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Fate of Autumn—Applied Metolachlor in a Clay Loam in the Northern U.S. Corn Belt

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ABSTRACT

Application of herbicides in autumn is of interest to land managers who seek to reduce the number of field operations during spring in the northern Corn Belt. A limited number of herbicides, however, posses the physical characteristics that are required to minimize loss from soil over winter. This study examined the fate of one of these herbicides, metolachlor, during three consecutive winters (1994–1995, 1995–1996, and 1996–1997) near Morris, MN. Metolachlor was applied to the top 5 cm of a clay loam that was packed into a 1.8-m long plastic pipe. The pipe was then set inside a larger diameter 1.8-m long plastic pipe that was buried vertically in the field. The gap between the pipes was insulated along the sides and sealed at the top; this configuration allowed collection of leachate and extraction of the smaller diameter pipe while the field soil was frozen. The experimental design was replicated thrice with sample date (date that the smaller diameter pipes were extracted from the field) as the main treatment. Pipes were extracted from the field at least twice during winter and sectioned into 2 cm or larger increments. The soil contained within these sections was then analyzed for metolachlor. Downward movement of metolachlor occurred in the soil profile during the autumn, but only in 1995. This movement was likely caused by exclusion during pore ice formation as the soil froze. At the time of complete soil thaw

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in spring, the majority of metolachlor was still detected in the zone of application (0–5 cm depth). Some metolachlor, however, was detected 1 to 3 cm below the zone of application in all three years. Downward movement during thaw was due primarily to infiltration of snowmelt and rain. Metolachlor was most vulnerable to degradation during spring, but some loss occurred in autumn prior to freeze-up. This study suggests that autumn-applied metolachlor moves little in a repacked clay loam profile during winter. Further studies are warranted in evaluating movement under a range of soil physical properties and management practices.

Key Words: Herbicide movement; Herbicide degradation; Fall-applied herbicide; Frozen soil; Soil freezing; Soil thaw; Winter.

INTRODUCTION

Herbicides are a vital resource to growers worldwide for controlling weeds that would otherwise diminish crop quality and yield. Yet, herbicides found in surface and ground water systems in the midwestern United States[1,2] potentially threaten the quality of our water resources. Detection of herbicides in ground and surface water is most apparent during the growing season, but is also evident in the spring prior to field application.[2,3]

Herbicides applied to the soil surface can be lost as a result of degradation, runoff, or leaching. Heavy precipitation events contribute to the likelihood of runoff and/or leaching and therefore to the movement of herbicides from fields to ground and surface waters in the north central United States. Autumn application of herbicide may minimize loss by runoff and leaching because heavy precipitation events are less likely to occur in the autumn than in spring in the northern Corn Belt.[4] Autumn-applied herbicides, however, may be vulnerable to degradation, runoff, and/or leaching from the upper soil profile because of the long residence time in soil prior to weed emergence in spring. Although cold soils will retard degradation of herbicides in northern regions,[5] little is known concerning the over winter fate of herbicides in soils. Clay et al.[6] found the mobility of herbicides, applied to frozen soil in late autumn, to vary over the course of winter at three locations in the northern Corn Belt. In their study, movement of both metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] and alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxy-methyl)acetamide] occurred throughout the spring in response to snowmelt and rainfall events. Metolachlor, however, was less mobile (no movement or contained in the upper 15 cm of the soil profile) than alachlor (moved to depths greater than 30 cm). Despite the variation in soil type and climate across these three locations, the short duration (one year) and method of application (to frozen soil) in their study negates any evaluation that can be made of over winter movement of metolachlor under site specific climate variability and recommended application practices.

Metolachlor is used for weed control in corn and soybean production systems in the northern Corn Belt. The positive correlation between metolachlor adsorption and soil clay and/or organic matter content[7] and high adsorption compared with other herbicides[8] has promoted application of metolachlor to fine-textured soils during autumn in cold regions.[9] Indeed, metolachlor is recommended for application to fine-textured soil by incorporating prior to soil freezing.[10] Yet, little information is available on the fate of metolachlor when applied to the soil during autumn. This study was therefore undertaken to assess movement of metolachlor in soil from the time of application in autumn to the time of sowing in spring in the northern US Corn Belt.

MATERIALS AND METHODS

This study was conducted at a field site located in west central Minnesota near Morris (45°35′N, 95°53′W). This region is characterized by a continental climate with cold and dry winters. The Morris area has a mean annual temperature of 5.3°C and receives 61 cm of precipitation throughout the year. January is the coldest (−8.2°C) and driest (1.8 cm) month of the year. There are more than 220 days between the first freeze in autumn (28 September) and the last freeze in spring (8 May). Snowfall during the winter averages 1.1 m and snow cover is persistent from 29 October in autumn to 23 April in spring.

Soil Columns

Movement of metolachlor over winter was assessed in the field using repacked soil columns. Hamerly clay loam (Aeric Calciaquolls) was used in this experiment since this soil series forms part of the Aastad–Hamerly–Barnes association and Chernozem soil group. This association and soil group respectively comprise 1.5 and 15% of the area in the North Central United States. The soil is characterized by a pH of 8.1 and an organic carbon content of 3.8%. Percent sand, silt and clay was respectively 30, 40, and 30%.

Soil columns (1.8-m long) were prepared in the laboratory and placed in the field in mid-autumn of 1994–1996. Laboratory preparation was accomplished in a temperature-controlled room maintained at 15°C; this temperature is representative of soil at a 2-m depth in mid-autumn in central Minnesota.[11] Water was added to air-dry Hamerly clay loam to achieve an initial water content of 0.25 g g^{-1} (equivalent volumetric water content of 0.30 cm^3 cm^{-3} and water potential of −50 kPa) which is typical of soils prior to freeze-up in western Minnesota.[12] Soil columns were then prepared by packing the moist soil into 10-cm diameter by 1.8-m long plastic pipe at a density of 1.2 g cm^{-3}. Soil was packed into the pipe by 5-cm layers. After each layer was packed, the surface of the soil was scratched prior to the addition of the next layer to minimize discontinuities between the packed soil layers. As each pipe was packed, a sample of untreated soil was sealed in a plastic bag, weighed, placed in a freezer at −20°C, and later analyzed for metolachlor concentration. The top 5 cm of each plastic pipe was packed with soil treated with metolachlor. Metolachlor was thoroughly incorporated into the moist clay loam by hand to attain a concentration of about 5.0 μg g^{-1}. As the top 5 cm of each pipe was packed, a sample of treated soil was collected, sealed in a plastic bag, weighed, frozen, and later analyzed for metolachlor concentration. These samples (treated and untreated) were used to determine the initial distribution of metolachlor within each soil column.

Repacked soil columns were capped and placed horizontally on a bench in the temperature-controlled room until preparations were complete. Installation of columns in the field was typically accomplished within 24 h after preparation. Metolachlor is not likely to move below the zone of application (below 5 cm) in the soil profile prior to installation in the field because diffusion of metolachlor is slow or negligible in relatively dry and cool soil.[13] Soil columns were then installed in the field on 9 November 1994, 6 November 1995, and 24 October 1996. Prior to these dates, there were 12, 15 and 4 days with diurnal air temperatures ranging above and below 0°C (freeze-thaw), respectively. The daily mean temperature was above 0°C until 18 November 1994, 2 November 1995 and 9 November 1996. The field soil remained frozen for the duration of winter after these dates. Frost depth was measured thrice weekly using duplicate frost tubes at the experimental site. In addition, hourly air temperature and daily precipitation were measured at a microclimate station located about 3 km from the site. These data were used in part to determine potential soil evaporation by the Blaney–Criddle equation.[14]

At the field site, each repacked soil column was placed inside a 15-cm diameter by 1.8-m long plastic pipe. The larger diameter pipes were buried vertically in the field soil profile on a 1.0×1.5 m spacing. The top of the larger diameter pipe was flush with the surface of the field soil; the field soil was devoid of vegetation and crop residue for the duration of the study. The larger diameter pipe was capped and sealed at the bottom. The gap between the smaller and larger diameter pipes was filled with fiberglass insulation to minimize lateral heat flow. A rubberized seal was placed between the gap at the top of the pipes. The top of the smaller pipe protruded 1 cm above the surface of the field soil to minimize the lateral flow of water across the top of the soil column. This assembly allowed collection of leachate inside the outer pipe; however, no leaching occurred through the soil column during the study. The experimental design was replicated thrice with sample date as the main treatment.

Three soil columns were extracted from the field on two dates during the 1994–1995 winter (5 January and 3 May) and on three dates during the 1995–1996 winter (12 December, 11 April, and 7 May) and 1996–1997 winter (14 November, 26 February, and 5 May). The first and last dates of each year corresponded to a time after freeze-up in the autumn and after complete thaw of the soil profile in the spring, respectively. The 11 April 1996 and 26 February 1997 sample dates characterized the state of soil during spring thaw and at the time of maximum penetration of frost in the soil profile, respectively.

The soil columns were sectioned into 2-cm increments from the 0–0.20 m depth, into 5-cm increments from the 0.20–0.50 m depth, and into 10-cm increments from the 0.50–1.80 m depth. The 2-cm increments provided the finest possible resolution for securing an intact sample of soil when sectioning the columns using a band saw. Soil from each sectioned sample was sealed in a plastic bag, weighed, and frozen at −20°C. About 900 s elapsed between the time the column was extracted from the field and the time the soil samples were placed in the freezer. Frozen soil samples were broken and a fraction removed for gravimetric determination of soil water. The remaining fraction was ground to pass a 0.5 mm sieve. Grinding of the soil was accomplished inside a walk-in freezer set at $-10°C$ to prevent thawing of the soil samples. Dry ice was ground between soil samples to minimize cross contamination of samples. Ground soil samples were kept frozen at $-20°C$ until analyzed for metolachlor concentration.

Chemical Analysis

Metolachlor analyses were performed on all 2 and 5 cm thick sections. A 20 g subsample (previously ground) was removed from the freezer to which was added 100 ml of 10% water in methanol. The soil-methanol mixture was boiled for 2 h in a reflux condenser. The mixture was filtered and collected in a volumetric flask. The volume of leachate was brought to 100 ml using 10% water in methanol. Twenty-five ml of the leachate-methanol mixture was removed to a separatory flask, to which was added 100 ml of water and 10 ml of saturated sodium chloride. This mixture was extracted thrice with 50 ml portions of hexane. The hexane extracts were combined and filtered through an anhydrous sodium sulfate pad. The pad was rinsed with 20 ml of hexane. The hexane mixture was evaporated using a rotary evaporator with a bath temperature of 30°C. Five ml of hexane was added to the remaining residue, samples of which were analyzed on a Gas Chromatograph (GC). Recovery of spiked samples using the above procedure was more than 91%. The detection limit of the GC was 0.5 $\mu g\ g^{-1}$.

RESULTS AND DISCUSSION

The winter season (November through April) was typified by wet atmospheric conditions in 1994–1995, cold and dry conditions during 1995–1996, and cold and wet conditions during 1996–1997. Air temperatures were near normal (1.0°C above the 100-year average of $-5.1°C$) during the 1994–1995 winter while temperatures were nearly 3°C below average during the latter two winters. Precipitation was 6 cm above average (100 year average was 16 cm) during the 1994–1995 winter, 6 cm below average during the 1995–1996 winter, and 10 cm above average during the 1996–1997 winter. Noteworthy was the particularly wet March of 1995 with 7 cm more precipitation than average and the dry spring (February through April) of 1996 with 6 cm less precipitation than average. Snowfall during successive winters amounted to 140, 135 and 205 cm. The soil froze to a depth of about 1 m during the first two winters and 0.75 m during the last winter.

Movement in Autumn

Repacked soil columns were placed in the field prior to freeze-up (the day when some portion of the soil profile remained frozen for the duration of winter) in all years except 1995 (Figures 1–3). In the autumn of 1995, columns were placed in the field four days after freeze-up. Cyclic freezing and thawing of soil, soil evaporation, and infiltration of rain prior to freeze-up were the environmental factors most likely

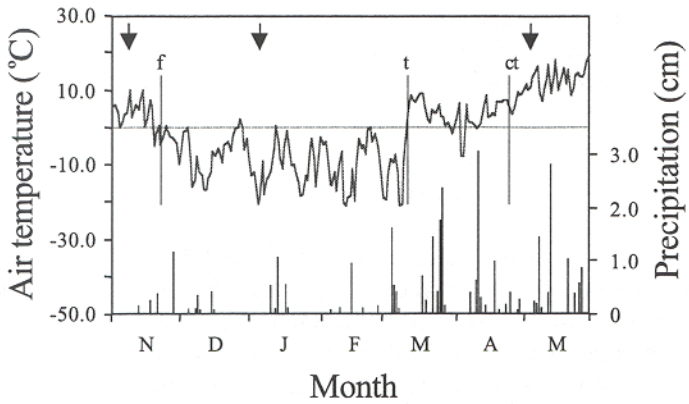

Figure 1. Daily air temperature and precipitation at Morris, MN from November 1994 through May 1995. Arrows signify sampling dates and vertical lines the onset of freeze-up (f), initial soil thaw in spring (t), and complete thaw of the soil profile (ct).

to cause redistribution of metolachlor in the soil profile during the autumn of 1994 and 1996. In the autumn of 1994, metolachlor did not move much beyond the zone of application (metolachlor may have moved below the applied depth of 5 cm, but it was not detected below a depth of 6 cm) from the day the soil columns were installed in the field on 9 November 1994 to the day of sampling after freeze-up on 5 January 1995 (Table 1). Lack of downward movement of metolachlor possibly resulted from little or no infiltration of precipitation during autumn. This is substantiated by the small amount of precipitation (0.7 cm) received over a 14-day interval from the day the columns were installed in the field to the day of freeze-up (9 to 22 November). After freeze-up, all precipitation (2.2 cm) was received in the form of snow.

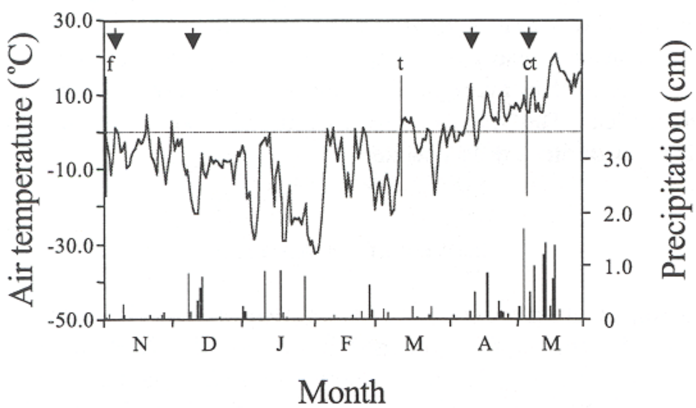

Figure 2. Same as Figure 1 except for November 1995 through May 1996.

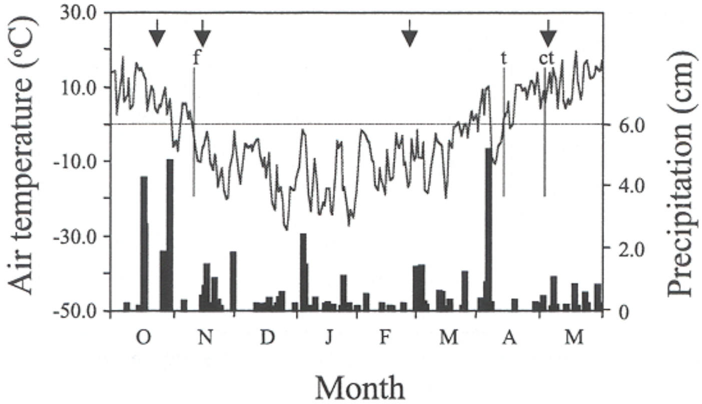

Figure 3. Same as Figure 1 except for October 1996 through May 1997.

In the autumn of 1996, infiltration of rain was likely substantial and may have caused downward movement of metolachlor in the soil profile. Nearly 7 cm of precipitation was received from the day the soil columns were installed in the field (24 October) to freeze-up (10 November). Metolachlor, however, was not detected much beyond the zone of application (at a depth greater than 6 cm) four days after freeze-up (Table 3). Any movement of metolachlor resulting from infiltration in autumn 1996 was likely compensated by that which occurred upward in response to soil freezing or evaporation. Soil freezing may induce upward movement of chemicals in the profile by convection as water moves from regions of high water potential (below the depth of freezing) to low water potential (near the freezing front) in the soil.[15] Soil freezing, however, did not induce any upward movement of metolachlor in the profile in the autumn of 1994 or 1995 (Tables 1 and 2).

Table 1. Metolachlor concentration in a clay loam profile from the time of autumn application in 1994 to complete thaw in Spring 1995 at Morris, MN.

	Metolachlor concentration[a] ($\mu g\ g^{-1}$)		
Depth (cm)	9 Nov	5 Jan	3 May
0–2	4.7 (0.1)[b]	4.6 (0.3)	4.0 (0.1)
2–4	4.7 (0.1)	4.0 (0.2)	4.4 (0.3)
4–6	2.4 (0.1)	2.4 (0.2)	3.3 (0.3)
6–8	0	0	0.7 (0.3)
8–10	0	0	0

[a]Dates correspond to installation of soil columns in the field prior to freeze-up, after freeze-up but prior to initial soil thaw in spring, and after complete thaw of the soil profile, respectively.
[b]Numbers in parenthesis are the standard errors of the means.

Table 2. Metolachlor concentration in a clay loam profile from the time of autumn application in 1995 to complete thaw in Spring 1996 at Morris, MN.

	Metolachlor concentration[a] ($\mu g\ g^{-1}$)			
Depth (cm)	6 Nov	12 Dec	11 Apr	7 May
0–2	5.6 (0.1)[b]	4.9 (0.2)	3.4 (0.8)	3.1 (0.3)
2–4	5.6 (0.1)	4.6 (0.2)	3.8 (0.4)	3.8 (0.2)
4–6	2.8 (0.1)	3.8 (0.5)	3.6 (0.3)	2.7 (0.1)
6–8	0	0	0.7 (0.2)	0
8–10	0	0	0	0

[a]Dates correspond to installation of soil columns in the field, after freeze-up, after initial soil thaw, and after complete thaw of the soil profile, respectively.
[b]Numbers in parenthesis are the standard errors of the means.

Soil freezing may also promote downward movement of chemicals in the soil profile as a result of exclusion of chemicals from an advancing freezing front.[15] Exclusion of metolachlor may have occurred in the soil profile during the autumn of 1995 (Table 2). An apparent increase in metolachlor was detected at the 4–6 cm depth from the day the columns were installed in the field (6 November) to the following sample date (12 December). Infiltration of precipitation did not cause this increase in metolachlor concentration because soil columns were installed in the field four days after freeze-up in autumn. In addition, all precipitation (1.8 cm) received over the 37-day interval from the day the soil columns were installed in the field (6 November) to the first sample date after installation (12 December) was in the form of snow. Infiltration of snowmelt from 6 November to 12 December 1995 was likely limited because strong winds had prevented the accumulation of snow cover (maximum depth of snow was 2 cm).

Movement in Spring

Metolachlor was detected below the depth of application prior to, during and after spring thaw (Tables 1–3). No metolachlor, however, was detected below a depth of 8 cm over the three years of this study. Prior to the 1997 spring thaw, metolachlor was detected at a depth of 6 to 8 cm in the soil profile (Table 3). Downward movement of metolachlor apparently occurred while the soil was frozen (between 14 November 1996 and 26 February 1997). Infiltration of snowmelt may have occurred over this time interval because air temperatures were sufficient to initiate melt of the snowpack. Maximum daily air temperatures did not exceed 5°C, but did exceed 0°C on 13 days between 14 November to 26 February. Although snowmelt may have infiltrated the frozen soil,[16,17] there was no detectable increase in water content in the upper soil profile.

After complete thaw of the soil profile in the spring of 1995 and 1997, metolachlor was detected at a depth of 6 to 8 cm below the soil surface (1 to 3 cm below depth of application). Downward movement of metolachlor was likely caused by

Table 3. Metolachlor concentration in a clay loam profile from the time of autumn application in 1996 to complete thaw in Spring 1997 at Morris, MN.

	Metolachlor concentration[a] ($\mu g\ g^{-1}$)			
Depth (cm)	24 Oct	14 Nov	26 Feb	5 May
0–2	4.6 (0.1)[b]	5.2 (0.6)	3.3 (0.7)	2.8 (0.2)
2–4	4.6 (0.1)	4.2 (0.3)	3.7 (0.2)	2.5 (0.5)
4–6	2.3 (0.1)	0.9 (0.6)	1.9 (0.6)	1.8 (0.3)
6–8	0	0	1.2 (0.4)	1.3 (0.4)
8–10	0	0	0	0

[a]Dates correspond to installation of soil columns in the field prior to freeze-up, after freeze-up, prior to initial soil thaw, and after complete thaw of the soil profile, respectively.
[b]Numbers in parenthesis are the standard errors of the means.

infiltration of snowmelt or rain. In the spring of 1995, more than 13 cm of rain fell from the day of initial thaw (12 March) to complete soil thaw (26 April). Although less than 0.5 cm of rain fell from the day of initial thaw (13 April) to complete soil thaw (3 May) in the spring of 1997, downward movement of metolachlor was likely aided by infiltration of snowmelt from a 45-cm thick snowpack. This snowpack potentially stored more than 11 cm of water based upon typical snowpack densities in western Minnesota.[18] This is in contrast to the thin snowpack (thinner than 15 cm during winter) and little precipitation (4 cm) received from the day of initial thaw (12 March) to complete thaw (6 May) in the spring of 1996. Although downward movement of metolachlor was detected during the thaw process in spring 1996 (Table 2), metolachlor below a depth of 6 cm had either degraded or moved up in the soil profile by the time of complete thaw. Water movement toward the soil surface in response to evaporation may have resulted in upward movement of metolachlor. Evaporative demand during spring thaw was accentuated in 1996 compared to the previous or subsequent year. For example, the effective evaporative demand (potential evaporation minus rainfall) from initial thaw to complete thaw in spring was 9 cm in 1996 compared to 1 cm in 1995 and 7 cm in 1997. Changes in soil water content during winter caused by infiltration or evaporation did not appear to influence metolachlor redistribution within the soil profile. An increase in soil water content was observed to a depth of at least 50 cm during all winters (Figure 4). Total water contained within the soil profile also increased over all winters. Although water is the primary transport mechanism by which chemicals move in the soil profile, the timing and magnitude of infiltration events also influence chemical movement.

Loss over Winter

Loss of metolachlor occurred during the winters of 1995–1996 and 1996–1997, but no loss was apparent during the 1994–1995 winter (Tables 1–3). Loss of metolachlor likely resulted from microbial degradation and not from leaching or surface runoff. Leaching was not evident since metolachlor was not detected below a depth of

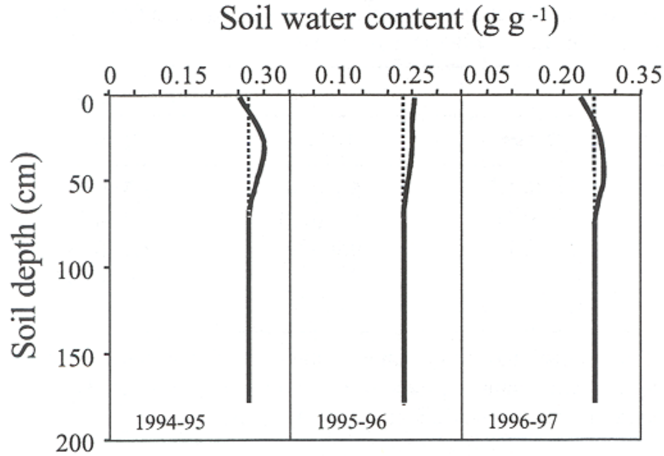

Figure 4. Water content in the soil profile at the time of application of metolachlor in autumn (dash line) and at complete thaw in spring (solid line).

8 cm and leachate did not appear in the larger diameter plastic pipes. Our experiment was designed to minimize runoff from the soil column by installing the columns with the top of the column protruding 1 cm above the surrounding field soil. Degradation of metolachlor was most apparent during spring thaw, but was also evident in autumn (Tables 2 and 3). Approximately 30 and 25% of metolachlor was lost (degraded) by the spring of 1996 and 1997, respectively. Microbial degradation is most likely to occur during spring thaw as a result of a burst in microbial activity as soils thaw.[19] Little or no degradation was apparent when the soil remained frozen; this was exemplified by the nearly same recovery of metolachlor after the time of freeze-up as at the time prior to initial thaw in spring (Table 3).

CONCLUSION

Some agricultural herbicides applied in autumn can potentially aid in controlling early spring weed infestations and minimizing the number of field operations in spring. Autumn application of metolachlor may be a viable management option for producers in the northern Corn Belt because little downward movement and loss occurred from a clay loam profile over three consecutive winters in west central Minnesota. Over winter movement of metolachlor was restricted to within 3 cm of the zone of application and largely occurred in spring as a result of infiltration of snowmelt or rain. Loss of metolachlor primarily occurred during spring thaw and was likely due to microbial degradation. Although the results of this study are encouraging in minimizing metolachlor loss from soils, further research is warranted on the over winter movement of metolachlor in soils with a range of physical properties and subject to various tillage management practices.

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