PESTICIDES IN THE WATER-COLUMN AND BOTTOM SEDIMENTS OF FOUR MANITOBA RIVERS

by

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ABSTRACT

Gamhewage, Mauli. M.Sc., The University of Manitoba, February, 2020. Pesticides in the water-column and bottom sediments of four Manitoba rivers. Co-advisors: Dr. Annemieke Farenhorst and Dr. Claudia Sheedy.

Pesticides are used to control pests in a variety of habitats including agricultural lands, forests, commercial lands, and domestic properties. Pesticide transport from such habitats to surface waters leads to environmental contamination. The objectives of this research were to compare the pesticide types present in the water-column and bottom-sediments of rivers flowing through intensively-managed and semi-natural habitats and to examine the extent of variations in MCPA and 2,4-D concentrations in the sediments that could be explained by measured laboratory parameters such as K_d, sediment organic carbon content and particle size distribution. This study screened water-column and sediment samples for 160 pesticide compounds which is substantially greater than what has been typically included in Prairie surface water research. River contamination primarily arises as a result of current-use pesticides applied in agricultural and urban habitats. For most compounds detected, there was no significant correlation between their concentrations detected in water and sediments, suggesting that pesticide concentration in the water-column is a poor indicator of the presence of pesticides in sediments. Pesticide mixtures were more common in water (72%) than sediments (51%) and dominated by broadleaf herbicides. The concentrations of pesticide mixtures detected in water never exceeded their calculated threshold value for the Pesticide Toxicity Index, indicating that the presence of pesticides in Prairie rivers continue to pose no significant risks to freshwater organisms. The

batch-equilibrium study found that regardless of the lower sorption to sediments, more frequent presence of MCPA in the water-column allowed for greater opportunities for MCPA to partition to sediments compared to 2,4-D. Thus, the water-column loadings of those compounds, and not sediment characteristics, are the driving force for determining their frequencies and concentrations in sediments. Since this study found that herbicides co-applied with MCPA and 2,4-D were often detected in river waters, future monitoring studies should focus on a wide variety of active ingredients that are co-applied with the top ranked active ingredients. Also, additional monitoring studies should focus on rivers flowing through urban and agricultural lands. Future batch-equilibrium studies could incorporate different concentrations of MCPA and 2,4-D mixtures to further examine chemical sorption under different environmental conditions.

FOREWARD

This thesis is prepared in manuscript style in accordance with the Department of Soil Science, University of Manitoba guidelines. This thesis consists of four chapters including introduction (Chapter 1), two stand-alone specific research chapters (2 to 3) and the overall synthesis (Chapter 4).

Chapter 3 has been published with the student M. Gamhewage being the first author (used with permission):

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Chapter 2 will be submitted to the Bulletin of Environmental Contamination and Toxicology.

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This thesis is dedicated to my loving and supportive dad, Sarath Gamhewage (1955 – 2002).

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1. INTRODUCTION

A wide range of chemicals have been detected in freshwater ecosystems such as rivers, including heavy metals, macro and micronutrients, pesticides and pharmaceuticals (Pal et al. 2010; Zbyszewski and Corcoran 2011; Outram et al. 2014; Ali et al. 2016). This thesis research focuses on a wide range of legacy and current-use pesticides and examines their detection in the water-column and bottom sediments of river segments in Manitoba. Contamination of freshwater ecosystems by pesticides has been widely discussed but previous studies have mainly focused on the water column (Glozier et al., 2012; Yang et al., 2015; Fairbairn et al., 2016; Challis et al., 2018). Pesticide molecules have been detected in surface waters such as rivers (Ricart et al. 2010; Bonansea et al. 2013; Stone et al. 2014), streams (Glozier et al. 2012; Fairbairn et al. 2016), lakes (Yuan et al. 2013; Papadakis et al. 2015), ponds (De Lorenzo et al. 2012) and wetlands (Poissant et al. 2008; Messing et al. 2011). Rivers and streams flowing through agricultural lands tend to have greater levels of pesticide contamination than rivers flowing through forests and grasslands (Sun et al. 2013; Fairbairn et al. 2016). Urban cities can be a significant source of pesticide contaminants to rivers (Pal et al. 2010; Wittmer et al. 2010; Glozier et al. 2012; Stone et al. 2014), partly because of the inefficiency of municipal water treatment processes to remove pesticides prior to releasing wastewater into the broader environment (Gerecke et al. 2002; Piel et al. 2012).

The contamination of surface water by pesticides results from various sources and pathways, and might pose a risk to aquatic organisms depending on the severity of contamination (Figure 1.1). Pathways by which pesticides enter surface waters include surface runoff and soil erosion, particularly when a high-intensity rainfall event occurs shortly after pesticide application (Gfrerer et al. 2001; Piel et al. 2012). Other sources include dry and wet atmospheric deposition (Jantunen et al. 2008; Messing et al. 2011), accidental spills of pesticides (Petit et al. 1995; Frank et al. 1990), as well as groundwater discharge (Székács et al. 2015; Reichenberger et al. 2007). Pesticides in surfaces water are subjected to a range of fate processes that include sediment sorption-desorption, and pesticide biodegradation, photolysis, volatilization and bioaccumulation (De Schepper et al. 2012; Holvoet et al. 2007; Mehmetli and Koumanova 2007; Warren et al. 2003; Petit et al. 1995).

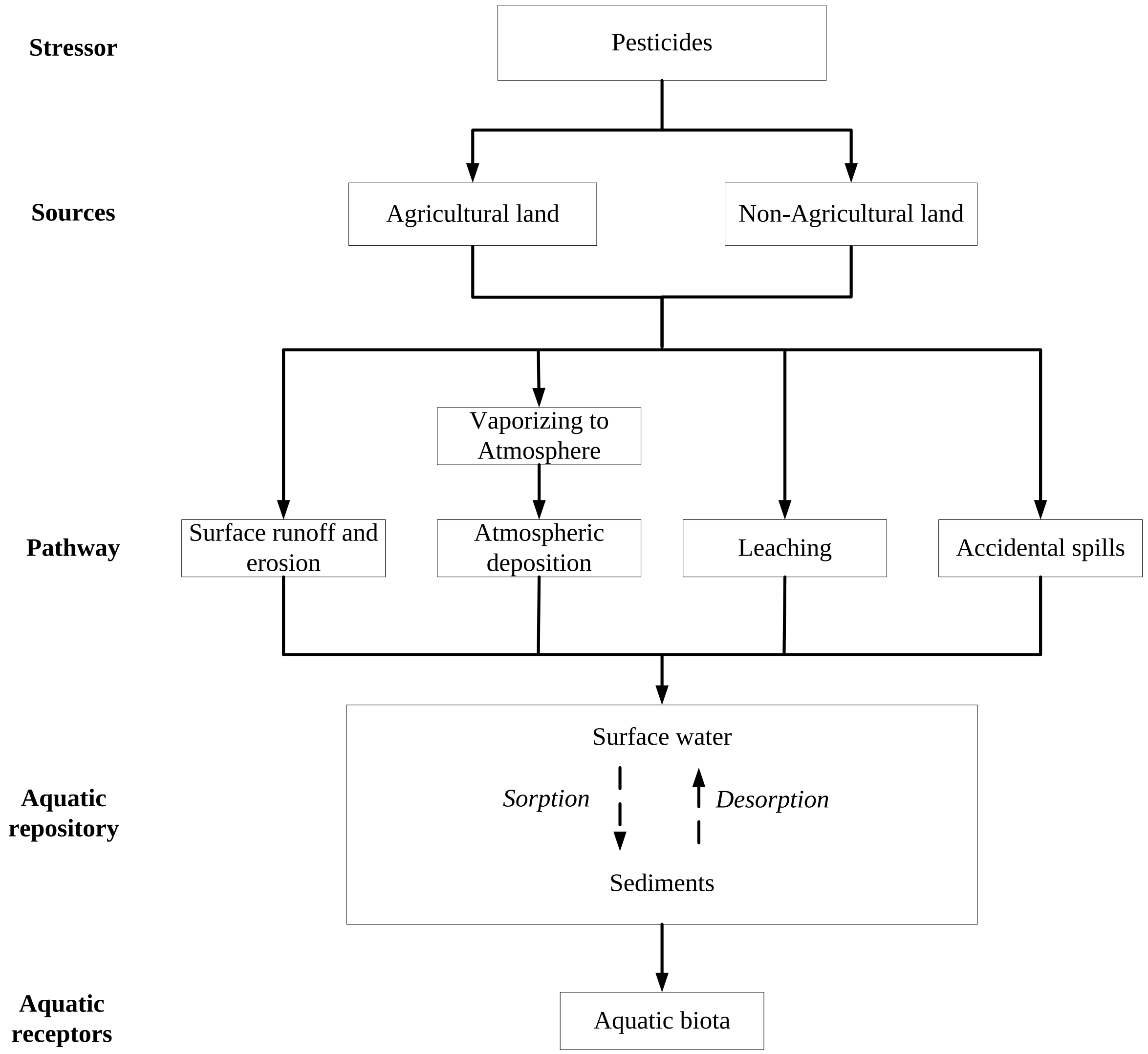

Figure 1.1 A generalized conceptual model of the sources and pathways of pesticide contamination of surface waters.

1.1 Use of Pesticides in Canada

Pesticide is "any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest; [as well as] any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant; [or] any nitrogen stabilizer" (USGPO 2018). The majority of the pesticides used are herbicides, insecticides and fungicides but a wide range of other pesticides exist (Whitacre and Ware 2004). For example, an antimicrobial is a pesticide as well. About 6,800 formulated pesticide products are registered for use in Canada and an estimated 100 million kg of pesticide products are sold each year (Health Canada 2014). Most of the pesticides sold are used in agricultural applications (75%), rather than non-agricultural (21%) and domestic (4%) applications (Health Canada 2014). Table 1.1 includes most commonly used pesticides in Manitoba and their agricultural applications. Herbicides account for about three-quarters of agricultural pesticides sold in Canada. MCPA (2-methyl-4-chlorophenoxyacetic acid) and 2,4-D (2,4-Dichlorophenoxy acetic acid) are among the top 10 pesticide active ingredients sold in Canada (Health Canada 2014) and among the top three pesticides sold in the Province of Manitoba (Environment Canada 2011). MCPA and 2,4-D are phenoxy acetic acids and commonly referred to as auxin herbicides. They are growth regulators (Group 4 Mode of Action) and are widely used for post emergence control of broadleaf weeds in cereal crop production systems. Chapter 3 of this thesis specifically focuses on the interaction of MCPA and 2,4-D with bottom sediments, including the concentration of these auxin herbicides in bottom sediments collected from river segments in Manitoba.

Table 1.1 Physio-chemical properties and agricultural application of commonly used pesticides in Manitoba (Lewis et al. 2016; Manitoba Agriculture 2019). Unavailable information is indicated as “NA”.

Pesticide compound	Water solubility (mgL^{-1} at 20ºC)	Log Kow (at pH 7, 20ºC)	Half-life in water (days)	Half-life in water+sediments (days)	Crops and staging
MCPA	29390	-0.81	13.5	17	Pea (3 to 6 expanded leaves); wheat, oats, rye (prior to flag leaf); corn, pasture (no restrictions)
2,4-D	24300	-0.82	7.7	18.2	Wheat, barley, rye (full tillering to flag leaf); corn, pasture (no restrictions)
Bentazon	7112	-0.46	80	716	Soy bean, corn, wheat (no restrictions); flax (after 5cm in height); Pea (3 leaf pairs to flowering)
Clopyralid	7850	-2.63	148	NA	Barley, wheat (3 leaf to flag leaf); flax and solin (5-10cm in height); canola (2-6 leaf stage); pasture (2-4 leaf stage)
Fluroxypyr	6500	0.04	10.5	34.7	Wheat, barley (2 leaf to stem elongation)
Atrazine	35	2.7	NA	80	Corn (pre-plant, pre-emergence, 1-6 leaf stage)
Metolachlor	530	3.4	88	365	Soybean, corn, potato (pre-plant, pre-emergence)
Dicamba	250000	-1.88	40	41	Wheat, barley, oat (2-5 leaf); rye (2-3 leaf); corn (2 weeks prior to 50cm height); pasture (no restrictions)
Bromoxynil	38000	0.27	13	13	Barley, wheat, oat,rye (2 leaf to early flag); corn (beyond 4 leaf); flax

					and solin (5-10cm in height); canola (pre-seed, pre-plant)
Boscalid	4.6	2.96	5	545	Potato (no restrictions); canola (20-50% flowering); filed pea, lentil (beginning of flowering)
Tebuconazole	36	3.7	42.6	365	Wheat (75% of wheat heads emerged to 50% of heads are in flower); soybean, barley, oat (no restrictions)
Azoxystrobin	6.7	2.5	6.1	205	Dry bean, lentil, field pea (until onset of flowering); soybean (R1-R3 stage)
Metalaxyl	8400	1.75	56	56	Soybean, lentil, pea, canola, sunflower, wheat, barley, oat, rye, triticale, corn, pasture (no restrictions)
Prothioconazole	22.5	2	NA	NA	Wheat (75% of wheat heads emerged to 50% of heads are in flower); barley (70% of barley heads emerged to 3 days after full head emergence); oat, soybean (no restrictions); corn (silking to silk browning); canola, flax (20-50% flowering); sunflower (10-50% disk flower bloom); lentil (beginning of flowering)
Mecoprop	250000	-0.19	37	50	Wheat, barley, oat (3 leaf to flag stage)
Propiconazole	150	3.72	6	561	Wheat, barley (growth stages 12-23); oat, corn, soybean, dry bean, lentil, field pea, (no restrictions); canola (rosette); canary seed (flag leaf emergence)

1.2 MCPA and 2, 4-D Characteristics

MCPA and 2,4-D molecules are similar except that at the position two of the benzene ring 2,4-D has a chlorine, whereas MCPA has a methyl group (Figure 1.2). Both compounds are highly soluble in water and have low K_{ow} values (Table 1.2) which indicate that they tend to remain in the water phase rather than partitioning into living or dead organisms (e.g., aquatic biota) or materials rich in organic matter (e.g., sediments). MCPA and 2,4-D are formulated as an amine salt or ester, with ester formulations being more volatile. In the environment, however, these amine and ester formulations are rapidly converted to the acid form and both MCPA and 2,4-D acids have a relatively low volatility as demonstrated by their low Henry's law constants and vapor pressures (NPIC 2019) (Table 1.2). Both herbicides have relatively short half-lives in soils, water and sediments (Table 1.2), and neither MCPA nor 2,4-D is considered environmentally persistent. In aquatic environments, 2,4-D degrades faster than MCPA in the water phase (Lewis et al. 2016).

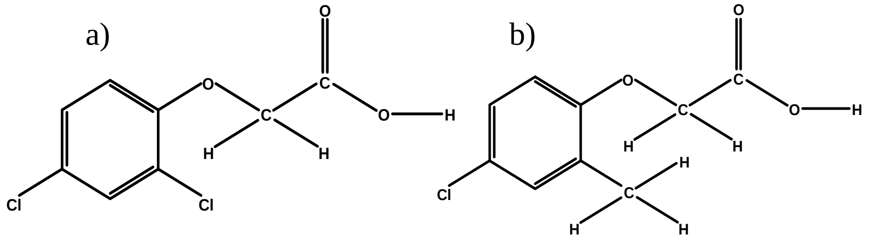

Figure 1.2 Chemical structure of 2, 4-D (a) and MCPA (b).

Table 1.2 Physio-chemical properties of MCPA acid and 2,4-D acid (Sattar and Paasivirta 1980; USEPA 2004, 2005; Lewis et al. 2016)

	MCPA	**2,4-D**
Molecular mass (g/mol)	200.62	221.04
Water solubility at 20ºC (mg/L)	29,390	24,300
Octanol/water partition coefficient (log Kow) at pH 7, 20ºC	- 0.81	-0.82
Half-life in water phase only (days)	13.5	7.7
Half -life in water + sediment phase (days)	17	18.2
Half-life in flooded soil (days)	24-48	24-48
Vapor pressure at 20ºC (mPa)	0.4	0.009
Henry's Law constant at 25ºC (Pa m^3/mol)	5.5×10^{-5}	4×10^{-6}

1.3 Retention of Pesticides by Sediments

A portion of pesticides entering surface waters is attached to wind and water eroded sediments, and these pesticides can partition into the water column over time. Likewise, pesticides entering the water-column of surface waters (e.g., via water runoff) can partition to river sediments (Ricart et al. 2010; Masia et al. 2013). The technical term "sorption" refers to the binding or partitioning of a chemical from the liquid or gaseous phase onto a solid phase (Kerle et al. 1994). The relative amounts of pesticide sorption by sediments can be described by the sorption distribution constant (K_d), with greater K_d values indicative of greater sorption. K_d is commonly measured using the batch equilibrium method in laboratory settings (OECD/OCDE 106 2000). K_d values can vary depending on the physio-chemical properties of the pesticide, as well as sediment characteristics particularly organic carbon content. Hence, the organic carbon normalized sorption coefficient, K_{oc} (L/Kg) is also determined where Kd values are divided by the fraction of the sediment organic carbon content (OECD/OCDE 106 2000). Larger K_{oc} values reflect greater pesticide sorption per unit of organic carbon in the sediment. Like sorption, desorption of pesticides from sediments to the water-column is also important for predicting the pesticide concentrations in rivers (Kawakami et al. 2007). Desorption is an additional step measured as part of the batch equilibrium sorption experiments (OECD/OCDE 106 2000), however, most studies focus on pesticide sorption without this additional step to determine desorption.

Studies have shown a positive correlation between sediment organic carbon content and pesticide sorption (Hiller et al. 2006, 2009; Lin et al. 2008; Gaultier et al. 2009; Xu et al. 2009; Gebremariam et al. 2011). Pesticide sorption has shown to be both positively (Budd et al. 2011; Hiller et al. 2009) and negatively (Xu et al. 2009; Vallee et al. 2014) associated with sediment clay content. Regardless of sediment properties, pesticide sorption is greater for hydrophobic pesticides with high Koc and low water solubility (Vallee et al. 2014).

1.4 Relative Toxicities of Pesticides for Freshwater Organisms

Pesticides in freshwater systems can pose a risk to aquatic life (Morrissey et al. 2015; Nowell et al. 2018). Most toxicological studies have focused on the impact of single pesticides on specific species. Most commonly used species for freshwater ecotoxicology experiments are: green algae, diatoms, and duckweed for aquatic plants; rainbow trout, fathead minnow, and bluegill for fish; and midge, scud, and daphnids for invertebrates. Higher sensitivity for pesticide compounds, greater availability of all stages of life cycle of the species throughout the year, and low demand for propagation and laboratory maintenance are some of the reasons for selecting those species for ecotoxicological experiments (Wolf et al. 1985; Lewis et al. 2018). EC50 (50% Effective Concentration) and LC50 (50% Lethal Concentration) values are commonly used to compare the relative toxicity of chemicals among species. The EC50 is defined as the concentration of a pesticide which inhibits 50% of population growth of the test organism at a given time. The LC50 value is defined as the pesticide concentration that kills 50% of the test organism at a given time. For example, Stoughton et al. (2008) reported that the insecticide imidacloprid can be toxic to a freshwater invertebrate midge (*Chironomus tentans*) and an amphipod (*Hyalella Azteca*) with LC50 (96h) values being 5,800 ngL^{-1} and 65,400 ngL^{-1}, respectively.

Macrophytes (e.g., *Lemna minor*) are generally more sensitive to herbicides than microalga (e.g., *Pseudokirchneriella subcapitata*); and some synthetic auxins (MCPA and mecoprop in particular) and glyphosate are virtually non-toxic to algae (Cedergreen et al. 2005). A study that examined the toxicity of 42 fungicides to aquatic organisms reported that invertebrates are more sensitive than fish to ethylene bisdithiocarbamate (EBDC) fungicides, but less sensitive than fish to non-EBDC fungicides (Maltby et al. 2009). For the non-EBDC fungicide captan, Boran et al. (2012) reported that the LC50 (96h) values for rainbow trout is 380,000 ngL^{-1}. Studies have also examined sub-lethal effects of pesticides on organisms. For example, for the organophosphate insecticide chlorpyrifos, the embryonic exposure of zebrafish (*Danio rerio*) at 100,000 ngL^{-1} resulted in the zebrafish having a declined swimming activity and impaired spatial discrimination (Levin et al. 2004). Chlorpyrifos can also cause longer-term neurobehavioral damage (Sledge et al. 2011).

A few studies have examined the impact of pesticide mixtures on aquatic organisms even though pesticides are usually detected as mixtures in aquatic environments (Smiley et al. 2014; Gustavsson et al. 2017). Depending on the types of pesticides included in the mixture, and the aquatic organisms involved, the effect of the pesticide mixture on a species can be additive, synergistic or antagonistic. Reylea (2009) compared the effects of single and mixture applications of ten pesticides on aquatic communities. Zooplankton and algea were exposed to pesticide concentrations ranging from 2,000 – 16,000 ngL^{-1} and the ecological risk (acute mortality) induced by any individual pesticide was nearly identical to the risk induced by pesticide mixtures. In contrast, Norgaard and Cedergreen (2010) reported that experimental data derived from exposing aquatic crustaceans to fungicide mixtures containing prochloraz showed 12 times greater toxicity (acute immobilization) than the calculated sum of the individual fungicide effects.

1.5 Monitoring Studies on Pesticides in Rivers

The presence and levels of pesticides in rivers have been monitored worldwide. Majority of these monitoring studies are focused on the water-column, in particular the frequency of detections of organochlorines (Sankararmakrishnan et al. 2005; Konstantinou et al. 2006; Rissato et al. 2006; Imo et al. 2007; Ize-Iyamu et al. 2007) and organophosphates (Rovedatti et al. 2001; Hela et al. 2005; Fadai et al. 2012; Lari et al. 2014).. Studies that have monitored pesticides in both river water-column and bottom sediments also most commonly screened for organochlorine pesticides (Pereira et al. 1996; Zhou et al. 2006; Yang et al. 2013). A few other studies collected both water-column and bottom sediments in rivers and screened for between one to 50 pesticide active ingredients pesticides, most often involving chemical families such as organophosphates, triazines, and phenoxy acids (Laabs et al. 2002; Masia et al. 2013).

1.6 Pesticides Detected in Rivers Flowing into Lake Winnipeg

This thesis focuses on river segments in Manitoba, with all four rivers studied entering Lake Winnipeg. Lake Winnipeg is the world’s tenth largest freshwater lake. It has a watershed of 1 million km^2 and has the largest watershed-to-lake area ratio in the world (40:1) (LWSB 2006; ECMWS 2011). Human activities in Lake Winnipeg’s watershed have a large potential to influence the types of contaminants entering rivers and streams, thus potentially the lake (LWIC 2005; ECMWS 2011). Major pollution concerns of Lake Winnipeg include extreme eutrophication (Kling et al. 2011; Schindler et al. 2012; Ulrich et al. 2016), pesticides (Rawn et al. 2000) and microplastics (Anderson et al. 2017).

Lake Winnipeg is a remnant of the Lake Agassiz and is located between the Precambrian shield and sedimentary rock of interior plains (Brunskill et al. 1980; LWSB 2006). Lake Winnipeg received most of its water from Precambrian shield rivers (Brunskill et al. 1980). This includes two rivers sampled in this research project: Winnipeg River (Winnipeg R) that accounts for about one-half of the total water flow into Lake Winnipeg, and the Manigotagan River (Manigotagan R) that accounts for less than 1% (Brunskill et al. 1980; ECMWS 2011). This thesis project also includes two rivers flowing from the southern and western watersheds (sedimentary strata), namely the Red River (Red R) and the Fisher River (Fisher R). The Red R accounts for about one-sixteenth of the total water flow into Lake Winnipeg, and the Fisher R accounts less than 1% (Brunskill et al. 1980; ECMWS 2011).

Previous studies have monitored for pesticide residues in the water column of the Red R and Saskatchewan River that flow into Lake Winnipeg (Gummer 1980; Rawn et al. 1999; Glozier et al. 2012; ECCC 2015; Challis et al. 2018). Comparing Rawn et al. (1999) with ECCC (2015), pesticide concentrations in the Red R water column might have risen over time. Rawn et al. (1999) quantified pesticide compounds in the Red R water-column from 1993 to 1995 and reported that 11 of 16 pesticides being screened for were detected in more than 50% of the samples (n=96). The median concentrations of these pesticides detected ranged from 0.01 to 11.1 ngL^{-1} (Rawn et al., 1999). ECCC (2015) monitored the Red R from 2006 to 2011 and reported that 6 of 47 pesticides being screened for were detected in more than 50% of the samples (n=77). The median concentrations of these pesticides ranged from 2.8 to 43.5 ngL^{-1} Both surveys have reported median concentrations for three herbicides in common (2,4-D, MCPA and metolachlor). From what was reported in Rawn et al. (1999) and ECCC (2015), 2,4-D concentrations increased more than thirty-fold (0.36 - 1.39 to 43.5 ngL^{-1}) and metolachlor concentrations increased more than two-fold (5.06 – 8.9 to 23.07 ngL^{-1}). However, median concentrations of MCPA did not appear to show a substantial increase over time (1.65 – 4.53 to 5.07 ngL^{-1}). There is no information on pesticides concentrations in sediments of the Red R other than that reported by Chacko and Gummer (1980), who detected 2,4-D in the water-column (including the suspended sediments), but not in bottom sediments.

1.7 Research Objectives and Hypotheses

The overall aim of this research was to collect water-column and bottom sediment samples from river segments in Manitoba for subsequent laboratory analysis to address the following research questions: 1) What are the types of pesticides present in the water-column and bottom sediments of rivers flowing through intensively-managed versus semi-natural habitats? Also do the concentrations of the pesticide mixtures in the water-column pose a potential risk to freshwater organisms? (Chapter 2); 2) To what extent can variations in the concentrations of MCPA and 2,4-D detected in bottom sediments be explained by measured laboratory parameters such as Kd values, sediment organic carbon content and particle size distribution (Chapter 3) ?.

The hypotheses of this research were: The types of pesticides present in the water-column are similar to those present in the bottom sediments (Chapter 2); Pesticide mixtures are more commonly found in river segments flowing through intensively-managed habitats than semi-natural habitats (Chapter 2); river bottom sediments sorb significantly greater MCPA than 2,4-D (Chapter 3); greater sediment organic carbon content and finer river bottom sediments positively affect MCPA and 2,4-D concentrations in those sediments (Chapter 3).

1.8 Thesis Outline

This thesis is prepared in manuscript style in accordance with the University of Manitoba's Department of Soil Science Guidelines. It has four chapters including the introduction (Chapter 1), two stand-alone manuscripts (Chapter 2 and 3), and the overall synthesis (Chapter 4).

Chapter 2: Pesticides in water and bottom sediments of four Manitoba rivers: impact of land-use and effects on aquatic organisms

A field survey that determined pesticides in the water-column and bottom sediments of Red River, Fisher River, Winnipeg River and Manigotagan River. Potential risks of pesticide mixtures on aquatic plants, fish and invertebrates were calculated.

Chapter 3: Phenoxy herbicides' interactions with river bottom sediments

A laboratory study that determined the sorption-desorption behavior of MCPA and 2,4-D in bottom sediments collected from the Red R, Fisher R and Winnipeg R. Sediment organic carbon content and particle size distribution, as well as MCPA and 2,4-D concentrations in the collected sediments, were determined and used in subsequent correlation analysis with Kd values derived from laboratory experiments.

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2. PESTICIDE MIXTURES IN THE WATER-COLUMN VERSUS BOTTOM-SEDIMENTS OF PRAIRIE RIVERS

2.1 Abstract

Water-column and bottom sediment samples were screened for 160 pesticide compounds to compare the types of pesticides present between these matrices and between river segments flowing through intensively-managed versus semi-natural habitats. Current-use pesticides accounted for 96% (water) and 76% (sediment) of the compounds detected. Pesticide mixtures were more frequently detected in water (72%) than sediments (51%) and predominantly consisted of broadleaf herbicides. Pesticide mixtures were most frequently detected and at greater concentrations in rivers flowing through intensively-managed habitats. For most compounds detected, there was no significant correlations between their concentrations detected in water and sediments, suggesting that monitoring the water-column is a poor indicator of the presence of pesticides in sediments. Despite evidence that the concentrations of some broadleaf herbicides were substantially greater in this study than in studies between 1993-2011, the concentrations of pesticide mixtures detected were below the threshold indicating no significant risks to freshwater organisms.

2.2 Introduction

Natural processes and human activities in watersheds influence river water quality. Lake Winnipeg in the Province of Manitoba, Canada has the largest watershed-to-lake area ratio in the world (40:1) and is also among the most impacted lakes by eutrophication (LWIC 2005; ECMWS 2011). Rawn et al. (2000) reported that concentrations of legacy insecticide DDT (dichlorodiphenyltrichloroethane) were greater in sediments from the south than north basin of the lake because its historical agricultural and urban use was concentrated in the south. There are more than 60 tributaries entering Lake Winnipeg, most notably the Red River (Red R) in the south, which is flowing through areas dominated by croplands and urban activities before entering Lake Winnipeg (Figure 2.1). Thus, although only accounting for about one-sixteenth of the total water flow into Lake Winnipeg (ECMWS 2011), it is the tributary most frequently studied for pesticide concentrations in its water column (Gummer 1979; Rawn et al. 1999; ECCC 2015; Challis et al. 2018). Comparing data from previous studies, the mean concentration of the herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) was 30-fold greater in late 2000s than in the mid-1990s (Rawn et al. 1999; ECCC 2015). An earlier study did not detect 2,4-D in bottom sediments of the Red R (Chacko and Gummer 1980). Studies comparing the presence of pesticides in the water-column versus bottom-sediments of rivers in various parts of the world frequently focused on legacy insecticides such as DDT (Pereira et al. 1996; Zhou et al. 2006; Yang et al. 2013) but have included up to fifty pesticides (Laabs et al. 2002; Masiá et al. 2013).

Canadian Water Quality Guidelines for the Protection of Aquatic Life have been set for a number of pesticide active ingredients, but not for pesticide mixtures. Although pesticide mixtures are commonly present in surface waters, there have been only two studies that assessed the impact of environmentally relevant concentrations of pesticide mixtures on aquatic organisms (Relyea 2009; Nowell et al. 2018). For small streams in the Midwestern United States, Nowell et al. (2018) reported that the concentrations of herbicide mixtures occasionally exceeded the acute toxicity thresholds for non-vascular plants (e.g., acute EC50s for green algae and diatoms).

In this study, we screened water-column versus bottom-sediment samples for 160 compounds, of which 86 were pesticide active ingredients registered for use in Canada and their metabolites, while the other compounds include legacy insecticides such as DDT and lindane and their metabolites. The objectives of this study were to compare the types of pesticides present in these two matrices and among rivers flowing through intensively-managed versus semi-natural habitats, and further calculate whether the concentrations of the pesticide mixtures in the water-column pose a potential risk to freshwater plants, fish and invertebrates.

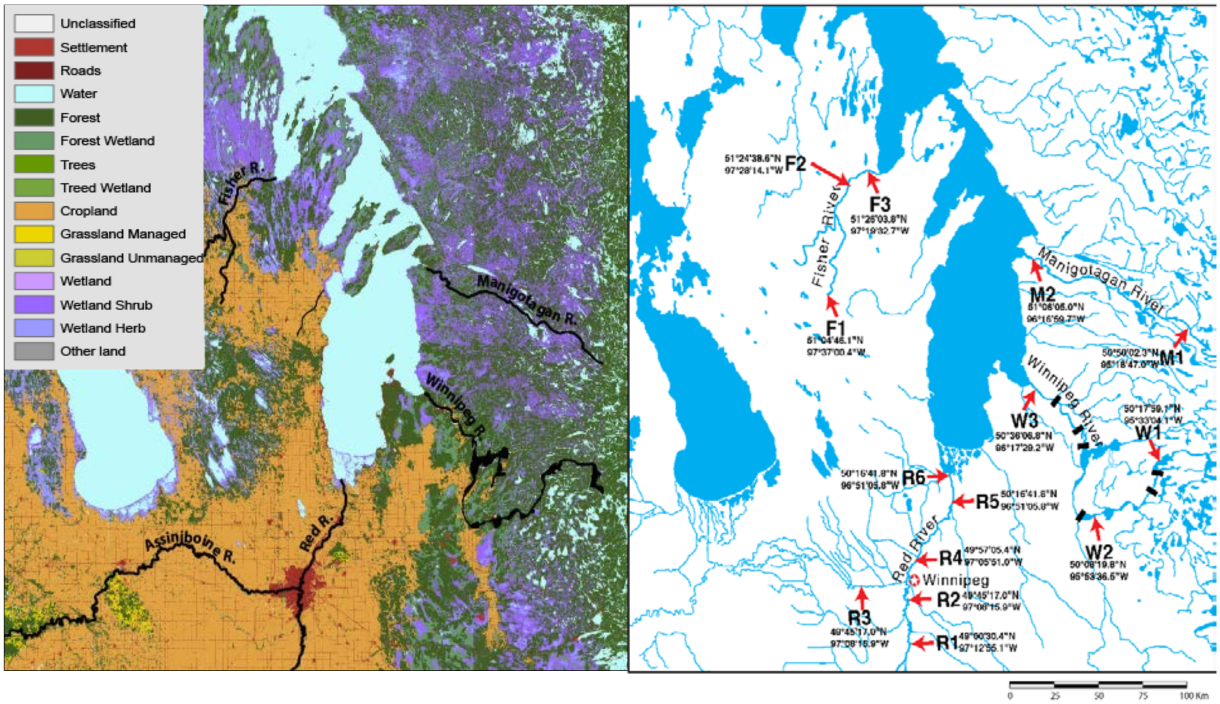

Figure 2.1 Land use classifications in Manitoba (A) and river sampling locations (B) of the study. Land use classification was obtained from Agriculture and Agri-Food Canada © Her Majesty the Queen in Right of Canada as represented by the Minister of Natural Resources http://www.agr.gc.ca/atlas/landu (A).The solid black lines in the Winnipeg River refer to the six hydroelectric generating stations which are towards the mouth of the river: Pointe du Bois, Slave Falls, Seven Sisters Falls, McArthur Falls, Great Falls and Pine Falls generating stations.

2.3 Materials and Methods

In addition to the Red R, this study also included the Winnipeg River (Winnipeg R), a river accounting for about half of the total water flow into Lake Winnipeg (ECMWS 2011); the Fisher River (Fisher R), a river flowing through the territory of the Fisher River Cree Nation, a First Nation reserve in Manitoba (MB); and the Manigotagan River (Manigotagan R), a bedrock river that is part of the Canadian Shield. Sampling locations are presented in Figure 2.1 and include the mouth of each river (R6 in the Red R, F3 in the Fisher R, W3 in the Winnipeg R and M2 in

Manigotagan R) prior to discharging into Lake Winnipeg. The Red R (~880 km along its main stem) has a drainage area of 288,000 km^2 (Newton 2016) with about 80% of its length flowing through the USA before entering MB in the border town of Emerson. In MB, the Red R flows through cropland (R1 to R2) then through the City of Winnipeg (pop. ~700,000) (R2 to R4) and sub-urban areas and cropland (R4 to R6). The Fisher R (~140 km along its main stem) originates in MB and first flows through cropland (F1 to F2) then wetland complexes (F2 to F3) with a total drainage area of ~3150 km^2 (Government of Manitoba 2018). The Winnipeg R (~260 km along its main stem) has a drainage area of ~150,000 km^2 with about one third flowing through the Province of Ontario (ON), Canada, before entering MB (Barth et al. 2013). In MB, the river predominantly flows through boreal forests and wetland complexes (W1 to W3) with some small sections of the river also intersecting with cropland (W2 to W3). There are six hydroelectric generating stations built along the Winnipeg R, where herbicides are part of the integrated vegetation management along transmission lines (Manitoba Hydro 2019). About 20% of the Manigotagan R (~150 km) flows through ON before entering MB with boreal forests and wetland complexes (M1 to M2) dominating its total drainage area of ~217 km^2 (Manitoba eco-network 2018).

Water-column samples (n=83) and bottom sediment samples (n=68) were collected at a total of 14 sampling locations (Figure 2.1) from May 9 to August 30, 2016. Water samples were collected eight times in the Red R, five times in the Fisher R and Winnipeg R, and four times in Manigotagan R. As part of these sample collection events, bottom sediments were collected seven times in the Red R, five times in the Fisher R and four times in Winnipeg R. Bottom sediments were not collected from the Manigotagan R because it is a bedrock river. Bottom sediments (3375 cm^3) were collected using an Ekman Dredge, and placed into sterile amber plastic bags (Fisher Scientific International Inc., USA). Samples were transported on ice to the laboratory and stored at -20°C until all sediment collections were completed in August. The grab sampling method was used to collect water into 1L amber glass bottles. Water samples were kept at 4°C prior to extraction and analysis within 7 days after collection.

Water and sediment samples were extracted and analyzed at the Lethbridge Research and Development Centre, Agriculture and Agri-Food Canada, Alberta. Methods used followed those described in Munira et al. (2018) and Gamhewage et al. (2019) to screen for 86 pesticide active ingredients and metabolites currently registered for use in Canada, and for 74 compounds that are active ingredients, metabolites or by-products in pesticide products not or no longer registered in Canada (Table 2S1). Briefly, suspended material in the water-column samples were filtered out using glass wool and pesticides were isolated from water using liquid-liquid extraction with dichloromethane. Bottom sediment samples were freeze-dried (-37°C for 24 hours) and extracted using the quick, easy, cheap, effective, rugged, and safe (QuEChERS) procedure. Extracts were analyzed using a 7890B gas chromatograph with a 7000C QQQ mass selective detector. The limit of detection (LOD) of most compounds was 25 ngL^{-1} (water-column) and 1,667 $ngKg^{-1}$ (freeze-dried sediments). Detections below LOD were considered as zero concentration (non-detect). The associations between pesticide concentrations detected in water versus those in sediments were determined using Spearman rank-order correlation (SAS, version 9.4). The significance level was set at $P<0.05$.

The Pesticide Toxicity Index (PTI) was used as an indicator (Nowell et al. 2014) to estimate the risk of pesticide mixtures present in the water-column on freshwater 1) vascular plants, 2) non-vascular plants, 3) invertebrates and 4) fish. Two different risk assessments were conducted for each of the four rivers. In the first risk assessment, water-column samples containing at least two detectable pesticides were taken into account and all pesticides were included in the calculations at the concentrations they were detected, including up to 19 pesticides for the Red R, up to eight pesticides for the Fisher R, and up to five pesticides for the Winnipeg R and Manigotagan R. The second risk assessment simulated a worst-case scenario by selecting the highest pesticide concentration detected in a river and then assuming that all pesticides in that river were detected at that concentration. Benchmarks obtained from USEPA (2018) were: 1) the effective concentrations inducing 50% inhibition (<10d EC50s) in vascular (i.e., duckweed) or non-vascular (i.e., typically green algae and diatoms) plants, and 2) lethal concentrations inducing 50% mortality (48-96h LC50s) in invertebrates (i.e., typically midge, scud and daphnia) or fish (i.e., typically rainbow trout, fathead minnow and bluegill). Toxicity quotients were calculated by dividing each pesticide concentration by the EC50 or LC50 for that pesticide. The PTI was calculated by summing the toxicity quotients for all pesticides. A value of PTI=1 was set as the threshold demonstrating significant harm, i.e., 50% of mortality/growth inhibition is expected at the threshold of 1.

2.4 Results and Discussion

Table 2.1 Pesticide concentrations (ng L^{-1} and ng Kg^{-1}) detected in the water-column and bottom sediments of the Red River. Numbers refer to (mean/maximum, detection frequency %). Compounds in **bold** were detected in both water and sediment samples. All compounds are current-use pesticides except for herbicides that are *italicized* and are either *metabolites (M)* or herbicides not registered for use in Manitoba *(NR).*

Current-use herbicides *or their metabolites (M) and herbicides not registered for use (NR)*
Water-column: **MCPA**(236/1,436, 90%); **2,4-D**(130/726, 86%); **Clopyralid**(101/311, 84%); **Mecoprop**(101/311, 84%); **Bentazon**(226/986, 82%); **Fluroxypyr**(127/1,378, 78%); Atrazine(79/214, 78%); **Metolachlor**(90/254, 65%); Dicamba(58/1500, 59%); **Bromoxynil**(113/1,772, 42%); **Imazethapyr**(16/302, 7%); **Triallate**(3/36, 7%); EPTC(7/243, 5%)
Bottom sediments: **MCPA**(55,318/266,252, 96%); **Clopyralid**(4,727/44,308, 60%); **2,4-D**(3,203/28,302, 43%); **Fluroxypy**(1,074/9,056, 31%); **Bentazon**(1,187/24,174, 22%); *NR:Dimethachlor* (610/8,848, 10%); **Imazethapyr**(1,121/31,310, 8%); **Bromoxynil**(432/12,131, 8%); **Mecoprop**(90/3,094, 5%); *M:2,4-Dichlorophenol*(256/10,728, 3%); **Metolachlor**(44/1,826, 2%); **Triallate**(38/1,585, 2%)
Current-use fungicides *or their metabolites (M)*
Water-column: **Boscalid**(29/137, 46%); **Tebuconazole**(59/189,44%); **Azoxystrobin**(116/646, 42%); **Propiconazole** (19/290, 13%); Metalaxyl(15/61, 38%), ***M: Prothioconazole-Desthio***(15/67, 36%); Pyraclostrobin(9/241, 5%); Fludioxonil(3/71, 5%); Picoxystrobin(1/36, 2%)
Bottom sediments: **Boscalid**(2,568/15,256, 46%); **Tebuconazole**(5,672/28,264, 41%); **Azoxystrobin**(8,414/44,207, 39%); Difenoconazole(5,706/35,232, 34%); **Propiconazole**(1,700/11,362, 24%); ***M:Prothioconazole-Desthio***(562/3,564, 22%)
Current-use insecticides *or their metabolites (M) and insecticides not registered for use (NR)*

Water-column: *NR:p,p-DDE*(1/25, 2%)

Bottom sediments: *NR:Dieldrin*(160/6,684, 2%); *NR:p,p-DDT*(142/5,928, 2%); *NR:Trans-Permethrin*(83/3,448 ,2%); Chlorpyrifos(50/2,087, 2%); *NR:Cis-Permethrin*(45/1,869,2%)

Table 2.2 Pesticide concentrations (ng L^{-1} and ng Kg^{-1}) detected in the water-column of the Fisher River, Winnipeg River and Manigotagan River. Numbers refer to (mean/maximum, detection frequency %). Compounds in bold were detected in the water column of all three rivers. Italicized compounds are metabolites.

Fisher River	Winnipeg River	Manigotagan River
Current-use herbicides *or their metabolites*		
MCPA(4,227/50,450, 54%);	**Bentazon**(10/39, 34%);	**MCPA**(11/61, 38%);
2,4-D(142/778, 34%);	**2,4-D**(36/373, 17%);	**Bentazon**(19/79, 38%);
Fluroxypyr(77/511, 34%);	**MCPA**(14/154, 17%);	**2,4-D**(78/591, 25%);
Bentazon(46/411, 27%);	**Clopyralid**(22/261, 9%);	Mecoprop(5/28, 25%);
Bromoxynil(7/30, 27%);	**Bromoxynil**(10/119, 9%);	**Bromoxynil**(5/25, 25%);
Clopyralid(120/1,796, 7%);	Mecoprop(1/9, 9%)	**Clopyralid**(2/11, 13%)
Picloram(6/77, 7%)		
Current-use fungicides		
Tebuconazole(11/95, 14%); Boscalid(10/78, 14%);		
Prothiconazole-Desthio(1/11, 7%)		

Current-use pesticides accounted for 96% (water) and 76% (sediment) of the compounds detected. However, 59 current-use pesticides were never detected (Table 2S1). The number of compounds detected decreased in the order of Red R > Fisher R > Winnipeg R > Manigotagan R (Tables 2.1 and 2.2), further suggesting that river contamination primarily arises because of current-use pesticides applied in agricultural and urban habitats. Sampling point R1 (Figure 2.1) typically demonstrated similar types and concentrations of pesticides in the water-column than other sampling locations in the Red R (Figure 2.2), highlighting transboundary contamination as previously noted (Challis et al. 2018). Current-use fungicides were only detected in the Red R (Table 2.1) and Fisher R (Table 2.2), suggesting that they are present because of their use in agriculture (Figure 2.1).

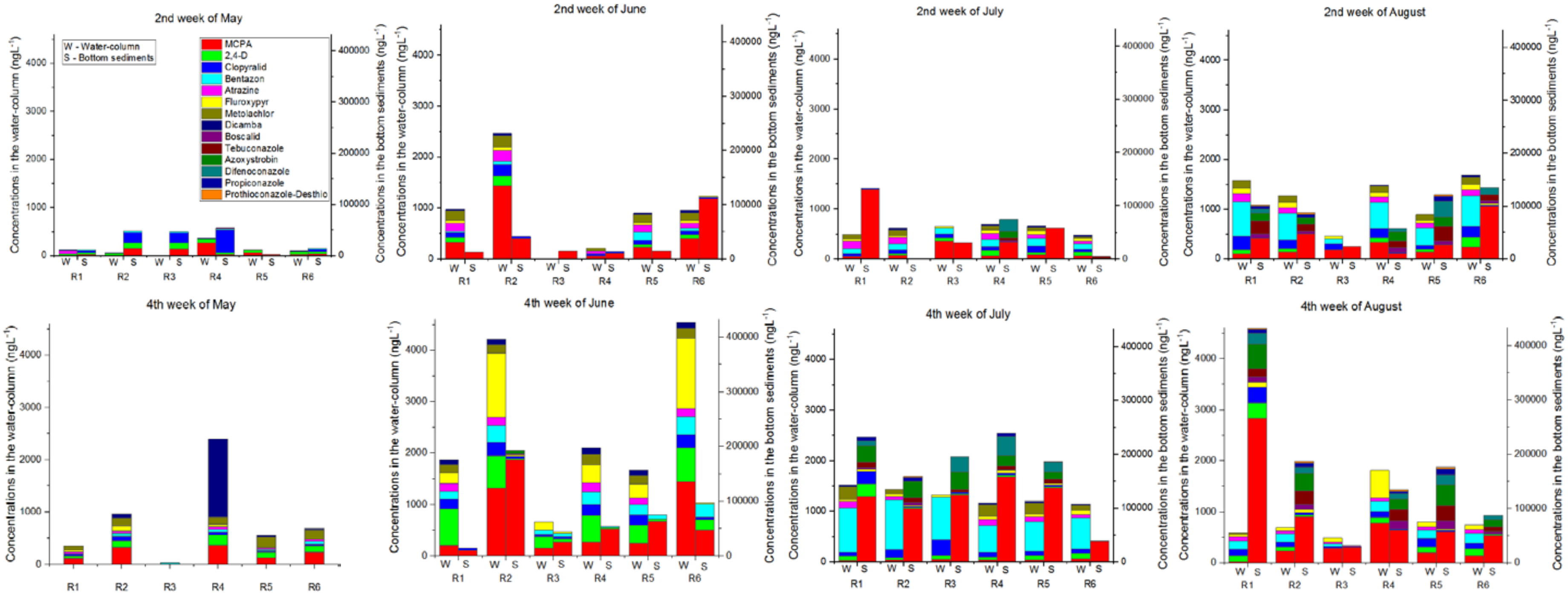

Figure 2.2 Cumulative concentrations of pesticides detected in more than 50% of the samples in the water column, and in over 20% of the bottom sediments of the Red R from May to August 2016. Bottom sediment samples were not collected in the 4th week of May 2016.

Fourteen current-use herbicides were detected in the water-column. MCPA, 2,4-D, bentazone, bromoxynil and clopyralid were detected in all four rivers (Table 2.1 and 2.2). Auxin herbicides such as MCPA and 2,4-D are widely used in Prairie agriculture, in addition to being formulated together in several formulations (e.g., MCPA or 2,4-D with bromoxynil or clopyralid). Of the five broadleaf herbicides, MCPA, 2,4-D and clopyralid are also registered for use in forests and woodlots, as well as industrial and domestic non-food sites for vegetation control (HCPMRA 2007, 2011, 2017). As well, all five herbicides have the potential to enter surface waters by atmospheric deposition, including MCPA in air (Messing et al. 2011, 2014). Previous studies have reported the frequent detection of auxin herbicides in Prairie rivers, including that of 2,4-D, clopyralid and MCPA among the top three pesticides detected out of 47 pesticides monitored for (ECCC 2015). The median concentrations of MCPA and 2,4-D in the Red R were between 2 and 210 times greater than reported for studies between 1993-2011 (Rawn et al. 1999; ECCC 2015), suggesting that the contamination of the Red R by these current-use herbicides has increased over time.

No insecticides were detected in the water column (Table 2.2) but p,p-DDE (a metabolite of DDT) was detected in the Red R water-column (Table 2.1). Eight current-use fungicides (Figure 2.2), as well as prothioconazole‘s metabolite prothioconazole-desthio were detected in the water-column (Table 2.1 and 2.2). Prothioconazole-desthio is more environmentally persistent in aquatic environments than its parent compound (USEPA 2007).

Two current-use insecticides (bifenthrin and chlorpyrifos) were detected in sediments. These insecticides have both a low water solubility (<2 mgL^{-1} at $20^{o}C$) and an octanol-water partition coefficient (Log P) greater than 4 (Lewis et al. 2016) implying the tendency of these insecticides to move from the water-column to sediments in rivers. Prothioconazole-desthio as well as five current-use fungicides were detected in sediments; the water solubility of these compounds at $20^{o}C$ ranges from 4.6 mgL^{-1} (azoxystrobin) to 150 mgL^{-1} (propiconazole). The ten current-use herbicides detected in sediments included MPCA, 2,4-D, bentazone, bromoxynil and clopyralid; all possess a high water solubility (>7,000 mgL^{-1} at $20^{o}C$). MCPA was detected in sediments of all the rivers (except Manigotagan, which was not sampled for sediments), due to its wide use across all watersheds. Two-thirds of the 15 herbicides and half of the ten fungicides and metabolites detected in the Red R were detected in both water and sediments (Table 2.1). These herbicides and fungicides are applied to one or more of the dominant crops grown in the Red R basin, particularly cereal (e.g., spring wheat), oilseed (e.g., canola) and legume (e.g., soybeans) crops (Manitoba Agriculture 2019). For azoxystrobin, boscalid, and tebuconazole, prothioconazole-desthio, and the herbicide triallate, there was a positive correlation ($p<0.05$) between their detected concentrations in water and sediment samples. None of the other compounds showed significant associations between their concentrations detected in water and sediments (Table 2.1). Ten compounds were detected in sediments but not in water-column samples. Thus, with a few exceptions, monitoring only the water-column (as typically is done) is a poor indicator of understanding the full range of pesticides present in rivers.

Pesticide mixtures were more frequently detected in water (72%) than sediment (51%) samples (Figure 2.2). Cumulative concentrations of pesticides detected in water and sediments of the Red

R were relatively lower in the second week of May than in most other sampling rounds (Figure 2.2). This suggests that the pesticides detected in Red R water and sediments are because of pesticide applications in the year of sampling, including via runoff, spray drift and atmospheric deposition. Auxin herbicides (e.g., 2,4-D, clopyralid, dicamba fluroxypyr, MCPA) dominated the contaminants in the Red R water-column in May and June (Figure 2.2). MCPA was among the most frequently detected herbicides across all sampling sites and times, and demonstrated an apparent partitioning into bottom sediment (e.g., in June, July and August) despite its reported short half-life in water (13.5 days) (Lewis et al. 2016). In the current study, MCPA concentrations in bottom sediments were many folds larger than those of other pesticides, suggesting that MCPA frequently enters rivers and partitioning to sediments despites its relatively high-water solubility (>25,000 mgL^{-1}) (Lewis et al. 2016). Contact herbicide bentazon appeared in notable concentrations in the Red R water-column towards the end of July and mid-August (Figure 2.2), most likely reflecting its use in legume and cereal crop production in the region (e.g., dry bean, soybean, spring wheat). Bentazon has a high water solubility (7112 mgL^{-1}at 20°C) and a low octanol-water partition coefficient (Log P) value (-0.46) (Lewis et al. 2016), and did not appear to move into sediments perhaps because of its lesser use relative to MCPA (Manitoba Agriculture 2019).

Pesticide mixtures were dominated by herbicides (Figure 2.2, tables 2.1 and 2.2), hence aquatic plants were more sensitive to the pesticides detected than fish and invertebrates (Figure 2.3). Under the realistic risk assessment scenario, the calculated PTI was largest for non-vascular plants in the Red R (0.39), and for vascular plants in the Fisher R (0.39). None of the pesticide mixtures detected in the water column of any of the rivers sampled exceeded the PTI threshold value of 1, suggesting that the current pesticide concentrations in those rivers do not pose a risk to aquatic organisms, including in the river most heavily impacted by human activities in its watershed. With the worst-case scenario, the PTI score was >1 for non-vascular plants in the Red R (3.48) and Fisher R (1.39), and for vascular plants in the Fisher R (1.17). Given that this worst-case risk includes concentrations for pesticide mixtures that exceed those typically encountered, we conclude that the types and concentrations of pesticides detected in Manitoba rivers do not pose a risk to aquatic non-vascular and vascular plants, invertebrates or fish.

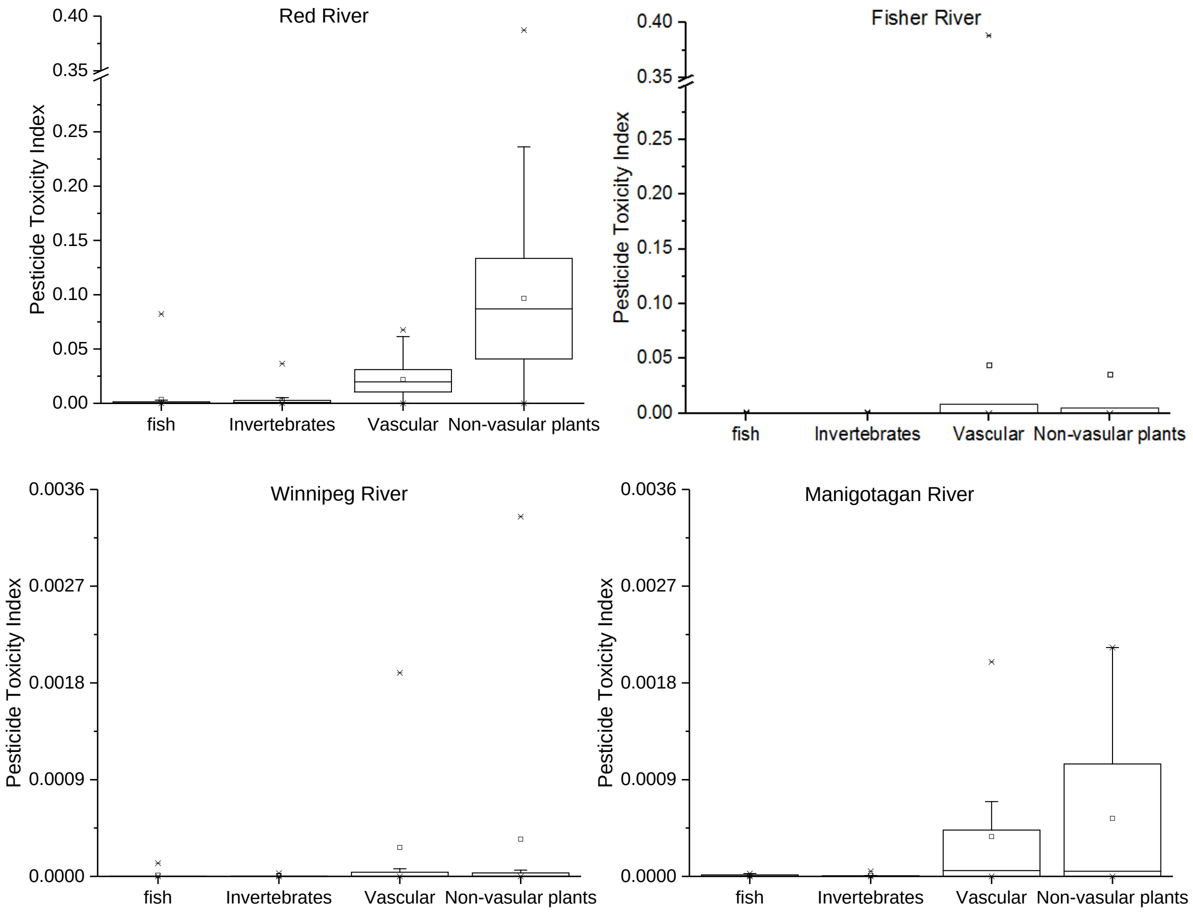

Figure 2.3 Pesticide Toxicity Index (PTI) for fish, invertebrates, vascular and non-vascular plants in river waters using every pesticide detected at least once during the sampling period. The upper and lower boundaries of the boxplots are the 25th and 75th percentiles. The medians are marked as the horizontal line across the boxes. □ and ∗ indicate the mean, and maximum and minimum values respectively

2.5 Conclusion

This study screened for 160 pesticide compounds and 72% (water) and 51% (sediment) of all water (n=83) and sediment (n=68) samples contained pesticide mixtures. Current-use pesticides accounted for 96% (water) and 76% (sediment) of the 34 pesticide compounds detected, with MCPA and other broadleaf herbicides being the most dominant compounds detected. Pesticide mixtures were detected in 94% (water) and 79% (sediment) of the river flowing almost exclusively through intensively-managed habitats (cropland and urban) whereas samples collected from other rivers showed less (17% to 60% in water) and 7% to 9% in sediment). Based on the types and timing of pesticides detected from May to August, pesticide contamination appeared to occur because of recent pesticide applications (during the year of sampling), including the partitioning of pesticides from the water-column into bottom sediments. However, for most compounds detected, there was no significant correlation between their concentrations detected in water and sediments suggesting that monitoring the water-column is a poor indicator of the presence of pesticides in sediment. Despite evidence that the concentrations of some broadleaf herbicides were substantially greater in this study than in previous studies between 1993-2011, the concentrations of the mixtures of compounds detected were below the threshold indicating significant risks to aquatic plants, invertebrates and fish.

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3. PHENOXY HERBICIDES' INTERACTIONS WITH RIVER BOTTOM SEDIMENTS

3.1 Abstract

Purpose: MCPA (2-methyl-4-chlorophenoxy acetic acid) and 2,4-D (2,4-dichlorophenoxy acetic acid) have a relatively high water solubility (>20,000 mg L^{-1} at 20°C) and a few studies have examined the affinity of these herbicides for river sediments. The aim of this study was to evaluate whether the concentrations of MCPA and 2,4-D quantified in bottom sediments were associated with the characteristics and herbicide sorption-desorption parameters determined for these sediments.

Materials and methods: Sixty surface bottom sediments samples (15 cm^3) and water-column samples (1 L) were collected from twelve sampling sites distributed across selected rivers in a Prairie province of Canada, with each site being sampled four to seven times during the summer 2016. The concentrations of MCPA and 2,4-D in the sediment and water-column samples were quantified by gas chromatography coupled to triple quadrupole mass spectrometry. Sediment characteristics included determination of the organic carbon content (OC), the percentages of sand, silt and clay by the pipette method, as well as detailed particle size distributions (PSD) as determined using a laser diffraction particle size analyzer. Sorption of 2,4-D and MCPA by sediments was determined using the standard batch equilibrium method.

Results and discussion: Sediments with larger OC contents had relatively larger sorption and smaller desorption when their unimodal PSD had a narrow range (1 to 60 µm), but relatively smaller sorption and larger desorption when their unimodal PSD had a broader range (1 to 1,000 μm) thus coarser particle sizes. Sediments with smaller OC contents always had relatively smaller sorption and larger desorption. The detection frequencies and concentrations in sediments were substantially greater for MCPA than 2,4-D even though batch-equilibrium experiments showed that sediments sorbed significantly less MCPA than 2,4-D. Neither MCPA nor 2,4-D concentrations detected in sediments were significantly correlated with sediment properties or their sorption-desorption characteristics. However, the detection frequencies and concentrations in water-column samples were also substantially greater for MCPA than 2,4-D.

Conclusions: Relatively to 2,4-D, MCPA was more frequently detected in the sediments and in greater concentrations because the more frequent presence of MCPA in the water-column allowed for greater opportunities for MCPA to partition to sediments. Thus, the water-column loadings of MCPA and 2,4-D, and not sediment characteristics, are the driving force for determining their frequency and concentrations in sediments.

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3.2 Introduction

Auxin herbicides such as 2,4-D and MCPA are frequently detected in the water-column of surface waters (Kock et al. 2010; Ricart et al. 2010; Glozier et al. 2012; Ensminger et al. 2013). This includes rivers in the Prairie Region of Canada where more than 80% of Canada's cropland is located and auxins are widely applied to control broadleaf weeds in cereal crops. In a study from 2006-2011, 2,4-D and MCPA were among the most frequently detected pesticides in the water-column of three Prairies rivers (Environment and Climate Change Canada 2015). When the source of drinking water consisted of surface water reservoirs integrated in Prairie agricultural landscapes, 2,4-D and MCPA were detected in both the source and treated drinking water (Donald et al. 2007).

2,4-D and MCPA molecules only differ at position two of their benzene ring where MCPA has a methyl group and 2,4-D a chlorine. Despite their relatively larger water solubility (>20,000 mg L^{-1} at 20°C), it has been demonstrated under laboratory (Gaultier et al. 2009; Xu et al. 2009) and field (Degenhart et al. 2011) conditions that 2,4-D and MCPA are sorbed by wetlands bottom sediments. The environmental concentrations of 2,4-D and MCPA in sediments have less frequently studied. In a research conducted more than 20 years ago, the concentrations of 2,4-D and MCPA were examined, but not detected in river sediments (Albanies et al. 1995). However, Ricart et al. (2010) have detected the herbicides in river bottom sediments at concentrations ranging from 500 to 2000 ng Kg^{-1} for MCPA and from 200 to 7000 ng Kg^{-1} for 2,4-D. Hence, further studies on the environmental concentrations of 2,4-D and MCPA in river sediments are required.

For many herbicides, including 2,4-D and MCPA, batch equilibrium sorption experiments have demonstrated that herbicide sorption increases with increasing sediment OC content (Hiller et al. 2006, 2009; Gaultier et al. 2009; Xu et al. 2009). Sediment textural characteristics are often reported on the basis of three broad classes of particle size ranges (sand 50-2000 μm; silt 2-50 μm; clay <2 μm) and some studies (but not all) suggest that there is a significant negative correlation between sediment clay content and the amount of auxin herbicides sorbed (Xu et al. 2009; Vallee et al. 2014). More detailed information on the sizes of particles in sediment samples is relevant to sorption studies. For example, Gao et al. (1998) examined the sorption of a range of pesticides by different sediment particle size fractions. In general, the fractions with particle sizes <6.3 μm and between 63 to 200 μm showed greater pesticide sorption than those of 6.3 to 63 μm.

Laser diffraction techniques are widely used to identify the sizes of particles in a sample. For example, a laser diffraction technique was utilized to provide detailed information about the sizes of particles and their distribution in powders, emulsions and ashes (Hogan et al. 2001; Cordeiro et al. 2009; Liu et al. 2011), but such technique has never been used in combination with herbicide sorption studies by sediments. Previous studies have examined the sorption-desorption of MCPA and 2,4-D to sediments in order to predict their mobility in water systems, but to the best of our knowledge, none of the studies have compared it with the environmental concentrations of these herbicides. The objective of this study was to examine the impact of OC and sediment PSD (as determined by a laser diffraction technique) on the sorption and desorption of MCPA and 2,4-D by river sediments, and to what extent the variations observed for environmental detections of MCPA and 2,4-D in these sediments could be explained by measured laboratory parameters.

3.3 Materials and Methods

3.3.1 Study Area and Sample Collection

Sixty surface bottom sediment samples (15 cm^3) and water-column samples (1 L) were collected from twelve sampling sites in Manitoba, Canada as indicated in Figure 3.1. Water-column samples were collected in amber glass bottles using grab sampling method. Sediment samples were collected in sterilized amber plastic bags (Fisher Scientific International Inc, NH, USA) using an Ekman dredge. Sediment samples were collected from the center of the Ekman dredge to avoid possible contamination from the walls of the sampler. After each sample collection, remaining sediment was removed from the walls by using tap water and a brush followed by rinsing the Ekman dredge with milli-Q water. Samples were collected between May to August 2016 with the same sampling locations being sampled seven times (Red River sampling sites: R1 to R6), five times (Fisher River sampling sites: F1 to F3), and four times (Winnipeg River sampling sites: W1 to W3). This included sampling near the location where the Red River (R6), the Winnipeg River (W3) and Fisher River (F3) discharge into Lake Winnipeg. Lake Winnipeg (23,750 km^2) is the largest lake in Manitoba and the tenth largest freshwater lake in the world (Environment Canada 2011).

The Red River (885 km long) starts in the USA at the Minnesota-North Dakota border and enters Canada at the North Dakota-Winnipeg border near the town of Emerson, Manitoba (R1). In Manitoba, the Red River flows through croplands from R1 to R2, and then flows through the city of Winnipeg (pop. ~700,000) (R2 to R4) and sub-urban areas such as Selkirk (R5). The Assiniboine River (R3) is the largest tributary of the Red River and confluences with the Red River in the city of Winnipeg between sampling points R2 and R4. The Winnipeg River (260 km long) begins in the USA in Minnesota, then flows through Lake of the Woods in the Province of Ontario, Canada, before entering Manitoba. In Manitoba, the Winnipeg River's watershed consists of forests and wetlands (W1 to W2) and then forests and agricultural land towards the mouth of the river (W2 to W3). There are six hydroelectric generating stations built along the Winnipeg River (Grand Falls, McArthur, Pine Falls, Pointe du Bois, Slave Falls, and Seven Sisters generating stations). The Fisher River originates in Manitoba with uplands mainly comprised of agricultural land (F1 to F2) and then wetland complexes (F2 to F3).

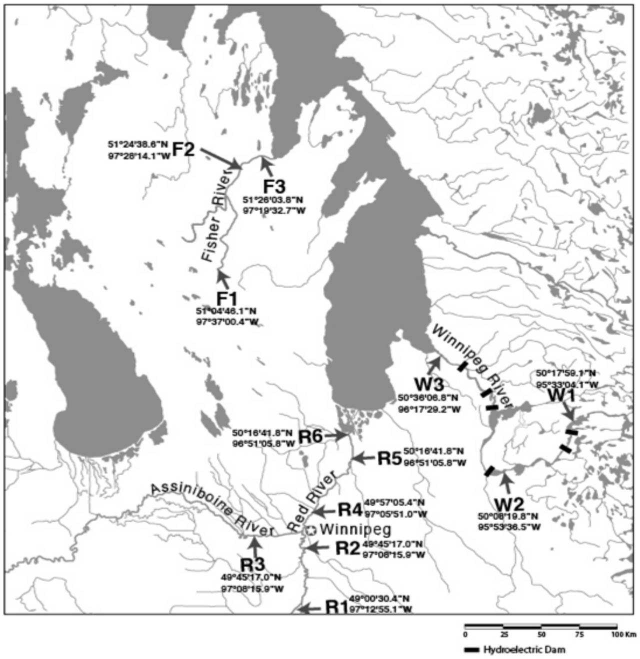

Figure 3.1 Locations of sampling sites in the Red River, Assiniboine River, Fisher River and Winnipeg River for bottom sediments during May to August 2016

3.3.2 Determination of 2, 4-D and MCPA Residues

Water-column samples were processed within 3 (minimum) to 7 (maximum) days, including collection in the field, transportation to the laboratory, and extraction and analysis. Water-column samples were transported to the laboratory on ice and stored in the fridge (4˚ C) until extracted and analyzed as described by Munira et al. (2018). Briefly, suspended material in the water-column samples were filtered out using glass wool. The filtered water-column samples were acidified to pH 2 with concentrated sulfuric acid. Using dichloromethane, pesticides in the water-column samples were extracted by liquid-liquid partitioning. Dichloromethane extracts were dried using acidified Na_2SO_4, followed by methylation with diazomethane and addition to hexane (40 mL). The excess diazomethane was removed using nitrogen gas. The final volume of esterified extract was adjusted to 10mL using a rotary evaporator. Extracts were analyzed using an Agilent™ 7890B gas chromatograph coupled to an Agilent™7000C triple quadrupole mass spectrometer as described below. The study reported here focuses on the detections of 2,4-D and MCPA for which 25 ng L^{-1} was the lower limit of quantification for either herbicides. Any detection below 25 ng L^{-1} was considered as zero concentration (0 ng L^{-1}).

Sediments were stored in a freezer (-20 °C) prior to extraction and analysis. Sediment samples were then freeze dried (Scientific freeze dryer, Harvest Right™, USA) at -37 °C for 24 hours. Freeze-dried sediments (3 g) were extracted using the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method (Lehotay 2007). Briefly, a solution of acetonitrile with 1% acetic acid was added to freeze-dried sediments and vortexed (2 minutes) followed by the addition of QuEChERS salt ($MgSO_4$/NaOAc 4/1, w/w) (PN 5982-6755, Agilent Technologies, Santa Clara, CA, USA). Materials were again vortexed (5 minutes) and then centrifuged at 3220 x g for 10 min to separate phases. The supernatant was methylated with diazomethane (2 mL) followed by the addition of hexane (40 mL) and reducing hexane extracts to 2 mL by a rotary evaporator prior to analysis as described below. The study reported here focuses on the detections of 2,4-D and MCPA with the detection limits being 1667 ng kg^{-1} for either herbicides on a freeze-dried basis.

An autosampler (Agilent™ 7693) with splitless injection was used to inject extracts (2 μL) of water-column and sediment samples 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 $°Cmin^{-1}$, at 3 $°Cmin^{-1}$ to 200 °C, and at 8 $°Cmin^{-1}$ 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. Compounds were identified by monitoring retention times and the presence of target and qualifier ions.

3.3.3 Measured Laboratory Parameters

Sediments were air-dried, sieved (<2 mm) for sediment characterization and use in sorption/desorption experiments. OC content was determined by the Walkley-Black method

(Nelson and Sommers 1996) and the percentages of sand (50-2000 μm), silt (2-50 μm), and clay (<2 μm) by the pipette method (Gee and Or 2002). Detailed data on the sizes of particles (i.e., 100 different sizes ranging from 0.02-2000 μm) and their relative proportions in sediments were quantified using a Mastersizer 2000 laser diffractometer and Hydro 2000 SA wet dispersion unit (Malvern Instruments Ltd, Worcestershire, UK). For this, a portion of sediment (5 g) was dispersed in RO water (100 mL), sonicated for 2 minutes with a Q125 Sonicator (Qsonica LLC, CT) to minimize overestimation of median grain size, and then injecting the suspensions into the diffractometer with parameter settings being a refraction Index of 1.52 with an obscuration range of 15-20% and a pump speed of 2000 rpm (Sperazza et al. 2004).

Sorption of 2,4-D and MCPA by sediments was determined using the standard batch equilibrium method (OECD/OCDE 106 2000). Herbicide solutions were prepared in 0.01 M $CaCl_2$ by combining ^{14}C-ring labeled chemicals (specific activity of 55 mCimmol^{-1}; 99% radiochemical purity; American Radiolabeled Chemicals, St. Louis, MO, USA) with analytical grade chemicals (Sigma-Aldrich, St. Louis, MO). Duplicate 5 g sediment samples in glass tubes were fortified with either 2,4-D or MCPA at environmentally relevant concentrations of 2000 ng L^{-1} (95th centile of MCPA concentrations as determined for the water-column samples collected in this study) and rotated for 24 hours to establish equilibrium. Samples were centrifuged at 7000 rpm (8200 x g for 20 min) and duplicate 1 mL subsamples of the equilibrium solution were added to 7 mL scintillation vials containing 3 mL of Ultima Gold scintillation cocktail (PerkinElmer Inc., Waltham, MA, USA). Radioactivity in vials was quantified by Tri-Carb 4910TR Liquid Scintillation Counter (LSC) (PerkinElmer, Inc, Waltham, MA, USA) with a maximum counting time of 10 minutes. The sorption distribution constant (K_d, in Kg L^{-1}) was calculated using K_d =

Cs/Ce where Cs = the amount of MCPA or 2,4-D sorbed by sediments at equilibrium (mg Kg^{-1}) and Ce = the concentration of MCPA or 2,4-D in solution at equilibrium (mg L^{-1}). The K_d values were divided by the fraction of OC to calculate the OC normalized sorption coefficient, K_{oc}. Greater K_d or K_{oc} values indicate greater sorption. To quantify MCPA or 2,4-D desorption, the remaining supernatant (5 mL) was removed from the glass tubes and replaced by a 0.01M $CaCl_2$ solution (7 mL). Samples were again rotated for 24 hours to equilibrate and centrifuged at 7000 rpm (8200 x g for 20 min) to quantify the amount of radioactivity in the equilibrium solution by LSC. The percentage of desorption was calculated by (M_{des} / M_{ads}) *100 where M_{des} = the mass of MCPA or 2,4-D desorbed from sediments after 24 hours (µg) and M_{ads} = mass of MCPA or 2,4-D sorbed by sediments at equilibrium (µg). M_{des} was calculated as the mass of MCPA or 2,4-D in the supernatant at desorption equilibrium minus the mass of MCPA or 2,4-D remaining in the soil and the 3 mL solution at sorption equilibrium.

3.3.4 Statistical Analysis

Data were tested for normality using the Shapiro-Wilk normality test with a cut-off of W statistic >0.9 (SAS, version 9.4). All data were normally distributed except for MCPA concentration, 2,4-D concentration, OC content, and PSD. MCPA K_d versus 2,4-D K_d, and %MCPA desorption versus %2,4-D desorption was compared using a paired t-test (SAS, version 9.4). The associations between sediment characteristics, and sorption and desorption parameters were measured by Pearson product-moment correlation for normally distributed data and by Spearman rank-order correlation for data that were not normally distributed (SAS, version 9.4). The significance level was set at $P < 0.05$. In addition, correlation coefficient (r) values ≤0.3 were considered insignificant correlations as only ≤9% of the total variation of the dependent variable (y) is explained by the independent variable (x)'s variation (Taylor 1990; Mukaka 2012). For samples collected from the Red River, samples were split in sediments showing 2,4-D detections (44%) and those that did not (56%) and an independent t-test was used to compare the two groups for their sediment characteristics (percentages of sand, silt, clay; OC content), their 2,4-D K_d values and their %2,4-D desorption. All data used in the independent t-test were normally distributed except for %OC that was transformed to be log-normally distributed. Sediments almost always showed MCPA detections (83%), particularly in the Red River (94%), hence a similar independent t-test was not done for MCPA. Principal Component Analysis (PCA) (SAS, version 9.4) was used to reduce the number of variables (OC content, PSD, %sand, silt and clay, MCPA K_d and 2,4-D K_d values and %MCPA and %2,4-D desorption) into a small number of linear combinations of variables (principal components) and to plot the distribution patterns of sampling locations within the principal components space (Statheropoulos et al. 1998; Golobocanin et al. 2004).

3.4 Results and Discussion

Despite of their large water solubility, both MCPA and 2,4-D were detected in the bottom sediments. Therefore, our study adds to the evidence (Ricart et al. 2010) that 2,4-D and MCPA partition to bottom sediments. MCPA was detected in the sediments of all rivers with a detection frequency of ~83% out of 60 sediment samples and a maximum concentration of 266,252 ng Kg^{-1} (Table 3.1). Mean concentrations of MCPA in sediments significantly decreased in the order Red River (57,995 ng Kg^{-1}) > Winnipeg River (7,000 ng Kg^{-1}) ≈ Fisher River (7,651 ng Kg^{-1})

(Table 3.1). The detection frequency of 2,4-D in sediments was only 25% and all these detections were in the Red River with a maximum concentration of 28,302 ng Kg^{-1} (Table 3.1). The maximum concentrations of MCPA and 2,4-D detected in the freeze-dried sediments of this study were about 100-fold and 8-fold greater, respectively, than those reported for these herbicides in river sediments collected from a river in Spain (Ricart et al. 2010). The MCPA and 2,4-D maximum concentrations were for samples collected in late August at site R1 and concentrations detected at other sampling times at R1 ranged from 2,214 to 130,050 ng Kg^{-1} for MCPA and from 3,600 to 23,406 ng Kg^{-1} for 2,4-D (Figure 3.2). Considering the positive detects of MCPA or 2,4-D in sediments, the mean concentration of MCPA (45,286 ng Kg^{-1}) was significantly greater than that of 2,4-D (7,449 ng Kg^{-1}). Sediments that had detectable concentrations of 2,4-D almost always (except in one sample) showed detectable concentrations of MCPA as well.

Sediment OC content ranged from 0.25 to 3.91% (Table 3.1). Sediment textural classes ranged from sandy loam to silty clay loam. Sediments had a wide range of percentages of clay (0.04 to 50.32%) and particularly silt (3.73 to 99.18) and sand (0.79 to 90.32%) (Table 3.1).

MCPA was detected in 94% (Red River), 73% (Winnipeg River) and 62% (Fisher River) of the total sediment samples collected in those rivers. Considering the positive detections of MCPA in the sediments of each river system separately, MCPA concentrations were not significantly correlated ($p>0.05$) with OC content, or with the percentages of clay, silt or sand in any of the rivers, except for a significantly negative correlation with %silt in the Red River ($r=-0.41$). 2,4-D was detected in 44% of Red River sediments but the 2,4-D concentrations were not significantly correlated (p>0.05) with the OC content, or with the percentages of clay, silt or sand in these sediments. In addition, there was no significant difference (p>0.05) in the mean OC content, or the mean percentages of clay, silt or sand, in sediments with or without 2,4-D detections.

Table 3.1 Summary statistics of bottom sediments collected from Red River, Fisher River and Winnipeg River with the K_d (sorption distribution constant), K_{oc} (organic carbon normalized sorption coefficient) and desorption determined by batch equilibrium experiments, and conc. (concentration) of MCPA or 2,4-D quantified in freeze-dried sediments.

Property	Mean	Median	Min	Max	Q1	Q3
<u>Fisher River (n=13)</u>						
Organic C (%)	2.33	3.12	0.34	3.66	0.78	3.58
Sand (%)	39.91	22.07	3.00	90.32	20.16	72.80
Silt (%)	36.19	47.37	3.73	54.10	21.64	51.69
Clay (%)	23.90	28.50	3.00	43.83	10.42	28.81
MCPA K_d (L Kg^{-1})	0.84	0.90	0.17	1.48	0.32	1.34
MCPA Dt%	20.15	18.31	0	67.57	5.33	22.31
2,4-D K_d (L Kg^{-1})	1.09	1.10	0.05	1.92	0.62	1.48
2,4-D K_{oc} (L Kg^{-1})	52.47	45.05	3.00	182.49	29.81	53.61
2.4-D desorbed (%)	14.60	11.79	0	38.16	3.45	19.99
MCPA conc (ng Kg^{-1})*	7,651	5,056	<1,667	28,226	<1,667	12,897
2,4-D conc. (ng Kg^{-1})**	<1,667	<1,667	<1,667	<1,667	<1,667	<1,667
<u>Red River (n = 36)</u>						
Organic C (%)	1.30	1.23	0.60	3.91	1.05	1.35
Sand (%)	23.46	20.08	7.03	66.32	13.92	29.70
Silt (%)	43.12	42.87	22.36	59.70	38.81	48.05
Clay (%)	33.42	32.73	11.32	50.32	26.80	40.11
MCPA K_d (L Kg^{-1})	1.23	1.26	0.47	2.26	1.00	1.44
MCPA K_{oc} (L Kg^{-1})	101.25	95.62	36.79	177.88	79.62	121.52
MCPA Dt%	11.73	5.08	0.33	56.30	2.09	18.46
2,4-D K_d (L Kg^{-1})	1.39	1.42	0.57	2.33	1.05	1.74

2,4-D K_{oc} (L Kg^{-1})	115.86	112.70	39.78	234.34	90.66	148.03
2.4-D desorbed (%)	13.07	9.38	0.05	64.30	3.78	19.30
MCPA conc.* (ng Kg^{-1})	57,995	37,699	<1,667	266,252	13,634	88,601
2,4-D conc.** (ng Kg^{-1})	3,150	<1,667	<1,667	28,302	<1,667	2,494
Winnipeg River (n=11)						
Organic C (%)	0.61	0.48	0.25	1.34	0.34	0.76
Sand (%)	55.22	56.42	0.79	89.03	47.14	69.81
Silt (%)	22.14	12.71	6.14	99.18	8.19	19.17
Clay (%)	22.64	26.64	0.04	46.08	6.00	32.54
MCPA K_d (L Kg^{-1})	0.43	0.29	0.10	1.18	0.18	0.56
MCPA K_{oc} (L Kg^{-1})	79.58	62.19	15.89	217.07	34.66	110.67
MCPA Dt%	25.12	25.05	13.59	33.97	22.24	29.11
2,4-D K_d (L Kg^{-1})	0.44	0.22	0.11	1.24	0.17	0.59
2,4-D K_{oc} (L Kg^{-1})	80.02	53.63	18.40	255.15	29.09	99.01
2.4-D desorbed (%)	25.44	24.46	9.55	39.25	20.76	29.40
MCPA conc.* (ng Kg^{-1})	7,000	6,890	<1,667	21,109	1,460	9,712
2,4-D conc.** (ng Kg^{-1})	<1,667	<1,667	<1,667	<1,667	<1,667	<1,667

2,4-D K_d ranged from 0.05 to 2.33 L Kg^{-1} and 2,4-D desorption from 0.05 to 64.3% (Figure 3.2). MCPA K_d ranged from 0.1 to 2.26 L Kg^{-1} and MCPA desorption from 0.33 to 67.6% (Figure 3.2). 2,4-D K_d values were significantly greater than MCPA K_d values ($t=-3.93$, $P<0.001$). Studies comparing 2,4-D and MCPA sorption for soil samples also found that K_d values are somewhat greater for 2,4-D than MCPA (Harberhauer et al. 2000; Hiller et al. 2008). 2,4-D and MCPA only differ at position two of their benzene ring where MCPA has a methyl group and 2,4-D a chlorine. Harberhauer et al (2000) have shown that the substitution of a methyl by a chlorine group creates a negative free standard sorption energy, and results in increased sorption of 2,4-D in soil than MCPA. 2,4-D K_{oc} values (15 to 255 L Kg^{-1}) were significantly greater than

MCPA K_{oc} values (14 to 217 L Kg^{-1}) (t=-3.69, P<0.001). There were no significant differences between 2,4-D and MCPA desorption (t=0.19, p=0.85).

2,4-D K_d and MCPA K_d values were each positively correlated with %OC, %clay and %silt, with correlation coefficients ranging from r=0.53 to 0.62 (Table 3.2). Thus, 2,4-D K_d and MCPA K_d values were negatively correlated with %sand (Table 3.2). The percentage of 2,4-D and MCPA desorption was negatively correlated with %OC, %clay and %silt, and positively correlated with %sand (Table 3.2). Thus, both the percentage of 2,4-D (r=-0.45) and MCPA (r=-0.43) desorption was negatively correlated with their respective herbicide sorption (K_d) values. Both 2,4-D K_{oc} and MCPA K_{oc} values were positively correlated with %clay (Table 3.2), suggesting that the presence of smaller sized particles is an indicator of greater herbicide sorption per unit of OC in sediments. However, for sediments with 2,4-D or MCPA detections, there were no significant correlations between the measured 2,4-D or MCPA sorption-desorption characteristics (K_d or K_{oc} values and %desorbed) and the concentrations of 2,4-D or MCPA that the sediments contained. Sediments with (44%) and without (56%) 2,4-D detections also showed statistically similar 2,4-D K_d (means of 1.4 and 1.3 L Kg^{-1}, respectively), K_{oc} values (means of 119 and 114 L Kg^{-1}, respectively) and percentage of desorption (10 and 15%, respectively).

Table 3.2 Pearson and Spearman correlation coefficients among sediment properties and chemical characteristics on bottom sediments collected from Red River/Assiniboine River, Fisher River and Winnipeg River

	%OC	**%Sand**	**%Silt**	**%Clay**
MCPA K_d	0.57	-0.72	0.53	0.62
MCPA K_{oc}	NS	NS	NS	0.4
MCPA Dt%	-0.39	0.54	-0.42	-0.44
2,4-D K_d	0.58	-0.72	0.56	0.59
2,4-D K_{oc}	NS	NS	NS	0.4
2.4-D Dt%	-0.35	0.5	-0.36	-0.45
MCPA concentrations	NS	NS	NS	NS
2,4-D concentrations	NS	NS	NS	NS

NS = Correlation not significant ($\alpha = 0.05$)

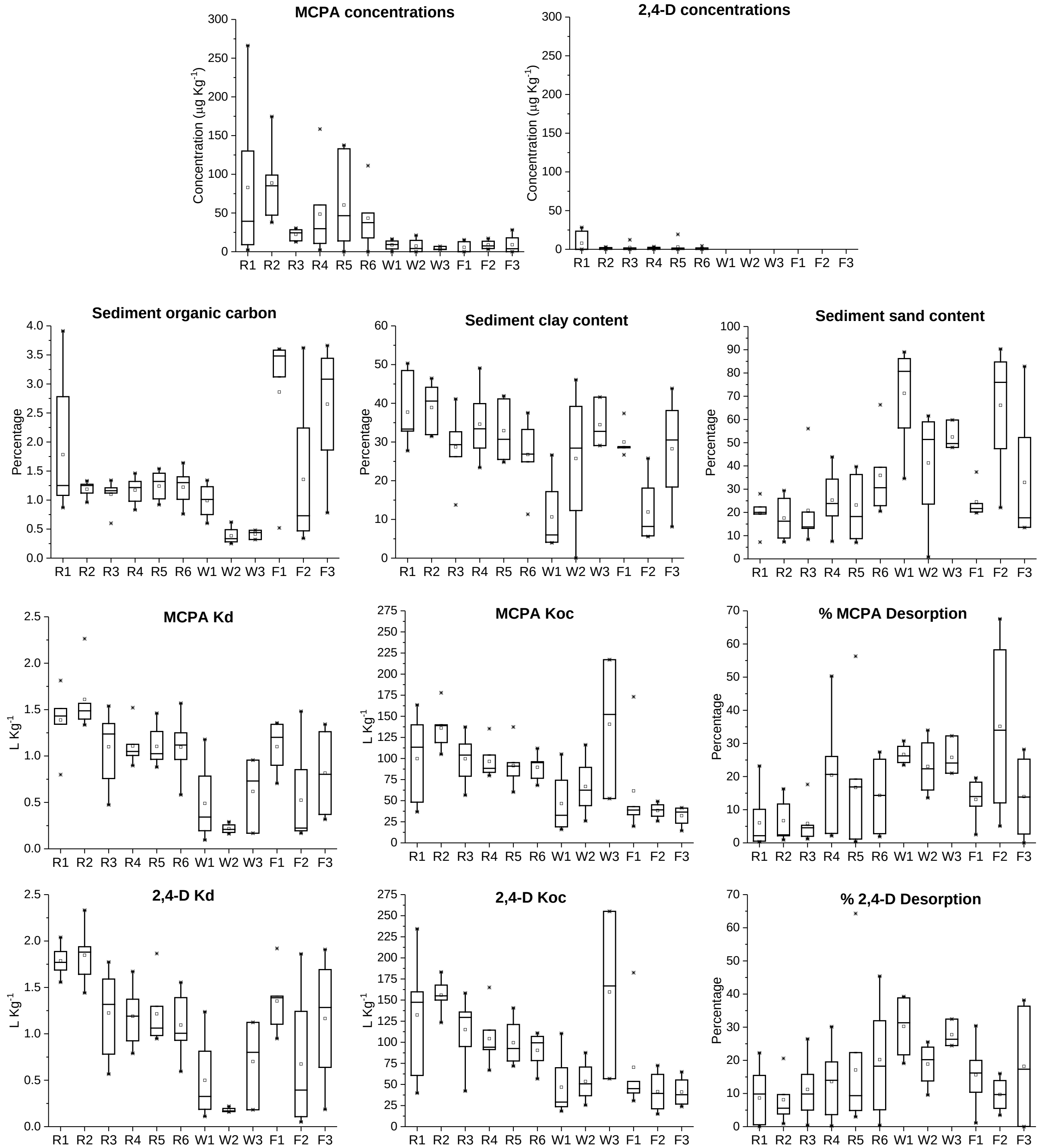

Figure 3.2 Box plots of sediment characteristics and pesticide concentrations of bottom sediments from the Red River (R1, R2, R4, R5, and R6), Assiniboine River (R3), Winnipeg River (W1, W2, and W3) and Fisher River (F1, F2, and F3). The upper and lower boundaries of the boxplots are the 25th and 75th percentiles. The medians are

marked as the horizontal line across the boxes. □ and ∗ indicate the mean, and maximum and minimum values respectively

Sediment particle sizes ranged from 0.03 to 1905.5 µm, with particle sizes >1 µm more dominant for all sampling locations and times except for all samples collected from sites W2 and W3 which are downstream from a series of hydroelectric generating stations in the Winnipeg River (Figure 3.1). Sediments collected from W2 and W3 demonstrated distinct bimodal distributions with peaks ranging from 0.03 to 1 μm and from 1 to 80 μm (Figure 3.3). Principal Component one and two accounted for 64% of the total variance with three distinct groupings (Figure 3.4). Sediments of group 1 had a relatively low OC content and consequently relatively smaller 2,4-D and MCPA K_d values, and relatively larger percentages of 2,4-D and MCPA desorption. Most of these samples had a bimodal PSD with its peaks ranging from 0.03 to 1μm and from 1 to 80 μm. In contrast, sediments of groups 2 and 3 had unimodal PSDs and larger OC contents. Sediments of group 2 had a narrow unimodal PSD with most particle sizes ranging from 1 to 60 μm, whereas sediments of group 3 had a broader unimodal PSD with most of its particle sizes ranging from 1 to 1,000 μm and thus having a larger sand content than sediments in group 2. MCPA and 2,4-D sorption is negatively correlated with %sand, and MCPA and 2,4-D desorption is positively correlated with %sand (Table 3.2). Thus, sediments of group 3 with most of its particle sizes ranging from 1 to 1,000 μm had smaller herbicide sorption and greater herbicide desorption than sediments of group 2 with most particle sizes ranging from 1 to 60 μm (Figure 3.4). In addition, when either MCPA or 2,4-D were plotted separately by PCA, the sampling locations had the same distribution pattern as they were plotted together. Thus, this study shows for the first time the impact of particle size distribution, as measured by the laser diffraction method, on pesticide sorption-desorption by sediments. Riefer et al. (2011) have shown that most of the bound residues of MCPA (within 48 hours) can be detected in the clay fraction of the soil, hence soils with finer texture have greater MCPA sorption. This is a plausible reason why sediment samples with its particle sizes ranging from 1 to 60 μm demonstrated greater sorption than sediment samples with a boarder particle size distribution.

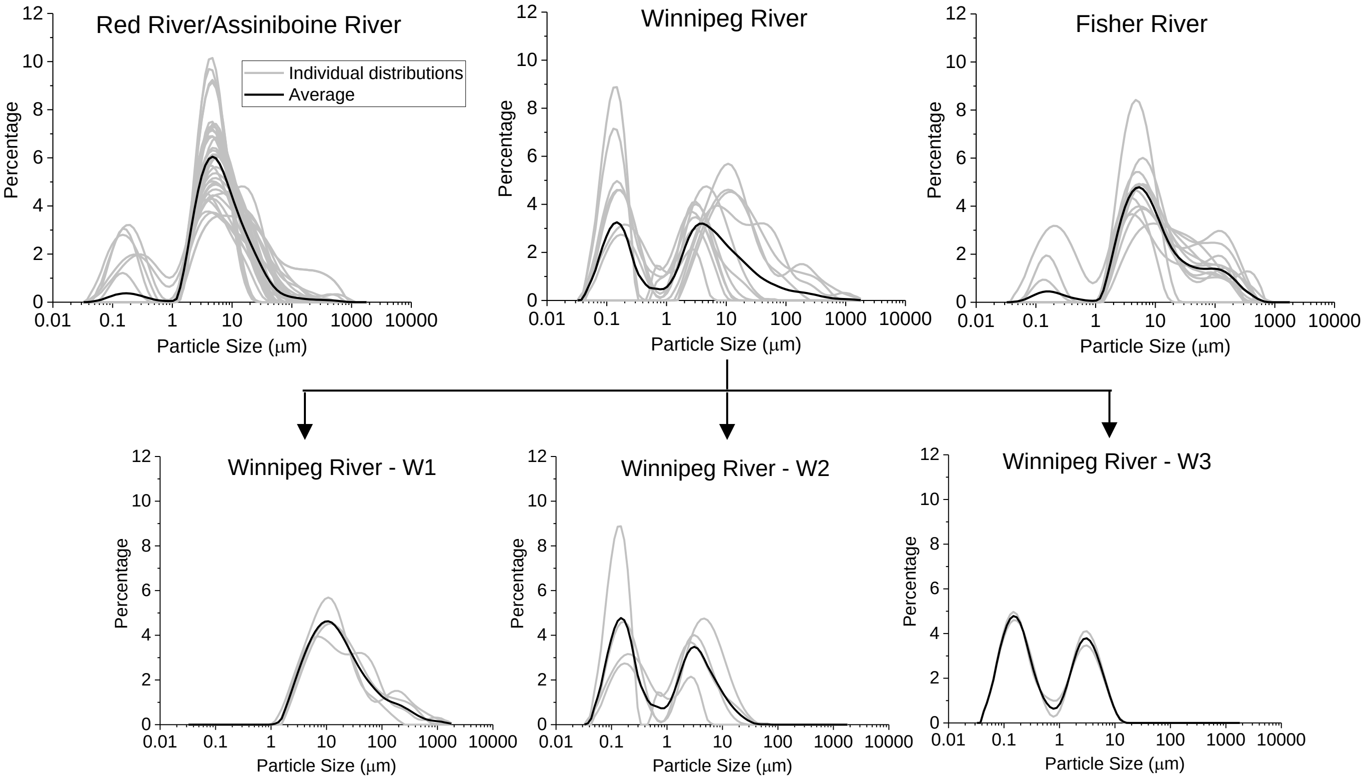

Figure 3.3 Particle size distributions of bottom sediments collected from different rivers

The Red River predominately flows through agricultural land, as well as urban and sub-urban areas; the Fisher River predominantly flows through agricultural land and wetland complexes; the Winnipeg River predominantly flows through forests and wetlands. The detection frequencies of MCPA and 2,4-D in the Red River (92% and 83%, respectively) and in the Fisher River (62% and 38%, respectively) were relatively large when compared to their detection frequencies in the water-column of the Winnipeg River (18% for both MCPA and 2,4-D). In addition, for both MCPA and 2,4-D, the concentrations detected in the water-column of the Red River and Fisher River were larger than those detected in the water-column of the Winnipeg River (Table 3.3). Thus, overall, these results suggest that the loadings of both MCPA and 2,4-D into rivers intensify because of pesticide use as part of agricultural and urban settings.

MCPA was detected at significantly greater frequencies and concentrations in our river bottom sediments compared to 2,4-D and the results of the batch equilibrium sorption-desorption experiments indicate that this cannot be explained by differential retention of MCPA versus 2,4-D in sediments. Water-column samples collected in the Red River (92%) and Fisher River (62%) frequently contained MCPA and in relatively larger concentrations with a maximum concentration of 50,449 ngL^{-1}. In contrast, 2,4-D was detected in the water- column of 83% (Red River) and 38% (Fisher River) with a maximum concentration of 778 ng L^{-1}. Data on the amount of pesticides used in Canada are limited but recent sales data (2015) for a Prairie Province indicate that the active ingredient MCPA (920,000 kg) exceeds that of 2,4-D (640,000 kg) in Alberta (AEP 2015). Thus, greater agricultural and non-agricultural usage of MCPA versus 2,4-D in the Prairies, including Manitoba, might explain its greater loadings into the water-column of rivers and hence bottom sediments of the Red River and Fisher River.

Table 3.3 Summary statistics of MCPA and 2,4-D concentrations in the water-column samples collected from Fisher River, Red River and Winnipeg River. Concentrations units are ng/L. Q1 and Q3 are first and third quartiles respectively.

River	**Mean**	**Median**	**Min**	**Max**	**Q1**	**Q3**
MCPA						
Fisher River	4,876	46	<25	50,449	<25	749
Red River	230	143	<25	1,435	45	263
Winnipeg River	15	<25	<25	154	<25	<25
2,4-D						
Fisher River	164	<25	<25	778	<25	164
Red River	125	77	<25	726	46	109
Winnipeg River	38	<25	<25	372	<25	<25

In addition to the fact that sediments are likely exposed to greater levels of MCPA than 2,4-D because of greater MCPA loadings into the rivers we examined, it is also possible that MCPA (DT50 = 13.5 days) is relatively more persistent than 2,4-D (DT50 = 7.7 days) in the water-column, hence allowing sediments to be more continuously exposed (Lewis et al. 2016). An added plausible reason for the greater frequency and concentrations of MCPA detected in sediments could be that MCPA is more persistent in sediments than 2,4-D, but data that compares the persistence of auxin herbicides in sediments is lacking. It is known that MCPA persists about twice as long in flooded soils than under moist soil conditions (Sattar and Paasivirta 1980). In contrast, Yoshida and Castro (1975) reported that the degradation rates of 2,4-D in moist and flooded soils were relatively comparable, with one flooded soil showing almost no 2,4-D remaining at 28 days.

A significant increase in the finer sediment particles (<1 μm) was observed in the Winnipeg River after it flows through hydroelectric generating stations. Bogen and Bonsnes (2001) also observed sediments to contain finer sediments at river locations sampled after hydroelectric generating stations. However, the sampling locations in the Winnipeg River were limited to only one location prior to (W1) and two locations (W2 and W3) after hydroelectric generating stations. The sediments of the Winnipeg River are also influenced by a variety of natural sources with different geologies and the impact of these sources are spatially dependent with respect to the length of the river (Matile et al. 1988). In particular, when a river flows through a reservoir, coarser sediments tend to settle in the bottom of the reservoir leaving finer sediments to move towards and perhaps settle to the outflow of the river in our case towards sampling points W2 and W3. Techniques such as the Malvern Mastersizer laser diffraction method could be used to provide further insight towards the impact of hydroelectric generating stations and/or natural sources on PSD distributions in sediments.

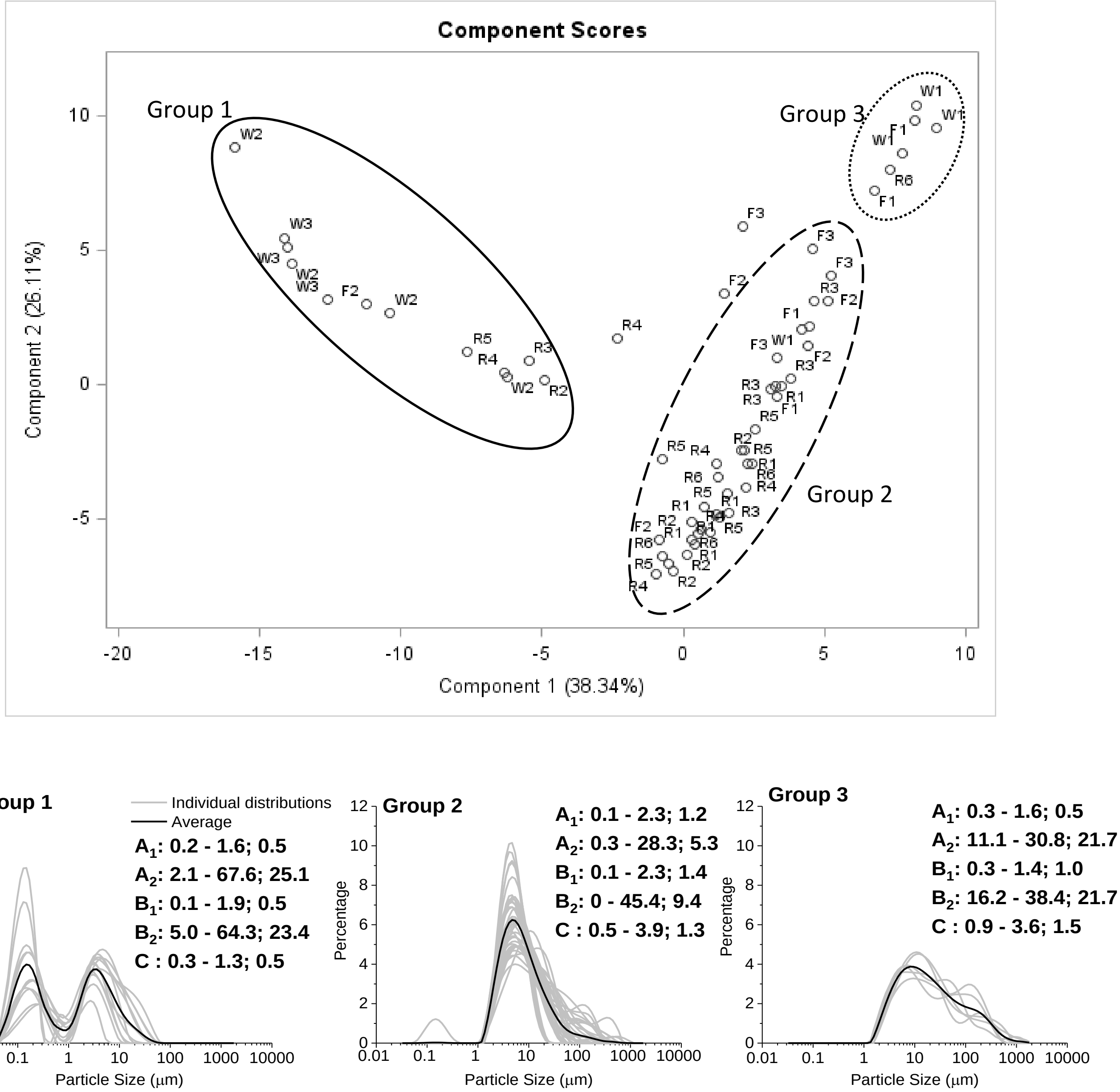

Figure 3.4 Principal component analysis: groups of sampling locations with similar sediment properties and sorption characteristics and their sediment properties and sorption characteristics. A_1 = MCPA Kd (L Kg^{-1}), A_2 = % MCPA desorption, B_1 = 2,4-D Kd (L Kg^{-1}), B_2 = % 2,4-D desorption, C = % SOC, with numbers for each variable referring to the minimum and maximum; and median values.

3.5 Conclusion

Water-column and sediments samples were collected from several rivers in Manitoba. The detection frequencies and concentrations in sediments were substantially greater for MCPA than 2,4-D even though batch-equilibrium experiments showed that sediments sorbed significantly less MCPA than 2,4-D. The detection frequencies and concentrations in water-column samples were also substantially greater for MCPA than 2,4-D, suggesting that the greater presence of MCPA in bottom sediments was due to greater opportunities for MCPA to partition into sediments. Monitoring studies in rivers typically only include water-column samples, and our study suggests that for auxin herbicides, their frequency of detection in the water-column is a good indicator of the frequency at which these auxins might partition and persist in bottom sediments.

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4. OVERALL SYNTHESIS

4.1 Summary of Research

This thesis examined pesticide concentrations in the water-column and bottom sediments of Manitoba rivers and further quantified factors influencing the sorption and desorption of pesticides by these bottom sediments. The strength of this study is that it screened water-column and bottom sediment samples for 160 active ingredients, metabolites or by-products in pesticide products; and this is substantially greater than the number of pesticide compounds that have been typically included in surface water research in the Prairie region (Rawn et al. 1999; Glozier et al. 2012; ECCC 2015). Also, previous studies in North America and elsewhere frequently focused on hydrophobic legacy pesticides such as DDT (e.g., Malik et al. 2009; Chen et al. 2011; Yang et al. 2013). However, the current study screened for pesticide compounds with a wide range of physiochemical properties, including active ingredients of pesticide products currently registered for agricultural use in Canada, and active ingredients, metabolites or by-products in pesticide products not or no longer registered in Canada. Most of the compounds detected in rivers were current-use pesticides, suggesting that the watersheds' existing pesticide use was contributing to river contamination by pesticides. This study also identified that the river flowing through the watershed with greatest human activities had a larger likelihood for detecting a wider range of herbicide mixtures, as well as mixtures of herbicides and fungicides. Fungicides are not likely to be present in rivers that flow through watersheds without significant urban or agricultural activity, perhaps suggesting that long-range atmospheric transport is not likely to occur for current-use fungicides. Most importantly, based on the types and concentrations of the pesticides detected in the water-column of rivers included in this study, there was no evidence that the pesticide mixtures present pose a risk to aquatic organisms, including the river most heavily impacted by human activity in its watershed.

MCPA is widely used in Manitoba both in agricultural and non-agricultural applications, and this is a contributing factor to why this auxin herbicide was detected in all four rivers. The auxin herbicide MCPA was the most frequently detected pesticide in bottom sediments, and was detected at the highest concentrations. 2,4-D, another auxin herbicide with a relatively similar molecular structure and use pattern in Manitoba as MCPA, was detected at substantially lower frequencies and concentrations in bottom sediments. Previous studies have collected sediments to examine the sorption-desorption of MCPA and 2,4-D in order to predict their mobility in water systems, but these studies typically used concentrations much greater than the environmentally-relevant concentrations detected in this study. Thus, a component of the current study was focused on environmentally-relevant concentrations for quantifying the impact of organic carbon and sediment particle size distribution (as determined by a laser diffraction technique) on the sorption and desorption of MCPA and 2,4-D by river sediments. The batch-equilibrium experiments showed that sediments sorbed significantly less MCPA than 2,4-D, although numerically the differences were small. Since MCPA was detected more frequently and at greater concentrations than 2,4-D in bottom sediment samples, the measured laboratory parameters could not explain the differences observed for environmental detections of MCPA versus 2,4-D in these sediments. As such, the study concludes that the greater presence of MCPA in bottom sediments is likely due to greater entry of MCPA than 2,4-D in rivers in Manitoba and hence the opportunities for MCPA to partition from the water-column to suspended and bottom sediments.

4.2 Practical Implications of the Research

The monitoring study described in Chapter 2 provides valuable information on current pesticide contamination in Manitoba rivers, and this data can be used as baseline information for future (long-term) monitoring studies. Since this study found that the frequency of detection and the concentration of pesticides were largest for river segments with greater urban and agricultural activities in their surroundings, additional monitoring studies should (continue to) focus on rivers flowing through urban and agricultural land. Chapter 2 also demonstrated that for herbicides that are co-applied with auxin herbicides MCPA and 2,4-D, these herbicides are often detected as mixtures in the water-column of rivers. For example, although MCPA and 2,4-D are not formulated together in pesticide products, both MCPA and 2,4-D are often formulated with other herbicides such as bromoxynil, fluroxypyr, and clopyralid. All these other herbicides were frequently detected with MCPA or 2,4-D. This information suggest that future monitoring studies should not only focus on active ingredients that are widely applied, but also on the wide variety of other active ingredients that might be co-applied with the top ranked active ingredients. Because 72% of the water-column samples examined in this study contained pesticide mixtures, this study also highlights the need for the development of Canadian Water Quality Guidelines for pesticide mixtures that are commonly present in Canadian rivers.

Flooding from spring snowmelt and summer rainfall in the Canadian Prairies enhances runoff from agricultural lands; and this runoff is a major source of surface water contamination (Tiessen et al. 2011). Pesticides are introduced to surface waters via runoff (Gfrerer et al., 2001; Piel et al., 2012). This study identified that the pesticides present in the water column of rivers are mainly herbicides with aquatic half-lives less than 150 days. Moreover, if only considering MCPA and 2,4-D (most frequently detected pesticides in all rivers), their aquatic half-lives is less than 20 days. Hence, if runoff water can be captured prior to entering surface water, and held for a sufficiently long period of time to degrade the pesticides, this could be a way by which pesticide pollution of rivers could be mitigated. A good application might be field-edge retention ponds that are designed for nutrient management and used to detain the runoff water from agricultural fields (Baulch et al. 2019). Water can be held which allows for opportunities for pesticide degradation prior to releasing the water to rivers or reusing the water trapped in retention ponds on agricultural fields. Retention ponds also trap and retain runoff sediments. As such, retention points would also mitigate the transport of sediment-sorbed pesticides to rivers.

This study provides data about the types of current-use pesticides detected in rivers, as well as their frequency of detection. These findings are important as they determine priority inputs to be included into pesticide fate models. Specifically, because auxin herbicides were among the most frequently detected compounds, the study suggests that collecting data on the use and fate parameters of auxin herbicide in Prairie watersheds would be useful to improve on assigning values to pesticide fate input parameters. Pesticide fate models are widely used by regulatory agencies and researchers as they are cost-effective and their information can augment monitoring studies (Chen et al. 2017). Pesticide use data are critical when applying pesticide fate models at a large scale (Gagnon et al. 2016). Unfortunately, detailed data on pesticide use remains largely unavailable in Canada, including for auxin herbicides that are widely used. So, regulatory agencies such as Pest Management Regulatory Agency of Canada should prioritize strategies to obtain and use such information, particularly when re-evaluating of registrations of current herbicide products, such as recently done for 2,4-D (HC-PMRA 2017).

4.3 Limitations of the Research and Recommendations for Future Studies

In this study, most of the compounds detected in rivers were current-use pesticides. So future studies should focus on examining the types and concentrations of current-use pesticides in rivers, rather than restricting studies to include only legacy chemicals. Chapter 2 of this thesis identified that greater the human activities in the watershed, the larger the likelihood for detecting a wider range of herbicide mixtures, as well as mixtures of herbicides and fungicides. Fungicides are not likely to be present in rivers that flow through watersheds without significant urban or agricultural activity. It will be interesting to further examine which type of human activity is influencing which types pesticide loadings into rivers, or to determine whether it is even possible to make such a distinction as many of the pesticides detected in the rivers are used in both agricultural and non-agricultural applications. In order to examine the impact of agriculture versus urban influences on the types and concentrations of pesticides present in Manitoba rivers, a future study can be designed where water and sediment samples will be collected from upstream and downstream of lands such as agricultural farms, golf courses, and points where sewage treatment plants release the treated water into rivers.

Grab sampling, which is a point sampling method was used to collect water-column samples. Although this sampling method only gives a single snap-shot of pesticide contaminants in river water at a given time and location, samples were collected every two weeks and is likely to be a close representation of the types and concentrations of pesticides present in the rivers sampled from May to August. However, between sampling times, some pesticides may have been present in the river that were not detected at the time of sampling, for example because they rapidly degraded in the water-column. A future monitoring study can include continuous *in situ* monitoring of pesticides in river water such as polar organic chemical integrative samplers (POCIS) in order to examine types and concentrations of pesticides passed through a certain point of a river over a longer period of time (e.g., 21 days for POCIS) (Challis et al. 2016). That way, the types, frequencies and concentrations of pesticides detected in both sampling methods can be compared. The monitoring study of this thesis consisted of biweekly sampling, but was limited to four months during the summer season. Further studies can be conducted including year-round sampling including core sampling during winter in order to understand seasonal and annual occurrence of pesticides in rivers.

Fluctuations in the river water discharge could impact the pesticide mass in the water-column. For example, when a herbicide such as MCPA is present at a concentration of 100 ng/L at both sampling stations A and B, the mass of pesticides moved at those sampling locations would be the greatest for the station with the greatest water discharge. However, the mass of pesticides was not calculated in the study because river discharge data were not available for most of the sampling locations. If further data are to be collected from these rivers, some of the sampling locations were near hydrometric stations and should therefore be included in these future monitoring studies. Water discharge data at these stations could be used to estimate the masses of pesticides transported at a given time and location.

Chapter 3 of this thesis focused on the sorption of environmentally relevant concentrations of MCPA and 2,4-D (2000 ngL^{-1}) into river bottom sediments. The sediment samples were fortified with individual pesticides, however in rivers, they present as mixtures. Hence, a further study can be designed incorporating different concentrations of MCPA and 2,4-D mixtures in order to further examine sorption behaviors of those chemicals under different environmental conditions.

Chapter 3 of this thesis also observed an increase in the finer sediment particles (<1 μm) in the Winnipeg River after it flows through hydroelectric generating stations. Bogen and Bonsnes (2001) also observed sediments to contain finer sediments at river locations sampled after hydroelectric generating stations. However, the sampling locations in the Winnipeg River were limited to only one location prior to (W1) and two locations (W2 and W3) after hydroelectric generating stations. In a future study, repetitive sediment samples can be collected from upstream and downstream of each hydroelectric station in the Winnipeg River (from East to West: Pointe du Bois station, Slave Falls station, Seven Sisters Falls station, McArthur Falls station, Great Falls station, and Pine Falls station). Detailed particle size distribution measured using laser diffraction technique and the sorption of MCPA and 2,4-D into sediments collected from upstream verses downstream of a hydroelectric station can be compared.

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APPENDICES

Supplementary Information: Chapter 2

Table 2S1 Pesticides included in the analytical suite of the study. Compounds with asterisk mark (*) are metabolites. R= Registered/Currently used; NR=Not Registered; H= Historical

Pesticide name	Status	Chemical family	Detection (Yes/No)
	Herbicides		
2,4-D	R	Auxin	Yes
2,4-DB	R	Auxin	No
2,4-Dichlorophenol *	R	Auxin	Yes
Alachlor	H	Chloroacetanilide	No
Allidochlor	NR	Amide	No
Atrazine	R	Triazine	Yes
Benfluralin	NR	Dinitroaniline	No
Bentazon	R	Diazinone	Yes
Benzoylprop-Ethyl	NR	Arylalanine	No
Bromacil	R	Uracil	No
Bromoxynil	R	Nitrile	Yes
Butachlor	NR	Chloroacetanilide	No
Butralin	NR	Dinitroaniline	No
Butylate	H	Thiocarbamate	No
Carfentrazone-ethyl	R	Triazolone	No
Chlorthiamid	NR	Thioamide	No
Clodinafop-propargyl	R	Aryloxyphenoxypropionic	No
Clomazone	H	Oxazole	No
Clopyralid	R	Auxin	Yes
Cycloate	H	Thiocarbamate	No

Desmetryne	NR	Methylthiotriazine	No
Dicamba	R	Auxin	Yes
Dichlobenil	R	Benzonitrile	No
Dichlorprop	R	phenoxypropionic	No
Diclofop	H	Aryloxyphenoxypropionate	No
Dimethachlor	NR	Chloroacetanilide	Yes
Diphenamid	H	Amide	No
EPTC (S-ethyl dipropylthiocarbamate)	R	Thiocarbamate	Yes
Ethalfluralin	R	Dinitroaniline	No
Ethofumesate	R	Benzofuran	No
Fenoxaprop	R	Aryloxyphenoxypropionate	No
Flamprop-Isopropyl	H	Arylalanine	No
Flamprop-Methyl	H	Arylalanine	No
Fluazifop-p-butyl	R	Aryloxyphenoxypropionic	No
Flumioxazin	R	Dicarboximide	No
Fluroxypyr	R	Auxin	Yes
Hexazinone	R	Triazinone	No
Imazamethabenz	R	Imidazolinone	No
Imazethapyr	R	Imidazolinone	Yes
MCPA	R	Phenoxyacetic, auxin	Yes
MCPB-methyl	R	phenoxybutyric	No
Mecoprop	R	phenoxypropionic	Yes
Metolachlor	R	Chloroacetanilide	Yes
Monolinuron	H	Phenylurea	No
Napropamide	R	Amide	No
Oxyfluorfen	R	Nitrophenyl ether	No
Pendimethalin	R	Dinitroaniline	No
Picloram	R	Auxin	Yes
Prometon	NR	Methoxytriazine	No
Prometryn	R	Methylthiotriazine	No

Propham	NR	Carbanilate	No
Propyzamide	R	Amide	No
Quinclorac	R	Guinolinecarboxylic acid	No
Quizalofop-ethyl	R	Aryloxyphenoxypropionic	No
Simazine	R	chlorotriazine	No
Sulfentrazone	R	Triazolinone	No
Terbacil	R	Uracil	No
Terbutryne	NR	Triazine	No
Triallate	R	Thiocarbamate	Yes
Triclopyr	R	Auxin	No
Trifluralin	R	Dinitroaniline	No
	Fungicides		
Azoxystrobin	R	Strobilurin	Yes
Benalaxyl	NR	Anilide	No
Boscalid	R	Anilide	Yes
Bupirimate	NR	Pyrimidine	No
Captan	R	Phthalimide	No
Chloroneb	H	Aromatic	No
Chlorothalonil	R	Chloronitrile	No
Cyprodinil	R	Anilinopyrimidine	No
Difenoconazole	R	Conazole	Yes
Etridiazole	R	Thiadiazole	No
Famoxadone	R	Oxazole	No
Fenamidone	R	Imidazole	No
Fludioxonil	R	Pyrrole	Yes
Folpet	R	Phthalimide	No
Ipconazole	R	Conazole	No
Iprodione	R	Dicarboximide	No
Metalaxyl	R	Acylamino acid	Yes
Metconazole	R	Conazole	No
Myclobutanil	R	Conazole	No

Picoxystrobin	R	Methoxyacrylate strobilurin	Yes
Procymidone	NR	Dichlorophenyl dicarboximide	No
Propiconazole	R	Conazole	Yes
Prothioconazole-Desthio*	R	Conazole	Yes
Pyraclostrobin	R	Carbanilate	Yes
Pyrimethanil	R	Anilinopyrimidine	No
Quintozene	H	Aromatic	No
Tebuconazole	R	Conazole	Yes
Trifloxystrobin	R	Strobilurin	No
Triticonazole	R	Conazole	No
Vinclozolin	NR	Oxazole	No
Zoxamide	R	Benzamide	No
		Insecticides	
Aldrin	NR	Organochlorine	No
Azinphos-methyl	H	Organophosphate	No
Bifenazate	R	Carbazate	No
Bifenthrin	R	Pyrethroid	Yes
Bromophos-Ethyl	NR	Phenyl organothiophosphate	No
Carbaryl	R	Carbamate	No
Carbofuran	H	Carbamate	No
Chlormephos	NR	Organophosphate	No
Chlorpyrifos	R	Organophosphate	Yes
Chlorpyrifos-Methyl	NR	Organophosphate	No
Chlorthal-Dimethyl	R	Phthalic acid	No
cis-Chlordane	H	Cyclodiene	No
cis-Permethrin	NR	Pyrethroid ester	Yes
Cyfluthrin	R	Pyrethroid	No
Cyhalothrin lambda	NR	Pyrethroid	No
Cypermethrin-beta	R	Pyrethroid	No
Cypermethrin-zeta	R	Pyrethroid	No
Deltamethrin	R	Pyrethroid	No

Diazinon	R	Organophosphate	No
Dichlorvos	H	Organophosphate	No
Dieldrin	NR	Cyclodiene	Yes
Dimethoate	R	Organophosphate	No
Dioxathion	NR	Organophosphate	No
Endrin	NR	Organochlorine	No
Ethion	H	Organophosphate	No
Etrimfos	NR	Organophosphate	No
Fenchlorphos	NR	Organophosphate	No
Fenthion	H	Organophosphate	No
Fonofos	H	Organophosphate	No
HCH-α *	H	Organochlorine	No
HCH-β *	H	Organochlorine	No
HCH-δ *	H	Organochlorine	No
Heptachlor	NR	Organochlorine	No
Isofenphos	NR	Organophosphate	No
Lindane	H	Organochlorine	No
Malathion	R	Organophosphate	No
Methoprene	R	Juvenile hormone mimics	No
Methoxychlor	H	Organochlorine	No
Mirex	NR	Cyclodiene	No
Naled	R	Organophosphate	No
o,p-DDD *	H	Organochlorine	No
o,p'-DDE *	H	Organochlorine	No
o,p-DDT *	H	Organochlorine	No
p,p- DDT *	H	Organochlorine	Yes
p,p-DDD *	H	Organochlorine	Yes
p,p'-DDE *	H	Organochlorine	Yes
Phorate	R	Aliphatic organothiophosphate	No
Pirimicarb	H	Dimethylcarbamate	No
Pirimiphos-Ethyl	NR	Organophosphate	No

Pirimiphos-Methyl	NR	Organophosphate	No
Propetamphos	H	Phosphoramidothioate	No
Propoxur	R	Phenyl methylcarbamate	No
Pyridaben	R	Pyridazinone	No
Spiromesifen	R	Tetronic acid	No
Sulfotep	H	Organophosphate	No
Sulprophos	NR	Organophosphate	No
t-Chlordane	NR	Organochlorine	No
Terbufos	H	Organophosphate	No
Tetramethrin	R	Pyrethroid	No
trans-Permethrin	NR	Pyrethroid ester	Yes
tr-Heptachlor Epoxide	M	Organochlorine	No
α-Endosulfan	R	Organochlorine	No
		Insecticide Synergist	
Piperonyl butoxide	R	Cyclic aromatic	Yes
		Acaricides	
Bromopropylate	NR	Bridged diphenyl	No
Diclofenthion	NR	Organophosphate	No
Flumetralin	NR	Growth inhibitors	No
Nitrapyrin	NR	Nitrification inhibitors	No
Tetradifon	NR	Bridged diphenyl	No
Tetrasul	NR	Bridged diphenyl	No