INVESTIGATION OF PESTICIDES IN RIVERS AND AN ON-FARM MITIGATION STRATEGY FOR REDUCING POINT-SOURCE POLLUTION

by

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ABSTRACT

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By screening for up to 172 pesticide compounds (primarily herbicides and insecticides), this research investigated the types and concentrations of pesticide compounds present in water-column and bottom-sediment samples collected from four rivers in the Province of Manitoba, Canada. A total of 34 unique compounds were detected in the water-column (n=202) with broadleaf herbicides among the most frequently detected (2,4-D, bentazone, clopyralid, MCPA), in addition to herbicides atrazine and metolachlor that are widely used in the United States Corn Belt. Herbicide triclopyr was only detected after the Red River entered urban landscapes in Manitoba but many other unique active ingredients were already detected in the first sampling station immediately after the Canadian-United States border. Only 6 unique compounds have set Canadian Water Quality Guidelines for the Protection of Aquatic Life, and their guidelines were never exceeded. A total of 32 unique compounds were detected in bottom sediments (n=94) of which 78% are current-use active ingredients in Manitoba. In addition to sediments, pesticides can be sorbed to other constituents present in rivers such as microplastics which are believed to be carriers of legacy insecticide DDT (dichlorodiphenyltrichloroethane). This study investigated the sorption of current-use herbicides (2,4 D, atrazine, glyphosate) by microplastics which was virtually negligible, except for glyphosate sorption by PVC (35%). In contrast, the sorption of DDT by these same microplastics was always >50% (of the initial DDT in solution). Finally, this study investigated the efficiency of single and dual-cell biobeds in the Prairies to minimize point-

source pollution by allowing the capture and degradation of pesticide residues associated with sprayer rinsing. With a few exceptions (clopyralid, fluroxypyr and imazethapyr), biobeds always showed to be highly effective in reducing pesticides concentrations in rinsate. The PTI (Pesticide Toxicity Index) values determined for a range of indicator species were always much larger for influent than effluent samples, suggesting ecological benefits to the broad adoption of biobeds in Prairie municipalities and on-farms. Biobeds were least effective for current-use pesticides that have relatively high GUS values (> 2.8) suggesting that further improvements in biosystem design need to be made for optimizing the recycling of these pesticides.

FOREWARD

This thesis is prepared in manuscript style in accordance with the Department of Soil Science and Faculty of Graduate Studies, University of Manitoba guidelines. This thesis consists of five chapters including an Introduction (Chapter 1), three stand-alone specific research chapters (Chapters 2 to 4) and an Overall Synthesis (Chapter 5).

Chapter 2 is under preparation for submission to the Journal of Environmental Quality:

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1. INTRODUCTION

1.1 Pesticides and Environmental Fate

Pesticides, which include herbicides, insecticides and fungicides, are routinely applied to control various pests that would otherwise interfere with crop production or other human activities. Understanding the environmental fate of pesticides is of interest because pesticide active ingredients and their degradation products can move from agricultural land to surface water and ground water and become contaminants. The fate of pesticides in the environment includes sorption, transformation and transport processes. Pesticide sorption is influenced by the pesticide' physiochemical properties (e.g. octanol water partition coefficient, sorption coefficient, water solubility), as well as the characteristics of the environmental compartment that the pesticide resides in (e.g., organic carbon content or clay content of soil and sediments) (Hall et al. 2015; Kasozi et al. 2012; Reichman et al. 2011; Tülp et al. 2009; Vryzas 2018; Wauchope et al. 2002; Borggaard and Gimsing 2008). Sorption of pesticides by soil and sediment includes pesticide molecules that are readily desorbed, those that are strongly bound and do not readily desorb, as well as bound residues that are irreversible sorbed. Sorption also includes the absorption of pesticides by organisms such as fish. Pesticide transformation usually occurs by biodegradation involving microorganisms, but also occurs due to chemical degradation such as photolysis, hydrolysis, and oxidation.

Pesticides may move into broader environment by a variety of pathways such as spray drift (Caldwell 2007), wind erosion of surface soil (Larney et al. 1999), as well as rainfall, snowmelt or irrigation related surface runoff (Dabrowski et al. 2002; Donald et al. 2005; Gaultier et al. 2009). Atmospheric deposition (wet and dry) is also an important non-point source pathways by which surface waters can become contaminated with pesticides (Hill et al. 2003; Jantunen et al. 2008; Messing et al. 2011). The

release of waste water effluent in surface water is also known to contribute to pesticide point source pollution in surface waters (Münze et al. 2017; Sheedy et al. 2019; Challis et al. 2020). Pesticide leaching in soils can contribute to ground water contamination (Kolpin et al. 1998; Elliott et al. 2000; Munira et al. 2018). There are insufficient data to determine the cost of this water pollution to Canadian society, but water pollution by pesticides costs the United States an estimated $2 billion per year (Pimentel 2005). In a recent report, it was estimated that overall pollution is costing Canada billions of dollars per year (Smith and McDougal 2017). It is estimated that for more than 15 million hectares of Canada's agricultural land, the risk of water contamination by pesticides is greater now than it was in the 1980s (Gagnon et al. 2014; Clearwater et al. 2016).

1.2 Pest Control Product Sales in Canada

There are no public records in Canada that provide for a quantitative assessment of the timing and rates of pesticides applied in a specific geographical location or region. Available data on recent Pest Control Product Sales (2012-2018) indicate that the amount of pesticide active ingredients annually sold in Canada varies from about 90 to 130 million kg. Out of this total, about three-fourths are pesticide sales in the agricultural sector, and one-fourth in the non-agricultural (~20%) and domestic (~5%) sectors. As an example, the amount of pesticide active incredients sold in Canada was around 120 million kg in 2016 and 2018, and 132 million kg in 2017 (Health Canada 2018). Furthermore, it is estimated that the three Prairie Provinces (Alberta, Saskatchewan and Manitoba) account for 85% of the total agricultural pesticides used which is not surprising since these Prairie Provinces contain about 83% of Canada's cropland (Statistics Canada 2016). The majority of pesticides used in the agricultural sector are herbicides (~73%), followed by fungicides (~15%), insecticides (~4%), antimicrobials (~4%) and others (~4%) (Health Canada 2018).

Table 1.1 Top 10 active ingredients and pesticides sold in Canada in 2018 (Source: Health Canada 2018)[1]

Rank	Overall sold active ingredients				Active ingredients sold in agriculture sector
	All active ingredients and pesticides	Herbicides	Insecticides	Fungicides	
1	Glyphosate*	Glyphosate*	Mineral oil	Prothioconazole*	Glyphosate
2	Available chlorine, present as sodium hypochlorite	Glufosinate ammonium*	Hydrogen peroxide	Tebuconazole*	Prothioconazole*
3	Creosote	Bromoxynil*	Sulphur	Mancozeb	Glufosinate ammonium*
4	Prothioconazole*	MCPA*	DEET	Metam-sodium	Available chlorine, present as sodium hypochlorite
5	Glufosinate ammonium*	2,4-D*	Chlorpyrifos*	Chlorothalonil*	Bromoxynil*
6	Bromoxynil*	Corn gluten meal	Thiamethoxam*	Chloropicrin	MCPA*
7	MCPA*	S-metolachlor and R-enantiomer	Paradichlorobenzene	Trifloxystrobin*	Surfactant blend
8	Surfactant blend	Bentazon*	Imidacloprid*	Mono and dibasic sodium, potassium, and ammonium phosphites	2,4-D*
9	*Borates*	Metam-sodium	Imidacloprid*	Sulphur	Tebuconazole*
10	*2,4-D**	Clethodim	Silicon dioxide	Metiram	Mineral oil

[1]*Pesticides with * were analyzed for the river water and sediment samples in this research.*

1.3 Pesticide Residues in Canadian Prairie Surface Waters

Agricultural practices in the proximity of surface waters can affect the types and concentrations of pesticides entering surface water (Xing et al. 2012; Fairbairn et al. 2016; Main et al. 2016). Pesticides are used not only on agricultural land, but also in other applications such as for weed control along railway tracks and roads, on industrial terrains, and in parks and golf courses. Hence, it is documented that pesticide use in urban settings can also lead to surface water contamination (Glozier et al. 2012).

Pesticides have been frequently detected at low levels in Prairie surface waters including wetlands (Messing et al. 2011; Main et al. 2016), lakes (Rawn et al. 2000), as well as streams and rivers (Rawn et al. 1999; Charest et al. 2015; Basiuk et al. 2017; Challis et al. 2018; Gamhewage et al. 2019; Sheedy et al. 2019).These studies have focused on monitoring the water-column, and there are relatively few studies that have examined the types and concentrations of pesticides in sediments of rivers, lakes and rivers in the Prairies (Donald and Syrgiannis 1995; Gamhewage et al. 2019; Kurek et al. 2019). Pesticides and other chemicals are known to enter rivers flowing through agricultural and urban landscapes (Pal et al. 2010; Wittmer et al. 2010; Glozier et al. 2012; Stone et al. 2014). 2,4-D and MCPA are herbicides that are frequently detected in Prairie rivers (Rawn et al. 1999; Gamhewage et al. 2019; Sheedy et al. 2019). Glyphosate is another widely used herbicide in Canada and was detected in the water-column of Prairie rivers by Glozier et al. (2012) and Basiuk et al. (2017).

1.4 Pesticides Sorption by Solid Substances in Rivers

Depending on the physico-chemical characteristics of the pesticide, a pesticide in surface water can reside in the aqueous phase or in the solid phase such as sorbed by suspended sediments or bottom sediments. Investigating the sorption-desorption of pesticides by sediments is of great interest,

particularly for environmental and ecological reasons. Specifically, pesticide sorption by sediment directly impacts the other environmental fate processes, including pesticide degradation, bioavailability and transport, hence it also controls the persistence and the possible effects of the pesticide on non-target organisms in the aquatic environment (Karickhoff et al. 1979; Gao et al. 1998). Sorption, or the attraction and binding of a pesticide to a sorbent, tends to reduce pesticide mobility within the broader environment. The sorption of pesticides is influenced by the physio-chemical properties of the pesticide such as its water solubility and octanol water partition coefficient (Log Kow), as well as the characteristics of the sediment such as organic carbon content (Vryzas et al. 2018).

In addition to sediments, a range of other materials can be present in rivers, particularly microplastics.The increased production and use of plastics in the past decades have resulted in escalating the detection of these polymers in marine and fresh water systems (Anderson et al. 2016). The term ‘‘microplastics’’ was first used by Thompson et al. (2004) to describe microscopic plastic pieces in the marine environment defined as pieces <5mm in diameter (Arthur et al. 2009). Substantial research has been conducted since then, predominantly for marine environments but also for freshwater and terrestrial systems (Thompson et al. 2009; Claessens et al. 2011; Wagner et al. 2014; Ballent et al. 2016; Rodrigues et al. 2018). The abundance of microplastics in marine and freshwater systems is increasingly seen as a global threat to ecosystems (Cole et al. 2011; Eerkes-Medrano et al. 2015). A number of studies have reported on microplastics in the water column or sediments of rivers and lakes in Canada (Castañeda et al. 2014; Corcoran et al. 2015; Anderson et al. 2016; Warrack et al. 2017). Microplastics are considered contaminants and it is also shown that microplastics can be cariers of chemical contaminants such as persistent organic pollutants including polychlorinated biphenyls, polyaromatic hydrocarbons and organochlorines(e.g., DichloroDihenylTrichloroethane (DDT)) (Rios et al. 2007; Teuten et al. 2007; Barnes et al. 2009; Eerkes-Medrano et al. 2015; Anderson et al. 2016).

Other materials present in rivers include fly ash which is a by-product from coal-fired power or energy stations. Fly ash is alkaline in nature and this mineral residue typically contains macro and micronutrients (for example, P, K, Ca, Mg, Zn, Fe, Cu, Mn, B and Mo) (Ahmaruzzaman, 2010; Ghosh & Singh 2013). The release of millions of tons of fly ash due to human activities are contributing to environmental pollution including water contamination by the ash (Ahmaruzzaman 2010; Lokeshappa and Dikhshit 2011). Charcoal, which is like ash a component of what is considered black carbon, is another solid constituent that is present in rivers. Charcoal is generally produced from wood or biomass by thermal degradation, when oxygen is limited, and considered as a popular fuel product in many countries (Kammen and Lew 2005). Loading of ash and charcoal into surface water are well documented, including that such loading occurs in regions impacted by natural or human-induced forest fires (Mitra et al. 2002; Hockaday et al. 2007; Eriksen et al. 2013; Parks Canada 2018; Alberta Agriculture and Forestry 2019; Woodward 2020; Alexandra & Finlayson 2020).

1.5 Chemicals included in this Research

This Ph.D. research included field studies whereby samples were screened for 172 compounds of which 97 were pesticide active ingredients (and some of their metabolites) that are currently registered for agricultural use in Canada (Table 2S1). The other 75 compounds included historical pesticides that are no longer registered (e.g., DDT, lindane, clomazone) along with some of their isomers or metabolites (e.g., p,p´DDE, p,pDDD, HCH-α, HCH-β, HCH-γ), as well as pesticides never registerd in Canada(e.g., dimethachlor, chlorthiamid, terbutryne).Of the total 172 compounds, the majority were insecticides (~41%), followed by herbicides (~38%), fungicides (~18%) and others included bactericides, acaricides, nematicides, growth regulator (~3%).

This research also included batch equilibrium sorption studies in the laboratory that utilized four pesticide active ingredients with distinct properties (Table 1.2). This included three current use pesticides (2,4-D, atrazine, glyphosate) and legacy compound DDT. 2,4-D (weak-acid, pKa=3.40 at 25^{o}C) is a selective, systemic post emergent herbicide applied to control broad-leaf weeds. This herbicide has been registered for use in USA and Canada since the 1940s (USEPA 2005). 2,4-D is registered for use in a wide range of agricultural crops, as well as for use in urban areas, for example, on golf courses (Meftaul et al. 2020; Smith and Bridges 1997). It has high water solubility (24,300 mg L^{-1}at 20^{o}C) and is non-persistent in soil (typical half-life 4.4 days) (Lewis et al. 2016). Studies show frequent detection of 2,4-D in Prairies surface water and sediment (Donald and Syrgiannis 1995; Donald et al. 1999; Gamhewage et al. 2019; Sheedy et al. 2019).

Table 1.2 Molecular structure and physicochemical properties of the pesticides used in the study (Sprankle et al., 1975; Lewis et al. 2016; PubChem Compound Database, 2020)

Properties[1]	2,4-D	Atrazine	Glyphosate	DDT
Molecular mass (g/mol)	221.04	215.68	169.1	354.49
Water solubility at 20ºC (mgL^{-1})	24,300	35	10,500	0.006
Octanol/water partition coefficient (log Kow) at pH 7, 20ºC	-0.83	2.70	-3.20	6.91
Dissociation constant pKa at 25^{0}C	3.40	1.70	2, 2.6, 5.6, 10.6	-
Soil sorption coefficient Koc	39.3	100	1424	151,000
Typical ½-life (days)	4.4	75	15	6,200
Water-sediment ½-life (days)	18.2	80	9.9	>150 years
Vapor pressure at 20^{0}C (mPa)	0.009	0.039	0.0131	0.025
H at 25ºC (Pa m^3/mol)	$4X10^{-06}$	$1.5X10^{-04}$	$2.1X10^{-07}$	$8.43X10^{-01}$

[1]log Kow = Octanol/water partition coefficient; H = Henry's law constant

Atrazine (weak-base, pKa=1.7 at 25^{o}C) is a selective, systemic pre- and post-emergent herbicide used to control broad-leaf weeds and grasses. It has a relatively low water solubity in water (35mg L^{-1}in water at 20ºC) and is moderately persistent in soil (typical half-life 75 days) (Lewis et al. 2016). Atrazine has been used in North American agriculture since the 1960s, and is particularly widely used

in the cornbelt of the United States (Hansen et al. 2019; Mahler et al. 2017; Van Metre et al. 2017). Atrazine has been frequently detected in the Red River of which ~80% is flowing in North-Central United States before entering the Province of Manitoba, Canada (Rawn et al. 1999, Challis et al. 2018). However, the herbicide is less frequently detected in other Prairie rivers which do not originate in the USA (Sheedy et al. 2019).

Glyphosate (zwitterion) is a broadspectrum, non-selective, systemic, post-emergent herbicide. Although first registered for use in Canada in 1976, the introduction of glyphosate-tolerant varieties (canola, soybean, maize and cotton) since the mid 1990s has particularly increased glyphosate use in North America and other regions in the world (Beckie et al. 2014; Duke and Powles 2008). Glyphosate has a relatively high water solubility (10,500 mg L^{-1} at 20ºC) and is non-persistent in the soil (typical half-life 17 days) (Lewis et al. 2016). Despite being listed as non-persistent in water-phase of surface waters as well (half-life 9.9 days) (Lewis et al. 2016), Glozier et al. (2012) frequently (>50%) detected glyphosate in the water column of some Canadian Prairie rivers and streams.

DDT (nonpolar) is a broadspectrum, non-selective, non-systemic insecticide. Prior to its deregistration in 1973, DDT was widely used in North-America for the control of insects that interfered with crop production (e.g., Colorado potato beetle) and that are vectors of human diseases (e.g., lice, fleas and mosquitoes). DDT was banned because of its demonstrated negative impact on organisms (e.g., Bald Eagle) as well as the increasing development of insect resistance to DDT (Stokstad, 2007; Davies et al., 2007). DDT has a very low water solubility (0.006 mg L^{-1}) and high persistency in the soil with a typical half-life of 6,200 days (Lewis et al. 2016). Despite that DDT had been banned for decades, the active ingredient continued to be detected in the water-column and bottom sediments of Canadian lakes (Lembcke et al. 2011; Kuo et al. 2012; Kurek et al. 2019) and rivers (Pham et al. 1993, 1996).

There is substantial information about the sorption of 2,4-D, atrazine, glyphosate and DDT by soil and soil constituents (e.g., clay, humic acids), including sorption mechanisms. For nonionic pesticides, such as DDT, hydrophobic bonding is most common, but other possible mechanisms include charge-transfer complexes, covalent bonding, hydrogen bonding and Van der Waals attractions (Senesi and Chen 1989, Senesi 1992). For ionizable pesticides such as 2,4-D, atrazine and glyphosate,studies have shown that a diverse range of bonding mechanisms is possible, including common findings that include charge-transfer (electron donor-acceptor) complexes, hydrogen bonding, ligand exchange, and Van der Waals attractions (Fusi et al. 1988, Senesi and Chen 1989, Hermosin and Cormejo 1993, Piccolo and Celano 1994, Senesi et al. 1995, 1997, Ferreira et al. 2002, Sheals et al. 2002). Covalent bonding is also possible for weakly-acidic or weakly-basic pesticides (Hayes 1970; Senesi and Chen 1989), and hydrophobic bonding (partitioning) and ionic bonding are possible mechanisms for weakly-basic or zwitterionic pesticides (Senesi and Chen 1989, Senesi et al. 1997, Martin-Neto et al. 2001, Ferreira et al. 2002). Cationic bridging and enzyme-mediated bonding has also been proposed for some weakly-acidic pesticides such as 2,4-D (Fusi et al. 1988, Senesi and Chen 1989, Hermosin and Cormejo 1993).

1.6 Use of Biobeds to Mitigate Pesticide Point Source Pollution

Pesticide handling areas are locations used for the filling and cleaning of agricultural spraying equipment and could contribute to water contamination by point-source pollution resulting from runoff and leaching (Helweg 1994). Biobeds have shown to be an effective, attractive, cheap and an alternative approach to trap pesticide waste in the farm site (Torstensson 2000). A biobed is an above- or in-ground container structure that holds a biomixture that is typically derived from a combination of plant dry matter, humified organic matter and soil (Bergsveinson et al. 2018; Cessna et al. 2017). The

collected sprayer rinsate are usually trickled or sprayed over the top of the biobed and let to percolate through the biomix (Braul et al. 2018). This biomix may facilitate to retain and degrade the pesticides and lessen their environmental concentration and detection in the effluent, thereby minimizing point-source pollution. Invented by a Swedish farmer in the 1990s, on-farm biobeds have been adopted in some regions of the World, particularly Europe and Latin America, but remain largely unknown to farmers in Canada (Dias et al. 2020).

1.7 Research Objective and Hypothesis

This research quantified pesticide residues in the water-column and bottom sediment of four Manitoba rivers. For selected pesticide, active ingredients, the study further investigated the relative sorption of pesticides by bottom sediments and other constituents in rivers such as microplastics. In addition, the research examined the performance of four on-farm biobeds utilized in the Canadian Prairies for recycling pesticide rinsates. The objectives and hypothesis for the three studies of this graduate research were:

Study 1: Pesticides in Water-column and Bottom Sediment Samples of Prairie Rivers

Objective: To compare for river segments influenced by agricultural and non-agricultural pesticide applications, the types of pesticides detected in water columns versus bottom sediments, and examine reasons for variations in pesticide concentrations by sampling location and time.

Hyphothesis: A portion of current-use pesticide active ingredients detected in bottom sediments will not be detected in the water-column (see chapter 2)

Study 2: Sorption of Pesticides by Microplastics, Charcoal, Ash, and River Sediments

Objective: To investigate to what extent 2,4-D, atrazine and glyphosate are sorbed by microplastics (i.e., fiber, polyethylene beads, polyvinyl (PVC) and tire fragments) and other river constituents (i.e., ash, charcoal, and suspended and bottom sediments), and how this compares to the sorption potential of legacy pesticide DDT by these river constituents.

Hypothesis: Pesticides will each show distinct characteristics in their relative affinity for common constituents detected in rivers, including sediments, ash, charcoal and a range of microplastics (see chapter 3)

Study 3: Using the Pesticide Toxicity Index to Show the Potential Ecosystem Benefits of On-Farm Biobeds

Objective: To measure, through quantifying pesticide concentrations and Pesticide Toxicity Index (PTI) values, the efficiency of single- and dual-cell biobeds as it applies to pesticides commonly used in Prairie agriculture.

Hypothesis 1: The pesticides detected in biobed effluents are more likely to be pesticides that have greater Ground Water Ubiquity Score (GUS) values (see chapter 4)

Hypothesis 2: The mean Pesticide Toxicity Index (PTI) of biobed effluent will be significantly smaller than the mean PTI of biobed influent (see chapter 4).

1.8 Thesis Outline

This thesis is prepared in manuscript style in accordance with the Department of Soil Science, University of Manitoba Guidelines. It has five chapters including the introduction (Chapter 1), three stand-alone specific research chapters (Chapter 2, 3 and 4), and the overall synthesis (Chapter 5).

Chapter 2: Pesticides in Water-column and Bottom Sediment Samples of Prairie Rivers

The study investigated the types and concentrations of wide range of pesticide compounds present in water column and bottom sediments at various sampling locations in the Red River and three of its tributaries. Although a wide range of studies have examined pesticide residues in the water column in Canada, this research added to scientific knowledge by examining for a wider range of current-use and legacy active ingredients, and also taking into consideration bottom sediments.

Chapter 3: Sorption of Pesticides by Microplastics, Charcoal, Ash, and River Sediments

This is the first batch equilibrium study to contrast the relative sorption of current-use versus legacy pesticides by a range of constituents present in rivers, including sediments and a range of microplastics.

Chapter 4: Using the Pesticide Toxicity Index to Show the Potential Ecosystem Benefits of On-Farm Biobeds

This is the first study to apply the Pesticide Toxicity Index to show the effectiveness of four on-farm biobeds to recycle a wide range of pesticides widely applied in crop production in the Canadian Prairies.

My contributions to Chapters 2 to 4 include: planning and conducting field work to collect river water and sediment samples including their extraction in the laboratory for pesticide residues; laboratory experiments to generate sorption data on microplastics, charcoal, ash and river sediments for 2,4-D, atrazine, glyphosate and DDT; calculating the Pesticide Toxicity Index for a data set that was provided by Agriculture and Agri-Food Canada and included four biobeds situated in the Prairies, data management and statistical analysis; preparing tables and figures that facilitated the interpretation of the analyzed data; writing, improving, and finalizing manuscripts for submission to peer-reviewed journals and addressing reviewer comments as needed.

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2. PESTICIDES IN WATER-COLUMN AND BOTTOM SEDIMENT SAMPLES OF PRAIRIE RIVERS

2.1 Abstract

This study screened for up to 172 pesticide compounds (primarily herbicides and insecticides) in water-column (n=202) and bottom-sediment (n=94) samples of four rivers in the Province of Manitoba, Canada. Rivers in watersheds with clay-rich soils each showed 25 unique compounds (i.e., in the Red River and La Salle) whereas rivers in watersheds characterized by coarse textured soils showed 15 (Assiniboine River) and 16 (Seine River) unique compounds. Around 62% (water-column) and 60% (bottom-sediment) of the unique active ingredients detected in the Red River were already present in the first sampling location after the Canadian-United States border (i.e., location R1), suggesting transboundary contamination. 95 % of the compounds detected in the water-column samples at the point of the Red River discharging into Lake Winnipeg (i.e., locations R11 or R12) were also detected at R1 or R2. In contrast, about 40 % of the compounds detected in the bottom sediment samples at R11 or R12 were never detected at R1 or R2 suggesting that pesticides are partitioning from the water-column to bottom sediments and there was also evidence that this partitioning readily occurred in the swampy area (R11, R12).In 2016, 96% of the samples taken at five locations (R1, R2, R10, R11, R12) in the Red River showed 2,4-D, clopyralid and MCPA to be present in the water-column as mixtures, but for the same locations this was only 23% of the samples in 2017 which was a drier year. Insecticide malathion and herbicide triclopyr were only detected after the Red River entered suburban environments, and these active ingredients are in products sold in retail stores in the City of Winnipeg. Only six of the forty pesticide compounds detected in the water-column across two years have set Canadian Water Quality Guidelines for the Protection of Aquatic Life and their individual concentrations in the water-column were always well below their respective guidelines. Seventeen

active ingredients were detected in bottom sediments but never in the water-column of which 59% were current-use active ingredients, including glyphosate and its primary metabolite AMPA that were detected at much greater concentrations in bottom-sediments than other pesticides. Fungicides tebuconazole (72%), boscalid (67%) and propiconazole (61%) and herbicides MCPA (68%) and glyphosate (55%) were the top five most frequently detected current-use pesticide active ingredients in bottom sediment. A total of 57 current use active ingredients were never detected in the rivers.

2.2 Introduction

Surface waters in the Canadian Prairies have shown to contain a wide range of pesticides at low concentrations in the water-column of rivers (Rawn et al. 1999), lakes (Harris and Miles 1975; Rawn et al. 2000) and wetlands (Grover et al. 1997; Waite et al. 2002; Donald et al. 2007; Main et al. 2015). Current-use auxin herbicides and neonicotinoid insecticides are among the most frequently detected compounds (Glozier et al. 2012; Anderson et al. 2015; Main et al. 2015; Schaafsma et al. 2015; Sheedy et al. 2019), but legacy pesticides such as dichlorodiphenyltrichloroethane (DDT: banned in 1972) and ϒ- hexachlorocyclohexane (lindane: banned in 2004) are also being detected (Pham et al. 1996; Crosley et al. 1998; Donald et al. 2009; Vijgen et al. 2011; Kurek et al. 2019).

Pesticides are being detected in both the water-column and bottom sediments of rivers (Frank and Logan 1988; Rawn et al. 1999; Smalling et al. 2013; Keurek et al 2019) with the active ingredients and their concentrations varying between sampling locations and also changing over time (Struger et al. 2004; Byer et al. 2011). Determining whether a pesticide molecule is present in the water-column versus bottom sediments at a given location and time is important because the compartment in which it resides influences both the transport and degradation potential of the pesticide (Karickhoff et al. 1979; Luthy et al. 1997; Gao et al. 1998). The physico-chemical characteristics that have an influence on

whether the pesticideis likely to persists in the water-column or sediments includes the pesticide sorption coefficient (Koc) and the pesticide octanol water partition coefficient (Kow).

Lake Winnipeg in the Province of Manitoba, Canada has a large watershed-to-lake area ratio (40:1) and is heavily impacted by eutrophication (LWIC 2005; ECMWS 2011). At least 60 tributaries enter Lake Winnipeg of which the Red River enters from the South (LWIC 2005). In the past three decades, the water-column of the Red River has shown to contain detectable concentrations of herbicides such as 2,4-D, atrazine, bromoxynil, chlorpyrifos and MCPA (Rawn et al. 1999, Gamhewage et al. 2019). A previous study that collected sediments from Lake Winnipeg concluded that the concentrations of legacy insecticide DDT were largest in the south basin of the lake because its historical urban and agricultural use was primary in the south, including in the City of Winnipeg (Rawn et al. 2000). DDT has never been monitored for in the Red River water-column or sediments.

Pesticides are used in both agricultural and non-agricultural applications and can enter rivers by non-point sources such as atmospheric dry and wet deposition, as well as snowmelt runoff (Donald et al. 1999; Main et al. 2016; Messing et al. 2011; Sheedy et al. 2019). The release of wastewater effluent is also known to contribute to pesticide point source pollution in rivers, including 2,4-D, mecoprop, and triclopyr (Sheedy et al. 2019). The City of Winnipeg releases treated wastewater in the Red River, and in years with heavy rain is also releasing untreated sewage in the Red River as part of emergency measures (CBC 2022).

Almost all previous studies on pesticide active ingredients in Canadian rivers monitored the water-column only (e.g., Frank & Logan 1988; Rawn et al. 1999; Xing et al. 2012; Struger et al. 2008, 2015, 2016) and these studies included up to 25 pesticide active ingredients. In this study, we analyzed for up

to 172 pesticide compounds that according to the Pesticide Properties Data Base (PPDB) (Lewis et al. 2016) ranged in Koc values from 5 to 10,240,000 and in Log Kow values from -6.28 to 6.91. The pesticide water-sediment half-lives ranged from <1 to 1053 days (Lewis et al. 2016). About one-half (57%) are current-use active ingredients registered in Canada for use in agricultural and/or non-agricultural (e.g., golf course maintenance) applications. The remaining compounds were a few metabolities of current-use active ingredients, deregistered active ingredients, and pesticides never registered in Canada. The 172 compounds were primarily herbicides (38%), insecticides (41%) and fungicides (18%) with the remaining being classified as acaracides, or as a bactericide, nematicide or growth regulator. Their typical soil half-lifes ranged from <1 to 6,200 days (Lewis et al. 2016).

The objective of this study was to compare for river segments influenced by agricultural and non-agricultural pesticide applications, the types of pesticides detected in water-columns versus bottom sediments, and examine possible reasons for variations in pesticide concentrations by sampling location and time.

2.3 Materials and Methods

2.3.1 Rivers Samples

This study focused on the Red River and three of its tributaries (Assiniboine River, La Salle River and Seine River) (Figure 2.1). Annual cropland accounts for much of the land use (80%) in the Red River Valley of Manitoba and the watersheds of the Assiniboine River (58%) and Seine River (46%) (Painter et al. 2021; ARWAC 2006; AAFC 2005a). About one-half (46%) of land use along the La Salle River

is classified as cropland (Graveline and Larter 2006). The Red River is a major North American river that is 880 km long by channel length and has a drainage basin of 288,000 km^2. It originates from the confluence of the Bois de Sioux and Otter Tail River to form the border of Minnesota and North Dakota in the United States, before entering Manitoba where it has 20% of the river length until discharging into Lake Winnipeg. The Red River basin with its heavy clay soils is prone to flooding, particularly during snowmelt in the Spring. The Red River accounts for close to 70% (phosphorus) and 34% (nitrogen) of total P and N loadings to Lake Winnipeg even though, on average, it only accounts for ~15% of the total inflow to Lake Winnipeg (ECCC 2020).The Assiniboine River is the largest western tributary of the Red River which originates in southeastern Saskatchewan and is 1,070 km long with a drainage basin of 163,000 km^2 (Marsh 2015; Brooks and George 2015). The La Salle River is a southwesterly tributary of the Red River. This river converges with the Red River in St. Norbert, at the southern perimeter of the City of Winnipeg and has a watershed over 2,400 km^2 (Government of Manitoba 2010). The Seine River has a watershed of about 2,500 km^2 and is a southeasterly tributary that originates in the Sandilands Provincial Forest, Manitoba (Government of Manitoba 2009).

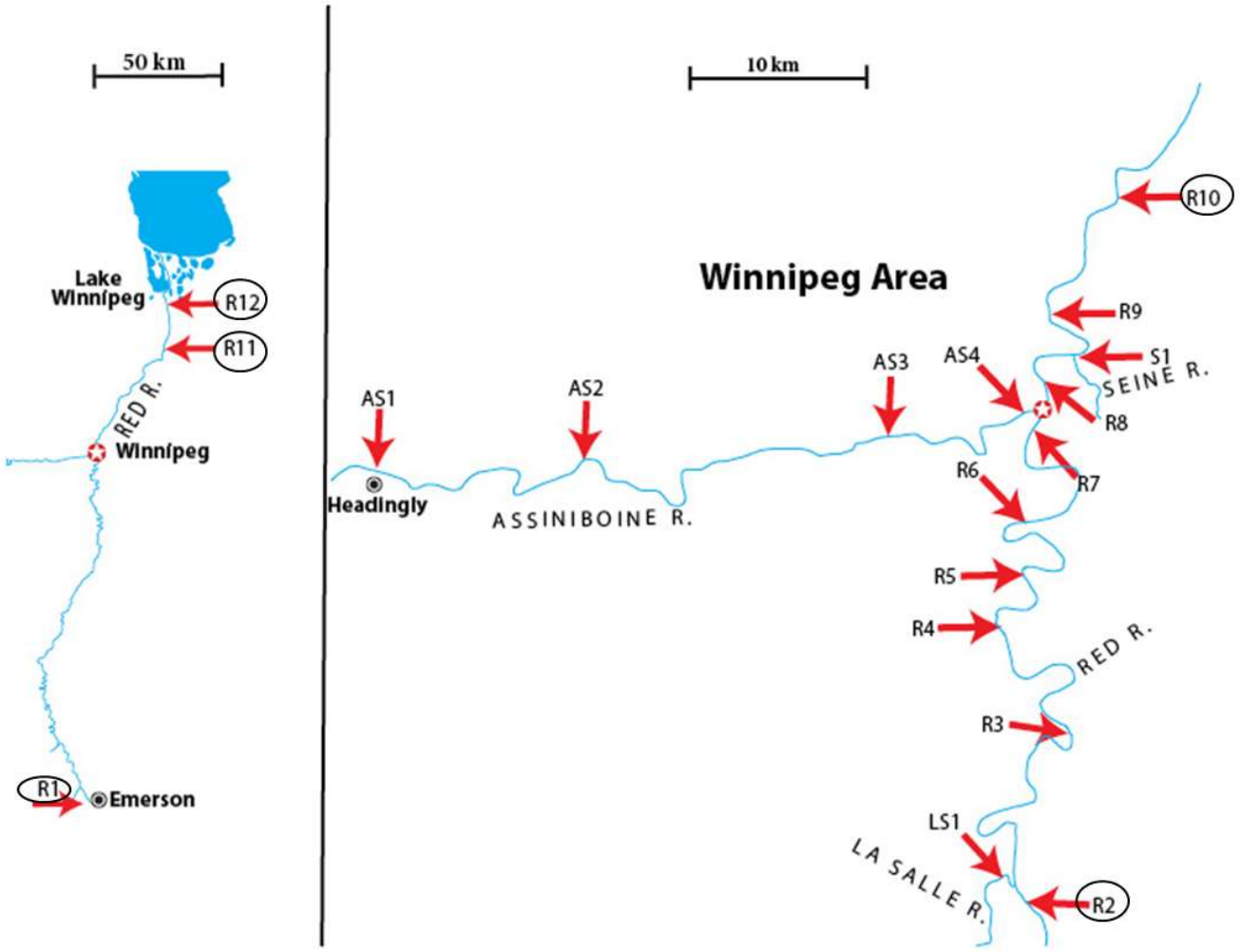


Figure 2.1: Map of sampling locations in 2017 (with the five sampling locations in 2016 identified by circled numbers). The left portion highlights the Canadian portion of the Red River from the US border to the dischargeat Lake Winnipeg. The right portion highlights all other sampling locations.

2.3.2 Sample locations and collection

Segments between two sampling locations were selected so that some segments were flowing through agricultural land, and other segments were flowing through urban land uses, including golf courses. Sampling location R1 is the point at which the Red River enters Canada from the United States (Figure 2.1). R12 is in the discharge zone of the Red River into Lake Winnipeg with a mostly swampy area between R11 to R12. Some sampling locations were chosen to include river segments flowing through

annual cropland such as upstream from R1, between R1 and R2, and upland from AS1. Other river segments were flowing through urban landscapes with golf courses and other urban spaces in which pesticide applications might occur. This included river segments flowing through the City of Winnipeg (i.e., between R4 and R5, from R5 to R10, and from AS2 to AS4) and its suburban areas (i.e., from R2 to R4, from R10 to R11, between AS1 and AS2, and upland from LS1 and S1). Location R4 is adjacent to a large cemetery and municipal park; R5 to a large municipal park; R6 to a municipal park and golf course; and R11 to a golf course. As well, R9 is just after Winnipeg's largest cemetery and R10 is just after Winnipeg's largest municipal park, golf course and North End Sewage Treatment Plant.

Samples were collected on a biweekly basis from May 1 to August 30, 2017, which corresponds to the timing of pesticide applications in the region. Water-column samples (n=162) were collected from all 18 locations and bottom sediments (n=54) were collected from five locations in the Red River (R1, R2, R10, R11, R12) and from one location in the Assiniboine river (AS1). These five locations in the Red River had also been sampled biweekly from May to August in 2016 (Figure 2.1), for a total of 40 water and 40 bottom sediment samples in 2016. Water samples (1 L) were collected by grab sampling at a distance of ~10 m from the riverbank and a depth of ~40 cm below the surface of the water and preserved in autoclaved 1 L amber bottles stored at 4^{o}C. Samples were extracted and analyzed within 3-5 days of collection. Bottom sediments were collected using an Ekman dredge at a distance of ~5 m away from the riverbank and stored in black sterile sampling bag at -20^{o}C until extraction were performed at the end of the sampling season.

2.3.3 Sample Extractions and Quantifications

A total of 202 water-column and 94 bottom sediment samples were collected across 17 sampling times. All samples collected in 2016 were screened for 160 pesticide compounds. Bottom sediment samples in 2017 were screened for 165 pesticide compounds. Water-column samples in 2017 were screened for 172 pesticide compounds, including seven neonicotinoids that were not screened for in bottom sediments. The small differences in the number of pesticide compounds analyzed in each year reflected new method development in the Agriculture and Agri-food Canada Lethbridge Research and Development Centre, which is an ISO17025 federal government laboratory. All mass spectrometric analyses used validated in-house quantitative methods including multiple reaction monitoring and surrogate internal standards. The detected concentrations below the limit of quantification were assigned values of zero. All pesticide chemicals were identified and quantified by gas chromatography mass spectrometry (GC-MS), except for ten current active-ingredients that were identified and quantified by liquid chromatography tandem mass spectrometry (LC-MS/MS). These were herbicide glyphosate and its main metabolite aminomethylphosphonic acid (AMPA), as well as herbicide glufosinate-ammonium, and the seven neonicotinoid insecticides.

Water samples: For the pesticide chemicals analysed by GC-MS, river water samples were filtered through ashed glass wool and transferred into 2 L separatory funnels for liquid-liquid extraction described in Munira et al. (2018). Briefly, each sample was extracted using dichloromethane, extracts were dried using acidified Na_2SO_4 and methylated with the addition of diazomethane. Diazomethane was neutralized with hexane, nitrogen gas (flow rate 7-10 psi) was used to remove the remaining diazomethane from the sample afterwards and final volume was adjusted to 10 ml. For glufosinate, glyphosate and AMPA extraction of water sample was done by adding internal standard mixture of

glufosinate-d_3, glyphosate-^{13}C, AMPA-^{13}C, then concentrated HCl and acetonitrile sequentially to the sample. After centrifuging at 4000 rpm for 5 min. at 5°C, borate buffer (4.75g disodium tetraboratedecahydrate in 250 ml deionized water and pH adjusted to 10 with NaOH) and FMOC-Cl (1.5mg flurenylmethyloxycarbonil chloride- per ml acetonitrile) were added to the collected top layer. Formic acid was added after 30 min. incubation of the samples. The final extracts were filtered into vials through 0.2µm PTFE 13 mm acrodisc filters prior to analysis by LC-MS/MS. Water sample extraction for neonicotinoids followed only filtration using 0.2µm PTFE luer lock cartridges and analyzing directly by LC-MS/MS along with control samples.

Sediment Samples: Wet sediments were freeze dried (Scientific freeze dryer, Harvest Right™, USA; -37^{0}C for 24 hours) and stored at -20^{0}C until extracted as described Gamhewage et al. (2019). Briefly, freeze-dried sediment samples were extracted using $MgSO_4$ salt in the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method. The supernatant was methylated with diazomethane followed by transferring to hexane and adjusting the final volume to 2 mL using a rotary evaporator.Sediment samples extraction for glufosinate, glyphosate and AMPA followed the same procedure as water samples except using .6M KH_2PO_4 for repeated extraction prior to adding internal standard mix and other chemicals.

2.3.4 Statistical Analysis and Other Data Collection

PROC TTEST in SAS 9.4 (SAS Institute Inc. 2013) was used with significance level $P < 0.05$ to determine treatment effects for 7 frequently detected pesticides in water column. This analysis was done for the pesticides flux in two locations (R1, R11) and 2 years (2016, 2017).

In addition, to facilitate the 2017 data interpretation, we calculated the relative proportions of major crops grown in the stretch of land spanning 3 km along both sides of the Red River. Data for the calculations were obtained from raster maps (Government of Canada 2019) followed by processing in ArcMap 10.4.1. Subsequently, the types of pesticides registered for use on these crops were obtained from the Guide to Crop Protection 2017, Manitoba (MGCP 2017) along with regional information about the stage of crop growth and timing of pesticide spray applications from the 2017 Manitoba Crop Report (MCR 2017). In addition, upstream (R1) and downstream (R11) in the Red River, the pesticide flux (μg/day) was calculated for selected active ingredients by multiplying their concentrations (μg/l) in the water-column by the discharge flow rate (m^3/s) data available at these sampling locations (Government of Canada 2022).

2.4 Results and Discussion

About 70% of the 172 pesticide compounds screened for in 2017 were not detected, including 57 current-use active ingredients. Around 62% (water-column) and 60% (bottom-sediment) of the active ingredients detected were already present in R1 samples because of transboundary contamination as previously reported (Challis et al. 2018; Gamhewage et al. 2021). (In 2016, this was 73% and 67%, respectively). Samples taken at R1 and R2 contained a total of 21 unique active ingredients in the water-column, similar to the number of unique active ingredients in the water-column at R11 and R12 combined. 95 % of the compounds detected in the water-column samples of R11 or R12 were also detected at R1 or R2, suggesting that the compounds are either persistent in the river system and/or are degraded and added as the river flows from the Canadian-US boarder to Lake Winnipeg. Among the herbicides most frequently detected in the water-column, in both years, 2,4 D and clopyralid had significantly higher mean flux ($p< 0.05$) at R11 than at R1 because of greater concentration and

discharge flow rate at that location. The atrazine mean flux was also greater at R11 than at R1 but only in 2017. Flux data for these pesticides in R1 and R11 sampling location, 8 sampling weeks and both the years are displayed in (Figure 2.2). There were no significant differences in bentazone, dicamba, MCPA, metolachlor flux between Emerson (R1) and Selkirk (R11) locations. Insecticide malathion was detected in the water-column of R11 or R12 but not in R1 or R2, and was first detected at La Salle River (LS1), Assiniboine River (AS2) and Seine River (S1). Herbicide triclopyr was found only in urban areas such as locations adjacent to golf courses, and not in agricultural locations.

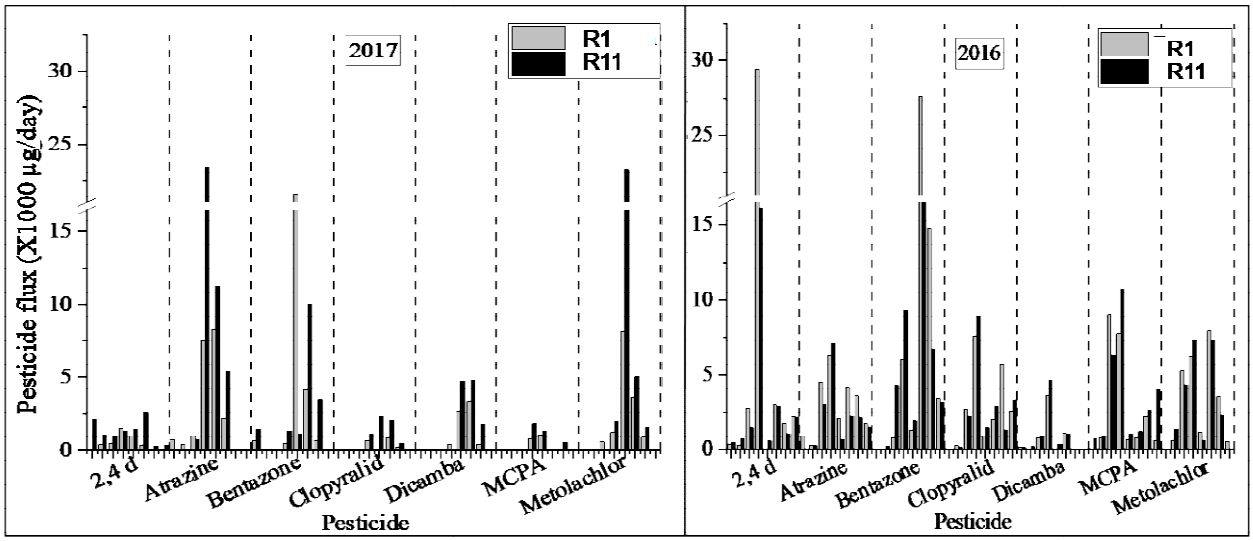


Figure 2.2: Pesticide flux by frequently detected pesticides for 8 sampling weeks in Red River in 2017 and 2016

Samples taken at R1 and R2 contained a total of 20 unique active ingredients in bottom-sediments whereas 19 unique active ingredients were detected in bottom sediments at R11 and R12 combined. About ~40 % of the compounds detected in the sediment samples of R11 or R12 were not detected at R1 or R2, which suggests that pesticides are partitioning from the water-column to bottom sediments in the Red River, and it further appears that this particularly occurred in the swampy area (R11, R12). Specifically, those detected in sediment of R11 or R12 but not R1 or R2 were first detected at R11

(herbicide carfentrazone, insecticide p,p-DDT), R12 (fungicides etridiazole and iprodione and insecticide isofenphos) and AS1 (herbicide bentazone).

A total of 34 unique compounds were detected in the water-column (Figure 2.3) of which 62% were herbicides, 18% were insecticides, and 20% were fungicides. Of those detected (n=34), 88% were active ingredients in pest control products registered for current use in Manitoba with the other compounds being legacy (6%) or active ingredients never registered for use in Canada (6%). Eight current-use active ingredients were detected in the water-column of all four rivers including four insecticides (i.e., clothianidin, imidacloprid, malathion, thiamethoxam), three herbicides (i.e., 2,4-D, bentazone, MCPA), and one fungicide (boscalid). Current-use active ingredients such as atrazine, bentazone and metolachlor were detected at relatively larger concentrations in the water-column than other active ingredients (Figure 2.3). Only six of the detected active ingredients in the water-column have set Canadian Water Quality Guidelines (CWQG) for the Protection of Aquatic Life (CCME, 2022) and their individual concentrations in the water-column were always below their respective guidelines (Table 2.1).

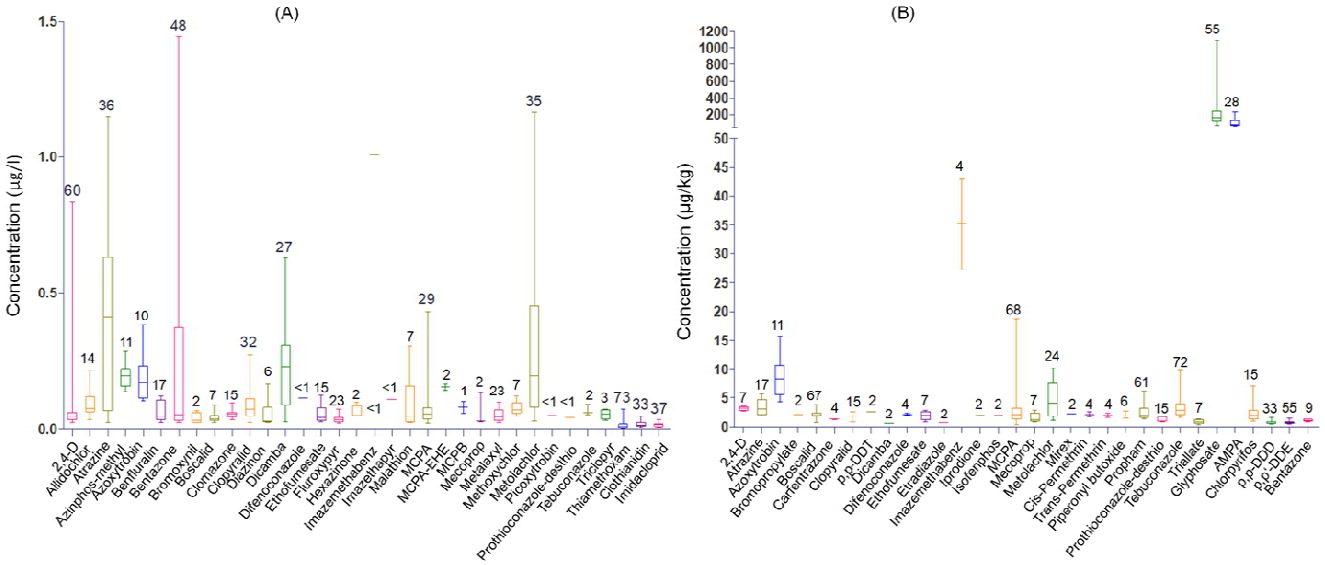


Figure 2.3: Box plots of each pesticide compounds detected in water (A) and sediment (B) during this study. Shown are the minimum, maximum, 25% and 75% quartiles, and the median. The values above the data are the detection frequencies (%).The pesticides detected in the water grab samples (n=162) and sediment samples (n=54) taken in the four rivers from May 1 to Aug 31, 2017

Table 2.1 Maximum concentrations and detection frequency (%) of pesticides in water samples of Red River and tributaries during the entire growing season (May- August 2017) Red River (n=108), Assiniboine River (n=35), La Salle River (n=9), and Seine River (n=9). Pesticides indicated in bold were detected in sediment as well. River with underlined detection frequency contained maximum concentration of each pesticide, ND= none detected, NG= no guidelines

	Detection Frequency (%)				Maximun Concentration ($\mu g\ L^{-1}$)	CWQG ($\mu g\ l^{-1}$)
	Red R	Assiniboine R	La Salle R	Seine R		Fresh water
Chemical			**Herbicide**			
2,4-D	70	23	78	78	0.835	4
Bentazon	53	28	78	34	1.444	NG
MCPA	31	17	56	22	0.435	2.6
Triclopyr	ND	ND	56	ND	0.075	NG
Metolachlor	52	ND	11	ND	1.165	7.8
Atrazine	50	ND	11	34	1.15	1.8
Dicamba	38	ND	11	22	0.629	10
Clopyralid	36	28	22	ND	0.274	NG
Fluroxypyr	33	9	ND	ND	0.075	NG
Ethofumesate	22	ND	ND	ND	0.123	NG
Benfluralin	21	ND	22	22	0.123	NG
Clomazone	20	ND	22	ND	0.097	NG
Allidochlor	19	ND	22	ND	0.213	NG
MCPB-methyl	ND	ND	ND	22	0.103	NG
Mecoprop	ND	ND	11	22	0.136	NG
Bromoxynil	3	ND	ND	11	0.070	5
Hexazinone	ND	11	ND	ND	0.100	NG
MCPA-EHE	ND	6	ND	ND	0.166	NG
Imazamethabenz	ND	3	ND	ND	1.008	NG
Imazethapyr	1	ND	ND	ND	0.109	NG
			Insecticide			
Thiamethoxam	78	70	67	34	0.076	NG
Imidacloprid	39	14	56	11	0.047	0.23
Clothianidin	49	9	11	22	0.035	NG

Malathion	6	3	22	22	0.305	NG
Azinphos-methyl	15	ND	22	ND	0.286	NG
Diazinon	7	ND	11	22	0.167	NG
Methoxychlor	10	ND	11	ND	0.123	NG
	Fungicide					
Boscalid	1	9	67	11	0.090	NG
Metalaxyl	34	ND	11	11	0.100	NG
Azoxystrobin	13	3	11	ND	0.385	NG
Tebuconazole	2	ND	11	ND	0.094	NG
Picoxystrobin	ND	ND	11	ND	0.052	NG
Prothioconazole-Desthio	ND	ND	11	ND	0.042	NG
Difenoconazole	ND	3	ND	ND	0.115	NG

A total of 32 unique compounds were detected in bottom sediments of which 78% are current-use active ingredients in Manitoba (Figure 2.3). More than one-half of the unique compounds detected in bottom sediments were insecticides (28%) and fungicides (28%), with the remaining compounds being herbicides (44%) or acaricides (3%). Current-use fungicides tebuconazole (72%), boscalid (67%) and propiconazole (61%) and current-use herbicides MCPA (68%) and glyphosate (55%) were the top five most frequently detected pesticide compounds in bottom sediment. Glyphosate (mean 224 µg/kg; max. 1,088 µg/kg) and its primary metabolite AMPA (mean 106 µg/kg; max. 229 µg/kg) were detected at much greater concentrations in bottom sediments than other pesticide compounds (Figure 2.3). Glyphosate and AMPA were never detected in water-column samples (Figure 2.3). Current-use herbicide imazamethabenz was also detected at relatively large concentrations in bottom sediments while only detected once in the water-column.

Although about the same number of active ingredients were detected in the water-column and bottom sediments, only 15 active ingredients were detected in both compartments (67% herbicides and 33% fungicides). The 17 active ingredients detected in bottom sediments but not in water-column included 23% herbicides, 53% insecticides, 18% fungicides, and 6% acaricide of which 59% were current-use

active ingredients. The 15 active ingredients detected in the water-column but not bottom sediments are all current-use pesticides (54% herbicides, 33% insecticides, and 13% fungicides). More legacy active ingredients were detected in bottom sediments (9%) than the water-column (6%).

In 2017, water-column (86%) and bottom sediments (77%) frequently contained two or more compounds. In 2016, this was 100% and 85% respectively. Other water-column samples showed single (9%) or no (5%) detections. Similarly, only 6% of the bottom sediment samples showed a single detection and 7% had no detections. Seven water-column samples without detections came from the Assiniboine River (last two sampling weeks in August) and two water-column samples without detections came from the Seine River (first and third sampling weeks in May). Bottom sediment samples showing no detections also came from the Assiniboine River and were obtained during the last four sampling cycles in July-August 2017.

The La Salle River has a watershed that is at least 100-fold smaller than the Red River but both the La Salle River (25 total unique compounds) and the Red River (25) had the largest number of unique compounds detected in water-column samples. The La Salle River with its relatively small drainage basin (2,400 km^2) had a more diverse range of unique compounds (25) than the Assiniboine River (15) and the Seine River (16). Both the Red River and La Salle watersheds are characterized by clay-rich soils (AAFC, 2009) and this might have increased pesticide loadings into the rivers for example during rain- or snowmelt runoff that is common in the area known as the Red River Valley. This compares to the Assiniboine River and Seine River basins that are characterized by sand-rich soils that are less prone to runoff (AAFC 2009). The Assiniboine River has a large drainage basin (163,000 km^2) and during the 2017 sampling period (May to August) its mean water discharge was 388.6 m^3 s^{-1}. (Government of Canada 2022) and such relatively high discharge rate might have contributed to the

dilution of pesticide concentrations. For example, the La Salle River had a mean water discharge of 0.38 m^3 s^{-1} during respected sampling period (Government of Canada 2022).

For the pesticides that were detected in the water-column of all four rivers,the three neonicotinoids (i.e., clothianidin, imidacloprid, thiamethoxam) were always detected at concentrations < 0.08 µg L^{-1} which is well below the CWQG for the Protection of Aquatic Life for imidacloprid (clothianidin and thiamethoxam do not have guidelines) (CCME 2022). Thiamethoxam (73 %) was more frequently detected than clothianidin (33%) and imidacloprid (36%) (Figure 2.3). These neonicotinoids are predominantly used as seed treatment in oilseed and cereal crops widely grown in the Prairies and have moderate to high water solubilities ranging from 340 to 4,100 mg/L and are moderately to very persistent in soil with typical soil half-lives ranging from 50 to 545 days (Lewis et al. 2016). Other studies in Canada detected these neonicotinoids at typically larger concentrations, in the ranges of 0.059 to 3.11 µg L^{-1} for clothianidin, 0.0047 to 6.10 µg $L^{-1}$for imidacloprid, and 0.83 to 1.49 µg $L^{-1}$for thiamethoxam (Government of Quebec 2011; Lalonde and Garron 2020; Main et al. 2014).

Auxins 2,4-D and MCPA were also detected in all four rivers despite both herbicides being classified as non-persistent in the environment, i.e., typical soil half-lives of <25 days (Lewis et al. 2016). Both molecules have a high water solubility (>20,000 mg/L) and are similar except for a slight difference at position two of the benzene ring (MCPA has a methyl versus 2,4-D has a chlorine); they are environmentally mobile (Lewis et al. 2016). Both active ingredients continue to be popular and have been used for decades to provide for broad spectrum weed control management in small grains and in non-agricultural applications such as vegetation control along rights-of-ways such as railway tracks (Health Canada 2010).

Herbicides bentazone, fungicide boscalid and insecticide malathion were also detected in all four rivers. Boscalid is very persistent in soil (DT50=484 days) and has low water solubility (4.6 mg/l) (Lewis et al. 2016). Boscalid transport into Canadian rivers by snowmelt and rainfall runoff has been reported (Metcalfe et al. 2019). Both bentazone (DT50=20 days) and malathion (DT50 <1 day) are non-persistent in soil but have high (bentazone=7,112 mg/l) and moderate (malathion=148 mg/l) water solubilities (Lewis et al. 2016). Studies have reported on malathion surface runoff from agricultural fields and urban sites (Newhart, 2006). Bentazone surface runoff from agricultural fields into rivers and streams also has been reported (Kratzer 1998; Riise et al. 2004).

In 2016, there were a total of 22 (water-column) and 27 (bottom-sediment) active ingredients detected at sampling locations R1, R2, R10, R11 and R12. Herbicides 2,4-D (95%), MCPA (95%), atrazine (90%), clopyralid (88%) and bentazone (83%) were the top 5 most frequently detected active ingredients in water-column samples in 2016. In 2017, at these same sampling locations, this was also 2,4-D, atrazine, bentazone and clopyralid, as well as metholachlor with MCPA ranking sixth. Auxin herbicides such as 2,4-D, MCPA and clopyralid have been frequently detected herbicides in other surface water studies of Canada (Grover et al. 1997; Waite et al. 2002; Donald et al. 2007).

The year 2017 was comparatively a drier year than 2016 which played role on the difference of the detection pattern of pesticides in Red River (Figure 2.4). Both the total concentrations and the number of unique compounds in samples also varied during the season and to a lesser extent between sampling locations (Figure 2.5). Auxin herbicides were often present as mixtures in the water-column and bottom sediments but there were notable differences between years for the five locations samples . For example, almost all (93%) of the water-column samples in 2016 contained 2,4-D, clopyralid and MCPA as mixtures whereas this was only 23% of the water-column samples taken from the same

locations in 2017. As well, only a total of 12 active ingredients were detected in the water-column in both years. This included 75% herbicides (2,4-D, atrazine, bentazone, bromoxynil, clopyralid, dicamba, fluroxypyr, MCPA, and metolachlor) and 25% fungicides (azoxytrobin, boscalid, and metalaxyl). In addition to the parent compounds, it is well known that transformation products, both biotic and abiotic, of chemical mixtures can still pose risks to non-target organisms in fluvial systems (de Jongh et al. 2012). Thus, pesticide mixtures are comprised of more than the active ingredients that were the focus of this study and so the concentrations of mixtures can in fact be more extensive than assessed here.

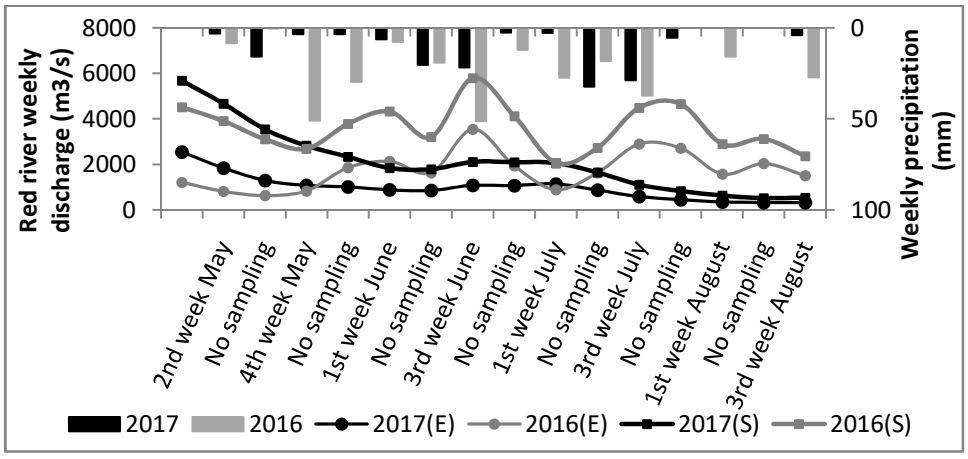


Figure 2.4 Weekly discharge data (lines) of Red river from R1 (E-Emerson) and R11 (S-Selkirk); precipitation data (bars) from Winnipeg International Airport weather station (Government of Canada, 2017, 2022)

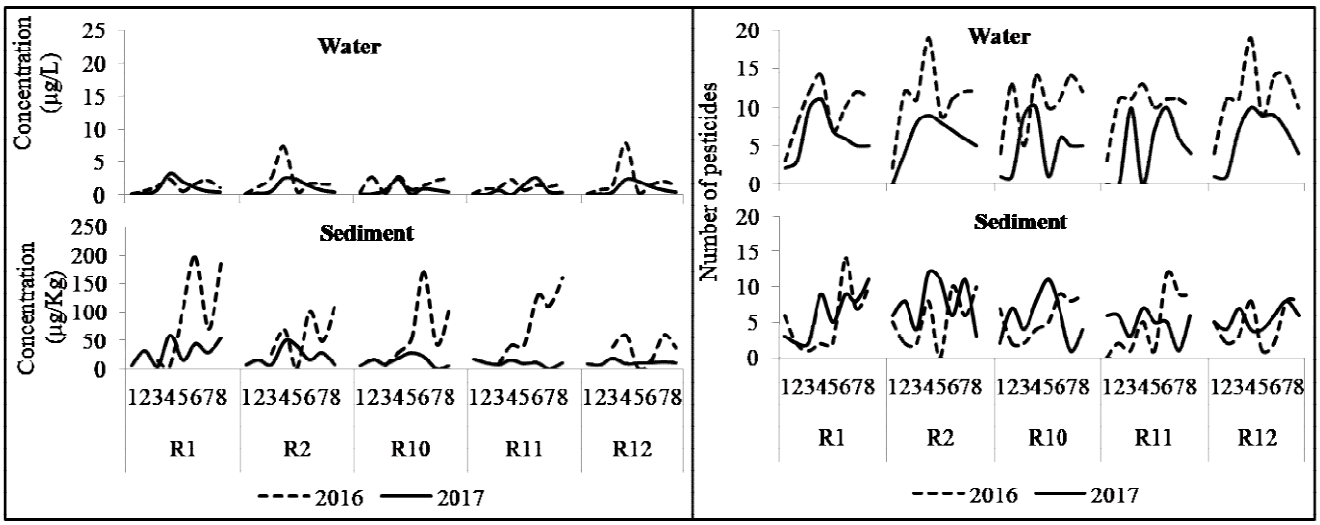


Figure 2.5 Pesticides as mixture in water and sediment of Red river

Herbicides MCPA (77%) and clopyralid (51%), and fungicides tebuconazole (48%), boscalid (48%) and azoxytrobin (46%) were the top 5 most frequently detected active ingredients in bottom sediment samples in 2016. In 2017, at these same sampling locations, tebuconazole, MCPA and boscalid were also within the top 5 most frequently detected, with the other active ingredients being metolachlor and propiconazole. For the five sampling locations, commonly a total of only 15 active ingredients were detected in the bottom sediments in both years. These were 47% herbicides (2,4-D, bentazone, clopyralid, MCPA, mecoprop, metolachlor and triallate), 40% fungicides (azoxytrobin, boscalid, difenoconazole, propiconazole, prothioconazole-desthioand tebuconazole) and 13% insecticides (clorpyrifos and the synergist piperonil butoxide).

Along the Red River in 2017, the relative proportions of annual crops grown were soybean (32%), wheat (26%), canola (23%), corn (10%) and oat (9%). As a comparison, the relative proportions of crops grown at the provincial scale decreased in the order of canola 32% > wheat 26% > soybean 24% > corn 5% >oats 5% and other crops 8% (sunflower, beans, pea, rye, lentil, potato etc.) (MASC 2017).

Table 2.2 shows the pesticides detected in this study and at what crop stage these current-use pesticides are typically applied. Pesticide detections in the water-column most frequently occurred in the post-emergence stage although 2,4-D and mecoprop was often detected in the pre-emergence stage as well (Table 2.3). Water-column samples were relatively free of pesticides at the post-harvest stage (Table 2.3), suggesting that they were degraded and/or were partitioning into bottom sediments. Pesticides were perhaps more consistently detected in bottom-sediments regardless of the crop stage (Table 2.3), suggesting that current-use pesticides can be persistent in sediment and/or are readily partitioning from the water-column to the bottom sediment in the growing season. In general, temporal variability of pesticide concentrations in sediment samples is less compared to water samples (Vryzas et al. 2018). Moreover, pesticide concentration in sediment is affected less by extreme rainfall and runoff events compared to water samples.

Table 2.2 Pesticides registered for use in the crops grown on land adjacent to the Red River in Manitoba, Canada (MGCP 2017)

Crops	Seed treatment, Pre emergent	Post emergent	Pre harvest
Soybean	Azoxytrobin, Bentazone, Carfentrazone, glyphosate, Thiamethoxam	2,4 D, Boscalid, Imazethapyr, Tebuconazole	Boscalid, Carfentrazone, glyphosate
Corn	Atrazine, Carfentrazone, Clothianidin, glyphosate, Metolachlor, Thiamethoxam	2,4 D, Atrazine, Azoxytrobin, bentazon, Dicamba, MCPA	Carfentrazone
Wheat	Carfentrazone, Clothianidin, Dicamba, Thiamethoxam	2,4 D, Bromoxynil, Clopyralid, Dicamba, MCPA, Mecoprop, Tebuconazole, Fluroxypyr	Carfentrazone, glyphosate
Canola	Carfentrazone, Clothianidin, glyphosate, Thiamethoxam	Azoxytrobin, Boscalid, Imazethapyr, bromoxynil, MCPA	Glyphosate
Oat	Carfentrazone	Fluroxypyr, MCPA, Mecoprop, Tebuconazole	Glyphosate

Table 2.3 Detection (%) of active ingredients (a.i) among commonly used pesticides within the pre-emergence, post emergence and pre harvest pesticides application completion period (MCR 2017) (Application completed for pre emergence a.i. by 2nd week of June, post emergence 3rd week of July, pre harvest 3rd week of August; W= water-column, S=sediment)

Active ingredients (a.i)	Pre emergence stage (sampling 1st week May to 1st week Jun.)	Post emergence stage (sampling 3rd week Jun. to 3rd week Jul.)	Pre harvest stage (sampling 1st week to 5th week Aug.)
Atrazine	8% (W)	90% (W), 67% (S)	2% (W), 33% (S)
Azoxytrobin	17% (S)	100% (W), 50% (S)	33% (S)
Bentazone	18% (W), 40% (S)	82% (W), 40% (S)	20% (S)
Boscalid	18% (W), 42% (S)	82% (W), 44% (S)	14% (S)
Bromoxynil		100% (W)	
Clopyralid	4% (W), 67% (S)	94% (W), 33% (S)	2% (W)
Clothianidin	23% (W)	77% (W)	
Dicamba		100% (W), 100% (S)	
2,4-D	28% (W), 50% (S)	63% (W), 50% (S)	9% (W)
Fluroxypyr		100% (W)	
Imazethapyr		100% (W)	
MCPA	4% (W), 32% (S)	94% (W), 49% (S)	2% (W), 19% (S)
Mecoprop	33% (W), 50% (S)	67% (W), 50% (S)	
Thiamethoxam	43% (W)	57% (W)	

2.5 CONCLUSION

The results from this study reveal that both agricultural and urban areas play a role to load pesticides into river systems, but there was no clear impact of these different land use systems on the types and concentrations of compounds detected across sampling locations. Sampling years influenced both the number and concentrations of pesticides detected in water and sediment samples and hence multi-year studies are important to delineate such differences. Concentration and number of detected pesticides were higher in water and sediment samples in 2016 than 2017. The year 2017 was comparatively a drier year than 2016 which played role on the difference of the detection pattern of pesticides in the Red River. The most frequently compounds detected were auxin herbicides and neonicotinoid insecticides in water-column samples and fungicides and herbicide glyphosate in bottom sediment samples. In general, there were substantial differences in types of active ingredients detected in water-

column versus bottom sediments, indicating the importance of sampling both matrices to fully understand river contamination by pesticides. None of the concentrations detected exceeded the Canadian Water Quality Guidelines for the Protection of Aquatic Life, but only 6 out of 40 detected pesticide compounds have guidelines established. Pesticides were frequently present as mixtures and there is a need to establish water quality guidelines in Canada that take such mixtures in to consideration.

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3. SORPTION OF PESTICIDES BY MICROPLASTICS, CHARCOAL, ASH AND RIVER SEDIMENTS

3.1 Abstract

In addition to sediments, pesticides can be sorbed to other constituents present in rivers including ash, charcoal and microplastics. Pesticide sorption by microplastics has been studied for hydrophobic compounds such as the legacy insecticide DDT (dichlorodiphenyltrichloroethane) but not for current-use herbicides. The purpose of this study was to investigate to what extent 2,4-dichlorophenoxyacetic acid(2,4-D) (weak-acid), atrazine (weak-base) and glyphosate (zwitterion) are sorbed by microplastics (i.e., fiber, polyethylene beads, polyvinyl chloride (PVC) and tire fragments) and other river constituents (i.e., ash, charcoal, suspended and bottom sediments). DDT was included in the study to provide reference data that could be compared to known literature values. Batch equilibrium experiments were conducted following guidelines 106 of the Organisation for Economic Co-operation and Development (OECD106, 2000). Experiments utilized either a 1:100 solid/solution ratio with 0.1g of a river constituent as the sorbent, or a 1:5 solid/solution ratio with the sorbents consisted of 1.9 g bottom sediments mixed with 0.1 g of a river constituent. Background solutions included 0.01 M $CaCl_2$ or 0.01 M KCl, deionized water and river water. Individual microplastics always sorbed >50% of DDT. Current-use herbicides had a weak affinity for microplastics (< 6%) except that a substantial amount of glyphosate was sorbed by PVC (32-36%) in 0.01M KCl and DI water. When river water was used as a background solution, rather than 0.01M KCl or deionized water, there was much less glyphosate sorption by PVC, ash, charcoal, and both sediments. This suggested that ions present in river water competed for sorption sites with glyphosate molecules. Across background solutions, sorption by sediments decreased in the order of DDT (91-95%) > glyphosate (36-88%) >atrazine (5-13%) >2,4-D (2-5%).Sorption of 2,4-D, atrazine and DDT by ash and charcoal was always > 90%, but < 35% for glyphosate. Relative to bottom sediments alone, the presence of ash or charcoal [5% by

weight] with sediments significantly increased the sorption of 2,4-D, atrazine and DDT. Microplastic additions [5% by weight] had no impact on all 4 pesticides sorption by sediments. Microplastics are not a strong sorbents for current-use herbicides, although there are exceptions such as glyphosate by PVC. Ions present in river water competed with glyphosate for sorption sites of river constituents. Hence, the types and concentrations of ions present in rivers might have some influence on the partitioning of glyphosate between the water-column and solid phase, including glyphosate fate processes in rivers.

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3.2 Introduction

Pesticides enter rivers due to a number of processes such as atmospheric wet and dry deposition, rainfall and snowmelt runoff, as well as ground water recharge (Squillace et al. 1993; Waite et al. 2004; Cabrerizo et al. 2019). Depending on their physico-chemical properties, pesticides in rivers reside in either the water-column or sediments, or in both matrices (Rawn et al. 1999; Glozier et al. 2012; Ensminger et al. 2013; Ronco et al. 2016; Gamhewage et al. 2019). Mathematical models that estimate pesticide fate in rivers commonly include a sorption parameter (e.g., Kd, Koc) because when a pesticide is sorbed by sediments, it has different degradation rate and transport potential than when the same pesticide is dissolved in the water-column. There is substantial information available on pesticide sorption parameters as it relates to sediments (Chefetz et al. 2004; Gaultier et al. 2009; Dollinger et al. 2015; Gamhewage et al. 2019), but less so as it relates to other potential constituents present in rivers such as microplastics, ash and charcoal.

A wide range of studies have highlighted the persistence of microplastics in surface waters in North America, Europe as well as Asia (Moore et al. 2011; Eriksen et al. 2013; Castañeda et al. 2014; Free et al. 2014; Lechner et al. 2014; Anderson et al. 2017). For example, the water-column of the Red River was found to contain more than 800,000 microplastics/km^2 at a sampling location in the Province of Manitoba, Canada (Warrack et al. 2017). Microplastics are per definition particles ≤5 mm and might include fiber, polyethylene (PE) beads, polyvinyl (PVC) and tire fragments, all of which have been detected in surface waters (Thompson et al. 2009; Arthur et al. 2009; Castañeda et al. 2014; Wagner et al. 2014; Warrack et al. 2017; Sighicelli et al. 2018; Wang et al. 2018; Leads & Weinstein 2019). Microplastics are present in the water-column but also in bottom sediments because microplastics are likely to settle at some rate depending on factors such as polymer density. Graca et al. (2017) found

that the density of microplastics were predominantly >1 g cm^{-3} when detected in the surface layer of marine bottom sediments but <1 g cm^{-3} when detected in the surface layer of beach sediments.

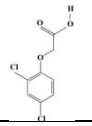
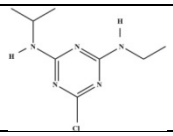
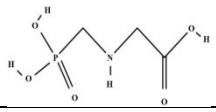
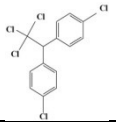
When present in water systems, microplastics are believed to act as carriers for transporting contaminants but studies have predominantly focused on persistent organic pollutants such as legacy insecticide DDT (dichlorodiphenyltrichloroethane), as well as on pharmaceuticals and personal care products. For example, in batch equilibrium studies these chemicals were shown to have a high sorption affinity for materials such as PVC, PE powder, polystyrene and tire fragments (Bakir et al. 2014; Lee et al. 2014; Wu et al. 2016; Hüffer et al. 2019; Sharma et al. 2020). DDT and some of its metabolites have been detected in microplastics residing in surface waters, at concentrations ranging from 22 to 7,100 ng/g microplastic (Rios et al. 2007). DDT also continues to be detected in bottom sediments of surface waters throughout North America and elsewhere (Lembcke et al. 2011; Kuo et al. 2012; Kurek et al. 2019).

Current-use herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) (weak-acid; pKa=2.87 at 25^{o}C), atrazine (weak-base; pKa=1.70 at 25^{o}C) and glyphosate (zwitterion; pKa= 2, 2.6, 5.6 and 10.6 at 25^{o}C) are being detected in both the water-column and bottom sediments of North American rivers (Wan et al. 2006; Glozier et al. 2012; Ronco et al. 2016; Basiuk et al. 2017; Gamhewage et al. 2019). It is well known that carbon-rich substances such as ash and charcoal might retain these herbicides to some extent (Alam et al. 2000; Karapanagioti et al. 2004; Igwe et al. 2012; Ghosh & Singh 2013). Ash and charcoal loadings to rivers particularly occur when large regions are impacted by forest fires such as in recent years in Australia and Canada (Parks Canada 2018; Alberta Agriculture and Forestry 2019; Woodward 2020). In addition to atmospheric deposition of ash and charcoal, the increased surface runoff and erosion occurring post fire is responsible for enhancing the transport of sediment, ash,

charcoal and other debris to surface waters (Anshari et al. 2001; Karapanagioti et al. 2004; Smith et al. 2011; Mansilha et al. 2019; Rhoades et al. 2019). Coal fly ash released by coal burning power plants can also enter surface waters, for example due to waste water discharge or atmospheric deposition (Eriksen et al. 2013).

The objective of this batch equilibrium study was to investigate to what extent 2,4-D, atrazine and glyphosate are sorbed by microplastics (i.e., fiber, polyethylene beads, polyvinyl (PVC) and tire fragments) and other river constituents (i.e., ash, charcoal, and suspended and bottom sediments), and how this compares to the sorption potential of legacy pesticide DDT by these river constituents. We hypothesize that because of their contrasting physicochemical properties (Table 3.1), pesticides will each show distinct characteristics in their relative affinity for common constituents detected in rivers, including sediments, ash, charcoal and a range of microplastics.

Table 3.1 Molecular structure and physicochemical properties of the pesticides used in the study (Sprankle et al., 1975; Lewis et al. 2016; PubChem Compound Database, 2020). Solubility = Solubility in Water (mgL^{-1}) at 20^0C; log Kow = log Kow at pH 7, 20^oC; Soil ½-life = Soil half-life (days) at 20^oC; Sediment ½-life = Sediment half-life (days), except for DDT (years).

	2,4-D	Atrazine	Glyphosate	DDT
				
Solubility	23,180	35	10,500	0.006
logKow	-0.83	2.70	-3.20	6.91
pKa@25°C	2.87	1.70	2, 2.6, 5.6, 10.6	-
Koc	39.3	100	1424	151000
Soil ½-life	4.4	75	15	6,200
Sediment ½-life	18.2	80	9.9	>150 years

3.3 Materials and methods

3.3.1 Pesticides and sorbents

Pesticides used were 2,4-dichlorophenoxy acetic acid [ring-^{14}C(U)] (>99% radiochemical purity; specific activity 55 mCi/mmol) with analytical grade 2,4-D (99%);atrazine [ring-^{14}C(U)] (>99%, 160 mCi/mmol) with analytical grade atrazine (99%); glyphosate [phosphonomethyl-^{14}C](>99%,55 mCi/mmol) with analytical grade glyphosate (99% chemical purity); and 4,4'-dichlorodiphenyltrichloroethane [ring-^{14}C(U)] (>99%, 12.8 mCi/mmol) with analytical grade DDT (99%). Pesticides were purchased from American Radio labeled Chemicals Inc. St. Louis, MO, USA and Sigma-Aldrich Co. St. Louis, MO, USA.

Sorbents were suspended- and bottom sediments, ash, charcoal, as well as fiber, PE beads, PVC and tire fragments because these are among the most globally reported microplastics detected in the environment (Thompson et al. 2009; Engler 2012; Warrack et al. 2017; Hüffer et al. 2019). Sediments were collected from the Red River at a location near Selkirk, Manitoba (50°08'42.2"N 96°51'51.3"W). The Red River (~880 km) has a drainage area of 288,000 km^2 (Newton 2016) with ~80% of its length flowing through the USA before entering Canada. A continuous flow centrifuge (US Centrifuge M512) was used to collect suspended sediments in centrifuge aluminum bowl while water was pumped continuously through the device using high power generator for 4-6 hours. Bottom sediments (15 cm^3) were collected using an Ekman Dredge. Sediments were placed into sterile amber plastic bags (Fisher Scientific International Inc., Fair Lawn, NJ) and transported to the laboratory. Samples were air-dried and sieved (<2mm). Activated Charcoal Norit® and fly ash BCR® were purchased from Sigma-Aldrich Co. St. Louis, MO, USA. The Activated Charcoal is a chemically activated (by phosphoric acid) powder derived from wood with particle sizes ranging from 10-90 µm and a specific surface area (SSA) of 1400 m^2/g. According to the manufacturer, the charcoal contained calcium (200 mg/kg), iron

(150 mg/kg), and phosphate (3.5% on a mass basis). The fly ash is derived from pulverized coal with trace elements with particle sizes ranging from 0.5-40 μm and a SSA of 900 m^2/g. PE microbeads with particle sizes of 250-300 μm were used as model polymer typical of personal care products, and purchased from Cospheric LLC (Santa Barbara, CA, USA). Tire pieces (<5 mm) were collected from Reliable Tire Recycling Center, Winnipeg, Manitoba. Polyvinyl chloride (PVC) pipes were purchased from The Home Depot, Winnipeg, Manitoba and finely shredded into small pieces (<5 mm). Polyester fibers (<5 mm) were gathered from the insides of a newly bought pillow.

3.3.2 Batch equilibrium experiments and data analyses

Experiments were done in triplicate. One experiment utilized a 1:100 solid/solution ratio (0.1g/10mL) and included the four pesticides (2,4-D, atrazine, glyphosate, DDT), eight individual sorbents (suspended- and bottom sediments, ash, charcoal, PE beads, PVC and tire fragments), and three background solutions (0.01 M $CaCl_2$ or 0.01 KCl, deionized water, river water). The other experiment utilized a 1:5 solid/solution ratio (2g/10mL) and sorbents consisted of 1.9 g bottom sediments mixed with 0.1 g of each of the eight sorbents (suspended- and bottom sediments, ash, charcoal, fiber, tire, PVC, and PE beads). Although studies to date lack consistent and standardized methods/protocols to quantify microplastics present in bottom sediments (Campanale et al. 2020), we selected this ratio because the concentrations for microplastics, charcoal or ash in rivers are relatively small in volume compared to bottom sediments (Corcoran et al. 2015; Anderson et al. 2016; Warrack et al. 2017; Campanale et al. 2020).

Stock solutions of pesticides were prepared at a concentration of 2.5 μg l^{-1}. A total of 3 different background solutions were used in experiments. This included standard ionic solution of 0.01 M $CaCl_2$ (pH of 5.97) for 2,4-D, atrazine and DDT, and of 0.01 M KCl (pH of 6.24) for glyphosate (OECD 106,

2000), as well as deionized water (pH 6.35) and river water (pH 8). Pesticide solutions are usually prepared in 0.01M $CaCl_2$, but glyphosate forms complex formation with Ca^{2+} in the solution and hence KCl is the preferred electrolyte in batch equilibrium studies using glyphosate (Glass 1987; Munira et al. 2018). The river water was analyzed for a range of chemicals such as total calcium (69.3 mg/l), magnesium (49.1 mg/l) and others (Table 3S2). Prior to use in experiments, river water was filtered through Whatman glass fiber membrane filters (0.45 μm pore size, 47 mm), as well as autoclaved at 121°C for 20 minutes. Pesticide solutions (10 mL) were added to 50 mL glass centrifuge tubes (PYREX™ Round Bottom Glass Centrifuge Tubes) containing sorbents (0.1 or 2.0 g). Tubes were rotated in the dark for 24 hrs at 5°C. Tubes were removed and centrifuged at 7,000 rpm for 50 min at 5°C. Subsamples (1 mL) of supernatant were added to duplicated 6 mL scintillation vials, each containing 3 mL UltimaGold™ scintillation cocktail (Perkin-Elmer Inc., Waltham, MA, USA). Vials were lightly shaken and placed in dark for 24 hours to reduce false positives by photoluminescence or chemiluminescence. Radioactivity was quantified using Liquid Scintillation Counter (Tri-Carb 4910 TR, Perkin Elmer Inc.,MA, USA) with a counting time of 10 minutes.

For each pesticide and background solution separately, one-way analysis of variance (ANOVA) (GLIMMIX procedure, SAS 9.4) were performed on percent pesticide sorbed. The percentage sorption data followed a beta distribution and treatment mean differences were evaluated at $\alpha=0.05$ with the Tukey multiple comparison procedure.

3.4 Results and discussion

As individual sorbents (0.1 g), microplastics never sorbed more than 6% of 2,4-D or atrazine (Figure 3.1). Glyphosate also showed a weak sorption by microplastics, except that PVC fragments showed between 32-36% glyphosate sorption in 0.01M KCl and DI water (Figure 3.1). Previous studies have reported that some fungicides and insecticides, as well as a flame retardant tris (2-chloroethyl) phosphate, also showed an affinity for PVC (Chen et al. 2020; Gong et al. 2019; Tatarczak-Michalewska et al. 2021). In contrast to these current-use herbicides, legacy compound DDT showed between 85-94% sorption by fiber, tire or PVC fragments and between 55-66% sorption by PE beads (Figure3.1). Using batch-equilibrium studies, Bakir et al. (2014) also reported that DDT has a strong affinity for PVC and PE. Microplastics have hydrophobic properties and hence DDT and other hydrophobic chemicals with relatively large octanol-water partition coefficients have a large affinity for microplastics (Moyo et al. 2014; Wu et al. 2016; Beckingham & Ghosh 2017; Li et al. 2018; Llorca et al. 2018; Zuo et al. 2019). Partitioning interaction and pore filling are the predominant mechanisms controlling the sorption of DDT to microplastics (Bakir et al. 2012; Endo & Koelmans 2016; Wang et al. 2020).

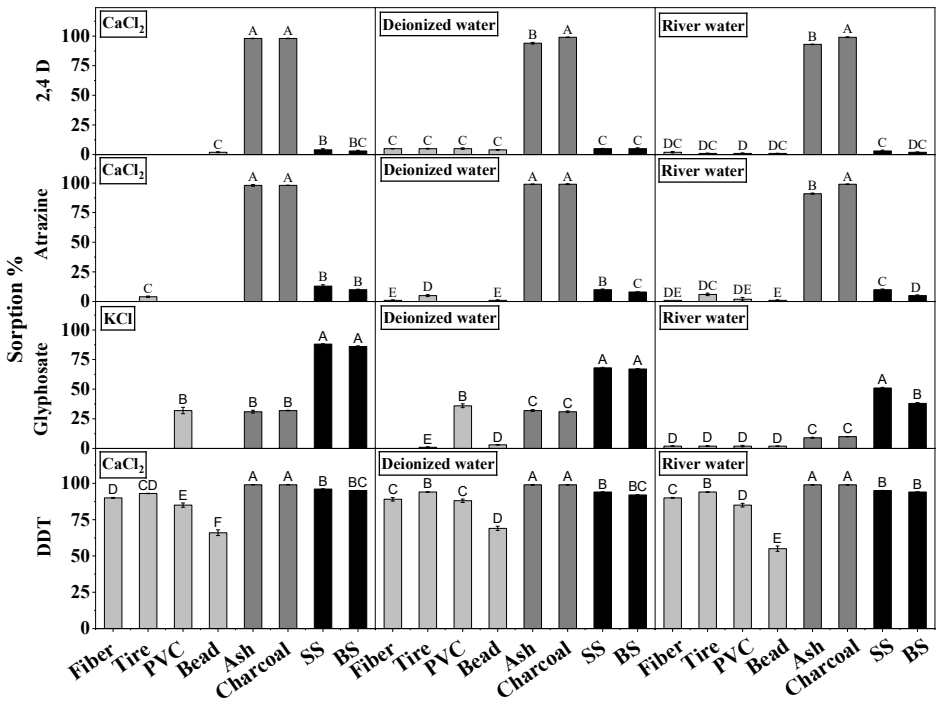


Figure 3.1 Pesticides sorption by individual solid constituent in $CaCl_2$, KCl, deionized water and river water solutions (1:100 solid/solution ratio) (letters on the top of the bars represent mean differences)

Ash and charcoal tend to have relatively high specific surface areas and as individual sorbents, ash (0.1g) and charcoal (0.1g) sorbed> 90%of 2,4-D, atrazine and DDT (Figure3.1). Previous studies reported that ash or charcoal sorbed between 54-87% of 2,4-D (Deokar et al. 2016), 32-99% of atrazine, and > 90% DDT (Gupta and Ali 2001; Ghosh and Singh 2013; Gonzalez et al. 2020). Suspended (0.1 g) or bottom (0.1 g) sediments sorbed> 90% DDT as well, but both 2,4-D (2-5%) and atrazine (5-13%) showed a weak affinity for sediments (Figure3.1). As individual sorbents (0.1 g), both suspended-and bottom sediment sorbed a substantial amount of glyphosate in 0.01M KCl (86-88%) and DI water (67-68%). However, the amount of glyphosate sorbed by suspended-and bottom sediment was only between 38-51% in the presence of river water (Figure 3.1). This suggests that ions present in river water competed with glyphosate for sorption by suspended-and bottom sediments. The river water contained a range of chemicals (Table 3S2) that are known to be sorbed by sediments including

phosphorus, lead, cadmium, copper and zinc (Phillips et al. 2004; Oh et al. 2009; Huang et al. 2015; Yin et al. 2016). As individual sorbents, ash (0.1g) and charcoal (0.1g) showed ~30% glyphosate sorption in 0.01M KCl and DI water solutions (Figure 3.1). However, both PVC (~2%) and ash or charcoal (~10%) showed a much lesser glyphosate sorption in the presence of river water (Figure 3.1). This suggests again that ions in river water competed with glyphosate for sorption by river constituents, including PVC, ash and charcoal. The river water contained a range of chemicals (Table 3S2) that are known to be sorbed by PVC such as lead, arsenic and cesium (Wankasi and Dikio 2014; Sing et al. 2020; Chen et al. 2020). Similarly, phosphate in river water might have competed with glyphosate for sorption by ash and charcoal because, for example, glyphosate sorption by wood biochar (also a carbon rich substance) was reduced in the presence of phosphate because of competitive sorption mechanism (Cederlund et al. 2016; Hall et al. 2018). In addition, river water had a pH of 8 whereas the pH of the other two background solutions was less than 6.5. Previous studies have shown that the sorption of glyphosate by clays, soils and sediments decreases with increasing pH because glyphosate is becoming increasingly negatively charged (McConnell and Hossner 1985; de Jonge and de Jonge 1999; Gimsing et al. 2003; Dollinger et al. 2015). Specifically, glyphosate sorption is reduced because of the increased negative charges of both soil and glyphosate result in greater electrostatic repulsion with rising pH (de Jonge and de Jonge 1999; Wauchope et al. 2002; Candela et al. 2007; Ololade et al. 2014).

Regardless of the background solution, the amount sorbed of the legacy compound DDT, as well as of current-use herbicides 2,4-D and atrazine, typically decreased in the order of ash/charcoal >sediments>microplastics. Glyphosate sorption typically decreased in the order of sediments>ash/charcoal>microplastics. Consequently, regardless of the pesticide, microplastics tend to be less likely to sorb pesticides than other river constituents. For none of the four pesticides, there was a significant impact of the type of microplastics present in sediments on % pesticide sorbed by

sediments. Bottom sediments with or without microplastics sorbed< 20% 2,4-D, ~55-58% atrazine but > 95% of glyphosate and DDT (Figure 3.2). In contrast, the presence of 0.1 g of either ash or charcoal with 1.9 g bottom sediments, significantly increased the sorption of 2,4-D, atrazine and DDT relative to 2.0 g bottom sediments only. The increased sorption was particularly profound for current-use herbicides 2,4-D and atrazine (Figure 3.2). Relative to 2.0 g bottom sediments only, the presence of 0.1 g charcoal with 1.9 g bottom sediments significantly decreased glyphosate sorption. However, numerically, the differences between these two treatments were extremely small because > 95% of glyphosate was sorbed in both cases (Figure 3.2). Other studies reported on the strong sorption of glyphosate by sediments (Xu et al. 2009, Degenhardt et al. 2012; Dollinger et al. 2015) and by soil (Shushkova et al. 2010; Munira et al. 2016; Munira and Farenhorst 2017; Munira et al. 2018).

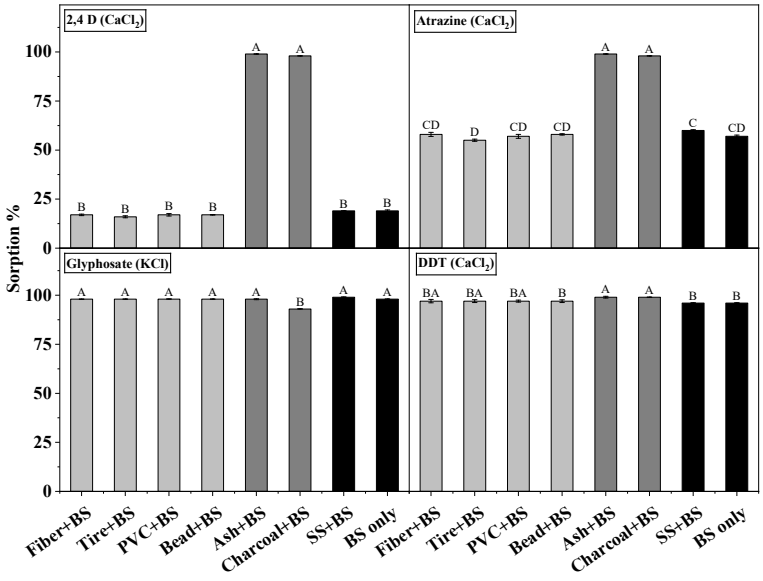


Figure 3.2 Pesticides sorption by mixture of bottom sediment and other solid constituents in $CaCl_2$ and KCl solution (1:5 solid/solution ratio) (letters on the top of the bars represent mean differences)

3.5 Conclusion

Based on the batch equilibrium conditions studied, we conclude that it is unlikely that microplastics will accumulate current-use herbicides such as 2,4-D, atrazine and glyphosate. Although glyphosate is

potentially retained by PVC, ions in river water appear to interfere with this glyphosate sorption. This might warrant including the types and concentrations of ions present in rivers when describing on glyphosate fate processes in rivers, including sorption by river constituents such as sediments and PVC. The amount of DDT sorbed by microplastics was substantial and hence such partitioning coefficients should be included when modeling the fate of DDT in river systems. The presence of ash/charcoal in regions impacted by large forest fires is likely to increase the removal of 2,4-D and atrazine from the water column, both in the short-term when ash/charcoal are suspended in the water-column, and in the long-term when ash/charcoal have settled in bottom sediments. In contrast, the presence of microplastics are unlikely to impact the removal of 2,4-D, atrazine and glyphosate from the water-column in rivers.

3.6 Acknowledgement

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4. USING THE PESTICIDE TOXICITY INDEX TO SHOW THE POTENTIAL ECOSYSTEM BENEFITS OF ON-FARM BIOBEDS

4.1 Abstract

The influent and effluent of two single-cell biobeds (Province of Alberta, Canada) and two dual cell-biobeds (Province of Saskatchewan, Canada) were monitored during a number of growing seasons. A total of fifty-nine unique pesticide active ingredients were detected, with all biobed influent samples (n=54) and 93% of effluent samples (n=54) containing pesticide mixtures. About one-half of the effluent samples in both single- (56%) and dual-cell (45%) biobeds contained active ingredients that have GUS values greater than 2.8 and so were more likely to move through the biomatrix materials into effluent. The Pesticide Toxicity Index (PTI) calculated for aquatic indicator species (i.e., vascular and non-vascular plants, invertebrates and fish) was always larger for influent samples (e.g., median PTI >500 for invertebrates in dual-cell biobed) than effluent samples (i.e., median PTI < 1). As such, this study demonstrates the potential ecosystem benefits of the broad adoption of on-farm biobeds in the Canadian Prairies for recycling tank rinsate as part of strategies to accelerate a green economy. Although biobeds were highly effective in reducing the concentrations for pesticides with a wide range of Koc and half-life values, the biobed effectiveness was relatively poor for herbicides clopyralid, diclofop, fluroxypyr and imazethapyr. Clopyralid (3.02), fluroxypyr (3.70) and imazethapyr (3.90) all have relatively high GUS values (> 2.8) and are thus more likely to be detected in effluent than active ingredients with smaller GUS values. This suggests that further improvements in biosystem design need to be made for optimizing the recycling of these pesticides.

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4.2 Introduction

Pesticide handling areas result in point-source pollution that can account for up to 90% of the total pesticide loadings in water resources (Frede et al. 1998; Neumann et al. 2002). By capturing the pesticide residues associated with the filling and cleaning of spraying equipment, biobeds are designed to minimize this point-source pollution (Torstensson 2000). A biobed is an above- or in-ground container structure that holds a biomixture that is typically derived from a combination of plant dry matter (e.g., straw), humified organic matter (e.g., peat) and soil. Previous studies have shown that the retention and degradation of pesticides in a biomatrix are influenced by the physico-chemical properties of the pesticide (e.g., half-life, sorption coefficient), the composition of the biomatrix (i.e., only soil versus mixture of plant dry matter and humified substrate), biobed water management (i.e., frequency and volume of wastewater loading) and other factors (e.g., ambient temperature) (Spliid et al., 2006; Coppola et al., 2007; Karanasios et al. 2012; Knight et al. 2016; Cooper et al. 2016; Delgado-Moreno et al. 2017; Lescano et al. 2018).

Invented by a Swedish farmer in the 1990s, on-farm biobeds have been particularly adopted in Europe (Karanasios et al. 2012) but remain largely unknown to farmers in Canada that operate a combined 37.8 million hectares of cropland (Braul et al. 2018). About 83% of Canada's cropland is located in the Prairies and four on-farm biobeds became operational in 2014 and 2015 (Table 4.1). The construction, maintenance, and operation of the four biobeds followed guidelines developed for the Canadian Prairies (Braul et al. 2018). This study evaluates these biobeds effectiveness for processing rinsate containing pesticides typically applied in Prairie agricultural and non-agricultural applications. Pesticides most frequently applied to the biobeds included herbicides such as 2,4-D, bromoxynil, clopyralid, MCPA, and mecoprop.

Table 4.1. Summary information of the four biobeds included in this study.

Location	Biomatrix (2:1:1)	Surface area (m^2)	Sampling period (# samples)
	Single-cell biobeds in the Province of Alberta		
Grand Prairie[1]	Wheat straw, compost, soil	44 m^2	08/2015-10/2015 (8) 08/2016-10/2016 (8)
Vegreville[2]	Wheat straw, peat, soil	8 m^2	06/2015-08/2015 (12) 06/2016-09/2016 (16) 07/2017-08/2017 (8)
	Dual-cell biobeds in the Province of Saskatchewan		
Outlook[2]	Wood chips, peat, soil	6 m^2	07/2014-09/2014 (8) 06/2015-09/2015 (14) 06/2016-09/2016 (14)
Simpson[2]	Wood chips, peat, soil	4.5 m^2	07/2015-09/2015 (8) 06/2016-10/2016 (12)

[1]Below ground biobed, [2]Above ground-biobeds.

A parameter for predicting the relative ranking of pesticides moving towards groundwater is the Groundwater Ubiquity Score (GUS) or Tier-1 assessments (GUS) (Hall et al., 2015; Kolupaeva et al., 2019).GUS is calculated by(log(DT50)×(4 – log(Koc)), whereby DT50 is the soil half-life of the pesticide and Koc is the normalized organic carbon sorption coefficient (Gustafson 1989).GUS values greater than 2.8 indicating that a pesticide has a high potential to move to groundwater (Zheng and Cooper 1996; Laabs et al. 2002; Soares et al. 2012; Close and Humphries 2019; Zambito Marsala et al. 2020). Given that GUS provide for a relative measures of pesticide movement through a matrix such as soil, we hypothesize that the pesticides detected in biobed effluents are more likely to be pesticides that have greater GUS values.

The Pesticide Toxicity Index (PTI) is a known tool to quantify the relative toxicity of pesticide mixtures to indicator species of aquatic organisms. The PTI is a Tier-1 type assessment that combines measured pesticide concentrations with acute toxicity data base values through an additive toxic-unit model (Munn et al. 2010; Nowell et al. 2014). In a river water study, a variety of pesticide mixtures were detected depending on sampling location and time and the PTI was used to compare the relative risk of these pesticide mixtures to aquatic organisms (Nowell et al. 2014). For Prairie rivers, PTI values

tend to be larger for non-vascular and vascular plants than for invertebrates or fish because pesticide mixtures in Prairie rivers tend to be dominated by herbicides (e.g.,2,4-D, bentazone, clopyralid, fluroxypyr and MCPA) rather than insecticides or fungicides (Rawn et al. 1999; Challis et al. 2018; Gamhewage et al. 2021). In this study, we quantified the PTIs for samples containing pesticide mixtures and hypothesize that in all cases (non-vascular plants, vascular plants, invertebrates and fish), the mean PTI of biobed effluent will be significantly smaller than the mean PTI of biobed influent.

The objective of this study was to measure, through quantifying pesticide concentrations and PTI values, the efficiency of single- and dual-cell biobeds as it applies to pesticides commonly used in Prairie agriculture.

4.3 Materials and Methods

4.3.1 Sampling and Pesticide Analysis

This study included two single-cell biobeds located in the Province of Alberta (AB) and two dual-cell biobeds in the Province of Saskatchewan (SK) (Table 4.1). Although there were differences in biobed configurations, particularly between provinces, biomixtures always had a 2:1:1 ratio by volume of plant dry matter (i.e., straw or wood), humified organic matter (i.e., peat or compost), and local topsoil. At each site, pesticide rinsate was collected and held in storage influent tanks, and then drip-irrigated or manually applied onto the surface of the biomatrix in the single-cell biobeds in AB or onto the first cell of the dual-cell biobeds in SK. The outflow of the first cell was further drip-irrigated onto the surface of the second biobed cell. The outflow of single-cell biobeds in AB or the second cell of dual cell biobeds in SK was directed to storage effluent tanks and held to facilitate sampling. For each of 54 sampling times in total, samples from influent and effluent storage tanks were collected in 1 L amber

glass bottles on the same day and kept at 4^{o}C to quantify pesticide residues within three days from the time of collection. Pesticides detected in influent were considered an indication of the types and concentrations of the pesticides added to a biobed. Pesticides detected in effluent were considered an indication of the types and concentrations of the pesticides not degraded or retained by the biobed.

All mass spectrometric analyses were conducted by the ISO17025 federal government laboratory-Lethbridge Research and Development Centre, in Agriculture and Agri-food Canada using validated in-house quantitative methods including multiple reaction monitoring and surrogate internal standards. Samples were extracted and analyzed for 142 to 160 compounds (i.e., an increasing number of compounds in more recent years) and this multi-residue method has been previously published (Munira et al. 2018; Bergsveinson et al. 2018; Gamhewage et al. 2019). Briefly, samples were filtered (glass wool), acidified to pH 2 (sulfuric acid) and extracted from water using liquid-liquid partitioning with dichloromethane. Extracts were dried (acidified Na_2SO_4) and concentrated, methylated (diazomethane), neutralized (hexane) and adjusted to 10 ml using rotary evaporator. Esterified extracts were injected (2µl) in an Agilent 7890B gas chromatograph coupled with a 7000C QQQ mass selective detector and multiple reaction monitoring (MRM) and a HP-5MS UI (30m×0.25mm ×0.25µm) column. The temperature programming was 70°C for 2 min, ramp of 25°C min^{-1} to 150°C, ramp of 3°C min^{-1} to 200°C, and ramp of 8°C min^{-1} to 280°C for 7 min, for a total run time of 38.86 min. Compounds were identified at expected retention time by monitoring one target ion and at least two qualifier ions. The lower limit of quantification was 25 ng/L for most pesticides and detections below this limit were considered not detected. Glyphosate, which was detected in both biobed influent and effluent was only included in the analytical suite in 2017, hence data were relatively limited for this widely used herbicide in North America.

4.3.2 Pesticide Detections and Calculated Parameters

For each pesticide active ingredient detected in influent or effluent samples, values for its Groundwater Ubiquity Score (GUS), typical half-life (DT50) and soil organic carbon coefficient (Koc) were obtained from the Pesticides Properties DataBase (Lewis et al. 2016). Koc values were not available in PPDB for 15 pesticide active ingredients and in these cases, the pesticide Koc value was calculated from the listed GUS and DT50 values. Pesticides detected in influent or effluent samples were assigned into one of four GUS categories (extremely low < 0; low 0-1.8; moderate 1.8-2.8; or high > 2.8; NPIC 2021). We here define GUS as relative likelihood of pesticides being detected in the biobed effluent. For example, a high GUS value would mean that there is a high potential of the pesticide to be detected in effluent because it is both persistent and/ or mobile in the biobed. DT50 categories (low <16 d; moderate 16-59 d; high >60 d; NPIC 2021), and Koc categories (highly mobile <10; mobile10-100; moderately mobile 100-1,000; slightly mobile 1,000-10,000; hardly mobile 10,000-100,000; immobile >100,000; FAO 2000) were also assigned based on literature recommended classes.

For the two single cell biobeds combined, and the two dual cell biobeds combined, the relative proportions of the assigned categories were calculated for the influent and effluent separately. For example, for the influent of single cell biobeds, the relative proportion of highly mobile pesticides (Koc <10) was calculated by the sum of the number of highly mobile pesticides (Koc <10) detected in influent samples divided by total detects in the influent; and expressed as a percentage (%).

For the PTI calculation, for each pesticide active ingredient detected in influent or effluent samples, the aquatic life benchmarks data were obtained from the United States Environmental Protection Agency database (USEPA, 2018). These benchmarks data are based on the toxicity values of selected indicator species in standardized tests namely the acute 48-96h LC50 (lethal concentrations inducing 50%

mortality) for fish (rainbow trout, fathead minnow, or bluegill) or aquatic invertebrates (midge, scud, or daphnids), or the acute < 10d EC50 (effective concentration inducing 50% growth inhibition) for aquatic vascular (green algae or diatoms) or non-vascular (duckweed) plants. Toxicity quotients were calculated by dividing each pesticide concentration present in the influent or effluent by the aquatic life benchmarks data of indicator species relevant for that pesticide. The PTI was then calculated by summing the toxicity quotients of all pesticides in an influent or effluent sample. The 7% of effluent samples that did not contain pesticide mixtures were excluded from the PTI calculations.

4.3.3 Statistical Analysis

For each of the top 5 most frequently detected pesticide active ingredients in biobed influent, the PROC TTEST in SAS 9.4 for Windows (SAS Institute Inc. 2013) with a significance threshold of $P < 0.05$ was used to determine significant differences in pesticide concentrations between biobed influent versus effluent. These analyses were done for all biobeds combined, as well as for single- and dual-cell biobeds separately. Single- and dual-cell biobeds data were kept separate for all other statistical analyses in which the PROC TTEST ($P < 0.05$) was used to determine significant differences between influent versus effluent samples for PTI values.

4.4 Results and Discussion

A large portion (87 %) of the 58 (Table 4S3) unique active ingredients detected in influent samples had concentrations > 1µg/l. Active ingredients were always detected as mixtures with the number of unique active ingredients per influent sample ranging from 6 to 31. In total, 31 herbicides, 14 fungicides, 12 insecticides, as well as nematicide dichlofenthion were detected in influent. Only 40 unique active ingredients were detected in effluent and almost two-third (64%) of these were detected at

concentrations < 1 µg/l. The majority (93%) of the effluent samples still contained pesticide mixtures ranging from 3 to 21 unique active ingredients per sample. However, three samples had zero detections and another effluent sample had a single detection of 2,4-D at 0.02 µg/l. In total, 22 herbicides, 10 fungicides, 7 insecticides, as well as nematicide dichlofenthion were detected in effluent.

Of the top 5 most frequently detected active ingredients in biobed influent, the mean effluent concentrations of 2,4-D (2.6 µg/l), dicamba (16.4 µg/l), MCPA (124 µg/l), mecoprop (0.4 µg/l) and bromoxynil (0.8 µg/l) were significantly smaller than the mean influent concentrations of these active ingredients (2,4-D=7,441 µg/l, dicamba=152.8µg/l, MCPA=7,946 µg/l, mecoprop=134 µg/l and bromoxynil=1,476 µg/l respectively). When single- and dual-cell biobeds were considered separately, these differences remained significant for both types of biobeds except that the mean concentration of mecoprop was statistically similar in influent and effluent in case of dual-biobeds. Although the total mean active ingredient concentration in influent was much larger for single-cell (4,390 µg/l) than dual-cell (527 µg/l) biobeds (Figure 4.1), both single- and dual-cell biobeds appeared to be effective for a range of the same pesticides (Table 4.2). The mean active ingredient concentration in effluent was 286 µg/l for single-cell and 99 µg/l for dual-cell biobeds (Figure 4.1). Given that the single-cell biobeds had received pesticide concentrations in much greater concentrations than dual-cell biobeds, we highlight that these data demonstrate that the single-cell biobeds performed remarkably well under Prairie conditions. This is the first study worldwide that allows for a comparison of the performances of single versus dual-cell biobeds.

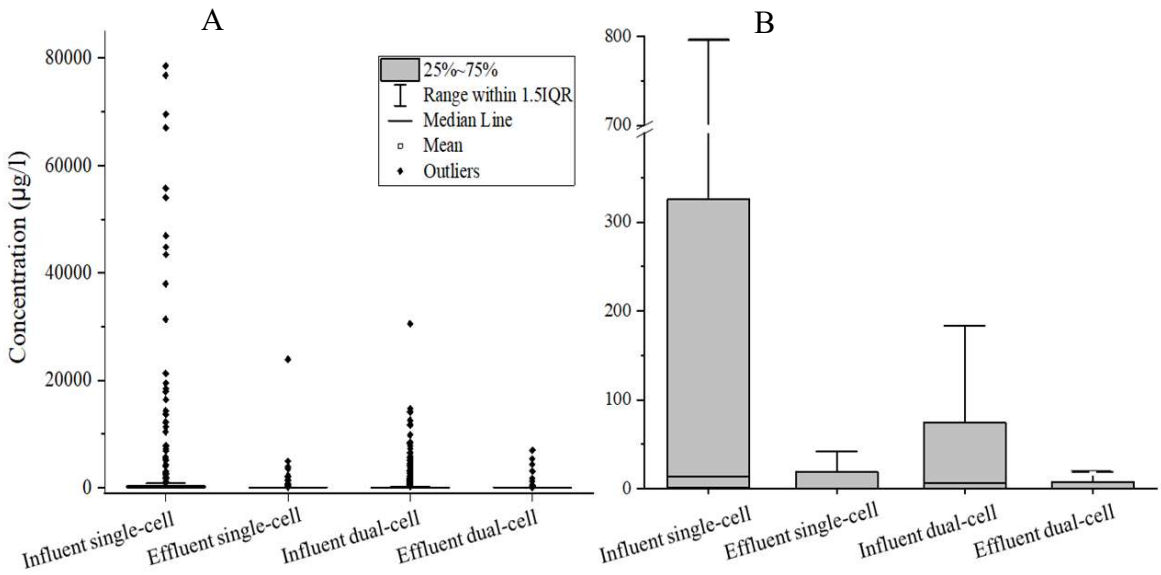


Figure 4.1. Concentrations of active ingredients in single- and dual-cell biobed influents and effluents with graphs showing (A) all outliers and a closer view of the interquartile ranges (B).

Table 4.2. Mean concentration of ten active ingredients in the influent of single- and dual-cell biobeds and the percent reduction of that mean concentration in the effluent. A reduction of 100% indicates that the active ingredient is not detected in the effluent. Numbers in brackets refer to the number of detections of the active ingredient in influent.

Active ingredient	Single-cell biobeds		Dual-cell biobeds	
	Mean influent conc.(µg/l)	% Reduction	Mean influent conc. (µg/l)	% Reduction
Metolachlor	<1 (2)	100	142 (16)	99.23
Boscalid	208 (11)	100	30 (15)	99.91
Fenoxaprop	1,841 (13)	99.80	<1 (14)	100
EPTC	<1 (2)	100	1,845 (14)	99.95
Propiconazole	16 (13)	98.53	4 (17)	99.22
Bromoxynil	14 (15)	99.41	2,451 (21)	99.96
MCPA	13,206 (17)	98.28	2,734 (23)	99.45
2,4-D	14,695 (17)	100	2,105 (23)	99.79
Dichlofenthion	2 (8)	96.70	7 (18)	95.29
Dicamba	115 (8)	97.66	164 (26)	84.56

A total of 27 unique active ingredients were detected in single-cell influent with detections being largest for herbicides glyphosate (maximum=76,798 µg/l), 2,4-D (69,561µg/l), MCPA (67,030 µg/l) and clopyralid (37,971 µg/l) (Figure 4.1). Dual-cell influent received a much broader range of unique active ingredients (n=52) but with a maximum detection of 30,543 µg/l (bentazone). Although 80% of the unique active ingredients detected in single-cell influent were also detected in single-cell effluent,

dual-cell effluent only contained 65% of the unique active ingredients detected in dual-cell influent. The active ingredients that were detected in influent but not in effluent had a wide range of Koc, DT50 and GUS values. Interesting, pesticide never detected in effluent all had GUS values <2.8, thus none had a high potential to being detected in the biobed effluent (Table 4.3).

Table 4.3. Pesticides detected in influent but not effluent. Pesticides indicated in italic under single-cell biobeds were detected in dual-cell biobeds influent and effluent. Pesticides indicated in italic under dual-cell biobeds were detected in single-cell biobeds influent and effluent. Abbreviations are explained in the footnote*

Pesticide	Max. Conc. [µg/l]	Koc [L/Kg]	DT50 [days]	GUS
Single-cell biobeds				
Atrazine (H^1)	0.06	100 (M^1)	75 (H)	2.57 (M)
EPTC (H^1)	0.41	300 (MM)	6 (L)	2.17(M)
Metolachlor (H^1)	0.06	120 (MM)	90 (H)	2.36(M)
Boscalid (F)	0.05	1,040 (SM)	484 (H)	2.64(M)
Picoxytrobin (F)	0.04	965 (MM)	24 (M)	1.35(L)
Spiromesifen (I)	27.83	30,900 (SM)	4 (L)	-0.16(EL)
Dual-cell biobeds				
2,4 DB (H^1)	2.46	224 (MM)	4 (L)	1.68 (L)
Benfluralin (H^1)	25.78	10,777 (SM)	120 (H)	-0.62 (EL)
Dichloprop (H^1)	0.24	74 (M^1)	10 (L)	2.39 (M)
Ethalfluralin (H^1)	2.94	6,364 (MM)	45 (M)	0.47 (L)
Fenoxaprop (H^1)	3.59	11,354 (HM)	5 (L)	0.02 (L)
MCPB (H^1)	0.3	114 (MM)	7 (L)	1.64 (L)
Oxyfluorfen (H^1)	2.65	85 (M^1)	35 (M)	0.23 (L)
Quizalofop ethyl (H^1)	29.84	540 (MM)	45 (M)	2.25 (M)
Trifluralin (H^1)	15.24	15,800 (HM)	<1 (L)	0.15 (L)
Carbaryl (I)	2.72	300 (MM)	16 (L)	2.02 (M)
Chlormephos (I)	419	1,100 (SM)	20 (M)	1.25 (L)
Cypermethrin-beta (I)	183	115,009 (I)	27 (M)	-1.52 (EL)
Cypermethrin-zeta (I)	106	44,146 (HM)	49 (M)	-1.09 (EL)
Methoprene (I)	0.45	2,535 (SM)	10 (L)	0.60 (L)
Methoxychlor (I)	1.47	80,000 (HM)	120 (H)	-1.88 (EL)
Fludioxonil (F)	8.02	145,600 (I)	164 (H)	-1.47 (EL)
Pyrimethanil (F)	1.04	535 (MM)	60 (M)	2.17 (M)
Triticonazole (F)	13.75	374 (MM)	237 (H)	2.7 (M)

*Abbreviations: H[1]=herbicide; I=insecticide; F=fungicide; EPTC = S-Ethyl DipropylThioCarbamate; 2,4 DB = 2,4-dichlorophenoxy butyric acid; for Koc: M[1]= mobile, MM= moderately mobile, SM= slightly mobile, HM= hardly mobile and I=immobile; For DT50: L= low, M= moderate and H= high; For GUS: EL= extremely low, L=low, M=moderate, and H=high.

Biobeds were not fully efficient in recycling pesticide rinsate. Thirty-eight percent of the unique active ingredients detected in single-cell effluent had concentrations > 1 µg/l, or 9 active ingredients in total. This included MCPA in 55% of effluent samples, as well as dicamba (42%), 2,4-D (14%) and mecoprop (10%). Thirty-three percent of the unique active ingredients detected in dual-cell effluent had concentrations > 1 µg/l, or 12 active ingredients in total including MCPA (40%), 2,4-D (20%), dicamba (14%) and bromoxynil (9%).These active ingredients have typically short half-lives in soil (i.e., one day to 3.5 weeks) (Lewis et al. 2016). As well, for laboratory incubations, Ngombe et al., (2011) reported that almost all 2,4-D was degraded within 10 days following its incorporation into biomatrices. However, these auxin herbicides have relatively large water solubility (i.e., >20,000 mg/L) (Lewis et al. 2016) which would make these active ingredients relatively mobile in the biobed and hence to appear in effluent rather than being fully degraded in the biobed.

Herbicide clopyralid was among the most frequently detected active ingredients in effluent (single-cell 88% of effluent samples; dual-cell 75%) while also being detected in among the largest concentrations (single-cell max. conc. 23,898 µg/l; dual-cell 3,044 µg/l). In dual-cell biobed effluent, herbicides bentazone (71%) and imazethapyr (64%) were also frequently detected with a maximum concentration of 3,044 µg/l for bentazone and 51µg/l for imazethapyr. All three herbicides, clopyralid (Koc=5 L/Kg, DT50=23days; GUS=3.02), bentazone (Koc=55L/Kg, DT50=20 days; GUS=1.95) and imazethapyr (Koc=52 L/Kg, DT50=90 days; GUS=3.9) might be considered somewhat environmentally mobile by water. Despite their relatively large concentrations in effluent, there was evidence that the herbicides were retained and/or degraded in the biomatrices to some extent because their mean concentrations

were significantly smaller in the effluent (dual cell- bentazone 987 µg/l, imazethapyr 26 µg/l) than influent (dual cell- bentazone 3501 µg/l, imazethapyr 66 µg/l). The exception was clopyralid which showed numerically greater mean concentrations in effluent (225 µg/L) than influent (181 µg/L), however the differences were not statistically significant.

It is possible that the materials used in the biomatrix (wheat straws, wood chips, composts, peats, soils) already contained these herbicides and that these residues became available for transport into effluent. For single-cell biobeds only, there were four active ingredients that were detected in effluent samples but never in influent samples. This included three detections of fungicide tebuconazole (maximum concentration = 0.21 µg/l) and a single detection of fungicides metconazole (1.18 µg/l) and prothioconazole-desthio: (0.02 µg/l),and insecticide pyridaben (0.68 µg/l).In previous studies, tebuconazole, metconazole and prothioconazole-desthio were detected as contaminants in straw and hay meant for livestock feed (Mol et al. 2014, Kang et al. 2016, Lin et al. 2017).In some biobeds, the overall concentrations of clopyralid, diclofop, fluroxypyr or imazethapyr were greater in effluent than influent (Table 4.4). Both clopyralid and imazethapyr are known to be relatively persistent in some soils (O'Sullivan et al. 1998, Seefeldt et al. 2014).

Table 4.4**.** Mean percentage reduction of concentration of four pesticides by single and dual cell biobeds. Mean percentage indicated in italic were increased from influent to effluent. Numbers in brackets refer to the number of detections of the active ingredient in influent.

Pesticide	Single cell (%)	Mean influentconc. (µg/l)/Det. No.	Dual cell (%)	Mean influentconc. (µg/l)/Det. No.
Clopyralid	56.67	4508 (18)	***24.17***	181 (22)
Diclofop	***100.67***	5.87 (1)	97.92	1.71 (3)
Fluroxypyr	78.87	447 (17)	***36.91***	0.25 (3)
Imazethapyr	***2.66***	0.32 (1)	60.91	66.13 (17)

The effluent of both single-cell biobeds (56%) and dual-cell biobeds (45%) had relatively large proportions of pesticides that are highly likely to be detected in biobed effluent (GUS>2.8). In contrast, the proportion of pesticides that have GUS>2.8 was only 48% in single-cell biobeds and 21% in dual-cell biobeds influent (Figure 4.2). Active ingredients that showed a proportionally greater presence in effluent included clopyralid (from 8.78% to 13.61% in single-cell biobeds, and from 3.66% to 8.13% in dual-cell biobeds), MCPA (from 3.83% to 6.59% in dual-cell biobeds), and imazethapyr (from 2.83% in influent to 6.98% in effluent of the dual-cell biobeds). These active ingredients all have GUS values of >2.8.Thus, overall, our results demonstrate that our hypothesis is true because the pesticides detected in biobed effluents are more likely to be pesticides that have greater GUS values. Influent and effluent samples of both single- and dual-cell biobeds showed a remarkably similar distribution of DT50 values and hence the proportional changes observed for GUS values were primarily driven by differences in Koc values (Figure 4.2).

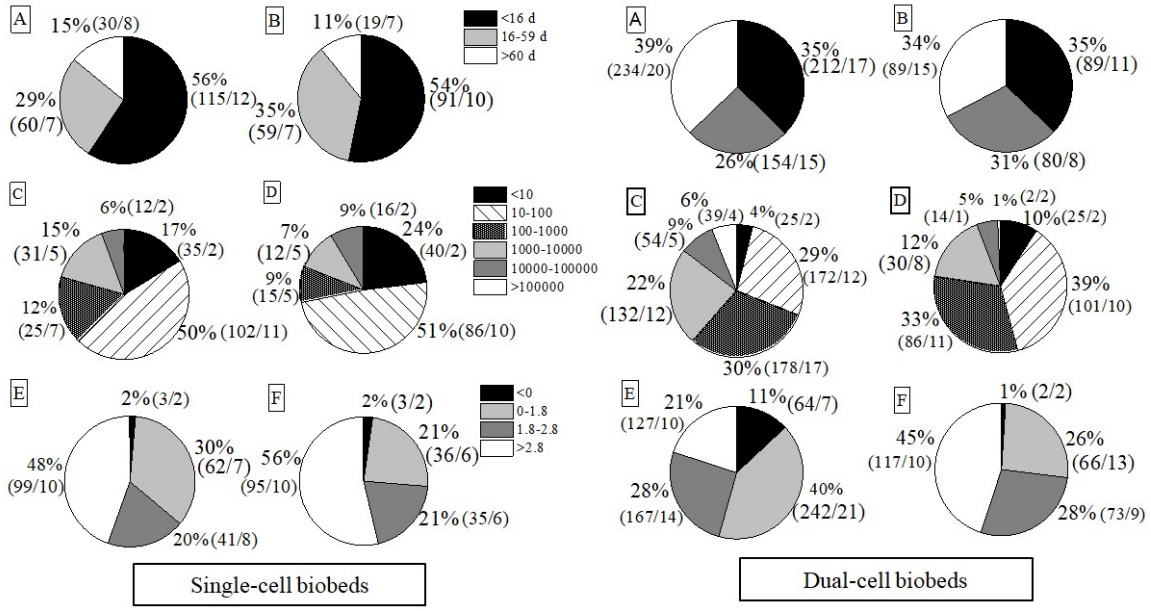


Figure 4.2. Proportional (%) detection of active ingredients by category of DT50 values (A= influent, B=effluent), Koc values (C=influent, D=effluent) and GUS values (E= influent, F=effluent) for the single-cell (left) and dual-cell (right) biobeds. The numbers in parenthesis refer to the total number of active ingredients detected in the category/the total number of unique active ingredients detected in the category.

Regardless of the aquatic organism indicator, both single- and dual-cell biobeds influent showed significantly greater PTI values than effluent samples. Many single- and dual-cell biobed influent samples had PTI values greater than one. For example, for fish, 48% (single-cell) and 64% (dual-cell) of the influent samples had PTI >1 (Figure 4.3). A PTI >1 means that 50% of the indicator species die or are inhibited in their growth. The concentrations of pesticide mixtures in influent samples also resulted in a high number of influent samples showing PTI >1 for invertebrates (48% and 64%), vascular (88% and 75%) and non-vascular (88% and 71%) plants. Despite the greater concentrations of active ingredients in the influent of single-cell than dual-cell biobeds (Figure 4.1), the PTI for fish and invertebrates was notably larger for dual-cell than single-cell influent (Figure 4.3) due to the influence of a number of active ingredients that were only detected in dual-cell biobed influent samples. This included five insecticides (chlorpyrifos, cyhalothrin lambda, cypermethrin zeta, deltamethrin and diazinon) and well as fungicide pyraclostrabin which all have very low OPP aquatic life benchmarks (ranging from 0.0018 to 7.85 µg/L).

In contrast to the influent samples, both single- and dual-cell biobed effluent samples often had PTI<1, including for fish (96% and 92 % of samples for single- and dual-cell biobed influent samples, respectively) and invertebrates (96 % and 84 %), as well as for vascular (84% and 40 %) and non-vascular plant (88% and 88 %). Given that for each of aquatic organism indicators, there was a sharp reduction in PTI values from influent to effluent samples (Figure 4.3), our study clearly shows that the mean PTI of biobed effluent is significantly smaller than the mean PTI of biobed influent (Figure 4.3).The PTI is a benchmark measure for pesticide mixtures and hence these data again suggest that for most current-use pesticides, biobeds are effective in retaining and/or degrading active ingredients. As such the broad adoption of on-farm biobeds in the Prairies for recycling tank rinsate can become an important strategy to accelerate a green economy in North America.

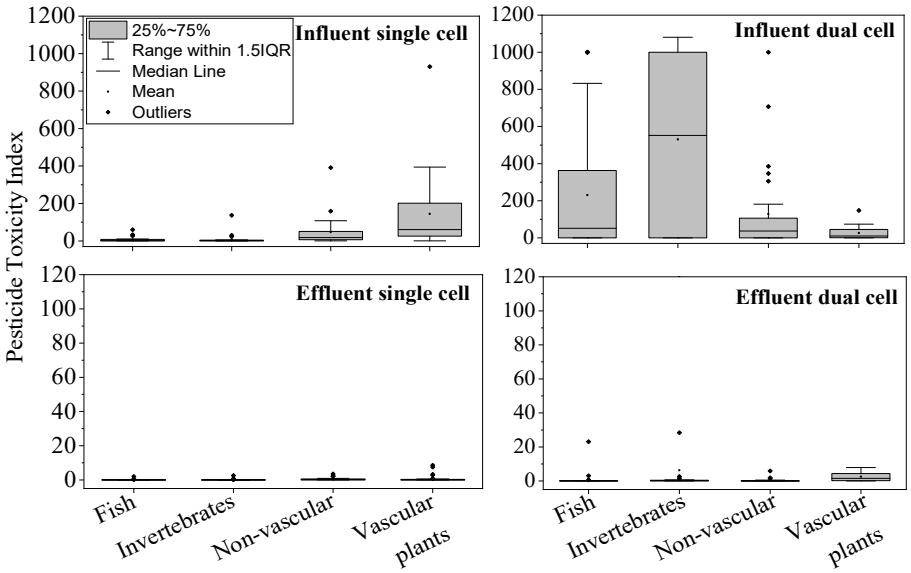


Figure 4.3. Pesticide Toxicity Index from influent and effluent of single and dual cell biobed for a range of aquatic organism

4.5 Conclusion

We conclude that biobeds are a very effective approach in colder climates for minimizing the risk of pesticides entering the broader environment. Both single- and dual-cell were effective for the same active ingredients by allowing for the retention and/or degradation of pesticides in biomatrices. Biobeds effectively reduced the PTI of pesticide rinsate from a value of several hundred (influent samples) to often close to zero (effluent samples). As such, we are demonstrating that the broad adoption of biobeds for recycling pesticide rinsate has potential ecological benefits. However, for some pesticides the biobeds were less effective and further studies are required to investigate such discrepancies. As well, this study did not include the many possible metabolites of the active ingredients measured, as well as that it did not account for pesticide molecules perhaps binding together to form other derivatives or molecules with large molecular mass. Such efforts might require the development of more advanced analytical quantification methods.

4.6 Acknowledgments

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5. OVERALL SYNTHESIS

5.1 Summary of the Research

This thesis first examined the pesticide concentrations in the water-column and bottom sediments in segments of the Red River and some of its tributaries that flow through crop lands or urban areas with golf courses that have known pesticide use. Samples were collected in 2016 (Gamhewage et al. 2019; 2021) and 2017 and analyzed for 97 current-use pesticide active ingredients (44 herbicides, 28 insecticides, 25 fungicides), a few of their metabolites (e.g., 2,4 dichlorophenol), as well as pesticide active ingredients no longer used (e.g., dichlorodiphenyltrichloroethane). The screening of water-column and bottom sediment samples for this wide range of pesticide compounds is much greater than was accomplished in previous studies in the Prairies (e.g., Rawn et al. 1999; Glozier et al. 2012; ECCC 2015). In agreement with these previous studies, current-use broadleaf herbicides such as 2,4-D, bentazone, clopyralid and MCPA were among the most frequently detected. The type of crops grow in the watershed was an important indicator of the types of pesticides detected with the relative proportions of annual crops grown along the Red River in 2017 being soybean (32%), wheat (26%), canola (23%), corn (10%) and oat (9%). A range of pesticide active ingredients applied in these crops, including seed treatments, were detected in the Red River during the 2017 growing season, with pesticide detections in the water column most frequently occurring in the post emergence stage. Water-column samples at the post-harvest stage often contained fewer pesticide compounds, suggesting that pesticides degraded in the water-column or partitioned into bottom sediments.There was some evidence that river segments flowing through urban landscapes introduced herbicides into the Red River because herbicide triclopyr was first detected after the Red River had left flowing through agricultural land. Most of the pesticide compounds detected in the Red River across the twelve sampling stations in

Manitoba, were already detected at the first sampling station in Canada, showing that a portion of the river pesticide pollution might have originated in the United States.

Water flow data was obtained for some locations in the Red River to calculate pesticide masses at these locations in the river in both 2016 and 2017. Such calculations showed that the concentration and loadings of frequently detected pesticides (such as 2,4-D, bentazone, clopyralid, MCPA, and metolachlor) were greater in 2016 than 2017. In 2017, when the number of sampling stations were extended to include tributaries of the Red River, the watersheds of tributaries with coarse textured soils showed 15 (Assiniboine River) and 16 (Seine River) unique pesticide compounds whereas the Red River and its La Salle tributary have watersheds with clay-rich soils and each showed 25 unique pesticide compounds across the growing season. This could suggested that flooding on clay-rich soils contributes to greater risks of river contamination by pesticides.

Both current-use and legacy pesticides were detected in bottom sediments. Most legacy pesticides such as DDT tend to be hydrophobic and hence are likely to partition to sediments that tend to be rich in organic carbon. Current-use pesticides, particularly herbicides, tend to be hydrophilic and thus are expected to have a smaller affinity for sediments relative to DDT. However, current-use herbicide glyphosate was detected in more than one-half (55%) of bottom-sediment samples and together with its main metabolite (AMPA) was detected in much greater concentrations than any other pesticide compound in sediment. The detection frequency of DDT (~3% out of 94 bottom-sediment samples) and its metabolites (33 to 50%; n=94) in bottom-sediment samples shows the persisting nature of these compounds in the environment given that DDT was banned decades ago from use in Canada.

In addition to suspended and bottom sediments, there are a range of other constituents in rivers including microplastics, ash and charcoal. Thus, the second study in this Ph.D research focused on the sorption of current-use herbicides (2,4-D, atrazine, glyphosate) versus DDT by river constituents. The sorption experiment included three different background solutions: 1) water enriched with ions ($CaCl_2$ or KCl); 2) de-ionized water; and 3) Red River water because this allowed for the investigation of water quality could have an impact on the sorption of pesticides by constituents by sediments, microplastics, ash and charcoal. Overall, although water quality had an impact, sorption was particularly influenced by the physio-chemical characteristics of the pesticide, and the nature of the sorbent. For 2,4-D, atrazine and DDT, charcoal and ash demonstrated the greatest sorption potential. Glyphosate sorption was significantly greater for suspended and bottom sediments than other constituents.The results of these laboratory experiments are in line with the results of the bottom-sediment samples collected in the field in that 55% of the bottom-sediments contained glyphosate up to a maximum of 1,088µg/Kg per freeze-dried sediment. This compares to 7% and ~ 4 µg/Kg for 2,4-D and 17% and ~ 6µg/Kg for atrazine, respectively. Microplastics had no significant affinity to sorb current-use herbicides (<6%) except for the sorption of glyphosate by PVC (32-36%). However, microplastics always strongly sorbed DDT (55-94%).

Pesticide rinsate areas are documented to contribute to point source pollution in the surface water (Frede et al. 1998; Neumann et al. 2002). Biobeds are designed to reduce this point source pollution by treating pesticide rinsate through biomatrix contained in a biobed system. This study examined under Prairie conditions both single- and dual-cell biobeds for their efficiency to treat pesticide rinsate that comes from the cleaning of sprayers. This pesticide rinsate contained current-use pesticides widely applied on the Prairies such as 2,4-D, bromoxynil, clopyralid, dicamba, and MCPA. By quantifying the concentrations of pesticides detected in the rinsate (influent to biobeds) and comparing them to a

toxicity quotient, the median Pesticide Toxicity Index was calculate. For both single and dual cell biobeds, the influent contained pesticide mixtures at concentrations that would by direct exposure, cause significant harm to several indicator species of aquatic organisms. In contrast, the median Pesticide Toxicity Index of the effluent of the single or dual cell biobeds were substantially smaller and perhaps indicated the potential to cause no harm upon environmental dispersal. As such, this study suggests that biobeds are well capable to minimize the risk for environmental pollution by current-use pesticide activate ingredients.

Biobeds were effective in reducing the concentrations of a wider range of current-use pesticides, including auxin herbicides such as 2,4-D, MCPA and dicamba that are widely used in crop production in the Prairies and were also among the most frequently detected pesticide compounds in the Red River included in this study. Both single and dual cell biobeds worked equally well for these herbicides but the tested biobeds showed a relatively poor performance for some other current-use herbicides such as clopyralid and bentazone, which are also frequently-used in the Prairies. Current-use herbicides that were relatively frequently detected in the effluent of the biobeds had generally high GUS values (>2.8), meaning that the Groundwater Ubiquity Score (GUS) might be a good indicator to use to predict current-use pesticides that are moving through the biobed to the effluent at a more consistent rate than other active ingredients

5.2 Practical Implications of the Research

A wide range of pesticides were detected in in the water-column and bottom sediment of the Red River. Only six of the 172 active ingredients detected in the water-column have individual Canadian Water Quality Guidelines for the Protection of Aquatic life and these guidelines were never exceeded. Water-column samples often contained both herbicides 2,4-D and MCPA (23% of total) or both herbicides

2,4-D and clopyralid (22%), and in 14% of 162 water-column samples all three herbicides herbicide 2,4-D, clopyralid and MCPA awere present. The Canadian Water Quality Guidelines must start including such pesticide mixtures that are commonly detected in surface waters. More than 8 out of 10 river water-column samples taken in this study contain pesticide mixtures, hence it is essential that the Government of Canada moves forward to setting aquatic water quality guidelines for pesticide mixtures which is necessary for aquatic ecosystem risk analysis.

The Government of Canada has been using models to estimate the impact of agriculture activities on the environment, for example as part of Agriculture and Agri-Food Canada's (AAFC) National Agri-Environmental Health Analysis and Reporting Program (NAHARP).The Canadian Indicator of Water Contamination by Pesticides (IROWC-Pest) was developed and refined under NAHARP over an about 15-year time frame (Cessna et al. 2004, 2005, 2010, Gagnon et al. 2016).The risk to surface water and ground water contamination is estimated using the Pesticide Root Zone Model (PRZM) linked to stochastic models (Gagnon et al. 2014). Examples of input parameters into PRZM includes crops and pesticides used, as well as soil texture. Output parameters are the estimated pesticide mass in surface water and groundwater in Soil Landscaped of Canada (SLC) polygons. Based on the results obtained for the four rivers studied in this PhD research, rivers in watersheds with clay-rich soils showed a much greater number of unique pesticide compounds in the water-column than rivers in watersheds with coarse-textured soils. It would be of interest to examine whether SLC polygons with clay-rich soils show greater risks for surface water contamination by pesticides, relative to SLC polygons with course-textured soils. Thus, the data collected in this Ph.D research can assist the Canadian Govenmnet in helping to validate IROWC-Pest.

Between 2008 and 2016, the Red River accounted for 12% of the inflow to Lake Winnipeg (Brunskill et al. 1980; LWIC 2005; ECCC 2020). This study quantified the concentrations of pesticides at sampling locations close to Lake Winnipeg. Such data can be informative to the Government of Manitoba in addressing the question to what extent the Red River contributes to pesticide loadings to Lake Winnipeg.

The basis of pesticide fate models is to understand the movement of pesticide from its point of application to broader environment (Wagenet and Rao 1990). Sorption coefficients are key input parameters in pesticide fate models, for example in predicting the mass of pesticides moving from the water column to bottom sediments. This Ph.D research calculated such sorption coefficients and compared them to sorption coefficients determined for other river constituents such as different types of microplastics, as well as ash and charcoal. It did so by following OECD approved methods of preparing the initial pesticide solutions such as glyphosate in 0.01MKCl. However, batch equilibrium experiments were also conducted with autoclaved river water and glyphosate sorption coefficients were distinctly different from those determined with the background KCl solutions. Thus, this PhD research shows the importance for including environmental water when determining glyphosate sorption coefficients for sediments or other river constituents.

In general, glyphosate sorption was shown to be lesser when using river water, suggesting that ions present in river water were competing with glyphosate molecules for sorption. Pesticide fate models need to be refined to take this competition into consideration, which would require further batch equilibrium studies on pesticide sorption by using environmental water.

A few studies (Besseling et al. 2013, Koelmans et al. 2015) have shown bioaccumulation of PCBs in marine organism and that a contributing factor was the ingesting of contaminated microplastics by organisms. This Ph.D research revealed that such bioaccumulation is of less concern for current-use pesticides, except for the sorption of glyphosate by PVC. As such, this study indicates that is unlikely for fresh water organisms to bioaccumulate pesticides because of ingesting microplastics. In complex, large-scale modeling such as at the global-scale, such bioaccumulation models can be switched off when quantifying environmental pesticide fate.

Although, using biobed is a well-known agricultural practice in Europe and Latin America, it is quite new in Canada. This research demonstrates the practical outcome of using operational on-farm biobeds. The results in this study show the drastic reduction in pesticide concentration from influent to effluent, indicating the efficient performance of single- and dual-cell biobeds under Prairie environmental conditions. As such, this Ph.D research provides farmers and other pesticide applicators with a practical option to protect the environment.

As a practical implication, the way farmers can get to know the effectiveness of biobed without doing expensive pesticide analysis is seeding mixture of grasses on the top of dual-cell biobed and may notice very poor plant growth on first cell depending on the type of pesticide mix, volume and concentration of rinsate. But farmers should notice bettergrowth of plants as the rinsate is already treated once by first cell. In the same way, farmers can use the effluent from single-cell biobeds and irrigate a potentially sensitive plant (e.g., a tomato plant is very sensitive to 2,4-D residues); if there is no or little negative impact onthe plant, the biobed is working.

This study shows that both single and dual-cell biobeds work equally well for most of the commonly used pesticides. The construction of a dual-cell biobed costs more than that of a single-cell biobed. This study demonstrates that single-cell biobeds work extremely well under Prairie conditions, thereby showing costs savings in protecting pesticide point-source pollutions in the environment.

5.3 Recommendations for Future Studies

In the first chapter of this thesis the types, concentrations and detection frequencies of pesticides in the water-column and bottom sediments of rivers were determined.There are limitations in grab sampling because it is just a quick snapshot in time. It is well documented that passive sampling (e.g. POCIS) can provide for a much more comprehensive overview of the presence of organic contaminants such as pesticides through a time-weighted average sampling (Challis et al. 2016, 2018). The main reason why these were not used is due to the issue of calibration of some of these samplers being primarily dependent on flow rate of the fluvial system, and so this is longer term work that subsequent studies should pursue. Future studies could also pursue taking grab samples approximately 24h after a major rainfall event such as has been done in some nutrient monitoring (Rattan et al. 2017).

Batch equilibrium experiments performed under this Ph.D research suggest that it is unlikely for the microplastics to contain current-use pesticides such as 2,4-D and atrazine. These herbicides are widely present in the water column of rivers such as the Red River, but this Ph.D study suggests that microplastics collected from the Red River should show no detections of these herbicides in microplastics.Future studies should also include sampling of microplastics from rivers to examine current-use pesticide concentrations in these samples, including screening for 2,4-D and atrazine to check whether these herbicides indeed do not partition into microplastics under environmental conditions.

In this study, in order to maximize recoveries, sediments were freeze-dried to obtain the pesticide residues in the sample. But moisture content was not accounted in the procedure. Future studies must include determining the moisture content of wet sediments to back calculate pesticide residues in bottom sediments so that comparison can be done with standards set under the Canadian Sediment Quality Guidelines.

The sorption study was accomplished using an equilibrium time period of 24 hours as done often in batch equilibrium studies. Ash and charcoal already sorbed ~100% of all the chemicals individually at equilibrium time. Future experiment can be conducted with shorther and longer time periods, and at different temperatures, to better understand sorption kinetic rates. In addition, studies need to be conducted to observe if there is any desorption of pesticides from the river constituents studied.

River water was collected at one time (mid-summer) to conduct this sorption study. Further studies can be conducted with river water collected at different time such as mid-winter or during the snowmelt period to observe whether the river water quality is different deopending on the time of year and how this might influence sorption cofficents.

This study measured the pesticide concentrations in biobed influent and effluent. However, the biomatrices of the single- and dual-cell were not analyzed for pesticide residues. There is a chance of plant dry matter or the topsoil use to prepare the biomatrix contained some pesticide residues and measuring pesticide concentration in the biomatrix over time helps with the interpretation of the results of some pesticide active ingredients which were detected in the effluent but not influent (e.g., metconazole, pyridaben, and tebuconazole in single-cell biobeds), or at greater concentration in the

effluent than influent (e.g., diclofop and imazethapyr in single-cell and clopyralid and fluroxypyr in dual-cell biobeds). Future studies must include the analysis of pesticides in biomatrices over time.

Further research should be conducted on modifications of the biomatrix to further optimize the efficiency of biobeds for pesticides that have large GUS values. The biobeds used for this research were single-cell and dual-cell biobed systems whose effluent needs to be disposed of such as by irrigating a grass strip or a shelterbelt. Future research should focus on closed biobed systems where the effluent continuously recirculates within the biobed system so no effluent would come out to the broader environment. Also, monitoring should be done to investigate if pesticides continue to build up in biomatrix and, if so, such levels could decrease microbial populations to the extent that pesticide degradation rates slow down.

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APPENDICES

Supplementary Information

Chapter 2

Table 2S1: List of 172 pesticide compounds analyzed with GC-MS/MS and LC-MS/MS for river water and sediment samples

Pesticide (Chemical compound	Status	Chemical class
	Herbicide	
MCPA	R	Phenoxyacetic, auxin
2,4-D	R	Phenoxyacetic, Auxin
Bentazon	R	Thiadiazine
Clopyralid	R	Auxin
Fluroxypyr	R	Auxin
Metolachlor	R	Chloroacetanilide
Bromoxynil	R	nitrile
Mecoprop	R	phenoxypropionic
Triallate	R	Thiocarbamate
Imazethapyr	R	Imidazolinone
Atrazine	R	Triazine
Dicamba	R	Auxin
EPTC (S-ethyl dipropylthiocarbamate)	R	Thiocarbamate
Picloram	R	Auxin
Dimethachlor	NR	Chloroacetanilide
2,4-Dichlorophenol (Metaboilte)	R	Phenoxyacetic, Auxin
Triclopyr	R	Auxin
Butylate	H	Thiocarbamate
Cycloate	H	Thiocarbamate
Diclofop	H	Aryloxyphenoxypropionate
Allidochlor	NR	Amide
Diphenamid	H	Amide
Napropamide	R	Amide
Propyzamide	R	Amide
Benzoylprop-Ethyl	NR	Arylalanine
Flamprop-Isopropyl	H	arylalanine
Flamprop-Methyl	H	arylalanine
Fenoxaprop	R	Aryloxyphenoxypropionate

Clodinafop-propargyl	R	aryloxyphenoxypropionic
Quizalofop-ethyl	R	aryloxyphenoxypropionic
Fluazifop-p-butyl	R	aryloxyphenoxypropionic
Ethofumesate	R	Benzofuran
Dichlobenil	R	Benzonitrile
Propham	NR	Carbanilate
Alachlor	H	Chloroacetanilide
Butachlor	NR	chloroacetanilide
Simazine	R	Chlorotriazine
Flumioxazin	R	dicarboximide
Benfluralin	NR	Dinitroaniline
Butralin	NR	Dinitroaniline
Ethalfluralin	R	Dinitroaniline
Pendimethalin	R	Dinitroaniline
Trifluralin	R	Dinitroaniline
Imazamethabenz	R	Imidazolinone
Prometon	NR	Methoxytriazine
Desmetryne	NR	Methylthiotriazine
Prometryn	R	Methylthiotriazine
Oxyfluorfen	R	nitrophenyl ether
Clomazone	H	Oxazole
MCPB-methyl	R	Phenoxybutyric
2,4-DB	R	Phenoxybutyric, Auxin
Dichlorprop	R	Phenoxypropionic
Monolinuron	H	Phenylurea
Quinclorac	R	quinolinecarboxylic acid
Chlorthiamid	NR	Thioamide
Terbutryne	NR	Triazine
Hexazinone	R	Triazinone
Sulfentrazone	R	Triazolinone
Carfentrazone-ethyl	R	Triazolone
Terbacil	R	Uracil
Bromacil	R	uracil
MCPA-EHE (MCPA 2 Ethylhexyl ester	R	Phenoxyacetic
Glyphosate	R	None
AMPA(Aminomethylphosphonic acid-Metabolite)	NR	None
Glufosinate	R	None
	Insecticide	
p,p'-DDE (Metaboilte)	H	organochlorine
Dieldrin	NR	Cyclodiene
p,p-DDD (Metaboilte)	H	organochlorine
p,p- DDT (Metaboilte)	H	organochlorine

Chlorpyrifos	R	Organophosphate
Bifenthrin	R	Pyrethroid
cis-Permethrin (Isomer)	R	pyrethroid ester
trans-Permethrin (Isomer)	R	pyrethroid ester
Phorate	R	aliphatic organothiophosphate
Carbaryl	R	Carbamate
Carbofuran	H	Carbamate
Bifenazate	R	Carbazate
cis-Chlordane	H	Cyclodiene
Mirex	NR	Cyclodiene
Pirimicarb	H	Dimethylcarbamate
Methoprene	R	juvenile hormone mimics
Aldrin	NR	Organochlorine
Endrin	NR	Organochlorine
HCH-α (Metaboilte)	H	Organochlorine
HCH-β (Metaboilte)	H	Organochlorine
HCH-δ (Metaboilte)	H	Organochlorine
Heptachlor	NR	Organochlorine
Lindane	H	Organochlorine
Methoxychlor	H	Organochlorine
t-Chlordane	NR	Organochlorine
tr-Heptachlor Epoxide	NR	Organochlorine
α-Endosulfan	R	Organochlorine
o,p-DDD (Metaboilte)	H	organochlorine
o,p'-DDE (Metaboilte)	H	organochlorine
o,p-DDT (Metaboilte)	H	organochlorine
Azinphos-methyl	H	Organophosphate
Chlormephos	NR	Organophosphate
Chlorpyrifos-Methyl	NR	Organophosphate
Diazinon	R	Organophosphate
Dichlorvos	H	Organophosphate
Dimethoate	R	Organophosphate
Dioxathion	NR	Organophosphate
Ethion	H	Organophosphate
Etrimfos	NR	Organophosphate
Fenchlorphos	NR	Organophosphate
Fenthion	H	Organophosphate
Fonofos	H	Organophosphate
Isofenphos	NR	Organophosphate
Malathion	R	Organophosphate
Naled	R	Organophosphate
Pirimiphos-Ethyl	NR	Organophosphate
Pirimiphos-Methyl	NR	Organophosphate

Sulfotep	H	Organophosphate
Sulprophos	NR	Organophosphate
Terbufos	H	Organophosphate
Propoxur	R	phenyl methylcarbamate
Bromophos-Ethyl	NR	phenyl organothiophosphate
Propetamphos	H	Phosphoramidothioate
Chlorthal-Dimethyl	R	phthalic acid
Cyfluthrin	R	Pyrethroid
Cyhalothrin lambda	NR	Pyrethroid
Cypermethrin-beta	R	Pyrethroid
Cypermethrin-zeta	R	Pyrethroid
Deltamethrin	R	Pyrethroid
Tetramethrin	R	Pyrethroid
Pyridaben	R	Pyridazinone
Spiromesifen	R	tetronic acid
Piperonylbutoxide	R	Cyclic aromatic
Imidacloprid	R	Chloronicotines
Thiamethoxam	R	Chloronicotines
Clothianidin	R	Chloronicotines
Acetamiprid	R	Chloronicotines
Thiacloprid	R	Chloronicotines
Dinotefuron	NR	Chloronicotines
Nitenpyram	NR	Chloronicotines
	Fungicide	
Boscalid	R	Anilide
Tebuconazole	R	conazole
Azoxystrobin	R	Strobilurin
Prothioconazole-Desthio	R	Conazole
Propiconazole	R	Conazole
Metalaxyl	R	acylamino acid
Pyraclostrobin	R	carbanilate fungicides
Picoxystrobin	R	methoxyacrylatestrobilurin
Fludioxonil	R	pyrrole
Difenoconazole	R	Conazole
Benalaxyl	NR	Anilide
Cyprodinil	R	Anilinopyrimidine
Pyrimethanil	R	anilinopyrimidine
Chloroneb	H	Aromatic
Quintozene	H	aromatic
Zoxamide	R	Benzamide
Chlorothalonil	R	Chloronitrile
Ipconazole	R	Conazole

Myclobutanil	R	Conazole
Triticonazole	R	Conazole
Metconazole	R	conazole
Iprodione	R	Dicarboximide
Procymidone	NR	Dichlorophenyldicarboximide
Fenamidone	R	Imidazole
Famoxadone	R	Oxazole
Vinclozolin	NR	Oxazole
Captan	R	Phthalimide
Folpet	R	Phthalimide
Bupirimate	NR	Pyrimidine
Trifloxystrobin	R	Strobilurin
Etridiazole	R	thiadiazole
	Acaricide	
Bromopropylate	NR	bridged diphenyl
Tetrasul	NR	bridged diphenyl
Tetradifon	NR	bridged diphenyl
Bactericide		
Nitrapyrin	NR	nitrification inhibitors
	Nematicide	
Diclofenthion	NR	Organophosphate
	Growth Regulator	
Flumetralin	NR	Growth inhibitors

Chapter 3

Table 3S2: Red River water analytical parameters (mg/L)

Inorganic compounds
Nitrate and Nitrite as N [1.12], Nitrate (as N) [1.07], Nitrite (as N) [0.045], Total Kjeldahl Nitrogen [1.39]
Organic compounds
Total phosphorus (P) [0.478], Sulfate (SO4) [217]
Total metals (water)
Aluminum (Al) [1.02], Antimony (Sb) [$3.5X10^{-4}$], Arsenic (As) [$7.09X10^{-3}$], Barium (Ba) [$8.06X10^{-2}$], Beryllium (Be) [$<1.0X10^{-4}$], Bismuth (Bi) [$5X10^{-5}$], Boron (B) [0.085], Cadmium (Cd) [$9.39X10^{-5}$], Calcium (Ca) [69.3], Cesium (Cs) [$1.84X10^{-4}$], Chromium (Cr) [$1.9X10^{-3}$], Cobalt (Co) [$1.38X10^{-3}$], Copper (Cu) [$6.0X10^{-3}$], Iron (Fe) [1.83], Lead (Pb) [$1.52X10^{-3}$], Lithium (Li) [0.0565], Magnesium (Mg) [49.1], Manganese (Mn) [0.175], Molybdenum (Mo) [$2.32X10^{-3}$], Nickel (Ni) [$8.07X10^{-3}$], Phosphorus (P) [0.414], Potassium (K) [8.68], Rubidium (Rb) [$5.01X10^{-3}$], Selenium (Se) [$1.53X10^{-3}$], Silicon (Si) [14.9], Silver (Ag) [$1.3X10^{-5}$], Sodium (Na) [37.7], Strontium (Sr) [0.286], Sulfur (S) [74.0], Tellurium (Te) [$<2.0X10^{-4}$], Thallium (Tl) [$4.4X10^{-5}$], Thorium (Th) [$3.4X10^{-4}$], Tin (Sn) [$<1.0X10^{-4}$], Titanium (Ti) [0.0296], Tungsten (W) [$<1.0X10^{-4}$], Uranium (U) [$5.04X10^{-3}$], Vanadium (V) [0.0108], Zinc (Zn) [0.0110], Zirconium (Zr) [$1.5X10^{-3}$]

Chapter 4

Table 4S3: List of all unique active ingredients detected in the influent and effluent of single and dual-cell biobeds

Herbicides
2,4-D, 2,4-DB, atrazine, benfluralin, bentazone, bromoxinil, carfentrazone-ethyl, chlorthiamid, clopyralid, dicamba, dichlobenil, dichloprop, S-ethyl dipropylthiocarbamate, ethalfluralin, fenoxaprop, fluroxypyr, imazethapyr, MCPA, MCPA-EHE, MCPB-methyl, mecoprop, metolachlor, oxyfluorfen, picloram, quizalofop-ethyl, sulfentrazone, terbacil, triallate, triclopyr, trifluralin, glyphosate
Insecticides
Carbaryl, chlormephos, chlorpyrifos, cyhalothrin-lambda, cypermethrin-beta, cypermethrin-zeta, deltamethrin, diazinon, methoprene, methoxychlor, pyridaben, spiromesifen, sulfotep
Fungicides
Azoxytrobin, boscalid,chlorothalonil, difenoconazole, fludioxonil, metalaxyl, metconazole, picoxytrobin, propiconazole, pyraclostrobin, pyrimethanil, tebuconazole, trifloxystrobin, triticonazole
Nematicide
Dichlofenthion