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ISSN 0805 - 7214

Rapportens tittel og forfatter(e):

Sorption properties of isoproturon in soils

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Rapport nr : 8/2001 (98)

Distribusjon: Fri (01.05.02)

Dato: 29.10.01

Prosjektnummer:

Faggruppe: Pesticider

Geografisk område:
S-Ø Norge

Antall sider (inkl. bilag) 10

Oppdragsgivers ref.:

Oppdragsgiver: Statens landbrukstilsyn

Sammendrag:

Det er gjennomført sorpsjons- og desorpsjonsforsøk med pesticidet isoproturon i topp- og undergrunnsjord fra Skuterud, Ås i henhold til OECD guideline 106 (1997).

Sorpsjons- og desorpsjonsisotermene for isoproturon er lineære over et stort konsentrasjonsområde (0,0001 – 1,0 mg/l) i topp- og undergrunnsjord fra Skuterud. Tilpasning til Freundlich isotermer var også god ($r^2 > 0,99$). Additiver i handelsproduktet Tolkan-WG (Rhone Poulenc) hadde ingen signifikant innvirkning på sorpsjonen av isoproturon i de undersøkte jordtypene.

Sorpsjonen av isoproturon er sterkt avhengig av jordas innhold av organisk materiale, og sorpsjonen var følgelig høyere for toppjord enn for undergrunnsjord med K_d -verdier på henholdsvis 2,9 og 1,06. Fordelingskoeffisienter korrigert for jordas innhold av organisk karbon viste liten variasjon for de to jordtypene, med verdier på 96 og 107.

Sorpsjons- og desorpsjonsprosessene er tilnærmet reversible i topp-og undergrunnsjord fra Skuterud.

4. Emneord, norske

1. Pesticider
2. Sorpsjon
3. Desorpsjon
4. Fordelingskoeffisienter

Prosjektleder:

4. Emneord, engelske

1. Pesticides
2. Sorption
3. Desorption
4. Partitioning coefficients

For administrasjonen:

Troud Børnsen

Preface:

This report is carried out as a part of the project: "Norske scenarier og modellevalueringer" run by Statens landbrukstilsyn.

Gunnhild Riise (associate professor)

Sorption properties of Isoproturon in soils

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Introduction

Soil-water distribution coefficients are used in a variety of models for predicting the fate of organic chemicals entering the soil environment. Interaction of organic chemicals with a solid phase is of great importance, because sorption directly affects plant uptake, retention, volatilisation, biodegradation and transport of organic chemicals in soils and waters. In this work we have determined sorption and desorption isotherms of isoproturon for two soil samples according to the OECD-guideline 106 (1997). The soil samples include one top soil and one subsoil from Skuterud, Ås, with different content of organic carbon and clay minerals. The time required for reaching the sorption equilibrium, was estimated based on kinetic experiments.

Freundlich and linear sorption models are often used for describing the sorption of organic chemicals in soil-water systems.

The Freundlich sorption coefficient, K_F^{ads} is obtained by fitting the experimentally determined sorption data with the Freundlich model:

$$C_s^{ads}(eq) = K_F^{ads} C_{aq}^{ads}(eq)^{1/n}, \quad (1)$$

where $C_s^{ads}(eq)$ and $C_{aq}^{ads}(eq)$ are the equilibrium concentration of the test substance in the solid phase (in $\mu\text{g g}^{-1}$) and in the aqueous phase ($\mu\text{g cm}^{-3}$), respectively. The K_F^{ads} express the extent of the sorption and n indicates the linearity of the sorption isotherm. In the case of $n=1$, the Freundlich sorption model is converted into the linear sorption model :

$$K_d = \frac{C_s^{ads}(eq)}{C_{aq}^{ads}(eq)} \quad (2)$$

where K_d is defined as the distribution coefficient for the sorption reaction.

As organic matter often is the main sorbent for organic chemicals in soils, especially for hydrophobic compounds, the distribution coefficients are often normalised for content of organic carbon (C_{org} , in %) according to the formulae:

$$K_{OC} = 100 K_F^{ads} / C_{org} \quad (3)$$

In this work the coefficients K_F^{ads} and K_d are used for describing the sorption process and K_F^{des} and K_{des} for the desorption process. The coefficient K_{OC} is used for characterising the sorption of isoproturon to soil organic matter.

Materials and methods

Soil materials

Two soil samples from Skuterud, Ås, were provided by the Norwegian Crop Research Institute, Plant Protection Centre. The soil samples were air-dried and sieved to < 2 mm. The physical and chemical characteristics of the soil samples are summarised in Table 1.

Table 1 : Physical and chemical characteristics of soil samples from Skuterud, Ås

Sample No	Depth (cm)	water content (%)	C_{org} (%)	Clay (%)
RG1 (top soil)	0- 20	5,6	2,52	25,1
RG2 (subsoil)	20-40	2,4	1,07	27,4

[¹⁴C]isoproturon and non-labelled isoproturon

¹⁴C ring labelled isoproturon [3-[4-isopropylphenyl]-1,1-dimethylurea] with a specific activity of 4 MBq/mg was used in all the experiments. The purity was > 97 % (Institute of Isotopes Co., Ltd., Budapest). For experiments with pesticide concentration higher than 1 µg cm⁻³, non labelled isoproturon, the commercial product Tolkan-WG was added in a proportion of 1:4 (labelled / non labelled). The purity of Tolkan –WG was 83% (Rhône Poulenc).

[¹⁴C]isoproturon was first dissolved in methanol (purity >99.7 %, Riedel de Haen) to a concentration of 9.2x10² µg cm⁻³. The methanol solution was then diluted with 0.01 M CaCl₂ to a concentration of 9.2 µg cm⁻³. The stock solution was further diluted with 0.01 M CaCl₂ to different concentrations.

Determination of [¹⁴C] isoproturon by liquid scintillation

0.5 to 1.0 ml aqueous solution containing [¹⁴C]isoproturon were transferred to a 20 ml vial and mixed with 9 ml scintillation cocktail (opti-Fluor, high flash-point LSC-cocktail for aqueous sample, Packard). The ¹⁴C activity of this solution was determined by liquid scintillation (Packard Tri-Carb 4530 liquid scintillation counter). The relation between the solute concentration and the activity of the solution was tested by linear correlation within the concentration range used for the sorption experiment.

Kinetic measurements

A fixed amount of air-dried soil (5.000 g, d < 2 mm) was weighed into a polypropylene centrifuge tube (Nalgene, USA) and mixed with 10 ml of 0.01 M CaCl₂. After 16 h shaking with an automatic rotating shaker, 10 ml of 0,01 M CaCl₂ spiked with [¹⁴C]isoproturon (1.12 µg cm⁻³) was added, and shaken for further 24 h. After 1 h, 5 h, 24 h and 48 h, samples (1 ml) were taken for ¹⁴C measurements. The samples were centrifuged at 10 000 x g for 10 minutes (Beckman Centrifuge) prior to the separation. Sorption was determined

by difference according to the formulae: $C_s(eq) = \frac{(C_0 - C_{aq}(eq))}{(m_{soil}/V_0)}$, where C_0 is the initial concentration in $\mu\text{g cm}^{-3}$, $C_{aq}(eq)$ the liquid concentration in $\mu\text{g cm}^{-3}$ after reaction with the solid phase, m_{soil} is the weight of the sample in g and V_0 the volume of the suspension in cm^{-3} .

Measurement of sorption isotherms

In the lower concentration range (initial concentration from 1×10^{-4} to $0.14 \mu\text{g cm}^{-3}$), the sorption and desorption experiments were carried out with pure [^{14}C]isoproturon, and in the higher concentration range (initial concentration from 0.1 to $1 \mu\text{g cm}^{-3}$) with a mixture of [^{14}C]isoproturon and the commercial fungicide containing 84% of isoproturon.

A fixed amount of air-dried soil (5.000 g, $d < 2$ mm) was weighed into a polypropylene centrifuge tubes (Nalgene USA) and mixed with 10 ml of 0.01 M CaCl_2 . After 16 h shaking with an automatic rotating shaker, the suspensions were equilibrated with 10 ml of 0.01 M CaCl_2 spiked with [^{14}C]isoproturon in different concentrations. After a further shaking for 24 h, the suspensions were centrifuged at $9600 \times g$ for 10 minutes (Beckman Centrifuge). Analyses of ^{14}C were run on 1 ml samples taken from the upper portion of the centrifuge tube.

Control experiments with different solute concentrations, without soil samples, were conducted to test the possible sorption to the walls of the tubes. The decrease in concentration in the control tubes was not significant.

The background activity of the supernatant was tested based on tubes with soil suspension not containing [^{14}C]isoproturon.

Measurement of desorption isotherms

After achieving pseudoequilibrium in soil suspensions containing [^{14}C]isoproturon, the

liquid phase was separated by centrifugation. 10 ml of the supernatant was then removed and replaced by 10 ml of 0.01 M CaCl₂. The suspension was shaken for 24 h and centrifuged again. The quantity of [¹⁴C]isoproturon in the liquid phase was determined by liquid scintillation.

Results and discussion

Sorption kinetics

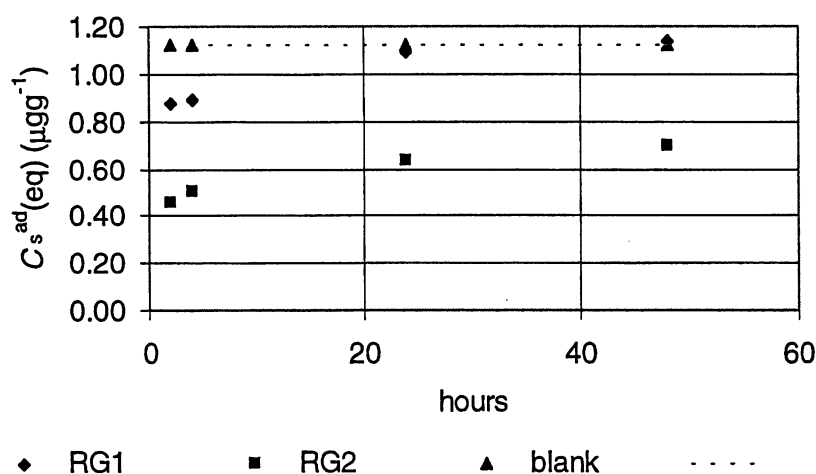


Fig. 1: Sorption kinetics of isoproturon in topsoil (RG1) and subsoil (RG2) from Skuterud, Ås.

Initially the sorption of isoproturon to the soil samples were rapid (Fig. 1). After 24 h., there was no significant increase in the amount of isoproturon that was sorbed to the soil. It was assumed that a pseudoequilibrium was reached within 24 h., and 24 h. was chosen as the reaction time in the sorption experiments.

The sorption isotherms

The linear relationships between the amount of isotroturon in the solid and liquid phase at psuedoequilibrium were generally good (Figs. 2a and 2b). Within the chosen concentration range, a linear model can therefore be used for describing the sorption and desorption of isotroturon on the soil samples from Skuterud, Ås. The K_d values calculated from the linear regression for the whole concentration range are summarised in Table 2.

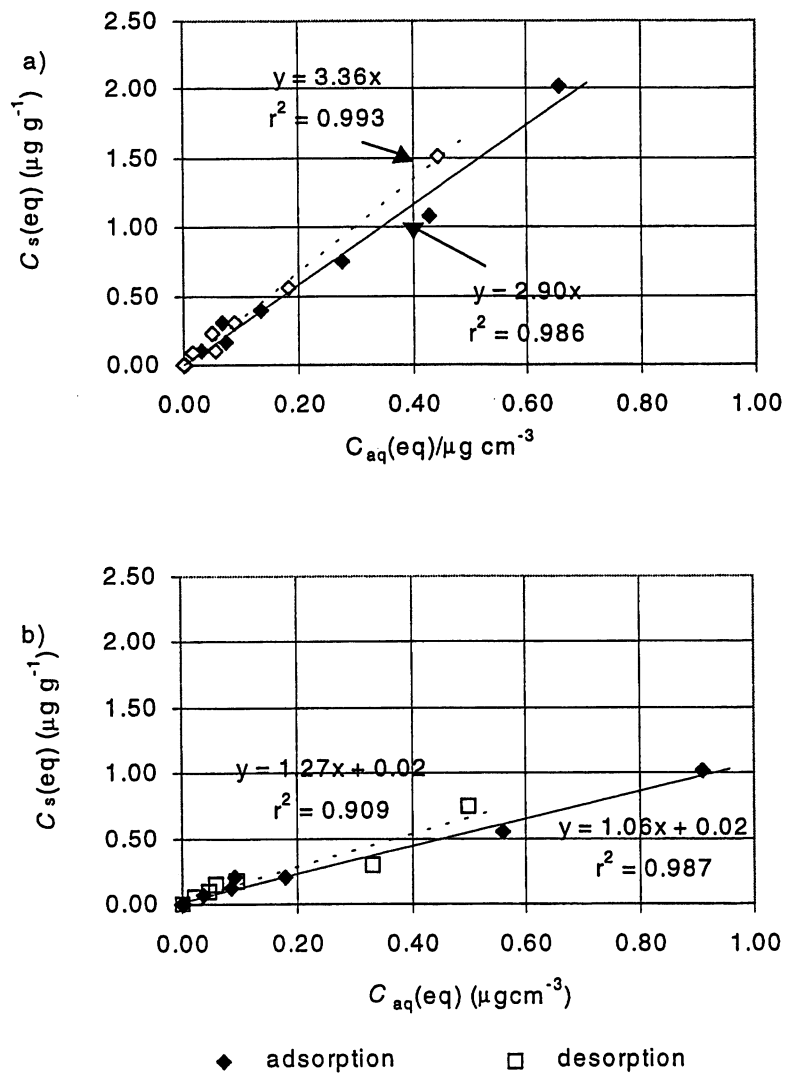


Figure 2: Adsorption- and desorption isotherms of isotroturon on soil samples from Skuterud, Ås , a): topsoil (RG1) and b): subsoil (RG2)

In Figs. 3a and 3b the sorption and desorption data are transformed into logarithmic relationships. The correlation coefficients for the logarithmic relationships were also high, and the data could therefore be fitted into the Freundlich sorption model, as well. The resulting values of K_F^{ads} , r^2 and n are presented in Table 2.

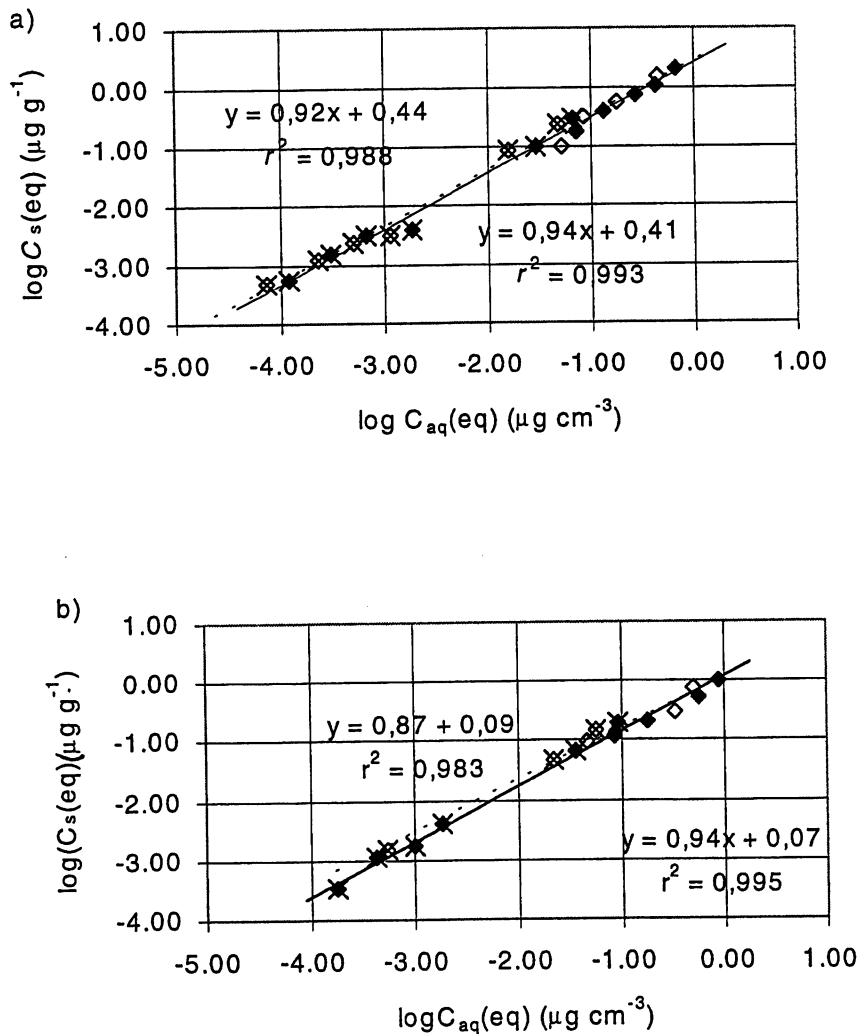


Figure 3: Freundlich adsorption- and desorption isotherms of isoproturon on a): topsoil (RG1) and b): subsoil (RG2).

adsorption: * (pure isoproturon) and \blacklozenge (commercial product),
 desorption: \otimes (pure isoproturon) and \diamond (commercial product)

The sorption of the pure and the commercial product of isoproturon is compared in Fig.3. The adsorption isotherms of both the pure and the commercial product of isoproturon are

found to conform the Freundlich model. This can be seen in the high coefficient of determination, r^2 . t-test further indicates that the difference between the regression lines of the pure and the commercial isoproturon are not significant at a $\alpha=0.05$ level. Two conclusions can be drawn from this results. First, the pure and the commercial isoproturon have the same sorbtivity to the soils tested. This implies that the additives in the commercial product have not significant influences on the sorption of isoproturon. Second, the Freundlich sorption models holds in a wide concentration range from $1 \times 10^{-4} \mu\text{g cm}^{-3}$ to $1 \mu\text{g cm}^{-3}$, which stretches over 4 orders of magnitude. The values of n in the Freundlich model, both for the sorption and the desorption, are not significantly different from 1. This implies that the sorption is highly linear.

Table. 2: The adsorption- and desorption coefficients of isoproturon on soil samples from topsoil (RG1) and subsoil (RG2) Skuterud, Ås.

	Adsorption				desorption				K_{OC}
	K_F^{ads}	n	r^2	K_d	K_F^{des}	n	r^2	K_{des}	
RG1	2.57	1.06	0.993	2.90	2.75	1.08	0.988	3.36	96
RG2	1.17	1.06	0.995	1.06	1.23	1.14	0.983	1.27	107

Using the equation (3) we have also calculated the K_{OC} values, the organic carbon normalised sorption coefficients for isoproturon (see Tab. 2). The K_{OC} values of the two soils, RG1 and RG2 are quite similar. The high sorption coefficient of the topsoil (RG1) can therefore be attributed to its high content of organic carbon (2,5 % org. C). We have also calculated some K_{OC} values using the sorption data reported in the literature (Pedersen et al. 1995 and Gaillardon 1997). The K_{OC} values obtained from the literature lie between 66 and 166 , which are in the same range as the K_{OC} value measured in our experiment ($K_{OC}=96-107$).

The K_{OC} values of many organic chemicals can be found in Rippen (1991). Based on K_{OC} values, Blume (1992) has classified the sorbtivity of different chemicals as very low (K_{OC} : 1-100), low (K_{OC} : 100-300), middle (K_{OC} : 300-1000), high (K_{OC} : 1000-10 000) and very high ($K_{OC}>10 000$). According to this classification isoproturon with a mean value of K_{OC} of 102, has a relatively low sorbtivity to soil organic matter.

The desorption isotherms

The desorption isotherms of isoproturon are presented in Figs. 2 and Fig. 3. The desorption data fit both with the linear and the Freundlich model, giving the apparent desorption coefficient, K_{des} and the Freundlich desorption coefficient, K_F^{ads} (see Tab. 2).

The high coefficients of determination (r^2) indicate a good fit of the desorption data with these two models.

Comparing the adsorption- and desorption isotherms in Fig. 2 or Fig. 3, only very weak hysteresis is observed, which implies high reversibility of the sorption-desorption process of isoproturon in soils. This result is in agreement with that observed by Gaillardon (1997) for a clay loam soil, where the desorption of isoproturon is achieved rapidly within a few hours and the desorption showed no hysteresis.

Conclusions

1. The sorption of isoproturon on the tested soils reaches its pseudo-equilibrium within 24 hours
2. The sorption of isoproturon is linear over a wide range of sorbate concentration between 1×10^{-4} and $1 \mu\text{g cm}^{-3}$
3. The additives in the commercial product Tolkan-WG (Rhone Poulenc) do not significantly affect the sorption of isoproturon
4. The sorption is strongly dependent on the content of soil organic carbon

5. The sorption-desorption process is highly reversible

Literature

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