Science of the Total Environment 610–611 (2018) 367–376

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Thiacloprid adsorption and leaching in soil: Effect of the composition of irrigation solutions

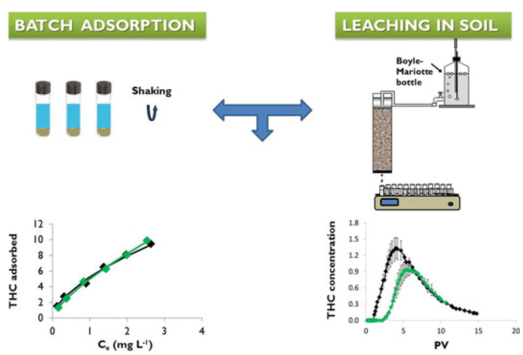
José Antonio Rodríguez-Liébana, M. Dolores Mingorance, Aránzazu Peña *

Instituto Andaluz de Ciencias de la Tierra (IACT), Consejo Superior de Investigaciones Científicas-Universidad de Granada (CSIC-UGR), Avda. de las Palmeras, 4, 18100, Armilla, Granada, Spain

HIGHLIGHTS

- Thiacloprid sorption was not greatly affected by irrigation solution and amendment.
- Thiacloprid batch adsorption was not modified in the DOC range tested (3–300 mg L^{-1}).
- In leaching studies DOC solutions and fertiormont enhanced thiacloprid retention.
- Pesticide co-transport is facilitated at high DOC concentrations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 May 2017
Received in revised form 18 July 2017
Accepted 2 August 2017
Available online 11 August 2017

Editor: D. Barcelo

Keywords:
Pesticide
Adsorption
Mobility
Treated wastewater
Amendment
Dissolved organic matter

ABSTRACT

Pressure on groundwater resources has increased during the last decades due to the growing demand, especially in arid and semiarid regions, such as the Mediterranean basin, with frequent drought periods. In order to partially remediate this environmental problem of world concern, irrigation of agricultural lands with adequately treated wastewaters (TWW) is becoming a common management practice. The complex composition of these low-quality waters may influence the behavior of organic contaminants in soils. A calcareous soil with low organic carbon content was selected for the assessment of the adsorption and leaching of the neonicotinoid insecticide thiacloprid (THC). Different solutions were evaluated: TWW after a secondary treatment, a saline solution and solutions with a range of dissolved organic carbon concentration (DOC, 3–300 mg L^{-1}). The addition of an organic fertilizer (fertiormont) to the soil was also assessed, in an attempt to reduce THC mobility. Sorption of thiacloprid, a relatively polar pesticide, was similar under all the conditions considered, though an adsorption decrease was observed when DOC concentration increased. The transport of THC through soil columns was retarded with all the treatments, with the lower effects corresponding to TWW and the saline solution. Addition of fertiormont and irrigation with DOC at 3 mg L^{-1} resulted in a reduction of pesticide leached (34% and 38%, respectively) in comparison with the control (66%), but surprisingly not for DOC at high concentration (55%), possibly due to co-elution of the pesticide with DOC. Therefore the transport of polar compounds, like THC, could be affected by the composition of the irrigation solutions, altering their impact to environmental water resources.

1. Introduction

Agricultural pesticides are an effective means to control pests and weeds but, once in soil, their environmental fate remains a serious

* Corresponding author.
E-mail address: aranchaph@iact.ugr-csic.es (A. Peña).

http://dx.doi.org/10.1016/j.scitotenv.2017.08.028

problem that needs to be assessed. Historically applied insecticides, such as those belonging to the organochlorine or organophosphorous families, were persistent and/or harmful to mammals, generating concern as a consequence of their environmental pollution and high toxicity (UNEP, 2004). Therefore, the general trend for modern pesticides is the design of less toxic and environmentally disruptive products to minimize both drawbacks, searching compounds with either more selective modes of action or else more polar and less persistent (Unsworth, 2010). These chemicals are then safer but, due to their polarity, may be more mobile and more easily transported to deeper soil layers and may pollute groundwater.

Neonicotinoids have been increasingly used in the last decades because of their systemic activity and selective effectiveness against insects, while remaining relatively safe to mammals (Jeschke et al., 2011). On the contrary, many aquatic invertebrates (Morrisey et al., 2015; Prosser et al., 2016), soil invertebrates (de Lima e Silva et al., 2017) and pollinators, such as honey bees and bumble bees (Schmuck and Lewis, 2016; Auteri et al., 2017) are sensitive to these insecticides at very low concentrations (up to 1 μg L^{-1}), all of which has forced governmental agencies to establish guidelines concerning neonicotinoids concentration thresholds in surface waters or to impose severe restrictions on their use (Prosser et al., 2016; Auteri et al., 2017). Due to their stability to hydrolysis and relatively high water solubility, the recommended concentration thresholds in surface waters are largely exceeded all over the world (Morrisey et al., 2015).

Given that water shortage is becoming endemic to a large world population, arid regions have resorted to reuse practices, such as irrigation with wastewaters, an increasingly attractive option for extending water supplies. Reuse of wastewater may result in an increase of soil organic matter and available nutrients together with an elevation of soil microbial activity (Friedel et al., 2000), favoring agricultural sustainability and promoting food production. However, at the same time, this practice may also affect soil quality, by inducing changes in soil hydraulic and chemical properties, such as the increase of sodicity and salinity and the reduction of soil hydraulic conductivity (Fernández-Gálvez et al., 2012; Lado et al., 2012; Assouline et al., 2016).

Moreover, the mobility in the soil profile of polar pesticides may be enhanced when using wastewater and increase their presence in groundwaters, since wastewater contains relatively high concentrations of dissolved organic matter (DOM) and of inorganic salts that could interact with the contaminants. Competitive effects and interaction between organic molecules (pesticides, pharmaceuticals) and DOM may decrease solute sorption, while at the same time co-sorption has been reported to increase soil retention (Chefetz et al., 2008; Rodríguez-Liébana et al., 2011, 2014a; ElGouzi et al., 2012; Borgman and Chefetz, 2013). These effects depend on solute properties and on the nature and composition of DOM.

To delve into the knowledge of wastewater irrigation on the fate of modern polar pesticides, experiments using either wastewater or solutions of different composition were performed using a soil from the metropolitan area of Granada (Southeastern Spain) devoted to agricultural activities. Solutions consisted in extracts from sewage sludge at various concentrations, as DOM sources, as well as saline solutions to explore the influence of wastewater on the adsorption and mobility of thiacloprid (THC), an insecticide from the neonicotinoid family. In an attempt to increase THC adsorption by soil and to reduce its mobility to water bodies, the addition of an organic fertilizer was also assessed. Experimental data from thiacloprid adsorption isotherms were fitted to the Freundlich and linear equations, and those from soil columns to the CXTFIT code to derive parameters that could be used to interpret the factors that may govern pesticide behavior.

2. Materials and methods

2.1. Soil and organic amendment

The plough layer (20 cm) of an agricultural soil (SV, typic xerofluvent) was collected, air-dried and sieved (<2 mm) in the laboratory. This soil is located in a fertile alluvial area of intensive agricultural activity in the province of Granada (Southeastern Spain) and corresponds to a Mediterranean type of climate. It is a calcaric fluvisol devoted to different irrigated crops such as corn, tobacco and fruit trees. The main physicochemical properties of SV soil are shown in Table 1.

A commercial organic fertilizer, solid fertiormont (Fertilizantes Orgánicos Montaño, S.L., Spain) (Table 1), which is composed of vegetal residues composted for two years, was sieved (<2 mm) and used to amend SV soil at a rate of 1% (w:w) and named FERT treatment. To ensure homogeneous mixing, dry soil and fertilizer were mechanically shaken end-over-end overnight at room temperature.

2.2. Pesticide and influent solutions

Thiacloprid (THC) [(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide] is an insecticide of the neonicotinoid family, whose mechanism of action involves disruption of the nervous insect system by stimulating nicotinic acetylcholine receptors. It has an activity not only against sucking insects but also against weevils, leaf miners and various beetle species. Its octanol/water partition coefficient (log K_{ow}) is 1.26, and its water solubility 185 mg L^{-1} (Lewis et al., 2016). A THC standard with purity ≥98% was used without further purification (Dr. Ehrenstorfer, Germany).

Apart from Milli Q (MQ) water (control) different solutions were used in both adsorption and leaching 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, 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} dissolved organic C (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_2HPO_4 50 mM during 24 h as in previous works (Rodríguez-Liébana et al., 2011, 2014a) to produce a suspension rich in organic matter (5.8 g L^{-1} DOC). Solutions with 3, 9, 30, 90, 150 and 300 mg $L^{-1}$of DOC (DOC 3, DOC 9, DOC 30, DOC 90, DOC 150 and DOC 300, respectively) used in the experiments were obtained by dilution of this extract with MQ water.

Additionally, solutions of $CaCl_2$ (Panreac, Spain) and $(NH_4)_2SO_4$ (Probus, Spain), both at 5 mM, were assayed. They had similar EC to that of TWW (1.2 and 1.3 dS m^{-1}, respectively).

2.3. Adsorption isotherms

THC adsorption by amended and non-amended SV soil was conducted by the batch equilibration method using 30 mL glass Pyrex tubes. The

Table 1
Properties of the soil and the organic fertilizer (Fertiormont).

	Soil	Fertiormont
Sand (%)	31	
Silt (%)	58	
Clay (%)	11	
FC (%)	27	
pH	8.1	8.8
EC (dS m^{-1})	1.2	3.7
CEC ($cmol_+$ kg^{-1})	8.1	
$CaCO_3$ (%)	26	
OC (%)	1.2	26
OM (%)	2.1	
DOC (g L^{-1})		1.7
Total C (%)	5.5	
C/N	6.9	

FC, field capacity; EC, electrical conductivity; CEC, cation exchange capacity; OC, organic carbon; OM, organic matter; DOC, dissolved organic carbon.