PESTICIDE SORPTION/DESORPTION ON MEDITERRANEAN SOILS MODIFIED BY SOLUTION COMPOSITION

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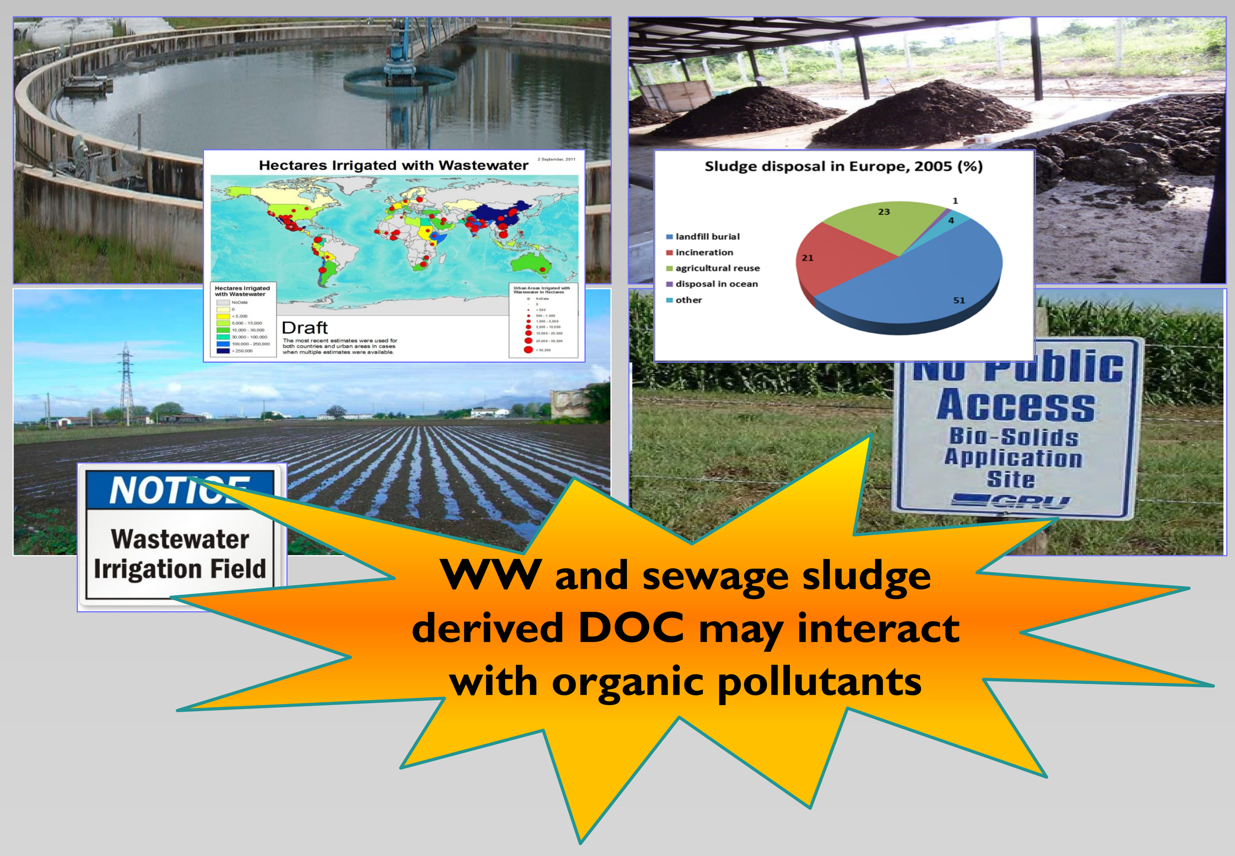
Introduction

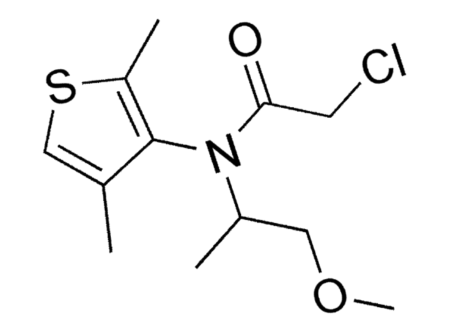
The relatively frequent water shortage periods in arid and semiarid regions, such as the Mediterranean basin, have led to irrigation with low-quality waters. This practice can modify the adsorption-desorption behaviour of pesticides onto soil, thus affecting the potential risk of surface- and groundwater contamination. We have assessed the impact of urban wastewater (WW) and dissolved organic carbon (DOC) solutions (30, 90 and 300 mg L^{-1} DOC) from sewage sludge on the adsorption-desorption behaviour of two pesticides of contrasting properties on agricultural soils from Granada province (Spain)



Materials and Methods

Table 1. Soil properties

	SV	RM1	RM3
Soil use	Irrigated crops	Rainfed crops	Olive orchards
Soil type (FAO/UNESCO)	Calcaric fluvisol	Chromic vertisol	Calcic cambisol
Sand (%)	31	10	19
Silt (%)	58	39	50
Clay (%)	11	51	31
Cation exchange capacity (meq_z/100g)	8.4	18.3	12.3
$CaCO_3$ (%)	24.9	42.1	58.7
pH	8.5	7.9	8.1
OC (%)	0.92	0.61	0.79

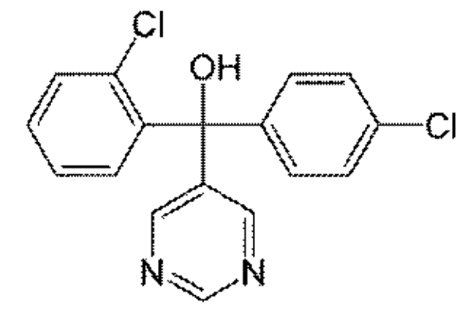


Dimethenamid (DIM)

Class: chloroacetamide herbicide

Water sol. (mg L^{-1}): 1200 (25 ºC)

Log K_{ow}: 2.15



Fenarimol (FEN)

Class: pyrimidine fungicide

Water sol. (mg L^{-1}): 13.7 (25 ºC)

Log k_{ow}: 3.69

Table 2. Solution properties

solution	Abbrev.	pH	EC (S m^{-1})	DOC (mg L^{-1})
MilliQ (control)	MQ	6.6	8.9x10^{-4}	b.d.†
Wastewater	WW	7.8	978x10^{-4}	25
Sewage sludge extract dilutions	DOC 30	6.5	28.8x10^{-4}	30
	DOC 90	7.0	80.3x10^{-4}	90
	DOC 300	7.1	247x10^{-4}	300

†below detection

Adsorption-desorption isotherms

- 5g soil/20 mL solution (24 h, 20°C)
- Pesticide analysis by HPLC-DAD
- Pesticide concentration range: 0.5-5 µg mL^{-1}
- Desorption (4 steps) with the highest concentration of the adsorption isotherm

FREUNDLICH EQUATION

$$X = K_f \, x \, C_e^{1/n}$$

HYSTERESIS COEFFICIENT

$$H = \frac{1/n_d}{1/n_a}$$

Results and Discussion

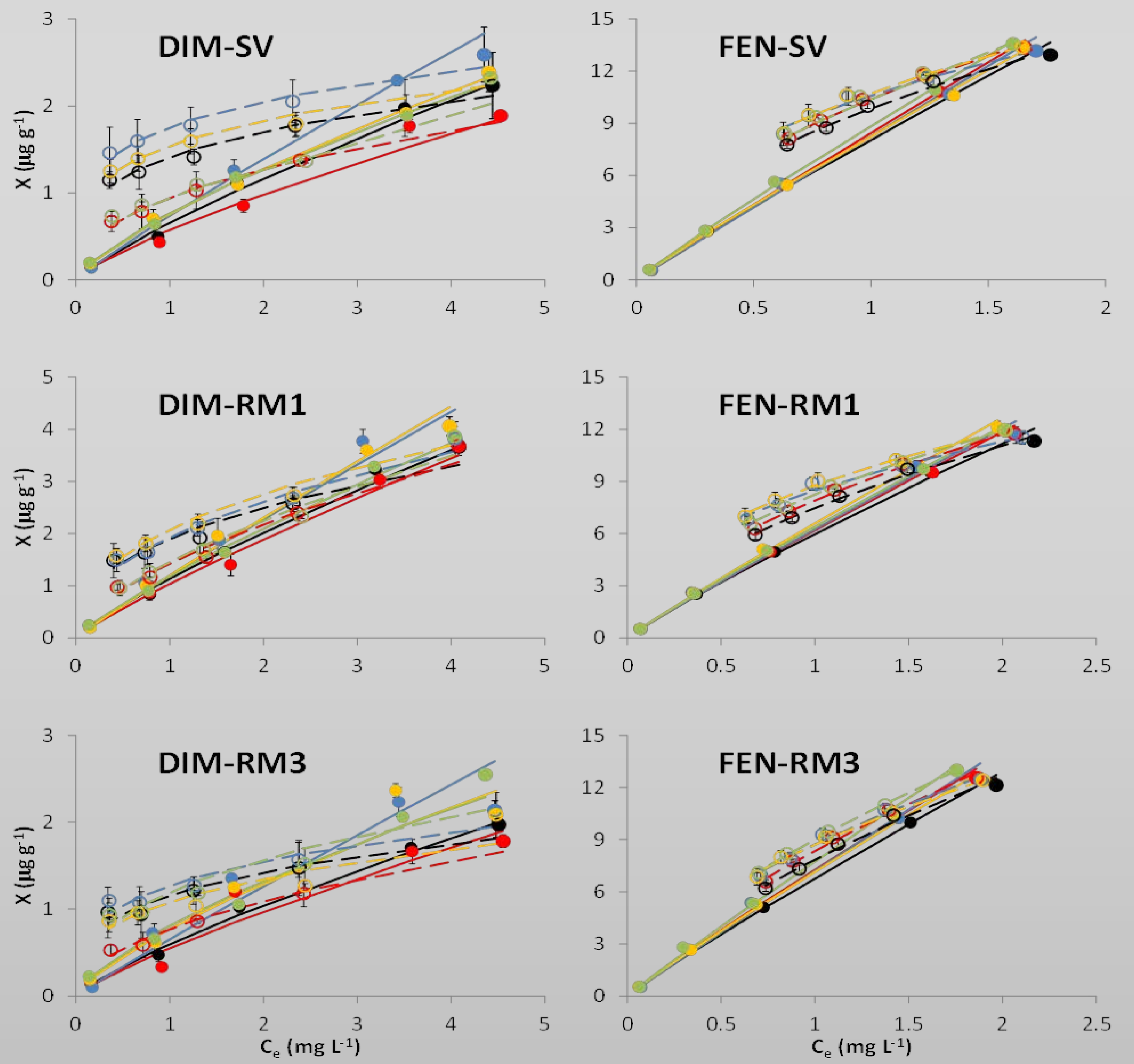


Figure 1. Sorption and desorption isotherms of FEN and DIM on three soils

- FEN adsorption increased with soil OC content (Tables 1 and 3) (Oliver et al. 2003; Rodríguez-Liébana et al. 2013)
- DIM adsorption was related to soil mineral fraction (Archangelo et al. 2004).
- WW did not influence pesticide adsorption
- DOC solutions increased adsorption: linearly for FEN ($R^2 \geq 0.87$; $P \leq 0.05$) in SV and RM3 soils, but without statistical relationship for DIM (Figure 1)

Table 3. Sorption-desorption parameters of the fitting to the Freundlich equation

		K_f	1/n	H	D †(%)	K_f	1/n	H	D †(%)
Soil			DIM				FEN		
SV	MQ	0.66 ± 0.03	0.83 ±0.04	0.33	48 ± 5	8.07± 0.28	0.93 ± 0.02	0.55	40 ± 1
	WW	0.58 ± 0.03	0.77 ±0.04	0.56	64 ± 7	8.46± 0.18	0.96 ± 0.01	0.55	39 ± 1
	DOC 30	0.74 ± 0.05	0.91 ± 0.06	0.24	44 ± 4	8.25± 0.28	0.98 ± 0.03	0.42	37 ± 3
	DOC 90	0.76 ± 0.02	0.75 ± 0.02	0.33	48 ± 3	8.27± 0.11	0.93 ± 0.01	0.48	37 ± 2
	DOC 300	0.77± 0.02	0.72 ± 0.02	0.63	68 ± 2	8.85± 0.09	0.93 ± 0.01	0.56	38 ± 0
RM1	MQ	1.14 ± 0.04	0.83 ± 0.03	0.47	60 ± 8	6.00 ± 0.09	0.90 ± 0.01	0.63	48 ± 2
	WW	1.04 ± 0.04	0.86 ± 0.03	0.71	74 ± 0	6.21 ± 0.17	0.93 ± 0.02	0.61	47 ± 0
	DOC 30	1.20 ± 0.06	0.93 ± 0.04	0.47	62 ± 2	6.28 ± 0.24	0.94 ± 0.03	0.45	42 ± 1
	DOC 90	1.20 ± 0.07	0.94 ± 0.05	0.44	61 ± 2	6.61 ± 0.18	0.94 ± 0.02	0.47	42 ± 2
	DOC 300	1.19 ± 0.03	0.83 ± 0.02	0.76	75 ± 3	6.41 ± 0.07	0.93 ± 0.01	0.57	45 ± 0
RM3	MQ	0.60 ± 0.02	0.80 ± 0.03	0.38	51 ± 16	6.78 ± 0.14	0.93 ± 0.02	0.75	49 ± 1
	WW	0.55 ± 0.06	0.82 ± 0.09	0.61	70 ± 2	7.28 ± 0.10	0.94 ± 0.01	0.73	48 ± 1
	DOC 30	0.66 ± 0.06	0.94 ± 0.07	0.30	50 ± 1	7.21 ± 0.24	0.98 ± 0.03	0.59	44 ± 1
	DOC 90	0.77 ± 0.04	0.74 ± 0.04	0.43	59 ± 3	7.16 ± 0.13	0.93 ± 0.01	0.59	45 ± 2
	DOC 300	0.82 ± 0.04	0.70 ± 0.04	0.56	64 ± 2	7.75 ± 0.36	0.95 ± 0.03	0.68	45 ± 0

†Desorbed amount after the 4 desorption steps

- DIM desorption was more hysteretic (lower H) than that of FEN
- FEN desorbed less than DIM, due to higher affinity for soil particles
- Desorbed percentages (D) were not considerably affected by DOC 30 and DOC 90 solutions (Table 3)
- D_{DIM} was higher with the solutions that exhibited less hysteresis, i.e., WW and DOC 300

Conclusions

- Soil organic matter and DOC are the main responsible for FEN adsorption
- The role of mineral fractions for DIM cannot be excluded
- Desorption of FEN was practically not affected by the solutions
- Adsorption of DIM with WW and DOC 300 solutions was more reversible (higher H) showing the highest desorption percentages
- The **composition of the irrigation solution** may modify the **potential risk of groundwater contamination** for non-ionic pesticides of intermediate hydrophobicity, such as DIM, which is weakly adsorbed on soil

References

- OLIVER D.P., KOOKANA R.S. & SALAMA R.B. (2003). Aust. J. Soil Res., 41 (5), 847-860.
- RODRÍGUEZ-LIÉBANA J.A., MINGORANCE M.D. & PEÑA A (2013). Colloid Surface A, 435, 71-77.
- ARCHANGELO E.R., KARAM D., FERREIRA F.A., PRATES H.T., FERREIRA L.R. & CARDOSO A.A. (2004). Planta Daninha, 22 (3), 467-477.

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