Sediment and the Environment (Proceedings of the Baltimore Symposium, May 1989) IAHS Publ. no. 184, 1989.

The role of sediment in metolachlor transport from agricultural fields

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ABSTRACT Examination of metolachlor concentrations and loads in the dissolved and suspended phases in runoff water revealed that sediment can be an important transport vector in the movement of relatively soluble herbicides from site of application. The proportion of total metolachlor yield carried on sediment ranged from 9-70 % for natural rainstorms on experimental plots. Near-stream water table conditions appear to determine whether field exports of metolachlor and sediment enter adjacent streams or are deposited in footslope areas.

INTRODUCTION

The increased use of herbicides in agricultural activities has heightened public concern over their potential to contaminate surface and subsurface waters. Relatively little is known about the fate of many herbicides in terms of their residence times and types and rates of movement from site of application. In particular, there is considerable debate as to whether the dominant transport vector for many compounds is in solution or bound onto particulate matter. Recent research has emphasized the importance of sediment in conveying contaminants in fluvial systems (e.g. Ongley et al. 1981), and while there is a wide range in concentrations of various herbicides in the sediment phase and in bulk (sediment plus water), there is a general tendency for concentrations to be higher in the former than the latter. Thus investigations of atrazine losses (Hall et al. 1972; Hall 1974; Smith et al. 1978; Bailey et al. 1974; White et al. 1967) suggest that on average atrazine concentrations on sediment are 7 times those in bulk. However, concentrations alone are of limited utility in assessing the relative importance of the adsorbed and solution transport vectors; the total load of herbicide carried in each phase needs to be determined.

The herbicide under investigation in this study is metolachlor (2chloro-N-(2-ethyl-6 methylphenyl)-N-(2 methoxy-1-methylethyl) acetamide), which is used in the control of grassy weeds in a variety of crops, including corn, soybeans, beans and potatoes. Metolachlor has a moderate solubility in water (550 ppm at 20^oC), and leaching studies by Spillner et al. (1983) suggest that as a result it is very mobile relative to similar herbicides. However, it is not known whether this moderate solubility implies that metolachlor moves primarily in solution in surface runoff. In addition, there is some question as to the applicability of laboratory findings to transport under field conditions, where the herbicide may be in contact with flowing water for shorter time periods than are used in adsorption/desorption laboratory studies. This paper presents the results of a two year investigation of the hydrological pathways of metolachlor transport from application site to receiving water bodies. In particular, it examines the role of sediment in metolachlor transport.

STUDY AREA AND METHODS

The study site is a 5.5 ha field planted in corn, located 15 km south of Peterborough, Ontario $(44^{\circ} 6' 55"N, 78^{\circ} 20' 20"W)$ (Fig. 1). The regional climate is modified continental, with moderately cold winters and warm summers. The site has an average ground slope of 6%, and drains to a small stream. Soil cover consists of Orthic Grey Luvisols in upslope areas and Orthic Grey Luvisols and Gleyed Grey Luvisols on the footslopes. Soil organic matter contents range from averages of 2.7% in upslope areas to 4.7% in the footslope zone. Poor drainage in the footslope zone has led to the installation of two tile drainage systems approximately 1 m below the ground surface, both of which discharge to the stream (Fig. 1).



- TILE DRAIN OUTFALL
- V-NOTCH WEIR
- GAUGING STATION + AUTOMATIC SAMPLER • WEATHER STATION

Fig. 1 Study site topography, instrumentation and soil sampling zones.

On May 29, 1986 metolachlor (formulated as $Dual^{R}$ herbicide) was applied to the field as a preemergence surface broadcast treatment (PRE) at a rate of 3.45 L ha⁻¹. This represents 18.4 kg of active ingredient applied to the field, or 334.1 mg m⁻². In 1987 the field was subdivided into two segments and metolachlor was applied to each at a rate of 2.75 L ha⁻¹ on June 4. Segment 1 (1.4 ha) received 3.7 kg of active ingredient (264.3 mg m⁻²) as a preemergence surface broadcast treatment, while on segment 2 (4.1 ha) 10.8 kg of metolachlor was incorporated to a 15 cm depth prior to planting (PPI), representing an application of 263.4 mg m⁻².

Soil samples were taken prior to herbicide application, 1 h after application, and at intervals of 1, 2, 3, 4, 6, 8, 10, 12, 16, 20 and 24 weeks following application. In 1986 soil samples were taken in two zones - across the entire field and in the footslope zone bordering the stream. In 1987 sampling for metolachlor persistence in soil was conducted in four zones - whole field PRE, whole field PPI, the footslope zone, and an ephemeral channel that cuts across the PPI segment (Fig. 1).

Table 1 summarizes the sampling strategy employed during the 1986 and 1987 field seasons. Sampling site locations are indicated on Fig. 1. HOFA and HOFB runoff plots were intended to monitor any runoff produced as a result of Horton overland flow. The other two plots (SOFA and SOFB) were installed at the base of the slope in an area that was observed to generate saturation overland flow following spring snowmelt. Differences in discharge and sediment loads measured at WLRA and WLRB were assumed to represent total export from the subcatchment defined by the two stations, while differences in metolachlor loads measured at these two sites were assumed to represent total herbicide export from the treated field. In 1987 two V-notch weirs (WA and WB) measured runoff from the PRE treatment, while runoff from the PPI segment was monitored at the WC V-notch weir.

MONITORIN SITE	G DEFINITION	TARGET	!	FIELD SEASON	DISCHARGE MEASUREMENT	WATER SAMPLING
HOFA HOFB SOFA SOFB	23.8 m² runoff plots	runoff, metc & sediment per unit	olachlor export area	1986,1987	continuous	integrated; one per event
TDA TDB	tile drain outfalls	metolachlor e shallow grou	export via Indwater	1986,1987	spot	spot
WA WB WC	V-notch weirs	metolachlor a export from ex treatmer	a sediment operimental nts	1987	continuous	spot sampling during storm events
WLRA WLRB	gauging stations & automatic samplers in stream	field export of & subcatchmer sedime	f metolachlor nt export of ent	1986,1987	continuous	hourly during storm events
Met	weather station	temperature, humidity, pre amount & ir	, relative ecipitation ntensity	1986,1987	-	-

Table 1 Monitoring strategy employed in the study

All water and soil samples were analyzed for metolachlor at the Agriculture Canada London Research Centre, using a gas chromatograph fitted with a N/P detector and employing an extraction procedure derived by R.A. Chapman and C. Harris of the London Research Centre.

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1986 water samples were analyzed for bulk metolachlor contents (i.e. in solution and adsorbed onto sediment). In 1987 water samples from the runoff plots were split, and metolachlor concentrations in solution and adsorbed onto sediment were determined separately. Sediment concentrations in water samples were determined by filtration.

RESULTS AND DISCUSSION

Metolachlor vields in the sediment and solution phases

Table 2 summarizes metolachlor concentrations and loads in solution and adsorbed onto sediment for those 1987 storm events that generated measurable runoff volumes from the runoff plots. Metolachlor concentrations on sediment were consistently greater than those in solution, and the former exceeded the latter by an average of 21 times for events where both were determined. When the total load of metolachlor carried in solution and on sediment is determined, it is evident that sediment can be an important transport vector for relatively soluble herbicides such as metolachlor. Despite variations in both metolachlor concentrations on soil particles and total sediment yield, the percentage of total metolachlor yield in

Table 2	Metolachlor	and	sediment	concentrations	and	yields,	1987
runoff p	lot data						

DATE	PLOT	METOLACHLOR IN WATER (pg/l)	CONCENTRATION ON SEDIMENT (ng/g)	SUSPENDED SEDIMENT CONCENTRATION (mg/l)	SEDIMENT YIELD (g/m²)	NETOLACHI IN SOLUTION (µg,	LOR YIELD ON SEDIMENT /m ²)	<pre>% OF TOTAL YIELD ON SEDIMENT</pre>
June 26	HOFA	270	-	234009	177.0	204.2	_	-
July 3	HOFA	293	-,	57397	60.3	307.8	-	-
	HOFB	10	370	42514	17.9	20.6	6.6	24
July 14	HOFA	46	560	12837	6.5	23.2	3.6	14
July 20	HOFA	122	350	812992	3381.8	507.5	1183.6	70
-	HOFB	36	230	181856	443.2	87.7	101.9	54
	SOFB	5	-	4952	2.7	2.7	-	-
Aug 2	HOFA	72	230	242373	835.1	248.1	192.1	44
2	HOFB	6	-	12340	7.3	3.5	-	-
	SOFB	3	-	2062	0.2	0.3	-	-
Aug 7	HOFA	66	320	288244	775.1	177.5	248.0	58
-	HOFB	26	140	18562	14.8	20.8	2.1	9
	SOFA	79	1640	6284	79.2	995.8	129.9	12
	SOFB	25	490	30528	30.8	25.2	15.1	37
Aug 9	HOFA	24	240	66486	717.9	259.2	172.3	40
	HOFB	12	120	89527	316.0	42.4	37.9	47
	SOFA	23	1360	12072	140.5	267.7	191.1	42
	SOFB	4	380	7924	9.0	4.5	3.4	43
Aug 31	HOFA	18	160	42423	23.2	9.8	3.7	27
	n	19	14	19	19	19	14	14
	x	60	471	113967	370.4	168.9	163.7	37
	ŝ	84	457	192215	781.8	245.8	306.3	18
C	V(%)	140	97	169	211	146	187	49

surface runoff carried as adsorbed load was appreciable. It is worth noting that water samples were separated into water and sediment fractions several weeks after sampling. If any movement from the adsorbed to the dissolved phase did occur following sampling, this would mean that the "% of total yield on sediment" values in Table 2 are underestimates, and that sediment transport is of even greater importance in metolachlor loss than has been suggested here.

There appears to be little relationship between the adsorbed metolachlor concentration and either "metolachlor yield on sediment" or the "percentage of total metolachlor yield carried on sediment". However, the results suggest that both indices have positive relationships with the sediment yield for the runoff event. This is not surprising, since by definition adsorbed metolachlor yield is a function of sediment yield, and because the event-to-event and plotto-plot variations in adsorbed concentrations are less that the variations in sediment yield (Table 2). Nevertheless, the importance of sediment yield to metolachlor export from site of application has implications for reducing herbicide loadings to streams, and reinforces the role of soil conservation measures in safeguarding water quality.

Hydrological controls on metolachlor loadings to streams

The 1986 and 1987 field seasons differed greatly in their general rainfall characteristics (Table 3), and can be considered to represent two distinct conditions.

	MONTHLY RAI	NFALL AND NUMB	ER OF DAYS WITH MEASURABLE PRECIPITATIO		
	MAY	JUNE	JULY	AUGUST	SEPTEMBER
1986	76.0 * (14) ^B	99.6 (12)	59.8 (12)	93.5 (17)	178.4 (16)
1987	41.6 (11)	73.1 (14)	44.4 (13)	84.1 (12)	85.2 (15)
30 YEAR MEANS (1951-1980)	57.1 (12)	60.4 (10)	77.9 (10)	74.2 (10)	72.9 (11)
	A - monthly	rainfall dept	h in mm; B - nu	umber of days	with rainfall

Table 3 Monthly precipitation data, Peterborough Airport

<u>1986 results</u> 1986 experienced an exceptionally wet spring and early summer, with above-average rainfalls in May and June. These resulted in a large number of early season runoff events, many of which exceeded the capacity of the runoff collecting barrels used on the runoff plots. Thus it was not possible to determine metolachlor

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loads for many of the individual storms. All four plots responded to large rainfall events during the early field season. However, for several storms that occurred from late June to mid-July, SOFA and to a lesser extent SOFB did not generate any runoff, while both HOFA and HOFB responded.

Fig. 2a shows the temporal trends in metolachlor persistence in the two sampling areas. While both zones experienced an expected decrease with time (cf. Patni, 1987), regression equations describing the rate of metolachlor dissipation show a significant difference in the slope coefficients at the 95% level, indicating that metolachlor dissipation is slower in the footslope zone than for the whole field. This could be the result of reduced degradation in the footslope zone due to wetter conditions there, as well as the deposition of metolachlor transported from upslope both in solution and adsorbed onto sediment.



Fig. 2 Metolachlor dissipation in soils: (a) 1986; (b) 1987.

The largest metolachlor yields in the receiving stream were observed for early season runoff events, with a storm on 19 June providing the peak yield of 42 g. Yields experienced a marked decline throughout the remainder of the field season, and it is estimated that less than 1% of the total applied active ingredient was exported from the subcatchment.

<u>1987 results</u> In contrast to 1986, the 1987 field season experienced below-average rainfalls in May, leading to low water table elevations in the footslope area and no surface saturation. This is manifested in the runoff plot outputs (Fig. 3a), where only the Horton overland flow plots made significant responses to early season rainfall events. Data from the V-notch weirs indicate that little runoff from the field entered the stream during these events, suggesting that much of the metolachlor and sediment that was being entrained on upslope portions of the field was being deposited in footslope areas prior to entry to the channel.

This is supported by the trends in metolachlor persistence in the soil sampling zones (Fig. 2b). Concentrations in whole field PRE,

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whole field PPI and epheneral channel soils decreased with time in a similar fashion to the 1986 results, and there were no significant differences in the slope coefficients of regression equations describing metolachlor dissipation in these zones. However, metolachlor levels in footslope soils responded very differently. These increased throughout late-June and July, implying that metolachlor entrained by upslope Horton overland flow was being deposited in this area. Metolachlor concentrations in the footslope soils dropped abruptly in August, coinciding with the large response of the SOF plots to prolonged heavy rainfall from 7-10 August (Fig. 3a). The cause of this increased saturation overland flow was a rapid rise in near-stream water table levels during this period, as indicated by the marked response of the tile drain discharges to the rainfall of 7-10 August (Fig. 3b). In addition to the generation of



Fig. 3 1987 precipitation and runoff responses: (a) runoff plot cumulative output; (b) tile drain discharges.

saturation overland flow as the water table intersected the ground surface in the footslope zone, Horton overland flow could now make its way to the stream channel in large quantities. As a result, metolachlor was flushed into the stream, accounting for the drop in metolachlor persistence in footslope soils to levels similar to those of the other sampling zones following this rainfall event. The 7-10 August storm produced the largest metolachlor yield observed in the stream (233 mg). This was less than 1% of the maximum metolachlor yield observed in 1986, and in contrast to the previous year occurred 66 days after herbicide application. A comparison of the 1986 and 1987 results highlights the importance of near-stream water table conditions during early season runoff events in governing metolachlor and sediment inputs to streams. While many workers have noted that the critical runoff events in terms of herbicide loss are those that occur shortly after application, it is the near-stream hydrologic conditions which determine whether field exports will enter the stream. The results also suggest that erosional and depositional processes must be considered when examining temporal trends in herbicide persistence in soils.

ACKNOWLEDGEMENTS This work was funded by the Pesticides Advisory Committee of the Ontario Ministry of the Environment. The author would like to thank J. Sanderson and T. Sawyer for their cooperation and assistance, B. Harris, G. Ward and A. Mennaman for invaluable support in the field and laboratory, and R.A. Chapman for the metolachlor analyses.

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