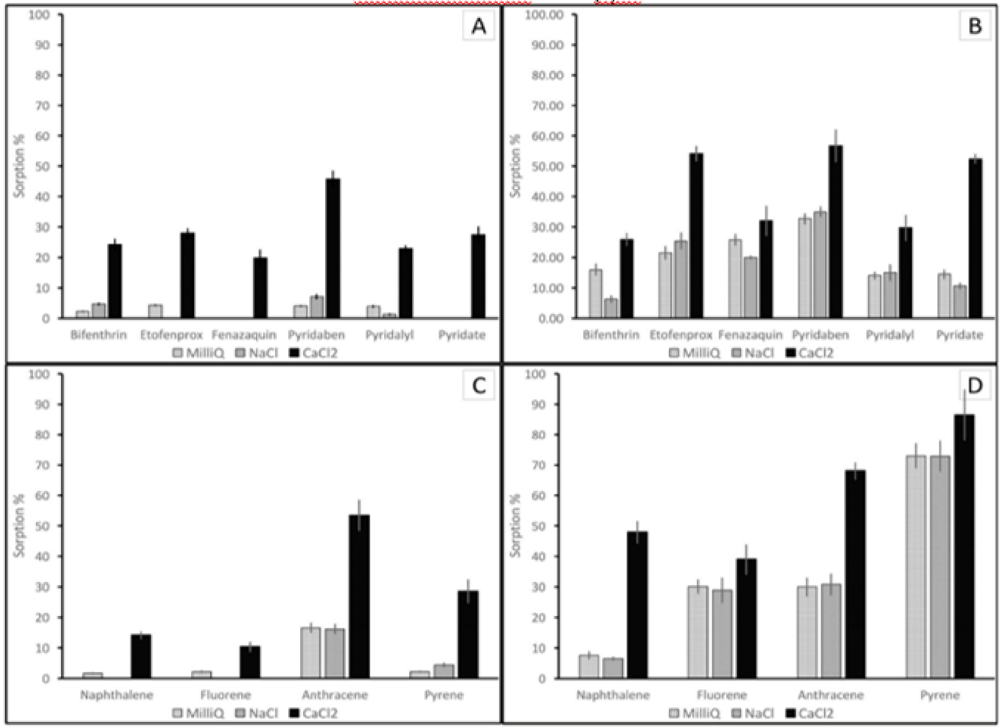


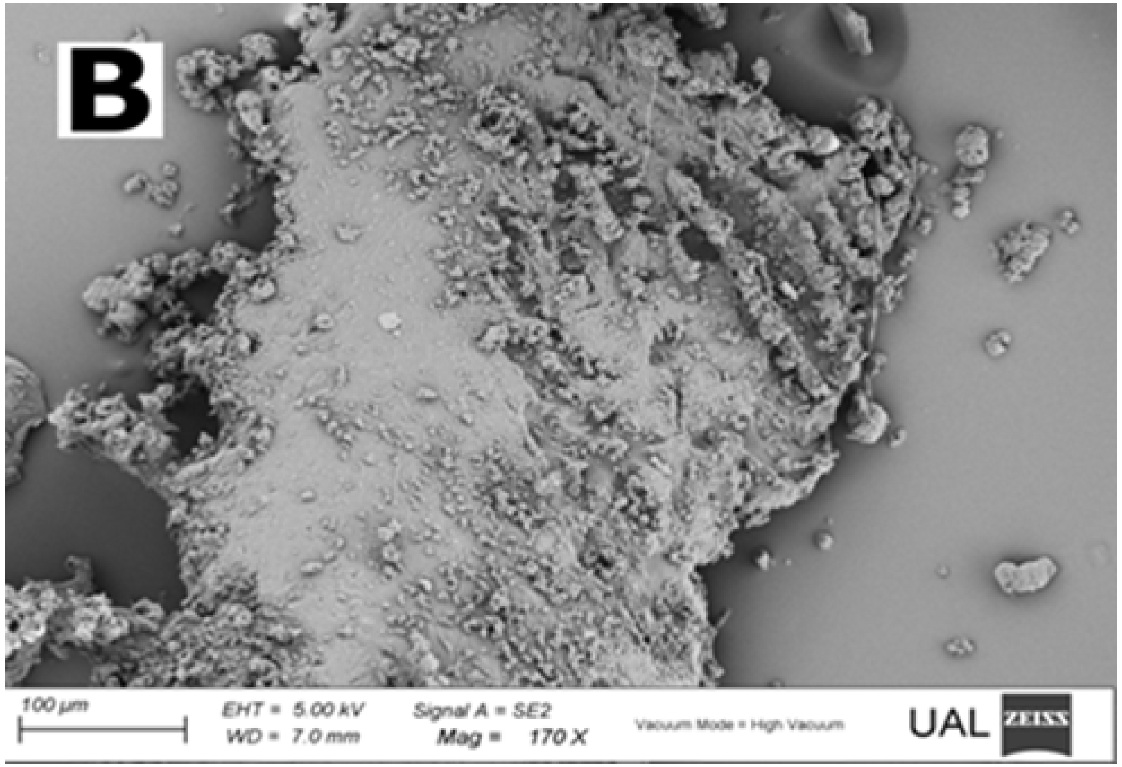
Exposure: polystyrene nanospheres
particle sizes: 200 nm - 500 nm
concentrations: 300 ppb – 50 ppm

Log Kow versus sorption (%) in PE (comercial mulch film)
(A) Pesticides (5 µg/L) and (B) PAHs (20 µg/L) in distilled water



Sorption of pesticides and PAHs in PE (pure) and PE (comercial mulch film)
Effect of ionic strengh (i) distilled water (ii) NaCl (iii) $CaCl_2$
Concentration 200 ppb

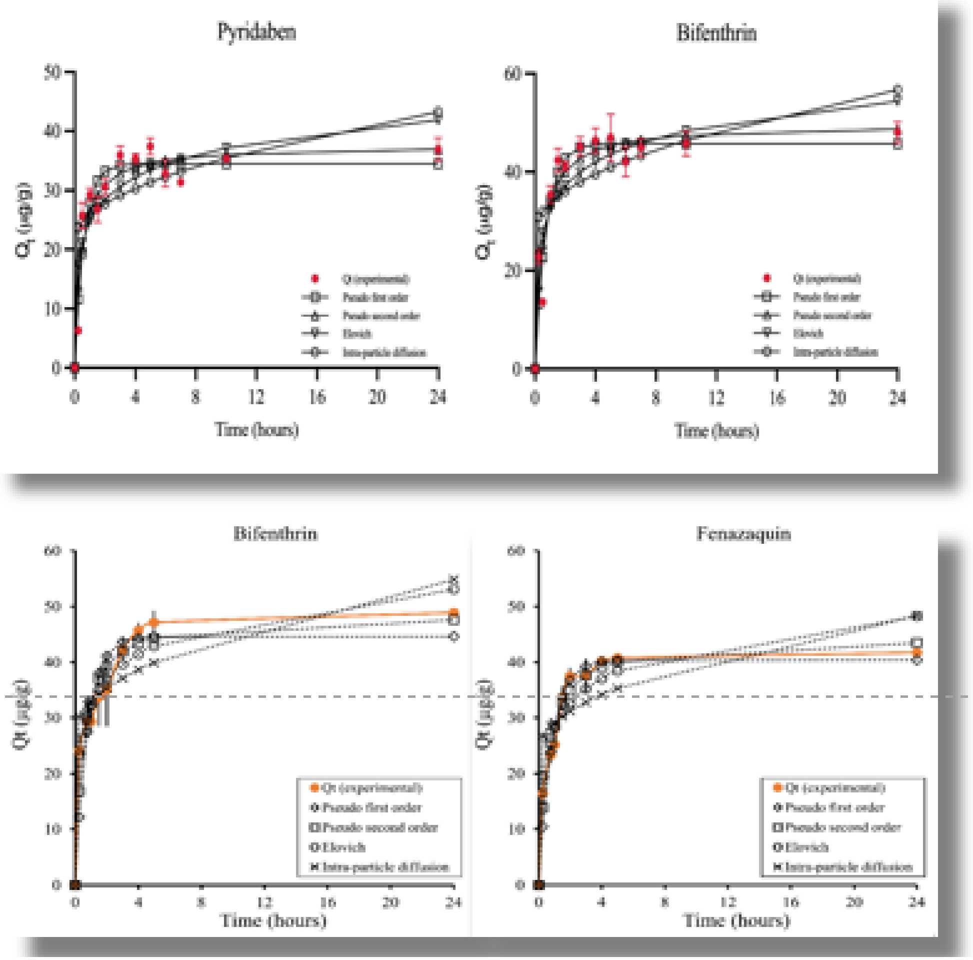




Sorption in conventional and biodegradable MPs

Conventional

Biodegradable

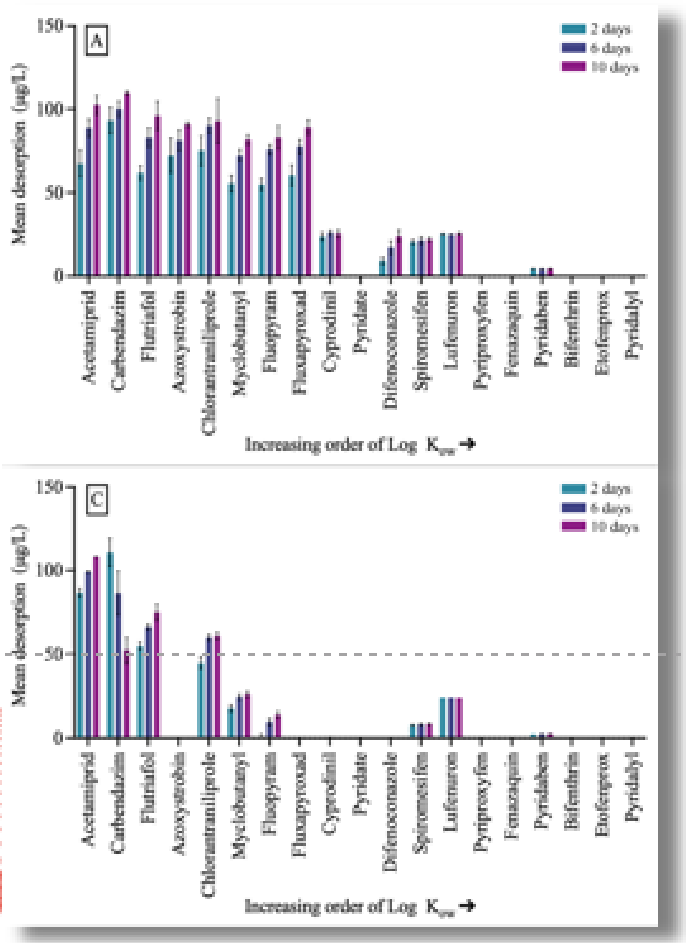


- Modelling the process of sorption
- Mechanism behind the sorption process: physisorption or chemisorption
- Differences between pure microspheres and mulch film MPs
- Differences between conventional and biodegradable microplastics
- Factors that influence the process

Desorption and Retention in Conventional Plastic Mulch Films vs Biodegradable Mulch Films

Conventional

Biodegradable



- Comparison between both plastic types.
- Higher sorption and retention in biodegradable plastic type
- Effect of log Kow
- Effect of temperature over desorption

Publications

ELSEVIER
Chemosphere
Volume 333, August 2023, 138959

Exploring sorption of pesticides and PAHs in microplastics derived from plastic mulch films used in modern agriculture

Harshit Sahai [a b c], Mar García Valverde [b], María Murcia Morales [b], María Dolores Hernando [a], Ana M. Aguilera del Real [b], A.R. Fernández- Alba [b]

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CONCLUSIONS

- -Agricultural use of regenerated water
- -Chemicals present, crop uptake, and risk associated
- -Soil contamination
- -Presence of MPs. Standarization?
- -Effect of MPS in cops
- -Are MPs a Troy Horse?

Acknowledgments

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