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Laboratory persistence in soil of thiacloprid, pendimethalin and fenarimol incubated with treated wastewater and dissolved organic matter solutions. Contribution of soil biota

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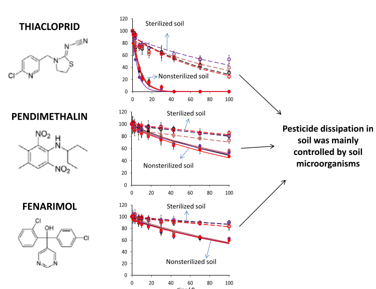
HIGHLIGHTS

- Treated wastewater and dissolved organic matter solutions were assayed.
- Soil microorganisms were mainly responsible for pesticide degradation.
- Treated wastewater only retarded slightly the decay rate of pendimethalin.
- Extracts of municipal sludges affected differently the persistence of the compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Reutilization of treated wastewater (TWW) in agriculture has continued to grow, especially in areas prone to frequent drought periods. One of the major aspects derived from this practice is the addition of important amounts of organic carbon (OC) that could interfere with the fate of organic contaminants in soils. This study has evaluated the impact of irrigation with a secondary TWW and dissolved OC (DOC) solutions from sewage sludge in the dissipation of thiacloprid (THC), pendimethalin (PDM) and fenarimol (FEN) in an OC-poor agricultural soil under laboratory conditions. The effect on soil microbial activity was also assessed through the measurement of dehydrogenase activity. Biotic processes were the main responsible for the degradation of the three compounds. Results showed that while THC was rapidly degraded ($DT_{50} \leq 5.5$ d), PDM and FEN were moderately persistent in soil ($DT_{50} \geq 93$ d). Incubation with TWW did not modify the decay rate of the three pesticides, but initially inhibited soil biota. Solutions of DOC did not alter the dissipation of FEN, but contrasting effects were observed for THC and PDM. Low DOC concentrations (30 mg L^{-1}) accelerated THC disappearance, a fact explained by stimulation of endogenous biota rather than by the presence of exogenous microorganisms from the solution. On the other hand, high DOC concentrations (300 mg L^{-1}) had more influence on the activity of microorganisms at longer times, and showed a trend to enhance the disappearance of the moderately persistent PDM.

1. Introduction

Degradation is a biological and physicochemical process that directly controls the attenuation of pesticide residues in soils.

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Therefore, it is widely used to predict the fate of pesticides and their potential risk of environmental contamination. The relative importance of this process depends on soil physicochemical and biological properties, climatic conditions, and pesticide characteristics (Kah et al., 2007; Grenni et al., 2012). As the breakdown of pesticides occurs mainly in the soil solution (Guo et al., 1999; Beulke et al., 2005), adsorption and degradation are in general negatively correlated due to the reduction of pesticide bioavailability with increased adsorption (Alexander, 1995; Guo et al., 1999; Grenni et al., 2012).

Although abiotic factors may be important (Delgado-Moreno and Peña, 2007, 2009), decomposition of most chemicals in the soil environment is mainly carried out by soil microorganisms (biotransformation), essentially bacteria and fungi (Alexander, 1995; Kulshrestha et al., 2000), converting them generally into less toxic compounds. The extent of biotransformation can range from minor changes without significantly compromising the compounds' chemical and toxicological properties to complete mineralization. In most cases, soil microorganisms use pesticides as a direct source of energy and nutrients (Briceño et al., 2007), or through cometabolism, metabolizing them with another substrate used for growth (Sánchez et al., 2004).

Crops have been historically irrigated with untreated municipal wastewaters, mainly in areas with water scarcity (Pedrero et al., 2010; Müller et al., 2012). In the last decades, stringent regulations concerning treatment of wastewater have become indispensable to avoid environmental contamination episodes and human health hazards. Jiménez and Asano (2008) estimated that 4.5 million ha were irrigated with low-quality waters, such as treated wastewaters (TWW), whose use for agricultural purposes has continued to grow, due to the dramatic increase in the demand of fresh water for domestic use (Pedrero et al., 2010; Sato et al., 2013). These alternative non-conventional water 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. But through irrigation with TWW important amounts of dissolved organic carbon (DOC), salts and microorganisms may be incorporated to the soil environment (Gloaguen et al., 2007), which could interact with pesticides (Ilani et al., 2005; Rodríguez-Liébana et al., 2011), and alter soil microbial populations (Kayikcioglu, 2012; Frenk et al., 2014). DOC can also potentially affect degradation and mineralization kinetics of pesticides in two ways: on one side, increasing the solubility of hydrophobic compounds, thus decreasing their adsorption and enhancing their availability to soil microorganisms, by forming stable pesticide–DOC complexes in solution or competitive adsorption (Li et al., 2005; Barriuso et al., 2011; Rodríguez-Liébana et al., 2011). On the other side, higher adsorption has been also reported due to pesticide–DOC–soil interactions (Flores-Céspedes et al., 2006; Ling et al., 2006), driving to reduced bioavailability, which is directly related to xenobiotics degradability (Briceño et al., 2007; Dalkmann et al., 2014). Therefore, the role of DOC in pesticide biotransformation is a subject of debate, since it depends on its source, nature and concentration, on the soil type, and pesticide characteristics.

In the present study, the laboratory dissipation of three non-ionic pesticides (thiacloprid, fenarimol and pendimethalin), with a wide range of physicochemical properties (K_{ow} from 1.26 to 5.18), was determined in a soil with intense agricultural activity. The effects on pesticide decay of irrigation with TWW, as well as the role of DOC from fresh sewage sludge were investigated. Two concentrations of DOC were evaluated, one close to the one normally encountered in TWW (30 mg L^{-1}) and a 10-fold higher concentration (300 mg L^{-1}), which would represent values close to non-treated wastewater (Friedel et al., 2000). Soil was sterilized to evaluate the biotic contribution to pesticide transformation, and dehydrogenase activity (DHA) was determined to assess the effects of the treatments on soil microbial community.

2. Materials and methods

2.1. Pesticides

Three pesticides representative of different families with contrasting physicochemical properties were used. Thiacloprid (THC) is an insecticide of the neonicotinoid family, with activity against sucking insects, weevils, leaf miners and various beetle species. Fenarimol (FEN) is a systemic fungicide with protectant, curative and eradicating properties of the group of substituted pyrimidines. Pendimethalin (PDM) is an herbicide of the dinitroaniline class used in pre- and post-emergence applications (FOOTPRINT, 2011).

The three pesticides are non-ionic compounds, with low to moderate water solubility (all in mg L^{-1}: THC 184, PDM 0.3 and FEN 13.7) and low to moderate-high hydrophobicity (log K_{ow}: THC 1.26, PDM 5.18 and FEN 3.69). FEN has been reported to be sensitive to sunlight irradiation while PDM is relatively volatile (Table S1). Pesticide standards with purity $\geq$ 98% were used without further purification (Dr. Ehrenstorfer, Germany).

2.2. Soil and solutions

Soil (SV) was located in a fertile alluvial area with intensive horticultural activity (Vegas del Genil, Granada, SE Spain) and collected from the upper layer (20 cm). Once in the laboratory, it was air dried and passed through a 2 mm sieve. The soil texture corresponds to a silt loam soil (31% sand, 58% silt, 11% clay). It had pH 8.1 (1/2.5 soil/water ratio), 27% of water content at field capacity (FC) (1/3 bar), 8.1 $cmol_{+} kg^{-1}$ cation exchange capacity, 26% $CaCO_3$ and 1.2% organic carbon (OC) content.

In order to estimate the biological contribution to pesticide disappearance, soil was sterilized (SSV samples) by tyndallization at 100 °C and atmospheric pressure for 1 h d^{-1} for 3 consecutive days (Delgado-Moreno and Peña, 2007; ElGouzi et al., 2015). No microbial growth was observed when sterilized soil suspensions were spread on Petri dishes containing LB (Lysogeny Broth) as culture medium (Fig. S1).

Different aqueous solutions were used for soil pre-treatment and to provide soil humidity: MilliQ water (MQ) as control, treated wastewater (TWW) and sewage sludge extracts. TWW was collected from the effluent of the secondary sedimentation tank of the wastewater treatment plant (EMASAGRA S.A.) of Granada Sur (Granada, Spain). Average properties of TWW were pH 7.8, electrical conductivity (EC) 0.98 dS m^{-1}, 24 and 88 mg O_2 L^{-1} biological and chemical oxygen demand respectively, 23 and 575 mg L^{-1} suspended and dissolved solids respectively, and 25 mg L^{-1} DOC.

Dewatered and anaerobically digested secondary sewage sludge was sampled from the same wastewater treatment plant. After drying and sieving (<2 mm) in the laboratory, the sludge rich in OC (33%) was used as a DOC source similar to that of TWW. Metal concentration of the sewage sludge was (all in mg kg^{-1}): Cr 60, Pb 349, Cd 2.5, Ni 103, Cu 284 and Zn 772 (Rodríguez-Liébana, 2016). To produce a DOC-rich suspension (5.8 g L^{-1} DOC), 1 g of sewage sludge was shaken with 10 mL of Na_2HPO_4 50 mM during 24 h (Rodríguez-Liébana et al., 2011). Solutions with 30 and 300 mg $L^{-1}$of DOC (DOC 30 and DOC 300 respectively) used in the experiments were obtained by dilution of this extract with MQ water. They had a conductivity of 0.14 and 1.3 dS m^{-1}, respectively.