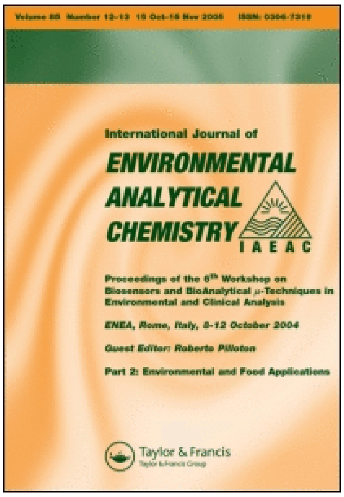

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Lucía Cox[a]; M.Carmen Hermosín[a]; Juan Cornejo[a]
[a] Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, 41080 Sevilla, Spain

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INFLUENCE OF ORGANIC AMENDMENTS ON SORPTION AND DISSIPATION OF IMIDACLOPRID IN SOIL

LUCÍA COX*, M.CARMEN HERMOSÍN and JUAN CORNEJO

Instituto de Recursos Naturales y Agrobiología de Sevilla,
CSIC, P.O. Box 1052, 41080 Sevilla, Spain

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The effect of organic amendments (OA) on imidacloprid sorption and dissipation in soil was investigated. A sandy soil was treated at a rate of 10% w/w with three OA: one liquid (Liquid Fertiormont, LF) and two solid (Solid Fertiormont, SF, and Alperujo, A). Sorption was measured using a batch equilibration method. Dissipation studies in the dark were performed by incubating pesticide-treated soils at moisture content of − 0.33 KPa and 20 ± 2°C for 28 days, whereas imidacloprid photolysis studies in soils were performed by irradiation of treated soils at water holding capacity in a Suntest apparatus with a xenon lamp for 32 h. In both cases, soils were sampled periodically and extracted for their imidacloprid content. Solid OA (SF and A) increased imidacloprid sorption by soils, whereas similar sorption was observed in soil amended with LF. Imidacloprid half-lives obtained from incubation studies in the dark remained unaffected upon amendment, whereas OA decreased the photolysis rate of imidacloprid in soils. However, no relation was observed between increase in sorption and decrease in the photodegradation rate of imidacloprid.

Keywords: Imidacloprid; Soils; Organic amendments; Sorption; Dissipation; Photodegradation

INTRODUCTION

Sorption and degradation are two processes affecting the fate of organic contaminants in the environment which may find application as natural remediation techniques. Sorption determines the amount of chemical that can reach the target organism and the amounts available for other processes such as volatilization, degradation and leaching [1, 2]. Sorption determines the availability of pesticides for microbial degradation, since a variety of studies have suggested that only pesticide in solution is available for biodegradation. Organic matter is mainly responsible for sorption of the insecticide imidacloprid [3].

Dissipation of imidacloprid in soils is a combination of degradation to metabolites and mineralization, with half-lives reported varying from 40 to 129 d [4]. Degradation under irradiation or photolysis can be a significant abiotic degradation process affecting pesticides and other organic contaminants in water, soils and plants.

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*Corresponding author. Fax: +34-954-624002. E-mail: lcox@irnase.csic.es

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The soil, as a whole, generally induces a decrease in the photolysis by a screening effect [5], whereas some of its components such as organic matter or humic acids have been shown to produce a photosensitizing effect [6]. The photolytic decomposition of imidacloprid in water has already been studied [7, 8]. These studies reported half-lives between 43 and 144 min, depending on formulation and type of water, and have identified 1-(6-chloro-3-pyridinyl)-methyl-2-imidazolidinone as the main degradate by several analytical techniques.

Soil amendments, inorganic [9] and organic [10, 11] have been shown to affect soil processes affecting pesticides, such as sorption [10, 12–14], volatilization [15], leaching [16–18] and biodegradation [19–21]. However, this is an issue very seldom considered when making decisions about fertilizing soil or disposing of organic wastes. The aim of this study was to investigate the influence of three soil organic amendments (OA) in sorption and dissipation (in the dark and under irradiation) of imidacloprid in soils. To our knowledge, there is no published work concerning the effect of the addition of organic amendments on photodegradation rates of soil-applied pesticides.

EXPERIMENTAL

Chemical, Soil and Amendments

Pure analytical imidacloprid (chemical purity >99%) was supplied by Bayer Corporation. The soil selected for this study was a sandy soil amended with the organic amendments (OA) LF, SF and A at 10% w/w. LF and SF are liquid and solid, respectively, commercial humic amendments of agricultural origin, and A is a solid waste from olive oil production. Some physicochemical properties of the soils (original and amended) and the OA are given in Table I.

Sorption Studies

Sorption isotherms were measured using a batch equilibration method. Duplicates of 5 g of each soil were treated with 10 mL of imidacloprid solutions with concentration (C_i) ranging from 5 to 100 μM made up in 0.01 M $CaCl_2$. The suspensions were shaken at 20 ± 2°C for 24 h and centrifuged at 12 000 rpm at the same temperature. Supernatants were filtered and equilibrium concentrations (C_e) determined by HPLC [22]. Isotherms were fitted to the Freundlich equation and sorption coefficients K_f and n_f calculated:

$$C_s = k_f \cdot C_e^{n_f} \tag{1}$$

TABLE I Physicochemical properties of original soil, amended soils and organic amendments

Soil	*pH*	*Sand* (%)	*Silt* (%)	*Clay* (%)	*Organic matter* (%)
Original	7.1	75	9	16	1.14
Soil + LF	6.5	75	9	16	1.82
Soil + SF	7.7	75	9	16	3.34
Soil + A	6.2	75	9	16	5.34
LF	5.1	–	–	–	26
SF	9.4	–	–	–	32
A	5.9	–	–	–	50

Sorption was also calculated as a function of organic carbon (OC) content:

$$K_{OC} = \frac{K_f}{\%OC} \times 100 \qquad (2)$$

Dissipation Studies in the Dark

For dissipation studies in the absence of light, duplicate amounts (500 g) of soils (original and amended with LF, SF or A) were treated with an aqueous solution of imidacloprid to give a concentration of 5 mg/kg dry soil. The appropriate volume of water was added to each soil to have a final moisture content of −0.33 KPa. Soil samples were thoroughly mixed by passing them at least three times through a sieve, and then transferred to kilner jars where they were incubated in the dark at $20 \pm 2°C$ for 28 days. Moisture content was maintained constant throughout the experiment by adding distilled water as necessary. Soils were sampled after 0, 7, 14, 21 and 28 days of incubation and imidacloprid extracted by shaking 10 g of soil with 20 mL of methanol for 24 h (recoveries $>90\%$). Methanol extracts were analyzed by HPLC [22]. Imidacloprid dissipation curves were fitted to first-order kinetics ($C = C_i e^{-Kt}$) and half-lives ($t_{1/2}$) calculated.

Photolysis Studies

Duplicate amounts of original and amended soils (5 g) were treated with imidacloprid (5 mg/kg) and moisture content adjusted to their water holding capacity in 4-cm diameter dishes, which were irradiated for 32 h in a Suntest photoreactor equipped with a xenon lamp and a permanent filter selecting wavelength >290 nm. This apparatus exhibits a radiation very close to natural sunlight [6]. Moisture content was maintained constant by addition of water after 30 min of irradiation. After 1, 2, 4, 8, 16 and 32 h of irradiation, soil samples were extracted with methanol (1/2 w/v) and extracts analyzed by HPLC for their imidacloprid content. Photodegradation curves of imidacloprid as a function of irradiation time were fitted to first-order kinetics and half-lives calculated.

RESULTS AND DISCUSSION

Sorption Studies

Imidacloprid sorption isotherms in original and amended soils are given in Fig. 1, and sorption coefficients after fitting isotherms to the Freundlich equation in Table II. Most isotherms are C–L-type, according to Giles *et al.* [23], although the imidacloprid sorption isotherm on soil amended with A displays a clear L-type isotherm, as also indicated by its much lower n_f coefficient when compared with the other soils. This type of isotherm indicates a reduction in specific sorption sites when concentration in solution increases and is indicative that sorption is not just a partitioning between the soil and the soil solution.

Sorption coefficients K_f (Table II) significantly increased in the case of the soils amended with SF and A of higher organic matter content (Table I). In the case of LF, the increase in sorption in relation to non-amended soil was not significant

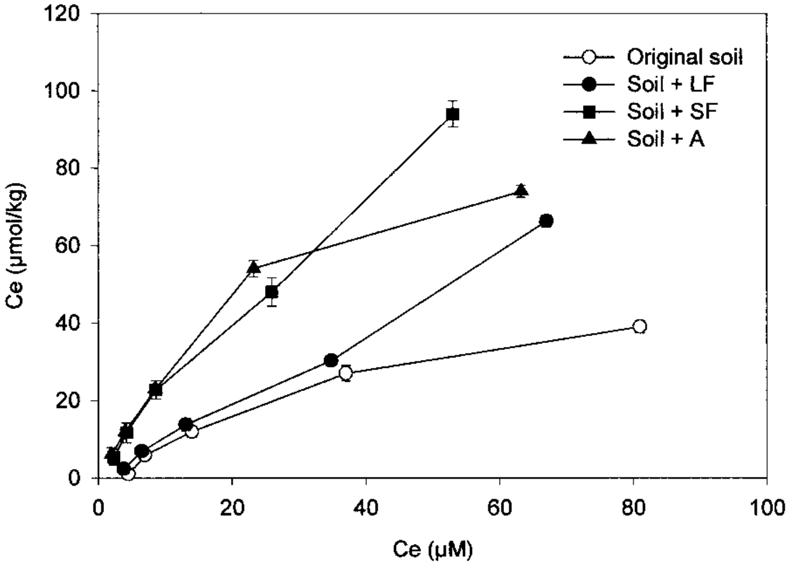

FIGURE 1 Imidacloprid sorption isotherms in original and amended soils.

TABLE II Imidacloprid sorption coefficients by original soil and amended soils and half-lives obtained from dissipation curves in the dark and under irradiation (photolysis)

Soil	*Original*	*Soil + LF*	*Soil + SF*	*Soil + A*
Sorption				
K_f	0.39(0.87–0.178)[a]	0.75(1.00–0.56)	3.03(3.51–2.61)	4.25(5.13–3.51)
n_f	1.12 ± 0.26[b]	1.06 ± 0.09	0.87 ± 0.05	0.74 ± 0.07
K_{OC}	59	70	156	137
r^2	0.99	0.99	0.99	0.97
Dissipation (dark)				
$t_{1/2}$(d)	61 ± 6.1[c]	60 ± 3.2	63 ± 6.3	65 ± 3.3
r^2	0.93	0.93	0.87	0.89
Photolysis				
$t_{1/2}$(h)	18	230	71	39
r^2	0.98	0.23	0.95	0.98

(Table II). This can be attributed to the lower organic matter content of the LF-amended soil when compared with SF- and A-amended soils (Table I). Also, the dissolved organic matter of this liquid amendment has been shown to interact with other pesticide molecules [16] and also to sorb on soil sorption sites giving rise to competitive sorption [10]. Both processes should contribute to the lower sorption of imidacloprid on soils amended with LF of high content in dissolved organic matter as compared with the other amended soils.

The variability of sorption coefficients K_{OC} (Table II) between soils did not diminish, which can occur when qualitatively homogeneous organic matter is the main soil component affecting sorption [24]. The variability in K_{OC} values also indicates a contribution from soil mineral components, such as clay minerals. In fact, the high sorption of other pesticides by montmorillonite has been shown to yield erroneously high K_{OC} values [25]. Previous studies have indicated that imidacloprid can also sorb on clay minerals [26], especially on montmorillonite.

Dissipation Studies in the Dark

Figure 2 shows the changes in total imidacloprid recovered from original and amended soils incubated in the dark *versus* incubation time, and Table II the half-lives calculated from fitting dissipation curves to first-order kinetics. The mean half-life of imidacloprid (60 days) falls in between the reported half-lives in field experiments [4].

As shown in Table II, differences in half-lives between original and amended soils are not significant, which is in disagreement with Rouchaud *et al.* [21], who found an increase in imidacloprid sorption and an increase in soil persistence upon recent organic fertilizer treatment. However, OA have been shown in many cases to enhance pesticide biodegradation owing to the increase in organic C of the soil and subsequent increases in microbial population and/or activity [12, 27]. Even at low application rates of OA such as 0.5% w/w, enhancement of degradation of herbicides has been observed [11]. In our case, we attribute these results to the increase in sorption upon amendment, which would protect imidacloprid from biodegradation, compensating for the effect of any increase in microbial population and, hence, yielding similar half-lives in unamended and amended soils.

Photolysis Studies

Imidacloprid photodegradation in aqueous solution (5 mg/L), together with the control in the dark, is shown in Fig. 3A, and photodegradation of imidacloprid in soils (original and amended) in Fig. 3B. Half-lives ($t_{1/2}$) after 32 h of irradiation are given in Table II. These $t_{1/2}$ values were calculated after fitting dissipation curves to first-order kinetics. Under the conditions studied, the imidacloprid half-life in aqueous solution is 0.9 h, while the imidacloprid concentration in the dark control (under the same conditions except for the light) did not significantly decrease.

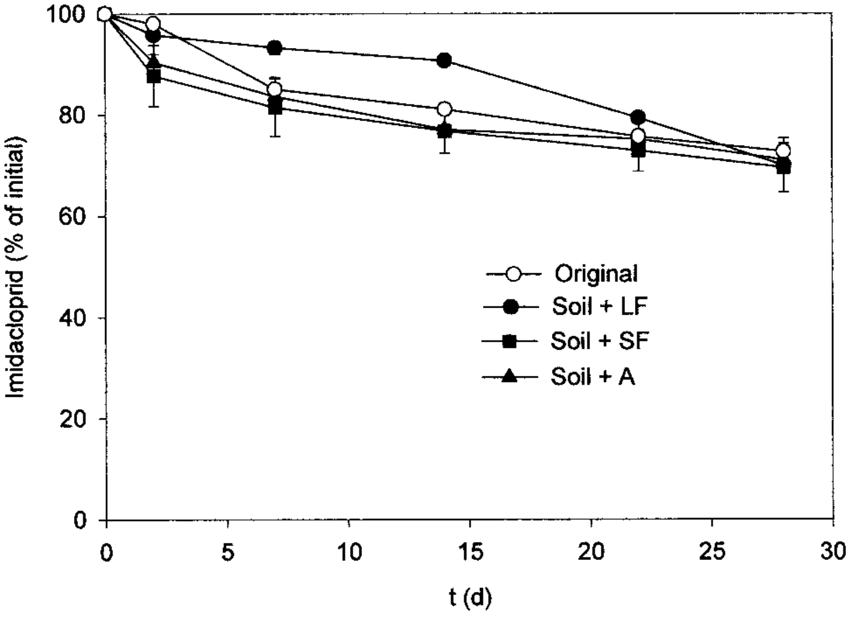

FIGURE 2 Imidacloprid dissipation in soils (original and amended) incubated in the dark.

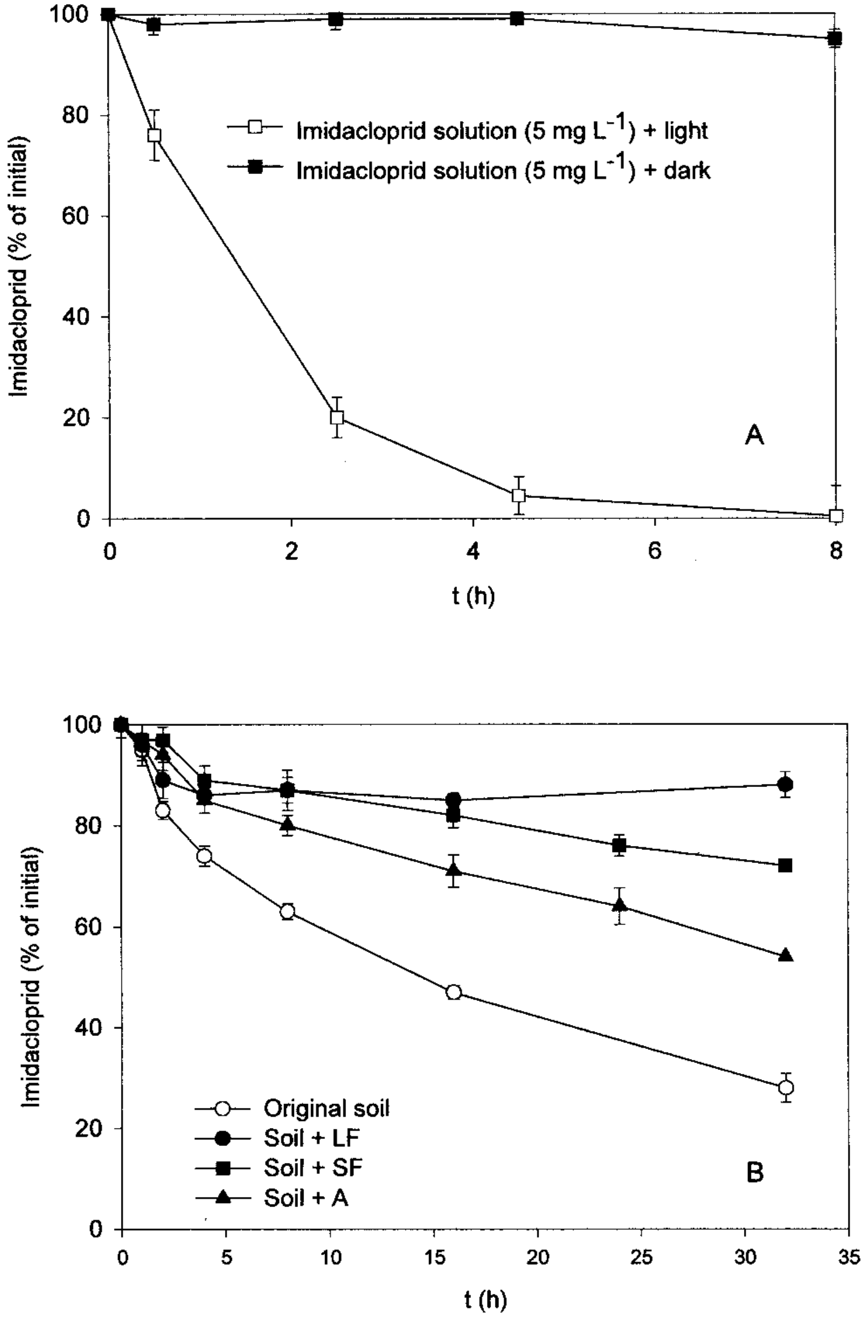

FIGURE 3 Photodegradation of imidacloprid in solution (A) and in original and amended soils (B).

In the original unamended soil (Fig. 3B) the calculated half-life of imidacloprid increased from 0.9 to 18 h, which is attributed to absorption of light by soil components and screening or light attenuation effects of the soil particles [12]. When the soil was amended with the different OA, $t_{1/2}$ increased in every case. We did not observe a photosensitizing effect of the organic matter of OA as reported for other pesticides in the presence of humic acids [6, 28]. This higher stability of imidacloprid in amended soils under the conditions studied is particularly significant in the case of LF, where the imidacloprid concentration remained very high ($>80\%$ of initial concentration) after 32 h of irradiation. The very dark color of the LF-amended soil, when compared with the other amended soils, would lead to higher absorption of light and, hence, protection of imidacloprid molecules from photodegradation. Also, as shown in Fig. 3B and Table II, there is no negative relation between sorption and photodegradation: imidacloprid is more stable in the low sorptive system (soil + LF) than in the highest sorptive soil (soil + A).

CONCLUSIONS

Soil sorption of imidacloprid increased with organic matter content of the solid organic amendments (SF and A), but this increase in sorption did not affect imidacloprid dissipation in soils under dark conditions. In the case of the liquid amendment LF, other factors such as interactions between dissolved organic matter and imidacloprid and/or competition between dissolved organic matter and imidacloprid for the same soil sorption sites must be involved in its low sorption behavior.

Organic amendments protect imidacloprid from photodegradation, and photolysis rates do not reveal that sorption processes have any type of “protecting effect” on imidacloprid against photochemical reactions.

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