



## Research article

# Adsorption-desorption of dimethenamid and fenarimol onto three agricultural soils as affected by treated wastewater and fresh sewage sludge-derived dissolved organic carbon

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## ABSTRACT

The use of treated wastewaters (TWW) in agriculture is widening in areas suffering drought, such as southern Europe, to preserve freshwater supply for human consumption. The composition of TWW, especially concerning their organic carbon (OC) content, has been demonstrated to influence the processes governing the behavior of non-ionic pesticides in soils. Three OC-poor agricultural soils (SV, RM1 and RM3) from the province of Granada (Spain) were chosen for the assessment of the adsorption and desorption of the herbicide dimethenamid (DIM) and the fungicide fenarimol (FEN). TWW and sewage sludge extracts at different dissolved OC (DOC) concentrations (30, 90 and 300 mg L<sup>-1</sup>) were considered to evaluate their effect on pesticide adsorption-desorption. As expected by their properties, DIM and FEN were weakly and moderately adsorbed to the soils, respectively. Soil OC seemed to be the major factor controlling FEN adsorption, whereas the mineral fraction played a key role in DIM adsorption, especially in RM1 with high clay:OC ratio. Although TWW did not significantly modify the adsorption of pesticides, it enhanced DIM desorption from the three soils. Adsorption of FEN to SV and RM3 was directly related to the concentration of DOC, possibly due to co-sorption phenomena. Hysteretic desorption was found in all cases, indicating partially reversible adsorption. While FEN desorption was not altered by the solutions, the use of sludge extracts at the highest DOC concentration (300 mg L<sup>-1</sup>) enhanced DIM desorption as occurred with TWW. Interactions with DOC in solution seemed to predominate for this less hydrophobic compound, thus increasing the risk of natural waters contamination if TWW will be used.

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## 1. Introduction

Over the last few decades, agricultural management has involved the use of synthetic pesticides to a large extent in order to ensure crop production for the growing world demand. Once in soil, pesticides are subjected to several physicochemical processes that will determine their environmental fate. Among them, adsorption-desorption phenomena have been catalogued as of paramount importance since they control the concentration of the chemicals in the soil solution, hence affecting other processes, such as degradation, leaching or plant uptake (Koskinen and Harper, 1990; Boesten and van der Linden, 1991).

Residues of pesticides, usually detrimental for human health (Colborn, 2006; Gill and Garg, 2014), have been frequently found in environmental water bodies, even in drinking water reservoirs (Hladik et al., 2008; Gill and Garg, 2014). These pollution episodes have led to the design of less harmful and less persistent compounds. At the same time cultural strategies to control pesticide use and environmental impact have been implemented, such as the addition to soil of organic materials or irrigation with treated wastewater (TWW).

Crops have been historically irrigated with municipal wastewaters, mainly in areas with intense water scarcity, due to its eco-friendly nature and minimal cost (Müller et al., 2012). Beyond the indispensable TWW reuse to reduce their discharge to natural waters, these non-conventional resources can be considered a reliable water supply, quite independent from seasonal drought and weather variability, and able to cover peaks of water demand, reducing the risk of crop failure and income losses. Consequently,

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and due to the necessity of allocating freshwater sources for human consumption, irrigation with TWW is continuously growing worldwide (Sato et al., 2013). In fact, maximization of TWW reuse is considered a top priority by European Authorities (European Commission, 2012).

Moreover, TWW often contain significant amounts of organic matter, which may increase crop productivity by improving soil structure and physicochemical properties, which will in turn increase moisture content and fertility (Sousa et al., 2011). Nonetheless, it has been widely reported that addition of dissolved organic matter (DOM) through effluent irrigation affects the interactions between hydrophobic organic molecules and soil colloids. This behavior is highly dependent on the chemical nature and composition of DOM, as well as on soil and pesticide properties, and has been postulated to occur in two different ways. Firstly, DOM may decrease pesticide retention to soils by increasing pesticide solubility thus favoring the formation of stable pesticide–DOM complexes in solution (Li et al., 2005; Barriuso et al., 2011), especially for highly hydrophobic compounds (Rodríguez-Liébana et al., 2011). On a second hand, pesticide adsorption may be enhanced due to co-sorption with DOM on the soil surface (Flores-Céspedes et al., 2006; Ling et al., 2006).

Due to the potential toxicity of pesticides in the environment, the research was focused on the herbicide dimethenamid and the fungicide fenarimol. Some chloroacetamide herbicides, the chemical family to which dimethenamid belongs, have been classified as mutagenic or potentially carcinogenic (Souissi et al., 2013). On its part fenarimol has displayed antiandrogenic effects in *in vivo* studies with male rats (Vingaard et al., 2005). The main goal of this work was then to examine the effects of TWW irrigation and the role of DOC from fresh sewage sludge on the adsorption–desorption behavior of dimethenamid and fenarimol. To do this, three agricultural soils from different locations in the province of Granada (SE Spain) were selected. DOC concentrations ranged from 30 mg L<sup>-1</sup>, a value normally encountered in TWW, to 300 mg L<sup>-1</sup> which would represent values close to those found in non-treated wastewaters.

## 2. Materials and methods

### 2.1. Pesticides studied

Standards of dimethenamid (DIM, 97.5% purity) and fenarimol (FEN, 99% purity) were purchased from Dr. Ehrenstorfer (Germany). Individual stock solutions were prepared at 1 g L<sup>-1</sup> in acetone HPLC grade (Panreac, Spain), stored at -20 °C, and subsequently diluted for the adsorption–desorption experiments. The chemical structures of both pesticides as well as some of their physicochemical properties are depicted in Table 1.

DIM is a selective pre-emergence herbicide belonging to the chloroacetamide family. It is non-volatile and resistant to degradation in aqueous solutions. FEN is a systemic fungicide with protectant, curative and eradicating properties of the group of substituted pyrimidines. In aqueous solutions, it is stable to hydrolysis but susceptible to rapid photolysis.

### 2.2. Characteristics of soils and aqueous solutions

Three soils, SV, RM1 and RM3, collected in the province of Granada (Southeast Spain), were used in this study and represent typical soils of the Mediterranean semiarid climate (Table 2). The soil SV was taken from an agricultural irrigated crop field, RM3 from an olive grove and RM1 from a rainfed crop field. Soil samples were collected from the upper layer (20 cm), and were air-dried and sieved (<2 mm) in the laboratory before adsorption–desorption experiments.

The soil particle size distribution was determined by sieving and sedimentation, applying the Robinson's pipette method after organic matter had been removed with H<sub>2</sub>O<sub>2</sub> (SSEW, 1982). The measurement of pH and electrical conductivity (EC) was carried out in soil/deionized water suspensions, 1/2.5 (w/v). Soil organic carbon (OC) content was determined by a modified Walkey and Black method (Mingorance et al., 2007), after oxidising the OC with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in the presence of H<sub>2</sub>SO<sub>4</sub>. Cation exchange capacity (CEC) was determined using a method based on the triethylenetetramine–Cu complex (Meier and Kahr, 1999) and calcium carbonate was measured by the pressure gauge method after reaction with HCl. The mineralogical composition of the soils was determined by X-Ray Powder Diffraction using a Panalytical X-Pert Pro diffractometer (Rodríguez-Liébana et al., 2016). Random powder diffraction and oriented-aggregates (normal, ethylene glycol and heated to 550 °C) were prepared on glass slides. The clay mineral proportions were estimated from the glycolated diffractograms.

Apart from Milli Q (MQ) water as control, different solutions were used in the experiments. Treated wastewater (TWW) and sewage sludge were collected from the effluents of the secondary sedimentation tank of the wastewater treatment plant of Granada Sur (EMASAGRA S.A.). Average properties of TWW were pH 7.8, EC 0.98 dS m<sup>-1</sup>, 24 and 88 mg O<sub>2</sub> L<sup>-1</sup> biological and chemical oxygen demand, respectively, 23 and 575 mg L<sup>-1</sup> suspended and dissolved solids, respectively, and 25 mg L<sup>-1</sup> dissolved organic carbon (DOC).

After drying and sieving (<2 mm) in the laboratory, dewatered and anaerobically digested sewage sludge (33% OC) was used as a DOC source similar to that of TWW. With this purpose, 1 g of this residue was shaken with 10 mL of Na<sub>2</sub>HPO<sub>4</sub> 50 mM during 24 h as in previous works (Rodríguez-Liébana et al., 2011, 2018) to produce a suspension rich in organic matter (5.8 g L<sup>-1</sup> DOC). Solutions with 30, 90 and 300 mg L<sup>-1</sup> of DOC (DOC 30, DOC 90 and DOC 300 respectively) used in the experiments were obtained by dilution of this extract with MQ water.

### 2.3. Adsorption–desorption experiments

The adsorption of DIM and FEN by the three Mediterranean soils was carried out with the batch equilibration method (OECD, 2000) using 30 mL glass Pyrex tubes. The soil (5 g) was suspended with 20 mL of the different aqueous solutions previously spiked with the pesticides at concentrations ranging from 0.5 to 5 mg L<sup>-1</sup>. The concentrations used were only semirealistic, in particular for DIM (Table 1), but was estimated necessary to achieve analytical sensitivity, especially during desorption. The suspensions were shaken in a rotary shaker placed at 20 °C for 24 h, enough time to reach equilibrium (unpublished data), and then centrifuged at 1500 g during 15 min. The amount of sorbed pesticide was calculated as the difference between initial and equilibrium concentrations in the supernatants. Each treatment was replicated three times and a blank without soil was also included to rule out possible losses by volatilization, degradation and/or retention in the walls of the tubes.

The adsorption data were fitted to the linear model,

$$C_s = K_d \times C_e \quad [1]$$

where  $C_s$  (mg kg<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) correspond to pesticide concentrations in the solid and liquid phases at equilibrium, respectively.  $K_d$  (L kg<sup>-1</sup>) is the distribution constant of the pesticide between the soil and the liquid phase. The adsorption constant normalized to the OC content (%) of the soil ( $K_{OC}$ ) (L kg<sup>-1</sup>) was calculated as  $K_{OC} = \left(\frac{K_d}{OC}\right) \times 100$ .

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