The influence of pesticide physicochemical properties on their sorption on a calcareous Mediterranean soil irrigated with treated wastewater

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INTRODUCTION

The reuse of treated wastewater (WW) in agricultural irrigation ensures a constant and safe water source even in the driest years. Irrigation with WW can modify the adsorption of pesticides in soils because WW contains different levels of dissolved solids, nutrients (N and P) and other substances, such as salts and dissolved organic carbon (DOC), not completely eliminated during the treatment, which involves a potential environmental hazard for contamination of groundwater.

Due to this the sorption behaviour of various pesticides covering a wide range of physicochemical properties has been evaluated in a representative Mediterranean soil, in the presence of WW.

METHODS

Table 1. Pesticide properties

Name	Water solub. (mg L^{-1})[a]	Log P[a]
α-cypermethrin (insecticide)	0.004-0.0007	6.94
Deltamethrin (insecticide)	0.0002	4.60
Pendimethalin (herbicide)	0.33	5.18 4.18
Fenarimol (fungicide)	13.7	3.69
Dimethenamid (herbicide)	1200	2.15
Thiacloprid (insecticide)	184	1.26

P: octanol-water partition coefficient
[a]*Tomlin* (2003). [b]*Sharma & Singh* (2007)

Table 2. Soil physicochemical parameters

OC %	pH 1/2.5 (soil/water)	CEC cmol+/kg	$CaCO_3$ %	sand %	silt %	clay %
1.1	8.1	7.9	25	31	58	11

OC: organic carbon; CEC: cation exchange capacity

BATCH EQUILIBRATION METHOD

MQ WATER (CONTROL) — TREATED WW

0.5 mg L^{-1} of each pesticide prepared in MQ or WW

20 mL solution + 0.4/5 g soil (depending on pesticide properties); 24 h agitation (20ºC)

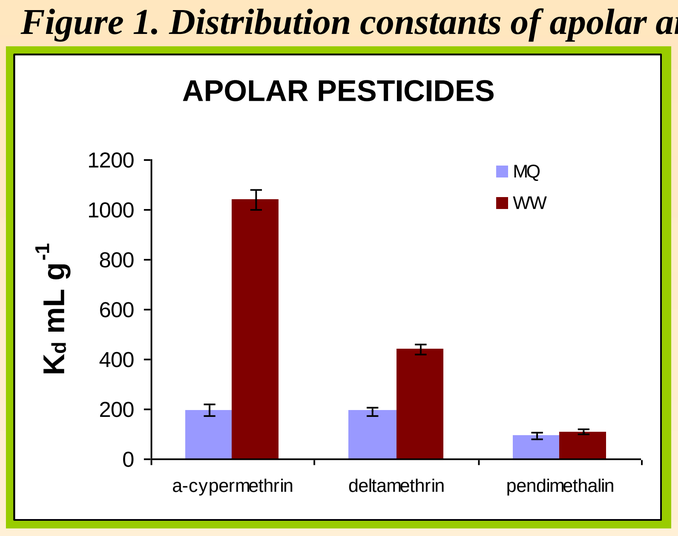
Pesticide concentration in supernatant (C_e) was determined by GC-μECD or HPLC-DAD

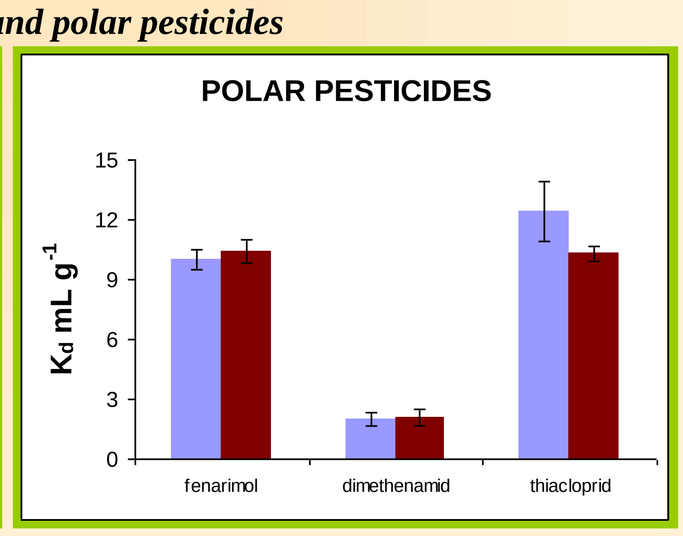
PESTICIDE DISTRIBUTION CONSTANTS:
K_d (mL g^{-1})= X (mg g^{-1})/C_e (mg mL^{-1})

RESULTS AND DISCUSSION

Figure 1. Distribution constants of apolar and polar pesticides

Figure 1 shows that sorption is ranged according to pesticide hydrophobicity *(Table 1)*, higher for apolar than for polar compounds.





WW enhances significantly (P<0.05) the sorption of the pyrethroid insecticides α-cypermethrin and deltamethrin, more hydrophobic than the others, with respect to MQ water (*Figure 1*). This increase cannot be only explained by soil OC content at the end of the batch method, which does not differ from that corresponding to control water *(Table 3)*.

The main differences in solution properties lie in a slight increase in DOC and the high conductivity of WW with respect to MQ water *(Table 3)*. Previous studies *(Turner, 2003)* reported that dissolved ions in solution could reduce the aqueous solubility of pesticides favoring their sorption on soil particles by a partitioning mechanism. This effect seems to be relevant for highly apolar compounds and for low soil/solution ratios (1/50 ratio) *(Spark and Swift, 2002)*.

Table 1. Some properties of the solutions used for sorption assays, as well as supernatant and soil properties after batch equilibration (confidence interval at α = 0.05) (n = 4).

Soil/solution ratio		Original solution DOC[a] (mg L^{-1})	Original solution pH		Original solution Conductivity x 10^{-4} (S m^{-1})		Supernatant pH		Supernatant Conductivity x 10^{-4} (S m^{-1})		Supernatant DOC[a] (mg L^{-1})		Soil OC[a] (%)	
1/50	MQ	0	5.9	0.1	0.5	0.0	8.8	0.1	109	1	16.4	0.1	1.12	0.11
	WW	30	7.6	0.0	922	1	7.5	0.1	1003	2	35.9	0.2	1.23	0.09
1/4	MQ	0	5.9	0.1	0.5	0.0	7.7	0.0	918	6	25.0	0.1	1.14	0.04
	WW	30	7.6	0.0	922	1	7.4	0.0	1628	3	31.2	0.4	1.05	0.01

[a]DOC: dissolved organic carbon (*Mingorance et al.*, 2007)

CONCLUSIONS

Our results suggest that both, the higher DOC of supernatants as well as the higher concentration of inorganic salts in WW, may play an important role in the sorption behavior of the two more hydrophobic pesticides, while the retention of the more polar compounds remains unchanged. Two effects could be occurring at the same time: a salting-out effect, which would reduce pesticide solubility in water increasing its sorption to soil, and enhanced DOC solution concentration, which would increase pesticide solubilization *(Rodríguez-Liébana et al., 2011)*. Pesticide properties, such as water solubility or octanol-water partition coefficient, are revealed as crucial factors for the prevalence of each one. Due to the complexity of the WW matrix, further evaluations are necessary to assess the effects of each component on pesticide retention.

REFERENCES
Mingorance, M.D., Barahona, E. and Fernández-Gálvez, J. (2007). *Chemosphere* 68, 409-413
Rodríguez-Liébana, J.A., Mingorance, M.D. and Peña, A. (2011). *J. Environ. Manaege*. 92, 650-654
Sharma, S.D. and Singh, M. (2007). *Bull. Environ. Contam. Toxicol.* 78, 91-94
Spark, K.M., and Swift, R.S. (2002). *Sci. Total Environ.* 298, 147-161
Tomlin, C.D.S. (2003). The Pesticide Manual. 13th Edn. British Crop Protection Council. 1344 pp
Turner, A. (2003). *Sci. Total Environ.* 314-316, 599-612

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