

HERBICIDE DYNAMICS IN PRAIRIE WETLANDS

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By

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ABSTRACT

Prairie wetlands are affected by agricultural activities, in particular herbicide contamination of wetland ecosystems. The environmental fate of herbicides in wetlands is determined by their persistence and transport. Currently, little is known about the persistence of commonly used herbicides in wetland water and sediment. The objective of this dissertation was to determine the importance of wetland sediments in influencing the fate of commonly used herbicides in prairie wetlands.

Sediment sorption is an important dissipation pathway for herbicides. The effects of land use on physicochemical properties of wetland sediment, and the associations between these properties and herbicide sorption characteristics for four herbicides (trifluralin, atrazine, 2,4-D and glyphosate), were examined for 17 wetlands. The sorption of herbicides in sediment increased in the order of 2,4-D < atrazine < glyphosate < trifluralin. Overall, sediments from wetlands that were recently cultivated had lower total organic carbon (TOC), total inorganic carbon (TIC), electrical conductivity (EC), exchangeable cation (EXCAT), cation exchangeable capacity (CEC), and sorption coefficient (K_d) values (2,4-D, trifluralin, and atrazine) than sediments from semi-permanent and riparian ephemeral wetlands. Although TOC content was correlated to the sorption of 2,4-D, trifluralin and atrazine, riparian wetland sediments despite having a lower TOC content than semi-permanent wetland sediments, had the highest herbicide sorption capacity for 2,4-D, trifluralin and atrazine.

To further examine the link between land use and herbicide sorption by sediment, a multi-residue analytical method was developed to quantify seven sulfonylurea herbicides commonly used in crop production (thifensulfuron-methyl, tribenuron-methyl, ethametsulfuron-methyl, metsulfuron-methyl, rimsulfuron, nicosulfuron and sulfosulfuron) in sediment from 17 wetlands. Sediment was extracted with deionized water using pressurized liquid extraction and the resultant extracts were cleaned-up using Oasis HLB solid-phase extraction cartridges. Quantification and confirmation were performed using liquid chromatography interfaced with positive ion electrospray tandem mass spectrometry, and multiple reaction monitoring. Calibration curves were linear with correlation coefficients greater than 0.994 and limits of quantification ranged from 1.0 to 2.0 $\mu\text{g kg}^{-1}$. Ethametsulfuron-methyl, sulfosulfuron

and metsulfuron-methyl, the three most environmentally persistent of the seven sulfonylurea herbicides monitored in this study, were most frequently detected in wetland sediment. The concentrations of sulfonylurea herbicides were higher in sediments from the semi-permanent wetland, which received surface runoff from a larger catchment.

To assess the relationship between herbicide dissipation and sorption to sediment, seven commonly used herbicides (glyphosate, dicamba, bromoxynil, 2,4-D, MCPA, mecoprop-P and dichlorprop) were applied to one half of an ephemeral (E) and a semi-permanent (SP) prairie wetland to mimic a direct overspray event, a worst-case scenario for wetland contamination. Water and sediment samples collected over a 77-d study period (early June to late August) were analyzed for herbicide concentration; aminomethylphosphonic acid (AMPA), the degradation product of glyphosate, was also monitored. Glyphosate dissipated rapidly in the water column of each wetland with DT_{50} values of 3.7 d for wetland E and 6.9 d for wetland SP. The mass of AMPA in each wetland increased with a concomitant decrease in the mass of glyphosate, suggesting that glyphosate degradation was occurring in the water column. In addition, glyphosate was also lost from the water column via sorption to bottom sediment, as evidenced by its detection in sediment samples up to 42-d post-treatment (39.0 – 224.5 $\mu\text{g kg}^{-1}$). The DT_{50} of the other six acid herbicides ranged from 2.3 d (bromoxynil) to 31 d (dichlorprop). The two chiral herbicides, mecoprop-P and dichlorprop, were the most persistent acid herbicides in the water column. Sorption to sediment was also an important dissipation route for these six herbicides in water, especially in wetland E. After 77 d in the semi-permanent wetland and 56 d in the ephemeral wetland, the concentrations of bromoxynil, dicamba and 2,4-D were below the Canadian Water Quality Guidelines for the Protection of Aquatic Life. Concentrations of the more persistent herbicides (mecoprop-P and dichlorprop) remained at levels above the guidelines.

Use of bromide ion as a conservative tracer indicated that some of the water loss from both wetlands was via infiltration. Because there was a strong correlation between the decrease in bromide ion and herbicide mass in the water column, it is possible some herbicides were lost from the water column along with the infiltrating water. Infiltration

to wetland margins during this part of the growing season would have been largely driven by the riparian vegetation surrounding both wetlands.

Overall, this thesis demonstrated the importance of sediment in the dissipation of currently used herbicides in wetland ecosystems. Both laboratory sorption studies and whole-wetland experiments provided insights on the sorptivity of herbicides in sediment as well as their persistence in water and sediment.

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LIST OF ABBREVIATIONS

AMPA	aminomethylphosphonic acid
CEC	total cation exchange capacity
E	ephemeral
E4G	ephemeral wetlands in a grassland catchment established 4 years ago
E20G	ephemeral wetlands in a brome grass catchment established 20 years ago
EC	electrical conductivity
ECNR	ephemeral wetlands with no riparian vegetation zone in a cultivated catchment
ECR	ephemeral wetlands with riparian vegetation in a cultivated catchment
EXCAT	exchangeable cation
<i>K_d</i>	sorption coefficient
<i>K_{oc}</i>	herbicide sorption per unit organic carbon
LC/MS/MS	liquid chromatography tandem mass spectrometry
LOQ	limit of quantification
MDL	method detection level
MRM	multiple reaction monitoring
<i>pK_a</i>	acid dissociation constant
PLE	pressurized liquid extraction
SP	semi-permanent
SPE	solid-phase extraction
SRM	single reaction monitoring
TIC	total inorganic carbon
TOC	total organic carbon content

1.0 INTRODUCTION

Wetland protection and preservation are essential to the biodiversity and ecosystem health of the Prairie Pothole Region of Canada, which may contain 1.6 to 4.0 million wetlands in any given year (Batt et al., 1989). The risk of herbicide contamination in wetlands located within agricultural fields is high and many studies have reported herbicide contamination in these important aquatic ecosystems (Donald and Syrgiannis, 1995; Donald et al., 1999; Donald et al., 2001; Donald et al., 2007; Grover et al., 1997; Waite et al., 2002; Waite et al., 2004).

Characteristics of wetland sediments will influence the distribution, transport, persistence of herbicides. Consequently, it is important to understand how sediment characteristics in various wetlands will affect these processes. The goal of this dissertation is to elucidate the importance of wetland sediments in influencing the fate of commonly used herbicides in wetlands. Aside from a single study published by Donald and Syrgiannis (1995) who investigated herbicide concentrations in wetland sediment, little is known about the role sediment plays in herbicide dissipation.

The objectives of this research were to:

- (a) Assess the effects of land use and riparian zone on the physicochemical properties of prairie wetland sediments, and determine the associations between these sediment properties and four herbicide sorption coefficients,
- (b) Develop extraction and analytical methods to determine seven sulfonylurea herbicides as well as six acid herbicides in wetland sediment,
- (c) Assess how land use practices affect the types and amounts of herbicides detected in sediments of prairie wetlands and,
- d) Using a whole-wetland study to determine dissipation routes of seven herbicides in two distinctly different wetlands.

Herbicide sorption to sediment will reduce the amount of herbicide loss via degradation (photolytic, chemical and microbial) and non-degradation (infiltration, volatilization and uptake by biota) pathways (Pionke and Chesters, 1973). The sorption coefficient (K_d) is used to compare the sorptivity of various herbicides by different matrices and K_d value is determined through batch equilibrium sorption experiments. The K_d value of most commonly used herbicides has been determined for various types of soils (Wauchope et al., 2002), and recently Gaultier et al. (2009) established 2,4-D sorption by sediment samples from 41 prairie wetlands. Generally, physicochemical properties that most influence herbicide sorption in soil are organic matter, clay and metal oxides. Herbicide sorption to these soil components has been well documented (Bailey and White, 1970; Farenhorst, 2006; Glass, 1987; Laird et al., 1994; Novak, 1999; Piccolo et al., 1996; Sannino et al., 1997). It is uncertain whether wetland sediment and soil differ in these physicochemical properties that affect herbicide sorption and it is also unclear if those properties are influenced by land use of wetland catchment and presence of riparian zone. Apart from carbon and sulfur characterization on wetland sediment by Jokic et al. (2003), little is known about the physicochemical properties of prairie wetland sediments. In Xu et al. (2009) (Chapter 3), the physicochemical properties of 13 wetlands are determined along with the K_d values for four herbicides (atrazine, 2,4-D, trifluralin and glyphosate).

The scarcity in literature related to herbicide residues in sediment is partly due to the complexity of the sediment matrix and lack of appropriate methodology for herbicide extraction and analysis. In Degenhardt et al. (2010b) (Chapter 4), a new analytical methodology is described for the extraction and analysis of seven sulfonylurea herbicides in wetland sediment. This methodology was used to quantify sulfonylurea herbicides residues from sediment samples collected from 17 wetlands across the prairies.

Due to reasons related to cost and logistics, whole wetland experiments are rarely used in studies to simulate pesticide dissipation in wetlands. Whole wetland experiments are more advantageous compared to mesocosm studies because the issues of appropriate scaling of sediment-water interactions, ensuring representative biodiversity, and simulating infiltration/recharge processes are avoided (Schindler,

1998). The last two research chapters (Chapter 5 and 6) present results from a whole-wetland study. Seven herbicides (glyphosate, dicamba, bromoxynil, 2,4-D, MCPA, mecoprop-P and dichlorprop) were added to the treated half of two distinctly different wetlands to mimic a direct over-spray event, representing the worst-case scenario for wetland contamination. Herbicide residues were monitored in the water as well as the sediment over a 77-d period. Glyphosate and its degradation product aminomethylphosphonic acid results are presented in Chapter 5 and the results of the other six acid herbicides are presented in Chapter 6.

Chapters 3 to 6 have been written as stand alone research papers that contain an appropriate literature review relevant to each paper. Chapter 2 provides a broader literature review on the subjects of this dissertation. Chapters 3 and 4 have been published in peer-reviewed journals and Chapters 5 and 6 have been submitted to a peer-review journal for publication. The final chapter (Chapter 7) presents an overall synthesis and conclusion of the results and implications for future research.

2.0 LITERATURE REVIEW

2.1 Pesticides

Pesticides are used extensively on the Canadian prairies for weed, insect and disease control. Because Canada is one of the few developed countries that do not require reporting of pesticides sales (Brimble et al., 2005), it is difficult to account for the type and amount of pesticides applied each year. This knowledge gap prevents our ability to assess environmental pesticide effects. Provincial governments in Saskatchewan and Manitoba do not collect pesticide sales data, although the Manitoba Agricultural Services Corporation has compiled a comprehensive pesticide use record for crop insurance purposes (Manitoba Agriculture Service Corporation, 2007). Saskatchewan is in the process of developing a similar database, but, because sales data are currently unavailable, I can only refer to primary literature and private consulting reports to determine pesticides used there.

Herbicides are the most frequently used pesticides in both Saskatchewan and Manitoba (Brimble et al., 2005). From 1996 to 2006, herbicide application in Manitoba accounted for approximately 95% of total pesticide applied to an equivalent of 19.0 million ha of land (Shymko et al., 2008). From 1996 to 2006, the top active ingredients applied to the greatest area of agricultural crops in Manitoba include: glyphosate (3.5 million ha), MCPA (3.1 million ha), bromoxynil (1.9 million ha), 2,4-D (1.0 million ha), thifensulfuron methyl (0.9 million ha) and tribenuron methyl (0.6 million ha). According to a private consulting report solicited by the Department of Fisheries and Oceans, most commonly used herbicides (based on amount applied) in Saskatchewan were (in decreasing order): ethalfluralin, glyphosate, MCPA, 2,4-D and bromoxynil (North/South Consultants Inc., 2003).

Much is known about herbicides and their mode of action. Some herbicides work by targeting a specific site, i.e. enzymes, while others work by targeting the photosynthetic systems or cell growth (Hall et al., 1999). Based on their mode of action and target sites, herbicides are classified into various groups. Often herbicides in the same group have the same application methods, constraints and toxicological profile. The herbicides investigated in this dissertation include herbicides from groups 2, 3, 4, 5, 6 and 9, and their respective target sites are listed in Table 2.1.

Because most herbicides are applied to plant foliage, the effectiveness of the herbicide in reaching the target site depends on its solubility and acid dissociation constant (pK_a) (Table 2.1). Solubility indicates how readily herbicides dissolve in water; and, pK_a measures the ease of the herbicide to hydrolyse or lose a proton (H^+) and become more soluble. Weak acids are those with pK_a values between -2 to 12 in water (Hall et al., 1999). Consequently, water solubility and pK_a values are the two important properties which determine herbicide movement in the environment. With the exception of trifluralin and atrazine, the herbicides under investigation in this dissertation are weak acids and relatively soluble in water (Table 2.1).

2.2 Herbicide contamination in aquatic environments

The Prairie Pothole Region, which encompasses over $777\,000\text{ km}^2$ of south central Canada and north central United States, has millions of water-holding wetlands of glacial origin (Sloan, 1972). Wetlands are important habitats and breeding grounds for waterfowl in North America; as much as 40–60% of annual waterfowl production depends on wetlands in the Prairie Pothole Region (Poiani and Johnson, 1991). Crop production is the predominant land use throughout this region. Currently used herbicides in surface waters (including wetlands) have been found in many studies. Those investigated in this dissertation are listed on Table 2.1. Some wetlands provide recharge to shallow groundwater and groundwater is often used for drinking water by local families (Donald et al., 2007). If wetlands are contaminated with herbicides which subsequently enter groundwater, human health related concerns result. Although few studies have found herbicide residue levels above the Canadian Water Quality Guidelines for the Protection of Aquatic Life set out by the Canadian Council of

Table 2.1. Classification of herbicides under investigation grouped by their mode of action and their chemical structure.

Group	Mode of action	Chemical family	Herbicides under investigation	Water solubility	<i>K_{oc}</i>	Vapour Pressure	<i>pK_a</i>	Product trade name
				mg L ⁻¹	mL g ⁻¹	mPa		
2	Acetolactate synthase (ALS) inhibitors	Sulfonylurea	ethametsulfuron-methyl	50 (pH 7)	85		4.6	Muster Gold
			metsulfuron-methyl	2790 (pH 7)	57	3.3×10^{-7}	3.3	Ally, Escort
			nicosulfuron	12200 (pH 7)	37	$<7.5 \times 10^{-2}$	4.6	Accent
			rimsulfuron	7300 (pH 7)	49	1.5×10^{-3}	4.0	Prism
			sulfosulfuron	1627 (pH 7)	33		3.5	Sundance
			thifensulfuron-methyl	6270 (pH 7)	28	1.7×10^{-5}	4.0	Harmony, Pinnacle
			tribenuron-methyl	280000 (pH 6)	52	5.2×10^{-5}	5.0	Express
3	Seedling root growth inhibitors	Dinitroaniline	Trifluralin	2 (pH 7)	4000/5120	6	–	Advance, Bonanza, Rival, Treflan
			2,4-D	311 (pH 1)	46/48	0.11	2.6	2,4-D
4	Growth regulators	Phenoxy acid	MCPA	734 (pH 7)	74/110	0.023	3.1	Dyvel, Curtail M
			Dichlorprop	350 (pH 7)	44/170	<0.01	3.0	Dichlorprop-D
			Mecoprop	734 (pH 7)	119	0.31	3.8	Compitox
			dicamba	6500 (pH 7)	5/13	4.5	1.9	Banvel
5	photosystem II inhibitors	Benzoic acid	atrazine	33 (pH 7)	93/147	0.039	1.7	Shotgun
6	Photosystem II inhibitors	Nitrile	bromoxynil	130 (pH 7)	202/190	<1	3.9	Pardner
9	5-enolpyruvyl-shikimate-3-phosphate (EPSP) synthase inhibitor		glyphosate	12000 (pH 7)	6920	<0.01	2.6, 5.6, and 10.3	Glyfos, Roundup, Vantage Plus

Table 2.2. Maximum concentrations detected of each herbicide in surface water surveillance studies conducted across Canadian prairies.

Herbicide Under Investigation	Study Location	Maximum Concentration Detected	References	Freshwater Aquatic Life Guideline [†]	Canadian Drinking Water Guideline [‡]
		($\mu\text{g L}^{-1}$)		($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)
2,4-D	Central SK	2.04	Donald et al. (2001)	4	100
	Central SK	4.13	Donald et al. (1999)		
	South-central SK	2.67	Grover et al. (1997)		
	South-central SK	5.8	Cessna and Elliott (2004)		
	South-central SK	0.43	Donald and Syrgiannis (1995)		
	Southern MB	1.85	Donald et al. (2007)		
	Southern MB	0.29	Rawn et al. (1999b)		
	South-central AB	1.24	Byrtus et al. (2004)		
Bromoxynil	Central SK	0.30	Donald et al. (2001)	5	5
	Central SK	0.15	Donald et al. (1999)		
	South-central SK	0.33	Grover et al. (1997)		
	Southern SK	0.03	Waite et al. (2004)		
	Southern MB	0.28	Rawn et al. (1999b)		
	Southern MB	0.38	Donald et al. (2007)		
	Dicamba	Central SK	1.06		
Central SK	5.43	Donald et al. (1999)			
Southern QC	0.13*	Poissant et al. (2008)	10	120	
South-central SK	11.2	Grover et al. (1997)			
Southern SK	0.21	Waite et al. (2004)			
South-central SK	4.5	Cessna and Elliott (2004)			
Dichlorprop	Southern MB	1.04	Donald et al. (2007)	4	—
	Central SK	0.27	Donald et al. (2001)		
	Central SK	1.59	Donald et al. (1999)		

	Southern MB	0.02	Rawn et al. (1999b)		
MCPA	Central SK	0.76	Donald et al. (2001)		
	Central SK	8.94	Donald et al. (1999)		
	South-central SK	1.97	Grover et al. (1997)		
	Southern SK	0.33	Waite et al. (2004)	2.6	—
	South-central SK	0.14	Cessna and Elliott (2004)		
	Southern MB	0.99	Rawn et al. (1999b)		
	South-central SK	0.37	Donald et al. (2007)		
Mecoprop	Central SK	0.29	Donald et al. (2001)		
	South-central SK	5.8	Cessna and Elliott (2004)	4	—
	South-central SK	0.08	Donald et al. (2007)		
Trifluralin	Central SK	0.20	Donald et al. (2001)		
	Central SK	0.04	Donald et al. (1999)		
	South-central SK	0.11	Grover et al. (1997)		
	South-central SK	0.71	Cessna and Elliott (2004)	0.2	45
	Southern MB	0.01	Rawn et al. (1999b)		
	Southern MB	0.001	Donald et al. (2007)		
Glyphosate	Central AB	1.07	Humphries et al. (2005)	65	280
Atrazine	Southern QC	0.53*	Poissant et al. (2008)		
	Southern MB	0.22	Rawn et al. (1999b)	1.8	5
	Southern BC	0.001	Woudneh et al. (2009)		
Ethametsulfuron-methyl	Southern MB	0.08	Donald et al. (2007)	—	—
Tribenuron-methyl	Southern MB	0.03	Donald et al. (2007)	—	—
Sulfosulfuron	Southern MB	0.04	Donald et al. (2007)	—	—
Thifensulfuron-methyl	Southern MB	0.01	Donald et al. (2007)	—	—
	Midwestern USA	0.015	Battaglin et al. (2000)		
Metsulfuron-methyl	Southern MB	0.002	Donald et al. (2007)	—	—
	Midwestern USA	0.01	Battaglin et al. (2000)		
Nicosulfuron	Midwestern USA	0.27	Battaglin et al. (2000)	—	—

*Canadian Council of Minister of the Environment (2007). †Health Canada (2009).

Ministers of the Environment (Table 2.2), it is important to keep in mind that this guideline is for individual herbicide active ingredient residues and not for herbicide mixtures, which are commonly found in the environment. Because the risk assessment required by Pest Management Regulatory Agency (PMRA) for herbicide registration is specific to the individual active ingredient, effects of herbicide mixtures on aquatic life are rarely investigated. Unless PMRA changes its requirements for herbicide registration to encompass multiple herbicide active ingredients for environmental risk assessments, changes to the environmental guidelines regarding herbicide residue levels are unlikely.

2.3 Effects of herbicides on wetland biota

Prairie wetlands are important breeding habits for the duck population in Canada (Batt et al., 1989). Wetlands also serve as a unique habitat for a number of amphibians, insects and crustaceans (Donald, 1983; Hartland-Rowe, 1966). The toxicological effects of older herbicides such as atrazine, 2,4-D and glyphosate, are more widely studied compared to sulfonylurea herbicides, that came into the agrochemical market in the 1990s. Atrazine has been found to reduce chlorophyll a, and diversity in the algal community (DeLorenzo et al., 1999; Pratt et al., 1988). Numerous studies have linked glyphosate and 2,4-D to the reduction of larval amphibians in wetland mesocosm studies (Relyea, 2005a; Relyea, 2005b; Relyea, 2005c). Furthermore, laboratory studies have confirmed endocrine and toxic effects in mammalian cells from glyphosate-based herbicides (Benachour and Seralini, 2009; Gasnier et al., 2009; Richard et al., 2005). Very little is known about the toxicity and fate of surfactants that are used in agrochemical products. Surfactants such as polyethoxylated tallowamine (POEA) have been found to display similar environment fate as glyphosate (Giesy et al., 2000). Non-ionic surfactants such as POEA may have negative effects on aquatic organisms by disrupting their respiratory surfaces (Lindgren et al., 2006). Aquatic toxicity tests on surfactants as well as herbicide mixtures are not conducted as part of herbicide use registration with PMRA, and hence little is known regarding the effects of surfactants and herbicide mixtures on aquatic biota.

2.4 Routes of herbicide entry to wetlands

The environmental fate of herbicides in wetlands is determined by herbicide persistence and transport as well as dissipation. Herbicides enter surface waters within the agriculture landscape through application drift (Wolf and Cessna, 2004), wet and dry atmospheric deposition (Yao et al., 2006), rainfall and snowmelt runoff (Cessna et al., 1994; Fischer et al., 1995; Waite et al., 1992), deposition of wind-eroded soil (Larney et al., 1999), and by eroded soil in surface runoff (Cessna et al., 1994; Waite et al., 1992). Off-target transport of herbicides into wetlands could potentially affect the health not only of aquatic biota (plants and animals) but riparian biota as well.

2.4.1 Surface runoff

Surface runoff or overland flow is defined as water and suspended and/or particulate particles that leave a field, catchment, or watershed by surface drainage (Grover, 1988). Runoff commences when the rate of rainfall/snowmelt exceeds the rate of soil infiltration. Conditions found to be most favourable for herbicide deposition by rainfall runoff occur when herbicides are applied to crop residue just prior to a heavy rainstorm when soil is already saturated from previous rainfall events (Grover, 1988). Herbicide concentrations tend to be highest at the beginning of a rainfall event and progressively decrease towards the end (Goolsby et al., 1997; Hill et al., 2002). Donald et al. (2005) have shown that, after a torrential storm, as much as 38% of applied herbicide could be mobilized and discharged to a nearby water body.

Spring snowmelt runoff events can also be a route of entry for herbicides into wetlands, because several studies have detected fall-applied herbicides in spring snowmelt runoff (Muir, 1991; Williamson, 1984). Researchers have found a strong correlation between concentrations in runoff and herbicide concentrations in the first one cm of watershed soil, also referred to as the mixing zone (Leonard et al., 1979; Smith et al., 1978). One study detected fall-applied 2,4-D in spring snowmelt runoff with a mean concentration of $31.0 \mu\text{g L}^{-1}$, comparable to rainfall runoff losses from a severe precipitation event following 2,4-D application (Nicholaichuk and Grover, 1983). Herbicide loss from snowmelt runoff was also greater after autumn than spring spraying, especially if it was preceded by a wet autumn and a cold winter (Felding et al., 1995).

Herbicides lost via runoff may end up in wetlands located in the agricultural landscape. Factors that influence this loss include: herbicide characteristics (i.e. solubility, *pKa*, persistence and vapour pressure), length and intensity of the precipitation event (Donald et al., 2005), landscape slope and drainage pattern, soil texture and farming practices (i.e. tillage, ground cover or mulching and buffer strips) (Elliott et al., 2000; Moore et al., 2001).

2.4.2 Atmospheric deposition

Herbicides enter the atmosphere via spray drift, evaporation/volatilization, or wind erosion of treated soil. Once in the atmosphere, they may be transported and redistributed, degraded or deposited directly or indirectly to wetlands through wet deposition (snow or rain) and dry deposition (dust). Several studies have reported atmospheric deposition of currently used herbicides in Canada (Table 2.3). Because there are no regulatory limits for herbicide concentrations in air, it is difficult to determine whether levels found are biologically significant. That being said, acid herbicides were frequently detected in air monitoring studies conducted in Saskatchewan (Waite et al., 2002; Waite et al., 2004; Waite et al., 2005a; Waite et al., 2005b). Concentrations of these herbicides peaked in mid to late June coinciding with the herbicide application period for most prairie farmers (Waite et al., 2005b). Acid herbicide concentrations in rainfall also peaked in late June, with detected concentration ranging from 150 ng L⁻¹ (bromoxynil and MCPA) to 30 ng L⁻¹ (dicamba) (Waite et al., 2005b). The Canadian Atmospheric Network for Current Use Pesticides has also provided some of the most recent surveillance data on pesticide levels in air and precipitation in Canada. Their air surveillance program found that herbicides were the most reported pesticides across the Canadian prairies. Herbicides most frequently detected at high levels in Saskatchewan include triallate, bromoxynil, MCPA, 2,4-D, dicamba, trifluralin and ethalfluralin (Yao et al., 2008).

Table 2.3. Maximum concentration detected of each herbicide in air samples from air surveillance studies conducted across Canada

Herbicide under investigation	Study location	Maximum concentration detected	References
		(pg m ⁻³)	
2,4-D	Bratt's Lake, SK	1460	Yao et al. (2006)
	Bratt's Lake, SK	781	Yao et al. (2008)
	Fraser Valley, BC	15700	Belzer et al. (1998)
	Lethbridge, AB	100	Kumar (2001)
	South of Regina, SK	3900	Waite et al. (2002)
	South of Regina, SK	680	Waite et al. (2005a)
	Saskatchewan	2730	Waite et al. (2005b)
	Southern MB	3500	Rawn et al. (1999a)
Bromoxynil	Bratt's Lake, SK	791	Yao et al. (2006)
	Bratt's Lake, SK	1840	Yao et al. (2008)
	Saskatchewan	1530	Waite et al. (2005b)
	Lethbridge, AB	300	Kumar (2001)
	South of Regina, SK	4200	Waite et al. (2004)
	Southern MB	1600	Rawn et al. (1999a)
Dicamba	Bratt's Lake, SK	626	Yao et al. (2006)
	Bratt's Lake, SK	538	Yao et al. (2008)
	Lethbridge, AB	50	Kumar (2001)
	South of Regina, SK	3700	Waite et al. (2004)
	South of Regina, SK	320	Waite et al. (2005a)
	Saskatchewan	1120	Waite et al. (2005b)
Dichlorprop	Southern MB	930	Rawn et al. (1999a)
	MCPA		
MCPA	Bratt's Lake, SK	4960	Yao et al. (2006)
	South of Regina, SK	390	Waite et al. (2004)
	Southern MB	13000	Rawn et al. (1999a)
	Saskatchewan	1900	Waite et al. (2005b)
Mecoprop	Bratt's Lake, SK	6700	Yao et al. (2008)
	Trifluralin		
Trifluralin	Bratt's Lake, SK	816	Yao et al. (2006)
	Bratt's Lake, SK	1690	Yao et al. (2008)
	South-central, ON	50	Gouin et al. (2008)
	South of Regina, SK	3220	Waite et al. (2004)
	Saskatchewan	640	Waite et al. (2005b)
	Glyphosate	Vegreville, AB	890
Atrazine			
Bratt's Lake, SK		53.1	Yao et al. (2006)
St. Anicet, QC		2720	Yao et al. (2008)
Baie St. Francois, QC		668	Yao et al. (2008)
	Fraser Valley, BC	14500	Belzer et al. (1998)

2.4.3 Application drift

Pesticides that end up in the atmosphere via spray drift increase the risk of water contamination through wet (precipitation) and dry (particulate) atmospheric deposition. Application drift depends not only on meteorological conditions, but also on application equipment and pesticide formulation (Wolf and Cessna, 2004). Buffer zones (Brown et al., 2004; de Snoo and de Wit, 1998) in conjunction with good agronomic management practices, such as the use of low-drift delivery technology (Nordby and Skuterud, 1975), low vapour pressure pesticides (Threadgill and Smith, 1975) and conservation tillage (Hall et al., 1991) can help to reduce the amount of pesticide entering a wetland. The combination of a 20-m buffer zone and a 10-m field margin with a dense windbreak was found to be effective in protecting wetlands against spray drift even under high wind speed conditions ($> 4.0 \text{ m s}^{-1}$) (Brown et al., 2004).

2.4.4 Leaching

Herbicides that are weak acids and with high water solubility, (e.g. phenoxyacetic herbicides and sulfonylurea herbicides), have the most potential to leach from soil to wetland via lateral water movement in subsurface or interflow. The leachability of a herbicide also depends on its sorption characteristics. For example, even though glyphosate (weak acid) is relatively soluble in water, it is strongly sorbed to organic matter and hence immobile in soil (Borggaard and Gimsing, 2008), whereas sulfonylurea herbicides (weak acids) are weakly sorbed to soil and therefore readily leached (Hollaway et al., 2006). Aside from herbicide characteristics, soil structure and texture and climatic conditions can also affect herbicide leaching. Leaching of glyphosate, for example, is much greater in sandy, oxide-poor soils (Borggaard and Gimsing, 2008). Because the risk of herbicide leaching is difficult to determine on a field scale, few published field leaching herbicide studies have been undertaken (Borggaard and Gimsing, 2008; Hall et al., 1991; Hollaway et al., 2006; Malone et al., 2004).

2.5 Routes of herbicide dissipation in wetlands

Pesticides exit wetlands through lateral flow, groundwater recharge and volatilization (Bailey and White, 1970; McCarty et al., 1981; Weber, 1994). Any pesticides that remain can be taken up by biota, or go through cycles of sediment

sorption/desorption and then finally be degraded through chemical or microbial transformation (Gavrilescu, 2005; Grover, 1988; Senesi and Testini, 1983; Wauchope, 1978). Environmental fate of pesticides is determined by their chemical properties and reactivities. Volatilization is a pathway by which volatile pesticides move from water into the atmosphere. Hence, extremely volatile chemicals are of concern because airborne pesticides can be spread quickly over large areas under the right conditions. Non-volatile chemicals, on the other hand, tend to accumulate in either sediment or water and are transported away from the source of release.

Biotic and abiotic degradation are the two general processes by which pesticides breakdown in the environment. Rates of pesticide degradation, in turn, depend on the chemical structure of the pesticide (reactivity of the functional groups). Some pesticides are more persistent than others and therefore may remain in the environment for a long period of time.

2.5.1 Microbial degradation

Pesticide breakdown by microorganisms is a primary degradation route. Microorganisms secrete enzymes which degrade pesticides and the substrates (carbon and nitrogen) generated are used for microbial growth. Degradative processes include dehalogenation, dealkylation, hydrolysis, oxidation, reduction, ring hydroxylation and ring cleavage (Grover, 1988). Very little is known about the microbial degradation rate of pesticides in sediment. The rate at which microbial degradation occurs in the soil is influenced by nutrient status, soil moisture, temperature, aeration, pH and organic matter content. Optimal conditions for biodegradation are well aerated soils at 50 to 100% field capacity, temperatures between 27–32 °C, pH between 6.5–8.0 and organic matter content >1% (Grover, 1988). Biodegradation rate is also influenced by pesticide molecular structure, concentration, and bioavailability of the pesticide as well as the microbial community structure.

2.5.2 Photolysis in aquatic ecosystems

Pesticides can also be degraded in the water via direct and indirect photolysis (Katagi, 2004). Direct photolysis is defined as the degradation of a molecule by UV light

while indirect photolysis is the reaction of a ground-state molecule with either a photo excited molecule or photochemically produced reactive species. In the latter form of indirect photolysis, the most reactive species are peroxide, singlet oxygen ($^1\text{O}_2$) and hydroxyl radicals ($\text{OH}\cdot$) produced via photolytic degradation of humic substances in dissolved organic carbon (DOC) and NO_3^- (Katagi, 2004). The photolytic half-lives of pesticides are affected by the suspended particles and DOC in the water column. Some of the high molecular weight aromatic humic compounds are able to absorb UV light (Arts et al., 2000; Waiser and Robarts, 2004) and therefore attenuate the photolysis of pesticides. Also if the pesticide is sorbed to suspended particles, the rate of photolysis may be reduced because suspended particles provide a shielding effect against photolysis (Oliver and Carey, 1979).

2.5.3 Hydrolysis

Pesticides that are soluble in water tend to degrade via hydrolysis, a chemical reaction that uses water to break a covalent bond (Grover, 1988). Pesticides having urea bonds (i.e. sulfonylurea herbicides) or carboxyl or phosphoryl ester linkages are more likely to be degraded by enzymatic hydrolysis via esterases and amidases (Sarmah and Sabadie, 2002). Although the hydrolysis of sulfonylurea herbicides is favoured in low pH environments, the primary degradation route is via microbial breakdown of the sulfonylurea linkage by *Pseudomonas fluorescens* (Zanaradini et al., 2002).

2.5.4 Volatilization

One of the losses of pesticides in the aquatic environment is the volatilization from water. Meteorological conditions and physical properties such as pesticide vapour pressure (Table 2.1) may strongly influence the rate of volatilization. The volatilization of phenoxy acids and dicamba from water at neutral pH is negligible (Mackay and Leinonen, 1975; Scifres et al., 1973). The vapour pressures of herbicides under investigation here are relatively low, with the exception of trifluralin (Table 2.1). It has an evaporation half-life from moist soil surfaces or shallow water of a few to 50 hours (Sanders and Seiber, 1983). The volatilization of trifluralin has been measured at 14% from the soil over 24-d period (Smith et al., 1997) and only 0.1% from water (Mackay

and Leinonen, 1975). Mackay and Leinonen (1975) concluded that the volatilization of a pesticide is insignificant if the water pH is greater than the pK_a of the pesticide.

2.5.5 Partitioning into aquatic sediment

Sorption is one of the most important processes affecting pesticide fate in sediment-water environments. Pesticide sorption is partially reversible. This phenomenon, known as hysteresis, can be studied by comparing the difference between sorption and desorption isotherms. Hysteresis is dependent not only on sorption mechanisms but the type of bonds formed between pesticide and the sorbent. Sorption for most neutral pesticides can be described by the Freundlich equation (Wauchope et al., 2002).

Environmental pesticide movement is largely dependent on pesticide partitioning between liquid (overlying water) and solid (sediment/soil) phases (the movement via vapour phase is not within the scope of this study). Pesticides can be sorbed on both the inorganic and organic soil constituents, with the importance of each constituent dependent on the quantities and properties of the constituents, as well as chemical properties of the pesticides (Briggs, 1981; Chiou et al., 1979; Karickhoff et al., 1979). Four pesticide structural factors affect their adsorption-desorption on soil colloids: (1) nature of functional group(s), (2) nature of substituting groups, which change the behaviour of functional groups, (3) position of substituting groups, which may enhance or reduce intramolecular bonding and (4) amount and degree of unsaturation in the molecule, which affects their solubility in water (Bailey and White, 1970).

2.5.5.1 Organic matter

Soil organic matter is an important sorbent for pesticides. Non-polar organic pesticides sorption by soils has been correlated to the amount of soil total organic carbon (TOC) (Schwarzenbach and Westall, 1981). Generally, for soil with TOC greater than 0.1%, the predominant sorbent for non-polar organic compounds is organic matter (Haderlein and Schwarzenbach, 1993; McCarty et al., 1981; Stevenson, 1976). Properties that influence pesticide sorption by soil organic matter include functional groups of humic substances (number, type and availability), pH, moisture, temperature,

exchangeable cations and other soil components (oxides and clay minerals) (Stevenson, 1976). Pesticide properties that influence their organic matter sorption capacity include carboxyl, alcoholic hydroxyl and amine functional groups, all of which have high affinity for organic matter (Senesi, 1992; Stevenson, 1976; Stevenson, 1982).

2.5.5.2 Clay

Clay refers to small particles with diameter equal or less than 0.002 mm (Sposito, 1989). Small particles such as clay play an important part in pesticide sorption because they have relatively high surface areas. In sediments or aquifers with low TOC, the properties of mineral surfaces may become an important sorbent for non-polar organic compounds (Weber, 1994). Isomorphous substitution (permanent) and pH-dependent charges (temporary) create negative charges on clay minerals which have also been reported to bind basic pesticides (Weber, 1994).

2.5.5.3 pH

Pesticides that are weak acids and bases are generally more affected by pH than nonionizable pesticides; their sorption has been found to be inversely related to soil pH (Karickhoff, 1984; Karickhoff et al., 1979). Phenoxy acid herbicides tend to be negatively charged at neutral pH, while if the soil has a slight negative charge, phenoxy acid herbicides sorption will not be as significant because of repulsion between the soil and herbicide.

2.5.5.4 Temperature

Adsorption processes are exothermic, while desorption processes are endothermic. An increase in temperature should reduce adsorption and increase desorption, especially for molecules bonded to the adsorbent through weak physical forces such as van der Waal forces (Grover, 1988). Molecules adsorbed through strong electrostatic forces are strongly bound to colloidal surfaces and these reactions tend to be temperature independent (Grover, 1988).

2.5.5.5 Salinity

An increase in salt content in water will generally decrease the amount of pesticide sorbed, especially of cationic pesticides. This is due to competition over the limited number of negative bonding sites in the soil/sediment. Acid herbicides sorption may increase with increases in salinity at pH above the pK_a of the acid. Neutral pesticides may show increased sorption with increasing salinity, due to the increase in activity coefficient of neutral molecules and saturation (Chao et al., 2004; Mackay and Leinonen, 1975; Smith et al., 1981). An increase in salinity can also affect pesticide sorption by changing the interlayer spacing of clays and soil organic matter morphology (Hayes et al., 1975)

2.5.6 Uptake by biota

Research on the uptake of pesticides by aquatic macrophytes is scarce. Aquatic macrophytes which usually include bryophytes, macroalgae and angiosperms can play an important part in pesticide fate (Hand et al., 2001). The sorption of λ -cyhalothrin to macrophytes was found to be rapid and extensive in Hand et al., (2001) as well the sorption is generally irreversible. Aquatic macrophytes such as duckweed (*Lemna* sp.) has been found to rapidly accumulate high levels of deltamethrin and the degradation products of deltamethrin were detected in plant tissue (Muir et al., 1985). In the same study deltamethrin concentration in filamentous algae were found at levels higher than those in duckweed. In an outdoor artificial pond study, permethrin was readily sorbed by duckweed but was not consistently detected throughout the study (Rawn et al., 1982). Aquatic macrophytes are able to degrade pesticides and thus does not generally act as a sink for pesticides in aquatic environments (Hand et al., 2001; Muir et al., 1985; Rawn et al., 1982).

2.5.7 Hydrological recharge and lateral flow to wetland margins

For a typical ephemeral wetland of glacial origin, infiltration to the shallow wetland margin accounts for approximately 75% of water loss (Parsons et al., 2004), while water loss to an underlying aquifer is considered to be minimal with the net recharge rate of 1 to 3 mm year⁻¹ (Hayashi et al., 1998). The movement of pesticides via

the lateral movement of water in the subsurface or interflow has never been studied. Because of the low vertical infiltration rate of these prairie ephemeral wetlands, there might be a significant amount of herbicide loss to the surrounding margin, especially if the herbicide is water soluble and has a low affinity for organic matter.

3.0 LAND USE AND RIPARIAN EFFECTS ON PRAIRIE WETLAND SEDIMENT PROPERTIES AND HERBICIDE SORPTION COEFFICIENTS

3.1 Introduction

The Prairie Pothole Region, which encompasses over 777 000 km² of south central Canada and north central United States, has millions of water-holding depressions of glacial origin known as sloughs or wetlands (Sloan, 1972). In North America, wetlands are important waterfowl habitat and breeding grounds. As much as 40–60% of annual North American waterfowl production depends on wetlands in the prairie pothole region (Poiani and Johnson, 1991). Crop production is the predominant land use throughout this area and previous studies showed that wetlands in this region are contaminated with a number of herbicides (Cessna and Elliott, 2004; Donald et al., 2001; Waite et al., 2002; Waite et al., 2004). Herbicides enter agricultural wetlands through application drift, wet and dry atmospheric deposition, surface runoff and deposition of wind/water-eroded soil (Cessna et al., 2000; Larney et al., 1999; Waite et al., 1995; Wolf et al., 2003).

The sorption coefficient (K_d) is the most sensitive input parameter in herbicide leaching models and has been widely studied for soils with different physicochemical properties (Boesten and van der Linden, 1991; Dann et al., 2006; Farenhorst, 2006). These studies demonstrated that percent total organic carbon (TOC) is an important soil property that can influence herbicide sorption in soils. Hence, the sorption coefficient K_{oc} , which is K_d normalized to TOC, is often used to assess other physicochemical properties that can effect herbicide binding in soil (Wauchope et al., 2002).

Herbicide sorption coefficient values are rarely published for prairie wetland sediments despite the frequent detection of a wide range of herbicides in these ecosystems. The present study was conducted at two long-term study sites in Canada that hold typical prairie wetlands within the landscape: the St. Denis National Wildlife

Area in Saskatchewan and the Manitoba Zero Till Research Association Farm in Manitoba. The objectives of this study were (i) to assess the effects of land use and riparian zone on the physicochemical properties of prairie wetland sediments, (ii) to examine the associations between these sediment properties and herbicide sorption coefficients (K_d and K_{oc}), and (iii) to establish herbicide sorption coefficient trends among wetlands under different land uses and riparian management regimes.

3.2 Materials and Methods

3.2.1 Study Sites

3.2.1.1 St. Denis National Wildlife Area, Saskatchewan

The St. Denis National Wildlife Area study site is situated 40 km east of Saskatoon, Saskatchewan, Canada (52° 12'N latitude, 106° 5'W longitude) (Figure 3.1). The soils of St. Denis National Wildlife Area were predominantly fine-loamy, mixed, frigid, Typic Haplustolls on the mid slopes with Entic Haplustolls on the lower slopes and Typic Ustorthents on the knolls (Miller et al., 1985). Parent material is a mix of unsorted calcareous till and glacio-lacustrine sediments. Climate data from 1971 to 2000 indicate that the mean annual temperature for Saskatoon was 2.2 °C, mean annual precipitation 350 mm, and the mean annual snowfall 97 cm (Environment Canada, 2004). The predominant land use at the St. Denis site is the production of grain and oilseed crops.

Thirteen wetlands were selected at this site: 12 ephemeral wetlands and one semi-permanent (SP) wetland. In high snowfall years, the SP wetland receives snowmelt water from ponds located upslope in its catchment (Woo and Rowsell, 1993). A study at St. Denis National Wildlife Area by Hayashi et al. (1998) estimated that roughly 30–60% of snow in the drainage basin ended up in wetlands via snowmelt runoff. In addition to direct precipitation, ephemeral wetlands selected generally receive runoff only from the surrounding catchment and, although they spill over to wetlands downslope in wet years, they typically do not receive spill-over water from upslope wetlands. Bedard-Haughn et al. (2006) reported that following multiple years of below-

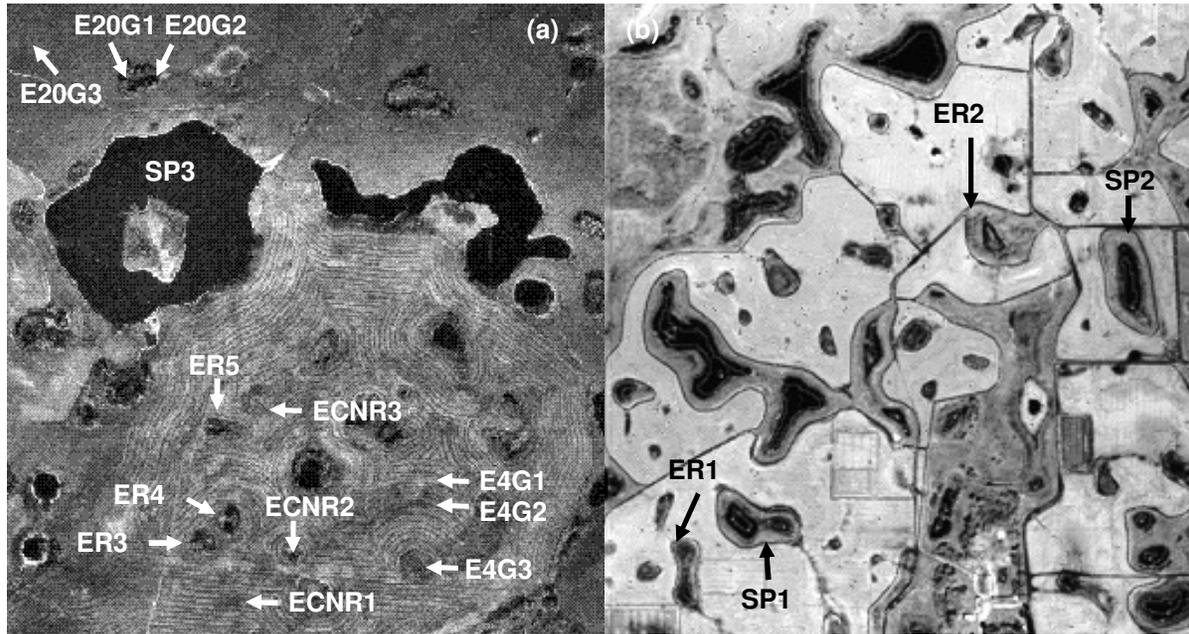


Figure 3.1. Aerial photograph of the research sites: (a) at the St. Denis National Wildlife Area and (b) Manitoba Zero Till Research Association.

average precipitation, ephemeral wetlands in the St. Denis National Wildlife Area were cropped in Springs when little or no water was present in the basins.

Aside from wetland permanence, the wetlands were also grouped into five classes based on land use and the presence or absence of a vegetation/riparian zone around the wetland. The five land use/riparian classes are: (i) ephemeral wetlands with no riparian vegetation zone in a cultivated catchment (ECNR), (ii) ephemeral wetlands with riparian vegetation in a cultivated catchment (ECR), (iii) ephemeral wetlands in a grassland catchment established 4 years ago (E4G), (iv) ephemeral wetlands in a brome grass catchment established 20 years ago (E20G), and (5) SP wetlands with multiple-land use catchments upslope. The ECNR wetlands are often cropped when lack of water permits seeding in the spring. The ECR wetlands encompass a vegetative buffer transition zone and therefore are not cropped or cultivated. The vegetative buffer zone is formed by an established stand of vegetation, such as willow (*Salix* spp.), trembling aspen (*Populus tremuloides* Michx), balsam poplar (*Populus balsamifera*), and cattail (*Typha* spp.). The E4G wetlands were not cropped or cultivated in the 4-yr period preceding sampling, and the E20G wetlands had not been cropped or cultivated in at least 20 yr. The SP wetland was never cropped due to the permanence of its water.

3.2.1.2 Manitoba Zero Till Research Association farm, Manitoba

The Manitoba Zero Till Research Association farm is situated approximately 20 km north of Brandon, Manitoba, Canada (49° 53' N, 99° 58' W) (Figure 3.1). The site is on gently sloping hummocky terrain; soils at the site were fine-loamy, mixed Udic Haploboroll. Climate data from 1971 to 2000 indicated that the mean annual temperature for Brandon is 2.4 °C and mean annual precipitation 474 mm, including approximately 101 cm of snowfall (Environment Canada, 2004).

At the Manitoba Zero Till Research Association farm site, four wetlands were selected: two ECR wetlands and two SP wetlands (Figure 3.1). The ECR wetlands were surrounded by cattail (*Typha* spp.), reed (*Phragmites* spp.) and sedge (*Carex* spp.). The SP wetlands had an open-water phase at the center, with the deepest part of the wetland enclosed by a deep-marsh zone predominantly consisting of undifferentiated grass-like plants, such as tall rush (*Scirpus* spp.) and cattail (*Typha* spp.). Similar to the SP

wetland at the St. Denis National Wildlife Area, the two SP wetlands at the Manitoba Zero Till Research Association farm were not cropped due to standing water. The dominant land use at this site is annual cropping, with a 6-yr cropping rotation of canola (*Brassica napus* L.), wheat (*Triticum aestivum* L.), field pea (*Pisum* L.), canola (*Brassica napus* L.), wheat (*Triticum aestivum* L.), and flax (*Linum usitatissimum* L.).

3.2.2 Field Sampling

Each wetland was sampled once in the 2007 growing season. A hand core sediment sampler (Wildco, New York, USA) was used to collect sediment samples from ephemeral wetlands, while a Kajak–Brinkhurst corer (Wildco) was used to sample SP wetlands. In all ephemeral wetlands and the two SP wetlands in Manitoba (SP1 and SP2), five sampling points were set along two intersecting transects, with three equally spaced points along the long axis and two along the short axis. Four cores were taken at each sampling point, and the cores were segmented into two depths, 0–5 cm and 5–10 cm. Depth segmented cores from each sampling point were bulked and mixed thoroughly to create one homogenous sample for sediment characteristic and sorption analyses. The SP wetland at the St. Denis National Wildlife Area, (SP3) was larger than all other wetlands (Figure 3.1) and hence was sampled as described above along a 10–point transect. Immediately before sediment sample collection, a water sample was collected from each wetland for water chemistry analysis using a Horizontal Alpha water sampler (Wildco, New York, USA).

3.2.3 Sediment Properties Characterization

The sediment samples were air-dried and ground to pass through a 2-mm mesh sieve. Sediments were analyzed for TOC, percent total inorganic carbon (TIC), pH, electrical conductivity (EC), exchangeable cation (EXCAT), total cation exchange capacity (CEC), and percent clay (%clay) according to Methods of Soil Analysis (Sparks, 1996). A Leco CR–12 Carbon Analyzer (LECO Corporation, Ontario, Canada) was used to analyze TOC and percent total carbon at 840 and 1100 °C, respectively. The TIC of sediments was calculated by subtracting TOC from %total carbon. A solution containing a 1:2 ratio of sediment:water (w/v) was used to determine sediment

pH (Acumen 50 pH meter; Thermo Fisher, Texas, USA) and EC (Radiometer Copenhagen Conductivity Meter, Bach–Simpson Ltd., Ontario, Canada). The determination of EXCAT and CEC was conducted using the ammonium acetate method at pH 7.0 (Lavkulich, 1981). Exchangeable Na^+ , Mg^{2+} , Ca^{2+} and K^+ were measured using an atomic adsorption spectrophotometer (Varian SpectrAA 220, Mulgrave, Australia). Total ammonium levels were determined colorimetrically using a Technicon AutoAnalyzer II (Technicon Industrial Systems, New Jersey, USA). The sediment samples were analyzed for %clay content using the Horiba LA–950 laser particle size analyzer (Horiba, California, USA). Before particle size analysis, organic matter in the sample was removed via combustion at 840 °C for 90 s. By monitoring the concentration of CO_2 gas released during combustion, we determined that the method was sufficient at removing more than 95% of the organic carbon in the sample. After combustion, the samples were dispersed by treatment with sodium hexametaphosphate and subsequent sonication. The clay fraction from sediments was also examined by x-ray diffractometry. This technique can provide a qualitative identification of the different clay minerals in each fraction. Clay separation was done by super-centrifugation, as described by Wang and Huang (2003). X-ray diffraction was done on a Rigaku Rotaflex 200SU (Tokyo, Japan) with a rotating Fe anode and graphite monochromator. The method used was modified from Whittig and Allardice (1986); the scans were performed at 40 kV and 160 mA, from $2\theta = 4$ to 80° , at a step size of 0.02° at a scanning rate of 0.1° s^{-1} .

3.2.4 Water Chemistry Analysis

Water samples were kept at 4 °C prior to being analyzed for pH, EC, major cations (Na^+ , Mg^{2+} , Ca^{2+} and K^+), anions (SO_4^{2-} , Cl^-) and alkalinity (HCO_3^-). Water pH and EC were measured in the field with a portable pH meter (Accumet AP85 pH meter; Thermo Fisher, Texas, USA) and a handheld conductivity meter (YSI Model 3000 T–L–C meter, YSI Inc., Ohio, USA), respectively. Major cations were measured using a SpectrAA atomic adsorption spectrophotometer (Varian SpectrAA 220, Mulgrave, Australia). Major anions were determined colorimetrically using a Technicon AutoAnalyzer II (Technicon Industrial Systems, New Jersey, USA). Alkalinity was

measured using Autotitrator Titalab Tim 850+SAC 90 titrator (Radiometer Analytical, Lyon, France) with H₂SO₄ added to the appropriate end point (Robarts et al., 1992).

3.2.5 Herbicide Sorption Analyses

Four herbicides, representing a wide range of chemical properties, were chosen for this study: trifluralin (2,6-dinitro-*N,N*-dipropyl-4-trifluoromethylaniline), atrazine (2-chloro-4-(ethylamine)-6-(isopropylamine)-*s*-triazine), 2,4-D (2,4-dichlorophenoxyacetic acid), and glyphosate (*N*-(phosphonomethyl) glycine). 2,4-D, atrazine, trifluralin and glyphosate sorption to sediment was determined in duplicate using batch equilibrium experiments. Analytical grade 2,4-D (95+% chemical purity; Sigma-Aldrich Co., St. Louis, MO), ¹⁴C U-ring labelled 2,4-D (99+% radiochemical purity, specific activity 521.7 MBq mmol⁻¹; Sigma-Aldrich Co.), atrazine (95+% chemical purity; Ultra Scientific, North Kingstown, RI), ¹⁴C U-ring labelled atrazine (99+% radiochemical purity, specific activity 81.4 MBq mmol⁻¹; Sigma-Aldrich Co.), trifluralin (99.3% chemical purity; Riedel-de-Haen, Seelze, Germany), ¹⁴C U-ring labelled trifluralin (99+% chemical purity, specific activity 81.4 MBq mmol⁻¹; Sigma-Aldrich Co.), glyphosate (99% purity; Chem Service, West Chester, PA), and (phosphonomethyl-¹⁴C) glyphosate (95% purity, specific activity 344.1 MBq mmol⁻¹; Sigma-Aldrich Co.) were used. The concentrations of herbicide and radiolabelled herbicide in each solution were 1 µg mL⁻¹ and 16.7 Bq mL⁻¹, respectively. For each herbicide, a concentrated stock solution (1000×; containing analytical grade and radiolabelled herbicide) was prepared in 25-mL of 95% ethanol. Then 1-mL of stock solution was added to 1-L of 0.01 mol L⁻¹ CaCl₂, and this diluted solution was used for experiments. The glyphosate stock solution was added to 1-L of deionized water instead of CaCl₂ because of observed solubility issues in CaCl₂. Each herbicide solution (10 mL) was added to 1 g of air-dried sediment, ground to pass through a 2-mm mesh sieve, placed in Teflon tubes, and rotated in growth chambers set to 20 °C until equilibrated (24 h). Samples were then centrifuged at 7550 g for 10 min. Aliquots (1 mL) of supernatant were removed from each tube and used to determine the amount of herbicide remaining in solution. The amount of radioactivity in herbicide solutions and samples from experiments was determined using a liquid scintillation counter with

automated quench correction (#H method) (LS 7500; Beckman Instruments, Fullerton, CA). Radioactivity was measured using 10 mL of Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ) and a maximum counting time of 10 min.

Amounts of radioactivity in the initial solution and remaining in the supernatant were used to calculate the sorption partition coefficient Kd ($L\ kg^{-1}$) for each of the four herbicides:

$$Kd = \frac{Cs}{Ce} \quad [3.1]$$

where Cs is the amount of herbicide sorbed by the sediment ($g\ kg^{-1}$) and Ce is the herbicide concentration of the sediment solution at equilibrium ($g\ L^{-1}$). The amount of herbicide sorption per unit organic carbon, Koc ($L\ kg^{-1}$), was also determined:

$$Koc = \frac{Kd}{\%TOC} \times 100 \quad [3.2]$$

3.2.6 Statistical Analyses

Data are presented as mean \pm standard error. The data failed the Kolmogorov–Smirnov normality test and therefore the nonparametric Kruskal–Wallis test was used to investigate the statistical significance of mean differences in sediment properties, herbicide sorption between sediment depths, and spatial variability in sediment properties between the five samples taken from each wetland. For the land use comparisons, Conover–Inman pairwise comparisons (StatsDirect Ltd., Cheshire, UK) with $\alpha = 0.05$ were used to determine the statistically significant differences in sediment properties and herbicide sorption between land uses. Spearman’s pairwise correlation analysis was used to identify associations between sediment properties and herbicide sorption among all land use groups at each depth section. The correlation between EC and herbicide sorption coefficients was omitted because herbicide sorption analyses were done under constant ionic strength, and therefore the EC of the sediment should not affect sorption. Forward stepwise regression analysis using SAS, version 8.01 (SAS Inst., Cary, NC) was used to determine the sediment properties that best predicted 2,4–D, atrazine, trifluralin and glyphosate sorption for sediment samples from all 17 wetlands. The model that best fit the data was determined by the r^2 value. To prevent

over fitting, the best predicted model was also selected based on having the closest Mallows' Cp value (Mallow, 1973) to the number of variables used in the model:

Mallow's Cp is defined as:

$$Cp = \frac{RSS}{\sigma^2} - (n - 2p) \quad [3.3]$$

where RSS = the residual sum of squares (equal to the error sum of squares for the model with p regressors), σ^2 is the error mean square from fitting the whole model with all regressors considered, n is the sample size, and p is the number of variables in the regression. Each variable entered into the model had to meet a 0.05 significance level.

3.3 Results

Water chemistry parameters such as EC, major cations and major anions were significantly different between the five land use groups (Table 3.1). The ECNR, E4G and ECR wetlands had lower EC and lower concentrations of major cations and anions relative to the E20G and SP wetlands, indicating a smaller solute load in the former wetlands. The ranges for EC and ion concentrations are within the ranges reported for wetlands in the study region (Driver and Peden, 1977).

There were no significant differences in sediment properties or herbicide sorption coefficients between the five sampling points in each of the ephemeral wetlands and the SP1 and SP2 wetlands ($P > 0.05$), indicating that sediments in these wetlands are not spatially different. In contrast, the 10-point sampling transect in wetland SP3 showed differences in various sediment properties across the transect (Figure 3.2). Overall, sediment TOC, EC, EXCAT, and CEC were significantly greater in the deeper portion of the wetland (sampling points 7 and 8) compared with the shallower portion of the wetland (sampling points 1, 2, 3, 4, 5, 6, 9, and 10) (Table 3.2). Because the other SP wetlands were of similar depth to the shallower portion of SP3 wetland, and given that sediment samples from points 7 and 8 had very different properties than the rest of the sediment samples from SP3, these two points were omitted from all ANOVA analyses of the impact of land use on sediment properties and herbicide sorption.

Table 3.1. Summary of water chemistry from wetlands in this study.

Land Use [†]	Wetland Designation	Wetland Number	pH	EC (dS m ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	Source [‡]
ECNR	ECNR1	112	7.3	0.2 ^{all}	28.0 ^a	8.9 ^a	21.5 ^a	0.4 ^a	4.2 ^a	3.3 ^a	80.8 ^{ac}	1
	ECNR2	107A	7.7	0.4 ^a	42.8 ^a	11.8 ^a	29.8 ^a	1.4 ^a	3.9 ^a	3.3 ^a	122.2 ^{ac}	1
	ECNR3	114	7.7	0.4 ^a	42.8 ^a	10.6 ^a	24.8 ^a	0.0 ^a	5.3 ^a	4.1 ^a	136.3 ^{ac}	1
			7.6±0.1 [§]	0.3±0.5 [§]	37.9±5 [§]	10.4±0.8 [§]	25.4±2 [§]	0.6±0.4 [§]	4.5±0.4 [§]	3.6±0.3 [§]	113.1±17 [§]	
E4G	E4G1	104	6.7	0.2 ^a	20.2 ^b	7.0 ^a	17.1 ^{ab}	0.0 ^a	6.1 ^a	6.4 ^{ab}	66.0 ^b	1
	E4G2	102	7.0	0.2 ^a	19.7 ^b	5.2 ^a	19.0 ^{ab}	1.7 ^a	6.8 ^a	8.1 ^{ab}	59.8 ^b	1
	E4G3	104A	7.6	0.2 ^a	20.8 ^b	7.2 ^a	16.6 ^{ab}	1.2 ^a	5.3 ^a	6.4 ^{ab}	62.5 ^b	1
			7.1±0.3	0.2±0.01	20.2±0.3	6.5±0.6	17.6±0.7	1.0±0.5	6.1±0.4	7.0±0.6	62.8±2	
ECR	ECR1	201E	7.7	0.3 ^a	26.8 ^{ab}	9.0 ^a	14.7 ^b	1.1 ^a	7.5 ^b	7.3 ^a	85.9 ^{ab}	2
	ECR2	101E	7.0	0.2 ^a	51.1 ^{ab}	35.2 ^a	15.7 ^b	14.7 ^a	60.9 ^b	8.9 ^a	129.2 ^{ab}	2
	ECR3	110	6.7	0.2 ^a	19.4 ^{ab}	6.3 ^a	18.5 ^b	0.1 ^a	6.4 ^b	4.1 ^a	60.1 ^{ab}	1
	ECR4	111	6.6	0.2 ^a	21.1 ^{ab}	6.5 ^a	13.5 ^b	0.0 ^a	4.3 ^b	1.7 ^a	74.4 ^{ab}	1
	ECR5	113	6.5	0.2 ^a	15.3 ^{ab}	4.7 ^a	12.5 ^b	0.0 ^a	5.0 ^b	1.7 ^a	48.3 ^{ab}	1
			6.9±0.2	0.2±0.1	26.7±6	12.3±6	15.0±1	3.2±3	16.8±11	4.7±2	79.6±14	
E20G	E20G1	2	7.6	2.0 ^b	124.3 ^c	113.5 ^b	17.9 ^a	54.7 ^b	216.5 ^c	18.5 ^b	181.6 ^d	1
	E20G2	3	7.2	1.7 ^b	141.7 ^c	84.1 ^b	20.9 ^a	21.9 ^b	121.6 ^c	14.0 ^b	231.4 ^d	1
	E20G3	15	7.3	0.6 ^b	53.6 ^c	24.1 ^b	25.7 ^a	4.5 ^b	35.2 ^c	7.3 ^b	192.3 ^d	1
			7.4±0.1	1.4±0.4	106.5±27	73.9±26	21.5±2	27.0±15	124.4±52	13.3±3	201.8±15	
SP	SP1	201P	7.7	1.0 ^b	68.6 ^c	68.8 ^b	16.4 ^a	25.7 ^b	129.5 ^c	8.9 ^b	143.6 ^{cd}	2
	SP2	101P	7.7	0.9 ^b	52.2 ^c	59.6 ^b	17.5 ^a	24.6 ^b	107.6 ^c	10.6 ^b	112.0 ^{cd}	2
	SP3	1	N/A	0.8 ^b	72.3 ^c	52.7 ^b	36.0 ^a	13.0 ^b	267.0 ^c	15.3 ^b	194.0 ^{cd}	3
			7.7±0	0.9±0.3	64.4±7	60.4±5	23.3±5	21.1±6	168.0±4	11.6±2	149.9±24	

[†]Land Use: ECNR, cultivated ephemeral wetlands with no riparian vegetation; ECR, ephemeral wetlands with riparian vegetation in a cultivated catchment; E4G, ephemeral wetlands in a grassland catchment established 4 years ago; E20G, ephemeral wetlands in a brome grass catchment established 20 years ago; SP, semi-permanent wetlands in multi-land use catchments.

[‡]Sources: 1 – data from this study collected on May 10, 2007; 2 – data from this study collected on May 15, 2007 and 3 – data are the means of 3 sampling dates in 2005, provided by Ducks Unlimited Canada.

[§]Mean ± standard error.

^{a-c} Means within groups with the same case letter are not significantly different (pairwise comparison Conover-Inman, $\alpha = 0.05$), properties with no letters are not significantly different between the land use groups.

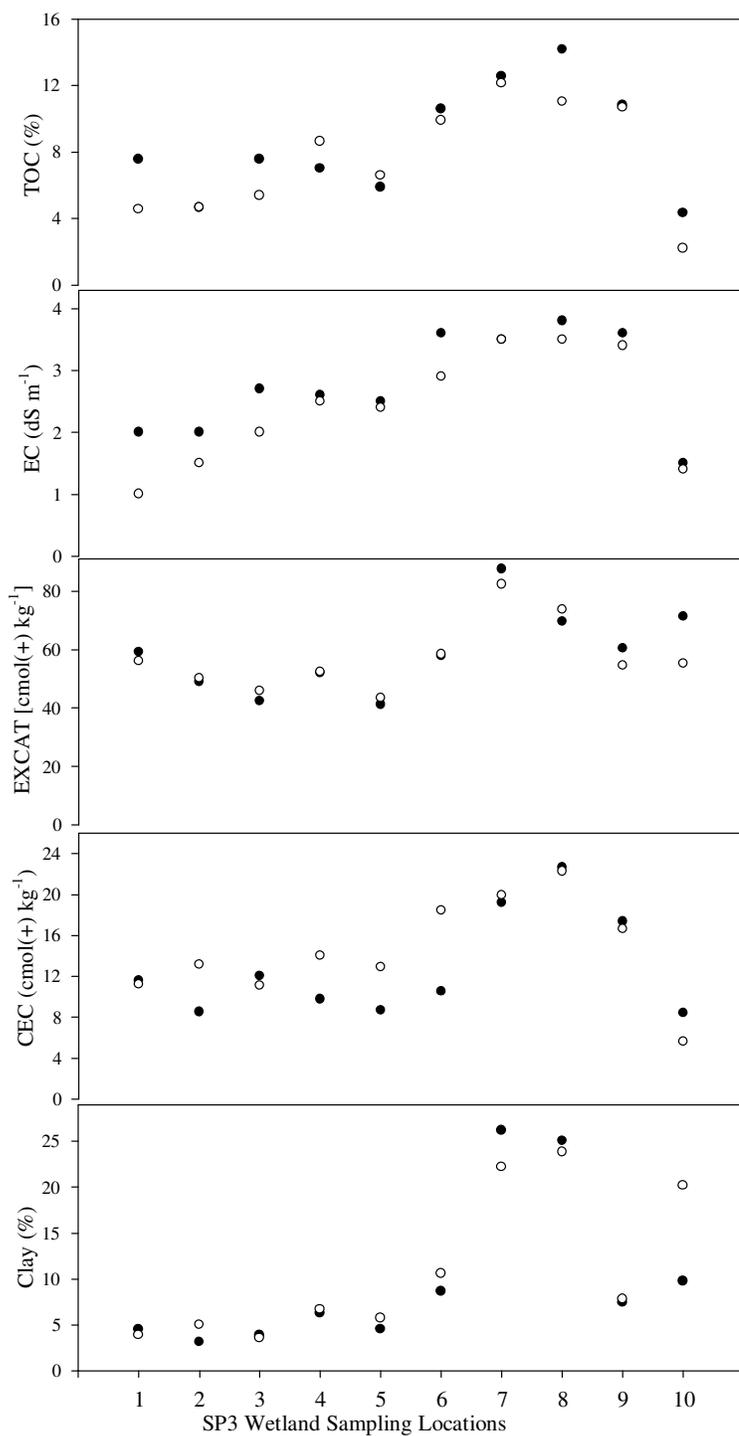


Figure 3.2. Sediment properties for wetland SP3 for 10 points along the sampling transect. Solid dots represent 0 to 5 cm section, open dots represent 5 to 10 cm section.

Table 3.2. Independent t-test results comparing means[†] of sediment properties[‡] between deep and shallow points[§] of the semi-permanent wetland (SP3) in the cultivated field at St. Denis National Wildlife Area.

Sediment properties	Means		t statistic	P>t [¶]
	Shallow points	Deep points		
TOC	6.9 ± 0.7	12.5 ± 0.7	-4.02	<0.001
TIC	1.6 ± 0.2	2.2 ± 0.4	-1.60	0.127
pH	7.4 ± 0.04	7.2 ± 0.08	1.57	0.133
EC	2.4 ± 0.2	3.6 ± 0.08	-3.04	<0.01
EXCAT	53.0 ± 2	78.2 ± 4	-5.73	<0.0001
CEC	11.9 ± 0.9	21.0 ± 0.9	-5.01	<0.0001
%Clay	6.9 ± 1.0	24.3 ± 0.9	-8.00	<0.0001
Med PS	0.06 ± 0.004	0.02 ± 0.001	4.534	<0.0001

[†]Mean ± standard error. N=8 for shallow points and N=2 for deep points.

[‡]TOC, total organic carbon (%); TIC, total inorganic carbon (%); EC, electrical conductivity (dS m⁻¹); EXCAT, exchangeable cations [cmol(+) kg⁻¹], CEC, total cation exchange capacity [cmol(+) kg⁻¹] and Med PS, median particle size (mm).

[§]Shallow points – points 1, 2, 3, 4, 5, 6, 9, and 10 and deep points – points 7 and 8.

[¶]When P = 0.05, t = 1.98 (Degrees of freedom = 18).

Significant differences were found in some sediment properties and in the atrazine K_d between the upper (0–5 cm) and the lower (5–10 cm) sections of sediment (Table 3.3). Specifically, compared with the lower section, upper sections had larger TOC ($P < 0.001$) and higher atrazine sorption coefficient ($P < 0.01$) but smaller %clay ($P < 0.01$) (Table 3.4). Due to differences between the sections, associations between TOC, %clay, and K_d for atrazine were evaluated separately for each section.

For all properties examined except TIC, differences were observed between wetlands that had been recently cultivated (ECNR and E4G) and wetlands that had not been cultivated in the last 20 yr or more (E20G, ECR, and SP) (Table 3.4). In general, mean sediment properties TOC, TIC, EC, EXCAT, and CEC ranked in the order of SP > E20G > E4G > ECNR. Clay content did not follow the same trend, ranking in the order of E4G > ECNR > E20G > SP > ECR.

Across all five land use classes, trifluralin had the largest K_d value, followed by glyphosate, atrazine, and 2,4-D (Table 3.5). The K_d values for 2,4-D and atrazine were observed to be different between recently cultivated wetlands (ECNR and E4G) and never cultivated/long-term uncultivated wetlands (E20G, ECR, and SP). Trifluralin sorption was also correlated to land use. Trifluralin K_d increased in the order ECNR < E4G < ECR < E20G < SP. For all sediment samples, K_{oc} for each herbicide was higher in the lower section (5–10 cm) than in upper section (0–5 cm). The K_{oc} for atrazine did not respond to land use in either depth section, whereas the K_{oc} for 2,4-D and trifluralin differed between land uses in the upper section, with K_{oc} values greater in ECNR, E4G, and ECR wetlands than in E20G and SP wetlands. Glyphosate sorption did not respond to land use, and K_{oc} was not calculated for glyphosate because its K_d did not correlate to TOC (Table 3.6).

Sediment TOC was significantly correlated to EXCAT ($r = 0.65$; $P < 0.0001$), CEC ($r = 0.64$; $P < 0.0001$), and %clay ($r = -0.44$; $P < 0.0001$) (Table 3.6). Sediment TOC was also weakly correlated to pH ($r = 0.17$; $P < 0.05$). Sediment TIC was positively correlated to pH ($r = 0.42$; $P < 0.0001$) and EXCAT ($r = 0.19$; $P < 0.05$) and negatively correlated to CEC ($r = -0.20$; $P < 0.001$). Sediment pH was also found to have a positive correlation with EXCAT ($r = 0.52$; $P < 0.0001$). Sediment EXCAT was

Table 3.3. Means and variability[†] of the soil properties[‡] and four herbicide sorption coefficients measured on wetland sediment samples as affected by section[§].

	Sediment Properties							Herbicide Sorption Coefficients <i>K_d</i>			
	TOC %	TIC %	pH	EC dS m ⁻¹	EXCAT cmol(+) kg ⁻¹	CEC cmol(+) kg ⁻¹	Clay %	2,4-D L kg ⁻¹	Trifluralin L kg ⁻¹	Atrazine L kg ⁻¹	Glyphosate L kg ⁻¹
All sediments	5.6 ± 0.2	0.7 ± 0.04	6.7 ± 0.06	0.9 ± 0.08	36.2 ± 2	23.9 ± 1	8.0 ± 0.3	5.5 ± 0.2	296.2 ± 9	10.6 ± 0.6	182.1 ± 8
	Section										
Upper	6.8 ± 0.4	0.7 ± 0.05	6.7 ± 0.07	1.0 ± 0.1	37.6 ± 3	26.2 ± 2	7.3 ± 0.5	5.7 ± 0.3	299.0 ± 14	11.3 ± 0.7	196.4 ± 13
Lower	4.5 ± 0.3	0.7 ± 0.06	6.8 ± 0.07	0.8 ± 0.09	34.8 ± 3	21.7 ± 1	8.7 ± 0.4	5.3 ± 0.3	278.1 ± 12	9.8 ± 0.7	170.1 ± 9
	Statistical Significance										
Section	***	ns	ns	ns	ns	ns	**	ns	ns	**	ns

** and *** denote $P < 0.01$ and $P < 0.001$ levels of significance, respectively by Kruskal-Wallis test; ns denotes no significance at $P \geq 0.01$.

[†]Mean ± standard error. All sediments N=148, upper and lower section N=74.

[‡]TOC, total organic carbon; TIC, total inorganic carbon; EC, electrical conductivity; EXCAT, exchangeable cations; CEC, total cation exchange capacity.

[§]Upper, 0 to 5 cm; Lower, 5 to 10 cm.

Table 3.4. Means and variability[†] of sediment properties[‡] as affected by land use[§].

Land Use [§]	Sediment Properties						
	TOC	TIC	pH	EC	EXCAT	CEC	Clay
	%	%		(dS m ⁻¹)	cmol(+) kg ⁻¹	cmol(+) kg ⁻¹	%
ECNR	3.2 ± 0.1 ^a	0.47 ± 0.04	6.7 ± 0.1 ^{ab}	0.2 ± 0.01 ^a	18.3 ± 1 ^a	13.3 ± 1 ^a	9.1 ± 0.5 ^{ab}
	2.6 ± 0.1 ^A						9.9 ± 0.6 ^{AC}
E4G	3.8 ± 0.1 ^a	0.50 ± 0.05	6.4 ± 0.1 ^a	0.2 ± 0.08 ^a	19.9 ± 1 ^{ab}	16.8 ± 1 ^a	11.3 ± 0.7 ^b
	2.9 ± 0.1 ^{AB}						11.9 ± 0.6 ^A
ECR	6.8 ± 0.5 ^b	0.57 ± 0.05	6.4 ± 0.1 ^a	0.6 ± 0.07 ^b	32.3 ± 3 ^{ab}	24.8 ± 2 ^{ab}	4.9 ± 0.4 ^c
	3.8 ± 0.3 ^B						6.7 ± 0.4 ^B
E20G	8.7 ± 0.8 ^{bc}	0.65 ± 0.07	7.2 ± 0.1 ^b	0.9 ± 0.1 ^b	42.3 ± 3 ^{bc}	33.1 ± 4 ^b	5.6 ± 0.5 ^c
	5.1 ± 0.4 ^{BC}						7.3 ± 0.5 ^{BC}
SP	9.6 ± 0.9 ^c	0.86 ± 0.1	7.1 ± 0.1 ^b	2.0 ± 0.1 ^c	61.5 ± 3 ^c	31.9 ± 3 ^b	6.7 ± 0.6 ^{ac}
	7.1 ± 0.5 ^C						8.8 ± 1.0 ^C

[†]Mean ± standard error. N=12 for ECNR, E4G, E20G, N=20 for ECR and N=10 for SP.

[‡]TOC, total organic carbon; TIC, total inorganic carbon; EC, electrical conductivity; EXCAT, exchangeable cations; CEC, total cation exchange capacity.

[§]Land Use: ECNR, ephemeral wetlands with no riparian vegetation in a cultivated catchment; ECR, ephemeral wetlands with riparian vegetation in a cultivated catchment; E4G, ephemeral wetlands in a grassland catchment established 4 years ago; E20G, ephemeral wetlands in a brome grass catchment established 20 years ago; SP, semi-permanent wetlands in multi-land use catchments.

^{||a-b}Means within groups with the same case letter are not significantly different (pairwise comparison Conover-Inman, $\alpha = 0.05$), properties with no letters are not significantly different between land uses. Data given for TOC, % clay and atrazine sorption are for 2 sediment sections, 0 to 5 and 5 to 10 cm.

Table 3.5. Means and variability[†] of herbicide sorption coefficients[‡] as affected by land use[§].

Land Use [§]	Herbicide Sorption Coefficients						
	<i>K_d</i>				<i>K_{oc}</i>		
	2,4-D L kg ⁻¹	Trifluralin L kg ⁻¹	Atrazine L kg ⁻¹	Glyphosate L kg ⁻¹	2,4-D L kg ⁻¹	Trifluralin L kg ⁻¹	Atrazine L kg ⁻¹
ECNR	3.3 ± 0.1 ^{¶a}	168.1 ± 5 ^a	6.2 ± 0.3 ^a 5.0 ± 0.2 ^A	172.9 ± 16	110.4 ± 5 ^a 119.6 ± 6	5467.3 ± 185 ^a 6163.4 ± 432	189.3 ± 10 193.6 ± 9
E4G	3.9 ± 0.1 ^{¶ab}	242.7 ± 8 ^b	5.8 ± 0.2 ^a 4.9 ± 0.2 ^A	152.6 ± 15	111.0 ± 5 ^a 125.4 ± 6	6584.9 ± 449 ^a 8293.7 ± 217	155.1 ± 6 170.9 ± 7
ECR	7.5 ± 0.5 ^c	283.5 ± 18 ^{bc}	15.8 ± 2 ^b 13.0 ± 2 ^B	251.9 ± 21	125.5 ± 11 ^a 188.3 ± 12	5202.7 ± 391 ^a 7301.1 ± 678	246.8 ± 25 325.5 ± 25
E20G	6.1 ± 0.3 ^c	310.0 ± 12 ^{cd}	11.4 ± 0.7 ^b 8.2 ± 0.7 ^B	193.1 ± 16	85.1 ± 8 ^{ab} 117.1 ± 9	4013.2 ± 426 ^b 6471.2 ± 494	145.9 ± 17 167.8 ± 15
SP	6.0 ± 0.6 ^{bc}	406.0 ± 22 ^d	14.0 ± 2 ^b 14.4 ± 1 ^B	124.9 ± 9	50.6 ± 6 ^b 83.7 ± 13	4344.4 ± 419 ^b 5866.7 ± 318	154.4 ± 10 213.3 ± 17

[†]Mean ± standard error. N=12 for ECNR, E4G, E20G, N=20 for ECR and N=10 for SP.

[‡]*K_d*, herbicide sorption coefficient; *K_{oc}* herbicide sorption per unit organic carbon.

[§]Land Use: ECNR, ephemeral wetlands with no riparian vegetation in a cultivated catchment; ECR, ephemeral wetlands with riparian vegetation in a cultivated catchment; E4G, ephemeral wetlands in a grassland catchment established 4 years ago; E20G, ephemeral wetlands in a brome grass catchment established 20 years ago; SP, semi-permanent wetlands in multi-land use catchments.

^{¶a-d}Means within groups with the same case letter (lower case for 0 to 5 cm and upper case for 5 to 10 cm) are not significantly different (pairwise comparison Conover-Inman, $\alpha = 0.05$), properties with no letters are not significantly different between land uses. Data given for atrazine sorption are for 2 sediment sections, 0 to 5 and 5 to 10 cm.

Table 3.6. Relations among sediment properties[†] and herbicide sorption coefficients[‡] for all wetland sediments measured by Spearman correlation coefficients.

Sediment Properties	Sediment Properties					
	TOC	TIC	pH	EXCAT	CEC	%Clay
TOC	1.00					
TIC	—	1.00				
pH	0.17*	0.42***	1.00			
EXCAT	0.65***	0.19*	0.52***	1.00		
CEC	0.64***	-0.20**	—	0.70***	1.00	
%Clay	-0.44***	—	—	—	-0.26***	1.00
	Herbicide Sorption Coefficients					
<i>K_d</i>						
2,4-D	0.43***	-0.25**	-0.21**	0.25**	0.66***	-0.44***
Trifluralin	0.67***	0.16*	0.15*	0.41***	0.37***	-0.31***
Atrazine	0.73***	—	—	0.57***	0.62***	-0.51***
Glyphosate	—	-0.17*	-0.47***	-0.32***	—	-0.18*
			<i>K_{oc}</i>			
2,4-D		-0.25**	-0.35***	-0.34**	—	—
Trifluralin		—	—	-0.41***	-0.44***	0.22**
Atrazine		-0.196**	-0.19*	—	—	—
Glyphosate		—	-0.43***	-0.67***	-0.42***	0.20**

*, ** and *** denote $P < 0.05$, $P < 0.001$, $P < 0.0001$ level of significance.

[†]TOC, total organic carbon; TIC, total inorganic carbon; EC, electrical conductivity; EXCAT, exchangeable cations; CEC, total cation exchange capacity.

[‡]*K_d*, herbicide sorption coefficient; *K_{oc}* herbicide sorption per unit organic carbon.

positively correlated to CEC ($r = 0.68$; $P < 0.0001$). Clay content was negatively correlated to CEC ($r = -0.26$; $P < 0.001$).

The K_d values of 2,4-D, trifluralin, and atrazine were positively correlated to TOC, EXCAT, and CEC and negatively correlated to %clay (Table 3.6). Glyphosate K_d had a weak negative relationship with TIC, pH, EXCAT, and %clay. The K_{oc} value for 2,4-D was negatively correlated to TIC, pH, and EXCAT; trifluralin K_{oc} was negatively correlated to EXCAT and CEC and positively correlated to %clay. Atrazine K_{oc} was negatively correlated to TIC and pH, whereas glyphosate K_{oc} was negatively correlated to pH, EXCAT, and CEC and positively correlated to %clay.

Stepwise regression analysis showed that CEC, %clay, and pH accounted for 56% of the variation in 2,4-D sorption averaged across all wetland sediments (Table 3.7). For trifluralin, sorption was significantly dependent on TOC in the best regression model. The best predictor of atrazine sorption was achieved by a regression model containing TOC, %clay, and CEC. The most optimal prediction of glyphosate sorption was obtained with variables pH, %clay, and CEC.

3.4 Discussion

Sorption at the dynamic sediment–water exchange interface is an important process influencing herbicide fate in wetlands. Understanding herbicide sorption behaviour can improve prediction of their movement in wetland ecosystems. In this study, 2,4-D, atrazine, trifluralin, and glyphosate sorption by wetland sediment was primarily controlled by herbicide properties and the sediment sorption capacity.

The selected herbicides exhibited different surface charge under the pH range for prairie wetland sediment. Atrazine can be either positively charged at $\text{pH} < 7$ or neutral at $\text{pH} > 7$. Glyphosate and 2,4-D were negatively charged under our experimental pH conditions. Trifluralin was the only non-ionic herbicide. Ionic and non-ionic herbicide sorption can occur through chemical and physical forces such as ion exchange, charge-transfer, hydrogen bonding and van der Waal forces (Muir, 1991). Organic matter has been shown to be the most important component in the sorption of various herbicides. The physicochemical property CEC is often used to characterize sorption properties important in herbicide retention because it is highly dependent on the amount and

composition of organic matter and clay minerals (Parfitt et al., 1995). Given the low percentage of clay found in our sediment samples, CEC was predominantly correlated with TOC. There were significant differences in the TOC content in sediment between wetlands of various land uses, and therefore, herbicides that have strong affinity for TOC showed significant difference in sorption behaviour between land uses.

The EC and cation compositions of the water and sediment were also affected by land use. Those variables may directly influence herbicide sorption by competing for the available sorption sites or indirectly affect herbicide sorption by changing the surface charge.

Atrazine sorption to sediment was predominately controlled by TOC (Table 3.7). Similar to other studies, we found a positive relationship between TOC content and atrazine K_d (Table 3.6) (Novak, 1999). Atrazine sorption was significantly greater in sediments with higher TOC, such as those from ECR, E20G, and SP wetlands.

Similar to other findings, the TOC content was the single best predictor of trifluralin sorption (Table 3.7) (Peter and Weber, 1985; Solbakken et al., 1982). For ECNR, E4G and ECR wetland sediments, with TOC content ranging from 2.6 to 6.8%, the sorption coefficients were consistent with the upper-range sorption values reported in literature for agricultural soils with similar TOC content (Table 3.5) (Cook et al., 2004). For sediments with higher TOC content, such as those from E20G and SP wetlands, their sorption coefficients were two-fold greater than trifluralin sorption values reported for soil.

Using the measured physicochemical properties, the predictability of glyphosate sorption to sediment was quite low ($r^2 = 0.33$). There were no significant differences between glyphosate sorption between the different land use groups (Table 3.5). We found that sediment pH, clay content and CEC exerted the most influence on glyphosate sorption (Table 3.7). The negative relationship between pH and glyphosate sorption has been reported in other studies (de Jonge and de Jonge, 1999; McConnell and Hossner, 1986). The pH dependency was due to the increasing attraction between the negative glyphosate ion and the increasing positive charge on surfaces at decreasing pH. In contrast to results from other studies (Gimsing and Borggaard, 2002; Glass, 1987),

Table 3.7. The most suitable models to predict herbicide sorption coefficients following forward stepwise multiple linear regression and various sediment properties[†]. Significant levels for the predicted models are P<0.001 in all cases. The most suitable model was determined to be the model with the largest r^2 value. All variables in the model met a 0.05 significance level.

	Regression Equation	r^2	P
2,4-D <i>Kd</i>			
Sediment properties	0.12 CEC – 0.18 %Clay – 0.87pH + 10.1	0.56	<0.001
Trifluralin <i>Kd</i>			
Sediment properties	25.5TOC + 151.2	0.43	0.006
Atrazine <i>Kd</i>			
Sediment properties	0.55TOC – 0.30%Clay + 0.19CEC + 5.6	0.44	0.001
Glyphosate <i>Kd</i>			
Sediment properties	-74.3pH – 7.16%Clay - 0.87CEC + 762.7	0.33	<0.001

[†]TOC, total organic carbon (%); TIC, total inorganic carbon (%); EXCAT, exchangeable cations c. CEC, total cation exchange capacity [cmol(+) kg⁻¹].

we found a negative relationship between glyphosate sorption and clay content.

Glyphosate sorption to clay could be impeded by the presence of other competitive anions like phosphate (Gimsing and Borggaard, 2002; Hill, 2001). Therefore, sediments that have lower anion load and clay content, such as sediments from ECR wetlands, were found to have larger glyphosate sorption coefficients.

Total organic carbon and CEC were found to be positively correlated to 2,4-D sorption (Table 3.6). This is in agreement with other studies that have also found TOC content to be the predominate controlling factor in 2,4-D sorption (Farenhorst et al., 2008; Gaultier et al., 2006; Picton and Farenhorst, 2004). Despite the elevated TOC content in SP wetland sediments, 2,4-D sorption was greater in ECR and E20G wetlands (Table 3.5). This could be due to their lower clay content because clay was found to be negatively correlated to 2,4-D sorption (Table 3.6). Under alkaline and neutral pH conditions, 2,4-D exists in its anionic form and would be repelled by the negatively charged clay minerals. Findings from studies conducted with montmorillonite clay (a type of clay also found in the wetland sediment from this study [Table 3.8]) showed a strong negative relationship with 2,4-D sorption (Hermosin and Cornejo, 1993; Sannino et al., 1997). Wetland sediments have lower 2,4-D sorption coefficients than soils with the same TOC content (Gaultier et al., 2008). Hence, weakly bound 2,4-D may be relatively mobile in sediment, with the risk of contaminating groundwater under high water table and rapid recharge conditions.

In the wetland ecosystem, herbicide sorption to sediment is an important parameter in determining herbicide fate. The wetlands selected for this study were representative of the types of wetland that are widespread in the Prairie Pothole region. We have found that aside from water permanence and land use practice in the surrounding catchment, the size of wetlands can affect physicochemical sediment properties. In small and shallow wetlands, the sediment had little spatial variation in physicochemical properties partly because the suspended solid concentration was evenly distributed in the wetland. For larger and deeper wetlands, such as SP3 wetland, physicochemical properties, particularly clay content, may be affected by wave action in the near-shore areas and sedimentation process in the deeper areas

Table 3.8. Minerals identified in the sediments by x-ray diffraction.

Land Use [†]	Primary Minerals	Secondary Minerals		
		Layer Silicates	Carbonates	Sulfates
ECNR	Present	Present (montmorillonites, smectite, kaolinite)	Present (calcite)	Absent
E4G	Present	Present (montmorillonites, smectite, kaolinite)	Present (calcite)	Absent
ECR	Present	Present (montmorillonites, smectite, vermiculite, kaolinite)	Present (calcite)	Absent
E20G	Present	Present (Illite, muscovite, montmorillonites, kaolinite)	Present (dolomite, calcite)	Present (gypsum)
SP	Present	Present (montmorillonites, smectite, kaolinite)	Present (dolomite, calcite)	Present (gypsum)

[†]Land Use: ECNR, ephemeral wetlands with no riparian vegetation in a cultivated catchment; ECR, ephemeral wetlands with riparian vegetation in a cultivated catchment; E4G, ephemeral wetlands in a grassland catchment established 4 years ago; E20G, ephemeral wetlands in a brome grass catchment established 20 years ago; SP, semi-permanent wetlands in multi-land use catchments.

(Bengtsson and Hellstrom, 1992). Because our study encompassed only one large wetland, the effects of clay content as result of wetland size cannot be fully determined.

Overall, the best predictors of the capacity of sediment to sorb herbicides were the TOC and clay content. Averaged across all wetlands, although TOCs were 1.2- to 1.8-fold greater in the upper sediment section (0–5 cm) than in the lower section (5–10 cm), *K_d* values were not significantly different (except for atrazine). TOC *K_{oc}* values were also higher in the lower than the upper section. Although organic matter composition was not analyzed in our study, the higher *K_{oc}* in the lower sediment be a result of organic matter composition difference between the two depth sections, as has been previously reported by (Ding et al., 2002).

3.5 Conclusions

Prairie wetlands are water-holding depressions that vary in size, depth, water permanence, water chemistry, and sediment properties. In this study, we have determined that TOC and ion composition of the sediment were affected by land use. As well, sorption coefficients for atrazine and trifluralin were strongly influenced by TOC, and different sorption behaviours were noted in the various wetland types. A weaker relationship was established between 2,4-D sorption and TOC, whereas no relationship was found between glyphosate sorption and TOC. Despite having lower TOC content than semi-permanent wetland sediment, riparian wetland sediments have the highest herbicide sorption capacity for all four herbicides. The understanding of herbicide fate in wetlands will become increasingly important because the numbers of riparian and semi-permanent wetlands in the Prairie Pothole region are predicted to increase as more effort is put forth to increase carbon storage by creating and restoring wetlands and their riparian zones.

4.0 TRACE LEVEL DETERMINATION OF SELECTED SULFONYLUREA HERBICIDES IN WETLAND SEDIMENT BY LIQUID CHROMATOGRAPHY ELECTROSPRAY TANDEM MASS SPECTROMETRY

4.1 Introduction

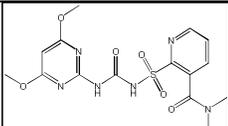
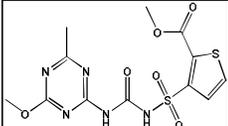
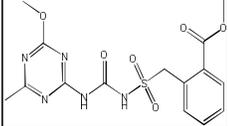
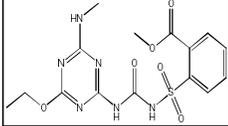
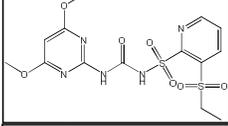
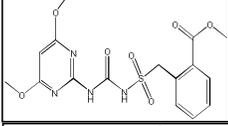
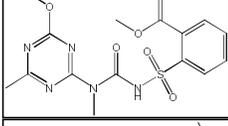
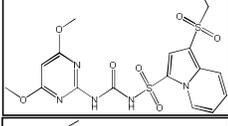
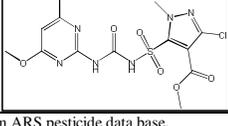
Sulfonylurea herbicides are used worldwide at relatively low application rates (2 to 75 g active ingredient ha⁻¹) to control a wide range of broad-leaved and grassy weeds in more than 25 crops. Although they express low acute mammalian toxicity, they are highly phytotoxic and chronic exposure to low level residues can affect the growth of sensitive plants (Brown, 1990). If present in aquatic ecosystems at µg L⁻¹ concentrations, sulfonylurea herbicides can be highly toxic to some micro-algae and periphyton communities (Nyström and Blanck, 1998; Nyström et al., 1999; Thompson et al., 1993).

The general structure of sulfonylurea herbicides consists of an aryl group, the sulfonylurea bridge and a heterocyclic portion that can be a symmetrical pyrimidine or triazine group. The molecular structures of the seven sulfonylurea herbicides selected for this study are illustrated in Table 4.1 (Beyer et al., 1988). Sulfonylurea herbicides are highly soluble in water (Table 4.1), weakly sorbed to soil, and non-volatile with vapour pressures typically in the order of 10⁻⁶ to 10⁻¹² mPa (Schmuckler et al., 2000). The sulfonylurea herbicides are weak acids (*pKa* values ranging from 3.3 to 5.0) (United States Department of Agriculture - Agricultural Research Service (USDA-ARS), 2001), due to the effect of the electronegativity of the carbonyl and sulfonyl moieties on the adjacent urea nitrogen.

The main degradation pathways of sulfonylurea herbicides in soil are hydrolysis and microbial degradation. Microbial degradation is relatively important in alkaline soils whereas hydrolysis is more rapid in warm, moist, light-textured and low pH soils (Hall et al., 1999). In alkaline soils, sulfonylurea herbicides are not only more slowly

hydrolyzed but, because they are weak acids, have increased mobility because they are present as anions and hence are not strongly sorbed to soil. Consequently, these

Table 4.1. Chemical structures, molecular weights, formulas, water solubility and *K_d* values for thifensulfuron-methyl, tribenuron-methyl, ethametsulfuron-methyl, metsulfuron-methyl, rimsulfuron, halosulfuron-methyl, nicosulfuron, bensulfuron-methyl, and sulfosulfuron.

Name	Molecular Structure	MW	Formula	Water solubility [†] g L ⁻¹	<i>K_d</i> in soil [†] mL g ⁻¹
Nicosulfuron		411.2	C ₁₅ H ₁₈ N ₆ O ₆ S	12.2 @ pH 7	0.3–2.6
Thifensulfuron-methyl		388.0	C ₁₂ H ₁₃ N ₅ O ₆ S ₂	6.3 @ pH 7	0.1–8.6
Metsulfuron-methyl		381.4	C ₁₄ H ₁₅ N ₅ O ₆ S	2.8 @ pH 7	0.4–1.4
Ethametsulfuron-methyl		411.8	C ₁₅ H ₁₈ N ₆ O ₆ S	0.05 @ pH 7	0.4–4.1
Rimsulfuron		432.0	C ₁₄ H ₁₇ N ₅ O ₇ S ₂	7.3 @ pH 7	0.3–1.6
Bensulfuron-methyl		411.5	C ₁₆ H ₁₈ N ₄ O ₇ S	0.9 @ pH 8	0.3–1.4
Tribenuron-methyl		396.2	C ₁₅ H ₁₇ N ₅ O ₆ S	280 @ pH 6	0.2–2.0
Sulfosulfuron		471.1	C ₁₆ H ₁₈ N ₆ O ₇ S ₂	1.6 @ pH 7	0.1–5.3
Halosulfuron-methyl		435.5	C ₁₃ H ₁₅ ClN ₆ O ₇ S	1.6 @ pH 7	0.3–3.6

[†]Water solubility and *K_d* values from ARS pesticide data base.

characteristics make them more susceptible to leaching in the calcareous soils (high pH) typically found in the Canadian Prairies.

Millions of wetlands are scattered across the Prairie Pothole Region of North America, which encompasses more than 777 000 km² of south central Canada (including parts of Saskatchewan and Manitoba) and the north central United States (Sloan, 1972). The most predominant land use throughout this region is crop production and several studies have shown that associated wetlands are contaminated with a wide range of herbicides used in crop production (Anderson, 2005; Grover et al., 1997; Waite et al., 2002; Waite et al., 2004). Twenty-seven herbicides were recently detected in drinking water reservoirs in this region, including five sulfonylurea herbicides (Donald et al., 2007). Herbicides can enter surface waters situated within the agriculture landscape through application drift (Wolf and Cessna, 2004), wet and dry atmospheric deposition (Yao et al., 2006), deposition of wind-eroded soil (Larney et al., 1999) and by surface runoff and deposition of water-eroded soil (Cessna et al., 1994; Waite et al., 1992). The off-target transport of sulfonylurea herbicides into wetlands could potentially affect the health of both riparian biota (plants and animals) and aquatic biota in those environments. Because the ecotoxicological effects of sulfonylurea herbicide mixtures in wetland ecosystems have yet to be published, it is important to have a robust multi-residue analytical method for assessing their concentrations in both wetland water and sediment.

Sulfonylurea herbicide residues in soil have been determined using plant bioassays (Hollaway et al., 1999), as well as analysis of soil extracts either by capillary electrophoresis (Chen et al., 2000; Dinelli et al., 1995) or high performance liquid chromatography (HPLC) (Font et al., 1998; Powley and de Bernard, 1998) with UV detection or enzyme-linked immunoassay techniques (Hollaway et al., 1999). The only study regarding sulfonylurea herbicide residues in sediments involved fortification of sediment/water slurries with 12 sulfonylurea herbicides and analysis by capillary electrophoresis with UV detection (Berger and Wolfe, 1996). Herbicide concentrations (100 to 10,000 µg L⁻¹) in the slurries, were however, high relative to environmental concentrations expected in wetland sediments. Consequently, we believe that there is a need for a robust analytical method using liquid chromatography tandem mass spectrometry (LC/MS/MS) that allows fast, sensitive and reliable monitoring for sulfonylurea herbicide residues in wetland sediment. Furthermore,

detection limits in low $\mu\text{g kg}^{-1}$ levels are required because only a fraction of the low application rates at which the sulfonylurea herbicides are applied enter surface waters and partition into sediment. Liquid chromatography coupled with tandem mass spectrometry has been used to determine sulfonylurea herbicides in a prairie wetland (Cessna et al., 2006) and reservoir (Donald et al., 2007) waters. It is a promising technique for sediment analysis because it has the potential to provide sufficient specificity to reduce interference from co-extractives in the complex sediment matrix while achieving good sensitivity at low $\mu\text{g kg}^{-1}$.

The objectives of this study were to a) develop a multi-residue method to determine the concentrations of seven sulfonylurea herbicides (nicosulfuron, thifensulfuron-methyl, metsulfuron-methyl, ethametsulfuron-methyl, rimsulfuron, tribenuron-methyl and sulfosulfuron) commonly used in prairie crop production in wetland sediment, and b) use this method to quantify sulfonylurea herbicide concentrations in sediment samples collected from 17 wetlands in Saskatchewan and Manitoba, Canada.

4.2 Materials and methods

4.2.1 Study Sites

Two study sites for monitoring sulfonylurea herbicide concentrations in wetland sediment were utilized in this study. The first site is the St. Denis National Wildlife Area encompassing 360 ha of agricultural land, 40 km east of Saskatoon, Saskatchewan, Canada ($52^{\circ} 12' \text{N}$ latitude, $106^{\circ} 5' \text{W}$ longitude) and the second site is the Manitoba Zero Till Research Farm, a smaller area (130 ha) located approximately 20 km north of Brandon, Manitoba, Canada ($49^{\circ} 53' \text{N}$ latitude, $99^{\circ} 58' \text{W}$ longitude). The dominant land use at the St. Denis National Wildlife Area is the production of grain and oilseed crops, whereas that at the Manitoba Zero Till Research Farm involves a six year cropping rotation of canola (*Brassica napus* L.), wheat (*Triticum aestivum* L.), field pea (*Pisum* L.), canola, wheat, and flax (*Linum usitatissimum* L.). According to the management history provided for both sites, no sulfonylurea herbicides were applied at these sites in the past five years prior to sampling. Seeding at these sites typically begins in mid May, herbicide application from mid May to mid July, and harvest in September/October. The mean annual precipitation is 350 mm and 474 mm at the St. Denis National Wildlife Area and the Manitoba Zero Till Research Farm,

respectively (Environment Canada, 2004). The corresponding average amounts of snowfall are 97 cm and 101 cm.

Thirteen wetlands were selected at the St. Denis National Wildlife Area and included 12 ephemeral wetlands (wetlands 1 to 12) and one large semi-permanent wetland (wetland 13) (Figure 4.1a). Nine of the ephemeral wetlands (wetland 1 to 9) and the semi-permanent wetland had riparian vegetation. Vegetation has been shown to be effective in mitigating droplet spray drift (Hewitt, 2001; Richardson et al., 2002; Ucar and Hall, 2001); however, spray drift reduction is dependent on vegetative height and porosity. The riparian vegetation in the ephemeral and semi-permanent wetlands generally consisted of a mixture of willow (*Salix* spp.), trembling aspen (*Populus tremuloides* Michx), balsam poplar (*Populus balsamifera* L.), tall rush (*Scirpus* spp.) and cattail (*Typha* spp.), all of which have been shown to be effective in reducing application droplet drift using both conventional and air-induced low drift nozzles (Wolf and Cessna, 2004). In contrast, the agricultural land surrounding the other three ephemeral wetlands (wetland 10 to 12) was cultivated to the edge of the water. The catchment areas for all 12 ephemeral wetlands are contained within the study site; however, the catchment area for the large semi-permanent wetland (wetland 13) extends well beyond the study area and drains into the wetland at a single point of runoff inflow. There was also a 65-ha field of perennial grass within the Wildlife Area with a centrally situated wetland surrounded by willow and poplar trees. This field did not receive herbicide application and sediment from this wetland contained no detectable residues of any of the sulfonylurea herbicides selected for study. Consequently, sediment from this wetland was fortified with the seven sulfonylurea herbicides plus the surrogate compound in recovery experiments.

Four wetlands on cultivated land, each with riparian vegetation consisting mainly of tall rush and cattail were selected for study at the Manitoba Zero Till Research

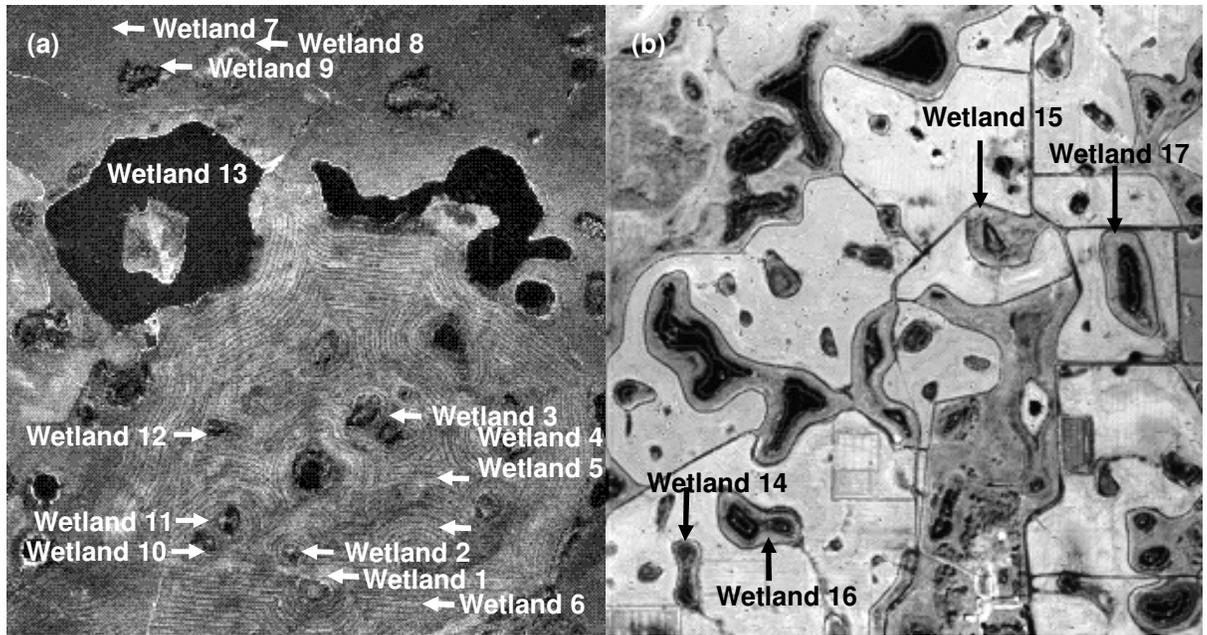


Figure 4.1. Aerial photograph of the research sites with the locations of the wetlands sampled: (a) at the St. Denis National Wildlife Area, provided by Canadian Wildlife Services, Environment Canada and (b) Manitoba Zero Till Research Farm, provided by Manitoba Zero Till Research Association.

Farm. The wetlands selected at this site included two ephemeral wetlands (wetlands 14 and 15) and two semi-permanent wetlands (wetlands 16 and 17) (Figure 4.1b). The catchment areas for these four wetlands were also contained within the study site.

4.2.2 Wetland Sampling

All wetlands at each study site were sampled in May 2007, after bottom sediment had thawed. A hand core sediment sampler (Wildco, New York, USA) was used to collect sediment samples from the ephemeral wetlands. For the deeper semi-permanent wetlands, a Kajak–Brinkhurst corer (Wildco, New York, USA) was used. In all but wetland 13 (Figure 4.1a), sediment was sampled in five points along two intercepting transects with three equally spaced points along the long axis and two points on the short axis. Sampling points on each axis were approximately 3 to 5 m apart, depending on the size of the wetland. At each sampling point, four cores consisting of the top five cm of sediment were collected and each core was placed in a Whirl-Pak polyethylene bag (Nasco, USA), which was then placed in an amber polyethylene bag. The large semi-permanent wetland at the St. Denis National Wildlife Area (wetland 13) was similarly sampled along a 10–point transect beginning at the point of runoff inflow (point 1). From the St. Denis National Wildlife Area site, samples were transported on ice to the National Hydrology Research Centre, Saskatoon, SK and maintained at -40 °C until they were freeze-dried. Initially, samples from the Manitoba Zero Till Research Farm were similarly transported to an on-site freezer maintained at -10 °C. Later, the samples were shipped on dry ice to the National Hydrology Research Centre, Saskatoon, SK for freeze-drying.

A water sample was collected from each wetland prior to sediment sampling for the purpose of sulfonylurea herbicide residue analysis. However, the water samples were compromised by the inadvertent addition of sulfuric acid to pH = 2 to stabilize the samples until extraction. Because sulfonylurea herbicides are rapidly hydrolyzed at pH = 5, (United States Department of Agriculture - Agricultural Research Service (USDA-ARS), 2001) these samples were not analyzed once we became aware of this circumstance.

4.2.3 Chemicals and Reagents

Certified ACS-grade formic acid and OmniPur ammonium acetate (>97%) were obtained from EMD Chemicals Inc (San Diego, CA). Ottawa sand (20–30 mesh) and pesticide grade methanol, ethyl acetate and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA). Deionized water (18 MΩ) was supplied from a Milli-Q Gradient A10 purification system (Millipore, Billerica, MA). Analytical grade sulfonylurea herbicide standards (thifensulfuron-methyl, tribenuron-methyl, ethametsulfuron-methyl, metsulfuron-methyl, rimsulfuron, nicosulfuron and sulfosulfuron) as well as the surrogate (nicosulfuron) and internal standards (bensulfuron-methyl) were purchased from Chem Service Inc (West Chester, PA) in solid form with 98% or greater purity.

4.2.4 Preparation of Standard Solutions

Stock solutions (1 mg L⁻¹) of each of the seven sulfonylurea herbicides were prepared in acetonitrile and stored in the dark at 4 °C. Stock solutions (1 mg L⁻¹) of two sulfonylurea herbicides not used in Canadian prairie crop production were also prepared in acetonitrile for use as surrogate (halosulfuron) and internal (bensulfuron-methyl) standards. A calibration stock solution containing all seven sulfonylurea herbicides each at 100 µg L⁻¹ was then prepared in acetonitrile such that it contained the surrogate standard (halosulfuron) and the internal standard (bensulfuron-methyl) at 100 µg L⁻¹ and 50 µg L⁻¹, respectively. Seven additional calibration standard solutions (1 to 50 µg L⁻¹) were prepared by serial dilution of the calibration stock solution with methanol and surrogate and internal standards added such that they were present in each solution at 100 µg L⁻¹ and 50 µg L⁻¹, respectively. All calibration standard solutions were prepared within 24 h of sample extract analysis.

4.2.5 Sediment Fortification

Recoveries of the seven sulfonylurea herbicides were determined from sediment from the control wetland fortified with the sulfonylurea herbicide mixture. This sediment had physicochemical properties similar to that collected from the wetlands on the St. Denis National Wildlife Area and the Manitoba Zero Till Research Farm (Table 4.2) and contained no detectable levels of the sulfonylurea herbicides. Freeze-dried sediment (5 g) was fortified at two levels (2 and 10 µg kg⁻¹) with the seven sulfonylurea herbicides by the addition 10 and

50 ng of each herbicide plus 100 ng of halosulfuron dissolved in methanol (1 mL). The sediment was mixed well and placed in a fume hood until methanol had completely evaporated. The fortified sediment was extracted within 48 h. Unfortified sediment was treated similarly with methanol only.

4.2.6 Pressurized Liquid Extraction

The four cores from each sampling point were freeze-dried individually using a Labconco freeze-dry system (Kansas City, USA), and then combined and mixed thoroughly using a mortar and pestle to create a homogenous sample for herbicide residue analysis.

Freeze-dried sediment (5 g) was mixed with Ottawa sand (40 g) and placed in a 33-mL stainless steel extraction cell equipped with two GF/X filter papers at the exit end of the cell and one filter paper at the inlet end. Additional Ottawa sand was used to completely fill the cell. The sample was then extracted with deionized water using a pressurized solvent extraction system (ASE 200; Dionex, Sunnyvale, CA) using the following operating conditions: temperature, 70 °C; static mode time, 5 min at 1500 psi; two static cycles; 75% flush volume with each cycle; and 140 s purge time with ultra-high purity nitrogen at the end of each run. The total volume of extraction solvent was approximately 50 mL or equivalent to approximately 1.5 times the cell volume.

4.2.7 Sediment Extract Cleanup

The Oasis HLB cartridge (Waters, Milford, MA) has been used previously for the solid-phase extraction (SPE) of sulfonylurea herbicides from environmental waters (Baker et al., 2005; Carabias-Martínez et al., 2004; Cessna et al., 2006; Perreau et al., 2007); therefore, it was selected for sediment extract cleanup. Using a 12-position vacuum manifold (Supelco, Gland, Switzerland), the SPE cartridges were conditioned with 10 mL methanol followed by 10 mL of deionized water. Sample extracts were loaded under a slight vacuum (600 mm Hg) onto the SPE cartridges at a flow rate of approximately 0.5 mL min⁻¹. The cartridges were then rinsed with 10-mL deionized

Table 4.2. Physicochemical properties of all sediment samples analyzed.

Sediment Samples	Sediment Properties					
	Total Organic Carbon Content	Total Inorganic Carbon	pH	Electrical Conductivity	Total Cation Exchangeable Capacity	Clay
	%	%		dS m ⁻¹	cmol(+) kg ⁻¹	%
Fortified Wetland Sediment	6.8 ± 0.5	0.57 ± 0.1	6.4 ± 0.1	0.6 ± 0.1	24.8 ± 2	4.9 ± 0.4
Wetland Sediment Samples [†]	6.8 ± 0.4	0.7 ± 0.1	6.7 ± 0.1	1.0 ± 0.1	26.2 ± 2	7.3 ± 0.5

[†]n=4, mean value for the sediment samples collected from the St. Denis National Wildlife Area and the Manitoba Zero Till Research Farm.

water and dried under a gentle stream of N₂ gas using the vacuum manifold equipped with the Visiprep SPE drying attachment (Supelco, Gland, Switzerland). The SPE cartridges were eluted with 4.5-mL of methanol and the extracts were evaporated and concentrated to near dryness under a gentle stream of nitrogen gas using the same drying attachment. Internal standard (bensulfuron-methyl; 50 ng in 50 µL of methanol) was added to the extract residues, which were reconstituted with deionized water resulting in a final volume of 1 mL for LC/MS/MS analysis.

4.2.8 Liquid Chromatography Tandem Mass Spectrometry

A Waters LC system consisting of the Model 1525 µ binary pump and a column oven (30 °C) was used with a Gemini C6-phenyl (150 mm x 2.0 mm i.d., 3-µm particle size) column (Phenomenex, Torrance, CA) and a C6-phenyl guard column (4 mm x 2.0 mm i.d.). Injection was achieved using the CTC Combi Pal autosampler (Leap Technologies, Carrboro, NC). All injection volumes were 10 µL. Mobile phase consisted of 0.1% formic acid in 2 mM ammonium acetate at a flow rate of 200 µL min⁻¹. Isocratic elution of the seven sulfonylurea herbicides plus the surrogate and internal standards from the column resulted in retention times ranging from 8.42 to 26.67 min (Table 4.3). To prevent carry-over from the injection port, consecutive injections (50 µL) of ethyl acetate and methanol were made before and after each sample extract analysis and vented from the injection port. Instrumental conditions were as follows: source temperature, 120 °C; cone voltage (Table 4.3); capillary voltage, 3.10 kV; desolvation temperature, 350 °C; nitrogen desolvation gas flow rate, 750 L h⁻¹; nitrogen cone gas flow rate, 150 L h⁻¹; extractor voltage, 4 V; RF lens 0 V. The cone voltage (20 to 25 eV) and collision energy (15 to 30 eV) were dependent on the multiple reaction monitoring (MRM) channel. Ultra high purity argon was used as collision gas for MRM at a pressure sufficient to increase the pirani gauge of the collision cell to a reading of 1.5 E⁻³ mbar. The software QuanLynx (Waters, Milford, MA) was used for data processing.

The sulfonylurea herbicides were quantified and confirmed using the Quattro Premier triple-quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray ionization (ESI) source set to positive ion mode which provided

Table 4.3. Liquid chromatography-tandem mass spectrometry (LC/MS/MS) retention time (R_t), and multiple reaction monitoring (MRM) transitions with their respective response ratio using electrospray ionization for sulfonylurea herbicides and internal standard.

Analyte	MRM m/z Quan (Qual)	Collision	Cone	R_t min
		Energy eV	Voltage eV	
1. Nicosulfuron	411.2 > 182.8	20	25	8.42
	(411.2 > 213.8)	15	25	8.42
2. Thifensulfuron-methyl	388 > 167.2	20	20	9.00
3. Metsulfuron-methyl	382 > 167.6	20	25	9.33
4. Ethametsulfuron-methyl	411.8 > 168.3	30	20	9.66
	(411.8 > 196.9)	15	20	9.66
5. Rimsulfuron	432 > 182.3	25	25	10.25
	(432 > 325.7)	15	25	10.25
6. Bensulfuron-methyl	411.5 > 150	25	25	13.66
7. Tribenuron-methyl	396.2 > 156.5	15	20	13.83
	(396.2 > 181.9)	20	20	13.83
8. Sulfosulfuron	471.1 > 211.4	25	20	17.49
	(471.1 > 218.2)	25	20	17.49
9. Halosulfuron	435.5 > 182.5	20	25	26.67

maximum sensitivity (Cessna et al., 2006). Ionization and MS/MS conditions were optimized by infusing a 50 $\mu\text{g L}^{-1}$ solution [50:50 (v/v) acetonitrile: water] of each sulfonylurea herbicide into the ion source with a syringe pump. The protonated molecule $[\text{MH}]^+$ for each herbicide was selected for collision induced dissociation using the first quadrupole. Argon gas was introduced into the collision cell (hexapole) and the third quadrupole was used to monitor the resulting major product ions. For most of the sulfonylurea compounds, two or three product ions were observed in the product ion scan; however, only the most intense transition was selected for quantification purposes. The second most intense transition was used for confirmation purposes along with retention time and the ratio of the quantitative/qualitative ion transitions. In some cases (Table 4.3), a second fragment ion was not observed and for these sulfonylurea herbicides only the single MRM transition was available for quantification. Maximum sensitivity was achieved by optimizing the cone and collision energy.

The main cleavage of the sulfonylurea herbicide molecule involved the sulfonylurea bridge (between the carbonyl group and the amino nitrogen attached to the sulfonyl moiety). Because some of the sulfonylurea herbicides have similarly substituted triazine or pyrimidine rings, the same product ion was monitored when quantifying the different sulfonylurea herbicides. For example, thifensulfuron-methyl, tribenuron-methyl and metsulfuron-methyl have triazine rings similarly substituted with methyl and methoxy groups, whereas rimsulfuron, halosulfuron, nicosulfuron, bensulfuron-methyl and sulfosulfuron possess pyrimidine rings similarly substituted with methoxy groups (Table 4.1).

4.3 Results and discussion

4.3.1 Optimization of Pressurized Liquid Extraction Parameters

The efficiency of extracting herbicides from soil has improved in recent years with development of newer techniques, including microwave assisted extraction (Font et al., 1998), supercritical fluid extraction (Berdeaux et al., 1994) and pressurized liquid extraction (PLE) (Kremer et al., 2004). One of the advantages of using the PLE technique is that a wide range of solvents can be used for extraction. The ideal extraction solvent should be selective for the analytes of interest but also minimize the

extraction of organic co-extractives in order to simplify extract cleanup. For example, Kremer et al. (2004) found that PLE using water and acetonitrile eluted less lipophilic substances from soil compared to methanol. However, when greater than 5% of an organic solvent is used in the extraction solvent, it is necessary to concentrate the extract and then reconstitute with water prior to SPE cleanup. If the amount of organic solvent in the reconstituted extract is less than 5%, then the extract may be subjected to SPE in the same manner as a water sample (Waters, 2000).

In the present study, the PLE method used for wetland sediment extraction was finalized after investigating various extraction solvents and the number of extraction cycles. Based on the extraction of soil by Kremer et al. (2004) water and water containing 5% acetonitrile were considered for the extraction of the seven sulfonylurea herbicides from wetland sediment. Sulfonylurea herbicides are relatively soluble in water (Table 4.1), therefore efficient PLE extraction with water or aqueous acetonitrile was expected. Sulfonylurea herbicides are weak acids and their water solubility and mobility in soil increases with increasing pH (Hollaway et al., 2006). Therefore, we also investigated extraction under alkaline conditions using 0.5 mM sodium hydroxide solution (pH = 9.5). Using sediment from the control wetland (n = 6) fortified with the seven sulfonylurea herbicides at 10 $\mu\text{g kg}^{-1}$, the operating conditions of PLE using each of the above extraction solvents were: temperature – 70 °C, pressure – 1500 psi, extraction time – 5 min, flush volume – 75%, and 1 or 2 extraction cycles.

The recovery for six out of the seven sulfonylurea herbicides from the fortified wetland sediment using one extraction cycle with water as the extraction solvent gave consistent results, with percent recoveries ranging from 77.3 \pm 2% for metsulfuron-methyl to 100 \pm 2% for thifensulfuron-methyl. The recovery for tribenuron-methyl, the sulfonylurea herbicide most susceptible to hydrolysis at pH = 7, (Syracuse Research Corporation, 2009) was significantly lower at 47.3 \pm 2%. The addition of 5% acetonitrile or 0.5 mM sodium hydroxide to water as extraction solvents did not markedly improve the mean (n = 6) herbicide recoveries from fortified sediment (Table 4.4).

Table 4.4. Pressurized solvent extraction efficiency for various optimization parameters.

Compounds	Extraction Efficiency (%) [†]			
	Pressurized Solvent Extraction Optimization Parameters			
	Deionized water (1 cycle)	Deionized water (2 cycles)	Deionized water with 5% acetonitrile (1 cycle)	Deionized water with 0.5 mM NaOH (1 cycle)
Nicosulfuron	95.2±2	97.0±3	92.2±3	89.7±3
Thifensulfuron- methyl	100.0±2	104.9±2	99.1±2	102.8±2
Metsulfuron- methyl	77.3±2	94.5±3	75.5±4	77.6±2
Ethametsulfuron- methyl	96.8±3	99.4±3	95.6±2	96.7±3
Rimsulfuron	93.9±3	97.2±2	82.5±3	92.7±3
Tribenuron- methyl	47.3±2	56.2±5	46.9±3	45.0±4
Sulfosulfuron	87.3±4	92.4±2	87.4±2	86.5±3

[†]Extraction efficiency is the mean ± standard deviation calculated based on the mean extraction efficiency of six fortified sediment samples.

Because the addition of acetonitrile or sodium hydroxide to water did not improve recoveries, the effect of a second extraction cycle was investigated with water as the extraction solvent. The additional extraction cycle improved recoveries of the individual sulfonylurea herbicide by approximately 5 to 10% such that, with the exception of tribenuron-methyl, recoveries for the other six herbicides ranged from $92.4 \pm 2\%$ for sulfosulfuron to $104.9 \pm 2\%$ for thifensulfuron-methyl (Table 4.4). The additional cycle also increased the recovery of tribenuron-methyl from $47.3 \pm 2\%$ to $56.2 \pm 4\%$. Kremer et al. (2004) found that an additional extraction cycle increased extraction efficiency when a single extraction cycle was insufficient for quantitative recovery.

With a mean recovery for all seven herbicides greater than 90%, the relatively high organic carbon content of the sediments (Table 4.2) did not appear to significantly reduce herbicide recoveries. This was not unexpected because the log K_{ow} values for the seven sulfonylurea herbicides are quite low, ranging from -0.051 to -1.7 (United States Department of Agriculture - Agricultural Research Service (USDA-ARS), 2001). When the six fortified sediment samples were subjected to a third extraction with water, none of the seven sulfonylurea herbicides was detected in the resulting sediment extracts. Consequently, water with two extraction cycles was used to extract all of the wetland sediment samples.

4.3.2 Herbicide Separation and Quantification

The total MRM LC/MS/MS chromatogram for the seven selected sulfonylurea herbicides ($50 \mu\text{g L}^{-1}$), the internal standard ($50 \mu\text{g L}^{-1}$) and the surrogate standard ($100 \mu\text{g L}^{-1}$) is shown in Figure 4.2 (a). Under the chromatographic conditions used, baseline separation was not achieved within a 30-min run time for metsulfuron-methyl (peak 3; 9.33 min), ethametsulfuron-methyl (peak 4; 9.66 min) and rimsulfuron (peak 5; 10.25 min) and for bensulfuron-methyl (peak 6; 13.66 min) and tribenuron-methyl (peak 7; 13.83 min). Incomplete chromatographic resolution of the co-eluting sulfonylurea herbicides was resolved by the use of tandem mass spectrometry, with the exception of thifensulfuron-methyl and metsulfuron-methyl, because different product ions were produced for the most intense transitions monitored for the co-eluting herbicides. Even

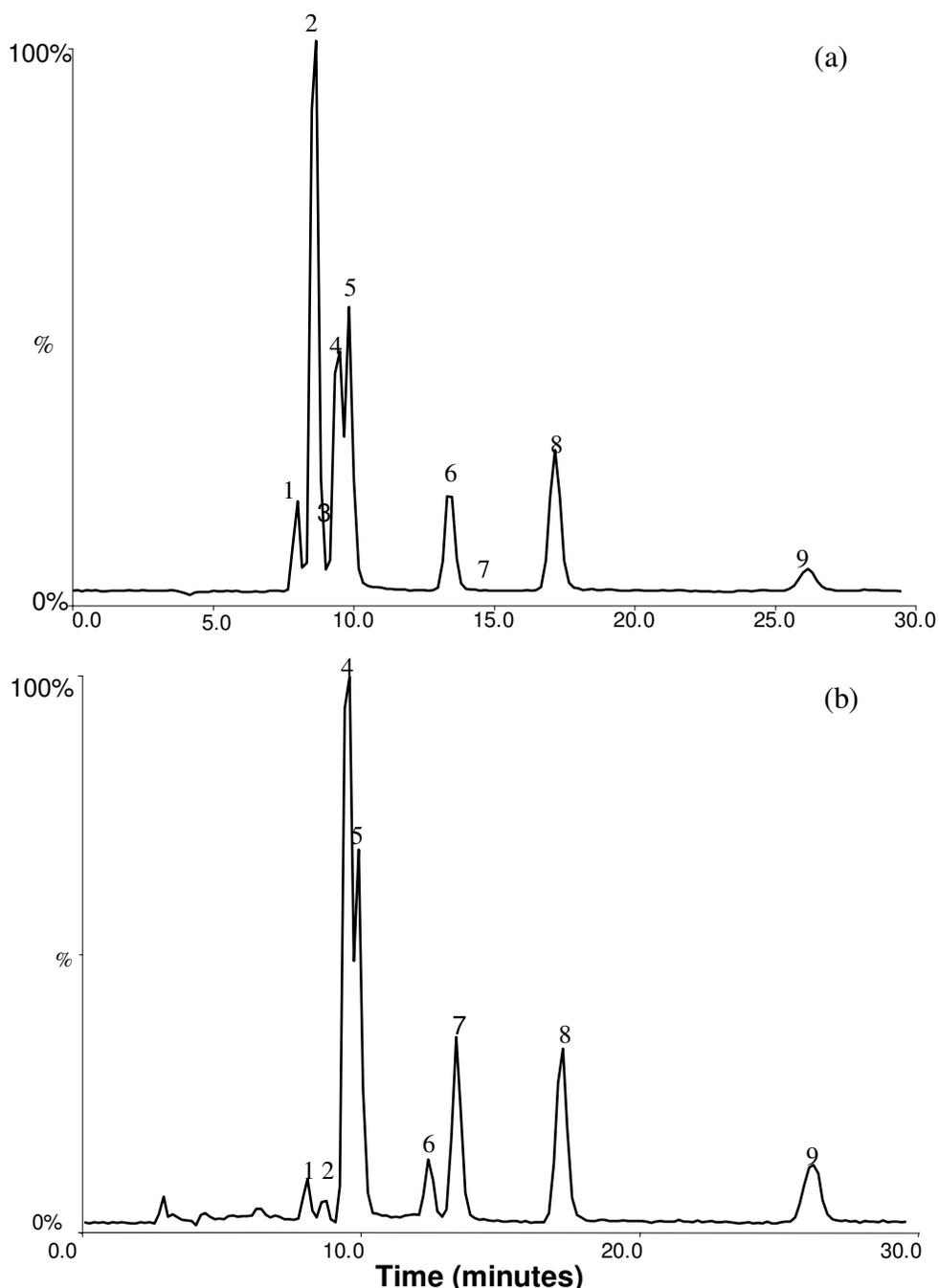


Figure 4.2. Total multiple reaction monitoring (MRM) chromatogram of (a) the nine sulfonyleurea herbicides from the injection of 10 μL of a standard mixture at $50 \mu\text{g L}^{-1}$ for all sulfonyleurea except for halosulfuron-methyl at $100 \mu\text{g L}^{-1}$. 1, nicosulfuron; 2, thifensulfuron-methyl; 3, metsulfuron-methyl; 4, ethametsulfuron-methyl; 5, rimsulfuron; 6, bensulfuron-methyl (internal standard); 7, tribenuron-methyl; 8, sulfosulfuron and 9, halosulfuron-methyl (surrogate standard) and (b) of wetland sediment sample: (1) nicosulfuron $3.0 \mu\text{g kg}^{-1}$ (8.33 min); (2), thifensulfuron-methyl $0.42 \mu\text{g kg}^{-1}$ (9.00 min); (4) ethametsulfuron-methyl $17.7 \mu\text{g kg}^{-1}$ (9.83 min); (5) $6.1 \mu\text{g kg}^{-1}$ (10.16 min); (6) bensulfuron-methyl (internal standard) $55.2 \mu\text{g kg}^{-1}$ (13.66 min); (8) sulfosulfuron $13.5 \mu\text{g kg}^{-1}$ (17.49 min); and (9) halosulfuron-methyl (surrogate standard) $99.3 \mu\text{g kg}^{-1}$ (26.32 min). Metsulfuron-methyl (3) and tribenuron-methyl (7) were not detected in this sediment sample.

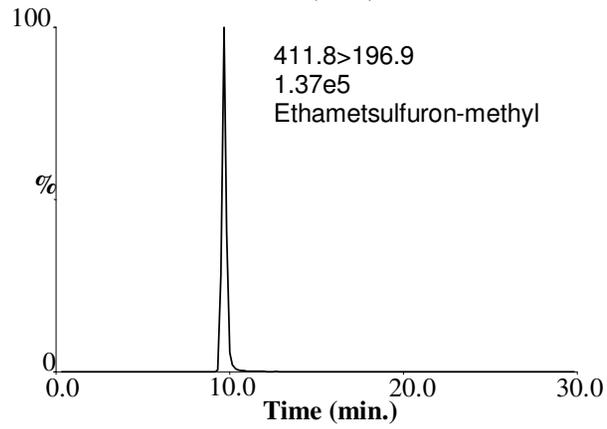
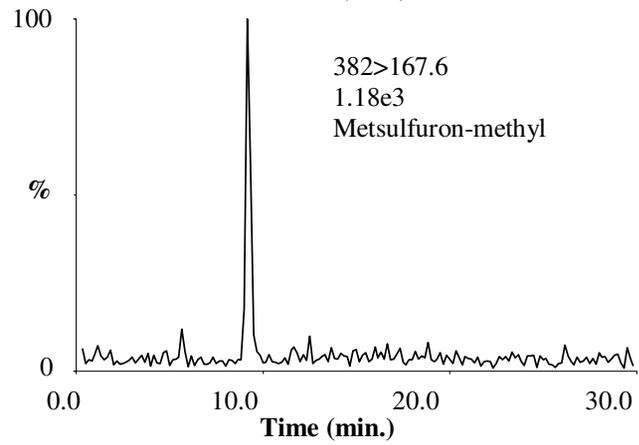
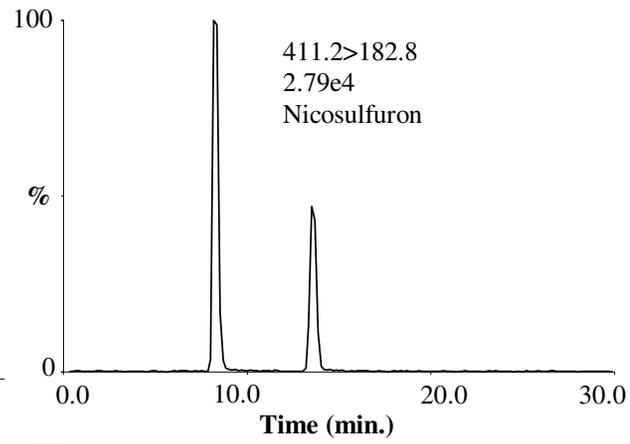
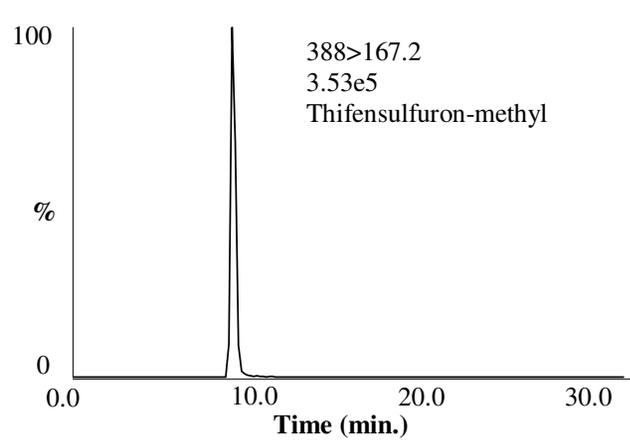
though the masses of the protonated molecules of thifensulfuron-methyl and metsulfuron-methyl are different, each protonated parent molecule gives a specific transition to the same product ion (Figure 4.3, Table 4.3). Although the same product ions were produced, there was no crosstalk between the two MRM channels for these herbicides. This is demonstrated in Figure 4.3 where all seven herbicides were analyzed separately and all 14 transitions (Table 4.3) were monitored.

Using eight-point calibration curves (1 to 100 $\mu\text{g L}^{-1}$), herbicide concentrations in the sediment extracts were quantified by using the most predominant precursor-product ion transition for each sulfonylurea herbicide precursor ion in the full-scan MS/MS mass spectrum (Figure 4.3). Strong linear correlations ($r^2 > 0.994$) were observed between the observed peak areas versus concentration over the entire calibration range of each herbicide. The instruments detection limit for each of the seven sulfonylurea herbicides was in the order of 10 pg (equivalent to 1 ng L^{-1}), the method detection limit or limit of detection determined using blank sediment was 0.5 $\mu\text{g kg}^{-1}$. The limit of quantification (LOQ), defined as half of the minimum fortification concentration of each sulfonylurea herbicide used in the recoveries studies, was 1 $\mu\text{g kg}^{-1}$ for all sulfonylurea herbicides except for tribenuron-methyl for which the LOQ was 2 $\mu\text{g kg}^{-1}$.

4.3.3 Analysis of Wetland Sediment Samples

As part of the quality assurance/quality control protocol, sediment from the control wetland fortified at 10 ($n = 10$) and 2 ($n = 10$) $\mu\text{g kg}^{-1}$ with each sulfonylurea herbicide was analyzed with each set of ten wetland sediment samples. Results of the fortifications at 10 $\mu\text{g kg}^{-1}$ demonstrated that the herbicide recoveries were similar to those obtained during method development with recoveries ranging from $57.9 \pm 13.0\%$ for tribenuron-methyl to $98.2 \pm 17.0\%$ for ethametsulfuron-methyl (Figure 4.4a). At the 2 $\mu\text{g kg}^{-1}$ fortification level, recoveries were lower and ranged from $24.9 \pm 5.4\%$ for tribenuron-methyl to $73.6 \pm 16.5\%$ for sulfosulfuron (Figure 4.4b).

Analysis of sediment samples collected from the 17 wetlands on the two study sites in Saskatchewan and Manitoba resulted in the detection of at least one of seven sulfonylurea herbicides in each of the 90 sediment samples analyzed in our study (Table



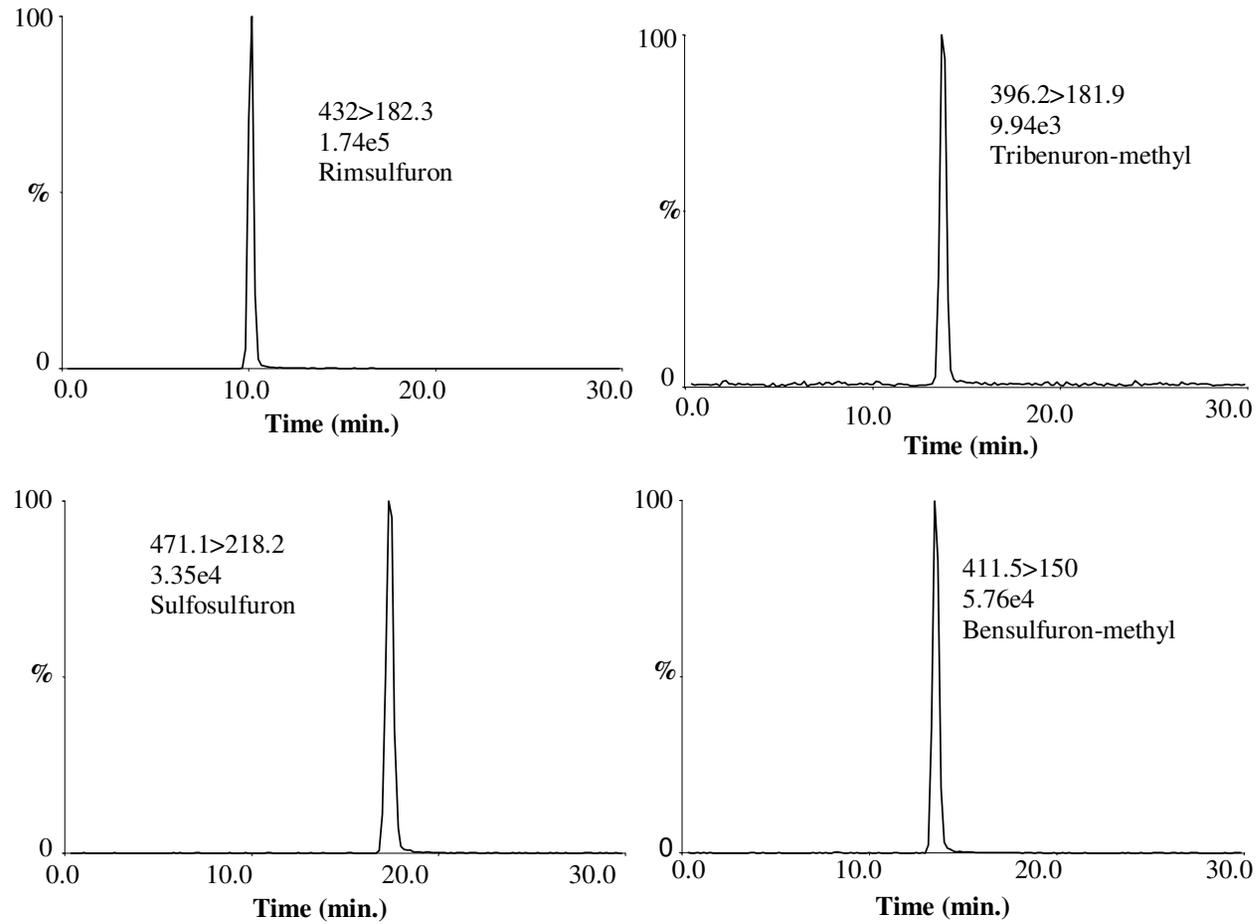


Figure 4.3. Individual multiple reaction monitoring (MRM) chromatograms of nicosulfuron, thifensulfuron-methyl, metsulfuron-methyl, ethametsulfuron-methyl, rimsulfuron, tribenuron-methyl, sulfosulfuron and bensulfuron-methyl (internal standard) for quantitative transitions. Injection of 10 μL standard at 50 $\mu\text{g L}^{-1}$.

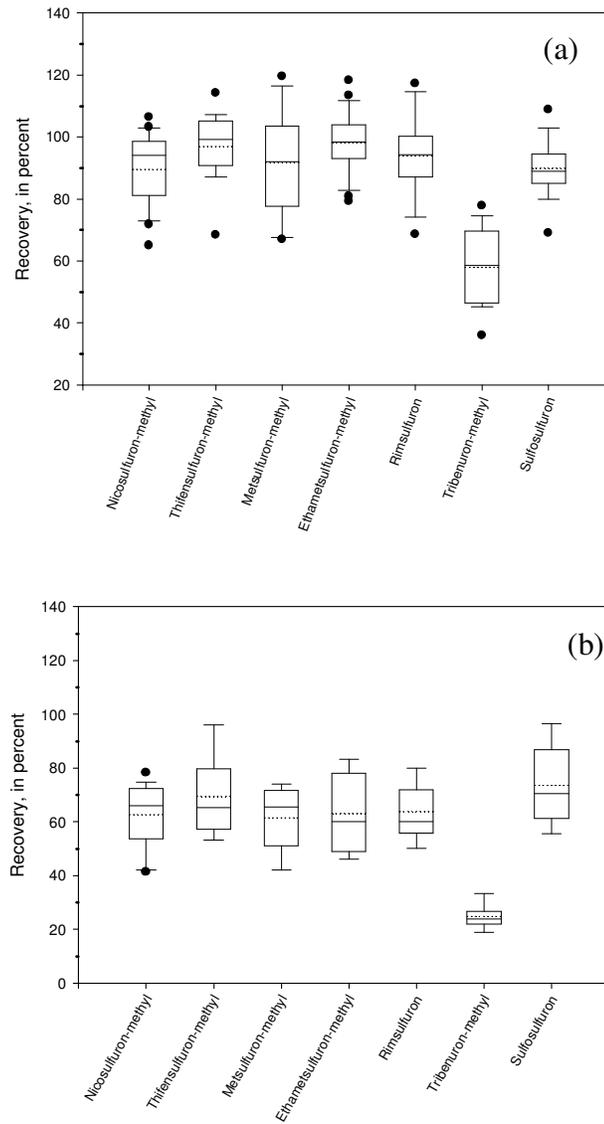


Figure 4.4. Recovery of herbicides fortified in sediment at a concentration of (a) 10 µg kg⁻¹ and (b) 2 µg kg⁻¹. The hinges indicate median recoveries, while the dotted line indicates the mean recovery. The boxes indicate 25th and 75th percentiles, and whiskers indicate 5th and 95th percentiles. The solid circle indicates outlier recoveries.

4.5). The chromatogram in Figure 4.2 (b) illustrates the analysis of the extract of a sediment sample collected from wetland 13 on the St. Denis National Wildlife Area. Five sulfonylurea herbicides were detected including: nicosulfuron (1), thifensulfuron-methyl (2), ethametsulfuron-methyl (3), rimsulfuron (4) and sulfosulfuron (6). The chromatogram shows that SPE cleanup of the sediment extract resulted in very little interference from matrix co-extractives.

In 2006, approximately 270,000 ha of cropland in Manitoba were treated with the seven sulfonylurea herbicides monitored in the current study (Manitoba Agriculture Service Corporation, 2007). The area treated with these herbicides decreased in the following order: thifensulfuron-methyl (~76%) \approx tribenuron-methyl (~75%) > rimsulfuron (~8%) \approx nicosulfuron (~8%) > ethametsulfuron-methyl (~5%) > metsulfuron-methyl (~1%) > sulfosulfuron (<1%). Mixtures of thifensulfuron-methyl and tribenuron-methyl are applied to cereal crops [wheat (spring, durum, winter), barley (*Hordeum vulgare* L.), oat (*Avena sativa* L.)], nicosulfuron to corn (*Zea mays* L.), rimsulfuron to corn and potato (*Solanum tuberosum* L.) and ethametsulfuron-methyl to canola, mustard (*Brassica juncea* L.) and sunflower (*Helianthus annuus* L.). Data on the use of these herbicides in the province of Saskatchewan were not available. However, because the same crops are grown in both provinces and, with the exception of more potato in Manitoba, in essentially the same proportion, the Manitoba sulfonylurea herbicide use data should approximate that in Saskatchewan.

The proportional use of each of the seven sulfonylurea herbicides in the provinces of Manitoba and Saskatchewan appeared to have no relation to the frequency and levels of sulfonylurea herbicides detected in the 90 wetland sediment samples. For example, the two herbicides used on the greatest area of cropland, thifensulfuron-methyl and tribenuron-methyl, were detected in sediment from the fewest wetlands and only in trace concentrations; that is, at concentrations less than the LOQ. Tribenuron-methyl was not detected in wetland sediment from the Manitoba Zero Till Research Farm. In contrast, ethametsulfuron-methyl was detected in sediment samples from all wetlands with 39% of samples having concentrations greater than the LOQ. Similarly, sulfosulfuron was detected in a high proportion (96%) of samples, also with 39% of samples having concentrations greater than the LOQ. Rimsulfuron and nicosulfuron

were detected in 89% and 81% of sediment samples, respectively, but concentrations greater than the LOQ were detected only in sediment from the large semi-permanent wetland on the St. Denis National Wildlife Area.

The presence of the seven sulfonylurea herbicides in the wetland sediments was more closely correlated with their persistence in the environment. The environmental persistence of the seven sulfonylurea herbicides reflects to a large extent the susceptibility of the sulfonylurea herbicides to hydrolysis and decreases in the following order: sulfosulfuron (7 to 120 d) > metsulfuron-methyl (8 to 105 d), > ethametsulfuron-methyl (16 to 54 d) > nicosulfuron (14 to 49 d) > rimsulfuron (5 to 23 d) > thifensulfuron-methyl (6 to 17 d) > tribenuron-methyl (2 to 23 d) (United States Department of Agriculture - Agricultural Research Service (USDA-ARS), 2001). This order of environmental persistence closely reflects the frequency of detection of the sulfonylurea herbicides in wetland sediment as well as the frequency of detection of concentrations greater than the LOQ; that is, the greater the environmental persistence of a sulfonylurea herbicide, the greater its frequency of detection in wetland sediment (Table 4.5). The mean concentrations of the three most environmentally persistent herbicides (sulfosulfuron, metsulfuron-methyl, and ethametsulfuron-methyl) ranged from 1.2 to 10.0 $\mu\text{g kg}^{-1}$ in sediment from individual wetlands. The maximum concentration for any sulfonylurea herbicide in wetland sediment was that for ethametsulfuron-methyl (17.7 $\mu\text{g kg}^{-1}$; Figure 4.2b).

The method developed in this paper provided > 85% analyte recovery for six out of the seven sulfonylurea herbicides (Table 4.4, Figure 4.4). Tribenuron-methyl had significantly lower recovery compared to the other six sulfonylurea herbicides; consequently the LOQ for tribenuron-methyl was also higher, at 2 $\mu\text{g kg}^{-1}$. In addition to its relatively short environmental persistence, the low recovery of tribenuron-methyl may also have contributed to its low detection frequency in the sediment samples.

Pesticides are known to move from treated agricultural areas and it is generally accepted that such movement is associated with atmospheric transport and transport in water. Because sulfonylurea herbicides had not been applied to the study sites within the last five years, their presence in wetland sediment could only have resulted from

atmospheric deposition directly into the wetlands or deposition within the catchment area and subsequent transport in snowmelt runoff entering the wetlands. Because the

Table 4.5. Sulfonylurea herbicide concentrations ($\mu\text{g kg}^{-1}$) in wetland sediment from the St. Denis National Wildlife Area (SK) and the Manitoba Zero Till Research Farm (MB). The limit of quantification (LOQ) is $1 \mu\text{g kg}^{-1}$ for all seven sulfonylurea except tribenuron-methyl, which the LOQ is set at $2 \mu\text{g kg}^{-1}$. The number samples in which herbicides were detected is indicated in parentheses.

Site Location	Wetland number	Nicosulfuron	Thifensulfuron-methyl	Metsulfuron-methyl	Ethametsulfuron-methyl	Rimsulfuron	Tribenuron-methyl	Sulfosulfuron
SK	1	<LOQ (n=3)	0	0	<LOQ (n=5)	<LOQ (n=5)	<LOQ (n=4)	<LOQ (n=3)
SK	2	<LOQ (n=5)	<LOQ (n=2)	<LOQ (n=1)	<LOQ (n=5)	<LOQ (n=4)	<LOQ (n=4)	<LOQ (n=3)
SK	3	<LOQ (n=3)	0	0	<LOQ (n=5)	<LOQ (n=4)	<LOQ (n=4)	1.2 ± 0.6 (n=5)
SK	4	<LOQ (n=5)	0	<LOQ (n=3)	<LOQ (n=5)	<LOQ (n=3)	<LOQ (n=2)	<LOQ (n=5)
SK	5	<LOQ (n=5)	0	<LOQ (n=3)	<LOQ (n=5)	<LOQ (n=1)	<LOQ (n=2)	<LOQ (n=5)
SK	6	<LOQ (n=2)	0	<LOQ (n=3)	<LOQ (n=5)	<LOQ (n=5)	0	<LOQ (n=5)
SK	7	<LOQ (n=4)	<LOQ (n=5)	<LOQ (n=1)	<LOQ (n=5)	<LOQ (n=5)	<LOQ (n=1)	3.4 ± 5.8 (n=5)
SK	8	<LOQ (n=5)	<LOQ (n=5)	1.4 ± 2.0 (n=5)	<LOQ (n=5)	<LOQ (n=5)	<LOQ (n=2)	<LOQ (n=5)
SK	9	<LOQ (n=5)	<LOQ (n=4)	<LOQ (n=2)	1.3 ± 0.5 (n=5)	<LOQ (n=5)	<LOQ (n=1)	7.1 ± 2.5 (n=5)
SK	10	<LOQ (n=3)	0	1.4 ± 1.0 (n=5)	<LOQ (n=5)	<LOQ (n=5)	<LOQ (n=1)	<LOQ (n=5)
SK	11	<LOQ (n=4)	0	<LOQ (n=1)	<LOQ (n=5)	<LOQ (n=3)	0	<LOQ (n=5)
SK	12	<LOQ (n=1)	0	0	<LOQ (n=5)	<LOQ (n=5)	0	2.8 ± 4.5 (n=5)
SK	13	2.0 ± 0.6 (n=10) [†]	<LOQ (n=10)	<LOQ (n=4)	10.0 ± 4.0 (n=10)	2.6 ± 2.5 (n=10)	0	5.5 ± 3.3 (n=10)
MB	14	<LOQ (n=5)	<LOQ (n=5)	<LOQ (n=2)	1.6 ± 0.5 (n=5)	<LOQ (n=5)	0	<LOQ (n=5)
MB	15	<LOQ (n=4)	<LOQ (n=4)	0	4.0 ± 5.7 (n=5)	<LOQ (n=5)	0	<LOQ (n=5)
MB	16	<LOQ (n=5)	0	0	2.6 ± 1.0 (n=5)	<LOQ (n=5)	0	1.2 ± 0.4 (n=5)
MB	17	<LOQ (n=4)	0	0	2.5 ± 2.4 (n=5)	<LOQ (n=5)	0	<LOQ (n=5)
% detections	-	81	39	31	100	89	23	96
% detections >LOQ	-	11	0	11	39	11	0	39

[†]Each sulfonylurea herbicide concentration is the mean concentration of five sediment samples taken from each wetland, except for wetland 13, which is the mean of 10 sediment samples. Mean sulfonylurea herbicide concentrations detected in wetland sediment are not corrected based on corresponding recoveries from fortified sediment.

wetlands in our study are situated in areas of intensive agricultural production, sulfonylurea herbicides in the wetland sediment could have resulted from deposition of spray drift from neighbouring fields (Wolf et al., 2008), or via longer range atmospheric deposition (Tuduri et al., 2006). In the case of wetland 13 on the St. Denis National Wildlife Area, the herbicide concentrations in the sediment samples showed a distinct spatial pattern (Figure 4.5). Higher concentrations of ethametsulfuron-methyl, sulfosulfuron and rimsulfuron were detected near the point of runoff inlet (points 1 and 2) of wetland 13. This wetland typically receives snowmelt runoff from a large catchment area that extends beyond the study site. Thus, given the timing of our sampling and the spatial pattern of the sulfonylurea concentrations in this wetland, the main source of these herbicides was likely from snowmelt runoff.

Because the water samples collected simultaneously with the sediment samples were compromised by the addition of sulfuric acid, we have no sulfonylurea herbicide concentration data in the water column relative to corresponding concentrations detected in the sediment. However, the two sulfonylurea herbicides (ethametsulfuron-methyl and sulfosulfuron) most frequently detected in our sediment samples were also detected in drinking water reservoirs situated in regions near the St. Denis National Wildlife Area and Manitoba Zero Till Research Farm study sites (Donald et al., 2007). Nevertheless, concentrations of these herbicides in the water columns of these reservoirs (1.4 to 25 ng L⁻¹) were two to three orders of magnitude lower than corresponding concentrations detected in wetland sediments in the present study (Table 4.4). Interestingly, tribenuron-methyl and thifensulfuron-methyl, which demonstrate the least environmental persistence of the seven herbicides studied, were also detected in 20% and 3% of drinking water reservoir samples, respectively. In another surveillance study, conducted in 11 Midwestern States in the USA, nicosulfuron was detected in concentrations above the method reporting limit (10 ng L⁻¹) in 52% of samples collected from surface water reservoirs (Battaglin et al., 2000). The concentrations of sulfonylurea herbicides that we detected in wetland sediment are not likely to have a significant biologic effect on non-target aquatic plants. However, they do contribute to the overall pesticide load present in wetland ecosystems and, at this point, the ecotoxicological effect of herbicide mixtures on aquatic biota is still unclear.

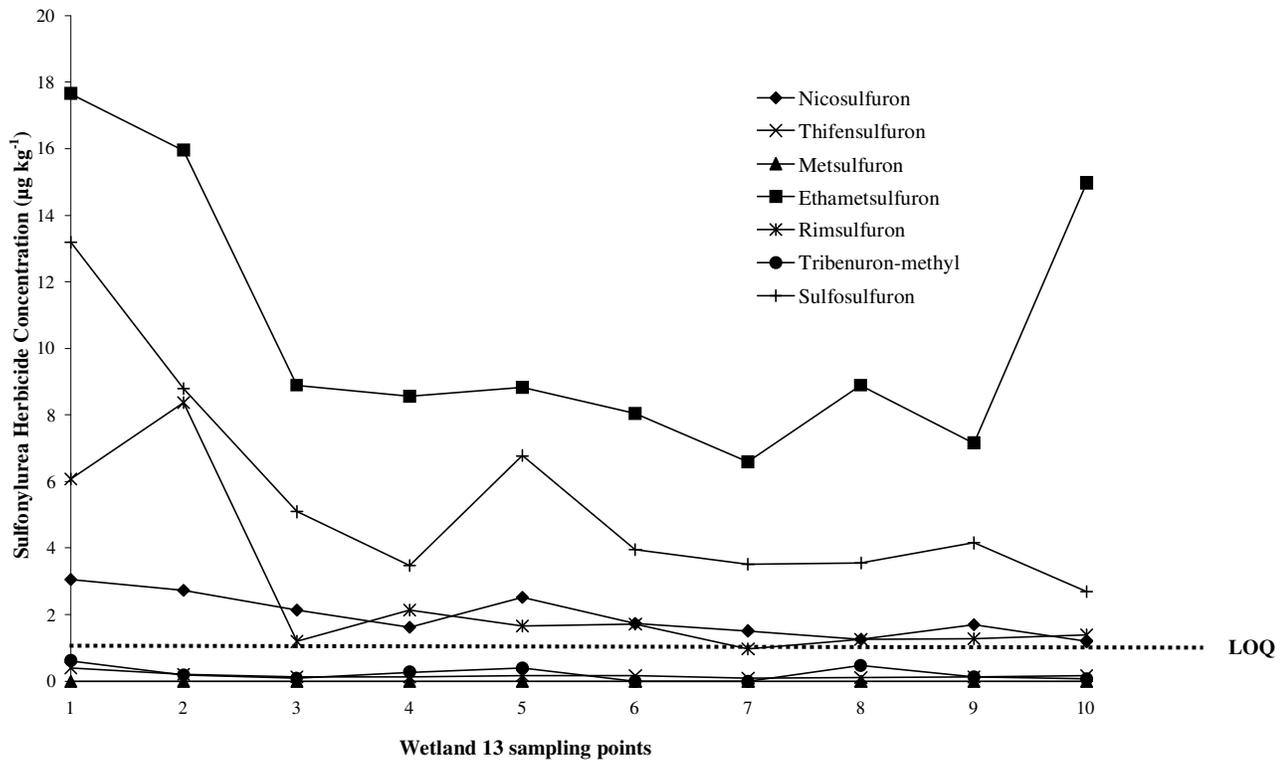


Figure 4.5. Sulfonylurea herbicide concentrations from sediment samples collected from 10 sampling points in wetland 13 from St. Denis National Wildlife Area, Saskatchewan, Canada. The dashed line represents the limit of detection (LOQ) for all seven sulfonylurea herbicides except tribenuron-methyl, for which the LOQ was set at $2 \mu\text{g kg}^{-1}$.

4.4 Conclusions

The multi-residue analytical method developed proved to be robust and reliable for the purpose of quantifying environmental concentrations (LOQ from 1 to 2 $\mu\text{g kg}^{-1}$) of sulfonyleurea herbicide mixtures in wetland sediment. This study has demonstrated the usefulness of both PLE and LC/MS/MS for the routine determination in wetland sediment of seven sulfonyleurea herbicides widely used in crop production on the Canadian prairies. The method developed in this paper should prove useful for routine monitoring of sulfonyleurea herbicides, as well as determining the effects on aquatic flora and fauna in wetlands of low-level exposure to sulfonyleurea herbicide mixtures. Findings from those studies will be critical for establishing environmentally relevant standards for herbicide mixtures.

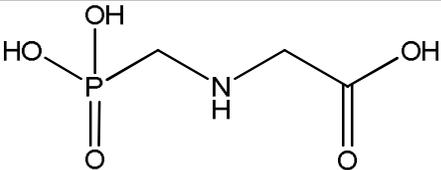
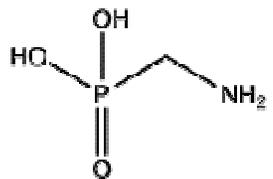
5.0 DISSIPATION OF HERBICIDES IN WATER AND SEDIMENT OF TWO CANADIAN PRAIRIE WETLANDS. PART I. GLYPHOSATE AND AMINOMETHYLPHOSPHONIC ACID

5.1 Introduction

Glyphosate (*N*-phosphonomethyl glycine) is a broad spectrum, non-selective herbicide. In western Canada, it is predominately used for pre-seeding and post-harvest weed control in agricultural crop production. Glyphosate use has increased in the past 10 years as has the area seeded to glyphosate tolerant crops such as canola (*Brassica napus* L.), field and silage corn (*Zea mays* L.) and soybean (*Glycine max* L. Merr.). As well, glyphosate is the most widely used herbicide active ingredient in Manitoba, accounting for 18% of the total pesticide treated area (Shymko et al., 2008). Glyphosate is a weak organic acid comprised of glycine and a phosphonomethyl moiety (Table 5.1), which inhibits 5-enolpyruvylshikimate-3-phosphate synthase, an enzyme essential for the synthesis of plant amino acids (Duke, 1988).

Knowledge of glyphosate dissipation in the prairie pothole region of the North American Great Plains is important for several reasons. The millions of wetlands here are susceptible to pesticide contamination because of their location in agricultural fields where pesticides are regularly used. Pesticides enter wetlands via application drift (Wolf and Cessna, 2004), wet and dry atmospheric deposition (Yao et al., 2006), deposition of wind-eroded soil (Larney et al., 1999), and by surface runoff (Cessna et al., 1994; Degenhardt et al., 2010b; Waite et al., 1992). Commonly used pesticides have been detected in the waters of prairie wetlands in several studies (Cessna and Elliott, 2004; Donald et al., 1999; Grover et al., 1997; Waite et al., 2004). Concerns regarding pesticide contamination in wetlands are growing because of the reported negative impacts of agricultural chemicals on wetland biota (Donald et al., 1999; Perez et al., 2007; Relyea, 2005a). Most recently, both endocrine and toxic effects of

Table 5.1. Table of some physicochemical properties of glyphosate and aminomethylphosphonic acid (AMPA) (Tomlin, 2000; Traas and Smit, 2003).

Compound	Structural formula	Molecular mass (g mol ⁻¹)	Water solubility (g L ⁻¹)	Vapour pressure mPa	pKa	Photolysis DT ₅₀ in water (day)	Log <i>K_{ow}</i>	DT ₅₀ in soil (day)
Glyphosate		169.1	10.1	< 1 x 10 ⁻⁵	< 2, 2.6, 5.6, 10.6	69	-2.8	12
AMPA		111.0	5.80	No data	0.9, 5.6, 10.2	No data	-2.2	No data

glyphosate-based herbicides were observed in mammalian cells (Benachour and Seralini, 2009; Gasnier et al., 2009; Richard et al., 2005).

Biodegradation of glyphosate to its major metabolite aminomethylphosphonic acid (AMPA) is an important dissipation pathway in surface waters, while photolytic decomposition and chemical degradation are comparatively minor (Mallat and Barcelo, 1998). Glyphosate dissipation in boreal forest wetlands was rapid with first-order half-lives (DT_{50}) ranging from 1.5 to 11.2 d (Feng et al., 1990; Goldsborough and Beck, 1989; Goldsborough and Brown, 1993; Newton et al., 1994). In fact, AMPA has been detected in wetland water as early as 24-h after glyphosate addition (Goldsborough and Beck, 1989). In various surface water quality studies conducted in the USA, AMPA occurred more frequently than glyphosate and, often, concentrations of AMPA were higher than those of glyphosate (Battaglin et al., 2005; Scribner et al., 2003; Scribner et al., 2007). In soil, the sorption coefficient (K_d) of AMPA is similar to that of its parent compound ($K_d > 100 \text{ L kg}^{-1}$) (Grunewald et al., 2000). Persistence of trace levels of AMPA in the environment (Baker et al., 2006) is likely due to the low penetration of AMPA into microbial cell walls which in turn leads to lower rates of microbial degradation (United States Environmental Protection Agency, 1984).

Although glyphosate dissipation in boreal forest wetlands has been reported (due to the widespread use of glyphosate in silviculture), glyphosate and AMPA dissipation in prairie wetland water or sediment have not been studied. Given that prairie wetlands and boreal forest wetlands have very different hydrological, environmental and biological attributes (e.g. temperature, water and sediment characteristics, microbial populations and activities), dissipation of glyphosate may differ significantly in prairie wetlands from that in boreal forest wetlands. During summer, evaporation is an important water loss pathway, especially in semi-permanent wetlands. However, greater than 70% of water loss from ephemeral wetland is via infiltration to wetland margin (Parsons et al., 2004). This may or may not be an important route of dissipation of glyphosate because it is strongly sorbed to surficial sediment ($K_d = 196.4 \text{ L kg}^{-1}$) (Xu et al., 2009).

Due to cost and logistical reasons, mesocosms have been used in studies to simulate pesticide dissipation in wetlands. In comparison, whole wetland experiments

avoid the issues of appropriate scaling of sediment-water interactions, ensuring representative biodiversity, and simulating infiltration/recharge processes (Schindler, 1998). This study was conducted in two wetlands (an ephemeral (E) and a semi-permanent (SP) wetland) divided by polyvinyl curtains in order to investigate the dissipation of glyphosate and its major degradation product AMPA in water and sediment of over a growing season.

5.2 Materials and methods

5.2.1 Study sites

The study site was at the Manitoba Zero Till Research Farm located approximately 20 km north of Brandon, Manitoba, Canada (49° 53'N latitude, 99° 58'W longitude). A detailed description of this site has been published elsewhere (Xu et al., 2009). Two isolated wetlands within a cultivated field, each with a riparian zone, were selected: a smaller wetland E and a larger wetland SP (Figure 5.1). In wet years, wetland E would exist as a single wetland whereas in dry years, such as when this study was carried out, it would exist as two separate smaller wetlands. Both wetlands were colonized by emergent macrophytes, such as tall rush (*Scirpus* spp.) and cattail (*Typha* spp.). An aquatic moss (*Fontinalis antipyretica*) was also found in water column of wetland SP. According to the management history provided by Manitoba Zero Till Research Association, commercially available products containing glyphosate have been applied annually to catchments of both wetlands at label-recommended rates for the preceding seven years.

Laminated polyvinyl curtains, which divided each wetland into 'control' and 'treated' halves, were installed in May 2008, approximately one month prior to glyphosate treatment (Figure 5.1). Contact of the lower edge of each curtain with bottom sediment was ensured by inserting a metal chain into a pocket sewn across the width of each curtain which provided about three kg of weight per meter across the curtain. To ensure the curtain did not shift due to wind/wave action, sandbags were also placed on top of the chain on the control half of the wetland to help hold the curtain in place.

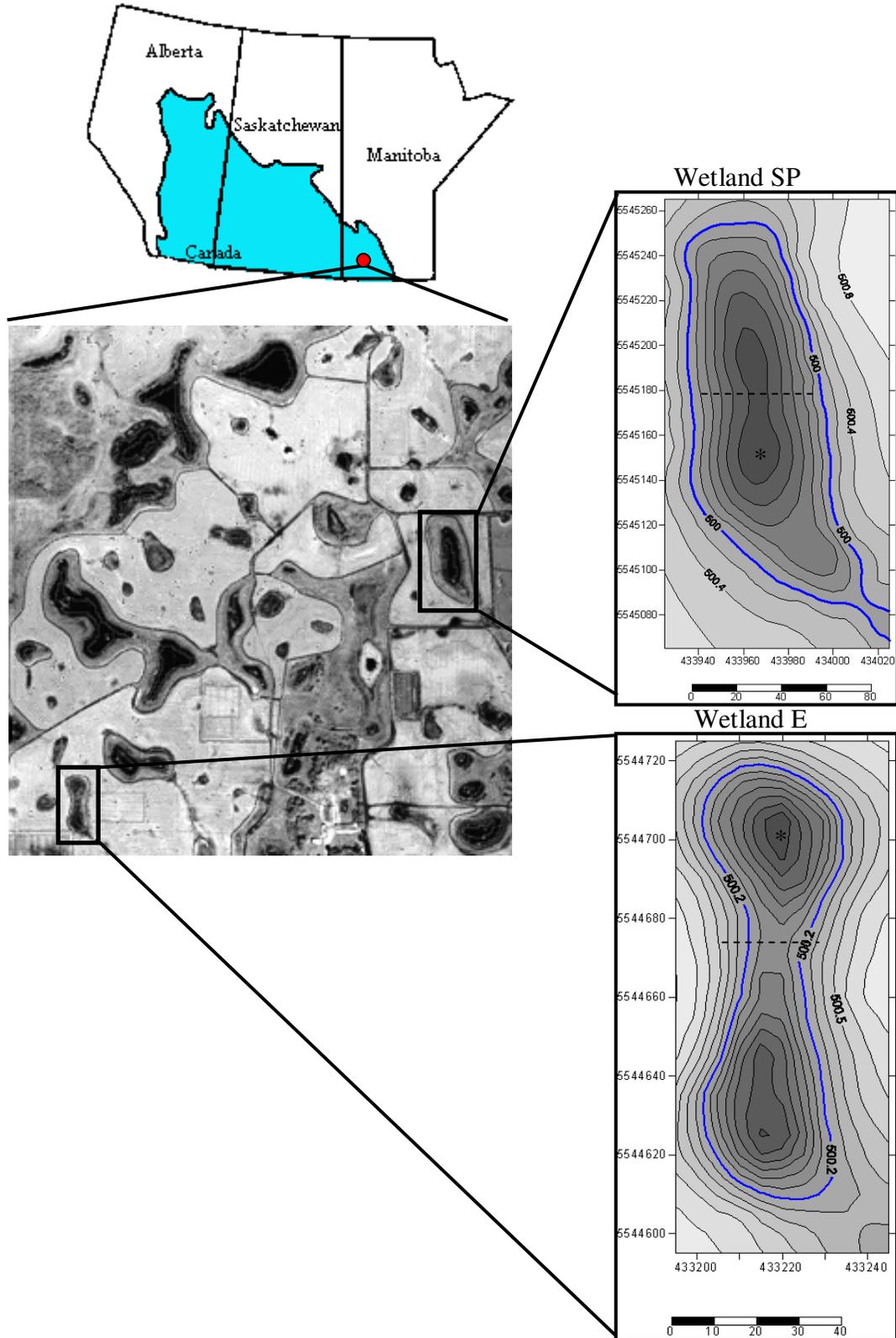


Figure 5.1. A map of the Prairie provinces in Canada highlighting the prairie pothole region and the location of the study site indicated by a circle. The expanded panel shows an aerial photograph of wetland E and wetland SP. The dashed lines represent the curtains that divide each wetland into two halves. The treated half is indicated by the *.

5.2.2 Water and sediment properties

Wetlands E and SP were selected for this study because they were representative of the most common types of wetlands found in prairie pothole region. The two wetlands differed in size (Table 5.2) and water permanence, as well as in some water and sediment properties important to pesticide sorption (Table 5.3) (Xu et al., 2009). Surficial sediment characterization was conducted as part of an earlier study and a detailed discussion on water chemistry and sediment characteristics of the two wetlands can be found in Xu et al. (2009).

5.2.3 Conservative Tracer application

A conservative tracer was required in this study to confirm no cross contamination from the treated to the control half of wetlands E and SP, as well as to determine the extent of water infiltration from the wetlands and to assess solute transport processes (Parsons et al., 2004). Bromide ion is widely used as a hydrological tracer due to its relatively non-reactive nature and naturally occurring low concentration in water and soil (Levy and Chambers, 1987). Sodium bromide was added on 6 June 2008, to the treated half of wetlands E and SP, when the estimated corresponding wetland volumes were 54 m³ and 1136 m³. Sodium bromide was first dissolved in water (20 L) contained in polyethylene carboy equipped with a spigot. The solution was released from the spigot on the carboy into wetland SP from an inflatable raft paddled around the wetland. Wetland E was too shallow to deploy an inflatable raft and, therefore, the sodium bromide solution was applied using the same carboy as wetland SP from the edge of the wetland. Amounts of sodium bromide added to wetlands E and SP to reach the target bromide concentration of 20 mg L⁻¹ were 1.1 kg and 23 kg, respectively (Table 5.4). Target bromide concentration was determined, in part, by detection limit for bromide ion as well as previous work by Parsons et al. (2004).

5.2.4 Herbicide target concentration and treatment

The commercially available formulation “GLYFOS” [360 g acid equivalent (a.e.) L⁻¹ glyphosate as its isopropylamine salt; Cheminova, Denmark] was used in this study. The fortification target concentration of glyphosate (72 µg L⁻¹) was calculated by

Table 5.2. Summary of physical characteristics and water chemistry of each basin from semi-permanent (SP) wetland and ephemeral (E) wetland prior to herbicide application, along with estimated wetland volume at time of spiking and glyphosate target concentration.

Parameter	Wetland SP (large)		Wetland E (small)	
	Control	Treated	Control	Treated
Length, m	55	70	30	40
Width, m	65	65	20	20
Area, m ² , at spiking	1600	2300	325	425
Estimated Volume at spiking, m ³	-	1253	-	71.3
Target concentration, ng L ⁻¹	0	70.2	0	70.2
pH	7.9	7.6	7.0	7.0
Conductance (μS cm ⁻¹ @ 25 °C)	1290	1171	469	813
Total Alkalinity (mg CaCO ₃ L ⁻¹)		144		129
DOC (mg L ⁻¹)	20.6	22.2	40.5	40.2
Na ⁺ (mg L ⁻¹)	36.6	34.7	10.6	22.6
Ca ²⁺ (mg L ⁻¹)	87.2	82.1	46.8	77.2
Mg ²⁺ (mg L ⁻¹)	106	98.5	18.7	44.4
K ⁺ (mg L ⁻¹)	25.0	25.3	44.4	45.9
Cl ⁻ (mg L ⁻¹)	10.0	9.8	8.0	10.5
SO ₄ ²⁻ (mg L ⁻¹)	442	414	105	214
NH ₃ ⁻ (mg L ⁻¹)	0.04	0.05	0.2	0.2
NO ₃ /NO ₂ ⁻ (mg L ⁻¹)	<0.01	<0.01	0.01	<0.01
Total Phosphorus (mg L ⁻¹)	0.7	1.8	0.8	1.8

Table 5.3. Summary of surficial (0 to 5 cm) sediment characteristics for the semi-permanent (SP) and the ephemeral (E) wetland. Each value is the mean of five sediment samples taken from both the control and treated halves of the wetland in May 2007 (Xu et al., 2009).

Parameter	Wetland SP	Wetland E
Total Organic Carbon (%)	12.1	7.6
Total Inorganic Carbon (%)	0.5	0.4
pH	7.2	6.3
Electrical Conductivity (dS m ⁻¹)	2.4	0.9
bulk density (g cm ⁻³)	0.44	0.57
Cation Exchange Capacity [cmol(+) kg ⁻¹]	50.5	47.6
Sand (%)	43.7	69.5
Silt (%)	48.7	26.4
Clay (%)	7.6	4.1

Table 5.4. Wetland volume, bromide ion concentration and mass, and changes in volume and bromide ion mass in treated half of the semi-permanent (SP) and the ephemeral (E) wetland.

Days after spiking	Rain	Wetland SP – treated half					Wetland E – treated half				
		volume	Br ⁻ conc [†]	Br ⁻ mass [‡]	Δ volume [§]	Δ Br ⁻ mass [¶]	volume	Br ⁻ conc [†]	Br ⁻ mass [‡]	Δ volume [§]	Δ Br ⁻ mass [¶]
		m ³	mg L ⁻¹	g	m ³	g	m ³	mg L ⁻¹	g	m ³	g
-4	1.3	1246	< MDL	-	-	-	54.3	< MDL	-	-	-
-3	0.0	1136	18.6	21125.9 [#]	-109.8	-	54.3	19.4	1053.4 [#]	0	-
0	16	1253	-	-	116.8	-	71.3	-	-	17	-
1	24	1272	8.1 ^{**}	10339.7	19.2	-10786.1	87.1	11.8 ^{**}	1027.8	15.8	-25.6
2	0.0	1272	12.8	16228.2	0	5888.4	87.1	3.4	294.4	0	-733.4
3	37	1488	11.0	16424.2	215.9	196.0	168	6.0	1014.7	80.9	720.3
5	12	1527	9.1	13883.2	39.6	-2541.1	178	4.3	765.5	9.6	-249.3
7	5.8	1527	9.1	13883.2	0	0.0	178	3.9	692.6	0	-72.8
14	8.1	1448	8.4	12205.8	-79.4	-1677.4	163	2.9	478.5	-14.3	-214.2
21	16	1408	8.3	11686.4	-39.9	-519.4	149	2.7	397.6	-14.4	-80.9
28	0.0	1310	8.6	11268.6	-97.7	-417.8	124	2.1	254.6	-25.3	-142.9
35	28	1272	8.8	11191.8	-38.5	-76.7	103	2.4	246.5	-20.9	-8.1
42	36	1330	9.2	12233.2	57.9	1041.4	118	1.5	177.5	15.6	-69.0
49	1.0	1233	9.8	12085.4	-96.5	-147.9	97.7	1.1	107.5	-20.6	-70.0
56	24	1253	9.6	12025.0	19.4	-60.4	71.3	1.2	85.6	-26.4	-21.9
63	7.1	1116	9.4	10491.3	-136.5	-1533.6	34.6	0.6	20.8	-36.7	-64.8
77	29	996	9.3	9265.6	-119.8	-1225.8	0 ^{‡‡}	-	-	-34.6	-

[†]Bromide ion concentration. [‡]Bromide ion mass.

[§]Change in volume of treated half of wetland calculated as the difference between the volume of water from the previous sampling day and the volume of water at time t.

[¶]Change in bromide ion mass calculated as the difference between the mass of bromide ion from the previous sampling day and the mass of bromide ion at time t.

[#]Mass of bromide ion added to each wetland. ^{**}Concentrations are in error most likely because of incomplete mixing of the wetland after rainfall runoff.

^{‡‡}Wetland was dry.

assuming that a typical prairie wetland of 0.5-m depth was inadvertently over-sprayed at the recommended application rate of 360 g a.e. ha⁻¹. This target concentration represents a worst-case scenario for prairie wetland contamination (Cessna et al., 2006).

Wetland herbicide fortification was conducted on the morning of 9 June 2008 with 14.1 and 316 mL of the “GLYFOS” formulation (equivalent to 5.08 and 113.8 g of glyphosate, respectively) added to wetlands E and SP, respectively. “GLYFOS” was mixed with six other herbicides discussed in Part II of this study (Degenhardt et al., 2010a), into approximately 30 L of water in the tank of a hand-operated sprayer equipped with a 1.5-m wand and then injected below the water surface. For wetland SP, an inflatable raft was used to inject herbicide solution at varying depths by moving the wand from just beneath the water surface to a depth of 1.5 m. To ensure a more homogeneous application of herbicide, the raft was pulled in a zigzag pattern over the width and length of the wetland using ropes. Wetland E was too shallow to deploy an inflatable raft, and the herbicide solution was similarly applied by wading into the wetland and moving in a zigzag pattern to ensure homogeneity of the herbicide application.

5.2.5 Sample collection

Water: To establish bromide ion as well as glyphosate and AMPA residue levels prior to fortification, water samples were collected on 5 June 2008 from the centre of both halves of each wetland. The day after glyphosate fortification (10 June 2008), three water samples were collected from different points in the treated half of each wetland to determine homogeneity of both glyphosate and bromide ion applications. Water samples for glyphosate analyses were subsequently collected from treated and control sides of each wetland on Days 2, 3, 5, 7, 14, 21, 28, 42, 56 and 77. Sampling was more frequent in the first week post-treatment because glyphosate concentrations were known to decrease more rapidly in surface water during the first 7 d post-treatment (Goldsborough and Brown, 1993). In addition to the sampling times for glyphosate analysis, water samples for bromide ion analysis were also collected on Days 35, 49 and 63.

Water samples were collected from the same location in both the treated and control side of Wetland SP and the centers of both treated and control halves of wetland E. Water samples were collected through a polyethylene tube (interior diameter (i.d.) 4 cm) into a 1-L polyethylene bottle at a rate of 300–400 mL min⁻¹ using a variable speed peristaltic sampling pump placed 40 to 60 cm below the water surface. Water was then transferred into 250-mL amber high density polyethylene bottles through a 153- μ m mesh NITEX screen to remove large seston materials and zooplankton. The water samples were maintained at -10 °C in an on-site freezer and later shipped on ice to the Alberta Research Council in Vegreville, AB for glyphosate and AMPA analysis.

Sediment: Bottom sediment sampling was achieved using a hand-core sediment sampler (Wildco, New York) in wetland E and a Kajak-Brinkhurst corer (Wildco, New York) in wetland SP. On 5 June 2008, four sediment cores from different locations within the treated and control halves of each wetland were collected to establish glyphosate and AMPA residue levels before fortification. Sediment samples from both treated and control halves of the wetland were then collected at 1, 3, 7, 14, 21, 28, 42, 56 and 77-d after fortification as follows: a sediment core was collected at four sites (center and three peripheral sites) from the treated and control halves of the wetland and the top 5 cm of each core was placed in a Whirl-Pak polyethylene bag (Nasco, USA), which was then placed in an amber polyethylene bag. The sediment samples were stored similarly as the water samples and then shipped the Alberta Research Council for analysis.

5.2.6 Glyphosate and AMPA analysis

Water samples: Once in water, glyphosate rapidly hydrolyzes from the formulated isopropylamine salt to the free acid. Consequently, analyses were only carried out for the free acid and the analysis of glyphosate was conducted as follows: ¹³C₂¹⁵N₁-Glyphosate (Cambridge Isotope laboratories, Andover, MA) and ¹³C₁¹⁵N₁D₂-AMPA (CDN Isotopes, Pointe-Claire, QC, Canada) were added as surrogate standards to a 5-mL aliquot of each water sample, which was then concentrated ten-fold with a stream of nitrogen gas (water bath at 90 °C). A 50- μ L aliquot of the concentrated

sample was derivatized *in situ* with heptafluorobutanol and trifluoroacetic anhydride at 40 °C. After derivatization, the solution was evaporated to dryness (water bath at 40 °C) and the residue dissolved in ethyl acetate prior to analysis by gas chromatography ion trap mass spectrometry (Varian Inc, Walnut Creek, CA) using selective ion monitoring. Deuterated phenanthrene (CDN Isotopes, Pointe-Claire, QC, Canada) was added as an internal standard to monitor performance of the mass spectrometer. The limits of quantification (LOQ) for glyphosate and AMPA were 0.2 µg L⁻¹ and 1.0 µg L⁻¹, respectively.

Sediment: As with water samples, isotopically labelled glyphosate and AMPA were added as surrogate standards to 20 g of freeze-dried sediment. Extraction solvent (0.25 M aqueous NH₃OH/0.01 M KHPO₄; 80 mL) was added and the mixture sonicated for 30 min. The mixture was then centrifuged (2000 rpm) for 20 min and the supernatant (10 mL) decanted into a test tube containing 10 mg activated carbon and sonicated for 10 min. Approximately 200 µL of the extract was filtered using 0.2-µm syringe filter with nylon membrane (Whatman, Maidstone, UK) and kept at 4 °C until derivatization and analysis. A more detailed description of quantification methods for glyphosate and AMPA in water and sediment is described elsewhere (Humphries et al., 2005). The LOQ for glyphosate and AMPA were 30 and 150 µg kg⁻¹, respectively.

5.2.7 Bromide Ion Analysis

The concentration of bromide ion was measured in filtered (0.45 µm nylon filter; Chromspec, Ontario, Canada) water samples using a Dionex ICS-3000 dual ion chromatography system (Dionex, Sunnyvale, CA). The method detection limit (MDL) for bromide ion was 0.6 mg L⁻¹.

5.2.8 Calculations

Wetland volume calculation

Wetland area and volume calculations were based on a digital elevation model (DEM) of the site, which included measured wetland bathymetry, surrounding catchment topography, as well as water level measurements taken throughout the study.

The algorithm for area and volume calculation was based on an algorithm given in Planchon and Darboux (2001). According to this algorithm, the wetland and its catchment are initially inundated with a thick layer of water and excess water is removed in 0.1 mm increments until the water depth equals the measured wetland water depth. The depth of water in each DEM cell (5 m by 5 m in this study) was then calculated from wetland bathymetry. The sum of the depth by area measurements for each cell then is the wetland volume at that time. Wetland volume calculation by this method is accurate because it is based on actual wetland bathymetry rather than an idealized elliptical basin form (Li, S., personal communication).

Mass of glyphosate, AMPA and bromide ion

Water: The mass ($mass_t$) of each compound at a given sampling time (t) was calculated using the following equation:

$$mass_t = concentration_t \times volume_t \quad [5.1]$$

where $concentration_t$ is the concentration of glyphosate, AMPA, or bromide ion at time t and $volume_t$ is the volume of water in the treated or control half of each wetland at time t .

Sediment: The mass of glyphosate or AMPA ($mass_t$) in the surficial sediment (0–5 cm) at a given sampling time (t) was calculated by:

$$mass_t = area \times depth\ of\ sediment\ sampled \times bulk\ density \times concentration_t \quad [5.2]$$

where $area$ is the maximum area underwater on the treated half of wetland E or SP. In order to account for all of the surficial sediment that could have been under water at any point during the 77-d study period, we used the maximum area instead of the area at each sampling event. The bulk density of top 5 cm of the sediment was determined in a previous study (Xu et al., 2009), and $concentration_t$ is the concentration of glyphosate or AMPA at time (t).

The dissipation of half-life for glyphosate

The DT_{50} for glyphosate is the time required for 50% of the glyphosate concentration or mass to dissipate from the water column of the treated half of each

wetland. Using a first-order kinetics approximation, the DT_{50} value for glyphosate was calculated using the following equation:

$$DT_{50} = \frac{\ln 2}{k} \quad [5.3]$$

where k is the degradation rate (d^{-1}) obtained from the linear correlation between \ln [concentration/initial concentration (C_0)] and time, or \ln [mass/initial mass (m_0)] and time (Grover, 1988).

5.3 Results and Discussion

5.3.1 Initial bromide ion concentrations

Prior to bromide ion addition, concentrations in both wetlands were less than the MDL (0.6 mg L^{-1}) (Table 5.4). On bromide ion fortification day (Day -3 – three days before the addition of glyphosate), average wind speed was 6 m s^{-1} , which would have resulted in relatively rapid mixing of these shallow water bodies (Cessna et al., 2006). Consequently, shortly after tracer addition, bromide ion concentrations (18.6 and 19.4 mg L^{-1} in wetlands SP and E, respectively) were close to the target concentration of 20 mg L^{-1} .

5.3.2 Wetland hydrology

In the week following tracer addition, the study site received approximately 90 mm of rainfall. Because of the rainfall and accompanying runoff, wetland SP volume increased 30%, whereas that of wetland E increased 330%. As a result, 7-d after bromide ion addition (Day 3 – three days after the addition of glyphosate), bromide ion concentrations were diluted to 11.0 and 6.0 mg L^{-1} in wetlands SP and E, respectively (Table 5.4).

Wetlands SP and E acted in a hydrologically similar manner. Though the study site received approximately 240 mm of precipitation over the 77-d study period, water volume in both wetlands continued to decrease with time (Table 5.4). Under the semi-arid climate of the study site (Environment Canada, 2004), water loss exceeded water gained through precipitation, and by Day 65, wetland E was completely dry. At the end of the study, wetland SP had lost approximately 35% of its maximum volume (Days 5 and 7). Because the water volumes in the wetlands were known at each sampling time,

bromide ion as a conservative tracer was used to determine which hydrological processes were operative: increases in bromide ion concentration were considered to be due to evaporation, decreases in bromide ion mass due to infiltration, and increases in bromide ion mass due to recharge (Parsons et al., 2004).

Although there was adequate time for complete mixing of both wetlands by Day 0, because of rainfall and surface runoff into the wetlands, reliable bromide ion masses were not obtained until Day 2 for wetland SP and Day 1 for wetland E (Table 5.4). Maximum wetland volumes were observed on Day 7. From that point on, bromide ion mass and wetland volume generally decreased continuously in the treated halves of both wetlands suggesting the principal mechanism of water loss was dominated by infiltration to riparian areas most likely driven by the rapid vegetation growth in these areas. In wetland SP, bromide ion mass decreased more rapidly in the first half of the study [9 June (Day 0) to 14 July (Day 35)]. An increase in bromide mass which occurred between Day 42 and Day 56 was likely due to recharge. Bromide ion concentration also increased on Day 35 despite a slight decrease in bromide mass indicating that evaporation had also become a significant mechanism of water loss in wetland SP. In wetland E, both bromide ion mass and concentration decreased continuously indicating that infiltration was the dominant mechanism of water loss throughout the study.

5.3.3 Glyphosate dissipation in the water column

At 4 d pre-treatment, glyphosate was not detected from either half of wetlands SP and E (Table 5.5). Additionally, glyphosate was never detected above MDL on the control sides of wetlands SP and E throughout the 77-d study period. Initial concentrations of glyphosate on Day 1 were 87.6 ± 46 and $73.8 \pm 43 \mu\text{g L}^{-1}$ ($n = 3$) in wetlands SP and E, respectively, and were within 24 and 5%, respectively, of the target concentration ($70.2 \mu\text{g L}^{-1}$). The high standard deviations most likely reflect incomplete mixing of the wetlands following the 16 mm of rain received the night previous to sampling (Table 5.4). As with bromide ion, incomplete wetland mixing due to subsequent rainfall and resulting runoff on Days 1 and 3 likely accounts for low glyphosate concentrations on Days 2 and 3 in wetland SP and on Day 3 in wetland E.

Table 5.5. Wetland volume, herbicide concentration and mass, and changes in volume and herbicide mass in treated half of the semi-permanent (SP) and the ephemeral (E) wetland.

Days after spiking	Wetland SP – treated half							Wetland E – treated half						
	Volume	Gly conc [†]	AMPA conc [‡]	Gly mass [§]	AMPA mass [¶]	Δ Gly mass [#]	Δ AMPA mass ^{††}	Volume	Gly conc [†]	AMPA conc [‡]	Gly mass [§]	AMPA mass [¶]	Δ Glyph. mass [#]	Δ AMPA mass ^{††}
	m ³	μg L ⁻¹		g		g		m ³	μg L ⁻¹		g		g	
0	1253	–	–	114 ^{‡‡}	–	–	–	71.3	–	0.0	5.0 ^{‡‡}	–	–	0.0
1	1272	88±46 ^{§§}	0	111	0	-2	0.0	87.1	74±43	0.6 [*]	6.4	0.1	1.4	0.1
2	1272	41	0	52	0	-59	0.0	87.1	20	0.0	1.7	0.0	-4.7	0.0
3	1488	43	0	64	0	12	0.0	168.0	5.7	0.0	–	0.0	-0.8	0.0
5	1527	48	1.5	74	2.3	10	2.3	178	9.7	1.3	1.7	0.2	0.8	0.2
7	1527	18	0.9 [*]	27	1.4	-47	-0.9	178	1.4	0.5 [*]	0.3	0.1	-1.5	-0.1
14	1448	7	9.4	10	14	-17	12	163	0.9	3.2	0.2	0.5	-0.1	0.4
21	1408	38	11	53	15	43	1.2	149	0.8	4.0	0.1	0.6	0.0	0.1
28	1310	1.5	6.1	2.0	8.0	-51	-6.7	124	0.0	0.0	0.0	0.0	-0.1	-0.6
42	1330	0.0	2.2	0	2.9	-2.0	-5.1	118	0.0	5.6	0.0	0.7	0.0	0.7
56	1253	0.0	4.4	0	5.5	0.0	2.6	71.3	0.0	3.6	0.0	0.3	0.0	-0.4
77	996	0.0	3.2	0	3.2	0.0	-2.3	0.0	–	–	–	–	–	–

[†]Concentration below the method detection limit.

[†]Glyphosate concentration.

[‡]AMPA concentration. [§]Glyphosate mass.

[¶]AMPA mass.

[#]Change in glyphosate mass calculated as the difference between the mass of glyphosate from the previous sampling day and that at time t.

^{††}Change in AMPA mass calculated as the difference between the mass of AMPA from the previous sampling day and that at time t.

^{‡‡}Amounts of glyphosate added to the wetlands.

^{§§}n=3.

Glyphosate concentrations decreased to levels below MDL on Day 42 in wetland SP and Day 28 in wetland E (Table 5.5). This relatively rapid rate of glyphosate dissipation is consistent with that in forest wetlands (Goldsborough and Beck, 1989; Goldsborough and Brown, 1993). In both wetlands, glyphosate concentrations were below the Canadian Water Quality Guideline for the Protection of Aquatic Life ($65 \mu\text{g L}^{-1}$) by Day 2. Possible reasons for rapid glyphosate dissipation include microbial degradation, photolysis, partitioning to sediments, infiltration and uptake by aquatic macrophytes.

Plotting the natural logarithm of the concentration versus time demonstrated that glyphosate dissipation in both wetlands followed first-order kinetics ($r^2 = 0.79$ for wetland E and $r^2 = 0.95$ for wetland SP), with an estimated DT_{50} of 2.4 d and 6.9 d in E and SP, respectively (Table 5.6). Volumes of both wetlands, however, changed continuously over the study duration (Table 5.5) due to rainfall, rainfall runoff, infiltration and evaporation. As a result of incomplete mixing with the rainfall/runoff water, sampling after major rainfall and rainfall runoff events caused an increase in glyphosate mass in wetland SP (Day 3, 5, 21, Table 5.5). A corresponding increase in glyphosate mass was only observed in wetland E on Day 5, indicating that complete mixing may have occurred sooner in this smaller wetland. To determine whether the changes in wetland volume affected glyphosate dissipation kinetics, the natural logarithm of the calculated mass of glyphosate was plotted versus time. This approach did not produce a stronger relationship between observed residue mass and estimated residue mass ($r^2 = 0.78$ for $r^2 = 0.95$ for wetland SP) (Table 5.6). The corresponding DT_{50} values were 2.9 and 4.8 d for wetlands E and SP.

Decrease in bromide ion mass over Days 3, 7, 14, 21 and 28 was strongly correlated with glyphosate mass ($r^2 = 0.99$ wetland SP, $r^2 = 0.90$ wetland E). This correlation suggests either glyphosate most likely moved out of the wetland with the infiltrating water thus accounting for the continually decreasing mass of glyphosate during that 4 week period, or both glyphosate and Br^- were lost to the aquatic macrophytes and shorelines sediments on the wetland margin as the surface area of the wetland decreased overtime.

Table 5.6. Modeled first-order dissipation kinetics ($C_t = C_0e^{-kt}$) of glyphosate in the ephemeral (E) and semi-permanent (SP) wetland water.

	Wetland SP		Wetland E	
	Concentration	Mass	Concentration	Mass
r^2	0.77	0.81	0.73	0.88
C_0 ($\mu\text{g L}^{-1}$)	87.6		73.8	
Mass ₀ (g)		113.8		5.06
K	0.10	0.11	0.29	0.18
$t_{1/2}$ (d)	6.9	6.4	2.4	3.7

5.3.4 AMPA dissipation in the water column

The appearance of AMPA in surface waters containing glyphosate has been deemed to be *prima facie* evidence of glyphosate degradation (Goldsborough and Brown, 1993). In the present study, AMPA was not detected in water samples taken 4 d pre-treatment from either half of wetlands SP and E (Table 5.5). Additionally, AMPA was never detected above MDL on the control sides of wetlands SP and E throughout the 77-d study period. AMPA first appeared in both wetlands on Day 5. The total mass of AMPA increased from Day 5 to a maximum concentration on Day 21 for wetland SP and Day 42 for wetland E. Initially (Day 5), total masses of AMPA in both wetlands were lower than the corresponding masses of glyphosate, but by Day 14, the total mass of AMPA in each wetland exceeded that of glyphosate. AMPA was detected in both wetlands throughout the rest of study. Presence of AMPA in the water column may have been due, in part, to microbial, photolytic and chemical degradation and possibly rain washout on surface of riparian macrophytes. However, glyphosate may have also been taken up by submerged macrophytes (e.g. aquatic moss *Fontinalis antipyretica*) present in abundance in wetland SP (Badiou, Ducks Unlimited, data unpublished). Aquatic moss is known to metabolize glyphosate through enzymatic degradation (Van Eerd et al., 2003). Subsequent release of AMPA may have occurred during moss decomposition. Such release and possibly rainfall runoff between Days 35 and 42 may also explain AMPA presence in wetland SP and wetland E after glyphosate has dissipated.

It was not possible to determine the degradation rate for AMPA in each wetland due to the continued production of AMPA associated with glyphosate degradation and its possible release from decaying moss and riparian plant tissue. Previous studies have shown that AMPA, which has no herbicidal properties, is more stable than its parent compound and thus persists longer in the environment (Baker et al., 2006; Simonsen et al., 2008). The results of our study support this conclusion.

5.3.5 Glyphosate and AMPA dissipation in surficial sediment

Glyphosate and AMPA were not detected in surficial sediment (0–5 cm) in either wetland 4 d prior to the treatment with glyphosate (Table 5.7). Glyphosate and AMPA were also not detected in the surficial sediments taken from the control side of

both wetlands throughout the 77-d study. Because glyphosate has a high affinity for wetland sediment (Xu et al., 2009), sorption to sediment was expected. Sediment samples taken from wetlands SP and E on Day 1 contained $102 \mu\text{g kg}^{-1}$ and $116 \mu\text{g kg}^{-1}$ glyphosate (on a dry-weight basis), respectively. Maximum concentrations of glyphosate detected in sediments occurred on Day 14 in wetland SP ($224.5 \mu\text{g kg}^{-1}$) and Day 21 in wetland E ($155.0 \mu\text{g kg}^{-1}$). Glyphosate was still detectable on Day 42 in wetland E ($39.0 \mu\text{g kg}^{-1}$), whereas glyphosate was last detected in wetland SP on Day 28 ($69.5 \mu\text{g kg}^{-1}$). In contrast, AMPA was never detected above MDL ($150 \mu\text{g kg}^{-1}$). Because of the linear correlation observed between glyphosate mass and bromide ion mass in the water column, glyphosate may have dissipated via water loss to lateral flow. Even though AMPA has a similar log K_{ow} value to that of glyphosate (Table 5.1), it was not detected in the sediment of either wetland during the 77-d study and this may be due to a higher LOQ of AMPA concentrations in sediment compared to water (150 versus $30 \mu\text{g kg}^{-1}$).

The maximum mass of glyphosate present in the upper 5 cm of surficial sediment in each wetland corresponded to the maximum concentrations which occurred on Day 14 in wetland SP and Day 21 in wetland E (Table 5.7). Based on maximum glyphosate concentration detected in surficial sediments, the upper 5 cm of sediment sorbed approximately 67% of the total glyphosate added to wetland E. For wetland SP, surficial sediments sorbed significantly less, accounting for only 10% of the amount added. This is in accordance with results from our previous work, where glyphosate K_d was determined to be much higher in wetland E (251.9 L kg^{-1}) than wetland SP (124.9 L kg^{-1}) (Xu et al., 2009). One of the other major differences between the two wetlands is the presence of aquatic moss in wetland SP, which may have taken up and/or sorbed glyphosate. On this basis, we hypothesize that a greater proportion of glyphosate may have been taken up or sorbed by moss and suspended seston in wetland SP relative to wetland E, thus accounting for the smaller proportion sorbed to sediment. Glyphosate is

Table 5.7. Wetland area, glyphosate concentration and mass in sediment and AMPA concentration and mass in sediment for the treated half of wetland SP and E.

Days after spiking	Wetland SP – treated half					Wetland E – treated half				
	Area	Gly conc [†]	AMPA conc [‡]	Gly mass [§]	AMPA mass [¶]	Area	Gly conc [†]	AMPA conc [‡]	Glyph mass [§]	AMPA mass [¶]
	m ²	µg kg ⁻¹		g		m ²	µg kg ⁻¹		g	
-4	2300	0.0	0.0	0.0	0.0	425.0	0.0	0.0	0.0	0.0
0	2175	–	–	–	–	475.0	–	–	–	–
1	2175	102	0.0	5.3	0.0	500.0	116	115 [*]	2.6	2.5
3	2375	95.0	127 [*]	5.0	6.0	750.0	101	0.0	2.2	0.0
7	2375	84.0	0.0	4.4	0.0	775.0	83.5	0.0	1.8	0.0
14	2350	225	0.0	11.8	0.0	725.0	112	0.0	2.5	0.0
21	2300	177	0.0	9.2	0.0	700.0	155	0.0	3.4	0.0
28	2175	69.5	0.0	3.6	0.0	650.0	112	0.0	2.5	0.0
42	2200	0.0	0.0	0.0	0.0	650.0	39.0	70 [*]	0.9	1.5
56	2175	28 [*]	0.0	1.5	0.0	475.0	0.0	46 [*]	0.0	1.0
77	2075	21 [*]	53 [*]	1.1	2.5	0.0	30.0	53 [*]	0.7	1.2

^{*}Concentration below the method detection limit.

[†]Glyphosate concentration.

[‡]AMPA concentration.

[§]Glyphosate mass.

[¶]AMPA mass.

also known to form complexes with divalent cations (Ca^{2+} and Mg^{2+}) (Glass, 1987; Subramaniam and Hoggard, 1988). Because wetland SP had higher levels of these divalent cations, the complexation of glyphosate with these ions in the water column could also explain, in part, the lower sorption to the sediment.

5.4 Conclusion

Our results showed that for prairie wetlands, glyphosate sorption to sediment and infiltration are important pathways for the dissipation of glyphosate in water. This is especially true in the ephemeral wetland, where a significant portion of the glyphosate was bound to sediment. Overall, in prairie wetland ecosystems, glyphosate is dissipated rapidly in the water (DT_{50} 3.1 to 6.7 d), which may effectively reduce aquatic biota exposure. Based on EC_{50} value of $770 \mu\text{g L}^{-1}$ for the most sensitive organism, a marine diatom (*Skeletonema costatum*) (Solomon, 2003), our results suggest that acute toxic effects of glyphosate contamination in water will be limited even for a worst-case scenario with a direct overspray event. Presently, we are not aware of any guidelines for glyphosate residues in sediment; hence, it is not clear whether the maximum levels of glyphosate detected in the sediment (155 to $225 \mu\text{g kg}^{-1}$) would negatively impact sediment dwelling organisms and other organisms that spend part of their lifecycle in sediment.

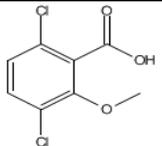
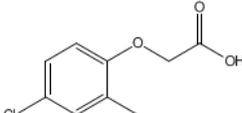
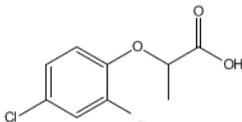
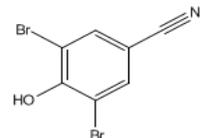
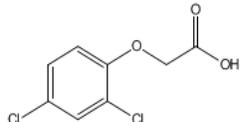
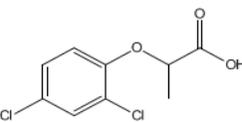
6.0 DISSIPATION OF HERBICIDES IN WATER AND SEDIMENT OF TWO CANADIAN PRAIRIE WETLANDS. PART II. ACID HERBICIDES

6.1 Introduction

Some of the oldest and most widely used herbicides in the world are haloalkyl/aryl acid herbicides; they generally contain carboxylic acid and phenolic functional groups. Acid herbicides consist of several families of compounds that have similar chemical properties (Table 6.1) and biological target sites. In this study the acid herbicides investigated are the ones that were most frequently detected in prairie aquatic ecosystem (Donald et al., 2001; Donald et al., 2007). They include phenoxyacetic acid [2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA)], phenoxypropionic acid [(RS)-2-(2,4-dichlorophenoxy) propionic acid (dichlorprop) and (R)-2-(4-chloro-*o*-tolylxy) propionic acid (mecoprop-P)], benzoic acid [3,6-dichloro-2-methoxybenzoic acid (dicamba)] and a phenol [3,5-dibromo-4-hydroxybenzotrile (bromoxynil)]. Acid herbicides may be used alone, formulated as mixtures or tank mixed with other herbicides to control annual and perennial broadleaf weeds. With the exception of bromoxynil, this group of herbicides mimics auxin, the plant growth regulator, promoting unregulated plant growth which eventually leads to plant death (Hall et al., 1999). Acid herbicides are registered for agricultural use on various crops including: cereals [wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), oats (*Avena sativa* L.), rye (*Secale cereale* L.), triticale (*Triticale hexaploide* L.), corn (*Zea Mays* L.)], oil seed [flax (*Linum usitatissimum* L.)], legumes [peas (*Pisum sativum* L.)] and perennial grasses (Saskatchewan Agriculture, 2008). They are also commonly used on summer fallow and stubble fields for weed control.

Acid herbicides are formulated either as alkaline metal (potassium) or amine (dimethylamine) salts or esters (iso-octyl esters). The hydrolysis of the salts to the corresponding free acids is rapid (few hours) compared to iso-octyl esters for which

Table 6.1. Table of various physicochemical properties of dicamba, bromoxynil, MCPA, 2,4-D, mecoprop-P, dichlorprop (Agriculture and Environment Research Unit, 2007)

Compound	Molecular Structure	Molar mass	Water solubility	Vapour pressure	<i>pKa</i>	Photolysis	DT ₅₀ in Soil
		g mol ⁻¹	g L ⁻¹	mPa		DT ₅₀ in water (day)	(day)
Dicamba		221.0	4.5	4.5	1.87	14-50	<14
MCPA		200.6	0.83	0.2	3.12	24	<7
Mecoprop		214.6	0.62	0.3	3.11	42	21
Bromoxynil		276.9	0.13	0.006	3.06	stable	<7
2,4-D		221.0	0.90	0.02	2.80	7.5	10
Dichlorprop		235.1	0.71	0.01	2.86	4	10

complete hydrolysis may take up to 48 h (Aly and Faust, 1964; Muir, 1991; Zepp et al., 1975). Each year, approximately 1.5 million kg each of MCPA and 2,4-D are sold or used in Canada, and these two herbicides rank second and third as the most widely used pesticide active ingredients in Canada (Brimble et al., 2005). Bromoxynil, dicamba and mecoprop-P are also heavily used in Canada, with approximately 250,000 to 500,000 kg of each active ingredient sold or used each year. The six herbicides under investigation are typically tank mixed together in groups of two or three to provide a broader spectrum of weed control in prairie agriculture (Saskatchewan Agriculture, 2008)

Over three quarters of Canada's arable land is located in Alberta, Saskatchewan and Manitoba, all of which coincidentally has high density of wetlands. Prairie wetlands are important breeding habitats for the duck population in North America (Batt et al., 1989). Wetlands also serve as a unique habitat for a number of amphibians, insects and crustaceans (Donald, 1983; Hartland-Rowe, 1966). As part of crop production systems within the Prairie region, a diverse range of pesticides is applied each year either by ground or aerial application mainly from early May to mid July. Wetlands are susceptible to pesticide contamination through application drift (Wolf and Cessna, 2004), wet and dry atmospheric deposition (Yao et al., 2006), snowmelt and rainfall runoff as well as deposition of soil from wind erosion and surface runoff (Cessna et al., 1994; Donald et al., 2005; Xu et al., 2009). Once in the wetland, pesticides can dissipate from the water column through the physical processes of volatilization, sorption to suspended particles, sediment and biota, and infiltration to groundwater and wetland fringes (Pionke and Chesters, 1973). Pesticides can also be degraded biologically via microbial degradation and chemically via direct and indirect photolysis or hydrolysis.

Water concentrations of some acid herbicides have been reported (Cessna and Elliott, 2004; Donald et al., 1999; Grover et al., 1997) to exceed the Canadian Water Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment, 2007). Those which most often exceeded aquatic life guidelines were 2,4-D, dicamba and MCPA. Although acute toxic effects of acid herbicides to fish and invertebrates are quite minimal (Mayer and Ellersieck, 1986), 2,4-D has recently been linked to reduction of larval amphibians in wetland mesocosm studies (Relyea, 2005a).

Furthermore, the effects of acid herbicide mixtures on primary producers in aquatic ecosystems have yet to be determined, and indirect effects (mediated through consumer-resource interactions) of acid herbicides on wetland biota may be of significance.

The objective of this study was to determine dissipation rates of six commonly used acid herbicides (dicamba, bromoxynil, MCPA, 2,4-D, mecoprop-P, and dichlorprop; Table 6.1) in the water column and sediment of one semi-permanent (SP) wetland and one ephemeral (E) wetland, over a 77-d study period. To our knowledge, only one study has ever investigated the fate of acid herbicides in prairie wetlands (Muir et al., 1991).

6.2 Materials and Methods

6.2.1 Study site

Two wetlands within a cultivated field, each with a riparian zone, were selected at this site: a smaller ephemeral wetland (wetland E) and a larger semi-permanent wetland (wetland SP). In the case of wetland SP, a polyvinyl curtain dividing the wetland into halves, was installed in May 2008, approximately one month prior to herbicide treatment (Degenhardt et al., 2010c). One half of the wetland was selected as the control and the other to be treated with herbicide. In the case of wetland E, this wetland in wet springs would exist as a single wetland after snowmelt whereas in dry years, such as when this study was carried out, it existed as two separate smaller wetlands. One of the smaller wetlands was chosen as the control and the other to be treated with herbicide. However, a polyvinyl curtain was installed between the separated wetlands in case of sufficient rainfall which would result in the merging of the two wetlands.

2,4-D and MCPA based herbicide products had been applied annually to the catchments of both wetlands at label-recommended rates for seven years preceding study initiation. All site information water and sediment properties, wetland volume calculation and tracer application are described in Part I of this study (Degenhardt et al., 2010c), along with wetland volume calculation and bromide ion tracer application.

6.2.2 Herbicide selection and treatment target concentrations

The “treated” half of each wetland was fortified with a mixture of glyphosate, dicamba, MCPA, 2,4-D, mecoprop-P and dichlorprop, each of which is widely used in crop production on the Canadian prairies. The glyphosate results can be found in Part I of this study (Degenhardt et al., 2010c). The fortification target concentration of each herbicide was calculated by assuming that a hypothetical wetland of 0.5-m depth was inadvertently over-sprayed at the recommended application rate (Cessna et al., 2006). A commercially available formulation of each active ingredient was used and the corresponding fortification target concentrations are listed in Table 6.2. Herbicide application, which occurred on 9 June 2008, has been described previously (Degenhardt et al., 2010c).

6.2.3 Water and sediment sample collection and handling

Water samples were collected from the treated and control halves of each wetland on Day -4, 2, 3, 5, 7, 14, 21, 28, 42, 56, 77 post treatment. Each sample was filtered through a 153- μ m mesh screen, and then transferred to 1-L amber glass bottle equipped with a Teflon lined cap. The filtered samples were acidified on-site to pH 3.5 with concentrated sulfuric acid. The solid-phase extraction (SPE) of each water sample (~250 mL) was conducted within 24 h following sample collection according to the protocols established by Raina and Etter (2010).

Four sediment cores from different locations within the treated and control halves of each wetland were collected 4 d pre-treatment to establish baseline residue levels. Sediment samples from both treated and control halves of each wetland were then collected at 1, 3, 7, 14, 21, 28, 42, 56 and 77 d after fortification. Each sediment sample was made up of four cores, and only the top 5 cm of each core was retained for the residue analysis. The composite sample was placed in a Whirl-Pak polyethylene bag (Nasco, USA), which in turn, was placed in an amber polyethylene bag. The sediment cores from each sampling day were kept on-site in a freezer maintained at -10 °C, and then samples were shipped on dry ice to National Hydrology Research Centre,

Table 6.2. List of commercial products, its formulation, active ingredient and target concentration used in the study, as well as the Canadian Water Quality Guidelines for the Protection of Aquatic Life for each active ingredient.

Active ingredient	Commercial product	Supplier	Formulation	Active ingredient concentration in formulation	Wetland target concentration	Freshwater Aquatic Life Guideline [†]
				g L ⁻¹	(free acid) µg L ⁻¹	(free acid) µg L ⁻¹
Dicamba	Oracle	Gharda Chemicals Ltd.	Dimethyl amine salt	480	93.6	10
MCPA	Nufarm MCPA Amine 500	Nufarm Agriculture Inc.	Dimethyl amine	500	125.0	2.6
Mecoprop-P	Mecoprop-P	United Agri Products	Potassium salt	150	178.6 wetland E 168.9 wetland SP	4
Bromoxynil	Pardner	Bayer Crop Science Inc.	Iso-octyl ester	280	61.6	5
2,4-D	Nufarm Estaprop PLUS	Nufarm Agriculture Inc.	2-Ethylhexyl ester	282	98.7	4
Dichlorprop	Nufarm Estaprop PLUS	Nufarm Agriculture Inc.	2-Ethylhexyl ester	300	105.0	4

[†]Canadian Water Quality Guidelines for the Protection of Aquatic Life set by the Canadian Council of Minister of the Environment (2007).

Saskatoon, SK for freeze-drying using a LabConco freeze-dry system (Kansas City, KA). Freeze-dried sediment samples were stored at -20 °C prior to residue extraction. water and sediment sample collection has been described in detail in Part I of this study (Degenhardt et al., 2010c).

6.2.4 Chemicals and Reagents

Certified ACS-grade sulfuric acid from EMD Chemicals Inc (San Diego, CA) was used. Pesticide grade methanol and acetonitrile as well as Ottawa sand (20-30 mesh) were purchased from Fisher Scientific (Pittsburgh, PA). Milli-Q water (18 MΩ) was obtained using a Milli-Q Gradient A10 purification system (Millipore, Billerica, MA). Analytical grade acid herbicide standards (dicamba, bromoxynil, MCPA, 2,4-D, mecoprop-P and dichlorprop) in solid form with 98% or greater purity were purchased from Chem Service Inc. (West Chester, PA). Isotopically labelled bromoxynil (ring-¹³C₆) and 2,4-D [(2,4-dichlorophenoxy-3,5,6-d³-acetic-d²-acid) d⁵-2,4-D] were purchased from Cambridge Isotope Laboratories Inc. (Andover, MA) and used as surrogate and internal standards, respectively.

6.2.5 Preparation of standard solutions

Stock solutions (50 mg L⁻¹) of each acid herbicide as well as the surrogate and internal standards, were prepared in acetonitrile and stored in the dark at 4 °C. A calibration stock solution containing all six herbicides at 100 µg L⁻¹, as well as the surrogate standard [bromoxynil (ring-¹³C₆)] at 50 µg mL⁻¹ was also prepared in acetonitrile.

6.2.6 Sample extraction

Water: Solid-phase extraction of the water samples was achieved using Supelco Superclean ENVI-Chrom-P cartridges (1 g, 6 mL; Sigma-Aldrich, Oakville, ON, Canada). The water sample (250 mL) was passed through the cartridge at a rate of 200 mL h⁻¹ under vacuum using a Supelco Visiprip DL SPE extraction manifold (Sigma-Aldrich). The herbicide residues were eluted from the cartridge and concentrated to ~0.95 mL and the surrogate standard (50 µL of 50 µg mL⁻¹) was added to give a total

volume of 1 mL. A detailed description of the SPE clean-up can be found in Raina and Etter (2010).

Sediment: Freeze-dried sediment (5 g) was mixed with approximately 40 g of Ottawa sand and transferred to a 33-mL stainless steel pressurized liquid extraction (PLE) cell equipped with two GF/X filter papers at both the inlet and the exit end of the cell. The sample was extracted with acetonitrile/water (10 : 90 v/v) using a PLE system (ASE 200; Dionex, Sunnyvale, CA) under the following operating conditions: temperature, 70 °C; static mode time, 2 min at 1500 p.s.i.; two static cycles; 90% flush volume with each cycle; and 60 s purge time with ultra-high purity nitrogen at the end of each run. After two extraction cycles, the combined volume of extract was approximately 60 mL. The extract was then diluted with deionized water to approximately 100 mL and then acidified by the addition of 3 M sulfuric acid (0.5 mL).

Recovery experiments for the six acid herbicides from sediment were conducted using control sediment collected from a wetland situated within a catchment that had not received any pesticide application in the past 5 years. Sediment samples (n = 6) from this wetland contained no detectable residue of any of the acid herbicides used in this study. Freeze-dried sediment (5 g) was fortified at two levels (5 µg kg⁻¹ and 20 µg kg⁻¹) by the addition of 25 and 100 ng of each acid herbicide plus 50 ng of bromoxynil (ring-¹³C₆) dissolved in methanol and extracted within 48 h. Unfortified sediment was treated similarly with methanol only. The recovery experiment protocols have been described in detail previously (Degenhardt et al., 2010b).

6.2.7 LC/MS/MS analysis

A Waters LC system connected to a Quattro Premier triple quadrupole mass spectrometer (Waters-Micromass, Milford, MA, USA) equipped with electrospray ionization set to negative ion mode was used for the analysis of both the sediment and water extracts. Based on the minimum standard concentration showing 25% deviation of peak area from the best-fit regression line of the calibration curves determined over 2–150 ng L⁻¹, the method detection limits (MDLs) for the water samples were 10 ng L⁻¹ for 2,4-D, mecoprop-P and dichlorprop, 5 ng L⁻¹ for bromoxynil and MCPA and 30 ng L⁻¹ for dicamba (Table 6.3). The MDLs for the sediment samples were 1 µg kg⁻¹ for

Table 6.3. Herbicide recoveries at given conditions[†] from fortified sediment at 5 and 20 $\mu\text{g kg}^{-1}$.

Compounds	Spiked concentrations (% recovery \pm standard deviation)	
	20 $\mu\text{g kg}^{-1}$ (n = 6)	5 $\mu\text{g kg}^{-1}$ (n = 6)
Dicamba	55.4 \pm 7 [†]	41.7 \pm 10
MCPA	98.8 \pm 3	49.5 \pm 4
Mecoprop-P	65.2 \pm 3	59.2 \pm 11
Bromoxynil	87.8 \pm 2	60.3 \pm 6
2,4-D	92.4 \pm 3	45.4 \pm 2
Dichlorprop	64.1 \pm 7	76.6 \pm 24

[†]Pressurized liquid extraction (PLE) conditions: heat for 5 min, 2 cycles at 2 min at 70°C and flush volume 90%, purge 60 sec. Blank samples (n = 2) no acid herbicides detected at concentration above method detection limit (MDL). Re-extracted 4 sediment samples spiked at 100 ppb by PLE again, no acid herbicides were detected at concentration above MDL.

bromoxynil, MCPA and dichlorprop, $2 \mu\text{g kg}^{-1}$ for 2,4-D and mecoprop-P, and $6 \mu\text{g kg}^{-1}$ for dicamba. A detailed description of the LC/MS/MS analysis used for quantifying these six acid herbicides can be found in Raina and Etter (2010).

6.3 Results and Discussion

In general, the two wetlands had similar hydrological patterns throughout the 77-d study (Degenhardt et al., 2010c). Rainfall and runoff events contributed to the increase in wetland volumes (Tables 6.4 and 6.5), especially in the first week post-herbicide treatment when the study site received approximately 95 mm of rainfall and volumes of wetland SP and E were increased by 30% and 330%, respectively. However, because of the semi-arid climate in this region, evapotranspiration and infiltration losses in both wetlands exceeded precipitation. By Day 65, wetland E was completely dry and, by the end of the 77-d study wetland SP had lost about 35% of its maximum volume.

According to the bromide ion concentration and water volume data, water loss from wetland E was dominated by infiltration, while evaporation was the dominant water loss pathway for wetland SP (Degenhardt et al., 2010c). In a study of a typical ephemeral wetland in Saskatchewan, Parsons et al. (2004), similarly reported infiltration, most likely to vegetated wetland margins, to be the main route of water loss.

6.3.1 Acid herbicide dissipation in water column

We did not detect residues of any of the six herbicides in either treated or control half of wetland SP in pre-treatment samples collected 4 d prior to herbicide addition. We also did not detect any herbicide residues in the control half of wetland E, however, MCPA, 2,4-D and mecoprop-P were detected in the treated half of wetland E in the pre-treatment samples (Table 6.4). This probably occurred because each of the separated wetlands received surface runoff from a different portion of the catchment. The concentrations of MCPA, 2,4-D and mecoprop-P, which ranged from 0.12 to $0.56 \mu\text{g L}^{-1}$, were low relative to the corresponding concentrations measured in the treated half of wetland E. Herbicides were not detected in the control half of either wetland after fortification.

Table 6.4. Wetland volume, herbicide concentration and mass in the water samples from the treated half of the ephemeral (E) wetland. Bolded concentrations are above the Canadian Water Quality Guidelines for the Protection of Aquatic Life.

		Wetland E (small) Treated half											
Days after spiking	Volume	Amine Salts				Potassium salt				Esters			
		Benzoic		Phenoxyacetic		Phenoxypropionic		Hydroxybenzointrile		Phenoxyacetic		Phenoxypropionic	
		Dicam conc [†]	Dicam mass [‡]	MCPA conc [§]	MCPA mass [¶]	Mecop conc [#]	Mecop mass ^{††}	Brom conc ^{‡‡}	Brom mass ^{§§}	2,4-D conc ^{¶¶}	2,4-D mass ^{##}	Dichp conc ^{†††}	Dichp mass ^{‡‡‡}
m ³	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	
-4	54.3	0.00	0.00	0.12	0.01	0.56	0.03	0.00	0.00	0.2	0.01	0.00	0.00
0	71.3	–	6.75*	–	9.01*	–	12.9*	–	4.44*	–	7.12*	–	7.57*
1	87.1	70.5±17^{§§§}	3.79	135±25	11.8	182±39	15.8	41.9±8^{¶¶¶}	3.65	59.9±10^{¶¶¶}	5.22	26.8±5^{¶¶¶}	2.33
2	87.1	49.0	4.27	128	11.1	170	14.8	50.2	4.37	77.5	6.75	48.9	4.26
3	168	47.5	7.98	59.9	10.1	82.7	13.9	25.0	4.19	38.9	6.54	29.9	5.02
5	178	50.3	8.94	54.4	9.65	74.6	13.2	15.8	2.80	39.3	6.98	29.4	5.22
7	178	51.0	9.05	31.7	5.63	42.1	7.47	7.60	1.35	23.8	4.23	19.6	3.49
14	163	39.6	6.46	24.4	3.99	29.2	4.76	1.00	0.16	19.0	3.10	16.3	2.66
21	149	5.92	0.88	14.4	2.14	18.8	2.80	0.00	0.00	13.0	1.94	13.6	2.03
28	124	7.96	0.98	12.4	1.53	20.8	2.57	0.00	0.00	10.8	1.34	16.2	2.01
42	118	5.44	0.64	9.72	1.15	31.1	3.68	0.00	0.00	6.88	0.81	24.0	2.84
56	71.3	0.00	0.00	3.08	0.22	16.4	1.17	0.00	0.00	1.88	0.13	10.5	0.75
70	0	–	–	–	–	–	–	–	–	–	–	–	–

[†]Mass determined from amount of each herbicide added

[†]Dicamba concentration.

[‡]Dicamba mass.

[§]MCPA concentration.

[¶]MCPA mass.

[#]Mecoprop-P concentration.

^{††}Mecoprop-P mass.

^{‡‡}Bromoxynil concentration.

^{§§}Bromoxynil mass.

^{¶¶}2,4-D concentration.

^{##}2,4-D mass.

^{†††}Dichlorprop concentration.

^{‡‡‡}Dichlorprop mass.

^{§§§}n=3.

^{¶¶¶}concentrations are low likely due to incomplete hydrolysis of the ester to free acid.

Table 6.5. Wetland volume, herbicide concentration and mass in the water samples from the treated half of the semi-permanent (SP) wetland. Bolded concentrations are above the Canadian Water Quality Guidelines for the Protection of Aquatic Life.

		Wetland SP (large) Treated half											
Days after spiking	Volume	Amine Salts				Potassium salt				Esters			
		Benzoic		Phenoxyacetic		Phenoxypropionic		Hydroxybenzoxynitrile		Phenoxyacetic		Phenoxypropionic	
		Dicam conc [†]	Dicam mass [‡]	MCPA conc [§]	MCPA mass [¶]	Mecop conc [#]	Mecop mass ^{††}	Brom conc ^{‡‡}	Brom mass ^{§§}	2,4-D conc ^{¶¶}	2,4-D mass ^{##}	Dichp conc ^{†††}	Dichp mass ^{###}
m ³	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	µg L ⁻¹	g	
-4	1246	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	1253	–	152	–	203	–	274	–	99.9	–	160	–	170
1	1272	126±17 ^{§§§¶¶¶}	74.2	229±28 ^{¶¶¶}	291	283±42 ^{¶¶¶}	360	41.0±8 ^{###}	52.2	66.1±11 ^{###}	84.1	34.6±13 ^{###}	44.0
2	1272	162	206	112	142	157	200	88.4	112	124	158	77.1	98.0
3	1488	22.3	33.2	110	164	142	211	55.4	82.4	98.9	147	82.2	122
5	1527	–	–	88.5	135	120	184	38.9	59.4	71.6	109	68.8	105
7	1527	–	–	113	172	145	221	38.4	58.6	90.2	138	84.8	130
14	1448	14.4	20.9	82.5	119	128	185	12.0	17.4	64.2	92.9	64.8	93.8
21	1408	36.8	51.9	60.6	85.3	86.1	121	1.20	1.69	50.2	70.6	49.2	69.3
28	1310	16.7	21.9	44.9	58.9	84.8	111	0.00	0.00	39.7	52.0	42.5	55.7
42	1330	22.6	30.1	17.4	23.1	74.3	98.8	0.00	0.00	17.8	23.6	56.6	75.3
56	1253	1.34	1.68	2.28	2.86	12.5	15.7	0.00	0.00	3.72	4.66	10.4	13.0
70	1031	2.28	2.35	1.04	1.07	5.68	5.86	0.00	0.00	2.12	2.19	4.56	4.70
77	996	2.28	2.27	0.48	0.48	4.08	4.06	0.00	0.00	2.08	2.07	4.60	4.58

[†]Mass determined from amount of each herbicide added

[†]Dicamba concentration.

[‡]Dicamba mass.

[§]MCPA concentration.

[¶]MCPA mass.

[#]Mecoprop-P concentration.

^{††}Mecoprop-P mass.

^{‡‡}Bromoxynil concentration.

^{§§}Bromoxynil mass.

^{¶¶}2,4-D concentration.

^{##}2,4-D mass.

^{†††}Dichlorprop concentration.

^{###}Dichlorprop mass.

^{§§§}n=3.

^{¶¶¶}concentrations are low likely due to incomplete mixing of the wetland after rainfall runoff.

^{###}concentrations are low likely due to incomplete hydrolysis of the ester to free acid.

Three random water samples were collected from the treated half of both wetlands 24 h post-treatment (Day 1) when mixing of the wetlands due to wind action would be expected to be more complete. Standard deviation values associated with initial concentrations ranged from ± 12 to $\pm 38\%$ (Tables 6.4 and 6.5) indicating that the wetlands were not as well mixed as expected, most likely due to 40-mm rainfall and resulting rainfall runoff which occurred on Days 0 and 1.

On Day 1, the concentrations of dicamba, MCPA and mecoprop-P in wetland E (applied as salts) were much closer to their target concentrations than in wetland SP (Tables 6.4 and 6.5). Both the smaller size of wetland E which facilitated mixing and the rapid hydrolysis of the salts may have been factors in how quickly the target concentrations of dicamba, MCPA and mecoprop-P were achieved. By Day 2, concentrations of dicamba, MCPA and mecoprop-P in wetland SP were much closer to target concentrations indicating a more uniform mixing after 48 h. It also required 48 h for concentrations of herbicide esters (bromoxynil, 2,4-D and dichlorprop) in both wetlands to reach their respective target concentrations. According to Smith, (1972), esters would require approximately 48 h to completely hydrolyze to the corresponding free acids. Because the herbicide analysis method here only extracts the free-acid, the lower than target concentrations on Day 1 may be attributed to the incomplete hydrolysis of herbicide esters.

In general, herbicide concentrations in both wetlands decreased throughout the 77-d study period (Tables 6.4 and 6.5). We did, however, see increased herbicide concentrations on Day 2, 3 and 7, most likely because of incomplete mixing in the wetlands due to the amount of rain (~95 mm) and associated rainfall runoff during the first week post-herbicide treatment (Degenhardt et al., 2010c). Significant amounts of precipitation fell on Days 1 (24 mm) and 3 (37 mm). Plotting the natural logarithm of herbicide concentration versus time showed that dissipation of all six acid herbicides in wetland SP and E followed first-order kinetics with regression correlations values (r^2) of 0.79–0.96 and 0.43–0.99, respectively (Table 6.6). To account for changes in wetland volume due to rainfall, rainfall runoff, infiltration and evaporation, we plotted the natural logarithm of the calculated mass of the herbicides in each wetland against

Table 6.6. Modeled first-order dissipation kinetics ($C_t = C_0e^{-kt}$) of each acid herbicide in the water column of ephemeral (E) and semi-permanent (SP) wetland.

	Wetland E (small)												
	Dicamba		Bromoxynil		MCPA		2,4-D		Mecoprop-P		Dichlorprop		
	Conc.	Mass	Conc.	Mass	Conc.	Mass	Conc.	Mass	Conc.	Mass	Conc.	Mass	
r^2	0.85	0.73	0.99	0.93	0.89	0.96	0.93	0.96	0.62	0.84	0.43	0.64	
C_0 ($\mu\text{g L}^{-1}$)	93.6		61.6		125		98.7		178		105		
Mass ₀ (g)		6.75		4.44		9.01		7.12		12.9		7.57	
k	0.07	0.06	0.30	0.24	0.06	0.07	0.06	0.07	0.04	0.04	0.02	0.03	
$t_{1/2}$ (d)	9.8	11	2.3	2.8	11	11	12	11	18	16	31	26	
	Wetland SP (large)												
	r^2	0.79	0.82	0.90	0.89	0.96	0.96	0.96	0.96	0.92	0.93	0.83	0.83
	C_0 ($\mu\text{g L}^{-1}$)	126		61.6		161		98.7		231		105	
Mass ₀ (g)		152		99.9		203		160		274		170	
k	0.05	0.05	0.18	0.18	0.07	0.08	0.05	0.06	0.05	0.05	0.03	0.04	
$t_{1/2}$ (d)	14	14	3.9	3.9	9.6	9.0	13	12	14	13	23	17	

time. The r^2 values for MCPA, 2,4-D, dichlorprop and mecoprop-P improved for wetland E and this was not unexpected because herbicide concentrations here were more affected by changes in volume. For wetland SP, the r^2 value calculated using herbicide mass were similar to those derived using herbicide concentration. The first-order rate constant (k) of each herbicide for both wetlands was consistent whether using concentration or mass for fitting dissipation kinetics. Based on herbicide concentration, the dissipation half-lives (DT_{50}) for the acid herbicides in wetland SP ranged from 3.9 d (bromoxynil) to 23 d (dichlorprop) (Table 6.6). In wetland E, the DT_{50} values ranged from 2.3 d (bromoxynil) to 31 d (dichlorprop). The order of persistence amongst the six herbicides was essentially the same for both wetlands. Photolysis of organic contaminants in wetland waters is expected to be relatively slow because most prairie wetlands have high DOC ($>20 \text{ mg L}^{-1}$) contents, which significantly attenuate UV light and decrease photolysis (Arts et al., 2000; Waiser and Robarts, 2004). Therefore the main route of acid herbicide breakdown in these wetlands was likely microbial degradation. In both wetlands, bromoxynil degraded most rapidly followed by the phenoxyacetic acids (2,4-D and MCPA) which were less persistent than the corresponding phenoxypropionic acids (dichlorprop and mecoprop-P) (Tables 6.4 and 6.5). The persistence of dicamba was similar to that of the phenoxyacetic acid herbicides. Only the phenoxypropionic acid (mecoprop-P and dichlorprop) concentrations remained above their respective guidelines for the protection of aquatic life on the last day of sampling. Because mecoprop-P and dichlorprop are chiral compounds, their longer persistence may result from resistance to microbial degradation due to their chemical structures. The commercial products used in our study were formulated to contain the herbicidally active R-(+)-isomer of mecoprop-P or the racemic mixture of dichlorprop. Chiral compounds are known to express enantiometric selectivity in reactions involving biological systems, especially microbial degradation. Garrison et al. (1996) showed that the degradation of dichlorprop occurred with enantiometric selectivity and the S-(-) isomer was degraded more rapidly than the R-(+) isomer.

Other dissipation pathways, such as volatilization, sorption to suspended particulates, sediment and biota, and transport with infiltrating water, are more likely to

influence the fate of those acid herbicides with longer DT_{50} values. Volatilization of esters may be an important dissipation route before hydrolysis to the free acids (Grover et al., 1994; Grover et al., 1985; Zepp et al., 1975). Herbicide loss via infiltration can be determined by examining the correlation between bromide ion mass and herbicide mass over time (Degenhardt et al., 2010c). We found a correlation between the decrease in bromide ion mass in wetland SP and that of bromoxynil ($r^2 = 0.63$) [n = 7], dicamba ($r^2 = 0.59$) [n = 8], 2,4-D ($r^2 = 0.76$) [n = 9], MCPA ($r^2 = 0.62$) [n = 9], mecoprop-P ($r^2 = 0.62$) [n = 10] and dichlorprop ($r^2 = 0.63$) [n = 10]. This relationship was even stronger in wetland E with r^2 ranging from 0.8 to 0.95 (n = 9). Stronger correlations were expected because the majority of the water loss in wetland E was via infiltration (Degenhardt et al., 2010c). The transport of these herbicides with infiltrating water may have been enhanced by the high DOC concentrations (wetland SP = 22 mg L⁻¹ and wetland E = 40.2 mg L⁻¹) in the water. Dissolved organic carbon can form soluble complexes with herbicides and thereby facilitate their transport with the infiltrating water (Baskaran et al., 1996).

6.3.2 Acid herbicide dissipation in sediment

The analytical method developed in this paper provided 41.7 to 76.6 % recovery for all six acid herbicides from sediment fortified at 5 µg kg⁻¹ (Table 6.3). The limit of quantification (LOQ), defined as half of the minimum concentration of herbicide determined by the recoveries studies, was 2.5 µg kg⁻¹ for each of the acid herbicides, except for dicamba which had a MDL of 4 µg kg⁻¹. This extraction method proved to be efficient and reliable for the purpose of quantifying environmental concentrations of the acid herbicides in wetland sediment.

None of the six acid herbicides analyzed in our study were detected in surficial sediment in either wetland prior to herbicide treatment (Tables 6.7 and 6.8). Throughout the 77-d study, we did not detect any herbicides in sediment collected on the control half of either wetland. In wetland E, sediment samples collected from the treated half on Day 1 contained the highest concentrations of all six acid herbicides, and samples taken on subsequent sampling periods showed decreased herbicide concentrations (Table 6.7). For wetland SP, the highest concentrations of mecoprop-P,

Table 6.7. Wetland area, herbicide concentration and mass in the sediment samples from the treated half of the ephemeral (E) wetland.

		Wetland E (small) Treated half											
Days after spiking	Area	Amine Salt				Potassium salt				Ester			
		Benzoic		Phenoxyacetic		Phenoxypropionic		Hydroxybenzotrile		Phenoxyacetic		Phenoxypropionic	
		Dicam conc[†]	Dicam mass[‡]	MCPA conc[§]	MCPA mass[¶]	Mecop conc[#]	Mecop mass^{††}	Brom conc^{‡‡}	Brom mass^{§§}	2,4-D conc^{¶¶}	2,4-D mass^{##}	Dichp conc^{†††}	Dichp mass^{‡‡‡}
m ²	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	
-4	425	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	475	–	–	–	–	–	–	–	–	–	–	–	–
1	500	34.8	0.77	61.1	1.35	67.4	1.49	73.4	1.62	171	3.77	73.1	1.61
3	750	16.7	0.37	28.8	0.63	32.0	0.71	14.0	0.31	26.2	0.58	21.7	0.48
7	775	13.3	0.29	20.6	0.45	21.7	0.48	6.90	0.15	68.1	1.50	46.0	1.01
14	725	5.00	0.11	13.7	0.30	13.7	0.30	3.00	0.07	56.0	1.23	60.1	1.32
21	700	6.30	0.14	8.50	0.19	10.4	0.23	5.80	0.13	13.3	0.29	17.2	0.38
28	650	8.00	0.18	10.3	0.23	8.70	0.19	0.00	0.00	47.1	1.04	83.6	1.84
42	650	7.90	0.17	8.30	0.18	8.00	0.18	0.00	0.00	18.4	0.41	22.2	0.49
56	475	9.00	0.20	8.00	0.18	10.7	0.24	0.00	0.00	15.4	0.34	41.8	0.92
77	0	9.50	0.21	0.00	0.00	7.60	0.17	0.00	0.00	0.00	0.00	14.7	0.32

†Dicamba concentration.

‡Dicamba mass.

§MCPA concentration.

¶MCPA mass.

#Mecoprop-P concentration.

††Mecoprop-P mass.

‡‡Bromoxynil concentration.

§§Bromoxynil mass.

¶¶2,4-D concentration.

##2,4-D mass.

†††Dichlorprop concentration.

‡‡‡Dichlorprop mass.

Table 6.8. Wetland area, herbicide concentration and mass in the sediment samples from the treated half of the semi-permanent (SP) wetland.

		Wetland SP (large) Treated half											
Days after spiking	Area	Amine Salts				Potassium salt				Esters			
		Benzoic		Phenoxyacetic		Phenoxypropionic		Hydroxybenzotrile		Phenoxyacetic		Phenoxypropionic	
		Dicam conc [†]	Dicam mass [‡]	MCPA conc [§]	MCPA mass [¶]	Mecop conc [#]	Mecop mass ^{††}	Brom conc ^{‡‡}	Brom mass ^{§§}	2,4-D conc ^{¶¶}	2,4-D mass ^{##}	Dichp conc ^{†††}	Dichp mass ^{‡‡‡}
		m ²	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹	g	µg kg ⁻¹
-4	2300	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	2300	–	–	–	–	–	–	–	–	–	–	–	–
1	2175	14.3	0.75	38.8	2.03	55.1	2.89	99.1	5.19	185	9.70	139	7.26
3	2175	5.40	0.28	18.9	0.99	18.0	0.94	30.6	1.60	59.2	3.10	27.7	1.45
7	2375	17.2	0.90	35.7	1.87	46.7	2.45	23.8	1.25	73.5	3.85	71.6	3.75
14	2375	23.4	1.23	43.0	2.25	45.8	2.40	2.60	0.14	101	5.27	102	5.36
21	2350	5.20	0.27	10.5	0.55	11.3	0.59	6.50	0.34	23.2	1.21	23.9	1.25
28	2300	1.90	0.10	10.0	0.52	13.5	0.71	5.40	0.28	19.0	0.99	17.4	0.91
42	2175	6.40	0.34	4.10	0.21	5.80	0.30	0.00	0.00	4.10	0.21	6.30	0.33
56	2200	5.60	0.29	3.50	0.18	6.80	0.36	0.00	0.00	2.70	0.14	7.70	0.40
77	2075	7.80	0.41	0.00	0.00	9.20	0.48	0.00	0.00	0.00	0.00	25.4	1.33

[†]Dicamba concentration.

[‡]Dicamba mass.

[§]MCPA concentration.

[¶]MCPA mass.

[#]Mecoprop-P concentration.

^{††}Mecoprop-P mass.

^{‡‡}Bromoxynil concentration.

^{§§}Bromoxynil mass.

^{¶¶}2,4-D concentration.

^{##}2,4-D mass.

^{†††}Dichlorprop concentration.

^{‡‡‡}Dichlorprop mass.

bromoxynil, 2,4-D and dichlorprop were detected on Day 1 (Table 6.8). In contrast, the concentrations of dicamba and MCPA increased overtime, reaching their maximum concentrations in sediment on Day 14. Bromoxynil became undetectable in the sediment samples from both wetlands after Day 42, while MCPA and 2,4-D were detected until Day 56. Dicamba, mecoprop-P and dichlorprop remained detectable in sediment from both wetlands on the last day of sampling (Day 77).

Using the maximum herbicide concentration detected in the sediment and the wetland area, we calculated herbicide mass which was sorbed in the upper 5 cm of sediment (Tables 6.7 and 6.8). Based on the total herbicide mass added to wetland E, the upper 5 cm of sediment sorbed approximately 53% of 2,4-D, 37% of bromoxynil, 21% of dichlorprop, 15% of MCPA, 12% of mecoprop-P, and 11% of dicamba. Though herbicide concentrations in sediment were similar between the two wetlands, surficial sediment in wetland SP sorbed a smaller proportion of total herbicide added compared to wetland E. Surficial sediment in wetland SP sorbed only 6% of 2,4-D, 5% of bromoxynil, 4% of dichlorprop, and approximately 1% of dicamba, mecoprop-P and MCPA.

The differences in herbicide loading in sediments from the two wetlands may be attributed to the differences in their herbicide sorption capacity. The sorption coefficients of 2,4-D in the sediment of these two wetlands were evaluated in a previous study by Xu et al. (2009). While a study on prairie wetland sediments found a positive correlation between 2,4-D sorption and total organic carbon (TOC) content (Gaultier et al., 2009), the sorption coefficient of 2,4-D was found to be greater in wetland E ($K_d = 7.5$) with lower TOC content (TOC = 7.6%), than to wetland SP ($K_d = 6.0$) with higher TOC content (TOC = 12.1%) (Xu et al., 2009). The authors speculated the higher clay content in sediment from wetland SP may have repelled the anionic herbicide from binding to the sediment. Furthermore, wetland SP was colonized by an aquatic moss (*Fontinalis antipyretica*), with an average density of 130 g (dry weight) m⁻² during the study period (Badiou, Ducks Unlimited, unpublished data). Because herbicides can be taken up and metabolized by this moss via enzymatic metabolism (Roy and Hanninen, 1990), we speculate that the acid herbicides in the water column of the wetland SP may

be captured by the aquatic moss and hence less herbicide was available for sorption to the sediment.

6.4 Conclusions

The fate of acid herbicides in prairie wetlands was examined in our study. Our results showed that, in water, the DT₅₀ of the six acid herbicides ranged from 2.3 d (bromoxynil) to 31 d (dichlorprop). The two chiral herbicides, mecoprop-P and dichlorprop, were the most persistent acid herbicides in the water column. Sorption to sediment and infiltration were the important dissipation routes for herbicides in water, especially in wetland E. After 77 d in the semi-permanent wetland and 56 d in the ephemeral wetland, the concentrations of bromoxynil, dicamba and 2,4-D were below the Canadian Water Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment, 2007). Concentrations of the more persistent herbicides (mecoprop-P and dichlorprop) remained at levels above the guidelines. Presently, there are no guidelines for acid herbicides in sediment, and this fact prevents an evaluation of the relevance of our sediment data with respect to ecotoxicity to aquatic biota. Given our findings, we believe herbicide guidelines are needed for sediment given the large number of organisms known to inhabit in wetland sediments (Euliss et al., 1999).

7.0 SYNTHESIS AND FUTURE RESEARCH NEEDS

7.1 Synopsis of previous work related to thesis

The presence of agricultural chemicals in wetlands is increasingly alarming as new studies have linked these contaminants to negative effects on wetland biota (Chapter 2). In prairie agriculture, herbicides are used more than any other group of pesticides. Except for atrazine, which is predominantly used in eastern Canada, and midwestern and northeastern United States, herbicides examined in this thesis are amongst some of the most commonly used herbicides in prairie agriculture (Brimble et al., 2005; National Center for Food and Agricultural Policy, 2004). Many wetlands are closely interspersed within cropland and some ephemeral wetlands may be cropped in dry years, resulting in the direct application of herbicides in these wetlands. Herbicides can also be transported into wetlands via surface runoff, spray drift and atmospheric deposition (Figure 7.1). Off-site movement of herbicides can vary depending on application method, weather conditions and physicochemical properties of the herbicide. Concentrations of herbicides in prairie wetlands vary temporally during the year, reflecting seasonal agricultural activities and spring snowmelt events. Spring snowmelt runoff events in the prairies can be an important route of entry for herbicides into wetlands, with relative importance depending on slope and drainage pattern in the landscape, as well as the size and the extent of the wetland catchment. Herbicide susceptibility to runoff may be affected by physicochemical properties, such as water solubility, persistence in the soil and pKa , as well as other factors such as length and intensity of snowmelt/precipitation events.

Once transported into wetlands, herbicide fate is dependent on destructive and non-destructive dissipation processes (Fig 7.1). Destructive dissipation processes include photolysis, microbial degradation, hydrolysis and enzymatic degradation;

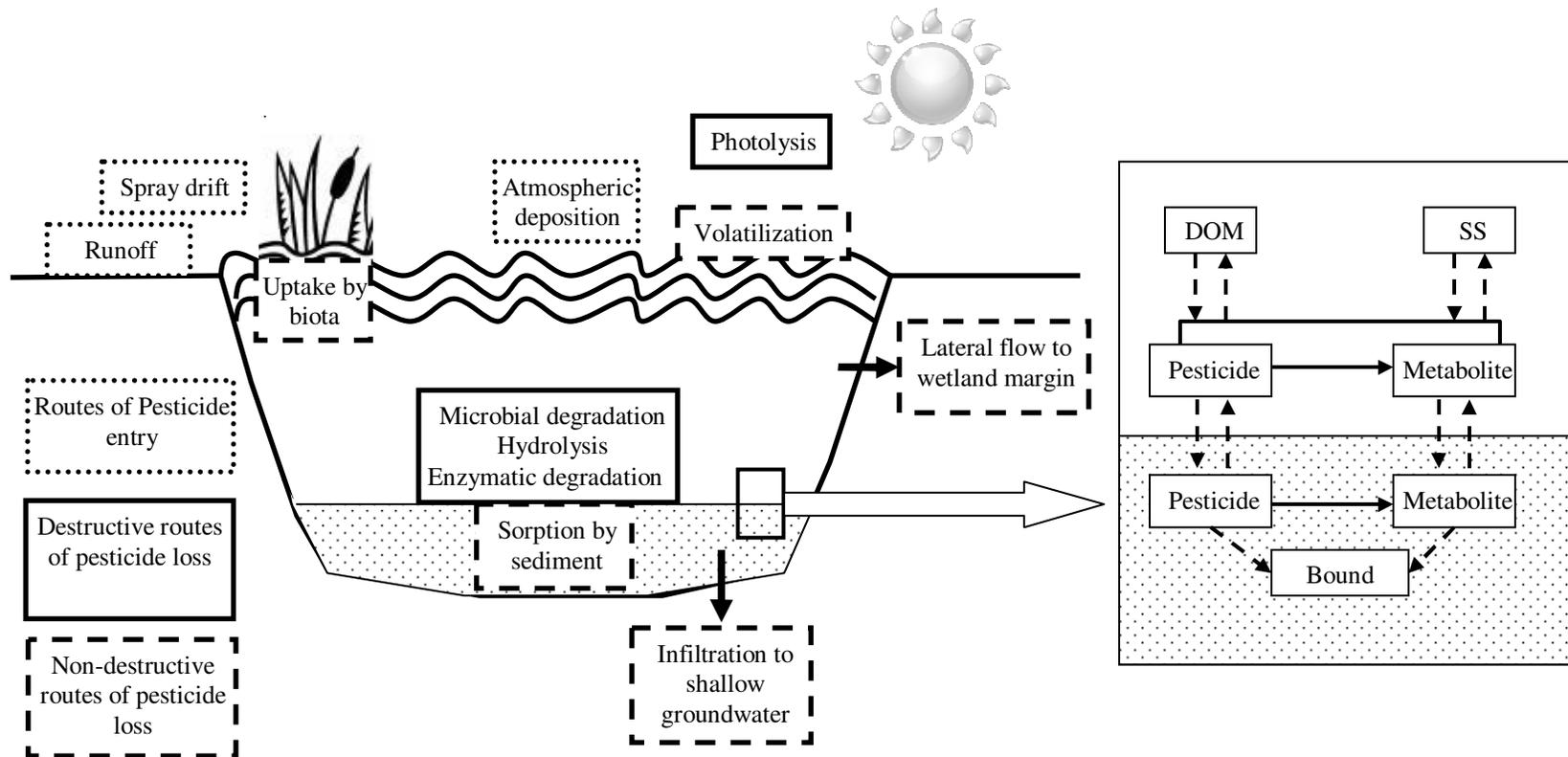


Figure 7.1. Transport and transformation processes of pesticides in wetlands. DOM, dissolved organic matters, SS, suspended solids. Dashed arrows represent non-destructive routes of pesticide/metabolite transformation and solid arrows represent destructive routes of pesticide transportation.

while non-destructive dissipation processes include volatilization, infiltration to shallow ground water and wetland margins, as well as sorption to suspended particulates, sediment and sorption/uptake by biota.

Sediments are important in wetland ecosystems, because they serve as habitat, food source and breeding ground for aquatic organisms. Despite the large volume of data on herbicide contamination in wetland waters, and the increasing interest from the public and governments regarding wetland conservation, very few studies have reported herbicide concentrations in wetland sediment (Goldsborough and Beck, 1989; Goldsborough and Brown, 1993; Newton et al., 1994). This lack may be due to the complexity of the sediment matrix, and absence of analytical methods for quantification. Only one study has been published on sorption and desorption of 2,4-D to wetland sediment (Gaultier et al., 2009); here, the authors reported that the potential for 2,4-D accumulation in wetland sediments was small, because most of the 2,4-D sorbed by sediments was released after 8 hours. The link between results garnered by herbicide sorption/desorption studies in sediment, and the persistence of herbicides in real wetland systems is unclear.

7.2 Synthesis of present work

The goal of this dissertation was to investigate whether herbicide sorption behaviors reflect the persistence of herbicides in wetland sediment. This thesis has advanced scientific knowledge by: 1) determining effects of wetland size, water permanence and riparian vegetation on various physicochemical properties of wetland sediment, and herbicide sorption by sediment; 2) detecting currently used sulfonylurea herbicides in sediment from 17 wetlands using a newly developed analytical method and 3) establishing half-lives of seven acid herbicides in the water columns of two prairie wetlands, as well as establishing their persistence in wetland sediment.

In the first study, we determined that the upper 5-cm sediment horizon from 17 wetlands were rich in organic carbon (OC). Semi-permanent wetlands contained higher OC content ($8.7\% \pm 0.8$) in the upper five cm than cultivated ephemeral wetlands ($3.2\% \pm 0.1$). Wetlands with riparian vegetation also contained higher OC content in the upper portion of the sediment ($6.8\% \pm 0.5$). We have determined the sorption coefficients

(*K_d*) of 2,4-D, trifluralin and atrazine in sediments from these 17 wetlands. They were correlated to the OC content of the sediment which is indirectly related to land use in the catchment and the presence of riparian vegetation. The results of this study provided insights into the effects of cultivation, vegetation cover in the catchment and riparian vegetation on the physicochemical properties of prairie wetland sediments. This study also permitted the elucidation of the relationship between *K_d* values and various sediment properties.

For the second study (Chapter 4), we analyze residues of seven sulfonylurea herbicides in the same sediments used in the batch equilibrium sorption study (Chapter 3). The goal of the study was to investigate the relationship between land use (tillage and vegetation cover) in wetland catchments and concentration of sulfonylurea herbicides in wetland sediment. Sulfonylurea herbicides were selected in this study because they are a relatively new class of herbicides in Canadian prairie agricultural production. Due to the complexity of the sediment matrix, protocols were developed for herbicide extraction and extract cleanup. At least one of the seven sulfonylurea herbicides analyzed in this study was detected in all of the sediment samples from the 17 wetlands. The results from this study suggest that the low levels of sulfonylurea herbicides found in sediments likely entered the wetland via atmospheric deposition, and the concentrations were not dependent on tillage or vegetation cover in the wetland catchment. Higher levels of sulfonylurea herbicide found near the delta and the edge of a large SP wetland likely came from surface runoff.

Study 3 (Chapters 5 and 6) examined the relationship between sorption data generated in the laboratory (Study 1) and the persistence of herbicides in actual wetlands. This study determined the dissipation rate of seven herbicides (glyphosate, dicamba, bromoxynil, 2,4-D, MCPA, mecoprop-P and dichlorprop) in water columns of two wetlands, and the herbicide concentrations in sediment over the 77-d study period. With the aid of bromide ion as a conservative tracer, the main hydrological routes of water loss from the two wetlands were determined. Infiltration and evaporation were the two most important water loss pathways in the studied wetlands. The dissipation half-lives (time for herbicide concentration to decrease by 50%) of herbicides in the water column ranged from several days (bromoxynil) to over a month (dichlorprop).

Herbicide dissipation half-lives were similar between the ephemeral wetland and the semi-permanent wetland. All seven herbicides were detected in wetland sediment. Based on total herbicide mass added, sediment in the ephemeral wetland sorbed more 2,4-D than the semi-permanent wetland, and this finding was in agreement with our sorption results from Study 1. Despite the high Kd value (125 L kg^{-1} for wetland SP and 250 L kg^{-1} for wetland E) determined for glyphosate, it only persisted in the sediment of wetland SP and E for 28 and 42 days, respectively. Whereas 2,4-D exhibited much lower Kd values (6 L kg^{-1} for wetland SP and 7.5 L kg^{-1} for wetland E), but persisted in the sediment of both wetlands for 56 days. In conclusion, the sorption data can provide information on herbicide sorption capacity of sediments from various wetlands, but it cannot be used to accurately estimate herbicide persistence.

7.3 Future Research

Simplistically, the wetland system in our study can be considered to consist of two heterogeneous phases, water and sediment. However, other components such as interstitial porewater, suspended solids and biota may play an integral role in herbicide dissipation processes in wetland ecosystems. Appropriate study design in the future should consider these components, because they are crucial in providing a complete understanding of pesticide behaviour in natural aquatic environments.

7.3.1 Interstitial porewater phase

Interstitial porewater is a key phase that needs to be considered, especially when dealing with toxicological effects of pesticides on bottom dwellers like chironomids. Interstitial porewater has been found to contain higher dissolved organic carbon (DOC) content than the overlying water phase (Thurman, 1985). Studies have found that DOC can facilitate degradation of herbicides by the production of oxidative species (Cessna and Muir, 1988). We are not aware of any studies that have investigated the fate of herbicides in interstitial porewater.

7.3.2 Suspended solids

Suspended solids or the colloid fraction in the water phase had high affinity for organic contaminants (Simpson et al., 2004). Suspended solids are detrital material

derived from decomposition. Due to the increase in adsorptive surface area, suspended solids have the potential to sequester herbicides in the water column. The sorptive nature of suspended solids is unknown, and further work is needed to investigate the importance of suspended solids in herbicide dissipation in water.

7.3.3 Biota

Wetlands are generally richer in diversity and more biologically productive than other aquatic bodies (Mitsch and Gosselink, 1993). The presence of both submersed and emergent plant growth can significantly increase enzymatic degradation of pesticides by plant tissue (Muir et al., 1985). Biofilms on all submerged surfaces including macrophytes have a highly reactive and extensive area which can increase sorption and degradation of herbicides (Headley et al., 1998; Lawrence et al., 2001). Whole-wetland studies in the future should include macrophyte and biofilm samples for herbicide residue analysis. If possible, plant litter should be separated from the sediment for separate residue analysis. Algae are an important component to consider in terms of pesticide sinks and degradation, especially at the air-water interface where biofilms are formed by their growth. Algae can also act as light scattering suspended particles that can shield pesticides from photolysis (Miller and Zepp, 1979; Zepp and Schlotzhauer, 1983). Because algal abundance is linked to agricultural activities (fertilizer runoff), their presence in wetlands may correlate with pesticide levels, and the interaction of the two requires more elucidation.

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