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OSLO

On the environmental fate of two endocrine disrupting chemicals in agricultural soils using wastewater for irrigation

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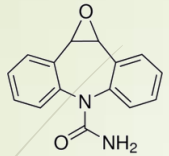
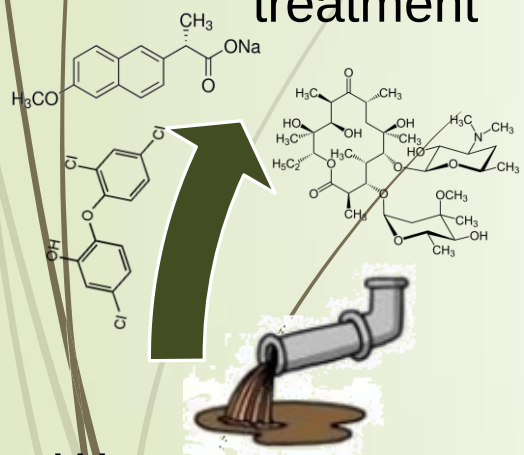
Wastewater is the main entrance of emerging pollutants into environment

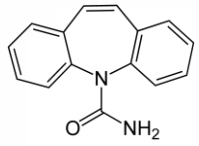
Wastewater treatment



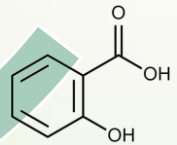
Water source

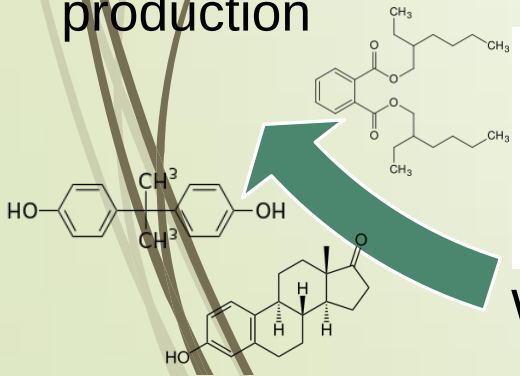


Wastewater production



Drinking water treatment





Water use

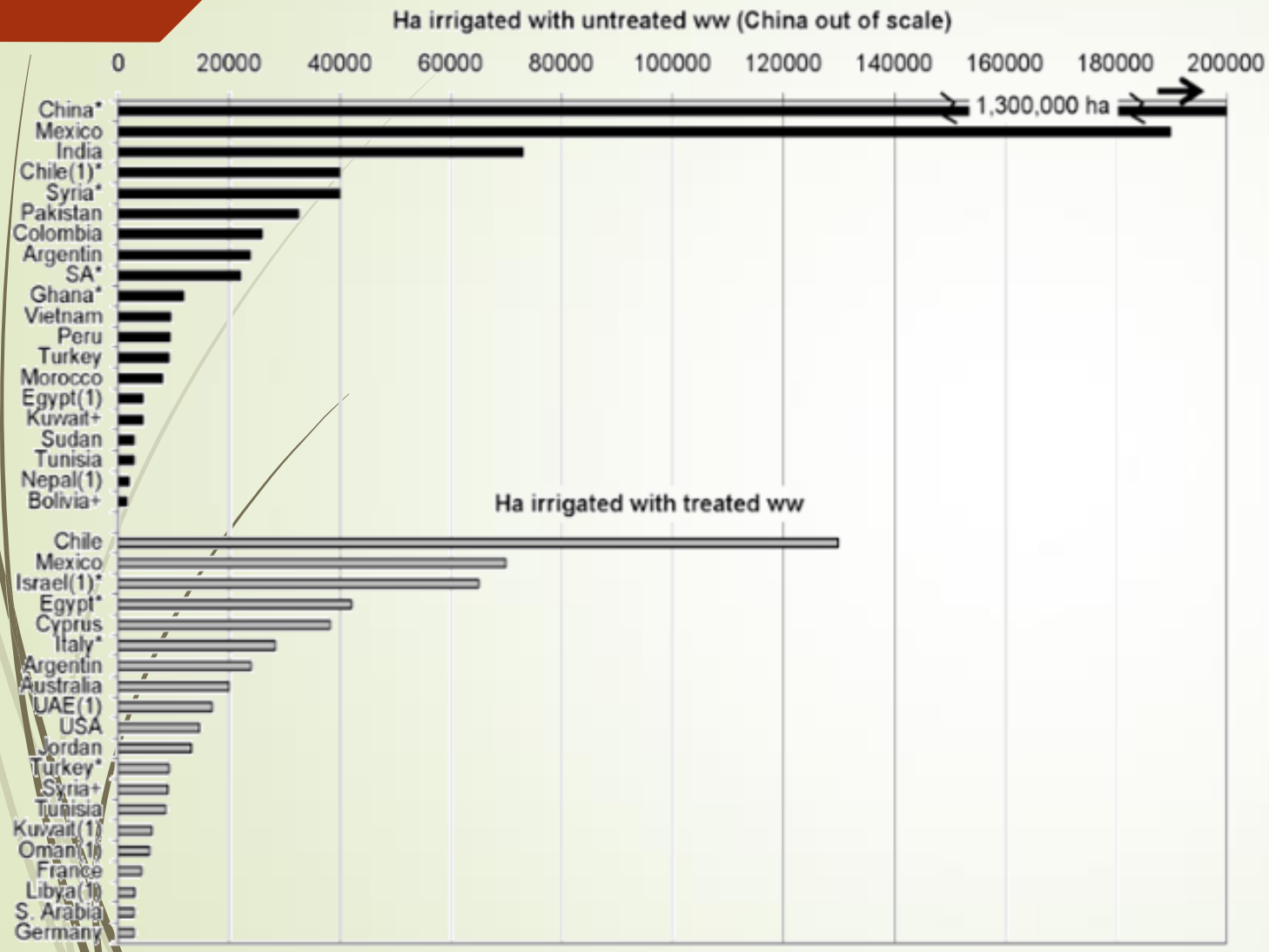
Emerging pollutants

Pharmaceuticals
- Analgesics
- Antibiotics
- Psychiatric drugs
- Antihypertensives
- Hormones

Personal care products
- Fragrances
- Sunscreens
- Disinfectants

Industrial
- Surfactants
- Flame retardants
- Plasticizers
- Additives

Soil receives emerging pollutants during irrigation



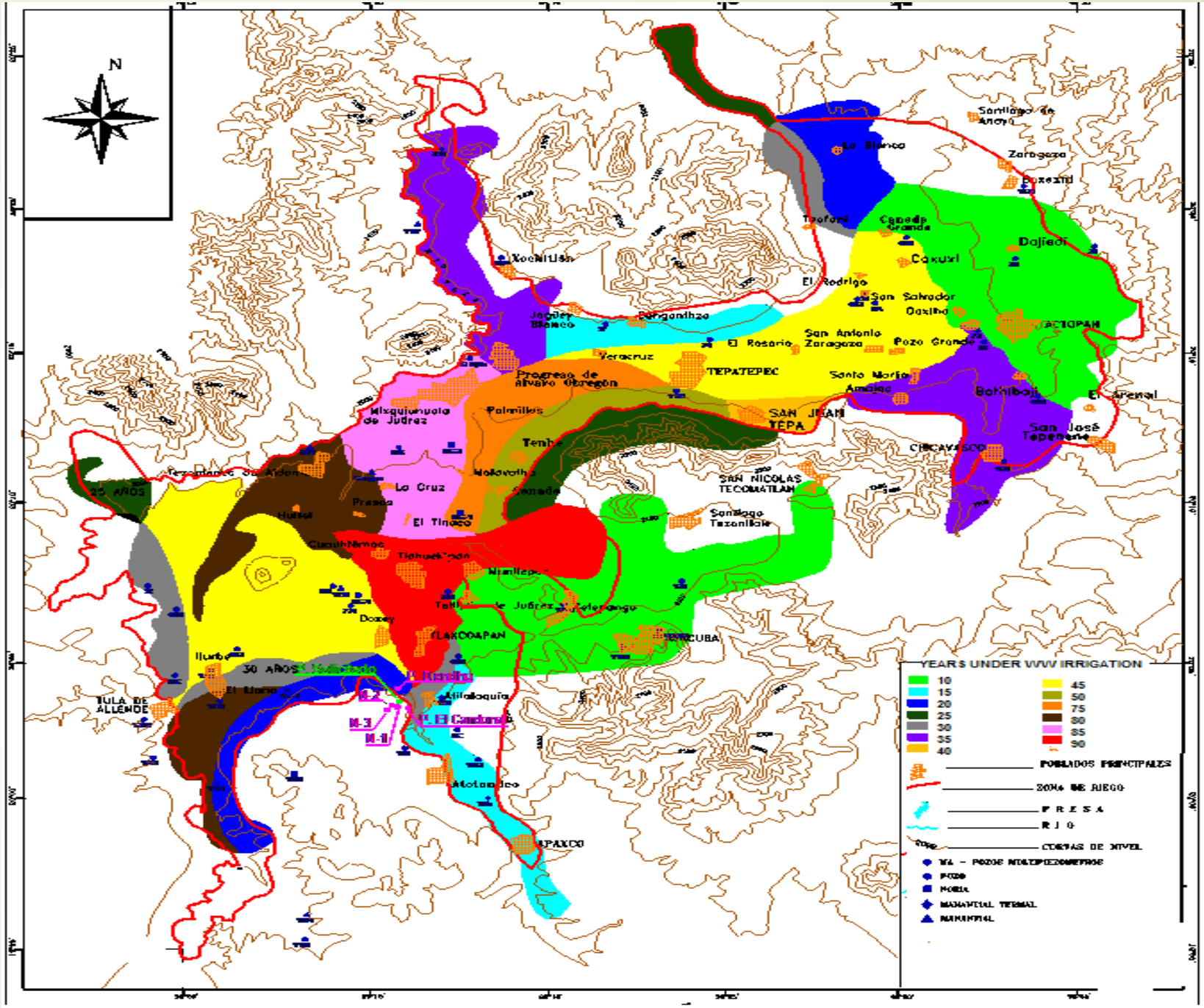
Reuse of untreated wastewater in agricultural irrigation worldwide (Jimenez and Asano, 2008)

Case study in Mexico

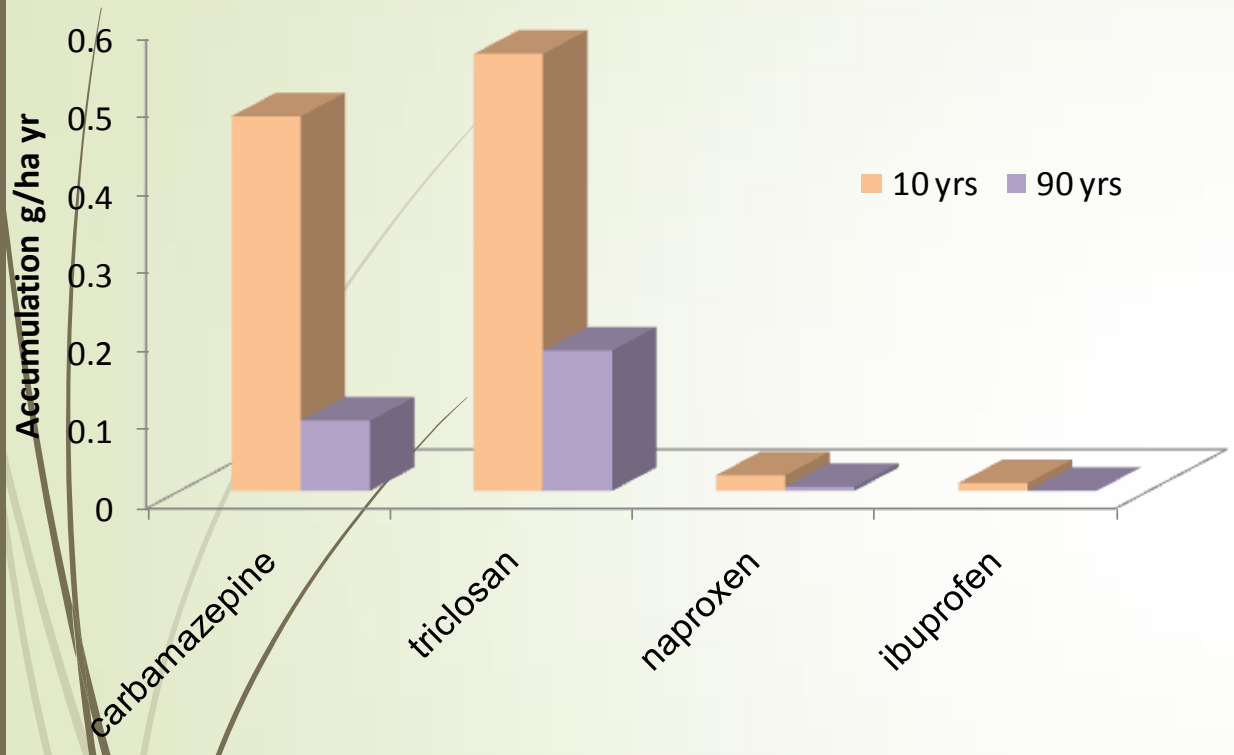
- Wastewater from Mexico City (75 m^3/s) is sent to Tula Valley 80 km north Mexico City.
- 90,000 ha of croplands are irrigated using untreated wastewater.
- Infiltration of wastewater through the soil.
- Non-intentional recharge of aquifer
- Wastewater purification by infiltration results in drinkable water.

Sites with different time under irrigation

- Irrigation using untreated wastewater started in 1914.
- Irrigated area gradually increased
- Accumulation of heavy metals in soil



Occurrence of emerging pollutants in Tula Valley



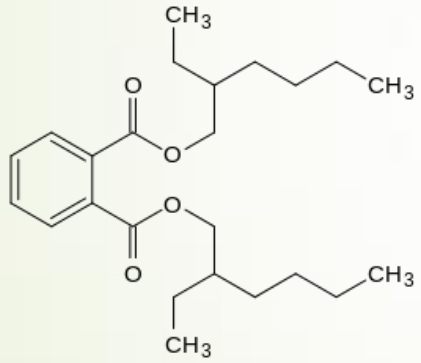
Analyte	LOD (ng/g)	Phaeozem	Leptosol
Clofibric acid	2.0	<LOD	<LOD
Ibuprofen	0.1	0.25 ± 0.04	<LOD
2,4-D	2.0	<LOD	<LOD
Gemfibrozil	2.0	<LOD	<LOD
Naproxen	0.2	0.55 ± 0.01	0.73 ± 0.20
Ketoprofen	1.0	<LOD	<LOD
Diclofenac	1.0	<LOD	<LOD
Carbamazepine	0.5	6.48 ± 0.59	5.14 ± 0.48
4-Nonylphenols	25	41 ± 6	123 ± 9
Triclosan	1.0	4.4 ± 0.1	18.6 ± 1.2
Bisphenol-A	2.0	<LOD	14.8 ± 3.2
Di-*n*-BuP	25	244 ± 43	552 ± 57
BuBeP	25	131 ± 23	346 ± 50
DEHP	25	820 ± 87	2079 ± 201
Estrone	1.0	<LOD	<LOD
17β-Estradiol	1.0	<LOD	<LOD
EE2	2.5	<LOD	<LOD

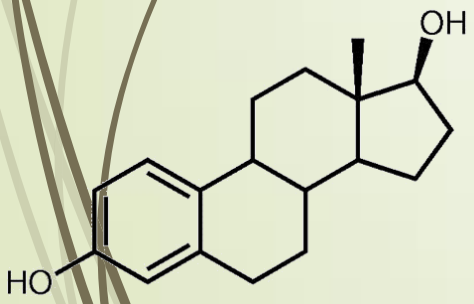
- Soil accumulates organic matter provided by wastewater.
- Comparison between two ages under irrigation.
- Greater accumulation in soils with 10 years under irrigation.
- Possible increased biodegradation in soils with 90 years under irrigation.

Aim

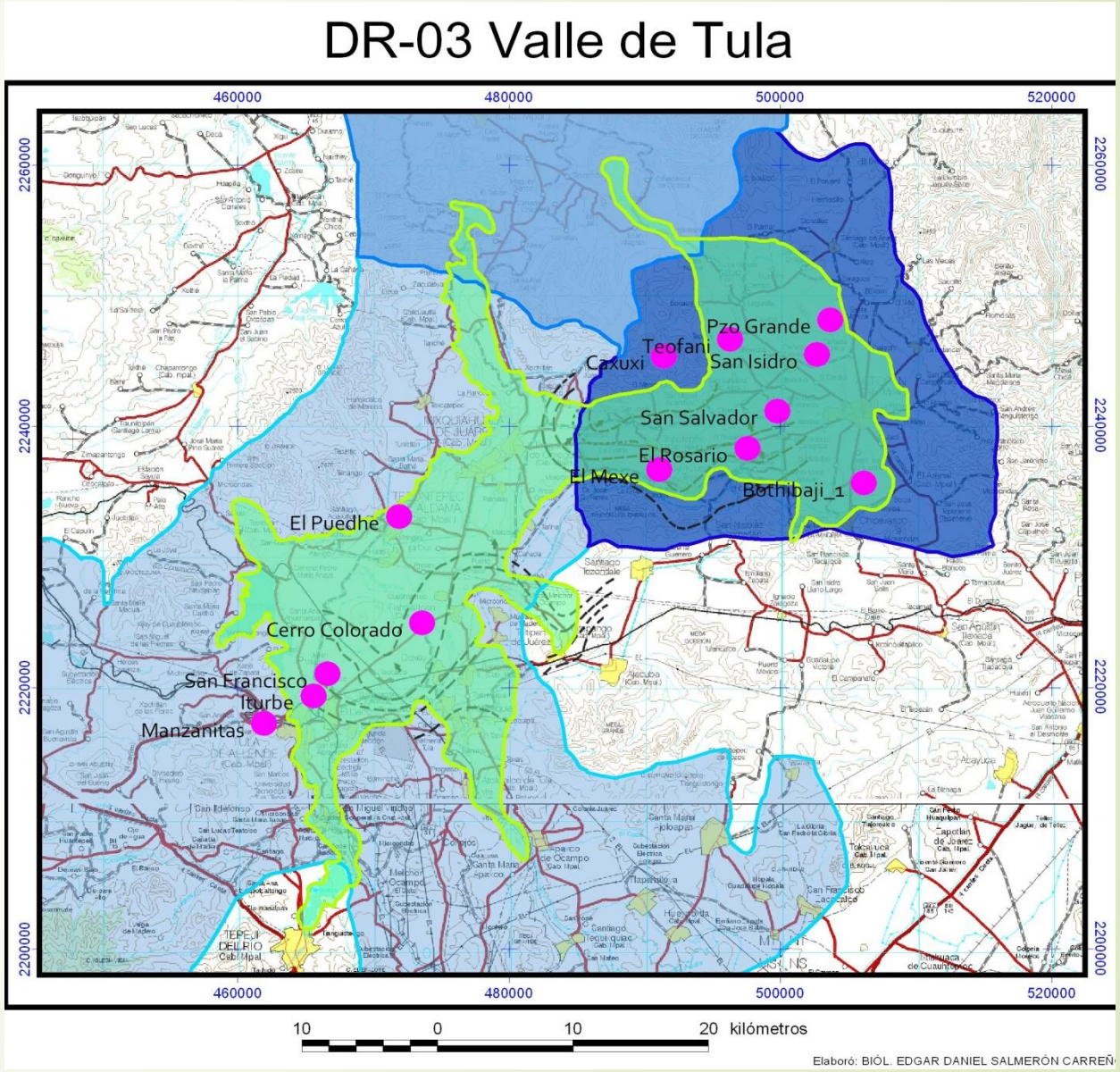
To asses the impact of long term wastewater irrigation on the biodegradation and mobility of two emerging pollutants in wastewater irrigated soils.

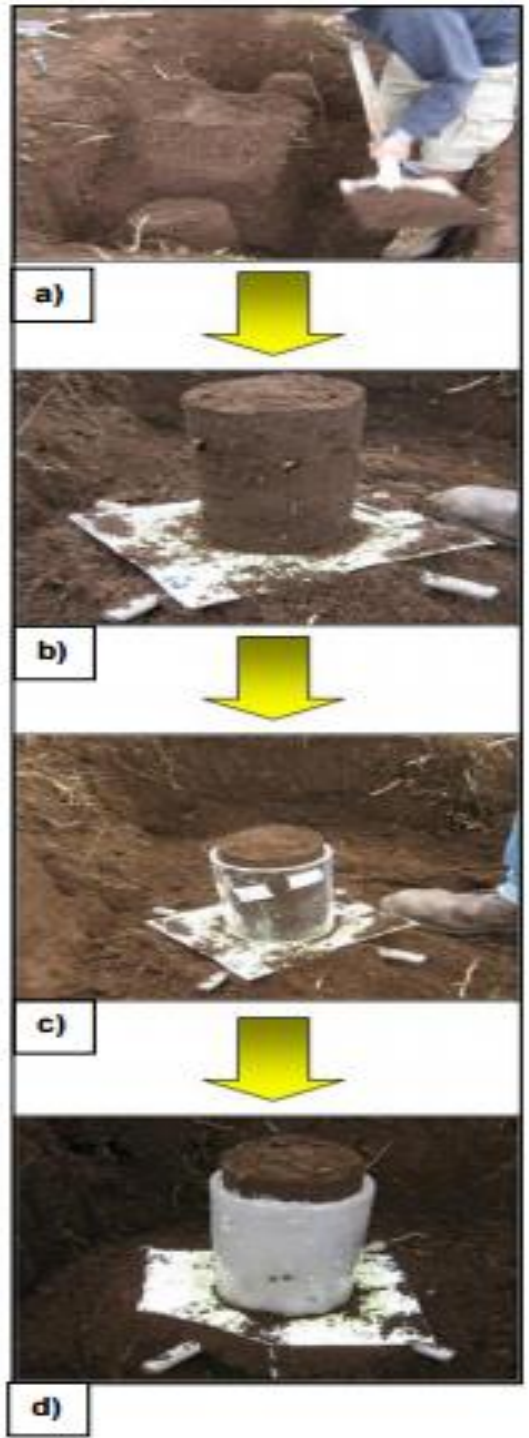
Bis ethyl hexyl phthalate (DEHP)





17β Estradiol





Soil sampling: 0, 35, 65 and 100 years under irrigation

Superficial soil was taken for batch biodegradation tests

Superficial layer above soil removed

500 g of soil samples taken in glass bottles

Soil preservation at -20°C until experiments

Dynamic sorption-desorption processes were assessed in undisturbed soil columns experiments

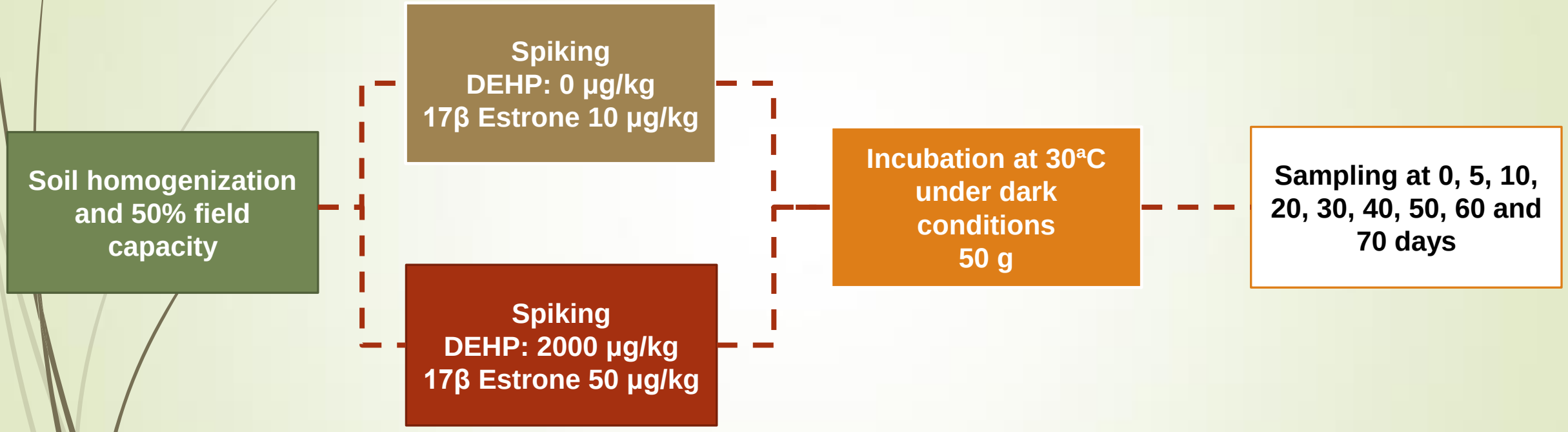
Soil characterization

Age (years)	pH	Conductivity (mS/cm)	Total organic carbon (%)	Clay Content (%)	Slit cntent (%)	Sand Content (%)	Hydraulic conductivity (cm/h)
0	7.23	4.7	**2.8 ± 0.6**	40	46.3	13.7	1.3
35	6.82	5.	**3.49 ± 0.4**	35.7	50.9	13.4	1.3
65	7.25	5.4	**4.25 ± 0.2**	40	47.9	12.1	1.0
100	6.76	4.8	**6.3 ± 1.1**	32	48.9	19.1	1.2

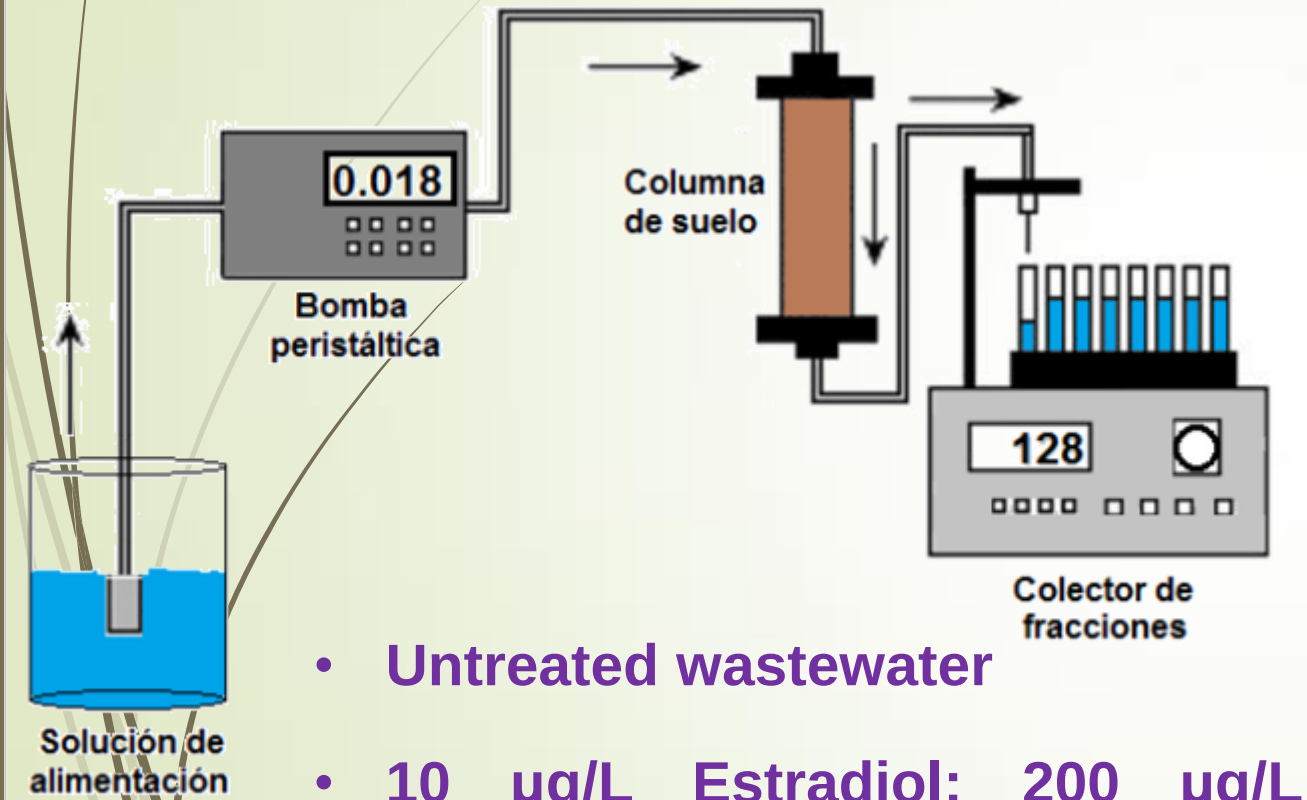
Soil	DEHP (µg/kg)	17β Estradiol (µg/kg)
0 years	215 ± 69	<LDD
35 years	1048 ± 111	2.5 ± 0.8
65 years	1025 ± 85	< LDD
100 years	829 ± 129	1.8 ± 1

Residual concentrations of target compounds were found in soil samples

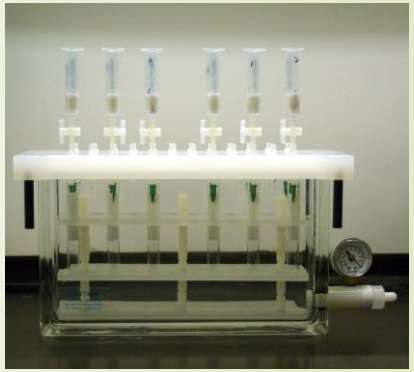
Biodegradation batch tests

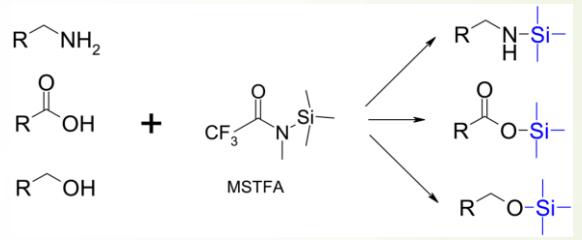


Dynamic sorption-desorption tests



- Untreated wastewater
- 10 µg/L Estradiol; 200 µg/L DEHP
- Steady state flow conditions





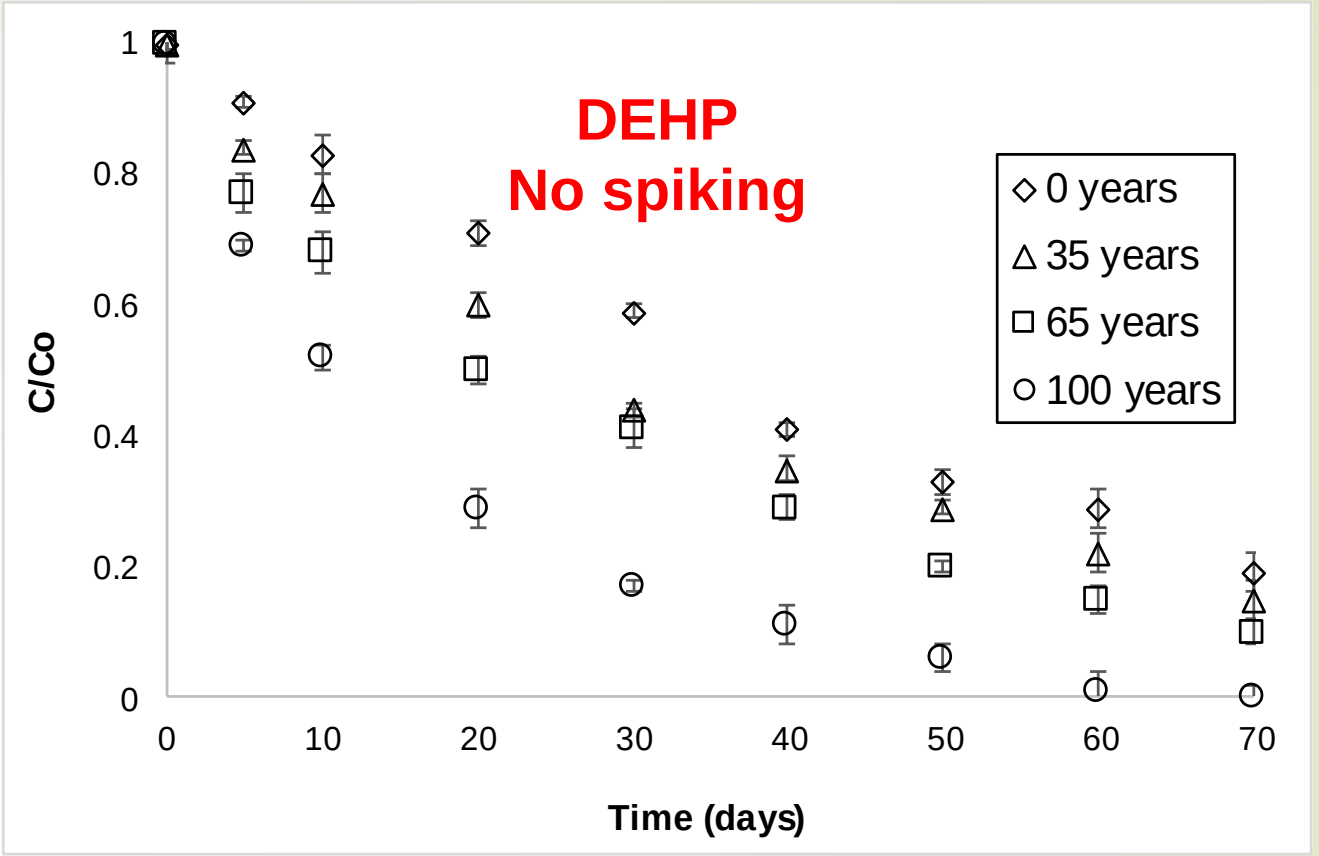
Instrumental analysis

Extraction efficiency in aging experiments

Aging (days)	DEHP Spiked 2000 µg/kg)	17β Estradiol Spiked 50 µg/kg)
0	102 ± 2	89 ± 2
20	104 ± 2	87 ± 2
40	100 ± 1	90 ± 1
60	99 ± 3	88 ± 3
80	97 ± 3	87 ± 3
100	93 ± 3	84 ± 3

Biodegradation rates

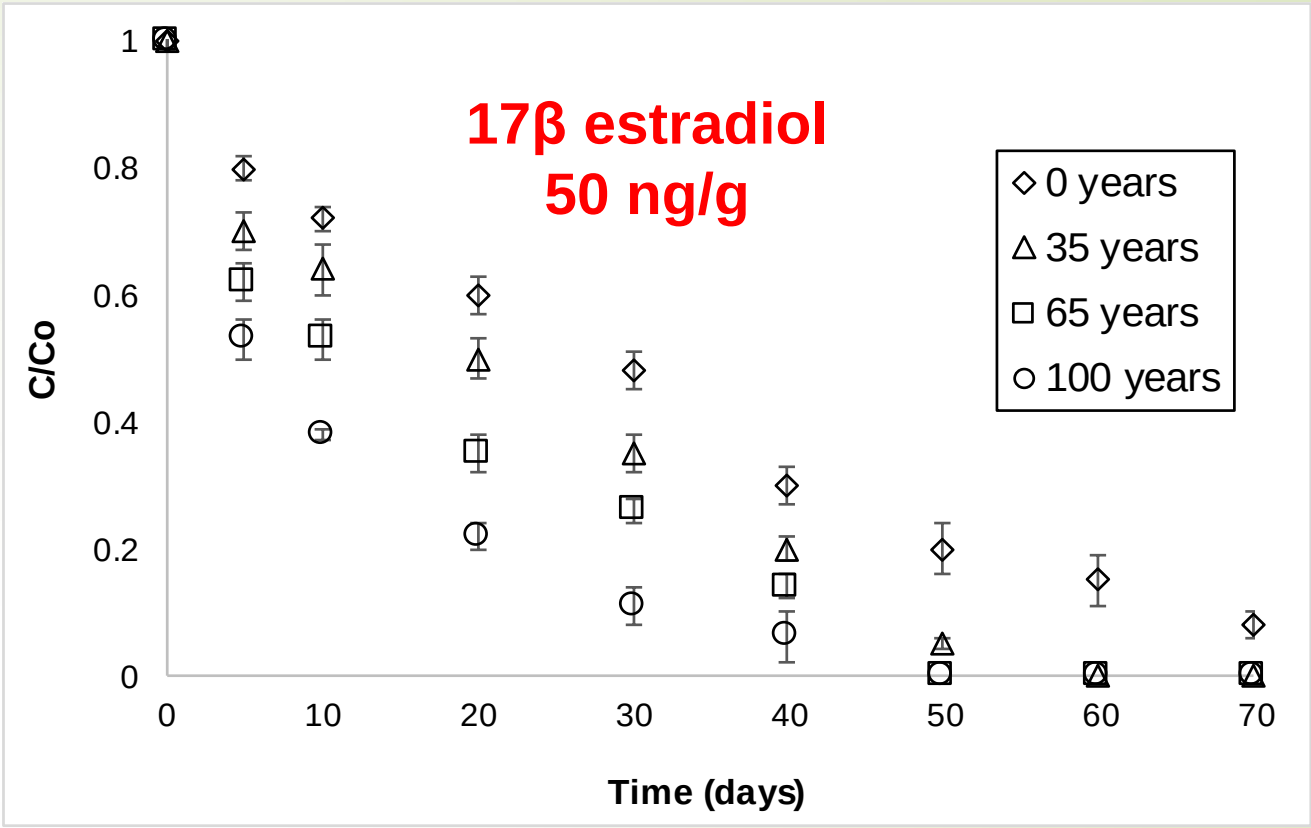
- Higher biodegradation of DEHP as increased time under irrigation.
- Increased initial concentration had no effect biodegradation rate.



Years under irrigation	*k* (d^{-1}) no spiking	*k* (d^{-1}) spiking	Half life (days)		
			This study	Agricultural soil, China (Cu et al., 2008)	Compost amended soil (Chang et al., 2009)
0	0.019 ± 0.003	0.013 ± 0.004	35.5	30.8	5
35	0.029 ± 0.003	0.03 ± 0.002	24.8		
65	0.034 ± 0.004	0.035 ± 0.007	20.3		
100	0.064 ± 0.007	0.061 ± 0.005	11.1		

Biodegradation rates

- 17β estradiol was readily degraded compared to DEHP.
- Degradation rate increased with time under irrigation.
- Effect of high initial concentration.

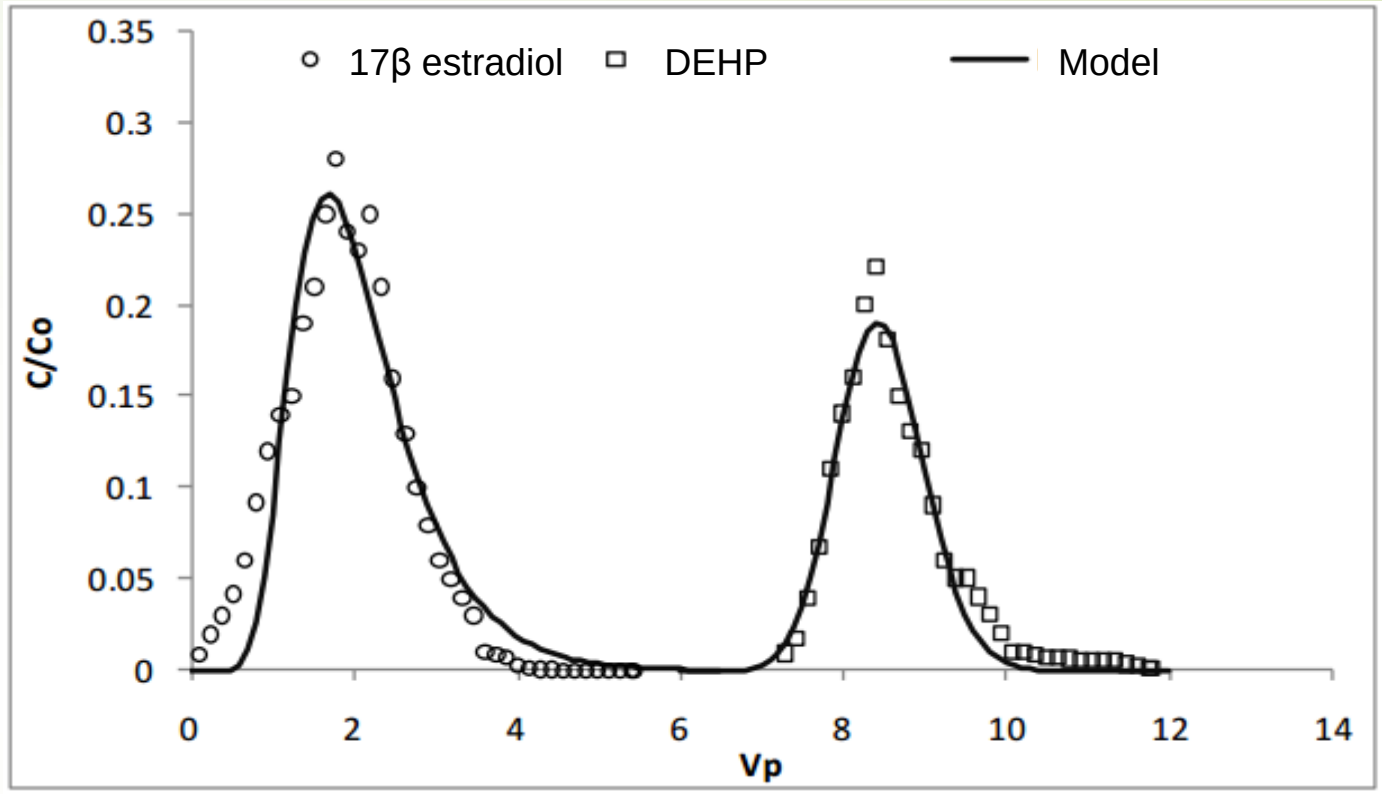


Years under irrigation	*k* (d^{-1}) spiking 10 ng/g	*k* (d^{-1}) spiking 50 ng/g	Half life (days)		
			This study	Agricultural soil, China (Jacobsen et al., 2005)	Soil amended with manure (Lucas et al., 2006)
0	0.033 ± 0.004	0.023 ± 0.004	21-29.7	12	1.3
35	0.049 ± 0.004	0.035 ± 0.003	14.1-20		
65	0.077 ± 0.004	0.061 ± 0.006	9-11.3		
100	0.19 ± 0.004	0.12 ± 0.002	3.7-5.8		

BTC of 17β estradiol and DEHP in 65 years irrigated soil

Mobility in undisturbed soil columns

- Higher retardation factor as increased time under irrigation.
- Higher biodegradation rates compared with batch tests.



Years under irrigation	17β estradiol			DEHP		
	Retardation factor	Degradation rate (d^{-1})	Remaining in soil (%)	**Retardation factor**	Degradation rate (d^{-1})	Remaining in soil (%)
0	**1.4**	0.13	2.8	**7.7**	0.1	4.18
35	**1.9**	0.13	< 2	**8.4**	0.17	3.6
65	**1.8**	0.2	< 2	**8.7**	0.09	2.5
100	**2.5**	0.25	< 2	**>14**	0.36	5.1

Concluding remarks

- **Agricultural soils are able to degrade and retain the tested micropollutants.**
- **Biodegradation occurs more rapidly under dynamic conditions than in batch tests.**
- **Increment of soil organic matter, which is supplied by wastewater increases the retention capacity, especially for non polar compounds.**

Long term Irrigation using untreated wastewater increases the soil capacity to cope with organic pollutants by biodegradation and retention processes.

Acknowledgments

- National Autonomous University of Mexico
- Mexico City's Council of Science, Technology and Innovation
- Postgraduate students in environmental chemistry

Thank you for your kind attention

Floor is open to question and discussion!!