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Trial of solar heating methods (solarization and biosolarization) to reduce persistence of neonicotinoid and diamide insecticides in a semiarid Mediterranean soil

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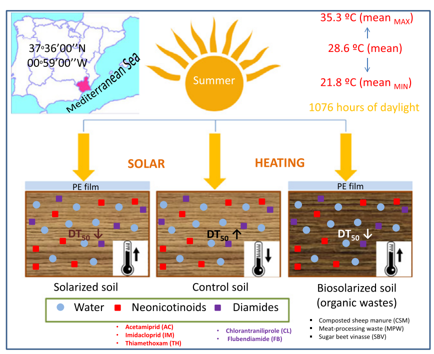
HIGHLIGHTS

- Solar heating techniques were assessed to study insecticide persistence in soils.
- Degradation rates of neonicotinoid and diamide insecticides were tested.
- Composted manure, meat-processing waste and sugar beet vinasse were used as organic wastes.
- Both, solarization and biosolarization decrease DT50 of insecticides in the soil.
- Increase in soil temperature and organic matter are decisive in their behaviour.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports the use of solar heating techniques, solarization (S) and biosolarization (BS) as a strategy for the environmental restoration of soils containing neonicotinoid, acetamiprid (AC), imidacloprid (IM) and thiamethoxam (TH), and diamide, chlorantraniliprole (CL) and flubendiamide (FB) insecticide residues. For this, a semiarid Mediterranean soil (Haplic calcisol) was covered with low-density polyethylene (LDPE) during the hot season, to raise the maximal soil temperatures. Compost from sheep manure (CSM), meat-processing waste (MPW) and sugar beet vinasse (SBV) were used as organic wastes. The results showed that both S and BS increase insecticide disappearance rates compared with the non-disinfected soil, the increase in soil temperature and added organic matter playing a key role. The dissipation rates of TH and AC in soil were satisfactorily described by first-order (monophasic) kinetics, while IM, CL and FB showed a deviation from exponential behaviour. For them, the best results were obtained applying biphasic kinetics with a rapid initial degradation followed by a slower decline of their residues. The findings suggest that S and BS (especially using MPW) can be considered as a valuable tool for enhancing the detoxification of soils polluted with these insecticides.

Abbreviations: AC, acetamiprid; BS, biosolarization; CL, chlorantraniliprole; CSM, composted sheep manure; DT, disappearance time; FB, flubendiamide; IM, imidacloprid; LDPE, low density polyethylene; MPW, meat-processing waste; RH, relative humidity; S, solarization; SBV, sugar beet vinasse; SFO, single first order; TH, thiamethoxam.

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1. Introduction

The main challenge faced by modern agriculture is how to improve the quality and quantity of food production while avoiding any adverse effect on the environment or natural resources. However, the widespread use of pesticides in agriculture to combat pest and diseases introduce these compounds and their metabolites into soils. Once a pesticide appears in the soil, the major processes conditioning its behaviour and fate in the environment are adsorption, migration and degradation (Gavrilescu, 2005; Navarro et al., 2007; Kah et al., 2007).

From an agronomic point of view, it is desirable that agrochemicals persist the necessary time to control pests throughout the cultivation cycle. However, from an environmental point of view, persistent compounds are undesirable for different reasons. Many of them are intrinsically toxic and consequently they can affect humans, domesticated animals, agricultural crops, wildlife, and fish and other aquatic organisms or microorganisms. The longer the molecule remains in the environment, the greater the risk of exposure of susceptible individuals or populations and the greater is the risk.

At present, neonicotinoids are the most widely used insecticides in the world due to their desirable features such as low application rates, versatile application methods, broad-spectrum activity, and upward systemic movement in plants (Goulson, 2013; Bass et al., 2015). They have been in use since the early 1990s, imidacloprid being the first commercially launched compound in 1991. Other insecticides of this class, including acetamiprid, thiamethoxam and thiacloprid were marketed in succession from 1995 to 2000. All these insecticides are selective agonists of the insect nicotinic acetylcholine receptors (nAChRs) located in the central nervous system of insects (Tomlin, 2009). However, being systemic, they are also found in the nectar and pollen of treated crops, which can, in turn, lead to the exposure of honeybees (Fairbrother et al., 2014). As a consequence, the European Commission following a reassessment of the risks involved by the European Food Safety Authority (EFSA) restricted the use of certain neonicotinoid insecticides (imidacloprid, clothianidin and thiamethoxam) in crops where they would have adverse effects on bees and other pollinators (European Commission, 2013). Moreover, neonicotinoids can persist and accumulate in soils and are prone to leaching through the soil profile with the consequent risk of groundwater pollution (Goulson, 2013; Raina-Fulton, 2016).

On the other hand, anthranilic and phthalic diamides (available since 2008), such as chlorantraniliprole or cyantraniliprole and flubendiamide, respectively, belong to a recently developed class of insecticides that disrupt the ryanodine (Ry) receptors in intracellular calcium channels (RyR)-Ca^{2+} that play a central role in muscle and nerve functions (Qi and Casida, 2013; Jeanghuenat, 2013). These insecticides specific site activity, a wide pest spectrum, little or no cross resistance with other classes and a favourable toxicological profile (Teixeira and Andaloro, 2013), being flubendiamide more persistent chorantranilipole in soil (Malhat et al., 2012; Sharma and Parihar, 2013).

The toxicity of these agrochemicals, especially neonicotinoids, means that soil remediation strategies are necessary in order to protect consumers from exposure to unacceptable levels of their residues in food and water. Besides the traditional techniques proposed for the treatment of pesticide-polluted soils such as confinement/isolation, biological, physical-chemical, thermal and others (Castelo-Grande et al., 2010), solarization and biosolarization, are proposed as efficient techniques to enhance the degradation and natural attenuation of insecticides (Fenoll et al., 2011), fungicides (Fenoll et al., 2010a) and herbicides (Navarro et al., 2009; Fenoll et al., 2010b, 2014) in soils during the last years.

Both chemical and non-chemical methods are used for soil disinfestation. The yield of many different crops has relied during the last few decades on methyl bromide (MBr) as the main fumigant to control soil-borne diseases, weeds and nematodes. However, the *Montreal Protocol on Substances that Deplete the Ozone Layer* and re-evaluation of pesticide usage worldwide in 2005 has dramatically reduced its use because although extremely effective as soil disinfectant is also recognised as an ozone-depleting substance. Consequently, many soil-borne diseases have become more difficult to manage and the search for soil disinfestation alternatives has been intense. Nowadays, solarization, biofumigation and biosolarization are considered three attractive methods for soil disinfestation and they are extensively used as non-chemical alternatives on different crops in the Mediterranean Basin.

In its present form, soil solarization (also termed solar heating), which originated during the 1970s, is based on covering the soil with transparent polyethylene during the hot season in an attempt to raise the maximal soil temperatures, thereby killing pathogens, reducing diseases and increasing yields (Katan, 2015). The initial definition of biofumigation as a process referring to the breakdown of *Brassica* tissues was later expanded to describe the process of biological decomposition of plant or animal by-products leading to the production of volatile compounds with disease and pest suppressive effects (Ploeg, 2008). Mulching with transparent polyethylene (biosolarization) prevents the escape of these volatiles and improves the control (Gamliel, 2000).

Although these techniques were originally developed for soil disinfestation to control soilborne plant pathogens, other additional uses have been developed in the years that followed. For this reason, the aim of this work was to assess the effectiveness of solar heating techniques (solarization and biosolarization) for the remediation of soils containing residues of two groups of insecticides: i) neonicotinoids, with serious environmental concerns and ii) diamides, a relatively new type of compounds. Both groups are widely used at level around 200–500 g a.i. Ha^{-1} for crop protection in many areas of the world at the present time.

2. Material and methods

2.1. Active ingredients, commercial formulations and reagents

Analytical standards of imidacloprid (IM), acetamiprid (AC), thiamethoxam (TH), chlorantraniliprole (CL), and flubendiamide (FB) which were used for standardization of the analytical procedures, were purchased from Dr. Ehrenstorfer (Augsburg, Germany), with purity > 99%. Table 1 shows the main physical and chemical properties of the insecticides. Experimental values of the octanol-water partition coefficient (log K_{OW}), aqueous solubility (S_W), Henry's law constant (H), and predicted value of soil organic partition coefficient (K_{OC}) were taken from the EPI Suite version 4.1 computer program provided by the U.S. Environmental Protection Agency (US EPA, 2015). GUS (Groundwater Ubiquity Score) indexes were taken from The Pesticide Properties DataBase (PPDB, 2016).

The commercial formulations (Actara 25WG, thiamethoxam 25% w/w; Couraze, imidacloprid 20% w/v SL; Epik, acetamiprid 20% w/w; Rynaxypyr 35 WG, chlorantraniliprole 35% w/w; and Fenos 24 WG, flubendiamide 24% w/w) were all purchased from Fitodolores SL (Murcia, Spain).

Acetonitrile for residue and HPLC analysis was provided by Scharlab (Barcelona, Spain). Deionized water was obtained from a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). Formic acid (98% purity) and sodium chloride were ordered from Fluka–Sigma–Aldrich (Steinheim, Germany).

2.2. Soil and amendments

The soil samples were taken from Campo de Cartagena, Murcia (southeastern Spain). The selected soil (Haplic calcisol) mainly occurs in arid, semi-arid, Mediterranean and steppe climates. Soil samples were collected from the surface (top 20 cm), air-dried, and passed through 2 mm sieve. The characteristics of the soil (clay loam) were as follows: pH (H_2O) 7.3 ± 1.5, Electric conductivity (dS m^{-1}) 7.3 ± 2.2; Organic carbon content (g kg^{-1}) 18 ± 3.5; Total nitrogen (g kg^{-1})