

**PESTICIDE RESIDUES IN GROUNDWATER AND SOIL OF A PRAIRIE
PROVINCE IN CANADA**

by

Kamala Sapkota

A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

In partial fulfilment of the requirements of the degree of

MASTER OF SCIENCE

Department of Soil Science

University of Manitoba

Winnipeg

Copyright © May, 2017

ABSTRACT

Sapkota, Kamala. M.Sc., The University of Manitoba, May 2017. Pesticide Residues in Groundwater and Soil of a Prairie Province in Canada. Professors: Claudia Sheedy & Annemieke Farenhorst

The study was conducted to monitor pesticide residues in groundwater of two agriculturally intensive regions of Alberta, to determine the occurrence of pesticide residues in soil and groundwater of an experimental plot in southern Alberta, and to investigate the influence of land management factors and soil depth on pesticide residues in soil. A total of 440 groundwater samples were collected in three years (2013-2015) and analyzed for the presence of 142 pesticides using Liquid-liquid Extraction (LLE) in combination with Gas Chromatography- Mass Selective Detector (GC-MSD) and Gas Chromatography - Tandem Mass Spectrometry (GC-MS/MS). Ten herbicides, seven insecticides, and six fungicides were detected. Herbicides 2,4-D, MCPA, and clopyralid were the most frequently detected, and the only pesticides consistently detected every year in both regions. Pesticides were detected more frequently in summer and fall compared to spring. 4.5% of the samples were contaminated with more than one pesticides. No pesticides exceeded the Guidelines for Canadian Drinking Water Quality. Similarly, a total of 213 groundwater samples (December 2014-November 2015) and 61 soil samples (in December 2014) in duplicates were analysed from the experimental plots in Lethbridge. Soil samples were collected at various depths (0-75 cm) and analyzed for the presence of 130 pesticides. A linear mixed effect model was fitted to determine the effect of soil depth, cropping systems and manure amendments on pesticide concentration in soil. In groundwater, bentazone, 2,4-D, and MCPA occurred most frequently and

pesticide detection frequency varied seasonally with greater detections in July and September compared to other months. 37 different pesticide compounds were detected, and DDT isomers, 2,4-D, difenoconazole, MCPA and trans-heptachlor epoxide accounted for 85% of all detections. p,p'-DDE, 2,4-D, p,p-DDT, difenoconazole and MCPA occurred throughout the soil column and all of these except p,p-DDT were detected in underlying groundwater. Bentazone was found in groundwater throughout the year but not in soil. A greater number and higher concentrations of pesticides were found in soil. However, not all of them leached to groundwater. Soil depth and cropping system were significantly associated with total pesticide and total DDT concentration in the soil. Manure amendments had no affect pesticide concentrations.

ACKNOWLEDGEMENTS

First, I would like to acknowledge Alberta Innovates - Energy and Environment Solutions (AI-EES) and the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding this research. I express my sincere appreciation and deep gratitude to my supervisors, Drs. Claudia Sheedy and Annemieke Farenhorst for their outstanding supervision, continuous encouragement, profound support throughout and during the completion of this thesis. I could not have asked for better supervisors than them. I am very thankful Dr. Benjamin Ellert for his supervision and insightful ideas during my stay at LeRDC and for being so kind to me. Also, I thank Dr. Genevieve Ali, for her constant willingness to help me whenever needed.

I feel so fortunate to have been able to work with awesome people like Denise Nilsson and Tara Vucurevich. A million thanks to both of them for helping me out, and creating friendly and family environment in the lab. My time in the lab went in a flash because of you. Special thanks to Lynda Miedema, Jacqueline Kohn and their team for groundwater sampling, data collection, and managing field visits. So many people helped me directly and indirectly during my research at AAFC, and I thank you all from the bottom of my heart. Four months in Winnipeg was truly amazing due to buddies like Geethani, Mauli, Mayowa, Theresa, Ahamed, and Vidura, so big thanks to them. I cannot remain without thanking Dr. Ross McQueen, Dr. Inoka D. Amarakoon, Dr. Francis Zvomuya (University of Manitoba) and Dr. Fabien Mavrot (University of Calgary) for their help in statistical analysis and GIS mapping. I would also like to thank Bikash Khatiwada, Monique

Dawson, Jessa Drury, Aiden Martindale, Scott Splengler, Melissa Fry and Moritz Haben for the technical support in the lab and field.

Finally, there are not enough words to thank my beloved husband Dr. Pratap Kafle for his infinite love and support during this venturesome journey. Thank you for keeping me on track when I could not keep myself on track. I must thank Pratima Kafle (Sister), Shree Dhakal (brother), Kashiram Kafle (father-in-law) and Chitra Kafle (mother-in-law) for encouraging me always. This journey would not have been possible without enormous moral support from my family here and back home. I thank my little girl Priscilla whose little kicks inside my belly, always motivated me to complete this thesis. Finally, I can never forget the ever-optimistic motivation from my brother-in-law Kashiram Khanal, who laid the foundation for my education and first inspired me to dream big, so thank you Venaju - I am here because of you. Last but not the least, mom Bishnudevi Sapkota, you are the inspiration of my life, so this is for you!

Thank you

Namaste!

Dedication

to my beloved mother, Mrs. Bishnudevi Sapkota, who continually supported me, and in
the memory of my father, Late Mr. Kaladhar Sapkota

TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iv
DEDICATION.....	vi
TABLE OF CONTENTS.....	vii
LIST OF TABLES	x
LIST OF FIGURES.....	xi
1. INTRODUCTION	1
1.1 History of pesticide use.....	1
1.2 Environmental fate of pesticide.....	2
1.3 Pesticide residues in soil and water.....	4
1.4 Groundwater and pesticide contamination.....	5
1.5 Research focus.....	7
1.6 Research objectives.....	9
1.7 References.....	10
2. PESTICIDE RESIDUES IN GROUNDWATER OF A PRAIRIE PROVINCE IN CANADA.....	17
2.1 Abstract.....	17
2.2 Introduction.....	18
2.3 Materials and methods.....	21
2.3.1 Chemicals and reagents.....	21

2.3.2 Site description.....	21
2.3.3 Sampling.....	22
2.3.4 Pesticides analyzed and percent recovery.....	24
2.3.5 Pesticide extraction and quantification.....	25
2.4 Results.....	26
2.5 Discussion.....	33
2.6 Conclusion.....	37
2.7 Acknowledgments.....	37
2.8 References.....	38

3. PESTICIDE RESIDUES IN SOIL AND GROUNDWATER OF A LONG TERM

CROP ROTATION SITE OF SOUTHERN ALBERTA.....	49
3.1 Abstract.....	49
3.2 Introduction.....	50
3.3 Materials and methods.....	52
3.3.1 Analytical reagents.....	52
3.3.2 Study site.....	53
3.3.3 Groundwater sampling and extraction.....	57
3.3.4 Soil sampling and extraction.....	58
3.3.5 Quantification of pesticides by GC-MS/MS.....	60
3.3.6 Statistical analysis.....	60
3.4 Results and discussions.....	61
3.5 Conclusion.....	75
3.6 Acknowledgements.....	76

3.7 References.....	77
4. OVERALL SYNTHESIS.....	86
4.1 Research summary.....	86
4.2 Practical implications.....	89
4.3 Recommendations for future studies.....	90
4.4 Final conclusions.....	92
4.5 References.....	93
APPENDICES.....	96
I. Pesticides included in the analytical suite of this study with their recovery percentages. Compounds 1 to 105 were included in all years. Compounds 106 to 142 were added to the analytical suite in 2015.....	96
II. Average % recoveries (%Relative Standard Deviation) of fortified pesticides included in the sand and soil samples for method validation using QuEChERS sample preparation, liquid-liquid extraction and GC-MS/MS analysis.....	106
III. Pesticide application history at Rotation U.....	113
IV. Pesticides detected in groundwater (sampled from December 2014 to November 2015) and soil (sampled in December 2014) of rotation u site, with their chemical group, detection frequencies (in soil, in groundwater), water solubility (mg/L, 20°C), soil organic carbon sorption coefficient (KOC), Half-life (in days), GUS, Leaching potential, Henry's constant and volatility.....	116

LIST OF TABLES

	Page
Table 2.1 Pesticide detections summarized by season, year, sampling area, the number of pesticides per sample (2013-2015) for 105 pesticides. Seasonal pesticide detections for 2015 is calculated for all 142 compounds. Seasonal pesticide detections were expressed as total pesticide detections per hundred samples.....	28
Table 2.2 Summary of pesticides detected in central and southern Alberta from 2013-2015 and their leaching potential and Canadian water quality guidelines.....	29
Table 3.1 List of soil properties along with number of samples analyzed from different soil depth, where gravimetric moisture content (%), soil pH, soil organic carbon and total carbon are expressed in average \pm coefficient of variation (CV%). Soil samples were collected in December 2014.....	56
Table 3.2 Detection frequency (DF), median, minimum, maximum and average \pm standard deviation of pesticide concentrations through soil depth.....	63

LIST OF FIGURES

	Page
Figure 2.1 Map showing the sampling regions of central (top) and southern (bottom) Alberta and the locations of sampling sites 1 to 5 (Map source: Lorenz et al. 2014).....	23
Figure 3.1 Layout of the experimental plots at the Rotation U site.....	55
Figure 3.2 Temporal variation in the maximum concentration ($\mu\text{g/L}$) of pesticides in groundwater at the Rotation U site at the Lethbridge Research and Development Centre, and total daily precipitation recorded during sampling period.....	67
Figure 3.3 Monthly variation in the detection frequencies of pesticide residues in shallow groundwater. Detection frequency represents the number of samples having at least one pesticide, divided by total number of samples analyzed, expressed as percentage. Total number of samples per month was 15-17.....	68
Figure 3.4 Detection frequencies of pesticides detected in groundwater at the experimental plots. Detection frequency is the proportion of samples contaminated with pesticide and total samples analyzed, expressed in percentage.....	69
Figure 3.5 Variation in 2,4-D and DDT concentration with soil depth.....	74

1. INTRODUCTION

Pesticides encompass a broad group of natural and synthetic compounds used to kill or suppress weeds, insects and other unwanted organisms harmful to crop, livestock, and human health. Pesticides are also applied to prevent spoilage during processing and storage of food and feed products. Pesticides are broadly classified per their target organism, the most common classes of pesticides being herbicides - used against weeds; insecticides - used to kill harmful insects; and fungicides - used against fungal infestations. Other categories of pesticides exist, including acaricides, rodenticides, defoliants, desiccants and growth regulators.

1.1 History of pesticide use

Pesticide use has a long history. Examples date as far back as 4,500 years ago, when Sumerians used sulfur-containing compounds against mites and insects. About 3,200 years ago, mercury and arsenic compounds were used to control body lice in Chinese civilizations. For several thousands of years, various plant and animal extracts, as well as smoke, were used as bio-insecticides in some regions of the world (Unsworth, 2010). This includes pyrethrum, a plant derived insecticide, used for over 2,000 years by Persians to protect stored grains considerably earlier than in Europe (McLaughlin, 1973). The development of synthetic pesticides, such as organochlorines, accelerated during the second world war due to the imminent need to protect soldiers and citizens from potential outbreaks of malaria and yellow fever (Edmund, 1999). From the 1940s until the 1970s, the use of organochlorines, including DDT (dichlorodiphenyltrichloroethane), in

agriculture rapidly expanded, and numerous ecological and health hazards were widely publicized by Carson (1962) and led to their elimination from domestic use in North America in the 1970s (Sibbald 2002). Numerous other synthetic organic pesticides have been and are being developed since the 1940s.

Health Canada's Pest Management Regulatory Agency (PMRA) regulates the use of pesticides in Canada (Health Canada 2009). At present, over 6,800 different pesticide products are registered for use in Canada, among which as many as 2,638 pesticide products were reportedly used in 2014 (Health Canada 2014). Over 101 million kg active ingredients of pesticides were sold in Canada in 2014 (Health Canada 2014). In the province of Alberta (where this thesis research was conducted) about 15 million kg of pesticide active ingredients were sold in 2013, of which about 95% was sold to the agriculture sector (Alberta Environment and Parks, 2015). Herbicides are the dominant group of pesticides used in Alberta, as well as in Canada, with 2,4-D, glyphosate, and MCPA being among the most commonly used herbicides (Environment Canada 2011; AEP 2015). Insecticides and fungicides account for most of the other pesticides sales in Alberta and Canada.

1.2 Environmental fate of pesticides

Enormous benefits have been derived from the use of pesticides in agriculture (Aktar et al. 2009). Among others, yield losses due to pests and diseases have been substantially reduced. Pesticides are therefore an integral part of today's agricultural operations (Gill and Garg 2014). Despite the benefits, widespread use of pesticides has led to environmental contamination.

When pesticides are applied, they can be taken up by plants and animals; they can volatilize to the atmosphere; be degraded (hydrolysis, photolysis, chemical and microbial degradation); they can be carried to surface water through runoff, remain adsorbed to soil and/or leach to groundwater. These processes are dependent on the physicochemical properties of the pesticides, the receiving soil as well as prevailing environmental conditions (Gavrilescu 2005). For example, pesticides like aldrin, dieldrin, DDT, and heptachlor are considered highly persistent because of their ability to resist photolytic, chemical and biological degradation at varying degrees. The soil sorption coefficient (K_{oc}) is one of the major factors determining the fate and eventual degradation of any chemical compound in the environment. It is the measure of a given pesticide's tendency to bind to soil, and it is influenced by soil type, pesticide physicochemical properties, soil moisture, soil pH, soil organic matter as well as the kind of pesticide formulation (Kerle et al. 2007). Pesticides can persist in soil for some time, and move to greater depths with soil water through a process called leaching. Factors governing pesticide leaching include their physicochemical properties (water solubility, adsorption, persistence), soil properties (organic matter content, texture), hydrogeological conditions, management practices (pesticide application rates and methods, irrigation) and climate (Arias-Estévez et al. 2008; Buttler et al. 1998; Tiriyaki and Temur 2010). The rate and extent of pesticide leaching to groundwater is also correlated with the amount of precipitation, snowmelt, and irrigation (Leistra and Boesten 2010). Leaching potential of a pesticide strongly depends on how strongly the pesticide sorbs to soil: weakly-sorbed pesticides such as 2,4-D and MCPA typically have a strong leaching potential (Hiller et al. 2006). Compounds strongly adsorbed to soil coupled with low water solubilities such as DDT and heptachlor

do not readily leach to groundwater (Miglioranza et al. 1999). However, even these hydrophobic compounds with strong sorption to soil can contaminate groundwater if rain occurs shortly after application through a process referred to as preferential flow (Elliott et al. 2000). Thus, all these factors determine a pesticide's fate in the environment and should be considered to minimize residues in the environment.

1.3 Pesticide residues in soil and water

Pesticide residues are present in the environment at various concentrations. These compounds can adversely impact human, wildlife and ecosystem health (Goulson 2013; Hernández et al. 2013; Gibbons et al. 2015). Long-term and frequent application of pesticides can potentially cause significant irreversible damage to the soil microbiota including nitrification bacteria and symbiotic mycorrhizal fungi which are essential for the maintenance of soil ecosystems by transforming and mineralizing organic matter and making nutrients available for plants (Gill and Garg 2014). Soil microorganisms can also contribute to pollutants and pesticides detoxification; thus, their loss can have a significant impact on the functioning of the terrestrial ecosystem (Sanchez-Bayo et al. 2011). If present at high concentrations in drinking water, pesticide residues can adversely affect human health when consumed (Agrawal et al. 2010). Research has found that the risk of Parkinson disease increases by 3% for every 1µg/L pesticide in groundwater (James and Hall 2015). Farm animals' exposure to different types of pesticides and doses through feed and the ensuing carry-over effects in animal products have been previously studied (Kan and Meijer 2007). Similarly, pesticide residues in irrigation water can also damage crops and plants. For example, MCPA in irrigation

water is toxic to legumes and can cause yield reductions, mortality in cereals, pastures and rangeland crops (Canadian Council of Ministers of the Environment, 2001).

1.4 Groundwater and pesticide contamination

Groundwater is the water beneath the earth's surface. It is found in cracks and spaces of soil, sand, and rock. Groundwater is recharged by surface water as well as infiltration of precipitation and ultimately flows back to surface in the form of rivers, seeps, wetlands, etc. Groundwater constitutes almost 90% of world's freshwater and is a vital source of freshwater for approximately 20% of the global population (Diop et al. 2002). Nearly 60% of withdrawn groundwater is used in agriculture, while the remainder is used in the industrial and domestic sectors (Vrba and van der Gun 2004). In North America, groundwater remains the primary source of freshwater. In Canada, approximately 30% of the population depends on groundwater for water supply, and 23% of Albertans rely on this resource for domestic use (Côté 2006). The government of Alberta estimates that more than 600,000 rural Albertans use groundwater for drinking purposes (AEP 2016). In Alberta, 16.9 % of groundwater is allocated for agricultural operations, 0.4% of which is used for irrigation (unlike other provinces where groundwater constitutes a significant portion of irrigation water). Livestock watering is one of the major agricultural uses of groundwater in Alberta (Rutherford 2004).

Groundwater is one of the most valuable natural resources. Although it is considered less vulnerable to pollution than surface water, pesticide residues are detected in groundwater worldwide (Toccalino et al. 2014; Jurado et al. 2012; Singh et al. 2005). Groundwater is a significant but often unrecognized natural resource and receives less attention compared to

surface water due to the inadequate understanding of its role when environmental planning, assessment, and protection is conducted (Daly 2009). In Canada, pesticide residues have been detected in groundwater of all provinces (Environment Canada 2011). In Alberta, studies have shown that groundwater is contaminated by a wide variety of pesticides. Miller et al. (1995a) detected hexazinone in 27% of groundwater samples in Lethbridge, AB. In the same study, 2,4-D and bromoxynil were reported in 48% and 34% of groundwater samples respectively from Taber, AB. Dicamba, mecoprop, MCPA, and diclofop were also detected in 9 to 21% of those groundwater samples (Miller et al. 1995a). Similarly, Miller et al. (1995b) found residues of bromoxynil, diclofop and MCPA in groundwater sampled at a manured site near Lethbridge, AB where bromoxynil and diclofop concentrations exceeded the Canadian Water Quality Guidelines. Rodvang et al. (2001) detected herbicides in groundwater samples from eight piezometers of Battersea Drain area (southern Alberta), and the herbicide dicamba concentrations exceeded the Canadian guideline for irrigation water. Hill et al. (1996) detected 2,4-D, bromoxynil, diclofop, MCPA and triallate in 17 to 61% of groundwater wells sampled in a three-year (1991-1993) study at Lethbridge. The study also revealed that herbicide concentrations were higher when rainfall or irrigation was heavy shortly after pesticide application, while pesticide concentrations were lower even after a heavy rain if gentle rain and drying occurred immediately after application (Hill et al. 1996). Previous studies that examined pesticide residues in groundwater of Alberta were limited to only a few pesticides (e.g., Hill et al.(1996) and Miller et al. (1995a) included only seven herbicides in their studies). A much broader analytic suite is necessary to have a better understanding of the types of pesticide residues present in groundwater, considering the current diversity of pesticide active ingredients in use across the province. The advances in analytic capabilities and

sample preparation techniques like QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) and solid-phase extraction using various sorbent materials, gas chromatography and tandem mass spectrometry (GC/MSMS), liquid chromatography and tandem mass spectrometry (LC/MSMS), on/in-line mode of extractions enabling sensitive detections with small sample volumes, have all contributed to the expansion of pesticide monitoring. Consequently, a large number of pesticides can be monitored at any given time (Masiá et al. 2014; Wen et al. 2014; Vázquez et al. 2016).

1.5 Research focus

This M.Sc. research is a part of a larger groundwater monitoring program undertaken in 2008 and administered by Alberta Agriculture and Forestry (formerly Alberta Agriculture and Rural Development) to assess the overall groundwater quality in Alberta. Additional stakeholders and participants in the program included crop and livestock producers in the study areas, and the Natural Resources Conservation Board, Alberta Irrigation Projects Association, Alberta Environment and Parks (formerly Alberta Environment and Sustainable Resources Development), Agriculture and Agri-Food Canada, the University of Alberta, the University of Saskatchewan and the University of Manitoba. The study sites consisted of two distinct regions of Alberta: Lacombe-Ponoka (central Alberta) and Battersea Drain area (southern Alberta). Also, this M.Sc. research included soil and groundwater sampling at long-term experimental plots (known as Rotation U site) located in a field adjacent to the Lethbridge Research and Development Centre in southern Alberta.

Lacombe-Ponoka (central Alberta)

The Lacombe-Ponoka lies slightly north of Red Deer and approximately 125 km south of Edmonton in Central Alberta. This area represents a mixed-grain agricultural production system typical of the Canadian Prairies. Groundwater is a primary source of drinking water for the residents in the area (Nowlan 2007; Alberta Wilderness Association 2016). The Lacombe-Ponoka region receives an annual precipitation of about 486 mm (average of 1981-2010) and has a mean annual temperature of $3.7 \pm 1.1^{\circ}\text{C}$ (Environment Canada 2016). Irrigation is uncommon, and crops are rain-fed. The specific sampling sites in this region were distributed among three locations (sites 1, 2 and 3) and included a total of 23 groundwater wells, 12 piezometers. Wells and piezometers depth for all sites varied from 2 to 30 m.

Battersea drain area (southern Alberta)

The Battersea drain area is located approximately 25 km north of Lethbridge and is delimited by the Oldman River (south), the Little Bow River (east) and the town of Picture Butte (west) in southern Alberta. Intensive livestock operations and associated cropping activities for feeding animals are common in this area (Turchenek 2014). Crops are dominantly barley, alfalfa and corn (Rodvang et al. 2004). The groundwater is not used as a source of drinking water; communities rather rely on the city of Lethbridge treated water sourced from the Oldman river for human consumption (City of Lethbridge 2017). The region is semi-arid, with an annual precipitation of about 380 mm (average of 1981-2010) and mean annual temperature of $5.9 \pm 1.1^{\circ}\text{C}$ (Environment Canada 2016). This area is part of the Lethbridge Northern Irrigation District (LNID), and approximately 70% of the Battersea watershed is irrigated (Turchenek 2014). This study involved

groundwater sampling at 31 locations including 15 water table wells (WTWs) and 16 piezometers with a depth varying from 2 to 20 m.

Rotation U

Rotation U is a long-term experimental crop rotation site of 9.7 acres, located at the Lethbridge Research and Development Centre, in Lethbridge, Alberta, Canada. Fourteen shallow WTWs and three piezometers were sampled at Rotation U. The piezometer depths were of 3.05 m, 6.1 m and 9.14 m and all were located north of the field. Twelve wells were located inside the field, representing two rotations, three replicate plots (blocks), one fertilizer rate and two manure rates. The other two wells were large-diameter wells located immediately north and west of the field. There were two cropping systems: corn-based: corn-wheat-corn-wheat-barley and alfalfa-based: alfalfa-alfalfa-alfalfa-wheat-barley. A single application rate of fertilizer (33 tons/hectare/year phosphorus) and two manure application rates (control and 33.5 tons/hectare/five-year) were used. Sampling at Rotation U was added to this research project because I had access to data (pesticides use, crops grown and soil properties), which allowed me to examine the impact(s) such factors have on pesticide fate and transport to groundwater.

1.6 Research objectives

The overall aim of this M.Sc. research project was to determine the concentrations of historical and current-use pesticides in soil and groundwater samples collected at selected sites in Alberta to better understand their spatial and temporal occurrence patterns in groundwater and soil. The first study, described in chapter 2, investigated the spatial and

temporal variation of pesticide residues in groundwater across central and southern Alberta over three years (2013-2015). This study was undertaken to understand the types and concentrations of pesticide residues in groundwater of non-irrigated (central Alberta) and irrigated (southern Alberta) agricultural systems. The study contributed to the overall groundwater quality assessment project led by Alberta Agriculture and Forestry. In a second study, described in chapter 3, the primary objectives were to monitor pesticide residues throughout the year and investigate the impact of various agricultural practices on pesticide occurrence in soil. Pesticide residues were monitored in shallow groundwater collected on a monthly basis for one year (December 2014-November 2015). Pesticide residues in soil samples collected adjacent to the wells were determined, and the potential influence of factors like soil depth, land use practices (manure treatment, cropping system) on the occurrence of pesticide residues was investigated. Collectively, this thesis will contribute to the existing body of knowledge on pesticide residues in groundwater and factors affecting the distribution of pesticides in the soil column.

1.7 References

- Agrawal, A., Pandey, R. S., & Sharma, B. 2010.** Water pollution with special reference to pesticide contamination in India. *Journal of Water Resource and Protection* **2 (5)**: 432.
- Aktar, W., Sengupta, D. and Chowdhury, A. 2009.** Impact of pesticides use in agriculture: their benefits and hazards. *Interdisciplinary toxicology* **2 (1)**: 1-12.

Alberta Environment and Parks (AEP). 2015. Overview of 2013 Pesticide Sales in Alberta. Land Policy Branch. Edmonton, AB. 80 pp.

Alberta Environment and Parks (AEP). 2016. Accessed: January 31 2017. Available at: <http://aep.alberta.ca/water/programs-and-services/groundwater/default.aspx> Accessed on: January 31 2017.

Alberta Wilderness Association. 2016. Available at :
<https://albertawilderness.ca/issues/wildwater/groundwater/>.

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C. and García-Río, L. 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, ecosystems & environment* **123 (4)**: 247-260.

Buttler, T. M., Martinkovic, W. and Nesheim, O. N. 1998. Factors influencing pesticide movement to ground water. University of Florida Cooperative Extension Service, Institute of Food and Agriculture Sciences, EDIS.

Canadian Council of Ministers of the Environment (CCME). 2001. Canadian water quality guidelines for the protection of agricultural water uses: MCPA. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Carson, R. 1962. Silent spring. New York, NY. Houghton Mifflin Harcourt.

City of Lethbridge. 2017. Accessed: January 30, 2017. Available at:
<http://www.lethbridge.ca/living-here/water-wastewater/Pages/Water.aspx>.

- Côté, F. 2006.** Freshwater Management in Canada: IV. Groundwater, Library of Parliament. [http://www. parl. gc. ca/information/libra ry/PRBpubs/prb0554-e. html](http://www.parl.gc.ca/information/library/PRBpubs/prb0554-e.html).
- Daly, D. 2009.** Groundwater – The ‘Hidden Resource’, Biology and Environment. Proceedings on the Royal Irish Academy **109B**: 221-236
- Diop, S., M'mayi, P., Lisbjerg, D. and Johnstone, R. 2002.** Vital water graphics: an overview of the state of the world's fresh and marine waters, UNEP/Earthprint.
- Edmund, R. 1999.** The strange career of DDT: Experts, federal capacity, and environmentalism in World War II. Technology and Culture **40(4)**: pp.770-796.
- Elliott, J.A., Cesna, A.J., Best, K.B., Nicholaichuk, W., Tollefson, L.C., 2000.** Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. J. Environ. Qual. **29**: 1650–1656.
- Environment Canada 2011.** Presence and levels of priority pesticides in selected Canadian aquatic ecosystems. Water Science and Technology Directorate. 8pp.
- Environment Canada. 2016.** Canadian climate normals 1981–2010. National Climate Data and Information Archive. Accessed: July 20, 2016. Available in: http://climate.weatheroffice.gc.ca/climate_normals/index_e.html.
- Gavrilescu, M. 2005.** Fate of pesticides in the environment and its bioremediation. Engineering in Life Sciences **5 (6)**: 497.
- Gibbons, D., Morrissey, C. and Mineau, P. 2015.** A review of the direct and indirect effects of neonicotinoids and fipronil on vertebrate wildlife. Environmental Science and Pollution Research **22 (1)**: 103-118.

- Gill, H. K. and Garg, H. 2014.** Pesticides: environmental impacts and management strategies. Pesticides—toxic aspects. InTech: 188-230.
- Goulson, D. 2013.** Review: An overview of the environmental risks posed by neonicotinoid insecticides. *Journal of Applied Ecology* **50** (4): 977-987.
- Health Canada. 2009.** Available at: <http://www.hc-sc.gc.ca/ahc-asc/branch-dirigen/pmra-arla/index-eng.php>
- Health Canada. 2014.** Pest Control Products Sales Report for 2014.
- Hernández, A. F., Parrón, T., Tsatsakis, A. M., Requena, M., Alarcón, R. and López-Guarnido, O. 2013.** Toxic effects of pesticide mixtures at a molecular level: their relevance to human health. *Toxicology* **307**: 136-145.
- Hill, B., Miller, J., Chang, C. and Rodvang, S. 1996.** Seasonal variation in herbicide levels detected in shallow Alberta groundwater. *Journal of Environmental Science & Health Part B* **31** (4): 883-900.
- Hiller, E., Khun, M., Zemanová, L., Jurkovic, L. and Bartal, M. 2006.** Laboratory study of retention and release of weak acid herbicide MCPA by soils and sediments and leaching potential of MCPA. *Plant Soil and Environment* **52** (12): 550.
- James, K. A., & Hall, D. A. 2015.** Groundwater pesticide levels and the association with Parkinson disease. *International journal of toxicology*, **34** (3): 266-273.
- Jurado, A., Vázquez-Suñé, E., Carrera, J., de Alda, M. L., Pujades, E., and Barceló, D. 2012.** Emerging organic contaminants in groundwater in Spain: a review of sources,

recent occurrence and fate in a European context. *Science of the total environment* **440**: 82-94.

Kan, C. A., & Meijer, G. A. L. 2007. The risk of contamination of food with toxic substances present in animal feed. *Animal feed science and technology*, **133 (1)**: 84-108.

Kerle, E. A., Jenkins, J. J., & Vogue, P. A. 2007. Understanding pesticide persistence and mobility for groundwater and surface protection (<http://extension.oregonstate.edu/catalog/html/em/em8561-e/>, verified 05/2010). Extension Service, Oregon State University.

Leistra, M. and Boesten, J. J. 2010. Pesticide leaching from agricultural fields with ridges and furrows. *Water, Air, & Soil Pollution* **213 (1-4)**: 341-352.

Masiá, A., Blasco, C. and Picó, Y. 2014. Last trends in pesticide residue determination by liquid chromatography–mass spectrometry. *Trends in Environmental Analytical Chemistry* **2**: 11-24.

McLaughlin, G. A. 1973. History of pyrethrum. *Pyrethrum: The Natural Insecticide*, 1-15.

Miglioranza, K. S. B., de Moreno, J. A., Moreno, V. J., Osterrieth, M. L., & Escalante, A. H. 1999. Fate of organochlorine pesticides in soils and terrestrial biota of “Los Padres” pond watershed, Argentina. *Environmental pollution*, **105 (1)**: 91-99.

Miller, J., Foroud, N., Hill, B. and Lindwall, C. 1995a. Short Communication: Herbicides in surface runoff and groundwater under surface irrigation in southern Alberta. *Canadian Journal of Soil Science* **75 (1)**: 145-148.

Miller, J., Hill, B., Chang, C. and Lindwall, C. 1995b. Residue detections in soil and shallow groundwater after long-term herbicide applications in southern Alberta. Canadian Journal of Soil Science **75 (3)**: 349-356.

Nowlan, L. 2007. Out of sight, out of mind? Taking Canada's groundwater for granted. In Eau Canada: The Future of Canada's Water. UBC Press. Vancouver, British Columbia. 55–83

Rodvang, J., Ryan, C., Zilkey, M., Dash, T. and Hill, B. 2001. Protecting groundwater in irrigated areas of Southern Alberta. Western Canada Agronomy Workshop.

Rodvang, S., Mikalson, D. and Ryan, M. 2004. Changes in ground water quality in an irrigated area of southern Alberta. Journal of Environmental Quality **33 (2)**: 476-487.

Rutherford, S. 2004. Groundwater use in Canada, West Coast Environmental Law.

Safe use of pesticide around home, Pennstate extension. Available at:

<http://extension.psu.edu/pests/pesticide-education/applicators/fact-sheets/pesticide-safety/safe-use-of-pesticides-around-the-home>

Sánchez-Bayo, F. 2011. Impacts of Agricultural Pesticides on Terrestrial Ecosystems". Ecological Impacts of Toxic Chemicals 2011: 63 – 87.

Sibbald, B. 2002. DDT use finally eliminated in North America. Canadian Medical Association Journal, **166 (10)**: 1322-1322.

Singh, K. P., Malik, A., Mohan, D., & Sinha, S. 2005. Persistent organochlorine pesticide residues in alluvial groundwater aquifers of Gangetic plains, India. Bulletin of environmental contamination and toxicology **74 (1)**:162-169.

- Tiryaki, O. and Temur, C. 2010.** The fate of pesticide in the environment. *Journal of Biological and Environmental Sciences* **4(10)**.
- Toccalino, P. L., Gilliom, R. J., Lindsey, B. D., & Rupert, M. G. 2014.** Pesticides in Groundwater of the United States: Decadal-Scale Changes, 1993–2011. *Groundwater*, **52 (S1)**: 112-125.
- Turchenek, J. 2014.** Defining the distribution, source, fate and transport of nitrate in groundwater beneath an agriculturally intensive region using high-resolution profiling methods. Master's thesis. University of Saskatchewan Saskatoon.
- Unsworth, J. 2010.** History of pesticide use. International union of pure and applied chemistry. Available at:
http://agrochemicals.iupac.org/index.php?option=com_sobi2&sobi2Task=sobi2Details&catid=3&sobi2Id=31
- Vázquez, P. P., Hakme, E., Uclés, S., Cutillas, V., Galera, M. M., Mughari, A. and Fernández-Alba, A. 2016.** Large multiresidue analysis of pesticides in edible vegetable oils by using efficient solid-phase extraction sorbents based on quick, easy, cheap, effective, rugged and safe methodology followed by gas chromatography–tandem mass spectrometry. *Journal of Chromatography A* **1463**: 20-31.
- Vrba, J. and van der Gun, J. 2004.** The world's groundwater resources. International Groundwater Resources Assessment Centre, Utrecht.
- Wen, Y., Chen, L., Li, J., Liu, D. and Chen, L. 2014.** Recent advances in solid-phase sorbents for sample preparation prior to chromatographic analysis. *TRAC Trends in Analytical Chemistry* **59**: 26-41.

2. PESTICIDE RESIDUES IN GROUNDWATER OF A PRAIRIE PROVINCE IN CANADA

2.1 Abstract

This three-year study examined the seasonal occurrence of pesticide residues in groundwater of central (Lacombe-Ponoka) and southern (Picture Butte) Alberta, two regions of Canada with intensive agriculture and livestock production. Four hundred and forty groundwater samples were collected from 38 water table wells and 28 piezometers (1.8 to 20 m depth). The analytical suite included 105 herbicides, insecticides, fungicides, and other pesticides in 2013 and 2014, and 142 pesticides in 2015. Out of the 131 positive detections above the detection level of 0.025µg/L, ~82% were herbicides; ~11% were fungicides, and ~8% were insecticides, with < 4% (5 detections) of the compounds being legacy pesticides (deregistered). Ten herbicides, seven insecticides and six fungicides were detected. Most samples contained a single pesticide with 11.2% (n=125), 16.1% (n=155) and 29.4% (n=160) of the samples in 2013, 2014 and 2015 respectively. Pesticide mixtures were only detected in 4.5% of total samples. When all data were considered, the pesticide detections per hundred samples were generally greater in summer (35.2, n=159) and fall (35.1, n=145) than in spring (17.6, n=136). However, the spring showed greater detections than other seasons in southern Alberta in 2013 and in central Alberta in 2014. In all three summers, the pesticide detections were greater in southern Alberta where irrigation practices on coarse to fine-textured soils are a common component of agricultural production, relative to central Alberta which is a predominantly non-irrigated region with fine textured soils. However, there was no apparent consistent difference between regions in the spring or fall. Herbicides 2,4-D,

MCPA, and clopyralid were the most frequently detected pesticides and the only pesticides consistently detected every year in both regions. The concentrations of herbicides MCPA, dicamba and simazine always exceeded their individual thresholds for the Protection of Agricultural Water Uses under the Canadian Water Quality Guidelines. Ten out of the twenty-three pesticides detected in this study have set Canadian Guidelines for Drinking Water Quality and at no time did their detected concentrations surpassed their individual thresholds. The Albertan population relying on potable groundwater sources is at low risk based on these guidelines, and based on the more conservative drinking water quality guidelines set by the European Union, a small portion of the samples in this study exceeded the 0.1 µg/l (~6% of total samples) and 0.5 µg/l (1.1% of total samples) thresholds for individual and total pesticides, respectively.

2.2 Introduction

Pesticides are chemical compounds widely used in agriculture for protecting crops and livestock from harmful weeds, insects, and pathogens. They are also commonly applied for controlling pests in non-agricultural settings (e.g., forestry, lawn care). There is evidence that this widespread use of pesticides has resulted in environmental contamination (Donald et al. 2007; Messing et al. 2012; Main et al. 2014; Pose-Juan et al. 2015; Abdallah and Abdel-Halim 2016; Ccancapa et al. 2016). Groundwater and surface waters within or near intensive agricultural regions are particularly vulnerable to pesticides contamination (Goss et al. 1998; Hildebrandt et al. 2008; Vryzas et al. 2009; Saha and Alam 2014). The presence of pesticides in water resources can have adverse effects on flora and fauna (Palma et al. 2014; Tiam et al. 2014; Morrissey et al. 2015;

Vassiliou 2016) as well as on humans (Soto et al. 1994; Hernández et al. 2013; Mesnage et al. 2014; Parrón et al. 2014; James and Hall 2015). Thus, the presence of pesticides in water is believed to result in significant socio-economic and environmental costs (Dearmont et al. 1998; Pimentel 2005; Bourguet and Guillemaud 2016).

In Canada alone, about 500 pesticide active ingredients in the form of about 7,000 pesticide products are in use (Brimble et al. 2005; Yao et al. 2006) with 109 million kg of pesticide active ingredients sold in 2013 (Health Canada 2013). In the Province of Alberta, where our study was conducted, 15.2 million kg active ingredients were sold in 2013, predominantly for agricultural applications (>95%), of which herbicides represented about 87% of the total sales (AEP 2015). More than 80% of farmland in Canada is in the Prairie Provinces including Alberta, Saskatchewan, and Manitoba. These provinces have similar agricultural production systems and pesticide use patterns, but Alberta is the province with the largest irrigation infrastructure (Statistics Canada 2013).

After application, pesticides can reach their target organisms, break down into degradation products, be retained by soil, or move to off-target sites including surface and ground water (Tiryaki and Temur, 2010; Keesstra et al. 2012; Edwards et al. 2016).

Groundwater is a valuable natural resource in Canada with a quarter of the total population depending on groundwater for potable water, including in the Province of Alberta (Environment and Climate Change Canada 2013). About two decades ago, two studies reported on the widespread occurrence of pesticide residues in shallow groundwater of Alberta and pesticide levels exceeding the Canadian Water Quality Guidelines (CWQG) for drinking water set for some pesticides (Miller et al. 1995a; Hill et al. 1996). The lack of recent studies, limited scope and analytical suite of previous

studies highlight the need for a more current investigation of the occurrence of pesticides in Alberta's groundwater.

Pesticides typically enter groundwater by moving through the soil profile and, collectively, studies have demonstrated that the concentrations of pesticides in groundwater can be influenced by climatic (Nolan et al. 2008; McGrath et al. 2010; Larsbo et al. 2014; Steffens et al. 2014) and hydrogeological (Baran et al. 2008; Aisopou et al. 2015) factors, as well as land management decisions (Cessna and Elliott 2004; Fait et al. 2010; Aisopou et al. 2015) and the physio-chemical properties of the pesticides applied (Mackay et al. 2006; Larsbo et al. 2014). Together, these factors bring spatial and temporal heterogeneity in pesticide residue levels detected in soil and groundwater, and no two sites are the same (Ccanccapa et al. 2016). Pesticides in groundwater have residence times ranging from weeks to decades depending on the geochemical and geobiological conditions of the groundwater in which the pesticides reside, and the rate at which the pesticides move and are transformed given their physio-chemical properties (Jablonowski et al 2011; Toccalino et al 2014).

The objective of this three-year study was to examine the seasonal occurrence of pesticides in groundwater of irrigated and non-irrigated agricultural region of Alberta. The irrigated region is in southern Alberta and dominated by sandy loam to clay soils whereas the non-irrigated region is in central Alberta and dominated by clay loam soils.

2.3 Materials and methods

2.3.1 Chemicals and reagents

Pesticide standards were purchased from Chem Service Inc. (West Chester, PA, USA) with an average purity of 98.7%. HPLC-grade dichloromethane (DCM), acetone, *n*-Hexane, toluene and ethyl ether were purchased from VWR® (Mississauga, ON, Canada). Ultra-high quality water was obtained through Milli-Q water purification system purchased from EMD Millipore (Etobicoke, ON, Canada). Anhydrous sodium sulfate was purchased from Sigma-Aldrich (St. Louis, MO, USA) and was acidified in the laboratory. Diazomethane used in methylation was prepared in the laboratory by dissolving 7.6 g of hydrogen peroxide in 7.6 ml of milliQ water and adding 83 ml of ethyl ether and 5 g of *n*-methyl-nitrosoguanidine.

2.3.2 Site description

Groundwater samples were collected in central Alberta near Lacombe-Ponoka which is located 25 km North of Red Deer (52°28' N, 113°44' W) and in southern Alberta near Picture Butte which is located 27 km North-East of Lethbridge (49° 52' N, 112° 46' W). Agricultural land use in both regions includes cereal (wheat, barley, oat, corn) production, oilseeds (canola, mustard) and alfalfa, as well as livestock operations dominated by beef cattle and dairy (AAF 2009). The central region is characterized by clay soils in which crops are typically grown without irrigation, with an annual precipitation of 486 mm (1981-2010 mean) and mean annual temperature of 3.7±1.1°C (Environment Canada 2016). The majority of the rural population in this region utilizes groundwater as a

potable water source (J. Kohn Pers. Comm., August 2015). The southern region is characterized by sandy loam to clay soils, and irrigation is typically applied to crops given an annual precipitation of 380 mm (1981-2010 mean) and mean annual temperature of $5.9 \pm 1.1^{\circ}\text{C}$ (Environment Canada 2016). People in this region relies on surface water (rather than groundwater) for potable water (City of Lethbridge 2017).

2.3.3 Sampling

A total of 440 groundwater samples were collected in spring (May/June), summer (July/August) and fall (Sept/Oct) of 2013 to 2015, inclusively, with the exception that central Alberta was not sampled in spring 2013. In central Alberta, sampling was done from 12 piezometers, 23 water table wells (WTWs) and one dugout across sites -1, 2 and 3 (Figure 2.1). In southern Alberta, 16 piezometers and 15 WTWs were sampled, across two sites (sites -4, 5) (Figure 2.1). WTW and piezometer depths ranged from 1.8 to 20 m, with WTWs on average shallower than piezometers with a mean (\pm standard deviation) depth of 4.88 ± 2.2 m (southern Alberta) and 6.54 ± 0.8 m (central Alberta) for WTWs and 11.57 ± 5.1 m (southern Alberta) and 15.08 ± 3.6 m (central Alberta) for piezometers. Purging, to remove standing water in the wells and piezometers, was done using a Waterra Pump (Waterra Power Pump II, Rice Engineering, Edmonton, Canada) and a polyethylene bailing tube (Single Sample® Bailers, Rice Engineering, Edmonton, Canada) a few days or up to two weeks prior to groundwater sampling. Recharge rate affected the number of WTWs and piezometers sampled in each of the three seasonal sampling rounds and across the three years. Groundwater was collected in an amber glass bottle (1L) using the polyethylene bailing tube. Samples were transported to the

laboratory in ice-packed coolers and stored in the fridge (4°C) until processed. All the samples were extracted within seven days following collection.

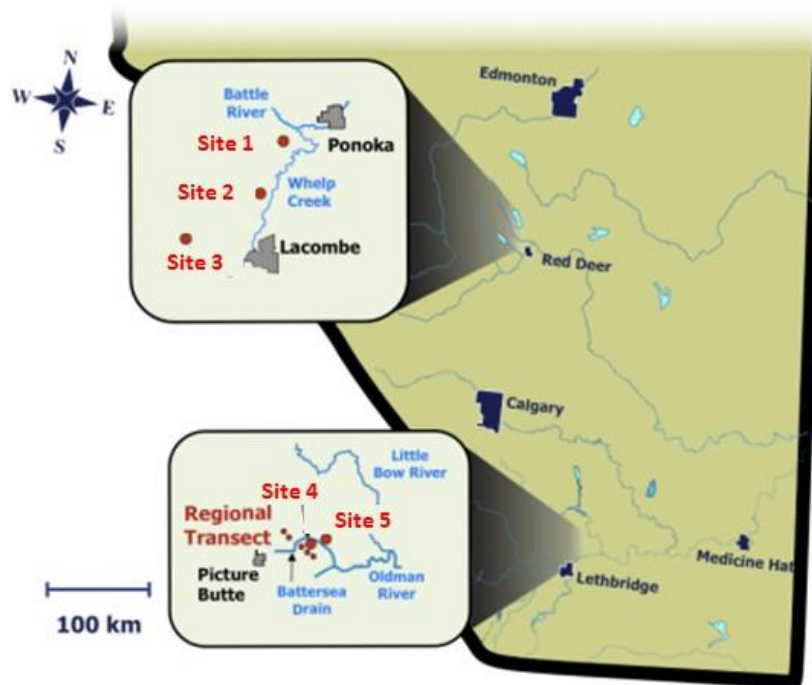


Figure 2.1 Map showing the sampling regions of central (top) and southern (bottom) Alberta and the locations of sampling sites 1 to 5 (Map source: Lorenz et al. 2014).

2.3.4 Pesticides analyzed and percent recovery

The analytical suite in 2013 and 2014 consisted of 105 pesticide active ingredients (47 herbicides, 45 insecticides, eight fungicides, three acaricides, a bactericide and a nematicide). Twelve herbicides, ten insecticides, 14 fungicides and an insecticide synergist were added to the analytical suite in 2015, increasing the total to 142 compounds. The analytical suite (Appendix I) included most of the historical and current used pesticides in Alberta, including current-use herbicides that were previously detected in surface drinking water and groundwater in Alberta such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), bromoxynil, clopyralid and dicamba (Hill et al. 1996; Donald et al. 2007).

Pesticide stock solutions were prepared in acetone, toluene or dichloromethane (DCM) at low (0.005-0.282 $\mu\text{g/mL}$) and high (0.026-1.41 $\mu\text{g/mL}$) concentrations. Aliquots (10 mL) of stock solutions were pipetted into a 250mL round bottom flask and maintained at a pH of 2 by adding 50 μL of 0.45M sulphuric acid, followed by methylation with diazomethane (2 mL), neutralization with n-hexane (40 mL) and concentration by rotary evaporator to determine the pesticide concentrations in the stock solution. Concentrations in the calibration standard varied by pesticide because the limit of detection (LOD) for each pesticide in our analytical suite varies. For determining the percent recovery of each compound (Appendix I), aliquots (10 mL) of stock solutions were pipetted into 1 L of MilliQ water and extracted and quantified as described below. The percent recovery was calculated by dividing the pesticide concentration obtained in the MilliQ water spiked samples by the pesticide concentration obtained using the stock solution and multiplying by 100.

2.3.5 Pesticide extraction and quantification

Groundwater and MilliQ water (blank) samples were filtered through glass wool and transferred into separatory funnels (2 L) for liquid-liquid extraction following previously published procedures (Bruns et al. 1991; Hill et al. 2002). Sample bottles were rinsed once with 30 mL acetone, which was also added to the separatory funnel. Each sample was extracted three times using 100, 100 and 50 mL of DCM. Sulphuric acid (30 drops, approximately 1.5 mL) was added once (after first DCM addition) to acidify samples to pH 2. This was followed by manually shaking the separatory funnels for 2 to 3 minutes and allowing the phases to separate. Following phase separation, DCM extracts were collected in 500 mL Erlenmeyer flasks and dried with acidified sodium sulfate by shaking at 200 rpm for 1 hour prior to concentration by rotary evaporator. Samples were incubated at 21°C circa 40 minutes with occasional swirling after the addition of diazomethane (2 mL) to form methyl esters and neutralization with hexane (40 mL). Nitrogen gas (flow rate 7-10 psi) was used to remove the remaining diazomethane in the sample. *n*-Hexane was added to adjust the final volume to 10 mL. Quality control included laboratory and field blanks consisting of 1 L MilliQ water, and no pesticides were detected in the blanks.

In 2013 and 2014, pesticides were quantified using gas chromatography-mass selective detection (GC-MSD) with a Hewlett-Packard (HP) 6890 C gas chromatograph interfaced to a 5973- mass selective detector operating in selected ion monitoring mode. The GC was equipped with a DB-1701 capillary column (30m x 0.25µm x 0.25mm id) to perform separation of pesticide compounds. The column temperature was programmed to start at 55°C for 2 min, increased to 130°C at 30°C/min, at 6°C/min to 250°C, and at 30°C/min to

280°C, and held for 10 min at 280°C with a total run time of 35.5 min. For 2015 samples, an autosampler (Agilent™ 7693) with splitless injection was used to inject extracts (2 µL) into an Agilent™ 7890B gas chromatograph coupled to an Agilent™ 7000C triple quadrupole mass spectrometer. The analysis was performed using multiple reaction monitoring (MRM) with electron impact (EI) ionization mode. Separation was performed using p/n 19091S-433UI column (30 m X 0.25 mm X 0.25 µm, HP-5ms Ultra Inert column from Agilent Technologies) with helium as the carrier gas and at a constant pressure so that the flow rate changed with temperature. The column temperature was programmed to start at 70°C for 2 min, increased to 150°C at 25°C/min, at 3°C/min to 200°C, and at 8°C/min to 280°C, and held for 7 min at 280°C with a total run time of 38.8 min. The temperature of the injection port, transfer line, and ion source were 280°C, 300°C, and 280°C, respectively. Pesticides were identified by monitoring retention times and the presence of target and qualifier ions. The lower limit of detection was 0.025 µg/L, which was based on the lowest standard used for analysis. Detections below this value were assigned values of zero (none detected).

2.4 Results

About one-quarter of the total samples collected in southern (~23 % of 207 samples) and central (~24% of 233 samples) Alberta showed at least one pesticide detection over three years (Table 2.1). The variety of pesticides detected was greater in the spring (13) and summer (11) than fall (9). Pesticides were detected in three-quarter of the 31 sampling points in southern Alberta and 80% of the 36 sampling points in central Alberta. Twenty-three pesticides (10 herbicides, seven insecticides, and six fungicides) were detected across the three years with the types and concentrations of individual pesticides varying

within and between the regions (Table 2.2). Out of the 131 positive detections, ~82% were herbicides; ~11% were fungicides, and ~ 8% were insecticides. Ten herbicides, five insecticides, and a fungicide were detected in 2013 and 2014, out of the 105 compounds screened for in both years. The addition of 37 pesticides to the analytical suite in 2015 resulted in the detection of seven new compounds, of which five were fungicides and two insecticides. Only 2.5 % of the samples contained at least two pesticides and < 1% of the samples contained three pesticides, the maximum number of pesticides detected in a sample considering 115 total detections for 105 pesticides all three years (Table 2.1). However, when all 131 detections and 142 pesticides are considered, 4.5% sample contained at least two pesticides with 3.4%, 0.7% and 0.5% samples containing two, three and four pesticides respectively (data not shown).

Table 2.1 Pesticide detections summarized by season, year, sampling area, the number of pesticides per sample (2013-2015) for 105 pesticides. Seasonal pesticide detections for 2015 is calculated for all 142 compounds. Seasonal pesticide detections were expressed as total pesticide detections per hundred samples.

Year	Location	Total detections per 100 samples			Percentage of samples with pesticides detections		
		Season			Number of pesticides per sample		
		Spring	Summer	Fall	One	Two	Three
2013	Central (n=55)	No sampling	7.70	17.24	12.70%		
	Southern(n=70)	22.22	16	0	5.71%	4.29%	
2014	Central (n=90)	17.2	6.45	13.33	10%	1.11%	
	Southern (n=65)	4.30	44	52.90	24.62%	1.54%	1.54%
2015	Central (n=88)	20	66.67	82.14	36.36%	4.54%	1.14%
	Southern (n=72)	22.22	77.27	43.47	22.22%	2.80%	1.40%
Overall	Central (n=233)	18.64	27.60	36.78	20.60%	2.15%	0.43%
	Southern (n=207)	16.88	44.44	32.80	17.40%	2.90%	0.97%
Average	n=440	17.64	35.22	35.17	84 (19.1%)	11 (2.5%)	3 (0.7%)

Table 2.2 Summary of pesticides detected in central and southern Alberta from 2013-2015 and their leaching potential and Canadian water quality guidelines.

Pesticide	Year§	% of total detection	Detection frequency %	Central Alberta	Southern Alberta	Max. concentration	GUS Index**	Aquatic life†	Irrigation water‡	MAC (Drinking water)
				Average ± SD						
Herbicides										
2,4-D	1,2,3	29.77	8.86	0.066±0.089	0.060±0.041	0.361	1.69	na	na	100
MCPA	1,2,3	21.37	6.36	0.089±0.079	0.185±0.341	1.293	2.94	2.6	0.025	100
Clopyralid	1,2,3	16.79	5.00	0.071±0.053	3.305±3.314	7.121	5.06	na	na	na
Propyzamide	2,3	6.87	4.38	nd	0.092±0.085	0.299	1.80	na	na	na
Fluroxypyr	3	2.29	0.68	0.040±0.003	0.042	0.042	2.42	na	na	na
Bromoxynil	3	1.22	0.63	0.027	nd	0.029	0.00	5	0.330	5
Dicamba	1	0.76	0.23	nd	0.027	0.027	1.75	10	0.006	120
EPTC	3	0.76	0.23	0.044	nd	0.044	1.34	na	na	na
Imazethapyr	1	0.76	0.23	0.211	nd	0.211	6.19	na	na	na
Simazine	2	0.76	0.23	nd	1.568	1.569	2.00	10	0.5	na
Insecticides										
Naled*	3	2.44	1.25	0.036±0.011	nd	0.043	0.0	na	na	na
Ethion	2	2.29	0.68	nd	0.076±0.034	0.113	0.0	na	na	na
Deltamethrin*	3	1.22	0.63	0.469	nd	0.469	-4.26	0.0004	na	na
Chlorpyrifos	3	1.53	0.45	0.117±0.131	nd	0.209	0.17	0.02	na	90
β-HCH	1	0.76	0.23	nd	0.038	0.038	3.95	na	na	na
cis-permethrin	1	0.76	0.23	nd	0.026	0.026	-1.11	0.004	na	na
Diazinon	2	0.76	0.23	0.166	nd	0.166	1.14	na	na	20
Fungicides										
Metalaxyl*	3	8.54	4.38	nd	0.046±0.019	0.082	2.79	na	na	na
Boscalid*	3	2.44	1.25	nd	0.594±0.093	0.659	2.66	na	na	na

Chlorothalonil*	3	2.44	1.25	0.109	0.343	0.109	0.62	0.18	5.8	na
Difenoconazole	3	1.22	0.63	nd	0.035	0.035	0.90	na	na	na
Prothioconazole -desthio*	3	1.22	0.63	nd	0.052	0.052	-0.18	na	na	na
Tebuconazole*	3	1.22	0.63	0.078	nd	0.078	2.85	na	na	na

†Canadian Water Quality Guidelines for the Protection of Aquatic Life

‡Canadian Water Quality Guidelines for the Protection of Agriculture for Irrigation Water

||Canadian Drinking Water Quality Guidelines

†‡Guideline values are obtained from CCME, 2014. ||Health Canada, 2017. *Compounds only monitored in 2015. na – Not available, nd- Not detected, MAC – Maximum admissible concentration.

§Pesticide detected in different sampling years is displayed as 1,2,3 indicating 2013, 2014 and 2015 respectively.

All the pesticide concentrations are expressed in µg/L.

**GUS index and leaching potential values were obtained from Lewis et al. 2016.

When comparing only the 105 compounds screened for in all three years, pesticides were more frequently detected in 2015 than in previous years (total detections per hundred samples being 51.3 in 2015 versus 20.6 in 2014 and 13.6 in 2013). Although the total number of individual pesticides detected was similar across the years (seven in 2013, seven in 2014, eight in 2015), there were annual variations in the types, concentrations and detection frequencies of pesticides (Table 2.2). When all data were combined, the total pesticide detections per hundred samples was numerically greater in the summer (~ 35, n=159) and fall (~ 35, n=145) than spring (~ 18, n=136). However, the spring showed greater detections than other seasons in southern Alberta in 2013 and in central Alberta in 2014 (Table 2.1). Regardless of the year, central Alberta always showed numerically greater total detections per hundred samples in the fall than summer (Table 2.1). In all three summers, the total detections per hundred sample was higher in southern Alberta where irrigation practices on coarse to fine textured soils are a common component of agricultural production, relative to central Alberta which is a predominantly non-irrigated region with fine textured soils. However, there was no apparent consistent difference between regions in the spring or fall.

2,4-D (8.9 %, n=440), MCPA (6.4 %), and clopyralid (5.0 %) were the most common pesticides detected in our study, and the only pesticides consistently detected in both regions and all three sampling years (Table 2.2). Thirty percent of the samples that contained more than one pesticide consisted of 2,4-D, MCPA, and/or clopyralid mixtures. Central (8.6%, n=233) and southern (9.2%, n=207) Alberta had similar 2,4-D detection frequencies ($P > 0.05$, Fisher's exact test), but there was substantial variation across years in 2,4-D detection (2.4%, n=125 in 2013; 8.4%, n=155 in 2014; 14.4%, n=160 in 2015).

The detection frequency also varied between years for MCPA (3.2% in 2013; 1.3% in 2014; 13.8% in 2015) but remained rather consistent across years for clopyralid (4.8% in 2013; 5.2% in 2014; 5.0% in 2015). MCPA was detected at the same frequencies in southern (6.3%) and central (6.4%) Alberta ($P > 0.05$, Fisher's exact test), while clopyralid was detected more frequently in central (8.2%) than southern Alberta (1.4%) ($P < 0.05$, Fisher's exact test). The mean concentrations of both MCPA and clopyralid were substantially greater in southern than central Alberta, but the mean concentration of 2,4-D was similar in both regions (Table 2.2). Only in southern Alberta did the pesticide concentrations exceed one $\mu\text{g/L}$, and this occurred three times for clopyralid, once for MCPA, and once for simazine.

The clopyralid concentration significantly ($r = -0.6$, Spearman test) decreased with increasing well depth but did not vary with piezometer depth. Well or piezometer depths did not significantly influence 2,4-D or MCPA concentrations. The detection frequency of MCPA significantly decreased with increasing piezometer depth ($r = -0.5$, Spearman test) but not with well depths. Well or piezometer depths did not significantly influence the frequencies of clopyralid or 2,4-D detections.

Few studies have reported variation in pesticide detections with well depth (Sievers and Fulhage 1992; Barbash et al. 2001). Pesticide detection was highly correlated with well depth in agricultural areas of Missouri (Sievers and Fulhage 1992). Barbash and Resek (1996) also found an inverse relation between well depth and pesticide detection frequency. Shakerkhatibi et al. (2014) found no correlation between well depth and

pesticide concentration. However, Toccalino et al. (2004) reported the variation in pesticide detection depending on well type and structure.

2.5 Discussion

2,4-D, MCPA, and clopyralid have been frequently detected in other studies, including in samples collected from groundwater in southern Alberta (Miller et al. 1995a; Miller et al. 1995b; Hill et al., 1996; Rodvang et al. 2001) and Prairie wetlands (Donald et al. 1999; Elliott et al. 2001; Messing et al. 2012), surface drinking-water reservoirs (Donald et al. 2007) and rivers (ECCC, 2013). 2,4-D and MCPA are among the most widely applied pesticides in the Prairie region of Canada, including Alberta (Cessna and Elliott 2004; Environment Canada 2011, Messing et al. 2012, AEP 2015). Clopyralid is less widely used in the Prairies (Wilson 2012) but is included with MCPA in a number of pesticide products (AAF 2017). 2,4-D (24,300 µg/L), MCPA (29,390 µg/L) and clopyralid (143,000 µg/L) have relatively high water solubility (Lewis et al. 2016). Based on the GUS index MCPA (2.94) and particularly clopyralid (5.06) are considered relatively mobile in soils (Table 2), as noted by several studies in the Prairie Provinces of Canada (Elliot et al. 2000, Hiller et al. 2006).

The study results indicate that groundwater is more prone to pesticide contamination in southern than central Alberta during the summer season. In 2013 (AEP 2015), the municipality of Lethbridge in which our sampling sites in southern Alberta are located, reported greater pesticide sales than the municipality of Lacombe/Ponoka in which our sampling sites in central Alberta are located. Previous studies reported increased pesticide detection in regions with greater pesticide use (Konstantinou et al. 2006, Messing et al.

2013, Messing et al. 2014). Since only in the summer did southern Alberta (~ 44, n=72) show substantial greater total pesticide detections per hundred samples than central Alberta (~ 28, n=88) it is possible that the common practice of cropland irrigation in southern Alberta increases the risk of groundwater contamination by pesticides. Examining the transport of the herbicide terbutylazine and its metabolite desethylterbutylazine, Fait et al. (2010) reported an increased risk of pesticide transport to groundwater in areas under different irrigation systems, relative to non-irrigated areas of sandy loam to clay loam soil of northern Italy.

Insecticides represent only 1.3 % of total pesticide sales in Alberta (AEP 2015). The insecticides detected in southern (cis-permethrin) and central (chlorpyrifos, deltamethrin, naled, and diazinon) are current-use pesticides used in feedlot operations to control livestock insects, as well as in crop production (AAF 2016). The detection of these insecticides was rather localized, in two wells at site-1 in central Alberta, and in four wells at site-4 and site-5, in southern Alberta where confined feedlot operations are present, suggesting that insecticide application in confined feeding operations can be a source of groundwater contamination.

Five of the six fungicides detected in the study were only screened for in 2015 (Table 2.2). The types and frequency of the detections were greater in southern than central Alberta, suggesting that irrigation practices may increase the risk of fungicide transport to groundwater. Tebuconazole and propiconazole are the most commonly used fungicides in Alberta (AEP 2015) but were less frequently detected than metalaxyl (Table 2.2).

Metalaxyl is commonly used in Alberta (AEP 2015) and is highly soluble in water with a moderate leaching potential in soils (Lewis et al. 2016).

Of the 23 compounds detected, three were legacy compounds, with levels ranging from 0.038 µg/L to 0.166 µg/L. This includes the organophosphate insecticide diazinon, deregistered for use in 2013 (Health Canada 2013), and detected in our study in 2014. This also included the insecticide ethion (deregistered in 2001), and β-HCH which was, until the early 1970s, a byproduct of the insecticide lindane. Recent studies in Asia also report the presence of ethion and β-HCH in groundwater (Wu et al. 2014; Abdallah and Abdel-Halim 2016; Oginawati and Pratama 2016). Neither compounds are particularly mobile in soil because of their strong sorption to soil (Seech et al. 2008; Nuro et al. 2014, Lewis et al. 2016), but ethion (half-life: 90 days) and β-HCH (half-life: 980 days, lindane) (Lewis et al. 2016) have relatively long-half lives in soil hence their detection may be the result of a slow, long-term downward movement over time or, otherwise, the compounds were transported through the soil profile by preferential flow and had persisted for decades in groundwater.

The concentrations of pesticides detected ranged from a minimum of 0.026 µg/L for cis-permethrin (an isomer of the insecticide permethrin, a pyrethroid compound) to a maximum of 7.121 µg/L for clopyralid. Only 26% of the detected pesticides in this study have set Canadian drinking water guidelines (Table 2.2) and this included herbicides 2,4-D (100 µg/L), MCPA (100 µg/L), bromoxynil (5 µg/L), dicamba (100 µg/L) and insecticides chlorpyrifos (90 µg/L), diazinon (20 µg/L). None of these pesticides was ever detected at a concentration exceeding their individual thresholds suggesting that the

Albertan population relying on potable groundwater sources is at low risk. The European Union has set the maximum concentration for individual pesticides in drinking water at 0.1 µg/L (European Union 2000), and ~6% of our samples exceeded that guideline. No CWQG have been developed for pesticide mixtures, but four samples in southern Alberta and one sample in central Alberta contained pesticide mixtures exceeding 0.5 µg/L, which is the drinking water guideline set by the European Union for pesticide mixtures (European Union 2000). Within the regions studied, only in central Alberta is groundwater used as potable water. The concentration of MCPA always exceeded the CWQG for irrigation. Dicamba and simazine exceeded these guidelines but were only detected once each. The exceedances of CWQG for irrigation did not pose a threat because surface water is typically used as the main source of irrigation water. Chlorpyrifos, deltamethrin and cis-permethrin were occasionally detected and exceeded the CWQG for the Protection of Aquatic Life (freshwater), but most aquifers are nutrient-poor, without light and anaerobic (Stevens 1997) and hence do not support aquatic indicator species upon which the guidelines are based. However, groundwater may discharge to surface waters such as springs and seeps, wetlands and streams (Howard and Merrifield 2010) and groundwater can be an important habitat for microbial communities (Thulin et. al. 2008; Deharveng et al. 2009; Griebler and Avramov 2015).

We conclude that the types and concentrations of pesticides detected in groundwater pose a low risk to human and ecosystem health. However, future studies, about which types of irrigation systems in southern Alberta can reduce the risk of pesticide transport to groundwater, are warranted. It is important to note that more than one hundred of current-use pesticides were screened for but not detected. This includes herbicides triallate and

ethalfluralin, as well as fungicides pyraclostrobin and iprodione, which are among the top 25 active ingredients sold in Alberta (AEP 2015).

2.6 Conclusion

Ten (out of 59) herbicides, seven (out of 55) insecticides and six (out of 22) fungicides were detected in groundwater samples of southern and central Alberta. Detection frequencies and concentrations in the summer seasons were greater in southern than central Alberta, most likely due to greater pesticide use and irrigation practices in the southern location. However, the concentrations detected in both regions suggest that there is a low risk to human and ecosystem health based on various guidelines set for some individual pesticides in Canada. Occasionally, the concentrations detected exceeded the more conservative European Drinking Water Quality Guidelines. 2,4-D, MCPA, and clopyralid were the only pesticides consistently detected in both regions and on all three sampling years. These herbicides are widely used in Alberta and are relatively mobile in soil. Given that these herbicides were frequently detected, further studies are warranted about which land and irrigation practices can be implemented to minimize the risk of 2,4-D, MCPA and clopyralid transport to groundwater.

2.7 Acknowledgements

We gratefully acknowledge funding for this study by Alberta Innovates - Energy and Environment Solutions (AI-EES) and Natural Sciences and Engineering Research Council of Canada (NSERC) grant to Dr. Farenhorst for student financial support. The authors thank Alberta Agriculture and Forestry for the contributions to site access and sampling and Oldman Watershed Council, Alberta Health Services, Agriculture and Agri-

Food Canada for their additional support. The technical assistance from Tara Vucurevich, Monique Dawson, Jessa Drury and Aiden Martindale (last three co-op students) is highly acknowledged.

2.8 References

Abdallah, S. M. and Abdel-Halim, K. Y. 2016. Pesticides in Indoor Dust and Shallow Groundwater in Rural Egypt. *Journal of High Institute of Public Health* **40 (4)**:705-723.

Aisopou, A., Binning, P. J., Albrechtsen, H. J. and Bjerg, P. L. 2015. Modeling the Factors Impacting Pesticide Concentrations in Groundwater Wells. *Groundwater* **53 (5)**: 722-736.

Alberta agriculture and forestry (AAF). 2009. Agriculture statistics factsheet.

Accessed September 06, 2016. Available at:

[http://www1.agric.gov.ab.ca/\\$department/deptdocs.nsf/all/sdd12807/\\$file/AgStats2016_853.pdf?OpenElement](http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/sdd12807/$file/AgStats2016_853.pdf?OpenElement)

Alberta agriculture and forestry(AAF). 2017. Crop protection 2017. Accessed

September 06, 2016. Available at:

[http://www1.agric.gov.ab.ca/\\$Department/deptdocs.nsf/all/agdex32/\\$FILE/606-1.pdf](http://www1.agric.gov.ab.ca/$Department/deptdocs.nsf/all/agdex32/$FILE/606-1.pdf)

Alberta Environment and Parks (AEP). 2015. Overview of 2013 Pesticide Sales in Alberta. Land Policy Branch. Edmonton, AB. 80 pp.

Baran, N., Lepiller, M. and Mouvet, C. 2008. Agricultural diffuse pollution in a chalk aquifer (Trois Fontaines, France): Influence of pesticide properties and hydrodynamic constraints. *Journal of Hydrology*. **358 (1)**: 56-69.

- Barbash, J. E., & Resek, E. A. 1996.** Pesticides in ground water: distribution, trends, and governing factors. Ann Arbor Press.
- Barbash, J. E., Thelin, G. P., Kolpin, D. W. and Gilliom, R. J. 2001.** Major herbicides in ground water. *Journal of Environmental Quality*, **30** (3): 831-845.
- Bourguet, D. and Guillemaud, T. 2016.** The Hidden and External Costs of Pesticide Use Sustainable Agriculture Reviews. 35-120.
- Brimble, S., Bacchus, P. and Caux, P.-Y. 2005.** Pesticide utilization in Canada :a compilation of current sales and use data. Prepared in fulfilment of a requirement of the Environment Canada Pesticide Program Coordinating Committee.
- Bruns, G. W., Nelson, S. and Erickson D. G. 1991.** Determination of MCPA, bromoxynil, 2,4-D, trifluralin, triallate, picloram, and diclofop-methyl in soil by GC-MS using selected ion monitoring. *J. Assoc. Off. Anal. Chem.* **74**: 550–553
- Canadian Council of Ministers of the Environment (CCME). 2014.** Accessed: March 27, 2017. Available at http://www.ccme.ca/en/resources/canadian_environmental_quality_guidelines/
- Ccancapa, A., Masiá, A., Andreu, V. and Picó, Y. 2016.** Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers (Spain). *Science of the Total Environment*. **540**: 200-210.
- Cessna, A. J. and Elliott, J. A. 2004.** Seasonal variation of herbicide concentrations in prairie farm dugouts. *Journal of Environmental Quality*. **33** (1): 302-315.

City of Lethbridge. 2017. Accessed: January 30, 2017. Available at:

<http://www.lethbridge.ca/living-here/water-wastewater/Pages/Water.aspx>.

Dearmont, D., McCarl, B. A. and Tolman, D. A. 1998. Costs of water treatment due to diminished water quality: a case study in Texas. *Water Resources Research*. **34 (4)**: 849-853.

Deharveng, L., Stoch, F., Gibert, J., Bedos, A., Galassi, D., Zagmajster, M., Brancelj, A., Camacho, A., Fiers, F., Martin. P., Giani, N., Magniez, G. and Marmonier, P. 2009. Groundwater biodiversity in Europe. *Freshwater Biology* **54**: 709–726

Donald, D. B., Cessna, A. J., Sverko, E. and Glozier, N. E. 2007. Pesticides in surface drinking-water supplies of the Northern Great Plains. *Environmental health perspectives*. 1183-1191.

Donald, D. B., Syrgiannis, J., Hunter, F. and Weiss, G. 1999. Agricultural pesticides threaten the ecological integrity of northern prairie wetlands. *Science of the Total Environment*. **231 (2)**: 173-181.

Edwards, P. G., Murphy, T. M. and Lydy, M. J. 2016. Fate and transport of agriculturally applied fungicidal compounds, azoxystrobin and propiconazole. *Chemosphere*. **146**: 450-457.

Elliott, J. A., Cessna, A. J. and Hilliard, C. R. 2001. Influence of tillage system on water quality and quantity in prairie pothole wetlands. *Canadian Water Resources Journal*. **26 (2)**: 165-181.

Elliott, J. A., Cessna, A. J., Nicholaichuk, W. and Tollefson, L. C. 2000. Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. *Journal of Environmental Quality*, **29** (5): 1650-1656.

Environment and Climate Change Canada(ECCC). 2013. Groundwater. Accessed July 20, 2016. Available at: <http://www.ec.gc.ca/eau-water/default.asp?lang=En&n=300688DC-1#sub5>.

Environment Canada 2011. Presence and levels of priority pesticides in selected Canadian aquatic ecosystems. Water Science and Technology Directorate. 8pp.

Environment Canada. 2016. Canadian climate normals 1981–2010. National Climate Data and Information Archive. Accessed July 20, 2016. Available in: http://climate.weatheroffice.gc.ca/climate_normals/index_e.html.

European Union. 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October establishing a framework for Community action in the field of water policy Off. J. Eur. Comm. L 2000, **327**.

Fait, G., Balderacchi, M., Ferrari, F., Ungaro, F., Capri, E. and Trevisan, M. 2010. A field study of the impact of different irrigation practices on herbicide leaching. *European journal of agronomy*. **32** (4): 280-287.

Goss, M., Barry, D., & Rudolph, D. 1998. Contamination in Ontario farmstead domestic wells and its association with agriculture. Results from drinking water wells. *Journal of Contaminant Hydrology*. **32** (3): 267-293.

Griebler, C. and Avramov, M. 2015. Groundwater Ecosystem Services: A Review. *Freshwater Science* **34** (1): 355-67.

Health Canada. 2013. Pest Control Products Sales Report for 2013.

Health Canada. 2017. Guidelines for Canadian Drinking Water Quality—Summary Table. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario.

Hernández, A. F., Parrón, T., Tsatsakis, A. M., Requena, M., Alarcón, R. and López-Guarnido, O. 2013. Toxic effects of pesticide mixtures at a molecular level: their relevance to human health. *Toxicology*. **307**: 136-145.

Hildebrandt, A., Guillamón, M., Lacorte, S., Tauler, R. and Barceló, D. 2008. Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). *Water Research*. **42 (13)**: 3315-3326.

Hill, B. D., Harker, K. N., Hasselback, P., Inaba, D. J., Byers, S. D. and Moyer, J. R. 2002. Herbicides in Alberta rainfall as affected by location, use and season: 1999 to 2000. *Water quality research journal of Canada*. **37 (3)**: 515-542.

Hill, B., Miller, J., Chang, C. and Rodvang, S. 1996. Seasonal variation in herbicide levels detected in shallow Alberta groundwater. *Journal of Environmental Science & Health Part B*. **31 (4)**: 883-900.

Hiller, E., Khun, M., Zemanová, L., Jurkovic, L. and Bartal, M. 2006. Laboratory study of retention and release of weak acid herbicide MCPA by soils and sediments and leaching potential of MCPA. *Plant Soil and Environment* **52 (12)**: 550.

Howard, J. and Merrifield M. 2010. Mapping groundwater dependent ecosystems in California, *plos one* **5 (6)**: e11249.

- Jablonowski, N. D., Schäffer, A. and Burauel, P. 2011.** Still present after all these years: persistence plus potential toxicity raise questions about the use of atrazine. *Environmental Science and Pollution Research* **18 (2)**: 328-331.
- James, K. A. and Hall, D. A. 2015.** Groundwater pesticide levels and the association with Parkinson disease. *International journal of toxicology* **34 (3)**: 266-273.
- Keesstra, S., Geissen, V., Mosse, K., Piirainen, S., Scudiero, E., Leistra, M. and Schaik, V. L. 2012.** Soil as a filter for groundwater quality. *Current Opinion in Environmental Sustainability* **4 (5)**: 507-516.
- Konstantinou, I. K., Hela, D. G. and Albanis, T. A. 2006.** The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. *Environmental Pollution* **141 (3)**: 555-570.
- Larsbo, M., Koestel, J. and Jarvis, N. 2014.** Relations between macropore network characteristics and the degree of preferential solute transport. *Hydrology and Earth System Sciences* **18 (12)**: 5255-5269.
- Lewis, K. A., Tzilivakis, J., Warner, D. J., & Green, A. 2016.** An international database for pesticide risk assessments and management. *Human and Ecological Risk Assessment: An International Journal*, **22 (4)**: 1050-1064.
- Lorenz, K., Iwanyshyn, M., Olson, B., Kalischuk, A. and Pentland, J. 2014.** Livestock Manure Impacts on Groundwater Quality in Alberta: 2008 to 2011 Progress Report. Alberta Agriculture and Rural Development, Lethbridge, Alberta, Canada. 316 pp.

- Mackay, D., Shiu, W.-Y., Ma, K.-C. and Lee, S. C. 2006.** Handbook of physical-chemical properties and environmental fate for organic chemicals: CRC press.
- Main, A. R., Headley, J. V., Peru, K. M., Michel, N. L., Cessna, A. J. and Morrissey, C. A. 2014.** Widespread use and frequent detection of neonicotinoid insecticides in wetlands of Canada's Prairie Pothole Region. PLoS one **9** (3): e92821.
- McGrath, G., Hinz, C. and Sivapalan, M. 2010.** Assessing the impact of regional rainfall variability on rapid pesticide leaching potential. Journal of Contaminant Hydrology **113** (1): 56-65.
- Mesnager, R., Defarge, N., Spiroux de Vendômois, J. and Séralini, G.-E. 2014.** Major pesticides are more toxic to human cells than their declared active principles. BioMed research international, 2014.
- Messing, P. G., Farenhorst, A., Waite, D. T., McQueen, D. R., Sproull, J. F., Humphries, D. A., & Thompson, L. L. 2012.** Corrigendum to “Predicting wetland contamination from atmospheric deposition measurements of pesticides in the Canadian Prairie Pothole region” Atmos. Environ **45**: 7227–7234.
- Messing, P.G, Farenhorst, A., Waite D.T., Sproull, J. F. 2013.** Influence of usage and chemical-physical properties on the atmospheric transport and deposition of pesticides to agricultural regions of Manitoba, Canada. Chemosphere **90** (6): 1997–2003.
- Messing, P.G, Farenhorst, A., Waite D.T., Sproull, J.F. 2014.** Current-use herbicides in air as influenced by their estimated agricultural use at various distances from six sampling locations. Water, Air, & Soil Pollution, 225, DOI 10.1007/s11270-014-2013-y

- Miller, J., Foroud, N., Hill, B. and Lindwall, C. 1995a.** Herbicides in surface runoff and groundwater under surface irrigation in southern Alberta. *Canadian Journal of Soil Science* **75 (1)**: 145-148.
- Miller, J., Hill, B., Chang, C. and Lindwall, C. 1995b.** Residue detections in soil and shallow groundwater after long-term herbicide applications in southern Alberta. *Canadian Journal of Soil Science* **75 (3)**: 349-356.
- Morrissey, C. A., Mineau, P., Devries, J. H., Sanchez-Bayo, F., Liess, M., Cavallaro, M. C. and Liber, K. 2015.** Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review. *Environment International* **74**: 291-303.
- Nolan, B. T., Dubus, I. G., Surdyk, N., Fowler, H. J., Burton, A., Hollis, J. M., . . . Jarvis, N. J. (2008).** Identification of key climatic factors regulating the transport of pesticides in leaching and to tile drains. *Pest management science* **64(9)**: 933-944.
- Nuro, A., Marku, E., Murtaj, B. and Mance, S. 2014.** Study of Organochlorinated Pesticides, Their Residues and PCB Concentrations in Sediment Samples of Patoku Lagoon. *Journal Of International Environmental Application And Science* **9 (3)**: 452.
- Oginawati, K. and Pratama, M. 2016.** Identification and level of organochlorine insecticide contamination in groundwater and iridology analysis for people in Upper Citarum cascade. Paper presented at the *Journal of Physics: Conference Series*.
- Palma, P., Köck-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I., De Alda, M. L. and Barceló, D. 2014.** Risk assessment of pesticides detected in surface water of the

Alqueva reservoir (Guadiana basin, southern of Portugal). *Science of the Total Environment* **488**: 208-219.

Parrón, T., Requena, M., Hernández, A. F. and Alarcón, R. 2014. Environmental exposure to pesticides and cancer risk in multiple human organ systems. *Toxicology letters* **230 (2)**: 157-165.

Pfeiffer, M. 2010. Groundwater Ubiquity score (GUS). Pesticide training resources.

Pimentel, D. 2005. Environmental and economic costs of the application of pesticides primarily in the United States. *Environment, development and sustainability* **7 (2)**: 229-252.

Pose-Juan, E., Sánchez-Martín, M. J., Andrades, M. S., Rodríguez-Cruz, M. S. and Herrero-Hernández, E. 2015. Pesticide residues in vineyard soils from Spain: Spatial

Rodvang, J., Ryan, C., Zilkey, M., Dash, T. and Hill, B. 2001. Protecting groundwater in irrigated areas of Southern Alberta. Paper presented at the Western Canada Agronomy Workshop.

Saha, D., & Alam, F. 2014. Groundwater vulnerability assessment using DRASTIC and Pesticide DRASTIC models in intense agriculture area of the Gangetic plains, India. *Environmental Monitoring and Assessment* **186 (12)**: 8741-8763.

Seech, A., Bolanos-Shaw, K., Hill, D., & Molin, J. 2008. In situ bioremediation of pesticides in soil and groundwater. *Remediation* **19 (1)**: 87.

Shakerkhatibi, M., Mosaferi, M., Jafarabadi, M. A., Lotfi, E., & Belvasi, M. 2014.

Pesticides residue in drinking groundwater resources of rural areas in the northwest of Iran. Health promotion perspectives **4 (2)**: 195.

Sievers, D.M. and Fulhage, C. D. 1992. Survey of rural wells in Missouri for pesticides and nitrate. Ground Water Monit. Rev. **12**: 142–150

Soto, A. M., Chung, K. L. and Sonnenschein, C. 1994. The pesticides endosulfan, toxaphene, and dieldrin have estrogenic effects on human estrogen-sensitive cells. Environmental health perspectives **102 (4)**: 380.

Statistics Canada. 2013. Agricultural Water Use in Canada. Statistics Canada Catalogue no. 16-402-X. Ottawa. Version updated 2013

Steffens, K., Larsbo, M., Moeys, J., Kjellström, E., Jarvis, N., & Lewan, E. 2014. Modelling pesticide leaching under climate change: parameter vs. climate input uncertainty. Hydrology and Earth System Sciences **18 (2)**: 479-491.

Stevens, T. 1997. Lithoautotrophy in the subsurface. FEMS Microbiology Reviews, **20 (3-4)**: 327-337.

Thulin, B., Hahn, H. J. and Grundwasserökologie, A. 2008. Ecology and living conditions of groundwater fauna. SKB.

Tiam, S. K., Libert, X., Morin, S., Gonzalez, P., Feurtet-Mazel, A., & Mazzella, N. 2014. Single and mixture effects of pesticides and a degradation product on fluvial biofilms. Environmental Monitoring and Assessment **186 (6)**: 3931-3939.

- Tiryaki, O., & Temur, C. 2010.** The fate of pesticide in the environment. *Journal of Biological and Environmental Sciences* **4(10)**.
- Toccalino, P. L., Gilliom, R. J., Lindsey, B. D. and Rupert, M. G. 2014.** Pesticides in Groundwater of the United States: Decadal-Scale Changes, 1993–2011. *Groundwater* **52 (S1)**: 112-125.
- Toccalino, P. L., Norman, J. E., Phillips, R. H., Kauffman, L. J., Stackelberg, P. E., Nowell, L. H., Krietzman, S.J. and Post, G. B. 2004.** Application of health-based screening levels to ground-water quality data in a state-scale pilot effort. *US Geol. Survey Scientific Investigations Report*, 5174.
- Vassiliou, G. 2016.** Factors Affecting Risk Assessment of Pesticides in Water Bodies: A Review. *MedCrave Online Journal of Toxicology* **2 (1)**: 00030.
- Vryzas, Z., Vassiliou, G., Alexoudis, C., & Papadopoulou-Mourkidou, E. 2009.** Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece. *Water Research* **43 (1)**: 1-10.
- Wilson, J. 2012.** Agricultural pesticide use trends in manitoba and 2,4-d fate in soil. PhD thesis. University of Manitoba. Department of Soil Science.
- Wu, C., Luo, Y., Gui, T., & Huang, Y. 2014.** Concentrations and potential health hazards of organochlorine pesticides in shallow groundwater of Taihu Lake region, China. *Science of the Total Environment*: **470-471**: 1047-1055.
- Yao, Y., Tuduri, L., Harner, T., Blanchard, P., Waite, D., Poissant, L., . . . Li, Y.-F. 2006.** Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. *Atmospheric Environment* **40 (23)**: 4339-4351.

3. PESTICIDE RESIDUES IN GROUNDWATER AND SOIL AT A LONG TERM CROP ROTATION SITE IN SOUTHERN ALBERTA, CANADA.

3.1 Abstract

A field study was undertaken in Lethbridge, Alberta, to quantify pesticide residues in soil at 0-15, 15-30, 30-45, 45-60 and 60-75 cm depths in December 2014 and then monitor the monthly pesticide occurrence in groundwater from December 2014 to November 2015 at the same experimental site. Groundwater was obtained from wells ranging in depth from 2.1 to 4 m and from piezometers with depths of 3, 6 and 9 m and Liquid-Liquid Extraction (LLE) was used to extract residues from water samples (1L). QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction and clean-up with LLE were used for pesticide extraction from soil. Soil and groundwater extracts were analyzed for 130 and 142 pesticide active ingredients and metabolites respectively using gas chromatography and tandem mass spectrometry (GC-MS/MS). 95.9% of soil samples contained at least one pesticide, with a maximum number of 25 pesticides detected in a single soil sample. Thirty-seven different pesticide residues were detected in soil, with DDT isomers (p,p'-DDE, p,p'-DDT) (not applied on the site since 1972), 2,4-D, difenoconazole, MCPA and trans-heptachlor epoxide accounting for 85% of all detections. Soil depth and cropping system significantly affected total pesticide concentration, as well as Σ DDT concentration, while 2,4-D concentration was not significantly affected by depth, cropping system or manure amendments. Eleven different pesticide compounds were detected in groundwater with bentazone, 2,4-D and MCPA being most frequently detected and accounting for 79% of total detections. Bentazone was detected throughout the year. p,p'-DDE and difenoconazole were also detected in

groundwater. Greater detection frequency of pesticides was found in July and in September, which did not necessarily represent the pesticide application periods at the study site. Soil acts as a sink for many pesticides used in the past to present, however not all of them leach to groundwater.

3.2 Introduction

Pesticides usually enter agroecosystems by intentional application to plant foliage, to the soil and to seeds planted in the soil, but unintentional inputs may also occur via: i) atmospheric deposition (dry or wet deposition, typically in gaseous or dissolved forms, but also deposited as aerosols or wind-blown sediments) (Waite et al. 2005); ii) inputs with irrigation water; iii) sub-surface groundwater flow; iv) inputs with livestock manure (especially that derived from livestock fed or bedded with forages treated with herbicides like clopyralid) (Davis et al. 2010). Pesticides in soil may undergo a variety of processes including sorption, transformation by microorganisms, and transport by the matrix or preferential flow (McGrath et al. 2010; Tiriyaki and Temur 2010). Pesticide transport results in the distribution of pesticides throughout the soil profile (Zhang et al. 2006; Vonberg et al. 2014) and leaching to groundwater (Leistra and Boesten 2012; Delwiche et al. 2014). Pesticide degrades more slowly in groundwater compared to surface water due to cooler temperature and low microbial activity underground (Trautmann et al. 1989). Groundwater polluted by pesticides can have detrimental effects if used for human consumption (Fiore et al. 1986; James and Hall 2015). Higher concentration of pesticide residues in soil have been shown to adversely affect microbial populations such as *Azotobacter* (Murugan et al. 2013) and *Rhizobium sp.* (Arias and de Peretti 1993).

The extent to which pesticides are transported to depth in the soil profile and into groundwater depends on the pesticide physiochemical properties and soil properties, as well as climate and hydro-geologic conditions (Decker 1990; Rodriguez-Cruz et al. 2006; Arias-Estévez et al. 2008; Keesstra et al. 2012). Soil properties such as the soil organic carbon content (SOC) and soil pH affect pesticide sorption (Farenhorst 2006; Kah and Brown 2006; Wu et al. 2011), and greater sorption decreases the availability of pesticides for degradation and transport to depth and groundwater (Gaultier et al. 2008). Land management operations including the types of crops grown, the incorporation of organic amendments such as manure, and tillage practices are important factors influencing soil properties like SOC (Hueso-González et al. 2014). For example, cereal and forage crops are included in cropping systems typical of the Canadian prairies and are major factors affecting soil properties of prairie land-use systems (Entz et al. 2002).

Pesticides can persist in the soil and groundwater years after use (Vonberg et al. 2014; Venier et al. 2016). Residues of many organochlorine compounds (e.g., DDT, HCH) are still being detected in soil and groundwater despite their ban decades ago (Wu et al. 2014; Karadeniz and Yenisoy-Karakaş 2015). In Canada, several of organochlorine compounds (e.g., DDT, HCH) were phased out as early as in the 1970s, but subsequent studies have documented their presence in soil (Don Waite et al. 2005; Wan et al. 2005; Reyes et al. 2015) and groundwater (Woudneh et al. 2009). Continued monitoring of organochlorine pesticides is of particular importance because of their persistence, bioaccumulation, biomagnification, and toxicity poses risks to non-targeted organisms and ecosystem health (Walker et al. 2012). For current-use pesticides, the accumulation of pesticides in

Canadian soils and their subsequent leaching to groundwater under repeated annual application has been reported (Smith 1982; Smith et al. 1991; Miller et al. 1995b). For example, Miller et al. (1995a) detected residues of MCPA, bromoxynil and diclofop in shallow groundwater of southern Alberta, two of which surpassing the Canadian drinking water quality guidelines.

Rotation U, a long-term cropping systems experiment at the Lethbridge Research and Development Center (LeRDC), is representative of irrigated cropland in southern Alberta, and this province accounts for almost 75% of about 590,000 ha of irrigated land in Canada (Dubetz, 1983; Statistics Canada 2015). This experimental site provides an opportunity to investigate the patterns and processes underlying the occurrence of pesticide residues in groundwater and soil. The objectives of this study were to investigate the occurrence of pesticide residues in the soil profile under two cropping systems with and without cattle manure amendments and to determine the monthly variation of a wide array of pesticide residues in shallow groundwater at the experimental site.

3.3 Materials and methods

3.3.1 Analytical reagents

Acetonitrile (MeCN), *n*-hexane, dichloromethane (DCM), acetone, and toluene (chromatographic grade) were obtained from VWR® (Mississauga, ON, Canada).

Analytical grade pesticides with a purity ranging from 66.3 to 100 % were obtained from Chem Service Inc. (West Chester, PA, USA). Anhydrous sodium sulfate was purchased

from Sigma-Aldrich® (St. Louis, MO, USA) and was acidified in the laboratory.

Diazomethane used in methylation was prepared in the laboratory by dissolving 7.6 g of hydrogen peroxide in 7.6 ml of milliQ water and adding 83 ml of ethyl ether and 5 g of *n*-methyl-nitrosoguanidine. QuEChERS kits were obtained from Agilent™ Technologies (Santa Clara, CA, USA) and contained 6 g MgSO₄ and 1.5 g Na acetate. These kits were used for soil extraction.

3.3.2 Study site

The study site (49.7030°N, -112.7577°W, elevation 911 m) was the long-term irrigated cropping systems study known as rotation U, originally established in 1910 at the LeRDC of AAFC. The site has a mean annual air temperature (1981-2010) of 5.9±1°C and mean annual precipitation (1981-2010) of 380.2 mm (Environment Canada, 2016). Soil (Table 3.1) was classified as an Orthic Dark Brown Chernozem (sandy clay loam) with 47% sand, 21% silt and 32% clay (Helgason et al. 2014). The experiment (six plots in total, each 135.6 x 29.9 m) was set as a randomized complete block design with two treatment; cropping systems and manure amendments. The two cropping systems were alfalfa-based (alfalfa-alfalfa-alfalfa-wheat-barley) and corn-based (corn-wheat-corn-wheat-barley). The manure treatment was super-imposed on the cropping systems. The manure treatment consisted of a non-manured control and a plot that received 33.5 tons/hectare beef cattle feedlot manure (wet weight basis; ~35% dry matter) once every five years (most recently in early 2013). Thus, the experiment included 12 plots with four treatments in three replications (Figure 3.1). A shallow groundwater (GW) well consisting of a PVC pipe (60.3 mm outside and 48.3 mm inside diameter) 305 cm long was installed in each plot. The top ~30 cm extended above the soil surface, and a union fitting ~30 cm below the

soil surface enabled the upper portion (non-perforated) to be periodically removed to facilitate field operations (tilling, seeding, harvesting). The hydrologic setting and shallow GW at this site, and others in the irrigated region of southern Alberta have been described by Beke et al. (1993). Anecdotal evidence suggests that dichlorodiphenyltrichloroethane (DDT) was used for wireworm control until the 1970s. Applications of 2,4-D, triallate, and diclofop-methyl in the late 1940s to early 1960s have also been recorded by some researchers (Freyman et al. 1982, Campbell et al. 1990). Pesticide applications over the past five years are summarized in Appendix III.

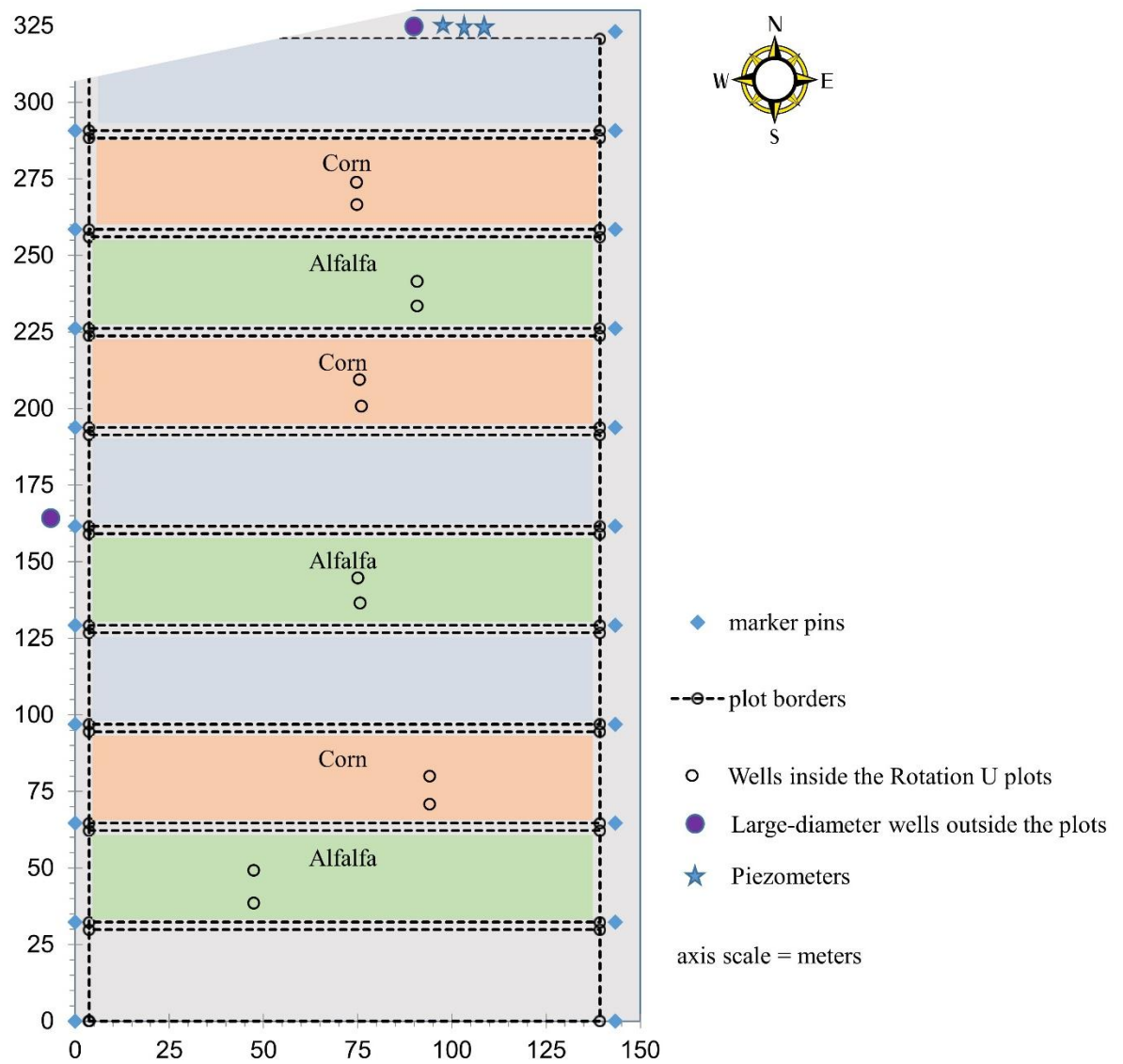


Figure 3.1 Layout of the experimental plots at the Rotation U site.

Table 3.1 List of soil properties along with a number of samples analysed from different soil depth where gravimetric moisture content (%), pH, soil organic carbon and total carbon are expressed in mean± coefficient of variation (CV%) . Soil samples were collected in December 2014.

Depth (cm)	Number of samples (n)	Gravimetric moisture content% (mean ± CV)	Average Bulk density (g cm⁻³)	pH (0.01M CaCl₂) (mean ± CV)	Average EC* (µs/cm)	Soil organic carbon% (mean ± CV)	Total carbon% (mean ± CV)
0-15	14	28.23±9.85	1.37	7.32±1.36	245.07	2.03±15.06	2.4±16.58
15-30	14	23.01±9.13	1.44	7.49±2.69	761.03	1.56±7.02	2.04±12.36
30-45	14	23.53±9.30	1.40	7.59±2.11	1285.30	1.07±8.27	2.42±42.83
45-60	14	22.67±7.59	1.44	7.58±2.33	1346.60	0.81±10.22	3.02±27.32
60-75	5	20.22±11.33	1.58	7.55±2.12	1165	0.68±22.09	3.03±10.43

*Electrical conductivity

3.3.3 Groundwater sampling and extraction

There were 12 GW wells within the experimental plots and samples were also collected from two additional large (250 mm) diameter wells (named as North well and West well). The well depth ranged from 2.1 m to 4 m (average depth of 2.7 m). Samples were also collected from a nest of three piezometers with depths of 3, 6 and 9 m respectively (Figure 3.1) on the periphery of the experimental area. At approximately monthly intervals, a total 213 GW samples were collected between December 2014 and November 2015 except that from June to November 2015, two WTWs dried up, and no groundwater could be collected from these wells. While sampling, the distance from the top of the well to the soil surface was measured using a ruler, and then the distance from the top of the well casing to the GW was measured using a level sensor (SPOHR-Messtechnik GmbH, Frankfurt). The sample intake tube was then inserted sufficiently below the GW surface to collect 1 L of water. Groundwater was collected into amber glass bottles using a Burkle's polyethylene MiniSampler (Burkle Inc., NY, USA) with 8 mm polytetrafluoroethylene tubing. All groundwater samples collected were stored at 4°C until processed using Liquid-liquid Extraction (LLE), which was typically within three days post-collection date. Samples were filtered through glass wool into separatory funnels (2 L), and emptied sample bottles rinsed with acetone (30 mL) that was also filtered and added to the separatory funnel to maximize pesticide recovery. For the extraction process, dichloromethane (DCM, 100 mL) was added to the separatory funnel and the pH of the sample adjusted to two by adding 0.45M H₂SO₄ (~1.5 mL). The content of the separatory funnel was then manually shaken five times, ten times, 15 times and 30 times, releasing the pressure between each set to prevent blow back, spillage and sample loss. The DCM layer was collected in a 500 mL Erlenmeyer flask, and the extraction

process was repeated twice, the first time with 100 mL DCM and the second time with 50 mL DCM. Acidified sodium sulfate was added to dry water present in the DCM and samples were shaken for an hour on an orbital shaker at 200 rpm. Samples were reduced to 2 mL using a rotary evaporator (Buchi Rotavapor R-300, Cole-Parmer®, Canada) followed by methylation with diazomethane (2 mL) at 20°C for 40 min. *n*-Hexane (40 mL) was added, followed by neutralization of the remaining diazomethane with nitrogen gas (7-10 psi) for 11 minutes and samples reduction to 2 mL by rotary evaporator. The volume was adjusted to 10 mL by adding *n*-hexane, and a subsample (2 mL) was transferred to a glass sample vial to quantify pesticides (Appendix I) by gas chromatography and tandem mass spectrometry (GC-MS/MS).

3.3.4 Soil sampling and extraction

Using a truck-mounted Giddings corer, soil cores were collected in December 2014 prior to groundwater sampling. Soil cores (5.08 cm in diameter) were collected in duplicates from soil surface to 0.75 m depth in each plot within 1 to 2 m distance from the wells sampled in this study. Soil cores were sectioned into five depth intervals (0-15, 15-30, 30-45, 45-60 and 60-75 cm) and frozen at -20°C until extracted in fall 2015. Soil samples were thawed at room temperature (20°C) and divided into two equal parts by cutting vertically through the column using a knife. Half of the sample was air-dried for routine soil chemical analyses, and the other half was refrigerated at field moisture content for subsequent pesticide extraction. The air-dried sample was first passed through a perforated drum mill to crush the aggregates to pass 2 mm openings (Waters and Sweetman 1955), and a representative sub-sample was taken for fine grinding using a roller mill (Arnold and Schepers 2004) for elemental microanalysis. Suspensions of

coarse (2 mm) soil in deionized water or 0.01 M CaCl₂ were prepared (5 g soil: 10 mL solution) for determination of soil EC or pH using Thermo Orion VersaStar meter with a DuraProbe 4-electrode conductivity cell and a Ross Ultra Triode pH combination electrode (Ellert et al. 2007). Soil total carbon was determined using an automated flash combustion-Dumas N technique (CE Instruments NA-2100 organic elemental analyzer, Milan Italy). Samples had a gravimetric moisture content ranging from 21 to 28%. For pesticide extraction, acetonitrile (15mL) was added to soil (15 g, wet weight) in Falcon tubes (50mL) and vortexed (2 min). Six g of MgSO₄ from QuEChERS kits was added to tubes, vortexed (2 min), and then allowed to rest to allow for the partitioning and dehydration of the reaction mixture. The mixture was centrifuged (Eppendorf 5810R) at 3220 x g (4000 rpm) for 10 min at 20°C. The supernatant (10-12 mL) was retrieved and cleaned-up by LLE in a separatory funnel (2L) containing 500ml of MilliQ water. The extraction process then followed the LLE protocol as described for the groundwater samples above.

The extraction method's efficiency was determined using soil from experimental plots, as well as sand (silicon dioxide, obtained from VWR®, Montreal, QC, Canada), as follows. Air-dried soil was ground (roller mill) and subsamples (15 g) including sand were spiked (1mL) with pesticides at a concentration ranging from 0.26 to 1.14 µg/mL. Pesticide stock solutions were prepared in toluene and acetone. Subsamples that were not spiked were run as controls to determine background levels of pesticides. Samples were extracted after 1hour incubation as described above and analyzed by GC-MS/MS.

Recovery varied by pesticide (Appendix II) and was on average, for 130 pesticides analyzed, $86.05\% \pm 14.6\%$ for sand and $64.6\% \pm 7.6\%$ for soil.

3.3.5 Quantification of pesticides by GC-MS/MS

The analytical suite included 142 pesticides in groundwater (Appendix I) and 130 pesticides in soil (Appendix II). Fewer compounds could be quantified in soil due to poorer recoveries in that matrix. GC-MS/MS analysis was performed using an Agilent™ 7890B gas chromatograph coupled with an Agilent™ 7693 autosampler and an Agilent™ 7000C triple quadrupole mass spectrometer. Analytes were separated with two HP-5 ms Ultra Inert Capillary columns from Agilent (30 m X 0.25 mm X 0.25 μm). The column head pressure was set at a constant rate so that the flow rate changed with temperature using helium as a carrier gas. The column temperature was programmed as follows: the initial temperature was 70°C (for 2 min), increased to 150 °C at 25 °C/min, ramped to 200°C at 3°C/min and at 8°C/min to 280°C then was held for 7 min at 280°C. The total run time was 38.8 min. The injection volume was 2.0 μL in splitless mode. The injection port, transfer line, and ion source temperatures were 280°C, 300°C, and 280°C, respectively. Nitrogen and helium were used as the collision gasses for all MS/MS experiments.

3.3.6 Statistical analysis

Results of pesticide residues in groundwater and soil were summarized using descriptive statistics performed in Microsoft Excel 2013 (Microsoft, Seattle, USA). A linear mixed effect regression (LMER) model (lme4 package in R Software Version 3.3.1.,

<http://www.cran.r-project.org>) was fitted to determine the influence of soil depth, cropping system (alfalfa-based and corn-based) and manure amendment (manured and non-manured) on total pesticide concentration (sum of the concentrations of all pesticides), Σ DDTs (sum of the concentration of all DDT metabolites) and 2,4-D concentration. The block was kept as a random effect. Model selection was based on Akaike's Information Criterion (AIC), and the model with the lowest AIC value was chosen as the final model. Correlation analysis was performed using Pearson's correlation tests (when data was lognormal) and Spearman rank test (when data did not meet normality assumptions).

3.4 Results and discussions

Of 130 compounds included in the analytical suite, 37 pesticides were detected in soil, namely 16 insecticides, 12 herbicides, eight fungicides and one acaricide (Table 3.2, Appendix IV). 96% of soil samples contained at least one pesticide, with a maximum number of 25 pesticides detected in a single soil sample. The most frequently detected pesticides in soil were p,p'-DDE, 2,4-D, p,p-DDT, o,p-DDT, pp-DDD, difenoconazole, MCPA and trans-heptachlor epoxide (Table 3.2). These pesticides accounted for 85% of all detections. Eight herbicides (2,4-D, bentazone, bromoxynil, fenoxaprop, imazamethabenz, MCPA, mecoprop, and picloram), two fungicides (azoxystrobin, difenoconazole) and one insecticide (p,p'-DDE) were detected in groundwater (Figure 3.3). One-hundred thirty-one (131) other pesticides were monitored for groundwater but not detected. Seven pesticides (2,4-D, MCPA, fenoxaprop, imazamethabenz, azoxystrobin, difenoconazole and p,p'-DDE) were detected in both groundwater and soil. 31.5% of groundwater samples contained at least one pesticide, with only a small portion

of the groundwater samples containing two (5.8%), three (1.9%) or four (0.5%) pesticides. Pesticide residues were detected throughout the year (Figure 3.2) with the frequency of detection being greater during summer and fall than winter (Figure 3.3). The largest number of different pesticides was detected in June, when five pesticides (2,4-D, bentazone, bromoxynil, difenoconazole and MCPA) were found across samples, and with one sample containing all compounds except bentazone. All pesticide detections in groundwater were at concentrations lower than 1µg/L.

Table 3.2 Detection frequency (DF), median, minimum, maximum and average \pm standard deviation of pesticide concentrations through soil depth.

Compounds	Type	Positive detections	DF%	Med	Min	Max	Concentration (average \pm SD), $\mu\text{g/kg}$				
							0-15 cm	15-30 cm	30-45 cm	45-60 cm	60-75 cm
p,p-Dichlorodiphenyldichloroethylene (p,p'-DDE)	Insecticide	104	85.25	0.92	<DL	20.14	5.89 \pm 5.22	6.98 \pm 6.73	1.77 \pm 2.77	0.33 \pm 0.39	0.27 \pm 0.31
2,4-Dichlorophenoxyacetic acid	Herbicide	91	74.59	1.82	<DL	61.29	2.21 \pm 2.21	2.57 \pm 2.57	2.19 \pm 2.15	2.75 \pm 1.41	7.98 \pm 18.22
p,p-Dichlorodiphenyltrichloroethane (p,p-DDT)	Insecticide	85	69.67	1.29	<DL	27.00	6.88 \pm 6.29	6.62 \pm 5.41	1.34 \pm 1.77	0.10 \pm 0.20	0.12 \pm 0.12
o,p-Dichlorodiphenyltrichloroethane (o,p-DDT)	Insecticide	44	36.07	0	<DL	7.48	1.11 \pm 1.54	1.35 \pm 1.89	0.21 \pm 0.42	nd	nd
p,p-Dichlorodiphenyldichloroethane (p,p-DDD)	Insecticide	44	36.07	0	<DL	3.38	0.69 \pm 0.76	0.74 \pm 0.89	0.18 \pm 0.34	nd	nd
Difenoconazole	Fungicide	25	20.49	0	<DL	60.20	2.08 \pm 3.32	1.99 \pm 7.41	4.02 \pm 14.8	0.18 \pm 0.69	0.19 \pm 0.4

MCPA (2-methyl-4-chlorophenoxyacetic acid)	Herbicide	24	19.67	0	<DL	3.73	0.24± 0.71	0.05± 0.1	0.06± 0.12	0.02± 0.06	0.04± 0.13
tr-Heptachlor Epoxide	Insecticide	23	18.85	0	<DL	10.01	1.94± 2.78	2.23± 3.38	0.27± 0.79	nd	nd
Ethalfuralin	Herbicide	16	13.11	0	<DL	87.85	14.30 ±23.2 1	0.08± 0.31	nd	nd	nd
o,p-Dichlorodiphenyldichloroethane (o,p-DDD)	Insecticide	11	9.02	0	<DL	0.42	0.03± 0.095	0.05± 0.13	0.03± 0.08	nd	nd
S-ethyl dipropylthiocarbamate (EPTC)	Herbicide	8	6.56	0	<DL	1.75	0.38± 0.63	nd	nd	nd	nd
Tebuconazole	Fungicide	8	6.56	0	<DL	8.18	0.06± 0.22	0.43± 1.68	0.43± 1.57	0.12± 0.49	nd
Hexazinone	Herbicide	6	4.92	0	<DL	8.43	nd	0.42± 1.68	0.49± 1.81	0.21± 0.84	nd
t-Chlordane	Insecticide	6	4.92	0	<DL	2.67	0.09± 0.31	0.16± 0.59	0.04± 0.16	nd	nd
Propiconazole	Fungicide	5	4.1	0	<DL	2.76	0.13± 0.49	0.1±0. 52	1.48± 0.18	nd	nd
Boscalid	Fungicide	4	3.28	0	<DL	7.37	nd	0.43± 1.63	0.47± 1.72	nd	nd

Fenoxaprop	Herbicide	4	3.28	0	<DL	30.26	nd	1.32± 5.81	0.25± 1.03	nd	nd
o,p- Dichlorodiphenyldichl oroethylene (o,p'- DDE)	Insecticide	4	3.28	0	<DL	0.30	0.02± 0.059	0.02± 0.069	nd	nd	nd
Azoxystrobin	Fungicide	3	2.46	0	<DL	4.64	nd	0.17± 0.88	0.29± 1.06	nd	nd
Prothioconazole- Desthio	Fungicide	3	2.46	0	<DL	0.65	nd	0.02± 0.12	0.04± 0.15	nd	nd
cis-Chlordane	Insecticide	2	1.64	0	<DL	0.93	nd	0.06± 0.21	nd	nd	nd
Clopyralid	Herbicide	2	1.64	0	<DL	5.43	0.19± 1.03	nd	nd	nd	0.45± 1.41
Fludioxonil	Fungicide	2	1.64	0	<DL	1.30	nd	nd	0.07± 0.28	nd	nd
Imazamethabenz	Herbicide	2	1.64	0	<DL	59.39	2.74± 11.58	nd	nd	nd	nd
Bifenthrin	Insecticide	1	0.82	0	<DL	0.89	nd	0.032 ±0.17	nd	nd	nd
Bromopropylate	Acaricide	1	0.82	0	<DL	1.80	nd	0.06± 0.34	nd	nd	nd
Carfentrazone-ethyl	Herbicide	1	0.82	0	<DL	2.25	nd	0.08± 0.42	nd	nd	nd

cis-Permethrin	Insecticide	1	0.82	0	<DL	1.03	nd	0.037 ±0.19	nd	nd	nd
Clodinafop-propargyl	Herbicide	1	0.82	0	<DL	1.89	nd	0.07± 0.36	nd	nd	nd
Cyhalothrin-lambda	Insecticide	1	0.82	0	<DL	1.89	nd	0.07± 0.36	nd	nd	nd
Deltamethrin	Insecticide	1	0.82	0	<DL	2.19	nd	0.08± 0.413	nd	nd	nd
Diclofop	Herbicide	1	0.82	0	<DL	0.49	nd	0.02± 0.09	nd	nd	nd
Hexachlorocyclohexa ne-delta	Insecticide	1	0.82	0	<DL	0.60	0.02± 0.11	nd	nd	nd	nd
Methoxychlor	Insecticide	1	0.82	0	<DL	1.07	nd	0.04± 0.20	nd	nd	nd
Quizalofop-ethyl	Herbicide	1	0.82	0	<DL	1.56	nd	0.06± 0.29	nd	nd	nd
trans-Permethrin	Insecticide	1	0.82	0	<DL	1.26	nd	0.05± 0.24	nd	nd	nd
Trifloxystrobin	Fungicide	1	0.82	0	<DL	0.85	nd	0.03± 0.16	nd	nd	nd

All concentrations are in µg/kg (dry weight). nd= not detected, DL=detection limit.
Mid= Median, Min= Minimum, Max=Maximum concentration

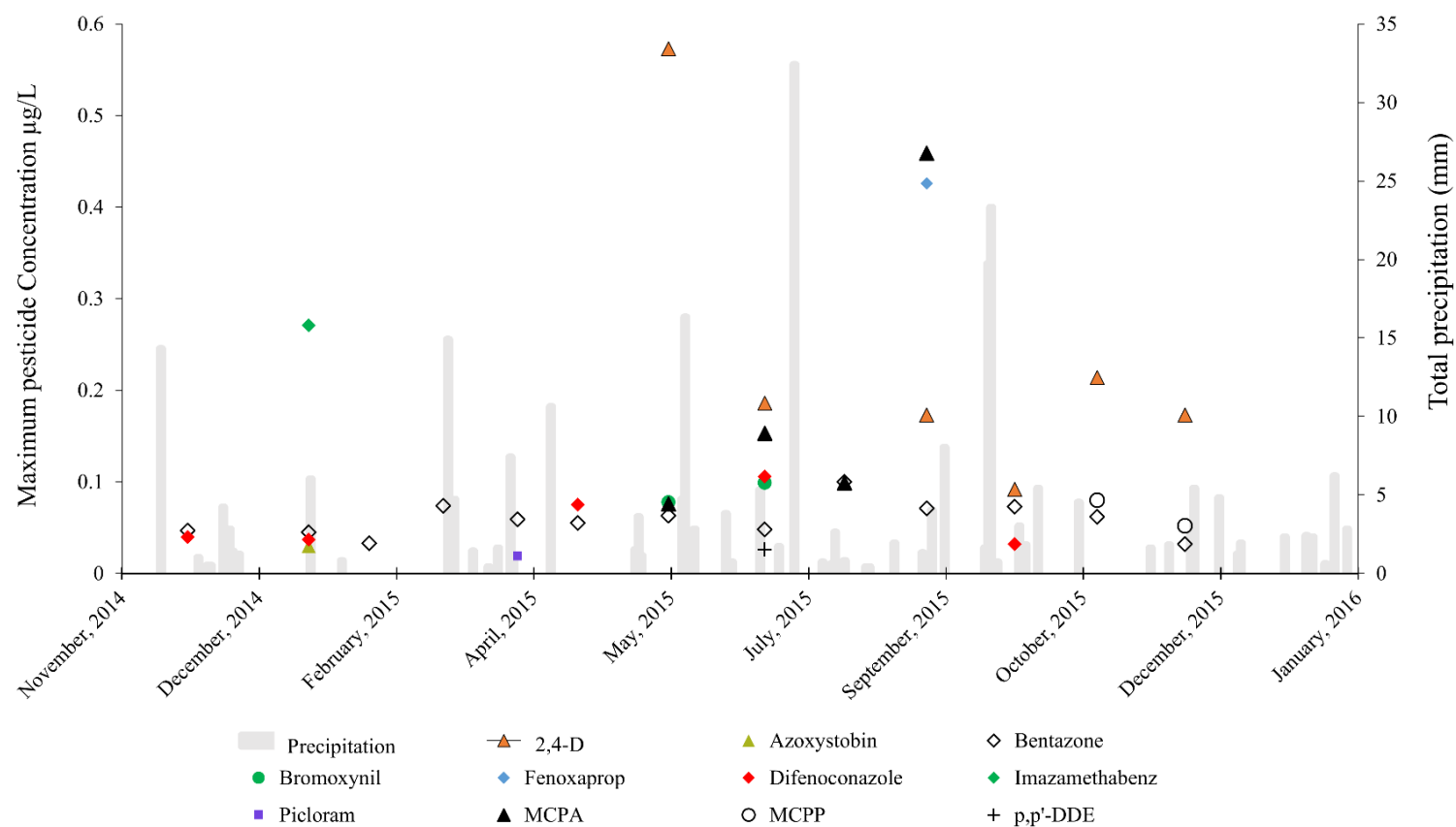


Figure 3.2 Temporal variation in the maximum concentration ($\mu\text{g/L}$) of pesticides in groundwater at the Rotation U site at the Lethbridge Research and Development Centre, and total daily precipitation recorded during the sampling period.

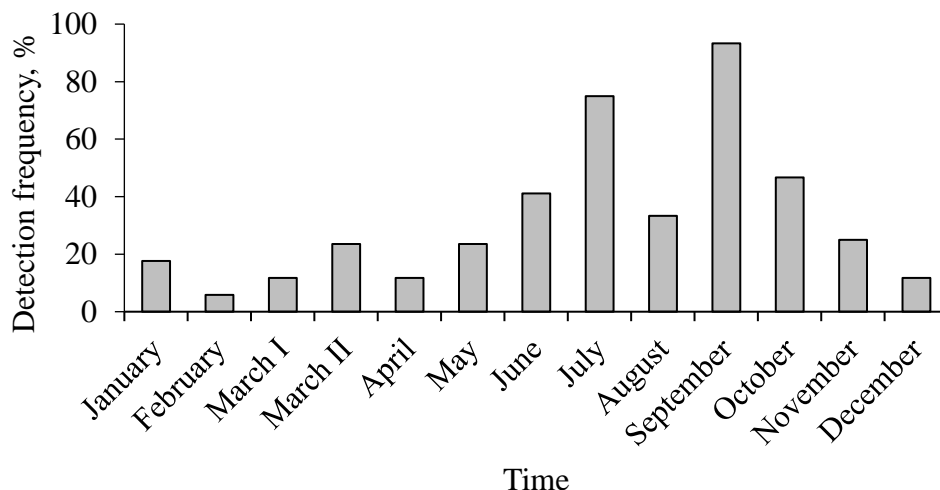


Figure 3.3 Monthly variation in the detection frequencies of pesticide residues in shallow groundwater. Detection frequency represents the number of samples having at least one pesticide, divided by total number of samples analyzed, expressed as percentage. Total number of samples per month was 15-17.

Bentazone (14.5%) and two phenoxy acetic acids, 2,4-D (12.7%) and MCPA (7.0%), were the most frequently detected pesticides in groundwater samples (Figure 3.4). The detections of these three herbicides accounted for 79.3% of a total of 92 positive detections. 2,4-D was detected in all the wells and piezometers at least once throughout the year. 2,4-D was detected in May through November with the highest concentration in May ($0.573 \mu\text{g/L}$), and MCPA was detected in May through August with the maximum concentration in August ($0.459 \mu\text{g/L}$). Bentazone was detected throughout the year with the largest concentration ($0.1 \mu\text{g/L}$) in July. Bentazone, difenoconazole, imazamethabenz and azoxystrobin were detected in groundwater at least once in the winter months (Figure 3.2). p,p'-DDE, a metabolite of DDT, was detected once in a groundwater sample despite

its low solubility in water (0.006 mg/L, Lewis et al. 2016) and high affinity towards soil organic matter (Semple et al. 2003).

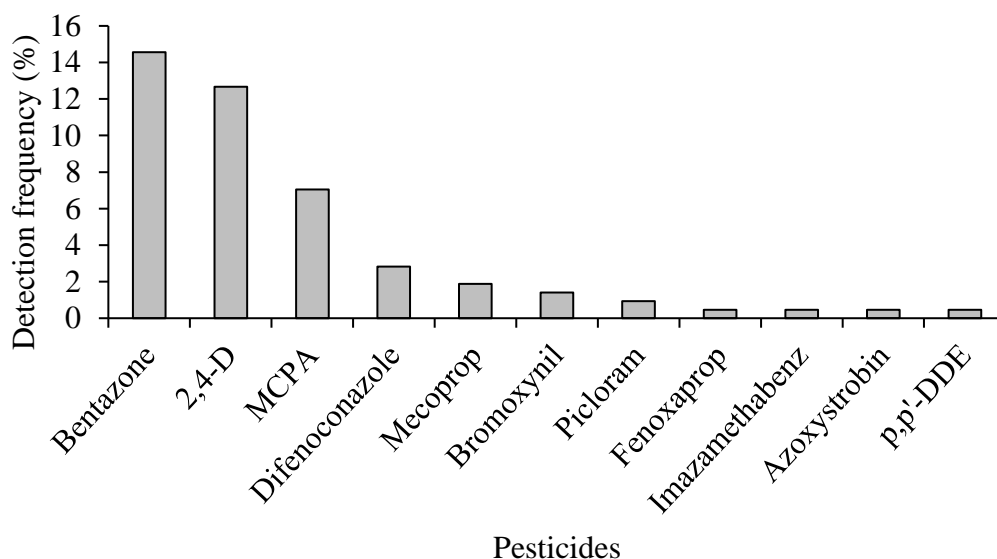


Figure 3.4 Detection frequencies of pesticides detected in groundwater at the experimental plots. Detection frequency is the proportion of samples contaminated with pesticide and total samples analyzed, expressed in percentage.

Of the pesticides charted in Figure 3.4, MCPA, 2,4-D and bromoxynil herbicides and difenoconazole fungicide had been applied since 2010 (Appendix III). Fungicides typically are used as seed treatments in May when crops are planted. Selective herbicides are used in early June when plants are in the seedling stage. In groundwater, the pesticides detection frequency not necessarily reflected the application time as well as major rainfall and irrigation events (Figure 3.2). Pesticides are applied in two main application periods per year, in June and in September /October (Appendix III). The occurrence of pesticides in groundwater in this study followed a similar pattern as

described in Greece by Albanis et al. (1998), who detected greater concentrations of alachlor and atrazine in groundwater from June through September when these herbicides are typically applied, followed by lesser alachlor and atrazine concentration during fall and winter.

Bentazone was frequently detected in groundwater but never in soil samples. Bentazone concentration in groundwater ranged from 0.028 µg/L to 0.100 µg/L (Fig 3.2), and the concentration remained similar throughout the year. Bentazone is a commonly used thiadiazole herbicide in Alberta (AEP 2015), but the high frequency of bentazon detection was unexpected, as it has not been used in the experimental plots for over ten years. Hence, the frequent detection of this herbicide in groundwater must either be due to its persistence in groundwater or transportation from adjacent fields. Bentazone was applied on fava beans which were grown sporadically in adjacent fields between 1991 to 2001, it is only weakly sorbed to the soil (Boivin et al. 2005) and is highly soluble in water (7112mg/L, Lewis et al. 2016). Bentazone photodegrades in both soil and water but is resistance to hydrolysis (USEPA, 1985). Once bentazone reaches groundwater, the dark conditions and its stability in water possibly make it persistent in groundwater. The repeated detection of bentazon at many sampling times (Fig. 3.2) suggests that this soluble and mobile herbicide entered the GW several years ago, and has become a persistent feature.

The phenoxy herbicides are widely used and have been commonly detected in various environmental matrices (e.g. Hill et al. 1996; Environment Canada 2011). 2,4-D and

MCPA are weakly acidic herbicides commonly used to control broadleaf weeds in Prairie agriculture and were applied to the field approximately three and two years, respectively, before the sampling period of the study. 2,4-D is considered mobile in soil because of its acidic carboxyl group (Aquino et al. 2007) and relatively large water solubility (24,300 mg/L at 20°C, Lewis et al. 2016), resulting in surface and sub-surface water contamination (Miller et al. 1995a; Donald et al. 2007). 2,4-D is non-persistent in soil with an average field half-life ranging from 1-14 days (NPIC 2012). However, under anaerobic laboratory conditions, the half-life can be as long as 333 days at 20°C (USEPA 2005). MCPA, similarly to 2,4-D, has a low persistence with a reported field half-life of 14 days to 1 month, and is highly soluble in water (29,390 mg/l at 20°C) making it a highly leachable pesticide (Lewis et al. 2016). Hiller et al. (2006) reported that phenoxy herbicides like MCPA exhibit low sorption, making them mobile in surface soil and likely to contaminate groundwater. 2,4-D and MCPA have been detected in soil and groundwater from the Canadian Prairies in the past (Miller et al. 1995a; Miller et al. 1995b; Hill et al. 1996) as well as from various agricultural sites in the central and southern Alberta (present study, see chapter 2 of the thesis).

The occurrence of mecoprop in GW likely is attributable to the periodic application of turfgrass herbicides used on the perimeter of the experiment to curtail the invasion of the alfalfa plots from dandelion (*Taraxacum officinale*) in the border areas. Difenconazole was the most common fungicide detected in both soil and groundwater. Its frequent detection along with that of metalaxyl and azoxystrobin result from the use of treated seeds of alfalfa, corn and wheat rather than direct application.

The levels of DDT (sum of o,p and p,p isomers), DDE (sum of o,p' and p,p' isomers) and DDD (sum of o,p and p,p isomers) in soil ranged between 0.26-25.69 µg/kg, 0.14- 20.14 µg/kg and 0.29-3.73 µg/kg, respectively. DDE (p,p'-isomer) was the most frequently detected pesticide in soil samples (detection frequency of 85.3%, 104 positive detections in 122 samples). The occurrence of organochlorine insecticides despite their ban decades ago results from their persistence. DDT was deregistered for use in Canada in 1972 but has been reported in soil and groundwater in some studies in Canada since then (Waite et al. 2005; Daly et al. 2007). Hebert et al. (1994) reported levels of DDT, DDE and DDD ranging to be 1.7 to 131.7 µg/kg, 4.0 to 342.6 µg/kg and up to 11.7 µg/kg, respectively, in soil samples from Ontario, Canada. DDT and its metabolites have a high affinity for SOC (Koc: 151,000, Lewis et al. 2016) and combined with their low water solubility (0.006mg/L, Lewis et al. 2016), their mobility through the soil profile and subsequent leaching to groundwater are minimal (Gavrilescu 2005). Our results seemingly support this, given a single detection of p,p'-DDE in groundwater samples and frequent detection in corresponding soil samples. The errant DDT detection (well 31) in the GW possibly was associated with contamination of surface soil, for example when the well extensions were removed or re-installed to facilitate field operations. This single detection could also be a result of the transport of soil particles to groundwater, for example through preferential flow paths, because the soil sample collected at the same site contained a large concentration of DDT. Past studies have reported the presence of DDT in groundwater samples (Toccalino et al. 2014; Karadeniz and Yenisoy-Karakaş 2015). The detection of other banned compounds such as chlordane (cis-, trans-), trans-heptachlor epoxide and δ-HCH in soil likely resulted from their traditional application for the control of sugarbeet root maggot in southern Alberta (Harper et al. 1961; McDonald 1961).

Sugar-beet was included in the rotation system at our experimental site before 1991 (Dubetz 1983).

Factors influencing pesticide concentration in soil

The final regression model (lowest AIC value) included all three variables of interest (depth, cropping system and manure amendment) as fixed factors and block as a random factor. Model outputs revealed that soil depth and cropping system significantly affected the total and Σ DDTs concentrations, but 2,4-D concentration was not affected by any of these factors. Manure amendment did not have statistically significant effect on total, Σ DDTs or 2,4-D concentrations ($P > 0.05$). Correlation analysis showed that 2,4-D was somewhat uniformly distributed through the soil depth (no strong correlation, $r = -0.03$, Pearson test) (Figure 3.5). Σ DDTs concentration, on the other hand, had significant negative correlation with soil depth ($r = -0.9$, Pearson test) (Figure 3.5). The alfalfa-based cropping system had a higher total pesticide concentration (range: non-detects to 101.52 $\mu\text{g/kg}$) with an average concentration of 22.38 $\mu\text{g/kg}$ compared to the corn-based cropping system (range: 0.17 to 104.52 $\mu\text{g/kg}$) with a mean concentration of 12.67 $\mu\text{g/kg}$. Similarly, alfalfa based cropping system had higher Σ DDTs concentration (range: non-detects to 40.87 $\mu\text{g/kg}$) than in corn-based cropping system (range: non-detects to 13.37 $\mu\text{g/kg}$). The concentration of 2,4-D in the alfalfa based cropping system ranged from non-detects to 61.29 $\mu\text{g/kg}$ with an average concentration of 3.33 $\mu\text{g/kg}$, and that in the corn-based system ranged as non-detects to 9.97 $\mu\text{g/kg}$ with an average of 2.59 $\mu\text{g/kg}$. Σ DDTs concentration was positively correlated with SOC ($r = 0.51$, Pearson test).

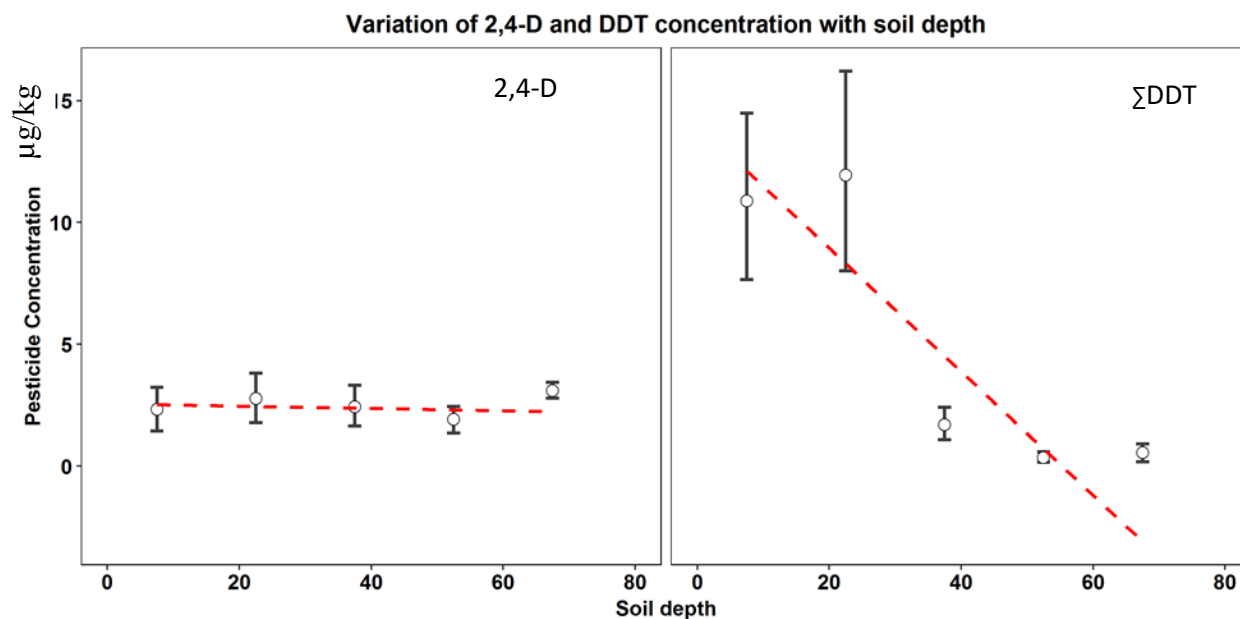


Figure 3.5 Variation in 2,4-D and DDT concentration with soil depth.

Pesticide residues in soil are affected by factors like soil physical and chemical characteristics (Farenhorst et al. 2008; Gaultier et al. 2008), land management practices (Wang et al. 2006; Murugan et al. 2013) and environmental factors (Edwards 1975). The key factors controlling the fate of pesticides in soil are degradation (chemical and biological) and sorption, which are influenced by soil properties like SOC and pH (McConnell and Hossner 1985; Farenhorst et al. 2008), as well as the nature of the pesticides themselves (Boivin et al. 2005). SOC is the versatile sorbent, which decreases with soil depth. Hence, pesticides which have high sorption coefficient show a negative correlation with soil depth. Our finding of negative correlation of Σ DDTs concentration with depth supports this (Koc for Σ DDTs -151,000, Lewis et al. 2016). (Figure 3.5). The

absence of correlation between 2,4-D concentration and depth is probably related to its low sorption coefficient ($K_{oc} = 39.3$, Lewis et al. 2016) and greater mobility.

Different cropping systems are often associated with differences in tillage, irrigation and pesticide application (type and rate). In turn, these farming practices can influence the level of pesticide residues in soil directly or indirectly by altering the soil environment (Alam et al. 2014; Hueso-González et al. 2014). A significant effect of cropping system on total pesticide concentration is an indication of the potential impact of various farming practices, and resultant variation in soil properties. SOC was slightly higher in the alfalfa-based cropping system (1.37 ± 0.57 , average \pm standard deviation) compared to the corn-based cropping system (1.28 ± 0.46), which might be due to the lower tillage activity in alfalfa based cropping system compared to corn-based cropping system. This finding is in line with Smith et al. (2012) who found that including perennial hay such as alfalfa in crop rotations increases the SOC levels in soil. Although we lack proper and updated pesticide application data on the plots, the possible differences of the pesticide inputs to the plots in the past cannot be undermined.

3.5 Conclusion

The detection of 11 different pesticides in groundwater and 37 different pesticides in soil in a long-term rotation experimental plot following typical prairie farming systems suggests that both currently and historically used pesticides occur in soil and groundwater in southern Alberta. This study demonstrates that pesticide levels in groundwater vary year-round, with overall higher detection frequencies during summer and fall, which correspond to pesticide application periods. Pesticides like bentazone can reach

groundwater at sites which did not receive it currently and can occur in groundwater throughout the year. The detection of a greater number of pesticides in the soil suggests that soil acts as a sink for pesticide residues and not all pesticides leach to groundwater. The occurrence of legacy organochlorine compounds such as DDT (all isomers), trans-heptachlor epoxide, cis-,trans-chlordane can be explained by their widespread use in the past for insect control and further confirm their longevity and persistence in the environment. Detection of 2,4-D, difenoconazole and MCPA throughout the soil column, and in groundwater, indicates that pesticides did leach from the surface to shallow groundwater. Significant effects of soil depth and cropping system on pesticide concentrations were observed in this study, and likely constitute valuable information regarding determinants of pesticide residues in soil. Our findings of different factors affecting 2,4-D and Σ DDTs concentrations in soil and water also suggested that such effects are substantially dependent upon the chemical properties of pesticides.

3.6 Acknowledgements

This research was funded by Alberta Innovates - Energy and Environment Solutions (AI-EES) and Natural Sciences and Engineering Research Council of Canada (NSERC) grant to Dr. Farenhorst for student financial support. The author would like to thank Tara Vucurevich, Scott Splengler, Melissa Fry and Moritz Haben for their technical support in the field during sampling. Support from Dr. Francis Zvomuya, Dr. Inoka Amarakoon (University of Manitoba), Dr. Fabien Mavrot, Dr. Pratap Kafle (University of Calgary) for data analysis is highly acknowledged.

3.7 References

- Alam, M. K., Islam, M. M., Salahin, N. and Hasanuzzaman, M. 2014.** Effect of tillage practices on soil properties and crop productivity in wheat-mungbean-rice cropping system under subtropical climatic conditions. *The Scientific World Journal* 2014.
- Albanis, T., Hela, D., Sakellarides, T. and Konstantinou, I. 1998.** Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia (N. Greece) by means of solid-phase extraction disks and gas chromatography. *Journal of Chromatography A* **823 (1)**: 59-71.
- Alberta Environment and Parks (AEP). 2015.** Overview of 2013 Pesticide Sales in Alberta. Land Policy Branch. Edmonton. 80 pp.
- Aquino, A., Tunega, D., Haberhauer, G., Gerzabek, M. and Lischka, H. 2007.** Interaction of the 2, 4-dichlorophenoxyacetic acid herbicide with soil organic matter moieties: a theoretical study. *European journal of soil science* **58 (4)**: 889-899.
- Arias, R. N. and de Peretti, A. F. 1993.** Effects of 2, 4-dichlorophenoxyacetic acid on *Rhizobium* sp. growth and characterization of its transport. *Toxicology letters* **68 (3)**: 267-273.
- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C. and García-Río, L. 2008.** The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, ecosystems & environment* **123 (4)**: 247-260.

- Arnold, S. L., & Schepers, J. S. 2004.** A simple roller-mill grinding procedure for plant and soil samples. *Communications in soil science and plant analysis*, **35** (3-4): 537-545.
- Beke, G. J., Entz, T., & Graham, D. P. 1993.** Aquifer characteristics and long-term ground-water levels. *Journal of irrigation and drainage engineering*, **119** (1): 129-141.
- Boivin, A., Cherrier, R. and Schiavon, M. 2005.** A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere* **61** (5): 668-676.
- Campbell, C. A., Zenter, R. P., Janzen, H. H., & Bowren, K. E. 1990.** Crop rotation studies on the Canadian prairies (No. 1841/E).
- Daly, G. L., Lei, Y. D., Teixeira, C., Muir, D. C. and Wania, F. 2007.** Pesticides in western Canadian mountain air and soil. *Environmental science & technology* **41** (17): 6020-6025.
- Davis, J., Johnson, S. E., & Jennings, K. 2010.** Herbicide carryover in hay, manure, compost and grass clippings: Caution to hay producers, livestock owners, farmers and home gardeners. NC State University. Ext. Pub. AG-727W.
- Decker, J. 1990.** Pesticide Use: Environmental Risks and Alternative. *Environs: Environmental Law & Policy Journal*. **14**: 46.
- Delwiche, K. B., Lehmann, J., & Walter, M. T. 2014.** Atrazine leaching from biochar-amended soils. *Chemosphere*, **95**: 346-352.

- Don Waite, P. B., Quinnett-Abbott, L. and Ripley, B. D. 2005.** Residues of DDT and other selected organochlorine pesticides in soils from Saskatchewan, Canada (1999). Canadian Journal of Soil Science **85** (2): 265-271.
- Donald, D. B., Cessna, A. J., Sverko, E. and Glozier, N. E. 2007.** Pesticides in surface drinking-water supplies of the Northern Great Plains. Environmental health perspectives: 1183-1191.
- Dubetz, S. 1983.** Ten-year Irrigated Rotation U 1911-1980. Agric. Can. Tech. Bull. 1983-21 E
- Edwards, C. 1975.** Factors that affect the persistence of pesticides in plants and soils. Pure and Applied Chemistry **42** (1-2): 39-56.
- Ellert, B. H., Janzen, H. H., VandenBygaart, A. J., & Bremer, E. 2007.** Measuring change in soil organic carbon storage. Soil sampling and methods of analysis, 25-38.
- Entz, M. H., Baron, V. S., Carr, P. M., Meyer, D. W., Smith, S. and McCaughey, W. P. 2002.** Potential of forages to diversify cropping systems in the Northern Great Plains. Agronomy Journal **94** (2): 240-250.
- Environment Canada. 2011.** Presence and levels of priority pesticides in selected Canadian aquatic ecosystem. Water Science and technology directorate.
- Environment Canada. 2016.** Canadian climate normals 1981–2010. National Climate Data and Information Archive. Accessed: July 20, 2016. Available in: http://climate.weatheroffice.gc.ca/climate_normals/index_e.html.

- Farenhorst, A., Papiernik, S., Saiyed, I., Messing, P., Stephens, K., Schumacher, J., Lobb, D., Li, S., Lindstrom, M. and Schumacher, T. 2008.** Herbicide sorption coefficients in relation to soil properties and terrain attributes on a cultivated prairie. *Journal of Environmental Quality* **37 (3)**: 1201-1208.
- Fiore, M., Anderson, H., Hong, R., Golubjatnikov, R., Seiser, J., Nordstrom, D., Hanrahan, L. and Belluck, D. 1986.** Chronic exposure to aldicarb-contaminated groundwater and human immune function. *Environmental Research* **41 (2)**: 633-645.
- Freyman, S., Palmer, C., Hobbs, E., Dormaar, J., Schaalje, G. and Moyer, J. 1982.** Yield trends on long-term dryland wheat rotations at Lethbridge. *Canadian Journal of Plant Science* **62 (3)**: 609-619.
- Gaultier, J., Farenhorst, A., Cathcart, J. and Goddard, T. 2008.** Degradation of [carboxyl-14 C] 2, 4-D and [ring-U-14 C] 2, 4-D in 114 agricultural soils as affected by soil organic carbon content. *Soil Biology and Biochemistry* **40 (1)**: 217-227.
- Gavrilescu, M. 2005.** Fate of pesticides in the environment and its bioremediation. *Engineering in Life Sciences* **5 (6)**: 497.
- Harper, A., Lilly, C. and Bergen, P. 1961.** An evaluation of insecticides for control of the sugar beet root maggot in southern Alberta.
- Hebert, C., Weseloh, D., Kot, L. and Glooschenko, V. 1994.** Organochlorine contaminants in a terrestrial foodweb on the Niagara Peninsula, Ontario, Canada 1987–89. *Archives of Environmental Contamination and Toxicology* **26 (3)**: 356-366.

Helgason, B., Gregorich, E., Janzen, H., Ellert, B., Lorenz, N. and Dick, R. 2014.

Long-term microbial retention of residue C is site-specific and depends on residue placement. *Soil Biology and Biochemistry* **68**: 231-240.

Hill, B., Miller, J., Chang, C. and Rodvang, S. 1996. Seasonal variation in herbicide

levels detected in shallow Alberta groundwater. *Journal of Environmental Science &*

Health Part B **31 (4)**: 883-900.

Hiller, E., Khun, M., Zemanová, L., Jurkovic, L. and Bartal, M. 2006. Laboratory

study of retention and release of weak acid herbicide MCPA by soils and sediments and

leaching potential of MCPA. *Plant Soil and Environment* **52 (12)**: 550.

Hueso-González, P., Martínez-Murillo, J. F. and Ruiz-Sinoga, J. D. 2014. The impact

of organic amendments on forest soil properties under Mediterranean climatic conditions.

Land Degradation & Development **25 (6)**: 604-612.

James, K. A. and Hall, D. A. 2015. Groundwater pesticide levels and the association

with Parkinson disease. *International journal of toxicology* **34 (3)**: 266-273.

Kah, M., Beulke, S. and Brown, C. D. 2007. Factors influencing degradation of

pesticides in soil. *Journal of agricultural and food chemistry* **55 (11)**: 4487-4492.

Karadeniz, H. and Yenisoy-Karakaş, S. 2015. Spatial distributions and seasonal

variations of organochlorine pesticides in water and soil samples in Bolu, Turkey.

Environmental Monitoring and Assessment **187 (3)**: 1-12.

Keesstra, S., Geissen, V., Mosse, K., Piirainen, S., Scudiero, E., Leistra, M. and van

Schaik, L. 2012. Soil as a filter for groundwater quality. *Current Opinion in*

Environmental Sustainability **4 (5)**: 507-516.

- Leistra, M., & Boesten, J. J. T. I. 2012.** Experiments on the movement of pesticides in sandy soils to groundwater: prospects of testing preferential transport models (No. 2291). Alterra Wageningen UR.
- Lewis, K. A., Tzilivakis, J., Warner, D. J., & Green, A. 2016.** An international database for pesticide risk assessments and management. *Human and Ecological Risk Assessment: An International Journal*, **22** (4): 1050-1064.
- McConnell, J. S. and Hossner, L. R. 1985.** pH-dependent adsorption isotherms of glyphosate. *Journal of agricultural and food chemistry* **33** (6): 1075-1078.
- McDonald, S. 1961.** The reduction of seedling sugar-beet stands by heptachlor-impregnated fertilizer. *Canadian Journal of Plant Science* **41** (1): 16-19.
- McGrath, G., Hinz, C. and Sivapalan, M. 2010.** Assessing the impact of regional rainfall variability on rapid pesticide leaching potential. *Journal of Contaminant Hydrology* **113** (1): 56-65.
- Miller, J., Foroud, N., Hill, B. and Lindwall, C. 1995a.** Short Communication: Herbicides in surface runoff and groundwater under surface irrigation in southern Alberta. *Canadian Journal of Soil Science* **75** (1): 145-148.
- Miller, J., Hill, B., Chang, C. and Lindwall, C. 1995b.** Residue detections in soil and shallow groundwater after long-term herbicide applications in southern Alberta. *Canadian Journal of Soil Science* **75** (3): 349-356.
- Murugan, A., Swarnam, T. and Gnanasambandan, S. 2013.** Status and effect of pesticide residues in soils under different land uses of Andaman Islands, India. *Environmental Monitoring and Assessment* **185** (10): 8135-8145.

NPIC (National Pesticide Information Centre). 2012. 2,4-D General Factsheet.

Archived at: <http://npic.orst.edu/factsheets/24Dgen.html#env>

Reyes, E. S., Liberda, E. N. and Tsuji, L. J. S. 2015. Human exposure to soil contaminants in subarctic Ontario, Canada. *International journal of circumpolar health* **74**.

Rodriguez-Cruz, M. S., Jones, J. E. and Bending, G. D. 2006. Field-scale study of the variability in pesticide biodegradation with soil depth and its relationship with soil characteristics. *Soil Biology and Biochemistry* **38 (9)**: 2910-2918.

Semple, K. T., Morriss, A. and Paton, G. 2003. Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. *European journal of soil science* **54 (4)**: 809-818.

Smith, A. E. 1982. Review Article: Prepared upon Invitation of the CSSS: Herbicides and the soil environment in Canada. *Canadian Journal of Soil Science* **62 (3)**: 433-460.

Smith, A., Hume, L., Lafond, G. and Biederbeck, V. 1991. A review of the effects of long-term 2, 4-D and MCPA applications on wheat production and selected biochemical properties of a Black Chernozem. *Canadian Journal of Soil Science* **71 (1)**: 73-87.

Smith, E. G., Janzen, H. H., Ellert, B. H. and Nakonechny, D. J. 2012. Rotation 120—Lethbridge, Alberta. *Prairie Soils Crops* **5**: 155-164.

Statistics Canada. 2015. Agricultural water use in Canada. Available in:

<http://www.statcan.gc.ca/pub/16-402-x/2013001/part-partie1-eng.htm>

Tiryaki, O. and Temur, C. 2010. The fate of pesticide in the environment. *Journal of Biological and Environmental Sciences* **4 (10)**.

Toccalino, P. L., Gilliom, R. J., Lindsey, B. D. and Rupert, M. G. 2014. Pesticides in Groundwater of the United States: Decadal-Scale Changes, 1993–2011. *Groundwater* **52** (S1): 112-125.

Trautmann, N. M., Porter, K. S. and Wagenet, R. J. 1989. Pesticides and groundwater: a guide for the pesticide user.

USEPA (United States Environmental Protection Agency). 1985. Pesticide Factsheet: Bentazone and Sodium Bentazone. Office of Pesticide and Toxic Substances, Washington, DC.

USEPA (United States Environmental Protection Agency). 2005. Reregistration Eligibility Decision for 2,4-D. March 2007 EPA 738-R-07-005. Accessed: 18 January 2017. Available: https://archive.epa.gov/pesticides/reregistration/web/pdf/24d_red.pdf

Venier, M., Salamova, A. and Hites, R. A. 2016. Temporal trends of persistent organic pollutant concentrations in precipitation around the Great Lakes. *Environmental Pollution*.

Vonberg, D., Hofmann, D., Vanderborght, J., Lelickens, A., Köppchen, S., Pütz, T., Buraue, P. and Vereecken, H. 2014. Atrazine soil core residue analysis from an agricultural field 21 years after its ban. *Journal of Environmental Quality* **43** (4): 1450-1459.

Waite, D. T., Bailey, P., Sproull, J. F., Quiring, D. V., Chau, D. F., Bailey, J., & Cessna, A. J. 2005. Atmospheric concentrations and dry and wet deposits of some herbicides currently used on the Canadian Prairies. *Chemosphere*, **58**(6): 693-703.

- Walker, C. H., Sibly, R., Hopkin, S. and Peakall, D. B. 2012.** Principles of ecotoxicology, CRC press.
- Wan, M. T., Kuo, J.-n. and Pasternak, J. 2005.** Residues of endosulfan and other selected organochlorine pesticides in farm areas of the Lower Fraser Valley, British Columbia, Canada. *Journal of Environmental Quality* **34 (4)**: 1186-1193.
- Wang, T.-Y., Lu, Y.-L., Dawson, R., Shi, Y.-J., Zhang, H. and Xing, Y. 2006.** Effects of environmental factors on organochlorine pesticide residues in soils of the Guanting Reservoir area, China. *Journal of Environmental Science and Health Part B* **41 (3)**: 309-321.
- Waters, D. F., & Sweetman, I. C. 1955.** The Rukuhia soil grinder. *Soil Sci*, **79**: 411-413.
- Woudneh, M. B., Ou, Z., Sekela, M., Tuominen, T. and Gledhill, M. 2009.** Pesticide Multiresidues in Waters of the Lower Fraser Valley, British Columbia, Canada. Part II. Groundwater. *Journal of Environmental Quality* **38 (3)**: 948-954.
- Wu, C., Luo, Y., Gui, T. and Huang, Y. 2014.** Concentrations and potential health hazards of organochlorine pesticides in shallow groundwater of Taihu Lake region, China. *Science of the Total Environment* **470-471**: 1047-1055.
- Zhang, H., Luo, Y., Zhao, Q., Wong, M. and Zhang, G. 2006.** Residues of organochlorine pesticides in Hong Kong soils. *Chemosphere* **63 (4)**: 633-641.

4. OVERALL SYNTHESIS

4.1 Research summary

Pesticides encompass a wide group of chemical compounds primarily used for preventing or reducing the impacts of pests (weeds, insects, fungi) on agricultural productivity. The increasing intensification of agriculture has led to a growing use of pesticide products (Matson et al. 1997; Tilman et al. 2001), which in turn has resulted in the contamination of the environment including soil and water. This environmental contamination is a concern because of the potential adverse effects of pesticides on human and ecosystem health. The soil is supporting almost if not all living beings, and groundwater represents one of the most valuable sources of drinking water (Morris et al. 2003; Kløve et al. 2014). High levels of pesticide residues in groundwater and soil can affect these ecosystems (Graymore et al. 2001; Bünemann et al. 2006; Rodríguez-Liebana et al. 2014) and can irreversibly reduce their quality (Dexter and Zebbiech 2006). In Canada, previous studies have reported pesticide residues in various environmental matrices (Waite et al. 1992; Wan et al. 2005; Kurt-Karakus et al. 2006; Donald et al. 2007; Messing et al. 2012) including soil and groundwater. Alarming, some studies have reported levels of pesticide higher than their respective water quality guidelines (Donald et al. 2007; Messing et al. 2012). This highlights the increasing need for pesticide monitoring in the environment to safeguard public and ecosystem health.

Pesticides reach soil through direct application, spray drift during foliar application, wash-off from foliage and atmospheric deposition. Pesticides in soil can reach

groundwater by leaching or preferential flow (Arias-Estévez et al. 2008). The fate of pesticides in soil is a function of various factors including physical and chemical properties of both pesticides and soil, land use as well as climate (Gavrilescu 2005; Arias-Estévez et al. 2008). Monitoring pesticide residues in the environment is crucial for getting first-hand information on the state of contamination, while knowledge of pesticide residues occurrence in groundwater and potential factors affecting pesticides leaching or accumulation in soil could be beneficial to design future pesticide management activities (Thodal et al. 2009).

The work reported in Chapters 2 and 3 was designed to address the above-mentioned concerns and aimed to monitor pesticide residues in Alberta's groundwater for three consecutive years, to study the monthly variation of pesticide residues in groundwater and to determine the effect of soil depth and land use (cropping system and manure treatment) in the concentration of pesticide residues in soil.

In Chapter 2, concentrations of pesticide residues in 440 groundwater samples collected in 2013-2015 from central and southern Alberta are reported and analyzed to monitor 142 pesticides in the groundwater. This study generated new knowledge on the occurrence of pesticide residues and their levels in groundwater of central and southern Alberta. 23 pesticides were detected as part of that study. Herbicides, insecticides as well as fungicides were detected at different levels throughout the growing season (May-September). However, none of the compounds surpassed the Canadian water quality guidelines for drinking water. Herbicides were detected most frequently, especially 2,4-D, clopyralid and MCPA. These findings are in accordance with their sales rankings in

Alberta (Alberta Environment and Parks 2015). Spatial variation in pesticide residues was observed, with five compounds detected in both sampled areas. Annual and seasonal variation were also evident, which can be linked to temporal variation in climatic conditions, pesticide application, and land use. Besides the regular monitoring, this study also presents the usefulness of broad-based analytical suites, allowing for the detection of pesticide compounds that could have been missed otherwise.

In Chapter 3 of this thesis, I report the results of a study conducted to monitor 142 pesticide compounds in shallow groundwater and 130 compounds in soil collected from experimental plots (Lethbridge Research and Development Centre) under long-term crop rotations. Pesticides concentrations in shallow groundwater (within 2.1-9 meters) and soil (0-75 cm) were determined. The variation in pesticide levels and occurrence with depth, cropping system and manure application were investigated. The results of this study showed that pesticides are found in shallow groundwater throughout the year, with the highest detection frequency in summer (June) and in fall (September). 11 different compounds were detected, in a total of 213 groundwater samples collected and analysed. The herbicide bentazone was detected every month throughout the year. From a total of 61 soil samples collected and analyzed (in duplicates), 37 different pesticides were detected. DDT, 2,4-D, difenoconazole, MCPA were the most frequently detected compounds in soil and were found from 0 to 75cm depth along with groundwater. Organochloride pesticides such as DDTs, trans-heptachlor epoxide, trans-, cis- chlordane which were discontinued decades ago, still persist in soil. The topmost soil layer (0 – 15 cm) contained fewer pesticides than the 15-30cm depth. Soil depth and cropping system

were significantly associated with total pesticide concentration and total DDT concentration in soil.

4.2 Practical implications

Chapter 2 provides valuable data on Alberta's groundwater contamination with pesticides. Since this study was focused on areas of intensive agriculture in Alberta, it provides a basis to assess the potential of groundwater contamination where pesticides are regularly applied. This study provides a comprehensive database on the occurrence of a significant number of pesticide residues in Alberta's groundwater, a welcome contribution to the existing literature in the field of pesticide monitoring. The findings from Chapter 3 provide insight into the temporal variation of pesticide occurrence in groundwater, and highlight the variability in pesticides residues and concentrations in soil and groundwater collected from the same sites. Monitoring studies can be useful in providing baseline information and determine priorities for long-term monitoring studies.

Overall, the results of this thesis show that pesticides do occur in groundwater and soil of cultivated areas in Alberta while exhibiting temporal and spatial variability. More compounds were found in soil than in the groundwater beneath it. Also, compounds currently not in use but with long half-lives and strong sorption to soil were present in significant quantities. Some compounds like bentazone were present in groundwater throughout the year but not present in the soil, likely resulting from either their physiochemical properties or groundwater flow. The presence of DDTs and other OCP

residues in soil decades after their last application shows the persistence of these pesticides in soil years after their application and studies have concluded that this persistence could impact microbial community and soil ecology (Megharaj et al. 2000). The concentration of pesticides in this study was never above available drinking water quality guidelines, which indicates no immediate health concern if groundwater is used for that purpose. Higher levels of pesticides in groundwater and soil could result in potential adverse effects on microbiota and fauna, but the lack of studies focused on this topic precludes further conclusions. Some of the samples surpassed quality guidelines for irrigation and the protection of aquatic life; if groundwater were to be used for such purposes, further assessment for single as well as mixtures of compounds would be recommended before use. Finally, the study also highlights the need for maximum residue limits for pesticide mixtures under the Canadian climate conditions, perspectives, and circumstances.

4.3 Recommendations for future studies

Although the analytical suite included up to 142 historically and currently used pesticides, common currently used pesticides such as glyphosate, certain sulfonylureas and neonicotinoids were missing due to limited analytical capabilities. Encompassing these very important groups of pesticides would be desirable to have a broader understanding of the diversity of pesticide residues in the environment. As part of my study (chapter 3), I detected monthly variation in pesticide residues in groundwater with pesticide(s) occurring in all seasons including winter. This suggests that the results on the pesticide residues in a given area will be influenced by when sampling is performed. Therefore, analysis of samples collected throughout the year including the winter season is suggested

to gain a complete understanding of pesticide contamination. Moreover, a longer-term monitoring study would be useful in reaching firm conclusions regarding pesticides' seasonal and annual occurrence.

In the experimental study (Chapter 3), I investigated factors potentially affecting pesticide levels in soil including depth, cropping system, and manure application. However, pesticide use, as well as climatic conditions, were not considered. Pesticide use data for historically used pesticides such as Σ DDT was not available, thereby limiting the conclusions. Incorporating these relevant factors would help gain a greater understanding of their role in pesticide occurrence. Monitoring data could also be incorporated in models like PEARL, MACRO, PRZM (Carsel et al. 1985; Giannouli and Antonopoulos 2015). Crop and pesticide use information is crucial to the success of monitoring studies, and can only be obtained by collaborating directly with farmers (land owners). This was not a possibility for the monitoring study of groundwater from the south and central Alberta, thereby limiting the scope of the study and its conclusions.

Water table wells in southern and central Alberta could not be sampled in winter due to logistical limitations, and lack of recharge also limited sampling of specific wells during the growth season. These issues can be avoided in future studies by careful selection of wells. Besides, the study only included wells and piezometers in proximity of feedlot operations and manure application sites. The inclusion of wells from other areas such as golf courses, residential areas in addition to agricultural sites would provide a wider understanding of the effect of land use on groundwater quality.

4.4 Final conclusions

The work undertaken in this thesis has shown that Alberta's groundwater is contaminated by pesticide residues but is safe for human consumption based on Canadian water quality guidelines. The lower levels of pesticides and infrequent non-compliance with the protection of aquatic life and irrigation water quality guidelines do not indicate any immediate threat because the groundwater is not used for irrigation purposes and does not contain extensive aquatic species. Similarly, analysis of soil samples revealed the presence of persistent compounds like organochlorides which were banned decades ago, suggesting the need for continued monitoring of these compounds. Although the overall levels of pesticide residues in groundwater and soil were lower in this study, the potential negative effects on microorganisms inhabiting different ecosystems and trophic levels (Margni et al. 2002) should not be ignored. The development of maximum residue limits for pesticide mixtures is desirable to ensure adequate safety to the ecosystem and public health.

4.5 References

- Alberta Environment and Parks (AEP).** 2015. Overview of 2013 Pesticide Sales in Alberta. Land Policy Branch. Edmonton, AB. 80 pp.
- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J. C., & García-Río, L. 2008.** The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems & Environment*, **123** (4): 247-260.
- Bünemann, E. K., Schwenke, G. D., & Van Zwieten, L. 2006.** Impact of agricultural inputs on soil organisms—a review. *Soil Research*, **44** (4): 379-406.
- Carsel, R. F., Mulkey, L. A., Lorber, M. N., & Baskin, L. B. 1985.** The pesticide root zone model (PRZM): A procedure for evaluating pesticide leaching threats to groundwater. *Ecological Modelling*, **30** (1-2): 49-69.
- Dexter, A.R., Zebisch, M.A., 2006.** Degradation: critical limits of soil properties and irreversible degradation. In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. second ed. Taylor and Francis, Philadelphia, PA, USA, pp. 411–415.
- Donald, D. B., Cessna, A. J., Sverko, E. D., & Glozier, N. E. 2007.** Pesticides in surface drinking-water supplies of the Northern Great Plains. *Environmental health perspectives*: 1183-1191.
- Gavrilescu, M. 2005.** Fate of pesticides in the environment and its bioremediation. *Engineering in Life Sciences*, **5** (6): 497.

- Giannouli, D. D., & Antonopoulos, V. Z. 2015.** Evaluation of two pesticide leaching models in an irrigated field cropped with corn. *Journal of environmental management*, **150**: 508-515.
- Graymore, M., Stagnitti, F., & Allinson, G. 2001.** Impacts of atrazine in aquatic ecosystems. *Environment international*, **26** (7): 483-495.
- Kløve, B., Ala-Aho, P., Bertrand, G., Gurdak, J. J., Kupfersberger, H., Kværner, J., ... & Uvo, C. B. 2014.** Climate change impacts on groundwater and dependent ecosystems. *Journal of Hydrology*, **518**: 250-266.
- Kurt-Karakus, P. B., Bidleman, T. F., Staebler, R. M., & Jones, K. C. 2006.** Measurement of DDT fluxes from a historically treated agricultural soil in Canada. *Environmental science & technology*, **40** (15): 4578-4585.
- Margni, M., Rossier, D., Crettaz, P., & Jolliet, O. 2002.** Life cycle impact assessment of pesticides on human health and ecosystems. *Agriculture, ecosystems & environment*, **93** (1): 379-392.
- Matson, P. A., Parton, W. J., Power, A. G., & Swift, M. J. 1997.** Agricultural intensification and ecosystem properties. *Science*, **277** (5325): 504-509.
- Megharaj, M., Kantachote, D., Singleton, I., & Naidu, R. 2000.** Effects of long-term contamination of DDT on soil microflora with special reference to soil algae and algal transformation of DDT. *Environmental Pollution*, **109** (1): 35-42.
- Messing, P. G., Farenhorst, A., Waite, D. T., McQueen, D. R., Sproull, J. F., Humphries, D. A., & Thompson, L. L. 2012.** Corrigendum to “Predicting wetland

contamination from atmospheric deposition measurements of pesticides in the Canadian Prairie Pothole region” *Atmos. Environ* **45**:7227–7234.

Morris, B. L., Lawrence, A. R., Chilton, P. J. C., Adams, B., Calow, R. C., & Klinck, B. A. 2003. Groundwater and its susceptibility to degradation: a global assessment of the problem and options for management (Vol. 3). United Nations Environment Programme.

Rodríguez-Liébana, J. A., Mingorance, M. D., & Peña, A. 2014. Pesticide mobility and leachate toxicity in two abandoned mine soils. Effect of organic amendments. *Science of the Total Environment*, **497**: 561-569.

Thodal, C. E., Carpenter, J., & Moses, C. W. 2009. Monitoring for Pesticides in Groundwater and Surface Water in Nevada, 2008 (No. 2009-3093). US Geological Survey.

Tilman, D., Fargione, J., Wolff, B., D'Antonio, C., Dobson, A., Howarth, R., ... & Swackhamer, D. 2001. Forecasting agriculturally driven global environmental change. *Science*, **292** (5515): 281-284.

Waite, D. T., Sommerstad, H., Grover, R., Kerr, L., & Westcott, N. D. 1992. Pesticides in ground water, surface water and spring runoff in a small Saskatchewan watershed. *Environmental toxicology and chemistry*, **11** (6): 741-748.

Wan, M. T., Kuo, J. N., & Pasternak, J. 2005. Residues of endosulfan and other selected organochlorine pesticides in farm areas of the Lower Fraser Valley, British Columbia, Canada. *Journal of environmental quality*, **34** (4): 1186-1193

APPENDICES

APPENDIX I. Pesticides included in the analytical suite of this study with their recovery percentages. Compounds 1 to 105 were included in all years. Compounds 106 to 142 were added to the analytical suite in 2015.

Compounds		Type	LOD (µg/L)	Solvent	Low Spike		High Spike	
					Average	RSD%	Average	RSD%
					recovery%	(n=3)	recovery%	(n=3)
1	2,4-D	Herbicide	0.0251	acetone	93.78	7.83	84.84	6.25
2	2,4-DB	Herbicide	0.0255	toluene	95.18	9.12	90.33	8.30
3	Alachlor	Herbicide	0.0248	toluene	95.14	3.51	92.61	7.25
4	Aldrin*	Insecticide	0.0258	toluene	97.30	6.83	84.63	11.21
5	Allidochlor	Herbicide	0.0258	toluene	94.23	11.18	92.44	7.26
6	Atrazine	Herbicide	0.0247	acetone	88.40	24.52	93.45	7.22
7	Benalaxyl	Fungicide	0.6372	toluene	104.55	7.59	96.75	8.38

8	Benfluralin	Herbicide	0.0253	toluene	94.03	13.89	96.35	7.37
9	Bentazon	Herbicide	0.0247	acetone	105.58	11.12	96.48	11.27
10	Benzoylprop-Ethyl	Herbicide	0.0243	toluene	105.69	8.55	100.27	9.82
11	HCH- α *	Insecticide	0.1036	toluene	93.74	3.99	91.66	5.20
12	HCH- β *	Insecticide	0.0254	toluene	97.73	7.78	90.95	4.65
13	HCH- δ *	Insecticide	0.0515	acetone	95.17	4.40	90.06	5.83
14	Bifenthrin	Insecticide	0.0247	toluene	97.12	12.40	92.50	9.02
15	Bromacil	Herbicide	0.0251	toluene	53.54	17.79	48.72	28.79
16	Bromophos-Ethyl	Insecticide	0.0247	acetone	80.77	29.58	91.78	5.32
17	Bromopropylate	Acaricide	0.0248	toluene	103.70	6.12	99.21	8.81
18	Bromoxynil	Herbicide	0.0255	acetone	95.29	3.18	92.75	8.65
19	Bupirimate	Fungicide	0.0251	toluene	94.87	3.42	87.38	7.09
20	Butachlor	Herbicide	0.0507	toluene	102.38	1.27	95.07	7.33
21	Butralin	Herbicide	0.0249	toluene	99.26	2.37	92.70	5.13
22	Butylate	Herbicide	0.025	toluene	91.76	2.35	89.75	5.61
23	cis-Chlordane*	Insecticide	0.032	toluene	99.62	14.06	88.79	5.29
24	t-Chlordane*	Insecticide	0.0251	toluene	98.52	2.23	88.08	6.59

25	Chlormephos	Insecticide	0.0253	toluene	95.56	9.46	91.25	5.81
26	Chloroneb	Fungicide	0.025	acetone	96.88	5.48	90.53	5.66
27	Chlorpyrifos	Insecticide	0.0247	toluene	104.45	10.72	93.27	4.40
28	Chlorpyrifos-Methyl	Insecticide	0.0251	toluene	99.04	4.79	90.50	5.82
29	Chlorthal-Dimethyl	Insecticide	0.0459	toluene	94.42	6.43	91.17	6.16
30	Chlorthiamid	Herbicide	0.0258	toluene	91.87	13.02	88.55	6.71
31	Clomazone	Herbicide	0.0267	toluene	96.03	7.49	89.26	7.78
32	Clopyralid	Herbicide	0.0248	acetone	68.28	15.55	64.43	12.91
33	Cycloate	Herbicide	0.1497	toluene	95.11	5.14	90.61	5.07
34	o,p-DDD*	Insecticide	0.0256	toluene	96.92	7.01	93.82	7.39
35	p,p-DDD*	Insecticide	0.0255	toluene	99.71	3.14	95.82	8.40
36	o,p'-DDE*	Insecticide	0.025	toluene	95.36	3.77	88.52	6.14
37	p,p'-DDE*	Insecticide	0.1577	toluene	95.78	3.14	90.94	8.47
38	o,p-DDT*	Insecticide	0.0249	toluene	89.18	3.41	85.60	8.46
39	p,p-DDT*	Insecticide	0.0247	toluene	90.69	14.23	84.31	12.49
40	Desmetryne	Herbicide	0.0254	toluene	56.47	30.21	49.91	17.25
41	Diazinon*	Insecticide	0.0255	toluene	97.83	4.05	89.14	9.35

42	Dicamba	Herbicide	0.0257	acetone	93.69	7.15	90.53	5.75
43	Dichlobenil	Herbicide	0.025	toluene	91.12	10.22	89.45	5.04
44	Dichlorprop	Herbicide	0.0251	acetone	96.19	6.32	91.23	4.20
45	Dichlorvos	Insecticide	0.0502	toluene	93.59	8.33	89.08	6.59
46	Diclofenthion	Nematicide	0.025	toluene	95.18	2.96	89.57	6.17
47	Diclofop	Herbicide	0.0248	toluene	98.01	7.81	96.79	13.27
48	Dieldrin*	Insecticide	0.0247	toluene	93.24	13.86	93.66	12.43
49	Difenoconazole	Fungicide	0.2507	acetone	113.42	21.97	107.62	6.61
50	Dimethachlor	Herbicide	0.1433	toluene	106.93	7.02	95.85	2.74
51	Dimethoate	Insecticide	0.0246	toluene	107.42	22.02	96.53	6.64
52	Dioxathion	Insecticide	0.0248	acetone	124.29	13.33	105.78	3.55
53	Diphenamid	Herbicide	0.025	toluene	102.73	3.92	96.27	3.53
54	α -Endosulfan	Insecticide	0.1168	toluene	92.20	6.44	91.56	4.37
55	Endrin	Insecticide	0.0462	toluene	99.95	5.61	93.89	10.14
	Eptc (S-ethyl							
56	dipropylthiocarbama	Herbicide	0.0257	toluene	83.36	14.01	90.65	6.84
	te)							

57	Ethalfuralin	Herbicide	0.0256	toluene	95.47	4.12	89.70	4.82
58	Ethion*	Insecticide	0.025	toluene	102.55	4.86	97.44	6.74
59	Ethofumesate	Herbicide	0.0247	toluene	96.10	2.54	93.33	7.90
60	Etriazole	Fungicide	0.0495	toluene	86.13	4.74	87.44	0.42
61	Etrimphos	Insecticide	0.0258	toluene	97.52	13.19	88.23	4.66
62	Fenchlorophos	Insecticide	0.0254	toluene	101.19	4.20	91.18	8.00
63	Fenoxaprop	Herbicide	0.0248	acetone	95.15	13.89	93.44	9.52
64	Fenthion	Insecticide	0.0253	toluene	99.14	4.12	87.95	0.61
65	Flamprop-Isopropyl	Herbicide	0.025	toluene	102.43	6.98	96.52	8.03
66	Flamprop-Methyl	Herbicide	0.0256	toluene	99.98	10.88	97.19	7.13
67	Flumetralin	Growth Reg	0.0249	toluene	97.49	5.89	96.09	5.99
68	Fluroxypyr	Herbicide	0.0247	acetone	98.31	10.30	91.67	8.07
69	Fonofos	Insecticide	0.1506	toluene	100.28	4.97	91.07	3.98
70	Heptachlor*	Insecticide	0.0252	toluene	92.67	5.94	85.85	4.33
71	tr-Heptachlor Epoxide*	Insecticide	0.0251	toluene	99.72	2.17	90.75	6.72
72	Imazethapyr	Herbicide	0.0256	acetone	126.54	30.52	126.59	12.61

73	Isofenphos	Insecticide	0.0254	toluene	98.24	2.12	92.57	5.24
74	Lindane*	Insecticide	0.0256	toluene	93.34	12.41	91.82	4.07
75	MCPA	Herbicide	0.6306	toluene	120.18	36.60	87.99	6.11
76	Mecoprop	Herbicide	0.6274	acetone	98.98	11.87	89.99	2.85
77	Methoxychlor	Insecticide	1.3751	toluene	97.07	12.91	89.27	14.97
78	Metolachlor	Herbicide	0.0254	acetone	95.28	3.70	90.71	5.69
79	Mirex	Insecticide	0.0508	toluene	93.13	6.39	85.50	11.81
80	Nitrapyrin	Bactericide	0.0425	toluene	92.47	9.95	92.11	0.89
81	cis-Permethrin	Insecticide	0.0486	toluene	100.39	30.82	99.94	10.66
82	trans-Permethrin	Insecticide	0.025	toluene	120.62	19.17	101.37	12.05
83	Phorate	Insecticide	0.0255	toluene	95.85	2.73	84.24	6.06
84	Picloram	Herbicide	0.0254	acetone	70.15	4.82	68.47	13.40
85	Pirimicarb	Insecticide	0.0257	toluene	40.03	11.57	37.65	7.94
86	Pirimiphos-Ethyl	Insecticide	0.0249	acetone	99.49	2.32	88.14	4.16
87	Pirimiphos-Methyl	Insecticide	0.0251	toluene	95.79	11.04	90.86	7.25
88	Procymidone	Fungicide	0.0253	toluene	101.87	7.08	91.47	4.79
89	Prometon	Herbicide	0.074	toluene	58.78	11.76	46.59	6.06

90	Propham	Herbicide	0.0258	toluene	96.40	5.19	88.06	2.64
91	Propiconazole	Fungicide	0.0255	acetone	100.20	5.05	98.58	8.46
92	Propyzamide	Herbicide	0.0307	toluene	95.83	1.20	91.90	4.75
93	Quinclorac	Herbicide	0.0525	toluene	76.56	29.67	97.47	3.61
94	Quintozene	Fungicide	0.0246	toluene	99.94	8.89	88.90	7.69
95	Simazine	Herbicide	0.0254	acetone	108.11	14.31	93.73	12.44
96	Sulfotep	Insecticide	0.0251	toluene	99.43	4.88	92.63	5.92
97	Sulprophos	Insecticide	0.09	toluene	103.69	10.89	94.47	12.07
98	Terbacil	Herbicide	0.0252	acetone	131.83	16.57	189.82	33.26
99	Terbufos	Insecticide	0.0255	acetone	93.15	1.04	83.26	7.95
100	Terbutryne	Herbicide	0.0249	acetone	91.99	4.26	88.48	7.10
101	Tetradifon	Acaricide	0.4382	toluene	91.82	13.38	99.55	6.70
102	Tetrasul	Acaricide	0.0697	toluene	101.79	6.91	93.26	7.20
103	Triallate	Herbicide	0.0259	toluene	93.96	3.78	91.37	6.63
104	Triclopyr	Herbicide	0.0251	acetone	102.71	9.90	90.62	7.11
105	Trifluralin	Herbicide	0.0257	toluene	100.70	8.01	88.07	7.27
106	Azinphos-methyl	Insecticide	0.0813	acetone	124.15	17.71	96.06	19.04

107	Azoxystrobin	Fungicide	0.02529	acetone	146.21	60.26	141.52	28.01
108	Boscalid	Fungicide	0.0252	acetone	114.34	22.98	108.43	11.43
109	Captan	Fungicide	0.0836	acetone	59.84	67.36	80.25	14.90
110	Carbaryl	Insecticide	0.0254	acetone	112.65	27.32	95.46	15.23
111	Carbofuran	Insecticide	0.0253	acetone	97.50	11.88	99.93	7.75
112	Carfentrazone-ethyl	Herbicide	0.031	acetone	106.83	5.12	97.94	7.49
113	Chlorothalonil	Fungicide	0.025	acetone	112.61	31.20	1253.11	83.53
114	Clodinafop- propargyl	Herbicide	0.0257	acetone	104.86	19.93	104.59	10.32
115	Cyhalothrin lambda	Insecticide	0.0257	acetone	97.32	5.56	97.81	5.50
116	Deltamethrin	Insecticide	0.0249	acetone	268.95	103.39	101.75	10.61
117	Fluazifop-p-butyl	Herbicide	0.0249	acetone	101.11	7.55	97.11	6.73
118	Folpet	Fungicide	0.0254	acetone	49.62	98.59	70.07	29.07
119	Hexazinone	Herbicide	0.0249	acetone	107.90	25.48	103.78	2.87
120	Imazamethabenz	Herbicide	0.0252	acetone	66.84	24.89	55.35	14.87
121	Iprodione	Fungicide	0.0763	acetone	106.99	16.04	102.99	7.47
122	Malathion	Insecticide	0.0246	acetone	99.17	1.11	92.22	5.83

123	MCPB-methyl	Herbicide	0.025	acetone	96.27	3.60	91.42	7.26
124	Metalaxyl	Fungicide	0.0319	DCM	95.76	17.28	98.62	0.92
125	Methoprene	Insecticide	0.0253	acetone	98.30	5.94	90.62	4.01
126	Monolinuron	Herbicide	0.0248	acetone	100.00	4.92	93.77	13.46
127	Naled	Insecticide	0.1521	toluene	176.95	81.09	115.42	35.05
128	Napropamide	Herbicide	0.0255	acetone	106.47	5.19	98.27	7.48
129	Oxycarboxin	Fungicide	0.0604	acetone	95.83	11.17	108.10	6.79
130	Oxyfluorfen	Herbicide	0.0251	acetone	97.30	8.00	100.88	6.39
131	Pendimethalin	Herbicide	0.0259	acetone	91.45	7.91	91.14	5.47
132	Piperonyl butoxide	Insecticide	0.0591	ethanol	115.44	24.58	107.86	17.36
		Synergyst						
133	Prometryn	Herbicide	0.0249	acetone	97.96	5.57	88.37	6.96
134	Propoxur	Insecticide	0.196	toluene	96.25	12.79	95.52	5.85
135	Prothioconazole- Desthio	Fungicide	0.0249	acetone	101.24	4.29	97.07	6.17
136	Pyraclostrobin	Fungicide	0.0448	acetone	133.05	31.35	108.60	7.09
137	Pymetrozine	Insecticide	0.0253	acetone	80.55	3.05	119.83	46.32

138	Quizalofop-ethyl	Herbicide	0.0244	acetone	153.59	46.89	114.21	21.24
139	Tebuconazole	Fungicide	0.0479	toluene	104.61	12.10	101.62	5.30
140	Trifloxystrobin	Fungicide	0.0254	acetone	102.81	7.84	98.54	6.97
141	Triticonazole	Fungicide	0.0254	acetone	90.26	51.31	101.35	3.84
142	Vinclozolin	Fungicide	0.025	acetone	86.01	8.84	89.85	6.25

LOD - limit of detection

RSD - relative standard deviation (ratio of standard deviation and average recovery, expressed in 100).

* Compounds deregistered for use in Canada.

APPENDIX II. Average % recoveries (%Relative Standard Deviation) of fortified pesticides included in the sand and soil samples for method validation using QuEChERS sample preparation, liquid-liquid extraction and GC-MS/MS analysis.

	Compounds	High spike (pg/μl)	Recovery % in sand	Average recovery % in soil	RSD % (n=2) for soil
1	2,4-DB	28.4366	67.69	50.84	6.70
2	2,4-D-methyl	33.3874	17.04	11.80	2.52
3	Alachlor	23.6247	85.76	73.68	23.24
4	Aldrin	24.0375	93.16	63.77	9.24
5	Allidochlor	27.342	80.95	60.74	0.24
6	Atrazine	25.984	84.06	63.04	1.08
7	Azinphos-methyl	368.4035	111.69	80.97	14.61
8	Azoxystobin	28.6917	119.38	123.95	3.23
9	Benalaxyl	22.6164	80.32	63.08	0.63
10	Benfluralin	23.3444	83.6	63.56	17.31
11	Bentazone	25.3258	80.65	60.72	1.30
12	Benzoylprop-	23.343	82.89	64.28	3.14
	ethyl				
13	BHC-alpha	23.891	84.79	61.86	5.41
14	BHC-beta	24.3317	80.95	61.90	2.08
15	BHC-delta	138.3839	84.15	62.64	4.09
16	BHC-	24.683	87.24	62.20	7.32
	gamma(Lindane)				

17	Bifenthrin	23.5101	92.96	68.77	10.90
18	Boscalid	22.7391	82.29	70.31	1.17
19	Bromophos-ethyl	23.1756	88.54	63.23	10.14
20	Bromopropylate	47.5364	86.82	65.14	5.20
21	Bromoxynil	26.0263	61.42	47.78	11.68
22	Bupirimate	23.8873	72.56	53.17	1.74
23	Butachlor	76.3469	87.35	63.99	11.70
24	Butralin	26.0189	90.49	65.81	5.42
25	Butylate	22.6535	87.78	62.96	5.86
26	Captan	29.7804	87.55	49.22	33.38
27	Carbaryl	31.8797	79.85	56.37	17.85
28	Carbofuran	27.6983	78.27	65.34	0.75
29	Carfentrazone-	54.6509	77.88	64.03	0.44
	ethyl				
30	Chlordane-	24.7338	93.02	66.59	5.81
	cis(alpha)				
31	Chlordane-	23.78	89.98	64.09	11.13
	trans(gamma)				
32	Chlormephos	24.4639	84.36	61.73	4.55
33	Chloroneb	26.5493	91.27	63.92	8.93
34	Chlorpyrifos-	37.6457	83.52	59.50	8.59
	methyl				

	Chlorthal-				
35	demethyl,DCPA	24.6851	84.13	62.02	6.45
36	Chlorthiamid	27.8375	80.79	58.79	0.49
	Clodinafop-				
37	propargyl	141.6917	80.18	70.77	4.02
38	Clomazone	28.924	82.36	62.67	7.11
39	Clorpyrifos	23.6454	87.06	64.26	5.30
40	Cycloate	24.5996	87.86	62.61	10.13
	Cyhalothrin-				
41	lambda	24.1095	91.49	70.28	4.89
42	DDD-o,p'	24.4525	86.42	62.26	8.28
43	DDD-p,p'	24.2036	84.69	63.38	8.88
44	DDE-o,p'	48.3415	88.04	62.91	9.41
45	DDE-p,p'	24.8126	86.99	68.41	21.07
46	DDT-o,p'	22.9132	85.23	49.90	56.79
47	DDT-p,p'	53.2807	89.06	71.78	1.53
48	Deltamethrin	23.8432	96.12	88.38	1.13
49	Diazinon	24.1006	86.99	62.11	4.95
50	Dicamba-methyl	25.6807	83.03	61.09	5.51
51	Dichlobenil	30.1004	83.77	60.01	3.32
52	Dichlofenthion	24.2469	87.09	61.99	8.71
	Dichloprop-				
53	methyl	25.2466	84.68	60.54	7.50

54	Diclofop-methyl	23.53	88.37	66.72	7.02
55	Dieldrin	22.2956	89.76	69.77	10.64
56	Difenoconazole I	36.2444	80.39	78.27	4.26
57	Dimethachlor	24.8404	92.43	68.25	0.20
58	Dimethoate	309.7517	80.94	62.69	1.29
59	Dioxathion	142.2736	108.64	83.43	12.38
60	Diphenamid	24.1117	77.7	62.47	1.78
	Endosulfan I-				
61	alpha	78.7211	91.37	65.04	5.84
62	Endrin	26.9968	78.17	57.91	5.93
63	EPTC	24.0782	89.41	65.16	4.08
64	Ethalfuralin	107.2427	85.79	68.71	15.74
65	Ethion	51.219	88.27	67.41	7.03
66	Ethofumesate	25.1303	77.99	63.36	0.09
67	Etridiazole	24.8955	92.08	63.93	9.08
68	Etrimfos	22.5342	83.44	57.11	10.45
69	Fenchlorphos	20.3085	83.27	59.03	8.35
70	Fenthion	20.2599	93.89	70.55	6.05
	Flamprop-				
71	isopropyl	24.7977	79.79	62.19	0.33
72	Flamprop-methyl	24.2079	76.73	61.83	0.18
73	Fluazifop-p-butyl	23.909	87.89	63.90	4.49
74	Fludioxonil	22.1938	74.42	59.25	14.41

75	Flumetralin	23.6703	89.77	67.75	3.59
76	Folpet	21.482	101.36	54.28	26.23
77	Fonofos	23.2758	88.91	64.14	8.26
78	Heptachlor	24.4153	87.88	62.71	8.25
	Heptachlor	67.6034	84.04		
79	epoxide-trans			63.64	7.62
80	Hexazinone	36.6416	86.5	59.54	17.04
81	Imazamethabenz	207.0213	51.49	43.58	5.89
82	Iprodione	26.1621	77.34	62.16	3.92
83	Isofenphos	46.473	86.98	64.61	5.24
84	Malathion	20.7728	77.46	60.09	1.52
85	MCPA-methyl	28.788	89.36	60.76	6.62
86	MCPB-methyl	27.3681	85.74	62.72	1.87
87	Metalaxyl	26.3721	78.59	64.23	0.07
88	Methoprene	51.0923	117.62	95.87	5.78
89	Methoxychlor	25.0295	87.39	65.51	5.98
90	Metolachlor	23.71	80.1	60.86	3.57
91	Mirex	22.2662	87.29	62.19	9.30
92	Monolinuron	827.6693	95.06	64.33	7.98
93	Naled	8.5936	94.25	14.50	43.69
94	Napropamide	23.8402	80.49	62.88	1.17
95	Nitrapyrin	26.8675	88.24	64.68	9.21
96	Oxycarboxin	306.4634	100.27	84.60	3.30

97	Oxyflurfen	33.9884	88.9	64.47	1.75
98	Pendimethalin	28.2784	87.3	63.80	0.41
99	Permethrin I (cis)	21.5269	95.64	71.74	12.34
	Permethrin				
		24.8959	95.68		
100	II(trans)			70.00	11.62
101	Phorate	30.9903	99.98	75.24	4.14
	Piperonyl				
		28.5389	96.09		
102	butoxide			75.36	8.33
103	Pirimiphos-ethyl	46.1348	85.28	61.04	7.47
	Pirimophos-				
		23.5826	84.69		
104	methyl			62.87	4.74
105	Procymidone	24.5788	79.61	61.04	0.03
106	Prometon	23.5834	53.45	44.64	14.75
107	Prometryn	23.8126	80.19	58.87	3.90
108	Propham	29.2014	85.3	60.61	3.79
109	Propiconazole I	77.4349	75.65	64.33	0.34
110	Propoxur	29.1902	79.94	63.52	2.50
111	Propyzamide	26.7175	79.86	62.68	1.78
	Prothioconazole-				
		23.9713	76.21		
112	desthio			60.88	2.33
113	Pymetrozine	184.2856	85.34	60.45	14.67
114	Pyraclostrobin	25.6456	95.91	80.34	2.76
115	Quintozene	42.6981	80.01	57.24	6.25

116	Quizalofop-ethyl	24.7834	98.94	75.98	6.38
117	Simazine	65.6558	74.98	59.19	0.55
118	Sulfotep	23.6515	80.1	60.31	8.02
119	Sulprofos	17.8868	102.42	72.68	7.55
120	Tebuconazole	28.4459	71.94	76.01	19.60
121	Terbacil	28.0047	190.63	156.44	14.13
122	Terbufos	35.7741	106.91	80.33	8.74
123	Terbutryn	22.5178	74.07	55.51	9.43
124	Tetradifon	23.3044	93.54	65.52	1.10
125	Tetrasul	22.8663	89.58	64.37	9.13
126	Triallate	24.0922	87.39	62.03	9.67
127	Trifloxystrobin	25.9971	80.94	62.63	0.36
128	Trifluralin	24.6234	82.35	61.74	5.69
129	Triticonazole	33.3754	70.06	65.69	0.46
130	Vinclozolin	25.7393	84.06	59.79	5.35

APPENDIX III. Pesticide application history at Rotation U.

Year	Crop	Pesticides used		Application rate	Application date	Purpose
		Trade name	Active Ingredient			
2010	Wheat	Achieve Extra Gold	tralkoxydim + bromoxynil + MCPA		May	Selective control of grassy and broadleaf weeds
2010	Wheat	Dividend XL RTA fungicide	Difenoconazole+Metalaxyl -m and s-isomer	325-360ML/100kg seed		Seed treatment
2010	Alfalfa		None			
2011	Maize		Difenoconazole+Metalaxyl -m and s-isomer	325-360ML/100kg seed	June	Seed treatment
2011	Maize	RT540	Glyphosate	1L/A	August	Broad-spectrum weed control in RoundUp-Ready Corn
2011	Alfalfa	RT 540	Glyphosate	2.5L/A	September	Terminate alfalfa
2011	Alfalfa	2,4-D Ester 700	2,4-D	400ml/A	September	Terminate alfalfa

2012	Wheat	Dividend XL RTA fungicide	Difenoconazole+Metalaxyl -m and s-isomer	325- 360ML/100kg seed		Seed treatment
2012	Wheat	SIMPLICIT Y	Pyroxsulam	200ML/A	June	Broadleaf control in wheat
2012	Wheat	BUCTRIL M	Bromoxynil +MCPA	404ML/A	June	Broadleaf control in wheat
2012		VELOCITY M3	Pyrasulfotole+Bromoxynil +Thiencarbazone-methyl			
2013	Barley	Dividend XL RTA fungicide	Difenoconazole+Metalaxyl -m and s-isomer	325- 360ML/100kg seed	May	Seed treatment
2013	Barley	Infinity	Pyrasulfotole+ Bromoxynil	0.33L/A	June	Broadleaf weed control in barley
2013	Barley	AXIAL BIA	Pinoxaden	500ML/A	June	Broadleaf weed control in barley
2013	All plots	STARTUP 540	Glyphosate	1L/A	October	Control fall weed
2013	All plots	HEAT	Salfufenacil	10.4G/A	October	Control fall weed
2013	All plots	MERGE	Surfactant	200ML/A	October	Control fall weed

2014	Alfalfa	Edge™Ethalf luralin	Ethalf luralin	6.9-11.3Kg/A	May	
2014	Alfalfa	Apron			May	
2014	Maize	MERGE	Surfactant	200ML/A	May	Control volunteer barley in Corn
2014	Maize	ROUNDUP 540	Glyphosate	1L/A	June	Weed control in Broad-spectrum weed control in RoundUp- Ready Corn
		HEAT	Salfufenacil	10.4G/A	June	
2015	Alfalfa		None			
2015	Wheat	Dividend XL RTA fungicide	Difenoconazole+Metalaxyl -m and s-isomer	325- 360ML/100kg seed	May	Seed treatment
2015	Wheat	AXIAL EXTREME	Pinoxaden +Fluroxypyr	0.5L/A	June	Grassy weed control in Wheat
2015	Wheat	Refine SG	Thifensulfuron methyl, Tribenuron methyl	12G/A	June	Grassy weed control in Wheat
2015	Wheat	HEAT	Salfufenacil	10.4G/A	October	Fall weed control
2015	Wheat	ROUNDUP 540	Glyphosate	1L/A	October	Fall weed control
2015	Wheat	MERGE	Surfactant	200ML/A	October	Fall weed control

APPENDIX IV: Pesticides detected in groundwater (sampled from December 2014 to November 2015) and soil (sampled in December 2014) of rotation u site, with their chemical group, detection frequencies (in soil, in groundwater), water solubility (mg/L, 20°C), soil organic carbon sorption coefficient (KOC), Half-life (in days), GUS, Leaching potential, Henry's constant and volatility.

Pesticides	Type	Found in	DF (%)	Solubility (mg/L)	KOC	Half life (Days)	GUS	Leaching potential	Henry's constant	Volatility
<i>Organochlorine group</i>										
p,p-Dichlorodiphenyldichloroethylene (p,p'-DDE)	I	S, GW	85.25/0.47	0.006	151000	2000	-3.89	low	3.32x10 ⁻⁰⁴	V
p,p-Dichlorodiphenyltrichloroethane (p,p-DDT)	I	S	69.67	0.006	151000	2000	-3.89	low	3.32x10 ⁻⁰⁴	V
p,p-Dichlorodiphenyldichloroethane (p,p-DDD)	I	S	36.07	0.006	151000	2000	-3.89	low	3.32x10 ⁻⁰⁴	V
o,p-Dichlorodiphenyltrichloroethane (o,p-DDT)	I	S	36.07	0.006	151000	2000	-3.89	low	3.32x10 ⁻⁰⁴	V
tr-Heptachlor Epoxide	I	S	18.85	0.056	24000	285	-0.93	low	4.47x10 ⁻⁰²	V
o,p-Dichlorodiphenyldichloroethane (o,p-DDD)	I	S	9.02	0.006	151000	2000	-3.89	low	3.32x10 ⁻⁰⁴	V
t-Chlordane ^a	I	S	4.92	0.1	20000	37-3500	-0.77	low	1.99x10 ⁻⁰⁴	V

o,p-Dichlorodiphenyldichloroethylene (o,p'-DDE)	I	S	3.28	0.006	151000	2000	-3.89	low	3.32x10 ⁻⁰⁴	V
cis-Chlordane ^a	I	S	1.64	0.1	20000	37-3500	-0.77	low	1.99x10 ⁻⁰³	V
Hexachlorocyclohexane-delta ^b	I	S	0.82	8.52	1270	980	3.95	High	6.1x10 ⁻⁰⁶	V
Methoxychlor	I	S	0.82	0.1	80000	120	-1.88	low	1.14x10 ⁻⁰⁴	V
<hr/> <i>Phenoxy group</i> <hr/>										
2,4-Dichlorophenoxyacetic acid	H	S, GW	74.59/12.68	24300	39.3	4.4	1.69	low	1.4x10 ⁻⁰⁹	NV
MCPA (2-methyl-4-chlorophenoxyacetic acid) ^c	H	S, GW	19.67/7.04	29390	74	24	2.94	High	1.1x10 ⁻⁰⁸	NV
Fenoxaprop	H	S, GW	3.28/0.47	0.9	9490	5	0.02	low	3.2x10 ⁻⁰⁷	MV
Clodinafop-propargyl ^c	H	S	0.82	4	1466	0.8	-0.08	low	3x10 ⁻⁰⁷	NV
Diclofop ^c	H	S	0.82	122700	288.6	23.9	2.12	Transition	3.39x10 ⁻¹⁵	NV
Quizalofop-ethyl	H	S	0.82	0.31	540	45	2.1	Transition	1.5x10 ⁻⁰⁵	MV

Mecoprop	H	GW	1.88	250000	47	8.2	2.29	Transition	1.4x10 ⁻⁹	NV
----------	---	----	------	--------	----	-----	------	------------	----------------------	----

Triazole, Triaxinone, Triazolinthione, Triazolone group

Difenoconazole ^c	F	S, GW	20.49/ 2.82	15	6120	130	0.9	low	7.31x10 ⁻¹⁰	NV
Tebuconazole ^c	F	S	6.56	36	1,000	365	2.85	High	5.14x10 ⁻⁰⁹	NV
Hexazinone	H	S	4.92	33000	54	90	4.43	High	8.3x10 ⁻¹¹	NV
Propiconazole	F	S	4.10	150	1086	71.8	1.89	Transition	1.7x10 ⁻⁰⁷	NV
Prothioconazole-Desthio ^c	F	S	2.46	300	1760	0.5	-0.18	low	1.88x10 ⁻¹⁰	NV
Carfentrazone-ethyl	H	S	0.82	29.3	866	1	0	low	1.01x10 ⁻⁰⁷	NV

Pyrethroid group

Bifenthrin	I	S	0.82	0.001	236610	102.2	-2.76	Low	4.1x10 ⁻⁰²	V
Cyhalothrin-lambda	I	S	0.82	0.004	180000	57	-2.2	low	4.62x10 ⁻¹¹	NV

Deltamethrin	I	S	0.82	0.0002	102400 00	26	-4.26	low	4.2x10 ⁻⁰⁶	MV
cis-Permethrin	I	S	0.82	0.2	100000	13	-1.11	low	7.76x10 ⁻⁰⁵	V
trans-Permethrin	I	S	0.82	0.2	100000	13	-1.11	low	7.76x10 ⁻⁰⁵	V

Pyridine carboxylic group

Clpyralid	H	S	1.64	143000	5	34	5.06	High	1.46x10 ⁻⁰⁸	NV
Picloram	H	GW	0.94	560	13	82.8	6.03	High	1.42x10 ⁻¹¹	NV

Others

Azoxystrobin* [¶]	F	S, GW	2.46/0 .47	6.7	589	84.5	2.65	Transition	2.72x10 ⁻¹²	NV
Trifloxystrobin ^{¶ c}	F	S	0.82	0.61	2377	2	0.19	low	9.18x10 ⁻⁰⁷	MV
Bromopropylate ^{¶ c}	A	S	0.82	0.1	6309	59	-0.35	Low	4x10 ⁻⁰⁷	MV
Bentazone [‡]	H	GW	14.55	7112	55.3	20	2.89	High	2x10 ⁻¹³	NV

Boscalid ^{§ c}	F	S	3.28	4.6	772	246	2.66	Transition	2.12x10 ⁻⁰⁸	NV
Ethalfluralin ^{‡‡}	H	S	13.11	0.01	6364	39.8	0.43	low	1.64x10 ⁻⁰¹	V
Bromoxynil ^{§§}	H	GW	1.41	38000	302	0.63	-0.34	low	1.46x10 ⁻⁰⁷	NV
Imazamethabenz ^{* c}	H	S, GW	1.64/0 .47	1110	35	47	2.21	Transition		
Fludioxonil [#]	F	S	1.64	1.8	145600	239	-2.67	low	2.15x10 ⁻⁰⁸	NV
S-ethyl dipropylthiocarbamate (EPTC) ^{¶¶}	H	S	6.56	370	300	6	1.34	low	9.6x10 ⁻⁰⁴	V

I – Insecticide, H – Herbicide, F – Fungicide, A – Acaricide

S – Soil, GW – Groundwater

KOC – Soil sorption coefficient, DF – Detection frequency, GUS – Groundwater ubiquity score

V – Volatile, NV – Non-Volatile, MV- Moderately volatile

[¶] - Strobilurin , [‡] Benzothiazinone, ^{||} Benzilate, [§]Carboxamide, ^{‡‡}Dinitroaniline, ^{§§}Hydroxybenzonitrile, ^{|| ||} Imidazolinone, [#]Phenylpyrrole,
^{¶¶}Thiocarbamate

All the data are taken from PPDB (Lewis et al. 2016) unless otherwise indicated.

^a Data taken from npic Chlordane technical factsheet

^bThese values are for Lindane.

^c Data taken from PAN pesticide database