

Pesticides in the Air, Atmospheric Deposits, and Surface Waters of Canada

by

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## ABSTRACT

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In Canada, more than 35 million kilograms of pesticide active ingredients are applied annually on agricultural land with about 84% of this mass applied in the Canadian Prairies Provinces. Pesticide residues may become airborne through post-volatilization losses from land, water or vegetative surfaces, via wind-eroded soil, and by spray drift during pesticide application. Once in the air, pesticides may be dispersed and transported as parent molecules or as degradation products. Currently used and legacy pesticide air concentrations were measured in the agricultural region of the Prairie Provinces and the northern subarctic and arctic regions of Canada in 2005 and 2007. More intensive air sampling was conducted across the province of Manitoba in 2008 and 2009. Separate wet versus dry atmospheric deposition samples and wetland water samples were also taken in these years. In general, pesticides were detected in the monitored environmental media as mixtures with the frequency and concentrations detected being largest for pesticides that were applied on-site. Although the most commonly used herbicides in western Canadian agriculture were frequently present in the air in the regions where they are applied, they appeared infrequently and at low levels in the Canadian Subarctic, Arctic, and remote sites far from agricultural pesticide applications. Results also indicated that the concentrations of legacy pesticides such as lindane ( $\gamma$ -HCH) and its manufacturing by-product prior to 1971 ( $\alpha$ -HCH) continued to decrease over time in the Canadian environment. Air concentrations of pesticides in agricultural regions, and subsequent wet

and dry atmospheric deposition, contaminated surface water following periods of pesticide application. Dry deposition contributed 12–51% of the total deposition. Calculations were performed to predict wetland water column pesticide concentrations based on total atmospheric deposits alone. The estimated concentrations were closest to actual concentrations for MCPA and predictions were also reasonable for a range of other herbicides, but a source other than atmospheric deposition was clearly relevant to the detection of clopyralid in the wetland water-column. Individual herbicide concentrations did not exceed Canadian water quality guidelines for the protection of aquatic life.

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## FORWARD

This is a manuscript style thesis prepared in accordance with the Department of Soil Science, University of Manitoba guidelines. Following the general introduction (Chapter 1) are four chapters prepared in a stand-alone, manuscript format. The final chapter (Chapter 6, Overall Synthesis) integrates the four data chapters by summarizing the research findings and implications, discusses the research limitations, provides future recommendations, and identifies the contribution of this thesis to knowledge.

Chapter 2 has been accepted by the Journal of Environmental Science and Health, Part B and chapter 3 has been submitted for publication.

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## LIST OF ABBREVIATIONS

- 2,4-D: [2,4-(dichlorophenoxy) acetic acid]
- A.I.: Active Ingredient
- AB: Alberta
- CUH: Currently-used herbicides
- AMPA: aminomethylphosphonic acid
- DEM: Digital Elevation Model
- DT<sub>50</sub>: Dissipation Time, 50%
- GC: Gas Chromatography
- HCH: Hexachlorocyclohexane
- K<sub>oa</sub>: octanol–air partitioning coefficient
- K<sub>oc</sub>: Soil organic sorption coefficient
- K<sub>ow</sub>: octanol-water partitioning coefficient
- LD<sub>50</sub>: lethal dose, 50%
- MB: Manitoba
- MDL: Minimum Detection Level
- MS: Mass Spectrometry
- MZTRA: Manitoba Zero-Tillage Research Association
- pK<sub>a</sub>: logarithmic measure of the acid dissociation constant
- PPR: Prairie Pothole Region
- PUF: Polyurethane Foam
- SK: Saskatchewan

# **1. INTRODUCTION**

## **1.1 Agricultural Pesticide Use and Importance to Canada**

Agriculture is an important industry in the prairies with total cash receipts equaling \$7.8, \$6.6, and \$3.7 billion in Alberta, Saskatchewan, and Manitoba respectively (Eilers, 2010). Total farm area for the three provinces equals 54.8 million ha with 21.1, 26.0, and 7.7 million ha in Alberta, Saskatchewan, and Manitoba respectively (Eilers, 2010).

At least 35 million kilograms of agricultural pesticides are currently applied in Canada each year (Cessna et al., 2010). Approximately 84% of this mass is applied in the prairie region of the three Prairie Provinces. Cessna et al. (2010) estimated that approximately 17.4, 8.4, and 4.6 million kg pesticides is applied on cropland in Saskatchewan, Alberta, and Manitoba respectively (Cessna et al., 2010). The majority of these applications are confined to the arable land in the southern portions of these provinces (Eilers, 2010). Approximately 96% of the pesticides applied to cropland in the Prairie Provinces are herbicides (Cessna et al., 2010). Using crop insurance data from Manitoba, Wilson (2012) provided more detailed calculations of agricultural herbicide use by producers and estimated that at least 2 million kg of agricultural pesticides are applied annually in this province encompassing ~ 60 different active ingredients.

## **1.2 Prairie Pothole Region of Canada**

The Prairie Pothole Region (PPR; Figure 1.1) of North America is an area of approximately 715,000 km<sup>2</sup> (Euliss et al., 1999) and contains millions of wetlands, a large

portion being closely associated with agricultural cropland. The geomorphological landscape of the Prairie Pothole Region was shaped in the Wisconsin Glacial Period resulting in numerous small topographic depressions forming prairie wetlands. The water balance components of these prairie wetlands are well understood (van der Kamp and Hayashi, 2009) and are controlled by the cold semi-arid climate (van der Kamp, et al., 2003). Movement of snow-derived water to the wetlands is critical to their existence (Hayashi et al., 1998) with 30 – 60% transferred from the upland to the wetland as snowmelt runoff in the spring. Summer surface runoff occurs only rarely during intense rainfall events (Hayashi et al., 1998). Due to the moderate rainfall the area receives and the geological age of the landscape there are few natural surface drainage systems and it is common for wetlands to be closed drainage basins (van der Kamp and Hayashi, 2009). Potential evapotranspiration often exceeds precipitation during the summer months (Conly and van der Kamp, 2001). Prairie wetlands are among the most productive ecosystems in the world, providing habitats for a wide variety of flora and fauna, such as 50 – 80% of the continent's duck population (Batt et al., 1989).

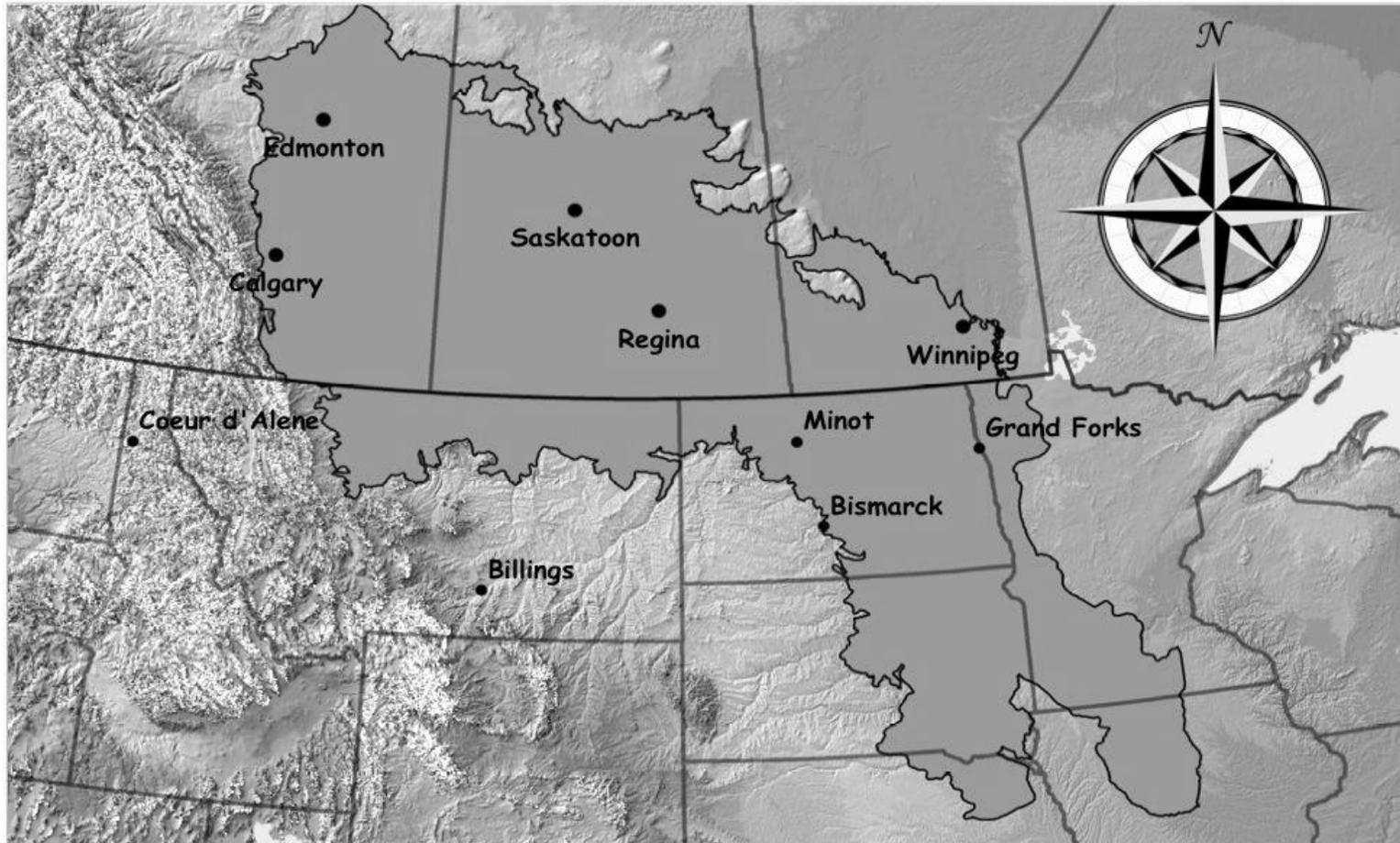


Figure 1.1. Prairie Pothole Region of North America.

### **1.3 Manitoba Zero-Till Research Association Research Farm**

The Manitoba Zero-Till Research Association Research Farm is located within the PPR on a section of farmland (260 ha) owned and operated by the Manitoba Zero-Till Research Association and Ducks Unlimited Canada, approximately 20 km north of Brandon, Manitoba (Figure 1.2).

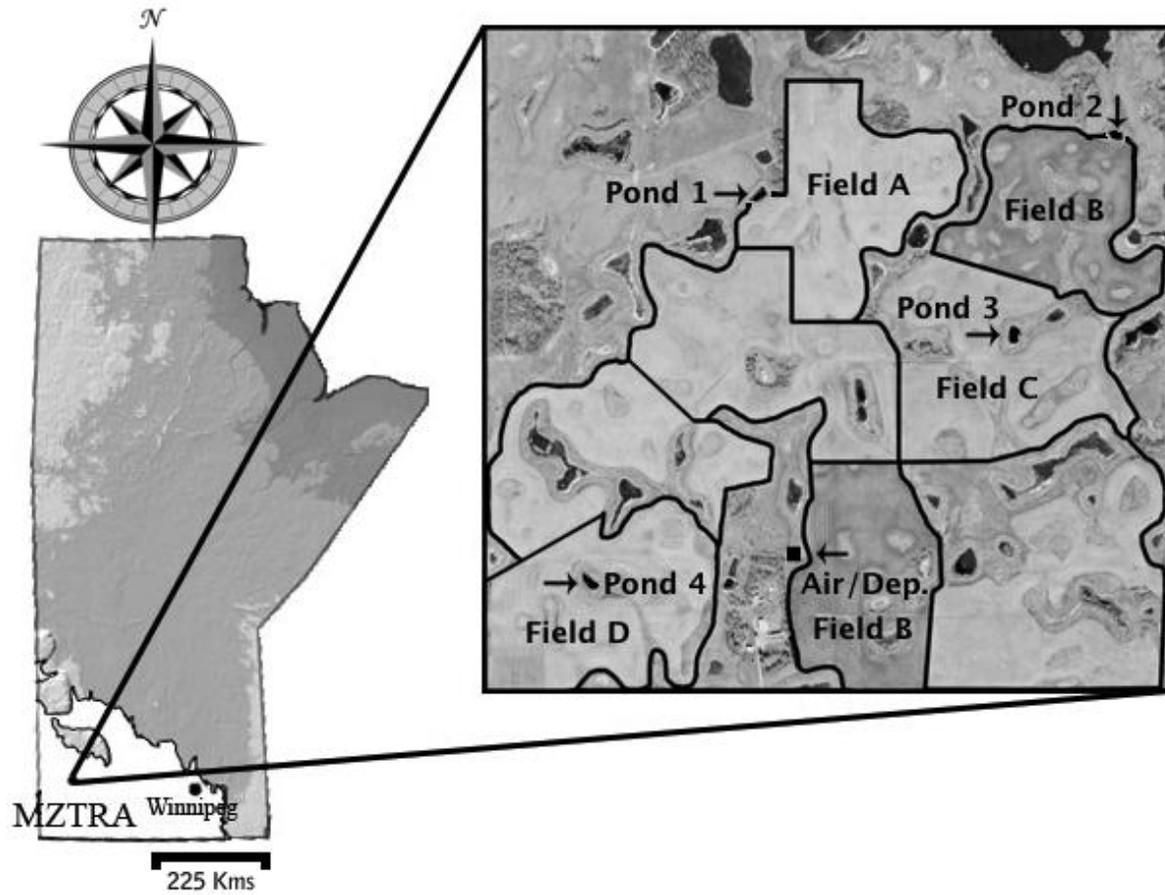


Figure 1.2. The extent of the Prairie Pothole Region (area in white) in the Province of Manitoba (entire map) with a close-up of the MZTRA farm (1.6 km<sup>2</sup>).

This research site has an undulating to hummocky landscape, dominated by Black Chernozemic soils as defined by the Agriculture and Agri-Food Canada Publication the Canadian System of Soil Classification, 3rd ed. (1998). Slopes range on the landscape from 5-35 degrees and the site contains approximately 200 wetlands. In 1993 the farm was converted from conventional to zero tillage production for field scale research. Agricultural management at the site includes a six-year annual crop rotation, a six-year forage and annual crop rotation and permanent pasture for livestock grazing. Zero tillage is practiced on all cultivated land.

#### **1.4 Pesticides in the Air**

Soon after the initiation of the commercial use of pesticide products in agriculture, it was reported that the vapours of pesticides have the potential to become air pollutants (Daines, 1952). Application and post application losses of pesticides to the air depend on the physicochemical characteristics of the active ingredient and the formulated product, the application method, and the environmental conditions (Caldwell, 2007; Waite et al., 2005; Donald et al., 2001). Pesticides may become airborne through application drift (Caldwell, 2007), post-volatilization losses from land, water, or vegetative surfaces, (Grover et al., 1985) and on wind-eroded soil (Larney et al., 1999). Once airborne, pesticides may be dispersed and transported to offsite locations as parent molecules or as degradation products (Shen et al., 2005). The distance transported is determined by atmospheric transport, atmospheric degradation, and deposition rates as well as revolatilisation rates (Gouin and Wania, 2007). Many studies have focused on historically used organochlorine pesticides and their ability to be transported great distances through long range transport processes (Wania and Mackay, 1993; Harner et al., 2006; Su et al.,

2008; Hoferkamp et al., 2010). However, currently used pesticides such as trifluralin and metolachlor have also been detected hundreds to thousands of kilometers from their site of application (Rice and Chernyak, 1997; Su et al., 2008; Hoferkamp et al., 2010).

### **1.5 Atmospheric Deposition of Pesticides**

Atmospheric deposition of pesticides is typically measured using samplers that collect precipitation only (Belzer et al., 1998; Hall et al., 1993; Rawn et al., 1999) or through bulk (dry and wet combined) deposition samplers (Hill et al., 2001; Waite et al., 1995). Bulk deposition has been shown to vary spatially in the prairies depending on the intensity of local and regional pesticide use (Hill et al., 2003).

To our knowledge, Canada is the only country worldwide to have compared simultaneous measurements of pesticide wet versus dry deposition. This work has been limited to one study site in the province of Saskatchewan (Waite et al., 2005). Using the Waite-Banner Atmospheric Dry/Wet Deposition Sampler (Waite et al., 1999), this single study demonstrated that total seasonal dry deposition may account for up to ~ 85 to 100% of the total bulk deposition mass (wet + dry) of triallate, trifluralin, 2,4-D, bromoxynil, dicamba, and MCPA (Waite et al., 2005). Prior to this Canadian study, it was reported that dry deposition contributed only to a minor extent of the total deposition of pesticides (Siebers et al., 1994).

### **1.6 Pesticides in Wetlands**

Previous studies have shown prairie wetlands in Canada to be contaminated with a suite of pesticides (Donald et al., 2001; Anderson, 2002; Waite et al., 2002). Pesticide loadings

to prairie wetlands may be due to atmospheric sources such as atmospheric wet and dry deposition, including gas exchange at the air-water interface (Waite et al., 1995; Jantunen et al., 2008), runoff events (Waite et al., 1992) and groundwater recharge (Waite et al., 1992). Donald et al. (1999) estimated that between 9 - 24% of the wetlands in the province of Saskatchewan contain levels of pesticides exceeding Canadian guidelines for the protection of aquatic life. Donald et al. (2001) used data on the atmospheric deposition of pesticides collected for four growing seasons (1984 to 1987), as reported by Waite et al. (1995), to calculate the average mass of three pesticides deposited during a growing season. Using these data, Donald et al. (2001) then calculated what the average concentration of each herbicide would be if a wetland had a depth of 50 cm. They found that these calculated concentrations were similar to the mean concentrations of 41 wetlands they monitored in the province of Saskatchewan. Based on these assumptions, Donald et al. (2001) concluded that atmospheric processes alone can account for detectable levels of herbicides in the wetlands of central Saskatchewan, but direct measurements linking atmospheric inputs of herbicides to concentrations found within prairie wetlands have not been published.

## **1.7 Objectives**

The overall goal of this study was to improve the knowledge of the environmental occurrence of pesticides in Canada. The specific objectives were: (1) To evaluate the concentration of currently used pesticides and legacy chemicals in the air at sites located along an east-west transect spanning the agricultural region of the Canadian Prairies, and northern subarctic and arctic locations in the Northwest Territories and Nunavut (Chapter 2). (2) To monitor pesticide air concentrations in the summer and winter seasons as a

function of local herbicide use and the spatial scale between samplers (Chapter 3), (3) To quantify, in an agricultural field site typical of the Prairie Pothole Region near Brandon, Manitoba, the relative amounts of 14 pesticides deposited as dry versus wet atmospheric deposition, and to relate their detections to airborne levels measured at the same site (Chapter 4), and (4) To quantify the contribution of atmospheric deposition on pesticide concentrations detected in the water-column of four prairie wetlands (Chapter 5).

### **1.8 Hypotheses**

The hypotheses are: (1) Currently used pesticides in the Canadian Prairies are not being transported in the air as parent molecules to Northern Canada. (2) Winter air concentrations of pesticides will be lower than those found in the summer due to lower application rates and decreased volatilisation with lower temperatures. (3) Spatial variability of air concentrations of pesticides increases as the distance between the samplers increases. (4) Dry deposition of pesticides is a significant contributor to total seasonal deposition and (5) Atmospheric depositions of pesticides will contribute a quantifiable amount to water concentrations of prairie wetlands.

### **1.9 Thesis Outline**

This is a manuscript style thesis prepared in accordance with the Department of Soil Science, University of Manitoba Guidelines. Specific research activities are divided into four, stand alone manuscripts (Chapters 2 through 5).

**Chapter 2: Air concentrations of currently used herbicides and legacy compounds in the Canadian prairies, subarctic, and arctic**

A study that monitored pesticide air concentrations in the summers of 2005 and 2007 with two east-west transects: four locations along the southern portion of the Prairie Provinces and five locations in the Arctic and northern Subarctic.

**Chapter 3: Summer and Winter Pesticide Air Concentrations at Seven Sites in Canada**

Pesticide air concentrations were monitored at seven sites in the summers of 2008 and 2009 and winter of 2009. The sites were located in a ~500 km east-west transect and a ~1000 km north-south transect. The site with the greatest estimated amount of local herbicide use had four separate sampling locations 0.5 to 1.5 km apart.

**Chapter 4: Influence of usage and chemical-physical properties on the atmospheric transport and deposition of pesticides to agricultural regions of Manitoba, Canada**

The masses of 14 pesticides deposited as wet (precipitation) versus dry (gaseous and particle) atmospheric deposition were quantified at a research farm in southwestern Manitoba, Canada. The air concentrations of these pesticides were also measured.

**Chapter 5: Predicting wetland contamination from atmospheric deposition measurements of pesticides in the Canadian Prairie Pothole region**

The masses of pesticides entering wetlands by atmospheric deposition were compared with the concentrations of pesticides detected in the water-column of prairie wetlands. Weekly air and bulk deposition samples were collected from

May 26<sup>th</sup> to Sept. 15<sup>th</sup>, 2008 at a research farm in southwestern Manitoba, Canada, with four on-site wetlands (approximate sizes 0.15 - 0.45 ha) monitored every second week. The air concentrations of pesticides were also measured.

My contributions to Chapters 2 through 5 include: conducting field and laboratory work; supervising student assistants who assisted with field and laboratory work. Statistical analysis using various software programs including Data Desk and Microsoft Excel; writing and submitting four manuscripts for publication in international peer reviewed journals (Chapters 2, 3, 4, and 5). Pesticide analyses were performed by Mr. Jim Sproull at the Prairie & Northern Laboratory for Environmental Testing, Environment Canada, Edmonton, Alberta, Canada and Dave Humphries at Sustainable Ecosystems, Alberta Innovates Technology Futures, Vegreville, Alberta, Canada.

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## **2. AIR CONCENTRATIONS OF CURRENTLY USED HERBICIDES AND LEGACY COMPOUNDS IN THE CANADIAN PRAIRIES, SUBARCTIC, AND ARCTIC**

### **2.1 Abstract**

Passive air samplers were installed in the summers of 2005 and 2007 for 90 days at four locations in the agricultural region of the Canadian Prairies and at five locations in the Canadian Subarctic and Arctic. The presence and masses of ten currently used herbicides and three legacy compounds in the polyurethane foam disks were quantified. Herbicides 2,4-D, bromoxynil, and MCPA were detected at all locations in the Canadian Prairies and in both years because these herbicides are widely applied to control broadleaf weeds in cereal crops that are an integral part of Prairie agricultural production systems. MCPA was also detected at one location in the Arctic in 2007. The detection of the other seven herbicides in the two years combined ranged from no detections (atrazine only) to five detections for the relatively volatile herbicides trifluralin and triallate. Triallate was the only other herbicide detected in the Arctic (2005). Legacy compounds were either not detected (alachlor) or at levels near their detection level ( $\gamma$ -HCH and  $\alpha$ -HCH).  $\gamma$ -HCH and  $\alpha$ -HCH were more frequently detected in 2005 than in 2007 indicating that their concentrations in Canadian air have decreased over time.  $\gamma$ -HCH, widely used as an insecticide in Prairie oilseed production until 2002, was detected at larger concentrations in the Canadian Prairies than in the Subarctic and Arctic.  $\alpha$ -HCH, a manufacturing by-product in technical HCH prior to 1971 in Canada, was not detected in the Canadian Prairies but was at detectable levels in the Subarctic and Arctic as the Arctic Ocean is reported to be a major source of  $\alpha$ -HCH to the atmosphere. We conclude that some of the most widely used herbicides in Canadian agriculture today are commonly present in the

air in regions where they are applied and that a portion of these herbicides may be traveling as parent molecules to the Canadian Arctic. To the authors' knowledge, this is the first evidence of the presence of MCPA and triallate in Arctic air samples, perhaps because previous research has seldom monitored for currently used herbicides in this region.

## 2.2 Introduction

Pesticides are widely applied in North American agricultural production systems. In Canada, more than 35 million kilograms of pesticide active ingredients are applied annually on agricultural land with about 84% of this mass applied in the Canadian Prairies in the provinces of Saskatchewan, Alberta, and Manitoba (Cessna et al., 2010). Approximately 96% of the pesticides applied to agricultural land in the Canadian Prairie Provinces are herbicides (Cessna et al., 2010).

Pesticide residues may become airborne through spray drift during pesticide application, through volatilization losses from land, water or vegetative surfaces, and via wind-eroded soil (Larney et al., 1999). In the agricultural region of the Canadian Prairies pesticides such as 2,4-D [2,4-dichlorophenoxyacetic acid], atrazine [6-chloro-N<sup>2</sup>-ethyl-N<sup>4</sup>-isopropyl-1,3,5-triazine-2, 4-diamine], bromoxynil [3,5-dibromo-4-hydroxybenzoxynitrile], clopyralid [3,6-Dichloro-2-pyridinecarboxylic acid], ethalfluralin [N-ethyl- $\alpha,\alpha,\alpha$ -trifluoro-N-(2-methylallyl)-2,6-dinitro-*p*-toluidine], lindane [ $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane], MCPA [(4-chloro-2-methylphenoxy)acetic acid], mecoprop [2-

(4-chloro-2-methylphenoxy)propanoic acid], metolachlor [2-chloro-6-ethyl-N-(2-methoxy-1-methylethyl)acet-*o*-toluide], triallate [S-2,3,3-trichloroallyl di-isopropyl (thiocarbamate)], and trifluralin [ $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-N,N-dipropyl-*p*-toluidine] have all been previously (1999 – 2008) detected in the air (Messing et al., 2011; Kumar, 2001; Waite et al., 2005; Yao et al., 2006) With the exceptions of atrazine, lindane, and metolachlor these pesticides are currently widely applied in prairie agriculture.

Distant locations from where agricultural pesticides are applied, such as the Subarctic and Arctic, may potentially be contaminated by persistent chemicals that undergo long-range transport (Scheringer, 2009; Wöhrnschimmel, 2012; Zhang et al., 2012). Many long-range transport studies have focused on the monitoring of historically used pesticides in the Arctic such as  $\gamma$ -HCH (lindane) and pesticide byproducts such as  $\alpha$ -HCH (Hoferkamp, et al., 2010; Hung et al., 2010; Su et al., 2008). However, currently used pesticides such as trifluralin and metolachlor have also been detected hundreds to thousands of kilometers from their site of application (Hoferkamp, et al., 2010; Su et al., 2008, Rice and Chernyak, 1997; van Dijk and Guicherit, 1999).

The objectives of this study were to evaluate the presence and masses of currently used herbicides in the air in regions where they are applied and to determine whether the herbicides detected travel as parent molecules to the Canadian Subarctic and Arctic. Three legacy compounds were also included in the study to compare their presence and masses with that of currently used herbicides.

## 2.3 Material and Methods

**2.3.1 Sampling Locations.** Passive air samplers were deployed at four locations in an east-west transect spanning ~1000 km along the southern portion of the Prairie Provinces of Alberta (AB), Saskatchewan (SK), and Manitoba (MB) and ~1300 km north of these at five locations in the Arctic and northern Subarctic in an east-west transect spanning ~1500 km in the Northwest Territories (NT) and Nunavut (NU) (Figure 1). The locations were situated adjacent to Environment Canada meteorological stations to monitor air temperature. The southern locations were located in rural areas surrounded by farmland and included (from west to east): Lethbridge Agricultural Research Station, AB; Swift Current Agricultural Research Station, SK; Indian Head Agricultural Research Station, SK; Brandon Agricultural Research Station, MB (Table 2.1). The Subarctic and Arctic locations included (from west to east): Nahanni National Park, NT; near the town of Ft. Simpson, NT; near the town of Yellowknife, NT; in the town of Arviat, NU; and in the town of Coral Harbour, NU (Table 2.1). The Coral Harbour, NU location was included in 2005 but transportation difficulties prevented accessibility in 2007 and the location was substituted with a location in the town of Cape Dorset, NU. At all locations, air samplers were deployed in duplicate. For those that had detections, the average coefficient of variation in the pesticide concentrations detected between the duplicated side-by-side samplers was 37% in 2005 and 42% in 2007.



Figure 2.1. Sampling locations.

Table 2.1. Sampling locations, coordinates, region, and periods for duplicate PUFs per location for 2005 and 2007.

<b>Sampling site</b>	<b>Latitude, Longitude</b>	<b>Region</b>	<b>2005 Sampling Period</b>	<b>2005 Days Deployed</b>	<b>2007 Sampling Period</b>	<b>2007 Days Deployed</b>
Brandon, MB	49.8653, -99.9817	Agricultural Prairie	May 5 - Aug. 9	96	May 3 - Aug. 15	104
Indian Head, SK	50.5333, -103.6667	Agricultural Prairie	May 5 - Aug. 9	96	May 4 - Aug. 16	104
Swift Current, SK	50.2850, -107.7928	Agricultural Prairie	May 25 - Aug. 11	78	May 1 - Aug. 9	100
Lethbridge, SK	49.6931, -112.8417	Agricultural Prairie	May 26 - Aug. 12	78	May 2 - Aug. 8	98
Coral Harbour, NU	64.1386, -83.1692	Arctic	May 26 - Aug. 7	73	NS	NS
Cape Dorset, NU	64.2303, -76.5408	Arctic	NS	NS	May 15 - Aug. 14	91
Arviat, NU	61.0956, -94.0717	Arctic	May 16 - Aug. 2	78	June 7 - Sept. 13	98
Yellowknife, NT	62.4544, -114.3764	Subarctic	May 11 - Aug. 25	106	May 14 - Aug. 15	93
Fort Simpson, NT	61.8167, -121.3136	Subarctic	May 18 - Aug. 9	83	May 25 - Aug. 23	90
Nahanni National Park, NT	61.4994, -125.5003	Subarctic	May 9 - Aug. 9	92	May 15 - Aug. 20	87

NS: No sample

**2.3.2 Sampling Devices and Pesticides Analyzed.** Passive air samples were collected for 90 days using polyurethane foam (PUF) disks mounted inside chambers consisting of two stainless steel bowls with holes drilled into them to act as a protective housing as designed by Shoeib and Harner (2002). PUF disks were precleaned by Soxhlet extraction for 16 hours using dichloromethane. PUF disks were collected at the end of the study period and shipped on the day of collection in ice packed coolers to the Prairie & Northern Laboratory for Environmental Testing, Environment Canada, Edmonton, Alberta, Canada. Samples were kept frozen and in the dark prior to extractions that occurred within 10 days of collection.

**2.3.3 Pesticide Extraction and Quantification.** PUF disks were analyzed for 10 currently used herbicides: 2,4-D, atrazine, bromoxynil, clopyralid, ethalfluralin, MCPA, mecoprop, metolachlor, triallate, and trifluralin. They were also analyzed for alachlor [2-chloro-2-(4-chlorophenyl)-N-methoxy-N-propylacetanilide] and lindane, two pesticides no longer registered for use in Canada, and for  $\alpha$ -HCH [ $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane] a manufacturing by-product in technical HCH prior to 1971 in Canada. (Tuduri et al., 2006). Producers in Canada were able to use lindane stocks until the end of 2002 and alachlor was de-registered in 1985 (Health Canada, 2012). Clopyralid and mecoprop were not analyzed in 2005.

The PUF disks were Soxhlet extracted with 500 ml acetone for 24 hours as described by Waite et al. (2005). Solvents (acetone, dichloromethane, ether and hexane) were pesticide

grade and were obtained from Caledon Laboratories (Georgetown, Canada). Pesticide standards were 98% purity or greater and were obtained from ChemService (West Chester, USA) and Riedel-de Haen (Seelze, Germany). 2,4-DCAA (2,4-dichlorophenyl acetic acid) was obtained from Sigma-Aldrich (Oakville, Ontario) to act as a surrogate to determine recoveries. One mL of acetone containing 1  $\mu\text{g}$  2,4-DCAA was added to each PUF in the laboratory prior to extractions to act as a surrogate. Acetone extracts were concentrated by rotary evaporation, methylated with three 2 ml aliquots of ethereal diazomethane and concentrated with a stream of pure nitrogen gas after each addition. The final concentrate was then made up to a final volume of 10 ml using hexane for the analyte quantification by GC-MS.

Quantification was performed using an Agilent Technologies (Palo Alto, CA) model 6890 GC interfaced with a Waters (Manchester, UK) model Quattro Micro GC triple-quadrupole mass spectrometer operated in electron impact ionization mode using multiple reaction monitoring. The GC column used was a HP-5ms 30-m x 0.25-mm internal diameter, film thickness 0.25  $\mu\text{m}$  of 5% phenyl-95% dimethylpolysiloxane. Helium was used as the carrier gas with a flow rate of 1 ml/minute. Extract aliquots (2  $\mu\text{L}$ ) were injected into the GC with an Agilent model 7683 automatic liquid sampler. Method detection limits were 0.01  $\mu\text{g}$  for all analytes with the exceptions of 2,4-D, atrazine, ethalfluralin, and trifluralin that had limits of 0.05  $\mu\text{g}$ . In addition to 2,4-DCAA, an internal standard (0.1  $\mu\text{g}$  4,4' dibromooctafluorobiphenyl in 0.1 ml of hexane) was added just prior to instrumental analysis. The data were normalized to a standard 90-day sampling period.

Protocols also included the use of field and laboratory blanks as well as matrix spikes. Field blank samples were taken by placing the PUF disks into the passive air samplers and then returning them to their amber glass jars at each of the agricultural locations. Matrix spikes included samples of clean matrix fortified prior to extraction with 1.0 µg of each of the analytes of interest including the surrogate. Matrix spikes and matrix blanks were analyzed throughout the study period at a frequency of at least 10% of the samples analyzed. Field and lab blanks for the PUF samples were below levels of detection for all analytes and therefore no blank correction was performed. Average pesticide recoveries ranged from 79 - 122% for the PUF spikes and no recovery correction was performed.

## **2.4 Results and Discussion**

Across the four locations in the Canadian Prairies, there were a total of 18 (2005) and 23 (2007) detections of currently used herbicides (Table 2.2). The number of herbicides detected at the locations ranged from four to six herbicides in 2005, and from five to seven herbicides in 2007. 2,4-D (0.06-0.81 µg sample<sup>-1</sup>), bromoxynil (0.03-0.52 µg sample<sup>-1</sup>), and MCPA (0.05-0.47 µg sample<sup>-1</sup>) were always detected because these herbicides are among the most widely used agricultural pesticides in the Canadian Prairies (Brimble et al., 2005; Wilson, 2012).

Table 2.2. Normalized mass ( $\mu\text{g sample}^{-1}$ ) of detected pesticides collected per sampler in 2005 and 2007. Sampling locations without detections have not been included in the table.

<b>2005</b>	<b>MCPA</b>	<b>Bromoxynil</b>	<b>2,4-D</b>	<b>Ethalfuralin</b>	<b>Trifluralin</b>	<b>Triallate</b>	<b>Metolachlor</b>	<b><math>\alpha</math>-HCH</b>	<b><math>\gamma</math>-HCH</b>	<b>Clopyralid</b>	<b>Mecoprop</b>
Brandon, MB	0.19	0.11	0.10	ND	0.05	ND	ND	ND	0.01	NA	NA
Indian Head, SK	0.13	0.13	0.11	0.03	0.13	0.03	ND	ND	0.02	NA	NA
Swift Current, SK	0.47	0.52	0.23	0.04	ND	ND	ND	ND	0.05	NA	NA
Lethbridge, AB	0.05	0.22	0.13	ND	0.85	ND	ND	ND	0.01	NA	NA
Coral Harbour, NU	ND	ND	ND	ND	ND	ND	ND	0.01	ND	NA	NA
Arviat, NU	ND	ND	ND	ND	ND	0.06	ND	0.01	0.01	NA	NA
Yellowknife, NT	ND	ND	ND	ND	ND	ND	ND	0.01	ND	NA	NA
Fort Simpson, NT	ND	ND	ND	ND	ND	ND	ND	0.01	ND	NA	NA
<b>2007</b>											
Brandon, MB	0.10	0.03	0.24	ND	ND	0.01	0.29	ND	ND	ND	0.30
Indian Head, SK	0.06	0.08	0.06	ND	0.09	0.03	0.03	ND	ND	0.02	ND
Swift Current, SK	0.06	0.16	0.11	ND	0.04	0.03	ND	ND	0.02	ND	0.02
Lethbridge, AB	0.05	0.11	0.81	ND	ND	0.03	ND	ND	ND	ND	0.03
Cape Dorset, NU	ND	ND	ND	ND	ND	ND	ND	0.01	ND	ND	ND
Arviat, NU	0.01	ND	ND	ND	ND	ND	ND	0.01	ND	ND	ND

NA = Not Analyzed

ND = No detection

The detection of the other seven herbicides in the two years combined ranged from no detections (atrazine only) to once for clopyralid ( $0.2 \mu\text{g sample}^{-1}$ ), twice for metolachlor ( $0.03$  and  $0.29 \mu\text{g sample}^{-1}$ ) and ethalfluralin (trace levels in both samples), three times for mecoprop ( $0.02$ - $0.30 \mu\text{g sample}^{-1}$ ), and five times for triallate ( $0.01$ - $0.03 \mu\text{g sample}^{-1}$ ) and trifluralin (trace levels- $0.85 \mu\text{g sample}^{-1}$ ). Ethalfluralin, triallate, and trifluralin all have vapor pressures higher than 9 mPa (Pesticide Property Database, 2012) and are expected to partition to the gas phase. The other herbicides have relatively low vapor pressures ranging from 0.04 to 1.7 mPa. Previous studies have demonstrated that these herbicides, which have relatively low vapor pressures, can be present in the atmosphere either partitioned to the gas phase or sorbed to atmospheric particulates (Kumar, 2001; Messing et al., 2011; Messing et al., 2012; Rawn et al., 1999; Waite et al., 2005; Yao et al., 2008).

Except for metolachlor, all other herbicides that we detected are commonly used in Prairie agriculture (Brimble et al., 2005; Wilson, 2012). Metolachlor is typically used in corn production east of the Canadian Prairies in the provinces of Ontario and Quebec, and south of the Canadian Prairies in the Mid-West region of the United States. This herbicide is relatively persistent in the environment and can be transported hundreds of kilometers from its areas of application (Hoferkamp et al., 2010; Su et al., 2008; Rice and Chernyak, 1997; van Dijk and Guicherit, 1999).

Triallate at  $0.06 \mu\text{g sample}^{-1}$  (2005) and MCPA at  $0.01 \mu\text{g sample}^{-1}$  (2007) were detected at the Arctic location in Arviat, Nunavut (Table 2.2). The mass of triallate detected at this Arctic location was numerically greater than the mass of triallate detected at each of the four locations in the Canadian Prairies. In contrast, the mass of MCPA in the Arctic sample was at the detection limit (Table 2.2). Few studies have monitored currently used herbicides in the Subarctic and Arctic but trifluralin and metolachlor have been previously detected in these regions (Hoferkamp et al., 2010; Su et al., 2008; Rice and Chernyak, 1997; van Dijk and Guicherit, 1999). This is the first study to report on detectable levels of triallate and MCPA in Arctic air samples.

The legacy chemical,  $\gamma$ -HCH, was detected in the Canadian Prairies at all four locations in 2005 but the sampled masses were relatively small and ranged from the detection limit of  $0.01$  to  $0.05 \mu\text{g sample}^{-1}$  (Table 2.2). Air concentrations of  $\gamma$ -HCH in the Canadian Prairies are clearly decreasing over time as, in our study,  $\gamma$ -HCH was only detected in one location in the Canadian Prairies in 2007 (Table 2.2). Since  $\gamma$ -HCH is relatively persistent in soil,  $\gamma$ -HCH detected in the air samples in the years after product deregistration in 2002 may be due to the volatilization of residual  $\gamma$ -HCH from Prairie agricultural soils (Yao et al., 2006; Scholtz and Bidleman, 2006). Yao et al. (2006) reported that the average air concentration of  $\gamma$ -HCH was  $5 \text{ ng m}^{-3}$  in 2003, numerically lower than the air concentrations of  $16$  and  $7 \text{ ng m}^{-3}$  reported by Waite et al. (2001) for locations in the Canadian Prairies in 1997 and 1998, respectively. In our study, there was evidence of long-range transport of  $\gamma$ -HCH, albeit the legacy compound was only detected once in the northern transect, this was at the Arctic location of Arviat, NU at the detection limit of

0.01  $\mu\text{g sample}^{-1}$  in 2005. The possibility of  $\gamma$ -HCH volatilizing from Canadian Prairie soils and transporting to Canadian Arctic air has been previously demonstrated (Waite, et al., 2005).

The legacy byproduct  $\alpha$ -HCH was not detected in the air samples collected in the Canadian Prairies.  $\alpha$ -HCH was frequently detected in Subarctic and Arctic locations in 2005 but at the detection limit of 0.01  $\mu\text{g sample}^{-1}$  (Table 2.2). In 2007, the detection of  $\alpha$ -HCH only occurred at the Arctic locations located on the coast of the Arctic Ocean. Previous research has suggested that the Arctic Ocean is the last major storage system of  $\alpha$ -HCH on Earth (Macdonald et al., 2000; Pućko et al., 2011; Wania et al., 1999).

In this study, the low detected quantities of  $\alpha$ -HCH and  $\gamma$ -HCH at the Subarctic and Arctic locations were expected as low concentrations have been reported for Arctic samples in other recent studies. (Hung, et al., 2010; Pozo et al., 2006; Pozo et al., 2009). Hung et al. (2010) found that air concentrations of HCHs are decreasing over time as was observed in the current study. The frequency of detection of  $\alpha$ -HCH and  $\gamma$ -HCH appears to be decreasing in the Subarctic and Arctic as degradation processes remove them from the environment. Pućko et al. (2011) have estimated that degradation processes could eliminate the majority of  $\alpha$ -HCH by 2020 in the Beaufort Sea.

## 2.5 Conclusion

Herbicides widely used in the Canadian Prairies were detected as mixtures in passive air samplers collected in the Provinces across this region in the summers of 2005 and 2007. Herbicides 2,4-D (0.06-0.81  $\mu\text{g sample}^{-1}$ ), bromoxynil (0.03-0.52  $\mu\text{g sample}^{-1}$ ), and MCPA (0.05-0.47  $\mu\text{g sample}^{-1}$ ) were detected in every sample, and MCPA was also detected at one location in Arctic air (0.01  $\mu\text{g sample}^{-1}$ ). Triallate was the only other herbicide detected in Arctic air (0.06  $\mu\text{g sample}^{-1}$ ) but in an amount greater than the masses of triallate detected in the air samples in the Canadian Prairies (0.01-0.03  $\mu\text{g sample}^{-1}$ ). Of the legacy compounds studied, the frequencies of detection of  $\gamma$ -HCH and  $\alpha$ -HCH were greater in 2005 than in 2007 indicating that the persistence of these legacy compounds in the air have decreased over time.  $\gamma$ -HCH (lindane) was more frequently detected in the Canadian Prairies possibly due to the volatilization of residual  $\gamma$ -HCH from Prairie agricultural soils as lindane was registered for use until 2002 and is relatively persistent in soil. In contrast,  $\alpha$ -HCH, a manufacturing by-product in technical HCH prior to 1971 in Canada, was only detected in air in the Canadian Subarctic and Arctic, more consistently at locations near the Arctic Ocean. This is the first study to report on detectable levels of triallate and MCPA in Arctic air samples suggesting a need for more intensive monitoring of currently used pesticides in Subarctic and Arctic regions.

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### **3. CURRENT-USE HERBICIDES IN AIR AS INFLUENCED BY THEIR ESTIMATED AGRICULTURAL USE AT VARIOUS DISTANCES FROM SIX SAMPLING LOCATIONS**

#### **3.1 Abstract**

Passive air samplers were deployed at six locations across the province of Manitoba, Canada to represent areas with, or at various distances from, agricultural herbicide applications. During the growing seasons in 2008 and 2009, the four southern sites always demonstrated mixtures of current-use herbicides (CUHs) in air but CUHs were not detected at the two northern sites that were 400 and 800 km away from Manitoba's most northern boundary of agricultural herbicide applications. The masses of the CUHs detected in the air were most strongly positively associated with their estimated masses typically applied in a ~100 km<sup>2</sup> township area surrounding the sampling sites ( $r = 0.70$  to  $0.74$ ) and to a lesser extent with their estimated mass applied in incrementally larger areas ( $r = 0.53$  to  $0.59$ ). The masses of CUHs detected in air were also significantly positively associated with their estimated masses applied at a provincial level ( $r = 0.45$  to  $0.52$ ), but not with their reported half-lives in air, suggesting that a system of maintaining records of herbicide use data, even at a coarse scale, can strongly improve agri-environmental risk assessments. Of the 9 CUHs detected, MCPA and bromoxynil, which are widely applied in Manitoba agriculture, were the only herbicides detected at all four southern sites. Triallate and metolachlor which have low use in Manitoba, were the only CUHs detected in the winter months, confirming that these herbicides are relatively persistent in the air and may undergo long-range transport. Four passive air samplers, installed each 0.5 to 1.5 km apart at the same location, showed variations in the herbicide

masses detected with the coefficient of variation ranging from 10% for bromoxynil in 2008 to 137% for MCPA in 2009. These variations were particularly observed for the two herbicides applied on-site (MCPA and clopyralid), but also for four herbicides transported into the area from longer distances (2,4-D, bromoxynil, ethalfluralin, and triallate). Future regional-scale research should therefore consider deploying multiple sets of passive air samplers at a site for obtaining a more representative measure of herbicide air concentrations.

### **3.2 Introduction**

Pesticides become airborne through application drift, volatilization losses from land, water vegetative surfaces, and by being attached to windblown sediment (Grover et al., 1985; Larney et al., 1999; Caldwell, 2007). Application and post application losses of pesticides to the air depend on the application method, the physicochemical characteristics of the active ingredient and the formulated product, as well as the environmental conditions (Donald et al., 2001; Waite et al., 2005; Caldwell, 2007). Pesticides in the atmosphere are dispersed and transported offsite with the distances transported determined by their atmospheric degradation and deposition rates as influenced by environmental conditions (Shen et al., 2005).

More than 28 million kg of herbicide active ingredients are annually applied to agricultural land in the Canadian Prairie Provinces (Manitoba, Saskatchewan and Alberta) (Cessna et al. 2010). The herbicides 2,4-D, atrazine, bromoxynil, clopyralid, ethalfluralin, MCPA, mecoprop, metolachlor, triallate and trifluralin have all been

detected in air samplers installed during the growing season in Manitoba, Saskatchewan or Alberta (Kumar, 2001; Messing et al., 2011; Waite et al., 2005; Yao et al., 2006). With the exceptions of atrazine and metolachlor these pesticides are currently widely applied in prairie agriculture. The herbicides MCPA, metolachlor, triallate and trifluralin have been also detected hundreds to thousands of kilometers from their site of application (Rice and Chernyak, 1997; Hoferkamp et al., 2010; Messing et al., 2014).

Previous studies have demonstrated that the mass of pesticides in bulk (wet and dry) deposition was largest in agricultural regions with greater pesticide use (Goolsby et al. 1997) or pesticide sales (Hill et al. 2001). The objective of this study was to determine the masses of ten current-use herbicides (CUHs) in passive air samplers as influenced by estimated herbicide use applications at various distances from six sampling locations in Manitoba, Canada.

### 3.3 Material and Methods

**3.3.1 Herbicides and their estimated use.** The study focused on 10 CUHs with a wide range of physical-chemical characteristics and use patterns in Manitoba agriculture (Table 3.1): 2,4-D [2,4-dichlorophenoxyacetic acid], atrazine [6-chloro-N<sup>2</sup>-ethyl-N<sup>4</sup>-isopropyl-1,3,5-triazine-2, 4-diamine], bromoxynil [3,5-dibromo-4-hydroxybenzoxynitrile], clopyralid [3,6-Dichloropyridine-2-carboxylic acid], ethalfluralin [N-ethyl- $\alpha,\alpha,\alpha$ -trifluoro-N-(2-methylallyl)-2,6-dinitro-*p*-toluidine], MCPA [(4-chloro-2-methylphenoxy)acetic acid], mecoprop [2-(4-chloro-2-methylphenoxy)propanoic acid],

metolachlor [2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)aceto-*o*-toluidide], triallate [S-2,3,3-trichloroallyl di-isopropyl (thiocarbamate)], and trifluralin [ $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-N,N-dipropyl-*p*-toluidine]. The applications of the 10 CUHs across Manitoba were estimated utilizing a database (Wilson, 2012) containing the formulated pesticide products applied to crops in each of the 1,124 townships of Manitoba with agricultural land. A township is 36 square miles (93.2 km<sup>2</sup>) with the division of land into townships dating back to the Dominion Land Survey (1869) conducted in western Canada to promote European settlement on arable land. The database reflected the types of pesticide products used by approximately 80% of the producers in Manitoba in years 2004, 2005 and 2006 (Wilson 2012). Years 2004 to 2006 were chosen because they provided the most recent data available at a township level prior to 2008 and 2009 when the 10 CUHs were monitored in the air. For each of the 1,124 townships and each year, the mass of each CUH applied was calculated using a computer program written in PERL (Practical Extraction and Report Language) that linked the information in the database with that in an Excel spreadsheet. The Excel spreadsheet listed the formulated products used in Manitoba containing the CUHs, along with their recommended maximum application rates on each crop that they are registered for (Manitoba Agriculture and Food, 2006). It was assumed that when a formulated herbicide product was reportedly used on a crop, it was only applied once in the growing season. Pesticide use estimates by Brimble et al. (2005) and by Cessna et al. (2010) also assumed one herbicide application at the maximum recommended rate.

Table 3.1 Mass of active ingredients applied in Manitoba (2004–2006 average) (Wilson, 2012), their physicochemical properties (Pesticide Properties Database, 2012) and atmospheric half-lives (U.S. EPA, EPI Suite. 2013).

Herbicide	Typical crops	Application timing	Mass applied in MB (kg)	Water solubility 20°C (mg L <sup>-1</sup> ) <sup>a</sup>	Vapour pressure at 25°C (mPa) <sup>a</sup>	Half-life in air (h) <sup>1</sup>
2,4-D	wheat, barley, rye	post-emergent	162,420 ± 10,036	23180	0.0187	38.7
Atrazine	corn	pre/post-emergent	18,171 ± 4,437	35	0.039	9.4
Bromoxynil	wheat, barley, oats	post-emergent	166,152 ± 12,196	90	0.17	1220
Clopyralid	wheat, barley, canola	post-emergent	19,160 ± 2,409	143000	1.36	468
Ethalfuralin	canola, alfalfa	pre-emergent	93,004 ± 9,256	0.01	12	3.2
MCPA	wheat, barley, oats	post-emergent	429,484 ± 60,604	29390	0.4	20.3
Mecoprop	wheat, barley, oats	post-emergent	4,961 ± 1,344	250000	1.6	14.8
Metolachlor	corn	pre-emergent	194 ± 123	530	1.7	4.6
Triallate	wheat, barley, canola	pre-emergent	7,190 ± 698	4.1	12	7.7
Trifluralin	wheat, barley, canola	pre-emergent	43,899 ± 2,831	0.22	9.5	10.7

<sup>1</sup>Estimated gas-phase persistence

**3.3.2 Research Locations and Sampling Devices.** Six research regions were chosen (Figure 3.1) to represent townships and adjacent townships with varying mass applications of the 10 CUHs (Table 3.2). Two northern sites were chosen to represent regions without agricultural herbicide use and these sites were located 400 (Northern Site 1) and 800 (Northern Site 2) km north of Manitoba’s most northern boundary of the agricultural region. The four southern sites included from west to east (Figure 3.1): A) a Parkland Agricultural Site (Manitoba Zero Tillage Research Association Farm, 2.6 km<sup>2</sup>) located in a township in which herbicides are widely used on undulating to hummocky soil-landscape terrains dominated by wheat, barley, and canola production; B) the largest marsh complex in Manitoba (Delta Marsh, ~ 120 km<sup>2</sup>) located in a township with low herbicide use; C) the largest city in Manitoba (City of Winnipeg, 463 km<sup>2</sup>) located in a township with no agricultural herbicide use; and D) a Red River Valley Agricultural Site (Glenlea Research Farm, 5 km<sup>2</sup>) located in a township with moderate herbicide use on near-level heavy-clay soils dominated by wheat, oat, canola and soybean production.



Figure 3.1. Passive air sampler locations in Manitoba: A) Parkland agricultural site (Manitoba Zero Tillage Research Association Farm); B) a marsh complex (Delta Marsh); C) urban site (City of Winnipeg); D) Red River Valley agricultural site (Glenlea Research Farm); E) Northern Site 1; F) Northern Site 2.

Table 3.2 Total mass of the 10 current-use herbicides applied (kg) on agricultural land in four incrementally larger areas (km<sup>2</sup>) surrounding the research locations of the passive air samplers.

Research Location	Herbicide Mass Applied (kg)			
	93.2 km <sup>2</sup> [1]	837.2 km <sup>2</sup>	2,331.0 km <sup>2</sup>	4,568.8 km <sup>2</sup>
Parkland Agricultural Site	1,849 ± 290	15,008 ± 2,296	31,620 ± 4,957	58,913 ± 9,326
Red River Valley Agricultural Site	596 ± 104	8,713 ± 1,548	22,662 ± 3,964	46,997 ± 8,235
Marsh Complex	29 ± 6	6,639 ± 954	21,718 ± 2,598	36,950 ± 4,459
Urban Site (City of Winnipeg)	0	3,206 ± 533	18,611 ± 3,321	44,470 ± 7,565
Northern Site 1	0	0	0	0
Northern Site 2	0	0	0	0

[1] Areas represent: township area (93.2 km<sup>2</sup>) in which the research location was situated, and this same township plus the adjacent blocks of eight townships (~ 837 km<sup>2</sup> area), twenty-four townships (~ 2,325 km<sup>2</sup> area), or forty-eight townships (~ 4,557 km<sup>2</sup> in area).

At the site with the largest regional herbicide applications (Parkland Agricultural Site), three additional sets of side-by-side samplers were installed. Each of the four samplers were installed 0.5 to 1.5 km apart in a section of farmland (1.6 km<sup>2</sup>) such that the impact of sampling location on the masses of herbicides detected could be assessed. The samplers were installed in the most central cultivated land on the farm (Parkland Agricultural-1), among native grasses that received no herbicide applications (Parkland Agricultural-2), adjacent to a wetland within cultivated land in the northwest corner of the farm (Parkland Agricultural-3), and adjacent to a wetland within cultivated land in the southwest corner of the farm (Parkland Agricultural-4).

**3.3.3 Sampling Devices and Pesticide Quantification.** Air samples were collected using polyurethane foam (PUF) disks mounted in chambers consisting of two stainless steel bowls with holes drilled into them to act as a protective housing as designed by Shoeib and Harner (2002). Prior to installation of the passive air samplers at the research locations, PUFs were precleaned by Soxhlet extraction using dichloromethane for 16 h. Side-by-side passive air samplers were deployed at each site adjacent to meteorological stations. Field blanks (placing the PUF-disk into the sampler and returning it to the amber

glass jar) were included in the study and were always below levels of detection for each of the herbicides analyzed.

At the southern locations the frost-free period typically ranges from mid and late May to early and mid September, during which time herbicides are applied as part of crop production (Agriculture, Food and Rural Development, 2013). Samplers were installed in the field for approximately 3 months during the growing season in both 2008 and 2009 and off-season in 2009 (Table 3.3). Variations in sampling periods and locations were due to difficulties in accessing sites because of remoteness and impassible roads resulting from snow or flooding. Samples in the off-season were only collected in the southern sites during which temperatures averaged  $-7 \pm 2$  °C. The mean temperature during growing seasons was  $17 \pm 1$  °C at southern sites and  $10 \pm 2$  °C at northern sites. PUF disks were kept frozen in the dark and analyzed within 10 days of collection at the Prairie & Northern Laboratory for Environmental Testing, Environment Canada, Edmonton, Alberta, using the same protocols as described in Waite et al. (2005). Briefly, 1 µg 2,4-dichlorophenyl acetic acid to act as a surrogate was added in acetone (1 mL) to each PUF prior to extractions. PUF disks were Soxhlet extracted with 500 ml acetone for 24 hours. Acetone extracts were concentrated with rotary evaporation, methylated with three 2 ml aliquots of ethereal diazomethane and concentrated with a stream of pure nitrogen gas after each addition. The final concentrate was then made up to a final volume of 10 ml using hexane.

Table 3.3. Summer growing season and Winter/Spring off-season sampling dates and number of days deployed.

Sampling Location	Latitude, Longitude	Summer/Fall Deployment				Winter/Spring Deployment	
		2008 Dates	# of Days	2009 Dates	# of Days	2009 Dates	# of Days
Parkland Agricultural Site	50.0596, -99.9254	May 20 - Aug. 18	90	May 20 - Aug. 18	90	Jan. 17 - Apr. 27	100
Red River Valley Agricultural Site	49.6453, -97.1579	May 21 - Aug. 19	90	Jun. 16 - Sept. 14	90	Jan. 24 - May 4	100
Marsh Complex	50.1826, -98.3821	May 20 - Aug. 18	90	May 20 - Aug. 18	90	Jan. 17 - May 7	110
Urban Site (City of Winnipeg)	49.8365, -97.1218	May 20 - Aug. 18	90	May 20 - Aug. 18	90	Jan. 24 - May 4	100
Northern Site 1	58.7655, -93.9355	July 23 - Oct. 21	90	June 6 - Sept. 4	90	ND	ND
Northern Site 2	55.8786, -98.4804	July 23 - Oct. 21	90	June 3 - Sept. 4	93	ND	ND

ND = Not Deployed

Quantification was performed using an Agilent Technologies (Palo Alta, CA) model 6890 gas chromatograph (GC) interfaced with a Waters (Manchester, UK) model Quattro Micro GC triple-quadrupole mass spectrometer operated in electron impact ionization mode using multiple reaction monitoring. The GC column used was a HP-5ms 30-m x 0.25-mm internal diameter, film thickness 0.25  $\mu\text{m}$  of 5% phenyl-95% dimethylpolysiloxane. Helium was used as the carrier gas with a flow rate of 1 ml/minute. Extract aliquots (2  $\mu\text{L}$ ) were injected into the GC with an Agilent model 7683 automatic liquid sampler. An internal standard (0.1 microgram 4,4'-dibromooctafluorobiphenyl in 0.1 ml of hexane) was added prior to instrumental analysis. Spiked PUFs and blank PUFs were included at a frequency of at least 10% of the samples analyzed. Spiked PUFs consisted of clean PUFs fortified prior to extraction with 0.5  $\mu\text{g}$  of each of the 10 pesticides analyzed for plus 2,4,5-T-d2. Recovery values typically ranged from 100 - 130% for the PUF spikes. Laboratory blanks for the PUF samples were always below levels of detection. Minimum detection limits (MDLs) were 0.01  $\mu\text{g}$  sample<sup>-1</sup> for all analytes with the exceptions of 2,4-D, atrazine, ethalfluralin, and trifluralin that had MDLs of 0.05  $\mu\text{g}$  sample<sup>-1</sup>. The herbicide masses detected in the side-by-side samplers were averaged to calculate the mass of each herbicide detected per

sampler. The mean coefficient of variation in herbicide masses detected in all of the side-by-side samplers deployed was 7% (2008) and 9% (2009), similar to the analytical variability of the PUF spikes (7% in 2008 and 11% in 2009). The data were normalized to a standard 90-day sampling period.

### **3.4 Results and Discussion**

**3.4.1. Growing season detections.** The southern region always demonstrated herbicide mixtures in air (Table 3.4) and this is in agreement with other studies (Messing et al., 2012; Waite et al., 2005; Yao et al., 2006). 2,4-D, bromoxynil, clopyralid, MCPA, mecoprop, triallate, and trifluralin were detected in both 2008 and 2009 (Table 3.4), most likely because these pesticides are commonly applied in Manitoba (Table 3.2) and their annual masses applied within the southern region are relatively similar between years (Wilson, 2012). The masses of herbicides detected ranged from 0.01  $\mu\text{g sample}^{-1}$  (detection limit) for several CUHs at several locations to a maximum of 0.74 (2009) and 1.78 (2008)  $\mu\text{g sample}^{-1}$  for MCPA in the Parkland Agricultural region (Table 3.4). In Canada, air quality guidelines for the protection of human health and the environment have not been developed for CUHs.

Table 3.4. Averaged normalized mass ( $\mu\text{g sample}^{-1}$ ) of detected pesticides in the duplicate side-by-side samplers at the six locations in 2008 and 2009.

Location	2,4-D	Ethalfluralin	Bromoxynil	Clopyralid	MCPA	Mecoprop	Metolachlor	Triallate	Trifluralin
2008									
Parkland Agricultural-1	0.21	ND	0.07	0.16	1.78	ND	0.02	0.02	ND
Red River Valley Agricultural Site	0.08	ND	0.11	0.07	0.69	0.01	ND	0.01	0.04
Marsh Complex Site	ND	ND	0.03	ND	0.06	ND	ND	ND	ND
Urban Site (City of Winnipeg)	ND	ND	0.01	ND	0.01	0.04	ND	ND	ND
Northern Site 1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Northern Site 2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Parkland Agricultural-2 <sup>a</sup>	0.08	ND	0.04	0.02	0.39	ND	ND	0.01	ND
Parkland Agricultural-3	0.12	ND	0.05	0.03	1.19	ND	ND	0.01	ND
Parkland Agricultural-4	0.11	0.04	0.05	0.10	0.87	ND	0.07	0.01	ND
2009									
Parkland Agricultural-1	0.32	ND	0.05	0.02	0.07	ND	ND	0.02	ND
Red River Valley Agricultural Site	ND	ND	0.04	0.01	0.13	ND	ND	ND	ND
Marsh Complex Site	ND	ND	0.04	ND	0.03	ND	ND	ND	0.06
Urban Site (City of Winnipeg)	ND	ND	0.01	ND	0.02	0.02	ND	ND	ND
Northern Site 1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Northern Site 2	ND	ND	ND	ND	ND	ND	ND	ND	ND
Parkland Agricultural-2 <sup>a</sup>	0.10	ND	0.06	0.02	0.08	ND	ND	0.04	ND
Parkland Agricultural-3	0.15	ND	0.05	0.06	0.74	ND	ND	0.04	ND
Parkland Agricultural-4	0.16	ND	0.05	0.02	0.12	ND	ND	0.03	ND

<sup>a</sup>Parkland Agricultural site had three additional sets of side-by-side samplers installed each 0.5 to 1.5 km apart in a section of farmland (1.6 km<sup>2</sup>). The coefficient of variation in herbicides masses among the four samplers was 56-137% for MCPA, 67-87% for clopyralid, 42-62% for 2,4-D, 29-40% for triallate and 10-24% for bromoxynil in 2008-2009, respectively.

2,4-D, bromoxynil, clopyralid, MCPA and triallate were detected in all four sampling locations at the Manitoba Zero Tillage Research Association Farm in the Parkland Agricultural region. The coefficient of variation among the four samplers in the herbicide masses detected ranged from 10% for bromoxynil in 2008 to 137% for MCPA in 2009 (Table 3.4). MCPA and clopyralid are annually applied on the farm on fields cropped to cereals (Messing et al. 2011) and demonstrated numerically larger coefficient of variations than 2,4-D, bromoxynil and triallate, which had not been applied on the farm (Table 3.4). Metolachlor and ethalfluralin were the only other herbicides detected in the Parkland Agricultural region but not in all four samplers, and only in 2008. There could be several reasons for the observed variations in herbicide masses among the four samplers including: herbicide application drift and post-volatilization losses may come from specific directions depending on which nearby farm fields are sprayed; wind speed and directions may vary during and after spraying operations. Also, the meteorological stations adjacent to the four passive air samplers demonstrated the micro-variability of the prairie atmosphere showing variations in the frequencies and amounts of rainfall across the 1.6 km<sup>2</sup> area. Such variations in rainfall occur at both local and larger scales, influencing the rate of herbicide washout by rain and thus the potential for herbicides to be transported long-range with prevailing winds.

The samplers at the Parkland Agricultural Site demonstrated a relatively high frequency of CUH detections in both 2008 (six detects) and 2009 (five detects) (Table 3.4) because herbicides are widely applied in this region (Table 3.2). In contrast, samplers at the Urban Site and Marsh Complex Site, located in areas with low to no use of the 10 CUHs (Table

3.2), showed a low frequency of CUHs detections (Table 3.4). There was a statistically significant positive association between the masses of CUHs detected in the air and their estimated masses typically applied in the townships in which the samplers were located (Figure 3.2; Table 3.5). The strength of the association was similar, regardless of which of the four samplers installed in the Parkland Agricultural region was included in the analyses (Table 3.5). Previous studies have demonstrated that there is a positive association between the masses of pesticides in bulk deposition and nearby pesticide use (Goolsby et al. 1997; Hill et al. 2001).

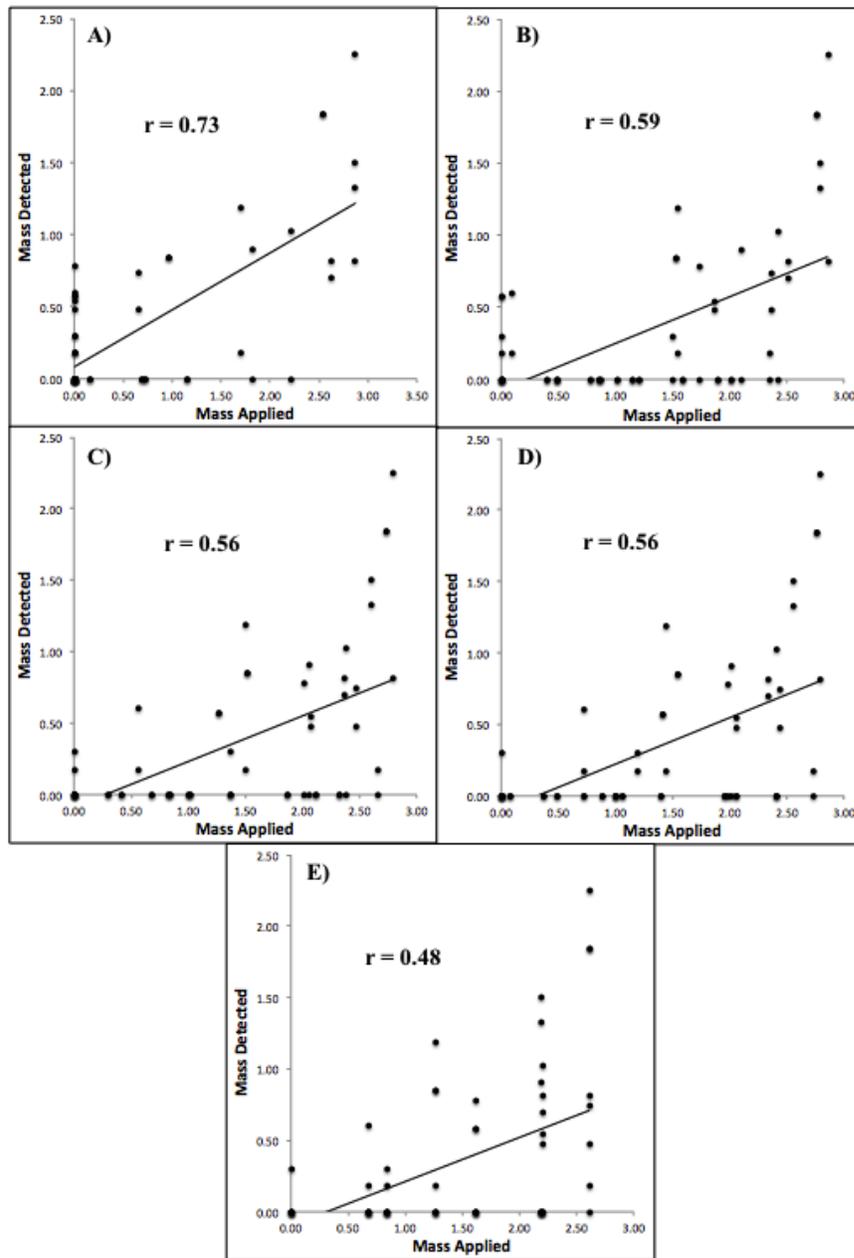


Figure 3.2. Scatterplots and correlation coefficients ( $P < 0.05$ ) between the masses of herbicides applied and the masses of herbicides detected in the passive air samplers. Graphs are for the estimated masses of herbicides applied within a  $93 \text{ km}^2$  (A),  $837 \text{ km}^2$  (B),  $2,331 \text{ km}^2$  (C) and  $4,569 \text{ km}^2$  (D) surrounding the sampling location, and on all  $104,802 \text{ km}^2$  agricultural land in Manitoba (E). All data was  $\log_{10}$  transformed to achieve normality.

Table 3.5 Correlation coefficients between mass applied and mass detected using either Parkland Agricultural 1, 2, 3 or 4

Research Location	Herbicide Mass Applied (kg)				
	93.2 km <sup>2</sup> [1]	837.2 km <sup>2</sup>	2,331.0 km <sup>2</sup>	4,568.8 km <sup>2</sup>	All of MB
All samplers including Parkland Agricultural 1	0.73	0.59	0.56	0.56	0.48
All samplers including Parkland Agricultural 2	0.70	0.58	0.56	0.53	0.45
All samplers including Parkland Agricultural 3	0.74	0.59	0.57	0.59	0.52
All samplers including Parkland Agricultural 4	0.70	0.58	0.57	0.59	0.52

[1] Areas represent: township area (93.2 km<sup>2</sup>) in which the research location was situated, and this same township plus the adjacent blocks of eight townships (~ 837 km<sup>2</sup> area), twenty-four townships (~ 2,325 km<sup>2</sup> area), or forty-eight townships (~ 4,557 km<sup>2</sup> in area).

The masses of CUHs detected in the air were to a lesser extent significantly positively associated with their estimated masses applied in areas at incrementally larger distances from their sampling locations, and with the estimated masses applied on all agricultural land in Manitoba (Figure 3.2, Table 3.5). There was no statistically significant association between the masses of CUHs detected in the air and their reported half-lives in the air, or their vapour pressure or water solubility (Table 3.1). Hence, data sets on the estimated mass of herbicides used, including at a coarse level, were a better indicator of the masses of CUHs detected in air than databases providing information about their physical-chemical properties.

MCPA and bromoxynil are widely applied in Manitoba agriculture (Table 3.1) and were the only CUHs detected at all of the southern sites in both 2008 and 2009 (Table 3.4). In the 837 km<sup>2</sup> area surrounding the sampling locations, MCPA and bromoxynil accounted for an estimated 38% (Marsh Complex Site), 58% (Parkland Agricultural Site), 82% (Red River Valley Agricultural Site), and 76% (Urban Site) of the total mass of the 10 CUHs applied. 2,4-D and bromoxynil are applied in approximately the same amount in Manitoba agriculture but because bromoxynil has a much longer half-life ( $t_{1/2\text{air}}$ ) than 2,4-

D (Table 3.1) it was more consistently detected across the southern research sites (Table 3.4). Thus, there was some indication that the atmospheric half-lives influenced the likelihood of detection for some CUHs, as previously observed for the fungicide chlorothalonil and herbicide pendimethalin in an atmospheric study by Hayward et al. (2010) in the province of Ontario, Canada.

Mecoprop was detected in the City of Winnipeg in both 2008 and 2009. Urban application of mecoprop is likely the predominant source of mecoprop contamination in the air because urban use of this herbicide is at least 50 times greater (Welch 2012) than we calculate is typically applied on agricultural land in the 837 km<sup>2</sup> township range around the city (11 kg).

None of the CUHs were detected in the northern sites in Manitoba, even though other atmospheric studies have detected MCPA, metolachlor, triallate, and trifluralin in subarctic and arctic locations in the North (Hoferkamp et al., 2010; Messing et al., 2014; Rice and Chernyak, 1997).

The northern sites had detections of legacy pesticides ( $\alpha$ -HCH and alachlor) in 2008, while these legacy pesticides were not detected in either year at our southern locations (data not shown). Persistent organic pollutants such as  $\alpha$ -HCH and alachlor tend to accumulate in polar regions through long range transport mechanisms known as global fractionation and cold condensation (Wania and Mackay, 1993).

**3.4.2. Off-season detections.** Metolachlor (0.10 µg/sampler) and triallate (0.03 µg/sampler) were the only two herbicides detected in the off-season, both at the Parkland Agricultural Site. Metolachlor has very limited applications in Manitoba (Tables 3.1) but is widely used south of Manitoba in the Mid-West region of the United States and east of Manitoba in the provinces of Ontario and Quebec in corn production (Byer et al., 2011). Although triallate and metolachlor have a reported short atmospheric  $t_{1/2\text{air}}$  (Table 3.1), other monitoring studies have demonstrated that these herbicides are relatively persistent in the atmosphere and have been detected hundreds of kilometers from where they were applied, including being detected in remote areas such as the Arctic (Messing et al., 2014; Muir and Zheng, 2007; Rice and Chernyak, 1997).

### 3.5 Conclusion

Mixtures of CUHs were detected in all four sets of passive air samplers installed from east to west across the agricultural region of Manitoba, but no CUHs were detected in samplers installed 400 and 800 km away from Manitoba's most northern boundary of agricultural land. The masses of CUHs detected in air were significantly associated ( $r = 0.70$  to  $0.74$ ) with their estimated masses applied in the  $\sim 100 \text{ km}^2$  township range in which the samplers were installed. MCPA ( $\sim 430,000 \text{ kg/y}$ ) and bromoxynil ( $\sim 170,000 \text{ kg/y}$ ) are among the most widely applied CUHs in Manitoba and were detected in all southern air samplers and in both growing seasons. Triallate ( $\sim 7,000 \text{ kg/y}$ ) and metolachlor ( $\sim 200 \text{ kg/y}$ ) that have a low use in Manitoba agriculture were the only CUHs detected in the winter months, suggesting that these herbicides are more persistent in air than the other monitored CUHs. Four passive air samplers installed each 0.5 to 1.5 km apart at the same agricultural location demonstrated variations in the herbicide masses

detected for both herbicides applied on the farm and those transported from longer distances. For obtaining a more representative measure of herbicide air concentrations, future regional-scale research should consider deploying multiple sets of passive air samplers at a research site.

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## **4. INFLUENCE OF USAGE AND CHEMICAL–PHYSICAL PROPERTIES ON THE ATMOSPHERIC TRANSPORT AND DEPOSITION OF PESTICIDES TO AGRICULTURAL REGIONS OF MANITOBA, CANADA**

### **4.1 Abstract**

This study quantified the masses of 14 pesticides deposited as wet (precipitation) versus dry (gaseous and particle) atmospheric deposition at a research farm in southwestern Manitoba, Canada. The concentration in air of these pesticides was also measured. Total bulk deposition amounts (wet + dry) ranged from 0.009 – 2.3  $\mu\text{g m}^{-2}$  for the 12 pesticides detected, and for the six pesticides with both wet and dry deposition detections, dry deposition contributed 12 to 51% of the total deposition over the crop growing season. Although not applied at the site, eight herbicides registered for use in Canada, as well as lindane ( $\gamma$ -HCH), were all frequently detected (92-100%) in the twelve air samples analyzed during the crop growing season, with by-product isomer  $\alpha$ -HCH (75%), clopyralid (50%) and atrazine (8%) detected to a lesser extent. The chemical's physicochemical properties and the relative mean mass of each agricultural pesticide applied in the province of Manitoba and in a thirteen kilometer radius were significant parameters in explaining the trends in the concentrations of pesticides detected in our samples. The important contribution of dry deposition to total pesticide deposition warrants greater attention in arid and semi-arid areas such as the prairie region of Canada, also because under a changing climate this region is estimated to experience more severe droughts while the more favorable conditions predicted for pest infestations could lead to increased pesticide applications in agricultural and urban areas.

## 4.2 Introduction

Wetlands of the Prairie Pothole Region of North America are among the most productive ecosystems in the world, providing habitats for a wide variety of flora and fauna such as 50 – 80% of the continent's duck population (Batt et al., 1989). Prairie wetlands in Canada are contaminated with a suite of pesticides (Anderson et al., 2002; Donald et al., 2001; Waite et al., 2002) with an estimated 9 - 24% of the wetlands in the province of Saskatchewan having levels exceeding the Canadian guidelines for the protection of aquatic life (Donald et al., 1999). Pesticide loadings to prairie wetlands can be caused by atmospheric sources such as pesticide wet (precipitation) and dry (gaseous and particle) deposition (Jantunen et al., 2008; Messing et al., 2011; Waite et al., 1995). Pesticides enter the atmosphere through application drift (Caldwell, 2007), post-application vapor losses (Grover et al., 1985) or on wind eroded soil (Larney et al., 1999).

Atmospheric deposition of pesticides is typically measured using samplers that collect precipitation only (Belzer et al., 1998; Hall et al., 1993; Rawn et al., 1999) or through bulk (dry and wet combined) deposition samplers (Hill et al., 2001; Waite et al., 1995). Bulk deposition has been shown to vary spatially in the prairies depending on the intensity of local and regional pesticide use (Hill et al., 2003).

To our knowledge, Canada is the only country worldwide to have compared simultaneous measurements of pesticide wet versus dry deposition. This work has been limited to one study site in the province of Saskatchewan (Waite et al., 2005). Using the Waite-Banner Atmospheric Dry/Wet Deposition Sampler (Waite et al., 1999), this single study demonstrated that total seasonal dry deposition may account for up to ~ 85 to 100% of the

total bulk deposition mass (wet + dry) of triallate, trifluralin, 2,4-D, bromoxynil, dicamba, and MCPA (Waite et al., 2005). Prior to this Canadian study, it was reported that dry deposition contributed only to a minor extent of the total deposition of pesticides (Siebers et al., 1994).

In Manitoba, approximately 2 million kg of agricultural pesticides are applied annually encompassing ~ 60 different active ingredients (Wilson, 2012). Quantifications of the concentrations of pesticides in air and atmospheric deposits in Manitoba have been limited to three studies: (1) high-volume air and rainwater (using a wet-only sampler) samples collected at a site near Miami (49° 19' 28" N, 98° 21' 50" W) between 1993 and 1996 (Rawn et al., 1999), (2) bulk deposition samples collected at a site near Minnedosa (50° 14' 39" N, 99° 50' 34" W) in 2000 and 2001 (Hill et al., 2003), and (3) high-volume air and bulk deposition samples collected at a site near Brandon (50° 03' 07" N, 99° 55' 26" W) in 2008 (Messing et al., 2011).

The objectives of this study were to quantify, in an agricultural field site typical of the Prairie Pothole Region near Brandon, Manitoba, the relative amounts of 14 pesticides deposited as dry versus wet atmospheric deposition, and to relate their detections to airborne levels measured at the same site.

### **4.3 Materials and Methods**

**4.3.1 Sampling Location.** The Manitoba Zero-Tillage Research Association (MZTRA) research site (260 ha) is located in south central Canada ~ 20 km north of Brandon (50° 03' 07" N, 99° 55' 26" W), Manitoba. Ambient air temperatures are highly variable with

extremes ranging from – 46.7 to 43.3 °C (Brandon Airport). The warmest month is July (daily mean of 18.9 °C) and the coldest month is January (daily mean of -17.9 °C) (Environment Canada, 2012). Mean annual precipitation is 474 mm of rainfall and 1,014 mm of snowfall. Mean wind speeds in the area are 15.2 km/h (Environment Canada, 2012).

**4.3.2 Sampling Devices and Pesticides Analyzed.** A high volume air sampler (Model PS-1, General Metals Works, Village of Cleves, OH) and the Waite-Banner Atmospheric Dry/Wet Deposition Sampler (Waite et al., 1999) were installed at the field site adjacent to a meteorological station that has been operational since April, 2007 through the Manitoba Ag-Weather Program. Samples were collected in the summer of 2007 and analyzed for 11 currently used herbicides and three pesticides no longer registered for use in Canada. During the sampling period none of the analyzed chemicals were applied on the research farm but both MCPA and clopyralid were applied the previous year. The currently used herbicides included three active ingredients with vapor pressures larger than 9 mPa (ethalfluralin, triallate, and trifluralin) and eight other active ingredients with vapor pressures below 2 mPa (Table 4.1). The legacy pesticides included lindane ( $\gamma$ -HCH), its by-product isomer  $\alpha$ -HCH, and alachlor. In Canada, producers were able to use lindane stocks until the end of 2002.  $\alpha$ -HCH was a manufacturing by-product in technical HCH only prior to 1971 (Tuduri et al., 2006). Lindane was primarily used on the prairies on canola seed (Waite et al., 2001) with 94% of total usage applied from 1970 – 2000 at approximately 8.5 million kg (Li et al, 2004). The herbicide alachlor was de-registered in 1985 (Health Canada, 2012).

Table 4.1. Mass of active ingredients applied in MB and in a 13 km radius around study site (2004 - 2006 average) (Wilson, 2012) and their physicochemical properties (The Pesticide Properties Database, 2011).

Active Ingredient	Mass applied in MB (kg)	% of total of all applied in MB	Rank out of the 59 A.I.s used in MB	Mass applied in a 13 km radius	Water Solubility 20°C (mg L <sup>-1</sup> )	Vapour pressure at 25°C (mPa)	Henry's law constant at 25°C (Pa m <sup>3</sup> mol <sup>-1</sup> )	Koc (mL g <sup>-1</sup> )	Kow at pH 7, 20°C
MCPA	439470	21	2	10880	29390	0.4	5.50 X 10 <sup>-05</sup>	74	1.55 X 10 <sup>-01</sup>
Bromoxynil	168146	8	4	3453	90	0.17	5.30 X 10 <sup>-04</sup>	174	1.10 X 10 <sup>-01</sup>
2,4-D	148936	7	5	6731	23180	0.0187	1.30 X 10 <sup>-05</sup>	56	1.48 X 10 <sup>-01</sup>
Ethalfuralin	93126	4	6	817	0.01	12	18	5356	1.29 X 10 <sup>-05</sup>
Trifluralin	41683	2	10	83	0.221	9.5	10.2	8765	1.86 X 10 <sup>-05</sup>
Dicamba	20537	1	16	260	250000	1.67	1.0 X 10 <sup>-04</sup>	12	1.32 X 10 <sup>-02</sup>
Clopyralid	19655	1	15	579	143000	1.36	1.80 X 10 <sup>-11</sup>	5	2.34 X 10 <sup>-03</sup>
Atrazine	18171	1	17	0	35	0.039	1.50 X 10 <sup>-04</sup>	100	5.01 X 10 <sup>-02</sup>
Triallate	7194	0	23	542	4.1	12	0.89	4301	1.15 X 10 <sup>-04</sup>
Mecoprop	5008	0	25	199	250000	1.6	2.20 X 10 <sup>-04</sup>	31	6.46 X 10 <sup>-01</sup>
Metolachlor	194	0	48	0	530	1.7	2.40 X 10 <sup>-03</sup>	200	2.51 X 10 <sup>-03</sup>
Lindane	0	0	NA	0	8.52	4.34	1.50 X 10 <sup>-01</sup>	1100	4.90 X 10 <sup>-03</sup>
α-HCH	0	0	NA	0	2.0	5.99	0.43 - 2.16 <sup>e</sup>	1888	6.61 X 10 <sup>-03</sup>
Alachlor	0	0	NA	0	240	2.9	3.20 X 10 <sup>-03</sup>	124	1.23 X 10 <sup>-03</sup>

NA (Not Applicable) - Not registered for use in Canada

**4.3.3 Sampling Frequencies.** The air samples were collected weekly for 12 weeks beginning on May 23 and ending on August 15, 2007. Air was sampled continuously throughout the week with the high volume air sampler field calibrated on set up and monitored daily during operation by integral Venturi/Magnahelic assemblies for a flow rate of  $2000 \text{ m}^3 \text{ week}^{-1}$ . The sampling head consisted of a 10.2 cm diameter glass fiber filter (Graseby, GMW) for particle collection and XAD-2 resin sandwiched between polyurethane foam for vapor phase collection. The filter and cartridge were extracted together as described below to obtain a 7 d total pesticide concentration per volume.

Weekly dry and wet deposition samples were collected for eight weeks beginning on May 23 and ending on July 18, 2007 using the Waite-Banner Atmospheric Dry/Wet Deposition Sampler. A detailed description of the sampler can be found in Waite et al., (1999). To summarize the unique sampling device and protocol, dry atmospheric depositions are collected on a sheet of water continuously flowing down a stainless steel tray that is 0.5 m x 1 m to simulate an open water surface. The water consisted of 18-megohm deionized water acidified to a pH of  $\sim 1$  with concentrated trace metal grade sulfuric acid (Fisher Scientific Ltd., Montreal, Quebec). Any particles or gases that partition into the sheet of water are swept into the sampler to pass through a glass fiber and XAD-2 resin sampling cartridge removing any organics (including the pesticides) from the water before being re-circulated back to the surface of the tray. The XAD-2 resin cartridge was removed and replaced by another each week and extracted to obtain a 7 d composite dry deposition sample. Prior to replacement the sampler was refilled with 18-megohm deionized acidified water to replace the water that evaporated during the week.

After replacement, the machine was run for 30 minutes through a XAD-2 clean-up column (identical to the sample columns) to ensure that no contaminants were present and to remove any that may have been in the water. A 1 L background water sample was then taken, extracted, and analysed. The sampler collects rainfall separately as rain triggers a sensor that both stopped the water flow and redirected any rainwater falling onto the steel tray to a separate stainless steel collection container outside of the sampler. The volatilization of pesticides from rainwater collected in the container was minimized because the container was closed off from air as soon as the rainfall stopped. After the 7 d sampling period the rainwater container was well mixed and a subsample was taken in a 1 L amber glass bottle with a Teflon sealed cap. Rainfall samples were preserved with the addition of 5 mL of concentrated trace metal grade sulfuric acid immediately following sample collection. The sampler is prone to breakdown which occurred in the week ending June 20 (weekly sample not taken) and it malfunctioned after July 18, leaving seven weeks of data available. Similar challenges with the equipment were reported in Waite et al. (2005).

**4.3.4 Pesticide Extraction and Quantification.** All reagents were reagent grade. Solvents (acetone, dichloromethane, ether and hexane) were pesticide grade and were obtained from Caledon Laboratories (Georgetown, Canada). Pesticide standards were 98% purity or greater and were obtained from ChemService (West Chester, USA) and Riedel-de Haen (Seelze, Germany). Deuterated pesticide standards were obtained from C/D/N Isotopes (Pointe Claire, Quebec). 2,4-DCAA (2,4-dichlorophenyl acetic acid) was obtained from Sigma-Aldrich (Oakville, Ontario) to act as a surrogate.

All samples were analyzed at the Prairie & Northern Laboratory for Environmental Testing, Environment Canada, Edmonton, Alberta (AB), Canada. Samples were shipped in an ice packed cooler from Manitoba to Alberta on the day of collection and then stored at 4°C in the dark prior to extractions which occurred within 10 days of collection.

The PUF/XAD-2 resin cartridge and glass fiber filter from the PS-1 high volume air sampler were Soxhlet extracted with 500 mL acetone for 24 h as described by Waite et al. (2005). One mL of acetone containing 1 µg 2,4-DCAA was added to the PUF in the laboratory to each sample prior to extractions. Acetone extracts were concentrated with rotary evaporation, methylated with three 2 mL aliquots of ethereal diazomethane and concentrated with a stream of pure nitrogen gas after each addition. The final concentrate was then made up to a final volume of 10 mL using hexane for the analytes quantification by gas chromatography-mass spectrometry.

For the extraction of the XAD-2 column from the dry/wet deposition sampler, the same 2,4-DCAA solution was added in the laboratory to the sampling inlet end of the column and flushed onto the column with 250 mL of reagent water. The reagent water that eluted from the column was discarded and a vacuum was applied to the outlet end of the column to remove any excess water which was also discarded. The XAD-2 column was extracted by back flushing it with 1000 mL of acetone as described by Waite et al. (2005). The acetone extract was concentrated using rotary evaporation until an aqueous phase remained from the water remaining in the column after the vacuum had been applied. The aqueous phase was transferred to a separatory funnel, combined with 100 mL of reagent water and acidified to a pH of 2 with 0.5 mL of concentrated sulfuric acid. The entire

volume was extracted with three 40 mL aliquots of dichloromethane. The dichloromethane extract was dried by passing through 30 grams of acidic sodium sulfate, and concentrated by rotary evaporation. Samples were then methylated and exchanged into hexane to a final volume of 10 mL, as described above.

The same 2,4-DCAA solution was added in the laboratory to the rainfall and background water samples from the dry/wet deposition sampler. Sodium chloride (150 g) was dissolved in each sample and samples were acidified to pH 2 with sulfuric acid and then extracted by liquid-liquid partitioning with three 60 mL aliquots of dichloromethane, as described in Cessna et al. (1985). The dichloromethane extract was then dried and concentrated as described above, after which the samples were methylated and exchanged into hexane to a final volume of 10 mL, also as described above.

Quantification was performed using an Agilent Technologies (Palo Alto, CA) model 6890 gas chromatograph (GC) interfaced with a Waters (Manchester, UK) model Quattro Micro GC triple-quadrupole mass spectrometer operated in electron impact ionization mode using multiple reaction monitoring. The GC column used was a HP-5ms 30-m x 0.25-mm internal diameter, film thickness 0.25  $\mu\text{m}$  of 5% phenyl-95% dimethylpolysiloxane. Helium was used as the carrier gas with a flow rate of 1 mL/minute. Extract aliquots (2  $\mu\text{L}$ ) were injected into the GC with an Agilent model 7683 automatic liquid sampler. Minimum detection limits (MDLs) were 0.01  $\mu\text{g sample}^{-1}$  for all analytes with the exceptions of 2,4-D, atrazine, ethalfluralin, and trifluralin that had MDLs of 0.05  $\mu\text{g sample}^{-1}$ . The accuracy of the calibration standards were verified by comparison to external standards obtained from an independent chemical supplier. In

addition to 2,4-DCAA, an internal standard (0.1 µg 4,4' Dibromooctafluorobiphenyl in 0.1 mL of hexane) was added just prior to instrumental analysis.

QA/QC protocols also included the use of field and laboratory blank matrices as well as matrix spikes. Field blanks consisted of two PUF/XAD-2 resin cartridges, two XAD-2 columns and two 1 L 18-megohm deionised water samples. The laboratory blanks included PUF/XAD-2 resin cartridges, XAD-2 columns and dechlorinated Edmonton, AB drinking water. Matrix spikes included samples of clean matrix fortified prior to extraction with 1.0 µg of each of the analytes of interest including the surrogate. Matrix spikes and matrix blanks were analyzed throughout the study period at a frequency of at least 10% of the samples analyzed. Recovery values typically ranged from 82 – 124% for the water spikes, 88 to 118% for the XAD-2 column spikes, and 75 – 113% for the PUF/XAD-2 resin cartridges spikes. However, XAD column spike recoveries for ethalfluralin & trifluralin were generally lower (37.9 to 75%). Blanks for all media and water background samples were below levels of detection with the following exceptions: 0.03 µg MCPA was found in XAD Column Method Blanks 1 and 2 and 0.01 µg of dicamba found in XAD Column Method Blank 2.

**4.3.5 Statistical Analysis.** Pearson product-moment correlation and multiple linear regression analyses were performed on  $\log_{10}$  transformed data in Data Desk 6.3 (Data Description Inc., Ithaca, NY, USA) to determine correlations and predictions of the physicochemical properties (vapour pressure, water solubility, Henry's law constant) (The Pesticide Properties Database, 2012), meteorological conditions (temperature and rainfall) and/or pesticide use data (mass applied within a 13 km radius of the research site,

mass applied in Manitoba) versus pesticide air concentrations and atmospheric deposits. The 13 km radius was chosen because the pesticides applied in this area would likely be able to transport to the study site given the known chemical half-lives of some pesticides in air and average wind speeds in the area. The 13 km radius is a conservative estimate as the atmospheric half-life for many of these chemicals is unknown.

## 4.4 Results

**4.4.1 Currently-Used Herbicides.** Metolachlor was not detected in any of the matrices. Except for atrazine, all other active ingredients were frequently detected (50-100%) in the air, with their detection generally being highest from May 30th to mid July (Table 4.2). Weekly air concentrations ranged from 0.00 – 1.23 ng m<sup>-3</sup> with ethalfluralin detected at the highest concentration. Ethalfluralin, triallate, MCPA, bromoxynil, trifluralin, dicamba, 2,4-D, and mecoprop were all detected in 92-100% of the air samples collected (Table 4.2). The mean air concentration of pesticides detected over the study period was strongly positively associated with their masses applied in a 13 km radius of the site and in Manitoba (Table 4.3). Among the regressions investigated, the mean air concentration was best predicted by a combination of the relative use of these active ingredients in Manitoba and their vapor pressures: mean air concentration = 1.032 active ingredient use in Manitoba + 0.509 vapour pressure - 3.498, R<sup>2</sup> = 0.83; with the p-values being 0.0003 for the active ingredient use in Manitoba, and 0.01 for the active ingredient vapor pressure.

Table 4.2. Atmospheric Concentrations of Herbicides (ng m<sup>-3</sup>) including detection frequencies and maximum concentrations (bold values are the maximum weekly concentrations).

Date	30-May	7-Jun	13-Jun	20-Jun	27-Jun	4-Jul	11-Jul	18-Jul	25-Jul	1-Aug	8-Aug	15-Aug	Detection Frequency (%)	Max. Conc (ng m <sup>-3</sup> )
Ethalfuralin	0.63	<b>1.23</b>	1.00	0.82	0.49	0.26	0.42	0.43	0.14	0.21	0.16	0.19	100	1.23
Triallate	0.12	0.15	<b>0.46</b>	0.19	0.26	0.17	0.10	0.13	0.09	0.07	0.07	0.05	100	0.46
MCPA	0.02	0.12	0.23	0.20	0.13	0.10	<b>0.46</b>	0.05	0.04	0.03	0.01	0.01	100	0.46
Bromoxynil	0.03	0.16	<b>0.32</b>	0.20	0.23	0.14	0.12	0.05	0.05	0.04	0.02	0.01	100	0.32
2,4-D	ND	0.18	<b>0.21</b>	0.16	0.14	0.10	0.11	0.05	0.10	0.10	0.04	0.04	92	0.21
Trifluralin	0.07	0.15	<b>0.21</b>	0.18	0.15	0.20	0.08	0.06	0.07	0.08	0.10	0.08	100	0.21
Mecoprop	ND	0.02	0.02	0.03	0.02	0.03	<b>0.14</b>	0.04	0.06	0.04	0.02	0.02	92	0.14
Dicamba	0.01	0.02	0.03	0.03	0.03	0.02	<b>0.11</b>	0.02	0.04	0.03	0.02	0.01	100	0.11
Clopyralid	ND	0.05	0.05	0.03	0.05	<b>0.06</b>	<b>0.06</b>	ND	ND	ND	ND	ND	50	0.06
Atrazine	ND	ND	<b>0.04</b>	ND	ND	ND	ND	ND	ND	ND	ND	ND	8	0.04
Lindane	0.02	0.03	<b>0.04</b>	0.03	0.03	0.03	0.03	0.02	0.03	<b>0.04</b>	0.03	0.02	100	0.04
α-HCH	0.01	0.02	ND	<b>0.02</b>	<b>0.02</b>	<b>0.02</b>	<b>0.02</b>	ND	0.01	ND	<b>0.02</b>	<b>0.02</b>	75	0.02

ND = no detection

Table 4.3. Correlation coefficients of log-transformed data between pesticides average air concentration, total wet deposition, total dry deposition, and total bulk deposition and physicochemical properties and pesticide use data.

	mean air conc.	dry dep.	wet dep.*	bulk dep. (wet + dry)
Mass applied in MB	0.79 <sup>B</sup>	0.82 <sup>B</sup>	0.78 <sup>B</sup>	0.88 <sup>A</sup>
Mass applied in a 13 km radius of the site	0.81 <sup>B</sup>	0.69 <sup>C</sup>	0.99 <sup>A</sup>	0.89 <sup>A</sup>
Water Solubility 20°C (mg L <sup>-1</sup> )	ns	ns	0.52 <sup>D</sup>	ns
Vapour pressure at 25°C (mPa)	ns	ns	ns	ns
Henry's law constant at 25°C (Pa m <sup>3</sup> mol <sup>-1</sup> )	ns	ns	ns	ns
Koc (mL g <sup>-1</sup> )	ns	ns	ns	ns
Kow at pH 7, 20°C	ns	ns	- 0.79 <sup>B</sup>	ns

\* excluding those active ingredients which partition to the air and were not found in the wet deposition samples

p-value: <sup>A</sup> < 0.001; <sup>B</sup> < 0.01; <sup>C</sup> < 0.05; <sup>D</sup> < 0.1

ns: not significant

All active ingredients were frequently detected in the dry deposition samples except atrazine, and trifluralin. Largest deposition rates occurred from May 30<sup>th</sup> to June 27<sup>th</sup> and then fell to lower levels or below detection limits throughout the remaining season except for a concentration increase of most herbicides in the week ending in the July 18<sup>th</sup> sample (Table 4.4). Ethalfuralin had the greatest rates of dry deposition followed by 2,4-D, MCPA, Triallate, and bromoxynil (Table 4.4). The total dry deposition of pesticides detected over the study period was strongly positively associated with their mass applied in Manitoba and to a lesser extent with those applied in a 13 km radius of the site (Table

4.3). Among the regressions investigated, total dry depositions are best predicted by the relative use of these active ingredients applied in Manitoba ( $R^2 = 0.68$ , Figure 4.1).

Six herbicides were detected in wet depositions in 14 to 86% of the samples (Table 4.5). Wet deposition rates were highest in the samples collected throughout most of June and in the week ending in July 11<sup>th</sup> (Table 4.5). Ethalfluralin, triallate, and trifluralin, all having vapor pressures larger than 9 mPa (Table 4.1), were not detected (Table 4.5). The total wet deposition of pesticides detected over the study period was strongly positively associated with their mass applied in a 13 km radius of the site and to a lesser extent with the mass applied in Manitoba. There was also a weaker positive correlation to water solubility and negative association with  $K_{ow}$  (Table 4.3). Among the regressions investigated, total wet deposition of detected pesticides (excluding those which partition to the air and were not found in the wet deposition samples) was best predicted by the annual mean mass of each pesticide applied in a 13 km radius surrounding the farm: total wet deposition of detected pesticides =  $0.841$  active ingredient use in a 13 km radius +  $0.082$ ,  $R^2 = 0.98$ ,  $P \leq 0.0001$ . For the three most frequently detected herbicides (all as mixtures in 86% of the samples), larger weekly wet deposition rates are predicted in weeks of greater precipitation (Figure 4.2).

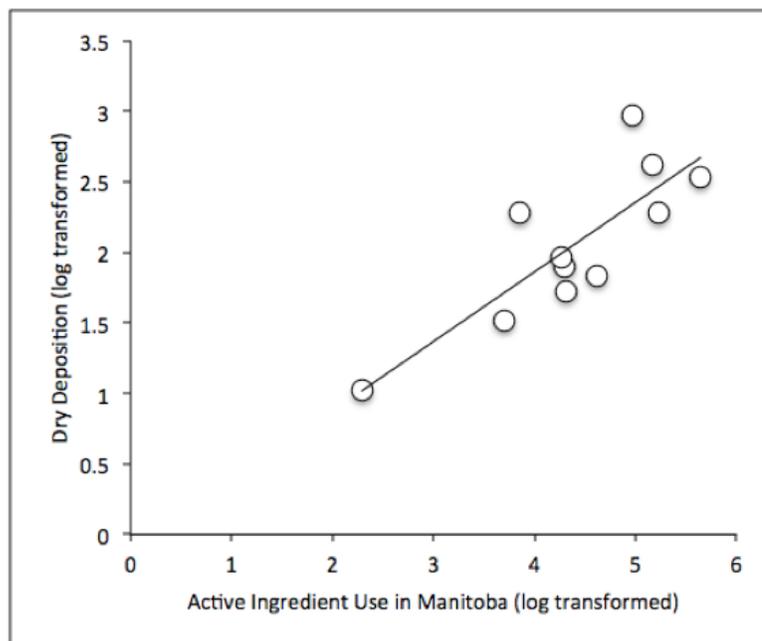


Figure 4.1. Total dry deposition of detected pesticides plotted against the relative use of these active ingredients applied in MB. Regression equation: total dry deposition mass = 0.493 active ingredient applied in Manitoba - 0.111,  $R^2 = 0.68$ ,  $P < 0.002$ .

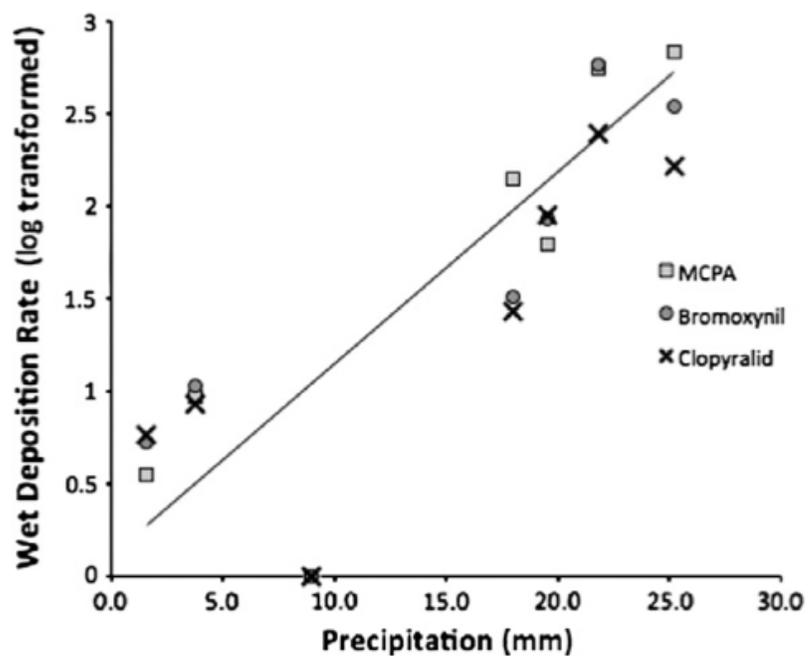


Figure 4.2. Wet deposition rate plotted against precipitation. Regression equation is wet deposition rate = 0.077 precipitation (mm) + 0.5773,  $R^2 = 0.86$ ,  $P \leq 0.0001$ .

Table 4.4. Herbicide dry deposition rate ( $\text{ng m}^{-2} \text{d}^{-1}$ ) and average temperatures including detection frequencies, maximum deposition rate, and total mass of dry depositions (bold values are the maximum weekly mass deposited).

Date	30-May	7-Jun	13-Jun	27-Jun	4-Jul	11-Jul	18-Jul	Detection Frequency (%)	Max. Deposition ( $\text{ng m}^{-2} \text{d}^{-1}$ )	Total Dry Deposition ( $\text{ng m}^{-2}$ )
Avg. Temp. ( $^{\circ}\text{C}$ )	8.6	14.2	15.6	17.0	16.5	18.7	17.5			
Ethalfuralin	218.79	<b>414.43</b>	93.04	98.20	19.34	ND	74.37	86	414.43	918.17
2,4-D	64.24	<b>122.97</b>	55.19	120.09	ND	ND	33.64	71	122.97	396.12
MCPA	32.05	87.71	48.56	<b>112.03</b>	7.79	11.51	38.23	100	112.03	337.88
Triallate	47.76	<b>51.52</b>	11.64	46.66	10.70	3.99	17.34	100	51.52	189.61
Bromoxynil	12.41	47.47	18.85	<b>88.70</b>	7.82	3.11	9.12	100	88.70	187.46
Clopyralid	11.96	<b>24.53</b>	6.94	23.63	ND	ND	7.14	71	24.53	74.20
Atrazine	<b>31.82</b>	18.16	ND	11.72	ND	ND	ND	43	31.82	61.71
Dicamba	11.41	11.96	5.04	<b>13.98</b>	2.20	2.63	4.81	100	13.98	52.04
Mecoprop	6.59	<b>8.34</b>	4.25	7.19	ND	2.43	ND	71	8.34	28.80
Trifluralin	ND	<b>17.42</b>	ND	11.37	ND	ND	ND	29	17.42	28.79
Lindane	<b>8.43</b>	6.29	4.72	4.80	ND	ND	4.41	71	8.43	28.65
$\alpha$ -HCH	<b>5.82</b>	ND	ND	ND	ND	ND	3.62	29	5.82	9.44

ND = no detection

Table 4.5. Herbicide wet deposition rate ( $\text{ng m}^{-2} \text{d}^{-1}$ ) and weekly precipitation (mm) including detection frequencies, total wet deposition, total (wet + dry) deposition, and dry deposition contribution to total deposition (bold values are the maximum weekly concentrations).

Date	30-May	7-Jun	13-Jun	27-Jun	4-Jul	11-Jul	18-Jul	Detection Frequency (%)	Max. Deposition ( $\text{ng m}^{-2} \text{d}^{-1}$ )	Total Wet Deposition ( $\text{ng m}^{-2}$ )	Total (wet + dry) Deposition ( $\text{ng m}^{-2}$ )	Dry Deposition Contribution to Total (%)
precipitation (mm)	9.0	25.2	21.8	19.6	1.6	18.0	3.8					
2,4-D	ND	<b>939.81</b>	932.61	ND	ND	ND	ND	29	939.81	1872.42	2268.55	17.46
MCPA	ND	<b>685.50</b>	549.72	60.58	2.57	139.41	8.22	86	685.50	1446.00	1783.88	18.94
Bromoxynil	ND	343.06	<b>582.05</b>	83.93	4.34	31.42	9.59	86	582.05	1054.39	1241.85	15.10
Clopyralid	ND	161.81	<b>246.93</b>	88.93	4.86	26.14	7.51	86	246.93	536.19	610.38	12.16
Dicamba	ND	52.37	58.79	ND	3.03	<b>86.34</b>	ND	57	86.34	200.53	252.57	20.60
Mecoprop	ND	ND	ND	ND	ND	<b>27.99</b>	ND	14	27.99	27.99	56.79	50.72
Ethalfuralin	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	918.17	100.00
Triallate	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	189.61	100.00
Atrazine	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	61.71	100.00
Trifluralin	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	28.79	100.00
Lindane	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	28.65	100.00
$\alpha$ -HCH	ND	ND	ND	ND	ND	ND	ND	0	0.00	0.00	9.44	100.00

ND = no detection

For those pesticides with both wet and dry deposition detections, dry deposition contributed 12 – 21% of the total deposition over the sampling period, except for mecoprop for which dry deposition accounted for 51% of total deposition (Table 4.5). Total bulk deposition amounts (wet + dry) ranged from 0.009 – 2.3  $\mu\text{g m}^{-2}$  with 2,4-D and MCPA accounting for the greatest mass deposited (Table 4.5). The total bulk deposition of pesticides detected over the study period was well correlated with their detected mean air concentrations ( $r = 0.75$ ). The total bulk deposition of pesticides detected over the study period was strongly associated with both the masses applied in a 13 km radius of the site and in Manitoba (Table 4.3). Among the regressions investigated, the total deposition was best predicted by a combination of the relative use of these active ingredients applied in a 13 km radius from the site and their vapor pressures: total deposition = 0.465 active ingredients applied in a 13 km radius - 0.223 vapor pressures + 2.007;  $R^2 = 0.88$ ; 13 km radius p-value  $\leq 0.0001$ ; vapor pressure p-value = 0.04.

**4.4.2 Pesticides No Longer Registered For Use in Canada.** Alachlor was not detected in any of the matrices. Air concentrations of Lindane and  $\alpha$ -HCH remained relatively consistent throughout the season (Table 4.2). Lindane was more frequently detected in the dry deposits than  $\alpha$ -HCH (Table 4.4). Lindane and  $\alpha$ -HCH were not detected in the wet deposition samples (Table 4.5).

## 4.5 Discussion

As none of the monitored pesticides were applied on the research farm, the detectable concentrations must have resulted from application drift (Caldwell, 2007), post-

application vapor losses (Grover et al., 1985) or on wind eroded soil (Larney et al., 1999) associated with off-farm pesticide applications. This dispersion and subsequent deposition of pesticides may contaminate non-target areas including biologically important ecosystems such as the numerous wetlands that are pervasive within the PPR. The detected air concentrations and depositions of pesticides were significantly correlated to estimates of the masses and physicochemical properties of pesticides applied. Levels of pesticide use are generally lacking for Canada as well as other countries (Boyd, 2001; Brimble et al., 2005). Physicochemical data for pesticides can be derived from sources such as the IUPAC Footprint data base (The Pesticide Properties Database, 2012). Our study provides direct evidence of well established theories that pesticides will more likely be associated with the water-phase (rain) when they have relatively small  $K_{ow}$  values and with the vapor-phase (air) when they have relatively large vapor pressures.

Donald et al. (2001) have previously proposed that applied pesticides are lost to the atmosphere and evenly distributed over the regional landscape within the province of Saskatchewan. The current study gives further indication that pesticides are dispersed throughout the landscape from their areas of application. In our study, the masses of pesticide wet deposition were more strongly associated with the masses of pesticides applied in a 13-km radius surrounding the site than with the masses of pesticides applied in Manitoba as a whole; in contrast, the masses of pesticide dry deposition were more strongly associated with the masses of pesticides applied in Manitoba as a whole than with the masses of pesticides applied in a 13-km radius surrounding the site. This suggests that currently-applied pesticides move relatively short distances before being deposited by rainfall as they are washed out of the atmosphere and are transported over

longer distances particularly when in the gas phase or associated with particulate matter. Dry deposition followed similar trends to the air concentrations and total dry deposition shared similar correlations with the same physicochemical properties as the average air concentrations.

Ethalfuralin and triallate were detected at the highest air concentrations among the pesticides studied because these active ingredients have high vapor pressures and low water solubilities (Table 4.1). Ethalfuralin was detected at higher concentrations than triallate because it is more frequently used in the province of Manitoba (Table 4.1). Trifluralin is used in larger quantities in the Province of Manitoba than triallate, but the concentrations detected were less than that of triallate possibly because of its lower vapor pressure. MCPA, bromoxynil and 2,4-D have vapor pressures ranging from 0.02 to 0.4 mPa but are widely applied in Manitoba and were within the top five maximum air concentrations (Table 4.2). Other studies have demonstrated that pesticides that have relatively low vapor pressures are present in the atmosphere partitioned in the gas phase or sorbed to atmospheric particulates (Yao et al., 2008; Rawn et al., 1999; Waite et al., 2005). Although mecoprop and dicamba were frequently detected in the air, their concentrations were lower than the other frequently detected pesticides, likely due to the lower amounts applied within Manitoba.

Although the highest concentrations of pesticides in wet deposition were found with low rainfall events, as previously discussed by Hill et al. (2003), greater total deposition was found with greater precipitation, at least this was evident for the pesticides frequently detected as wet deposits (MCPA, bromoxynil, and clopyralid; Figure 4.2). Evidence for

this was also found by Donald et al. (2005) who reported the frequent detection of some herbicides in wetlands (e.g., MCPA, 2,4-D, and dicamba) resulted most likely from direct atmospheric wet deposition rather than herbicide rainfall runoff from agricultural soils. Using the same sampler as the current study, Waite et al. (1999), also found positive correlations between precipitation and wet deposition concentrations of several herbicides (2,4-D, dicamba, and lindane) but no such correlations were found in a later study by Waite et al. (2005).

For those pesticides with both wet and dry deposition detections Waite et al. (2005) found that dry deposition contributed approximately 90% to the total herbicide deposition for 2,4-D, Bromoxynil, Dicamba, and MCPA. This is more than the proportional dry deposits observed in our study (12 – 51%) for these and other pesticides. The proportionally greater amount of dry deposits observed by Waite et al. (2005) is likely due to their study site being located in Saskatchewan, a province which typically receives less precipitation than Manitoba. Only 48 mm of rainfall was measured in the five weeks of the study by Waite et al. (2005) compared to 99 mm of rainfall in the seven weeks in the current study.

The pesticides no longer registered for use in Canada were found at very low concentrations in both the air and dry deposition samples suggesting that these chemicals with moderately high vapor pressures are still persistent in our environment at near background levels.

Drinking, Aquatic and Irrigation Water Quality guidelines in Canada are set for some individual pesticides, but not for pesticide mixtures which were commonly found in the

current study. In all of the samples that contained detectable levels of pesticides, at least three pesticides were detected. Of the pesticides screened in this study, Canadian Environmental Quality Guidelines (Canadian Council of Ministers of the Environment, 2012) for the Protection of Aquatic Life (Freshwater), Water Quality Guidelines for the Protection of Agriculture (Irrigation/Livestock), Air Quality Guidelines for the Protection of Human Health and the Environment are available for 9, 5/9, and 0 of pesticides respectively. The Guidelines for Canadian Drinking Water Quality are published by Health Canada and of the number of pesticides screened in this study 6 are available. The detected concentrations of individual pesticides never exceeded the respective Water Quality guidelines.

#### **4.6 Conclusion**

Monitoring studies often focus on precipitation only and may miss quantitatively important dry deposits, contributing 12 to 51% of the total deposition in the current study. Air concentrations and dry and wet deposition rates of pesticides were found to correlate to the mass and physicochemical properties of pesticide applied. In addition, an increasing amount of weekly rainfall demonstrated increasing masses of wet deposition by those pesticides more often detected in rainfall. This study represented only a small portion of the commonly-used herbicides in the prairie region, but all were frequently detected. Other pesticides applied in the region would contribute to greater total pesticide air concentrations and atmospheric depositions and further contribute to the chemical mixtures found in the environment. In order to reduce agricultural pesticide loadings to the atmosphere and to surface waters by subsequent atmospheric deposition, farm

extension efforts designed to minimize spray drift and post-volatilization losses should operate at the regional-scale.

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## **5. PREDICTING WETLAND CONTAMINATION FROM ATMOSPHERIC DEPOSITION MEASUREMENTS OF PESTICIDES IN THE CANADIAN PRAIRIE POTHOLE REGION**

### **5.1 Abstract**

Although it has been reported that atmospheric deposition alone can result in detectable levels of pesticides in wetlands of the Prairie Pothole Region of Canada, this is the first field study to compare the masses of pesticides entering wetlands by atmospheric deposition with those concentrations of pesticides detected in the water-column of prairie wetlands. Weekly air and bulk deposition samples were collected from May 26<sup>th</sup> to Sept. 15<sup>th</sup>, 2008 at the Manitoba Zero Tillage Research Association (MZTRA) Farm, Brandon, Manitoba, with four on-site wetlands (approximate sizes 0.15 - 0.45 ha) monitored every second week. Twelve pesticides were detected in the air, with MCPA (one of the three pesticides applied on the farm in 2008 in addition to clopyralid and glyphosate), triallate, and  $\gamma$ -HCH being detected every week. Calculations were performed to predict wetland pesticide concentrations based on bulk deposits alone for those pesticides that had detectable concentrations in the bulk deposition samples (in order of the highest total seasonal deposition mass to the lowest): MCPA, glyphosate, 2,4-D, clopyralid, bromoxynil, atrazine, dicamba, metolachlor, and mecoprop. The estimated concentrations were closest to actual concentrations for MCPA (Pearson correlation coefficient's = 0.91 to 0.98; p-values < 0.001) and predictions were also reasonable for a range of other herbicides, but a source other than atmospheric deposition was clearly relevant to detections of clopyralid in the wetland water-column. Although the types and levels of pesticides detected in the wetlands of the current study suggest that regional pesticide applications can contribute to pesticide surface water contamination following

atmospheric transport and deposition, the greater frequency and concentrations of clopyralid, MCPA, and glyphosate detections in wetlands confirm that on-farm pesticide applications have a greater impact on on-site water quality. Beneficial management practices that reduce application drift, as well as rainfall or snowmelt runoff, will be important measures in reducing pesticide loading into wetlands situated in agricultural fields of the Prairie Pothole Region of North America.

## **5.2 Introduction**

The Prairie Pothole Region of North America is an area of approximately 715,000 km<sup>2</sup> (Euliss et al., 1999) and contains millions of wetlands, a large portion being closely associated with agricultural cropland. The geomorphological landscape of the Prairie Pothole Region was shaped in the Wisconsin Glacial Period resulting in numerous small topographic depressions forming prairie wetlands. The water balance components of these prairie wetlands are well understood (van der Kamp & Hayashi, 2009) and are controlled by the cold semi-arid climate (van der Kamp et al., 2003). Movement of snow-derived water to the wetlands is critical to their existence (Hayashi et al., 1998) with 30 – 60% transferred from the upland to the wetland as snowmelt runoff in the spring. Summer surface runoff occurs only rarely during intense rainfall events (Hayashi et al., 1998). Due to the moderate rainfall the area receives and the geological age of the landscape there are few natural surface drainage systems and it is common for wetlands to be closed drainage basins (van der Kamp & Hayashi, 2009). Potential evapotranspiration often exceeds precipitation during the summer months (Conly & van der Kamp, 2001). Prairie wetlands are among the most productive ecosystems in the world, providing habitats for a wide

variety of flora and fauna, such as 50 – 80% of the continent's duck population (Batt et al., 1989).

North American agricultural production systems are reliant on pesticides with at least 35 million kilograms applied annually in Canada with approximately 84% of this mass applied in the prairie region (Cessna et al., 2010). Application and post application losses of pesticides depend on the formulated product, application method, environmental conditions and the chemical's physicochemical properties (Tuduri et al., 2006a).

Previous studies have shown prairie wetlands in Canada to be contaminated with a suite of pesticides (Donald et al., 2001; Anderson et al., 2002; Waite et al., 2002). Pesticide loadings to prairie wetlands may be due to atmospheric sources such as atmospheric wet and dry deposition, including gas exchange at the air-water interface (Waite et al., 1995; Jantunen et al., 2008); runoff events (Waite et al., 1992); or groundwater recharge (Waite et al., 1992). Donald et al. (1999) estimated that between 9 - 24% of the wetlands in the province of Saskatchewan contain levels of pesticides exceeding Canadian guidelines for the protection of aquatic life.

Donald et al. (2001) used data on the atmospheric deposition of pesticides collected for four growing seasons (1984 to 1987), as reported by Waite et al. (1995), to calculate the average mass of three pesticides deposited during a growing season. Using these data Donald et al. (2001) then calculated what the average concentration of each herbicide would be if a wetland had a depth of 50 cm (typical wetland in the area). They found that these calculated concentrations were similar to the mean concentrations of 41 wetlands

they monitored in the province of Saskatchewan. Based on these assumptions, Donald et al. (2001) concluded that atmospheric processes alone can account for detectable levels of herbicides in the wetlands of central Saskatchewan, but direct measurements linking atmospheric inputs of herbicides to concentrations found within prairie wetlands has yet to be confirmed. The purpose of this study was to quantify the contribution of atmospheric deposition on pesticide concentrations detected in the water-column of four prairie wetlands.

### **5.3 Materials and Methods**

**5.3.1 Sampling Location and Devices.** The study site (Figure 5.1) is a section of farmland (260 ha) located in south central Canada ~20 km north of Brandon (50° 03' N latitude, 99° 56' W longitude), in the Province of Manitoba. Weekly air and bulk deposition (dry and wet deposition) samples were collected for 17 weeks from May 26th to Sept. 15th, 2008 adjacent to a meteorological station operated by the Manitoba Ag-Weather Program. Air was sampled continuously throughout the week using a high volume air sampler (Model PS-1, General Metals Works (GMW), Village of Cleves, OH). Bulk deposition samples were collected using a one meter by one meter galvanized metal pan sampler that emptied into 23 L glass carboys shaded by plywood and covered with tinfoil to minimize pesticide photodegradation. Water samples were taken (grab samples) from the four wetlands every second week beginning May 26th and ending Sept. 15th for a total of 9 sampling events.

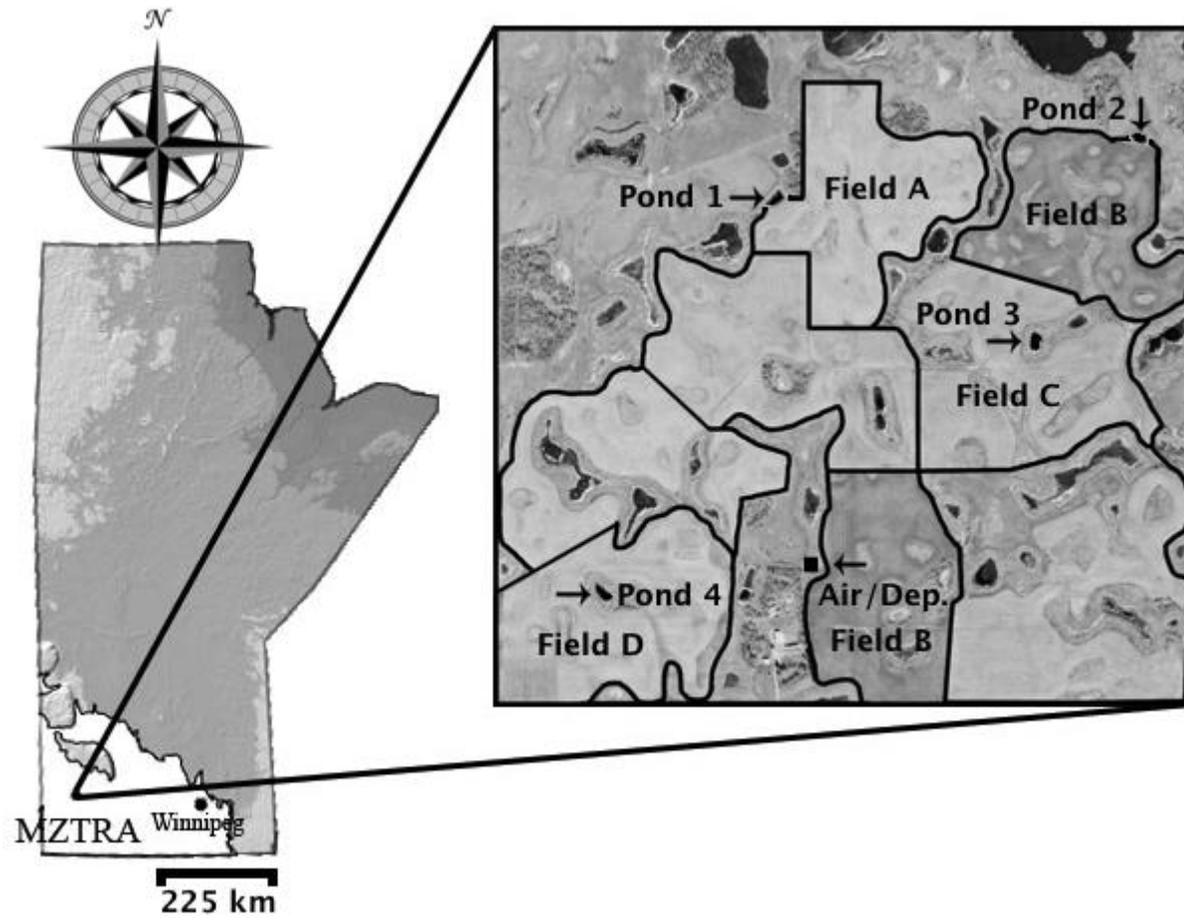


Figure 5.1. The extent of the Prairie Pothole Region (area in white) in the Province of Manitoba (entire map) with a close-up of the MZTRA farm (1.6 km<sup>2</sup>). Field B is composed of two separate areas that have identical farm management practices.

**5.3.2 Description of the Chemicals Analyzed.** Samples were analyzed for 17 chemicals that have a range of physicochemical properties (Table 5.1). Of the 17 chemicals, 13 chemicals are currently used herbicides in Manitoba (Table 5.2), including the active ingredients MCPA, clopyralid and glyphosate that were applied on-site in 2008 (Table 5.3, Figure 5.1). The primary metabolite of the active ingredient glyphosate, aminomethylphosphonic acid (AMPA), was also analyzed. Of the thirteen currently used herbicides, ethalfluralin, triallate, and trifluralin have vapor pressures larger than 9 mPa (Table 5.1). These three relatively volatile herbicides are widely applied in Manitoba (Table 5.2), generally in the spring prior to our sampling period and in the fall after our sampling period. The other ten currently used herbicides have vapor pressures below 2 mPa (Table 5.1). Dicamba, mecoprop, clopyralid, MCPA, bromoxynil, and 2,4-D are widely applied after crops emerge as part of cereal and oilseed production systems in Manitoba but may be applied throughout the season to maximize weed control (Table 5.3). Glyphosate and glufosinate are used throughout the season in Manitoba (Table 5.2) particularly on herbicide-tolerant canola varieties. Applications of atrazine and metolachlor are significantly less in Manitoba (Table 5.2) with the primary region of corn production occurring in Manitoba in the southwest and southeast near the borders with the provinces of Saskatchewan and Ontario, respectively (Yao et al., 2007). However, metolachlor and atrazine are widely used in corn production east of Manitoba in the provinces of Ontario and Quebec, and south of Manitoba in the Mid-West region of the United States. The legacy pesticides included lindane,  $\alpha$ -HCH, and alachlor. In Canada, producers were able to use lindane stocks until the end of 2002.  $\alpha$ -HCH was a manufacturing by-product in technical HCH prior to 1971 (Tuduri et al., 2006b). Lindane

was primarily used on the prairies on canola seed (Waite et al., 2001) with 94% of total usage applied from 1970 – 2000, approximately 8.5 million kg (Li et al., 2004). The herbicide alachlor was de-registered in 1985 (Health Canada, 2012).

Table 5.1. Active ingredient physicochemical properties (The Pesticide Properties Database, 2011, Degenhardt et al., 2011; Mackay et al., 2006;). A dash indicates that the data are not available.

Active ingredient	Water Solubility 20°C (mg L <sup>-1</sup> ) <sup>a</sup>	Vapour pressure at 25°C (mPa) <sup>a</sup>	Henry's law constant at 25°C (Pa m <sup>3</sup> mol <sup>-1</sup> ) <sup>a</sup>	Koc (mL g <sup>-1</sup> ) <sup>a</sup>	pKa at 25°C <sup>a</sup>	Kow at pH 7, 20°C <sup>a</sup>	Water phase only DT50 (days) <sup>a</sup>	Water-Sediment DT50 (days) <sup>a</sup>	Wetland DT50 (days) (same study site) <sup>b</sup>	Soil Degredation DT50 (days) <sup>a</sup>	Half-life Air <sup>c</sup>	Rat Acute Oral LD50 (mg kg <sup>-1</sup> ) <sup>a</sup>
Glyphosate	10500	0.0131	2.10 X 10 <sup>-07</sup>	21699	2.34	6.31 X 10 <sup>-04</sup>	2.5	87	2.4 - 6.9	12	NA	> 2000
Glufosinate	NA	NA	NA	NA	2	1.10 X 10 <sup>-04</sup>	NA	NA	NA	NA	NA	1625
Dicamba acid	250000	1.67	1.0 X 10 <sup>-04</sup>	12	1.87	1.32 X 10 <sup>-02</sup>	40	41	9.8 - 14	8	2.42 - 6 d	1581
MCPA acid	29390	0.4	5.50 X 10 <sup>-05</sup>	74	3.73	1.55 X 10 <sup>-01</sup>	13.5	17	9 - 11	15	NA	962
Bromoxynil	90	0.17	5.30 X 10 <sup>-04</sup>	174	3.86	1.10 X 10	13	13	2.3 - 3.9	1	NA	81
2,4-D acid	23180	0.0187	1.30 X 10 <sup>-05</sup>	56	2.87	1.48 X 10 <sup>-01</sup>	29	29	11 - 13	10	1.8 - 23.9 h	469
Clopyralid	143000	1.36	1.80 X 10 <sup>-11</sup>	5	2.01	2.34 X 10 <sup>-03</sup>	148	NA	NA	34	NA	> 2675
Mecoprop	250000	1.6	2.20 X 10 <sup>-04</sup>	31	3.11	6.46 X 10 <sup>-01</sup>	37	50	13 - 18	8.2	3.8 - 37.8 h	1166
Ethalfuralin	0.01	12	18	5356	no diss	1.29 X 10 <sup>05</sup>	10.5	13.5	NA	45	2 h	> 5000
Trifluralin	0.221	9.5	10.2	8765	no diss	1.86 X 10 <sup>05</sup>	13	5.5	NA	181	21 - 193 min	> 5000
Triallate	4.1	12	0.89	4301	no diss	1.15 X 10 <sup>04</sup>	104	57.4	NA	82	5 h	1100
Atrazine	35	0.039	1.50 X 10 <sup>-04</sup>	100	1.7	5.01 X 10 <sup>02</sup>	NA	80	NA	75	2.6 h	1869
Alachlor	240	2.9	3.20 X 10 <sup>-03</sup>	124	0.62	1.23 X 10 <sup>03</sup>	NA	2	NA	14	0.5 - 2.8 d	930
Metolachlor	530	1.7	2.40 X 10 <sup>-03</sup>	200	no diss	2.51 X 10 <sup>03</sup>	88	365	NA	90	NA	1200
a-HCH	2.0	5.99	0.43 - 2.16 <sup>e</sup>	1888	NA	6.61 X 10 <sup>03</sup>	NA	NA	NA	175	2.3 d - 4.4 yr	177
g-HCH	8.52	4.34	1.50 X 10 <sup>-03</sup>	1100	NA	4.90 X 10 <sup>03</sup>	36	90	NA	121	<1 d - 9.1 yr	88

NA = Not available

no diss = no dissociation

Table 5.2. Mass of active ingredient applied around a 13 km radius around the sampling sites (kg) and the total mass of these pesticides applied in Manitoba (MB) (represents pesticides used for agricultural use and insured through the MB Agricultural Services Corporation; Wilson, unpublished data).

<b>Active Ingredient (A.I.)</b>	<b>Mass applied in MB (kg)</b>	<b>% of total applied in MB</b>	<b>Rank out of the 59 A.I.s used in MB</b>	<b>Mass applied in a 13 km radius</b>	<b>% of total applied</b>
Glyphosate	627877	30	1	21742	36
MCPA	439470	21	2	10880	18
glufosinate	173611	8	4	5264	9
Bromoxynil	168146	8	4	3453	6
2,4-D	148936	7	5	6731	11
Ethalfuralin	93126	4	6	817	1
Trifluralin	41683	2	10	83	0
Dicamba	20537	1	16	260	0
Clopyralid	19655	1	15	579	1
Atrazine	18171	1	17	0	0
Triallate	7194	0	23	542	1
Mecoprop	5008	0	25	199	0
Metolachlor	194	0	48	0	0

\*The 13 km radius was chosen because the pesticides applied in this area would likely be able to transport to the study site due to chemical persistence and local wind speeds

Table 5.3. Three-year field history of pesticide applications at the MZTRA, in relation to the pesticides analyzed in the current study.

Field ID	Year	Field size (ha)	Seed Date	Crop	Pre seed Date	Active Ingredient	In Crop App 1 Date	In Crop App 1 Chemical	In Crop App 2 Date	In Crop App 2 Chemical
A	2006	13.8	5-May	Peas	28-Apr	glyphosate				
A	2007	16.2	12-May	Canola	10-May	glyphosate	05-Jun	glufosinate		
A	2008	16.2	9-May	Spring Wheat	26-May	glyphosate/clopyralid				
B	2006	12.5	NA	Alfalfa						
B	2007	12.5	NA	Alfalfa/Winter wheat					04-Sep	Glyphosate/2-4D
B	2008	12.5	8-Sep	Winter Wheat			23-Jun	clopyralid, MCPA	26-Aug	glyphosate
C	2006	16.2	18-May	Flax	7,10-May	glyphosate	17-Jun	clopyralid, MCPA		
C	2007	16.2	20-May	Canola/Alfalfa	18-May	glyphosate	15-Jun			
C	2008	16.2	NA	Alfalfa						
D	2006	17.0	11-May	Flax	10-May	glyphosate	14-Jun	clopyralid, MCPA		
D	2007	17.0	10-May	Canola	24-April/9-May	ethalfuralin/glyphosate	03-Jun	glufosinate		
D	2008	17.0	10-Sep	Winter Wheat			22-Jun	clopyralid, MCPA	26-Aug	glyphosate

NA = Not available

**5.3.3 Chemical Extraction and Quantification.** Analyses were performed at the Prairie & Northern Laboratory for Environmental Testing, Environment Canada, Edmonton, AB, Canada for all pesticides (Waite et al., 2005) except glufosinate, glyphosate, and its metabolite aminomethylphosphonic acid (AMPA). These were analyzed at the Environmental Monitoring & Health division of the Alberta Research Council, Vegreville, AB, Canada (Water Research Users Group, 2005) and did not include the air samples. Strict QA/QC protocols were followed including using field blanks, surrogate solutions as a check on extraction efficiency, matrix spikes, and blanks. Blanks for all media were below levels of detection. Minimum detection limits (MDLs) were  $0.01 \mu\text{g sample}^{-1}$  for all analytes with the exceptions of 2,4-D, atrazine, ethalfluralin, and trifluralin with a MDL of  $0.05 \mu\text{g sample}^{-1}$ ; glyphosate at  $0.2 \mu\text{g L}^{-1}$ ; and glufosinate and AMPA at  $1.0 \mu\text{g L}^{-1}$ .

**5.3.4 Predicting Wetland Contamination.** Wetland water depth was monitored using HOBO Water Level Loggers from MicroDAQ.com. The wetland bathymetry and upland topography was mapped using a Sokkia total station set 4110 and georeferenced using the Trimble AgGPS (global positioning system) 214. The topographical data was surfaced using the point kriging interpolation method to produce a high-resolution digital elevation model (DEM) with a cell size of 5 m in Surfer 8.00 (Golden Software Inc. 2002). This software was then used to calculate the water volume and water surface area of each wetland at measured water depths. The weekly total mass of pesticide entering a wetland through dry and wet deposition was estimated by multiplying the mass of pesticide deposited per square meter, as measured through the use of the bulk deposition samplers, by the water surface area of the wetland. A portion of this mass will dissipate over time

through degradation or movement out of the water column. The time required for 50% of the mass to dissipate is referred to as the dissipation half-life (DT50). For the pesticides detected in the water-column of the current study, we used their DT50 values as reported by Degenhardt et al. (2011) who studied the fate of these pesticides from the water-column and bottom sediment in two wetlands at MZTRA. The mass of pesticide deposited to the wetland each week was added to that remaining in the wetland following dissipation then divided by the volume of water to estimate the weekly concentration of the pesticide found in the wetland. The first monitored value of the start of season was taken as the initial concentration.

## 5.4 Results and Discussion

**5.4.1 Relatively Volatile Herbicides.** Of the relatively volatile currently used herbicides, triallate was detected in air for the longest period followed by trifluralin and then ethalfuralin (Table 5.4). Weekly averaged maximum air concentrations were highest from mid-June to mid-July ranging from 0.1 – 0.3 ng m<sup>-3</sup> (Table 5.4), and the detection of triallate, trifluralin, and ethalfuralin in the air may be, in part, due to volatilization from soil after their earlier application in the Spring. Smith et al. (1997) found that a total of 21%, 18%, and 14% of applied triallate, trifluralin, and ethalfuralin volatilized from soil under prairie spring conditions. Air concentrations steadily declined to trace levels or below detection by the end of the sampling period (Table 5.4), likely due to photodegradation in addition to removal by wet and dry deposition. Triallate was the only relatively volatile herbicide detected in the wetland water-column (Figure 5.2), twice in Pond 2 (Figure 5.1, Table 5.4). Triallate has a smaller Henry's Law constant than either ethalfuralin or trifluralin (Table 5.1), suggesting that triallate in the gas-phase is more

likely to be absorbed into the water column than ethalfluralin or trifluralin. Ethalfluralin, trifluralin, and triallate partition to the air as they have high vapor pressures and low water solubilities (Table 5.1) and were not detected in any of the bulk deposition samples (Figure 5.2). Hill et al. (2001) conducted 7-day stability tests with a similar bulk deposition sampler. Bottles were spiked with  $0.24 \mu\text{g L}^{-1}$  of herbicides and after 7 days recoveries ranged from  $13\% \pm 5\%$  for trifluralin and  $61\% \pm 12\%$  for triallate. Although not tested, they predicted low recovery rates for ethalfluralin as well. These pesticides may also revolatilize from the surface of the sampler as discussed by Waite et al. (1999). Hence, the lack of detections of triallate, trifluralin, and ethalfluralin in bulk deposition samples could be also due to the sampling protocol used.

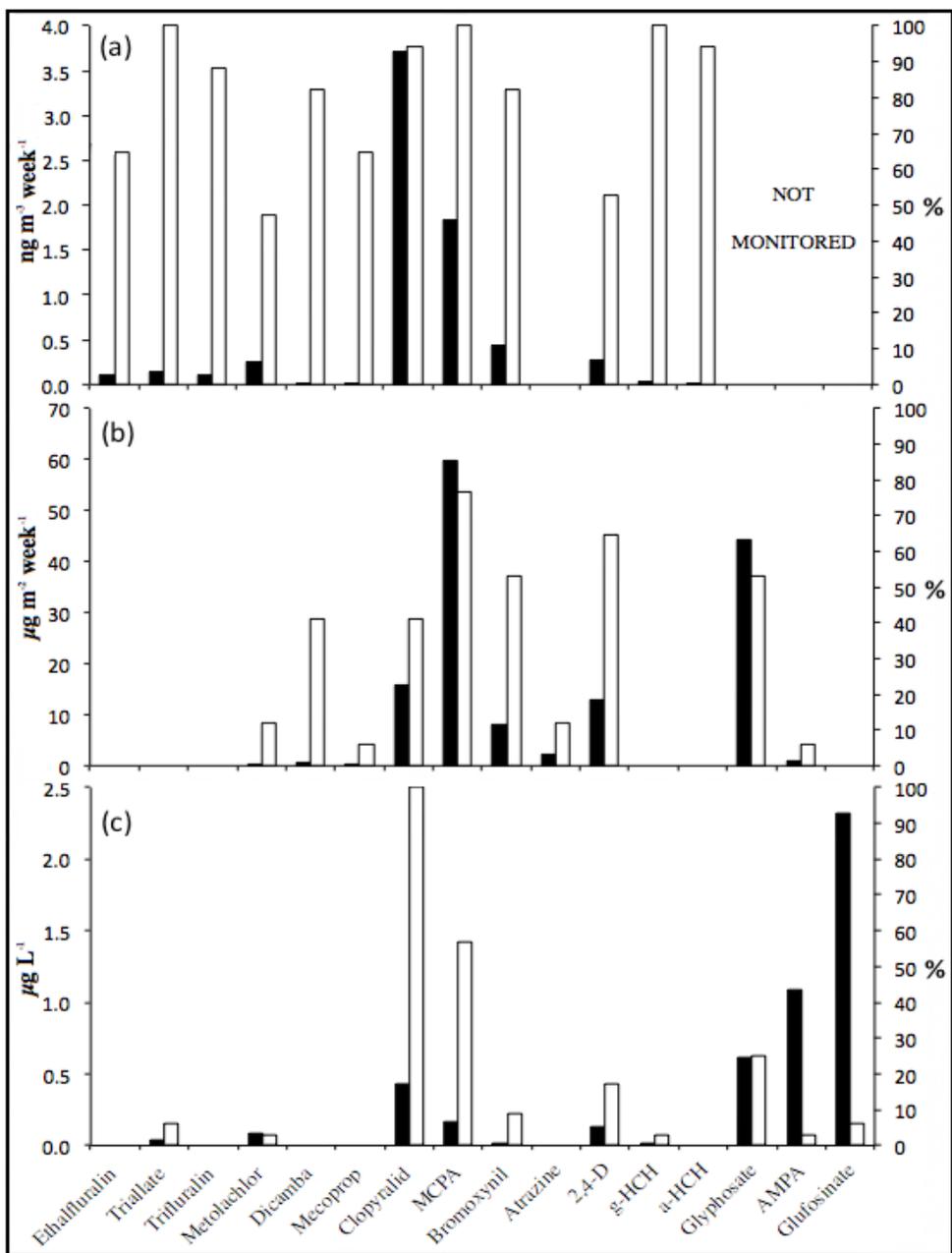


Figure 5.2. (a) Maximum weekly averaged atmospheric concentrations of pesticides ( $\text{ng m}^{-3} \text{ week}^{-1}$ ; black bar) and frequency of detection (white bar); (b) maximum weekly bulk (wet + dry) deposition ( $\mu\text{g m}^{-2} \text{ week}^{-1}$ ; black bar) and frequency of detection (white bar); and (c) maximum wetland grab sample concentrations ( $\mu\text{g L}^{-1}$ ; black bar) and frequency of detection (white bar).

Table 5.4. Average weekly atmospheric concentrations of detected herbicides (ng m<sup>-3</sup> week<sup>-1</sup>).

Date	26-May	2-Jun	9-Jun	16-Jun	23-Jun	30-Jun	7-Jul	14-Jul	21-Jul	28-Jul	4-Aug	11-Aug	18-Aug	26-Aug	1-Sep	8-Sep	15-Sep
Ethalfuralin	0.05	ND	0.07	0.06	0.05	0.1	0.04	0.1	0.03	0.04	0.04	0.04	ND	ND	ND	ND	ND
Triallate	0.02	0.02	0.1	0.09	0.06	0.07	0.03	0.07	0.06	0.06	0.05	0.04	0.05	0.03	0.02	0.02	0.01
Trifluralin	0.04	0.02	0.09	0.08	0.05	0.06	0.04	0.10	0.05	0.08	0.06	0.05	0.04	0.04	0.04	ND	ND
Metolachlor	ND	0.005	ND	ND	ND	0.3	0.2	0.02	0.02	0.005	0.01	0.01	ND	ND	ND	ND	ND
Dicamba	ND	0.005	0.01	0.005	0.02	0.02	0.01	0.005	0.005	0.005	0.005	ND	0.005	0.01	0.01	ND	0.005
Mecoprop	ND	ND	0.01	ND	0.02	0.01	0.01	0.005	0.01	0.01	0.01	0.01	0.01	0.009	ND	ND	ND
Clopyralid	ND	0.01	0.02	0.02	4	0.3	0.06	0.06	0.05	0.05	0.03	0.02	0.01	0.02	0.02	0.006	0.005
MCPA	0.01	0.02	0.06	0.04	2	0.3	0.09	0.03	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.005	0.005
Bromoxynil	0.01	0.02	0.07	0.03	0.4	0.4	0.2	0.03	0.03	0.02	0.02	0.02	0.01	0.01	ND	ND	ND
2,4-D	ND	ND	0.05	0.02	0.3	0.08	0.06	ND	ND	ND	0.02	ND	ND	0.04	0.06	ND	0.03
g-HCH	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.02
a-HCH	ND	0.005	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

ND = No detection

**5.4.2 Less Volatile Herbicides.** For the other currently used herbicides, MCPA and bromoxynil were the only less volatile herbicides detected in the air in late May (Table 5.4). However, by early June most of the less volatile herbicides had been detected at least once at trace levels (Table 5.4). Maximum air concentrations of the herbicides appeared at the end of June (Table 5.4) as most of the herbicides are widely applied after crop emergence. Clopyralid was found at the highest maximum weekly average concentration of  $4 \text{ ng m}^{-3}$  followed by MCPA at  $2 \text{ ng m}^{-3}$  on June 23rd (Table 5.4) because of herbicide applications on-site (Table 5.3, Figure 5.1). Given that we detected a wide range of other currently used herbicides (Figure 5.2), including those not being used on-site, pesticide air pollution at the site was also due to spray drift and/or post-volatilization associated with regional herbicide applications. In addition to regional applications and associated spray drift, the few detections of 2,4-D in the air in the fall (Table 5.4) also could be due to fall harvest operations when soil and plant particulates may become airborne, as was observed with fenpropimorph by Scharf and Bachmann (1993). Despite the very low use of metolachlor in Manitoba (Table 5.2), and metolachlor not being applied on site (Table 5.3), it was detected several times in the air, indicating that a broader region than Manitoba contributes to the air concentration of this pesticide.

Total seasonal bulk deposition amounts ranged from  $0 - 100 \text{ } \mu\text{g m}^{-2}$  with MCPA accounting for the greatest mass deposited (Figure 5.2, Table 5.5). The  $100 \text{ } \mu\text{g m}^{-2}$  is equivalent to  $1 \text{ gram ha}^{-1} \text{ yr}^{-1}$ , or approximately 0.5% of the average recommended application rate of  $313 \text{ g/ha}$  for MCPA. The highest weekly bulk deposition rate of glyphosate was  $40 \text{ } \mu\text{g m}^{-2} \text{ week}^{-1}$  during the week ending Aug. 26<sup>th</sup>, as a result of spray drift and/or post-volatilization losses associated with herbicide applications in fields B

and D (Table 5.3, Figure 5.1). The highest weekly averaged deposition rates of most other herbicides occurred on June 23<sup>rd</sup> or 30<sup>th</sup> (Table 5.5) during the same two weeks as the highest maximum averaged weekly air concentrations (Table 5.4). Glufosinate was not detected in any of the bulk deposition samples (Figure 5.2), despite being widely applied in Manitoba (Table 5.2). The herbicides 2,4-D, dicamba, and clopyralid were all detected in the deposition sample of Sept. 1<sup>st</sup> at levels significantly larger than trace amounts (Table 5.5), possibly reflecting their application in the region and/or fall harvest operations as discussed above for the air concentrations of 2,4-D.

Table 5.5. Rates of deposition of detected herbicides in bulk (wet + dry) deposition ( $\mu\text{g m}^{-2} \text{ week}^{-1}$ ), weekly precipitation (mm), and total seasonal depositions.

Date	26-May	2-Jun	9-Jun	16-Jun	23-Jun	30-Jun	7-Jul	14-Jul	21-Jul	28-Jul	4-Aug	11-Aug	18-Aug	26-Aug	1-Sep	8-Sep	15-Sep	Bulk Total Seasonal Deposition ( $\mu\text{g m}^{-2}$ )
precipitation (mm)	19.1	9.3	42.2	49.4	6.6	15.8	8.3	16.6	34.2	1.4	22.5	12	5.5	17.6	6	18	0.7	
Metolachlor	0.2	0.1	ND	ND	ND	ND	ND	ND	ND	MS	ND	ND	ND	ND	ND	ND	ND	0.4
Dicamba	ND	0.3	ND	ND	0.5	0.3	0.08	0.2	ND	MS	0.5	ND	ND	ND	0.2	ND	ND	2
Mecoprop	ND	ND	ND	ND	0.2	ND	ND	ND	ND	MS	ND	ND	ND	ND	ND	ND	ND	0.2
Clopyralid	ND	0.4	0.5	ND	20	10	0.2	0.2	ND	MS	ND	ND	ND	ND	0.06	ND	ND	30
MCPA	0.5	1	7	7	50	60	2	2	2	MS	0.9	0.2	0.2	ND	0.06	ND	ND	100
Bromoxynil	0.5	0.5	3	2	8	5	0.3	0.5	0.3	MS	ND	ND	ND	ND	ND	ND	ND	20
Atrazine	2	1	ND	ND	ND	ND	ND	ND	ND	MS	ND	ND	ND	ND	ND	ND	ND	4
2,4-D	1	2	8	9	10	5	0.9	1	2	MS	3	ND	ND	ND	0.7	ND	ND	50
Glyphosate	5	0.09	0.7	0.9	3	ND	ND	ND	ND	ND	ND	3	1	40	ND	ND	1	60
AMPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.9	0.9

ND = No detection; MS = Missing sample

Table 5.6. Monitored concentrations of detected herbicides in wetland grab samples and calculated concentrations in italics ( $\mu\text{g L}^{-1}$ ).

Pond 1	26-May	2-Jun	9-Jun	16-Jun	23-Jun	30-Jun	7-Jul	14-Jul	21-Jul	28-Jul	4-Aug	11-Aug	18-Aug	26-Aug	1-Sep	8-Sep	15-Sep
Clopyralid	0.3		MS		0.2		0.2		0.2		0.06		0.04		0.02		0.04
<i>Clopyralid</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.06</i>	<i>0.04</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
MCPA	ND		MS		0.2		0.2		0.09		0.03		ND		ND		ND
<i>MCPA</i>	<i>0</i>	<i>0.007</i>	<i>0.03</i>	<i>0.03</i>	<i>0.2</i>	<i>0.3</i>	<i>0.2</i>	<i>0.08</i>	<i>0.04</i>	<i>0.02</i>	<i>0.02</i>	<i>0.01</i>	<i>0.01</i>	<i>0.009</i>	<i>0.02</i>	<i>0.005</i>	<i>0.02</i>
Bromoxynil	ND		MS		0.01		ND		ND		ND		ND		ND		ND
<i>Bromoxynil</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0.006</i>	<i>0.03</i>	<i>0.02</i>	<i>0.01</i>	<i>0</i>									
2,4-D	ND		MS		0.08		ND		ND		ND		ND		ND		ND
<i>2,4-D</i>	<i>0</i>	<i>0.01</i>	<i>0.04</i>	<i>0.03</i>	<i>0.05</i>	<i>0.02</i>	<i>0</i>	<i>0.008</i>	<i>0.01</i>	<i>0.01</i>	<i>0.02</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.02</i>	<i>0</i>	<i>0</i>
Glyphosate	ND		0.05		ND		ND		0.1		ND		ND		ND		ND
<i>Glyphosate</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.03</i>	<i>0.02</i>	<i>0.7</i>	<i>0</i>	<i>0</i>	<i>0.05</i>
<b>Pond 2</b>																	
Clopyralid	0.06		0.04		0.04		0.05		0.04		0.05		0.02		0.03		0.04
<i>Clopyralid</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.05</i>	<i>0.04</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
MCPA	ND		0.04		0.1		0.2		0.08		0.03		ND		ND		ND
<i>MCPA</i>	<i>0</i>	<i>0</i>	<i>0.02</i>	<i>0.04</i>	<i>0.2</i>	<i>0.3</i>	<i>0.2</i>	<i>0.06</i>	<i>0.03</i>	<i>0.02</i>	<i>0.01</i>	<i>0.006</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
Bromoxynil	ND		ND		0.01		ND		ND		ND		ND		ND		ND
<i>Bromoxynil</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0.007</i>	<i>0.03</i>	<i>0.02</i>	<i>0.01</i>	<i>0</i>									
2,4-D	0.1		0.08		0.06		ND		ND		ND		ND		ND		ND
<i>2,4-D</i>	<i>0</i>	<i>0.008</i>	<i>0.03</i>	<i>0.03</i>	<i>0.04</i>	<i>0.02</i>	<i>0</i>	<i>0.005</i>	<i>0.009</i>	<i>0.01</i>	<i>0.01</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.006</i>	<i>0</i>	<i>0</i>
Glyphosate	ND		0.1		ND		ND		0.09		ND		ND		ND		ND
<i>Glyphosate</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0.006</i>	<i>0.3</i>	<i>0</i>	<i>0</i>	<i>0.02</i>
<b>Pond 3</b>																	
Clopyralid	0.1		0.2		0.1		0.1		0.1		0.1		0.1		0.1		0.4
<i>Clopyralid</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.03</i>	<i>0.02</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
MCPA	ND		0.03		0.08		0.07		0.03		0.02		ND		ND		ND
<i>MCPA</i>	<i>0</i>	<i>0</i>	<i>0.02</i>	<i>0.02</i>	<i>0.1</i>	<i>0.2</i>	<i>0.07</i>	<i>0.03</i>	<i>0.02</i>	<i>0.009</i>	<i>0.006</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
Bromoxynil	ND		ND		ND		ND		ND		ND		ND		ND		ND
<i>Bromoxynil</i>	<i>0</i>	<i>0</i>	<i>0.006</i>	<i>0</i>	<i>0.02</i>	<i>0.01</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
2,4-D	ND		ND		0.07		ND		ND		ND		ND		ND		ND
<i>2,4-D</i>	<i>0</i>	<i>0.005</i>	<i>0.02</i>	<i>0.02</i>	<i>0.03</i>	<i>0.01</i>	<i>0</i>	<i>0</i>	<i>0.005</i>	<i>0.006</i>	<i>0.006</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
Glyphosate	ND		0.1		ND		ND		ND		ND		ND		ND		ND
<i>Glyphosate</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.006</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.008</i>	<i>0</i>	<i>0.1</i>	<i>0</i>	<i>0</i>	<i>0</i>
<b>Pond 4</b>																	
Clopyralid	0.2		0.2		0.1		0.1		0.1		0.1		0.1		0.1		0.2
<i>Clopyralid</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.05</i>	<i>0.03</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
MCPA	ND		0.06		0.2		0.2		0.1		0.05		0.02		ND		ND
<i>MCPA</i>	<i>0</i>	<i>0</i>	<i>0.03</i>	<i>0.03</i>	<i>0.2</i>	<i>0.3</i>	<i>0.2</i>	<i>0.1</i>	<i>0.09</i>	<i>0.07</i>	<i>0.05</i>	<i>0.04</i>	<i>0.03</i>	<i>0.02</i>	<i>0.02</i>	<i>0.01</i>	<i>0.008</i>
Bromoxynil	ND		ND		0.01		ND		ND		ND		ND		ND		ND
<i>Bromoxynil</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0.005</i>	<i>0.03</i>	<i>0.02</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>
Atrazine	ND		ND		ND		ND		ND		ND		ND		ND		ND
<i>2,4-D</i>	<i>0</i>	<i>0.009</i>	<i>0.03</i>	<i>0.04</i>	<i>0.07</i>	<i>0.06</i>	<i>0.05</i>	<i>0.03</i>	<i>0.03</i>	<i>0.03</i>	<i>0.03</i>	<i>0.02</i>	<i>0.02</i>	<i>0.01</i>	<i>0.01</i>	<i>0.008</i>	<i>0.006</i>
Glyphosate	0.2		0.1		0.4		ND		ND		ND		ND		ND		ND
<i>Glyphosate</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0</i>	<i>0.01</i>	<i>0.007</i>	<i>0.2</i>	<i>0.02</i>	<i>0</i>	<i>0.008</i>

ND = No detection; MS = Missing sample

**5.4.3 Legacy Pesticides.** Although the detection frequency for lindane was 100% and for  $\alpha$ -HCH 94%, their maximum weekly air concentrations were relatively low (Figure 5.2).  $\alpha$ - and  $\gamma$ -HCH (lindane) compounds have been shown to be ubiquitous throughout the North American atmosphere (Shen et al., 2004). Lindane,  $\alpha$ -HCH, and alachlor were not detected in bulk deposition and wetland water samples with the exception of lindane being detected in one water sample at trace levels (Figure 5.2 and Table 5.5).

**5.4.4 Herbicides Detected in the Water-Column.** Herbicide detection frequencies were less than 10% for all herbicides with the exceptions of MCPA, 2,4-D, clopyralid, and glyphosate (Figure 5.2). In no instance did herbicide concentrations exceed Canadian water quality guidelines for the protection of aquatic life. Only 10 of the 16 analyzed pesticides currently have set guidelines (Table 5.7).

Table 5.7. Comparison of monitored concentrations of pesticides in wetland grab samples ( $\mu\text{g L}^{-1}$ ) to the Canadian Water Quality Guidelines for the Protection of Aquatic Life ( $\mu\text{g L}^{-1}$ ) (CCME, 1999).

Active Ingredient	Pond 1 Max.	Pond 2 Max.	Pond 3 Max.	Pond 4 Max.	Canadian Water Quality Guidelines for the Protection of Aquatic Life ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>
Ethalfuralin	ND	ND	ND	ND	NA
Triallate	ND	0.04	ND	ND	0.24
Trifluralin	ND	ND	ND	ND	0.2
Metolachlor	0.08	ND	ND	ND	7.8
Dicamba	ND	ND	ND	ND	10
Mecoprop	ND	ND	ND	ND	NA
Clopyralid	0.3	0.06	0.4	0.2	NA
MCPA	0.2	0.2	0.08	0.2	2.6
Bromoxynil	0.01	0.01	ND	0.01	5
Atrazine	ND	ND	ND	ND	1.8
2,4-D	0.08	0.1	0.07	0.07	4
$\gamma$ -HCH	0.01	ND	ND	ND	0.01
$\alpha$ -HCH	ND	ND	ND	ND	NA
Glyphosate	0.1	0.1	0.1	0.6	65
AMPA	ND	ND	ND	1	NA
Glufosinate	0.9	ND	2	ND	NA

NA = Not available; ND = No detection

MCPA concentrations were highest in the wetland water samples taken June 23<sup>rd</sup> and July 7<sup>th</sup> following maximum MCPA bulk deposition rates (Table 5.5 and 5.6) because of herbicide applications on-site (Table 5.3). 2,4-D was detected in Pond 2 following snowmelt runoff. This was the only wetland with its catchment situated partly in a field with a fall application of 2,4-D on Sept. 4<sup>th</sup>, 2007 (Field B in Figure 5.1, Table 5.3). Waite et al. (2002) also found 2,4-D concentrations in farm pond water to be highest in the spring and early summer suggesting transport with spring snowmelt. 2,4-D was also detected in all four wetlands following the maximum weekly averaged bulk deposition rates corresponding to regional application (Tables 5.5 and 5.6). Concentrations of 2,4-D in all four wetlands dissipated to levels below detection in subsequent weeks. In previous studies, 2,4-D dissipated in two weeks by 50% in the case of spiked pond water (Boyle, 1980) and by 64% in the case of a natural contamination (DeWeese, 1992) after 14 days. Herbicides in wetlands may dissipate through photochemical, hydrolytic, or microbial degradation; partitioning to bottom sediments and biota; volatilization; short-range lateral transport through soil infiltration; or through deep percolation into the groundwater system (Waite et al., 1992; Tuduri et al., 2006a). Concentrations may also become dilute with less contaminated rainfall.

The elevated concentration of clopyralid in Pond 1 on May 26<sup>th</sup> ( $0.3 \mu\text{g L}^{-1}$ ; Table 5.5) is associated with clopyralid applications to this wetland's riparian zone on the same day (Table 5.3, Figure 5.1). The spray drift did not reach the air sampler and bulk deposition sampler situated ~ 800 m from the pond (Figure 5.1) but ponds 1 – 4 all contained clopyralid in the May 26<sup>th</sup> sample (Table 5.5). Clopyralid is relatively persistent in both aquatic and soil environments (Table 5.1) and the detection of clopyralid in the four

ponds could be due to clopyralid carry-over in wetlands from previous years or due to the movement of clopyralid-containing water and soil by snowmelt erosion because the herbicide had been applied around the complete circumference of Ponds 3 and 4 in 2006 (Table 5.3, Figure 5.1). Pond 2, with no applications of clopyralid in the field next to it in the last two years (Table 5.3, Figure 5.1), had a maximum wetland concentration over three times lower than any other Pond. Previous work has found detectable levels of clopyralid in surface waters following snowmelt runoff (Cessna & Elliott, 2004). Rainfall runoff may have caused an increase in clopyralid concentration in Ponds 3 and 4 in the weekly wetland sample ending on June 9<sup>th</sup> (Table 5.6) as in the morning prior to its collection, on June 9<sup>th</sup>, 23 mm of rain had fallen (Table 5.5). Clopyralid wetland concentrations did not increase in Ponds 2 and 4 following application to Fields B and D on June 22<sup>nd</sup> nor in any of the wetlands during the highest weekly averaged atmospheric deposits.

Relative to the other pesticides, the MDLs for glyphosate, AMPA, and glufosinate are 4 to 100 times higher (Waite et al., 2005; Humphries et al., 2005). Glyphosate was detected in 25% of the surface water samples and was detected in all four wetlands in the samples taken on June 9<sup>th</sup> (Table 5.6). This was despite being applied to only one field on May 26, and not until August 26 to two other fields (Table 5.3, Figure 5.1). Concentrations of glyphosate in wetlands may be due to atmospheric deposition (Table 5.5). Elevated concentrations of glyphosate in Pond 4 ( $0.6 \mu\text{g L}^{-1}$ ) on Sept. 1<sup>st</sup> is primarily due to spray drift associated with glyphosate applications on Aug. 26<sup>th</sup> on Field D in which Pond 4 was situated (Table 5.3, Figure 5.1, Figure 5.3). The following sample, taken two weeks later, had glyphosate concentrations were below the level of detection. Previous studies

have shown that glyphosate dissipates rapidly from the water-column forest wetlands (Goldsborough & Brown, 1993). Glyphosate was also applied on Aug. 26<sup>th</sup> in Field B resulting in the maximum bulk deposition detection of glyphosate ( $40 \mu\text{g m}^{-2} \text{ week}^{-1}$ ; Table 5.6) but no detection in Pond 2 on Sept. 1<sup>st</sup> located on the northern edge of the field. Glyphosate was not detected in Pond 2 likely due to the wind blowing in the southerly direction for three days following application. Nor was it detected in ponds 1 and 3 (Table 5.6). Its metabolite AMPA was detected only once (Pond 4) (Table 5.6). Glufosinate was detected twice in the wetland water samples (Table 5.6), despite not being detected in any of the bulk deposition samples, nor being applied on-site (Tables 5.3 and 5.5).

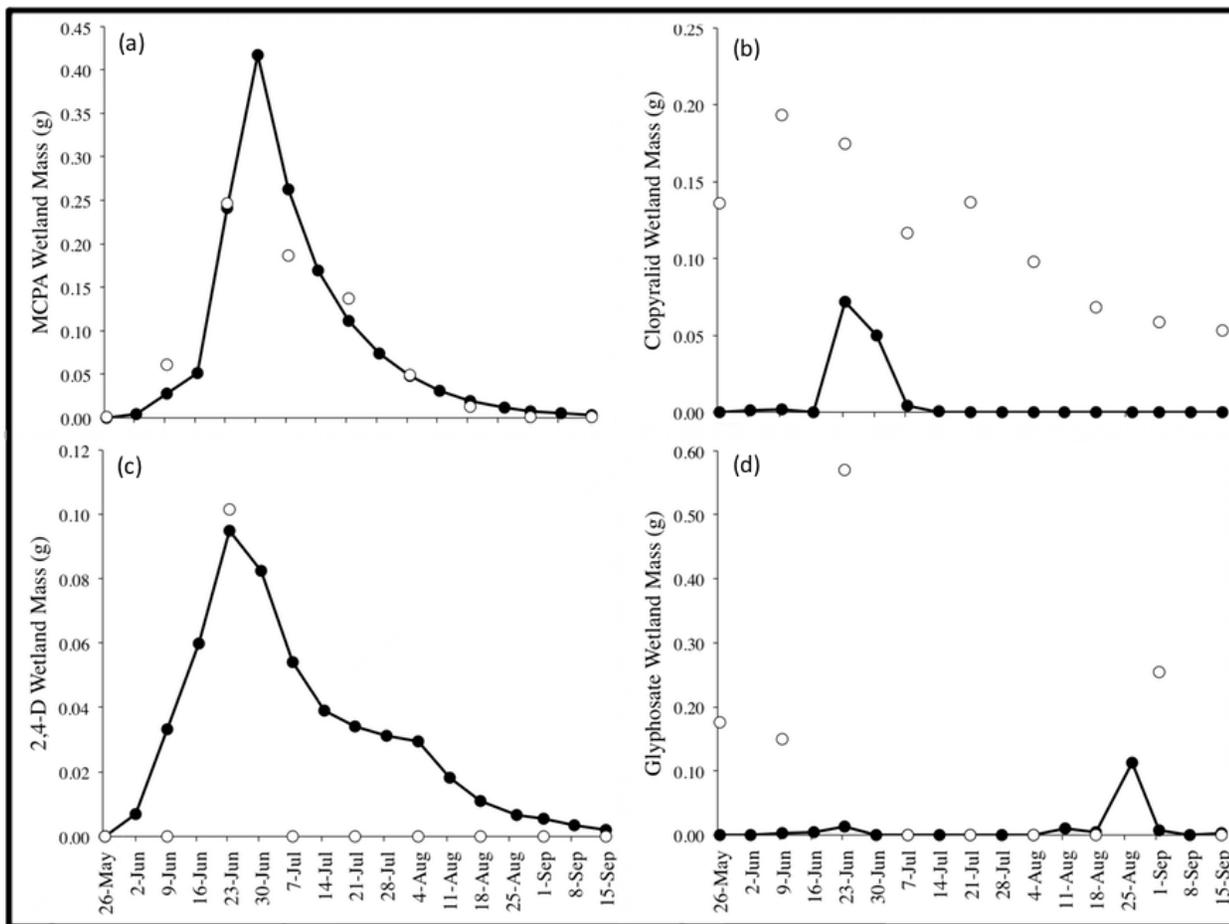


Figure 5.3. Comparison of measured masses (open circles) and calculated (solid circles) masses of select herbicides in one wetland (pond 4). Examples are given for herbicides (a) MCPA, (b) clopyralid (c) 2,4-D and (d) glyphosate. Mass is given as zero if monitored concentrations were below the minimum detection limits.

**5.4.5 Contribution of Atmospheric Deposition to Prairie Wetland Water Contamination.** Pesticides that had detectable concentrations in the bulk deposition samples were (in order of the highest rates of deposition to the lowest): MCPA, glyphosate, clopyralid, 2,4-D, bromoxynil, atrazine, dicamba, metolachlor, and mecoprop. MCPA, bromoxynil, and 2,4-D are among the top 5 pesticides applied in Manitoba and in a 13 km radius surrounding the site (Table 5.2). MCPA, glyphosate, and clopyralid were all applied on-site (Table 5.3).

Predicted MCPA wetland concentrations were close to monitored concentrations with Pearson correlation coefficient's of 0.98 (p-value = 0.00003), 0.91 (p-value = 0.00058), 0.97 (p-value = 0.00002), and 0.96 (p-value = 0.00005) for Ponds 1 to 4 respectively, suggesting that atmospheric dry and wet deposition is the main source of MCPA contamination of these prairie wetlands (Figure 5.3). Based on calculated predictions highest weekly concentrations of MCPA in the wetlands ranging from 0.2 to 0.3  $\mu\text{g L}^{-1}$  (Table 5.5) were missed due to bi-weekly sampling protocols (Figure 5.3). This demonstrates that monitoring programs with low sampling frequencies may easily underrepresent surface water concentrations of pesticides. To provide further evidence that atmospheric dry and wet deposition is a source of MCPA contamination of prairie wetlands, the measured wetland concentration of this herbicide was directly related to the surface area to volume ratios of the wetlands. Although volumes varied (0 – 1500  $\text{m}^3$ ) throughout the season and between the wetlands, three of the four had very similar ratios (3.14 to 3.56) during maximum herbicide deposition rates during the week ending June 23<sup>rd</sup>. This resulted in similar monitored concentrations of MCPA (0.1 – 0.2  $\mu\text{g L}^{-1}$ ) and

their equivalent predicted ( $0.2 \mu\text{g L}^{-1}$ ) concentrations (Table 5.6). Pond 3 had a lower surface area to volume ratio of two, resulting in lower measured and predicted herbicide concentrations (Table 5.5). The greatest mass of MCPA within the wetlands, ranging from  $0.08 - 0.3 \text{ g}$ , was largely dependent on their surface areas; those with the largest surface areas had the greatest mass. The greatest weekly averaged atmospheric deposition occurred in this season when the wetlands were at their greatest volume, which corresponded to a lower surface area to volume ratio for the studied wetlands. In dry years this ratio would be higher and could result in higher concentrations of MCPA within the wetlands.

2,4-D (Figure 5.3) and bromoxynil calculated concentrations were highest the same date as monitored concentrations (with the exception of 2,4-D in Pond 2) (Table 5.6), indicating that atmospheric deposition may be one possible pathway by which the on-site wetlands become contaminated with these herbicides.

Predicted wetland concentrations of atrazine, dicamba, and mecoprop were below their respective analytical detection limits with monitored values corroborating these predictions (Table 5.6). Although predicted concentrations were below detection limits for metolachlor there was one detection of metolachlor in Pond 1 on May 26<sup>th</sup> (Table 5.5). This coincided with detections in the bulk deposition samples the first two weeks of sampling ( $0.2 \mu\text{g m}^{-2} \text{ week}^{-1}$  on May 26<sup>th</sup> and  $0.1 \mu\text{g m}^{-2} \text{ week}^{-1}$  on June 2<sup>nd</sup>; Table 5.6).

Although predicted concentrations did not correlate well with the monitored concentrations of glyphosate (Table 5.5), all of the wetlands had detectable

concentrations on June 9<sup>th</sup>, which suggests atmospheric deposition of glyphosate as a possible source of wetland water contamination. Glyphosate applications account for the single largest mass of herbicide applications in Manitoba (Table 5.2). The most isolated wetland, Pond 4 (Figure 5.1), located in the southwestern corner of the field had detections in the spring samples of May 26<sup>th</sup> to June 23<sup>rd</sup> that may have resulted from spray drift associated with nearby adjacent farms, but spray drift did not reach the other wetlands. The two most northern ponds (Ponds 1 and 2; Figure 5.1) had detections of glyphosate on July 21<sup>st</sup> that, again, may have resulted from applications on nearby farms.

The predicted concentrations did not correlate with monitored concentrations for clopyralid (Table 5.5) suggesting that processes other than atmospheric deposition contribute to wetland water-column contamination by this herbicide, as discussed above. No increases in wetland concentrations were seen with the maximum deposition of clopyralid.

## **5.5 Conclusions**

Although the types and levels of pesticides detected in the wetlands of the current study suggest that regional pesticide applications can contribute to pesticide surface water contamination following atmospheric transport and deposition, the greater frequency and concentrations of clopyralid, MCPA, and glyphosate detections in wetlands suggest that on-farm pesticide applications have a greater impact on on-site water quality. Farm extension efforts designed to reduce pesticide loading into prairie wetlands need to focus on beneficial management practices that minimize application drift and post-volatilization losses, and that reduce rainfall or snowmelt runoff on agricultural land and from entering

wetlands.

### **5.6 Acknowledgment**

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## 6. OVERALL SYNTHESIS

### 6.1 Summary of Research Findings

This research used field and laboratory methods to examine concentrations of pesticides in the air, dry deposition, wet deposition, bulk deposition, and wetlands. In general the study results indicate that the frequency and level of detectable concentrations in the monitored environmental media are greatest for pesticides that are applied on-site, but that these pesticides are frequently detected as mixtures with pesticides applied off-site. The pesticide's physicochemical properties and its relative mean mass applied in the area surrounding the research sites were significant parameters in explaining the concentrations of individual pesticides detected in samples taken. For example, as shown in Chapter 3, the masses of the CUHs detected in the air were most strongly positively associated with their estimated masses typically applied in a ~100 km<sup>2</sup> township area surrounding the sampling sites.

The studies described in Chapters 2 and 3 are unique in that they provide for data on pesticide concentrations in air that were collected simultaneously in Arctic, Subarctic and southern agriculture sites in the Prairie Region of Canada. These study results indicate that some of the most commonly used herbicides in Canadian agriculture today are present in the air in the regions where they are applied but appear infrequently and at low levels in the Canadian Subarctic, Arctic, and other remote sites far from agricultural pesticide applications. This suggests that currently used pesticides do not have a strong potential to be transported long-range distances in air as parent compounds. Chapters 2 and 3 also agree with the results shown by other researchers that concentrations of legacy

pesticides such as lindane ( $\gamma$ -HCH) and its manufacturing by-product prior to 1971 ( $\alpha$ -HCH) continue to decrease over time in our environment including in the prairies as well as in the northern Subarctic and Arctic regions of Canada.

Herbicides that are widely used in the agricultural region of the Canadian Prairie Provinces were more frequently detected in environmental samples taken in this region than two other herbicides that were monitored and typical of crop production systems in the eastern Canadian provinces. Bromoxynil, MCPA, and 2,4-D are among the most frequently applied herbicides on the Canadian Prairies as part of grain and oilseed production and were detected in environmental samples at all of the agricultural prairie sites, with the exception that 2,4-D was not detected at the Glenlea Research station in 2009 (Chapter 3).

Pesticides were detected at lower frequencies and concentrations in the winter air than those found in the summer (Chapter 3). Pesticides are typically not applied in the winter time and hence there is little chance for application drift and subsequent air pollution. Snow cover and cold climatic conditions during most of the winter would have also decreased pesticide volatilization from land, water, and plant surfaces. Triallate and metolachlor were the only two pesticides detected in the winter. Triallate (2005) and MCPA (2007) were also the only currently used herbicides detected in the North, at one Arctic site in Nunavut. The mass of triallate detected at this Arctic location was numerically greater than the mass of triallate detected at each of the four locations in the Canadian Prairies. In contrast, the mass of MCPA in the Arctic sample was at the detection limit (Chapter 2). The research results demonstrate that these currently used

herbicides are relatively persistent in the environment and can be transported hundreds of kilometers where they are applied.

The agricultural sites in Chapters 2, 3, 4, and 5 demonstrated that pesticide mixtures are common in the air, atmospheric depositions, and wetland water columns. Air concentrations of pesticides have the potential to contaminate surface water through atmospheric deposition. In Chapter 5, for the pesticides that had detectable concentrations in the bulk deposits, calculations were performed to determine predicted wetland water column pesticide concentrations from deposition alone. The predicted concentrations were the closest to measured concentrations for MCPA and were reasonable for a range of other herbicides. Sources other than atmospheric deposition alone were clearly important to the detected concentrations of clopyralid in the wetland water-column. The Canadian water quality guidelines for the protection of aquatic life were not exceeded by any individual detected herbicide.

## **6.2 Present and Future Implications**

Given the extent to which pesticides are applied in the Prairie Provinces of Alberta, Saskatchewan and Manitoba it is critical that the environmental fate of currently used pesticides is understood to enable producers and policy makers to choose pesticides that have the lowest possible environmental impacts. One of the challenges is the lack of monitoring studies that simultaneously monitor agricultural sites where pesticides are applied and remote sites to determine if they undergo long-range transport. The results of this PhD thesis provide information over several years on the ability of current use pesticides to travel to remote sites such as potentially sensitive sites in the Arctic and

Subarctic. Chapter 3 demonstrates that the atmospheric concentrations of currently used herbicides decreases with increasing distance from areas in which their use was concentrated based on their estimated mass applied in incrementally larger areas surrounding the farm. The results in Chapter 2 also suggest that the currently used pesticides do not have a strong potential to be transported long-range distances in the air as parent compounds to Northern environments but are frequently found as mixtures in the air in regions where they are applied. As agricultural practices change and new products are introduced this too may change. Air concentrations of pesticides are of greatest concern in those regions where they are applied and monitoring efforts should be focused in agricultural regions. A system of maintaining records of herbicide use data, even at a coarse scale, can strongly improve agri-environmental risk assessments. It should be noted that the passive sampling devices utilized in the Northern environments sample a very small volume of air relative to powered devices such high volume air samplers. This may result in a lack of detections for those pesticides at low concentrations.

Chapters 2 and 3 agree with the results shown by other researchers that concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH in our environment continue to decrease over time in the Prairies as well as the Subarctic and Arctic sites. The need for continued monitoring of  $\alpha$ -HCH and  $\gamma$ -HCH has become less pertinent in these areas as these concentrations are falling to insignificant levels.

A challenge that is faced when determining the environmental fate of pesticides applied on-site or within a region is the lack of available data on the concentrations of pesticides in a variety of environmental compartments simultaneously. Chapter 5 provides both the concentrations of pesticides in the air and how they are deposited into wetlands. The results indicate that atmospheric depositions of some pesticides contribute a quantifiable amount to water concentrations of prairie wetlands and for others there must be an alternate route of contamination such as runoff. This gives a broader understanding of the potential of pesticides to cause wetland contamination and that pesticide movement within the environment is complex and not restricted to atmospheric deposition as some previous literature may have suggested for prairie environments (Donald et al., 2001). However, the types and levels of pesticides detected in the wetlands do suggest that regional pesticide applications strongly contribute to pesticide surface water contamination at a site following their atmospheric entry, transport, and deposition. On-farm pesticide applications showed an increased potential of wetland contamination indicating that spray drift prevention or reduction could be an important means of decreasing pesticide loading to wetlands in a wider region.

Chapter 4 provides details on the contribution of dry and wet atmospheric depositions of pesticides within the prairies in Manitoba and provides opportunities for spatial and temporal comparisons between dryer and wetter regions and years within the Prairies. The dry deposition of pesticides is a significant contributor to total seasonal depositions in Manitoban agricultural regions. The important contribution of dry deposition to total pesticide deposition warrants greater attention in arid and semi-arid areas such as the

prairie region of Canada, also because under a changing climate, this region is estimated to experience more severe droughts while the more favorable conditions predicted for pest infestations could lead to increased pesticide applications in agricultural and urban areas (Kharin and Zwiers, 2000).

Chapter 3 shows that spatial variability of air concentrations of pesticides at a small farm scale ranging from 10% for bromoxynil in 2008 to 137% for MCPA in 2009. While air samplers are commonly deployed to represent regional air concentrations (Yao et al. 2006; Yao et al. 2008) this chapter demonstrates that local or nearby applications of pesticides are highly influential on pesticide air concentrations. Spatial variability should be taken into consideration when determining the numbers and placement of samplers. Future regional-scale research should therefore consider deploying multiple sets of passive air samplers at a site for obtaining a more representative measure of herbicide air concentrations. Data should be collected on the pesticide products applied surrounding the sampling locations to help determine the sources of air pollution.

Pesticide mixtures commonly found in each of the study chapters are not taken into consideration in setting guidelines, such as water quality guidelines, in Canada. The potential for the contamination of surface waters by airborne pesticides is greatest in the agricultural regions in which they are applied, such as the Prairie Pothole Region of North America that includes millions of ecologically important wetlands. Government policies and toxicological studies should focus on chemical mixtures of those pesticides that are

applied in the greatest amounts in the region as these are found at greater frequencies in the environment.

### **6.3 Study Limitations and Future Recommendations**

Farm extension efforts designed to reduce pesticide loading into prairie wetlands need to focus on beneficial management practices that reduce application drift, as well as rainfall or snowmelt runoff, as these will be important measures in reducing pesticide loading into wetlands situated in agricultural fields of the Prairie Pothole Region of North America.

Chapters 2 to 5 utilized analytical methods that represented only a small portion of the commonly used herbicides in the prairie region. Other pesticides applied in the region would contribute to greater total pesticide air concentrations and atmospheric depositions and further contribute to the chemical mixtures found in the environment. It is recommended that future studies test for a wider range of pesticide products as these multi-residue methods become more widely available and focus on pesticides that are most commonly applied.

Passive air samplers have low air sampling volumes compared to active sampling methods. Although passive samplers are a cost effective means of monitoring contaminants in the air and are easily deployed in remote environments they may not collect detectable quantities of contaminants present at low air concentrations. It is recommended that studies utilize active air samplers when attempting to capture high-

resolution temporal changes in pesticide concentrations or when intending to monitor for low concentrations of contaminants.

Due to the variations at very small scales in pesticide air concentrations it is recommended that regional studies deploy multiple sets of side-by-side passive air samplers at each regional research site and pesticide use data should also be collected to help determine where they are to be deployed.

Levels of pesticide use are generally lacking for Canada as well as other countries (Boyd, 2001; Brimble et al., 2005). This makes it difficult to determine which pesticides to monitor in a given region and in many cases impossible to make correlations of pesticide use to environmental concentrations. Collection of use data is recommended prior to sampling in the area surrounding the site if these data are not available. Another challenge is the lack of a good understanding of the physicochemical properties of pesticides and their dissipation times in various environmental media. Future studies should focus on the determination of these properties and dissipation times especially for environmental compartments such as the air as very little information is currently available.

Few studies have focused on the detection of currently used pesticides in the Subarctic and Arctic. Future studies should focus on long term monitoring of currently used pesticides in the Subarctic and Arctic to determine if there is a potential of contamination

of these environments especially as new pesticides come into use. The studies in this thesis also lacked the ability to monitor air concentrations of some of the herbicides applied in the greatest amounts, such as glyphosate and glufosinate ammonium, and future work should monitor these as well.

The detected concentrations of individual pesticides never exceeded the respective Water Quality guidelines. However, Drinking, Aquatic and Irrigation Water Quality guidelines in Canada are not set for some of the individual pesticides studied and there are no guidelines for pesticide mixtures, which were commonly found. Future work should focus on the impact of mixtures of pesticides on ecosystems and human health, particularly in locations of greater agricultural activity.

#### **6.4 Contribution to Knowledge**

The currently used herbicides appeared infrequently and at low levels in the air in the Canadian Subarctic and Arctic. Chapter 2 was the first to detect levels of triallate (2005) and MCPA (2007) and both were found at the Arviat, Nunavut Territory site. This chapter also indicates that there is a continued decline of  $\alpha$ -HCH and  $\gamma$ -HCH in these regions.

The research presented in Chapter 3 is the first to measure spatial variability of air concentrations of pesticides at small farm scales. This chapter also demonstrates that local or nearby applications of pesticides is highly influential on pesticide air concentrations

and is the first study to correlate the estimated mass of pesticides in a nearby region with monitored pesticide concentrations in the air.

Chapter 4 shows good correlations were found between pesticide air concentrations and bulk depositions of pesticides and this is the first study to show that dry deposition of pesticides are significant contributors to total seasonal depositions of pesticides in Manitoba.

Chapter 4 was the first study to find significant correlations between the detected air concentrations and depositions of pesticides to estimates of the masses and physicochemical properties of pesticides applied. The masses of pesticide wet deposition were more strongly associated with the masses of pesticides applied in a 13-km radius surrounding the site than with the masses of pesticides applied in Manitoba as a whole; in contrast, the masses of pesticide dry deposition were more strongly associated with the masses of pesticides applied in Manitoba as a whole than with the masses of pesticides applied in a 13-km radius surrounding the site. Dry deposition followed similar trends to the air concentrations and total dry deposition shared similar correlations with the same physicochemical properties as the average air concentrations.

The research presented in Chapter 5 is the first study to provide direct evidence that atmospheric deposition of pesticides contribute a quantifiable amount to water

concentrations of prairie wetlands. On-farm pesticide applications have a greater impact on on-site water quality but regional pesticide applications can also contribute to pesticide surface water contamination following atmospheric entry, transport and deposition.

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