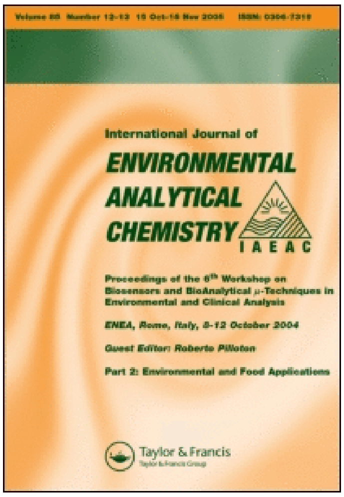

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DEGRADATION AND DISSIPATION STUDIES OF ISOPROTURON IN A SILTY CLAY LOAM FROM NORWAY

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Degradation and dissipation studies in laboratory and field were performed with isoproturon (IPU) to produce data for modelling the fate of an autumn applied pesticide in a Gleyic Podzoluvisol in Norway.

Transformation rate studies of IPU in the laboratory during 8 weeks displayed a DT_{50} of 13 days in topsoil (0–20 cm) and 21 days in subsoil (20–40 cm) at 20°C. In topsoil, a decline in the content of the metabolite monodesmethyl-isoproturon (MMU) was observed along with an initial production of didesmethyl-isoproturon (MU) after 4 weeks. In subsoil, the content of MMU was stabilized and no decrease was observed during the experiment. Only trace amounts of MU were found in the subsoil.

Field dissipation of IPU was investigated in a silty clay loam following post-emergence application to winter wheat (September 1999). A bromide tracer was used to monitor the water flow in the soil profile. Soil was sampled from the 0–20, 20–40, 40–60 and 60–80 cm layers after 1, 2, 4, 13, 62, 232 and 371 days. 13 days after herbicide application, the waterfront had reached a depth of 80 cm and as a result an amount of 7 mg IPU m^{-3} could be recovered from this depth, representing 2% of the initial amount of herbicide applied. Less than 9% of the herbicide applied could be seen to penetrate below 20 cm soil depth. After 62 days, only 18% of the initial IPU amount applied could be recovered from the profile. Using the results from the laboratory degradation study, a theoretical DT_{50} of IPU in the field was estimated to 18–25 days ($Q_{10} = 2.2$). The theoretical DT_{50} corresponded well with the actual dissipation of IPU observed in the field. This indicated that degradation of IPU was the primary contribution to the fast dissipation of IPU in the field, and that the risk of runoff of IPU was negligible.

Appearance of the major degradation product MMU in the field was monitored during the entire experimental period, at most representing 11% of the initial herbicide concentration. Field studies showed that MMU was more easily transported below the plough layer than isoproturon. Traces of IPU and MMU could be found in soil one year after application. A second degradation product, MU, could not be recovered in quantifiable amounts in the soil samples.

Keywords: Degradation; Isoproturon; Dissipation; Field

INTRODUCTION

Isoproturon (IPU) has a low solubility in water (70 mg l^{-1}) but is only weakly retained by sorption and is considered a risk compound for leaching to surface and ground waters [1]. According to the JOVÅ-monitoring programme on pesticides in Norway,

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IPU has been traced in 8 out of 52 samples collected from different streams and rivers in Norway from 1995 to 1999 [2]. These observations have been made in June–August only, that is, concurrently with field applications of IPU. The objectives of this study were to produce input data for the parameters of the two mathematical models MACRO and PRZM3 and to describe the fate of IPU in the field for validation of these two models. Data from the first year was meant for calibration of the models.

EXPERIMENTAL

Soil and Chemicals

The soil used was taken from the experimental field at Rustad, Ås, Norway. The physical and chemical properties of the soil are listed in Table I.

Analytical grade IPU and the metabolites monodesmethyl-isoproturon (MMU; *N′*-(4 isopropylphenyl)-*N*-methyl urea) and didesmethyl-isoproturon (MU; *N*-(4 isopropylphenyl)urea) were supplied by Dr. Ehrenstorfer GmbH.

Laboratory Experiments

Soil samples were collected from the topsoil (0–20 cm) and subsoil (20–40 cm), sieved to pass a 2 mm screen without previous air-drying. Initial soil moisture content was 17% (subsoil) and 23% (topsoil). The soil samples were pre-incubated in one week at 20°C and at 40% of their maximum water holding capacity. Soil, relative to 50 g dry mass, was weighed into separate beakers, and aqueous IPU was applied at a rate of 5 $\mu g\,g^{-1}$ in volumes of water needed to bring the soils to a water holding capacity of 60%. IPU was used formulated as the wettable powder Tolkan WG, which contains 83% a.i. The beakers were incubated in the dark at 20°C. At each sampling event, triplicate beakers were removed and analysed after 0, $\frac{1}{2}$, 1, 1, $1\frac{1}{2}$, $\frac{1}{2}$, 2, 4, 6 and 8 weeks.

Field Experiment

The experimental field was located at Rustad, Ås, and sown with winter wheat, which had reached approximately 5 cm shoot height at the time of herbicide treatment. IPU (Tolkan WG) was applied at a rate of 552 g a.i. ha^{-1} to four replicate plots (6 × 30 m) on the 16th of September 1999. Paper filters were distributed across the field prior to application to measure the herbicide applied. In addition, soil samples at a depth of 1 cm were collected on the day of application and the following

TABLE I Soil physical and chemical properties of the Rustad silty clay loam

Layer	*Depth* cm	*Sand* %	*Silt* %	*Clay* %	*Tot C* %	*CEC meq 100* g^{-1}	*pH*		*Soil density* g cm^{-3}
							H_2O	*$CaCl_2$*	
Ap	0–26	12.7	60.1	27.4	1.9	14.2	6.6	5.8	1.32
Eg/Bt	26–34	9.5	57.3	33.2	0.4	12.7	5.7	4.9	1.75
Bt	34–71	6.3	55.3	38.5	0.3	17.5	6.6	5.6	1.62
BCg	71+	8.8	53.2	38.1	0.3	16.4	7.1	6.1	1.75

day. Bromide, at a rate of 39 kg/ha^{-1}, was used as a non-interactive tracer in order to track the movement of water in the profile. The plots were sampled for herbicide and bromide at intervals between September 1999 and September 2000. Four days after herbicide and bromide application, soil samples at a depth of 30 cm were collected, whereas at 13, 62, 232 and 371 days after application, samples at a depth of 80 cm (0–20, 20–40, 40–60 and 60–80 cm) were collected with a 33 mm diameter cube corer from predetermined random positions on a grid. Triplicate samples from each plot were mixed together. The samples were stored at -20°C until analysis.

Extraction and Analysis

Isoproturon and the metabolites MMU and MU were extracted from the soil samples by mixing 25 g soil with 2×50 ml methanol for 10 min and centrifuging (5000 rpm, 10 min) to separate the soil from the extract. The methanol extract was diluted in 400 ml water and passed through an IST Isolute ENV+ cartridge (500 mg styrene divinylbenzene). The loaded cartridges were dried by passing a gentle stream of nitrogen before elution with methanol (5 ml). The eluate was reduced to dryness and re-suspended in methanol (1 or 5 ml). The IPU concentrations were determined by reversed-phase HPLC (Spectra-Physics SP8800 Ternary HPLC Pump, Gilson 234 Autoinjector) with injection through a 20-µl loop. 30% acetonitril in phosphatebuffer (20 mM, pH 7.1) was used to elute the sample through a Supelco C18 column (5 µm, 150×4.6 mm i.d.) at 1 ml min^{-1} with detection by a Shimadzu SPD-10A UV spectrophotometric detector at a wavelength of 242 nm. The limit of detection was 1 µg/kg for all compounds, and recovery values were in the range 87–107% for IPU, 84–86% for MMU and 54–77% for MU.

Bromide ion was extracted from the soil samples by mixing 25 g soil with 50 ml distilled water, shaking for 30 min and centrifuging (5000 rpm, 10 min) to separate the soil from the extract. Bromide concentrations were determined in solutions at room temperature using a bromide specific ion electrode (Orion Research, Boston MA). Calibration of the bromide ion electrode was accomplished by using a standard solution of NaBr. The recovery for bromide was in the range of 92–111%.

RESULTS AND DISCUSSION

Degradation Study in the Laboratory

In Fig. 1, the rate of degradation of IPU in the topsoil and subsoil samples are plotted on a logarithmic scale. The straight lines obtained indicate that the transformation of IPU follows first-order reaction kinetics. The half-life of IPU at 20°C, as derived from the slopes of the regression lines, was 13 ± 0.3 days in the topsoil and 21 ± 0.7 days in the subsoil.

The half-life for IPU in topsoil of a silty clay loam in this laboratory study is consistent with similar studies presenting half-lives in the range of 6–28 days (0–25 cm, 15–20°C) [3–6]. Former studies revealed a DT_{50} of IPU of 208 days in a heavy clay soil (25–50 cm, 15°C) [3]. Degradation in subsurface soil is generally reported to be slower than in surface soils, a fact that can be attributed to a lower microbiological activity in the subsoil [1,5,7].

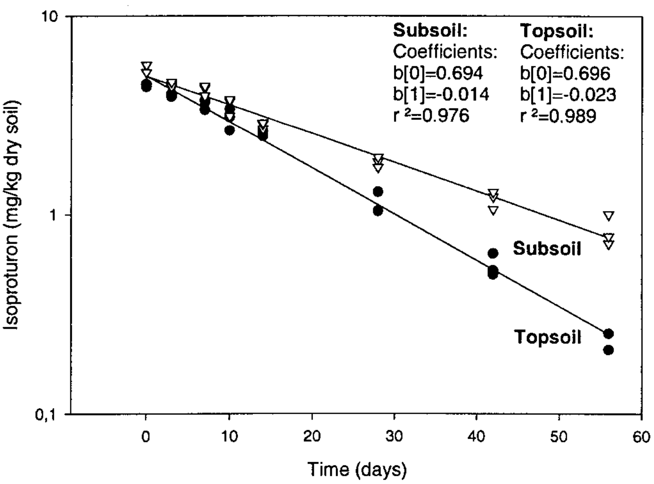

FIGURE 1 Degradation of isoproturon (IPU) at 20°C in topsoil and subsoil samples of a silty clay loam from Rustad ($n = 2$).

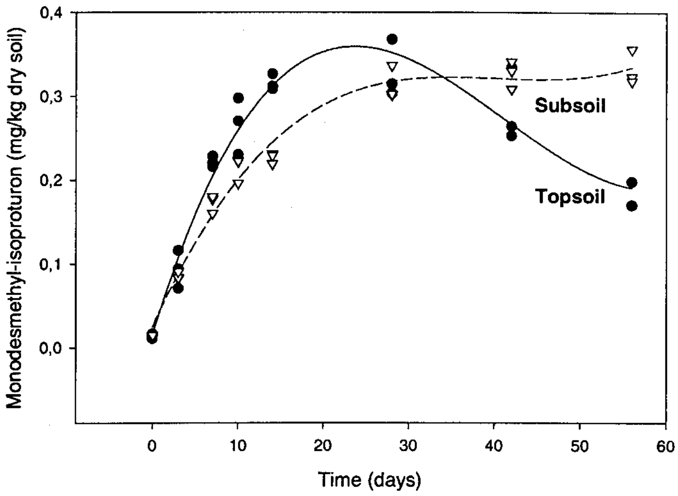

FIGURE 2 Production of monodesmethyl-isoproturon (MU) (mg/kg dry soil) in topsoil and subsoil (Rustad) ($n = 2$).

Transformation of IPU into MMU could be observed as a rapid increase in the concentration of the metabolite during the first three weeks until a maximum was reached (Fig. 2). In the topsoil, the concentration of MMU decreased after about 30 days, indicating that the transformation of the metabolite was the dominant degradation reaction in the soil. This was supported by an appearance of a quantifiable amount of MU in the soil samples at 28 days that kept increasing during the rest of the experiment.

As opposed to the situation in the topsoil, the level of MMU in the subsoil was increasing throughout the whole period (Fig. 2), reflecting a less pronounced transformation of both IPU and its metabolite in the subsoil. A production of MU was initiated after 28 days, but at a lower rate than in the topsoil. Benoit *et al.* [1] obtained similar results during an incubation study of IPU at 18°C where MMU appeared after 3 days, whereas a minor production of MU was detected after 35 days.

The concentration of MMU reached only 7% and 6% of the initial pesticide concentration in topsoil and subsoil, respectively, whereas MU constituted less than 0.16%. The low concentrations may indicate that transformation processes other than *N*-demethylation have been significant, for example, the formation of hydroxylated metabolites [6].

Dissipation Study in the Field

Meteorological Data

Figure 3 shows the daily rainfall and the average air temperatures from May 1999 to September 2000. From 16.09.99 to 29.09.99, a total rainfall of 174 mm was measured, whereas from 29.09.99 to 17.11.99 a total of 109 mm was precipitated.

The daily average soil temperatures at the depths of 1, 10 and 20 cm were not significantly different from each other and were approximately 13°C in September 1999 and decreased to 2°C in November 1999 (Fig. 4). From December 1999 to March 2000, the soil temperatures were at or below 0°C. From May to September 2000, the average temperature in the 1–20 cm soil layer was 15 ± 1°C (Fig. 4).

Distribution of Bromide

Bromide was used as a non-interactive tracer in order to track the movement of water and the water-soluble fraction of herbicides in the profile. The mean recovered mass of bromide from the soil after application was 39.0 kg ha^{-1} with a relative

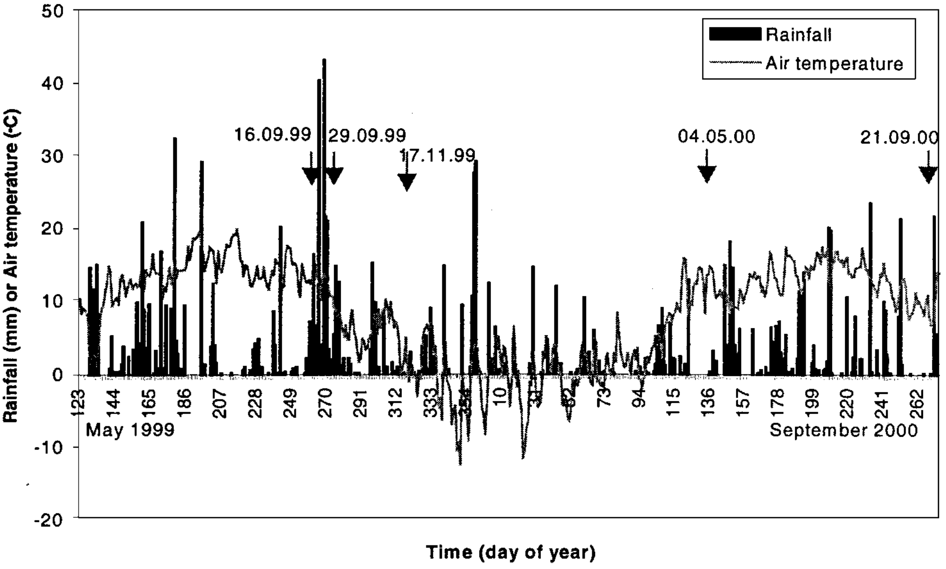

FIGURE 3 Rainfall and average air temperature from May 1999 to September 2000 at the Rustad site on a daily basis. The sampling dates are marked with arrows.

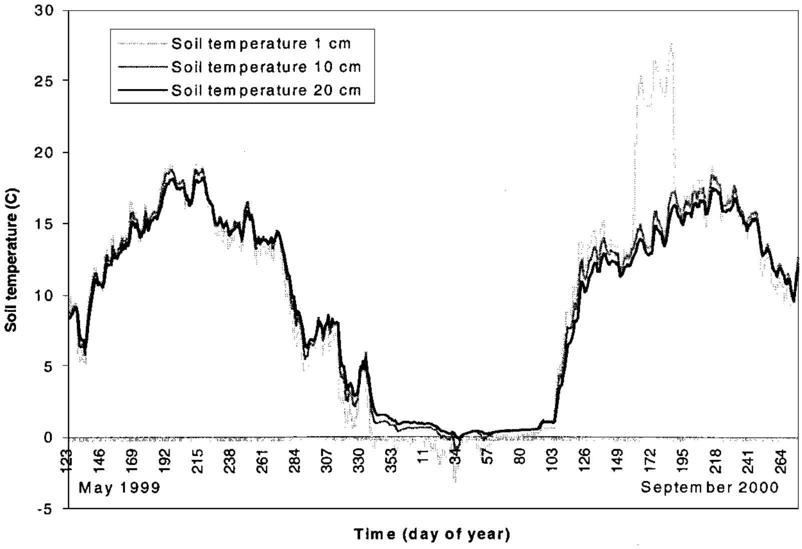

FIGURE 4 Soil temperature at three depths (l, 10 and 20 cm) from May 1999 to December 2000 at the Rustad site.

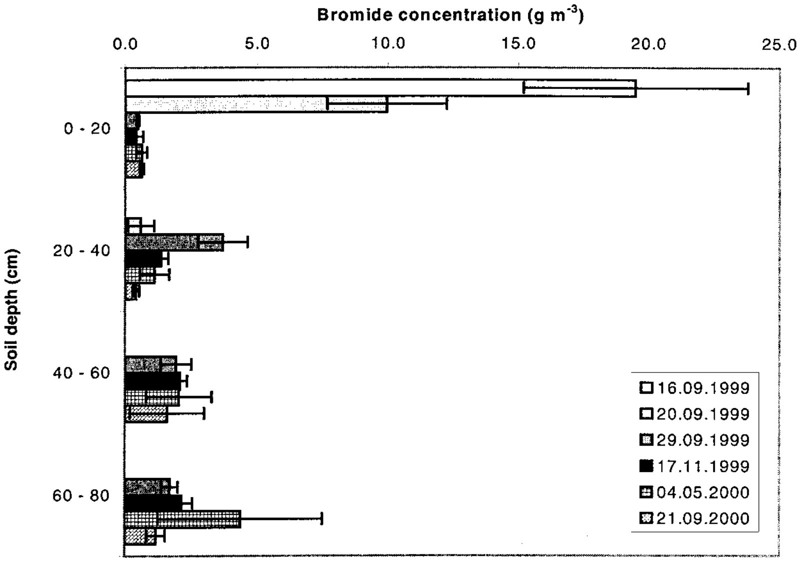

FIGURE 5 Bromide concentration (g m^{-3}) as a function of depth as measured at the experimental field from 16.09.99 to 21.09.00 ($n=3$).

standard deviation of mean of 22%. Bromide was sampled from the top 1 cm layer only on the two first sampling dates, and from the 0–40 cm layer on the third sampling day (Fig. 5).

Four days after application, a loss of 46% was found in the 0–40 cm layer, as the bromide had leached into the deeper soil layers. From 29.09.99 onwards, the water had reached a depth of 80 cm and sampling was performed from four layers (0–80 cm).

A loss of 60% of the bromide applied was observed between 20.09.99 and 29.09.99. Bromide is readily absorbed by plant roots, and as much as 86% of the applied bromide have been shown to be taken up by several monocotyledons [8–10]. After 62 days, the bromide concentration increased with increasing depth, implying that the waterfront was reaching below 80 cm. In the spring (04.05.00), there was a gain in total bromide mass found, probably owing to a release of bromide from decaying plant material. One year after application, only 19% of the bromide applied could be recovered from the profile.

Distribution of Isoproturon

At the day of application of pesticide to the field, the mean recovered mass of IPU from the soil was 628 g ha^{-1} with a relative standard deviation of mean of 13%. Filters spread across the field to measure the uniformity of application of pesticide displayed a mean concentration of 632 g ha^{-1}, with RSD = 18%, which corresponds well with the content measured from the soil. The theoretical concentration of IPU applied to the field would be 552 g ha^{-1}. The measured concentrations have not been corrected for recovery of the analytical method, which was in the range of 89–107%.

Figure 6 displays the mean concentrations of IPU as measured from the experimental field from 16.09.99 to 21.09.00. As only soil at a depth of 1 cm was sampled on the two first sampling dates, these results have been made valid for a 0–20 cm soil layer by averaging. The high recovery of IPU gained on 17.09.99 and 20.09.99 may be a result of variety in execution of the sampling and/or sampling at more concentrated areas. 13 days after herbicide application, the waterfront had reached a depth of 80 cm, and, accordingly quantifiable amounts of IPU were recovered from that depth.

Between the 20th of September and the 29th of September 1999, there was a total rainfall of 146 mm, and IPU could be found at a depth of 60–80 cm in the profile.

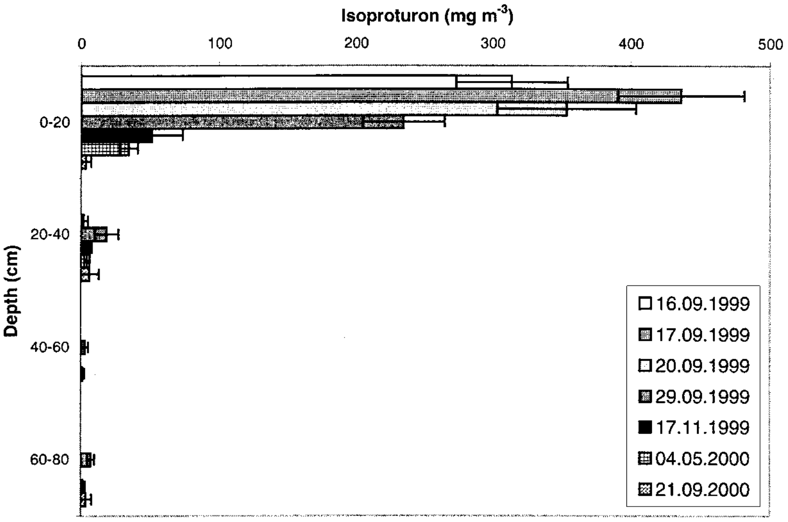

FIGURE 6 Concentration and distribution of isoproturon (IPU) (mg m^{-3}) as measured at the experimental field from 16.09.99 to 21.09.00 ($n = 3$).

The main concentration however, was still to be found in the topsoil (0–20 cm). A loss of 16% of IPU applied was observed, which might be attributed to either degradation, volatilisation or leaching beyond a depth of 80 cm. However, only minor concentrations (< 9% of applied) penetrated below 20 cm depth during the whole experimental period, and less than 3% of applied was found below 40 cm. Thus, there was no substantial movement of IPU from the top 20 cm soil layer. One year after application of IPU, 4% of the initial herbicide amount could be recovered from the profile.

The half-life of a chemical is defined as the time required for 50% of the chemical to dissipate. This is not a true chemical kinetic degradation rate and depends on many factors including volatilisation, binding to soil constituents, plant uptake, leaching and degradation [11] (Fig. 7).

In the autumn (16.09.99–17.11.99), the dissipation time of IPU in the topsoil was 21 ± 2 days (Fig. 8). In a similar field study in Germany, Gatzweiler *et al.* [12] found dissipation times for IPU corresponding to 7–20 days after autumn application, with only minor detections below 10 cm in a fine-textured soil.

The dissipation half-life in the field, however, did increase profoundly (> 290 days) during the winter (November 1999 to May 2000) probably due to a reduced microbial activity as the temperature in the soil declined. Beck *et al.* [13] also observed this trend for IPU residues in a clay soil in UK but obtained a median half-life value of 90 days (November 1990 to April 1991). Both temperature and moisture have been shown to affect degradation in subsurface soil [14]. There were still quantifiable amounts left of both IPU and its metabolite in the field one year after application.

An estimation of the theoretical degradation of IPU in the topsoil in the field can be made using the results from the laboratory degradation study, applying a Q_{10} of 2.2 and assuming comparable microbial populations and water contents in the soils. A calculated degradation half-life of 18 days gives a theoretical IPU concentration of 201 mg m^{-3} in the topsoil on the 29th of September 1999. The concentration left would be 52 mg m^{-3} on the 17th of November, using a calculated half-life of 25 days during this last period as the soil temperature had decreased (Table II).

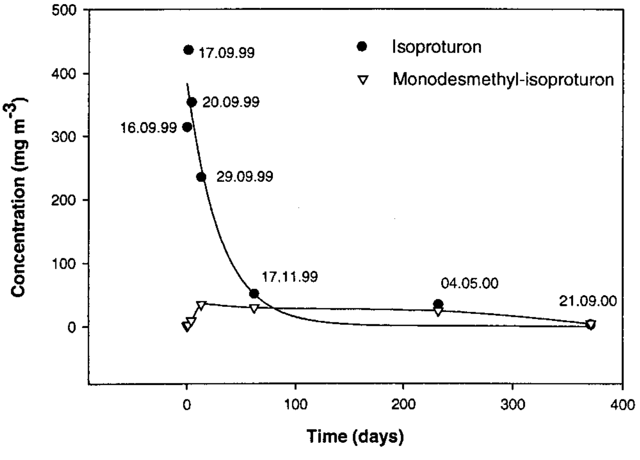

FIGURE 7 Concentration of isoproturon (IPU) and the metabolite monodesmethyl-isoproturon (MMU) (mg m^{-3}) at depth 0–20 cm in the experimental field from 16.09.99 to 21.09.00 ($n = 3$).

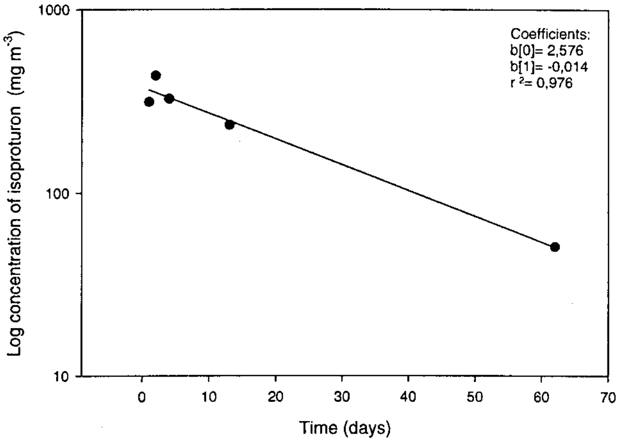

FIGURE 8 Dissipation of isoproturon (IPU) (mg m^{-3}) in the 0–20 cm soil layer from 16.09.99 to 21.09.00 at the experimental field showing a half-life of 21 days ($n = 3$).

TABLE II Concentrations of isoproturon (IPU) in the topsoil (0–20 cm): measured *vs.* theoretical values. Measured subsoil values represent leached IPU at the time

Date	*Topsoil IPU* (mg m^{-3})		*Subsoil IPU* (mg m^{-3})
	Measured	*Theoretical*	*Measured*
16.09.99	314 ± 41	314 ± 41	
29.09.99	235 ± 30	201 ± 26	29 ± 5
17.11.99	51 ± 23	52 ± 7	7 ± 2

The theoretically calculated IPU concentrations were lower than the actual total concentrations found in the field, implying that the degradation in the field was somewhat slower than calculated. This also shows that degradation is the principal reason for dissipation of IPU in the field and the risk of leaching of IPU in the profile is minimal. According to the JOVÅ-study, IPU has been traced in 8 out of 52 samples collected from different streams and rivers in Norway during 1995–1999. The IPU observations were made in June–August only, and therefore, concurrently with the application of IPU on fields [2].

A calculation of the theoretical degradation during May–September 2000 has not been accomplished, as the assumption of a Q_{10} factor of 2.2 has been observed to be valid for rather large initial pesticide concentrations only.

Distribution of Monodesmethyl-Isoproturon

The soil samples were analysed with regard to the metabolites MMU and MU, but only MMU could be found in quantifiable amounts. The content of MMU in the experimental field was seen to increase during the first two weeks after application of IPU (Fig. 9), at most representing 13% of the initial herbicide concentration. After 17.11.99, the total concentration of the metabolite was in retreat, probably due to a low level of the parent compound in the soil and an ongoing degradation of the metabolite itself.

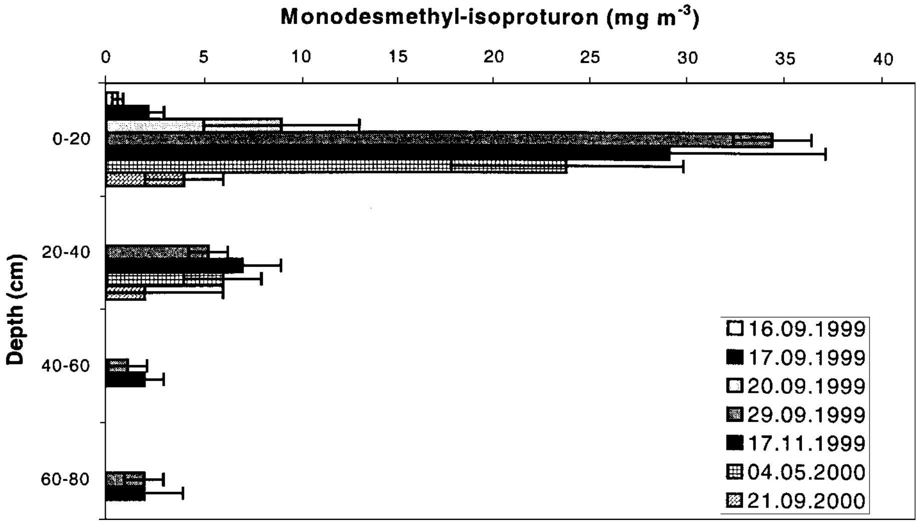

FIGURE 9 Concentration and distribution of the major metabolite monodesmethyl-isoproturon (MMU) ($\mathrm{mg\,m^{-3}}$) as measured at the experimental field from 16.09.00 to 21.09.00 ($n=3$).

During degradation, IPU is demethylated and converted into a more hydrophilic compound (MMU), which implies that MMU will be more susceptible to water flow events in the soil. This was indeed the case in the field experiment: whereas the amount of IPU in the 20–40 cm soil layer constituted less than 14% of the amount found in the 0–20 cm layer at anyone time, the content of MMU in the 20–40 cm soil layer represented up to 25% of the total metabolite amount found in the upper layer. That is, MMU was more readily transported below the plough layer than its parent compound.

CONCLUSION

lsoproturon, being only weakly retained by sorption, is considered a risk compound for leaching to surface and ground waters [1]. A field experiment in a silty clay loam from Norway, showed that IPU was not particularly susceptible to leach below 20 cm. A rapid degradation further prevented any long-term transport to subsurface regions. The metabolite MMU was more readily transported below the plough layer, but only in minor concentrations.

References

[1] P. Benoit, E. Barriuso, Ph. Vidon and B. Réal, *J. Environ. Qual.*, **28**, 121–129 (1999).
[2] G.H. Ludvigsen and O. Lode, Jordsmonnovervåking i Norge – Pesticider. (1999). Rapport Jordforsk: 22/01, SFT: TA-1786/2001 814/01.
[3] C.D.S. Tomlin, *The Pesticide Manual*, (11th Edn.), pp. 732–734. British Crop Protection Council, UK (1997).
[4] P.J. Mudd, R.J. Hance and S.J.L. Wright, *Weed Research*, **23**, 239–246 (1983).
[5] A. Walker, I.J. Turner, J.E. Cullington and S.J. Welch, *Soil Use and Management*, **15**, 9–13 (1999).
[6] B.M. Berger, *J. Agric. Food. Chem.*, **47**, 3389–3396 (1999).

[7] J.S. Conn, W.C. Koskinen, N.R. Werdin and J.S. Graham, *J. Environ. Qual.*, **25**, 1048–1053 (1996).
[8] R.R. Schnabel, W.L. Stout and J.A. Shaffer, *J. Environ. Qual.*, **24**, 888–892 (1995).
[9] L.B. Owens, R.W. Van Keuren and W.M. Edwards, *J. Environ. Qual.*, **14**, 543–548 (1985).
[10] J.M. Jemison, Jr. and R.H. Fox, *Soil Sci. Plant. Anal.*, **23**, 283–297 (1991).
[11] J.L. Miller, A.G. Wollum III, and J.B. Weber, *J. Environ. Qual.*, **26**, 633–638 (1997).
[12] E.W. Gatzweiler, B. Schmidt, M. Feyerabend, R.L. Jones and D.J. Arnold, In: A.A.M. Del Re, C. Brown, E. Capri, G. Errera, S.P. Evans and M. Trevisan (Eds.), *Human and Environmental Exposure to Xenobiotics*. Proceedings of the XI Symposium Pesticide Chemistry, September 11–15, Cremona, Italia (1999).
[13] A.J. Beck, G.L. Harris, K.R. Howse, A.E. Johnston and K.C. Jones, *Chemosphere*, **3**, 1283–1295 (1996).
[14] D.C. Bouchard, T.L. Lavy and D.B. Marx, *Weed Science*, **30**, 629–632 (1982).