



Behavior of the enantiomers of the herbicide imazaquin in agricultural soils under different application regimes



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ABSTRACT

Sorption, persistence, and leaching of the enantiomers of the herbicide imazaquin, *S*-imazaquin and *R*-imazaquin, in two soils under different application regimes were studied. Imazaquin dissipation was evaluated after a single application of the racemic herbicide and the pure enantiomers, and after a repeated application of the racemic herbicide. The effects of adding two olive-mill wastes (ALP and ALPc), biochar (BC), and organoclay (SA-HDTMA) on sorption, dissipation, and leaching of imazaquin enantiomers applied as racemic herbicide to the soils was also evaluated. For all treatments, sorption, dissipation, and leaching of imazaquin in the soils were either non-enantioselective or scarcely enantioselective. No interconversion of *R*-imazaquin to *S*-imazaquin or vice-versa was observed in the experiments with the pure isomers. Addition of ALP, ALPc, or BC did not enhance the negligible sorption of imazaquin enantiomers by the soils, but accelerated their dissipation. Addition of SA-HDTMA increased sorption of both enantiomers and delayed their dissipation and leaching. The results illustrate how agricultural practices can impact the behavior of imazaquin enantiomers in soils and support the suitability of replacing currently used racemic formulations of imazaquin with formulations based on the single biologically-active (*R*) enantiomer to reduce the environmental impact of this chiral pesticide.

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1. Introduction

Imazaquin is an imidazolinone herbicide used at low rates to control a wide spectrum of weed species by inhibiting the enzyme acetohydroxyacid synthase, mainly in soybean crop, turf, and ornamentals (Tan et al., 2005). This pesticide has a chiral carbon in its structure, and consequently can exist as two enantiomers: *R*-imazaquin and *S*-imazaquin (Fig. 1). Even though it has been reported that the herbicidal activity of the *R* enantiomer is greater than that of the *S* enantiomer (Lao and Gan, 2005; Ramezani et al., 2010), imazaquin is marketed and used as formulations consisting of 1:1 mixtures of its enantiomers, i.e. as racemic mixtures. As a consequence, the toxicity of the non-active enantiomer to non-target organisms is a matter of concern.

Imazaquin is an amphoteric compound with several functional groups with acid-base character. Values of pKa are: pKa₁ = 1.8 (NH⁺), pKa₂ = 3.8 (COOH), and pKa₃ = 10.5 (NH) (Fig. S1) (Weber et al., 2003). Because of this structure, one of the most relevant factors in the sorption of imazaquin in soils is the pH. At common agricultural

soil pH levels (pH > 5), the anionic form of imazaquin predominates (Aichele and Penner, 2005; Lee et al., 1990), and repulsive interactions with soil colloids lead to low or negative sorption and high leaching potential (Che et al., 1992; Loux et al., 1989a; Porfiri et al., 2015; Regitano et al., 2000; Stougaard et al., 1990). Another important factor in imazaquin sorption on soil is the soil organic matter content. Che et al. (1992) suggested that imazethapyr and imazaquin have higher affinity for organic matter than for clay. Other soil characteristics that can influence imazaquin sorption and leaching are texture (Weber et al., 2003), water retention (Regitano et al., 2002), and iron and aluminum oxides contents, particularly in soils with low amount of organic matter (Gennari et al., 1998; Rocha et al., 2002).

An important feature of the behavior of imazaquin in soils is its relatively long persistence (Basham et al., 1987). Degradation of imazaquin in soils is mainly because of photodegradation and biodegradation. Imazaquin hydrolysis is also possible, but this degradation process appears to be very slow at pH < 9 compared with the other two aforementioned (Barkani et al., 2005; Ramezani et al., 2008). Biodegradation of imazaquin has been related to soil pH and soil organic matter. Aichele and Penner (2005) found that the degradation of imazaquin in soils at pH = 7 was slightly faster than that at pH = 5. This was attributed to a greater herbicide sorption at lower pH that meant less amount of herbicide available to be degraded. Only a few studies about the enantioselectivity of biodegradation process of imazaquin have been conducted. Jarman et al. (2005) concluded that the degradation of

Abbreviations: ALP, fresh olive-mill waste; ALPc, composted olive-mill waste; BC, biochar; Rac, racemic; SA-HDTMA, hexadecyltrimethylammonium-modified Arizona montmorillonite.

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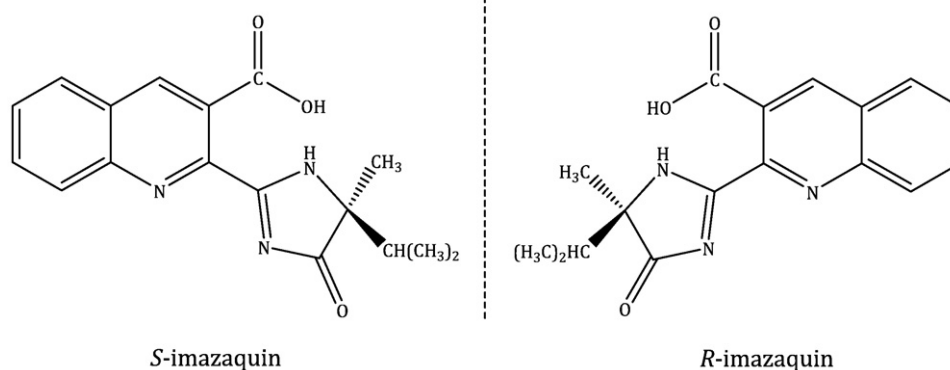


Fig. 1. Chemical structures of S-imazaquin and R-imazaquin.

imazaquin in aqueous soil slurries was non-enantioselective. Ramezani et al. (2010) found a slightly faster degradation of R-imazaquin compared to S-imazaquin in several Australian soils that presented a wide range of physico-chemical properties.

Several studies have evaluated the effects of organic amendments on the behavior of imazaquin in soils. Wang et al. (2007a) amended a sandy loam soil with farm litters and observed an increase in the degradation rate of imazaquin, which was attributed to the incorporation of new microbial population and a large quantity of nutrients. Undabeytia et al. (2004) added two organic amendments to four soils with different properties. The amendments generally led to a decrease in the sorption of imazaquin on the soils due to blocking of sorptive surfaces and equilibrium pH rises (Undabeytia et al., 2004). The effect depended on the nature of the organic amendment and the properties of the soils, such as pH, amount of organic matter, and amorphous iron oxide content. Clay materials, including pillared clays and organoclays, have also been studied as sorbents of imazaquin (Polubesova et al., 2002; Undabeytia et al., 2013). Park et al. (2014) developed a study using hexadecyltrimethylammonium-treated Arizona montmorillonite (SA-HDTMA) to remove imazaquin from aqueous solution and concluded that this organoclay was an excellent material to sorb imazaquin.

With very few exceptions (Jarman et al., 2005; Ramezani et al., 2010; Yi et al., 2007), previous studies on the behavior of imazaquin in soils did not explicitly account for the behavior of its individual enantiomers, treating the herbicide as if it was an achiral compound. However, considering the enantioselective behavior of chiral pesticides in the environment and possible differences between enantiomers is necessary to develop accurate environmental risk assessment, design successful remediation/prevention pollution strategies, and assess the suitability of using single (biologically-active) enantiomers for a more sustainable pesticide use (Celis et al., 2015; Gámiz et al., 2016; Magrans et al., 2002). In this work, we conducted an enantiomer-selective study to: i) evaluate the enantioselectivity of the sorption, dissipation, and leaching processes of imazaquin in two Mediterranean agricultural soils, ii) assess how the repeated application of the herbicide and its co-application with different soil amendments altered the individual behavior of imazaquin enantiomers, and iii) address the question of whether imazaquin enantiomers were configurationally stable in the soils.

2. Materials and methods

2.1. Herbicide

Imazaquin has a molecular weight of 331.3 g/mol, an aqueous solubility of 60 mg/L (25 °C), and a vapor pressure < 0.0013 mPa (60 °C) (Tomlin, 2006). Analytical standard-grade racemic-imazaquin (purity >99.9%) provided by Sigma-Aldrich (Spain) was used in this study.

Pure S-imazaquin and R-imazaquin aqueous solutions were obtained by semi-preparative HPLC using the same equipment and chromatographic conditions as those described in section 2.7, but with 0.001 M HCl:acetonitrile (60:40) as mobile phase instead of 0.01 M H₃PO₄:acetonitrile (60:40) to avoid the presence of the strongly competing phosphate anion in the purified enantiomer solutions. After injecting 50 µL of a 500 mg/L rac-imazaquin solution prepared in mobile phase into the HPLC analytical column, the peaks eluting at about 6.4 min (S-imazaquin) and 7.3 min (R-imazaquin) were collected and neutralized with 0.1 M NaOH to a pH ~ 6. Next, the acetonitrile was evaporated from the neutralized collected fractions using a gentle N₂ stream. The resulting aqueous solutions contained the individual enantiomers of imazaquin at a concentration of ~30 mg/L with an enantiomeric purity >99%.

2.2. Soils

Two agricultural soils from Seville (SW Spain) were collected (0–20 cm), air-dried, and then passed through a 2 mm sieve and stored at 4 °C. The selected soils had different texture and mineralogy, but presented similar alkaline pH values and low organic matter and Fe oxide contents. Soil 1 was a clay soil with 6% sand, 26% silt, 68% clay (20% montmorillonite, 38% illite, 10% kaolinite), 0.49% organic carbon, and a pH of 8.6. Soil 2 was a sandy loam soil with 74% sand, 6% silt, 20% clay (10% montmorillonite, 4% illite, 6% kaolinite), 0.50% organic carbon, and a pH of 8.3. The oxalate-extractable Fe₂O₃ content of both soils was <1%.

2.3. Amendments

Three organic amendments derived from the olive-oil processing industry were used. The first one was a fresh (uncomposted) solid byproduct, called “alperujo” (ALP), generated during the two-phase olive-oil extraction process. The second organic amendment was a stabilized alperujo (ALPc) which was obtained by subjecting a fresh ALP to a composting process for 5 months. Both amendments, ALP and ALPc, were ground, sieved (2 mm), and stored at 4 °C. The third organic amendment was a biochar (BC) that was made by heating ALPc at 400 °C for 4 h under a flow of N₂ at 1.5 L/min. The most important characteristics of ALP, ALPc, and BC are summarized in Table S1. The rate of ALP, ALPc and BC applied to the soils (2% w/w) was equivalent to 60 t/ha, considering a soil bulk density of 1.5 g/cm³ and a soil depth of 0–20 cm.

The fourth amendment used was hexadecyltrimethylammonium-saturated Arizona montmorillonite (SA-HDTMA) which was added to the soils at a rate of 2% or 5% (w/w). This organoclay was prepared by a cation exchange reaction according to Celis et al. (2007) and its characterization is detailed in Gámiz et al. (2015). It had 22.1% C, 1.26% N, and a basal spacing value of 2.25 nm, which indicated the successful

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