



Sorption, persistence and leaching of abscisic acid in agricultural soils: an enantiomer-selective study



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ABSTRACT

Little is known about the enantioselectivity of the processes that determine the efficacy and environmental fate of natural compounds with potential to be used as environmentally-friendly agrochemicals. We conducted incubation and column leaching experiments to examine the extent and enantioselectivity of the sorption, persistence, and leaching of (*RS*)-abscisic acid (ABA) in three agricultural soils. Sorption of ABA enantiomers was a non-enantioselective process that occurred only in the soil with pH close to the pK_a (4.8) of ABA enantiomers, but not in the two other (alkaline) soils. The degradation of (*RS*)-ABA was enantioselective for the three soils tested. (*S*)-ABA, the naturally-occurring enantiomer, was always degraded faster ($DT_{50} < 4$ days), compared to (*R*)-ABA ($DT_{50} > 8$ days). The movement of ABA enantiomers through the soil profile was enantioselective with column leachates being enriched in (*R*)-ABA enantiomer. Leaching was delayed in the soil that displayed sorption for both enantiomers. The results showed that the behavior of ABA enantiomers in soil was enantioselective and that the final fate of (*R*)-ABA and (*S*)-ABA depended on the soil type and appeared to be affected by their sorption on soil. The longer persistence of (*R*)-ABA should be considered when assessing the possibility of using this enantiomer or formulations containing enantiomer mixtures of ABA for crop management.

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1. Introduction

The development of synthetic agrochemicals has greatly contributed to achieve appropriate levels of high-quality food production in modern agriculture (Dayan et al., 2009; Vyvyan, 2002). Nonetheless, it has also led to concerns related to the potential impact of these compounds on the environment and human health and to evolution of pest resistance. In order to reduce these drawbacks, a growing interest exists to integrate the use of less harmful, naturally-occurring compounds as crop protection products, often included in the general term of biopesticides (Cantrell et al., 2012; Seiber et al., 2014; Villaverde et al., 2014).

Abscisic acid (ABA) has recently been registered by the European Union and United States Environmental Protection Agency as an active substance to be used as a plant growth regulator, and is considered a biopesticide (Cantrell et al., 2012; EC, 2014; USEPA, 2010). Abscisic acid is a chiral plant hormone typically studied in the framework of stress signaling during plant growth, although it is also involved in the control of certain developmental and physiological functions in non-stress situations (Milborrow, 1974; Rai et al., 2011). Currently registered formulations based on ABA contain only the naturally occurring enantiomer, (*S*)-ABA, which aids in plant growth by bolstering stress resistance, improving fruit set, and controlling the pace of

ripening and senescence (EC, 2013, 2014; USEPA, 2010). Nevertheless, it has been observed that the unnatural enantiomer, (*R*)-ABA, can also exert various physiological effects. These include inhibiting plant growth and seed germination or contributing to protect plant tissues from UV irradiation (Berli et al., 2010; Cutler et al., 2010; Lin et al., 2005; Palma et al., 2014). In fact, the potency of unnatural (*R*)-ABA has been a striking feature of many biological activity tests (Cutler et al., 2010; Milborrow, 1974).

Nowadays, one big challenge in agricultural and environmental science is to achieve a better knowledge of the enantioselectivity of the processes that determine the behavior and environmental fate of chiral agrochemicals. A large number of current use agrochemicals are chiral and their enantiomeric forms usually differ in their biological activities (Garrison, 2006), because they interact selectively with enzymes, receptors, or other (chiral) naturally occurring molecules (Garrison et al., 1996; Liu et al., 2009). Traditionally, chirality has not been contemplated when assessing the fate of pesticides and other agrochemicals in the environment (Wong, 2006); however, it is now widely accepted that chiral pesticide enantiomers can differ greatly in their toxicity to target and non-target organisms and in their environmental fate. Furthermore, environmental factors, such as soil type, pH, redox conditions, microbial populations, and agricultural practices, can alter the final enantioselective behavior of chiral pesticide enantiomers in soils (Buerge et al., 2003; Celis et al., 2015; Gámiz et al., 2013, 2016). Hence, all these parameters need to be considered and evaluated to optimize the use of chiral agrochemicals for crop protection.

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Different investigations have focused on the biological role of ABA and on how its activity can be used to improve the yield and/or quality of crops (Hussain et al., 2014; Li et al., 2010; Travaglia et al., 2010; Zhang and Dami, 2012). In contrast, there is very little published information on the fate of ABA once this compound has reached the soil, in particular concerning its possible enantiomer-selective behavior (Hartung et al., 1996). Natural levels of (*S*)-ABA in soils have been reported in the literature as ranging from 0.05 to 110 $\mu\text{g kg}^{-1}$ soil dry weight, but its use as a plant growth regulator can result in concentrations up to several thousand-fold greater than natural levels present in untreated soils (APVMA, 2010). Environmental toxicity tests have indicated that at such levels (*S*)-ABA could have toxic effects on aquatic plants and adverse effects on seedling emergence, survival, height, dry weight, or condition of several terrestrial plant species (APVMA, 2010; EFSA, 2013). In this regard, sorption, degradation, and mobility studies of ABA in soils are particularly lacking, even though these processes may determine the degree of exposure of target and non-target organisms and offsite movement of the compound to different environmental compartments.

In this work, we sought to get further information about the fate of ABA by assessing the sorption, persistence, and leaching behavior of its two enantiomers in three different agricultural soils. The information provided should be helpful for a better understanding of the environmental fate of ABA and for optimizing its use as a biopesticide for crop management.

2. Materials and methods

2.1. Abscisic acid and soils

Analytical standard grade racemic (*RS*)-ABA (chemical purity $\geq 98.5\%$) and enantiopure (*R*)-ABA (chemical purity $\geq 98.5\%$) were purchased from Sigma-Aldrich (Spain). (*RS*)-ABA was used in the incubation and leaching experiments, whereas (*R*)-ABA was employed to identify the elution order of the ABA enantiomers by HPLC. ABA is a weak acid with pK_a of 4.75 (Slovik et al., 1995), molecular weight of 264 g mol^{-1} , and water solubility of 3.2 g L^{-1} at 20 °C (PPDB, 2015). The structure of ABA enantiomers is shown in Fig. 1.

Three agricultural soils from Andalusia (Southern Spain) with markedly different physicochemical properties were used. All soils were sampled (0–20 cm soil layer), air-dried, sieved (2 mm mesh) and stored (4 °C) before used. The texture of the soils was determined by the hydrometer method (Gee and Bauder, 1986). The organic carbon and carbonate contents were determined by dichromate oxidation and the pressure calcimeter method, respectively (Nelson and Sommers, 1982; Nelson, 1982). Soil respiration was measured following the alkali trapping–titrimetric procedure described by Anderson (1982), by quantifying the amount of CO_2 released by the soils during 1 week under the same conditions as those used in the incubation experiments. The characteristics of the three soils are compiled in Table 1.

2.2. Incubation experiment

The sorption and dissipation of (*RS*)-ABA in soil was simultaneously studied by an incubation experiment. Portions of soil (200 g) were spiked with (*RS*)-ABA at a rate of 2 mg kg^{-1} dry soil by adding 8 mL of a 50 mg L^{-1} (*RS*)-ABA aqueous solution. The soils were thoroughly mixed with a spatula and then incubated in glass jars at 20 ± 2 °C in the dark for up to 8 days. The soil moisture content was adjusted and maintained at a constant level close to water content held by the soil columns used in the leaching experiment (see below) (40% for Soil 1 and Soil 3 and 30% for Soil 2) by adding deionized water as necessary. At times $t = 0.04, 0.25, 1, 1.25, 2, 3, 4$ and 8 days after treatment, the jars were opened and aerated, and aliquots of soil (3 g) were sampled in triplicate with a sterilized spatula and immediately frozen until analyzed. The total amounts of (*R*)-ABA and (*S*)-ABA in the soil samples were determined by extraction with 8 mL of a mixture (30:70) of acetonitrile:0.01 M H_3PO_4 aqueous solution ($\text{pH} = 2.2$), shaking during 24 h, followed by centrifugation, and enantioselective analysis of the supernatant solution by chiral HPLC. It was previously checked that this extraction procedure recovered more than 90% of the ABA enantiomers freshly added to the soils.

To assess sorption, 1 h and 24 h after spiking the soils with (*RS*)-ABA, the free amount of ABA enantiomers in the aqueous phase (C_e) was determined by sampling, in duplicate, 10 g of soil and removing an aliquot of the aqueous phase by centrifugation using Macrosep® Advance Centrifugal tubes (Pall Corporation) with polyethersulfone membranes (0.45 μm). The solution obtained after centrifugation was immediately analyzed by chiral HPLC to determine the aqueous concentration (C_e) of (*R*)-ABA and (*S*)-ABA.

2.3. Leaching experiment

The leaching of ABA enantiomers was studied in glass columns of 30 cm length \times 3.1 cm internal diameter hand-packed with air-dried soil. At the bottom of the column, glass wool and 10 g (5 cm) of sea sand were placed to prevent losses of soil during the experiment. The rest of the column was filled with soil (20 cm) and completed with additional sea sand (10 g) at the top of the column. The soil columns were saturated by adding 100 mL of distilled water to the top of the columns, and then allowed to drain for 24 h. The column pore volume (V_p) was determined as the amount of water (mL) held by the columns after saturation and 24 h-drainage. Next, 0.15 mg of (*RS*)-ABA (equivalent to the maximum agronomic application rate of 2 kg ha^{-1} established for ABA) was applied to the surface of the columns. Subsequently, 15 mL of distilled water was added daily to the top of the columns, and the leachates were collected in vials containing 5 mL of methanol and stored at 4 °C in the dark. A preliminary experiment indicated that the concentration of ABA enantiomers in aqueous soil extracts decreased during sample storage, but this effect could be completely suppressed by the addition of methanol as a sample stabilizer (Fig. S1). The individual concentrations

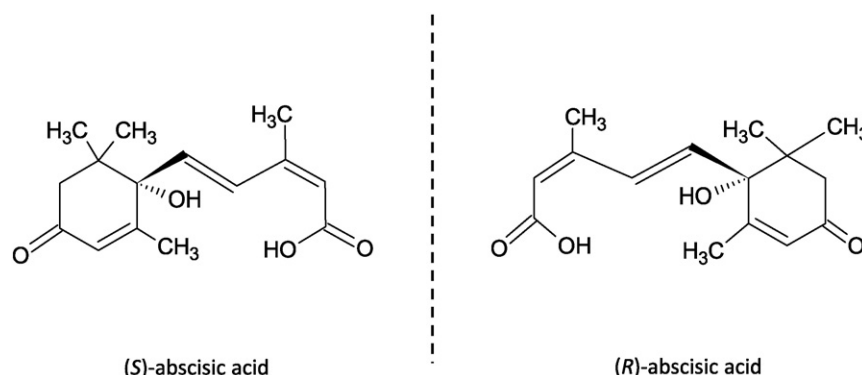


Fig. 1. Structures of (*S*)-abscisic acid and (*R*)-abscisic acid.

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