Fate of agricultural chemicals in soil, ground water and agricultural drainage water under farm conditions.

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1.0 RATIONALE/OBJECTIVES

Environmental concens have been raised because of the presence of fertilizer and pesticide residues in streams and ground water. Information is required on the contribution of agriculture to surface and subsurface water pollution under different cropping management practices in order to control and reduce loading of chemicals to water systems in the Great Lakes Basin.

The popularity of conservation tillage including zero or **no tillage (NT)** has grown steadily in Canada and the USA, mainly because of reduced costs and lower potential for surface water pollution compared to **conventional tillage (CT)**. The high residue cover left on non-tilled land and the improved soil aggregate stability associated with an increase in organic matter content under NT can reduce soil erosion by 50 to 90%, and thus decrease the transport of sediment-bound pollutants such as pesticides and phosphorus to nearby streams (Logan et al., 1987). Absence of tillage, however, will generally favour the formation of macropores or preferential flow channels, the continuity of which is not disturbed by cultivation. Macropores and reduced runoff under NT could permit an increased downward movement of water and thus increase leaching of water-borne pollutants to tile drains or ground water. In Ohio, Schwab et al. (1985) reported increased atrazine and reduced nitrate losses in tile effluents under NT compared to CT. Most of the reported research on tillage effects is based on plot studies. Conclusions from such research need to be validated in field studies.

Computer simulation models could be useful in the selection and development of the most promising and cost-effective remedial action plans for the abatement of pollutant transport in the Great Lakes Basin. Several models have been proposed to predict water and chemical transport/behaviour in soil-water systems. However, field results required to calibrate, verify, and adapt the various transport models to Canadian conditions are very limited at present. Model validation also requires an improved understanding of the field variability of the input parameters, and of processes by which applied agricultural chemicals and their degradation products are entrained, transformed, and transported through soil-water systems in the field.

This study was aimed at determining the long-term (1990-1993) fate of two commonly used herbicides, metolachlor and atrazine, and two pollutants of concern, nitrate and phosphorus, in tile drained, loam soil corn fields under **CT and NT treatments**. Chemical concentrations were determined in tile effluents and in soil and groundwater at various depths. Surface drainage water quality was also determined. Additional information required for model validation, such as water flow rates, water table elevations, precipitation, and various soil properties, was also obtained. Results from this field-scale study will complement other simultaneous studies at the detailed laboratory and plot scale, and less-detailed watershed scale, under the Great Lakes Action Plan of the Government of Canada.

This report describes study methodology, findings, conclusions, new technologies and benefits, implications for the Great Lakes basin ecosystem, technology transfer potential, and needs for future research. Publications based on this study are also listed. Some analysis of samples and data is still in progress at the time of writing this report.

2.0 METHODOLOGY

The study site

The experimental site is a 14 ha (approximately 450 x 315 m) field at the Greenbelt Research Farm of Agriculture and Agri-Food Canada, near Ottawa, Ontario. It consists of a Typic Haplaquent (Dalhousie Association, Brandon Series) soil with a loamy-textured Ap horizon and a clay loam B horizon underlain by heavy clay. The site was tile drained in the fall of 1986 with laterals 15 m apart and approximately 1 m below the soil surface. The field is nearly level with an average slope of about 0.2%.

From 1981 to 1986, the site was cropped to a mixture of alfalfa and brome grass. No atrazine or metolachlor was applied to the field between 1972 and the summer of 1986. From 1987 to 1989, it was planted to corn under conventional tillage and received applications of atrazine in 1986 (fall), 1987 and 1989, of cyanazine in 1987 and 1988, and of metolachlor in 1987, 1988, and 1989. Several studies had been conducted on the site prior to this one (Frank et al., 1991a, 1991b; Thooko et al., 1990, 1991; Warnock et al., 1990).

The study reported here was initiated in April 1990 when the 14 ha field was divided into four plots for the two experimental treatments, conventional tillage (CT) and no tillage (NT), with two replications each (Fig. 1). Each plot covers approximately 3 ha and is drained by four or more laterals. In the summer of 1990, three sites in each plot were equipped with four 75 or 100 mm dia. piezometric wells for sampling shallow ground water at 1.2, 1.8, 3.0, and 4.6 m depths, and a 3.0 m deep water table monitoring well. The subsurface drainage system was modified by November 1990 so that tile water from each plot was led to a separate station where flow was monitored with pre-calibrated H-flumes and the water sampled with automatic Buchler (Edmund Bühler GmbH & Co., Germany) samplers. Each tile flow monitoring site was sheltered and equipped with a flameless catalytic propane heater for winter sampling.

In the following year (1991), additional H-flumes were installed in each of the four plots to measure surface runoff. Berms, about 20 cm high, were built around the periphery of the plots to direct surface runoff to these flumes. Rainfall was measured on site using Belfort Universal rain gauges (Belfort Instrument Co., Baltimore, MD).

Study Procedures

Details of the cropping operations are given in Table 1. Both NT and CT plots were cultivated in the fall of 1989 and in the spring of 1990, when this study was initiated. The NT plots were not tilled thereafter while the CT plots were plowed every fall and disked or cultivated every spring.

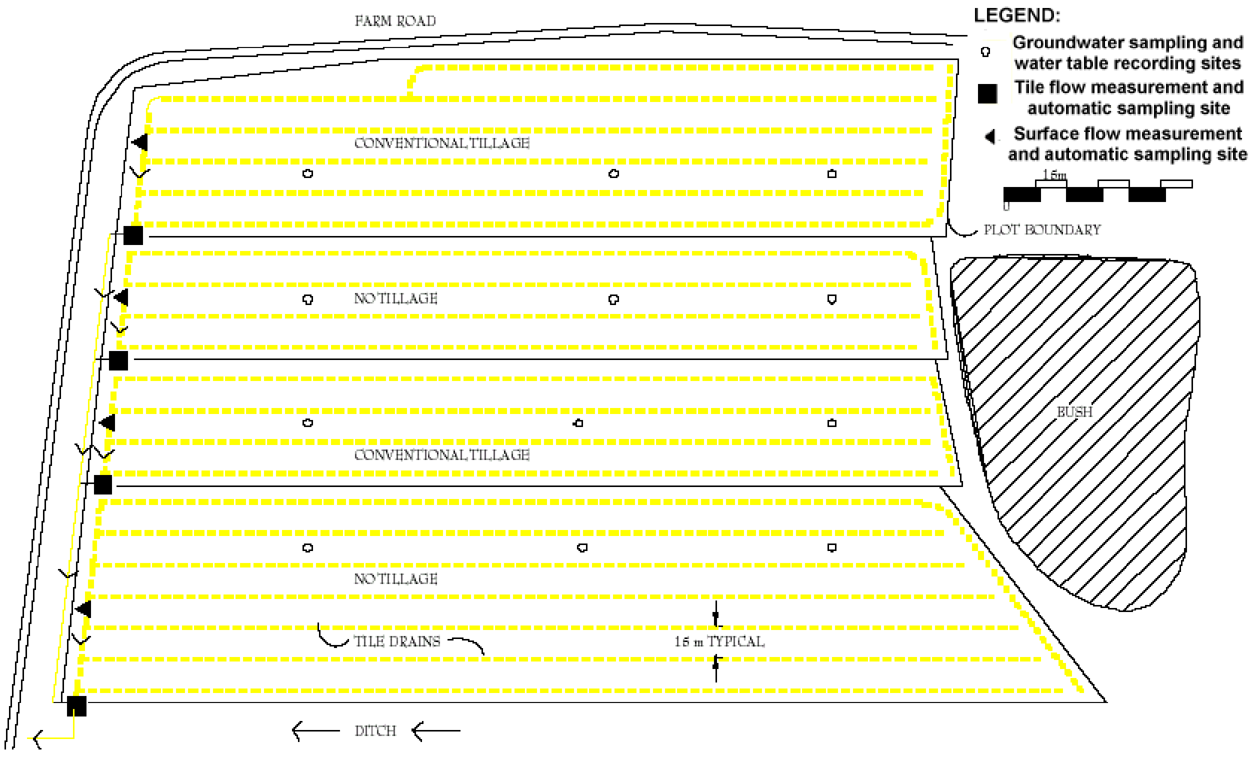

Figure 1. Site Plan at Experimental Field

Sampling

From June 1990 to December 1993, groundwater samples were collected monthly and after major storm events, except in the winter. Prior to sampling, stagnant water was removed from the wells which were then allowed to recharge for a few hours before samples were collected. Between December 1990 and December 1993, tile drainage water was sampled periodically (at one- to twelve-hour intervals depending upon flow rate) with automatic samplers,whenever tile flow occurred. Because of the flat topography of the field, surface water flow occurred only during the short snowmelt period every year. It was manually sampled once or twice a day in 1992 and 1993.

Table 1. Summary of annual cropping operations.

OPERATION	1990	1991	1992	1993
Disking or cultivating date for CT plots only	May 7	May 8	Apr 25	May 5
Planting date	May 10	May 10	May 11	May 11
Silage corn (seeds/ha)	66 700	66 700	66 700	66 700
Fertilizer 8-32-16 (kg/ha)	150	110	110	110
Herbicide application date (post-emergent)	May 31	May 24	May 26	Jun 7
Metolachlor (kg/ha)	2.6	2.6	2.6	2.4
Atrazine (kg/ha)	2.2	1.5	1.8	1.9
Anhydrous ammonia injection date	Jun 22	Jun 13	Jun 15	Jun 25
Application rate (kg N/ha)	100	140	120	115
Harvest date	Oct 3	Sep 19	Oct 6	Sep 21
Plowing CT plots only	Nov 5	Sep 25	Oct 6	Oct 3

Soil samples for chemical analysis were collected in the vicinity of the three groundwater sampling sites in each plot (Fig. 1) a few days prior to herbicide application (day -1), on the day of application (day 0) and on days 1, 7, 30, 90, and 150 after application. Composite soil samples were made from ten subsamples collected within a 10 x 10 m grid at each site. The same grid was used for subsequent sampling in a given year. Prior to planting and after harvest (days -1 and 150), 10 cm dia. x 1.2 m deep soil cores were collected with a truck-mounted hydraulic coring machine. The cores were sectioned into six depth segments, 0-7.5, 7.5-15, 15-30, 30-60, 60-90, and 90-120 cm. On other sampling days, soil was sampled at 0-7.5 and 7.5-15 cm depths using a spade. Additional six soil cores, 7.5 cm dia. x 7.5 cm deep, were collected at 0-15 and 15-30 cm depths in each plot in May 1991, August 1991, and May 1992 to determine bulk density, saturated hydraulic conductivity, and moisture retention capacity.

Analytical procedure: Herbicide residues in water and soil were determined using recommended procedures, at the Agricultural Laboratory Services of the Ontario Ministry of Agriculture, Food and Rural Affairs in Guelph, Ontario (1990-1992), and at the Agriculture and Agri-Food Canada Research Station in Harrow, Ontario (1993). The detection limit for atrazine, deethylatrazine, and metolachlor was 0.02, 0.03, and 0.05 µg/L (ppb) in water and 0.005, 0.005, and 0.01 µg/g (ppm) in soil, respectively.

In water, nitrate concentration was determined with a specific ion electrode (Model #93-07, Orion, Cambridge, MA), and soluble total phosphorus by filtration (glass fibre filter paper) followed by the ascorbic acid reduction method, according to the methods outlined in APHA (1989). Electrical conductivity and pH were also measured. Due to resource constraints, only a selected number of tile water samples collected by the automatic samplers were analyzed. In soil, nitrate, ammonia, total N, P, K, organic matter content and moisture retention capacity were determined according to the methods described by Sheldrick (1984). Saturated hydraulic conductivity was measured on soil cores by the constant head method (Reynolds, 1993). Bulk density was determined by drying the cores in an oven at 104°C for 48 hrs.

Data analysis

For statistical analysis, tile water data were pooled by the treatment and groundwater data by the treatment as well as site. All tile flow between December 1990 and December 1993 was divided into 20 "events". An event lasted from less than a week to over three weeks and generally went from an initial low (less than 0.05 mm/hr) or no flow condition to the next low or no flow condition. It consisted of one or more peaks on the hydrograph. In two instances, data for events with extremly low flows were grouped with the next event.

Flow in tile drains was calculated from the continuously recording strip charts. Tile effluent chemical concentration was determined in several samples during the rising portion, the peak and the receding portion of the hydrograph. Total flow (F_{event}), chemical loading (Q_{event}), and flow-weighted concentration (C_{fw}) during an event were calculated as:

$$F_{event} = \Sigma_{i=1,n} F_i$$

$$Q_{event} = \Sigma_{i=1,n} F_i C_i$$

$$C_{fw} = Q_{event}/F_{event}$$

Where, i = Part of event duration, ranging from one to several hours
n = number of time intervals used for the event flow calculation
F_i = Total flow during the i^{th} time-internal of an event
C_i = Average concentration during the i^{th} time-interval of an event

Tile and groundwater data were analyzed for significant difference between treatments during (a) the entire sampling period, (b) each calendar year, (c) each cropping year (planting to next planting), and (d) each season across all years. Four seasons were defined as (1) **snowmelt (SM)** which extended from start of permanent snow cover to the last day with snow on the ground, usually from late-December to mid-March, (2) **spring (SP)**, from the end of snowmelt to planting, (3) **growing season (GS)**, from planting to harvest, and (4) **fall (FA)**, from harvest to a permanent snow cover. The block x treatment error term was used in the Analysis of Variance (ANOVA) to check for significant treatment effect.

Due to the short duration of surface flow every year, not enough surface water samples were available for a meaningful statistical analysis. Statistical analysis was performed on bulk density, saturated hydraulic conductivity, and water retention capacity. Herbicide disappearance curves were used for field half-life calculation.

3.0 FINDINGS

Findings are discussed below in terms of water and soil characteristics under the two tillage treatments. Other related research conducted with collaborators is summarized without presentation of data which are available in listed publications.

3.1 Precipitation

Weekly rainfall during the study period is given in Figure 2. Tile flow in the two treatments during the 20 events recorded between December 1990 and December 1993 are shown in Figure 3. In the four years between 1990 and 1993, yearly rainfall was close to the 75-year regional average of 864 mm, except in 1991 when precipitation was 38% below average and the water table was more than 3 m below the soil surface for most of the growing season. That year, the tile drains had flow in March and April only (Fig 3). In 1992, the growing season was wet. The period from May 1 to Sep 30 had 20% more rainfall than the long-term average of 400 mm. July and August rainfall amounted to 282 mm, 54% above normal. It was the only year in which tile drains had flow during each of the four seasons (Fig 3). The spring of 1993 was particularly wet with 127 mm of rain in April, twice the average, and drains had flow intermittently until the end of June (Fig 3). During July and August, however, precipitation was 37% below average. Rainfall for the whole of 1993 was close to the regional mean.

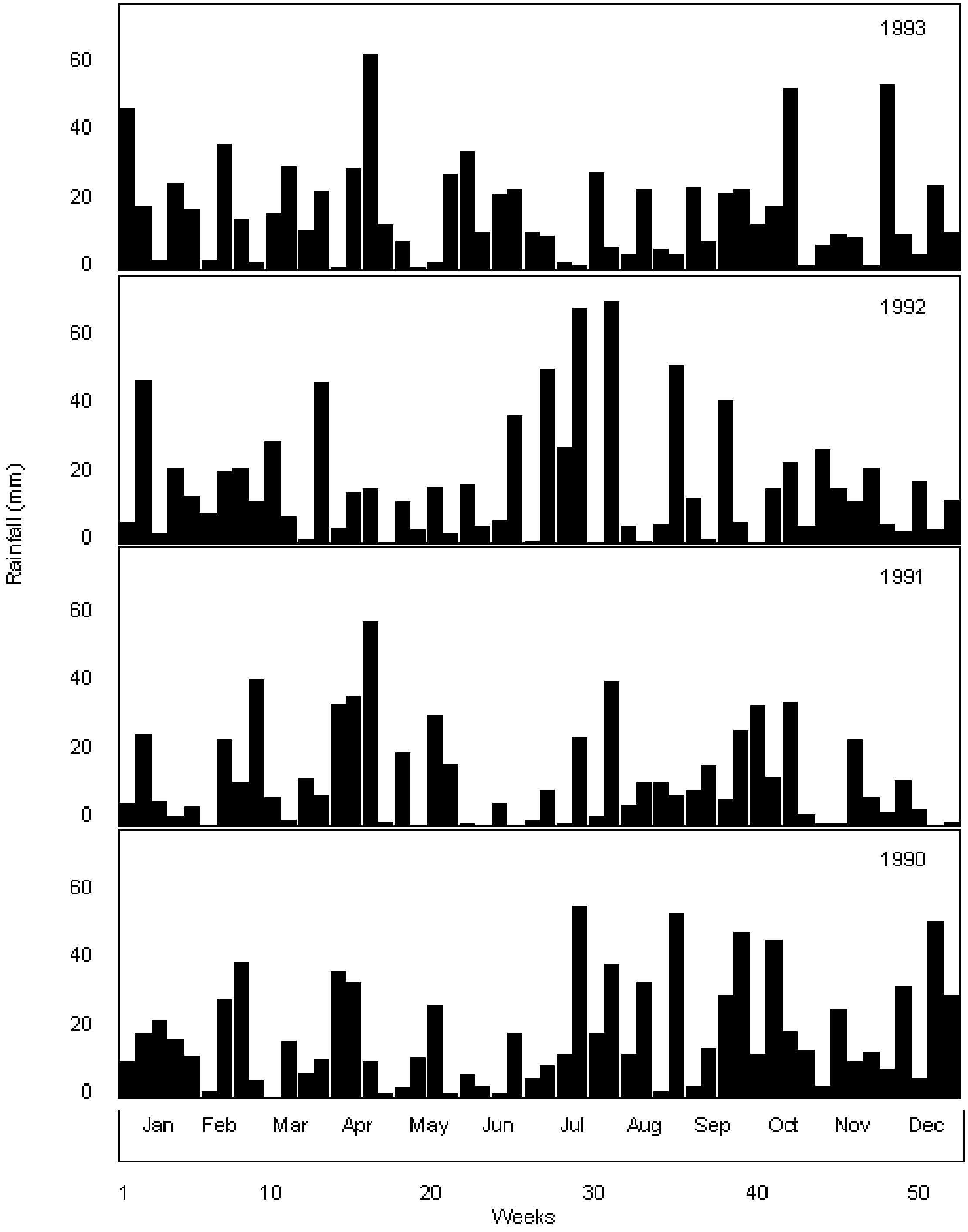

Figure 2. Weekly rainfall at the experimental site from 1990 to 1993

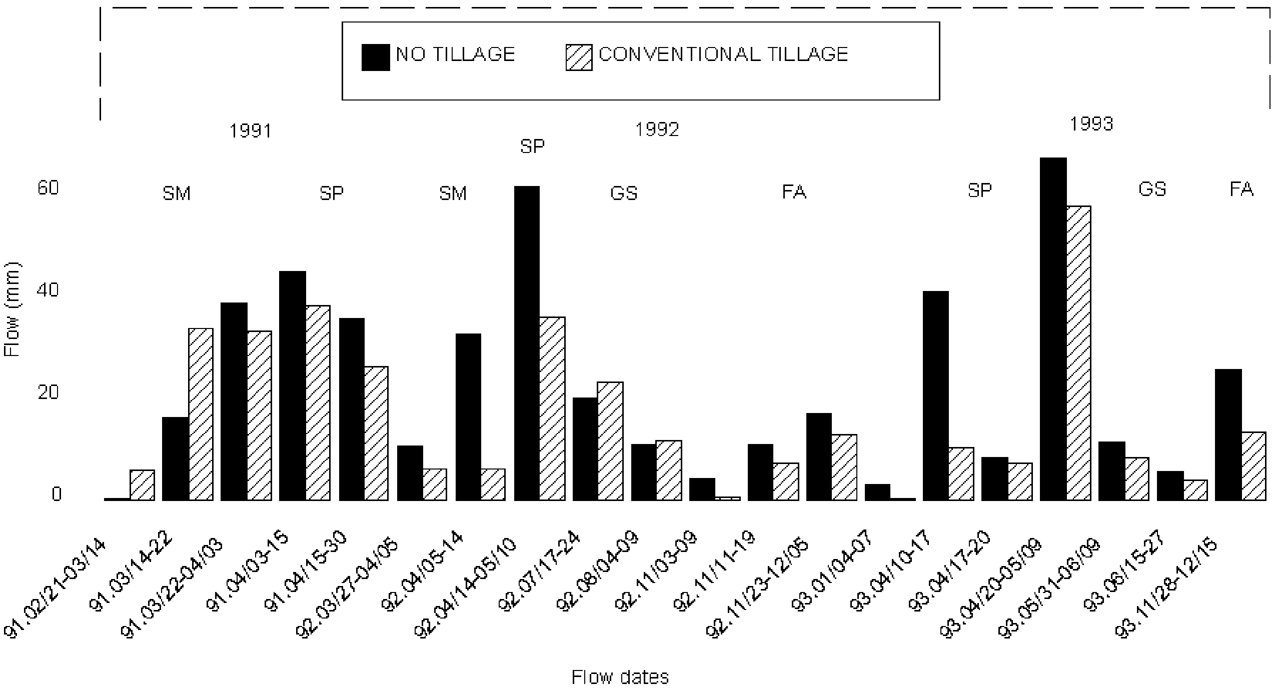

Figure 3. Tile drain flow during 20 events between December 1990 and December 1993. Vertical dasked lines separate the seasons of flow.
SM = snowmelt; SP = spring; GS = growing season; FA = fall

3.2 Tile Effluent

3.2.1 Flow

In 16 of the 20 events, flow was higher under NT than CT (Fig 3). Soil macropores or preferential flow channels may have contributed to the observed difference. Soil macropores remain undisturbed under NT, and thus the resistance to downward movement of water wouldbe less than under CT where pores at the surface are broken down by annual tillage operation. Another reason for higher flow under NT than CT could be the higher initial moisture conditions in the former. Laboratory tests and *in-situ* soil moisture measurements in 1993 indicated a significantly higher water retention capacity in the top 15 cm of soil under NT than CT.

Freeze-thaw cycles seemed to affect flow during snowmelt. The snowmelt period was characterized by freeze-thaw cycles in 1991 but not in 1992, when the thaw was practically continuous. Snowmelt period flow was greater under NT than CT in 1992 but not in 1991. During freeze-thaw cycles, the CT plots probably had more soil surface available for thawing during the day than the NT plots where frozen water may have blocked some of the large pores. In 1993, a rapid thaw caused flooding of the tiles during the snowmelt period, and flow started after the ground snowcover was gone.

Table 2 shows the observed flows during different time periods. Cumulatively over the three ears, the NT plots had 36% more flow than the CT plots (467 mm vs 344 mm). Whereas the tile flow was similar under the two treatments in 1991, in each of the two subsequent years, the NT plots had about 60% more flow than the CT plots. The total annual flow as a percent of the annual precipitation was 19% for both treatments in 1991, 19% for NT and 12% for CT in 1992, and 18% for NT and 12% for CT in 1993. Calculation of total flow by cropping years also indicated greater flow under NT than CT for the two years for which the complete data could be collected. Calculation of flow by seasons showed that flow was significantly greater under NT than CT during the snowmelt plus spring flow periods only (Table 3), that is, during the snowmelt-induced flow. During the growing season, tile flow was similar under both treatments because of factors such as precipitation interception by the crop canopy, high evapotranspiration, etc. In the fall events, flow was always higher under NT than CT but the difference was not statistically significant (Table 2).

Table 2. Tile flow between December 1990 and December 1993

Time period		No. of events	Flow (mm)		
			NT	CT	
Study duration		20	467	344	
Calendar year	1991	5	136	138	
	1992	9	171	105	
	1993	6	160	102	
Cropping year(1)	90-91	5	136	138	
	91-92	3	105	49	▲
	92-93	9	183	132	
	93-94	3	43	26	
Season (2) (all years)	GS	4	48	47	
	FA	5	61	35	
	SM	5	99	86	
	SP	6	259	176	
	SM+SP	11	358	262	*

Significant at $p <$ ▲ = 0.1, * = 0.05

(1) Cropping year covered the year from planting to planting. Flow results for cropping years 90-91 and 93-94 are incomplete because measurement started in December 1990 and ended in December 1993.

(2) GS = growing season (planting to harvest); FA = fall (harvest to snow cover); SM = snowmelt (snow cover on ground); SP = spring (end of snowmelt to planting).

Under both tillage treatments, about 75% of the calender-year annual tile flow occurred during the snowmelt and post-snowmelt spring periods prior to planting and chemical application. Consequently, chemical loading of most of the tile effluent in the calendar year resulted from chemical applications of the previous calendar year. This indicates the desirability of using the cropping year rather than the calendar year for mass balances, at least under eastern Canadian conditions.

3.2.2 Chemical concentrations in tile effluent

Concentration was measured in 615 samples for herbicides, 865 for nitrate-N, and 330 for soluble total phosphorus. Flow-weighted average concentrations of the herbicides and NO_3-N are shown in Table 3. In the following discussion, **average concentration** refers to the flow-weighted average value rather than the average of actual concentrations in samples.

Herbicide

Atrazine and deethylatrazine were almost always present in tile effluents with concentrations mostly below 5 µg/L, the Canadian drinking water guideline for atrazine. Average concentration was higher under NT than CT in 17 and 14 of the 20 flow events for atrazine and deethylatrazine, respectively. Treatment effect was significant for calendar year 1991, cropping years 90-91 and 92-93, and the snowmelt period for atrazine, and for calendar year 1992 for deethylatrazine (Table 3). Metolachlor was detected in a few samples during 8 out of the 20 flow events and concentrations were always below the Canadian drinking water guideline of 50 µg/L. Avergae concentrations were higher under NT than CT in 6 out of 8 events but treatment effect was not significant (Table 3).

During the 1992 growing season, there was one flow event seven weeks after herbicide application and a second event two weeks after the end of the previous one (Fig. 3). Two samples, one from each NT plot, showed atrazine concentrations of 9.4 and 6.8 µg/L, but average concentrations for those two events were 2.1 and 1.6 µg/L for NT and CT, respectively. Deethylatrazine average concentration was 2.2 µg/L under NT and 2.1 µg/L under CT. Metolachlor was not detected. These relatively low average herbicide concentrations during the growing season may be due to the dilution of residues by the large input of water. Herbicide concentration decreased rapidly as flow increased. Also, the herbicide may have had time to dissipate and/or was tightly adsorbed on the soil particles before the flow events.

High precipitation in the 1992 growing season and in the spring of 1993 (Fig. 2) may have contributed to higher average herbicide concentrations during the spring of 1993 than those in the two previous springs. In one NT sample, atrazine concentration reached 20.6 µg/L, the highest observed during the study. The CT plots had five samples with unusually high atrazine concentrations, between 5 and 10 µg/L. The mean herbicide concentrations were 1.6 and 1.9 µg/L for atrazine, 1.9 and 2.4 µg/L for deethylatrazine, and 1.1 and 0.86 µg/L for metolachlor, under NT and CT, respectively. These values were higher than the mean concentration in spring for all years (Table 3).

During the 1993 growing season, tile flow occured immediately before and eight days after herbicide application (Fig. 3). Atrazine and metolachlor levels were relatively low in the first event but, in the second one, average concentrations reached their highest levels during the study: 4.3 and 2.9 µg/L for atrazine, and 3.2 and 1.4 µg/L for metolachlor under NT and CT, respectively. The maximum level was 13.2 µg/L for atrazine and 11.7 µg/L for metolachlor. Atrazine concentration exceeded the drinking water guideline in 10 out of 33 samples, six under NT and four under CT.

Table 3. Mean values of flow-weighted average concentrations in tile effluent during flow events in different time periods

Time period		Atrazine (µg/L)		Deethylatrazine (µg/L)		Metolachlor (µg/L)		Nitrate-nitrogen (mg/L)	
		NT	CT	NT	CT	NT	CT	NT	CT
Study duration		1.29	0.88	1.66	1.52	0.47	0.29	21.9	25.3
Calendar	1991	1.21	0.58 ▲ 0.60	1.50	1.06	0.00	0.00	18.7	20.3
	1992	1.02		1.52	1.38 ▲	0.20	0.08	23.8	28.5
	1993	1.75	1.54	2.00	2.13	1.26	0.82	21.8	25.1
Cropping	90-91	1.21	0.58 ▲	1.50	1.06	0.00	0.00	18.7	20.3
year(1)	91-92	0.78	0.47	0.61	0.56	0.61	0.23	12.8	16.8
	92-93	1.29	1.09 ▲	1.97	2.03	0.19	0.30	25.4	30.2
	93-94	1.92	1.20	2.06	1.85	1.96	0.79	26.0	28.5
Season (2)	GS	2.34	1.62	2.18	2.13	1.38	0.53	27.8	29.8 *
(all years)	FA	0.64	0.17	1.87	1.56	0.07	0.06	28.5	35.1 ▲
	SM	0.99	0.43 ▲	1.06	0.76	0.37	0.14	13.7	15.3 ▲
	SP	1.37	1.30	1.64	1.74	0.28	0.43	19.4	23.4

Significant at p < ▲ = 0.1, * = 0.05

(1) Cropping year covered the year from planting to planting. Results for cropping years 90-91 and 93-94 are incomplete because measurement started in December 1990 and ended in December 1993.

(2) GS = growing season (planting to harvest); FA = fall (harvest to snow cover); SM = snowmelt (snow cover on ground); SP = spring (end of snowmelt to planting).

Over the three-year experiment, atrazine and metolachlor average concentrations were highest during the growing season and lowest in the fall (Table 3). Average concentrations were higher in the spring than in the fall events, even though no herbicide was applied in the meantime, suggesting possible release of bound residues. Deethylatrazine concentrations were also highest in the growing season but difference between seasons was not as pronounced (Table 3). The metabolite was generally detected in higher concentrations than the parent compound (Table 3). This observation is in agreement with that of Muir and Baker (1978).

Nitrate-nitrogen

The Canadian drinking water limit of 10 mg/L for nitrate-N was exceeded in 93% of all samples. Every year and season, average concentrations were higher under CT than NT by 1.5 to 6.6 mg/L only but the treatment effect was significant in every season except the spring (Table 3).

Greater nitrogen mineralization, lower denitrification, and thus higher NO_3-N concentrations may be expected under CT compared to NT (Gilliam and Hoyt, 1987). However, their effect may have been offset by higher leaching under NT than CT, thus accounting for the small concentration difference between the two tillage practices.

Nitrate-N concentration was mostly season dependent under both treatments. Maximum concentrations, approximately 50 mg/L under both treatments, were found in the fall. Average concentrations were highest in the fall and the growing season, with levels between 28 and 35 mg/L (Table 3). They were lowest during snowmelt and intermediate in the spring events (Table 3). Concentrations during a given season did not vary substantially from one year to the next. Seasonal coefficients of variation were usually below 30%. Variation was also low within an event unless flow became extremely low, in which case concentrations dropped below 10 mg/L. In 1993, NO_3-N concentrations in tile water was determined at a two-hour interval during the fall event. Coefficients of variation were below 10% in every plot.

During cropping years, average nitrate concentration appeared to depend on rainfall amount and on the seasons during which flow occurred. In the dry cropping year 91-92, average concentrations were low, only slightly above the drinking water limit, while in the wet cropping year 92-93, average levels were 2.5 to 3 times the drinking water limit (Table 3).

Soluble total phosphorus

Only soluble total phosphorus was determined in water samples. The Ontario water quality objective of 30 µg/L for total P was exceeded in 18% and 30% of the samples collected in 1991 and 1992, respectively. The maximum concentration was 1100 µg/L but most samples exceeding the objective had concentrations between 30 and 50 µg/L. Average concentrations were above 30 µg/L in two snowmelt and one growing season flow events. Tillage effect on phosphorus concentration was not evident from these preliminary results.

3.2.3 Chemical loading in tile effluent

Table 4 gives total loading and the loss relative to the amount of chemical applied in different cropping years. Cumulative loss of chemicals in tile effluent during the study period are shown in Figure 4 for herbicides and Figure 5 for nitrate-N.

Table 4. Total and relative losses in tile effluent.

	Atrazine		Deethylatrazine		Metolachlor		Nitrate-N	
Time period	NT	CT	NT	CT	NT	CT	NT	CT
Cropping year	(g/ha)		(g/ha)		(g/ha)		(kg/ha)	
90-91 (1)	1.88	0.91 ▲	2.10	1.54	0.00	0.00	27.2	28.8
91-92	1.15	0.33	0.89	0.38 **	0.49	0.04	16.5	10.2 ▲
92-93	2.70	2.11	3.24	2.77	0.57	0.62	40.6	39.2
93-94 (1)	0.43	0.17 *	0.83	0.46	0.44	0.16	11.6	8.3
Study duration	6.16	3.52 *	7.06	5.15 ▲	1.50	0.82	95.9	86.5
Cropping year	(% of applied)		(% of applied)(2)		(% of applied)		(% of applied)	
90-91 (1)	0.09	0.04	0.10	0.07	0.00	0.00	24.3	25.7
91-92	0.08	0.02	0.06	0.03	0.02	0.00	11.1	6.9
92-93	0.15	0.12	0.18	0.15	0.02	0.02	31.5	30.4
93-94 (1)	0.02	0.01	0.04	0.02	0.02	0.01	9.4	6.7
Study duration	0.08	0.05	0.10	0.07	0.01	0.01	18.7	16.9

Significant at $p <$ ▲ = 0.1, * = 0.05

(1) Cropping year covered the year from planting to planting. Results for cropping years 90-91 and 93-94 are incomplete because measurement started in December 1990 and ended in December 1993.

(2) Percent of applied atrazine

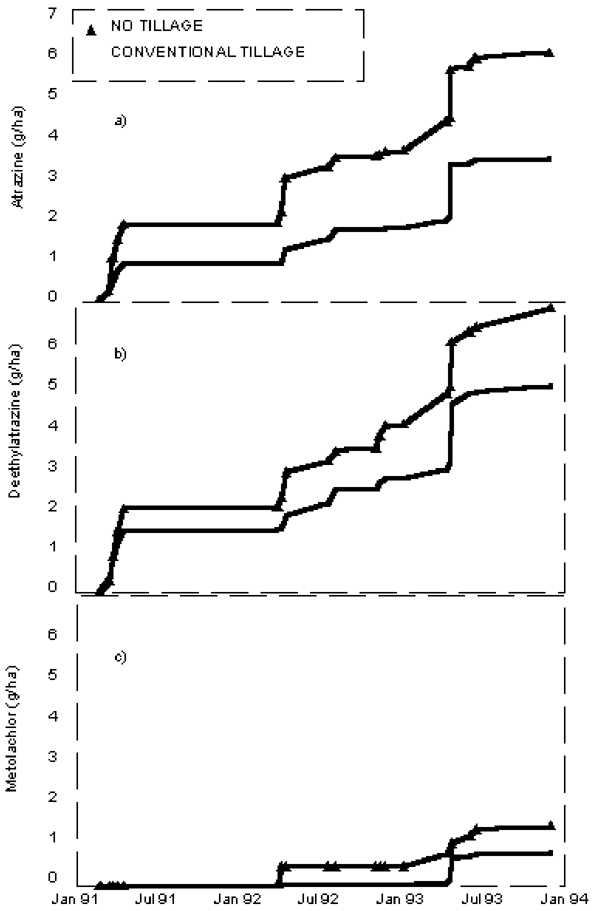

Figure 4. Cumulative loss of a) atrazine, deethyl-atrazine and c) metolachlor in tile drainage water between December 1990 and December 1993.

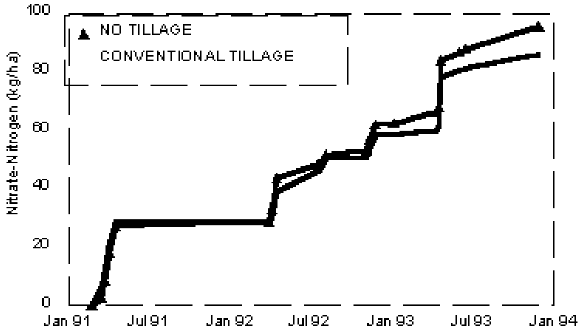

Figure 5. Cumulative loss of nitrate-nitrogen in tile drainage water between December 1990 and December 1993.

Herbicides

Chemical loading in tile effluent is a function of concentration and flow. For atrazine and its metabolite, both these variables generally had higher values under NT than CT. Consequently, atrazine and deethylatrazine cumulative losses in tile effluent during the study period were significantly higher under NT than CT (Table 4). Treatment effect was significant in cropping year 90-91 and 93-94 for atrazine and in cropping year 91-92 for deethylatrazine (Table 4). Metolachlor losses, however, were generally low and the difference between treatments was small and mainly due to one event in the spring of 1992 (Fig. 4).

Over 80% of all atrazine and 70% of all deethylatrazine losses occured during the high-flow snowmelt and spring events when concentrations were relatively low. During the growing season, concentrations were somewhat higher but, because of low flow, losses were not important under either tillage practice (Fig. 4). Flow, as opposed to concentration, appeared to have been the main factor in loading magnitude. This conclusion is in agreement with that of Muir and Baker (1978).

Herbicide losses in tile effluent, as percent of the amount applied, were always low (Table 4). The highest atrazine loss occurred in cropping year 92-93 when approximately 0.33% under NT and 0.27% under CT of applied atrazine was lost as atrazine plus deethylatrazine. In the dry cropping year 91-92, total atrazine losses represented 0.14% and 0.05% of applied, under NT and CT, respectively. The highest metolachlor loss was only 0.02% of the amount applied under both treatments (Table 4).

Nitrate-nitrogen

Cumulative nitrate-N losses in tile effluent were similar under both treatments (Fig. 5). The effect of higher concentrations under CT was balanced by that of higher flow under NT. In cropping year 91-92, higher flow under NT than CT caused significantly greater loss in the former (Table 4) even though the average concentration was higher in the latter (Table 3). As with herbicides, flow was more important than concentration for loading magnitude. Approximately 70% of the nitrate loss occurred in the snowmelt and the spring periods (Fig. 5) when concentration was generally the lowest and flow the highest.

Nitrate-N losses during the wetter cropping year 92-93 were much higher than those during the dry cropping year 91-92 (Table 4). Nitrate-N loss represented over 30% of applied fertilizer N in the wetter year and about 10% in the dry one (Table 4). Overall, NO_3-N loss amounted to less than 20% of the amount applied. This indicates the need for improved management of N in corn cropping.

Soluble total phosphorus

In the spring of 1991, P losses in tile drains amounted to about 20 g/ha in both tillage treatments, corresponding to 0.05% of applied phosphorus. In the spring of 1992, 30 and 20 g/ha left the field via the drain system under NT and CT, respectively, corresponding to 0.19 and 0.12% of the amount applied. In the two events during the growing season of 1992, only about 0.06% of the phosphorus applied that spring was lost in tile water. This indicates that phosphorus losses in tile effluent were not important under either tillage treatment.

3.3 Ground water

Ground water was sampled 29 times between June 1990 and December 1993. Herbicide and nutrient concentrations were measured in 103 samples at the 1.2 m depth, in 194 at 1.8 m, 295 at 3.0 m, and 327 at 4.6 m. The shallower sampling wells were dry more often than the deeper ones.

Atrazine and deethylatrazine concentration

Atrazine was detected in 84% and 62% of the samples collected under NT and CT, respectively. Samples with non-detectable levels were mainly from the 3.0 and 4.6 m depths. The maximum atrazine concentration was 5.4 µg/L, in a CT plot sample at the 1.8 m depth. The drinking water guideline was exceeded in two samples only. Deethylatrazine was detected in 92% and 78% of the NT and CT samples, respectively. Only one sample had deethylatrazine concentration above 5 µg/L.

Over the 43-month sampling period, the average atrazine concentration was significantly higher under NT than CT at the 1.8 and 3.0 m depths (Table 5). At the 1.2 m depth, average atrazine concentration was also higher under NT than CT but the difference was not significant. At the 4.6 m depth, atrazine concentrations were low under both tillage practices and there was no significant treatment effect.

Table 5. Average concentrations in ground water in 29 samplings between June 1990 and December 1993.

Depth	Atrazine (µg/L) NT	Atrazine (µg/L) CT		Deethylatrazine (µg/L) NT	Deethylatrazine (µg/L) CT		Metolachlor (µg/L) NT	Metolachlor (µg/L) CT	Nitrate-N (mg/L) NT	Nitrate-N (mg/L) CT
1.2 m	0.54	0.36		0.95	0.55		0.23	0.16	22.9	32.4
1.8 m	0.69	0.23	*	1.06	0.48		1.17	0.08	17.9	23.6
3.0 m	0.63	0.13	**	0.86	0.31	*	0.08	0.14	17.2	15.8
4.6 m	0.25	0.18		0.40	0.18		0.07	0.34	3.6	6.0

Deethylatrazine concentration was also higher under NT than CT at all depths but treatment effect was significant at the 3.0 m depth only (Table 5). Average concentration for deethylatrazine was higher than that for atrazine on most sampling dates, under both tillage practices (Figs. 6 and 7). Also, deethylatrazine was detected in more samples than the parent compound. In the CT plots during the dry growing season of 1991, most samples below the 1.2 m depth had concentrations under the detection limit for atrazine but not for deethylatrazine.

Higher and more numerous atrazine and deethylatrazine concentration peaks under NT than CT, especially at the 1.8 and 3.0 m depths (Figs. 6 and 7), suggest that rainfall events affected herbicide movement more under NT than CT. Between June 17 and July 22, 1992, 189 mm of rainfall was recorded, including four storms events with 20 mm or more rainfall. Ground water was sampled on June 17, July 15, and July 22. Atrazine and deethylatrazine concentrations under the CT plots were hardly affected by the precipitation (Figs. 6 and 7). In the NT plots, however, atrazine concentration doubled and deethylatrazine concentration increased by 150% between June 17 and July 15 at the 1.8 m depth. At the 3.0 m depth, atrazine concentration increased by 50%. On July 22, concentrations had decreased to the levels found in June, probably due to dilution of the residues by the 70 mm of rain that fell between the two sampling days. Tile drains started to flow on July 17 and water leaving the field via the drain system may also have further reduced herbicide movement to ground water. Results indicate that pollution of shallow ground water by atrazine and its metabolite was essentially absent even after several years of application, under the conditions of this study.

Metolachlor

Metolachlor was detected in only 25% of all groundwater samples and the maximum concentration was 15 µg/L. Metolachlor movement to ground water seemed to be erratic (Fig. 8). In October 1990, approximately one third of the samples showed detectable levels ranging between 0.50 and 5.6 µg/L. Then, until March 1993, all wells had non-detectable levels except at two sampling sites, one under each tillage practice, with higher sand content in surface soil than other sites. At these two (out of twelve) sites, some wells showed metolachlor residues up to 15 µg/L between August 1990 and May 1991. The storm events of July 1992 apparently did not result in any leaching of metolachlor. Between March and December 1993, groundwater samples started to show low metolachlor concentrations, generally below 1 µg/L. There was no apparent treatment effect on metolachlor movement to ground water (Table 5). Results again indicate low probability of shallow groundwater pollution from long-term use of metolachlor under conditions similar to those of this study.

Nitrate-Nitrogen

Nitrate-N concentrations in ground water exceeded the drinking water standard of 10 mg/L in over 80% of the samples collected at the three shallower depths and in 18% of those at the 4.6 m depth. Under CT, concentrations decreased steadily with depth (Fig. 9), with average concentrations going from 32 mg/L at 1.2 m to 6 mg/L at 4.6 m (Table 5). Under NT, average concentrations decreased from 23 mg/L at 1.2 m to 4 mg/L at 4.6 m, but concentrations were similar at the 1.8 and 3.0 m depths (Table 5). Average concentrations were mostly higher under CT than NT at all depths except at the 3.0 m depth (Fig. 9). However, there was no treatment effect on nitrate-N leaching to ground water at any depth (Table 5).

NO_3-N concentrations in ground water tended to be similar in every season. They were also comparable from one year to the next with the exception of a marked decrease in concentration at the 1.2 m depth under NT in 1993 (Fig. 9). Improved nitrogen management is required to reduced to reduce nitrate leaching into ground water.

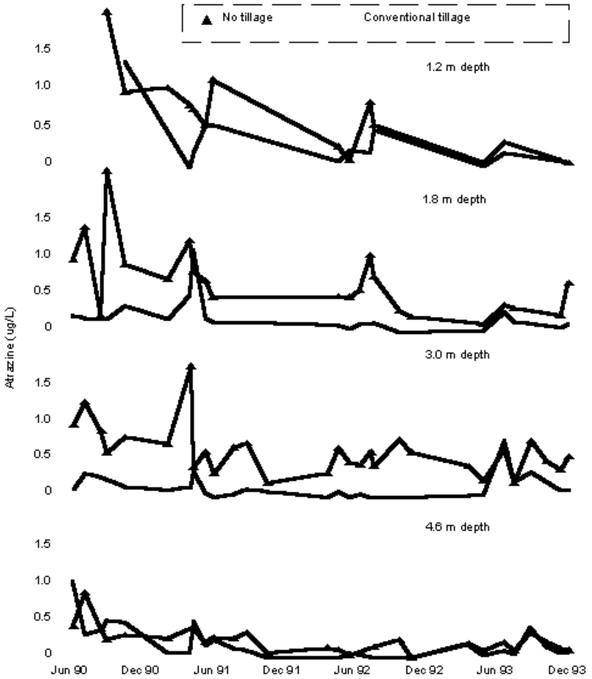

Figure 6. Atrazine concentration in groundwater at various depths between June 1990 and December 1993.

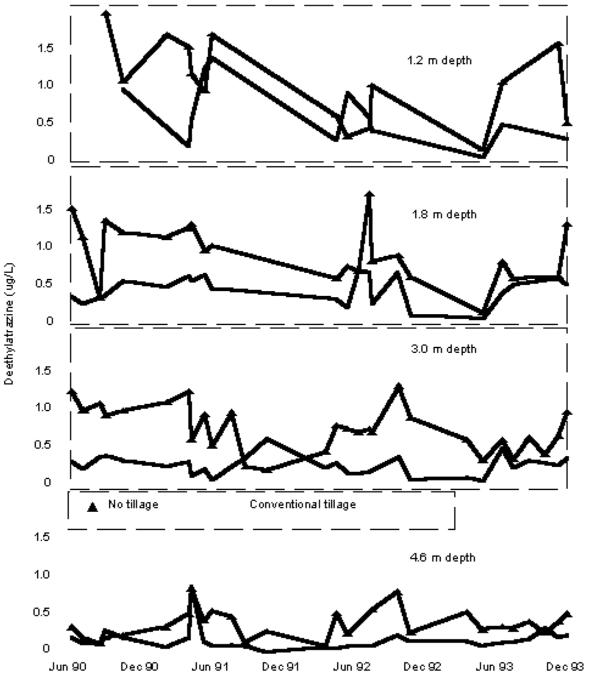

Figure 7. Deethylatrazine concentration in groundwater at various depths between June 1990 and December 1993.

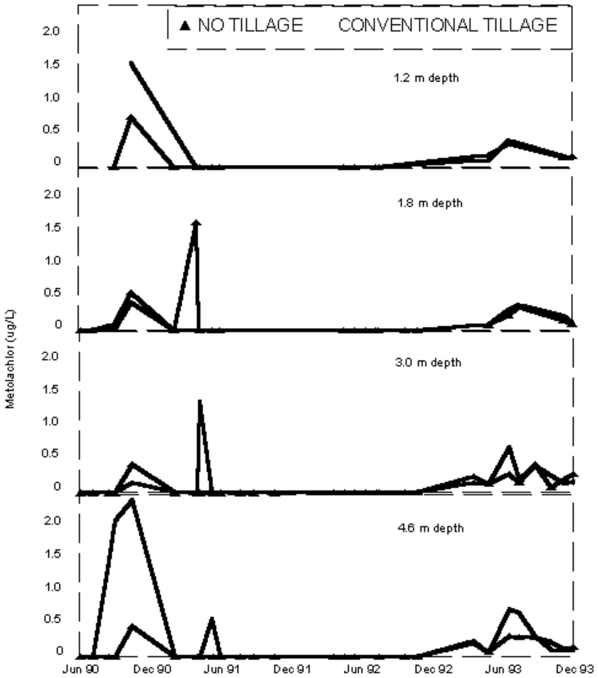

Figure 8. Metolachlor concentration in groundwater at various depths between June 1990 and December 1993.

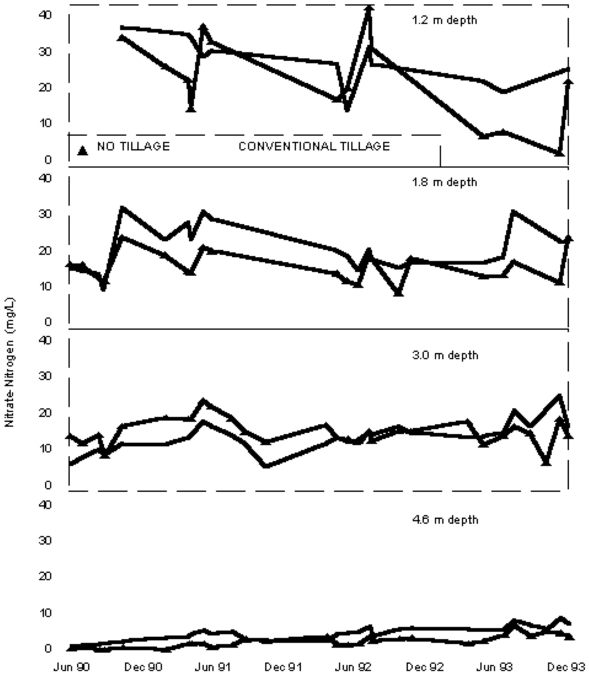

Figure 9. Nitrate-nitrogen concentration in groundwater at various depths between June 1990 and December 1993.

Soluble total phosphorus

The Ontario objective of 30 µg/L for total phosphorus in surface water was exceeded in approximately 65% of the samples collected at the 1.2 and 1.8 m depths, 50% of those at the 3.0 m depth, and 20% at the 4.6 m depth. Maximum concentrations exceeded 30 µg/L at every depth except at 4.6 m. Average concentrations exceeded the objective at all depths, except at 4.6 m, with 89 and 68 µg/L at 1.2 m, 61 and 60 µg/L at 1.8 m, and 50 and 44 µg/L at 3.0 m under NT and CT, respectively. There was no apparent treatment effect on phosporus leaching to ground water.

3.4 Surface Runoff

During the study, surface runoff occurred for a few days during the snowmelt period only. Lateral movement of snowmelt water between the plots was limited due to ponding in the plowed plots, corn stalk residues in the non-tilled plots, and a 20 cm high berm between the plots. The effect of such movement on water and chemical transport was also limited because of the large size of the plots (approx. 3 ha each) and the low concentration of chemicals and solids in the snowmelt water (Table 6). Total surface flow could not be determined during the study period because ice conditions in the flumes.

In 1992, surface runoff occurred during four days only. A total of 19 samples were analysed for nitrate-N and three for herbicides. In 1993, surface flow was observed in only one of the four plots for three days in late March. In early April, it occurred in every plot for five days. A total of 20 samples were collected for herbicide, nitrate, and solids analysis. Table 6 shows that chemical and solids concentrations were low in surface runoff. This suggests that snowmelt runoff from relatively flat fields is not likely to carry high pollutant concentrations under conditions similar to those present in this study.

Table 6. Surface drainage water quality - 1992-1993.

Parameters	Treat-ment	1992 Average	1992 Range	1993 Average	1993 Range	2-year Average
Atrazine	NT	1.05	0.20-1.90	1.38	0.10-5.56	1.33
(mg/L)	CT	0.70	(1)	0.88	0.32-1.92	0.87
Deethylatrazine	NT	0.20	0.10-0.30	0.43	0.01-1.12	0.39
(µg/L)	CT	0.30	(1)	0.62	0.08-1.21	0.59
Metalochlor	NT	2.70	ND-5.40	0.93	0.06-1.70	1.31
(µg/L)	CT	1.10	(1)	0.81	0.27-1.94	0.84
Nitrate-N	NT	2.2	1.1-3.5	1.12	0.5-1.9	1.68
(mg/L)	CT	2.5	1.3-4.0	1.13	0.8-2.0	1.74
Suspended solids	NT	31	5-112	34	0- 83	33
(mg/L)	CT	36	7-59	62	0-182	54
Total solids	NT	73	21-163	59	18-109	66
(mg/L)	CT	70	31-106	97	22-228	86

(1) Only one sample was collected.

3.5 Soil

Herbicide residues were not detected in the soil below 30 cm depth. At the 0-15 cm depth in 1992 and 1993, concentrations ranged from 0.77 and 1.16 µg/g on the day of application to 0.04 and 0.04 µg/g a year after application, for atrazine and metolachlor, respectively. Deethylatrazine concentrations remained below 0.05 µg/g throughout this period. At the 15-30 cm depth, concentrations varied between 0 and 0.03 µg/g for atrazine and deethylatrazine, and between 0 and 0.08 µg/g for metolachlor. Table 7 shows herbicide half-lives in 1992 and 1993 for each treatment. Half-life calculations were based on first-order herbicide disappearance in the top 15 cm of soil over a five-month period from the day of application. For both years, half-life values ranged between one to two months. There was no apparent differences between tillage treatments.

Table 7. Atrazine and metolachlor half-life in the 0-15 cm depth in soil, based on concentrations in the first 150 days after application

Year	Atrazine (days)		Metolachlor (days)	
	NT	CT	NT	CT
1992	64	52	54	58
1993	42	31	64	45

Average saturated hydraulic conductivity was also similar under the two tillage practices, between 3 and 4 mm/d, with coefficients of variation above 100%. Water retention capacity, however, was significantly higher under NT than CT at the 0-15 cm depth in two out of three sampling periods, at tensions between 5 and 350 cm of water.

3.6 Computer simulation modelling

Field data from the study site were used by collaborating investigators to improve and validate predictive models for water and chemical transport in the field. The pesticide component of GLEAMS was integrated with DRAINMOD to simulate pesticide load in tile drainage water under conventional tillage (Thooko et al. 1994). Although the integrated model tended to under-predict pesticide loads, the performance of the model was considered to be satisfactory in view of the limited data base. Field dissipation of atrazine and metolachlor was closely predicted using a dissipation model which was calibrated using laboratory data, although the model underestimated mineralization/volatilization and overestimated bound residue formation (Topp et al., 1994). Spatial and seasonal variations in input parameters for computer simulation modelling of chemical transport and hydrological phenomena in soil-water systems were examined under conventional tillage conditions (Gupta, 1993; Gupta et al. 1993a, 1993b, 1992, 1991). A deterministic-stochastic form of a model satisfactorily represented the observed saturated hydraulic conductivities and infiltration rates. The modelling effort is being continuing by collaborating investigators.

4.0 STUDY CONCLUSIONS

Tile drainage flow was higher under NT than CT during the spring/snowmelt period but was not significantly different in the two treatments during the growing season and in the fall. Atrazine and its degradation product deethylatrazine were almost always present in tile effluent, with concentrations mostly below 5 µg/L, the Canadian drinking water guideline for atrazine. Concentrations exceeding this limit were observed in both treatments after rainfall-induced flow events within a few weeks after herbicide application. Metolachlor was detected in a few tile effluent samples only at concentrations well below the Canadian drinking water guideline of 50 µg/L. In contrast, nitrate-nitrogen concentrations in tile water were above the drinking water limit of 10 mg/L in over 93% of the samples and were higher under CT than NT except during the spring period. Under both treatments, soluble total phosphorus exceeded the Ontario objective of 30 µg/L for total phosphorus in surface water, in about 25% of the 330 samples that were analysed. Annual loss in tile effluent ranged between 0.02 and 0.33% of the amount applied for herbicides, and between 7 and 32% for nitrogen in the nitrate form.

In **ground water**, atrazine concentrations met the drinking water guideline in over 99% of the 920 samples analysed. The maximum concentration in any sample was 5.4 µg/L. Atrazine and deethylatrazine concentrations were consistently higher under NT than CT up to 3.0 m depth. Metolachlor was detected in 25% of the samples and concentrations were well below the drinking water guideline. Under both tillage treatments, nitrate-nitrogen concentrations decreased with depth and were above the drinking water standard in over 80% of the samples collected at depths up to 3.0 m. Soluble total phosphorus concentrations exceeded 30 µg/L in over 50% of the samples collected up to 3.0 m depth in the two treatments.

5.0 NEW TECHNOLOGIES AND BENEFITS

1) **Establishment of a long-term, large data base on field-scale movement of water, herbicides and nutrients:** This field site was established in 1987 when field data collection was started. Long-term field data on chemical (atrazine, metolachlor, nitrate, and phosphorous) transport, soil characteristics and transformation, precipitation, and water regime has been collected for two tillage practices, conventional and no tillage. These data are essential for the calibration and verification of computer simulation models for agri-chemical transport and for providing information to the environmental protection and regulatory agencies.

2) **Establishment of a long-term monitoring site to study field-scale transport of agri-chemicals in soil and water under different management practices.** As far as can be established, this is the only highly-instrumented field-scale site in Canada to simultaneously study the effects on groundwater, tile water and surface drainage water. It includes: piezometric wells to monitor water table fluctuations and to sample shallow ground water at different depths; calibrated H-flumes (for flow monitoring) and automatic samplers for surface as well as tile drainage water; soil moisture probes and soil solution samplers at different depths in the soil; and heated shelters for flumes and samplers to enable year-round monitoring and sampling of drainage water. Since all possible avenues for the transport of water and chemicals are monitored, the site is suitable for a complete mass balance analysis under different management practices.

3) **Establishment of a network of multi-disciplinary experts and training of graduate students.** A collaborative research network, with multidisciplinary expertise has emerged which is evident in the names of associate investigators for this study. One Ph.D. and two Master's degree candidates have used the data collected at the site for their dissertation. In addition, four students from France have used the site for training in field research methodology.

6.0 IMPLICATIONS FOR GREAT LAKES ECOSYSTEM

1) Reduced and minimum tillage systems are being increasingly recommended for use in the Great Lakes Basin. Results from this study suggest a greater movement of atrazine and metolachlor to shallow ground water and tile drainage water under no tillage compared to conventional tillage. However, at the recommended rates of application, contamination of tile drainage or ground water by atrazine and metolachlor in excess of acceptable limits for drinking water would be unlikely under either tillage practice.

2) Nitrate-N concentrations in excess of the drinking water limit are likely to occur in tile effluent and shallow ground water in corn fields even at agronomically recommended N application rates. Subsurface drainage water could carry enough nitrate to cause a substantial loss of valuable nitrogen. Management practices which reduce nitrogen loss should be encouraged. For example, drainage water could also be retained in a surface or subsurface reservoir to be used subsequently as nitrogen-rich irrigation water. Nitrification inhibitors and winter catch crops could also be useful.

7.0 TECHNOLOGY TRANSFER POTENTIAL

1) The long-term field-scale data base will be available to other researchers for calibration and verification of computer simulation models and to test different hypothesis. Model predictions would then be useful in the development of remedial measures to abate pollution in the Great Lakes Basin.

2) This well-instrumented site will be available to others for research on pollutant movement on field-scale. Also, it will be an educational site for students and researchers interested in environmental research. It is already being used for this purpose.

3) Technical knowledge and experience acquired on field installations and instrumentation - electronics, machinery, data collection and analysis - has been, and is being made available to other researchers.

8.0 GAPS/NEEDS FOR FUTURE RESEARCH

1) A large proportion of the applied herbicides (atrazine and metolachlor) cannot be accounted for in ground water, tile drainage water and surface flow. The long-term fate of the parent compound as well as the degradation products of applied herbicides, including the formation and release of bound (nonlabile) residues needs to be determined more precisely than what is known at present.

2) Improved understanding is required of chemical transformations and transport in the period from harvest in the fall to chemical application in the spring, when most of the annual surface and tile flow and chemical loading occurs. The role and importance of macropores in chemical leaching also needs better understanding.

3) Information is required on pollutant transport to tile effluent and groundwater under crops other than corn in the Great Lakes Basin.

4) Strategies for manure utilization under reduced and no tillage systems need to be developed. Manure incorporation in normally recommended to control odour emission and reduce nitrogen loss as ammonia, and some tillage is therefore necessary.

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