

Effect of Crop Residue Management and Drainage on the Persistence and Movement of Isoproturon in a Structured Clay Soil over the Growing Season of a Winter Barley Crop

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The persistence of isoproturon [3-(4-isopropylphenyl)-1,1-dimethylurea] in the cultivated horizon and losses from mole drains in a structured clay soil sown with winter barley and managed by crop residue burning and ash incorporation were compared with those where the crop residues were chopped and plowed in. Desorption coefficients (K_{app}) increased over time as isoproturon concentration declined and were greater on the burnt plot than on the unburnt plot on every sampling occasion. By contrast, sorption coefficients (K_d) were more consistent at approximately 5.0 L/kg on both plots. The variability of sorption and desorption was sensitive to temporal variation of rainfall. Sorption nonideality was observed on every sampling occasion with the nonideality index (K_d/K_{app}), declining with time following isoproturon application. Twenty-seven days following the autumn pre-emergent herbicide application [2.475 kg of active ingredient (ai) on October 9, 1991] K_d/K_{app} was approximately 0.5 and after 97 days had fallen to approximately 0.2, where it stabilized until the post-emergent application (1.625 kg of ai/ha on May 4, 1992) three months later. The variability of all parameters was almost as great at the local scale as at the field scale. Total isoproturon losses in drainflow over the growing season were similar at 869 and 943 mg/ha for the burnt plot and unburnt plot, respectively. However, temporal variation in leaching losses was complex, being influenced by a number of factors including dilution effects, soil solution contact times, and possibly particle-assisted transport.

Keywords: Isoproturon; persistence; leaching; sorption; desorption; nonideality; variability; straw; ash; mole drainage channels

INTRODUCTION

Following the harvest of cereal crops and to a lesser extent oilseed rape, peas, and beans, farmers are faced with a major crop residue disposal problem. Typically, combine harvesting will yield in excess of 5 tonnes/ha wheat straw and 3 tonnes/ha barley straw (The Burning Brief, 1991). How a farmer disposes of this will primarily depend on his method of cultivation. Under conservation tillage practices, characterized by minimal soil disturbance, the residue is usually left as a combination of stubble and a layer of straw on the surface. By contrast, conventional cultivation provides the farmer with the option of either incorporating the straw directly or burning the straw first and incorporating the resulting ash. Regardless of which residue disposal option is chosen, the implications for the mobilization of existing soil-borne contaminants and the immobilization of those subsequently applied, and their potential to runoff as surface water or leach to groundwater, may be considerable. These issues are particularly pertinent in the European Union, where there have recently been moves

to limit straw burning and in some countries, e.g. the United Kingdom, to impose a complete ban.

Incorporation of either intact straw or ash will have a profound impact on both the abundance and composition of organic matter in the cultivated horizon. Consequently, it may have a marked effect on the behavior of those compounds, principally nonionic organics, controlled by sorption to organic matter. Incorporation of straw will result in a greater abundance of organic carbon relative to the incorporation of ash. The organic matter content of ash may vary widely, depending on the extent of oxidation induced by straw burning. Toth et al. (1981) reported that thiobencarb and molinate were strongly sorbed by activated carbon in ash from rice stubble, rendering more than 60% of these herbicides biologically unavailable. Dao (1991) reported that the greatest sorptive capacity of intact wheat straw for metribuzin and its *S*-ethyl derivative was associated with the lignin fraction of the straw, while the cellulose fraction was of little significance. Thus, when the wheat straw decomposed over the growing season, the sorptive capacity of the residue increased because the proportion of the more recalcitrant lignin fraction increased relative to cellulose. Boyd et al. (1990) have found that the sorption coefficients of corn residues for benzene, ethylbenzene, and 1,2,3-trichlorobenzene ranged from 35 to 60 times greater than a fine loam soil (Typic hapludalf) containing 1.9% organic matter. The sorptive characteristics of intact wheat straw for atrazine have

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been investigated by Ghadiri et al. (1984). They reported that 60% of a 1.7 kg/ha atrazine application was intercepted by stubble. However, after 3 weeks and 50 mm of rainfall, 90% and 63% of the atrazine intercepted had been lost from standing and flat straw, respectively. This is a particularly important result insofar as it demonstrates that while intact straw has a high capacity to sorb atrazine, sorption would appear to be easily reversible.

The agricultural productivity of heavy clay soils is frequently dependent on the installation of artificial drainage systems. However, the improved water management afforded by drainage systems frequently facilitates, or enhances, leaching of agrochemicals in the soil with an increased risk to groundwater or surface waters if the drainage system discharges into field drainage ditches (Beck et al., 1993). The installation and efficiency of different drainage systems for water management in agricultural soils has been discussed by Castle et al. (1984). The most frequently used systems in heavy clay soils are mole drainage channels. Harris et al. (1993a,b) have investigated the use of mole drains in water table management and their impact on leaching of the herbicides mecoprop and isoproturon. Isoproturon loadings in drainflow from a clay soil were twice as great in closely spaced pipes (21.9 g/ha) than in conventional mole drains (12.2 g/ha) or expanded mole drains (12.3 g/ha). Harris et al. (1993a,b) attributed their findings to the greater water removal efficiency and a reduction in the soil-solute contact time in land managed by closely spaced pipe drainage systems.

The primary objective of this study was to compare the persistence and mobility of the widely used herbicide isoproturon ($C_{12}H_{18}N_2O$; solubility, 70 mg/L in water at 20 °C; vapor pressure, 3.3×10^{-6} Pa) in structured clay soil subject to different crop residue management practices and drainage techniques. The persistence of isoproturon in the cultivated horizon of an experimental plot subjected to straw burning and subsequent incorporation of ash was compared to that in a plot where the straw was chopped and incorporated directly, over the growing season of a winter barley crop. These treatments were coupled with mole drainage channels drawn with no expander and mole drainage channels drawn with a 150 mm large expander, respectively, making it possible to compare the water removal efficiency of these two drainage techniques and their implications for isoproturon leaching. The effect of these treatments on isoproturon sorption (K_d) and desorption (K_{app}) coefficients was also investigated. Variability at the field scale was compared with that at the local scale in an effort to establish the importance of intrinsic factors, such as the natural heterogeneity of soil physicochemical characteristics, as opposed to extrinsic factors including cultivation, drainage, and crop residue management in controlling the persistence and mobility of isoproturon.

MATERIALS AND METHODS

Experimental Site. The experimental site, Brimstone Farm, was established jointly by ADAS Soil and Water Research Centre (formerly the Agriculture Development Advisory Service Field Drainage Experimental Unit) and the Institute of Arable Crops Research at Rothamsted Experimental Station in 1978. The site is located near Faringdon, Oxfordshire, in the United Kingdom (Ordnance Survey grid reference 248947). It covers an area of approximately 10 ha overlying a heavy clay soil of the Denchworth series (Typic

Table 1. Physicochemical Characteristics of Denchworth Series Soil (Typic haplaquept)^a

parameter	mean	SD	CV
% sand	9.63	2.15	0.22
% slit	22.00	13.30	0.61
% clay	68.30	13.30	0.20
% organic matter	8.56	1.12	0.13
bulk density (kg/m ³)	860	164	0.19
exch Na (mequiv/kg)	1.33	0.73	0.55
exch K (mequiv/kg)	6.08	1.34	0.22
exch Ca (mequiv/kg)	204	56.10	0.28
exch Mg (mequiv/kg)	5.92	1.19	0.20
CEC (mequiv/kg)	1909	579	0.30

^a Statistics based on 25 samples obtained from the burnt plot in Oct 1990.

haplaquept, see Table 1) at an altitude of 100 m on a gently undulating plateau with a 2% slope and a southeasterly aspect. The mean annual precipitation is 680 mm with a mean annual temperature of 10 °C [Smith and Trafford, 1976, cited in Cannell et al. (1984)].

Design of Experimental Plots. The site consists of 20 experimental plots, each subjected to different agricultural management practices. Comprehensive details of the original plot establishment are given by Cannell et al. (1984) and subsequent modifications by Harris et al. (1994). The overall dimensions of the plots are 59.0 m × 41.0 m. Each plot was hydrologically isolated to a depth of 1.1 m by installing a continuous sheet of polyethylene down the slope at the eastern and western boundaries of the plots. At the northern boundary of each plot, a 1 m deep × 0.1 m wide interceptor trench containing a 0.075 m in diameter clay pipe was backfilled with freely permeable material to intercept any water moving downslope. A 3.0 m wide grass verge/access roadway was maintained upslope of the interceptor trench to ensure that its efficiency in removing surface water was not impeded by clods falling on the surface of the backfill material during cultivation. To ensure that no surface movement of water occurs between plots, the polyethylene barrier was covered with an inverted 0.1 m in diameter PVC gutter. Plot drains were installed 46.0 m downslope of the interceptor trench at a depth of 0.9 m and backfilled with permeable fill to within 0.35 m of the surface, then soil. Mole drainage channels were drawn at right angles down the slope at 0.55–0.60 m depth to intercept the plot drain. A further 1.5 m downslope of the plot drain a single plow furrow was excavated to 0.2 m depth to collect a combination of surface runoff and water moving laterally downslope within the cultivated horizon. Contemporary agricultural practices employed on the two plots investigated during this study are given in Table 2.

Monitoring and Analysis of Plot Drainflow. Discharge of both drainflow and combined surface flow/throughflow (i.e. a combination of surface runoff and water moving laterally downslope within the cultivated horizon without infiltrating the subsoil) was monitored using V-notch weirs fitted with a float and potentiometer device which measured flow every 5 min except when no flow occurred (BS 3680, 1981). This system was calibrated for discharges over a range of 0–7.0 L/s (Talman, 1980). Water samples for pesticide residue analysis and dissolved organic carbon (DOC) measurements were collected from the "U" bend reservoir in the filter bin of the weir gauging systems. Epic programmable samplers, fitted with Teflon tubing and amber glass collection bottles, were used for sample collection. A vacuum evacuation system, containing polyethylene and rubber fittings and with clear glass bottles, was operated as a backup [see Cannell et al. (1984) and Harris et al. (1994) for more comprehensive details of discharge measurement and solution monitoring]. Isoproturon concentration in drainage water was measured by the CSL Ministry of Agriculture Fisheries and Food using HPLC and GC-MS techniques described elsewhere (Harris et al., 1991, 1994). Subsamples for DOC analysis were stored in 28 mL screw-capped glass vials or 50 mL medical flat soda glass bottles (baked in a muffle furnace at 450 °C overnight to remove trace organics) and placed in cold storage at 4 °C prior

Table 2. Past and Contemporary Agricultural Practices on Experimental Plots

cropping history	
harvest year	
1989	winter oats
1990	winter wheat
1991	winter wheat
1992	winter barley
isoproturon application	
1989/1990	2.488 kg of active ingredient/ha as Arelon WDG on Nov 15, 1989, and 1.625 kg of active ingredient/ha as Musketeer on March 11, 1990
1990/1991	2.475 kg of active ingredient/ha as Arelon WDG on Oct 8, 1990, and 1.625 kg of active ingredient/ha as Musketeer on April 10, 1991
1991/1992	2.475 kg of active ingredient/ha as Arelon WDG on Sept 10, 1991, and 1.625 kg of active ingredient/ha as Musketeer on May 14, 1992
cultivation technique	moldboard plowing
crop residue management	burnt plot: straw burnt and ash incorporated by plowing unburnt plot: straw chopped and incorporated by plowing
drainage system	burnt plot: moled, no expander unburnt plot: moled, large expander

to analysis. Twenty-five milliliter samples were filtered through Whatman GF/C glass fiber filter papers (ashed in a muffle furnace at 450 °C to remove trace organics) prior to analysis. The optical absorbance of all samples was determined in duplicate at 230, 240, 250, and 260 nm on a Phillips Pye Unicam PU 8610 UV-vis single-beam kinetics spectrophotometer fitted with an automatic flow cell. A representative subset of samples was selected for DOC quantitation on a Phase Separations TOCSIN aqueous carbon analyzer. DOC quantitation was based on duplicate analyses with an accuracy of ± 0.05 mg/L with the calibration carried out against potassium hydrogen phthalate over a range of 0–10 mg/L. Linear least-squares techniques were then used to identify the best relationship between optical absorbance and DOC concentration. This occurred at 330 nm, and all subsequent DOC analyses were determined by UV-vis spectroscopy according to eq 1 ($r^2 = 0.990$). Meteorological data were obtained from

$$\text{DOC (mg/L)} = 3.35 + 47.4(\text{UV absorbance } 330 \text{ nm}) \quad (1)$$

two fully automatic weather stations located on site. Further details of site instrumentation and data collection procedures for the Brimstone Farm site are reported elsewhere [see Cannell et al. (1984) and Harris et al. (1994)].

Soil Sampling. Twenty-five 1 m² sampling areas were designated on the agronomic area of each of the two experimental plots investigated using a quasi-random approach to avoid interferences to/from tramlines and experimental instrumentation. On each sampling occasion (nine in total) during 1991–1992, one sample was taken from one of the intersections of a hypothetical 0.3 m² Cartesian grid superimposed on the central 0.6 m² of each 1 m² area on each plot. This provided a total of 25 samples from each plot on each sampling date. The sampling interval was flexible to facilitate the collection of data as soon as possible following any significant rainfall event or drainflow from the plots. In the event that a long period elapsed without significant rainfall and/or drainflow, sampling was undertaken at intervals of approximately 1 month. The first set of samples were collected 2 days before the pre-emergent herbicide application (2.475 kg of isoproturon/ha) on October 9, 1991. Samples were collected on five occasions (November 5 and 21, 1991, and January 14, February 19, and March 31, 1992) during the winter months prior to a spring post-emergent isoproturon application of 1.625 kg/ha on April 5, 1992. Samples were collected on a further three occasions (April 13, May 13, and June 17, 1992) during the spring and early summer of 1992.

Samples were obtained to a depth of 0.2 m by using a specially made 25 cm \times 3 cm in diameter trowel. This was

the only feasible method to obtain consistent samples during the winter months when the soil was too wet and sticky to allow the use of small-bore coring devices. Although the use of coring devices would have been possible during 1992 when the soil was considerably drier, the trowel was used throughout to minimize sampling discrepancies. Only the cultivated horizon was monitored during 1991–1992 because previous studies on these plots had failed to detect isoproturon residues below this horizon (Nicholls et al., 1993; Beck, 1994). Vertical variation within the cultivated horizon (0.20 m) was ignored. Each individual sample was ground to <2 mm and homogenized to give an average for the whole cultivated horizon in each of the 25 sampling squares of the plot on each sampling date. To minimize disturbance to the plots, access to sampling points was achieved via tramlines and duckboards; hollows created by sampling were backfilled with adjacent topsoil from outside designated sampling areas.

Measurement of Isoproturon Residues and Associated Sorption/Desorption Coefficients in the Cultivated Horizon. Soil samples were air-dried, ground to <2 mm, extracted, and analyzed within 2 weeks of sampling. Isoproturon was extracted from 20 ± 0.001 g subsamples of the 25 collected samples from each plot on each sampling date by shaking with 30 ± 0.02 mL of 80% methanol/20% water solution in 50 mL polypropylene centrifuge tubes on a rotary shaker for 24 h. The extraction efficiency of this procedure was quantified at 95% for freshly added isoproturon but, because the effect of residue aging on extraction efficiency was unknown, data presented herein have not been corrected for this loss. The tubes were centrifuged at 4000 rpm for 30 min, and then the supernatant solutions were carefully decanted, made up to 30 mL with 80% methanol/20% water solution, and filtered through a Nalgene 0.22 μ m filter unit prior to HPLC analysis. Twenty-five replicate K_d and K_{app} measurements for each plot were made by shaking 10 ± 0.001 g of each sample plus 20 ± 0.02 mL of approximately 5 mg/L isoproturon solution in organic-free water or organic-free water alone, respectively, in 50 mL polypropylene centrifuge tubes on a rotary shaker over a 24 h equilibration period. The tubes were centrifuged at 4000 rpm for 30 min, and the supernatant solutions were carefully decanted and passed through a Nalgene 0.22 μ m filter prior to HPLC analysis. Where isoproturon concentrations in the aqueous systems were too low to be measured in the filtrate directly (only applicable to K_{app} measurements), the samples were concentrated by passing a 10 mL aliquot of the supernatant solution through a Waters C₁₈ Sep-Pak solid phase extraction cartridge. Isoproturon was then recovered by eluting the cartridge with 1.0 mL of methanol. Where concentrations of greater than 10-fold were necessary, the 1.0 mL methanol concentrate was reduced further on a Tecam Dri-Block under a stream of nitrogen. Maximum concentration factors employed in this study were 100-fold with an associated detection limit of 2.5 μ g of isoproturon/L. No isoproturon losses were detected due to sorption on the centrifuge tubes; however, losses on Nalgene cellulose acetate filters were found to range from 11% in solutions of 5.0 mg of isoproturon/L to 22% in solutions of 0.5 mg of isoproturon/L. All data reported here have been corrected in accordance with this filter loss. Single-point sorption and desorption distribution coefficients (these have been found to be consistent with sorption parameters derived from isotherms over the 0.5–5.0 mg of isoproturon/L range; Beck and Jones, unpublished data) were calculated in accordance with the usual procedure:

$$K_d \text{ (or } K_{app}) =$$

$$\text{isoproturon on solid phase/isoproturon in solution (L/kg)} \quad (2)$$

Assessment of Variation Associated with Methods Employed. The proportion of variation that arose from inherent methodological variation as opposed to variation arising from natural processes or anthropogenic influences occurring in the field was determined. The excess soil collected during the experiment was composited, passed through a 2 mm sieve, and mixed thoroughly several times to create a

homogeneous sample. Using the techniques described above, eight replicates each of the isoproturon extractions, K_d and K_{app} values were measured using the homogenized soil. All of the K_{app} measurements included sample concentration to ensure maximum variability of the method was characterized.

HPLC System Configuration and Analysis. The analytical system consisted of a Merck Hitachi LC organizer fitted with a Rheodyne injection port containing a 20 μ L sample loop, an L-6200 intelligent pump, and an L-3000 photodiode array detector. They were controlled using Merck Hitachi D-6000 DAD Manager and HPLC Manager software packages on an IBM model AT computer. A Hibar Merck LiChroSpher C₁₈ reversed phase column (250 \times 4 mm i.d.) was used throughout the study. Isoproturon separation in the aqueous phases used to measure sorption/desorption coefficients was achieved with a mobile phase of 60% acetonitrile/40% water (no acidic modifiers were required) and a flow rate of 0.8 mL/min. Identification and resolution of isoproturon in the chromatograms of the methanol-based soil extracts were complicated by the coextraction of a large number of unidentified substances. This problem was overcome by using the conditions described above with the exception that methanol was substituted for acetonitrile in the HPLC mobile phase. Isoproturon peak area used in quantitation was measured at a wavelength of 245 nm for all samples.

Chemicals. Isoproturon [3-(4-isopropylphenyl)-1,1-dimethylurea], 99.9% purity, used for standard preparation was obtained from Ehrenstorfer Laboratories. Organic-free water was prepared using Millipore Milli-RO 4 and Milli-Q purification systems. Acetonitrile (BDH HiPerSolv UV grade) and methanol (BDH HiPerSolv grade) were used for all HPLC analyses.

RESULTS AND DISCUSSION

A. Persistence of Isoproturon in the Cultivated Horizon. *A.1. Chronology.* The general trends of isoproturon dissipation, K_d and K_{app} , from autumn 1991 to early summer 1992 are shown in Figure 1. Isoproturon carryover from previous herbicide applications (see Table 2 for application dates and rates) was approximately 0.2 mg/kg. Isoproturon in the cultivated horizon declined rapidly following the pre-emergent herbicide application on the unburnt plot, but more slowly on the burnt plot (Figure 1a). This might suggest that biodegradation may be an important loss mechanism because biological activity on the burnt plot may have been reduced due to partial destruction of the microbial population by burning. The possible effects of the differences in mole drainage between the two plots is discussed later (section B.2).

K_d (Figure 1b) was relatively consistent on the burnt plot with mean values ranging from 4 to 7 L/kg throughout the sampling period with the exception of October 7, 1991 ($K_d = 15 \pm 5$), and June 17, 1992 ($K_d = 14 \pm 11$), when they were more variable and up to 3 times greater than on any other occasion. The differences observed on these dates were most likely related to changes in the moisture status of the soil, as evident from differences between rainfall inputs and drainage losses from the plots (see section B.1) and/or differences in ambient temperature. Similar behavior was observed for the unburnt plot, with the exception that K_d was much more variable on this plot than on the burnt plot on November 21, 1991 ($K_d = 7 \pm 9$), and February 19, 1992 ($K_d = 12 \pm 18$)—sampling dates that were preceded by major rainstorm events. A possible explanation for this behavior was that those isoproturon residues sorbed to intact wheat straw on the unburnt plot were more labile than those sorbed to ash particulates in the burnt plot, making them more susceptible to changes in the soil moisture status. This assertion is supported by the

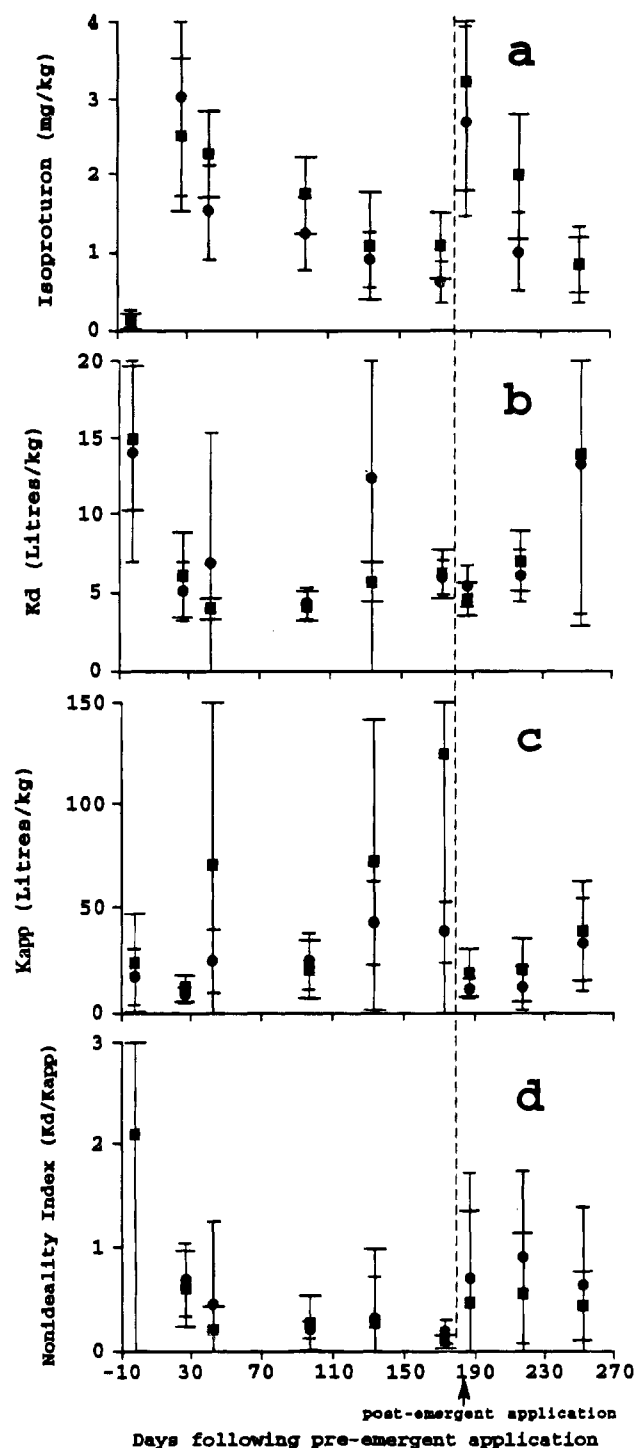


Figure 1. Trends in isoproturon concentration (a), K_d (b), K_{app} (c), and nonideality indices (d) in the cultivated horizon of burnt plots (■) and unburnt plots (●). Symbols and bars represent the mean and standard deviation, respectively, for $N = 25$ with the exception of the burnt plot 252 days after the pre-emergent application where $N = 23$. Statistically significant (0.05 level) differences between plots were observed for isoproturon concentration on October 7 and November 21, 1991, and January 14, March 30, and May 5, 1992; for K_d on April 13, 1992; for K_{app} on November 5, 1991, and March 30, April 13, and May 13, 1992; and for K_d/K_{app} on March 30, 1992.

results of Ghadiri et al. (1984), who reported that atrazine intercepted by flat and standing straw was easily desorbed by rainfall (see Introduction). By contrast, some of the more oxidized ash particulates closely resembled activated carbon or charcoal and, conse-

quently, their capacity for retention of sorbed residues was likely to be greater than that of intact straw. K_{app} was lowest on November 5, 27 days after the pre-emergent herbicide application, and then increased rapidly as isoproturon concentration of the cultivated horizon declined on both plots (Figure 1c). This trend was repeated again following the post-emergent application in spring. K_{app} exhibited the same sensitivity to changes in soil moisture content as K_d , becoming more variable on November 21, 1991, and February 19, 1992. It was also noticeable that extreme values were frequently observed, particularly for K_{app} , which were up to 5 times greater than respective mean values. This might be explained by distributed reactivity concepts (Weber et al., 1992). For example, the proportion of incorporated wheat straw or ash in each individual sample varied markedly.

Nonideality indices (K_d/K_{app}), i.e. the potential for sorbed residues to be mobilized, decreased with time following isoproturon application as reported elsewhere for atrazine and metolachlor (Pignatello and Huang, 1991) and simazine (Scribner et al., 1992). By January 14, 1992, 97 days following the pre-emergent application, the nonideality index on both plots had fallen to approximately 0.25, where it remained until the post-emergent application on April 4, 1992 (Figure 1d). Mean K_{app} values were typically 2–4 times greater than the corresponding K_d values over this period. Normalization of K_d values on a soil organic matter basis had little effect on their variability. Indeed, on January 14, 1992, normalization caused a slight increase from 29% to 30%, in agreement with the findings of a study of napropamide sorption in a sandy soil (Elabd et al., 1986). These results are in direct contrast to frequent reports that normalization acts to suppress variability due to the dominant influence of organic matter on sorption (Chiou et al., 1979; Rutherford et al., 1992) and indicates that great care must be taken if K_d values, used in contaminant modeling, are to be derived indirectly from soil organic matter contents.

A.2. Effect of Intrinsic and Extrinsic Factors on the Persistence of Isoproturon. The significance of the differences observed for isoproturon concentration, K_d , and K_{app} between the burnt and unburnt plots is given in Figure 1. Differences may have arisen because of intrinsic or extrinsic factors [see Donigian and Rao (1987) and Beck et al. (1993)] or more likely a combination of both. Only their effect on persistence is discussed here; the effect of agricultural practices on leaching is considered in section B.

The primary extrinsic factor contributing to the difference in persistence of isoproturon in the two plots investigated here was the method of crop residue management. This investigation would suggest persistence may be enhanced in the cultivated horizon of burnt land relative to that where crop residues were chopped and plowed in. The burnt plot was found to have significantly (0.05 level) greater isoproturon concentrations (five occasions of nine) and K_{app} values (four occasions of nine) than the plot where straw was incorporated (Figure 1). By contrast, K_d values were relatively consistent over the season and were significantly different for the two plots only on April 13, 1992, 9 days following the post-emergent herbicide application. The nonideality index was only significantly different (i.e. lower on the burnt plot) for the two plots on March 30, 1992, just before the post-emergent application of isoproturon. The sensitivity of the K_d on

Table 3. Comparison of the Variability of Isoproturon Concentration, K_d , and K_{app} at the Field Scale and the Local Scale with That of the Experimental Methods Employed

	method		subplot		whole plot	
	unburnt plot	burnt plot	unburnt plot	burnt plot	unburnt plot	burnt plot
<i>N</i>	8	8	9	9	25	25
isoproturon (mg/kg)						
mean	1.2	1.3	2.3	1.9	1.2	2.0
min	1.1	1.2	1.3	1.4	0.7	0.5
max	1.2	1.6	3.5	2.6	2.8	3.5
SD	0.1	0.1	0.8	0.3	0.5	0.8
CV	0.0	0.1	0.4	0.2	0.4	0.4
K_d (L/kg)						
mean	3.6	3.9	7.6	7.9	4.3	7.0
min	3.0	3.3	5.4	5.6	3.0	4.1
max	4.3	4.5	8.7	10.3	7.1	12.4
SD	0.4	0.4	1.3	1.6	1.0	2.0
CV	0.1	0.1	0.2	0.2	0.2	0.3
K_{app} (L/kg)						
mean	14.6	14.9		42.7	24.4	20.7
min	13.2	11.7		11.6	12.2	2.5
max	16.9	20.5		151.3	64.0	68.9
SD	1.1	3.0		43.1	13.3	15.1
CV	0.1	0.2		1.0	0.5	0.8

the unburnt plot and the K_{app} on both plots to rainfall was indicative of the importance of intrinsic factors as a source of variation.

Isoproturon concentration sometimes increased within individual 1 m² sampling areas on successive sampling dates up to and including March 30, 1992. No further isoproturon application was made until the post-emergent application on April 4, 1992, and it was unlikely that changes of the magnitude observed could be attributed to atmospheric deposition of the herbicide (Harris et al., 1992). Consequently, this phenomenon is indicative of the importance of variation at the local scale (i.e. within each 1 m² sampling area). To determine whether the variability reported in Figure 1 reflects extrinsic factors operating at the field scale or if it is merely a composite of intrinsic variation arising from the heterogeneity of soil physicochemical characteristics at the local scale, further studies were undertaken. On May 13 an additional sampling square was designated on each plot, and nine samples were taken from each of these sampling squares and the variability of isoproturon, K_d , and K_{app} within the individual square was compared with that for the whole plot (Table 3). Generally, variation within the 1 m² sampling areas was usually not much less than, or approximately equal to, that for the whole plot. This suggests that extrinsic factors such as cultivation did contribute to the variation in persistence of isoproturon but also that the natural intrinsic heterogeneity of the soil was also an important factor. However, these assertions must be made with great care. For example, the effect of agricultural practices (e.g. a plow furrow) might also be manifest within an area of 1 m². The variation associated with the experimental methods employed in this investigation are also given in Table 3. These data would suggest that, at most, approximately half (and frequently much less than this) of the variability reported for isoproturon concentration, K_d , and K_{app} within the 1 m² subplots and the whole plots could be attributed to methodological variation. Thus, we are confident that the variability reported here was an accurate reflection of intrinsic and extrinsic factors operating at the field scale.

B. Leaching of Isoproturon from Mole Drainage Systems. *B.1. Water Balance of Experimental Plots.* During the course of this experiment, October 1991 to June 1992, the total rainfall was 307.4 mm (45% of the long-term annual average) with potential evapotranspiration of 398.1 mm, resulting in a negative water balance of -91.0 mm. The amount of water lost by drainflow during this period was 4 times greater from the unburnt plot (11.01 mm) than from the burnt plot (3.1 mm). It should be stressed that these differences were due to the method of drainage in the plots (e.g. see below, Table 2; Harris et al., 1994) and not a reflection of burning. Approximately 50% of the total drainflow from the unburnt plot and 30% of that from burnt plot occurred during the months of November 1991 and February 1992 when rainfall exceeded potential losses by evapotranspiration and cracks in the soil remained open. This drainflow took place before a true watertable was established in these plots; therefore, drainflow early in the season, i.e. from November, must have been due to flow in cracks. These results are consistent with those reported by Harris et al. (1994) for the 1989-1990 and 1990-1991 winters. The drainage response was faster on the unburnt plot because the large expander mole drainage system, designed with the objective of closing the leg slot crack by increasing upward soil pressure and so creating a more stable channel, frequently failed due to roof collapse shortly after the channels were drawn. In effect, this opened a route for rapid water movement in a larger than normal channel. Furthermore, the no-expander mole channel system in the burnt plot effectively failed, resulting in little water movement from this plot. Despite rainfall exceeding 30 mm in March and 40 mm in April, May, and June 1992, there were only 1.41 and 0.6 mm of drainflow from the unburnt and burnt plots, respectively. This may be attributed to partial closure of cracks during March (although there was no direct evidence for this), increasing water use by the maturing wheat crop, and increasing evaporation as temperatures increased from spring to summer. During the 1991-1992 growing season, no measurable water loss occurred from either plot by either surface runoff or lateral movement downslope within the cultivated horizon.

B.2. Isoproturon Residues in Drainflow. Only limited data on isoproturon concentration in drainflow are available because samples were bulked for analysis on account of the low drainage responses. Isoproturon concentrations peaked in November 1991 after the pre-emergent herbicide application when rainfall led to through drainage. On the unburnt plot this was 0.03 mg/L and on the burnt plot it was 0.12 mg/L. There are several factors that may have contributed to this difference. First, the total volume of drainflow from the unburnt plot was greater than that from the burnt plot (see section B.1) so that the concentration may have been reduced due to dilution. Second, the rate at which the solute passed through the unburnt plot was greater than that through the burnt plot (Figure 2), resulting in a decrease in soil-solute contact times at the molecular scale. This may either enhance or suppress leaching depending on whether the compound of interest exists primarily in the solid or solution phase prior to leaching. Finally, it is possible that transport facilitated by the sorption to mobile particulate ash was partially responsible for the elevated isoproturon concentrations in the drainflow from the burnt plot. Graham et al.

(1992) have reported that particle-assisted (i.e. surficial soil material) transport may have been partially responsible for the occurrence of atrazine residues in vertisol cracks at depths of up to 1.25 m, while they were absent from the adjacent soil matrix. Although isoproturon does not bind strongly to soil particles, transport of isoproturon may be facilitated by ash particles which were frequently observed in cracks to a depth of 0.4 m and sometimes even as deep as 1.0 m during previous sampling efforts. The dilution effect would appear to be the major control in this instance given that the reversibly sorbed or labile fraction on the burnt plot was significantly lower than that on the unburnt plot, as evident from the nonideality indices (see section A.2), and the isoproturon was primarily soil sorbed. By contrast, during the April event, which followed the post-emergent application, the peak isoproturon concentration on the unburnt plot (0.105 mg/L) was nearly double that on the burnt plot (0.055 mg/L). This was an extremely interesting observation insofar as it may suggest that a fundamental change occurred in the mechanism controlling herbicide losses. The volume of water lost in drainflow from the unburnt plot was 3 times greater than that from the burnt plot (see section B.1), so a dilution effect was not responsible. Consequently, it would appear that isoproturon losses were controlled by the soil-solution contact time. Prior to this event, the "equilibrium" isoproturon solution concentration of the interstitial soil water of the unburnt plot was likely to be greater than that in the burnt plot because isoproturon residues in the unburnt plot were more labile, i.e. they had higher nonideality indices, than those in the burnt plot at the end of March 1992 (see section A.2). Consequently, when the interstitial solution was partially displaced by the April rainfall event, the drainflow concentrations may have been greater than those from the burnt plot. Furthermore, the faster drainage response of the unburnt plot relative to the burnt plot would reduce the soil-solution contact time in the subsoil, resulting in a lower potential for resorption of isoproturon further down the profile than in the burnt plot, albeit sorption of isoproturon by mineral soil is low (Beck, 1994). During the intervening months, December 1991 to March 1992, the pesticide concentrations declined to <0.005 mg/L—a background or residual level reported by Harris et al. (1994) to be typical of drainflow derived from a range of different agricultural practices.

Regardless of the temporal variation in isoproturon concentration, the total amounts of isoproturon lost in drainflow from the unburnt and burnt plots over the period November 1991 to February 1992 were similar at 178 and 164 mg, respectively, equivalent to <0.001% of the pre-emergent application. As discussed in section A, isoproturon was less persistent in the cultivated horizon of the unburnt plot than the burnt plot. Drainflow losses were unlikely to account for the differences observed in cultivated horizon concentrations between the plots or the total amount of isoproturon lost from either plot. Thus, other loss processes such as degradation, volatilization, or immobilization of leached isoproturon in subsoils (i.e. below the cultivated horizon) may have been important. The latter was unlikely to be a major factor because isoproturon is very weakly sorbed by soil mineral components (Beck, 1994) and has never been detected in soil samples collected below 0.2 m depth at this site (Nicholls et al., 1993; Beck, 1994). With a vapor pressure of 3.3×10^{-6} Pa and a Henry

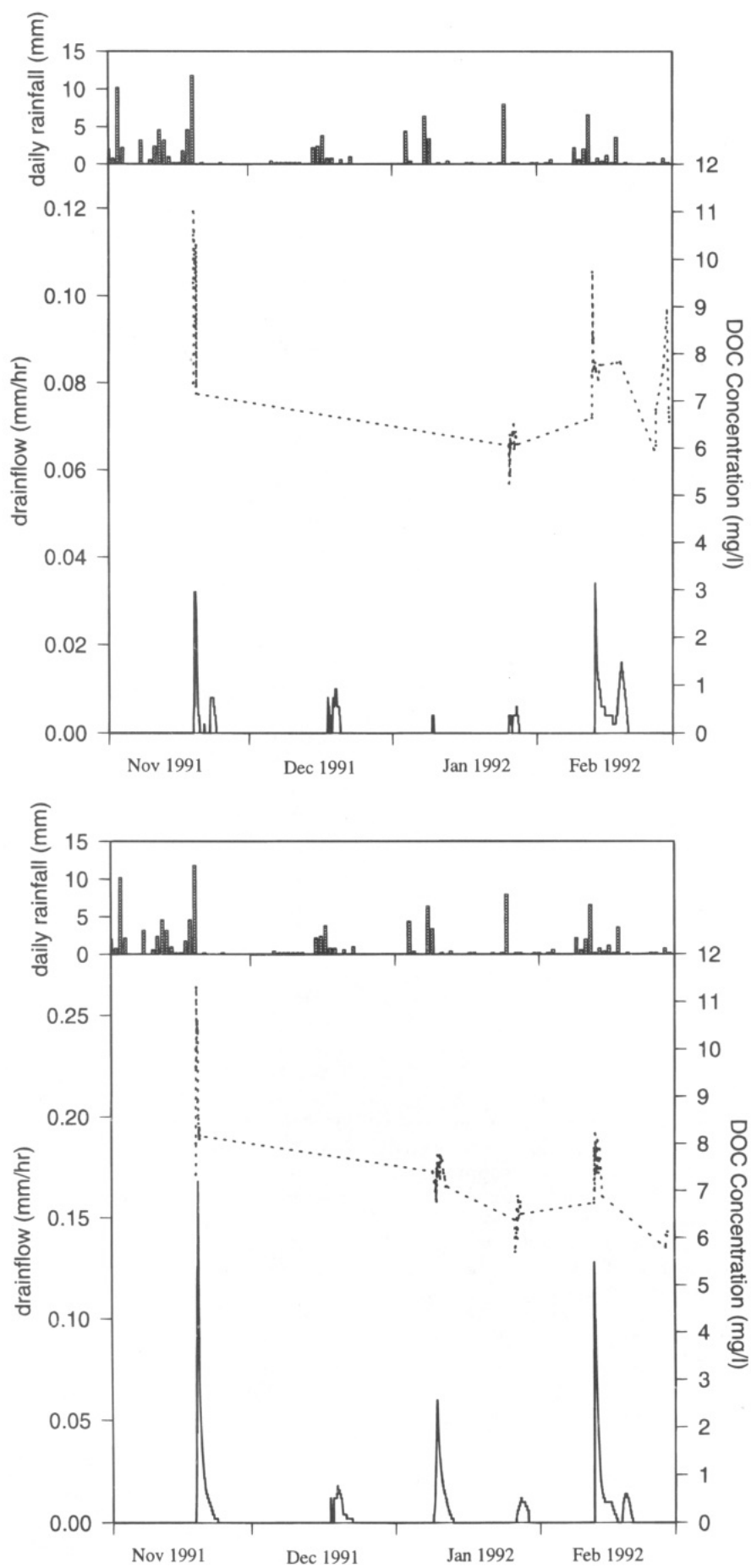


Figure 2. Discharge (—), daily rainfall, and DOC concentrations (---) in drainflow from the unburnt (a, top) and burnt plots (b, bottom).

constant of $1.33 \times 10^{-5} \text{ Pa m}^{-3} \text{ mol}^{-1}$ (P. Nicholls, Rothamsted Experimental Station, Harpenden, personal communication, 1994) volatilization is unlikely to be a major dissipation process. Biodegradation has now been well established for the phenylurea herbicides and so appears to be a likely cause of the results observed here. However, further investigation of isoproturon degradation in soils containing straw and ash in both the laboratory and the field will be necessary before any firm conclusions can be made.

The imbalance between the plots might also be attributable to partitioning into a third phase, e.g. dissolved organic matter or mobile colloidal material. Sorption/desorption experiments with wheat residues (Beck, 1994) have shown that the solutions mixed with intact straw were more colored than those mixed with ash. This suggests that greater solubilization of organic matter might be expected in the plot in which intact straw was incorporated than in the burnt plot. The presence of organic matter in solution has frequently been reported to enhance the solubility of organic contaminants (Chiou et al., 1986; La France et al., 1988; Barriuso et al., 1992; Lee and Farmer, 1989) and facilitate their transport in soils (Enfield et al., 1989; McCarthy and Zachara, 1989; Dunnivant et al., 1992). Neither of these assertions is supported by this field study. Dissolved organic carbon concentrations in the drainflow from the two plots investigated were not significantly different, ranging from 6 to 12 mg of DOC/L, with peak concentrations occurring in drainflow soon after major rainstorm events, suggesting that dissolved organic matter was in equilibrium with the soil solid phase (see Figure 2). This may be supported by the work of Jardine et al. (1989), who found that the capacity of clay soils to sorb dissolved organic matter was high. Given that total loss of organic carbon in drainflow from the unburnt plot was greater than from the burnt plot, the amount of isoproturon lost from the former plot should also be greater than that from the latter plot if DOC enhanced the solubility of the herbicide and facilitated transport. However, this was not so (see section B.1).

C. Summary and Conclusions. The persistence of isoproturon was greater in the cultivated horizon of soils where crop residues were burnt and the resulting ash incorporated than in soils where chopped straw was plowed in. Despite this, and regardless of differences in the drainage systems employed under these two crop residue management practices, no differences were observed in the total losses of isoproturon from mole drainage channels over the growing season of a winter barley crop. This suggested that processes other than leaching, most likely biodegradation, were partially responsible for isoproturon dissipation and, thus, further research is required. K_{app} was observed to increase over time while K_d remained relatively consistent. Consequently, sorption nonideality became increasingly pronounced with time following isoproturon application. Normalization of K_d on a soil organic matter basis failed to reduce the variability of this parameter at the field scale. Variability of all parameters was almost as great at the local scale as at the field scale, indicating that intrinsic factors, such as soil physicochemical characteristics and rainfall, may have been as important as extrinsic factors, such as crop residue management and drainage, in controlling the behavior of isoproturon in this soil. Drainflow was faster in soils drained with large expander mole drains, suggesting that transport

was dominated by preferential flow along cracks and voids. Temporal variation of isoproturon losses in drainflow were complex, being controlled by a number of different factors. These include dilution effects and soil-solution contact times. Further monitoring will be required in years with more typical rainfall and drainflows, if the importance of these mechanisms is to be elucidated. Investigations of the distribution of isoproturon in relation to soil morphological features should also contribute to our understanding of these mechanisms.

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