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A simple model for predicting solute concentration in agricultural tile lines shortly after application

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Abstract

Agricultural tile drainage lines have been implicated as a source of pesticide contamination of surface waters. Field experiments were conducted and a simple model was developed to examine preferential transport of applied chemicals to agricultural tile lines. The conceptual model consists of two linear reservoirs, one near the soil surface and one near the tile drain. The connection between the two reservoirs is via preferential flow paths with very little interaction with the soil matrix. The model assumes that only part of the field contributes solutes to the tile drain. The model was evaluated with data from the field experiments in which chloride, 2,4-D, and atrazine concentrations were measured on eight tile-drained plots that were irrigated twice. Atrazine was applied two months prior to the experiment, 2,4-D was sprayed just before the first irrigation, and chloride before the second irrigation. All three chemicals were found in the tile effluent shortly after the rainfall began. Generally, the concentration increased with increased flow rates and decreased exponentially after the rainfall ceased. Although the simple model could simulate the observed chloride concentration patterns in the tile outflow for six of the eight plots, strict validation was not possible because of the difficulty with independent measurement of the data needed for a preferential flow model applied to field conditions. The results show that, to simulate pesticide concentration in tile lines, methods that can measure field averaged preferential flow characteristics need to be developed.

Introduction

The use of pesticides and their effect on surface and subsurface waters has been under intense debate since Rachel Carson's book was published (Carson, 1962). Although pesticides are currently being detected on many occasions in shallow groundwater or surface waters, no agreement exists concerning their toxicological significance (Brown *et al.*, 1995). Surveys by the Environmental Protection Agency (1990, 1992) found that 10% of community drinking water supplies and 4% of rural domestic wells contained detectable levels of pesticides. Periera and Hostettler (1993) calculated that the Mississippi River annually carries over 300,000 kg of herbicides into the Gulf of Mexico. The concentrations found in surface waters are usually below 10 μg/l and rarely exceed 50 μg/l. Despite the lack of agreement on toxicological effects, treating drinking water to remove pesticides above legal limits is required by law and is extremely expensive (Brown *et al.*, 1995).

Agricultural tile lines play an important role in the contamination of surface waters (Traub-Eberhard *et al.*, 1995). Mackenzie and Viets (1974) suspected that pesticides might appear in agricultural drainage waters. This was confirmed for the first time by Muir and Baker (1976) who found atrazine and its by-products in tile water from corn plots. In many cases, pesticides in streams have been traced back to tile drain discharge (Rothstein *et al.*, 1996; Steenhuis *et al.*, 1990; Kladivko *et al.*, 1991; Flury, 1996; Milburn *et al.*, 1995). Preferential flow transports these pesticides much faster than predicted by their properties based on the convective-dispersive method (Traub-Eberhard, 1995; Kladivko *et al.*, 1991; Parlange *et al.*, 1988; Flury, 1996).

Although more than 40 models are available to simulate flow and transport in the vadose zone, (a list is given in Kramer and Cullen, 1995), very few can simulate transport in nonuniform or fractured media (Ma *et al.*, 1995; Jarvis *et al.*, 1991a,b; Hutson and Wagenet, 1995) and few can simulate the concentration of pesticides due to preferential transport in subsurface tile lines without excessive computer and data requirements (Utermann *et al.*, 1990; Grochulska and Kladivko, 1994). Furthermore, Flury (1996), in his overview article, points out that there is a lack of models which are able to simulate preferential flow.

The purpose of this paper is to assess how well a simple mathematical model can predict the high chemical concentrations in the subsurface tile lines that can occur shortly after application. The performance of the simplified model will be compared with data from eight tile drained fields in northern New York. Physically meaningful parameter values will be inferred from the measured breakthrough curves and goodness of fit and consistency between the different plots and three applied chemicals will be used as a measure of success of the predictions.

While more complicated models might explain the data better than the simple model developed here, complexity usually results in additional input parameters which are not always meaningful or are difficult to determine. Obtaining these parameters is not an easy task; even the present simplified model for pesticide prediction requires extensive input data which were not available.

Model Development

CONCEPTIONAL MODEL

The model called TAM-MO-DEL is patterned after models that have used a distribution layer near the surface successfully to simulate the concentration of preferentially moving solutes (Jarvis *et al.*, 1991a,b; Ma *et al.*, 1995; Ritsema and Dekker, 1994; Steenhuis *et al.*, 1994). The distribution layer is envisioned as a linear reservoir which distributes and supplies the water and solutes to the macropores in the subsurface.

The model employs a groundwater reservoir to simulate tile outflow. The two reservoirs are connected by preferential flow paths through which the water and solutes flow with little interaction with the soil (schematically depicted in Fig. 1). In accordance with previous research, the distribution layer has a fixed depth (Steenhuis *et al.*, 1994). The bottom reservoir volume can be variable. When a rainstorm starts, both reservoirs contain some water, the amount depending on the amount of evaporation and rainfall during the preceding period. After the top reservoir fills up (i.e., the distribution layer is near saturation), water and solutes flow to the lower reservoir where they 'mix' with the groundwater. After the rainfall stops, the movement through the preferential paths stops too. Because of the short time involved, it is unlikely that the whole area between the tile lines contributes water and solutes to the tile line. Consequently, the mass balance needs to be made over longer time periods (Richard and Steenhuis, 1988).

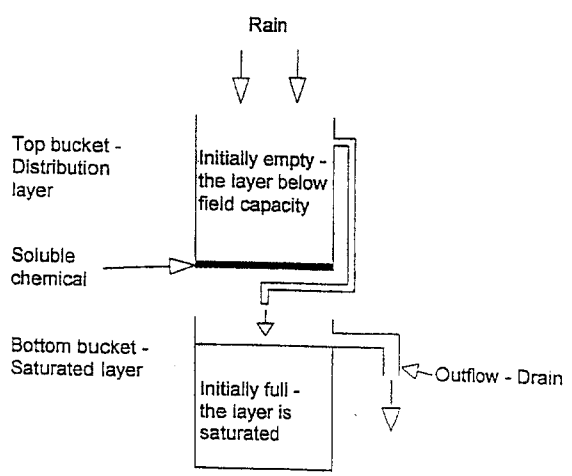


Fig. 1. *Description of the conceptual model, two-bucket system.*

The assumptions of the conceptual model can be stated formally as:

1. The distribution zone and the groundwater reservoir are linear reservoirs.
2. The travel time between two reservoirs is short.
3. The percolation through the macropores begins when the distribution layer is near saturation and ceases when the rainfall stops (or very shortly thereafter). Matrix flow may occur, but does not carry any solutes from the surface.
4. Not all the land area between the tile lines contributes water and solutes to the tile lines.

SIMULATION MODEL

Three separate periods are distinguished, defined as:

Period Ia. The period begins with the onset of the rainfall. The moisture content of the distribution layer increases ('fills up'). Rainwater 'mixes' with solutes in the distribution zone. There is no downward movement. Period Ia ends at time t_I when the distribution zone is near saturation and the preferential flow is initiated.

Period Ib. Rain continues to fall and the moisture content in the distribution layer remains the same (near saturation). The water and solutes move down through preferential flow paths where they come into contact and begin to mix with the water in the groundwater reservoir. The period ends at time t_{II} when the rain stops or ponding ceases.

Period II. Rainfall ceases and flow through the preferential flow paths ends. The groundwater continues to supply water and solutes to the tile line through redistribution.

Equations for the solute concentration in the distribution zone and groundwater during the different time periods are developed next.

Period I: During Rainstorm

Period Ia—Initiation of Rainfall Event: During this period, the water accumulates in the surface distribution layer. The solute concentration in the distribution layer at the end of this period is:

$$C_0^* = \frac{m_0^*}{m_a^*} \qquad (1)$$

where the superscript * indicates that the parameter values are associated with the surface distribution layer, m_0^* is the mass of solute per unit area in the distribution layer at time t_0, and w_a^* is the apparent water depth and includes the effect of adsorption. It is defined as:

$$w_a^* = h^*(\theta_s^* + \rho k_a^*) \tag{2}$$

where h^* is the thickness of the distribution layer, θ_s^* is the water content, k_a^* is the adsorption partition coefficient when the layer is being filled up, and ρ is the bulk density of the soil.

Period Ib: Solute Concentration in the Surface Distribution Layer: The solute concentration in the preferential flow from the distribution layer is given as (Steenhuis *et al.*, 1994):

$$C^* = C_0^* \exp\left(\frac{\int_{t_1}^{t} -R\,dt}{w_d^*}\right) \tag{3}$$

where C^* is the concentration of water in solutes in the distribution layer, R is the rainfall rate, t is time, t_1 is the time that Period Ib begins, and w_d^* is the equivalent water depth during outflow of the distribution layer which is equal to:

$$w_d^* = h^*(\theta_s^* + \rho k_d^*) \tag{4}$$

The terms in Eqn. (4) are similar to those in Eqn. (2) except that k_d is the desorption partition coefficient. For solutes that adsorb to the soil, the partition coefficients during adsorption, k_a, and desorption, k_d, are not necessarily the same due to hysteresis and nonequilibrium conditions (Steenhuis *et al.*, 1994). However, for nonadsorbing solutes, like chloride, both w_a^* and w_d^* are the same and are equal to the amount of water in the distribution layer.

Period Ib: Modelling the Concentration in the Tile Line: Gelhar and Wilson (1974) showed that the groundwater system behaves likes a linear reservoir. With this assumption, the gain and loss of the solutes from the groundwater within the contributing land area for Period I can be approximated by:

$$d\frac{m^{**}}{dt} = RC^* - \frac{Qm^{**}}{w_d^{**}} \tag{5}$$

where the ** superscript indicates that the parameter values are associated with the groundwater reservoir within the contributing area of the tile line, $w^*{}_d^*$—similar to Eqn. (4)—is the apparent groundwater volume per unit area, m^{**} is the mass of solutes per unit area, and Q is the rate of the tile outflow expressed as volume of water per unit time per unit area. All groundwater parameters are defined only for the contributing area. As will be seen later, the contributing area for summer storms is the area near the tile line where the groundwater table has a steep gradient. During early spring and winter when evaporation is small, it is likely that the whole field is contributing.

Substituting Eqn. (3) into Eqn. (5) gives:

$$\frac{dm^{**}}{dt} = RC_0^* \exp\left(\frac{\int_{t_1}^{t} -R\,dt}{w_d^*}\right) - \frac{Qm^{**}}{w_d^{**}} \tag{6}$$

A simplified solution can be obtained from Eqn. (6) by assuming (as suggested by the field experiments described later) that the amount of solute in the tile outflow is negligible during an actual (short term) precipitation event. Thus, by neglecting the second term on the right-hand side and assuming no solutes in the groundwater initially at time, t_I, Eqn. (6) becomes:

$$C^{**} = C_0^* \frac{w_d^*}{w_a^{**}}\left(1 - \exp\frac{\int_{t_1}^{t} R\,dt}{w_d^*}\right) \tag{7}$$

where C^{**} is the average groundwater concentration. As long as the solute loss is small during the rain event, the concentration in the tile line can be set equal to C^{**}.

Period II: After Rainstorm Ends: Once the rainfall has stopped and the downward flux of solutes through the preferential flow paths has ceased, Eqn. (5) can be rewritten:

$$\frac{dm^{**}}{dt} = -\frac{Qm^{**}}{w_d^{**}} \tag{8}$$

which is solved by the separation of variables for an average water depth $w^*{}_d^*$ as:

$$C^{**} = \frac{m_{II}{}^{**}}{w_a^{**}} \exp -\frac{\int_{t_{II}}^{t} Q\,dt}{w_d^{**}} \tag{9}$$

where $m^*{}_{II}^*$ is the amount of solutes in the groundwater per unit (land surface) area at the beginning of Period II, and can be found with help of Eqn. (7) for $t = t_{II}$.

Materials and Methods

Experiments were carried out on eight tile-drained plots planted with corn at the Willsboro Experimental Farm in northern New York near Lake Champlain (Fig. 2). The soil is classified as a somewhat poorly drained Rhinebeck variant fine sandy loam (Olson *et al.*, 1982) and consists of

five distinct layers: fine sandy loam (0–20 cm), clayey loam (20–40 cm), clayey hard pan (40–65 cm), gravely loam (65–100 cm), and gravely sand (>100 cm). The thickness of these soil horizons are average values and vary considerably. For example, plot 4 has the least amount of gravelly sand at shallow depth, while plots 1 and 8 have the gravelly sand starting closest to the surface. The soil surface has a slope of less than 3% in the SW to NE direction, with plot 8 the lowest and plot 1 the highest. Field observations during wet periods indicate that plots 5 through 8 (especially 6, 7, and 8) have some small springs within the plot. Apparently, the field perimeter drain depth is not adequate to collect all the subsurface flow from outside the area. Plot 8 also receives runoff from plot 7 and from the road between plots 7 and 8 (Fig. 2).

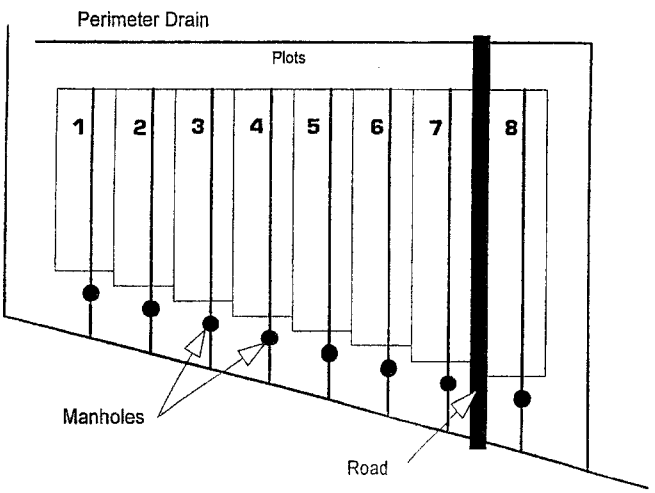


Fig. 2. *Layout of 8 tile drained plots at the Willsboro Research Farm.*

The plots are 18 m wide and 110 m (plot 1) to 150 m (plot 8) in length (Fig. 2). A single drainage line at an average depth of 80 cm in the E-W direction drains each plot. The tiles are offset 3 m in the downhill direction such that the water applied to the plot flows to the drain (Aburime, 1986). Tile lines 2 through 7 were installed in August 1984. In 1991, two more tile lines (1 and 8) and an additional perimeter drain were installed. At the end of each plot, the tile line passes through a manhole, where the flow rate is measured using a tipping bucket connected to a data logger (Campbell Scientific Model 21X). These outflow rates were verified by manual measurements. Water samples for chemical analysis were collected manually from the tile outflow.

Subplots just upslope of the manhole, with dimensions of 18 m (the width of the plot) by 55 m, were irrigated with water from Lake Champlain using a sprinkler system consisting of three lines of 4 sprinklers. The sprinklers were set up in a 12 m square grid and could irrigate two plots at a time. The sprinklers were set up in a line for plot 8 because it was separated by the field road from the other plots. Plot 8, therefore, had different irrigation intensities than the other seven plots.

Three no-till and five conventionally tilled plots were planted with corn for the third consecutive year on May 10. On May 20, atrazine (2-chloro-4-(ethylamino)-6-sopropylamine-s-triazine), was applied at a rate of 3.36 kg/ha. On June 29, 2,4-D (2,4-Dichlorophenoxyacetic acid) was sprayed at a rate of 1.68 kg/ha on corn plants approximately 30 cm high. As shown in Table 1, two irrigations were applied for 7 to 9 hours each. On June 29, plots 1 and 2 were irrigated. Each day thereafter, another pair of plots was irrigated. On July 6, a second round of irrigations were initiated, with a pair of plots irrigated each day.

Table 1. Summary of experiments performed and irrigation applications.

Plot	Tillage treatment	Date	Duration hours	Intensity mm/hr
week 1				
1	No-Till	6/29	7:00	4.1
2	Tilled	6/29	7:00	4.1
3	No-Till	6/30	8:35	4.6
4	Tilled	6/30	8:35	3.8
5	Tilled	7/1	7:15	4.3
6	No-Till	7/1	7:15	4.6
7	Tilled	7/2	9:20	3.8
8	Tilled	7/2	9:20	2.0
week 2				
1	No-Till	7/6	7:05	7.1
2	Tilled	7/6	7:05	7.1
3	No-Till	7/7	7:25	6.6
4	Tilled	7/7	7:25	4.1
5	Tilled	7/8	7:15	7.1
6	No-Till	7/8	7:15	7.4
7	Tilled	7/9	9:05	7.4
8	Tilled	7/9	9:05	3.3

The first irrigation with a low intensity of approximately 4 mm/hr was intended to leach the 2,4-D into the soil. The second irrigation one week later with an intensity of 7.5 mm/hr simulated a severe storm. Two hours prior to the second irrigation, 34 kg of chloride (in the form of 77% pure $CaCl_2.5H_2O$) was surface-applied to the irrigated area of each plot using a manual spreader.

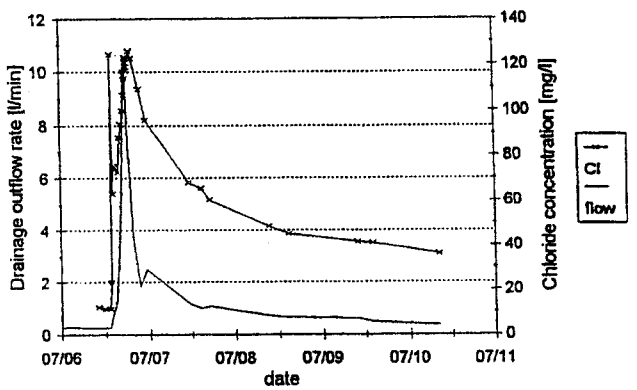
Water samples were analyzed for chloride, 2,4-D, and atrazine. Chloride analysis was performed using a Buchler Instruments digital chloridometer. Herbicide analysis was performed using RAPID immunosorbent assay kits supplied by Ohmicron, which have a reported maximum error of 20% (Ohmicron, 1994).

Results and Discussion

EXPERIMENTAL RESULTS

Typical hydrographs and breakthrough curves of chloride concentrations are shown for plots 1 and 3 (Figs. 3a and 3b). The chloride concentration increased with increase in flow. Conversely, the chloride concentration decreased when the flow decreased after the irrigation ceased. In some cases, a chloride concentration peak occurred ahead of the peak of water flow (Fig. 3). Some exceptions to this trend occurred on plots 5 and 6 during the second week of the experiment, when the concentration peaked a short time after the irrigation began and then decreased continuously.

(a)



(b)

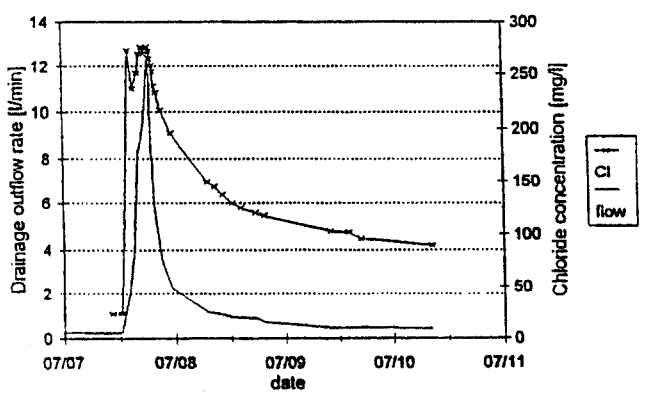


Fig. 3. *Chloride and flow rate as a function of time: (a) plot 1, (b) plot 3.*

Atrazine and 2,4-D concentrations (with a logarithmic scale) are plotted as a function of the cumulative tile outflow for plots 1 and 3 in Fig. 4. In these figures, the data points are given with an open circle. In addition, a filled triangle (week 1) and filled square (week 2) are used to indicate the data points that are used for the regression analysis for Period II. The pesticide breakthrough curves show the same general trend as chloride. During irrigation, when the tile discharge was increasing, the atrazine and 2,4-D concentrations increased. Concentrations became smaller with decreasing discharges after the irrigation stopped. The variability in pesticide data is larger than for chloride, likely due to the better precision of the chloride analytical method and possibly due to actual variations in pesticide tile line concentrations caused by differences in breakthrough of pesticides for individual pores.

The amount of chloride lost in the second event varied between 0.46 kg (1.4% of the amount applied) for plot 1 to 1.5 kg (4.5%) for plot 7 (Table 2). Loss of 2,4-D averaged 17 mg/plot/ event (0.01% of the amount applied per event), with a maximum of 0.05% (plot 2, event 1). Table 2 also shows that atrazine losses were on the same order as 2,4-D. Highest atrazine losses were from plot 1 during event 1 (60 mg, or 0.02% of the amount applied) and plot 3 during event 2 (52 mg). The base concentration of atrazine was higher than that for 2,4-D. Atrazine had been applied in previous years, and is persistent while 2,4-D, also applied in a prior year, degrades rapidly with no carry-over effect from year-to-year. On the other hand, the peak concentration for 2,4-D was higher than for atrazine. The tillage treatment did not seem to affect the observed concentrations with the possible exception of the peak atrazine concentrations being higher for the no-till treatment than for the conventionally tilled plots.

PARAMETER ESTIMATION

The amount of water in the groundwater reservoir, the pesticide adsorption partition coefficients, and the contributing area of the tile line are not known and need to be determined. Other values which are known or measurable are the amount of chemical applied, the rainfall intensity and duration, tile outflow rate, and solute concentration. The characteristics for the surface distribution layer were obtained from experiments on similar soils by Steenhuis *et al.* (1994) and Shalit and Steenhuis (1996).

The breakthrough curves for Period II after the irrigation ceased were used to obtain the apparent groundwater volumes per unit area, w^{**}_d within the contributing area. Because the contributing area is initially unknown, one must first determine the total groundwater volume, W^{**}_d within the contributing area. Other parameters to be determined are the concentration, C^{**}_{II}, and total solute amount, M^{**}_{II}, at the beginning of Period II within the contributing area. These parameters are defined as:

$$\begin{aligned} M^{**}_{II} &= A_c m^{**}_{II} \\ W^{**}_d &= A_c w^{**}_d \\ M^{**}_{II} &= C^{**}_{II} * W^{**}_{a/d} \end{aligned} \tag{10}$$

where $W^{**}_{a/d}$ is the apparent groundwater volume during either Period I or II and A_c is the actual contributing area to the tile line. Note that the assumption of different adsorption partition coefficients for Periods I and II results in different values for $W^{**}_{a/d}$. This, together with the fact that the dissolved solute concentration does not change

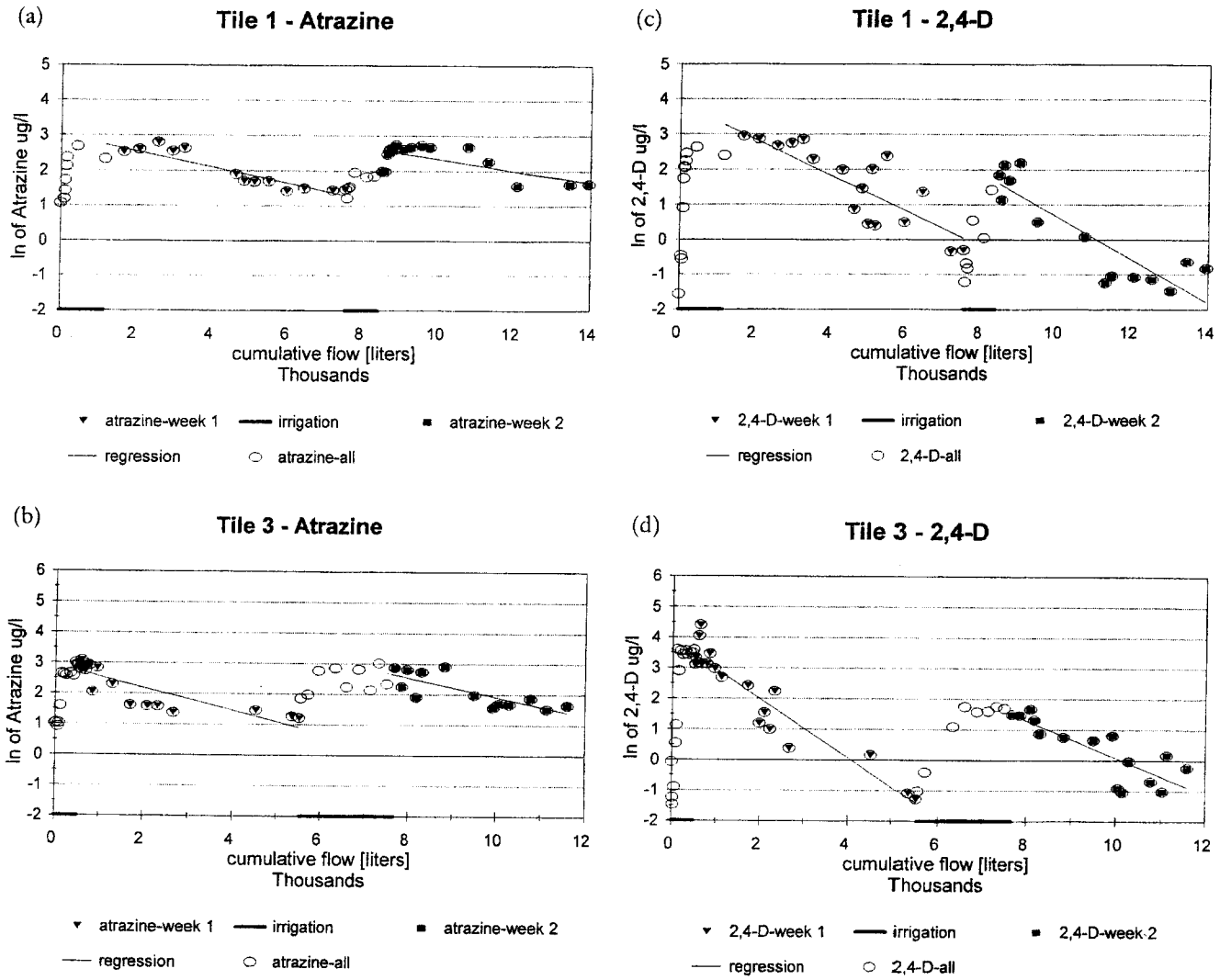


Fig. 4. *Pesticide loss as a function of cumulative water loss: (a) atrazine, plot 1, (b) atrazine, plot 3, (c) 2,4-D, plot 1, (d) 2,4-D, plot 3.*

between the two periods, results in an apparent change in mass of solutes in the groundwater from Period I to II. Physically, this means that a portion of the solutes is adsorbed strongly and, thus, is not available for loss in the drain water (Steenhuis *et al.*, 1994).

To determine the parameters, all breakthrough curves for Period II (as a function of the cumulative outflow since the irrigation cessation) are fitted for each plot for both weeks with a linear regression of the form:

$$\ln C^{**} = a Y_{II} + b \tag{11}$$

where a and b are the regression coefficients. Y_{II} is the cumulative outflow volume since the beginning of Period II, and is related to Q as:

$$Y_{II} = \int_{t_{II}}^{t} Q A_c dt \tag{12}$$

Comparing Eqns (9) and (11) shows that:

$$W_d^{**} = -\frac{1}{a} \tag{13a}$$

$$C_{II}^{*} = \exp b \tag{13b}$$

The regression constants together with the regression coefficients for the two irrigation events for the three chemicals and all 8 plots are shown in Table 3. Note that chloride was applied only at the beginning of the second irrigation event.

The calculated apparent groundwater volumes and the solute concentrations at the beginning of Period II—obtained by substitution of the regression values (Table 3) into Eqn. (13)—are given in Table 4. In general, the groundwater volumes are highest for plots 5 through 8. As will be discussed later, groundwater volumes based on 2,4-D are lower than for the other chemicals due to degradation.

The mass of chloride leached to groundwater at the beginning of Period II can be determined by combining Eqns (13a) and (13b) with W_a^{**} and W_d^{**} being equal.

Table 2. Amount lost, peak concentration and average concentration for chloride for second irrigation location; atrazine and 2,4-D in the tile water for the first and second irrigation events.

	CHLORIDE					ATRAZINE						2,4-D			
		peak	avg	amount in		peak	peak	avg	avg	amount in		peak	peak	avg	avg
	lost	conc	conc	tile drain		conc	conc	conc	conc	tile drain		conc	conc	conc	conc
plot/	kg	mg/l	mg/l	mg	mg	μg/l	μg/l	μg/l	μg/l	mg	mg	μg/l	μg/l	μg/l	μg/l
till	Ir 2	Ir 2	Ir 2	Ir 1	Ir 2	Ir 1	Ir 2	Ir 1	Ir 2	Ir 1	Ir 2	Ir 1	Ir 2	Ir 1	Ir 2
1/N	0.46	125	77	60	43	17	16	8	7	65	6	19	9	8	1
2/T	1.31	313	170	21	35	19	22	6	6	40	79	82	48	11	10
3/N	1.19	276	200	21	52	22	17	6	10	34	13	82	5	9	2
4/T	0.52	173	104	9	17	13	8	3	3	7	5	31	4	2	1
5/T	0.95	165	142	5	8	14	5	4	3	11	12	145	18	9	1
6/N	1.00	229	177	3	27	11	13	5	5	2	4	55	4	3	1
7/T	1.50	280	210	10	28	6	6	4	4	2	4	5	5	1	1
8/T	0.87	558	381	8	9	13	23	6	13	6	7	25	10	2	4

Table 3. Regression results for all tile lines.

		Week 1			Week 2		
Tile	Chemical	$a = \frac{-1}{W_d^{**}}$	$b = \ln\left(\frac{M_{II}^{**}}{W_m^{**}}\right)$	R^2	$a = \frac{-1}{W_d^{**}}$	$b = \ln\left(\frac{M_{II}^{**}}{W_m^{**}}\right)$	R^2
		$[m^{-3}]$			$[m^{-3}]$		
1/N	2,4-D	–0.51	3.27	0.69	–0.62	1.61	0.78
	Atrazine	–0.23	2.74	0.81	–0.17	2.59	0.47
	Chloride			–0.23	5.07	0.96	
2/T	2,4-D	–0.84	3.59	0.77	–0.47	3.17	0.71
	Atrazine	–0.50	2.62	0.83	–0.33	3.13	0.95
	Chloride	–0.32	5.86	0.97			
3/N	2,4-D	–0.96	3.42	0.90	–0.60	1.49	0.68
	Atrazine	–0.37	2.74	0.74	–0.31	2.65	0.61
	Chloride			–0.30	5.67	0.99	
4/T	2,4-D	–1.28	2.70	0.76	–0.57	1.98	0.91
	Atrazine	–0.48	2.40	0.80	–0.20	2.10	0.85
	Chloride			–0.32	5.17	0.93	
5/T	2,4-D	–3.28	3.71	0.91	–0.41	1.59	0.86
	Atrazine	–1.31	2.17	0.81	–0.13	1.49	0.97
	Chloride			–0.09	5.11	0.83	
6/N	2,4-D	–4.32	1.23	0.63	–0.15	–0.27	0.54
	Atrazine	–0.50	1.78	0.15	–0.19	2.08	0.68
	Chloride			–0.05	5.25	0.54	
7/T	2,4-D	–0.48	0.93	0.70	–0.48	0.97	0.73
	Atrazine	–0.11	1.48	0.73	–0.07	1.75	0.74
	Chloride			–0.09	5.68	0.80	
8/T	2,4-D	–1.03	2.97	0.86	–0.50	1.81	0.39
	Atrazine	–0.44	2.36	0.68	0.06	3.06	0.32
	Chloride			–0.03	6.30	0.08	

a and b are the slope and intercept of the regression line y=ax+b, where x depicts the cumulative outflow and y the logarithm of concentration. R^2 is the regression coefficient.

Table 4. Average groundwater volume and solute concentration at the beginning of Period II based on the regression data in Table 3.

Plot	Chloride Week 2	Atrazine Week 1	Atrazine Week 2	2,4-D Week 1	2,4-D Week 2
			Water Content W_d^{**}		
	m^3	m^3	m^3	m^3	m^3
1/N	4.4	4.4	6.0	2.0	1.6
2/T	3.1	2.0	3.1	1.2	2.1
3/N	3.3	2.7	3.2	1.0	1.7
4/T	3.2	2.1	5.0	0.8	1.7
5/T	11.1	0.7/8.0	7.8	0.3	2.4
6/N	18.3	2.0	5.3	0.2	6.7
7/T	10.6	8.8	13.5	2.1	2.1
8/T	38.5	2.3	n.a	1.0	2.0
			Concentration C_{II}^{*}		
	mg/l	µg/l	µg/l	µg/l	µg/l
1/N	159	15	13	26	5
2/T	351	14	23	36	24
3/N	290	15	14	31	4
4/T	176	11	8	15	7
5/T	166	9	4	41	5
6/N	191	6	8	3	1
7/T	293	4	6	3	3
8/T	545	11	21	19	6

Thus:

$$M_{II}^{**} = -\frac{\exp b}{a} \tag{14}$$

The results of this calculation are shown in Table 5. Although Table 5 shows that the chloride mass in the groundwater is highest in the last three plots, the results for plots 6 and 8 may be unreliable due to the low regression coefficients (see Table 3).

Table 5. Regressed chloride mass at the beginning of Period II and the observed cumulative loss of chloride in tile drainage water during Period I.

Plot	Mass of Chloride: Beginning Period II Estimated gram	Period I Tile Line gram
1/N	692	61
2/T	1096	359
3/N	967	49
4/T	550	115
5/T	1841	260
6/N	3497	278
7/T	3255	476
8/T	18152	0

CONTRIBUTING AREA

Assumption 4 stated that only a part of the area contributed flow towards the tile line. There are three ways to calculate the contributing area: Firstly, the contributing area, A_c^{Cl}, can be calculated as the quotient of M_{II}^{*} and the amount leached during Period I per unit area from the distribution zone (Eqns (1) and (3)). When the amount of solutes leached to the tile during Period I is also taken into account, the contributing area becomes:

$$A_c^{Cl} \frac{M_{II} + \int_{t_I}^{t_{II}} QC}{M_0^{*} \exp\left[-\frac{\int_{t_I}^{t_{II}} R\bar{dt}}{w^{*}}\right]} \tag{15}$$

Based on previous experiments (Steenhuis *et al.*, 1994) it was assumed that the distribution layer contained 10 cm of water.

Secondly, the contributing area, A_c^{w}, should also equal the quotient of the apparent groundwater volume and the depth of water recharged, i.e.:

$$A_c^{w} = \frac{W_d^{**}}{\int_{t_I}^{t_{II}} R\bar{dt}} \tag{16}$$

Thirdly, the contributing area, A_c^{Q}, can be determined simply by dividing the total outflow, Y_T by the depth of water recharged per unit area:

$$A_c^{Q} = \frac{Y_T}{\int_{t_I}^{t_{II}} R\bar{dt}} \tag{17}$$

Using the data from the chloride breakthrough curves, the contributing areas for plots 1–7 are calculated with Eqns (15) through (17) (Table 6). Plots 6 and 8 had low regression coefficients; the results for plot 8 are especially unrealistic.

MODEL ASSESSMENT

The validity of the model is assessed by comparing the trends and consistency of the parameters obtained from the regression analysis. The regression coefficients for events 1 and 2 (Table 3) for almost all plots are remarkably good for hydrology studies. Plots 6 and 8 are exceptions. The poor fit for plots 6 and 8 was not surprising: monitoring tile outflow for plot 8 in the dormant season showed more outflow than the rainfall, indicating some springs or surfacing of groundwater within the plot and plot 6 also had a higher base flow than the other plots,

Table 6. Calculation of contributing area (in percent of total) to tile line based on three different methods.

Plot	A_c^d Rcl/total	A_c^m TGW/rain	A_c^a rain/drain
1/N	0.09	0.06	0.13
2/T	0.06	0.11	0.16
3/N	0.07	0.08	0.13
4/T	0.06	0.05	0.10
5/T	0.22	0.16	0.14
6/N	0.35	0.27	0.11
7/T	0.17	0.23	0.15

indicating a small spring within its boundaries. Moreover, during irrigation event 1, the outflow atrazine concentrations had two distinctly different slopes. Thus, plots 6 and 8 did not satisfy the assumptions on which the model was based and were omitted from further analysis.

The calculated groundwater volumes of the groundwater reservoir (Table 4) are plotted in Fig. 5 and are all of the same order of magnitude. The groundwater volumes based on the atrazine data during the first week are slightly lower than for the second week. This is consistent with the smaller recharge and tile outflow during the first week compared with the second week. During week 2, the groundwater volumes based on the regressed atrazine and chloride concentration data are nearly equal (although atrazine-based volumes are slightly larger in some cases). In other words, the tangent of a plot of [ln C] vs. [cumulative outflow] is almost independent of the adsorption partition coefficient of the chemical. Because chloride is not adsorbed, this also means that atrazine behaves almost like a nonadsorbed chemical during Period II. This is similar to earlier experimental observations for the distribution layer (Steenhuis *et al.*, 1994). The trend in Fig. 5 shows that plots 2–4 have the smallest aquifers and plots 1 and 7 have more groundwater which is consistent with the soil information.

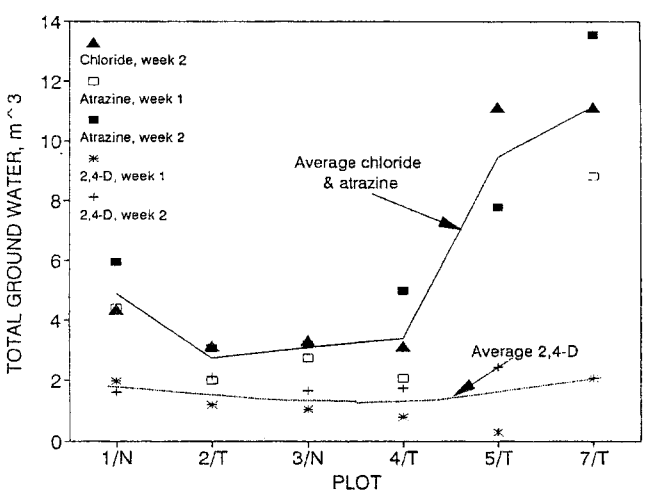


Fig. 5. *Groundwater volumes based on the regressed values of the three solutes for both irrigation events.*

Finally, apparent groundwater volumes are lower for 2,4-D than for atrazine and chloride because 2,4-D breaks down in macropores during the measurement period, as noted by Pivetz and Steenhuis (1995) in laboratory studies. Thus, 2,4-D cannot be considered conservative over the duration of the experiment. Rewriting Eqn. (8), adding a term for the first-order degradation rate, f, and integrating gives:

$$C^{**} = \frac{m_{II}^{**}}{w_a^{**}} \exp\left[-\left(\frac{Y_{II}}{w_d^{**}} + ft\right)\right] \qquad (18)$$

The equation shows that when regressing ln C with Y, a smaller groundwater volume is obtained, because the degradation of 2,4-D is neglected.

The contributing areas calculated with the three different methods (Fig. 6) show that for all methods for the second irrigation event, the area that contributes to the tile line is smaller than 25% of the total area during a rainfall event. The contributing area, A_c^Q, calculated with the method of Eqn. (17) is consistently and slightly higher than the contributing areas calculated with Eqns (15) or (16). However, in view of the uncertainty and assumptions on which the equations are based, the similarity does seem to be reasonable for field experiments, where considerable soil variation exists.

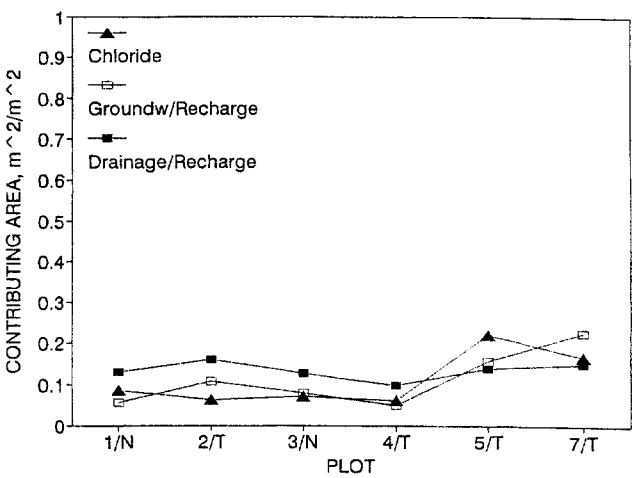


Fig. 6. *Predicted contributing areas calculated with Eqns (15), (16), and (17).*

Physical evidence that the contributing areas are reasonable can be derived from an earlier study by Aburime (1986) where the depth of the water table was measured at 0, 3, 8, and 13 m perpendicular to the tile line. Fig. 7 shows that for plot 2 the steepest gradients occurred 2–4 m from the tile line. It is likely that areas with the steep gradients can carry water and solutes to the tile line within

a reasonably short time and, thus, represents the contributing area. The distance between the tile lines is 20 m, giving a contributing area of 10–20% of the total area. This is very similar to that shown in Fig. 6.

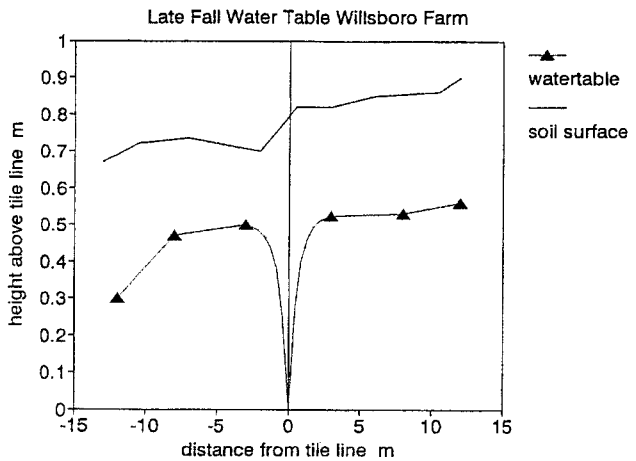


Fig. 7. *Water table depth in relation to the tile line at location 0 m.*

Discussion

Similar to several other studies, this study demonstrates that while pesticide concentrations in the tile outflow water were above the drinking water standards, the mass of the portion lost from the amount applied was very small (Table 2).

The finding that the pesticides and chloride were transported as fast as nonadsorbed solutes is confirmed by experiments in Maryland, where locations of pesticides and other nonadsorbed tracers in the subsoil were highly correlated (Kung *et al.*, 1995). Thus, all chemicals were transported the same distance, independent of the adsorption partition coefficient. This clearly differs from the predictions of the convective-dispersive equation where the adsorbed solutes move slower than the nonadsorbed solutes. The apparent discrepancy is explained if a very small portion of the pesticide is transported rapidly through preferential flow paths to the tile line; the convective-dispersive equation predicts only the average displacement of the bulk of the pesticides. The transport in the preferential flow paths is also too fast for sorption equilibrium to be reached.

It should be noted that, although the rate of transport of the chemicals is similar, the ratio of the peak concentration to the amount of chemical added is much lower for the pesticides than for the chloride. Clearly, adsorption and degradation, in case of 2,4-D, play a role here.

One of the original objectives of this experiment was to model pesticide outflow. Sufficient data was generated and collected to simulate the complete chloride breakthrough curve in the tile drainage water. The simulated breakthrough curve based on Eqns (7) and (9) for chloride on plot 4 is shown in Fig. 8. Input data for the model are the distribution zone water volume per unit area of 10 cm and the amount of rain applied minus the 21 mm evaporation that took place during the week. The observed rate of tile outflow was used. The model and the observed outflow breakthrough curves showed similar trends during Period I. The data for Period I were not used for curve fitting.

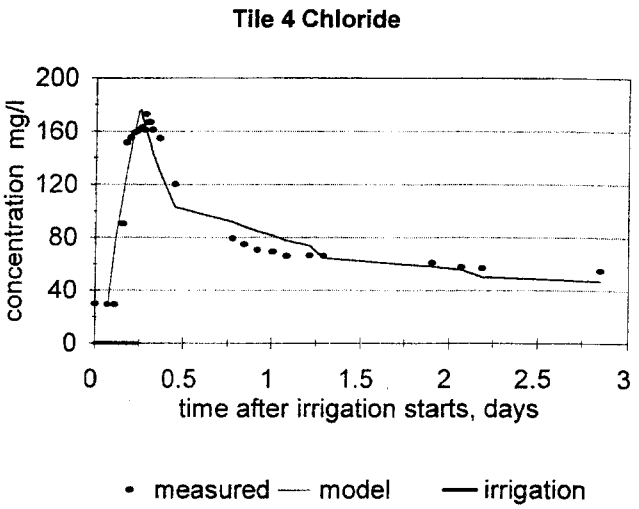


Fig. 8. *Predicted and observed chloride concentration for plot 4.*

To model the pesticides, the adsorption partition coefficient needs to be known during Periods I and II in the distribution zone and in the groundwater. Because the adsorption partition coefficient for atrazine and 2,4-D during Period I are not known, the pesticide breakthrough curves could not be simulated.

While Fig. 8 suggests that the proposed model has some of the characteristics necessary to simulate the initial breakthrough of solutes after application, more research is needed to determine if the calculated values for groundwater and contributing areas are consistent with other experimental studies. Furthermore, better ways of estimating the sorption characteristics of pesticides under field conditions in relatively short time scales need to be developed before the rapid transport of pesticides into the tile line can be predicted realistically.

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