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Appraising factors governing sorption and dissipation of the monoterpene carvone in agricultural soils

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ABSTRACT

The use of monoterpenes as agrochemicals has been proposed, but the behavior of this family of compounds once they reach the soil environment has not been completely examined. In this work, we investigated the sorption of the two optical isomers of the monoterpene carvone, *R*-carvone and *S*-carvone, on different soils and model sorbents, as well as their dissipation in selected soils. Sorption was a non-enantioselective process; from racemic initial solutions, *R*-carvone was sorbed to the same extent as *S*-carvone. Correlations with soil properties indicated that organic matter was the most important component determining the sorption of carvone on the soils. Accordingly, higher sorption of carvone enantiomers was measured on organic model sorbent (humic acid, $K_d = 28\,L\,kg^{-1}$) compared to mineral model sorbents (kaolinite, illite, montmorillonite, ferrihydrite, $K_d < 6.3\,L\,kg^{-1}$). Desorption from the soils was hysteretic, most likely because of the rapid degradation of the enantiomers in the soils. Dissipation of carvone in soils was microbial mediated and enantioselective, with *S*-carvone being degraded faster than *R*-carvone. The individual enantiomer dissipation rates and enantioselectivity depended on soil characteristics, such as pH. The findings of this study constitute a base for the understanding of the fate of monoterpenes in soils and for further investigations on their applicability as environmentally friendly agrochemicals.

1. Introduction

Modern agriculture needs to face the growing global demand for food due to the increasing world population, which is expected to reach about 9 billion in 2050 (Gerwick and Sparks, 2014). To achieve a proper yield of crop production and pest control, the intensive use of synthetic pesticides has been essential until now (Sparks et al., 2017). However, numerous undesirable side effects are derived from pesticide use, mainly related to environmental impacts resulting from water and soil contamination episodes (Cordeau et al., 2016) along with gradual pest resistance (Gerwick and Sparks, 2014). For these reasons, the legislation is becoming more restrictive and claims for new, alternative management strategies (and products) in order to pursue an environmentally sustainable agriculture (Sparks et al., 2017).

Primary and secondary metabolites produced by living cells have inspired the development of natural product-based pesticides, and have been proposed as a source of new pest control agents (Duke et al., 2000; Sparks et al., 2017). Two examples of this are the herbicide mesotrione and the fungicide azoxystrobin, based on triketone and strobilurin compounds, respectively (Gerwick and Sparks, 2014). Nevertheless, the direct use of natural products for crop protection still requires more investigation and has not been fully explored. Natural products are usually very unstable to exert their action in the environment and their structures are usually more complex than those of synthetic pesticides, factors that should be overcome to commercialize them as agrochemicals (Duke et al., 2000). Hence, a major challenge in agricultural science is to search for the ideal pesticides, that would be economically affordable and have low environmental impact while ensuring consumer safety (Cordeau et al., 2016).

Allelochemicals comprise a group of natural compounds which are responsible for the stimulatory or inhibitory effects of one organism (plants, insects, microbes, etc.) upon the growth, health, behavior, or population biology of neighboring organisms (Zeng et al., 2008). Monoterpenes, foremost constituents of essential oils, are one of the most promising families of allelochemicals to be used for pest management (Van Roon et al., 2005), since insecticidal, fungicidal, and herbicidal properties have been described for them (He et al., 2009; Inderjit et al., 1997; Marei et al., 2012; Vokou et al., 2003; Zeng et al., 2008). As an example, the monoterpenes eugenol, geraniol and thymol are currently approved in Europe as active substances (a.s.) to control botrytis infection in grapes, at application rates up to 0.26 kg a.s. ha^{-1} per treatment (EU Pesticides Database, 2018).

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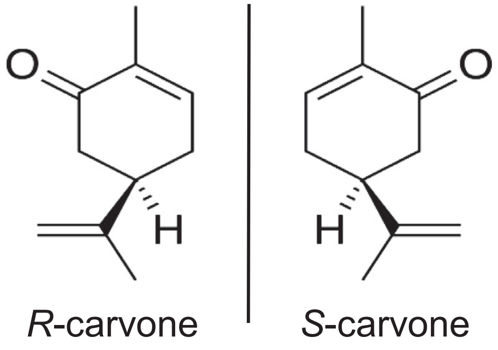

Fig. 1. Structures of *R*-carvone and *S*-carvone.

Carvone is a monoterpene which occurs naturally as two enantiomers, *S*-carvone and *R*-carvone (Fig. 1), and is a major constituent of the oils from caraway (S), gingergrass (both), and spearmint (R) (De Carvalho and Da Fonseca, 2006; EFSA, 2016). Both enantiomers have manifested striking pesticidal features, which potentially make carvone a target compound for being included as a new active ingredient in pesticide formulations. For example, Vokou et al. (2003) reported that both *R*- and *S*-carvone were extremely active in inhibiting seed germination of *Lactuca sativa*. Similarly, De Martino et al. (2010) found that *R*-carvone inhibited the radicle elongation for *Raphanus sativus* L. and *Lepidium sativum* L. Additionally, *R*-carvone has been shown to be effective against insects, and *S*-carvone as a fungistatic, bacteriostatic and potato sprout inhibiting compound (De Carvalho and Da Fonseca, 2006; Oosterhaven et al., 1995). In fact, the active substance *S*-carvone has already been authorized for use as a plant growth regulator (anti-sprouting agent) in Europe (EFSA, 2016), and *R*-carvone is registered as a biopesticidal active ingredient to be used in the manufacture of insect repellents in the United States (USEPA, 2009).

Recently, chirality has received progressive attention in the field of synthetic pesticides. The importance of enantiomers falls on the manifested selectivity in their responses, since one of the enantiomers usually reacts preferentially with the (chiral) host system to which it is exposed (Garrison, 2011). In addition, biodegradation of chiral pesticides is often an enantioselective process which will be influenced by soil composition, pH, redox conditions, and microbial populations (Buerge et al., 2003; Gámiz et al., 2017; Li et al., 2016; Matallo et al., 1998). In spite that abiotic processes, such as chemical distribution or transport processes, are often non-enantioselective, they can indirectly influence the relative abundance of one enantiomer over the other in the different environmental compartments by affecting biodegradation. It has been reported that sorption maintains enantiomer soil residues more racemic by reducing their bioavailability (Celis et al., 2013; Gámiz et al., 2016b) and even that sorption can turn into enantioselective when the starting initial pesticide solution is not racemic (Celis et al., 2015; Gámiz et al., 2016a). Consequently, the assessment of the enantioselective fate of chiral pesticides in various media has become an emerging area in agricultural and environmental science (Celis et al., 2015; Gámiz et al., 2016b; Li et al., 2016), which should be extrapolated to chiral allelochemicals such as carvone.

There is very little information regarding the fate of carvone in soils and even less concerning its possible enantiomer-selective behavior. Given that carvone can exit in nature as two enantiomers, both of them with pesticidal properties, its enantioselective behavior merits attention. In fact, few studies have addressed the enantiomer-selective behavior of natural compounds in soils. Gámiz et al. (2016b) found that the sorption of racemic abscisic acid (ABA) in soils was non-enantioselective and that ABA dissipation occurred with the natural *S*-enantiomer being degraded faster than the unnatural *R*-enantiomer. Likewise, the enantiomer dissipation rates were affected by amending the soil with organoclays and biochar (Gámiz et al., 2017).

The objective of this work was to provide insight into the behavior of the two enantiomers of the monoterpene carvone in agricultural soils. Correlations between sorption and soil properties were established and several model sorbents were used to ascertain the role of mineral and organic colloidal components in carvone sorption. The dissipation of carvone enantiomers in selected soils was also investigated. The information provided should be helpful to elucidate the behavior of this natural compound in soil and may also be valuable in the design of new carvone-based pesticide formulations intended for soil applications.

2. Materials and methods

2.1. Carvone, soils and model sorbents

Analytical standard-grade *S*-carvone and *R*-carvone with chemical purities of 98.5% and 99.9%, respectively, were purchased from Sigma-Aldrich (Spain). Carvone enantiomers are classified as monoterpenes with a molecular weight of 150.2 g mol^{-1}, a vapor pressure of 21.3 Pa at 25 °C, and a water solubility of 27 mg L^{-1} at 20 °C (BPDB, 2018). The racemic aqueous solutions of carvone (*RS*-carvone) used in this work (0.1–2 mg L^{-1}) were prepared by diluting a 200 mg L^{-1} (R + S) methanolic stock solution, which was made by adding 10 mg of each enantiomer to 100 mL of methanol.

Six agricultural soils (S1–S6) representative of Southern Spain were used in this study. Soil samples were collected from a 0–20 cm depth, air-dried, sieved to pass a 2 mm mesh, and stored at 4 °C. The soils were characterized by conventional methods described in the literature. The hydrometer method was used to determine soil texture (Gee and Bauder, 1986). The carbonate content was measured by the pressure calcimeter method and the organic carbon content by dichromate oxidation (Nelson, 1982; Nelson and Sommers, 1982). The amount of amorphous Fe-oxides was determined by extraction with oxalate (McKeague and Day, 1966). The phyllosilicate mineralogy was determined by X-ray diffraction analysis of oriented specimens of Mg^{2+}- and K^{+}-saturated soil clay (< 2 μm) samples, solvated with ethylene glycol and calcined at 550 °C, respectively (Brown, 1961). Soil pH values were measured in 1:2.5 soil:water slurries. The main physicochemical properties determined are compiled in Table 1. It is remarkable that the soils had relatively low organic carbon (OC) contents, as typical of Mediterranean soils (Gámiz et al., 2012), low amorphous Fe-oxide contents (< 1%, not shown), and variable clay contents and mineralogies. Additional details on the soils used are given in Supplementary Table S1.

Several model sorbents were chosen to assess the importance of soil constituents in the sorption of carvone: three reference phyllosilicates (kaolinite, illite and montmorillonite), a poorly crystallized Fe-oxyhydroxide (ferrihydrite), and a commercial humic acid (HA). The

Table 1
Selected properties of the soils used in this work.

Soil	Texture	Sand (%)	Silt (%)	Clay (%) (M, I, K)[a]	$CaCO_3$ (%)	OC (%)	pH
S1	Loamy sand	89	5	5 (2, 2, 1)	5.9	0.27	8.3
S2	Sandy loam	75	9	17 (9, 3, 5)	1.9	0.63	7.3
S3	Clay	26	32	41 (0, 36, 5)	1.0	1.06	8.6
S4	Loam	50	29	21 (11, 4, 6)	32.5	1.17	8.3
S5	Sandy loam	68	23	8 (0, 4, 4)	0.8	1.23	5.4
S6	Clay loam	22	51	27 (17, 9, 1)	24.0	1.37	8.3

[a] Percentage corresponding to montmorillonite (M), illite (I), and kaolinite (K).