

Institutt for jord og vannfag

Sorption and desorption of isoproturon and metalaxyl in soil from Heiabekken and Rustad, south-eastern Norway.

Qinglan Wu and Gunnhild Riise

Rapport nr.7/2001 (97)

**Institutt for jord og vannfag
Ås-NLH, 2001**

ISSN 0805-7214

INSTITUTT FOR JORD- OG VANNFAG

Norges Landbrukshøgskole

Postboks 5028, 1432 Ås Telefon: (09) 94 75 00 - Agriuniv. Ås

Telefax: (64) 94 82 11 Rapportarkiv: (64) 94 82 04

ISSN 0805 - 7214

Rapportens tittel og forfatter(e):

Sorption and desorption of isoproturon and metalaxyl in soil from Heiabekken and Rustad, south-eastern Norway

Rapport nr : 7/2001 (97)

Distribusjon: Fri (01.05.02)

Dato: 29.10.01

Prosjektnummer:

Faggruppe: Pesticider

Geografisk område:
S-Ø Norge

Antall sider (inkl. bilag) 19

Oppdragsgivers ref.:

Oppdragsgiver: Statens landbrukstilsyn

Sammendrag:

Det er gjennomført sorpsjons- og desorpsjonsforsøk med pesticidene isoproturon og metalaxyl i topp- og undergrunnsjord fra Heiabekken og Rustad gård i henhold til OECD guideline 106 (1997).

Sorpsjons- og desorpsjonsisotermene for isoproturon er lineære over et stort konsentrasjonsområde (0,002 – 2,0 mg/l) i toppjord og i et begrenset konsentrasjonsområde (0,02 – 0,02 mg/l) i undergrunnsjord fra Heiabekken. Resultatene for metalaxyl viser også god tilpasning til lineære isotermer i topp- og undergrunnsjord fra Heiabekken og undergrunnsjord fra Rustad gård, og til Freundlich isotermer i topp- og undergrunnsjord fra både Heiabekken og Rustad gård.

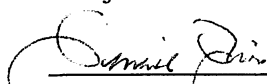
Sorpsjonen av isoproturon og metalaxyl er større for toppjord sammenlignet med undergrunnsjord, p.g.a. høyere innhold av organisk materiale. Både isoproturon og metalaxyl er mobile pesticider, isoproturon viser imidlertid større grad av binding til jord enn metalaxyl. Fordelingskoeffisienter korrigert for jordas innhold av organisk karbon viser høyere verdier for isoproturon (Koc: 94-107) sammenlignet med metalaxyl (Koc: 36-62).

For isoproturon er sorpsjons- og desorpsjonsprosessene tilnærmet reversible i topp- og undergrunnsjord fra både Heiabekken og Rustad gård. Hysteresis er observert for metalaxyl i topp og undergrunnsjord fra Rustad gård.

4. Emneord, norske

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

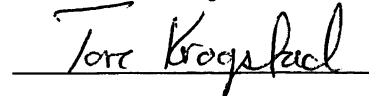
Prosjektleder:



4. Emneord, engelske

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

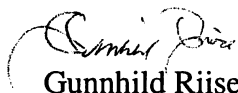
For administrasjonen:



Preface:

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

Ås, 29.10.01



Gunnhild Riise (associate professor)

Content

1	Introduction.....	1
2	Materials and methods.....	3
	2.1 Soil materials.....	3
	2.2 Chemicals.....	3
	2.3 Analytical methods.....	4
	2.4 Sorption and desorption isotherms.....	5
3	Results and discussion.....	8
	3.1 Sorption and desorption of isoproturon.....	8
	3.2 Sorption and desorption of metalaxyl.....	13
4	Conclusions.....	18
5	Literature.....	19

Sorption and desorption of isoproturon and metalaxyl in soils from Heiabekken and Rustad, south-eastern Norway

Qinglan Wu and Gunnhild Riise, Department of Soil- and Water sciences,

Agricultural University of Norway, P.O. Box. 5028, N-1432 Ås

1 Introduction

Interactions of organic chemicals with different compounds in the soil-water system are of great importance, because sorption and desorption reactions directly affects plant uptake, retention, volatilisation, biodegradation and transport of organic chemicals in soils and waters. Therefore, sorption and desorption parameters are used in a variety of models for predicting the fate of organic chemicals entering the soil environment.

In an earlier work, we have investigated the sorption and desorption of isoproturon on topsoil (RG1) and subsoil (RG2) from Rustad Gård (Wu and Riise, 2000). In this work, we have additionally determined the sorption and desorption isotherms of isoproturon for the topsoil (HB1) and subsoil (HB2) from Heiabekken, and that of metalaxyl for all the four selected soil samples (RG1, RG2, HB1 and HB2). The determination of the isotherms was carried out according to the OECD-guideline 106 (1997), so that the derived sorption parameters can be compared with other standardized data that are published. The selected soil samples differ in their contents of organic carbon (C_{org} in %) and clay minerals (clay in %). Influences of organic carbon and clay minerals on the sorption behaviour are discussed.

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

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

$$\frac{x}{m} = K_F^{ads} (C_{eq}^{ads})^{1/n}, \quad (1)$$

where $\frac{x}{m}$ and C_{eq}^{ads} are the equilibrium concentrations of the test substance in the solid phase (in mg/kg) and in the aqueous phase (mg/l), 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:

$$K_d^{ads} = \frac{\frac{x}{m}}{C_{eq}^{ads}}, \quad (2)$$

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

2 Materials and methods

2.1 Soil materials

Samples of the top- and subsoil from Rustad Gård (RG1 and RG2), Ås and Heiabekken (HB1 and HB2), Østfold were provided by the Norwegian Crop Research Institute, Plant Protection Centre. The samples RG1 and RG2 were air dried and sieved to < 2 mm, while the samples HB1 and HB2 were moist and contained 16,4% and 11,8% water, respectively. The physical and chemical characteristics of the soil samples are summarised in Table 1.

Table1: Physical and chemical characteristics of soil samples from Rustad Gård (RG1 and RG2) and Heiabekken (HB1 and HB2)*

Sample No	Depth/cm	pH (in CaCl ₂)	Water content (%)	C _{org} (%)	Clay (%)
RG1	0-20	n.d.	5.6	2.52	25.1
RG2	20-40	n.d.	2.4	1.07	27.4
HB1	0-35	5.5	16.4	2.2	11.4
HB2	35-56	5.1	11.8	0,2	5.1

*Data obtained from Norwegian Crop Research Institute, Plant Protection Centre

2.2 Chemicals

[¹⁴C] Isoproturon and non-labelled isoproturon

¹⁴C ring labelled isoproturon [3-[4-isopophylphenyl)-1,1-dimethylurea] with a specific activity of 4 MBq/mg was used in the sorption experiments. The purity was > 97 % (Institute of Isotopes Co., Ltd., Budapest). In experiments demanding high pesticide concentrations, non-labelled isoproturon, the commercial product (purity 83%, Tolkan WG) was added in a proportion of 1:4 (labelled / non labelled).

[¹⁴C] isoproturon was first dissolved in methanol (purity >99.7 %, Riedel de Haen) to a concentration of 8×10^3 mg/l. The methanol solution was then diluted with 0.01 M CaCl₂ to a concentration of 9.2 mg/l. The stock solution was further diluted with 0.01 M CaCl₂ to different concentrations.

Metalaxyl

Metalaxyl used for the sorption and desorption experiment is non-labelled, because the purchase of labelled chemical was failed. The purity of metalaxyl was > 99.3 % (Dr. Ehrenstorfer GmbH, Germany). The stock solution of metalaxyl was prepared by dissolving 49.1 mg Metalaxyl in 250 ml distilled water.

2.3 Analytical methods

Determination of 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. The ¹⁴C activity of this solution was determined by liquid scintillation (Packard Tri-Carb 4530 liquid scintillation counter). The linearity of the correlation between the solute concentration and the activity of the solution was tested within the concentration range used for the sorption experiment.

Determination of metalaxyl by HPLC

Metalaxyl in 20 ml water sample was first extracted into 5 ml of a methanol/water-mixture (1:1) using solid phase extraction techniques and then analysed by HPLC according to the method developed by Rolli (2001) at the Norwegian Crop Research Institute, Plant Protection Centre. The linearity of the measurement and the recovery rate of metalaxyl

were tested between 0.2 mg/l and 10 mg/l, the same concentration range as used for the sorption experiments. Within the concentration range tested, the linearity of the relationship between HPLC signal area and metalaxyl concentration is very high with a coefficient of determination of 0.9999 (r^2). Also the recovery rate of metalaxyl is very high, more than 95%.

2.4 Sorption and desorption isotherms

The sorption and desorption isotherms of isoproturon and metalaxyl were determined with batch experiments in 0.01 M CaCl₂ and at room temperature. The duration of the sorption experiments lasted for 24 hours and that of the desorption 72 hours, which is sufficient for reaching the apparent sorption and desorption equilibrium according to the kinetics measurements for isoproturon by Wu and Riise (2000) and that for metalaxyl by Olsen-Ingerø (1999).

Isoproturon

In the lower concentration range (initial concentration from 0.002 to 0.02 mg/l), the sorption and desorption experiments were carried out with [¹⁴C]isoproturon, and in the higher concentration range (initial concentration from 0.02 to 2.0 mg/l) with a mixture of [¹⁴C]isoproturon and a not labelled isoproturon.

A fixed amount of soil sample (5.000 g, d < 2 mm) was weighed into a polypropylene centrifuge tubes (Naglene USA) and mixed with 10 ml of 0.01 M CaCl₂. After 16 h end-over-end shaking, the suspensions were subsequently equilibrated with 10 ml of 0.01 M CaCl₂ spiked with [¹⁴C]isoproturon at different concentrations. After a further shaking for 24 h, the suspensions were centrifuged at 9600 x 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.

Tubes without soil were used to control the sorption to the tubes. The concentration change in the control tubes was not significant; therefore the sorption on the tubes was neglected.

The background activity of the supernatant was tested using blanks with soil suspension, but without [^{14}C]isoproturon. The background activity measured was so low that it can be neglected.

The desorption experiment was carried out by removing 10 ml of the supernatants from each centrifuge tube and replacing with 10 ml of 0.01 M CaCl_2 . The suspension was then shaken for another 72 h and centrifuged again. The quantity of [^{14}C]isoproturon in the liquid phase was determined by liquid scintillation.

Metalaxyl

A fixed amount of moist soil sample (20.000 g) was weighed into a 60 ml polypropylene centrifuge tubes (Naglene USA) and mixed with 20 ml of 0.01 M CaCl_2 . After 16 h end-over-end shaking, the suspensions were subsequently equilibrated with 20 ml of 0.01 M CaCl_2 spiked with metalaxyl at different concentrations. After a further shaking for 24 h, the suspensions were centrifuged at 4000xg for 30 minutes (Hereaus). The metalaxyl concentration in each supernatant was analysed using HPLC after a solid phase extraction into a methanol/water mixture (1:1).

Tubes without soil samples were used to control the sorption to the tubes. The decrease in concentration in the control tubes was about 10% of the initial concentration. The amount

~~of metalaxyl sorbed to the tubes has been accounted for during the calculation of the~~
sorption isotherms.

3 Results and discussion

3.1 Sorption and desorption of isotroturon

In Fig. 1 the sorption and desorption isotherms of isotroturon for the top soil from Heiabekken (HB1) are presented in the concentration range from 0.002 to 2.0 mg/l, a relative broad concentration range.

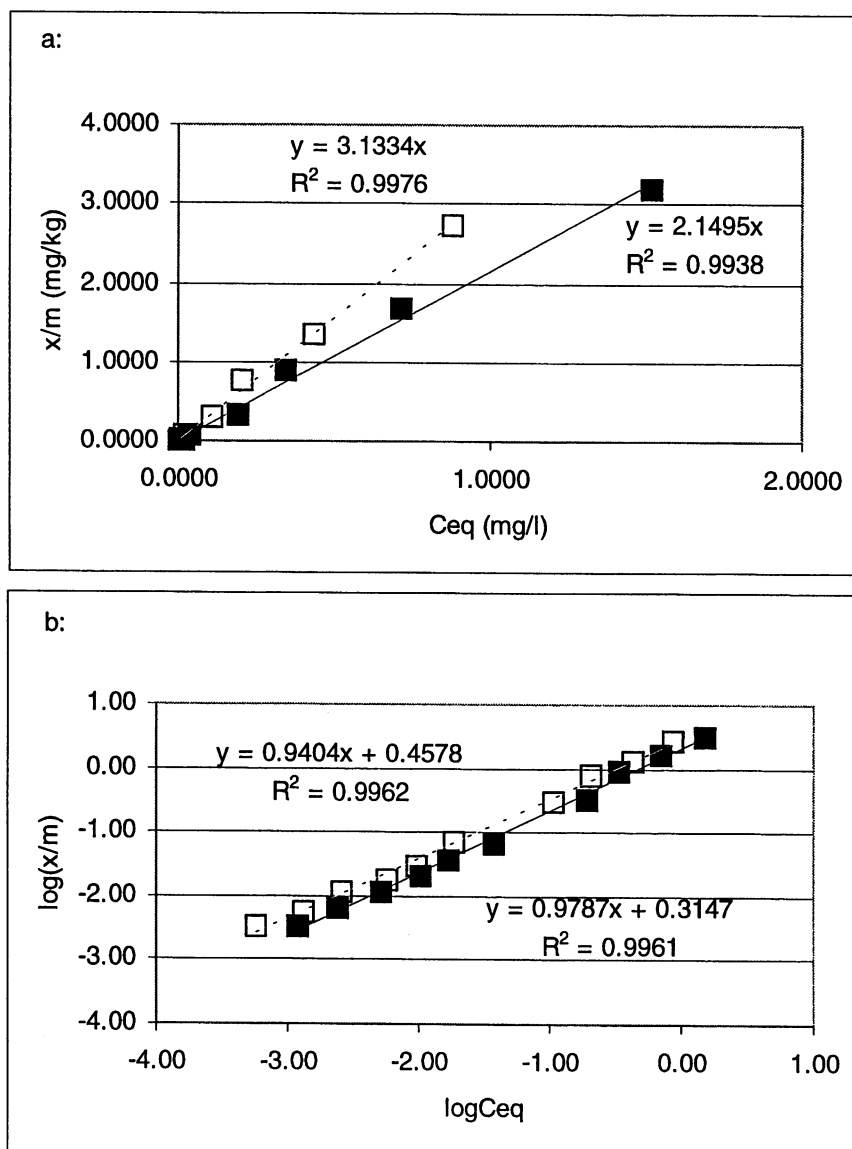


Figure 1: Sorption (■) and desorption (□) isotherms of isotroturon on the topsoil HB1 from Heiabekken a): in a normal scale according to the linear model; b): in a doubled logarithmic scale according to the Freundlich model

The linearity of the relationship between the amount of isoproturon in the solid and liquid phase at apparent equilibrium (see Fig. 1a) was generally very good, both for the sorption and desorption isotherms, as the large coefficients of determination r^2 indicate.

In Fig.1a, the experimental data are not evenly distributed over the whole concentration range. The data measured in the concentration range from 0.002 to 0.02 mg/l are all located near the coordinator's zero point. Details of the isotherms in this concentration range can be seen more clearly in Fig. 1b, a log-log plot, where the data are more evenly distributed over the x-coordinator.

The coefficients of determination for the logarithmic relationships were also high ($r^2 > 0.996$), and the data could therefore be fitted into the Freundlich sorption model, as well. The n-values, both for sorption and desorption, are not significantly different from one, which again indicates that the sorption and desorption are linear over the whole concentration range tested.

In contrast to the topsoil (HB1), the sorption and desorption isotherms for the subsoil from Heiabekken (HB2) are not linear over the whole concentration range tested. In order to show the details of the isotherm in the lower concentration range, the isotherms are presented in an enlarged scale in Fig. 2b. The sorption is only linear in the very lower concentration range from 0.002 to 0.02 mg/l, increases then rapidly with increasing equilibrium concentration up to 0.2 mg/l and decreases again in the more higher concentration range from 0.2 to 2.0 mg/l.

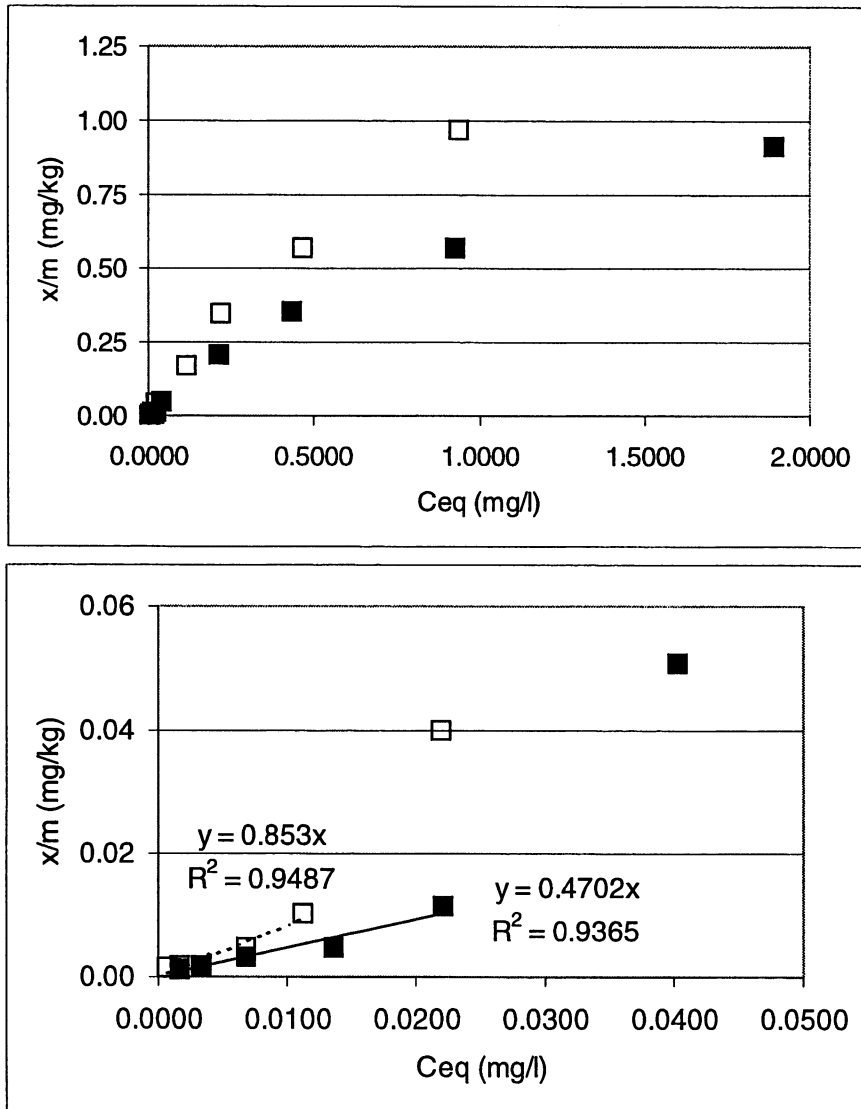


Figure 2: Sorption (■) and desorption (□) isotherms of isoproturon on subsoil from Heiabekken (HB2) over a concentration range **a**: from 0 to 2.0 mg/l and **b**: from 0 to 0.05 mg/l, fitted to a linear model

In Fig. 3 the sorption and desorption data are transformed into logarithmic relationships. In this diagram we can see even more clearly the S-form of the isotherms. The isotherms over the whole concentration range do not fit the Freundlich model. However, a part of the isotherm, in the high concentration range from 0.05 to 2.0 mg/l, fits well with the Freundlich model with a high coefficient of determination of $r^2=0.995$.

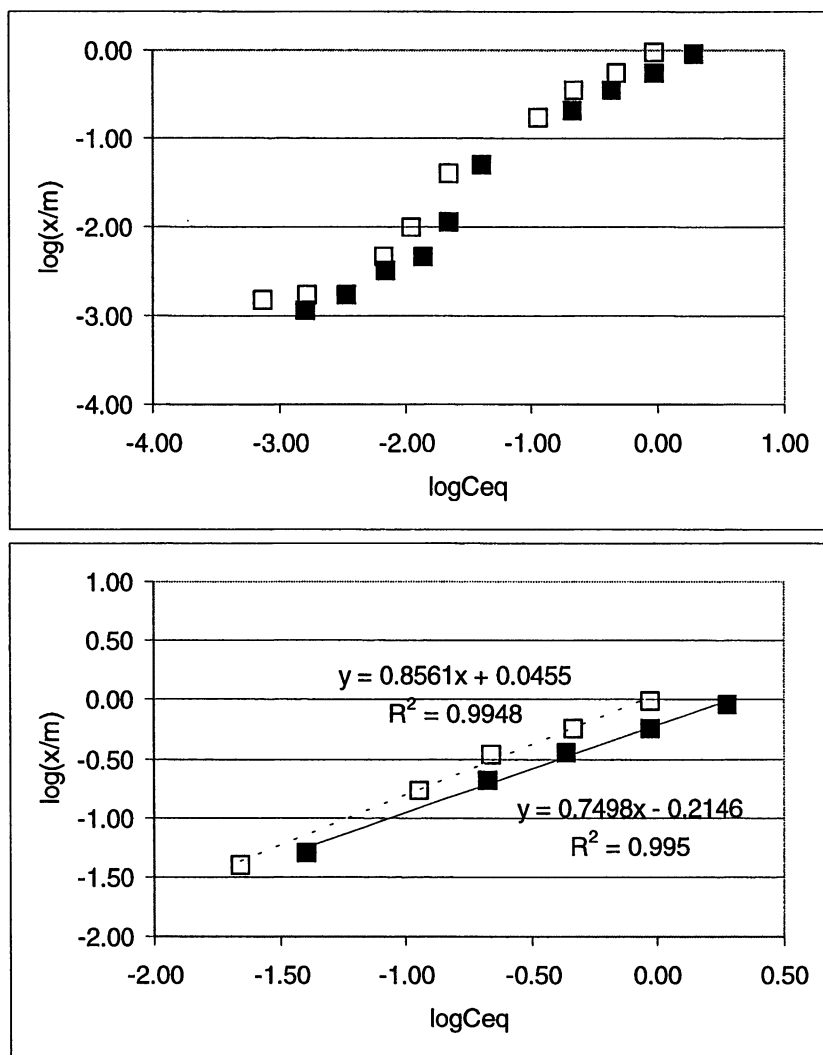


Figure 3: Log-log plot of the sorption (■) and desorption (□) isotherms of isoproturon on subsoil from Heiabekken (HB2), a: over the whole concentration range tested, from 0.002 to 2.0 mg/l, b: in the higher concentration range from 0.05 to 2.0 mg/l, fitted to the Freundlich model

The sorption and desorption characteristics derived from the fit to the linear and Freundlich model are summarised in Table 2. To compare the results with our earlier work on soils from Rustad Gård (Wu and Riise, 2000), sorption characteristics for soils RG1 and RG2 are also presented.

Table 2: Distribution coefficients (K_d^{ads} and K_d^{des}) and Freundlich coefficients for the sorption (K_F^{ads} and n^{ads}) and desorption (K_F^{des} and n^{des}) of isoproturon for soils from Rustad (RG1, RG2) and Heiabekken (HB1 and HB2).

Sample No	Concentration range (mg/l)	Sorption					Desorption					K_{OC}
		K_d^{ads}	r^2	K_F^{ads}	n^{ads}	r^2	K_d^{des}	r^2	K_F^{des}	n^{des}	r^2	
HB1	0.002-2.0	2.15	0.994	2.07	1.02	0.996	3.13	0.998	2.87	1.06	0.996	94
HB2	0.002-0.02	0.47	0.937	0.2	1.2	0.956	0.85	0.949	0.2	1.5	0.924	100
HB2	0.05-2.0	—	—	0.6	1.3	0.995	—	—	1.1	1.2	0.995	290
RG1	0.0001-1.0	2.9		2.57	1.06	0.993	3.36		2.75	1.08	0.988	96
RG2	0.002-2.0	1.06		1.17	1.06	0.995	1.27		1.23	1.14	0.983	107

Soils from these two places show the same trend that the sorption of isoproturon is larger in the topsoil compared to the subsoil. This can be attributed to the higher organic carbon content in the topsoil, as the organic matter is an important sorbent for hydrophobic chemicals, such as isoproturon.

We also have calculated the K_{OC} values. With the exception of HB2 in the higher concentration range, the derived K_{OC} values lie between 94 and 107, which are in the same range as reported in the literature (Pedersen et al. 1995 and Gaillardon 1997). The deviation for soil HB2 may arise from its low content of organic carbon (0.2%). Both uncertainty in the determination of organic carbon and the presence of sorbents others than organic matter, may be the reason for the high K_{OC} value of soil HB2.

By comparing the differences between K_d^{ads} and K_d^{des} , and between K_F^{ads} and K_F^{des} in Table 2, only a weak hysteresis can be observed, which means a high reversibility between sorption and desorption of isoproturon in these soils.

3.2 Sorption and desorption of Metalaxyl

In general, the accuracy of the measurement of metalaxyl by HPLC is lower than the measurement of isoproturon by ^{14}C liquid scintillation. In addition the sorption of metalaxyl on the tubes used in the batch experiment is about 10%, while that of isoproturon is less than 1%. Consequently, the isotherms determined for metalaxyl are not as accurate as that for isoproturon. Therefore, the isotherms of metalaxyl will not be discussed in the same detail as for isoproturon.

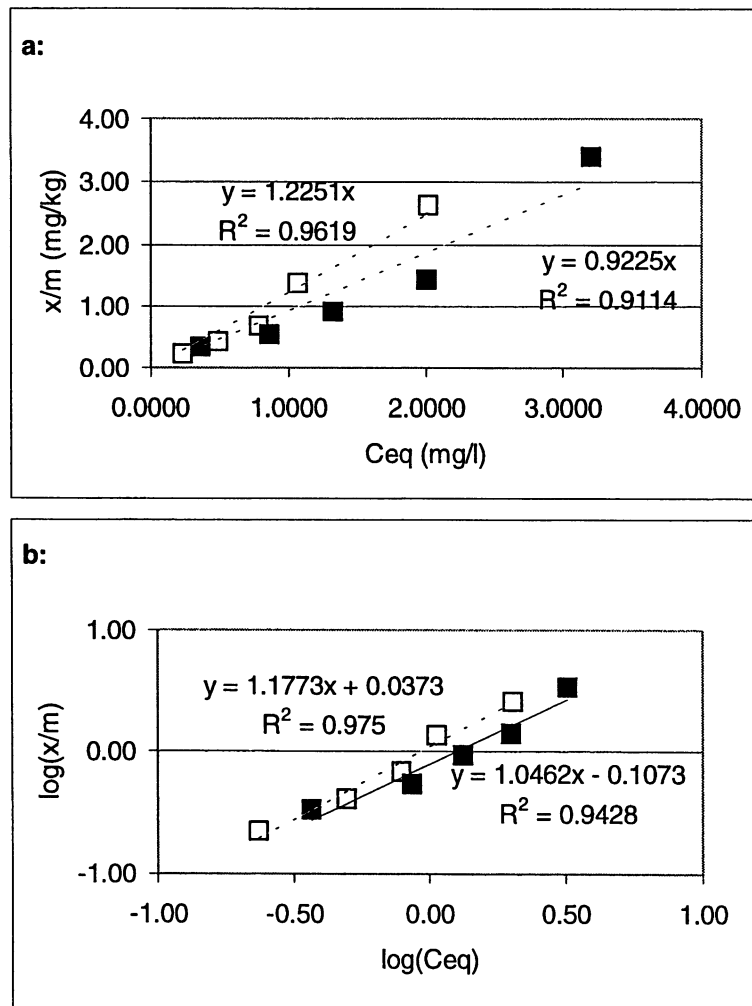


Figure 4: Sorption (■) and desorption (□) isotherms of metalaxyl for topsoil from Heiabekken (HB1), **a:** according to the linear model, **b:** according to the Freundlich model, in a log-log plot

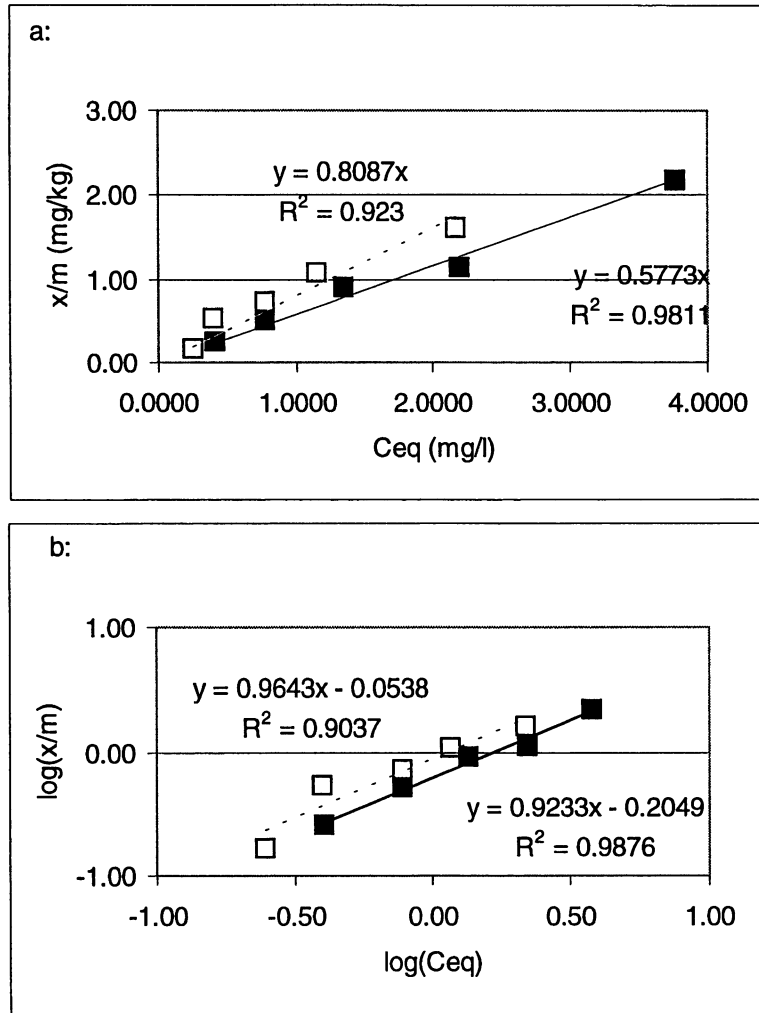


Figure 5: Sorption (■) and desorption (□) isotherms of metalaxyl on subsoil from Heiabekken (HB2), **a:** according to the linear model, **b:** according to the Freundlich model, in a log-log plot

The sorption and desorption isotherms of metalaxyl are presented in Fig. 4 for topsoil HB1 and in Fig. 5 for subsoil HB2. The experimental data were fitted both with the linear model and the Freundlich model. The relative large coefficients of determination ($r^2 > 0.9$) indicate a good fit of the experimental data with these two models. The resulting K_d -values, the Freundlich coefficients K_F and n , as well as the K_{oc} -values are summarised in Table. 3.

Comparing the sorption- and desorption isotherms in Fig. 4 and Fig. 5 only a very weak

hysteresis is observed, which implies a relative high reversibility of the sorption-desorption process of metalaxyl in soils HB1 and HB2.

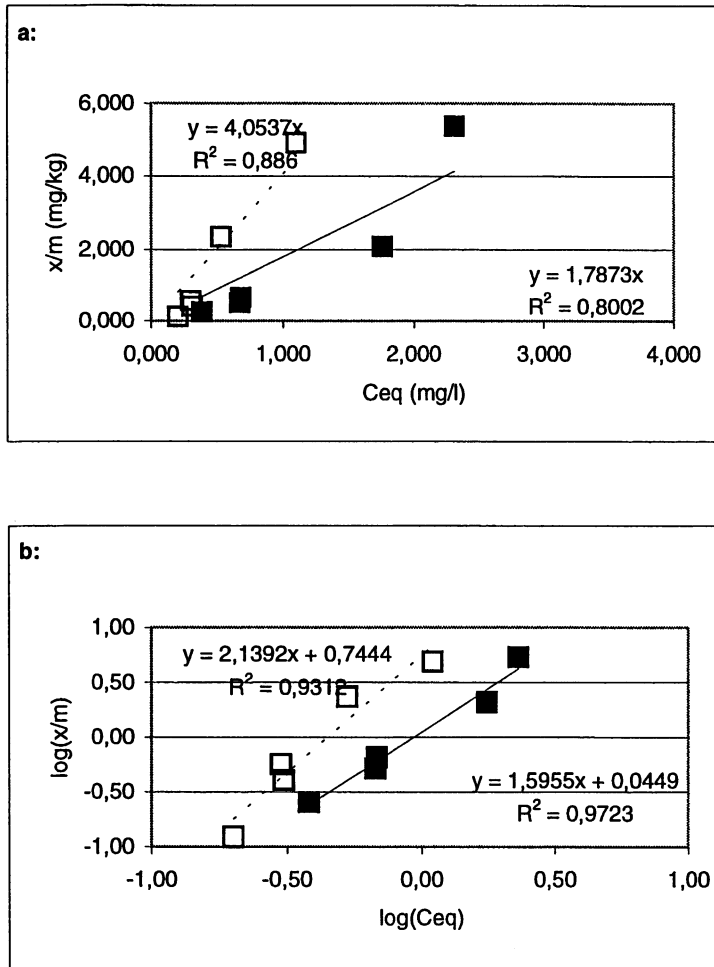


Fig. 6: Sorption (■) and desorption (□) isotherms of metalaxyl on topsoil RG1, **a:** according to the linear model, **b:** according to the Freundlich model, in a log-log plot

Fig. 6 and Fig. 7 show the sorption and desorption isotherms of metalaxyl for the topsoil RG1 and subsoil RG2 from Rustad Gård.

The linearity of the sorption isotherms for the topsoil from Rustad (RG1) is, with a coefficient of determination of 0.800, relatively low (Fig. 6). The fit with the Freundlich model in Fig. 6b is better with a large coefficient of determination ($r^2=0,973$). A n-value of 0.6 in the Freundlich model is largely deviated from one, which means a lower linearity of

the isotherm, which is in consistent with the small r^2 -value of the linear model.

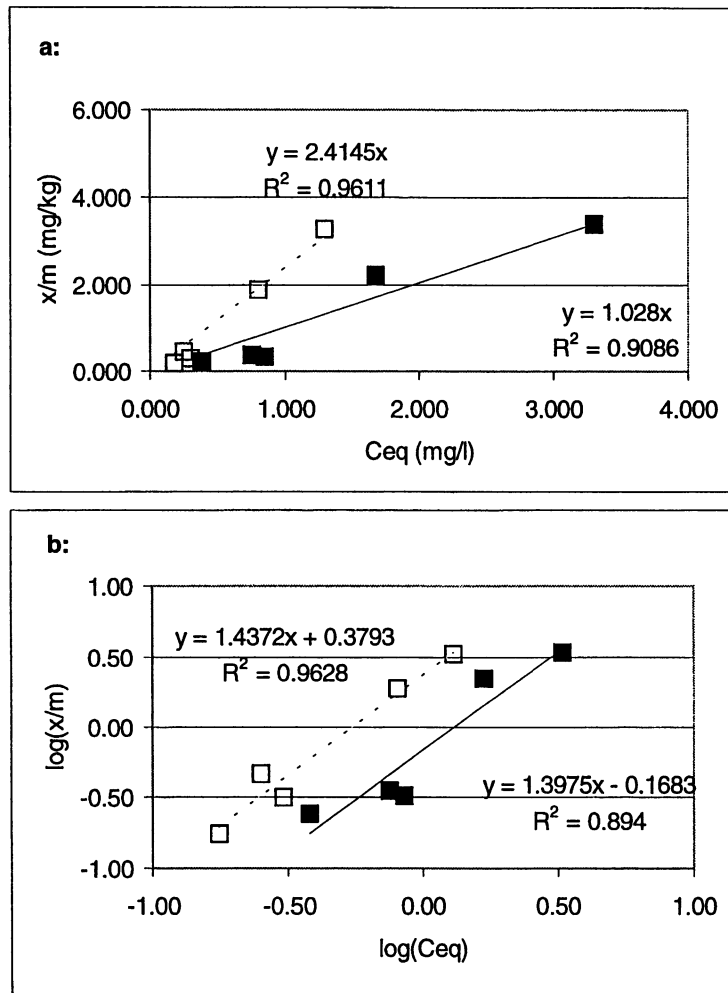


Figure 7: Sorption (■) and desorption (□) isotherms of metalaxyl on subsoil from Rustad (RG2), **a:** according to the linear model, **b:** according to the Freundlich model, in a log-log plot

Comparing the sorption isotherm with the desorption isotherm in Fig. 6 and Fig. 7, large hysteresis can be observed. This result implies that a part of the sorbed metalaxyl remains in the solid phase and cannot easily desorb again into the liquid phase.

The K_{OC} values calculated for the four tested soils are between 36 and 62, which are comparable to the K_{OC} -values (20-145) for the same soil determined by Olsen-Ingerø (1999) using one point distribution measurement.

The K_{OC} values of many organic chemicals can be found in Rippen (1991). In comparison to other organic chemicals, isoproturon with a mean K_{OC} -value of 102 and metalaxyl with a mean value of 49, have relatively low sorbtivity to soil organic matter according to the classification method of Blume (1992).

Table 3: Distribution coefficients (K_d^{ads} and K_d^{des}), Freundlich coefficients for the sorption (K_F^{ads} and n^{ads}) and desorption (K_F^{des} and n^{des}) and K_{OC} -values of metalaxyl for Heiabekken (HB1 and HB2) and Rustad (RG1 and RG2)

Sample No	Concentration range (mg/l)	Sorption					Desorption					Koc
		K_d^{ads}	R^2	K_F^{ads}	n^{ads}	R^2	K_d^{des}	r^2	K_F^{des}	n^{des}	r^2	
HB1	0.4-3.2	0.92	0.991	0.78	0.96	0.943	1.2	0.962	1.1	0.85	0.975	36
HB2	0.4-3.8	0.58	0.981	0.62	1.08	0.988	0.81	0.92	0.88	1.04	0.904	--
RG1	0.4-2.30	1.8	0.886	1.1	0.6	0.972	4.1	0.8	5.6	0.5	0.931	44
RG2	0.4-3.3	1.2	0.933	0.7	0.7	0.894	2.8	0.994	2.4	0.7	0.963	62

4 Conclusions

1. The sorption and desorption isotherms of isoproturon are linear over a wide concentration range (0.002 and 2.0 mg/l), for the topsoil from Heiabekken (HB1). However, for the subsoil from Heiabekken (HB2) the sorption and desorption isotherms are only linear in the very low concentration range from 0.002 to 0.02 mg/l. For the higher concentration range, from 0.05 to 2.0 mg/l the Freundlich model fits better to the isotherms.

2. The sorption and desorption isotherms of metalaxyl fit well to the Freundlich model for all the four soils tested in the concentration range from 0.4 to 3.0 mg/l. Except for the topsoil from Rustad Gård (RG1), the fit with a linear model also gives satisfactory results for the soils from Heiabekken (HB1, HB2) and the subsoil from Rustad gård (RG2).

3. The sorption of both isoproturon and metalaxyl is higher in the topsoil compared to the subsoil, as the organic carbon content decreases with the soil depth. The K_{OC} -value of metalaxyl (K_{OC} : 36-62) is in average lower than the K_{OC} -value of isoproturon (K_{OC} : 94-107).

4. The sorption-desorption process of isoproturon is highly reversible in all the four soils tested. For metalaxyl, relatively large hysteresis are observed in the soils from Rustad Gård.

5 Literature

- Blume, H.-P. (1992): *Handbuch des Bodenschutzes*. Ecomed Verlagsgesellschaft, Landsberg.
- Gaillardon, P. (1997): Desorption of diuron and isoproturon from undispersed clay loam soil. *Pesticide Science* 51, 185-193.
- OECD (1997): *OECD Guidelines for Testing of Chemicals: Adsorption/desorption using a batch equilibrium method*.
- Pedersen, H.J. Kudsk, P. And Helweg, A. (1995): Adsorption and ED50 values of five soil-applied herbicides. *Pesticide Science* 44, 131-136.
- Olsen-Ingerø, H.-K. (1999) Risiko for utlekking av plantevernmidler-undersøkelse av sorpsjon og nedbryting av metalaksyl i heiabekkområdet, Råde. Hovedoppgave ved Planteforsk Plantevernet, Avd. Ugras, NLH, Våren 1999.
- Rippen, G. (1995): *Handbuch der Umweltchemikalien*, Loseblattsammlung. Ecomed, Landsberg/Lech.
- Wu, Q. and Riise, G. (2001): Sorption properties of Isoproturon in soils. Report 8/2001 (98), Department of Soil- and Water Sciences, Agricultural University of Norway, Ås