

Diuron in Surface Runoff and Tile Drainage from Two Grass-Seed Fields

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ABSTRACT

The typical method of cool-season grass-seed production in Mediterranean climates briefly exposes surface waters to potentially high concentrations of the herbicide diuron [3-(3,4-dichlorophenyl)-1,1-dimethyl urea] during the initial season of growth. To better understand the process, and the degree, of diuron transport from agricultural fields, two grass-seed fields in the Willamette Valley of Oregon were monitored for diuron loss in surface runoff and tile drainage during the first wet season after planting. Initial diuron concentrations in surface runoff were high ($>1000 \mu\text{g L}^{-1}$ in one field and $>100 \mu\text{g L}^{-1}$ in the other), though they decreased by two orders of magnitude by the end of the season. Concentrations in the tile drains were as much as 1000 times lower than in the surface runoff during the first few weeks of runoff events, and they remained lower than surface water concentrations throughout the season. Total losses in surface runoff were between 1.3 and 3% of the amount applied — much higher than losses via the tile drains. It is also shown by means of a simple first-order decay model that, when little information is available, it may be best to describe diuron depletion in runoff water as a function of cumulative rainfall during the wet season.

THE PRESENCE of pesticides in surface waters is an ecological concern. In the Willamette Valley of Oregon in 1996, the pesticide applied in the greatest quantity by mass and area was diuron [3-(3,4-dichlorophenyl)-1,1-dimethyl urea] (Anderson et al., 1997). Diuron is applied in the valley principally in conjunction with grass-seed production, although it is also used to a much lesser extent with other crops (Anderson et al., 1997) and on roadsides (Wood, 2001). In 2003, roughly half of the agricultural land in the Willamette Valley (~200 000 ha) was devoted to grass seed (OAIN, 2004).

The typical method of grass-seed production poses a challenging problem in Mediterranean climates, as the fields are vulnerable to high surface runoff and erosion during the establishment period in the fall and early winter, the season of the greatest rainfall. Perennial ryegrass (*Lolium perenne* L.) and other grasses are usually planted in early to mid-October into a finely worked seedbed with rows spaced 25- to 36-cm apart. The grass seed is typically carbon-banded, with a 2.5-cm-wide band of activated charcoal slurry applied over the seed row, followed by an application of diuron. Weed seedlings germinating between the rows are killed by the diuron, while the carbon band protects the grass seed-

lings (diuron tightly adsorbs to charcoal). The seedbed must be smooth and compact for the charcoal system to function well. The compact surface, however, impedes infiltration, thus enhancing runoff and, potentially, diuron losses. Also, the crop remains small during the winter months when rainfall is heavy, resulting in little vegetative cover to protect the soil from sheet and rill erosion. During subsequent years, grass cover reduces herbicide losses until the field is tilled again in the fourth or fifth year.

There are few studies that have determined the direct transport of diuron from agricultural lands in Mediterranean climates like that of the Willamette Valley. The settings of some of these studies have been vineyards (Lennartz et al., 1997; Louchart et al., 2001) and roadsides (Huang et al., 2004a; Wood, 2001). For diuron transport associated with grass-seed production, there is very little data (Field et al., 2003), but these data suggest concern is justified. A review of other studies of diuron persistence in the environment can be found in Giacomazzi and Cochet (2004).

Field et al. (2003) examined diuron and its three major transformation products in soil and ground water in a level field under already established grass-seed production in the Willamette Valley. They also investigated a stream adjacent to the field. Of the transformation products, only DCPMU [3-(3,4-dichlorophenyl)-1-methyl-urea] was detected in ground water or stream water. Diuron and DCPMU were persistent in the soil year-round. They concluded that there was very little transport of diuron laterally through the A/E soil horizon from the field to the stream (see also Wigington et al., 2003). They also hypothesized that downward transport of diuron to the water table was mainly limited to the beginning of the wet season before preferential pathways were sealed by the swelling clay soils.

Field et al. (2003) did not measure surface runoff directly from the fields or diuron concentrations in the field runoff, but only in the adjacent stream; thus total losses of diuron from surface runoff were not known.

The main objectives of this study were to measure diuron concentrations over time and calculate total diuron losses in water leaving newly established grass-seed fields via both overland flow and tile drains. Thus, this investigation is an important complement to the findings of Field et al. (2003). In addition, the suitability of a first-order decay model for predicting diuron concentration in field discharge is examined.

MATERIALS AND METHODS

Site Description

The two fields studied (heretofore referred to as Fields 1 and 2) are located in the northern Willamette Valley, Oregon

Abbreviations: DCPMU, 3-(3,4-dichlorophenyl)-1-methyl-urea; OC%, percentage organic carbon.

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(see inset, Fig. 1). Surface and tile water draining from both fields enters ephemeral natural channels, which feed creeks that empty into the Yamhill River, a major tributary of the Willamette River. The soil classification in both fields is Woodburn silt loam (fine-silty, mixed, mesic Aquultic Argixeroll), which is reported to have a depth of approximately 1.6 m, a clay content of 10 to 30%, organic matter content of 3 to 5%, and a saturated hydraulic conductivity (K_{sat}) of 0.4 to 1.2 $m\ d^{-1}$ (Otte et al., 1974). For Field 1, Rupp et al. (2004) reported a field-scale K_{sat} of approximately 4 $m\ d^{-1}$ and soil depth $>2\ m$. The average slope of Field 1 is approximately 1% and the average slope of Field 2 is 3.6% (Table 1).

Because of topography and planting history, each field was divided into two subfields. Field 1-E and Field 1-W, corresponding to the east and west sides of Field 1 (Fig. 1), are two sides of a catchment. A depression running north-south divides the two fields. A low berm of soil running most of the length of the depression maintains separation of surface runoff from each field until it is allowed to mix above the outlet located at the south side of the fields. Field 2-N and Field 2-S are distinct catchments within Field 2 (Fig. 2).

There are important differences in the drainage systems of each field. In Field 1, a well-documented drainage system of plastic perforated pipe was installed by machine in 1990. The drains are at a depth of approximately 1.2 m and have a lateral

Table 1. Topographical properties of experimental sites.

Property	2001–2002		2002–2003	
	Field 1-W	Field 1-E	Field 2-N	Field 2-S
Area, ha				
Surface	4.34	†	1.48	0.88
Subsurface	1.4	1.0	unknown	no tile drain
Slope, %	0.8	~1	3.3	3.8

† The surface of Field 1-E was not surveyed.

spacing of 12.2 m (see also Rupp et al., 2004). In contrast, the clay tiles in Field 2 are thought to have been installed by hand 70 to 100 yr ago (based on conversations with local farmers). Probing revealed a single clay tile line ~1 m deep running west by northwest across Field 2-N but no drain in Field 2-S (Fig. 2). The tile-drain outlet and the Field 2-N watershed outlet empty into a highly eroded gully. The inlet to the tile drain is located in a ditch that separates Field 2 from a road on the east side. Because this ditch fills with water during large rainfall events, we installed a riser on the tile inlet to limit the amount of ditch water that enters the tile drain. The height of the riser was lower than the height of the field so that water would be allowed to enter the tile drain but not contribute to surface flow on the field.

Typical local crop rotations were followed. Field 1-E was planted with perennial ryegrass in the autumn of 2000 following corn (*Zea mays* L.) in 1999. Field 1-W was planted with tall fescue (*Festuca arundinacea* Schreb.) in the autumn of

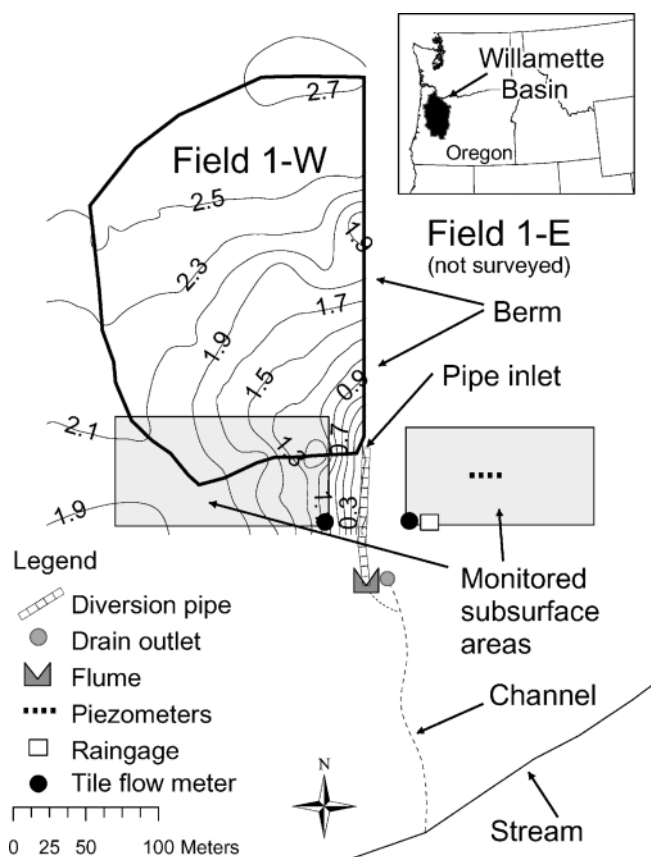


Fig. 1. Map of Field 1 with inset showing the location of the Willamette Basin, OR. Fields 1-W and 1-E are separated by a low berm running north-south to just south of the diversion pipe inlet. Sheet metal walls inserted 5 cm into the soil extend southwestward from the inlet of the diversion pipe to divert surface flow into the pipe. The heavy solid line bounds the surface area in Field 1-W monitored above the diversion pipe inlet. The gray rectangles show the approximate areas monitored by the flow meters inserted in the tile drain systems in Fields 1-W and 1-E.

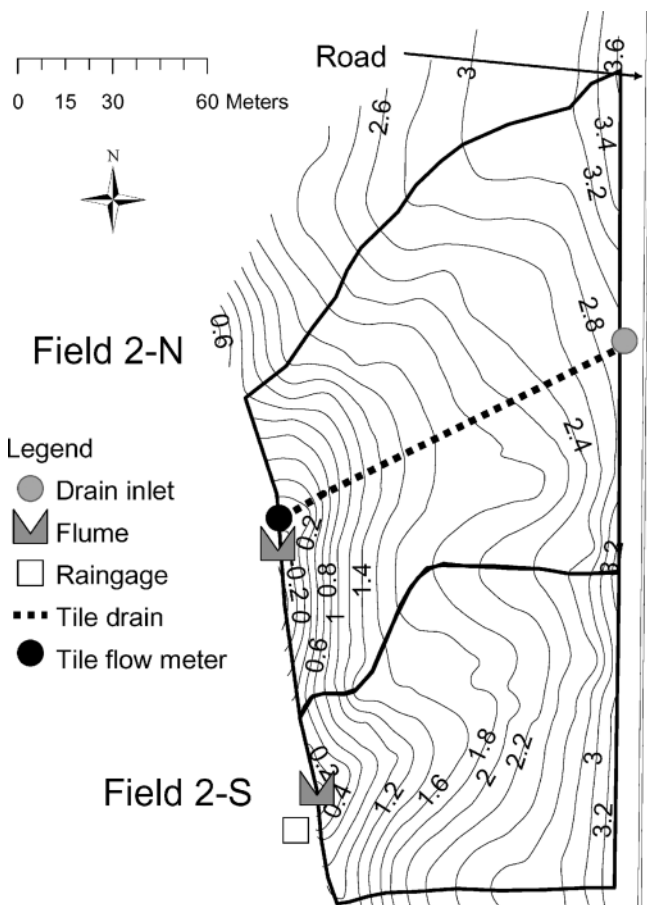


Fig. 2. Map of Field 2. A low berm on the west side of the field directs runoff toward the flumes. A ditch separates the field from the road to the east. The heavy solid line bounds the surface area monitored above the flumes.

2001 following corn in 2000. Fields 2-N and 2-S were both planted with perennial ryegrass in the autumn of 2002 following corn in 2001.

Hydrological Monitoring

Rainfall was measured on each field with a tipping-bucket rain gauge (0.2-mm resolution). Rainfall monitoring began at Field 1 on 30 Oct. 2001 and ended 30 Apr. 2002. At Field 2, rainfall was monitored from 1 Nov. 2002 to 18 June 2003. A rainfall accumulator was located next to the tipping-bucket rain gauge at Field 2 for calibration and verification. For rainfall that occurred before the installation of the rain gauges, hourly precipitation records were obtained from a National Weather Service rain gauge located < 5 km from the fields.

Surface runoff from Field 1-W was diverted by means of berms and sheet metal barriers into an irrigation pipe that delivered the water to an H-flume (for design, see Kilpatrick and Schneider, 1983) (Fig. 1). Water level in the flume was recorded every 5 min with a pressure transducer and data logger (miniTROLL, In-Situ, Laramie, WY). Measurements were made from 5 Nov. 2001 to 13 June 2002. On 1 and 6 Dec. 2001, improvements were made to the diversion barriers, which more than tripled the contributing uphill surface area. The contributing area to the irrigation pipe inlet was 4.34 ha after modifications. The appropriate area adjustments were made when calculating the discharge per unit surface area. Runoff was not monitored on Field 1-E.

On Fields 2-N and 2-S, surface runoff was measured at the field outlets in cylindrical flumes (for design, see Samani and Herrera, 1994) (Fig. 2). The water level in each flume was recorded every 5 min with a capacitance rod and data logger (TruTrack, Christchurch, New Zealand). Water levels were recorded from 11 Dec. 2002 to 26 Mar. 2003 in Field 2-N and from 7 Nov. 2002 to 26 Mar. 2003 in Field 2-S. The areas of Fields 2-N and 2-S are 1.48 and 0.88 ha, respectively.

The tile drains were fitted with turbine flow meters (Seametrics, Kent, WA) to measure drain discharge (details in Rupp et al., 2004). In Fields 1-W and 1-E, the flow meters were located below ground surface and measured flow from subsections of the tile system with areas of approximately 1.4 and 1.0 ha, respectively (Fig. 1). For Field 2-N, the flow meter was installed at the drain outlet (Fig. 2).

Diuron Application and Water Sampling

Diuron was applied in suspension using the commercial product Karmex 80 DF (DuPont, Wilmington, DE). The application dates and the rates, in terms of active ingredient only, for each field are given in Table 2.

An automated sampling device (ISCO, Lincoln, NE) collected water samples from the flumes at Fields 1-W and 2-S and from the tile drains at Fields 1-W, 1-E, and 2-N. Water was collected at a rate of one subsample (50–100 mL) every 48 min.

The device automatically placed 10 consecutive subsamples into one 0.5- or 1-L bottle; thus each sample represents an average for an 8-h period. Sample bottles were collected from the fields on a weekly basis. A small number of samples were collected manually from Field 2-N at the flume and from the roadside ditch near the tile drain inlet, where automated sampling devices were not located. Samples were stored at 2°C for up to 10 d before analysis.

For reasons of cost, a subset of all the samples was selected for analysis of diuron concentration. Total numbers of samples analyzed ranged from 40 to 74 per site. Surface runoff samples were chosen so that all the larger runoff events and some of the smaller ones were represented. By chance, the frequency distribution of total 8-h discharges corresponding to the surface runoff samples is indistinguishable from the distribution of all observed 8-h discharges (zeros excluded) based on a χ^2 test of the log-transformed values. For example, the χ^2 is only 0.35 with 10 degrees of freedom for the Field 1 surface data. The tile drain samples chosen typically coincided in time with the surface runoff samples, but ~10% of the tile samples were from low-flow periods between rainfall events.

For estimating cumulative mass loss of diuron from the field in surface runoff or tile drainage, the concentration of a given sample was assumed to be representative of the concentration in the surface or tile discharge occurring between when the sample and the previous sample were taken.

Analytical Methods

Fifteen-mL subsamples from each bottle were centrifuged for 5 min at 1600 rpm, placed in glass tubes, capped, and stored at 2°C. The remaining sample was filtered and the filter papers (6- μ m pore size, 0.39-mm thick) were stored at room temperature. A volume of water was extracted from the center of the glass tube and diluted by a factor of 100 for analysis. Diuron in the water was quantified by immunoassay (e.g., Guihot et al., 1996; Lee et al., 1995) using a commercial test kit (Envirogard urea herbicide plate kit, Strategic Diagnostics, Newark, DE). The calibrators for the test kit were for chlortoluron [3-(3-chloro-p-tolyl)-1,1-dimethylurea], but the reactivity of diuron is very close to that of chlortoluron and the kit manual provides for a correction. However, an independent laboratory provided diuron calibrators with which we analyzed approximately 20% of the samples. If concentrations fell outside of the calibration range, samples were reanalyzed at an appropriate dilution. The detection limit of the procedure was 0.02 μ g L⁻¹. Samples were also analyzed that contained known quantities of diuron added to surface water collected from a field where diuron had never been applied.

Ten samples were sent to an independent commercial laboratory for analysis of diuron and DCPMU. Other diuron transformation products were not tested for because they had not been detected in a previous study (Field et al., 2003). The analytical method of the independent laboratory was extraction

Table 2. Date and dosage of application and sampling period for each study site.

Property	2001–2002		2002–2003	
	Field 1-W	Field 1-E	Field 2-N	Field 2-S
Application date	15 Sept. 2001	14 Jan. 2002†	18 Oct. 2002	18 Oct. 2002
Dosage, kg ha ⁻¹	2.2	1.1†	2.5	2.5
Sampling period				
Surface	30 Oct.–6 Mar.	‡	§	14 Nov.–22 Mar.
Subsurface	21 Nov.–12 Mar.	1 Dec.–8 Feb.	15 Nov.–14 Mar.	–

† Diuron was also applied in late September 2000 at 2.2 kg ha⁻¹.

‡ Runoff was not sampled at Field 1-E.

§ Diuron was measured in only 3 grab samples from surface runoff at Field 2-N.

with methylene chloride and analysis by reverse phase high performance liquid chromatography and ultraviolet detection (USEPA, 1999).

Although the sample sediment was separated by filtration, it was not analyzed for herbicide content. Since samples spent as many as 7 d in the field and 10 d in a cooler for solid-liquid phase equilibrium to occur, an estimate could be made of the diuron present on the sediment from an estimate of the linear sorption coefficient, k_D , given the organic C content (OC% [v/v]) and the organic-C-normalized sorption (k_{OC} ; $k_D = 100k_{OC}/OC\%$). However, published values of k_{OC} for diuron range from 30 to 900 L kg⁻¹ (Huang et al., 2004b; Lennartz et al., 1997; Liu et al., 1970; Wauchope et al., 1992), and organic C content may only explain about half of the variability observed in k_D values among soils (Liu et al., 1970). Moreover, although the soil is composed of 3 to 5% organic matter, the organic matter content of the sediment samples is not known.

Nevertheless, to bound the mass that might have been sorbed to the sediments, we predicted the concentration of diuron adsorbed to the sample sediment as $C_s = k_D C_1$, where C_s (μg kg⁻¹) is the diuron concentration on the sediment and C_1 (μg L⁻¹) is the concentration in water. Average sediment mass per sample was calculated by measuring the filter papers in bulk (there was much uncertainty in the measurements of individual samples because individual papers were not measured before filtration and, when clean, they varied considerably in mass). To err on the high end, we assumed a high k_{OC} value of 900 L kg⁻¹, and an organic content of 5%. From the measurements of C_1 reported in runoff below, the diuron predicted on the sediment was 1–3% of the total diuron in the sample, on average, and as high as 10%.

Modeling of Diuron Concentration

A simple model for describing solute concentrations in surface runoff and preferential flow was compared to the observations of diuron in surface runoff and tile drainage. The model is based on Steenhuis and Walter (1980) and Steenhuis et al. (1994), but includes a sink term that lumps together all processes that remove diuron from the field other than liquid-phase advection (e.g., Darnault et al., 2004). These processes include biological degradation, photodegradation, hydrolysis, and erosion by wind or water.

Two principle assumptions of the model are (i) the presence of a mixing zone near the soil surface in which pesticide concentrations in the surface runoff, percolating water, and soil solution are equal, and (ii) that the adsorbed and desorbed phases are in equilibrium at all times. An extensive discussion of the mixing-zone model and the appropriateness of its assumptions is given in Ahuja (1986).

The concentration of unadsorbed diuron in the discharge water, C_1 (μg L⁻¹), is given by

$$C_1 = C_{1,0} \exp[-\int(r/w_d + 1/\alpha)dt] \quad [1]$$

where $C_{1,0}$ (μg L⁻¹) is the initial concentration, r (mm d⁻¹) is the rainfall rate, w_d (mm) is the apparent water content per unit surface area during the desorption phase, and α (d) is a first-order degradation coefficient. Furthermore, assuming that during many adsorption-desorption cycles, or rainfall and inter-rainfall periods, $w_d(t)$ and $\alpha(t)$ can be replaced by constant effective values, then the concentration in runoff during the course of the season can be expressed as

$$C_1 = C_{1,0} \exp[-(R/\hat{w}_d + t/\hat{\alpha})] \quad [2]$$

where R (mm) is the cumulative rainfall at time t (d) and \hat{w}_d and $\hat{\alpha}$ are effective values of w_d and α .

Equation [2] can be rewritten by introducing variables of dimensionless time t^* and dimensionless cumulative rainfall R^* at time t^* :

$$C_1 = C_{1,0} \exp\left[-\left(\frac{R_T}{\hat{w}_d} R^* + \frac{T}{\hat{\alpha}} t^*\right)\right] \quad [3]$$

The dimensionless time $t^* = t/T$, where T (d) is some arbitrary time since application, and the dimensionless cumulative rainfall $R^* = R/R_T$, where R_T (mm) is the cumulative rainfall per unit area at time T .

If degradation is the dominant cause of diuron depletion, then Eq. [3] can be reduced to a one-variable model and C_1 can be described as a function of time only:

$$C_1 = C_{1,0} \exp\left(-\frac{T}{\hat{\alpha}} t^*\right) \quad [4]$$

The constant $\hat{\alpha}$ then becomes proportional to the half-life, where the half-life equals $-\ln(0.5)\hat{\alpha}$, or $0.693\hat{\alpha}$. Likewise, if diuron depletion is primarily the result of being transported from the mixing layer by rainwater, then Eq. [3] can be reduced to a one-variable model where C_1 is only a function of cumulative rainfall:

$$C_1 = C_{1,0} \exp\left(-\frac{R_T}{\hat{w}_d} R^*\right) \quad [5]$$

In this case, the half-life can be viewed as being in units of cumulative rainfall (mm), and is equal to $0.693\hat{w}$.

RESULTS AND DISCUSSION

Surface Water

Diuron was detected in surface runoff and tile drainage from all fields for the duration of each observation season. The transformation product DCPMU was detected in only one of 10 runoff samples tested. Because of a lack of DCPMU detection, possibly due in part to the relatively high DCPMU detection limit (6 or 10 μg L⁻¹ for eight samples and 0.4 μg L⁻¹ for two samples), it is difficult to make comparisons to the study of Field et al. (2003) in this regard. The single positive sample was collected directly from a rivulet on the surface of Field 1-W and had a DCPMU concentration five times less than that of diuron, which is consistent with the findings of Field et al. (2003), who reported diuron/DCPMU ratios ranging from ~2 to 10 in creek water. However, the diuron concentrations in the other nine samples range from 2 to >40 times the DCPMU detection limit, which is consistent with the diuron in the surface runoff from Fields 1 and 2 undergoing less biodegradation than the diuron showing up in creek water at the sites of Field et al. (2003).

The first surface flow event on Field 1 was witnessed 45 d after application (30 Oct. 2000) and after 100 mm of accumulated rain. Though the flume installation was not complete on this date, two samples were collected by hand directly from a rivulet on Field 1-W. The concentration of diuron of the combined sample was 2160 μg L⁻¹. The first large flow event measured began 53 d after application (11 Dec. 2001), following 135 mm of rain. Up to 68 d (210 mm of rain) after application, concentrations remained >940 μg L⁻¹, with a maximum

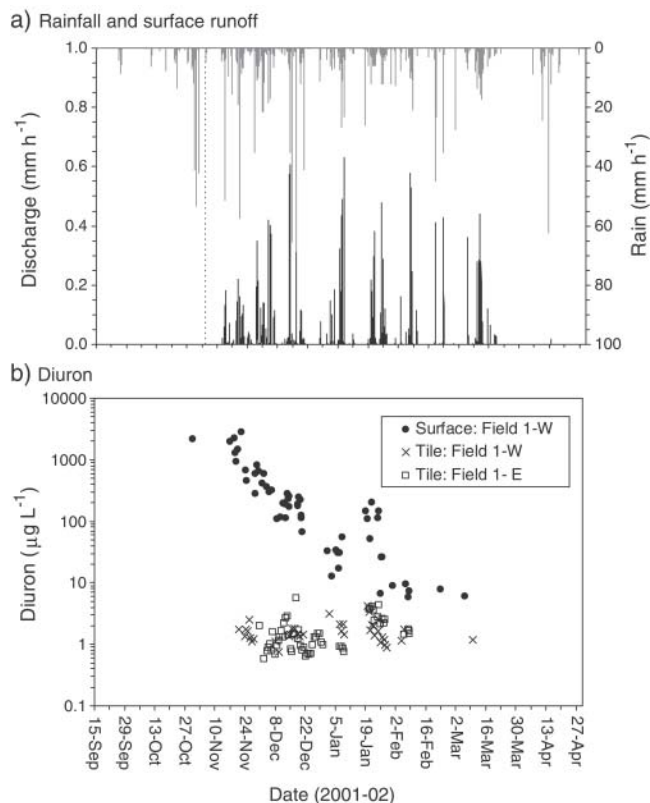


Fig. 3. Field 1 (a) rainfall and surface runoff intensity and (b) diuron concentrations in surface runoff and tile drainage for the 2001–2002 wet season. Diuron was applied on 15 Sept. 2001. Runoff monitoring began on 6 Nov. 2001 (dashed vertical line) and was stopped in June 2002. The detection limit is $0.02 \mu\text{g L}^{-1}$.

of $2830 \mu\text{g L}^{-1}$. Throughout the season, diuron concentrations showed a general exponential decline with time (Fig. 3), dropping by a factor of roughly 400 down to $6 \mu\text{g L}^{-1}$ during a period of 130 d (680 mm of rain).

Concentrations on Field 1-W show a sharp but short-lived increase beginning on 19 Jan. 2002 (Fig. 3). This initial increase occurred during the first runoff event following diuron application on the adjacent Field 1-E on 14 Jan. 2002. It is highly likely that this increase was due to unintentional spraying over the east side of Field 1-W, directly over the northsouth depression that delivers surface runoff southward toward the flume. By 25 Jan. 2002, diuron concentrations had decreased by more than an order of magnitude and resumed the declining pattern seen prior to this increase.

The first two surface flow events on Field 2 occurred 27 and 29 d after application (14 and 16 Nov. 2002) and after 58 and 64 mm of accumulated rain, although both events were very small (Fig. 4). On Field 2-S, the concentration of diuron for these events was $\sim 120 \mu\text{g L}^{-1}$. The first large runoff event occurred 53 d after application (10 Dec. 2002) or after 92 mm of rain. During several events between 10 and 15 Dec. 2002, concentrations remained $>130 \mu\text{g L}^{-1}$, with a maximum of $180 \mu\text{g L}^{-1}$. Similar to Field 1-W, diuron concentrations in Field 2-S showed a general exponential decline with time (Fig. 4), dropping by a factor of >100 during a period of 130 d (620 mm of rain). Diuron concentrations in the

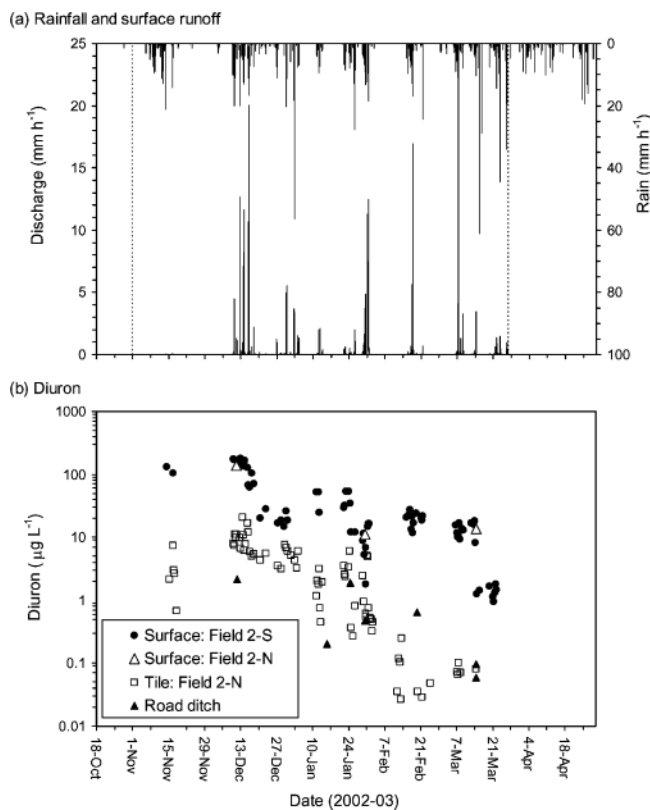


Fig. 4. Field 2 (a) rainfall and surface runoff intensity and (b) diuron concentrations in surface runoff and tile drainage for the 2002–2003 wet season. Diuron was applied on 18 Oct. 2002. The dashed vertical lines in (a) bound the period of surface runoff monitoring. The detection limit is $0.02 \mu\text{g L}^{-1}$.

three samples collected by hand from the flume at Field 2-N are similar to samples taken at the same time from Field 2-S (Fig. 4).

Surface runoff production from Field 1-W was $\sim 3\%$ of rainfall (Table 3). In contrast, surface runoff from Field 2-N and Field 2-S was 18 and 13% of rainfall, respectively. (Note that although the flume at Field 2-N was not operational until 11 Dec. 2002, the observed runoff from Field 2-S suggests that <2 mm of total runoff occurred before 11 Dec. 2002). The lesser slope and the presence of an effective drainage system are probably the primary factors for the lower surface runoff production from Field 1-W, although soil hydraulic properties, such as soil matrix hydraulic conductivity and macropore frequency, may also vary between fields.

Table 3. Rainfall, discharge, and diuron losses.

Site sampled	Rainfall	Discharge	Discharge/ rainfall		Diuron loss
	mm	mm	%	% of applied	g ha ⁻¹
Field 1-W†					
Surface	799	20	3	3.0	67
Tile drain§	799	125	16	0.12	2.6
Field 2-S‡	678	89	13	1.3	33
Field 2-N‡	678	122	18	–	–

† 15 Sept. 2001–6 Mar. 2002.

§ Missing data.

‡ 18 Oct. 2002–22 Mar. 2003; surface only.

Despite the lower surface runoff, the total diuron loss in runoff from Field 1-W was greater than from Field 2-S because the diuron concentrations in Field 1-W were an order of magnitude higher. Diuron losses were 67 g ha^{-1} (3.0% of applied) in Field 1-W and 33 g ha^{-1} (1.3% of applied) in Field 2-S (Table 3).

The diuron concentrations and their temporal pattern in surface runoff from Field 2 are consistent with those observed in vineyards with comparable climate and application rate (Louchart et al., 2001). The concentrations in Field 1 are much higher, however, and the disparity is surprising given the similarity of Fields 1 and 2 in soil characteristics, rainfall amounts and patterns, application rates, and lag times between application and the first major flow events (7–8 wk). Certainly the most notable difference between the fields is the runoff production, which is roughly five times higher in Field 2 than in Field 1. The higher concentrations in Field 1 are consistent with the mixing-zone model wherein a larger proportion of surface runoff water in Field 2 does not equilibrate in the mixing zone. Consider, for example, periods of rain when Field 2 is experiencing rill and sheet flow and much of the rain falling directly in rills and in the swale has no considerable contact with the soil before leaving the field.

Tile-Drain Water

Diuron concentrations in tile-drain water from Fields 1-W and 1-E were very low compared to surface runoff concentrations, and relatively constant in time (Fig. 3). A linear regression of concentration with time of the Field 1-W data reveals a slope of practically zero and an average concentration of $1.6 \mu\text{g L}^{-1}$. Concentrations in the Field 1-E tile drain increased by about a factor of 2 during the latter half of January 2002, which follows the diuron application on this field on 14 Jan. However, the average concentration of $1.7 \mu\text{g L}^{-1}$ was nearly the same as in Field 1-W.

Unlike Fields 1-E and 1-W, Field 2-N tile-drain water showed a large change in diuron concentration in time. The first samples collected in mid-November range from 0.7 to $7 \mu\text{g L}^{-1}$. Concentrations reached a maximum of $20 \mu\text{g L}^{-1}$ on Day 57 following application and afterward showed a general exponential decrease with time (Fig. 4), dropping by two orders of magnitude during the observation period. On average, the concentration of diuron in the tile drain was 11 times less than that in the surface runoff.

The similar temporal response of concentrations in surface and tile-drain discharge on Field 2 may be due to the importance of preferential flow on the field. An extreme case of preferential flow was first evident on 30 Jan. 2003, when a hole was observed in the main path of surface drainage $\sim 10 \text{ m}$ uphill from the watershed outlet at Field 2-N over where the tile drain was expected to be. Surface flow was seen entering the hole on this date. By 7 Feb. 2003, the hole was large enough to completely insert a boot and captured most of the surface runoff originating uphill from the hole. The red clay tile below was photographed by inserting a camera into

the hole at arm's length. On 11 Feb. 2003, the hole was filled with gravel and soil and sealed with bentonite. Curiously, the data show no obvious change in the pattern of diuron depletion when the hole was present, which was as long as 2.5 wk. It may be that the large scatter in the data masked any effect.

It is also possible that diuron was entering the tile drain at the drain inlet on the east side of the field, as water that accumulated in the ditch during large storms probably seeped into the drain despite the riser that was installed. Diuron was detected in the ditch water at concentrations similar to that found in the tile-drain water (Fig. 4). The roadside was sprayed with herbicide in the autumn of 2002 and in years past to control weeds. Although the principle herbicide used was Roundup (glyphosate [*N*-(phosphonomethyl)glycine], Monsanto Co., St. Louis, MO), diuron may also have been applied (Oregon Dep. of Transportation, Region 2, District 3, personal communication, 2004).

Difficulties with the flow meters at Field 1 complicated calculation of total drain discharge. Large and numerous gaps in the data, particularly for Field 1-E, when substantial flow was visible at the tile-drain outlet or in the Field 1-W tile drain, indicated malfunctioning. The disruptions in the flow meter in Field 1-W, which was excavated, were caused by fine roots, grass, or even soil particles. Two data gaps for Field 1-W totaling 27 d were detected in the record. These two gaps correspond to 35% of the rainfall that fell between the first measurable flow in the tile drain (21 Dec. 2001) and the end of the sampling period.

The total drain discharge per unit area measured from Field 1-W was 81 mm. Assuming, however, that the tile drain responded equally to rainfall during the data gaps as it did during the rest of the period between 21 Nov. 2001 and 6 Mar. 2002, the total outflow would have been 125 mm. This equals 16% of the total rainfall. The total loss of diuron was calculated to be 2.6 g ha^{-1} , or 0.12% of the total quantity applied (Table 2). For comparison, this is $<4\%$ of the diuron loss in surface runoff. Total losses from Field 1-E were not estimated.

The flow-meter readings from Field 2-N were unreliable because of repeated jamming of the turbine by debris, mainly grass and small roots; thus total diuron loss from tile drainage could not be estimated. The presence of debris may be viewed as evidence of macropore flow.

Modeling of Diuron Concentration

The model parameters in Eq. [3] to [5] were determined by linear regression of the log-transformed values of surface water concentration C_1 against t^* and/or R^* , and the results were compared in terms of the adjusted R^2 (hereafter referred to simply as R^2). For surface runoff in Fields 1-W and 2-S, and for tile-drain discharge in Field 2-N, cumulative rainfall explains slightly more of the variability in concentration than does time (Table 4, Fig. 5–7). Multivariable regression of $\ln(C_1)$ against both t^* and R^* is problematic because the two independent variables are highly correlated, and even results in a nonphysical negative value of $\hat{\alpha}$ for

Table 4. Initial diuron concentration ($C_{i,0}$), effective apparent water content (\hat{w}_d), effective degradation coefficient ($\hat{\alpha}$), and coefficient of determination (R^2) for the one-variable models of diuron depletion.

Site sampled	Model with variable time (t)			Model with variable cumulative rain (R)		
	$\hat{\alpha}$	$C_{i,0}$	R^2	\hat{w}_d	$C_{i,0}$	R^2
	d	$\mu\text{g L}^{-1}$		mm	$\mu\text{g L}^{-1}$	
Field 1						
Surface (1-W)	19	25 000	0.78	118	6400	0.81
Tile (1-W)	∞	1.6	–	∞	1.6	–
Tile (1-E)	∞	1.7	–	∞	1.7	–
Field 2						
Surface (2-S)	33	450	0.63	161	240	0.67
Tile (2-N)	20	170	0.64	98	58	0.66

Field 2-S. The result is that use of Eq. [4] instead of the simpler Eq. [6] does not improve the R^2 (Table 5).

The concentrations of diuron in the tile drains in Field 1 suggest half-lives that are much greater than the observation period (i.e., practically infinite for our purposes) (Table 4), so the regression results are not given.

The relative importance of degradation and advection from the mixing layer via rainfall on the wet-season diuron depletion cannot be clearly identified given the available data. The fact that cumulative rainfall explains more of the variability of diuron concentration in runoff water than time does, however, suggests that rainfall-driven advection played a major role in reducing diuron

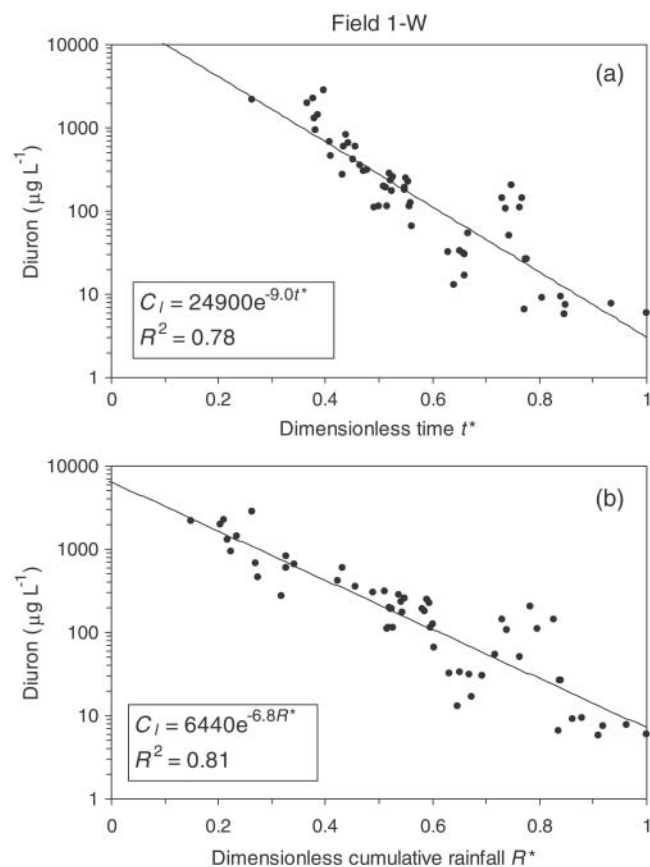


Fig. 5. Diuron concentration (C_i) in surface runoff against dimensionless time (t^*) and dimensionless cumulative rainfall (R^*) for Field 1-W.

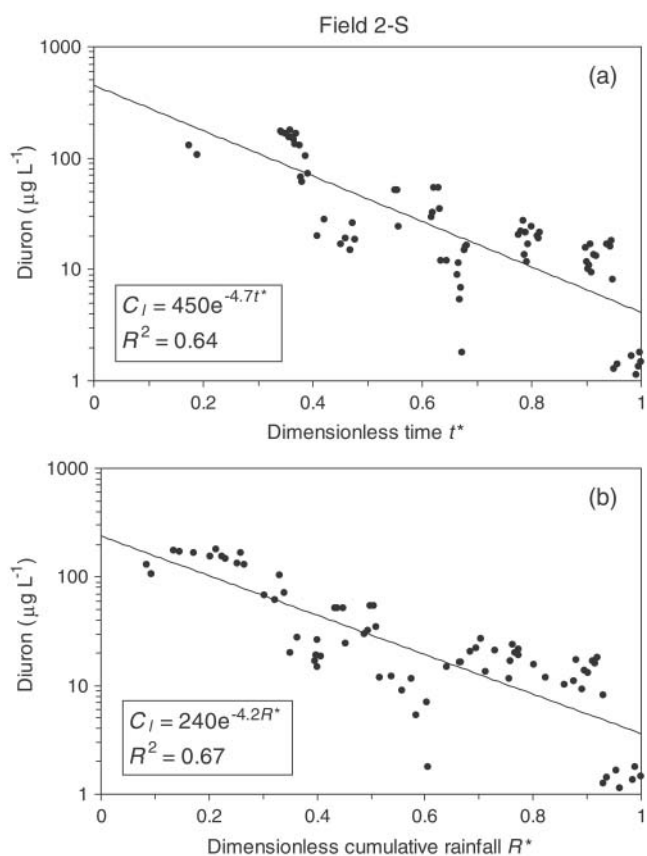


Fig. 6. Diuron concentration (C_i) in surface runoff against dimensionless time (t^*) and dimensionless cumulative rainfall (R^*) for Field 2-S.

in the upper layer of soil. Also, given the observed exponential depletion rates hypothesized by the model, linear and instantaneous desorption appears to describe the transfer of diuron from soil to water within the mixing zone in wet conditions, although results from other studies suggest otherwise, as discussed below.

It is of interest to compare the half-lives of diuron in the surface runoff computed from Eq. [5] to half-lives reported from other studies. At Fields 1-W and 2-S, the half-lives were 13 and 23 d, respectively. These values are consistent with half-lives of 13 to 35 d reported in surface runoff at two vineyards in southern France (Lennartz et al., 1997) and alongside a highway in northern California (Huang et al., 2004a). All of these values, however, are at the low end of, or lower than, earlier reports of “field” half-lives for diuron. A review of several studies by Wauchope et al. (1992), for example, revealed field half-lives ranging from 30 to 330 d, while half-lives as high as 4000 d have been measured in soils in the laboratory (Madhun and Freed, 1987).

Interestingly, both Lennartz et al. (1997) and Huang et al. (2004a) found the half-lives in surface runoff to be two to three times less than that in the upper 2 or 5 cm of soil. Lennartz et al. (1997) concluded that diuron content in soil with time as calculated by alcohol extraction does not indicate the herbicide depletion rate in surface runoff. Attempting to explain the discrepancy, Huang et al. (2004b) showed that decreasing desorbability with

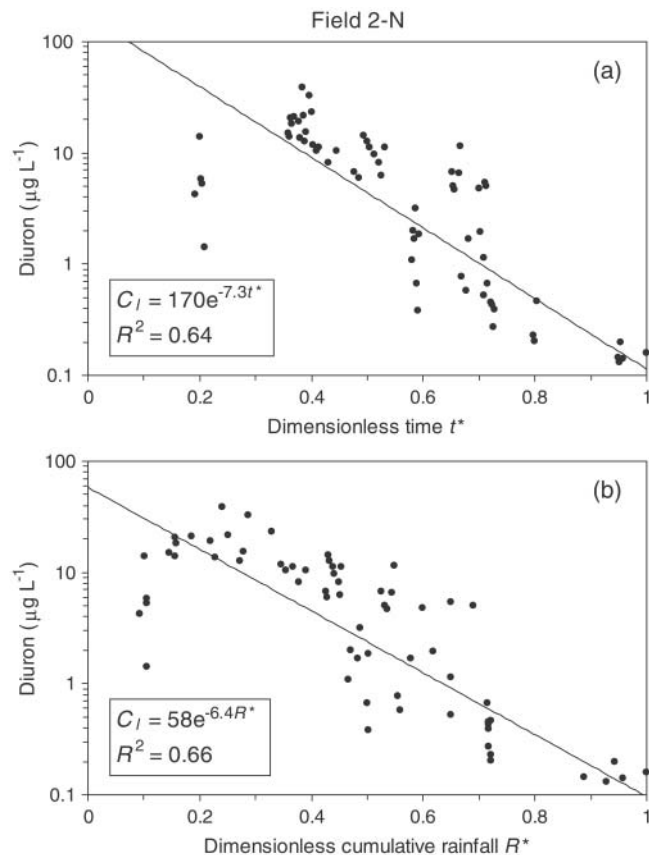


Fig. 7. Diuron concentration (C_i) in tile drainage against dimensionless time (t^*) and dimensionless cumulative rainfall (R^*) for Field 2-N.

herbicide age in soil samples was too small to be the dominant cause of faster diuron depletion in runoff than in the uppermost soil. This suggests that the controlling process is the changing spatial distribution of herbicide with time, such that the diuron that remains as time passes is progressively less accessible to transport by overland flow (e.g., Leonard et al., 1979). Although we did not measure diuron in the soil, our relatively low half-lives in runoff from grass fields provide further evidence that the oft-cited half-lives of diuron in field soils should not be used directly to predict diuron depletion in surface runoff.

CONCLUSIONS

The herbicide diuron was observed in surface runoff and tile drainage in two fields recently rotated to grass

Table 5. Effective apparent water content (\hat{w}_a), effective degradation coefficient ($\hat{\alpha}$), initial diuron concentration ($C_{i,0}$), and coefficient of determination (R^2) for the two-variable model of diuron depletion, with variables time (t) and cumulative rain (R).

Site sampled	$\hat{\alpha}$	\hat{w}_a	$C_{i,0}$	R^2
	d	mm	$\mu\text{g L}^{-1}$	
Field 1				
Surface (1-W)	90	147	8900	0.78
Field 2				
Surface (2-S)	-32	81	110	0.67
Tile (2-N)	577	101	61	0.65

for seed production. Initial concentrations of diuron during the first large runoff-producing rainfall events were 20 to 1000 times higher in surface runoff than in tile drainage, depending on the field. Total losses of diuron in a field with an 11-yr-old tile-drain system were 25 times greater in surface runoff than in tile drainage, even though total drain discharge exceeded surface discharge. Surface losses were 1.3–3.0% of the total amount of diuron applied.

In one field, concentrations in surface runoff remained $>1000 \mu\text{g L}^{-1}$ for the first 210 mm of accumulated rainfall, at levels of concern for aquatic invertebrates (Giacomazzi and Cochet, 2004), whereas concentrations in tile drainage were only $\sim 2 \mu\text{g L}^{-1}$. The implication for herbicide management is that a well-functioning tile drain system may improve water quality in streams if it reduces surface runoff, as long as preferential flow is minimal.

The persistence of diuron in surface runoff, in terms of half-life, was roughly 2 to 3 wk. During the first wet winter season after planting of grass seed, however, it may be more appropriate to consider the depletion of diuron in runoff as being controlled by rainfall, because at this time advection is probably the dominant process controlling diuron removal from the upper soil layer. A simple mixing-zone model supports this conclusion. As such, the half-life may be measured in terms of cumulative rainfall since time of application. The data indicate that diuron concentrations in surface runoff were reduced by half after ~ 80 to 110 mm of accumulated rainfall.

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