Residue detections in soil and shallow groundwater after long-term herbicide applications in southern Alberta

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Contribution No. 3879385. Received 14 June 1994, accepted 11 April 1995.

Miller, J. J., Hill, B. D., Chang, C. and Lindwall, C. W. 1995. **Residue detections in soil and shallow groundwater after long-term herbicide applications in southern Alberta.** Can. J. Soil Sci. **75**: 349–356. After herbicide applications for 1-24 yr, there were no detectable residues of glyphosate, dicamba, 2,4-D, bromoxynil or **methylchlorophenoxyacetic acid (MCPA)** in soil at two long-term tillage sites and one long-term manured site. The only detectable residues in soil were of diclofop and triallate. Residues of bromoxynil, diclofop and MCPA but not dicamba, 2,4-D or triallate, were detected in the groundwater at the manured site. Diclofop was detected in 6% and bromoxynil and MCPA in 2% of 84 water samples collected at the manured site. Maximum concentrations of bromoxynil (6.5 μg L^{-1}) and diclofop (47 μg L^{-1}) in the groundwater at the manured site exceeded levels set by the Canadian drinking water guidelines. Long-term application of herbicides has not caused accumulation of harmful residues in southern Alberta soils, but the presence of certain herbicides in the groundwater at concentrations above the level set by the drinking water guidelines is cause for concern.

Key words: Herbicide residues, tillage, manure, soil, groundwater

Miller, J. J., Hill, B. D., Chang, C. et Lindwall, C. W. 1995. **Détection des résidus dans le sol et dans la nappe superficielle à la suite de traitements herbicides de longue durée dans le sud de l'Alberta.** Can. J. Soil Sci. **75**: 349–356. Au terme d'années de traitements herbicides allant de 1 à 24 ans, on n'a observé aucun résidus décelables de glyphosate, de dicamba, de 2,4-D, de bromoxynil et de MCPA dans le sol à deux emplacements d'essais de longue durée de méthodes de travail du sol ainsi qu'à un emplacement d'essai de fumure organique. Les seuls résidus détectables dans le sol étaient ceux du dicloflop et du triallate. En outre, des résidus de bromoxynil, de diclofop et de MCPA étaient détectés dans la nappe phréatique à l'emplacement d'essai de fumure organique. Les concentrations maximales de bromoxynil (6,5 μg L^{-1}) et de diclofop (47 μg L^{-1}) dans la nappe à cet emplacement dépassaient les doses maximales fixées au Canada pour l'eau potable. On peut dire en conclusion que si les traitements herbicides de longue durée n'ont pas provoqué d'accumulation de résidus dangereux dans les sols du sud de l'Alberta, la présence de certains herbicides dans la nappe libre à des concentrations dépassant les doses admises dans l'eau potable demeure un sujet de préoccupation.

Mots clés: Résidus d'herbicides, méthode de travail du sol, fumier, sol, nappe

Repeated annual applications of commonly used herbicides to Canadian soils, under typical agronomic practices, have raised concerns about possible accumulation of residues in soils (Smith 1982) and leaching of these residues into the groundwater (Logan et al. 1991). Previous studies at long-term agricultural sites in Canada where different chemicals were repeatedly applied for 4-35 yr, found no significant accumulation of herbicides in soils (Smith 1982; Smith et al. 1991). These studies, however, did not examine possible residue accumulation of commonly used herbicides, such as bromoxynil, dicamba, diclofop, glyphosate and triallate, or the persistence of these herbicides under agricultural practices such as long-term conventional and conservation tillage, and long-term manure application.

Successful weed control during summerfallow periods or between crops in continuous cropped systems in North America requires three to five applications of paraquat or glyphosate, alone or in combination with 2,4-D, dicamba or bromoxynil (Brandt and Kirkland 1980; Lindwall and Anderson 1981). In-crop weed control (e.g., 2,4-D, diclofop-methyl, MCPA) is similar for crops seeded under conventional and conservation tillage, with the exception of soil-incorporated herbicides (e.g. triallate), which are generally not used under conservation tillage systems (Moyer et al. 1994).

Manure from cattle feedlots in southern Alberta is often applied to agricultural land, particularly to irrigated soils. Manure increases the organic matter content of soils, particularly the surface 30 cm (Sommerfeldt et al. 1988). The higher the organic matter content in soils, the greater is the adsorption of most pesticides (Yaron et al. 1985). The traditional concept of pesticide-organic matter interaction is that pesticide adsorption by organic matter concentrates pesticides near the soil surface, thereby decreasing the opportunity for leaching (Wagenet 1987). Few studies have examined field persistence of commonly used herbicides after repeated application to manured land.

The objective of this study was to determine whether there was residue accumulation and subsequent leaching into the groundwater after long-term herbicide application under agricultural practices in southern Alberta. We focussed our monitoring on two sites under conventional and conservation tillage and one site under long-term manure application.

MATERIALS AND METHODS

One site at Lethbridge and another at Carmangay, 60 km northwest of Lethbridge, Alberta, were used to investigate herbicide persistence in soil under long-term tillage practices. A third site at Lethbridge was used to examine herbicide persistence under long-term manure application. The topography of the Lethbridge site is uniform, and the slope of the land is < 1%, whereas the Carmangay site is undulating to inclined with slopes ranging from 2 to 3%. The Lethbridge plots (randomized complete block) are in a cereal-summerfallow rotation as part of a tillage experiment established in 1967 (Lindwall and Anderson 1981). A comparison of tillage and no tillage under continuous cropping and a crop-fallow rotation (randomized complete block) was initiated at Carmangay in 1979.

Soil textures at the Lethbridge site (0-120 cm depth) are clay loam (Chang and Lindwall 1989), and organic C values of surface (0-30 cm) soils are 1.7, 1.6 and 1.4% in the no-till, minimum tillage and conventional tillage plots, respectively (Dormaar and Lindwall 1989). Soil textures (hydrometer method) at the Carmangay site range from silty clay to clay (0-40 cm depth), and clay to heavy clay (40-80 cm depth). Organic C values, as determined by the difference of total C (automated combustion technique using Carlo Erba® Analyzer method) minus inorganic C (Amundson et al. 1988) of surface soils (0-20 cm), are 1.3, 1.3, 1.5 and 1.6% in the tilled fallow, no-till fallow, tilled continuous cropped, and no-till continuous cropped plots at Carmangay, respectively.

The tillage plots at Lethbridge were in summerfallow during 1991 and were subject to three tillage treatments: (1) conventional tillage or blade-only weed control and seedbed preparation by three to four passes yr^{-1} with a wide-blade (150-cm sweeps) cultivator at a depth of 90 mm or less; (2) minimum tillage or herbicide/fall blade weed control using herbicides and a single wide-blade cultivation in the fall; and (3) no-till weed control by herbicide only. The fallow plots at Carmangay were subjected to two tillage treatments: (1) conventional tillage using three or four passes yr^{-1} with either a heavy-duty cultivator and rod-weeder, or a wide-blade cultivator; and (2) no-till weed control using only herbicides. Since 1967 (Lethbridge) and 1979 (Carmangay) bromoxynil, diclofop-methyl and 2,4-D have been used when required for in-crop weed control, and glyphosate, dicamba and 2,4-D have been used for chemical summerfallow during non-crop periods (Table 1). Triallate, applied only at Carmangay, was broadcast on but not incorporated in the no-till plots.

In September 1991, soil cores were collected in 20-cm depth increments to 80 cm from three locations within each of the nine plots (three tillage treatments × three replicates) at Lethbridge, and the 12 plots (two tillage treatments × two crop rotations × three replicates) at Carmangay. The dimensions of the Lethbridge plots were 6.1 × 19.8 m; the Carmangay plots were 12 × 55 m (crop-fallow) and 6 × 45 (continuous cropped). Soil samples were collected using a truck-mounted Giddings drill, and composited into one sample for each depth increment in each plot. The stainless-steel core tubes (44.5 mm i.d.) were cleaned with brushes, rinsed in distilled water, and air-dried after each sample. Seventy-two soil samples from the two tillage sites (36 samples from each site) were collected in plastic bags, transported to the Lethbridge Research Centre in a portable cooler (4°C), and stored at -40°C.

Table 1. History of long-term herbicide applications at three sites in southern Alberta

Herbicide	Rate (g a.i. ha^{-1})	Years applied^z	Total number of yearly applications
Lethbridge tillage plots			
Bromoxynil	338-639	1967-1990	24
MCPA	398	1967-1984	17
Diclofop-methyl	404-781	1976, 1980, 1986, 1990	4
2,4-D	104-915	1976-1989	13
Glyphosate	61-890	1977, 1979, 1980, 1987, 1989, 1991	6
Dicamba	124-156	1974, 1981, 1986	3
Carmangay tillage plots			
Bromoxynil	338-596	1979-1988	9
MCPA	398-596	1979-1983	4
Diclofop-methyl	795-1069	1982-1988	7
2,4-D	320-517	1980-1989	10
Glyphosate	267-1517	1980-1987	8
Dicamba	120-168	1983-1989	7
Triallate	910	1989	1
Lethbridge manure plots			
Bromoxynil	338	1980-1991 (except 1981)	11
MCPA	336	1991	1
Diclofop-methyl	710-781	1980-1991 (except 1981, 1987)	10
Triallate	1350	1990	1

^{z}Soil and groundwater samples for the present study were taken in 1991, after any herbicide applications made in 1991.

A long-term (since 1973) manured site at the Lethbridge Research Centre was used for investigation of herbicide persistence in soil and possible leaching of residues into the groundwater. Details of the experimental layout (Fig. 1) and the manure used in this study were previously described (Sommerfeldt and Chang 1985). Manure was applied at 0, 30, 60 and 90 Mg ha^{-1} and 0, 60, 120 and 180 Mg ha^{-1} (wet wt.) to the nonirrigated and irrigated soils, respectively. The amounts were equal to one, two and three times the recommended rates (Alberta Agriculture 1980) for this soil type, under nonirrigated and irrigated conditions. Barley (*Hordeum vulgare* L. 'Galt') was grown annually on the plots under conventional tillage practices. Soil textures (hydrometer method) at the manure site (15-180 cm depth) range from sandy clay loam to clay loam. Organic C values of surface (0-15 cm) soil, estimated from percentage organic matter values (Chang et al. 1991), are 1.2, 1.7, 2.1 and 2.6% for the 0, 30, 60 and 90 Mg ha^{-1} treatments under dryland; and 1.3, 2.3, 3.6 and 4.6% for the 0, 60, 120 and 180 Mg ha^{-1} treatments under irrigation. Approximately 33 mm of water was applied to the irrigated plots on 16 July, and 51 mm on 19 July. Bromoxynil and diclofop-methyl have been used for weed control since 1980, and MCPA and triallate have been used only recently (Table 1).

Instrumentation installed as part of other ongoing studies at the manured plots was used for this investigation. Twenty-two water-table wells (2.54-5.08 cm i.d.) of perforated (to within 1 m of soil surface) polyvinyl-chloride

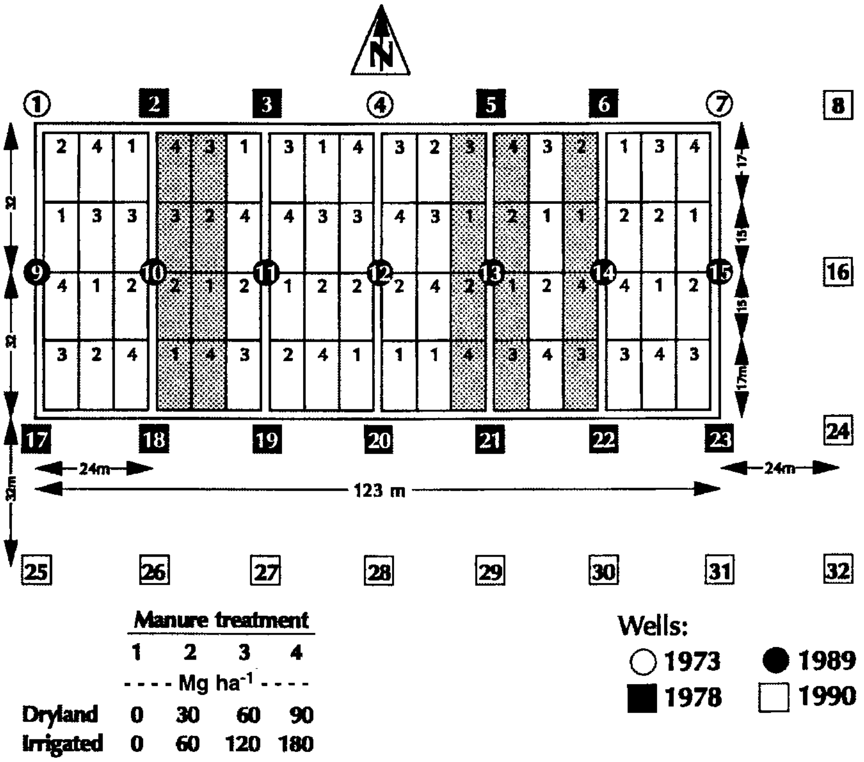

Fig. 1. Experimental design of manure plots at Lethbridge and location of monitoring wells. Shaded plots are those used in this study. Irrigated plots are on east half and dryland plots on west half of study site.

(PVC) pipe were installed in 1973, 1978, 1989 and 1990 within or adjacent to the plot area, and 3.81 cm (i.d.) perforated stainless-steel pipes were installed within 1 m of three of the PVC wells (Wells #5, 13 and 21) in the spring of 1991 (Fig. 1). All wells were installed using a solid-stem, continuous-flight auger to a depth of approximately 6.1 m below the ground surface. The annulus was backfilled with soil, and a cement or bentonite plug was inserted near the ground surface to prevent infiltration of surface water.

On 28 May, 11 June, 3 and 15 July, 7, 19, 20 and 23 August and 24 September 1991, 84 groundwater samples in total were collected from the manured plots in 1-L polyethylene (high density) bottles with aluminum-lined caps or in 1-L amber-glass bottles with teflon-lined caps. All bottles had been washed with soap and hot water, and rinsed with deionized water and acetone (pesticide grade). All wells were pumped dry the day before or on the day of sampling with a WaTerra® hand pump (Rice Engineering, Edmonton) or a copper or stainless-steel bailer, and samples were collected using a bailer. All groundwater sampling equipment was cleaned with water, and rinsed with distilled water before the next well was sampled. Groundwater samples collected in polyethylene bottles were stored at -40°C.

Soil from three replicates of the four manure treatments on irrigation and two replicates of each of the four manure treatments on dryland were sampled on 23 and 24 September 1991. Two sites in each plot were sampled and soil samples for each 20-cm depth increments were composited to a depth of 80 cm for each plot. Soil was sampled as described previously. Eighty soil samples were collected in plastic bags and stored at -40°C.

Water samples collected in glass bottles were stored at 4°C, and shipped to Edmonton in a portable cooler within 24 h of collection. Soil and water samples frozen at -40°C were stored for a maximum of 6 mo in Lethbridge. All soil and groundwater samples were transported to Edmonton, Alberta, in portable coolers (4°C) for analysis by Enviro-Test Laboratories. Storage stability studies indicated no significant degradation of the herbicides under the conditions of this study (Hill 1992). In Edmonton, frozen soil and water samples were stored at 20°C until extraction.

Herbicide residues (2,4-D, bromoxynil, dicamba, diclofop, MCPA and triallate) in soil were extracted using a double extraction procedure and analyzed by capillary column **gas chromatography (GC)** and **mass spectrometry (MS)** using **selected ion monitoring (SIM)** as described by Bruns et al. (1991).

Glyphosate and its metabolite, **aminomethylphosphonic acid (AMPA)**, were extracted and analyzed using chelation ion exchange, with subsequent quantitation by **high pressure liquid chromatography (HPLC)** with postcolumn reaction detection (Cowell et al. 1986). Approximately 50 g of soil was shaken with 150 mL of 0.3 M KOH at 60°C. After centrifuging, a 130-mL aliquot was placed in a 250-mL separatory funnel, the pH was adjusted to approximately 3 and the aliquot was partitioned into 50-mL of **dichloromethane (DCM)**. The DCM was discarded, and the aqueous layer was adjusted to pH 2.0 ± 0.4 and eluted through a Chelex 100 column. The eluent was discarded, and the adsorbed material was washed with 50 mL water and 100 mL HCl (0.2 M). After 27 mL HCl (6 N) was added to the column, 7 mL of eluent was discarded. The remaining eluent was mixed with 12 mL of concentrated

HCl, and added to an AG1-X8 column and the column was eluted with 10 mL HCl (6 M). All eluent batches were collected and concentrated to 2 mL with 5% MeOH/water. All samples were analyzed by HPLC/fluorescence using post-column derivatization and column switching. The HPLC operating conditions consisted of two Aminex A-9K (Bio-Rad Labs., Richmond, CA) ion exchange columns, a mobile phase of 4% MeOH and 0.005 M KH_2PO_4 (pH 2.1) at a flow rate of 0.6 ml min^{-1}, a detector sensitivity of 0.010 absorbency units, and an excitation wavelength of 230 nm.

Herbicide residues (2,4-D, bromoxynil, dicamba, diclofop, MCPA and triallate) in groundwater were determined using the following method adapted from Bruns et al. (1991). Each water sample was thawed and approximately 800-900 mL transferred to a 1-L separatory funnel. The pH was adjusted to 3 with H_2SO_4 (3 M), and the sample was extracted twice with dichloromethane and dried through acidified Na_2SO_4. The sample was concentrated to 1 mL using a rotary evaporator. After esterification with diazomethane, the extract was analyzed on a Hewlett-Packard 5971 mass-selective ion detector using a DB 1701 J & W column.

About 50 g of untreated soil from the study sites and 800-900 mL of tap water were fortified with 25-150 µL herbicide mix standard and allowed to equilibrate for 1 h. Soil was analyzed by the double extraction procedure (Bruns et al. 1991) and groundwater by the method described above. Recoveries on fortified (5-1000 µg kg^{-1}) soil samples ranged from 80.4 to 101% (SE = 2.1-12.5%, n = 9). The **minimum quantifiable limit (MQL)** based on fortified soil samples was 5 µg kg^{-1}, except for glyphosate and AMPA, where the MQL was 10 µg kg^{-1}. Recoveries on fortified (0.25-2.0 µg L^{-1}) water samples ranged from 86.8 to 97.9% (SE = 3.4-4.7%, n = 10). The MQL based on fortified water samples was 0.25 µg L^{-1}. The soil extraction method was considered appropriate for our weathered field samples because it had been previously validated and good recoveries have been mobtained using other aged soil samples (G. Bruns 1995, pers. commun.). The exhaustive double-extraction [overnight shaking in an acid medium followed by an ultrasonic extraction in KOH/H_2O as per Bruns et al. (1991)] ensured maximum recoveries for aged samples.

RESULTS AND DISCUSSION

Despite their use for 1-24 yr, residues of dicamba, 2,4-D, bromoxynil, MCPA and glyphosate were not detected in any soil samples at the three study sites (Tables 2, 3 and 4). This finding agrees with previous reports of low persistence of dicamba (Stewart and Gaul 1977), 2,4-D and MCPA (Smith et al. 1991) and bromoxynil (Smith 1980). Glyphosate had been recently applied (4 July 1991) to minimum till plots at Lethbridge, but was not detected in our samples, which is consistent with an average half-life in soil of < 30-40 d (Smith and Aubin 1993). The glyphosate metabolite, AMPA, was not detected at either tillage site.

After application of diclofop for 4-10 yr, its residues were detected in soil samples from all three sites (Tables 2, 3 and 4). Diclofop residues were detected in 3% (Lethbridge tillage site), 6% (Carmangay tillage site) and 5% (Lethbridge manured site) of soil samples. The greater persistence of diclofop is consistent with the finding of Smith et al. (1986). Although they reported rapid and complete hydrolysis of diclofop-methyl ester to diclofop acid within 9 d of application, diclofop acid underwent slow breakdown in the field soil, with 19% remaining after 126 d after application. Except for one sample detection at depth (60-80 cm) at the Lethbridge tillage plot, diclofop residues were restricted to the 0-20 cm or 20-40 cm depth at the other two sites. Residues in the soil, particularly at shallow depths, are likely indicative of solute transport through small soil pores (matrix flow) rather than preferential flow through macropores.

Triallate residues were detected in 14% of soil samples from the Carmangay plots 2 yr after a single granular application in the fall of 1989 (Table 3), as well as in 11% of soil samples from the manured plots 1 yr after a single granular application in the fall of 1990 (Table 4). Residues of triallate are carried over in field soils to the next crop year, particularly when granular formulations are applied (Smith 1982). Field persistence studies on triallate in Saskatchewan found that 12-23% of the initial triallate applied persisted in a surface soil after 20 wk (Smith 1979). Triallate residues were found at the Carmangay tillage plots (60-80 cm depth) and the Lethbridge manured plots (40-60 cm depth), suggesting leaching of this

Table 2. Herbicide concentration in soil under three tillage treatments at Lethbridge

Treatment	Depth (cm)	Herbicide (µg kg^{-1} soil)[z]					
		Dicamba	2,4-D	Bromoxynil	MCPA	Diclofop	Glyphosate
Conventional tillage	0-20	<5	<5	<5	<5	<5	<10
	20-40	<5	<5	<5	<5	<5	<10
	40-60	<5	<5	<5	<5	<5	<10
	60-80	<5	<5	<5	<5	9.7±9.7[y]	<10
Minimum tillage	0-20	<5	<5	<5	<5	<5	<10
	20-40	<5	<5	<5	<5	<5	<10
	40-60	<5	<5	<5	<5	<5	<10
	60-80	<5	<5	<5	<5	<5	<10
No tillage	0-20	<5	<5	<5	<5	<5	<10
	20-40	<5	<5	<5	<5	<5	<10
	40-60	<5	<5	<5	<5	<5	<10
	60-80	<5	<5	<5	<5	<5	<10

[z] Oven-dry basis.

[y] Mean of 3 samples ± standard error; 3% of 36 soil samples had detectable concentrations of one or more herbicides.

Table 3. Herbicide concentration in soil under two cropping practices and two tillage treatments at Carmangay

Treatment	Depth (cm)	Herbicide (μg kg^{-1} soil)[z]					
		Dicamba	2,4-D	Bromoxynil	Triallate	Diclofop	Glyphosate
				Crop-Fallow			
Conventional tillage	0-20	<5	<5	<5	24.5±8.9*a*[y]	<5	<10
	20-40	<5	<5	<5	<5	<5	<10
	40-60	<5	<5	<5	<5	<5	<10
	60-80	<5	<5	<5	<5	<5	<10
No tillage	0-20	<5	<5	<5	44.4±20.4*a*	<5	<10
	20-40	<5	<5	<5	<5	<5	<10
	40-60	<5	<5	<5	<5	<5	<10
	60-80	<5	<5	<5	5.6±5.6	<5	<10
				Continuous cropped			
Conventional tillage	0-20	<5	<2	<5	94.9±59.0*a*	14.2±3.7*a*	<10
	20-40	<5	<2	<5	<5	<5	<10
	40-60	<5	<2	<5	<5	<5	<10
	60-80	<5	<2	<5	<5	<5	<10
No tillage	0-20	<5	<2	<5	28.0±11.1*a*	4.8±2.4*a*	<10
	20-40	<5	<2	<5	<5	<5	<10
	40-60	<5	<2	<5	<5	<5	<10
	60-80	<5	<2	<5	<5	<5	<10

[z] Oven-dry basis.

[y] Mean of 3 samples ± standard error; 14% of 36 soil samples had detectable concentrations of one or more herbicides.

a Means (for each herbicide at the same depth within each crop rotation) followed by the same letter are not significantly different at $P = 0.05$ level.

herbicide. Although the solubility of triallate is relatively low (4 mg L^{-1}), long persistence (210 d) affords opportunity for this herbicide to leach to lower depths (Table 5).

The detections of diclofop and triallate but not glyphosate, MCPA, 2,4-D, bromoxynil or dicamba in the soil at the three sites are consistent with the relatively strong adsorption (high Koc values) and long persistence times (high $t_{1/2}$ values) of these two herbicides in soils (Table 5). Soil organic matter is the major factor controlling adsorption of most herbicides in soils (Yaron et al. 1985). Organic matter, however, has little effect on adsorption of glyphosate because as an acid, glyphosate undergoes ionic rather than hydrophobic interactions with soil and is adsorbed at positively charged sites on clay minerals (Reinert 1989) via the phosphoric acid moiety (Torstensson 1985).

Tillage and manure treatment effects among soil samples could not be discerned in this study because of the considerable number of non-detectable residues and because of the high standard error or variability between replicates that was caused by the small number (2-3) of cores sampled per plot. Future studies investigating these treatment effects should attempt to ensure detectable residues in the soil and should take more samples per plot to minimize the standard error.

Residues of bromoxynil, diclofop and MCPA but not dicamba, 2,4-D and triallate were detected in the groundwater at the manured site (Fig. 2). Diclofop was detected in 6% and bromoxynil and MCPA in 2% of the 84 water samples collected. This finding is consistent with the high solubilities of diclofop and MCPA and, to a lesser extent, bromoxynil (Table 5). The detection of diclofop in the groundwater, but not below the 40-cm depth in soil (Table 4), suggests the possibility of preferential flow through soil macropores and illustrates the insights gained by sampling both soil and groundwater. Manure treatment effects could not be discerned among the wells because of their location along the borders of the plots and because of the small size of the plots.

Maximum concentration of MCPA in the groundwater (8.9 μg L^{-1}) was in a well (well 28) adjacent to the plots on 3 July 1991 (Fig. 2). The Canadian drinking water guideline for MCPA is currently under development; however, the interim guideline for livestock water is 25 μg L^{-1} (P. Yves Caux 1994, pers. commun.). The maximum concentration of bromoxynil (6.5 μg L^{-1}) in a well (well 28) adjacent to the plots on 3 July 1991 exceeded the Canadian drinking water guideline of 5 μg L^{-1}. The maximum concentration of diclofop in groundwater (47 μg L^{-1}) in a well (well 14) within the irrigated plots on 15 July 1991, was above the Canadian drinking water guideline of 9 μg L^{-1} (Canadian Council of Resource and Environment Ministers 1987). MCPA, bromoxynil and diclofop were also detected in shallow groundwater at other irrigated sites in southern Alberta, and in some cases diclofop exceeded the level set by the Canadian drinking water guideline (Rodvang et al. 1992).

MCPA and bromoxynil applied to the manure plots might be expected to move with the groundwater toward well 28, because the water table beneath the manure plots slopes toward this well (data not shown). Transport of these herbicides in surface runoff to this well would be unlikely because of the level relief at this site. The detection of MCPA and bromoxynil in wells on 3 July was likely related to their application on 18 June 1991, followed by 110 mm of rainfall between 19 and 30 June (Fig. 2). Water table levels in the plot area rose by about 1 m from 13 to 27 June 1991, indicating significant groundwater recharge.

Table 4. Herbicide concentrations in soil under different manure treatments in dryland and irrigated plots at Lethbridge

Manure Treatment (Mg ha^{-1})	Depth (cm)	Herbicide (μg kg^{-1} soil)[z]			
		MCPA	Bromoxynil	Triallate	Diclofop
				Dryland	
0	0-20	<5	<5	97.2±6.2*a*[y]	5.6±5.6*a*
	20-40	<5	<5	<5	<5
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5
30	0-20	<5	<5	65.5±39.0*a*	8.1±1.1*a*
	20-40	<5	<5	<5	<5
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5
60	0-20	<5	<5	123.6±11.2*a*	<5
	20-40	<5	<5	<5	<5
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5
90	0-20	<5	<5	66.0±66.0*a*	6.7±0.5*a*
	20-40	<5	<5	<5	7.7±7.7
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5
				Irrigated	
0	0-20	<5	<5	61.8±43.7*a*	<5
	20-40	<5	<5	<5	<5
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5
60	0-20	<5	<5	145.2±61.9*a*	<5
	20-40	<5	<5	<5	<5
	40-60	<5	<5	32.6±32.6	<5
	60-80	<5	<5	<5	<5
120	0-20	<5	<5	534.1±116.1*b*	<5
	20-40	<5	<5	<5	<5
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5
180	0-20	<5	<5	305.8±70.5*ab*	<5
	20-40	<5	<5	<5	<5
	40-60	<5	<5	<5	<5
	60-80	<5	<5	<5	<5

[z] Oven-dry basis.

[y] Mean of 2 (dryland) or 3 (irrigated) samples ± standard error; 13% of 80 soil samples had detectable concentrations of one or more herbicides.

a,b Means (for each herbicide at the same depth within each dryland or irrigation treatment) followed by the same letter are not significantly different at $P = 0.05$ level.

Table 5. Solubility, adsorption to organic C (log K_{oc}), and half-lives ($t_{1/2}$) of herbicides examined in this study

	Solubility (mg L^{-1})	Log K_{oc}	$t_{1/2}$ (d)
Diclofop	122 700[z]	2.4[y]	14-21 (SL); 21-28 (HvC); >70 (SiC)[x]
Glyphosate	15 700[w]	NA[v]	<30-40[u]
Dicamba	4 500[w]	0.5[t]	<14[w]
MCPA	800-1 600[s]	2.0[r]	<7-14; 14-41[p]
2,4-D	900[w]	1.3[o]	<7-20;q 11-31[p]
Bromoxynil	130[w]	1.7[n]	14[m]
Triallate	4[w]	3.4[o]	210[l]

[z] Cessna et al. (1994); buffered at pH 7.0.

[y] Görlitz and Erzgräber (1992).

[x] Smith (1977); SL, sandy loam; HvC, heavy clay; SiC, silty clay.

[w] Weed Science Society of America (1994).

[v] NA, not applicable; glyphosate not adsorbed to organic carbon.

[u] Smith and Aubin (1993).

[t] Grover and Smith (1974).

[s] Sirons et al. (1982).

[r] Kenaga (1980).

[q] Smith et al. (1991).

[p] Foster and McKercher (1973).

[o] Wauchope et al. (1992).

[n] Estimated from solubility and melting point using eq. 13 of Karickhoff (1981).

[m] Royal Society of Chemistry (1986).

[l] Estimated from field persistence data (23-75% remaining after 30 wk) of Smith (1975).

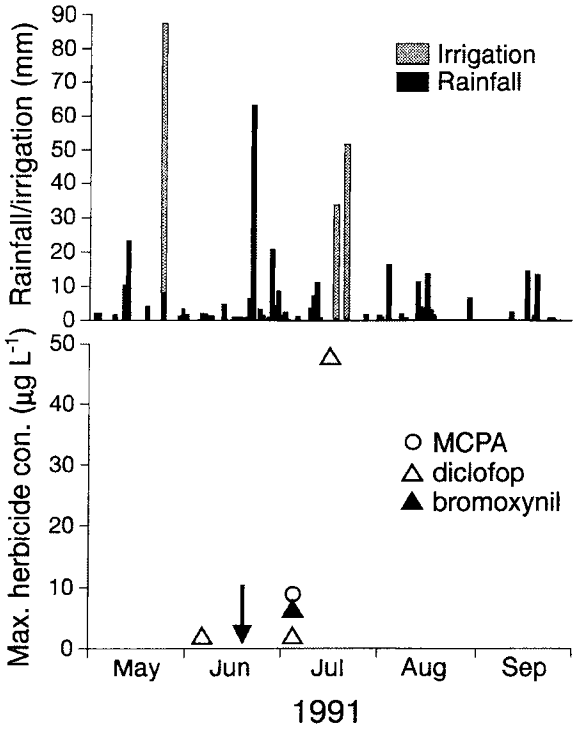

Fig. 2. Daily precipitation and irrigation from 30 April to 29 September 1991, at Lethbridge in relation to maximum herbicide concentrations in the groundwater. Vertical arrow indicates date of herbicide application (18 June). Ten percent of 84 water samples had detectable concentrations of one or more herbicides.

CONCLUSIONS

After repeated herbicide applications for 1-24 yr, there were no detectable residues of glyphosate, dicamba, 2,4-D, bromoxynil and MCPA in soil at the three sites. The only detectable residues in soil were of diclofop and triallate. Our findings support the claim that long-term application of commonly used herbicides under typical agricultural practices in Canada do not cause any significant residue accumulation in soils (Smith 1982). As noted by Smith, only repeated use of highly stable herbicides would lead to significant residue accumulation in soil. However, residues of MCPA, bromoxynil and diclofop in the shallow groundwater at the manured plots, with the concentrations of the latter two herbicides exceeding the levels set by the Canadian drinking water guidelines in some samples, is cause for concern, and may indicate that certain herbicides bypass the soil profile by rapid leaching in macropores. We recommend that future monitoring studies sample both the soil and the groundwater to account for possible macropore flow.

ACKNOWLEDGMENTS

This study was funded by the Environmental Sustainability Initiative of the Prairie Farm Rehabilitation Administration (PFRA). We are grateful to Brian Lamond and Dale Campbell for field sampling, and to the staff of the Land Evaluation and Reclamation Branch of Alberta Agriculture, Food and Rural Development for their assistance.

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