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Original article

Imidacloprid and pyrimethanil soil sorption

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Abstract – The sorption of imidacloprid and pyrimethanil was measured in different soils of southern Europe. Pyrimethanil sorption (Kf=1.2–4.60) was higher than that of imidacloprid (Kf=0.31–1.99). Sorption was influenced by organic carbon content and increased with time when the soil was incubated at 25 °C and 35% soil water content. Over a period of 14 days, the distribution coefficient between solid (soil) and solution phases increased by orders of magnitude of 2 and 4 respectively, for imidacloprid and pyrimethanil. The increment is consistent with the degradation rate measured, supporting the hypothesis of the two sites of sorption. Care should be taken when such values are used to predict pesticide fate in soil, particularly for regulatory purposes during pesticide registration.

imidacloprid / pyrimethanil / pesticide / soil sorption / soil dissipation

Résumé – Sorption de l'imidacloprid et du pyriméthanil dans le sol. La sorption de l'imidacloprid et du pyriméthanil a été mesurée dans divers sols d'Europe méridionale. La sorption du pyriméthanil (Kf = 1,2–4,60) était plus élevée que celle de l'imidacloprid (Kf = 0,31–1,99). Elle est influencée par la teneur en carbone organique et augmente avec le temps lorsque le sol est incubé à 25 °C et que sa teneur en eau est de 35 %. Sur une période de 14 jours, le coefficient de répartition entre la phase solide du sol et la phase liquide (solution) augmente d'un ordre de grandeur de 2 et 4 respectivement pour l'imidacloprid et le pyriméthanil. L'accroissement est en accord avec le taux de dégradation mesuré, ce qui confirme l'hypothèse de deux lieux de sorption. Il faut faire attention lorsqu'on utilise de telles valeurs pour prédire le devenir du pesticide dans le sol, en particulier dans des buts de réglementation au cours de la procédure d'enregistrement du pesticide.

imidacloprid / pyriméthanil / pesticide / sorption dans le sol / dissipation dans le sol

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1. Introduction

The sorption of pesticides by soil is a very important process because it strongly influences the amount of the applied pesticide that can reach the target organism and the amount that can be volatilised, degraded or leached. Sorption is influenced by the pesticide chemical properties but a very important role is played by the characteristics of the soil such as soil texture, organic matter content, pH. Liquid and gaseous soil phases can hold pesticides in a form available to be degraded or dissipated while the solid phase may be considered as a site of accumulation [2].

Imidacloprid [1-(6-chloro-3-pyrydilmethyl)-N-nitroimidazolidin-2-ylidineamine] and pyrimethanil [N-(4,6-dimethylpyrimidin-2-yl)-aniline] are new pesticides commonly used in southern Europe in both greenhouse and field situations. An estimate for the southern European market for 1999 indicates annual usage as 90 tons and 200 tons respectively, for imidacloprid and pyrimethanil for a variety of crop types. Imidacloprid is a systemic insecticide belonging to the chemical group of chloronicotynil, with activity against *Aphids* spp. Pyrimethanil is an anylopyrimidine fungicide used for the control of grey mould (caused by *Botrytis cinerea*) in a wide range of crops such as ornamentals, minor crops including tobacco, and major crops including top fruit. Although both pesticides are used at low dose rates (50–100 g/ha), they are usually applied more than once during the growing season. Therefore the assessment of the potential environmental impact must take into account likely maximum doses applied during a cropping season. Imidacloprid has a high water solubility (510 mg/l at 20 °C) and an apparent high persistence in soil in laboratory conditions (average DT50=190 days). However field experiments have demonstrated a greater rate of degradation, probably due to microbial activity (average DT50=48 days [8, 9]. Pyrimethanil with a water solubility of 121 mg/l at 25 °C is less soluble than imidacloprid, with an average DT50 of 30 days [11]. Based on these chemiodinamic values, imidacloprid and pyrimethanil are classified by a number of classifications systems as being highly mobile and moderately mobile in soil respectively [6].

The objective of this work was to analyse the sorption behaviour of imidacloprid and pyrimethanil in different soils representative of southern European agricultural areas.

2. Materials and methods

2.1. Chemicals

Analytical Imidacloprid (chemical purity 97%) Riedel de Hoën 46009 Pestanal®, Analytical Pyrimethanil (chemical purity 99.6%) AE B1 00309 00 1399 0001, acetonitrile Lichosolv® Gradient Grade for chromatography Merck (min. 99.8%), methanol purissimum cod. 141091 Panreac (min. 99.5%), Calcium Chloride anhydrous powder for analysis Panreac (95%), Confidor® 20 LS containing Imidacloprid 20% p/v Bayer, Scala® AgrEvo containing pyrimethanil 400 g/L.

2.2. Soils

Five different soils from three different southern European areas were selected (Tab. I). Two Italian soils, one from a greenhouse of Albenga (Savona) (three different layers: 0–30 cm, 60–90 cm, 100–110 cm) and the second from a field soil of Bologna (only the top layer). Two Spanish soils, one collected from the greenhouses of El Ejido (Almeria) (two different layers: amended soil=10–20 cm, native soil=20–60 cm) and the other from a field soil in Valencia (only the top layer). The fifth soil type was Greek field soil collected in Crete (only the top layer). These soils represent a broad spectrum from the south of Europe, although the Almeria soil is not a naturally occurring soil but an artificial one. It is prepared by adding layers on top of the existing soil when greenhouses are constructed. The main crops grown on these soils are both vegetables and ornamentals indoors (greenhouse) and tree crops such

as olives and oranges for the outdoor (field) conditions.

All the soils collected were air dried and passed throughout a 2 mm diameter sieve.

The soil texture was determined by the hydrometer method [7], the organic carbon soil content was measured by dichromate oxidation following the Walkley-Black method [13], the soil pH was determined using a glass electrode in 1:2.5 soil/water suspension [4].

2.3. Fast equilibrium sorption

The sorption experiment were done in accordance with the batch equilibration technique. Soils were air dried, then sieved, and 1 g was placed in several stoppered conical flasks with 2 ml of $CaCl_2$ (0.01M) containing imidacloprid or pyrimethanil with a concentration ranging between 0.5 and 2.5 mg/ml (three replicates for each point).

Every sample was shaken at 25 °C for a precise time corresponding to the equilibrium time, determined with previous sorption kinetics studies (Fig. 1) giving the following results: 24 hours for imidacloprid and 8 hours for pyrimethanil. After this time every sample was centrifuged at 10 000 rpm and the supernatant concentration was determined by high performance liquid chromatography (HPLC).

The amount of pesticide sorbed was calculated from the difference between the initial solution concentration and the equilibrium concentration. The sorption isotherm was obtained by fitting the values measured with the linear form of the Freundlich equation:

$$\log Cs = \log Kf + 1/nf \log Ce$$

where Cs is the concentration of the pesticide sorbed to the soil, Ce the concentration in water, 1/nf the power coefficient and Kf the Freundlich constant calculated from the slope and the intercept respectively.

2.4. Time dependent sorption

The sorption variation in the time was measured incubating the soil per 90 days (degradation trial) and then calculating the distribution coefficients (Kd) for each sampling point of the incubation trial using the OECD methodology [12].

The degradation trial was carried out in the following way. Solutions of imidacloprid pyrimethanil were prepared by diluting the commercial products Confidor® and Scala® with $CaCl_2$ 0.01 M in order to control the ionic strength. 14 ml of a 3.99 µg/ml solution of imidacloprid and 14 ml of a 1.23 µg/ml of pyrimethanil were respectively added to 40 g of a 0–30 cm depth Albenga soil. The soil had previously been air dried and passed

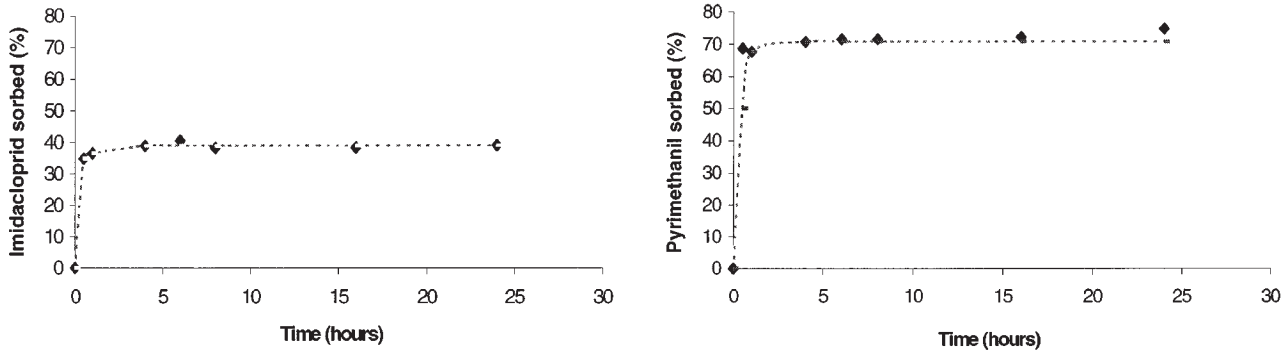

Figure 1. Sorption kinetic of imidacloprid and pyrimethanil in batch studies. The initial concentration was 1.2 and 0.985 mg/L for imidacloprid and pyrimethanil respectively.

through a 2 mm diameter sieve. The soil concentration obtained was 1.40 µg/g for imidacloprid and 0.43 µg/g for pyrimethanil, which are close to the normal field concentration rates.

The soil moisture reached was 35% (g/g) which is about 80% of the water holding capacity of the soil. Four replicates (40 g each) for imidacloprid and four for pyrimethanil were incubated at 25 °C for 12 weeks.

At every sampling time two replicates were analysed. The amount of pesticide degraded was calculated as the difference between the amount of pesticide applied at the beginning of the experiment and the amount recovered with methanol extraction at every sampling time.

Each of the other two replicates were transferred to PVC centrifuge tubes and centrifuged at 20 000 rpm for 15 minutes. The imidacloprid and pyrimethanil water supernatant concentrations were analysed by HPLC. The amount of pesticide sorbed was calculated as difference between the concentration of the sample and the concentration of the solution obtained by centrifugation at each sampling time.

2.5. Analysis of the samples

Analysis was carried out by HPLC Beckman equipped with Autosampler Beckman System Gold 507e, Programmable Solvent Module System Gold, Diode Array Detector Gold Module model 168, Waters^{TM} Steel Cartridge column (length of cartridge: 150 mm, internal diameter: 3.9 mm, filter size: 2 µm, cartridge prepacked with 4 µm Nova-Pack C-18 packing material).

The chromatographic conditions for imidacloprid determination were: mobile phase made up of 35% water and 65% acetonitrile, wavelength 269 nm, flow 1 ml/min, injection volume 20 µl. With this conditions the retention time was 1.8 min, the limit of determination 0.025 mg/kg and good linearity was achieved (R^2=0.999). For pyrimethanil analysis a gradient elution was necessary, starting with a mobile phase made up of 60% water and 40% acetonitrile, reaching a composition of 80:20 in 8 minutes; the wavelength was 270 nm, the flow 1 ml/min, the injection volume 50 µl. In these conditions the retention time for pyrimethanil was 6.1 min, the limit of determination 0.025 mg/kg and also in this case good linearity was achieved: $R^2 = 0.999$.

Soil samples were extracted adding 40 ml of methanol and, after 24 hours of shaking, centrifuged at 10 000 rpm for 10 minutes. The imidacloprid and pyrimethanil concentrations in the supernatant were then determined. Recovery tests done in the same conditions gave the following results: 100.8% ± 1.2 for imidacloprid and 113.9% ± 1.5 for pyrimethanil. Soil water samples were directly analysed after filtration on teflon 0.45 µm without previous solvent extraction.

3. Results and discussion

Pyrimethanil was adsorbed to soil more than imidacloprid by a factor 2: Freundlich constant (Kf) is in a range of 1.2 to 4.6 against values of 0.31 to 1.99 respectively (Tab. II). The adsorption of both pesticides increased proportionally with the organic carbon and clay content: Albenga>Bologna>Heraklion>Valencia>Almeria. The sorption also decreased with increasing depth in Albenga soil. This was due to the reduction of organic matter in the soil profile. Gonzales-Pradas [13] in similar soils found a good correlation between the distribution coefficient (Kd) and the organic carbon content and a poor correlation between the pesticide and clay. Results reported here show correlation coefficients much lower and a significant sorption dependence ($P < 0.05$) from the organic carbon. The isotherm obtained follows the Freundlich equation with a good approximation ($R^2 > 0.90$ on average) which indicates that sorption is fundamentally governed by a pesticide partition between the soil and aqueous solution (Fig. 2). Therefore the differences between the soils strongly influence the sorption, quantitatively and qualitatively, with the coefficient of variation of the Freundlich constant higher than 40% for both pesticides.

Table I. Measured soil properties.

Soil	Clay	Silt	Sand	Organic C	pH	Soil taxonomy[@]	USDA
Albenga (a)*	8.0	53.6	38.4	1.30	7.9	eutric cambisol	silt loam
Albenga (b)**	14.7	53.6	31.7	0.50	8.3	eutric cambisol	silt loam
Albenga ©***	15.0	53.1	31.9	0.10	8.5	eutric cambisol	silt loam
Bologna	19.2	33.5	47.3	1.40	8.4	vertisuol cambisol	loam
Almería (a)[#]	24.0	30.6	45.4	0.29	7.9	luvic xerosol	loam
Almería (b)[##]	20.0	27.7	52.3	0.49	8.6	calcic regosol	loam
Valencia	16.6	31.3	52.1	0.52	7.9	calcic cambisols	loam
Crete	21.4	31.0	47.6	0.85	7.5	lithosols	loam

*Soil collected at 0–30 cm deep; **60–90 cm deep, ***100–110 cm deep.
[#]Amended soil 10–20 cm deep; [##] native soil 20–60 cm deep.
[@] FAO (1998).

Table II. Freundlich constants calculated for imidacloprid and pyrimethanil in the different soils.

	Imidacloprid			Pyrimethanil		
Soil	Kf	1/nf	R^2	Kf	1/nf	R^2
Albenga (a)	1.62	0.93	0.99	4.60	1.00	0.99
Albenga (b)	1.22	0.89	0.95	2.41	0.73	0.98
Albenga ©	1.29	0.86	0.98	2.60	0.75	0.98
Bologna	1.99	0.94	0.97	3.84	0.88	0.99
Almería (a)	0.31	0.89	0.95	1.18	0.88	0.98
Almería (b)	0.88	0.45	0.87	1.99	0.83	0.86
Valencia	0.98	0.79	0.99	1.86	0.87	0.99
Crete	0.90	0.66	0.66	3.75	1.29	0.94
Mean	1.15	0.80		2.78	0.90	
Std. dev.	0.51	0.17		1.17	0.18	
Pearson coefficient	0.70 (organic carbon)* 0.60 (clay)			0.85 (organic carbon)* 0.55 (clay)		

*$P < 0.05$.

Kd of imidacloprid increases quickly in first 10 days of the incubation and then tends to approach the equilibrium (Fig. 3). Pyrimethanil's Kd increases quickly for 20 days then the amount of pyrimethanil in the aqueous phase is below the limit of determination. These data were consistent with the rates of degradation measured for both pesticides supporting the hypothesis that Kd increases due to degradation of readily available chemicals to soil water. The greater the degradation rate, the greater the increase of Kd with time.

Pyrimethanil is less persistent than imidacloprid, dissipating completely after 85 days. Its dissipation follows a first order kinetic ($R^2 = 0.99$) with a half-life (DT50) of 23 days. Imidacloprid is much more persistent and after 12 weeks more than 50% is still present in the soil. The imidacloprid concentration decreases rapidly in the first 10 days followed by a slower decrease in the total amount recovered (Fig. 4).

This phenomena may be explained assuming that there are two sites of adsorption [5]: the

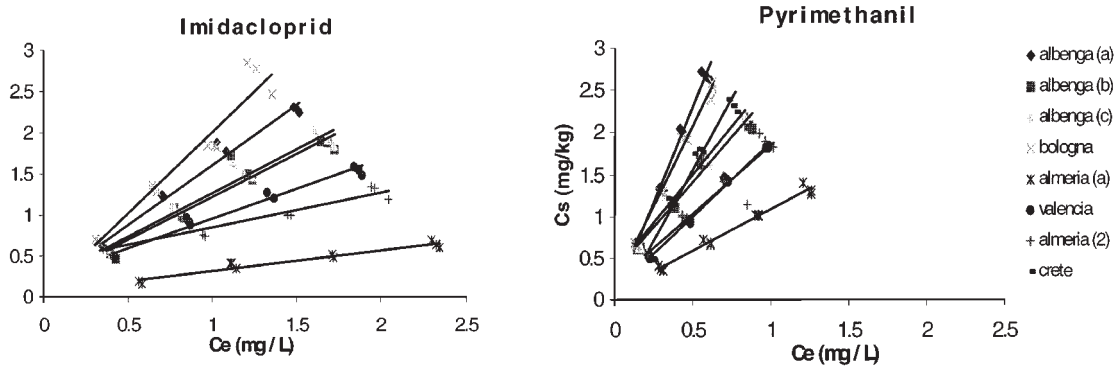

Figure 2. Sorption isotherms of pyrimethanil and imidacloprid in the different soils.

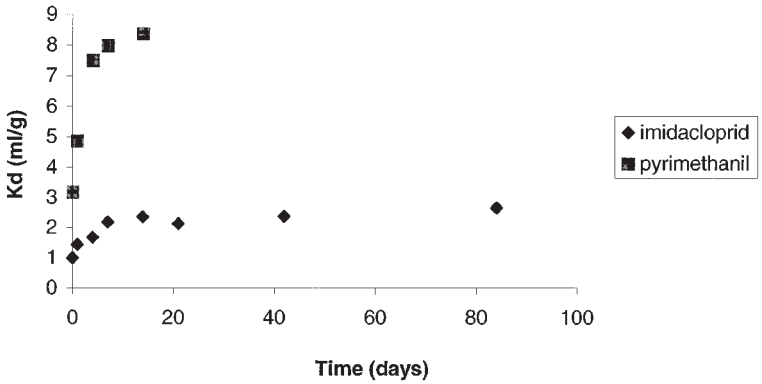

Figure 3. Changes in pesticide sorption coefficient (Kd) with incubation time in Albenga soil.

external sites, where the pesticide adsorption quickly reaches the equilibrium, and the internal sites, less accessible, where the soil-water equilibrium is reached more slowly. This means that besides the increasing of Kd with time due to degradation of available chemical, Kd may also increase due to diffusion processes to less accessible sites. This is true mainly in the soil with high organic carbon and clay content.

One of the consequences of this sorption increment is the potential effect on the pesticide classification hazard to groundwater pollution. The recent European Directive 91/414 requires the use of mathematical models for predicting the environmental concentration of pesticide in groundwater. If after 4 days of soil incubation, the distribution coefficient was increased by a factor 2 for both pesticides, and after 14 days by a factor 4 for pyrimethanil (Tab. III), this would have a great influence on model outputs. Sensitivity analysis obtained by varying the Kd with a magnitude order equal to three, produced on models such as PRZM or VARLEACH differences in soil-water concentration greater than 100% [1]. Recently Tiktak [10] reported the results of the sensitivity analysis carried out for the SOTRAS model: he found that the maximum concentration of the pesticide in the groundwater was very sensitive to Freundlich constants and, in some cases, changing the exponent by 1% resulted in a change of the maximum concentration of the pesticide in the groundwater by 65%.

4. Conclusions

The different Mediterranean soils tested have a great effect on pyrimethalin and imidacloprid soil

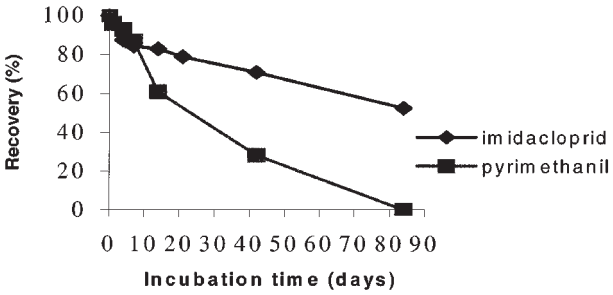

Figure 4. Dissipation of imidacloprid and pyrimethanil on Albenga soil (25 °C, 35% g/g soil moisture).

Table III. Distribution coefficient between solution phase and organic carbon calculated during the incubation.

Time (days)	Imidacloprid Koc (ml/g)	Pyrimethanil Koc (ml/g)
0	76.4	243.8
1	110.4	373.8
4	129.6	576.5
7	168.1	613.5
14	181.5	643.5
21	163.8	-*
42	183.1	- *
84	204.6	- *

*The pesticide was not detectable in the solution phase.

sorption. For both pesticides it has been assumed that both a coupled degradation-sorption and a diffusion process into the soil structure occurs. More research is needed to determine these mechanisms by measuring the distribution between the different chemical fractions of the soil, and also the effect that the ageing processes may have on soil sorption.

However, pyrimethanil was sorbed more than imidacloprid, and it dissipated faster resulting in less residues being measured in the soil. With time, the sorption increased, so increasing the distribution coefficient between soil and water solution. Furthermore the increase in sorption over time is greater for pyrimethanil than for imidacloprid by a magnitude of between 2 and 6.

The results confirm the need to develop a general theory of the two sites sorption to be applied to each of the pesticides and to be implemented in the mathematical models. From a legislative point of view this is essential for accurately predicting pesticide environmental concentration in soil, groundwater and surface water.

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