Environmental Fate of Chiral Pesticides in Soils

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Abstract Chirality has received progressive attention in the field of pesticides. Enantiomers of chiral pesticides have identical physicochemical properties but, commonly, they exhibit stereoselective response with chiral host systems and, therefore, enantioselectivity against the target pest. Despite this, approximately 30% of the pesticides in current use are formulated as mixtures of enantiomers or racemic mixtures. This has engendered new environmental problems, which demand exhaustive knowledge regarding the enantioselectivity of the processes that chiral pesticides may undergo in the soil environment. Changes in the enantiomer composition of chiral pesticides are caused mainly by biological interactions and, consequently, factors affecting the biodegradation of pesticides can also alter the

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enantioselectivity of the biotransformation of chiral pesticides in soils. Accordingly, soil parameters such as pH, redox conditions, texture, or agronomic practices have been reported to indirectly influence the final enantioselective behavior of these pesticides in soils, although there is limited knowledge in this regard. Hence, predicting the environmental behavior of chiral pesticides in soil turns challenging. This chapter summarizes the most recent enantioselective studies on chiral pesticide transfer and transformation processes in soils. Future research needs scientific foundations to establish under which agricultural and environmental conditions it is appropriate to replace racemic chiral pesticide mixtures with the biologically active purified enantiomers, the underlying mechanisms of enantioselective interactions, and the relationships between the soil microbial diversity and the biotransformation of chiral pesticides, which remain largely unknown.

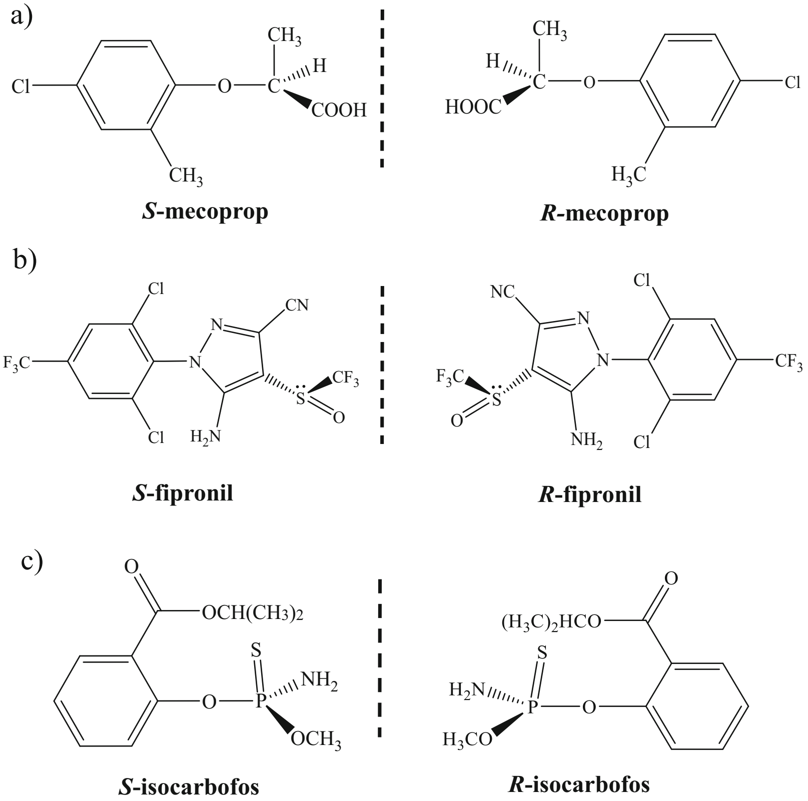
Keywords Chiral signature, Enantiomeric fraction, Enantiomers, Enantioselective behavior, Enantioselective degradation, Soil

1 Introduction

The search for new agrochemicals with higher specificity and efficiency for the control of weeds and pests in crops has led to the development of pesticides with increasingly complex structures, many of them chiral [1, 2]. Chiral pesticides have at least one asymmetric center in their structure that results in two enantiomeric forms (optical isomers or enantiomers), which are non-superimposable mirror images of each other [1]. Usually, the asymmetric or chiral center is a carbon atom attached to four different substituents, although chirality can also arise from the presence of asymmetric phosphorus or sulfur atoms [3] (Fig. 1).

The most accepted system to name the configuration of an asymmetric center is the Cahn-Ingold-Prelog convention that assigns a letter R or S to each center depending on the spatial distribution of its substituents. If this absolute configuration is unknown, then (+) and (−) prefixes, according to their interaction with plane-polarized light, can be used to name the enantiomers [4]. It should be noted that there is no universal relationship between the absolute configuration (R or S) and the direction (+ or −) in which the enantiomers rotate plane-polarized light, which can even change depending on the solvent used [5].

Unlike other types of stereoisomers, the enantiomers of a chiral compound have identical physicochemical properties in achiral environments. Nevertheless, enantiomers may differ in their behavior in chiral environments, either in the presence of a physical chiral medium, such as the plane-polarized light, or a chemical chiral one, such as solvents, reagents, or catalyzers [6, 7]. The soil offers a great chiral medium due to the presence of microorganisms, enzymes, and other chiral constituents. Thus, the behavior and fate of the enantiomers of a chiral pesticide in soil can differ, since the transfer and transformation processes that chiral pesticides undergo in soil may be enantioselective. To assess the enantioselectivity of these processes, the



***S*-mecoprop** ***R*-mecoprop**

***S*-fipronil** ***R*-fipronil**

***S*-isocarbofos** ***R*-isocarbofos**

Fig. 1 Examples of chiral pesticides whose asymmetric centers are C (**a**), S (**b**), and P (**c**) atoms

abundance of one enantiomer (E1) is compared with the other (E2) by determining the enantiomeric fraction, and its changes, according to the expression $EF = E1/(E1 + E2)$. EF values range from 0 to 1, with $EF = 0.5$ representing a racemic mixture and $EF \neq 0.5$ representing the predominance of one enantiomer over the other [8].

Many studies have reported that the effect of enantiomers on target and non-target organisms is usually different [9]. In most cases, only one of the enantiomers (active enantiomer) of a chiral pesticide is responsible for the biological activity against the target pest, as the molecular objective of the pesticide is usually an enzyme or a biological receptor whose active center is also chiral [10]. On the other hand, the behavior and final fate of inactive enantiomers are usually unknown. Consequently, the application of racemic mixtures of pesticides implies the addition of a substance without real functionality that could overload the self-recovery capacity of soils and affect non-target organisms. Therefore, the application of pure enantiomer formulations of chiral pesticides to fields is a green practice to consider in pest control [7]. Among the benefits of using the active enantiomer over the racemic mixture, besides reduction of environmental damage and ecological risk, is the reduction of

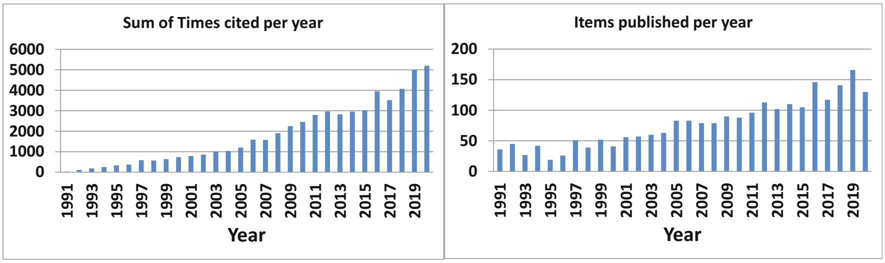


Fig. 2 Items published and sum of times cited to them on chiral pesticides per year. Source: ISI Web of Knowledge, Web of Science-Citation Report, April 2021. Search criteria: "chiral" and "pesticide"

application doses [3, 7], which means an increase in the profitability and the safety of the pesticide applicator. However, it is estimated that pesticide formulations consisting of pure enantiomers represent only 7% of the current pesticide market [11, 12]. This predominance in the use of racemic mixtures is in part due to the expenses associated with the production and/or purification processes, which makes their commercialization less profitable [2, 12]. However, currently, several methods are available to prepare chiral pesticides with sufficient efficiency to be produced at an industrial scale [2, 7].

The first studies about the enantioselective behavior of chiral pesticides go back to the 90's decade, although the interest in this kind of compounds has increased in recent years due to the unique environmental consequences associated with their use (Fig. 2). Currently, the application of chiral pesticides for pest control in the agro-industry is widespread all over the world [7]. It is estimated that approximately 30% of the active ingredients registered nowadays are commercialized as racemic mixtures of the enantiomers of these pesticides [2, 13, 14] and that more than 40% of the insecticides and herbicides used in China are chiral [9]. In addition, since 2015, a great development of chiral pesticides has been observed, a trend that seems to carry on [2].

The authorities have been more aware of the necessity of performing exhaustive studies on the possible enantioselectivity in the behavior and final fate of chiral pesticides in the environment, and even of recommending, in some cases, the use of the pure active enantiomer [15]. In fact, based on the different bioactivity of the enantiomers, several countries have taken action. For instance, the Dutch and Swiss authorities revoked the licenses for the use of racemic mixtures of chiral phenoxyalkanoic acids while the registration of products with the pure active isomer was approved. Another example is Sweden, where a tax as a function of the weight of chiral active ingredient was implemented [9]. Moreover, at the European level, regulation No. 1107/2009 [16] requires specifying the identity and content of isomers/diastereoisomers of the newly registered plant protection products and classifies those that contain a significant proportion of inactive isomers as candidate substances to be substituted. Based on this regulation and at the request of the European Commission, the European Food Safety Agency (EFSA) developed an

EFSA guidance on risk assessments for active substances in plant protection products that contain stereoisomers as components or impurities, or for transformation products of active substances which may have stereoisomers [17]. In the case of the USA, the Environmental Protection Agency (EPA) has issued an interim policy on the reevaluation of chiral pesticides for their replacement by pure enantiomers [18]. These international authorities (EFSA and EPA) have pointed out the lack of information on the stereoisomer-specific behavior of chiral active substances and have expressed their concern on how this ignorance could affect their risk assessment. For this reason, an exhaustive evaluation of the possible enantioselective behavior of chiral pesticides in soils is crucial. In this chapter, recent findings on the enantioselectivity of the main transfer and transformation processes to which pesticides are subjected in soil and their implications on the effects of chiral pesticides on target and non-target organisms are summarized.

2 Sorption of Chiral Pesticides in Soils

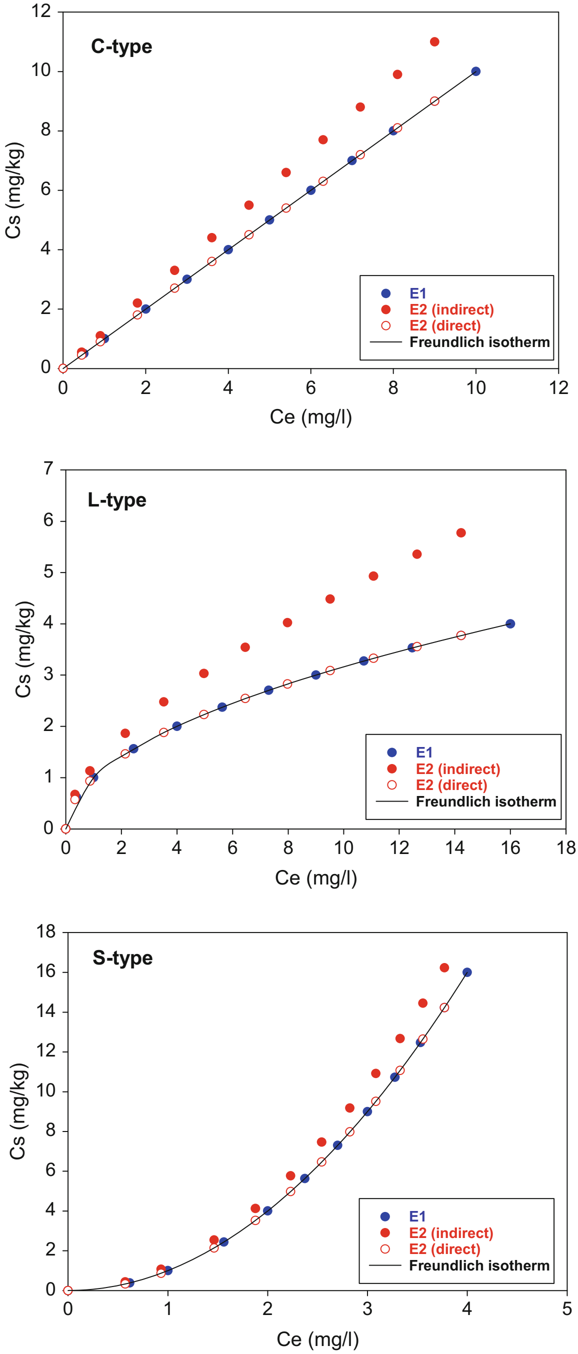
Sorption is a key process dictating the final fate of pesticides in soils, since it reduces the fraction of the pesticide available to be transported to deeper soil layers or to be degraded, while desorption causes the opposite effect. Because of the identical physicochemical properties of enantiomers, it is generally assumed that abiotic environmental processes, including sorption, are non-enantioselective [19]. If enantioselective soil sorption took place, other soil processes, such as leaching, runoff, or volatilization, would be altered, with the subsequent contribution to the prevalence of one enantiomer over the other in the various environmental compartments (e.g., soil, water, and air samples).

Sorption enantioselectivity requires the existence of a chiral soil environment, which is presumed possible since soils present chiral minerals and organic matter chiral regions with the potential of changing the chiral signatures of pesticide residues [20]. This link, however, has not been unequivocally proven, and the demonstration of the occurrence of enantioselective sorption in natural soils is still challenging [21–23]. Several reasons can explain the apparent difficulty to obtain such evidence. Achiral soil surfaces, for example, can be more abundant than chiral ones and hamper the observation of enantioselective sorption, which is difficult to observe under conventional batch sorption experiments [21, 22]. Furthermore, although different chiral sorption sites in soil may indeed be enantiomer-selective and cause enantioselective sorption at the local or microscale, because of the heterogeneity of soils, differences may be compensated at the global scale, resulting in an apparent lack of enantioselectivity [22, 23]. Hence, when sorption is measured by batch equilibration procedures at the macroscopic level, it is not projected that the interactions between the soil components and chiral pesticides in the soil solution are selective enough to discriminate between enantiomers [17, 21]. In this line, many studies have observed lack of sorption enantioselectivity in soils for chiral pesticides such as metalaxyl [24–28], benalaxyl and furalaxyl [29], tebuconazole [30], imazaquin [31], as well as for chiral natural compounds with the potential to be used as biopesticides, such as abscisic acid [32, 33] or carvone [34, 35]. Some of these studies also found that the lack of enantioselectivity remained after soil modification with different types of inorganic and organic amendments [26–28, 31, 35].

A less studied situation occurs when the chiral pesticide exists in the soil in a non-racemic form. This situation can arise when a particular chiral pesticide is applied as an enantiomer-enriched active ingredient or because of enantioselective biodegradation, as will be discussed in the next section. An enantiomer-enriched solution implies that the initial EF value of the pesticide differs from 0.5. In this regard, some investigations have aimed to establish whether enantioselective sorption can occur in soils from non-racemic pesticide enantiomer mixtures [36]. Hall [36] compared the sorption of racemic metalaxyl and metalaxyl-M (the R-enantiomer-enriched product of the fungicide metalaxyl) on bentonite and montmorillonite. Her experiments revealed that sorption of R-metalaxyl was higher than that of racemic metalaxyl on both sorbents, and it was proposed that enantioselective sorption of R-metalaxyl could have occurred. Subsequent investigations performed by Celis et al. [21] attempted to get additional insight into the possibility of the occurrence of enantioselective sorption of metalaxyl in soil using racemic and non-racemic initial solutions. The authors found that metalaxyl sorption in soil occurred enantioselectively when initial aqueous solutions enriched in R-enantiomer were used. Considering the shape of the sorption isotherms (S-type), it was proposed that metalaxyl solutions enriched in R-enantiomer could have induced an enantioselective sorption behavior whereby the R-metalaxyl enantiomer was preferentially sorbed over the S-enantiomer, probably at soil clay mineral surfaces, due to homochiral R-R interactions in the sorbed state being more favorable than heterochiral R-S interactions. This effect would lead to greater sorption of metalaxyl-M (R-enriched) compared to racemic metalaxyl (R + S) [21]. In addition, the mechanism was considered compatible with the absence of enantioselectivity observed for the sorption of metalaxyl in soil from racemic initial solutions and with previously reported differences between racemic metalaxyl and metalaxyl-M in their sorption to mineral samples [36].

An important experimental artifact that can influence the identification of the sorption enantioselectivity may arise from the preferential biodegradation of one enantiomer over the other during the sorption measurement. In the traditional batch equilibration technique, the amount of compound sorbed is commonly determined by calculating the difference between the amount initially added and that remaining in solution after equilibration. Consequently, the preferential biodegradation of one enantiomer over the other during the sorption measurement could be erroneously interpreted as enantioselective sorption. The relevance of this artifact is illustrated in Fig. 3, which represents the sorption isotherms for two enantiomers (E1 and E2) sorbed from individual enantiomer solutions in a hypothetical situation in which E1 was not biodegraded during the sorption experiment, whereas 10% of the initial amount of E2 was lost by biodegradation. The isotherms of the enantiomers were assumed to follow the Freundlich model with C-shape ($K_f = 1$; $1/n_f = 1$), L-shape ($K_f = 1$; $1/n_f = 0.5$), or S-shape ($K_f = 1$; $1/n_f = 2$), coinciding with the sorption

Fig. 3 Hypothetical sorption isotherms (C, L or S-type) separately obtained for two enantiomers (E1 and E2) which followed the Freundlich model where 10% of the initial amount of E2 is biodegraded during the sorption experiment. For E2, sorption points that would result after applying an indirect (solid symbols) or direct (open symbols) methodology to measure the sorbed amounts are shown. The solid line represents the actual Freundlich isotherm for the enantiomers ($C_s = K_f C_e^{1/nf}$). Calculations were performed assuming the following parameters: $K_f = 1$; $1/n_f = 1$ (C-type), 0.5 (L-type) or 2 (S-type); soil to solution ratio of 1:1; range of initial enantiomer concentrations of 0–20 mg/l



points expected for the enantiomer that is not biodegraded during the sorption experiment (E1). The sorbed amounts of E2, however, were assumed to be calculated either indirectly, analyzing the amount of enantiomer remaining in solution, or directly, by extracting the enantiomer actually sorbed. The sorption points for E2 will vary depending on the methodology used to determine the sorbed amount. While the direct methodology will accurately provide the actual amounts of E2 sorbed, following the same isotherm pathway as that of E1, the indirect methodology would lead to overestimating sorption of E2 and misinterpreting sorption as an enantiomer-selective process (E2 > E1). Similar experimental artifacts can arise from inaccuracy in the analytical determination of the enantiomers or because of enantiomer interconversion (enantiomerization) during sorption measurement [22], which should thus be discarded for a correct characterization of sorption enantioselectivity.

Experimental artifacts can also affect desorption experiments. Gámiz et al. [37] observed that biodegradation of R-metalaxyl during desorption from a Mediterranean soil resulted in artificially enhanced hysteresis of this enantiomer in non-sterilized soil. Sorption-desorption hysteresis and its enantioselectivity disappeared after autoclaving the soil to minimize microbial activity. It should be taken into account that the measurement of desorption requires longer shaking times and sample manipulation, which increases the risk of interferences by microbial degradation, even when using pre-sterilized soil samples.

Degradation during the sorption-desorption measurement has traditionally been described as a possible cause of hysteresis [38], but it may become particularly relevant when dealing with natural compounds, which are usually very rapidly biodegraded in soils [39]. Gámiz et al. [34], for example, observed hysteresis in the sorption-desorption of the monoterpene carvone in a pre-autoclaved sandy loam soil, obtaining thermodynamic indexes of irreversibility (TII), as hysteresis descriptors, of 0.38 for R-carvone and 0.65 for S-carvone. These values indicated that hysteresis was enantiomer-selective. An analysis of the sorption-desorption isotherms revealed that the hysteresis for S-carvone was particularly enhanced in the last desorption steps. The authors showed that assuming a total degradation of 10% during desorption was sufficient to explain the observed hysteresis for S-carvone [34].

3 Transformation of Chiral Pesticides in Soils

Enantioselective studies of pesticide degradation routes are important to accurately determine the residues of a particular chiral pesticide, control the contamination problems derived from its use, as well as to determine potential risks of enantiomeric residues to non-target organisms and their final presence in the food chain [17]. As in the case of achiral compounds, the transformation of chiral pesticides in soils can occur through biotic or abiotic pathways [40] and will be affected by factors such as the soil composition and texture, pH, redox conditions, and microbial populations

[24, 34, 41–46]. An additional process that may operate for chiral pesticides is enantiomer interconversion or enantiomerization [47]. Variations in enantiomer fractions should particularly be considered in the transformation of chiral pesticides in soils.

3.1 Abiotic Degradation of Chiral Pesticides

The abiotic transformation of chiral pesticides in soils mainly includes photolysis, hydrolysis, and oxidation/reduction reactions. Generally, abiotic reactions are not enantioselective, and consequently, no significant differences in the enantiomers degradation rate are detected [48]. Nevertheless, discerning the relative importance of abiotic against biotic dissipation processes can be difficult. For instance, the main degradation pathway described for metalaxyl in soils has been reported to be its microbial/enzymatic transformation, implying enantioselectivity in the process [24, 27, 42, 49]. However, Liang et al. [50] showed that, although biotransformation was indeed the predominant pathway for the elimination of R-metalaxyl in soil, both abiotic and biotransformation contribute to the degradation of S-metalaxyl. In the same line, the dissipation of the herbicide imazamox in soil involved both biodegradation and photodegradation [51], and the degradation of zoxamide occurred through hydrolysis and biodegradation [52]. Several mechanisms can thus simultaneously operate in the transformation of chiral pesticides in soils, which may hinder the identification of reactions specifically responsible for enantioselectivity.

3.2 Biotransformation of Chiral Pesticides

The biotransformation of chiral pesticides in the soil arises from the action of enzymes or biological receptors from different microorganisms [10]. The active centers of these macromolecules are usually chiral, whereby, despite the chemical similarity of the enantiomers of a chiral pesticide, the strength of the active center-enantiomer association is usually different. This is the main reason why the biotransformation of chiral pesticides can be enantioselective and why the enantiomers may have different bioactivity and toxicity on target and non-target organisms. Enantioselective biotransformation processes, which play a major role in determining the chiral signatures or enantiomeric fractions of chiral pesticides in the environment [14, 53, 54], can be produced by the following ways described by Müller and Kohler [55]:

1. Two enantioselective enzymes, each one transforming only one enantiomer.
2. Both enantiomers are transformed by the same enzyme at different rates.

3. One enzyme transforms sequentially both enantiomers, i.e., the enzyme initially converts one enantiomer and eventually the other, but only when the former has been completely transformed.
4. Transformation of one enantiomer by one enzyme and isomerization of the other by an isomerase.

3.2.1 Factors Affecting the Biotransformation of Chiral Pesticides in Soils

Data on the factors influencing enantioselective dissipation processes are essential to optimize the bioefficacy of chiral pesticides while preserving environmental safety. In general, soil parameters that influence the enantioselective transformation of chiral pesticides in soils are not fully understood [42, 53], as the biotransformation of chiral pesticides in soils is not always necessarily enantioselective. For example, the herbicide imazaquin, under alkaline and aerobic conditions, did not display changes in the enantiomer fraction during its dissipation in two Mediterranean soils [31]. Analogously, little enantioselectivity was observed in the degradation of the fungicide tebuconazole in soil, with enantiomeric fractions ranging between 0.452 and 0.475 after 180 days of incubation in seven soils under aerobic conditions [56]. Also for tebuconazole, Wang et al. [57] obtained EF values ranging from 0.474 to 0.481 in three soils with different characteristics. Likewise, in an investigation of the dissipation of the fungicide benalaxyl in six different soils, R-benalaxyl dissipated faster than S-benalaxyl in three of the studied soils, whereas the transformation of the fungicide was non-enantioselective for the rest of the soils [29]. In the same work, furalaxyl transformation was also assessed, and similar results were obtained. Different microorganisms present in the soils, together with different physicochemical characteristics and sorption behavior, were identified as the key factors modifying the enantioselectivity of the process [29]. The biotransformation of the chiral insecticide fluxametamide in soil under field conditions was also non-enantioselective [58]. These results are in contrast with other data found in the literature where the biotransformation of chiral pesticides in soils was markedly enantioselective [24, 42, 43, 46, 59, 60]. Differences in the enantioselective biotransformation of chiral pesticides in different soils may depend on the different microbial communities or enzyme levels according to soil properties and locations, variables which should be addressed to characterize the final fate of chiral pesticides in soil [24, 61]. Several important factors that can affect the biotransformation of chiral pesticides in the soil are discussed below (Fig. 4).

Sorption Although sorption is commonly considered a non-enantioselective process, it has been demonstrated that it can indirectly affect the enantioselective biotransformation of chiral pesticides through its influence on their availability to soil microbial degraders. As indicated above, sorption is the main factor controlling the bioavailability and the bioaccessibility of pesticides [62–64]. This became apparent when the environmental behavior of metalaxyl was evaluated in three

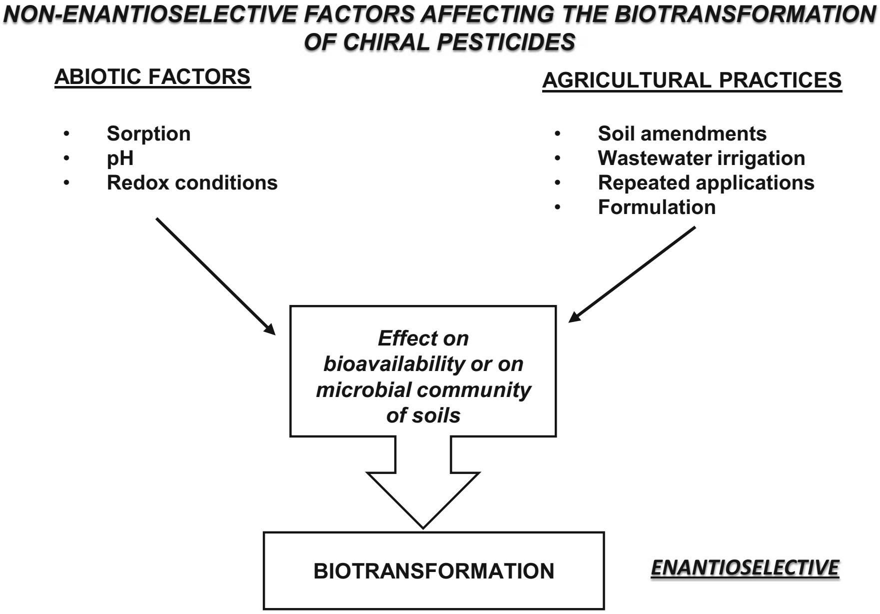


Fig. 4 Factors affecting the biotransformation of chiral pesticides in soils

slightly alkaline soils [24]. R-metalaxyl was preferentially degraded compared to S-metalaxyl in all soils, but the extent of the enantioselective biotransformation of metalaxyl was soil dependent, with the fraction of S-enantiomer in coarse-textured soils achieving greater values than those in fine-clayed soil. The greater sorption observed for metalaxyl in the soil with high clay content reduced the availability of both enantiomers, restraining their biotransformation compared to the coarse texture soils. The authors endorsed the protection of the chiral pesticide to sorption and entrapment in small-size pores, which resulted in longer persistence and more racemic metalaxyl residues in soil [24]. The indirect effect of sorption on the enantioselective biotransformation of chiral pesticides was also observed for the degradation of racemic abscisic acid in soils. Greater persistence and less variation in the enantiomeric fraction were detected in the soil with greater affinity for this acid [32]. Apart from sorption, the participation of soil-specific microorganisms in the biodegradation process could have also contributed to these results [32].

pH The pH has been demonstrated to modify the biotransformation of chiral pesticides in soils [42]. For example, the biotransformation of the herbicide beflubutamid was only slightly enantioselective in alkaline soil, with slower degradation of the bioactive-enantiomer, while the process was more enantioselective in acidic soil [65]. Remarkably, the metabolite of beflubutamid, phenoxybutamide, was also enantioselectively biodegraded in both soils, and interconversion between the enantiomers of the metabolite was observed [65]. Soil pH also altered the enantiomeric fraction of imazethapyr during its transformation under aerobic conditions [66]. In all soils tested, R-imazethapyr degraded faster than S-imazethapyr, with the extent in enantioselectivity (i.e., EF of imazethapyr residues) being soil pH-dependent. The authors attributed this observation to the low sorption and high bioavailability of imazethapyr at greater pH of the soils [66]. Variable behavior was observed for the herbicide imazamox during incubation experiments using soils with different pH, ranging from acidic to neutral. For soils with pH >6.5, the (+)-enantiomer was degraded faster than the (−)-enantiomer, whereas differences between enantiomers were not appreciable in slightly acidic soils. Furthermore, a change in the preferential degradation of the enantiomers occurred in strongly acidic soils [61]. Since biphasic degradation of imazamox enantiomers was detected in all cases, the changes in the transformation of imazamox in soils appeared to be microbial-mediated and dependent on the bioavailability of the herbicide, which has been described to decrease due to nonlinear and time-dependent sorption [61]. Further evidence that the effect of pH on the soil microbial population can modify the enantioselectivity of chiral compounds was observed in the dissipation of the natural compound carvone [34]. The biotransformation of the racemic mixture of carvone in slightly alkaline soil (pH 7.3) occurred very fast, with the S-enantiomer being degraded more rapidly than the R-enantiomer. By acidifying the same soil with HCl to a pH of 5.5, the dissipation of carvone became slower and scarcely enantioselective, with EF values of carvone residues close to 0.5 [34]. Given that the extent of sorption was similar in the pristine and acid-treated soil, the striking behavior was attributed to alterations in the soil microbial activity produced by the change in soil pH [34].

Redox Conditions Redox conditions represent an important parameter influencing the dissipation of chiral pesticides. In an incubation experiment using soil samples taken from 3 to 6 m soil-depth, the preferential degradation of the R-enantiomer of the phenoxyacetic acid herbicide mecoprop (MCPP) was observed under aerobic conditions and at environmentally relevant herbicide concentrations, whereas under anaerobic environments and higher MCPP concentration (mM) the prevalence in the degradation of S-MCPP was observed [67]. The authors found the existence of three types of microbial communities acting primarily depending on environmental conditions [67]. In another study, S-zoxamide was degraded faster than R-zoxamide under aerobic conditions, leading to an enrichment of the bioactive (R) enantiomer in the three types of soils studied, whereas, in an anoxic environment, differences in the degradation rates of S- and R-zoxamide were negligible. Aerobic microorganisms thus appeared to have dictated the biotransformation of zoxamide in an enantioselective manner in contrast to anaerobic microorganisms [52].

Agricultural Practices Agricultural practices and different application regimes of chiral pesticides can influence the availability of the enantiomers and also the nature and activity of the soil microbial population [28, 30, 37, 43, 68]. Furthermore, with the progress of modern agriculture, many novel additives, such as nanoparticles or nanoengineered materials, can reach the soil with consequences on the transformation and transport of chiral pesticides difficult to predict [35, 50].

One of the most extended agricultural practices is the application of organic amendments to improve the fertility of soils by increasing their organic matter and nutrient content. Organic amendments can trigger changes in the microbial activity

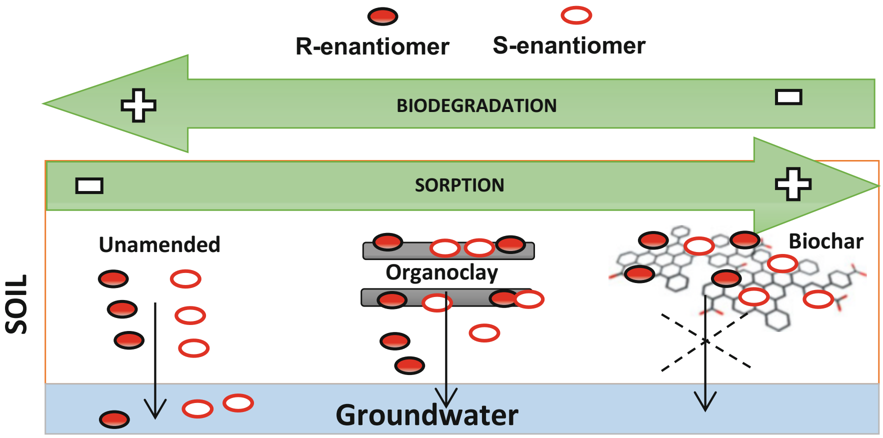


Fig. 5 Conceptual model of the effect of the addition of organic and nanoengineered sorbents to soil on the fate of chiral pesticides

of soils and, as a side effect, the sorption capacity of soils towards pesticides can be also modified [69–73]. Consequently, the enantioselectivity of the biotransformation of chiral pesticides can be influenced by changes in the microbial population, the bioavailability of the pesticide, or both (Fig. 5).

Soil incubation of racemic metalaxyl in unamended soil and in soil amended with olive-mill waste (OMW) resulted in different transformation patterns for the R- and S-metalaxyl enantiomers [28]. In unamended soil, the biotransformation of metalaxyl was highly enantioselective, with the biologically active enantiomer, R-metalaxyl, being preferentially degraded in comparison with S-metalaxyl. At the end of the experiment, the fraction of S-metalaxyl residues reached a value of 0.85. In OMW-amended soil, however, the biotransformation of metalaxyl showed little enantioselectivity and the fraction of S-enantiomer reached the value of 0.53. The organic waste increased the persistence of (active) R-metalaxyl and decreased the persistence of (non-active) S-metalaxyl [28]. Because OMW did not change the sorption capacity of the soil towards metalaxyl enantiomers, the effect of OMW was assigned to a change in the soil microbial population or in the activity of specific microbial degraders, as it had been previously suggested for the transformation of the chiral pesticide mecoprop in peat amended soil [74].

Recently, there has been a growing interest in the evaluation of nanoengineered materials, such as biochar, as amendments and mitigating tool to reduce the environmental impact of pesticides [75], but only a few works have addressed their effects on the enantioselective behavior of chiral pesticides when applied to soils [27, 30, 31, 37, 76]. Gámiz et al. [37] compared the enantioselective behavior of racemic metalaxyl in unamended soil and soil amended with composted olive-mill waste (OMWc) and its biochar. The biotransformation of metalaxyl was less enantioselective in biochar-amended soil, followed by OMWc-amended soil and unamended soil. This was attributed to an increase in the persistence of both metalaxyl enantiomers after the addition of biochar to the soil, caused by greater sorption and higher resistance of metalaxyl enantiomers to be desorbed, which maintained metalaxyl residues more racemic in the presence of biochar. The effect was in agreement with previous works describing the indirect effect of sorption on the availability of chiral pesticides in soils, although changes in the soil microbial activity could not be ruled out. The same trend was observed by López-Cabeza et al. [27], who compared the dissipation of racemic metalaxyl in soils amended with fresh olive-mill waste, composted olive-mill waste, and nanostructured elaidate-modified layered double hydroxide. They found that the amended soils with elaidate-modified layered double hydroxide displayed greater sorption of metalaxyl as compared to the rest of the amendments, which reduced the bioavailability of the enantiomers and maintained metalaxyl residues more racemic in the soils. A lower dissipation rate of metalaxyl enantiomers after the addition of woodchip biochar to a Chinese soil was also observed by You et al. [76]. In this work, although the preferential dissipation of the S-enantiomer as compared to the R-enantiomer occurred, the transformation was less enantioselective due to the indirect effect of metalaxyl sorption in biochar-amended soil. Interestingly, the reduction in the bioavailability of metalaxyl enantiomers led to a greater concentration of fungicide enantiomers in soil but triggered lower concentrations of R and S in the roots as compared to unamended soil. The authors also obtained calculated EF <0.5 indicating preferential accumulation of R-metalaxyl in the lettuce roots [76].

The addition of nanoengineered materials has also been proposed to increase the persistence of enantiomers of natural compounds with the potential to be used as biopesticides, such as abscisic acid (ABA) and carvone [33, 35]. The dissipation of both compounds was assessed in unamended soil and in soil amended with biochar and organically-modified bentonites. The dissipation of ABA mainly elapsed via biodegradation. Besides, the naturally occurring enantiomer S-ABA was always degraded faster than R-ABA (non-natural) in all treatments, and the enantioselectivity of ABA degradation was more pronounced in unamended soil compared to amended soils [33]. Sorption was determined in this work during the incubation experiment and a loss of sorption capacity of the organoclay-amended soil was observed in contrast to progressive sorption in biochar-amended soil, leading to more racemic residues in this latter case. Two different sorption mechanisms were described which explain this different behavior, i.e., surface sorption mechanisms for organoclays and slow (potentially pore filling) kinetics in biochar-amended soil [33]. A similar trend was observed for the dissipation of the monoterpene carvone in unamended soil and soil amended with organoclay and biochar [35]. Although S-carvone was preferentially degraded in all treatments, the greater sorption promoted by the addition of the amendments caused an increase in the half-lives of both enantiomers. The effect was more pronounced for biochar-amended soil, and the authors indicated that the bioavailability of carvone was dictated not only by the extent of sorption but also by the facility of the enantiomers to be desorbed, which was more limited in biochar-amended soil [35].

The addition of nanoparticles, such as TiO_2 or SiO_2, has also been shown to impact the behavior of racemic metalaxyl in soils by their influence on the chemical transformation or the bacterial community of soils [50, 77]. TiO_2 and SiO_2 promoted the chemical transformation of racemic metalaxyl in sterilized soils by the formation of reactive oxygen species (ROS) without changes in the preferential degradation of one enantiomer over the other [50]. DNA analysis demonstrated that the bacterial community was not modified after the addition of the nanoparticles to the soils, indicating that the enhanced transformation of rac-metalaxyl by TiO_2 addition was a chemical transformation [77]. The authors also evaluated the presence of mancozeb in the commercial formulation of metalaxyl and they observed that mancozeb did not induce changes in the enantiomeric fraction of metalaxyl in soil [77]. The addition of ZnO to soil did not affect the transformation of racemic quizalofop-ethyl, in contrast to what was reported for metalaxyl. The authors suggested that the rapid biotransformation of quizalofop-ethyl did not allow the chemical transformation induced by the presence of this photocatalyst [78].

Farming practices such as wastewater irrigation or sewage sludge application can modify the degradation of the chiral fungicide benalaxyl [79]. For example, while wastewater irrigation delayed the transformation of racemic benalaxyl in soil, sewage sludge promoted the degradation of the fungicide, with opposite enantioselectivity between soil and sewage sludge. In the case of sewage sludge, EF values were always >0.5 implying residues enriched in R-benalaxyl, whereas in soil irrigated with wastewater the values were lower than 0.5, representing S-benalaxyl abundance. As observed in the case of olive-mill wastes, this behavior would allow modulating the degradation of more toxic enantiomers, reducing environmental problems associated with their application to soils [79].

Repeated applications of pesticides can induce their accelerated biotransformation due to microbial adaptation [80, 81]. This was observed by Celis et al. [68], who investigated the effect of the repeated application of racemic metalaxyl to soils and found that the biotransformation of R-metalaxyl was enhanced after three successive applications. In contrast, the degradation rate of the non-active S-metalaxyl enantiomer became slower with the repeated applications, which was explained by the occurrence of several mechanisms comprising toxicity of the pesticide or its metabolites to S-metalaxyl degraders, easily degradable soil organic matter depletion with time, and/or time-dependent sorption effects [68].

3.3 Other Aspects to Consider in the Transformation of Chiral Pesticides in Soils

Most of the studies regarding the enantioselective biotransformation of chiral pesticides in soil have been done using racemic mixtures instead of pure enantiomers, due to the limited availability of commercial products. Only a few works have reported the dissipation of purified enantiomers separately in comparison with the racemates. Interestingly, López-Cabeza et al. [31] found that the herbicide imazaquin applied as pure enantiomers to Mediterranean soils was degraded faster than when applied as a racemic mixture of enantiomers. More recently, Gao et al. [82] evaluated the dissipation of the chiral organophosphorus insecticide isofenphos-methyl in soil, either as a racemic mixture or as purified enantiomers, and did not observe differences between them during an incubation experiment performed in three Chinese soils. The enantioselectivity in the biotransformation of this pesticide was suggested to be dependent on the enantiomer itself and its effect on the microbial community of the soils [82]. Therefore, more work is needed to understand possible differences between racemic mixtures and pure enantiomers concerning their degradation in the soil environment.

The recommendation to replace the racemic mixture of a certain pesticide with the corresponding purified active enantiomer requires a deep knowledge of the enantioselectivity of its behavior in the environment. Under certain environmental and even storage conditions, some biologically active enantiomers can be transformed, either biotically or abiotically, into the inactive enantiomer through a process of interconversion between enantiomers or enantiomerization [83]. In these cases, the substitution of the racemic mixture for the active enantiomer would be meaningless, especially under conditions where enantiomerization or racemization occurs rapidly [47]. For instance, the herbicide haloxyfop-methyl, which is rapidly degraded in soils, and its metabolite, haloxyfop acid, underwent enantiomer interconversion in such a manner that S-haloxyfop was converted to R-haloxyfop. The process was biologically mediated since neither degradation nor interconversion took place in sterile soil [84]. Similarly, Buerge et al. [65] did not observe enantiomer interconversion for the chiral pesticide beflubutamid, but did observe the enantiomerization of the main metabolite of this pesticide. This illustrates that assessment of enantiomerization is important not only for the parent compounds but also for their potential transformation products. In this context, in several European countries decreed that only the R-enantiomers of the herbicides dichlorprop and mecoprop will be used, as well as the R (active) enantiomers of all phenoxypropionic acid herbicides, to reduce the amount of herbicide used and avoid possible adverse impacts caused by the S (inactive) enantiomer [1]. It is, therefore, essential to acquire new knowledge when it comes to predicting the behavior of chiral pesticides after their application to agricultural soils, as well as to provide the scientific foundations that allow establishing under which agricultural and environmental conditions it is appropriate to replace racemic pesticide mixtures with the corresponding purified active isomers.

Few studies have been devoted to assessing the behavior of chiral pesticides under field conditions [85]. These can alter the degradation pattern of chiral pesticides affecting their degradation and eventually the enantioselectivity. In the field, several attenuation processes including leaching, runoff, volatilization, or chemical transformations can simultaneously operate [64]. This has been observed for the herbicide imazamox, which was found to be enantioselectively degraded via microbial attack when the dissipation experiment was performed under dark, controlled conditions in the laboratory [51], whereas non-enantioselective photolysis was identified as the predominant degradation pathway when degradation was appraised under natural sunlight exposure [51]. Several authors have studied the dissipation of tebuconazole in soils under real conditions and little enantioselectivity was observed for Chinese [86] and Mediterranean [30] soils. It was pointed out that the high half-lives of tebuconazole in soils probably hindered the development of enantioselectivity within the time-scale of the experiment [30]. Conversely, in the same field study, the enantioselective behavior of the fungicide metalaxyl was comparable to that observed in the laboratory, with R-metalaxyl being degraded more rapidly than S-metalaxyl in an alkaline soil under field conditions [30]. The addition of clay and biochar impacted the enantioselectivity of metalaxyl dissipation, with metalaxyl residues remaining more racemic in the amended soil due to the effect of sorption, as proposed previously in laboratory incubation studies [27, 37]. Li et al. [58] evaluated the degradation of the novel insecticide fluxametamide under field conditions and concluded that the process was non-enantioselective, whereby the application of the purified active S-enantiomer was encouraged to reduce the environmental impact and toxicity of this pesticide [58]. More studies to discern whether enantioselective data observed at laboratory scale are reproduced under real field conditions are particularly needed.

4 Leaching of Chiral Pesticides in Soils

The leaching of chiral pesticide enantiomers will be intimately related to their sorption-desorption and degradation in the soil. Consequently, if changes in the enantiomeric fraction occur during these processes, pesticide residues in leachates will reflect such changes (Fig. 6). Celis et al. [24] described several hypothetical leaching patterns which can be observed after the application of a racemic mixture of two chiral pesticide enantiomers to a soil column (Fig. 6).

If the enantiomers are equally sorbed and transformed during leaching, the elution curves of both enantiomers should overlap (Fig. 6a). This has been observed for the herbicide imazaquin; its rapid leaching and long persistence in soil did not generate significant variations in the EF values of the herbicide residues detected in leachates during a column experiment [31]. However, the most typical situation is depicted in Fig. 6b, where the enantiomers are sorbed to the same extent but one of them is degraded faster than the other during the vertical transport. This behavior has been observed after the application of racemic mixtures of metalaxyl, benalaxyl, and furalaxyl to soil columns [24, 29]. In these cases, the magnitude of the enantioselectivity in leaching will depend on the difference between the degradation rates of the enantiomers. EF values will be further from 0.5 with increasing enantioselectivity of the biotransformation process, which, in turn, may be affected by the sorption extent. Celis et al. [24], for example, observed noticeable enantioselectivity in the leaching of racemic metalaxyl in columns packed with a soil in which the fungicide displayed low sorption and strong enantioselective biotransformation. It should be noted, however, that divergences in degradation under incubation and column leaching conditions can occur. For instance, Gámiz et al. [32] detected greater amounts of the enantiomers of abscisic acid in column leachates from a soil where none of the enantiomers displayed a particularly long

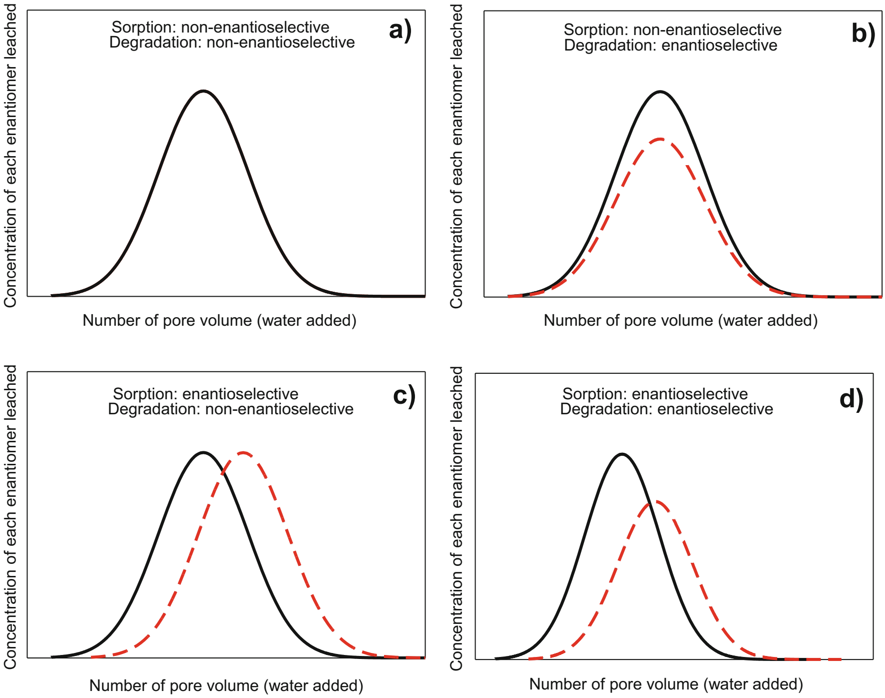


Fig. 6 Schematic representation of theoretical breakthrough curves for a racemic mixture of a chiral pesticide (black and red lines represent the two enantiomers) in soil columns where: (**a**) the two enantiomers are equally sorbed and degraded (**b**) the two enantiomers are equally sorbed but enantiomer 2 (red line) is degraded to a greater extent than enantiomer 1 (black line) during leaching, (**c**) the two enantiomers are equally degraded but enantiomer 2 (red line) is sorbed to a greater extent than enantiomer 1 (black line), and (**d**) enantiomer 2 (red line) is sorbed and degraded to a greater extent than enantiomer 1 (black line). The area below each curve represents the total amount of enantiomer leached. Adapted from Celis et al. [24]

persistence under incubation conditions. The authors attributed this behavior to a degradation lag phase during which abscisic acid rapidly leached through the soil column and the different experimental conditions in the incubation and column experiments (static and aerobic in the incubation tests versus dynamic and partially anaerobic in the column tests). It is known that the redox environment can affect the enantioselective biotransformation of chiral pesticides due to its impact on degrading microorganisms [42, 87], and the soil microbial community is expected to be affected by oxygen availability in saturated soil columns [32].

The leaching of non-racemic mixtures of chiral pesticide enantiomers has been little explored. Gámiz et al. [22] observed a change in the enantiomer fraction of a solution enriched in the R-enantiomer of metalaxyl during leaching through a soil column, even though the degradation of the enantiomers along the experiment was negligible. This behavior was attributed to the preferential sorption of the more abundant (R) enantiomer, as previously discussed in Sect. 2 [21]. The fact that, for both enantiomers, the total amount leached was >95% demonstrated that little degradation or enantiomer interconversion occurred during leaching. This case, which corresponds to that shown in Fig. 6c, provided direct evidence of how the enantioselective sorption of a chiral pesticide in soil, if it occurred, would affect the availability of its enantiomers to undergo other environmental processes.

The addition of organic amendments to soils can have an important impact on the leaching of chiral pesticide enantiomers, either by directly affecting their biodegradation patterns or by the indirect effect exerted by the sorption of the enantiomers on the amendments. Sorption can protect the enantiomers from biological degradation, but may also increase their residence time within the soil column, enhancing the chance of microbial degradation. Gámiz et al. [28] observed that the leaching of metalaxyl was less enantioselective in olive-mill waste-amended soil than in unamended soil. As the organic amendment had a negligible effect on the sorption of metalaxyl enantiomers, less enantioselective biodegradation of metalaxyl in the amended soil resulted in metalaxyl residues in leachates being more racemic compared to the unamended soil. In a subsequent study, the authors compared the leaching of a racemic mixture of R- and S-metalaxyl in soil columns amended with composted olive-mill waste and its biochar [37]. The mobility of both enantiomers was almost suppressed after amending the soil with biochar, whereas considerable amounts of R- and S-metalaxyl leached from unamended soil and from the composted olive-mill waste-amended soil. It was remarkable that while the fraction of S-enantiomer in leachates for the three treatments was similar (EF = 0.85–0.89), metalaxyl residues remaining in the biochar-amended soil columns had enantiomer fractions closer to 0.5 (EF = 0.70). It was concluded that the enhanced sorption in the biochar-amended soil columns protected metalaxyl from enantioselective biotransformation, maintaining metalaxyl residues within the soil column more racemic than those collected in the column leachates. Results of López-Cabeza et al. [31] did not reveal enantiomer-selective leaching of the herbicide imazaquin in two agricultural soils amended with composted olive-mill waste, organoclay, or biochar. Although some treatments impacted the sorption of the imazaquin enantiomers, a small incidence of biodegradation processes made the effect of the amendments on leaching enantioselectivity negligible [31].

It is worthy to note that the availability of the enantiomers of a chiral pesticide will depend not only on sorption but also on its desorption. The use of nanoengineered materials has been proposed to control the degradation and transport losses of natural compounds in soil, which can highly reduce their activity as biopesticides. Very promising results were obtained for the chiral compounds abscisic acid and carvone, for which organoclays and biochars increased sorption and delayed dissipation, allowing the enantiomers to remain longer in the soil [33, 35]. For both compounds, the influence of sorption was more noticeable for biochar-amended soil than for organoclay-amended soil. The amounts of abscisic acid and carvone leached from biochar-amended soils were lower than those from unamended or organoclay-amended soil, and abscisic acid and carvone residues remaining in the soil at the end of the experiment were more racemic. Weaker sorption and easier desorption of the enantiomers in unamended soil and organoclays-amended soil, in contrast to high resistance to desorption from biochar-amended soil, could explain these results [33, 35]. For these reasons, it is expected that biochar could protect these compounds from biotransformation and transport losses and increase their persistence in soils.

5 Effect of Chiral Pesticides on the Microbial Community of Soils

All factors that may influence, in one way or another, the soil microbial population or its activity have the potential to impact the enantioselectivity of the biotransformation of chiral pesticides in soils (Fig. 4). Current intensive agricultural practices alter the biodiversity of soils and their microbial populations [88], which claims for a better understanding of the effect of chiral pesticides on the soil microbial community and vice versa. To date, this aspect has been largely overlooked, probably due to the complexity of interactions between chiral compounds and soil microorganisms. The underlying mechanisms of these interactions, together with the relationships between the soil microbial diversity and the biotransformation of chiral pesticides, remain largely unknown [89]. Zhang et al. [90] observed that R- to S-enantiomer interconversion of the chiral phenylpyrazole insecticide ethiprole in soil proliferated within the groups *Luteimonas*, *Comamonadaceae*, and *Xanthomonadaceae* in bacteria. Zhou et al. [89] found that enantioselectivity in the biotransformation of racemic quizalofop-ethyl was correlated with bacterial structure, while the transformation rate was mainly dictated by the bacterial richness and abundance. At higher soil microbial diversity, the enantioselective transformation of quizalofop-ethyl became more complex and difficult to predict [89]. More recently, Liu et al. [91] demonstrated that imazethapyr enantiomers changed the *Arabidopsis thaliana* rhizosphere microorganism composition and root exudates, with only R-imazethapyr encompassing an inhibitory effect on plant biomass, but not S-imazethapyr. Furthermore, soil treatment with R-imazethapyr resulted in a greater increase in the relative abundance of beneficial rhizosphere microbes, such as *Bacillus* and *Ramlibacter*, compared to S-enantiomer treatment. This indicated the possible accumulation of some microorganisms in the rhizosphere in order to reduce herbicide stress [91]. In another work, the application of the novel acaricide cyflumetofen to soil altered the soil microbial population by reducing the bacterial abundance [92]. Such alteration was enantiomer-selective. The cyflumetofen enantiomers also had an impact on the abundance of N_2-fixing bacteria, in such a way that (+)-cyflumetofen could promote nitrification whereas (−)-cyflumetofen reduced the abundance of *amoA* gene, that is, negatively affected the nitrification in the nitrogen cycle [92]. These results encourage further research on the effects of pesticide chirality on soil microbial communities, which will influence the function and structure of the agricultural ecosystem. This information is essential for a better characterization of the global behavior and potential alterations caused by the presence of chiral pesticides in soils [90].

6 Effect of Chiral Pesticides on Target and Non-target Organisms

The final bioactivity and toxicity of chiral pesticides will be subjected to the transfer and transformation processes that they may undergo in soils. Both bioactivity and toxicity are commonly enantioselective since the molecular target of these pesticides is usually an enzyme or a biological receptor whose active center is also chiral, so it preferentially reacts with one of the enantiomers [10].

6.1 Enantioselective Bioactivity of Chiral Pesticides Against Target Organisms

In the case of chiral herbicides, some of the most common biochemical targets or modes of action that are inhibited by them are acetyl-coenzyme A carboxylase, an essential enzyme in long-chain fatty acid biosynthesis [93]; cellulose biosynthesis, acetohydroxy acid synthase/acetolactase synthase [94] and 4-hydroxy-phenylpyrovate dioxygenase [2]. Determining the structure of complexes formed between the enzymes and the herbicide enantiomer has been possible due to the availability of molecular docking computer tools (Autodock) [95]. For instance, imidazolinones are a group of chiral herbicides targeting acetohydroxyacid synthase, which is a key enzyme in the branched-chain amino acid biosynthesis pathway. By molecular docking, several studies demonstrated that the conformation of the R-enantiomer exhibited better binding modes than the S-enantiomer to the enzyme, which led to a greater inhibition [94, 96].

The bioactivity of fungicides against a large number of pathogens is also enantioselective. The main targets of fungicides are usually the respiratory chain, addressing the biochemical target succinate dehydrogenase [97] and cytochrome bc1; the cellulose biosynthesis by targeting the cellulose synthase 3 (CesA3) enzyme; the oxysterol-binding protein [98]; and the ergosterol biosynthesis, an essential component of the fungi's membrane, by targeting the CYP51B enzyme [2]. The latter is the mode of action of the triazole fungicides, a large and widely used group of fungicides of which approximately 84% are chiral [99]. The bioactivity of R-enantiomer of triazole fungicide is usually greater than that of S-enantiomer. In several works, the interaction between triazole fungicides and the CYP51B enzyme was studied and it was concluded that the R-enantiomers had better binding modes than S-enantiomers to the enzyme, which resulted in a more effective inhibition of the biosynthesis of ergosterol [99, 100].

The chiral insecticides also have enantioselective bioactivity due to different interaction between the enantiomers and the action site of the enzymes. An example is fluxametamide, whose stronger affinity of its S-enantiomer for the γ-aminobutyric acid receptor led to higher bioactivity [58].

6.2 Enantioselective Toxicity of Chiral Pesticides to Non-target Organisms

In most cases, the enantiomer active against the target weed is also the one that is most toxic to non-target plants since the objective enzyme is usually the same. Thus, for imidazolinone herbicides, the active R-enantiomer is more toxic than the inactive S-enantiomers both against target-active weeds (*Echinochloa crus-galli* or *A. thaliana*) and against non-target species such as *Oryza sativa* (rice) [101] and *Zea mays* L. (maize) [102]. Although the study of toxicology of herbicides is mainly focused on plants, these agrochemicals may be transported by runoff to water bodies and affect other organisms as cyanobacteria or microalgae. In the case of algae, the enantioselective effect of a chiral pesticide is usually opposite than vesicular plants [95]. Thus, the toxic effect of R-enantiomer of several chiral herbicides (including napropamide, acetochlor, propisochlor, and diclofop) on freshwater cyanobacteria and algae was less than that of the S-enantiomer [103, 104]. This inverse toxicity of the enantiomers suggested that the interaction pattern could differ greatly in different biological systems [104]. In this specific case, since the toxicity is mainly due to the S-enantiomer, the exclusive application of the active R-enantiomer may be less harmful than the application of the racemic mixture.

As a basis for the risk assessment, the enantioselectivity of toxicity to non-target organisms of chiral fungicides and insecticides must be evaluated in different terrestrial (nematodes, insects, and reptiles among others) and aquatic model organisms that cover different trophic levels (generally algae and crustaceans, fishes).

In toxicity assessments of chiral pesticides, the toxicity of the racemate is roughly intermediate between the toxicity of each enantiomer separately. However, on occasion, it has been observed that the toxicity of the racemic mixture is greater than or equal to that of the individual enantiomers, which would be indicative of a strong synergy between the toxic effect of the enantiomers against these species [56, 100, 105]. Thus, the effect of racemic mixtures on organisms cannot be predicted from the effect of the enantiomers and must be studied separately [56]. In these cases, the application of the active enantiomer instead of the racemate would maintain the activity and minimize risk on non-target organisms.

7 Future Perspectives

Future research in the field of chiral pesticides should be aimed at setting up the scientific foundations to establish under which agricultural and environmental conditions it would be appropriate to replace chiral pesticide racemic mixtures with the corresponding purified active enantiomer. This information can be valuable to the companies in the sector interested in the production of crop protection products at a large scale. Furthermore, information on the enantioselective environmental processes could influence policies and guidelines on management, conservation, and restoration of soils. For this purpose, the following issues are demanded:

- Better understanding of the effect of chiral pesticides and different agricultural practices on the soil microbial community and vice versa.
- To establish the interconnection of abiotic and biotic factors in the degradation of pesticides together with studies using pure enantiomers to assess the relevance of enantiomerization mechanisms. This is important not only for the parent compounds but also for their potential transformation products.
- To contrast the results obtained in laboratory-scale experiments with experiments regarding the environmental fate of chiral pesticides at field-scale studies, as the latter are very scarce.

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