Science of the Total Environment 538 (2015) 16–22

Contents lists available at ScienceDirect

Science of the Total Environment

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

Changes in the persistence of two phenylurea herbicides in two Mediterranean soils under irrigation with low- and high-quality water: A laboratory approach

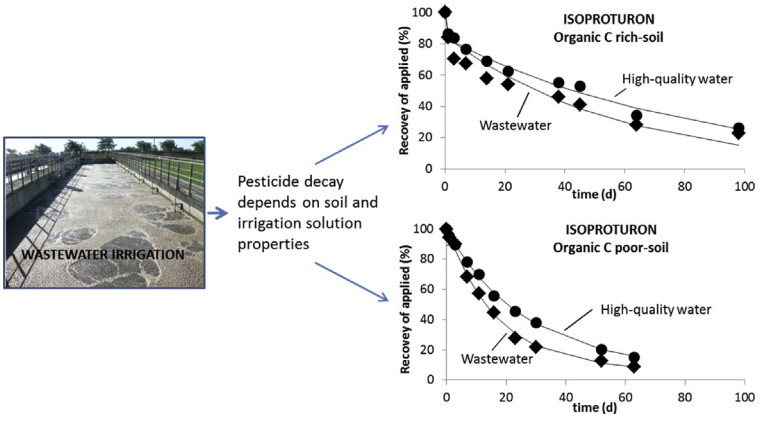
Siham ElGouzi [a,b], Khalid Draoui [b], E.H. Chtoun [b], M. Dolores Mingorance [a], Aránzazu Peña [a,*]

[a] Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Avda. de las Palmeras, 4, E-18100 Armilla, Granada, Spain
[b] Département de Chimie, Faculté des Sciences, Université Abdelmalek Essaadi, B.P. 2121, M'hannech II, 93002 Tétouan, Morocco

HIGHLIGHTS

- Use of low-quality water may modify pesticide dissipation behaviour in soil
- The wastewater effect on the disappearance of two phenylureas was assessed
- Wastewater effect on the OC-rich soil was negligible, likely due to the high OC load
- On the contrary wastewater speeded up pesticide decay in the OC-poor soil
- The structure of each pesticide was determinant for their disappearance rate

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 June 2015
Received in revised form 29 July 2015
Accepted 29 July 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Dissipation
Pesticides
Wastewater
Kinetic models

ABSTRACT

The disappearance of two phenylurea herbicides, chlorotoluron (CHL) and isoproturon (IPU), in two Mediterranean soils, an agricultural calcareous soil (S5) and an organic forest soil (S2), was assessed under irrigation with high- and low-quality water. Irrigation with wastewater, as opposed to irrigation with high-quality water, increased the degradation rate of both herbicides in both soils. For each soil, the decay rate of IPU was always higher than that of CHL, and both pesticides disappeared more rapidly from S5 with lower clay and organic carbon content than from S2. The degradation rate was inversely related with pesticide sorption on soil, because increased sorption would reduce pesticide bioavailability for decomposition. In most cases the residual concentration in soil of both phenylurea herbicides was better fitted to a bi-exponential decay model than to first-order or first-order with plateau models. Dehydrogenase activity, used as an indication of microbial activity, was very high in S2 in comparison with S5, but was not related to pesticide disappearance.

Abbreviations: CHL, chlorotoluron; DHA, dehydrogenase activity; DOC, dissolved organic carbon; DT_{50}, time to reach the 50% of the initial pesticide amount; IPU, isoproturon; k, kinetic degradation constant; K_f, Freundlich sorption constant; MQ, Milli Q water; OC, organic carbon; S2, organic forest soil; S5, agricultural calcareous soil; $t_{1/2}$, half-life time calculated from the fitting to a first-order degradation equation; WW, wastewater.

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

http://dx.doi.org/10.1016/j.scitotenv.2015.07.146
0048-9697/

1. Introduction

The use of low-quality water for irrigation is an alternative to safeguard fresh water, a natural resource vital for life, because a safe and abundant supply of water is required for the sustainable development of the world population. Considering that about 70% of the fresh water from rivers, lakes and aquifers (~820 × 10^7 m^3 d^{-1}) is used for irrigation, improvement of irrigation efficiency only in 10% could double the fresh water resources and redirect them to other purposes (O'Connor et al., 2008).

In the last decades treatment of wastewater (WW) is becoming ubiquitous in many countries, mostly due to increasing public awareness. In particular in Spain 71% of WW volume is used for irrigation (Iglesias et al., 2010). Similarly, in other regions suffering from water scarcity, i.e., the Middle East and North Africa, treated WW is also frequently employed for irrigation (Sato et al., 2013). Though treated WW is being produced in huge amounts and becoming more and more frequent as irrigation source, its use usually does not come without problems, either direct, such as potential infectious diseases or presence of contaminants like heavy metals, pharmaceuticals, surfactants or other organic chemicals (Pal et al., 2014; Zemann et al., 2014), or indirect, such as soil salinization, sodification, or changes in soil hydrophysical properties (Ruoss et al., 2008; Arienzo et al., 2009; Fernández-Gálvez et al., 2012), among others.

Pesticides are pollutants of environmental concern due to their occurrence in a wide range of ecosystems. Herbicides are usually applied to soils, where they can be subjected to different processes, such as sorption/desorption, transport and chemical or biological transformation. Several reports have addressed the effect of irrigation with urban treated WW on pesticide sorption/desorption (Drori et al., 2005; González et al., 2010; ElGouzi et al., 2012; Hernández-Soriano et al., 2012; Rodríguez-Liébana et al., 2011, 2014a) and on pesticide leaching (Graber et al., 1995; Seol and Lee, 2000; González et al., 2010; Peña et al., 2011; Müller et al., 2012), with variable results depending on pesticide and soil properties. However less information on pesticide degradation as affected by WW irrigation has been found in the literature (Vela et al., 2004; Hernández-Soriano et al., 2009; Dvorkin et al., 2012) and this is an aspect which deserves deeper attention, because it is a determinant process in the environmental fate of pesticides.

Specifically, in this study we have selected two phenylureas, (4-isopropylphenyl)-1,1-dimethyl urea (isoproturon) and 3-(3-chloro-p-tolyl)-1,1-dimethylurea (chlorotoluron), which share similar physicochemical properties but differ in chemical structure. Despite the similarity in their properties, such as water solubility or hydrophobicity, parameters commonly used to predict the environmental fate of organic pollutants, there are reports on differences in behaviour of both compounds (ElGouzi et al., 2012) which are worth exploring. Overall both herbicides degrade slowly in water and are quite persistent, so it is increasingly common to find the parent compounds and metabolites in groundwater in concentrations exceeding the drinking water threshold limit of 0.1 μg L^{-1} (Badawi et al., 2009; Carrier et al., 2009).

The aim of this work was to assess the effect of irrigation with high-quality water and WW on the dissipation behaviour of the phenylurea herbicides isoproturon (IPU) and chlorotoluron (CHL) in two soils with contrasting properties. Different kinetic models were used to fit the experimental data. At the same time the impact of pesticide application and WW irrigation on soil microbiota was evaluated by measuring the evolution of dehydrogenase activity (DHA).

2. Material and methods

2.1. Soils

The two soils considered in the current study were selected to contrast in their properties so that differences in the results could be obtained: An agricultural soil from the plain of Granada (SE Spain) (S5) and a forest soil from the area of Tetouan (North of Morocco) (S2). Soils were sampled from the upper layer (0–25 cm), dried and passed through a 2-mm sieve after discarding, in the case of the forest soil, the big vegetal remains. Physicochemical soil properties are shown in Table 1. The soil particle size distribution was determined by sieving and sedimentation applying the Robinson's pipette method, after elimination of organic matter with H_2O_2, using sodium hexametaphosphate as dispersing agent. pH (Eutech Instruments Cyberscan pH 2100, Singapore) and electrical conductivity (EC) (XS Instruments COND 510, Italy) were measured in soil/deionised water suspensions 1/2.5 (w/v). The method to determine cation exchange capacity (CEC) was based on the triethylenetetramine–Cu complex (Meier and Kahr, 1999). The $CaCO_3$ content was measured by the pressure gauge method after reaction with HCl. Total C was analysed by dry combustion (LECO TRUSPEC CN, Murcia, Spain). Organic C (OC) and dissolved OC (DOC), the latter at a 1/4 ratio (w/v), were determined by a modified Walkley and Black method (Mingorance et al., 2007). The determination of the soil humification index (HIX) was performed in 1/4 (w/v) soil/deionised water suspension, according to Zsolnay (2003).

Soil was autoclave sterilized (100 °C, at atmospheric pressure) for 1 h each day for three consecutive days (Sánchez et al., 2003; Hernández-Soriano et al., 2009). Solution sterilization was performed by heating for 1 h, in a water bath, at 90 °C.

2.2. Chemicals

Standards (99% purity, Dr. Ehrenstorfer, Augsburg, Germany) of two substituted phenylurea herbicides, IPU and CHL, were used. The partition coefficient (log K_{ow}) is 2.5 for both compounds and their water solubilities are 65 and 74 mg L^{-1} for IPU and CHL, respectively (Tomlin, 2003). Stock standard solutions for each analyte were prepared at 1 g L^{-1} in acetone.

Soil humidity was controlled by adding water of different quality: High quality Milli Q (MQ) water (Millipore, Bedford, MA, USA) and treated WW, from the effluents of the secondary sedimentation tank of the water treatment plant of Granada (EMASAGRA, Spain), a city of around 250,000 inhabitants. MQ had a pH 7.6, conductivity 10^{-3} dS m^{-1} and non-detectable OC content. On the other hand WW had a pH 7.5, conductivity 1.1 dS m^{-1} and 25 mg L^{-1} OC content. Besides, as reported from the treatment plant, WW also contained in average 39.7 mg L^{-1} total N, 6.9 mg L^{-1} total P, and had chemical and biological oxygen demands of 88 and 24 mg L^{-1}, respectively.

All solvents used were of HPLC analysis grade.

2.3. Pesticide dissipation

The soil samples (1 kg for each treatment) were preincubated with MQ water or with WW in a thermostatic chamber (Hotcold, Selecta) at 15.0 ± 0.1 °C for four days with a moisture level equivalent to 40% soil water holding capacity to stimulate the microbial activity (Hernández-Soriano et al., 2009). Then, the soil samples were homogeneously sprayed with a solution containing a mixture of CHL and IPU to reach a final pesticide concentration of 1.5 μg g^{-1} each. This pesticide dose is equivalent or even lower than field-recommended doses. After evaporation of the solvent sufficient volume of MQ or WW was added to reach 70% soil water holding capacity (Delgado-Moreno and Peña, 2009; Ruoss et al., 2011; Wang et al., 2014). The soil was then homogenised by thorough mixing and passed several times through a 2 mm sieve. Each soil treatment was split into two aliquots of ca. 500 g each, transferred to loosely capped glass containers and incubated in darkness at 15 ± 0.1 °C. Soil moisture content was maintained by periodic addition of MQ or WW, followed by homogenization. All treatments were sampled immediately after preparation and then at intervals during at least 63 days for non-sterile S5 soil and up to 100 days for sterile soils and non-sterile S2 soil, for which slower degradation rates were expected.