

**Measuring and modelling  
concentrations of plant protection products  
and trace metals in the South Saskatchewan  
River**

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## **Abstract**

Organic chemical pollutants are delivered to riverine habitats via basin land use and hydrology interactions. Aquatic organisms eventually absorb these substances, where they might have negative consequences. However, our capacity to reliably predict potential future changes in pollutant concentrations is now constrained by information gaps relating to the links between hydrological, chemical, and biological processes. In the South Saskatchewan River, Canada, in the years 2020 and 2021, concentrations of three pesticide classes (organochlorines, organophosphates, and herbicides) in the water, sediments, and fish were examined. Organochlorine pesticides have been prohibited in Canada since the 1970s; however, methoxychlor and lindane were occasionally found in samples of sediment and fish that may have been contaminated in the past. Organophosphate pesticides, with the exception of malathion and parathion, were close to detection limit in both sampling years in all matrices, while neonicotinoids were below detection in all samples. On the other hand, for both sampling years, consistent levels of the herbicides 2,4-D and dicamba were found in water samples from all locations. Concentrations were on average three times higher in 2020, when river discharge was two times greater, possibly pointing to contaminated sediments being disturbed by high flows, or run-off from the nearby watershed. Of the trace metals, copper and zinc concentrations at several sampling locations exceeded standards for sediment quality. About 18% of the water and sediment samples that were examined had mercury concentrations that were above recommended levels. These discoveries fill in the gaps in monitoring datasets and show significant connections between hydrology and chemistry that can be further investigated in computational models to forecast pollutant trends in freshwater systems.

Trace metal concentrations were used to model transport and fate in the South Saskatchewan River using an existing model developed for another freshwater system. The

River Analysis System from the Hydrologic Engineering Center was paired with a well-known 1-D modelling technique (HEC-RAS). The stream transport module for the WASP (Water Quality Analysis Simulation Program), TOXI, can calculate the flow of water, sediment, and dissolved constituents through branching and ponded segments and is integrated with flow routing for free-flow streams, ponded segments, and backwater reaches. Two metals with primarily anthropogenic and geogenic origins were chosen: copper and nickel. The South Saskatchewan River was analysed in 2020 and 2021 at 10 distinct locations, both upstream and downstream of the City of Saskatoon. By comparing model predictions with copper and nickel concentrations obtained earlier, model performance was assessed. The model functioned reasonably well for sediment samples and did a good job of estimating the levels of copper and nickel in water samples. In both the water and sediment sample segments, the model overestimated concentrations. Diffuse pollutant loads were increased to enable the model to work more precisely. This work shows the predictive power of merging WASP-TOXI and HEC-RAS models for the prediction of contaminant loading, even though numerous default parameter values had to be employed because primary historical data was unavailable. This proof-of-concept study will be useful for future research, including studies on the effects of climate change on the quality of water in the Canadian prairies.

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## Abbreviations

2,4 – D	2,4-dichlorophenoxyacetic acid
BCF	Bioconcentration Factor
BSAF	Biota-sediment Accumulation Factor
CCME	Canadian Council of Ministers
Cu	Copper
DDD	4,4'-dichlorodiphenyldichloroethane
DDE	4,4'-dichlorodiphenyldichloroethylene
DDT	4,4'-dichlorodiphenyltrichloroethane
DOC	Dissolved Organic Carbon
GC-MS	Gas Chromatography – Mass Spectrometry
GIS	Geographic Information System
HEC-RAS	Hydrologic Engineering Center – River Analysis System
HESI	Heated Electrospray Ionization
ISQG	Interim Sediment Quality Guidelines
LC-MS	Liquid Chromatography – Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MCPA	2-Methyl-4-chlorophenoxyacetic acid
MCPP	Methylchlorophenoxypropionic acid
Ni	Nickel
QA	Quality Assurance
QC	Quality Control

SPE	Solid Phase Extraction
SSR	South Saskatchewan River
SSRB	South Saskatchewan River Basin
TOC	Total Organic Carbon
TSS	Total Suspended Solids
WASP	Water Quality Analysis Simulation Program
WSC	Water Survey Canada



# **Chapter 1: GENERAL INTRODUCTION**

## **1.1. Introduction**

In recent decades, it has become increasingly evident that human activities can have harmful impacts on water quality. Many lakes, rivers, streams, and oceans and the organisms that inhabit these systems are being affected. Rapid industrialization and an increase in agricultural activities to meet the nutritional demand of a growing population are some of the major sources of pollution to water bodies. The use of synthetic fertilizers and pesticides to increase agricultural yields can result in run-off from fields to nearby water bodies (Nikolaidis, Mandalos, and Vantarakis 2008). Particularly, freshwater ecosystems have been affected by agricultural activities, resulting in impacts on various aquatic species (Revenga et al. 2000). More specifically, water contamination raises concerns over bioaccumulation of pesticides and other chemicals in fish, which are of commercial, ecological, and cultural importance (UNEP 2010).

The South Saskatchewan River is one of the most important river systems in Western Canada. The South Saskatchewan River Basin is home to 1.6 million people in Alberta and 460,000 people in the Saskatchewan portion of the basin (estimated from 2011 population census regions). More than half of the population of Saskatchewan depends on the South Saskatchewan River for its daily water needs (AMEC 2009). Major industrial water users include power production, fertilizer plants, potash mines, and petroleum-related operations (Alberta 2003).

Saskatchewan is well-known for its agriculture and is considered Canada's breadbasket (Statistics Canada 2017). Given the fact that more than half of Saskatchewan's residents rely on water from the South Saskatchewan River for daily activities, the consumption of water for irrigation and industries adds more stress. However, not only the quantity of water in the South Saskatchewan River Basin is under pressure; water quality is at risk of being impacted by contaminants from various sources. These include pesticides originating from areas of high

agricultural activity, petroleum hydrocarbons from oil and gas industries, pharmaceuticals and personal care products from municipal wastewater effluents, and urban run-off and stormwater from neighboring cities (Pomeroy et al. 2005).

Due to the relevance of the South Saskatchewan River Basin as an important source of water for many industries and residents of Alberta and Saskatchewan, it is crucial to improve our understanding of, and capabilities for, predicting water quality of the river along with current and future contamination trends considering the impacts of environmental factors.

## **1.2. Literature Review**

Various factors need to be considered to adequately understand the behavior of different contaminants in a water body. As mentioned above, Saskatchewan is an agriculture-intensive province, which results in increased use of pesticides, insecticides, and herbicides. Given the importance of the South Saskatchewan River, it is essential to understand how inorganic and organic contaminants behave in this water body. Various factors play an important role in determining the behavior of such contaminants, including water quality and its changes due to anthropogenic activities, uptake of these contaminants by aquatic organisms, such as fish, and the types and quantities of chemicals emitted on the prairies during agricultural and other activities. Predicting the fate of contaminants requires computational models fed with relevant data, the development of which is a central objective of this thesis.

### ***1.2.1. Water Quality***

Water quality, in general, refers to the condition or suitability of water to sustain ecosystems, as well as various uses and processes (Meybeck et al. 1988). Often, most of these uses have a common range of parameters that are required for the suitability of the water resource. Water quality is affected by a wide range of natural and anthropogenic factors. Natural factors mainly include geological, hydrological, and climatic changes. Anthropogenic

factors influencing water quality can be diverse, e.g., mining, agriculture, urbanization, nutrient loading, etc., and often lead to adverse effects on ecosystem health. Usually, several environmental and anthropogenic factors together govern the quality of water in an ecosystem. This means that for the comprehensive assessment of water quality in a given aquatic ecosystem, both environmental and anthropogenic processes, as well as their interactions might be responsible for any observed changes (Gove, Edwards, and Conquest 2001).

In the context of water quality, it is important to distinguish between contamination and pollution. According to Peter Chapman (2007), “contamination is simply the presence of a substance where it should not be or at concentrations above background. Pollution is contamination that results in or can result in adverse biological effects to resident communities.” Water pollution is often further classified into two categories: point source pollution originates from a single location, such as wastewater effluent, landfills, mines, etc. In contrast, non-point source pollution originates from various waterways spread across broad spatial scales, which may include groundwater, soil, agricultural and municipal run-off, etc. (Ritter et al. 2002).

### ***1.2.2. Pesticides***

Rising global pesticide use is known to contaminate surface and ground waters, which threatens the health of aquatic ecosystems (Ippolito et al. 2015; Malaj et al. 2014; Stehle and Schulz 2015; Sudo et al. 2004). Recently, total pesticide use was estimated at 5.8 billion pounds per annum globally (Atwood and Paisley-Jones 2017); however, given the fact that country-specific data availability is uncertain, these figures need to be viewed with caution. Canada mainly relies on the prairies region of Western Canada for agricultural production, which includes Alberta, Saskatchewan, and Manitoba (Statistics Canada 2017). As a result, the use of pesticides is greater on the Prairies in comparison with any other part of Canada (Malaj, Liber, and Morrissey 2019). Persistent usage of pesticides can lead to environmental problems.

It is well-documented that pesticides can be transported to aquatic ecosystems by surface run-off, erosion, and wind, which adds to agricultural contamination (Cessna et al. 2001). Further, the addition of excess water during irrigation after the soil has reached water saturation can lead to irrigation run-off entering drainage ditches, which in turn can carry cumulative run-off from multiple irrigated fields. For example, the South Saskatchewan River Irrigation District (SSRID) is the largest irrigation district in Saskatchewan. Most of its area is irrigated by backflood and sprinkler irrigation methods, and the drainage water from the irrigation is generally sent back to the river (Acreage et al. 2001; Cessna et al. 2001). Jame et al. (1999) suggest that water from the irrigated fields can be contaminated with pesticides and not be suitable for irrigating fields and other uses downstream of the outfall.

A study (Malaj, Liber, and Morrissey 2019) carried out in the Prairie Pothole Region estimated pesticide usage in 2015 at 39,236 metric tonnes for two widely grown crops, wheat and canola. They found that 55 herbicides, 27 fungicides, and 12 insecticides were commonly used on the Prairies. The study estimated the pesticide use patterns for three main groups (herbicides, fungicides, insecticides). Herbicide use density was the highest (24 – 183 kg/km<sup>2</sup>), followed by fungicides (0.4 – 23.8 kg/km<sup>2</sup>) and insecticides (0.4 – 3.6 kg/km<sup>2</sup>). The usage of pesticides varied across provinces yet was consistent to the wheat and canola crops. Some pesticides can stay in the environment for extended periods of time, depending on their physicochemical characteristics, as well as environmental factors, such as soil texture and precipitation (Malaj, Liber, and Morrissey 2019).

On the prairies, the pesticides most commonly used are the herbicides glyphosate, MCPA, and 2,4-D (Mackay 2001; Environment Canada 2011), and more recently, the neonicotinoid insecticides, thiamethoxam and clothianidin (Main et al. 2014). A study conducted by Mackay (2001) showed that MCPA and are some of the most commonly used herbicides in Central Saskatchewan.

### ***1.2.3. Trace Metals***

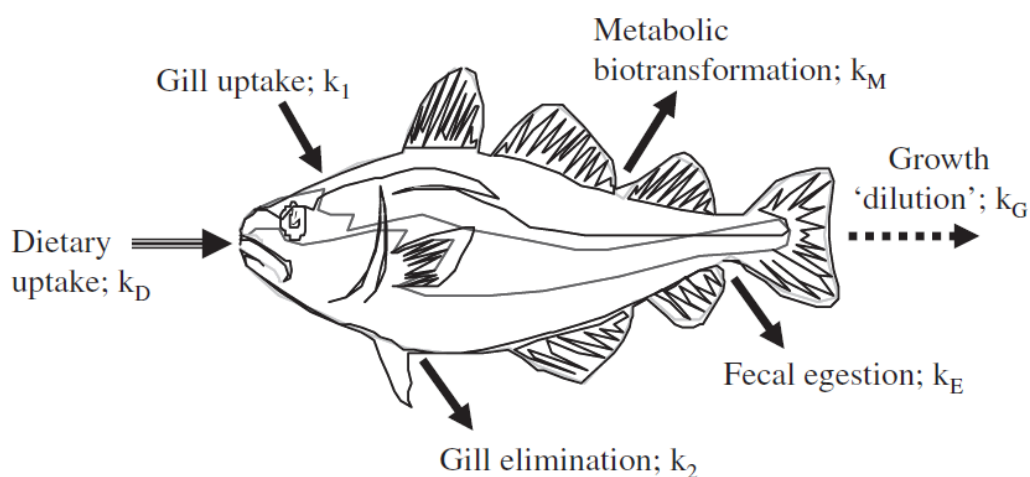
Trace metals have been deemed responsible for global water quality decline in the past few decades (Edet and Offiong 2002; Sollows 2015). Their environmental fate and bioavailability depend on several chemical properties. There are various chemical and potash plants, oil and gas wells, and pulp and paper mills located along the South Saskatchewan River (SSR) which are responsible in contributing effluents to the river with varied trace metal concentrations (South Saskatchewan River Watershed Stewards n.d.). Copper (Cu) is one such trace metal that is used in a plethora of activities such as electrical wiring, plumbing, industrial machinery, and construction materials. This contributes towards the anthropogenic release of Cu in the environment (Environment Canada 2016). Copper exists in four oxidation states, of which Cu (II) is the most important as it is generally found in water. The presence and bioavailability of Cu in surface waters is dictated by various physicochemical processes and factors such as pH, hardness, and DOC. Copper (II) is primarily linked to toxicity to aquatic life and with the sediments as well. Copper (II) binds with organic or inorganic matter depending on the pH and redox potential in that particular environment (EURAR 2008).

Nickel (Ni) is another trace metal which is naturally present in the earth's crust combined with other elements in soil, meteorites, and volcanic emissions (Genchi et al. 2020). Nickel can occur in various mineral forms and is resistant to corrosion by air, water, and alkali. It exists in five different oxidation states. The most common oxidation state in which Ni is found in the environment is Ni (II) (Clayton and Clayton 1994; Coogan et al. 1989). Nickel is widely distributed in the environment in air, water, and soil. Natural sources of Ni include dust, weathering of rocks and soils, volcanic emissions, and forest fires (Nieminen et al. 2007). Fate of Ni in freshwater systems is dependent on partitioning between soluble and particulate matter which is further affected by adsorption, precipitation, and complexation. Similar to Cu, Ni partitioning is influenced by pH and redox potential (Richter and Theis 1989).

#### ***1.2.4. Bioaccumulation***

Many pesticides display high chemical stability, resistance to metabolism, and high lipid solubility, making them some of the most hazardous substances present in the environment. In contrast to other environmental contaminants, pesticides are specifically produced to cause harm to pests. These properties, however, make pesticides also harmful to many non-target organisms in the environment, and sometimes also for humans (Dorr et al. 2007). In addition to knowing the toxicity of pesticides to non-target organisms, information regarding potential bioaccumulation is needed to assess whether a chemical is likely to reach concentrations in organisms that are elevated over environmental concentrations and a cause for concern. This information is important in determining environmental quality guidelines, establishing total maximum daily loadings, categorizing substances that are potential hazards, and quantifying the risk of chemicals to ecosystems and human health (Organization for Economic Co-operation and Development, Environmental Protection Agency). Empirical information is often preferable, but models are useful when empirical measurements do not exist or cannot be made for either technical or economic reasons (Arnot and Gobas 2006). The following are some key terms used to describe bioaccumulation.

*Bioconcentration* (Arnot and Gobas 2006): The process by which a chemical substance is taken up by an organism from the surrounding environment via the respiratory tract and dermal surface, excluding chemical exposure through their diet. It is the overall result of the uptake and elimination rate through respiration, fecal egestion, biotransformation of the compound, and growth dilution (Figure 1). The extent of bioconcentration that occurs is expressed as the bioconcentration factor (BCF).



**Figure 1.1.** Major routes and associated rate constants of chemical uptake and elimination in fish (Arnot and Gobas 2006).

Mathematically, bioconcentration can be represented by a one-compartment model, where the fish's body is represented by only one individual compartment. The chemical is assumed to be homogeneously distributed in both the fish and the surrounding bulk water. The model can be expressed as

$$\frac{dC_B}{dt} = (k_1 C_{WD}) - (k_2 + k_E + k_M + k_G) C_B \quad (1.1)$$

where  $C_B$  is the chemical concentration in the organism (mg/kg),  $t$  is a unit of time (d),  $k_1$  is the rate constant for chemical uptake from water at the respiratory surface (L/kg/d),  $C_{WD}$  is the dissolved chemical concentration in the water (mg/L), and  $k_2$ ,  $k_E$ ,  $k_M$ ,  $k_G$  are rate constants (1/d) for chemical elimination from the organism *via* respiratory surface, fecal egestion, metabolic biotransformation and growth dilution, respectively (Figure 1). When  $C_B$  and  $C_{WD}$  are in a steady state, i.e.,  $\frac{dC_B}{dt} = 0$ , the equation can be rearranged to calculate the bioconcentration factor (BCF) as



$$BCF = C_B/C_{WD} = k_1/(k_2 + k_E + k_M + k_G) \quad (1.2)$$

*Bioaccumulation* (Arnot and Gobas 2006): In this process, a chemical substance is taken up by an organism via all routes of exposure in the natural environment (including dietary sources). Bioaccumulation is the net result of chemical uptake into an organism at both respiratory surface and diet, and chemical elimination from an organism, including respiratory exchange, fecal egestion, metabolic biotransformation, and growth dilution. Figure 1 highlights all major routes of chemical uptake and elimination, as well as the corresponding rate constants in fish. Mathematically, bioaccumulation can be represented as

$$\frac{dC_B}{dt} = (k_1 C_{WD} + k_D C_D) - (k_2 + k_E + k_M + k_G) C_B \quad (1.3)$$

where  $k_D$  is the uptake rate constant for chemical in the diet (kg/kg/d), and  $C_D$  is the chemical concentration in the diet (mg/kg).

Bioaccumulation factor (BAF) is the degree to which bioaccumulation occurs and at a steady state, i.e.,  $\frac{dC_B}{dt} = 0$ , it can be represented as

$$BAF = \frac{C_B}{C_{WD}} = (k_1 + k_D(C_B/C_{WD}))/k_2 + k_E + k_M + k_G \quad (1.4)$$

BCF and BAF are distinct and not interchangeable quantities because of chemical exposure in the diet (potential biomagnification).

*Biomagnification* (Arnot and Gobas 2006): When the thermodynamic activity of a chemical in an organism exceeds the thermodynamic activity of its diet, the chemical is said to be biomagnified in the organism. Biomagnification can be expressed as the biomagnification factor (BMF) and is defined as the ratio of a steady-state chemical concentration in an organism relative to that in its diet.

$$BMF = \frac{C_B}{C_D}$$

(1.5)

In fish, invertebrates, and zooplankton,  $k_1$  can be viewed as a function of the gill ventilation rate  $G_V$  (L/d) and the diffusion rate of the chemical across the respiratory surface area (Gobas 1993; Gobas, Muir, and Mackay 1988):

$$k_1 = E_W G_V / W_B$$

(1.6)

where  $E_W$  is the gill chemical uptake efficiency (dimensionless) and  $W_B$  is the wet weight of the organism (kg). As  $k_1$  and  $k_2$  are involved in the same processes of ventilation and membrane permeation, the elimination rate constant  $k_2$  is determined by (Arnot and Gobas 2004):

$$k_2 = k_1 / BCF$$

(1.7)

As mentioned earlier, the equilibrium partitioning properties are represented by the  $BCF$ . The rate constants  $k_1$  and  $k_2$  play an important role in determining how fast or slow equilibrium partitioning will occur. This model is very sensitive to  $k_1$  and  $k_2$  for compounds that are absorbed from water and food or the ones which are eliminated predominantly by gill ventilation. The dietary uptake rate constant  $k_D$  and fecal elimination rate constant  $k_E$ , as well as growth dilution rate constant  $k_G$  vary according to a particular species' size, ambient temperature, food availability and quality, etc. The metabolic transformation rate constant  $k_M$  also depends on the species, life stage, temperature, food availability, as well as the chemical properties. However, empirical data for this process is often lacking. Therefore, many times, the value for  $k_M$  is assumed to be zero.

### **1.2.5. Water Quality Models**

For river systems, several models of varying complexity are available for predicting water quality. Simple screening models assume steady-state conditions in the river systems or are not spatially explicit and have relatively low requirements for input parameters. However, this also means that these models cannot reflect the dynamics of chemical concentrations in river systems in space and/or time (Kreuger and Tornqvist 1998; Neumann et al. 2002), e.g., EXAMS (Burns 2000; Lijzen and Rikken 2004), the Mackay Level III Model (Mackay 2001), and QUAL2E (Brown and Barnwell 1987). In-stream water quality models such as MIKE11 (Xiong, Zhang and Kuang 2017), ISIS (Wallingford and UK 1998), and RWQM1 (Modelling 2005) are based on various differential equations in order to predict chemical concentrations along a river. Depending on the specific model, parameter values can be static throughout the stream, or offer spatial variability.

Hydrologic Engineering Center River Analysis System (HEC-RAS) is one such model developed by the U.S Army Corps of Engineers. It is a multi-tasking software used for one-dimensional and two-dimensional hydraulic calculations for a network of river systems. The HEC-RAS system consists of four major components: (i) one-dimensional and/or two-dimensional steady flow simulation; (ii) one-dimensional and/or two-dimensional unsteady flow simulation; (iii) quasi unsteady or fully unsteady flow movable boundary sediment transport computations (1D and 2D); (iv) one dimensional water quality analysis. HEC-RAS is capable of geometric and hydraulic computation routines. It is also equipped with an extensive spatial data integration and mapping system (US Army Corps of Engineers 2021). HEC-RAS has been previously used for studies where it has been coupled with Water Quality Analysis Simulation Program (WASP) by providing segmentation of a river system (Sydor, DeBoer, and Cheng 1979; Sabokruhie et al. 2021).

WASP is another complex water quality model for aquatic systems. WASP7 was developed by the United States Environmental Protection Agency (US-EPA) and has been enhanced from

the original versions of the model. WASP is a dynamic mass balance model for simulating the fate and transport of contaminants of relevance to water quality in surface waters.

WASP consists of a number of kinetic sub-models that are based on transport and transformation equations. WASP is designed for aquatic systems, including both the water column and the underlying sediments, and calculates water flow through a stream network consisting of several segments. The model consists of various modules, including modules for advanced toxic chemicals (TOXI), sediment transport, eutrophication, and specific toxicant pollution (mercury, heavy metals, etc.). The capability of WASP to handle multiple pollutants and linking hydrodynamic models with watershed models makes it widely applicable to different water systems (Wool 2017, Ambrose and Wool 2009).

WASP allows the simulation of a variety of processes that may affect transport, transformations, and kinetic reactions of toxic chemicals. While focussing on trace metals, most of the simulations encompass sorption and one or two transformation processes that affect a chemical. The TOXI module is capable of simulating the transport and transformation of 1-3 chemicals, metals, and sediments and 1-3 types of particulate material. Every trace metal may exist in a neutral compound and 4 ionic species. These neutral and ionic species can exist in five possible phases: dissolved, sorbed to dissolved organic carbon (DOC), and sorbed to the other 3 types of solids classes (sand, silt, clay, inorganic, phytoplankton, and organic solids). Distribution of the metals among the chemical species and phases is determined by distribution/partition coefficients. Hence, a local equilibrium is assumed. This allows calculating the concentration of any trace metal in any phase *via* total chemical concentration, and only a single state variable pertaining to the total chemical concentration is needed for each trace metal (Ambrose and Wool 2009).

For the model implementation, the TOXI module needs a set of information such as Date and Times, Non-Point Source File (segment and system-specific data file), and Hydrodynamics (flow data). All the segment data is then added, which includes volume, velocity, depth, length, width, slope, etc. Finally, the flow data is provided, and the output display variables are defined (Ambrose and Wool 2009).

There are some drawbacks to the TOXI module to be kept in consideration while using it. Trace metal concentrations should be close to trace levels (half the solubility) since the assumptions of linear partitioning and transformation are inaccurate at higher concentrations. TOXI can furthermore not recognize the impact of high concentrations on pH, which may further alter the simulation. In the South Saskatchewan River, however, such high levels of contaminants are not expected, which makes WASP an ideal platform for modelling water quality in this system.

### **1.3. Objectives**

The overall goal of this research was to improve our understanding and predictive capabilities related to the intimate connection between hydrologic, chemical, and biological processes as key drivers of contaminant transport in the aquatic environment, and bioaccumulation in aquatic organisms.

Specifically, this research will address the following objectives:

- a. Collect environmental samples (water and sediment), as well as small-bodied fish at selected sampling locations along the South Saskatchewan River during two field seasons and measure concentrations of select pesticides and metals in these matrices;
- b. Use these newly created datasets to validate, and if necessary, calibrate a HEC-RAS model coupled with WASP - TOXI model;
- c. Extend an existing computational water quality model for the South Saskatchewan River with a chemical fate model for two trace metals, Cu and Ni.

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**Chapter 2: LEVELS OF PESTICIDES  
AND TRACE METALS IN WATER,  
SEDIMENT, AND FISH OF A LARGE,  
AGRICULTURALLY DOMINATED  
RIVER**

## Overview

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## 2.1. Abstract

Basin land-use interacts with hydrology to deliver chemical contaminants to riverine environments. These chemicals are eventually taken up by aquatic organisms, where they can cause harmful effects. However, knowledge gaps related to the connections between hydrological, chemical, and biological processes currently limit our ability to forecast potential future changes in contaminant concentrations accurately. In this study, concentrations of three pesticide classes (organochlorines, organophosphates, and herbicides) and a standard suite of trace metals were analyzed in the South Saskatchewan River, Canada in 2020 and 2021 in water, sediments, and fishes. Organochlorine pesticides have been banned in Canada since the 1970s, yet there were some detections for methoxychlor and lindane, predominantly in sediment and fish samples, which could be attributed to legacy contamination. Except for malathion and parathion, organophosphate pesticides were scarcely detected in both sampling years in all matrices, and neonicotinoids were below detection in all samples. Conversely, the herbicides 2,4-D and dicamba were detected consistently throughout all locations in water samples for both sampling years. Overall, concentrations were 3 times higher in 2020 when river discharge was ~2 times higher, suggesting run-off from the surrounding catchment or disturbance of contaminated sediments. Analysis for trace metals revealed that Cu and Zn exceeded sediment quality guidelines in some locations. Mercury concentrations exceeded the guidelines for about 18 % of the samples (water and sediment) analyzed. These findings fill gaps in monitoring datasets and highlight key links between hydrology and chemistry that can be further explored in computational models to predict future contaminant trends in freshwater systems.



## 2.2. Introduction

Water quality can be adversely affected by a wide variety of natural and anthropogenic factors (Boyd 2019). Natural factors mainly include geology, hydrology, and climate, while anthropogenic factors such as point- (e.g., wastewater effluent) and non-point (e.g., agricultural run-off) sources of pollution influence water quality in diverse ways and can often lead to adverse effects on ecosystem health. Most commonly, several environmental and anthropogenic factors together govern the quality of water in an ecosystem (Heathwaite 2010). While point sources can often be identified and addressed more easily in the case that environmental issues arise, non-point sources are notoriously difficult to address (EPA 1996).

Agricultural and municipal run-off are particularly important sources of pollution to surface water bodies in the sparsely inhabited and otherwise little industrialized Prairie region of Western Canada, which spans across Alberta, Saskatchewan, and Manitoba (Statistics Canada 2017). The Canadian Prairies are often considered Canada's breadbasket (Laforge, Corkal, and Cosbey 2021); as a result, the use of pesticides is greater there than in any other part of the country (Malaj, Liber, and Morrissey 2019). Persistent use of pesticides, however, can lead to environmental problems. Global pesticide use, estimated at 5.8 billion pounds per annum (Atwood and Paisley-Jones 2017), is known to contaminate surface and ground waters, which threatens the health of aquatic ecosystems (Ippolito et al. 2015; Malaj et al. 2014; Stehle and Schulz 2015; Sudo et al. 2004). A recent study (Malaj, Liber, and Morrissey 2019) carried out in the Prairie Pothole Region estimated pesticide usage in 2015 at 39,236 metric tonnes for two widely grown crops, wheat and canola. They found 55 herbicides, 27 fungicides, and 12 insecticides to be commonly used on the Prairies. Of these, herbicide use density was the highest (24 – 183 kg/km<sup>2</sup>), followed by fungicides (0.4 – 23.8 kg/km<sup>2</sup>) and insecticides (0.4 – 3.6 kg/km<sup>2</sup>). The most commonly used pesticides in Central Saskatchewan are the herbicides glyphosate, 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid

(2,4-D), and dicamba (Mackay 2001; Environment Canada 2011). More recently, the neonicotinoid insecticides, thiamethoxam and clothianidin, are also frequently used (Main et al. 2014).

It is well-documented that pesticides can be transported to aquatic ecosystems by surface run-off, erosion, and wind, which adds to agricultural contamination (Cessna et al. 2001). Yet the large rivers of the Prairie region derive most of their discharge from high elevation reaches in the Rocky Mountains, with few of the agricultural areas in the basin contributing directly to surface flow, meaning many contaminants may not reach the rivers and instead remain in geographically isolated wetlands (Main et al. 2014). However, the addition of excess water during irrigation after the soil has reached water saturation can lead to irrigation run-off entering drainage ditches, which in turn can carry cumulative run-off from multiple irrigated fields. The South Saskatchewan River Irrigation District (SSRID), for example, is the largest in Saskatchewan. Most of its area is irrigated by back flood and sprinkler irrigation methods, and the drainage water from the irrigation is generally sent back to the river (Acreage et al. 2001; Cessna et al. 2001).

Some pesticides can stay in the environment for extended periods of time, depending on their physicochemical characteristics, as well as environmental factors, such as soil texture and precipitation (Malaj, Liber, and Morrissey 2019). Several pesticides display high chemical stability, resistance to metabolism, and high lipid solubility, making them some of the most hazardous substances present in the environment. In addition to knowing the toxicity of pesticides to non-target organisms, information regarding potential bioaccumulation is needed to assess whether a chemical is likely to reach concentrations in organisms that are elevated and a likely cause for concern. This information is important for comparison with environmental-quality guidelines and thereby quantifying the risk these chemicals pose to

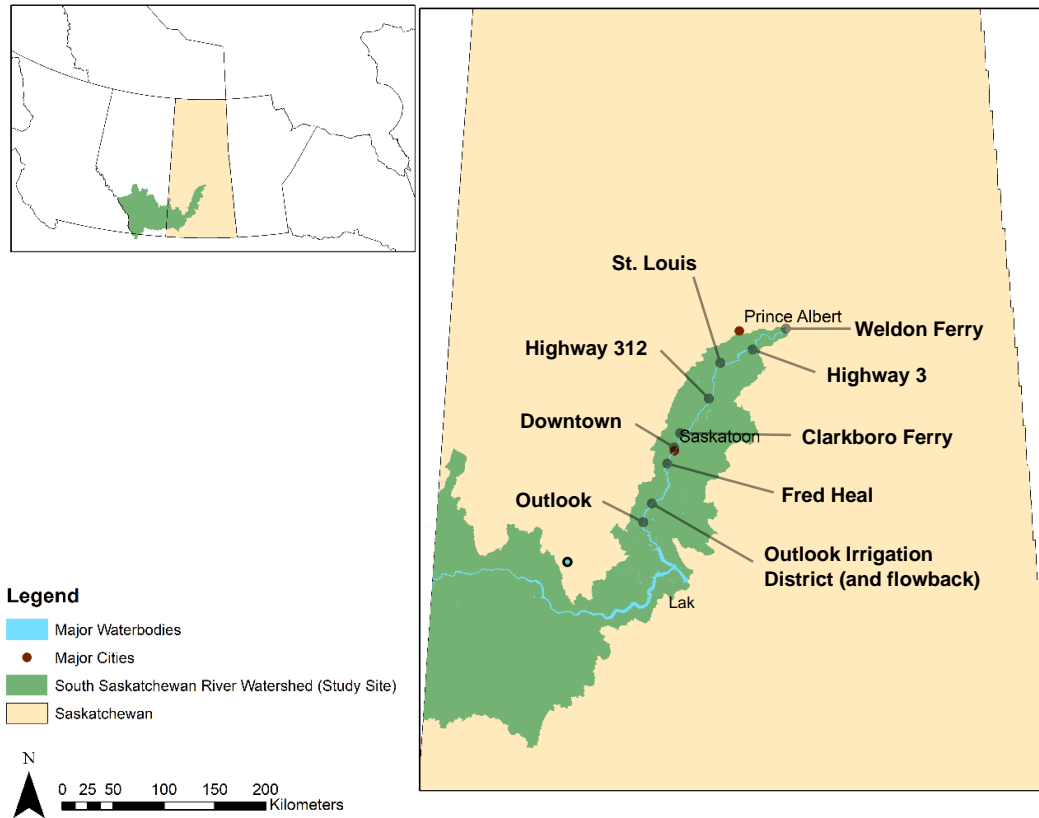
ecosystems and, ultimately, human health (OECD 2018). Unfortunately, empirical information is often unavailable, which complicates environmental risk assessments for a given watershed.

The aim of the present study was to fill some of these critical data gaps for a large, agriculturally dominated river, the South Saskatchewan River in Saskatchewan, Canada, by determining concentrations, as well as temporal and spatial dynamics, of a variety of pesticides, specifically insecticides and herbicides, in water, sediments, and small-bodied forage fish collected in spring and summer of both 2020 and 2021. The year 2020 was characterized by exceptionally high discharges (~ twice as much as 2021), while 2021 was a drought year with minimal discharge. In addition to measuring pesticides that depict impacts from agricultural run-off, a suite of trace metals, including mercury, was measured to identify potential additional impacts of municipal run-off from Saskatoon, the largest municipality in Saskatchewan, and to determine if long-term recovery from mercury contamination by a chlor-alkali production plant (Wobeser et al. 1969) was complete. Concentrations were compared with guidelines for the protection of aquatic life defined by the Canadian Council of Ministers of the Environment (CCME).

## **2.3. Materials and Methods**

### **2.3.1. Study Site**

The South Saskatchewan River Basin is situated in the southern parts of Alberta and Saskatchewan and covers major urban centers: Saskatoon, Swift Current, Red Deer, Calgary, Lethbridge, and Medicine Hat (Figure 1). The South Saskatchewan River Basin comprises Big Stick Lake, Bow River, Oldman River, Red Deer River, Seven Persons Creek, South Saskatchewan River, and the Swift Current Creek sub-basins (Lac and Colan 2004).



**Figure 2.1.** Sampling locations in the South Saskatchewan River Basin, Saskatchewan.

Fed by Rocky Mountain glaciers, the South Saskatchewan River results from the confluence of three mountain streams: the Red Deer, Bow, and Oldman rivers, the latter two of which join to form the South Saskatchewan River. From the headwaters, the South Saskatchewan River flows for 1,392 kilometers. At its mouth (Saskatchewan River Forks), it has an average discharge of 280 m<sup>3</sup>/s. It encompasses a watershed of about 146,100 km<sup>2</sup>, 1,800 km<sup>2</sup> of which are in Montana, USA, and 144,300 km<sup>2</sup> in Alberta and Saskatchewan (Alberta 2003). Agriculture accounts for more than two-thirds of the land cover in the basin (Rosenberg et al. 2005).

### 2.3.2. Field Sampling

Sample collection was carried out at ten different sampling sites along the river (Figure 1) during three timepoints in 2020 and two timepoints in 2021. The two years were characterized by marked differences in hydrology, with average discharges of 277 m<sup>3</sup>/s (min: 68 m<sup>3</sup>/s, max: 731 m<sup>3</sup>/s) in 2020 and 134 m<sup>3</sup>/s (min: 68 m<sup>3</sup>/s, max: 330 m<sup>3</sup>/s) in 2021 (both measured at the outlet of Lake Diefenbaker). Similarly, precipitation in southern Saskatchewan differed markedly between the two years, with a total average precipitation of 297.4 mm in 2020, and 180.7 mm in 2021 (ECCC historical weather data). Detailed discharge and precipitation data is provided in Table S7.

Duplicate grab samples of water (2 L) were taken in pre-cleaned glass jars, which were measured for concentrations of dissolved contaminants following filtration. Duplicate sediment samples were manually collected from the stream channel at each site below the water surface at a point with maximum water mixing. Both water and sediment samples were refrigerated on ice during transport and immediately frozen at -20°C once returned to the laboratory.

Small-bodied forage fish (fathead minnows, *Pimephales promelas*; spottail shiners, *Notropis hudsonius*; juvenile white suckers, *Catostomus commersonii*) were sampled using seine nets at corresponding sampling locations. In 2020, due to the high flow, fish sampling was limited to fewer sites as the sampling conditions were not conducive to seining. Fish were sorted and inspected for their health on site. All non-target fish were immediately released at the site of capture. All target fish (target quantity of 10 fish per species, site, and time-point), as well as any fish injured by sampling, were humanely euthanized using an overdose of metomidate, preserved on ice, and immediately frozen for subsequent analysis. Fish collections were carried out with permission of the University of Saskatchewan Animal Care Committee (protocol number 20200044) and the Saskatchewan Ministry of Environment (permit number 20AR008fp).

### 2.3.3. *Chemicals and Solutions*

A list of target chemicals was identified, which comprised commonly monitored priority pesticides, as well as those pesticides most commonly used on the Prairies (Malaj, Liber, and Morrissey 2019). Specifically, the list of analytes comprised legacy organochlorine pesticides, including alpha-hexachlorocyclohexane (alpha-HCH), lindane (gamma-HCH), beta-HCH, delta-HCH, heptachlor, aldrin, heptachlorepoxy isomer B,  $\gamma$ -chlordane,  $\alpha$ -chlordane, endosulfan I, endosulfan II, endosulfan sulfate, 4,4'-dichlorodiphenyldichloroethylene (DDE), 4,4'-dichlorodiphenyldichloroethane (DDD), 4,4'-dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, and methoxychlor; organophosphate pesticides, including carbophenothion, ethion, malathion, parathion, dichlorvos, ethoprophos, disulfoton, parathion-methyl, chlorpyrifos, fenchlorphos, and azinphos-methyl; the neonicotinoid pesticides thiamethoxam, imidacloprid, and clothianidin; as well as the herbicides atrazine, 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, and 2-methyl-4-chlorophenoxyacetic acid (MCPA), mecoprop (MCP), dichlorprop, and dinoseb.

These chemicals (organochlorines, organophosphates, and herbicides) were purchased from Sigma Aldrich (Milwaukee, USA) as certified ready-made mixtures that served as the calibration standards for subsequent chemical analyses. Malathion-d<sub>10</sub> (Sigma Aldrich, USA) was selected as an isotopically labeled internal standard and used to assess recovery of analytes during extraction and clean-up.

For neonicotinoid pesticides, all target chemicals were of >98% purity. Stable isotope standards were all of >99% isotopic purity. Atrazine (ATR), MP Biomedicals (Montreal, QC); ATR-d<sub>5</sub>, C/D/N Isotopes Inc. (Pointe-Claire, QC); Clothianidin (CLT), Sigma-Aldrich (Oakville, ON); CLT-d<sub>3</sub>, Sigma-Aldrich (Oakville, ON); Imidacloprid (IMI), Sigma-Aldrich

(Oakville, ON); IMI-d<sub>4</sub>, C/D/N Isotopes Inc. (Pointe-Claire, QC); Thiamethoxam (TMX), Sigma-Aldrich (Oakville, ON); TMX-d<sub>3</sub>, Sigma-Aldrich (Oakville, ON).

Native and isotopically labelled standards were made in methanol at 1 or 10 mg/L and used for making calibrations standards and internal standard spikes.

#### **2.3.4. Sample Extraction and Preparation**

Pesticides were extracted from water samples using solid-phase extraction (SPE). Prior to SPE, water samples were filtered through 0.45- $\mu$ m glass-fiber filters to remove suspended particulates. Oasis HLB 6 cc cartridges (Vac Cartridge, 500 mg sorbent per cartridge, 60  $\mu$ m) (Waters, USA) were used to carry out SPE for water samples. The cartridges were pre-conditioned with dichloromethane (DCM), methanol, and water before extracting 1-L water samples. After the extraction, they were eluted with 5 mL DCM and 5 mL methanol and were mixed thoroughly. The solution was further divided into two aliquots (for GC-MS and LC-MS analysis). Both aliquots were blown down to dryness with a gentle stream of nitrogen gas. One of the aliquots (for LC-MS) was reconstituted in 500  $\mu$ L of a 1:1, v/v methanol-water solution and the second aliquot (GC-MS) was reconstituted in 500  $\mu$ L acetone.

Fish and sediment samples for pesticide analyses were freeze-dried for 36-48 hours in a Dura-Dry microprocessor-controlled freeze-dryer at -92°C and ~9 mTorr vacuum, fortified with mass-labeled internal standard (5  $\mu$ L) and extracted using shake-flask extraction.

For extraction of pesticides, five grams of sediment or five grams of fish were added into falcon tubes with 10 mL of a hexane: acetone mixture (1:1, v/v) and shaken on a rotary shaker for 45 minutes. Subsequently, 10 mL of fresh solvent were added at a time and decanted after every 45 minute interval. This process was repeated three times. The combined extracts were collected, filtered into a new falcon tube, and concentrated to exactly 1 mL using a gentle

stream of nitrogen. For the sample clean-up, the concentrated extract was filtered through a 0.20 µm nylon disc filter (Fisherbrand) into vials for GC-MS analysis.

For neonicotinoid extractions, five grams of sediment or five grams of fish were added into falcon tubes with 30 mL of an ethyl acetate: acetonitrile mixture (1:1, v/v) and shaken on a rotary shaker for 45 minutes. Subsequently, 10 mL of fresh solvent were added at a time and decanted after every 45 minutes interval. This process was repeated three times. The combined extracts were collected, filtered into a new falcon tube, blown down to dryness by using a gentle stream of nitrogen, and reconstituted with the same solvent. For the sample clean-up, the concentrated extract was filtered through a 0.20 µm nylon disc filter (Fisherbrand) into vials for LC-MS analysis.

For analysis of trace metals, previously filtered water samples were acidified with ultrapure sulfuric acid to a pH of approx. 3. Sediment and fish samples were freeze-dried prior to analysis.

### ***2.3.5. Instrumental Chemical Analysis***

Instrumental analysis for organochlorine and organophosphorus pesticides, as well as select herbicides was conducted using a Thermo Scientific™ TRACE™ 1300 gas chromatograph with ISQ™ 7000 Single quadrupole GC-MS system and equipped with a split/splitless injector operating in splitless mode at a temperature of 300°C. The carrier gas used is helium (99.999% purity) at a 1.0 mL/min flow. The pesticides (organochlorine, organophosphate, and herbicide acids) were separated using an Agilent DB-5MS (30 m x 0.25 mm I.D., film thickness 0.25 µm) fused silica capillary column. The oven temperature program started at 60 °C (held for 1.0 min); ramped at 38.6 °C/min to 210°C, ramped at 4.20 °C/min to 260°C, and ramped at 11.40 °C/min to 300°C. The total run time was 20 min. The MSD transfer line temperature was set to 300°C. Data were acquired in SIM (Single Ion Monitoring) mode



and processing was performed using Chromeleon software (Thermo). Average internal standard recoveries for water samples across the 2020 and 2021 ranged from 93-159% and 69-98% for sediment and fish samples. While we did not correct data for varying recoveries, we assume that all concentration data are conservative because of the low recoveries.

Analysis of neonicotinoids was conducted using a Vanquish UHPLC and Q-Exactive<sup>TM</sup> HF Quadrupole-Orbitrap<sup>TM</sup> mass spectrometer (Thermo). LC separation was achieved with a Kinetex 1.7 $\mu$ m XB-C18 LC column (100  $\times$  2.1 mm) (Phenomenex, Torrance, CA) by gradient elution with 95% water + 5% methanol (A) and 100% methanol (B), both containing 0.1% formic acid at a flow rate of 0.2 mL min<sup>-1</sup> and column temperature of 40 °C. The gradient method started at 10%B, ramping linearly to 100%B over 7 min, held for 1.5 min, and returning to starting conditions for column re-equilibration between 8.5 – 11 min. Samples were ionized by positive mode heated electrospray ionization (HESI). The Q-Exactive Orbitrap method used the following source parameters: sheath gas flow = 35; aux gas flow = 10; sweep gas flow = 1; aux gas heater = 400 °C; spray voltage = 3.8 kV; S-lens RF = 60; capillary temperature = 350 °C. A Full MS/parallel reaction monitoring (PRM) method was used with the following scan settings: 120,000/15,000 resolution, AGC target =  $1 \times 10^6 / 2 \times 10^5$ , max injection time = 50 ms/50 ms, full MS scan range of 80-500 m/z and PRM isolation window of 2.0 m/z and multiplexing count of 4. All data acquisition and processing was conducted using Xcalibur v. 4.2 and TraceFinder<sup>TM</sup> v. 4.1 (Thermo-Fisher). This method was adapted from a previous method developed on a triple-quadrupole mass spectrometer (Challis, Hanson, and Wong 2016).

Batch analyses of both GC and LC samples were conducted by running calibration standards at the beginning and end of each sample batch along with blanks run between replicate treatment sets and single mid-point calibration standards every 15-20 samples as a QA/QC protocol. For GC samples, 7-point calibrations with concentrations ranging from 1-1000 ng/mL were used while for the LC samples, an eleven-point calibration curve ranging

from 0.05 – 500 ng/mL and spiked with 50 µg/L internal standard was used for quantification by isotope dilution (linearity > 0.99 for all analytes).

Trace metals of interest were analyzed using an Agilent 8800 ICP-MS Triple Quadrupole mass spectrometer, equipped with an ASX-500 autosampler and MassHunter software for instrument operation (Agilent, Santa Clara, USA). Use of the Octopole Reaction System (ORS, reaction/collision cell) provided efficient interference removal and improved the sensitivity and reliability of the system. For sediment samples, the dried subsamples were digested using a MARS 5 microwave system with closed Teflon vessels (CEM Corporation, Matthews, USA), following a standard operation protocol. Approximately 100 mg of each sample was weighed and transferred to Teflon vessels. Then, 5.0 mL of concentrated HNO<sub>3</sub> and 2.0 mL of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (ultra-trace analysis grade, Sigma-Aldrich) were added to the sample. The samples sat in the fume hood for ~30 min to allow the organic matter to react before adding 1.5 mL of 48% hydrofluoric (HF) acid (OmniTrace™, Ultra™, EMD Millipore™, Fisher Scientific, Toronto, Canada). Reagent blanks (containing digestion reagents only) and the certified reference material PACS-3 were run with the soil samples (10% of total samples). The vessels were tightly capped and placed in the microwave for digestion. The standard reference material (SRM), natural water 1640a was used as an instrument quality assurance sample (QA) to verify the instrument performance and analytical accuracy; while PACS-3, as a method quality control sample (QC) was used to evaluate the efficiency of metal extraction of the microwave digestion and general sample preparation. After passing the QA/QC checks, the samples were analyzed by ICP-MS. The QC check was repeated for every 10 samples to ensure its mean value fell within ±10% of the certified value. A duplicate check was also run for every 10 samples to evaluate the reproducibility and stability of the instrument.

Mercury concentrations in sediment and fish samples were analyzed using a Milestone DMA-80 (Direct Mercury Analyzer). The procedure followed was identical for both sediment

and fish samples, except for the weight of the samples. For sediment samples, 50±5 mg of sample was weighed into a metal boat while the sample weight for fish was 20±5 mg. Concentrations were calibrated with a certified reference material (TORT-3 lobster hepatopancreas) and secondary certified reference materials were analysed alongside samples and had acceptable recoveries (DORM-4 fish protein, 100 ± 11%,  $n = 3$ ; MESS-3 marine sediment, 118 ± 12%,  $n = 5$ ; DOLT-5 dogfish liver, 98% and 97%,  $n = 2$ ; PACS-2 marine sediment 107 ± 41%,  $n = 3$ ).

If not stated otherwise, the concentrations of all analytes in solid sediment and fish samples are reported on a dry weight basis.

### 2.3.6. Data Analysis

Limits of detection (LOD) and quantification (LOQ) were calculated from the regression lines of the calibration curves following DIN32645 2008 and propagated to the analyzed matrices based on extraction water volumes or sediment/fish masses, and the corresponding reconstitution volumes. Concentrations of various analytes for water, sediment, and fish samples for 2020 and 2021 were plotted as time-series plots created in GraphPad Prism 9 software (GraphPad, LaJolla, FL, USA). Biota-sediment accumulation factors (BSAF) were calculated for select sites depending on the availability of fish samples collected in the season by dividing measured concentrations in fish by those measured in sediments (Equation 1).

$$BSAF = \frac{\text{Concentration of Hg in Fish } \left(\frac{\mu\text{g}}{\text{kg}}\right)}{\text{Concentration of Hg in Sediment } \left(\frac{\mu\text{g}}{\text{kg}}\right)} \quad (2.2.1)$$

## 2.4. Results and Discussion

### 2.4.1. Pesticides

#### 2.4.1.1. Water

A variety of pesticides were detected in water samples collected during both field seasons in 2020 and 2021 (Figures 2A and 3A, Table S1 and S4). Herbicides, with detection frequencies above the limits of quantification ranging from 4% (MCPA) to 100% (dicamba) in 2020 and from 90% (MCPA) to 100% (dicamba) in 2021, were consistently measured at the greatest concentrations compared to the other pesticide classes. Among the herbicides, 2,4-D (mean: 0.16 µg/L, min: 0.06 µg/L, max: 0.36 µg/L) and dicamba (mean: 0.25 µg/L, min: 0.15 µg/L, max: 0.34 µg/L) are presented individually in Figures 2A and B because of their relevance (Malaj, Liber, and Morrissey 2020). None of these samples exceeded the long-term water quality guidelines for the protection of aquatic life established by the CCME, which are 2.6, 4.0, and 10 µg/L for MCPA, 2,4-D, and dicamba, respectively. Most of the sampling sites (except for downtown Saskatoon) are very close to agricultural areas, which explains the high detection frequencies and concentrations observed for the herbicides. In summer and fall, concentrations of herbicides tended to increase successively from the upstream to the downstream sampling sites, with a distinct drop in concentration in Saskatoon. This could be potentially caused by a weir located in the City of Saskatoon which can trap sediments and thereby reduce the pesticide load in water. A lack of an upstream-downstream trend in the spring might be related to the timing of herbicide application. In a 2007 study (Glozier et al. 2012), six samples were taken monthly in the summer from Wascana Creek, upstream and downstream of the city of Regina, Saskatchewan and were analyzed for 13 herbicides. Of the 13 herbicides, seven (2,4-D, dicamba, mecoprop, dichlorprop, clopyralid, bromoxynil, and MCPA) were detected in around 83% of the samples. Mean concentrations of 2,4-D and dicamba were higher than the rest of the detections with 0.37 µg/L and 0.32 µg/L respectively.

In a later national survey in 2007 (Glozier et al. 2012), prairie rivers were tested for herbicides. 2,4-D, dicamba, and MCPA were detected in all samples collected in Swift Current and Saskatoon. In the South Saskatchewan River, the mean concentration of 2,4-D ranged from 0.05 µg/L to 0.12 µg/L, in good agreement with levels measured in the present study.

Organophosphate pesticides were only detected at two sites in 2020 and were not detected at all in 2021 (Figures 2A and 3A). Malathion and parathion had detection frequencies of 7% and 25% respectively in 2020 and were consequently selected to represent this class of pesticides (Table S1-S6). Organophosphates are used as general-purpose insecticides on the Canadian Prairies (Malaj, Liber, and Morrissey 2020) (Mulla, Mian, and Kawecki 1981). However, their rapid environmental degradation in freshwater is well documented (Brown 1972; Fukuto and Metcalf 1969; Khan 1977; Miyamoto 1972). Both malathion and parathion are readily degraded in freshwater through abiotic and biotic processes. Chemical degradation in water and soil is dependent on various factors – pH, temperature, soil minerals, light, moisture, and organic matter. The low detection frequencies of organophosphates in water samples can be explained by their susceptibility to hydrolysis (Mulla, Mian, and Kawecki 1981). These findings are in line with previous reports by Spiller (1961) and Cowart, Bonner, and Epps (1971), who found that organophosphates were only sporadically detected in surface water samples from Canada.

Most analyzed organochlorine pesticides were not detected throughout most of the sites in both 2020 and 2021. Organochlorine pesticides were generally discontinued in Canada in the 1970s (PollutionTracker 2001); hence, any detections in the present study can be attributed to legacy contamination. In particular, two formerly popular organochlorine pesticides, methoxychlor and lindane ( $\gamma$ -hexachlorocyclohexane), were detected with the greatest frequencies of 46% and 100 %, respectively, in 2020. Neither of these pesticides was detected in 2021 (Figures 2A and 3B).

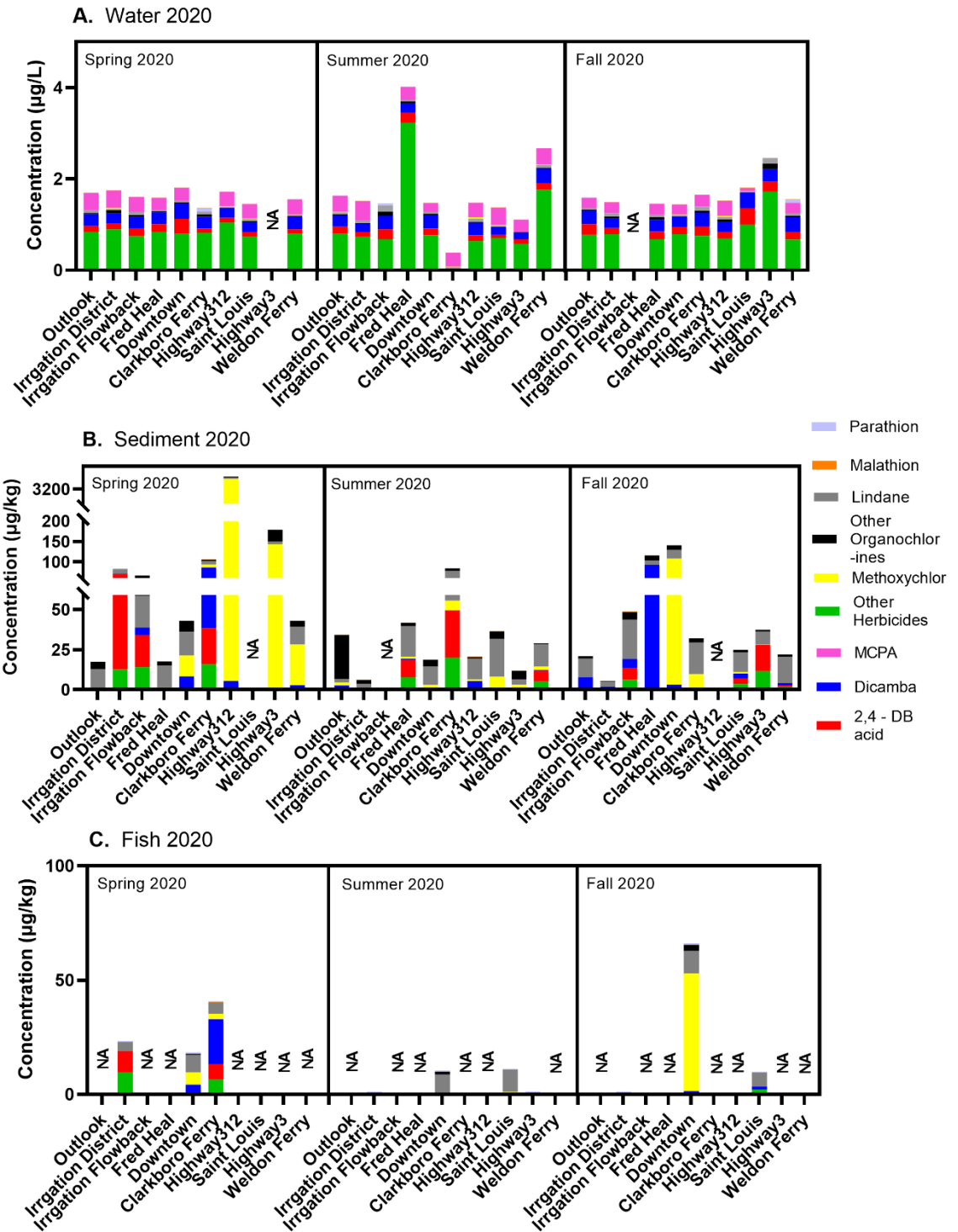
It is important to note that the hydrological conditions in the South Saskatchewan River differed markedly between the two sampled years: in 2020, the average discharge was around 277 m<sup>3</sup>/s (Real-Time Hydrometric Data for South Saskatchewan River) and in 2021, the average discharge recorded was approximately 134 m<sup>3</sup>/s. Concentrations of herbicides and other pesticides were on average 3 times greater in 2020 compared to 2021, which may be explained by the comparably greater contribution of agricultural run-off, as well as comparably greater turbulent mixing and sediment resuspension due to the high discharge during that field season.

#### *2.4.1.2. Sediment*

Herbicides were detected consistently in sediments for 2020 samples, with detection frequencies of 38% (2,4-D) and 67% (dicamba). Herbicides were sporadically detected for 2021 with detection frequencies of 20% (2,4-D) and 50% (dicamba). Concentrations of 2,4-D (mean: 6.45 µg/kg, min: 0.95 µg/kg, max: 56.6 µg/kg) and dicamba (mean: 7.39 µg/kg, min: 0.98 µg/kg, max: 92.2 µg/kg) in 2020 were higher than those in 2021 (2,4-D mean: 1.58 µg/kg, min: 0.58 µg/kg, max: 10.0 µg/kg; dicamba mean: 4.00 µg/kg, min: 0.56 µg/kg, max: 46.2 µg/kg) (Figure 2B and 3B). No sediment quality guidelines have been established by the CCME for these herbicides. High river flow rates in 2020 may explain consistent detections as the water level rises and erodes shore areas and mixes fresh sediment with higher concentrations. 2,4 – D, Dicamba, and MCPA are highly water soluble and are not likely to persist, which explains their absence in sediment samples. Herbicide loss by infiltration is well documented (Degenhardt et al. 2011). However other analytes in the herbicides group such as MCPP and dichlorprop are known to be only partially water soluble which explains some detections in sediments in both the seasons.

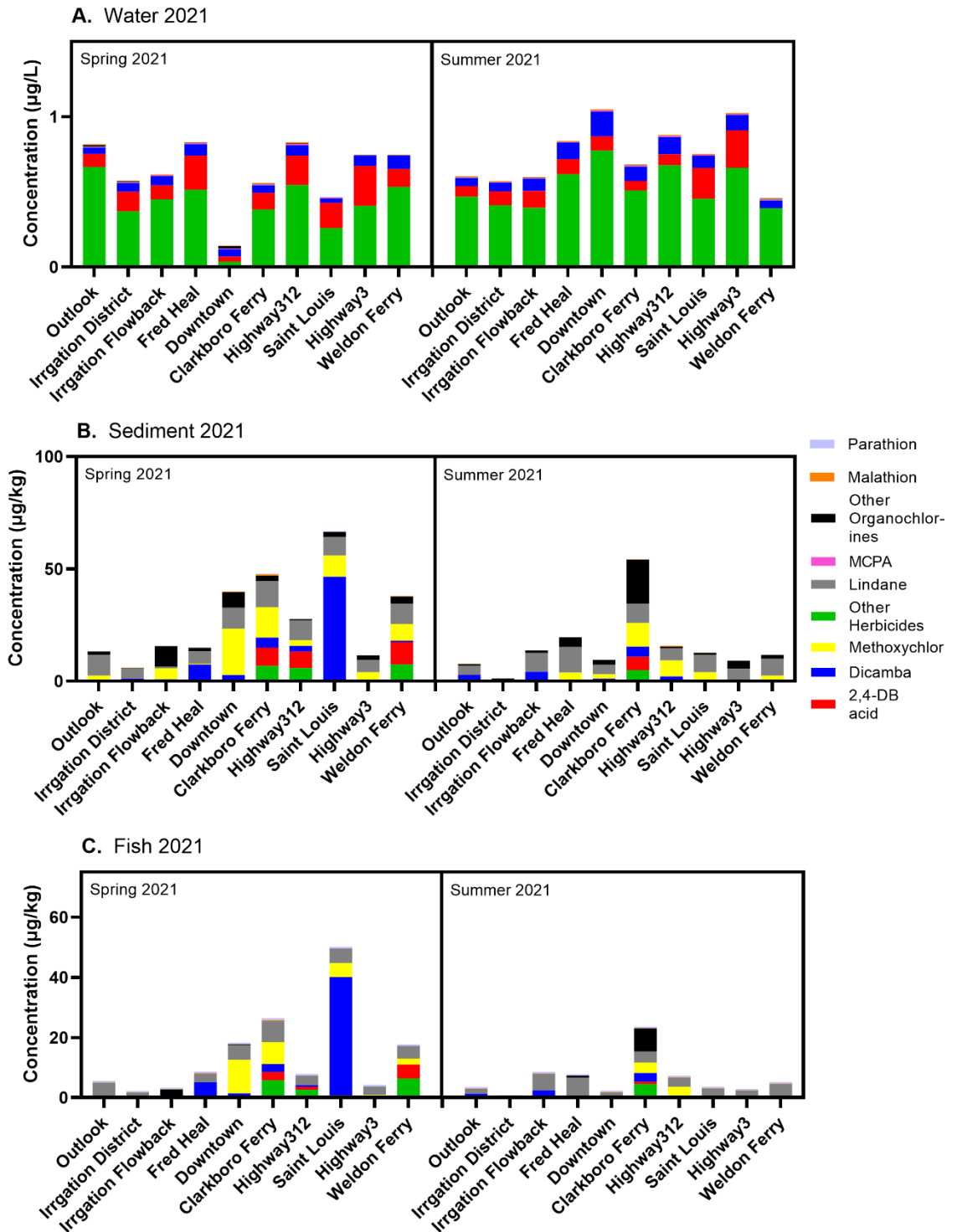
Organophosphate pesticides were only detected in sediments in Spring and Summer 2020 and only at two sites: Irrigation District (malathion: 0.78  $\mu\text{g}/\text{kg}$ ) and Clarkboro Ferry (parathion: 0.91  $\mu\text{g}/\text{kg}$ ). As mentioned above, both malathion and parathion are susceptible to degradation in water and sediment and hence may explain the lack of detections (Mulla, Mian, and Kawecki 1981).

Organochlorine pesticides were detected prominently in sediments in both years (Figures 2B and 3B). The detection frequencies for 2020 were 67% (methoxychlor) and 100% (lindane), and for 2021, the frequencies were 75% (methoxychlor) and 90% (lindane). Figure 3B shows individually presented methoxychlor (mean: 4.77  $\mu\text{g}/\text{kg}$ , min: 0.41  $\mu\text{g}/\text{kg}$ , max: 20.7  $\mu\text{g}/\text{kg}$ ) and lindane (mean: 6.79  $\mu\text{g}/\text{kg}$ , min: 4.22  $\mu\text{g}/\text{kg}$ , max: 11.5  $\mu\text{g}/\text{kg}$ ) for 2021. There were consistent detections in samples collected in 2021. This may be an indication of the flow variation between the two years as discussed above. It is important to note the high concentration value for methoxychlor at Highway 312 in Spring 2020. It may be suggestive of local accumulation. Lindane and other organochlorine pesticides were detected but at significantly lower concentrations. Organochlorines are still among the most abundant pesticides found in sediment due to their high lipophilicity and recalcitrance to biotic and abiotic degradation (Warren et al. 2003; Thevenon et al. 2013).



**Figure 2.2.** Concentrations of selected pesticides (insecticides and herbicides) during the 2020 field season for water (A), sediment (B), and fish (C) samples, respectively. NA: not analyzed.





**Figure 2.3.** Concentrations of selected pesticides (insecticides and herbicides) during the 2021 field season for water (A), sediment (B), and fish (C) samples respectively.

#### 2.4.1.3. Fishes

In 2020, herbicides were found in fishes with detection frequencies of 20% each for 2,4-D (mean: 1.58  $\mu\text{g}/\text{kg}$ , min: 6.61  $\mu\text{g}/\text{kg}$ , max: 9.23  $\mu\text{g}/\text{kg}$ ) and dicamba (mean: 2.64  $\mu\text{g}/\text{kg}$ , min: 4.07  $\mu\text{g}/\text{kg}$ , max: 19.7  $\mu\text{g}/\text{kg}$ ). Similarly, for 2021, the detection frequencies for herbicides were 10% (2,4-D) and 25% (dicamba). Mean concentrations for 2,4-D and dicamba in 2021 were 0.45  $\mu\text{g}/\text{kg}$  (min: 2.73  $\mu\text{g}/\text{kg}$ , max: 4.63  $\mu\text{g}/\text{kg}$ ) and 2.74  $\mu\text{g}/\text{kg}$  (min: 2.28  $\mu\text{g}/\text{kg}$ , max: 39.3  $\mu\text{g}/\text{kg}$ ), respectively.

Organochlorine pesticides were detected with frequencies of 40% (methoxychlor) and 70% (lindane) with concentration values - mean: 6.04  $\mu\text{g}/\text{kg}$ , min: 0.87  $\mu\text{g}/\text{kg}$ , max: 51.7  $\mu\text{g}/\text{kg}$  and mean: 5.31  $\mu\text{g}/\text{kg}$ , min: 4.13  $\mu\text{g}/\text{kg}$ , max: 9.95  $\mu\text{g}/\text{kg}$ , respectively (Figures 2C and Figures 3C). In 2021, methoxychlor (mean: 1.58  $\mu\text{g}/\text{kg}$ , min: 6.61  $\mu\text{g}/\text{kg}$ , max: 9.23  $\mu\text{g}/\text{kg}$ ) had a detection frequency of 40% whereas lindane (mean: 1.58  $\mu\text{g}/\text{kg}$ , min: 6.61  $\mu\text{g}/\text{kg}$ , max: 9.23  $\mu\text{g}/\text{kg}$ ) was found at a frequency of 90%. Organochlorines were predominant compared to the other classes of pesticides, which is in line with previous studies indicating their high bioaccumulation potential due to their high lipophilicity and recalcitrance (Warren et al. 2003; Thevenon et al. 2013). Like with sediment samples, this explains why organochlorines are still among the most abundant pesticides detected in fish, but not in water. The concentration of methoxychlor at Downtown in Fall 2020 was the highest. Interestingly, in Fall 2020, methoxychlor concentration was also significantly elevated in Downtown sediment samples, which might indicate a remobilization event of contaminated soils or sediments during the high flow season, which led to increased bioavailability for fish.

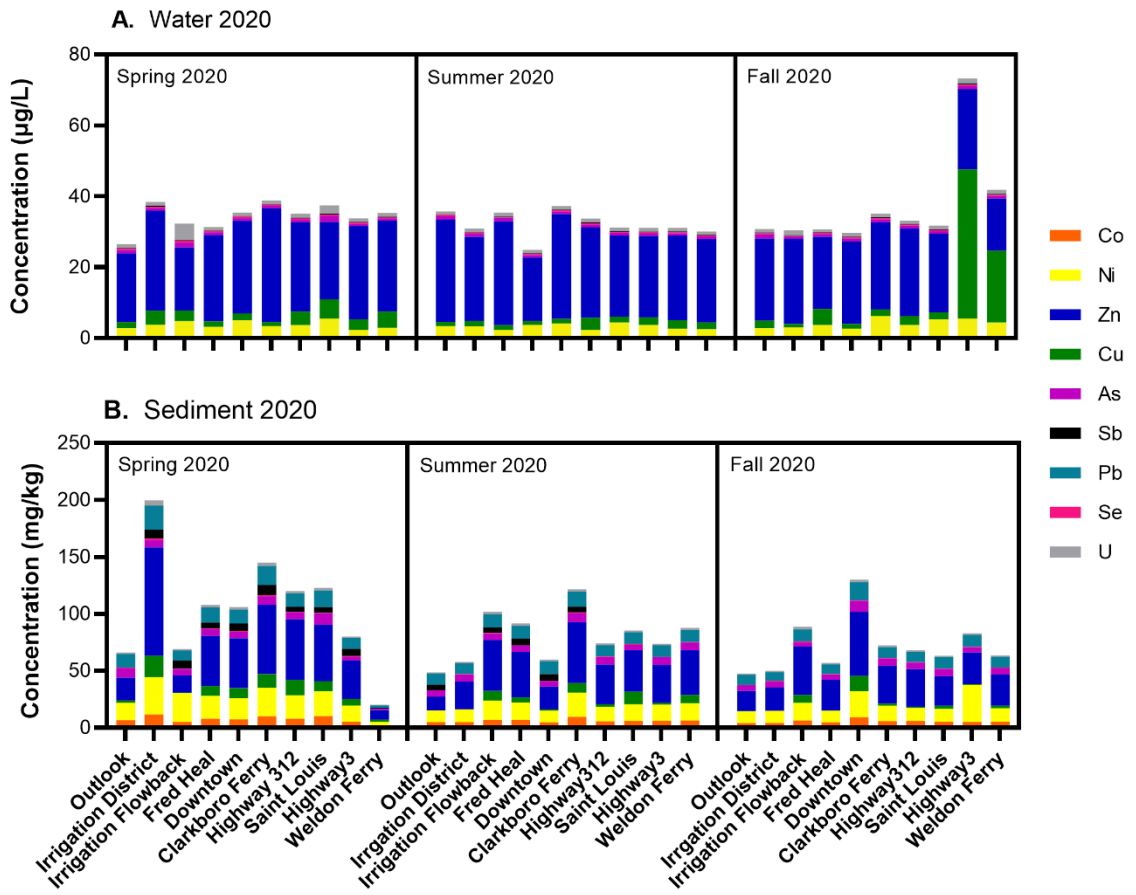
Organophosphates were not detected at all in fish samples during either year which can be explained by degradation through various factors such as hydrolysis, photolysis, and microbial activity.

Neonicotinoids were not found in any of the samples collected in 2020 and 2021 in water, sediment, and fish. The CCME guidelines for protection of aquatic life are set for atrazine and imidacloprid at 1.8 µg/L and 0.23 µg/L. Neonicotinoids have low volatility and can be rapidly photodegraded as most of them are present as aerosols (Fossen 2006; Peña, Rodríguez-Liébana, and Mingorance 2011). A half-life for clothianidin undergoing photolysis in water was determined to be less than a day (USEPA 2003) making photolysis a major removal process for neonicotinoids in water.

Biota-sediment accumulation factors (BSAFs) were calculated for 2,4-D, dicamba, methoxychlor, and lindane (SI – Mercury Data Spreadsheet). The resulting mean values and those at all individual sites were less than 1, indicating that fish are not being enriched with pesticides from sediment. A study carried out in the Black Sea reported the BSAF values for these chemicals to be lower than 1, ranging from 0.06 – 0.64 (Ozkoc, Bakan, and Ariman 2007).

#### **2.4.2. Trace metals**

Zn, Ni, Cu, Se, and U were the most predominant detections in 2020 water samples, while in 2021, Zn was the only commonly detected trace metal, with a few detects for Cu (Figures 4A and 5A). For sediment samples, trace metal composition was very similar across both years for Zn, Ni, Co, As, Pb, and U, both in terms of absolute concentrations and relative contributions to the overall levels (Figures 4B and 5B). High concentrations of Cu in Fall 2020 at Highway 3 and Weldon Ferry might be explained by ongoing roadway and bridge construction in this area (S. Prajapati, pers. obs.).



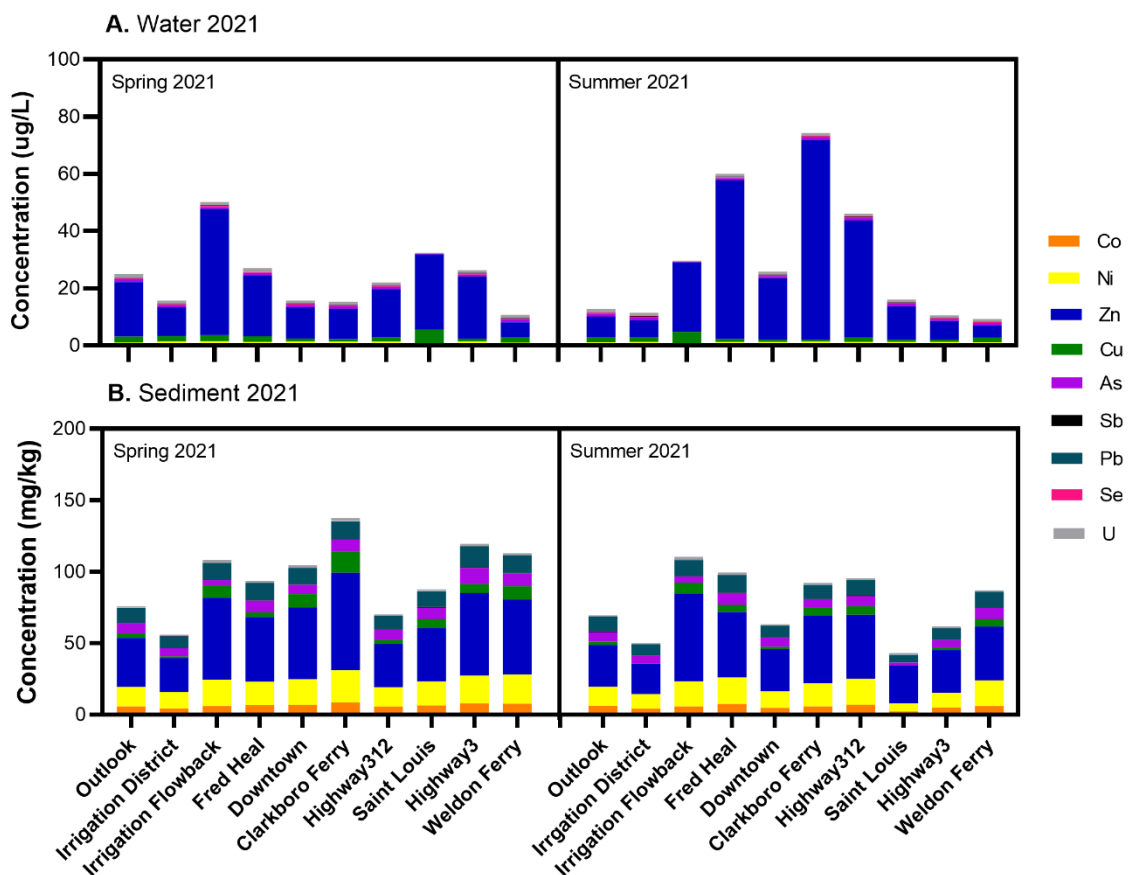
**Figure 2.4.** Concentrations of selected trace metal concentrations during the 2020 field season for water (A) and sediment (B) samples.

The CCME has developed water quality, sediment quality, and tissue residue guidelines for the protection of aquatic life from metal toxicity. Sediment guidelines include interim sediment quality guidelines (ISQGs) below which effects are unlikely to be observed, and probable effect levels (PELs), above which environmental impacts are likely, which can be used to evaluate the degree to which these elements can affect ecosystem health.

However, some of these concentrations exceeded the long-term CCME water guideline, which is calculated based on DOC, hardness, and pH as 28 µg/L. Hence, while short-term detrimental effects are not expected, long-term impacts on the aquatic community cannot be

excluded. For sediment samples, concentrations of Zn ranged from 9 mg/kg to 95 mg/kg in 2020 and 24 mg/kg to 68 mg/kg in 2021, all of which are under the CCME ISQG for Zn of 123 mg/kg.

Levels of Cu in the river water ranged from 1 µg/L to 42 µg/L in 2020 and 0.8 µg/L to 5 µg/L in 2021. Several of these measured concentrations exceeded the long-term CCME water quality guideline for Cu of 4 µg/L, which indicated that risk to aquatic life could not be excluded. In sediments, the concentration for Cu ranged from <LOQ to 19 mg/kg in 2020 and <LOQ to 15 mg/kg in 2021. Adverse effects are not expected as the results obtained are significantly below the CCME ISQG of 35.7 mg/kg.



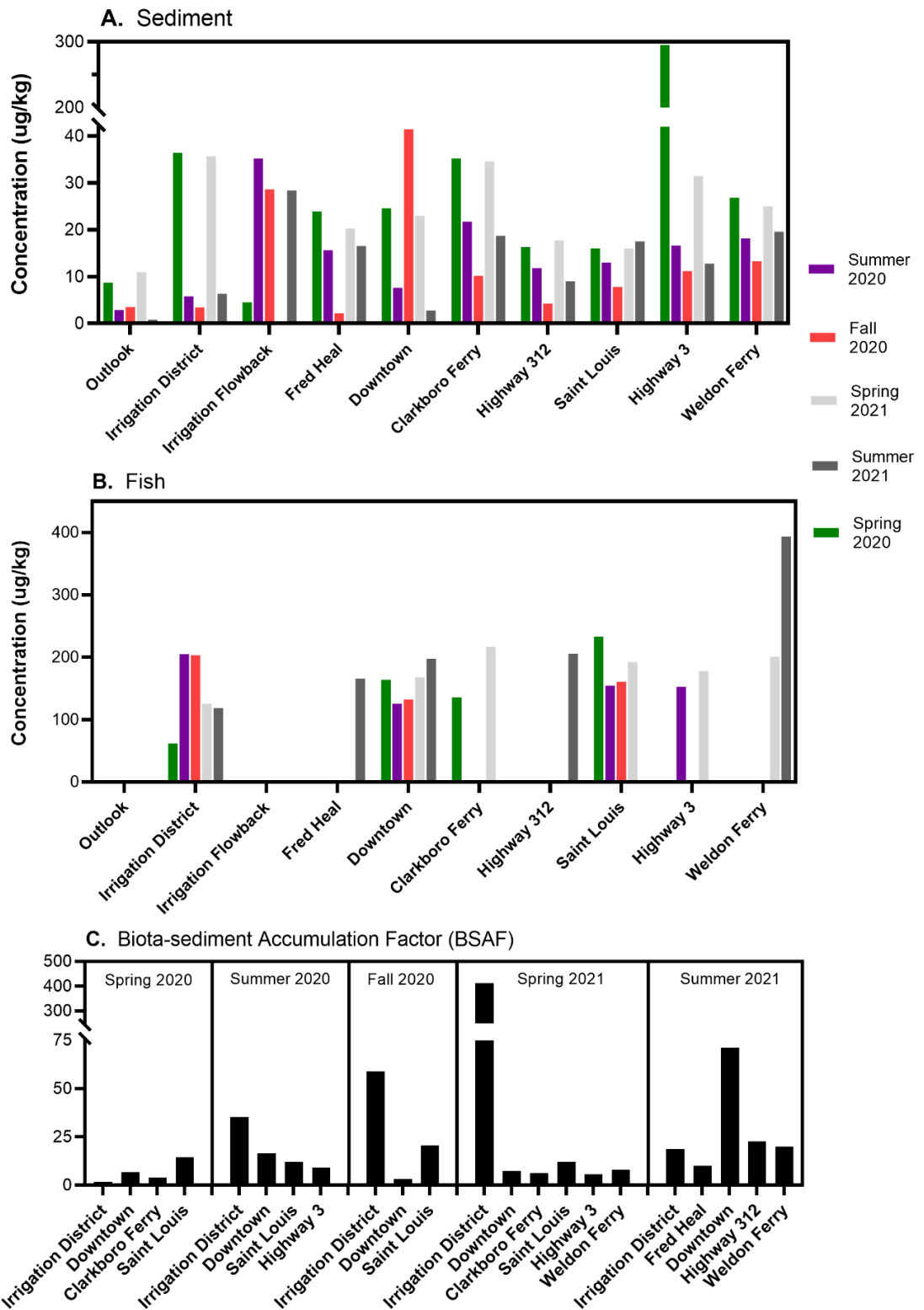
**Figure 2.5.** Concentrations of selected trace metal concentrations during the 2021 field season for water (A) and sediment (B) samples.

Concentrations of Ni, Se, and U in water were all below the CCME guidelines for the protection of aquatic life, indicating no risk to aquatic species. Sediment quality guidelines for these trace metals have not been established by CCME and thus cannot be compared with measured concentrations.

### **2.4.3. Mercury**

Concentrations of total mercury in sediments ranged from 1 µg/kg to 295 µg/kg (Figure 6A). One sediment sample collected in 2020 at Highway 3 was significantly higher (295 µg/kg) than the other sampling locations. However, the concentrations at the same site later in the year were very low and comparable to the other sites. This may be explained by sampling in a mercury-rich sediment area. Some studies have shown that sediments can be a sink for mercury deposition (Rudd and Turner 1983). In the remaining sites, the concentrations of total mercury were well below the CCME ISQG of 170 µg/kg.

Concentrations of total mercury in dry composite fish samples were in the range of 62 µg/kg to 394 µg/kg (Figure 6B), or 12 µg/kg to 79 µg/kg on a wet weight basis. The CCME guideline for tissue residue for the protection of wildlife consumers of aquatic biota is 33 µg/kg wet weight of methyl mercury and since methyl mercury typically represents about 80% of the total mercury concentration in small-bodied fishes (Lescord et al. 2018), the CCME guideline for methyl mercury would correspond to about 41.3 µg/kg wet weight of total mercury. Based on these findings, 18% of the fish samples obtained in the present study potentially exceeded the guideline.



**Figure 2.6.** Grouped plot distribution of mercury concentrations in sediment (A) and fish (B) samples across all the field seasons 2020 and 2021, as well as resulting biota-sediment accumulation factors (BSAFs, C). NA: not analyzed.

More than 50 years ago, the South Saskatchewan River was contaminated with mercury (Wobester, Nielsen, and Dunlop 1969). Wobester et al. (1969) found higher than normal mercury concentrations in fish at Clarkboro Ferry owing to inputs from a chlor-alkali plant that closed in the 1970s. At that time, the average concentrations (on a wet weight basis) in large-bodied predators (Goldeye, Northern Pike, Walleye, and White Sucker) were around 6700  $\mu\text{g}/\text{kg}$ , suggesting their prey had concentrations at or above 1000  $\mu\text{g}/\text{kg}$ , given mercury's fivefold increase with trophic level (Lavoie et al. 2013). This highlights the long-term attenuation of concentrations in the sediments and food web at this site following the cessation of a point source discharge. Several studies around the world have reported a decline in mercury concentrations following the closure of chlor-alkali plants (Kopec et al. 2019; Reis et al. 2009).

Biota-sediment accumulation factors (BSAFs) were calculated from Hg concentrations in sediment and Hg concentrations in fish to elucidate the linkages between enrichment of mercury in fauna compared to the surrounding environment. Values ranged from 1.7 to 411.5 (Figure 6C), far higher than values for bivalves in a Mexican estuary (Ruelas-Inzunza et al. 2009). Irrigation District had higher BSAF values than other sites in Summer 2020, Fall 2020, and Spring 2021. All values were greater than 1, suggesting that the fish are accumulating mercury from the sediment. BSAF values incorporate a wide range of factors, such as the trophic level of the fish, sediment-water equilibrium, and the diet of the fish, and are therefore considered to be site-specific (Burkhard 2009) (Table S12-S16).

## **2.5. Conclusion**

Our data revealed a mixture of legacy contaminants and current-use chemicals in water, sediment, and fishes. Organochlorine pesticides were found in sediment samples consistently



throughout the sites in both years but at very low concentrations. Considering these pesticides have been banned since the 1970s, their presence can be attributed to legacy contamination. The elevated concentrations of methoxychlor in sediment samples of the 2020 field season might be due to the high observed discharges, which would have led to fast currents and resuspension of deeper sediment layers. This hypothesis is also strengthened by the observations in the sediment data in 2021, where concentrations were significantly lower and more uniform.

Herbicides were found in greater concentrations in water samples compared to sediment and fish samples which can be easily explained by their high-water solubility. The concentrations of dicamba, MCPA, and 2,4-D in water were all well-below the CCME Water Quality Guidelines for the Protection of Aquatic Life. There is limited to no data about the toxicity and bioavailability of herbicides and their impacts in water, sediment, and fish. Presently, there are no guidelines for herbicides in sediment and tissue residues, representing an important shortcoming in our understanding of ecotoxicity to aquatic organisms, as these organisms are in direct contact with sediments and water. .

Organophosphate pesticides, especially malathion and parathion, were not detected at most of the sites and when detected, were significantly lower in concentrations than other pesticide classes. Prone to hydrolysis, malathion and parathion are very short-lived (Pehkonen and Zhang 2010).

Trace metals and mercury in the South Saskatchewan River are now below CCME guidelines for both sediment and water quality. However, regular monitoring would help in developing a database to understand the fate of trace metal toxicities and could also be applied to fate modelling.

Considering that the values of pesticides and trace metals are under their respective guidelines, it is safe to speculate that there is no imminent environmental risk from these

compounds. However, it is also important to note that availability of data is scarce and patchy which hinders detailed analysis. Impacts of changing hydrology due to upstream water resource development, land use change, and global climate change are pronounced in this region of Canada (Schindler and Donahue 2006), leading to potentially drastic differences in quantity and timing of discharges. Considering the apparent link between discharge and chemical concentrations observed here, further hydrological changes could ultimately change exposure to contaminants in large Prairie rivers.

## **2.6. Acknowledgements**

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**Chapter 3: MODELLING TRANSPORT  
AND FATE OF COPPER AND NICKEL  
ACROSS THE SOUTH  
SASKATCHEWAN RIVER USING  
WASP – TOXI.**

## Overview

A version of this chapter is currently under minor revisions in the Journal Water, Special Issue: Surface Water Quality and Modelling, Section: Water Quality and Contamination with the following details: Prajapati, Saurabh, Pouya Sabokruhie, Markus Brinkmann, and Karl-Erich Lindenschmidt. 2022. “Modelling transport and fate of Copper and Nickel across the South Saskatchewan River using WASP – TOXI”

### Author Contributions

**Saurabh Prajapati:** Research conceptualization, study design and implementation, methodology, software, validation, formal analysis, investigation, data curation, writing - original draft, reviewing, and editing, visualization.

**Pouya Sabokruhie:** Research conceptualization, study design and implementation, methodology, software, validation, formal analysis, investigation, data curation, reviewing, and editing, visualization.

**Markus Brinkmann:** Research conceptualization, funding acquisition, investigation, project administration, resources, supervision, writing – review & editing.

**Karl-Erich Lindenschmidt:** Research conceptualization, investigation, methodology, supervision, writing – review & editing.

### **3.1. Abstract**

Modelling trace metals in freshwater systems is complex because metals exist in two phases, dissolved and particulate. An established 1-D modelling approach was chosen and coupled with the Hydrologic Engineering Center's River Analysis System (HEC-RAS). The WASP (Water Quality Analysis Simulation Program) stream transport module, TOXI, is coupled with flow routing for free-flow streams, ponded segments, and backwater reaches and is capable of calculating the flow of water, sediment, and dissolved constituents across branched and ponded segments. Copper and nickel were chosen as two metals with predominantly anthropogenic and geogenic sources, respectively. Analysis was carried out at ten different sites along the South Saskatchewan River, both upstream and downstream of the City of Saskatoon, in the years 2020 and 2021. Model performance was evaluated by comparing model predictions with concentrations of copper and nickel measured in a previously published study. The model performed well in estimating the concentrations of copper and nickel in water samples and worked reasonably well for sediment samples. The model underestimated concentration values at certain segments in both water and sediment samples. In order to calibrate the model more accurately, extra diffuse contaminant loads were added. While several default parameter values had to be used due to the unavailability of primary historical data, our study demonstrates the predictive power of combining WASP-TOXI and HEC-RAS models for the prediction of contaminant loading. Future studies, including those on the impacts of global climate change on water quality on the Canadian prairies, will benefit from this proof-of-concept study.

### 3.2. Introduction

Contamination of the environment with various trace metals has been of significant concern for many decades due to their potential to cause deleterious impacts on exposed wildlife and humans. Trace metals have several unique chemical properties which dictate their environmental fate and bioavailability. Trace metals like copper (Cu), nickel (Ni), zinc, and lead are inclined to interact with other elements and organic molecules present in the environment. Assessments of environmental fate and risks of trace metal exposure to wildlife and humans historically only accounted for these interactions superficially and are most commonly based on total metal concentrations. Thus, there is a need to develop methods and strategies to overcome this limitation and help improve risk assessments for both anthropogenic metal contamination, e.g., with Cu, and geogenic background contamination, e.g., with Ni.

Copper reacts strongly with various functional groups present in soils and sediments, such as iron oxides and manganese oxides and carbonates (Tonkin, Balistrieri, and Murray 2004). Natural weathering and erosion of geological materials release Cu into surface waters and soils in Canada. Anthropogenic activities such as mining, municipal and industrial waste management, agriculture (use of Cu as a pesticide), and water treatment can contribute towards localized deposits (ATSDR 2004). Hence, Cu can enter water bodies through natural processes, anthropogenic activities, or from the corrosion of pipes/fittings in water distribution systems (WHO 1998; Ellingsen, Horn, and Aaseth 2007). Copper, owing to its malleability, conductivity, alloying potential, and resistance to corrosion and wear, is used in a diverse range of products such as pipes, paint pigments, antifouling agents, refinery oils, and construction materials (ATSDR 2004; WHO 2011; Ellingsen, Horn, and Aaseth 2007). Copper exists in four different oxidation states: Cu (0) (elemental copper), Cu (I) (cuprous ion), Cu (II) (cupric ion), and Cu (III) (Georgopoulos et al. 2001). Cu (II) is commonly occurring and the most frequently encountered species in water and sediment systems (Gaetke, Chow-Johnson, and Chow 2014).

Cu (I), due to its instability, is oxidized to Cu (II), which is further subjected to redox reactions and tends to be hydrated. The hydrated Cu (II) ion adsorbs to particulate matter, as well as dissolved organic and inorganic compounds (WHO 2011). Copper does not tend to bioaccumulate or even hydrolyze in any way in soil (Health Canada 2009). Copper speciation is complex and depends on various factors such as water hardness, water chemistry (dissolved oxygen, pH, and redox potential), and sediment-water interaction (Cuppett, Duncan, and Dietrich 2006). Water quality monitoring datasets from Environment and Climate Change Canada (ECCC) have been compiled for different provinces and territories. Total Cu concentrations of Canadian jurisdictions varied with an overall range from 0.002 (Ontario) to 5,723  $\mu\text{g/L}$  (Saskatchewan). The median Cu concentrations ranged from 0.3  $\mu\text{g/L}$  for Prince Edward Island (PEI) to 1.8  $\mu\text{g/L}$  for Manitoba.

The toxicity of Cu in freshwater is mainly driven by various chemical parameters and water quality. According to the biotic ligand model (BLM) proposed by Pagenkopf, Russo, and Thurston (1974), metal toxicity is driven by the accumulation of metal at a discrete site of action (biotic ligand). Metal speciation results in formation of inorganic and organic complexes (Santore et al. 2001). The ability of Cu (II) to adsorb to particulate matter and form dissolved complexes with both organic and inorganic ligands reduces its toxicity because of limited uptake (ECCC 2021).

Nickel is one of the most common elements on Earth and is widely distributed in the environment (Cempel and Nikel 2006). Nickel occurs mostly in mineral form at an average concentration of  $\sim 75,000 \mu\text{g/kg}$  in the Earth's crust. It is known to have a widespread distribution in the environment and is an essential component for many industrial and commercial uses. Various uses of Ni include electroplating, as a catalyst for fat hardening, coloring ceramics, electrical components, ammonia adsorption processes, and other metallurgical operations (IPCS 1991). Nickel is released into the environment in various forms,

predominantly from natural sources and few anthropogenic activities. Natural weathering and erosion of geological materials release Ni into surface waters and soils in Canada. Forest fires can be short-term but intense sources (Havas and Hutchinson 1983). Airborne Ni enters the environment through volcanoes, dust, sea salt, and particulate exudation from vegetation (NRCC, 1981; Richardson et al. 2001). Mining, smelting, petroleum refining, and manufacturing industries are other major emitters (Environment Canada 2007).

Nickel moves in both particulate and dissolved forms in natural waters. The transport and fate of Ni in freshwater rely on various factors such as the pH, redox potential, ionic strength, type, and adsorption type (Al. 1979)). Nickel toxicity is dependent upon the route of exposure and the solubility of a Ni compound (Coogan et al. 1989). The movement of Ni in the environment is high in acidic organic-rich soils, which can lead to groundwater contamination (Nieminen et al. 2007). In sediments and suspended solids, most of the Ni is distributed among organic materials, precipitated and coprecipitated particle coatings, and crystalline particles. Ni is distributed in Canada throughout areas with mafic and ultramafic bedrocks (Doyle 1991). Typically, Ni concentrations in Canadian surface waters are below 2 µg/L. Drinking water concentrations in Ontario, Saskatchewan, and Newfoundland were averaged at 2.9 µg/L (Health Canada 2011). In sediments, the concentrations in Canadian lakes ranged from 10 – 4000 mg/kg dw (Bradley and Morris 1986; Bodo 1989).

Studying metal speciation in freshwater systems is challenging, as the applied methodologies need to be very sensitive to be able to recognize minute differences in relative proportions of metal species at trace concentration levels. Various models have been used to compare predictions of metal speciation to experimental values, which has been documented in a few studies (Bryan, Tipping, and Hamilton-Taylor 2002; Dwane and Tipping 1998; Christensen and Christensen 1999; Oste et al. 2002). Models such as the biotic ligand model (BLM), the Windermere humic aqueous model (WHAM), the NICA-Donnan model, and the

Water Quality Analysis Simulation Program (WASP) (Ambrose and Wool 2009) have been developed to study or predict metal speciation in the environment at varying levels of complexity. BLMs determine metal speciation and predict metal toxicity to biota in aqueous systems using computational modeling. WHAM is based on the Humic Ion-Binding Model and assumes that proton and metal complexation occurs at two groups of discrete sites with strong and weak binding affinities (Tipping and Hurley 1992). The NICA-Donnan model considers carboxylic- and phenolic-type groups for determining site strengths (Kinniburgh et al. 1996). Sigg et al. (2006) modelled *in situ* concentrations of Cd, Cu, Ni, and Pb and compared these with measured values by employing different speciation techniques, specifically the Humic Ion-Binding Model VI (WHAM 6) and the NICA – Donnan model. Both models were reasonably accurate and performed consistently for metal speciation in freshwater. However, concentrations of total dissolved Cu and Pb were under-estimated by a large magnitude. While this finding is generally promising, the complexity of identifying anthropogenic versus geogenic sources of contamination, impacts of water chemistry/quality on the fate of metals, hydrology, and morphodynamics require an integrated modelling strategy that accounts for all of these processes.

In this study, we used WASP to model the fate of the metals Ni (predominantly from geogenic background) and Cu (predominantly from anthropogenic sources) between water and sediments in the South Saskatchewan River through the sampling periods of 2020 and 2021. The two years were characterized by marked differences in hydrology, with average discharges of 277 m<sup>3</sup>/s (min: 68 m<sup>3</sup>/s, max: 731 m<sup>3</sup>/s) in 2020 and 134 m<sup>3</sup>/s (min: 68 m<sup>3</sup>/s, max: 330 m<sup>3</sup>/s) in 2021 (both measured at the outlet of Lake Diefenbaker). Similarly, precipitation in southern Saskatchewan differed markedly between the two years, with a total average precipitation of 297.4 mm in 2020 and 180.7 mm in 2021 (ECCC historical weather data – SASKATOON RCS). This study makes use of trace metal concentrations and other physicochemical variables

recently published by our group (Prajapati et al. 2022). Comparing the predictive power of WASP for trace metal concentrations in sediment and water across two hydrologically different sampling periods, encompassing both a flood and a drought year, brings considerable potential to test the model across a wide range of hydrologic conditions and thus, the potential utility of this model in forecasting. This could enable an evaluation of secondary impacts of climate change where scenarios predict changes to hydrology in this river basin (Pomeroy et al. 2005).

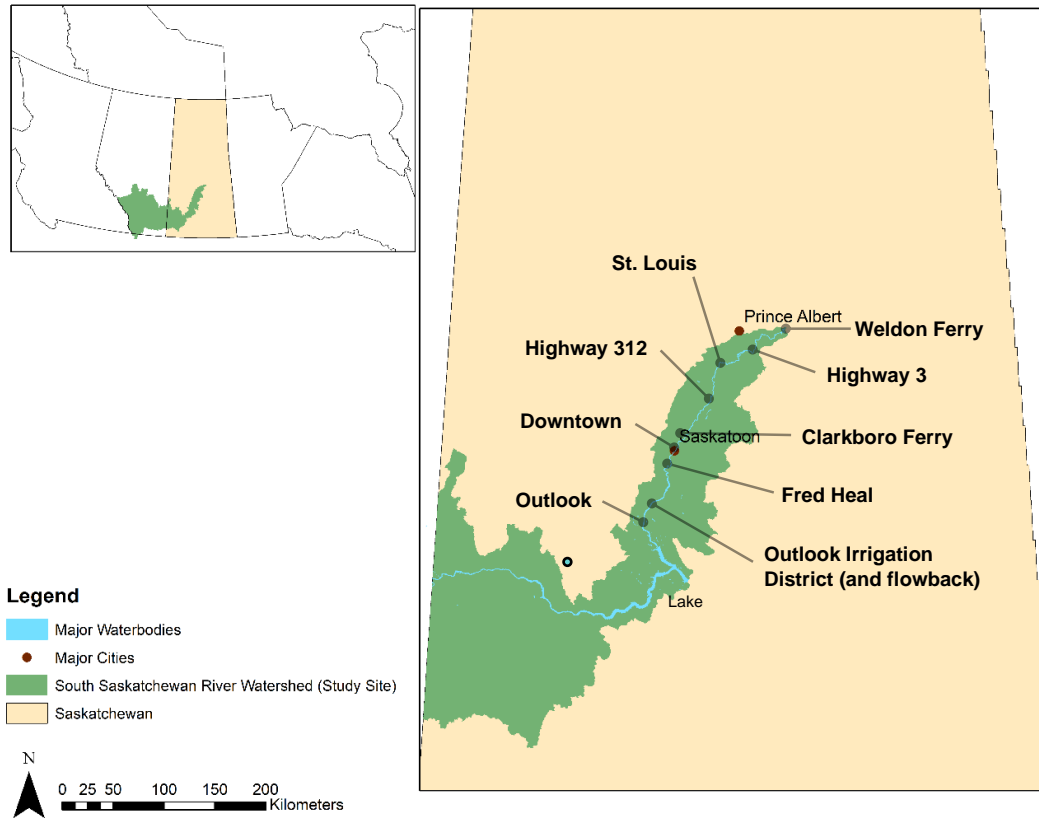
### **3.3. Materials and Methods**

#### **3.3.1. Study Site**

The Saskatchewan River System, which originates in Alberta's Rocky Mountain headwaters and flows through Canada's plains, is made up of the South and North Saskatchewan Rivers. The South Saskatchewan River Basin, which includes the major cities of Saskatoon, Swift Current, Red Deer, Calgary, Lethbridge, and Medicine Hat, is situated in the southern regions of Alberta and Saskatchewan (Figure 1). Big Stick Lake, Bow River, Oldman River, Red Deer River, Seven Persons Creek, South Saskatchewan River, and Swift Current Creek are all parts of the South Saskatchewan River Basin (Lac and Colan 2004).

The South Saskatchewan River is fed by the Rocky Mountain glaciers, resulting from the confluence of three mountain streams: the Red Deer, Bow, and Oldman rivers. From the headwaters, the South Saskatchewan River flows for 1,392 kilometers. At its mouth (Saskatchewan River Forks), it has an average discharge of 280 m<sup>3</sup>/s. It encompasses a watershed of about 146,100 km<sup>2</sup>, 1,800 km<sup>2</sup> of which are in Montana, USA, and 144,300 km<sup>2</sup> in Alberta and Saskatchewan (Alberta 2003). Agriculture accounts for more than two-thirds of the land cover in the basin (Rosenberg et al. 2005).





**Figure 3.1.** Sampling locations in the South Saskatchewan River Basin, Saskatchewan (Prajapati et al. 2022).

### 3.3.2. Modelling Approach

Concentrations of heavy metals in the South Saskatchewan River system was studied using WASP 7.52 (Athens, GA, USA) coupled with HEC-RAS as developed by the U.S. Army Corps of Engineers (USACE). Aquatic systems can be modelled by the WASP software to simulate hazardous water contamination using the concepts of mass, momentum, and energy conservation. The hydrodynamics of the model domain was simulated using the hydraulic model HEC-RAS 6.2. Since HEC-RAS has been developed by the USACE, all users and organizations have access to a free version of the model without requiring a license. This model can estimate sediment transport, water quality in one-dimensional (1D) steady and unsteady

flow, and two-dimensional (2D) unsteady flow of rivers. The model uses geometric data representation and geometric and hydraulic computer algorithms for a network of river channels. The HEC-RAS program can simulate an input flood using either a (1D) unsteady flow model or a (2D) unsteady flow model following these parameters.

Flow data was acquired from the Water Survey of Canada (WSC) station at Lake Diefenbaker, which has an operational gauge with records from 1966 to the present. The station is located about 13 km upstream of the modelling domain (gauge 07DA001–South Saskatchewan River Below Lake Diefenbaker).

A 1D modelling approach was chosen as the optimum method for simulating the South Saskatchewan River sites. 1D modelling can give results that are on par with or better than 2D models for rivers and floodplains where the predominant flow directions and forces follow the main river flow route, with less effort and computing resources. It was expected that the system was mixed both laterally and vertically. Previously 1D WASP and HEC-RAS coupling (Akomeah and Lindenschmidt 2017) and quasi-2D (K. E. Lindenschmidt, Sabokruhie, and Rosner 2022; Sabokruhie et al. 2021) have been done in the Athabasca River system for analyzing total suspended solids, chlorine, and vanadium etc. HEC-RAS carried on the hydrodynamic part of the modelling, and the output of the HEC-RAS model was used as an input (for water depth at each segment) for the WASP model.

### ***3.3.3. Setup for Water Quality Modelling***

The water quality part of the study was modelled using the Water Quality Analysis Simulation Program (WASP 7.32). Due to some stability problems, the newer version of WASP was not considered for the current study. WASP was first created in the 1980s and has undergone numerous improvements (Wool et al. 2020). The general dynamic model WASP

uses a segmentation network to solve the conservation of momentum, energy, and mass equations and simulate the transport of contaminants and sediment. The WASP model is frequently utilized to address sediment transport (Sabokruhie 2021), heavy metal transfer (K. E. Lindenschmidt, Sabokruhie, and Rosner 2022) and water quality issues (Mamani Larico and Zúñiga Medina 2019; Shabani et al. 2021). The WASP stream transport module, TOXI, is coupled with flow routing for free-flow streams, ponded segments, and backwater reaches and is capable of calculating the flow of water, sediment, and dissolved constituents across branched and ponded segments. Additionally, model boundary constraints and input parameters as defined.

Water flows through a network of branching streams, which may contain both free-flowing and ponded parts, and is calculated using the standard WASP8 stream transport model. Flow routing can be estimated for free-flowing stream reaches, ponded reaches, and backwater or tidally-influenced reaches for one-dimensional, branching streams or rivers. Advective transport can be driven through free-flowing portions with the simple yet practical kinematic wave flow routing method. The kinematic wave equation determines the propagation of flow waves and the fluctuations in flows, volumes, depths, and velocities that arise from the varied upstream inflow. This well-known equation is the solution to the one-dimensional continuity equation and a simplified form of the momentum equation that considers gravity and friction.

#### **3.3.4. *Kinematic Wave***

For most river systems, the kinematic wave formulation is appropriate. The kinematic wave calculates flow wave dissemination and flow velocity variation over a network of streams. The roughness of the slope and river bottom affect kinematic flow waves. By changing the Manning

equation (Equation 1) in the continuity equation and differentiating cross-sectional area with respect to time, the kinematic wave differential equation may be produced (Equation 2).

$$Q = \frac{1}{n} \frac{A^{5/3}}{B^{2/3}} S_0^{1/2} \quad (3.1)$$

$$\frac{\partial Q}{\partial x} + \alpha \beta Q^{\beta-1} \frac{\partial Q}{\partial t} = 0 \quad (3.2)$$

where  $Q$  is the flow rate,  $x$  is longitudinal distance in channel,  $t$  is time,  $\alpha$  and  $\beta$  are functions of hydraulic coefficients,  $S_0$  is the slope of the channel,  $n$  is the Manning friction factor,  $A$  is the cross-sectional area, and  $B$  is the channel width. The depth exponent is used along with segment geometries to estimate hydraulic coefficients, which are later used to calculate segment flow depths under specific flow rates. Wool et al. (2020) gives a complete description of WASP's stream transport equations.

### 3.3.5. Discretization

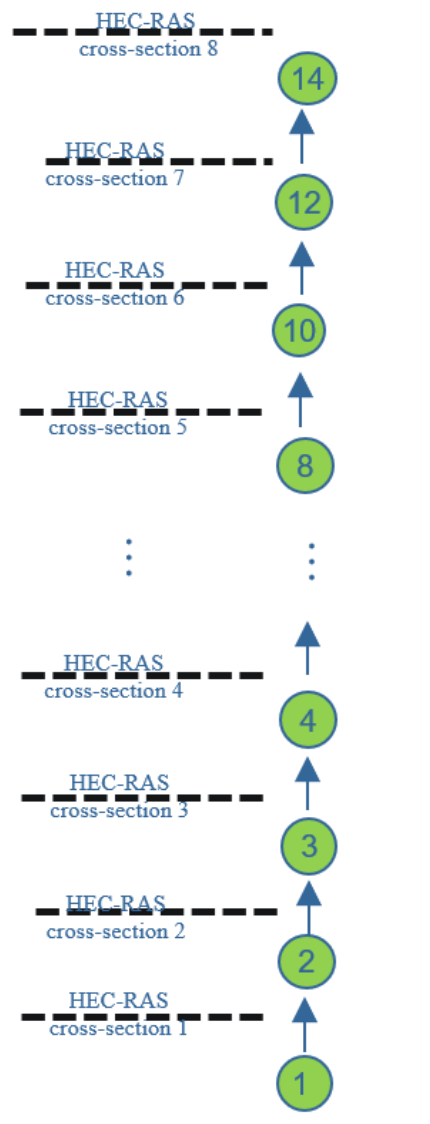
The river network was discretized using a 500 m interval. This led to 319 horizontal, one-dimensional water segments in WASP. Segment widths, average depths, and depth exponents were among the hydrodynamic metrics produced by HEC-RAS. The depth exponent controls channel shape in WASP. For these segments, a depth exponent value of 0.3 was used to simulate an uneven cross-section. These depths are used to determine segment depths during simulations, together with segment widths, slopes, and roughness factors.

The model's input variables include channel geometry, flow routing, boundary conditions, environmental time functions, loads, and initial segment conditions. Hydraulic parameters were obtained using a calibrated and validated HEC-RAS model and utilized as inputs for the flow functions in WASP (K.-E. Lindenschmidt, Sabokruhie, and Rosner 2022).

From the 319 HEC-RAS cross-sections separated by 500 m, geometry for the WASP segments (average depths, widths, and slopes) was derived. Based on the station's water quality data closest to the study region, spatial linear interpolation was used to identify the boundary and initial conditions for the current investigation.

The study's duration was from 2020 to 2021. Initial metal concentrations for each model component were derived by interpolating between two nearby long-term monitoring stations: the upstream boundary conditions were defined using the study from Prajapati et al. (2022) metal data, which was Outlook (1.23  $\mu\text{g/L}$ ). The boundary data for downstream was selected based on the data from Weldon Ferry (1.91  $\mu\text{g/L}$ ).

The chosen segment length of 500 m for modelling is deemed appropriate based on processing times, a reasonable uniform volume for segments, and an acceptable mixing. Benthic segments were inserted underneath each section of surface water to quantify erosion and sedimentation. The measured concentration at the upstream and downstream boundaries was used to calibrate the deposition rate of metals. The stretches between every two cross-sections of the HEC-RAS model were divided into single WASP segments. Output files of the hydrodynamic model (HEC-RAS) were specific for each cross-section. These results then needed to be averaged between two consecutive cross-sections to get the exact values for each WASP segment. This procedure is shown in Figure 2 and was implemented in Microsoft Excel for all input values.



**Figure 3.2.** Segmentation of the model domain. Left panel: HEC-RAS cross sections; right panel: WASP surface segments.

### 3.3.6. Visualization, Calibration, and Validation

The modelled metal concentrations and hydrodynamics were calibrated and validated. The calibration of metal concentrations involved several iterations in the parameter space

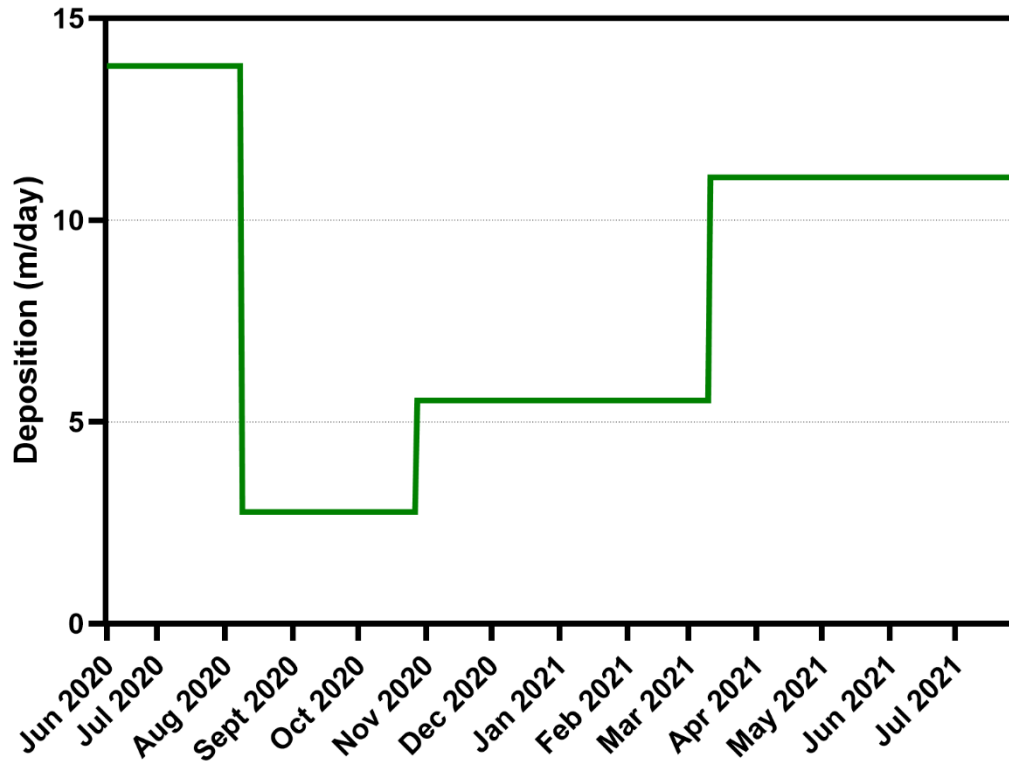
within reasonable parameters of the observed values. The best curve fitting with the observed data was achieved by choosing the optimum parameter values. To validate the model, a run with these values was compared against an independent set of field data.

An effective way to review model simulations and calibrate them using collected data is to use the Post-Processor (MOVEM). Results from every WASP run, as well as others, can be visualized using MOVEM. MOVEM allows the modeller the choice of two graphical representations of the results: Geometric Grid and x/y Plots. There is no restriction on how many geographical grids, x/y plots, or even model result files a user can employ in a session.

### **3.4. Results**

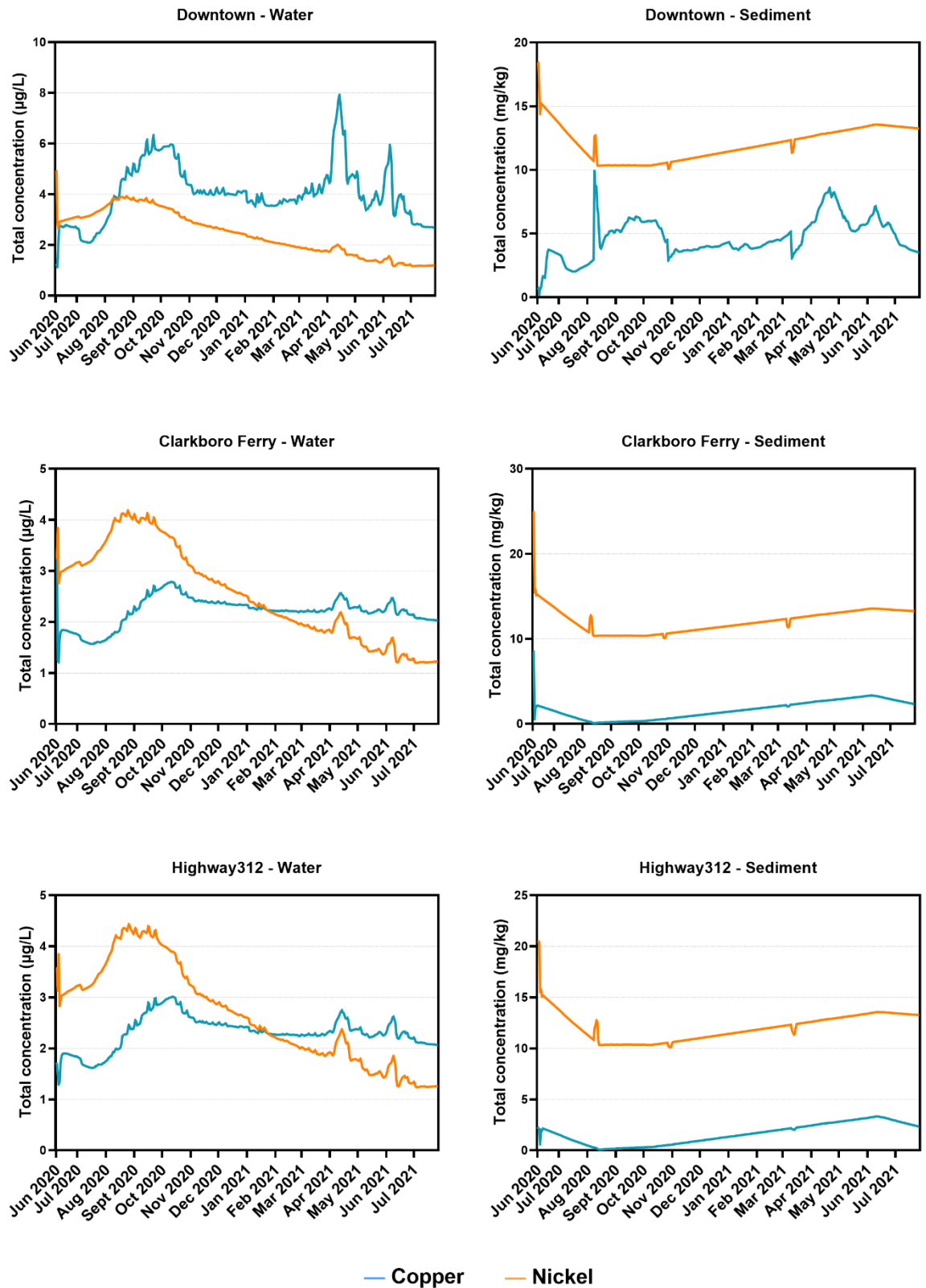
#### ***3.4.1. Deposition Rates and Overall Concentration Trends***

Deposition rates for Cu and Ni were calibrated using the sampled concentration at the upstream and downstream model boundaries (Figure 3.3). A previously developed model for sediment transport was used, and the model was calibrated with an acceptable range of deposition (K.-E. Lindenschmidt, Sabokruhie, and Rosner 2022). Concentration plots (Figure 3.4) show the trend for both trace metals at selected sampling sites (Downtown Saskatoon, Clarkboro Ferry, and Highway 312) for both water and sediment samples. This plot was achieved using calculations based on the mechanistic Van Rijn equation and the mechanistic Robert equation in an attempt to calibrate the model to match the observed values. Concentration values for all sites can be found in the Supplementary Information (Table S8-S11).



**Figure 3.3.** Calibrated deposition curve for both trace metals Cu and Ni. This plot was generated by using the existing observed values of Cu and Ni for calibration of the model.





**Figure 3.4.** Model predicted Concentrations of Cu and Ni in water and sediment for selected sites during the 2020 and 2021 field seasons.

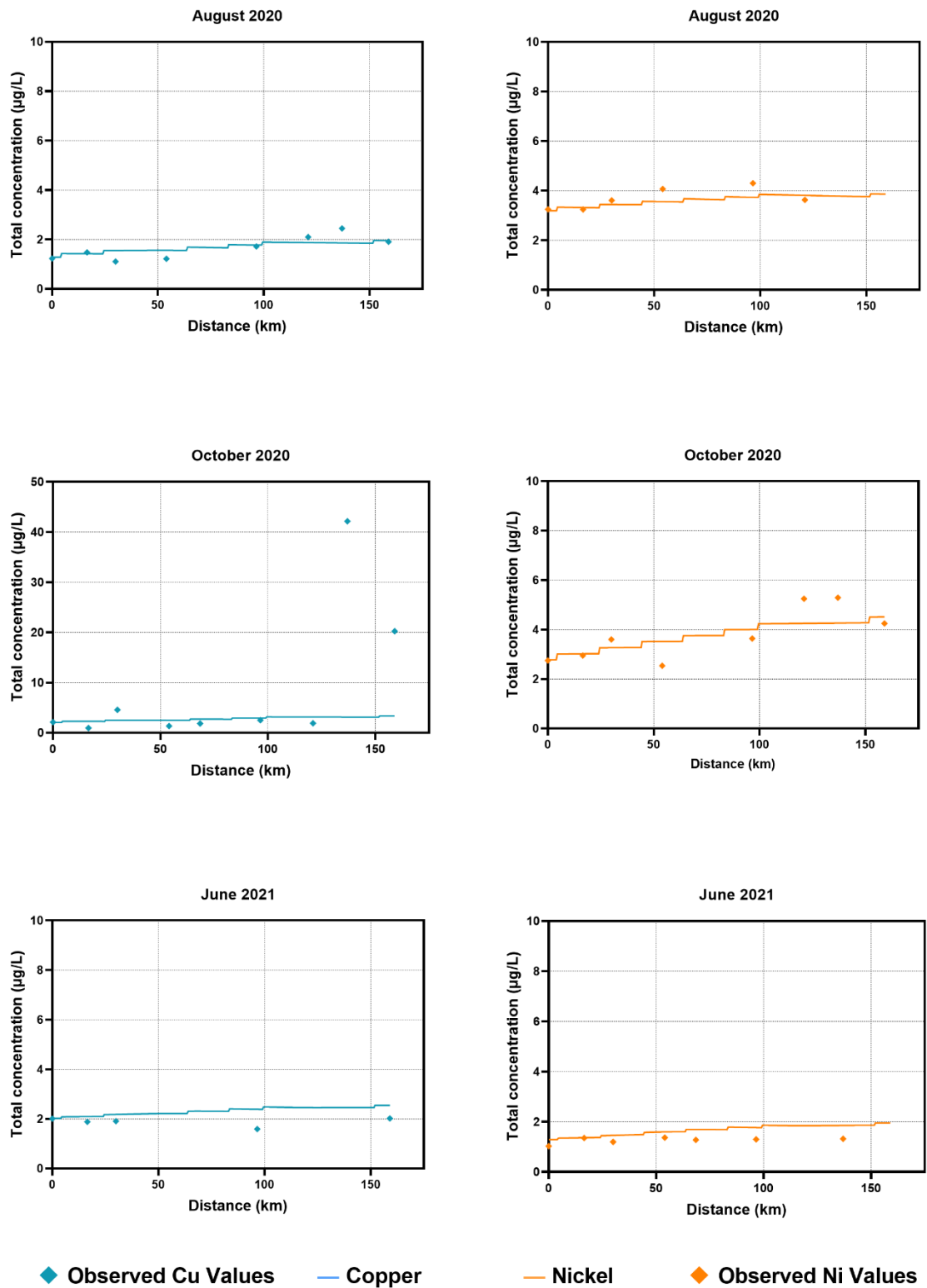
Both trace metals were modelled for the same time points for water and sediment in the years 2020 and 2021 and matched to the field sampling of water and sediment samples to maintain uniformity.

### **3.4.2. Copper**

In 2020, Cu concentrations were observed in the range of 1 – 5 µg/L except for two sites (Highway 3 and Weldon Ferry), with values at 42.2 µg/L and 20.2 µg/L, respectively (refer to Supplementary Information). Levels of Cu in river water in 2021 ranged from 0.8 µg/L to 5 µg/L. That the observed concentrations remained uniform, for the most part, is indicative of the complex mixing of copper across the sampling sites. On the other hand, elevated concentrations of Cu at Highway 3 and Weldon Ferry could be attributed to ongoing roadway and bridge construction in this area (S. Prajapati, pers. obs.). Several of these measured concentrations exceeded the long-term CCME water quality guideline for Cu of 4 µg/L at the given water hardness >180 mg/L CaCO<sub>3</sub>, which indicates that risks to aquatic life could not be excluded. In sediments, the concentrations of Cu ranged from <LOQ to 19 mg/kg in 2020 and <LOQ to 15 mg/kg in 2021 (Prajapati et al., 2022). Adverse effects are not expected as the results obtained are below the CCME ISQG of 35.7 mg/kg. Concentration values for copper in sediments ranged from 1 – 15 mg/kg, with Clarkboro Ferry being on the higher end for both sampling years, with values in the range of 12 –15 mg/kg.

Figures 5 and 6 show a longitudinal comparison of measured and modelled copper concentrations in water and sediment for 2020 and 2021. The concentrations modeled through the sampling time points almost uniformly increased between the upstream and downstream boundaries of the study area. Copper concentrations for water samples remained mostly consistent for June 2020, August 2020, and October 2020, but increased gradually and became more consistent in June 2021 and August 2021. Within the study period, discharge and flow

velocity of the South Saskatchewan River were highest in June 2020 (Figure 4), which can explain this observed pattern of copper concentrations, as increased discharge would cause significant erosion of river banks and stream beds. The modeled values were significantly close to the observed values which indicates successful consideration of high flow river data. Thereafter, longitudinal profiles for August 2020, October 2020, and June 2021 remained relatively consistent throughout the segments (Figure 5 and 6).

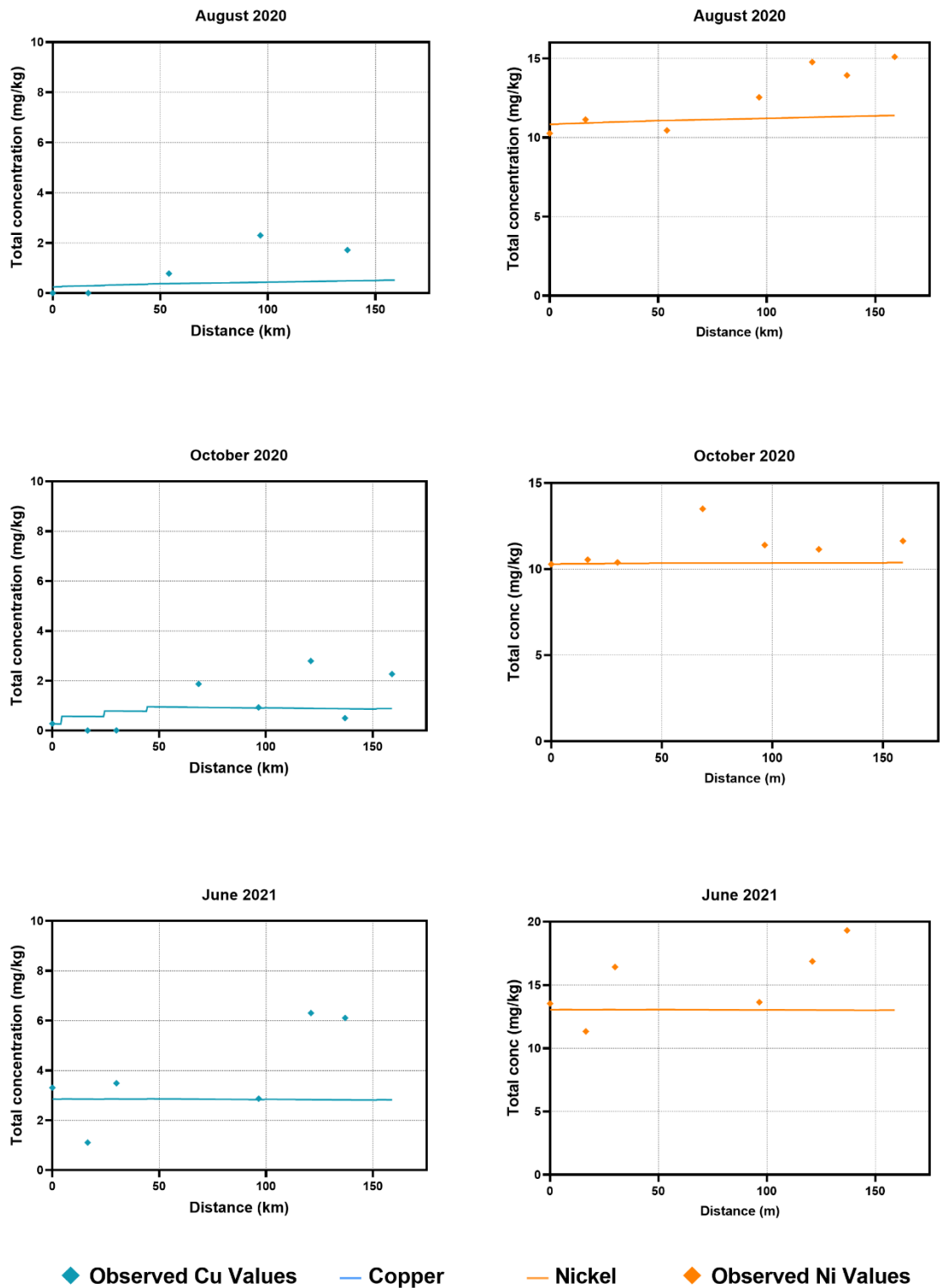


**Figure 3.5.** Longitudinal profiles of modeled water concentrations (lines) with observed values (points) for both trace metals in the 2020 and 2021 field seasons.

### 3.4.3. *Nickel*

In 2020, Ni concentrations ranged consistently from 2 – 6 µg/L for water samples and ranged from 0.3 – 1.4 µg/L in 2021. The high flow season in 2020 (due to elevated discharge and precipitation mentioned above) helps explain the almost 3 to 4-fold greater nickel concentrations in that year. Levels of Ni in sediments for 2020 ranged from 10.5 – 25 mg/kg and mostly remained consistent throughout the year. However, in contrast to concentration values for water samples, the concentration of nickel in 2021 remained around the same range with a very slight decrease, ranging from 10 – 20 mg/kg. None of the measured concentrations exceeded the long-term CCME water quality guideline for Ni of 150 µg/L at the given water hardness >180 mg/L CaCO<sub>3</sub>.

Longitudinal profiles for Ni (Figures 5 and 6) followed almost the same trend as those for Cu, with very little variability in concentration values during the different sampling time points. Nickel concentrations remained consistent for August 2020, October 2020, June 2021, and August 2021, with a slight gradual increment with every major segment (i.e., sampling station). The concentration values followed a similar trend of gradual increase. For sediment samples, the modeled progressions again followed similar patterns in August 2020, October 2020, and June 2021, with a consistent and slight decline throughout the study area. Again, high flow in 2020 could explain the 3 to 4-fold greater nickel concentrations in 2020 compared to 2021 water samples. Similarly, for sediment samples, settling and transverse mixing can contribute to consistent and slight declines in the concentration values.



**Figure 3.6.** Longitudinal profiles of sediment concentrations for both trace metals in the 2020 and 2021 field seasons.

### 3.5. Discussion

Modelled Cu concentrations in water were consistent and followed similar trends as the observed values for most of the sampling time points. An exception to that is the observed values in the October 2020 sampling time points, where the observed Cu concentration values were significantly higher than those simulated by WASP. This could be attributed to roadwork and bridge construction in the area, which would have been impossible for the model to cover. In sediment samples, the majority of the WASP simulated values were underestimated compared to the observed values with a few exceptions. This could be the result of the continuous accumulation of metals in sediments over many years, which was not accounted for in the current modelling exercise.

Modelled Ni concentrations in water samples across 2020 and 2021 also followed a similar trend without major discrepancies from the observed values. For sediment samples, there were a few instances where the observed values were higher than that of the modelled progression. The model tended to underestimate the Ni concentrations for sediment samples, following a similar trend to the Cu concentrations for sediment samples.

During initial simulations, the model underestimated concentrations at downstream segments. Additional diffuse loads were added to compensate and match the simulated values with measured values. This significantly improved the accuracy for both metals. For water samples, additional loads (~1 – 3 kg/day) were included at major segments (sampling stations) as a diffused load. The loads were increased 100 – fold for calibration for sediment samples. These amounts were determined through the calibration process. Copper and Ni are both known to sequester in the sediment bed and are less likely to be suspended in water. Copper, as mentioned above, enters the environment mainly through anthropogenic sources (Ellingsen, Horn, and Aaseth 2007). The release and remobilization of sediment-bound Cu have been well-documented in various studies; however, the overall impacts are minor (Costello,

Hammerschmidt, and Burton 2015; Teuchies et al. 2011; De Jonge et al. 2012). Mobility of Ni, on the other hand, is site-specific and depends on the soil type and pH (Richter and Theis 1989). These observations can attribute to the higher observed values of both Ni and Cu in the sediment samples in the current study.

The model used in the current study is an extension of the previously developed model 1D WASP and HEC-RAS coupling (Akomeah and Lindenschmidt 2017) and quasi-2D (Lindenschmidt, Sabokruhie, and Rosner 2022; Sabokruhie et al. 2021). In Lindenschmidt, Sabokruhie, and Rosner's (2022) study, mixing of vanadium and sediment was modelled with a quasi – 2D modelling approach in the lower Athabasca River. The authors observed a marked increase in vanadium concentration along the river. The model was successful in capturing the transverse mixing from tributary water with mainstream water. Trace metals have been modelled in other studies where the results were in line with the measured values. In a drinking water monitoring study in China, Xiao, Jia, and Wang (2015) reported that WASP-TOXI model performed well and the results were in line with measured values for calibration and validation. In a quarterly report by University of Houston and Parsons Water and Infrastructure, a study to monitor PCBs in Country Club Lake reported acceptable results working with WASP-TOXI (Rifai and Palachek 2007).

As mentioned earlier, freshwater systems are complex and challenging, which demands sensitive methods in order to get accurate results for different metals. With limited data availability, understanding metal speciation becomes difficult in such systems (Unsworth et al. 2006). The current study for the South Saskatchewan River system provides preliminary data focussing on trace metal transport and fate. This study also provides us with an understanding of how the concentration of trace metals (Cu and Ni) vary from upstream to downstream of the South Saskatchewan River. It was observed that the trace metal concentrations were the highest during the high flow season in 2020 with a few exceptions. This suggested that variation of



concentrations over time (presumably due to hydrology) was greater than the variation in space. There were a few CCME ISQG exceedances for Cu concentrations and there are no guidelines outlined for Ni (as of now). Although there may be no immediate potential for toxic effects in biota just yet, contamination to aquatic systems cannot be excluded. Further study involving more metals in the model with sufficient input parameters would be an ideal recommendation.

### **3.6. Conclusions**

The aim of this study was to better understand trace metal fate and interaction in the South Saskatchewan River. Two trace metals, Cu and Ni, were selected on the basis of their presence in the region. Copper is used in a wide range of products such as construction, pipes, industrial equipment, etc., resulting in widespread anthropogenic contamination. In contrast, Ni has a geogenic background in Saskatchewan and is transferred to the aquatic environment by effluents, leachates, and runoff from mining activities and the general land surface.

A 1-D modelling approach was successfully applied in studying the trends and patterns of trace metal fate in the river and sediment. The simulations provided useful data for both the trace metals and gave an insight into how the metals travel and react between water and sediment in the South Saskatchewan River.

A number of parameters values (volatilization exchange rate constant, atmospheric chemical concentration, water column decay rate constant, Newton-Raphson constant) were not available due to the lack of availability of consistent raw data regarding the processes in the freshwater system for the modelling of these two trace metals. Improved availability of these parameter values would help make the model more efficient and accurate in predicting future trends with increased/decreased flows.

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**Chapter 4: CONCLUSIONS AND  
RECOMMENDATION FOR FUTURE  
WORK**

## **2.1. General Conclusion**

Water quality is threatened by a variety of anthropogenic activities, many of which have had deleterious impacts on ecosystem health (UNEP 2010). In particular, leaching of pesticides and fertilizers from land cleared for agriculture have raised significant concern (Carsel et al. 1988; Rosenbom, Kjær, and Olsen 2010; Leistra and Boesten 2010). Global pesticide usage has been increasing significantly over the past decades, and pesticides are frequently found at levels high enough to raise concerns related to ecosystem health and source water quality (Malaj et al. 2014; Stehle and Schulz 2015). Urbanization, natural resource extraction, and other industrial activities are other major drivers of the global deterioration of water quality (Prüss et al. 2002).

As Canada's breadbasket, agriculture has been one of the key contributors to Saskatchewan's economy, and Saskatchewan supplies the largest share of Canada's agricultural products. Consequently, pesticide usage has been higher in Saskatchewan compared to the other provinces and territories due to large agricultural land base and to sustain high and reliable crop yields. The SSR is one of the most important river systems in Canada, and especially Saskatchewan, as most of its residents rely on the river for a variety of uses. Not a lot of studies related to water quality have been conducted in the SSR as a large-scale quantification process apart from Burke (2016) and Malaj, Liber, and Morrissey (2020). Assessing the concentrations of pesticides or other plant protection products in a place where the agriculture industry is dominant and thriving was necessary and needed to be carried out at this scale.

The purpose of this thesis was to quantify pesticide concentrations of different pesticides and trace metals, and then use modelling techniques to understand transport and fate of a selected subset of contaminants, specifically trace metals. Another objective of this thesis

was to generate a dataset for the discussed organic chemicals/plant protection products and trace metals with respect to their concentration and toxicity to freshwater, sediment, and fish species. This study is one-of-a-kind in the SSR and concentrated on the chemical analytical determination of various classes of pesticides (herbicides, organochlorines, organophosphates, and neonicotinoids), as well as trace metals in a variety of environmental media (Prajapati et al. 2022). The generated data from the previous study were then used in an existing water quality model for the SSR to understand transport and fate of these contaminants. Two representative trace metals (Cu and Ni) were selected for further modelling through WASP – TOXI.

#### **4.1. Pesticides in the SSR**

Chapter 2 quantified pesticides with respect to the CCME guidelines at several important sampling sites representing the SSR (upstream at Outlook followed by Irrigation District, Irrigation District Flowback channel, Fred Heal Canoe Launch, Downtown, Clarkboro Ferry, Highway 312, Highway 3, and finally downstream – Weldon Ferry). Organochlorines, organophosphates, herbicides, and neonicotinoids were the classes of pesticides that were selected for this study based on previous findings highlighting their relevance in the region (Malaj, Liber, and Morrissey 2019). In addition, samples were analyzed for trace metals to understand the transport and fate of various metals in freshwater. Even though it was a part in the 24-element trace metal analysis, mercury was analyzed separately in sediment and fish samples to understand BSAFs (biota sediment accumulation factors). I found a mixture of legacy contaminants (organochlorine pesticides) and other pesticides in water, sediment, and fish. Herbicides were present in abundance in the water samples due to their high solubility. Fortunately, most of the concentrations were under the CCME water quality guidelines which suggests there is no immediate concern from such farming practices. However, there is a significant lack of data regarding agrochemical use in the SSR system which would help track

major pesticides used for economically important crops. Publicly available pesticide use data would be a very desirable recommendation moving forward. This study complements the study carried out by Malaj, Liber, and Morrissey (2019) as it focuses on quantifying levels of specific pesticides relative to their toxicity by comparing them with environmental quality standards. Thereby, it helps shed more light on potential environmental concerns related to pesticide concentrations in river ecosystems.

Wetlands are an important part of our landscape in the ecosystem. Wetlands are known to provide a wide array of ecosystem services including fresh water, nutrient cycling, food production, carbon sequestration, flood mitigation, water purification, and water storage (Costanza et al. 2014; Mitsch and Gossilink 2000). A study carried out in the Prairie Pothole Region (Malaj, Liber, and Morrissey 2019) discussed agricultural pesticide products which contribute towards water quality degradation. This study focussed on ecologically important wetlands and estimated the spatial extent of pesticide use in the area. Furthermore, the study was successful in developing a Wetland Pesticide Occurrence Index (WPOI) to understand the exposure of pesticides to wetlands. Building on this study's pesticide index, this thesis focussed on transport and fate of pesticides, herbicides, insecticides, neonicotinoids, and trace metals in the freshwater river system (SSR).

#### **4.2. Trace metals in the SSR**

Trace metals are known to potentially have significant deleterious impacts on the environment. Based on their chemical properties, environmental fate and bioavailability of these trace metals can differ markedly. In this study, Cu was analyzed as a model trace metal with predominantly anthropogenic sources, whereas nickel was analyzed as a model trace metal with predominantly geogenic background contamination (Cempel and Nikel 2006).

#### **4.3. Water quality modelling using WASP-TOXI**

Two metals were modelled using WASP – TOXI for two significantly different flow seasons. The TOXI module allows for considerations in various parameters such as reaction kinetics, complexation with DOC, and pH. However, availability of all such parameters is not possible at this particular moment as not a lot of detailed water quality modelling studies have been conducted in the SSR. Even though a few parameters were unavailable, the calibration of the model was acceptable and followed by the predicted values being around the measured values. Hence, the modelling study conducted in Chapter 3 was successful and the results were acceptable. Chapter 3 provides the results with regards to trace metal trends and shows Cu and Ni concentrations to be consistent for the 2020 field season and increased gradually throughout the 2021 field season. High discharge and flow velocity are indicative of the observed results for Cu and Ni concentrations in 2020 field season. When observed Cu and Ni values were compared to the modelled longitudinal profiles, there were marked similarities with a few values being underestimated by the model. To counter this, additional diffused loads were added to the model to improve the accuracy in predicting concentrations of trace metals.

#### **4.4. Relationship between contaminant levels and hydro-climatic drivers**

Saskatchewan is known to experience low rainfall and less evaporation making the local water bodies or resources in general vulnerable to changes in climate and land cover (Pomeroy, Fang, and Williams 2009). As agriculture develops further, the water usage will be more efficient with improved crop varieties. The SSR originates in the province of Alberta and is subject to demands for irrigation and municipal use (Pomeroy et al. 2005). Saskatchewan is regarded as the breadbasket of Canada and agricultural development is at a rapid pace (Statistics Canada 2017). The efficiency of agriculture is increasing as it further develops and usage of water is expected to be optimized compared to the earlier agricultural systems, but there is also planned irrigation expansion which could lead to lower overall flows and higher concentrations of pesticides in agricultural return water. Changes in land management practices

would be an ideal solution to retain water for crop production and also ensuring that small wetlands which are important for the ecosystem do not dry out. As most of the provincial population is located in the southern part of Saskatchewan which are also the large urban centres, the SSR will be expected to provide enough water for industrial, urban, and agricultural water requirements. As Saskatchewan develops further, the water requirement is likely going to increase several-fold which could cause serious concerns over water supplies of the SSR. Hence, appropriate planning is required to use science and navigate this scenario effectively.

In this study, we observed two very different field seasons in 2020 and 2021. The 2020 sampling season observed exceptionally high flow which was twice as much compared with the 2021 sampling season. As discussed above in Chapter 2, high flow in rivers is linked to increased erosion and run-off which facilitates entry and mixing of organic contaminants at a higher rate. The high flow season can be attributed to wet-dry cycles, and deglaciation affects summer baseflows in the SSR (Clarke et al. 2015). If this doesn't change, the SSR will be more likely to experience variable flow seasons to a point of having no flow/drought scenarios in the near future. As most of Saskatchewan residents do rely on the SSR for various purposes, the responsibility to conserve this freshwater system is even more important.

#### **4.5. Constraints and Limitations**

While this study was successful on several accounts, it faced some limitations. One of the primary limitations was that the scope of this study had to be reduced due to COVID – 19, as travelling overnight for sampling was not possible in 2020 and 2021. The 2020 field season experienced a very high flow and as a result, water levels rose, which can cause non-representative sampling. Due to the high water level, sediment sampling may have occurred in the riparian zone instead of the river bed.

When conducting studies focussing on a broad suite of pesticide classes and/or trace metals, the resultant data set is generally large which naturally takes longer to analyse and process the data. Therefore, this study was confined to doing quantification analysis for all pesticide classes and trace metals, and modelling for only two trace metals. This data set, however, is very useful for further researchers and a plethora of studies can be built on this. A lack of consistent primary water quality data is evident when assessing publicly available resources, and inconsistent data make it difficult to accurately represent the river processes at work in the SSR.

#### **4.6. Future work**

Agriculture is not just an important part of Saskatchewan's economy but also for supplying an ever-increasing world population with nutritious crops grown on the prairies for consumption. With increasing demands for food, efficient farming practices have become vital. Hence, usage of pesticides has increased significantly in the agriculturally dominated river basin, the SSR. While this study has filled in some critical data gaps, they can be further advanced by focussing on individual classes of pesticides with greater depth. Following are the recommendations for future work based on the experience of this thesis:

1. Consistent availability of primary water quality data at major monitoring stations;
2. In depth studies on individual classes of pesticides with modelled progressions to understand transport and fate of individual chemicals and their interactions with water, sediment, and fish;
3. Similar studies with individual fish species and impacts of pesticides/trace metals, e.g., through biomarker analysis in exposed fish;
4. Application of other toxicity models to compare the results of the current study (Chapter 3); and,

5. Additional statistical analyses to identify different correlation patterns within chemicals and target sample.



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# APPENDIX

**Table S1.** Pesticide concentrations of water samples in field season 2020

Stes	2,4 - DB acid (ug/L)	Dicamba (ug/L)	MCPA (ug/L)	Other Herbicides (ug/L)	Methoxychor (ug/L)	Lindane (gamma-HCH) (ug/L)	Other Organochlorines (ug/L)	Melathion (ug/L)	Parathion (ug/L)
Outlook	0.132777759	0.258522333	0.382521687	0.83961413	0	0.05774681	0.013989764	0.004856391	0.003418823
Irrigation District	0.134488931	0.21783844	0.377749624	0.8962561	0.022150039	0.032889219	0.064321902	0.00404733	0
Irrigation Flowback	0.169487895	0.250880143	0.323417545	0.745749793	0	0.073283253	0.041081356	0.003514668	0
Fred Heal	0.168721584	0.250467699	0.265930966	0.841726299	0	0.026441364	0.022906995	0.003858106	0.001862806
Downtown	0.321399082	0.33620566	0.287389066	0.805965793	0.001623204	0.031717463	0.023351091	0.002548379	0.000638521
Clarkboro Ferry	0.088605779	0.259604443	0.287389066	0.822614913	0	0.051680377	0.051680377	0.009627897	0.066760064
Highway/312	0.105786673	0.216007053	0.31847303	1.044395792	0.012584469	0.06228761	0.003970758	0.003577074	0
Saint Louis	0.095799168	0.211715944	0.310648717	0.742353537	0.011749812	0.016855211	0.022408735	0.003414707	0.004766835
Highway/3				0			0		
Weldon Ferry	0.092282549	0.27664279	0.33262101	0.804563802	0.004707013	0.026992339	0.012869931	0.002527389	0.005405344
Outlook	0.144555714	0.247693191	0.355400136	0.808359742	0	0.041763398	0.023223181	0.004002284	0.00053772
Irrigation District	0.114812085	0.176547835	0.428652852	0.730502664	0	0.054379633	0.010760024	0.003330983	0
Irrigation Flowback	0.220208409	0.294561283	0	0.675340239	0	0.134261643	0.090305665	0.00452096	0.04684817
Fred Heal	0.216481877	0.207687491	0.283562905	3.22662622	0	0.033898946	0.044698756	0.003195982	0.004976305
Downtown	0.143192811	0.297325962	0.18984459	0.76822819	0	0.044313955	0.027080228	0.003749316	0.000402612
Clarkboro Ferry	0.104612224	0.162624478	0.30755671	0.239707805	0.010764195	0.014242994	0.014242994	0.003103293	0
Highway/312	0.127568262	0.266997003	0.317075645	0.642610425	0.022038425	0.076207517	0.017950715	0.004439564	0
Saint Louis	0.065531049	0.174264727	0.379328234	0.709308709	0.014729882	0.023441037	0.002426378	0.003655571	0
Highway/3	0.096124047	0.148467533	0.269885568	0.578658955	0	0.007711902	0.007711902	0.002800417	0
Weldon Ferry	0.134479877	0.31842873	0.358605302	1.768344825	0.011863177	0.059375881	0.01928812	0.003399769	0
Outlook	0.232608222	0.291890819	0.216666369	0.777310274	0.001888053	0.042144347	0.023850356	0.00293771	0.006204035
Irrigation District	0.135894477	0.222452962	0.232804963	0.788418322	0.004768034	0.07794347	0.027040651	0.003409313	0
Irrigation Flowback				0			0		
Fred Heal	0.169797664	0.259369207	0.241936166	0.679019097	0	0.052110391	0.052450465	0.00374404	0.001057092
Downtown	0.159829293	0.229755458	0.21783844	0.788569178	0.006410502	0.035688919	0	0.003707659	0.002783964
Clarkboro Ferry	0.207070914	0.304060229	0.244344609	0.753123025	0	0.092284613	0.038735183	0.01299686	0.002470517
Highway/312	0.14316345	0.216391528	0.321678191	0.699079425	0.022773602	0.057210128	0.05394144	0.012140572	0.005345059
Saint Louis	0.36157528	0.339767902	0.052427375	0.999460023	0.001762221	0.021335281	0.004705657	0.002838238	0.001149897
Highway/3	0.214519109	0.274487316	0	1.723026029	0	0.11272606	0.123386466	0.003005885	0
Weldon Ferry	0.169399196	0.313717036	0.234078713	0.67289382	0.002731782	0.046076278	0.036499255	0.003343821	0.075793424
LOD (ug/L)	0.0022929209	0.004623369	0.00398682	N/A	0.001900823	0.00489242	N/A	0.00489242	0.00489242
LOQ (ug/L)	0.013752541	0.031207739	0.025629599	N/A	0.006652882	0.020576818	N/A	0.020576818	0.018617121
Detection Frequency	100	100	89.28571429	N/A	46.42857143	100	N/A	7.142857143	25
Mean	0.159706203	0.251207164	0.258944105	0.799118702	0.005847601	0.050700176	0.027513458	0.00527389	0.008229311
Min	0.065531049	0.148467533	0	0.239707805	0	0.007040382	0.027513458	0.002827389	0
Max	0.36157528	0.339767902	0.428852852	3.22662622	0.022773602	0.134261643	0.123386466	0.02838238	0.075793424

**Table S2.** Pesticide concentrations of sediment samples in field season 2020.

Sites	2,4-DB acid (ug/kg)	Dicamba (ug/kg)	MCPA (ug/kg)	Other Herbicides (ug/kg)	Methoxychlor (ug/kg)	Lindane (Gamma-HCH) (ug/kg)	Other Organochlorines (ug/kg)	Malathion (ug/kg)	Parathion (ug/kg)	
Outlook	0	0.760361549	0	0	0	0.503702828	11.60116573	4.470342883	0.148528905	0.081287302
Irrigation District	56.61272824	0.993537067	0	0	12.549797	0	10.94855214	0.971076993	0.07855962	0
Irrigation Flowback	19.95874016	4.713021249	0	0	14.05735584	0	19.88345863	7.429928122	0.779662018	0.050925834
Fried Heal	0	0.730655746	0	0	0	0.747836791	13.3970664	2.715623622	0.167884136	0
Downtown	0	8.282972905	0	0	0	13.07315376	14.71190952	6.789697691	0.187085278	0
Clarkboro Ferry	22.37963104	47.66067466	0	0	15.9457631	8.916663454	8.916663454	3.790353277	0.415638046	0
Highway/312	0	5.443711702	0	0	0	3330.813631	15.38808804	14.21499742	0.376799711	0.1763419
Saint Louis	0	0	0	0	0	0	0	0	0	0
Highway/3	0	0	0	0	0	142.7663762	6.910962289	28.92427669	0.081379987	0
Weldon Ferry	0	2.928838371	0	0	0	25.20465535	11.05074765	3.741483785	0.128833329	0
Outlook	0	2.701607651	0	0	0	1.87667511	2.083254866	27.51380336	0	0
Irrigation District	0	0.438676644	0	0	0	0	3.868949181	2.313365437	0.212603026	0
Irrigation Flowback	10.64663773	0.979722422	0	0	7.792317489	1.211561162	19.05749267	2.045450693	0.046506611	0
Fried Heal	0	1.190173425	0	0	0	1.860946742	11.43598115	4.226718058	0.1111110504	0
Downtown	29.38072828	0	0	0	20.10295521	6.093121253	21.39766336	6.430439836	0.08894686	0.906233308
Clarkboro Ferry	0	5.393037376	0	0	0	1.017989916	13.03232111	0.952276961	0.306190577	0
Highway/312	0	1.100580481	0	0	0	6.945253081	23.73166707	4.536372127	0.290244885	0
Saint Louis	0	0.904693628	0	0	0	2.364672091	3.148023625	5.385612941	0.145267801	0
Highway/3	6.620699214	0.444087561	0	0	5.185729511	2.191835383	14.01887309	0.361921634	0.126098696	0.085433771
Weldon Ferry	0	0	0	0	0	0	0	0	0	0
Outlook	0	7.880369108	0	0	0	0	11.57479945	1.5304065	0	0
Irrigation District	0	1.872861981	0	0	0	0	3.162203959	0.376148538	0.024044392	0
Irrigation Flowback	7.459025953	5.317337035	0	0	6.291300573	0	24.57902446	4.683175445	0.449268152	0
Fried Heal	0	92.22758412	0	0	0.109410444	0	11.36614434	11.82861227	0.087081578	0
Downtown	0	3.217047316	0	0	0	104.5947478	21.64886542	10.96631772	0	0
Clarkboro Ferry	0	0	0	0	0	9.687350176	19.80290156	2.518705376	0	0
Highway/312	3.737744555	3.032619979	0	0	3.452856098	0.846978556	12.25683592	1.462913202	0.136025373	0
Saint Louis	16.441772544	0	0	0	11.57913291	0.24425388	8.179120315	0.87072813	0	0
Highway/3	0.95927	1.417298979	0	0	1.700170679	0	16.38919279	1.418231021	0.055107722	0
Weldon Ferry	0.609632036	0.955549288	0.477774644	N/A	0.303144647	1.061006263	0.757861617	0.776414064	0.776414064	0.776414064
LOQ (ug/kg)	3.779718623	6.449957691	3.583309829	N/A	1.061006263	3.183018789	0.776414064	3.260939068	3.260939068	2.950373442
Detection Frequency	37.03703704	66.66666667	0	0	66.66666667	100	6.017369619	3.703703704	3.703703704	3.703703704
Mean	6.450849282	7.393684102	0	0	3.558029217	13.07379882	0.361921634	0.164550637	0.048156375	0
Min	0	0	0	0	0	0	2.083254866	0	0	0
Max	56.61272824	92.22758412	0	0	20.10295521	24.57902446	28.92427669	0.779662018	0.906233308	0

**Table S3.** Pesticide concentrations of fish samples in field season 2020.

Sites	2,4 - DB acid (ug/kg)	Dicamba (ug/kg)	MCPA (ug/kg)	Other Herbicides (ug/kg)	Methoxychlor (ug/kg)	Lindane (Gamma-HCH) (ug/kg)	Other Organochlorines (ug/kg)	Malathion (ug/kg)	Parathion (ug/kg)
Outlook					0			0	
Irrigation District	9.225547412	0	0	0	9.635454157	0	0	0	0.402276633
Irrigation Flowback					0	4.136206751	0	0	
Fied Heal					0		0	0	
Downtown	0	4.073711053	0	0	0.201994937	5.461458129	0.349722453	0.050188299	0.552775904
Clarkboro Ferry	6.605875107	19.73487886	0	0	6.53870496	2.414404716	4.942120591	0.197937606	0.388271928
Highway/312					0		0	0	
Saint Louis					0		0	0	
Highway/3					0		0	0	
Weldon Ferry					0		0	0	
Outlook					0		0	0	
Irrigation District	0	0	0	0	0.097483768	0	0.620803536	0	0.459650473
Irrigation Flowback					0		0	0	
Fied Heal					0		0	0	
Downtown	0	0	0	0	0.136342278	0	8.52076111	0	0.520800119
Clarkboro Ferry					0		1.271246299	0	
Highway/312					0		0	0	
Saint Louis	0	0	0	0	0.179256423	0.871104154	9.764961046	0	0.414404082
Highway/3	0	0	0	0	0.162602821	0	0.628538319	0.022141882	0.477849567
Weldon Ferry					0		0	0	
Outlook					0		0	0	
Irrigation District	0	0.17388735	0	0	0.178100471	0	0.635775208	0	0.422455031
Irrigation Flowback					0		0	0	
Fied Heal					0		0	0	
Downtown	0	1.163092234	0	0	0.215285231	51.66275313	9.956238894	0	0.601480465
Clarkboro Ferry					0		2.59904764	0	
Highway/312					0		0	0	
Saint Louis	0	1.293700821	0	0	2.163126632	0	6.258833542	0.000732943	0.389902398
Highway/3					0		0	0	
Weldon Ferry					0		0	0	
LOQ (ug/kg)	1.1169551	1.78712816	0.89356408	N/A	0.48112277	1.202806926	N/A	1.271410466	1.266574062
LOQ (ug/kg)	6.92512162	12.06311508	6.7017306	N/A	1.683929696	5.051788039	N/A	5.339922938	4.812981436
Detection Frequency/	20	20	0		0.60963599	6.040972013	0	0.140667213	0.027100073
Mean	1.583142252	2.643927032	0		0.620803536	5.315847962	0	0.620803536	0.388271928
Min	0	0	0		0	0	0	0	0
Max	9.225547412	19.73487886	0		9.635454157	51.66275313	9.956238894	2.59904764	0.197937606

October

August

June

**Table S4.** Pesticide concentrations of water samples in field season 2021.

Sites	2,4 - DB acid (ug/L)	Dicamba (ug/L)	MCPA (ug/L)	Other Herbicides (ug/L)	Methoxychlor (ug/L)	Lindane (Gamma-HCH) (ug/L)	Other Organochlorines (ug/L)	Malathion (ug/L)	Parathion (ug/L)
Outlook	0.085882387	0.042255187	0.004168108	0.666279981	0	0.001693616	0.011852285	0	0
Irrigation District	0.131487483	0.0570777723	0.004606155	0.369648742	0	0.002059526	0.004476584	0	0
Irrigation Flowback	0.095082793	0.060229427	0.005222652	0.449781821	0	0.000700989	0	0	0
Fred Heal	0.228268538	0.075345383	0.00574135	0.514245942	0	0.001878845	0.000483637	0	0
Downtown	0.035281823	0.048951917	0.004756493	0.034557358	0	0	0.015096382	0	0
Clarkboro Ferry	0.111106394	0.050632464	0.004303391	0.382930864	0	0.00109344	0.0033160657	0	0
Highway 312	0.196680442	0.067831153	0.006789595	0.545492148	0	0.002280693	0.003815729	0	0
Saint Louis	0.16756694	0.029926908	0.004088692	0.259660305	0	0.000965598	0.00102751	0	0
Highway 3	0.264797629	0.068483909	0.003567186	0.407333055	0	0	0.000405462	0	0
Weidon Ferry	0.119485793	0.091007289	0	0.533008092	0	0	0.000499543	0	0
Outlook	0.069112398	0.055121681	0.001078415	0.468266665	0	0.002468905	0.002351248	0	0
Irrigation District	0.09057769	0.05897137	0.00364446	0.412538705	0	0.001774946	0.000637216	0	0
Irrigation Flowback	0.111731345	0.08168426	0.003906279	0.394268512	0	0.001055941	0.001576846	0	0
Fred Heal	0.099693422	0.109446404	0.004800632	0.617840587	0	0.001076969	0.000214119	0	0
Downtown	0.094340273	0.163694366	0.00800843	0.775089746	0	0.001829933	0.000326021	0	0
Clarkboro Ferry	0.063572949	0.094676564	0.004797561	0.509622198	0	0.004215926	0.001589961	0	0
Highway 312	0.074132514	0.11427943	0.006067468	0.67583348	0	0.002936825	0.001133821	0	0
Saint Louis	0.204427517	0.081229741	0.00435785	0.455567304	0	0.001984359	0.00042692	0	0
Highway 3	0.249128201	0.101717527	0.005055553	0.660855819	0	0.001921173	0.000736574	0	0
Weidon Ferry	0	0.049873704	0.003456591	0.393364501	0	0.009215673	4.36908E-05	0	0
LOD (ug/L)	0.003939582	0.006292836	0.003146418	N/A	0.001575833	0.003939582	N/A	0.003939582	0.003939582
LOQ (ug/L)	0.024425406	0.042476641	0.023598134	N/A	0.00515414	0.016546243	N/A	0.016546243	0.01497041
Detection Frequency	95	100	90			0			
Mean	0.124617826	0.075093009	0.004421343	0.476309291	0	0.001957668	0.00249271	0	0
Min	0	0.029926908	0	0.034557358	0	0	0	0	0
Max	0.264797629	0.163694366	0.00800843	0.775089746	0	0.009215673	0.015096382	0	0

August

June

**Table S5.** Pesticide concentrations of sediment samples in field season 2021.

Sites	2,4-DB acid (ug/kg)	Dicamba (ug/kg)	MCPA (ug/kg)	Other Herbicides (ug/kg)	Methoxychlor (ug/kg)	Lindane (Gamma-HCH) (ug/kg)	Other Organochlorines (ug/kg)	Malathion (ug/kg)	Parathion (ug/kg)
Outlook	0	0	0	0	2.392011094	9.370629804	1.405500998	0	0
Irrigation District	0	0.431747977	0	0.666907758	4.833247225	4.676984847	0.178554817	0	0
Irrigation Flowback	0	0.389511339	0	0.45728149	0.673674353	5.616757816	9.264493981	0.021082045	0.054721218
Fred Heal	0	7.401287018	0	0	0.408644191	9.292417127	1.429714672	0	0
Downtown	0	2.74364088	0	0	20.6756632	11.46691792	6.997016913	0.23229873	0
Clarkboro Ferry	8.140917765	4.50912591	0	6.810168125	13.5333294	8.932588505	2.601214372	0.560267233	0.183032595
Highway/312	7.313736267	2.493984204	0	5.876420465	2.555291204	8.20860151	0.502157192	0	0
Saint Louis	0	46.22162244	0	0.285816689	9.523716182	8.578762595	2.166570448	0.146722528	0.331017183
Highway/3	0	0	0	0	4.061415282	8.86801436	1.822752271	0.116683365	0
Weidon Ferry	10.03516056	0.560963991	0	7.454139434	7.485401454	0	3.299719027	0.16565697	0
Outlook	0	2.841678956	0	0	0	4.225619014	0.627863917	0	0
Irrigation District	0	0.58514203	0	0	0	8.372657176	0.611027777	0	0
Irrigation Flowback	0	4.233518229	0	0	0	11.3202875	1.096822624	0	0
Fred Heal	0	0	0	0	3.837039511	4.215691403	4.335247322	0.161217544	0
Downtown	0	1.183338632	0	0	1.950550561	8.547155645	2.093841038	0	0
Clarkboro Ferry	6.004137404	4.350618025	0	4.991336171	10.60806177	19.66425846	0.679350269	0	0
Highway/312	0	2.144886567	0	0	7.103820543	5.405203751	0.872924328	0.45770371	0
Saint Louis	0	0	0	0	4.005291178	7.811004399	0.872924328	0	0
Highway/3	0	0	0	0	2.501799276	5.566706111	3.540375157	0	0
Weidon Ferry	0	0	0	0	0	7.557033434	1.644148341	0	0
LOD (ug/kg)	0.609632036	0.955549288	0.477774644	N/A	0.303144647	0.757861617	N/A	0.776414064	0.776414064
LOQ (ug/kg)	3.779718623	6.449957691	3.583309829	N/A	1.061006263	3.483018789	N/A	3.260939068	2.950373442
Detection Frequency	20	50	0	0	75	90			
Mean	1.5746976	4.00455331	0	1.267866951	4.177276411	6.786308296	3.087312092	0.093081443	0.02843855
Min	0	0	0	0	0	0	0	0	0
Max	10.03516056	46.22162244	0	7.454139434	20.67566332	11.46691792	19.66425846	0.560267233	0.331017183

August



**Table S6.** Pesticide concentrations of fish samples in field season in 2021.

Sites	2,4 - DB add (ug/kg)	Dicamba (ug/kg)	MCPA (ug/kg)	Other Herbicides (ug/kg)	Methoxychlor (ug/kg)	Lindane (Gamma-HCH) (ug/kg)	Other Organochlorines (ug/kg)	Malathion (ug/kg)	Parathion (ug/kg)
Outlook	0	0	0	0	0.77863661	0	0	0	0.533899583
Irrigation District	0	0	0	0	0.146127181	4.189153346	0	0	0.44908019
Irrigation Flowback	0	0	0	0	0.2677865	1.5834432183	0	0	0.50746291
Fred Heal	0	4.91157953	0	0	0.140096422	0	2.523232885	0	0.514147692
Downtown	0	1.1713507628	0	0	0.257051356	2.991397653	0	0.27123143	0.106903554
Clarkboro Ferry	2.735726491	2.691488575	0	0	5.808134841	11.09827766	0	0.284469774	0.481314447
Highway312	0.937740222	0.49393278	0	0	2.673304291	7.016945728	0	0.284469774	0.664924034
Saint Louis	0	39.24897407	0	0	0.811282439	3.172885537	0	0	0.515917896
Highway3	0	0	0	0	0.224818543	4.892800378	0	0.000484324	0.535801821
Weldon Ferry	4.631068159	0	0	0	6.389368747	2.821929878	0	0.054650826	0.568515513
Outlook	0	1.119495281	0	0	0	4.17500581	0	0	0.535941481
Irrigation District	0	0	0	0	0.176596714	1.684285099	0	0	0.454297036
Irrigation Flowback	0	2.283585321	0	0	0.146595176	0	0	0	0.565477936
Fred Heal	0	0	0	0	0.151233049	5.554163806	0	0	0.507084751
Downtown	0	0	0	0	0.251020208	6.302868602	0.665243254	0.018758971	0.42363755
Clarkboro Ferry	0.775350522	2.874324532	0	0	0.125711562	1.629833564	0	0	0.436843743
Highway312	0	0.116156832	0	0	4.52505886	3.654106989	0	0.162163801	0.483683332
Saint Louis	0	0	0	0	0.393702034	3.033504007	0	0	0.45470651
Highway3	0	0	0	0	0.298290175	2.788123848	0	0	0.452869669
Weldon Ferry	0	0	0	0	0.128258676	1.971922343	0.12797434	0	0.54854844
LOD (ug/kg)	1.1169551	1.78712816	0.89356408	N/A	0.48112277	1.202806926	N/A	1.271410466	1.266574062
LOQ (ug/kg)	6.92512162	12.06311508	6.7017306	N/A	1.683929696	5.051789089	N/A	5.339923958	4.812981436
Detection Frequency	10	25	35	90					
Mean	0.45399427	2.745552227	0	0	1.149909448	1.620180079	0	0.535929487	0.031371563
Min	0	0	0	0	0	0	0	0	0.42363755
Max	4.631068159	39.24897407	0	0	6.389368747	11.09827766	7.016945728	0.284469774	0.664924034

August

**Table S7.** Discharge and Precipitation Data for varying seasons in 2020 and 2021.

Flow Data		2020	Flow Data		2021	Precipitation Data		2020	Precipitation Data		2021
Date	Flow		Date	Flow		Date	Precip		Date	Precip	
6/2/2020 0:00	385.8285211		6/9/2021 0:00	75.6		6/2/2020	0.6		6/9/2021	0.2	
6/3/2020 0:00	385.2706485		6/10/2021 0:00	70.3		6/3/2020	0		6/10/2021	22.2	
6/4/2020 0:00	345.687405		6/11/2021 0:00	81		6/4/2020	0		6/11/2021	0.2	
6/5/2020 0:00	348.1089728		6/12/2021 0:00	81		6/5/2020	0		6/12/2021	0	
6/6/2020 0:00	353.7310365		6/13/2021 0:00	69.1		6/6/2020	7.7		6/13/2021	0	
6/7/2020 0:00	377.4225221		6/14/2021 0:00	71.1		6/7/2020	40.8		6/14/2021	0	
6/8/2020 0:00	388.2392616		6/15/2021 0:00	70.7		6/8/2020	0		6/15/2021	1.2	
6/9/2020 0:00	376.6689224		Mean	74.11429		6/9/2020	0		Mean	3.4	
6/10/2020 0:00	388.6540116		SD	4.742943		6/10/2020	0		SD	7.685236	
6/11/2020 0:00	392.0316081		8/4/2021 0:00	71.1		6/11/2020	0		8/4/2021	0	
6/12/2020 0:00	394.1594278		8/5/2021 0:00	71.1		6/12/2020	0		8/5/2021	0	
6/13/2020 0:00	416.1113596		8/6/2021 0:00	86.7		6/13/2020	0		8/6/2021	0	
6/14/2020 0:00	407.5510543		Mean	76.3		6/14/2020	2.4		Mean	0	
6/15/2020 0:00	402.3492747		SD	7.353911		6/15/2020	0.8		SD	0	
6/16/2020 0:00	386.7602946		Overall Mean	74.77		6/16/2020	12.4		Overall Mean		
6/17/2020 0:00	398.6740281		Overall SD	5.742308		6/17/2020	19		Overall SD	2.38	
6/18/2020 0:00	359.4761099					6/18/2020	1.5		Overall SD	6.616011	
Mean	382.7484976					Mean	5.011765				
SD	19.85502947					SD	10.34891				
8/10/2020 0:00	164.474118					8/10/2020	0				
8/11/2020 0:00	151.415696					8/11/2020	0				
8/12/2020 0:00	187.1151322					8/12/2020	0				
8/13/2020 0:00	174.739145					8/13/2020	0				
8/14/2020 0:00	173.1826173					8/14/2020	0.2				
8/15/2020 0:00	173.1185551					8/15/2020	0				
8/16/2020 0:00	167.440516					8/16/2020	0				
8/17/2020 0:00	126.2079774					8/17/2020	0				
8/18/2020 0:00	133.1026749					8/18/2020	0				
8/19/2020 0:00	144.7599427					8/19/2020	0				
8/20/2020 0:00	137.493098					8/20/2020	0.2				
Mean	157.5499521					Mean	0.036364				
SD	19.03484067					SD	0.077139				
10/6/2020 0:00	112.5998414					10/6/2020	0				
10/7/2020 0:00	113.0011061					10/7/2020	0				
10/8/2020 0:00	116.2672921					10/8/2020	0				
Mean	113.9560799					Mean	0				
SD	1.642463562					SD	0				
Overall Mean	276.8271668					Overall Mean	2.76129				
Overall SD	118.7980931					Overall SD	8.05508				

**Table S8.** Trace metal concentrations of water samples in field season 2020.

Element	Be	Al	Ti	V	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Ag	Cd	Sn	Sb	Ba	Tl	Pb	U
Instrumental LOD (ppb)	<0.01	0.030	0.016	0.007	0.024	0.007	0.225	0.005	0.025	0.006	0.023	0.009	0.012	0.007	0.004	0.002	0.003	0.003	<0.01	0.003	0.003	0.001	<0.01
LOQ (ppb)	0.015	0.805	0.050	0.506	0.096	0.079	0.333	0.029	0.216	0.999	0.165	0.046	0.104	0.031	0.144	0.020	0.007	0.033	0.010	0.034	0.017	0.024	0.014
CCME Sediment - ISGC	No data	No data	No data	No data	37.3	No data	No data	No data	No data	35.7	123	5.3	No data	No data	No data	No data	No data	No data	No data	No data	No data	35	No data
CCME Sediment - PEL	4	No data	No data	130	64	No data	No data	40	45	63	250	12	1	No data	5	2000	1.4	5	20	No data	No data	70	23
CCME Soil - Agricultural	4	No data	No data	130	64	No data	No data	50	50	63	250	12	1	No data	10	2000	10	50	20	No data	No data	140	23
CCME Soil - Residential/parkland	8	No data	No data	130	87	No data	No data	300	89	91	410	12	2.9	No data	40	4000	22	300	40	200	1	260	33
CCME Soil - Commercial	8	No data	No data	130	87	No data	No data	300	89	91	410	12	2.9	No data	40	4000	22	300	40	200	1	260	33
CCME Soil - Industrial	8	No data	No data	130	87	No data	No data	300	89	91	410	12	2.9	No data	40	4000	22	300	40	200	1	260	33
Sample ID	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Outlook	<LOD	3.93	0.05	0.25	<LOD	0.51	1.64	0.05	2.74	1.71	19.37	0.94	0.39	234.46	1.39	<LOD	<LOD	0.49	0.13	177.64	0.01	0.04	1.05
Irrigation District	<LOD	2.16	0.09	0.26	<LOD	0.48	8.18	0.07	3.24	4.04	28.18	0.82	0.55	240.59	1.44	<LOD	<LOD	0.38	0.14	223.19	0.01	0.04	1.05
Irrigation Flowback	<LOD	3.02	0.06	0.39	<LOD	1.49	17.41	0.14	4.61	3.07	17.77	1.35	0.55	465.54	1.52	<LOD	<LOD	0.76	0.17	199.98	0.01	0.08	4.54
Fried Heil	<LOD	1.67	0.07	0.27	<LOD	0.31	1.31	0.06	3.09	1.57	24.34	0.75	0.36	213.03	1.19	<LOD	<LOD	0.72	0.15	176.38	0.01	0.02	0.98
Downtown	<LOD	2.42	0.08	0.3	<LOD	2.81	2.5	0.07	4.91	1.97	26.17	0.74	0.56	217.78	1.49	<LOD	<LOD	0.11	0.15	179.4	0.01	0.03	0.96
Clarkboro Ferry	<LOD	1.98	0.1	0.33	<LOD	5.25	3.3	0.1	3.25	1.13	32.06	0.76	0.33	220.36	1.47	<LOD	<LOD	0.02	0.15	190.79	0.01	0.02	1.01
Highway3	<LOD	2.98	0.13	0.3	<LOD	0.77	2.83	0.1	3.57	3.84	25.19	0.71	0.37	248.63	1.47	<LOD	<LOD	0.16	0.16	204.25	0.01	0.05	1.08
Saint Louis	<LOD	2.1	0.06	0.68	<LOD	1.1	5.55	0.22	5.25	5.41	21.9	1.73	0.35	352.16	1.56	<LOD	<LOD	0.36	0.18	188.13	0.01	0.04	2.36
Highway312	<LOD	32.8	0.05	0.24	<LOD	0.92	4.93	0.08	2.19	3.04	26.34	0.58	0.37	231.15	1.35	<LOD	<LOD	0.07	0.14	201.14	0.01	0.05	1.01
Weldon Ferry	<LOD	3.28	0.05	0.24	<LOD	0.52	2.33	0.06	2.84	4.59	25.67	0.56	0.32	237.82	1.38	<LOD	<LOD	0.23	0.14	187.34	0.01	0.03	1.11
Outlook	<LOD	1.8	0.06	0.34	<LOD	1.88	2.1	0.07	3.25	1.23	28.88	0.89	0.39	198.17	1.28	<LOD	<LOD	0.09	0.13	187.08	0.01	0.02	0.89
Irrigation District	<LOD	2.12	0.12	0.36	<LOD	0.46	8.18	0.07	3.24	1.48	23.73	0.93	0.25	216.83	1.34	<LOD	<LOD	0.95	0.14	186.67	0.01	0.03	1.06
Irrigation Flowback	<LOD	1.8	0.05	0.36	<LOD	2.31	6.69	0.05	2.23	1.36	29.21	1.08	0.2	197.6	1.4	<LOD	<LOD	0.23	0.13	208.19	0.01	0.03	1.06
Fried Heil	<LOD	1.87	0.04	0.31	<LOD	1.11	0.93	0.08	3.61	1.11	17.92	0.67	0.34	234.69	1.37	<LOD	<LOD	0.24	0.14	176.23	0.01	0.02	1.01
Downtown	<LOD	2.01	0.04	0.41	<LOD	6.69	1.6	0.09	4.07	1.22	29.64	0.66	0.27	219.83	1.37	<LOD	<LOD	0.04	0.16	194.56	0.01	0.03	0.98
Clarkboro Ferry	<LOD	2.6	0.08	0.48	<LOD	2.82	2.82	0.09	2.17	3.44	25.59	0.72	0.39	244.53	1.47	<LOD	<LOD	0.24	0.17	195.26	0.01	0.05	1.09
Highway3	<LOD	2.61	0.04	0.47	<LOD	0.41	1.36	0.07	4.3	1.72	22.77	0.75	0.31	230.61	1.43	<LOD	<LOD	0.66	0.16	172.51	0.01	0.04	1.02
Saint Louis	<LOD	2.64	0.06	0.42	<LOD	0.71	3.01	0.07	3.63	2.1	23.01	0.72	0.31	230.9	1.45	<LOD	<LOD	0.52	0.16	204.61	0.01	0.05	1.1
Highway312	<LOD	2.79	0.06	0.39	<LOD	0.59	5.99	0.08	2.5	2.45	23.85	0.7	0.3	224.04	1.41	<LOD	<LOD	0.48	0.16	185.63	0.01	0.05	0.96
Weldon Ferry	<LOD	7.27	0.05	0.47	<LOD	0.23	1.83	0.06	2.39	1.91	23.53	0.71	0.31	218.89	1.36	<LOD	<LOD	0.27	0.16	173.34	0.01	0.03	0.96
Outlook	<LOD	3.75	0.05	0.37	<LOD	1.62	12.99	0.07	2.75	2.11	23.18	1.09	0.38	230.12	1.35	<LOD	<LOD	0.12	0.14	182.97	0.01	0.03	0.99
Irrigation District	<LOD	4.24	0.09	0.27	<LOD	1.29	22.48	0.05	2.95	0.95	24.02	0.72	0.15	236.24	1.29	<LOD	<LOD	0.04	0.13	176.51	0.01	0.03	1.4
Irrigation Flowback	<LOD	2.93	0.05	0.36	<LOD	2.04	2.04	0.05	3.6	4.57	20.3	0.75	0.33	211.03	1.15	<LOD	<LOD	0.08	0.15	180.76	0.01	0.03	1.04
Fried Heil	<LOD	3.29	0.05	0.39	<LOD	1.56	5	0.07	2.54	1.33	23.33	0.8	0.36	228.98	1.35	<LOD	<LOD	0.26	0.14	188.97	0.01	0.02	1.07
Downtown	<LOD	2.09	0.06	0.53	<LOD	2.21	3.42	0.11	6.08	1.83	24.58	0.9	0.36	229.98	1.47	<LOD	<LOD	0.02	0.16	198.14	0.01	0.03	0.98
Clarkboro Ferry	<LOD	1.88	0.07	0.33	<LOD	1.12	1.75	0.05	3.64	2.51	24.73	0.77	0.32	215.28	1.39	<LOD	<LOD	0.03	0.14	186.64	0.01	0.03	0.94
Highway312	<LOD	2.59	0.07	0.26	<LOD	4.88	2.09	0.08	5.25	1.89	22.26	0.7	0.33	232.92	1.45	<LOD	<LOD	0.03	0.13	176.92	0.01	0.01	1.07
Saint Louis	<LOD	2.59	0.07	0.35	<LOD	1.62	2.09	0.14	5.29	42.16	22.65	0.83	0.45	304.01	1.78	<LOD	<LOD	0.1	0.12	220.21	0.01	0.16	1.36
Highway3	<LOD	4.71	0.09	0.35	<LOD	1.7	3.07	0.12	4.25	20.23	14.74	0.7	0.38	248.42	1.53	<LOD	<LOD	0.06	0.16	201.67	0.01	0.11	1.14
Weldon Ferry	<LOD	4.71	0.09	0.35	<LOD	1.7	3.07	0.12	4.25	20.23	14.74	0.7	0.38	248.42	1.53	<LOD	<LOD	0.06	0.16	201.67	0.01	0.11	1.14
Instrumental QA/QC - Certified Reference Material 1640f (n=4)	92.03	100.84	n/c	97.74	97.23	95.65	96.78	98.08	98.97	99.75	97.43	99.57	96.36	95.14	97.35	104.84	94.68	n/c	97.45	101.94	100.69	100.61	104.14
Avg % Recovery	1.50	1.95	n/c	1.68	1.40	2.63	1.98	2.14	2.48	2.94	2.67	0.76	1.95	0.85	2.02	1.08	2.27	n/c	1.33	1.76	1.13	2.39	0.57
SD	1.50	1.95	n/c	1.68	1.40	2.63	1.98	2.14	2.48	2.94	2.67	0.76	1.95	0.85	2.02	1.08	2.27	n/c	1.33	1.76	1.13	2.39	0.57

**1. General Information**  
 All results in ppb.  
 Samples were run using a multi-element Agilent Technologies 8800 ICP-MS Triple Quad.

**2. QA/QC**  
 Instrumental QA/QC - Measured values must be within ± 20% of certified value.  
 The instrumental certified reference materials 1640a, trace elements in natural water, obtained from the National Institute of Standards and Technology.  
 n/c = element not certified in reference material.  
 LOD = limit of detection of instrument  
 LOQ = limit of quantification  
**3. Note:** Contents of Be, Cr, Ag, Cd and Hg are very low, lower than the limit of quantification.



**Table S10.** Trace metal concentration of water samples in field season 2021.

Element	Concentration units	Be	Al	Ti	V	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Ag	Cd	Sr	Sb	Sb	Ba	Tl	Pb	U
Instrumental LOQ (ppb)	ug/L	0.005	0.394	0.094	0.007	0.006	0.020	0.051	0.002	0.038	0.015	0.009	0.006	0.010	0.008	0.005	0.002	0.003	0.005	0.001	0.008	0.002	0.018	0.001	
LOQ (ppb)	ug/L	0.044	0.138	0.080	0.045	0.041	0.027	1.434	0.004	0.110	0.078	0.184	0.094	0.043	0.016	0.761	0.005	0.005	0.339	0.004	0.004	0.050	0.018	0.060	0.013
CCOE Sediment - ISGC	No data	No data	No data	No data	No data	37.3	No data	No data	No data	No data	35.7	123	5.9	No data	No data	No data	No data	0.6	No data	No data	No data	No data	No data	35	No data
CCOE Sediment - PEL	4	No data	No data	130	64	90	No data	No data	40	45	63	250	12	1	No data	5	2000	1.3	5	20	750	1	70	23	
CCOE Soil - Agricultural	4	No data	No data	130	64	90	No data	No data	38	39	91	410	12	2.9	No data	18	4000	10	30	40	200	1	140	38	
CCOE Soil - Residential/semi/ind	8	No data	No data	130	87	87	No data	No data	300	300	300	410	12	2.9	No data	40	4000	22	300	40	200	1	260	30	
CCOE Soil - Industrial	8	No data	No data	130	87	87	No data	No data	300	300	300	410	12	2.9	No data	40	4000	22	300	40	200	1	600	30	
Sample ID	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	ug/kg dw	ug/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw
Outrock	<LOD	1.76	0.14	0.32	<LOD	<LOD	0.61	8.17	0.05	1.03	2.01	19.07	1.09	0.22	296.44	1.05	<LOD	<LOD	0.37	0.13	81.50	0.01	<LOD	<LOD	1.30
Irrigation District	<LOD	9.38	0.15	0.43	0.26	0.04	0.26	1.16	0.07	1.35	1.88	10.08	0.73	0.55	293.07	1.24	<LOD	<LOD	0.23	0.16	84.43	0.01	<LOD	<LOD	1.09
Irrigation Howland	<LOD	2.60	0.05	0.26	0.21	0.04	0.21	1.59	0.08	1.41	2.13	44.10	0.70	0.39	293.37	1.29	<LOD	<LOD	0.01	0.15	88.71	0.01	<LOD	<LOD	1.17
Field Soil	<LOD	2.14	0.10	0.29	<LOD	<LOD	0.28	2.59	0.05	1.20	1.91	21.32	0.92	0.34	279.35	1.12	<LOD	<LOD	0.62	0.13	81.16	0.01	<LOD	<LOD	1.20
Downtown	<LOD	3933	0.17	0.23	0.54	<LOD	0.54	2.84	0.05	1.37	0.01	10.96	0.81	0.38	287.26	1.19	<LOD	<LOD	0.23	0.12	73.29	0.01	<LOD	<LOD	1.04
Chabon Ferry	<LOD	2.52	0.07	0.14	<LOD	<LOD	0.32	0.97	0.07	1.28	1.60	16.06	0.82	0.38	289.26	1.17	<LOD	<LOD	0.20	0.13	75.29	0.01	<LOD	<LOD	1.11
Highway3	<LOD	10.07	0.18	0.26	<LOD	<LOD	0.32	1.68	0.05	1.59	1.59	14.54	0.78	0.39	282.64	1.03	<LOD	<LOD	0.14	0.08	36.63	<LOD	<LOD	0.38	
Highway312	<LOD	2.80	0.09	0.47	0.04	0.04	0.08	0.38	0.07	1.32	0.95	21.74	0.71	0.37	215.87	1.35	<LOD	<LOD	0.51	0.19	51.65	0.01	<LOD	<LOD	0.95
Weldon Ferry	<LOD	2.52	0.15	0.29	0.01	0.01	0.38	7.33	0.05	0.95	2.02	5.03	1.10	0.22	265.99	1.00	<LOD	<LOD	0.36	0.13	71.28	<LOD	<LOD	1.20	
Outrock	<LOD	2.26	0.15	0.28	<LOD	<LOD	0.48	5.06	0.05	1.09	1.90	7.11	1.02	0.27	276.83	1.01	<LOD	<LOD	0.49	0.13	74.35	<LOD	<LOD	1.15	
Irrigation District	<LOD	2.79	0.10	0.22	<LOD	<LOD	0.38	2.91	0.04	1.16	1.79	5.87	0.92	0.33	288.12	1.05	<LOD	<LOD	0.65	0.18	74.99	0.01	<LOD	<LOD	1.10
Irrigation Howland	<LOD	8.56	0.08	0.22	<LOD	<LOD	0.19	0.60	0.02	0.31	4.42	24.30	0.22	0.03	60.46	0.02	<LOD	<LOD	0.19	0.02	22.57	<LOD	<LOD	0.23	
Field Soil	<LOD	3.67	0.11	0.45	0.46	<LOD	0.36	0.77	0.07	1.18	0.94	55.58	0.71	0.36	306.47	1.13	<LOD	<LOD	0.31	0.14	72.32	0.01	<LOD	<LOD	0.97
Downtown	<LOD	3.55	0.09	0.22	0.22	<LOD	0.26	0.61	0.07	1.20	0.76	21.49	0.72	0.36	272.60	1.12	<LOD	<LOD	0.39	0.14	74.66	0.01	<LOD	<LOD	1.00
Chabon Ferry	<LOD	4.79	0.24	0.22	<LOD	<LOD	0.64	3.26	0.05	1.29	0.66	69.90	0.90	0.40	261.66	1.00	<LOD	<LOD	0.74	0.12	60.51	<LOD	<LOD	0.97	
Highway3	<LOD	2.25	0.14	0.26	<LOD	<LOD	0.21	0.85	0.05	1.14	1.59	40.93	0.79	0.40	261.66	1.00	<LOD	<LOD	0.76	0.12	72.12	0.01	<LOD	<LOD	0.96
Samtlouis	<LOD	1.92	0.10	0.40	0.04	<LOD	0.04	0.97	0.06	1.17	1.74	11.74	0.79	0.39	261.88	1.06	<LOD	<LOD	0.73	0.14	73.40	0.01	<LOD	<LOD	1.03
Highway312	<LOD	2.15	0.08	0.41	<LOD	<LOD	0.06	0.31	0.06	1.20	0.80	6.43	0.69	0.37	196.05	1.16	<LOD	<LOD	0.41	0.15	46.61	0.01	<LOD	<LOD	0.84
Weldon Ferry	<LOD	2.31	0.11	0.30	<LOD	<LOD	0.25	0.78	0.04	1.13	1.53	4.32	0.76	0.43	264.74	1.02	<LOD	<LOD	0.71	0.12	75.62	0.01	<LOD	<LOD	0.92
Instrumental QA/QC - 1640 (n=4)		Be	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Ag	Cd	Sr	Sb	Sb	Ba	Tl	Pb	U
Avg %Recovery		116.60	113.09	n/c	96.97	97.14	97.90	101.18	97.67	94.43	99.30	98.34	95.80	96.72	91.13	94.04	97.19	98.06	n/c	95.67	96.34	99.05	98.62	n/c	
SD		6.77	2.76	n/c	0.32	1.18	0.79	0.61	1.14	1.23	1.65	1.03	1.15	1.56	1.71	1.51	1.38	1.61	n/c	0.84	1.47	1.40	1.79	n/c	
<b>General Information</b> All results in ppb unless specified. Samples were run using a multi-element Agilent Technologies 8800 ICP-MS Triple Quad. QA/QC Instrumental QA/QC - Measured values must be within ±20% of certified value. n/c = element not certified in certified reference material. The instrumental certified reference material is 1640a, trace elements in natural water, obtained from the National Institute of Standards and Technology. LOD=Limit of Detection of instrument      LOQ= Limit of Quantification Notes: 1. Elements of Be, Ag, Cd, Hg and Pb have extremely low contents in samples and even below detection limit. The corresponding values are for reference only.																									

**Table S11.** Trace metal concentrations of sediment samples in field season 2021.

Instrument	Be	Al	Ti	V	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Ag	Cd	Sn	Sb	Ba	Tl	Pb	U	
Instrumental LOD (ppb)	0.02	0.025	0.020	0.005	0.044	0.044	0.067	0.004	0.061	0.021	0.041	0.003	0.029	0.016	0.008	0.015	0.006	0.014	0.002	0.006	0.001	0.008	<0.001	
LOQ (ppb)	0.121	2.285	0.912	0.039	0.916	0.956	4.707	0.031	0.349	0.891	6.628	0.085	0.196	0.348	0.526	0.352	0.032	3.991	1.768	0.277	0.022	0.176	0.284	
CODE Sediment - BSG	No data	No data	No data	No data	37.3	No data	No data	No data	No data	19.7	123	5.3	No data	No data	No data	No data	0.6	No data	No data	No data	No data	35	No data	
CODE Soil - Agricultural	4	No data	No data	130	64	No data	No data	No data	No data	45	63	12	1	No data	5	2000	3.5	No data	No data	No data	20	250	1	23
CODE Soil - Residential/parkland	4	No data	No data	130	64	No data	No data	No data	No data	45	63	12	1	No data	5	2000	3.5	No data	No data	No data	20	250	1	23
CODE Soil - Commercial	8	No data	No data	130	87	No data	No data	No data	No data	89	91	12	2.9	No data	40	4000	2.2	300	40	2000	1	60	30	
CODE Soil - Industrial	8	No data	No data	130	87	No data	No data	No data	No data	89	91	12	2.9	No data	40	4000	2.2	300	40	2000	1	60	30	
Sample ID	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw	
Outlook	0.52	28334.75	1076.05	34.90	14.84	237.35	11791.16	5.80	13.54	3.31	24.55	7.19	<LOD	199.83	0.22	<LOD	0.21	<LOD	0.11	731.30	0.28	10.36	1.06	
Irrigation District	0.24	19425.85	781.11	22.04	6.99	208.07	9494.37	4.52	11.33	1.11	23.88	5.62	<LOD	148.82	0.27	<LOD	0.07	<LOD	0.12	589.46	0.21	8.42	0.63	
Irrigation Howland	0.55	36779.65	2262.17	63.95	54.65	277.73	17526.73	6.12	18.60	8.59	57.19	8.53	0.28	188.16	0.27	<LOD	0.36	<LOD	0.22	748.40	0.46	11.86	2.19	
Fried Hill	0.55	35448.51	1969.97	46.70	31.76	379.60	15376.40	6.72	18.05	3.49	45.11	6.06	<LOD	274.54	0.16	<LOD	0.19	<LOD	0.26	986.37	0.34	12.19	1.50	
Downtown	0.52	36478.59	2113.03	60.16	44.97	340.90	17427.59	8.80	18.05	9.24	50.29	6.49	<LOD	228.21	0.24	<LOD	0.38	<LOD	0.32	814.22	0.34	11.45	1.67	
Clarksboro Ferry	0.74	35448.59	2113.74	42.04	46.55	452.00	20728.59	8.50	22.69	14.58	68.25	5.71	0.25	220.82	0.27	<LOD	0.32	<LOD	0.39	814.22	0.34	11.45	2.07	
Hilltop 3	0.72	35448.59	2113.74	42.04	46.55	452.00	20728.59	8.50	22.69	14.58	68.25	5.71	0.25	220.82	0.27	<LOD	0.32	<LOD	0.39	814.22	0.34	11.45	2.07	
Hilltop 2	0.72	35448.59	2113.74	42.04	46.55	452.00	20728.59	8.50	22.69	14.58	68.25	5.71	0.25	220.82	0.27	<LOD	0.32	<LOD	0.39	814.22	0.34	11.45	2.07	
Saint Louis 1	0.71	35448.59	2113.74	42.04	46.55	452.00	20728.59	8.50	22.69	14.58	68.25	5.71	0.25	220.82	0.27	<LOD	0.32	<LOD	0.39	814.22	0.34	11.45	2.07	
Hilltop 12	0.71	35448.59	2113.74	42.04	46.55	452.00	20728.59	8.50	22.69	14.58	68.25	5.71	0.25	220.82	0.27	<LOD	0.32	<LOD	0.39	814.22	0.34	11.45	2.07	
Wilson Ferry	0.61	33691.04	1609.57	55.73	30.01	343.70	18680.39	7.79	20.46	9.30	52.25	5.12	<LOD	226.75	0.16	<LOD	0.35	<LOD	0.19	729.02	0.36	11.39	1.44	
Outlook	0.38	36249.04	1393.21	35.25	14.49	308.24	13688.42	6.36	13.18	3.07	39.37	6.86	<LOD	221.14	2.72	<LOD	0.09	<LOD	0.52	702.91	0.22	10.26	0.92	
Irrigation District	0.38	22094.84	972.53	25.32	7.32	197.83	8706.54	4.35	10.05	0.37	21.23	5.52	<LOD	172.14	0.43	<LOD	0.12	<LOD	0.12	631.09	0.16	7.80	0.62	
Irrigation Howland	0.52	34797.80	2282.90	64.88	47.23	762.84	17193.73	7.52	17.51	7.84	61.27	3.97	0.28	188.35	0.50	<LOD	0.42	<LOD	0.12	686.66	0.32	11.47	2.03	
Fried Hill	0.56	38514.86	2238.98	55.97	41.15	378.29	18190.59	7.52	11.47	8.48	45.71	8.48	<LOD	290.03	0.37	<LOD	0.43	<LOD	0.13	695.96	0.31	11.23	1.70	
Downtown	0.26	21332.05	1654.04	35.85	35.28	292.57	13477.06	4.80	11.47	1.67	29.63	5.75	<LOD	196.03	0.17	<LOD	0.28	<LOD	0.13	609.94	0.18	8.54	0.90	
Clarksboro Ferry	0.28	29120.04	1707.26	51.65	35.28	292.57	13477.06	4.80	11.47	1.67	29.63	5.75	<LOD	223.18	2.27	<LOD	0.30	<LOD	0.15	700.96	0.28	9.78	1.30	
Hilltop 3	0.39	31268.43	1659.50	41.28	41.28	393.43	16399.29	7.10	12.97	5.89	45.04	7.05	<LOD	237.46	0.05	<LOD	0.41	<LOD	0.28	777.20	0.27	10.84	1.28	
Hilltop 2	0.05	18048.87	608.55	15.75	14.23	334.28	11191.30	2.29	5.04	<LOD	26.25	2.12	<LOD	159.06	<LOD	<LOD	0.05	<LOD	0.17	371.21	0.12	5.38	1.17	
Saint Louis	0.34	25331.46	1662.56	36.15	29.77	290.05	12651.90	4.93	10.49	1.73	29.93	5.15	<LOD	228.79	0.06	<LOD	0.25	<LOD	0.17	728.09	0.18	8.32	1.20	
Hilltop 12	0.41	29200.07	1444.21	45.99	29.58	373.14	16568.44	6.26	12.62	5.25	37.89	7.74	<LOD	221.69	0.12	<LOD	0.19	<LOD	0.45	745.27	0.27	10.69	1.20	
Wilson Ferry	0.41	29200.07	1444.21	45.99	29.58	373.14	16568.44	6.26	12.62	5.25	37.89	7.74	<LOD	221.69	0.12	<LOD	0.19	<LOD	0.45	745.27	0.27	10.69	1.20	
Instrumental QA/QC - 1681 (n=3)	Be	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Ag	Cd	Sn	Sb	Ba	Tl	Pb	U	
Avg % Recovery	100.93	97.75	n/c	97.51	100.82	95.77	99.75	94.12	94.66	93.48	100.23	97.95	93.52	101.74	101.03	89.25	99.23	n/c	102.79	98.37	89.70	91.66	n/c	
SD	5.10	2.98	n/c	0.95	0.58	1.22	0.95	0.79	1.33	0.97	1.60	2.08	3.20	3.33	1.26	0.90	2.71	n/c	2.77	3.75	4.14	4.51	n/c	
Method QA/QC - MESS 3 (n=3)	77.81	74.48	79.47	95.35	98.24	92.99	103.93	94.14	100.87	101.37	97.20	99.83	105.30	99.69	91.62	N/A	113.59	N/A	102.77	105.04	93.66	108.00	84.72	
Avg % Recovery	4.48	7.83	3.19	4.04	3.83	5.92	6.01	3.73	3.94	6.67	5.23	6.62	19.66	9.08	2.13	N/A	8.38	N/A	6.29	4.28	4.32	3.43	1.85	
General Information																								
All results in mg/kg unless specified.																								
Samples were run using a multi-element Agilent Technologies 8800-CP-MS Triple Quad.																								
QA/QC																								
Instrumental QA/QC - Measured values must be within ± 20% of certified value.																								
The instrument certified reference material is 1640a - trace elements in natural water, obtained from the National Institute of Standards and Technology.																								
n/c = element not certified in certified reference material.																								
LOD=Limit of Detection of Instrument																								
LOQ=Limit of Quantification																								
Notes:																								
1. Values of Sn and Sb element in samples are somewhat questionable due to high background of the method blanks.																								
Please interpret carefully.																								
2. Elements of Sn, Cd, Ag and Hg with recovery percentage in MESS 3 are out of the allowed range (70-130). Please interpret with caution.																								

**Table S12.** Mercury concentrations of sediment samples in field seasons 2020 and 2021.

<b>2021</b>		<b>2020</b>	
<b>Samples</b>	<b>Concentration (ng/g)</b>	<b>Samples</b>	<b>Concentration (ng/g)</b>
Outlook_Jun9_2021	10.94	Outlook_Jun9_2020	8.73
OID_Jun9_2021	35.69	OID_Jun16_2020	36.45
OID(FB)_Jun9_2021	0.31	OID(FB)_Jun16_2020	4.53
FH_Jun9_2021	20.25	FH_Jun2_2020	23.94
DT_Jun14_2021	23.03	DT_Jun2_2020	24.63
CF_Jun14_2021	34.61	CF_Jun2_2020	35.25
Hwy312_Jun14_2021	17.73	Hwy312_Jun3_2020	16.35
SL_Jun14_2021	16.00	SL_Jun3_2020	16.04
Hwy3_Jun15_2021	31.49	Hwy3_Jun18_2020	295.14
WF_Jun15_2021	24.99	WF_Jun18_2020	26.86
Outlook_Aug4_2021	0.85	Outlook_Aug10_2020	2.91
OID_Aug4_2021	6.34	OID_Aug10_2020	5.82
OID(FB)_Aug4_2021	28.41	OID(FB)_Aug10_2020	35.22
FH_Aug4_2021	16.54	FH_Aug10_2020	15.64
DT_Aug5_2021	2.77	DT_Aug19_2020	7.61
CF_Aug5_2021	18.75	CF_Aug17_2020	21.77
Hwy312_Aug5_2021	9.06	Hwy312_Aug20_2020	11.80
SL_Aug5_2021	17.53	SL_Aug19_2020	13.00
Hwy3_Aug6_2021	12.76	Hwy3_Aug20_2020	16.65
WF_Aug6_2021	19.59	WF_Aug20_2020	18.15
		Outlook_Oct6_2020	3.51
		OID_Oct6_2020	3.46
		OID(FB)_Oct6_2020	28.64
		FH_Oct6_2020	2.23
		DT_Oct7_2020	41.47
		CF_Oct7_2020	10.16
		Hwy312_Oct7_2020	4.27
		SL_Oct7_2020	7.80
		Hwy3_Oct8_2020	11.20
		WF_Oct8_2020	13.33





**Table S14.** BSAF calculated by mercury concentrations in fish and sediment.

<b>Sampling Sites</b>	<b>Hg Conc in Sediment (ng/g)</b>	<b>Hg Conc in Fish (ng/g)</b>	<b>BSAF</b>
OID_Jun16_2020	36.45	61.69	<b>1.692548</b>
DT_Jun2_2020	24.63	163.89	<b>6.653424</b>
CF_Jun2_2020	35.25	135.97	<b>3.856838</b>
SL_Jun3_2020	16.04	232.98	<b>14.52858</b>
OID_Aug10_2020	5.82	205.10	<b>35.24557</b>
DT_Aug19_2020	7.61	125.81	<b>16.52312</b>
SL_Aug19_2020	13.00	154.64	<b>11.89365</b>
Hwy3_Aug20_2020	16.65	152.78	<b>9.175622</b>
OID_Oct6_2020	3.46	203.28	<b>58.71965</b>
DT_Oct7_2020	41.47	132.35	<b>3.191321</b>
SL_Oct7_2020	7.80	160.73	<b>20.60632</b>
OID_Jun16_2021	0.31	125.66	<b>411.4831</b>
DT_Jun2_2021	23.03	167.88	<b>7.28819</b>
CF_Jun2_2021	34.61	216.90	<b>6.267262</b>
SL_Jun3_2021	16.00	192.40	<b>12.02828</b>
Hwy3_Jun18_2021	31.49	177.80	<b>5.647011</b>
WF_Jun18_2021	24.99	201.14	<b>8.047306</b>
OID_Aug10_2021	6.34	118.84	<b>18.74884</b>
FH_Aug10_2021	16.54	165.65	<b>10.01585</b>
DT_Aug19_2021	2.77	197.57	<b>71.25619</b>
Hwy312_Aug20_2021	9.06	205.81	<b>22.721</b>
WF_Aug20_2021	19.59	393.52	<b>20.08381</b>

**Table S15.** BSAF calculated by herbicide concentrations in sediment and fish.

Sampling Sites	2,4-D Conc in Sediment (ng/g)	2,4-D Conc in Fish (ng/g)	BSAF	Dicamba conc in sediment	Dicamba conc in fish	BSAF		
Outlook	0			0.760361549		0	June	2020
Irrigation District	56.61272824	9.225547412	0.162959	0.993537067	0	0		
Irrigation Flowback	19.95874016		0	4.713021249		0		
Fred Heal	0			0.730655746		0		
Downtown	0	0		8.282972905	4.073711053	0.491818		
Clarkboro Ferry	22.37963104	6.605875107	0.295174	47.66067466	19.73487886	0.41407		
Highway312	0			5.443711702		0		
Saint Louis								
Highway3	0			0				
Weldon Ferry	0			2.928838371		0		
Outlook	0			2.701607651		0	August	2020
Irrigation District	0	0		0.43667644	0	0		
Irrigation Flowback								
Fred Heal	10.64663773		0	0.979722422		0		
Downtown	0	0		1.190173425	0	0		
Clarkboro Ferry	29.38072828		0	0				
Highway312	0			5.393037376		0		
Saint Louis	0	0		1.100580481	0	0		
Highway3	0	0		0.904693628	0	0		
Weldon Ferry	6.620699214		0	0.444087561		0		
Outlook	0			7.880369108		0	October	2020
Irrigation District	0	0		1.872861981	0.17388735	0.092846		
Irrigation Flowback	7.459025953		0	5.317337035		0		
Fred Heal	0			92.22758412		0		
Downtown	0	0		3.217047316	1.163092234	0.36154		
Clarkboro Ferry	0			0				
Highway312								
Saint Louis	3.737744555	0	0	3.032619979	1.293700821	0.426595		
Highway3	16.41772544		0	0				
Weldon Ferry	0.95927		0	1.417298979		0		
Outlook	0	0		0	0		June	2021
Irrigation District	0	0		0.431747977	0	0		
Irrigation Flowback	0	0		0.389511339	0	0		
Fred Heal	0	0		7.401287018	4.91157953	0.663612		
Downtown	0	0		2.74364088	1.171507628	0.42699		
Clarkboro Ferry	8.140917765	2.735726491	0.336046	4.50912591	2.691488575	0.596898		
Highway312	7.313736267	0.937740222	0.128216	2.493984204	0.49393278	0.19805		
Saint Louis	0	0		46.22162244	39.24897407	0.849147		
Highway3	0	0		0	0	0		
Weldon Ferry	10.03516056	4.631068159	0.461484	0.560963991	0	0		
Outlook	0	0		2.841678956	1.119495281	0.393956	August	2021
Irrigation District	0	0		0.58514203	0	0		
Irrigation Flowback	0	0		4.233518229	2.283585321	0.539406		
Fred Heal	0	0		0	0	0		
Downtown	0	0		1.183338632	0	0		
Clarkboro Ferry	6.004137404	0.775350522	0.129136	4.350618025	2.874324532	0.66067		
Highway312	0	0		2.144886567	0.116156832	0.054155		
Saint Louis	0	0		0	0	0		
Highway3	0	0		0	0	0		
Weldon Ferry	0	0		0	0	0		

**Table S16.** BSAF calculated by organochlorine concentrations in sediment and fish.

Sampling Sites	Methoxychlor Conc in Sediment (ng/g)	Methoxychlor Conc in Fish (ng/g)	BSAF	Lindane conc in sediment (ng/g)	Lindane conc in fish ng/g	BSAF		
Outlook	0.503702828		0	11.60116573		0	June	2020
Irrigation District	0	0		10.94855214	4.136206751	0.377786		
Irrigation Flowback	0			19.88345863		0		
Fred Heal	0.747836791		0	13.39770634		0		
Downtown	13.07315376	5.461458129	0.417761	14.71190952	7.694240618	0.522994		
Clarkboro Ferry	6.707283299	2.414404716	0.359968	8.916663454	4.942120591	0.554257		
Highway312	3330.813631		0	15.33808804		0		
Saint Louis								
Highway3	142.7663762		0	6.910962289		0		
Weldon Ferry	25.20465535		0	11.05074765		0		
Outlook	1.87667511		0	2.083254866		0	August	2020
Irrigation District	0	0		3.368949181	0.620803536	0.184272		
Irrigation Flowback								
Fred Heal	1.211561162		0	19.05749267		0		
Downtown	1.860946742	0	0	11.43598115	8.52076111	0.745084		
Clarkboro Ferry	6.093121253		0	21.39766336		0		
Highway312	1.017989916		0	13.03232111		0		
Saint Louis	6.945253081	0.871104154	0.125424	23.73166707	9.764961046	0.411474		
Highway3	2.364672091		0	3.148023625	0.628538319	0.199661		
Weldon Ferry	2.191835383		0	14.01887309		0		
Outlook	0			11.57479945		0	October	2020
Irrigation District	0	0		3.162203959	0.635775208	0.201054		
Irrigation Flowback	0			24.57902446		0		
Fred Heal	0			11.36614434		0		
Downtown	104.5947478	51.66275313	0.493933	21.64886542	9.956238894	0.459897		
Clarkboro Ferry	9.687350176		0	19.80290156		0		
Highway312								
Saint Louis	0.846978556	0	0	12.25683592	6.258833542	0.51064		
Highway3	0.244253888		0	8.179120315		0		
Weldon Ferry	0			16.38919279		0		
Outlook	2.392011094		0	9.370629804	4.189153346	0.447051	June	2021
Irrigation District	0			4.696984847	1.583432183	0.337117		
Irrigation Flowback	4.833247225	0	0	0.673674353	0	0		
Fred Heal	0.408644191	0	0	5.616757816	2.991397653	0.532584		
Downtown	20.67566332	11.09827766	0.53678	9.292417127	4.923513799	0.529842		
Clarkboro Ferry	13.5333294	7.226119006	0.53395	11.46691792	7.016945728	0.61193		
Highway312	2.555291204		0	8.932588505	3.172885537	0.355203		
Saint Louis	9.523716182	4.673489808	0.490721	8.208060151	4.892800378	0.596097		
Highway3	4.061415282	0.679989716	0.167427	5.578762595	2.821929878	0.505834		
Weldon Ferry	7.485401454	1.981560776	0.264723	8.86801436	4.17500581	0.470794		
Outlook	0	0		4.225619014	1.684285099	0.398589	August	2021
Irrigation District	0	0		0	0			
Irrigation Flowback	0	0		8.372657176	5.554163806	0.663369		
Fred Heal	3.837039511	0.124671841	0.032492	11.3202875	6.302868602	0.556776		
Downtown	1.930550561	0	0	4.215691403	1.629833564	0.386611		
Clarkboro Ferry	10.60806177	3.506336906	0.330535	8.547155645	3.654106989	0.427523		
Highway312	7.103820543	3.113155871	0.438237	5.405203751	3.033504007	0.561219		
Saint Louis	4.005291178	0	0	7.811004399	2.788123848	0.356948		
Highway3	0	0		5.566706111	1.971922343	0.354235		
Weldon Ferry	2.501799276	0	0	7.557033434	4.171865603	0.552051		