Irrigation District Water Quality Project

Long-term patterns of pesticides in irrigation water of southern Alberta

VOLUME 4

Alberta

Irrigation District Water Quality Report Series

Volume 1: Salinity, major ions and physical characteristics in irrigation water of southern Alberta

Volume 2: Nutrients in irrigation water of southern Alberta

Volume 3: Metals in irrigation water of southern Alberta

Volume 4: Long-term patterns of pesticides in irrigation water of southern Alberta

Volume 5: Microbiological analysis of irrigation water of southern Alberta

Volume 6: Veterinary pharmaceutical analysis of irrigation water of southern Alberta

Volume 7: Water quality indices of irrigation water of southern Alberta

Volume 8: Water quality trends in irrigation water of southern Alberta

Volume 9: Effects of irrigation returns on river water quality of southern Alberta

Volume 10: Effects of land use on irrigation water quality of southern Alberta

Volume 4: Long-term Patterns of Pesticides in Irrigation Water of Southern Alberta

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In Memoriam

Dr. Claudia Sheedy was a Research Scientist for Agriculture and Agri-Food Canada (AAFC). Her main scientific interests were water quality and trace residue analysis of agricultural contaminants including pesticides, veterinary antibiotics and hormones. She worked tirelessly to understand the fate of pesticides, develop mitigation strategies and promote sustainable agriculture. She and her lab at the AAFC Research and Development Centre in Lethbridge were strong partners of the Irrigation District Water Quality project from the very beginning. Her enthusiasm and passion for putting science into action to inform and empower the agriculture and irrigation industry is reflected strongly in this report and will be deeply missed.

1974 to 2020

Photo credit: Andy Hurley

Executive Summary

More than 65% of Canada's irrigation occurs in southern Alberta's 13 irrigation districts. The associated irrigation conveyance network supplies water for crops and livestock production, as well as for rural communities and many rural homes. Irrigation water provides wildlife habitat and recreational activities such as fishing, boating, and camping on irrigation reservoirs. Good quality irrigation water is important for all these uses. The quality of irrigation water in Alberta has been previously monitored by several researchers, but differences in study design and objectives made the data difficult to compare. A 10-year study (2006 to 2007 and 2011 to 2018) was conducted by Alberta Agriculture and Forestry, Agriculture and Agri-Food Canada, and Alberta Irrigation Projects Association (now Alberta Irrigation Districts Association) to assess the quality of irrigation water within Alberta's irrigation districts using a long-term, consistent approach. This report is one of a series of reports based on data collected from the 10-year Irrigation District Water Quality project. The focus of this report is to examine the long-term patterns of pesticide presence in irrigation water of southern Alberta.

Inflow to Fincastle Reservoir in the Taber Irrigation District

Global agriculture is largely dependent on pesticides to manage pests that may threaten food production (i.e., fungi, weeds, insects). Currently, there are many pesticide products registered for use in Canada, with the largest user being the agricultural sector. While pesticides are important tools for pest management, the persistence of pesticides in soils, sediment, and water can have unintended environmental impacts, such as negative effects on aquatic food webs and damage to sensitive non-target crops. In addition, pesticide residue on food products can occur when irrigation water contains pesticides, which can have implications for food safety. Natural variation among different ecoregions leads to complex patterns in the movement of pesticides in the environment. Understanding the fate of pesticides in the environment is important for identifying agricultural and environmental risks, while providing insight for implementing beneficial management practices to ensure protection of water resources and irrigated crops.

Irrigation water was sampled in 12 irrigation districts from 2006 to 2018 and analyzed for a suite of pesticides as part of the Irrigation District Water Quality project. Overall, there were 54 different pesticides detected: 29 herbicides, three herbicide metabolites, 12 fungicides, and 10 insecticides. Herbicides were the most frequently detected pesticides and at the highest concentrations, which is not unexpected because herbicides have the greatest quantity of sales in Alberta. Most water samples (83%) contained at least one pesticide, with up to 13 pesticides being detected in a single sample. Pesticide concentrations were generally lower than guideline values for irrigation and livestock watering uses and the protection of aquatic life (PAL). Dicamba and 2-methyl-4-chloropheoxyacetic acid (MCPA) most frequently exceeded guideline values for irrigation water (17% and 23% of samples, respectively), but rarely exceeded livestock watering and PAL guidelines (<0.33%). All other pesticides rarely exceeded guideline values (<0.33%) and the exceedances were not consistent in time or space.

Irrigation of a mint crop in the St. Mary River Irrigation District

The prevalence of pesticides appeared to be associated with spatial factors, such as predominant land uses and proximity to source waters. Samples with greater number of pesticides were usually collected from irrigation districts with greater area under cultivation, and in particular, specialty crops. Districts in proximity to large urban centers had greater pesticide detections. Irrigation districts closest to the Rocky Mountains, which are the source of southern Alberta's irrigation water, generally had fewer pesticide detections.

Variable pesticide detection frequencies were observed at individual sampling sites, with patterns sometimes associated with irrigation districts and site types. No consistent year-to-year detection frequencies were observed, but the detection frequencies of several pesticides were higher in 2016, which was a wet year, compared to the drier years of 2015, 2017, and 2018. This indicates that precipitation somewhat influences pesticides movement into irrigation water. This pattern, however, is not consistent for all pesticides, indicating that there are other driving forces behind pesticide movement into irrigation water. Annually fluctuating pesticide concentrations and detection frequencies may be due to: climate, field management (including canal management), crop cover, pesticide applications, irrigation use, and irrigation conveyance networks.

Pesticides do not currently pose a concern to irrigation water quality in southern Alberta, but it is important to continue to monitor pesticides and the mechanisms of pesticide movement into irrigation water. This will ensure proper management and protection of water resources.

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1 Introduction

1.1 Project Background

More than 65% of Canada's irrigation occurs in Alberta's 13 irrigation districts. These districts encompass approximately 8,000 km of district- and government-owned irrigation infrastructure and more than 55 reservoirs that together serve 555,705 ha of irrigated agricultural land (AAF 2019). Irrigation is essential for high agricultural production and crop diversity in southern Alberta. The irrigation conveyance network supplies water to many rural homes and more than 30 communities for household potable water, municipal purposes, parks, and industrial use including food processing plants and factories. The conveyance network also supplies water for other important uses such as livestock production, wildlife habitat, and recreational activities such as fishing, boating, and camping on irrigation reservoirs. Good quality irrigation water is needed for all these uses. High yielding and safe food production requires low concentrations of salts, pesticides and pathogens in irrigation water. Low nutrient concentrations in water help prevent the growth of aquatic weeds and algae that would otherwise impede water conveyance. Good quality water is also important to minimize treatment costs for rural communities.

United Irrigation District Main Canal downstream of the Belly River diversion

The quality of irrigation water in Alberta has been previously monitored by researchers including Bolseng (1991), Cross (1997), Greenlee et al. (2000), Saffran (2005), Little et al. (2010), and Palliser Environmental Services Ltd. (2011). The extent of monitoring varied greatly among these studies, ranging from a one-time sampling of return sites in select irrigation districts (Bolseng 1991) to a comprehensive study throughout the irrigation districts (Little et al. 2010). Palliser Environmental Services Ltd. (2011) focused on only one irrigation district, whereas irrigation water quality reported by Saffran (2005) was part of a larger study on surface water quality within the Oldman River watershed. Cross (1997) carried out a review of irrigation district water quality based on several data sources from 1977 to 1996. Study designs, parameters, and methodology used among these studies varied, making the data difficult to compare.

A 10-year study (2006 to 2007 and 2011 to 2018) was conducted by Alberta Agriculture and Forestry, Agriculture and Agri-Food Canada, and Alberta Irrigation Projects Association (now Alberta Irrigation Districts Association) to assess the quality of irrigation water within Alberta's irrigation districts using a long-term, consistent approach. Although minor adjustments and additions were made during the study to accommodate secondary objectives and auxiliary projects, core sites and parameters remained unchanged. This project was supported by the Canada-Alberta Water Supply Expansion Program, the Irrigation Rehabilitation Program (special funding), and by Alberta's irrigation districts. This report is one of a series of reports based on the data collected from the 10-year Irrigation District Water Quality project. The focus of this report is to examine the long-term patterns of pesticide presence in irrigation water of southern Alberta.

Irrigation District Water Quality Project Objectives:

- Assess quality of irrigation water used for irrigation and livestock watering
- Assess quality of irrigation water for the protection of aquatic life
- Assess changes in water quality as water travels through the irrigation infrastructure
- Assess water quality among irrigation districts
- Assess cumulative effect of irrigation returns on river water quality
- Assess effect of land use on irrigation water quality

1.2 Pesticides in Irrigation Water

Global agriculture is largely dependent on pesticides to manage pests (i.e., fungi, weeds, insects) that may threaten food production (Aktar et al. 2009; Carvalho 2017; Pimentel 2009; Zhang 2018). Currently, there are 7753 pesticide products registered for use in Canada (Health Canada 2019), with the largest user being the agricultural sector. As of 2017, 93% of all farms reporting field crop production in Canada used herbicides, while 38% used fungicides, and 26% used insecticides (Statistics Canada 2020). While pesticides are important tools for pest management, the persistence of pesticides in soils, sediment, and water can have unintended environmental consequences (Morillo and Villaverde 2017), such as negative effects on aquatic ecology (Beketov et al. 2013; Muturi et al. 2017; Szöcs et al. 2017) and damage to sensitive non-target crops (Hill et al. 2002; Willett et al. 2019). In addition, pesticide residue on food products can occur when irrigation water contains pesticides, and this can have implications for food safety (Calderón-Preciado et al. 2011; Fantke et al. 2011). Natural variation among different ecoregions and climates leads to complex patterns in movement of pesticides in the environment

(Larson et al. 1997; Malaj et al. 2019). Understanding the fate of pesticides in the environment is important for identifying agricultural and environmental risks, while providing insight for implementing beneficial management practices to ensure protection of water resources (Stehle and Schulz 2015).

In southern Alberta, 97% of the irrigated land is contained within the South Saskatchewan River Basin (Bennett and Harms 2011). Maintaining good water quality in the region is critical for safe food production, healthy aquatic ecosystems, and sustainable rural development (Charest et al. 2015). In 2013, 15.2 million kg of pesticides were sold or shipped to Alberta, with 95% of these sales coming from the agricultural sector (Alberta Environment and Parks 2015). Little et al. (2010) comprehensively explored water quality and pesticides in Alberta's irrigation districts, and noted differences in pesticide detections across irrigation districts and types of features (primary, secondary, and return sites), with greater detection frequencies observed at return sites (unused irrigation water returning to the rivers), followed by secondary (mid-district), and then primary sites (source water entering districts). Herbicides were the most frequently detected pesticides in southern Alberta's irrigation waters, reflecting their prominent use. In 2006 and 2007, 2,4-Dichlorophenoxyacetic acid (2,4-D) was the most frequently detected herbicide in irrigation water; however, 2,4-D rarely exceeded water quality guidelines, while 3,6-dichloro-2-methoxybenzoic acid (dicamba) and 2-methyl-4-chlorophenoxyacetic acid (MCPA) were detected at lower frequencies, but often exceeded water quality guidelines for irrigation use (Little et al. 2010). The variable patterns of pesticide detections observed in Alberta's irrigation districts in 2006 and 2007 fueled the need to further investigate pesticide dynamics.

Speciality crops such as potatoes, often require the use of pesticides to maximize yields

2 Methods

2.1 Site Selection

Water sampling sites were defined as primary, secondary, and return site types. Primary sites were where source water entered an irrigation district, such as from a reservoir, a river diversion, or a main canal (Figure 2.1). Secondary sites were on lateral canals that branch off a main canal, or are immediately downstream of a mid-district reservoir. Return sites were located at the ends of the irrigation district conveyance network where unused irrigation water is returned to the rivers. Return sites are divided into watershed returns where water returns to rivers via coulees or natural drains, and infrastructure returns where water returns through constructed irrigation canals (Table 2.1). Additionally, three sites owned and operated by Alberta Environment and Parks (AEP) were included in pesticide analyses. These sites represent water diverted from rivers as it is conveyed towards irrigation districts: one on a canal that diverts water off the Bow River in the southeast part of the City of Calgary (AEP-P2); one on a canal that diverts water off the Bow River at Carseland,(AEP-P3); and one on a canal that diverts water from the Belly River to St. Mary Reservoir (AEP-S2).

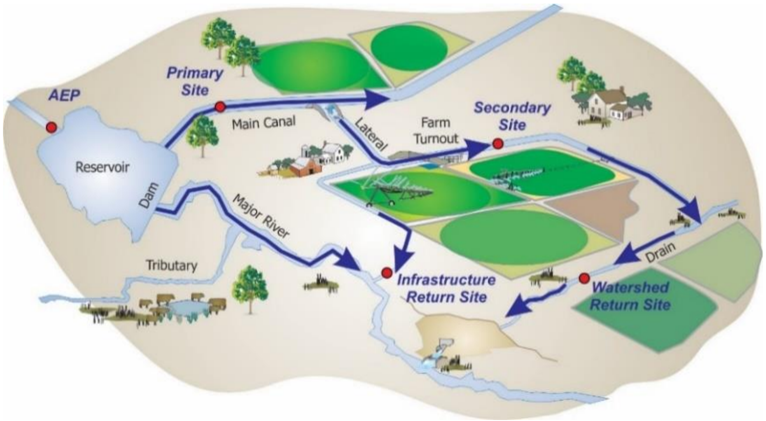

Figure 2.1 Schematic diagram of southern Alberta's irrigation conveyance network with Irrigation District Water Quality project site types.

The irrigation districts sampled were Mountain View (MVID), Aetna (AID), United (UID), Magrath (MID), Raymond (RID), Lethbridge Northern (LNID), Taber (TID), St. Mary River (SMRID), Ross Creek (RCID), Western (WID), Bow River (BRID), and Eastern (EID) (Figure 2.2). There were no sampling sites in the Leavitt Irrigation District (LID) as it is a small district and water quality upstream and downstream of the LID was captured by other sites. Sites were sampled for a suite of pesticides (Table A.1), four times per year during the growing season at approximately monthly intervals. For this report, sites that had fewer than seven years of monitoring during the 10-year period were not included in the analysis. This reduced the dataset from 105 to 80 sites; in 11 districts (Table 2.1), and reduced the number of samples from 3338 to 3000. A sub-set of sites were sampled at a reduced frequency (twice annually) from 2012 through 2016 for aminomethylphosphonic acid (AMPA), glufosinate, and glyphosate. This sub-set of sites included all return sites and a few primary and secondary sites (Table B.1).

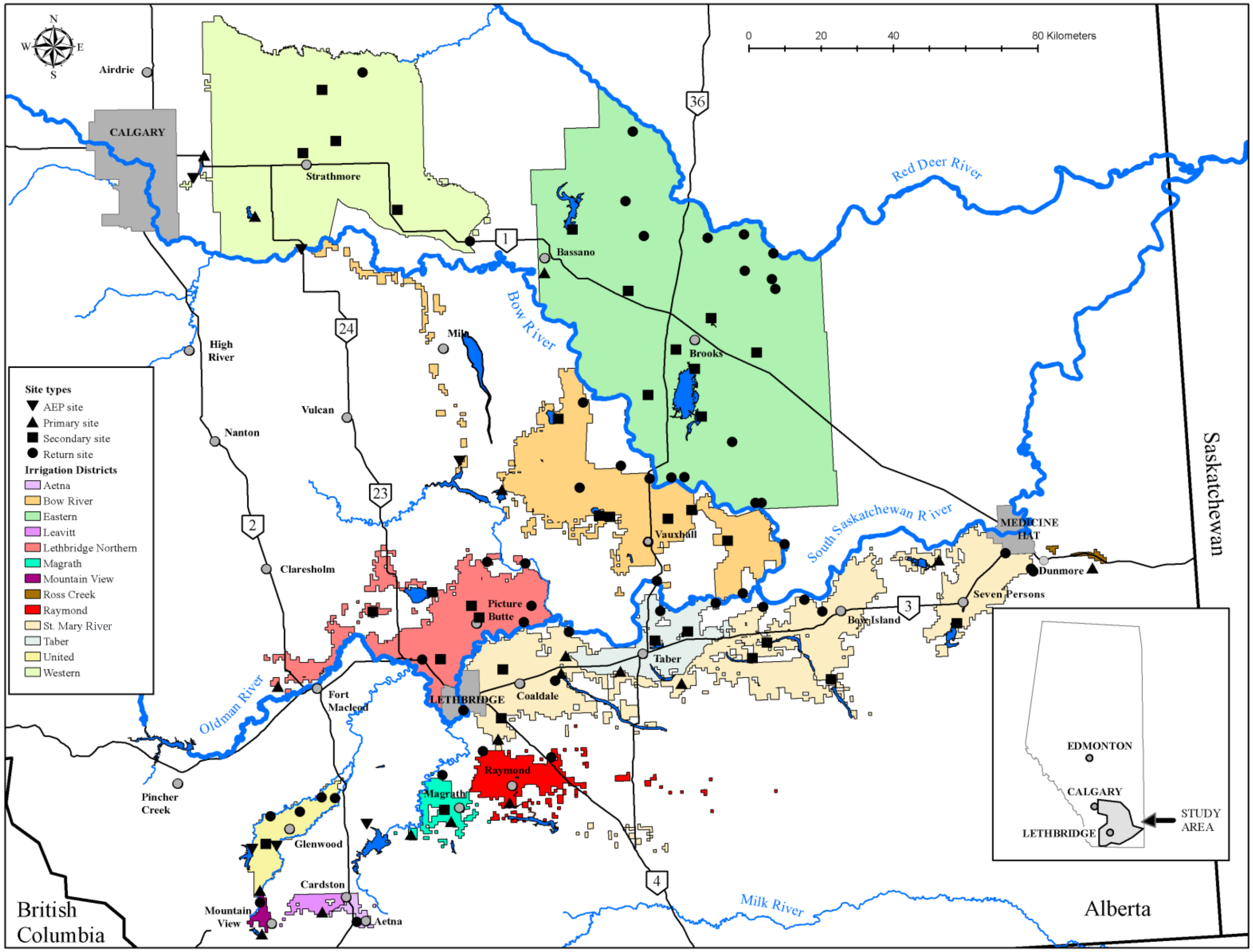

Figure 2.2 Irrigation District Water Quality project sampling site locations within Alberta's irrigation districts.

Table 2.1 Sites from which data were used in pesticide analyses.

District	Type	Site
MVID	Primary	MV-P1
	Return	MV-R1[z]
AID	Return	A-R1[y]
UID	Primary	U-P1
	Secondary	U-S1
	Return	U-R2[z]
MID	Primary	M-P1
	Secondary	M-S1
	Return	M-R1[y]
RID	Primary	R-P1
	Return	R-R1[y]
		R-R2[y]
LNID	Primary	LN-P1
	Secondary	LN-S1
		LN-S2
		LN-S3
		LN-S4
		LN-S5
	Return	LN-R1[y]
		LN-R2[y]
		LN-R3[z]
		LN-R4[z]
TID	Primary	T-P1a
		T-P2
	Secondary	T-S2
		T-S3
	Return	T-R1[z]
		T-R2[z]
SMRID	Primary	SMW-P1
	Secondary	SMW-S2
	Return	SMW-R1[y]
		SMW-R2[z]
	Primary	SMC-P1
	Secondary	SMC-S1
		SMC-S2
		SMC-S3
	Return	SMC-R1[z]
		SMC-R3[z]
		SMC-R4[z]
	Primary	SME-P1
	Secondary	SME-S1
	Return	SME-R1a[z]
		SME-R2[y]
WID	Primary	W-P1
		W-P2
	Secondary	W-S1
		W-S2
		W-S3
		W-S4
	Return	W-R1a[z]
		W-R2[y]
BRID	Primary	BR-P1
	Secondary	BR-S1
		BR-S2
		BR-S3
		BR-S4a
		BR-S5
	Return	BR-R1[z]
		BR-R2[y]
		BR-R3[y]
		BR-R4[y]
		BR-R5[z]
EID	Primary	E-P1
	Secondary	E-S1
		E-S2
		E-S3
		E-S4
		E-S5
		E-S6
		E-S8
	Return	E-R1[z]
		E-R2[z]
		E-R2a[y]
		E-R3[z]
		E-R4a[z]
		E-R5[z]
		E-R8a[y]
AEP canal		AEP-P2
		AEP-P3
		AEP-S2

[z] Infrastructure return
[y] Watershed return

2.2 Site Nomenclature

Sampling sites were identified using a prefix according to their location, either in an irrigation district (abbreviated to the first one or two letters of the district acronym), or outside of the districts (AEP = Alberta Environment and Parks canal). The St. Mary River Irrigation District was further divided into three areas as distinguished by a third letter in the prefix (W = western, C = central, and E = eastern). The site type and numeric identifier were included in the suffix of the hyphenated name. The site type (P = primary, S = secondary, R = return) preceded a numeral used to differentiate sites of the same type, within the same district. Numeric identifiers do not necessarily represent the sequence of sites moving downstream. Finally, the letter ‘a’ was appended to the end of some site names to indicate the replacement of a former site with a similar, but relocated site. Signs were located at each site to identify the site name and sampling location (Figure 2.3).

Figure 2.3 Sign post at SMW-R2.

2.3 Sampling Deployment and Intervals

Sites were grouped into sampling areas, with entire irrigation districts (except SMRID) being sampled on the same day. A single field team was responsible for collecting samples from each sampling area. Larger districts, such as BRID, LNID, EID, and WID, included two or three areas sampled on the same day. Smaller districts, such as AID, MVID, and UID were grouped in one area and sampled on the same day. This was also done for RID and MID. The three areas in the SMRID were sampled during three consecutive days.

Sampling was conducted from late May to the beginning of September, with two to five weeks separating four sampling events. Collection times were optimized to occur during active irrigation demand. The start of the season or individual sample collections were occasionally postponed as a result of reduced irrigation demand, usually due to rainfall. Three to four days were required to sample all sites during each sampling event.

2.4 Sample Collection

Grab samples were collected using a 1-L polyethylene bottle, attached to a telescopic pole with an extension range of four meters. The bottle was filled by pointing the mouth upstream, as close to the middle of the channel as possible, and mid-depth to avoid sampling the water surface or disturbing the bottom sediment (Figure 2.4a). The bottle was triple rinsed with sample water, and the rinse water emptied downstream of the sample site. A new sampling bottle was used at each site.

At each site, the sampling bottle was used to fill a 1-L glass bottle for the pesticide analytical suite, with a 125-ml polyethylene bottle filled at a sub-set of sites for AMPA, glufosinate, and glyphosate analyses (Figure 2.4b). Latex gloves and appropriate safety equipment were used when collecting the sample and filling the bottles. Samples were placed in coolers with ice while in the field. Pesticide suite bottles were delivered to Agriculture and Agri-Food Canada (AAFC) in Lethbridge, Alberta, where they were stored at 4°C, extracted within seven days of sampling and analyzed within 14 days of extraction. Samples collected for AMPA, glufosinate and glyphosate analysis were shipped on ice to Alberta Innovates-Technology Futures (AITF) in Vegreville, Alberta where they were stored at 4°C, extracted within 10 days of sampling and analyzed within 60 days of extraction.

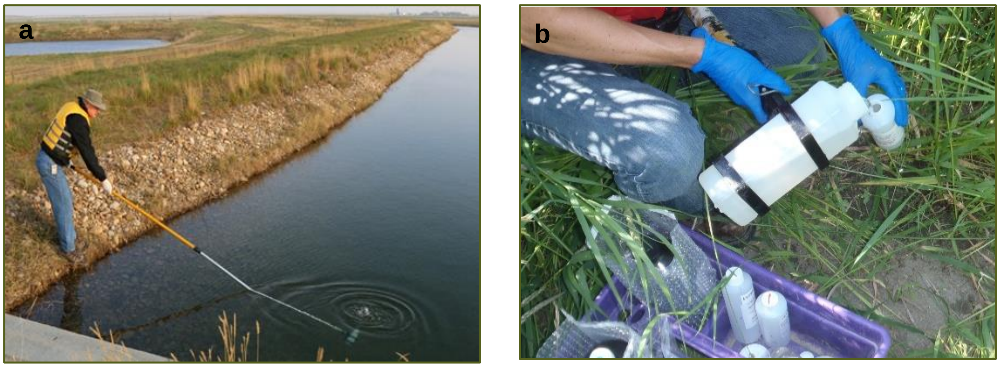

Figure 2.4 Water sampling an irrigation canal a) with a telescopic pole and b) by filling a laboratory bottle from sampling bottle.

2.5 Laboratory Methods

Pesticide residue analysis was conducted at AAFC in Lethbridge, AB. Water samples (1 L) were analyzed by gas chromatography-mass spectroscopy (GC-MS), using modified methods from Bruns et al. (1991) and Hill et al. (2002). Water samples were filtered through glass wool, acidified with concentrated sulphuric acid to pH 2, and extracted by liquid-liquid partitioning with dichloromethane. Extracts were then dried with acidified Na_2SO_4, concentrated under nitrogen gas, methylated using diazomethane, transferred to hexane, and adjusted to a final volume of 10 mL. Esterified extracts (2 µL injections) were analyzed in 2006 and 2007 using a Hewlett Packard 6890 Series GC with a HP 5973 mass selective detector in selected ion monitoring mode. While for the other years (2011–2018) esterified extracts (2 µL injections) were analyzed using an Agilent 7890B GC with a 7000C QQQ mass selective detector in multiple reaction monitoring mode. The column used was HP-5MS UI 30 m×0.25 mm×0.25 um, p/n 19091S-433UI. Temperature programing was 70°C for 2 min, ramp at 25°C/min to 150°C, ramp at 3°C/min to 200°C, and to 8°C/min to 280°C for 7 min, for a total analysis time of 38.87 min. One target ion and at least two qualifier ions were monitored. The limit of detection was 0.025 µg/L for most pesticides (refer to Table A.1 for specific detection limits). Detections below these limits were outside the range of the external standard curve and were assigned values of zero (none detected). Method blanks were run with each set of water samples analyzed.

Samples were collected from 2012 to 2016 and analyzed for AMPA, glufosinate, and glyphosate by AITF in Vegreville, AB. Water samples were collected in 125-mL plastic bottles for this analysis. Samples were derivatized with trifluoroacetic anhydride (TFA) and heptafluorobutanol (HFB) according to methods from Tsunoda (1993) and Alferness and Iwata (1994). The TFA reacts with the amine functional groups to form the corresponding trifluoroaectyl derivatives, while HFB reacts with the phosphoric and acetic acid functional groups to form the corresponding heptafluorobutal esters. Extracts were analyzed by GC-MS using a Varian Ion Trap with phenanthrene-d10 as an internal standard.

2.6 Data Acquisition

Information about the physical and chemical properties of pesticides were obtained from the Pesticide Action Network (PAN) Database (PAN 2019) and were used to investigate potential correlations with pesticide detection frequencies observed in Alberta's irrigation districts. Crop data were obtained from Alberta Agriculture and Forestry for all years of the study (Alberta Agriculture and Food 2007; Alberta Agriculture and Forestry 2015-2019; Alberta Agriculture and Rural Development 2008-2014). Crop-type definitions are in Table 2.2.

Daily precipitation data were obtained from Environment and Climate Change Canada for all sampling years (Environment and Climate Change Canada 2019) using the R package weathercan (LaZerte and Albers 2018). Data was gathered from seven stations in southern Alberta: Brooks (Station ID# 2180), Cardston (Station ID# 26971), Picture Butte West (Station ID# 2174), Raymond (Station ID# 42729), Strathmore (Station ID# 42725), Taber (Station ID# 2315), and Vauxhall (Station ID# 10889). Daily data were compiled by summing daily precipitation for the growing seasons (i.e., from May to September).

Table 2.2 Alberta Agriculture and Forestry (2019) crop type definitions.

Crop type	Specific crops
Cereals	Barley, Canada Prairie Spring (CPS) wheat, durum wheat, grain corn, hard red spring wheat, malt barley, oat, rye, soft wheat, triticale, winter wheat
Forages	Alfalfa (two & three cut, hay, and silage), barley silage, brome hay, corn silage, grass hay, green feed, milk vetch, native pasture, oat silage, sorghum/sudan grass, tame pasture, timothy hay, triticale silage
Oilseeds	Canola, flax, mustard, safflower
Specialty crops	Alfalfa seed, canary seed, canola seed, carrot, catnip, chickpea, dill, dry bean, dry pea, faba bean, fresh sweet corn, fresh pea, grass seed, hemp, lawn turf, lentil, market greens, mint, nursey, onion, potato, pumpkin, radish, seed potato, small fruit, soybean, sugar beet, sunflower, yellow pea
Other	Miscellaneous, non-crop, summer fallow, unknown

Base watershed polygon files used in GIS analysis were obtained from Alberta Environment and Parks (2018), and used to classify sites by sub-basin to compare with sales reports. Alberta Environment and Parks (2015) summary sales of pesticides data for 2013 were used as a qualitative comparison in this report.

2.7 Parameter Selection

The suite of pesticides analyzed by AAFC expanded from 29 pesticides in 2006 to 162 pesticides in 2017 and 2018. Therefore, different pesticides have differing number of years for which they were analyzed. Glufosinate, glyphosate, and AMPA were analyzed by AITF from 2012 to 2016, and less frequently (first and last samplings of each year) than the other pesticides. Pesticides that were not detected in any of the samples were not included in the analysis. Frequencies of detection are based on the periods of measurement, as different compounds were added to the analytical suite at different points in time. Additionally, sampling events were grouped into early, mid, and late season due to differences in the four sampling times per year. May 28 to June 15 represented early-season, while June 16 to August 3 and August 4 to September 4 represented mid- and late-seasons, respectively. These temporal divisions were decided upon with respect to average crop emergence times and the likely switch to foliar applications of pesticides. Further, the mid- and late-season divisions were made at August 3 to avoid separating the third sampling event in 2012 and 2013.

During the project's entire 10 years (2006–2007 and 2011–2018), 19 of the 28 continuously monitored pesticides were detected. From 2011 to 2018, 30 of the 100 continually measured pesticides were detected. Despite the increase in the number of compounds analyzed, the number of those detected only increased by 11 in 2011. During the study, compounds were added and removed. The number of added compounds with detections per year are shown in Table 2.3. Metribuzin, nicotine, oxycarboxin, and pymetrozine were only measured in 2015, and were removed afterwards given lack of analytical reliability.

Table 2.3 The number of pesticides analyzed, number of pesticides added, number of added pesticides detected, and added pesticides with detects per year.

Year added	No. of pesticides analyzed	No. of pesticides added	No. of added pesticides detected	Added pesticides with detects
2011	100	72	11	See Tables 3.3 to 3.5
2013	104	4	3	Bentazon, fluroxypyr, triclopyr
2014	106	2	1	Propiconazole
2015	146	40	16	See Tables 3.3 to 3.5
2016	161	19	2	Sulfentrazone, picoxystrobin
2017	162	1	1	MCPA-EHE

2.8 Statistical Analysis

Frequency calculations, statistical analyses, and graphs were calculated/produced using the statistical software R version 3.6.1 (R Development Core Team 2018) and the plotting package ggplot2 (Wickham et al. 2019). Visual maps were created using ArcMap 10.4.1 software. Minimum, maximum, median, and average concentrations were calculated for each pesticide. Here, three methods were used to calculate descriptive statistics: (i) averages based only on positive detections; (ii) averages of all samples where non-detects were substituted with zeroes; and (iii) averages, medians and standard deviations using Regression on Order Statistics (ROS). The ROS is a robust method that includes samples less than the detection limit by assuming a probable distribution and imputing non-detect values for summary statistic calculations (Helsel 2012). The ROS survival analysis technique was completed within the NADA package of R (Lee 2013) and only included those pesticides that had at least a 20% detection frequency as lower detection frequencies reduce the reliability of the ROS method. All three methods were completed in order to contrast the strength of the robust ROS method, which explicitly incorporates the method detect limits, to the other two methods that are commonly practiced but are known to be biased.

A cluster analysis was performed to group districts on an annual basis by predominant crop types in order to evaluate whether pesticide detection is influenced by cropping patterns. Euclidean distances on percent crop types per irrigation district and year were calculated using the vegan package of R (Oksanen et al. 2019). A hierarchical clustering of crop Euclidean distances was performed using the hclust function with the Ward's agglomeration method in R. Silhouette widths, a measure of the average distance between this object and all objects of its cluster, were calculated to determine the optimum number of cluster groups. The highest average silhouette width (i.e., the best number of clusters) was for three groups. This however, oversimplified the results and the next highest average silhouette distance was chosen: seven groups. The seven groups were then statistically tested using Kendall's coefficient of concordance and permutation tests. A global test on crop covers within each group was first conducted using a permutation test and then an *a posteriori* test to test the contribution of individual crops to the Kendall's coefficient of concordance (Legendre 2005). Global Kendall tests showed that the seven crop clusters were significant and *a posteriori* Kendall tests showed that all the irrigation districts by year in each cluster were concordant with each other (Table C.1, Table C.2).

Principal Component Analysis (PCA) was performed on detection frequency per sampling location for the six most frequently detected pesticides with at least seven years of data (2,4-D, MCPA, dicamba, fluroxypyr, mecoprop, and bentazon). Pesticide detection frequencies were centred and scaled (i.e., mean subtracted and divided by standard deviation) and a PCA was completed using the function prcomp in R. A biplot of the PCA was created to visualize the variation of the major pesticides detected across irrigation districts and type of irrigation infrastructure.

3 Results and Discussion

3.1 Pesticide Detections

Overall, in southern Alberta's irrigation districts, there were 54 different pesticides detected: 29 herbicides, three herbicide metabolites, 12 fungicides, and 10 insecticides (Tables 3.1 to 3.3). Herbicides have the greatest sales in Alberta (Alberta Environment and Parks 2015), and this is reflected in pesticide detections. Herbicides were the most frequently detected pesticides and at the highest concentrations (Table 3.1). The herbicide 2,4-D was by far the most frequently detected (78.1% of all samples collected), followed by MCPA (25.2%), dicamba (22.9%), glyphosate (17.4%), fluroxypyr (13.6%), AMPA (9.7%), mecoprop (7.4%), and bentazon (5.0%). The remaining detected pesticides were found in less than 5% of the samples analyzed during the 10-year period. These findings are consistent with previous studies in the region (Anderson 2005; Lorenz et al. 2008), where 2,4-D, MCPA, dicamba, glyphosate, bentazon, and mecoprop were detected in similar proportions of samples. However, other compounds that were more prevalent from 2011 to 2015, such as atrazine, clopyralid, and mecoprop (Charest et al. 2015), had lower detection frequencies when all years were considered.

Fungicides and insecticides were far less prevalent than herbicides in southern Alberta irrigation water (Tables 3.2 and 3.3). Boscalid was the most common fungicide observed, with detections mostly occurring in 2018 and in irrigation districts that grow specialty crops (e.g., SMRID, BRID, and TID) (Table 2.2, Table D.1,Table D.2). Alberta crop protection guidelines recommend the use of Lancer®, a product containing boscalid, on some specialty crops including: chickpea, lentil, bean, pea, and potato (Alberta Agriculture and Forestry 2020), all of which are grown in districts with boscalid detections. The only other fungicide detected in more than 1% of the samples was tebuconazole, which was detected mostly in 2015 in return sites within several irrigation districts (BRID, TID, SMRID, EID, UID). The source of tebuconazole detections are not clear; however, tebuconazole is recommended for use on cereal crops for the control of soil-borne pathogens such as *Fusarium spp*. (Alberta Agriculture and Forestry 2020). With significant amounts of cereal crops in BRID, TID, SMRID, and EID (Table 2.2, Table D.1), it is not unexpected that control products for *Furasium spp*. would be used. All insecticides occurred less than six times each, or in less than 0.4% of all samples.

Table 3.1 Summary of herbicides detected (2006–2007, 2011–2018) at sites monitored for at least seven years in southern Alberta irrigation districts.

Pesticide	Year added	Detection frequency (%)	No. of detections (No. of samples)	Detected average (µg/L)	Total average (µg/L)	Detected median (µg/L)	Detected min. (µg/L)	Detected max. (µg/L)
2,4-D	2006	78.1	2342 (3000)	0.206	0.161	0.089	0.013	37.384
MCPA	2006	25.2	755 (3000)	0.573	0.144	0.054	0.013	151.900
Dicamba	2006	22.9	686 (3000)	0.217	0.050	0.053	0.011	14.514
Glyphosate	2012[z]	17.4	77 (443)	0.427	0.074	0.270	0.047	3.900
Fluroxypyr	2013	13.6	253 (1855)	0.344	0.047	0.046	0.024	30.136
AMPA [y]	2012[z]	9.7	43 (443)	0.767	0.074	0.523	0.100	4.434
Mecoprop	2006	7.8	235 (3000)	0.094	0.007	0.057	0.011	2.331
Bentazon	2013	5.0	93 (1855)	0.199	0.010	0.058	0.025	8.179
Clopyralid	2006	3.1	93 (3000)	0.079	0.002	0.039	0.004	1.386
Hexazinone	2015	2.9	35 (1220)	0.188	0.005	0.113	0.027	0.540
EPTC	2011	2.5	61 (2464)	0.102	0.003	0.055	0.025	0.996
Simazine	2011	2.3	56 (2464)	0.242	0.006	0.104	0.039	2.363
Dichlorprop	2006	1.9	57 (3000)	0.033	0.001	0.030	0.012	0.090
Bromoxynil	2006	1.7	50 (3000)	0.149	0.002	0.046	0.012	1.444
Atrazine	2006	1.5	45 (3000)	0.077	0.001	0.043	0.024	0.528
MCPA-EHE [y]	2017	0.7	4 (602)	0.978	0.006	0.614	0.099	2.586
Triclopyr	2013	0.5	10 (1855)	0.120	0.001	0.060	0.025	0.745
Picloram	2006	0.5	15 (3000)	0.070	0.000	0.051	0.020	0.196
Sulfentrazone	2016	0.4	4 (903)	1.079	0.005	1.024	0.596	1.671
Flamprop-methyl	2011	0.2	6 (2464)	0.058	0.000	0.060	0.034	0.082
Metolachlor	2011	0.2	6 (2464)	0.055	0.000	0.034	0.031	0.161
Triallate	2006	0.2	6 (3000)	0.068	0.000	0.054	0.027	0.164
Imazamethabenz	2015	0.2	2 (1220)	0.739	0.001	0.739	0.719	0.759
2,4-DB [y]	2006	0.1	4 (3000)	0.195	0.000	0.062	0.039	0.617
Prometryn	2015	0.1	1 (1220)	0.031	0.000	0.031	0.031	0.031
Propyzamide	2011	0.1	2 (2464)	0.035	0.000	0.035	0.033	0.038
Bromacil	2006	0.1	2 (3000)	0.061	0.000	0.061	0.055	0.067
Diclofop	2006	0.1	2 (3000)	0.025	0.000	0.025	0.022	0.027
Imazethapyr	2006	0.1	2 (3000)	0.401	0.000	0.401	0.219	0.583
Desmetryn	2011	0.0	1 (2464)	0.031	0.000	0.031	0.031	0.031
Fenoxaprop	2006	0.0	1 (3000)	0.193	0.000	0.193	0.193	0.193
Trifluralin	2006	0.0	1 (3000)	0.049	0.000	0.049	0.049	0.049

[z]Glyphosate and AMPA were only analysed from 2012 to 2016.
[y]Metabolite

Table 3.2 Summary of fungicides detected (2006–2007, 2011–2018) at sites monitored for at least seven years in southern Alberta irrigation districts.

Pesticide	Year added	Detection frequency (%)	No. of detections (No. of samples)	Detected average (µg/L)	Total average (µg/L)	Detected median (µg/L)	Detected min. (µg/L)	Detected max. (µg/L)
Boscalid	2015	4.7	57 (1220)	0.059	0.003	0.042	0.025	0.319
Tebuconazole	2015	1.3	16 (1220)	0.188	0.002	0.055	0.025	1.322
Prothioconazole Desthio	2015	0.7	9 (1220)	0.060	0.000	0.033	0.025	0.198
Difenoconazole	2015	0.6	7 (1220)	0.095	0.001	0.105	0.025	0.133
Metalaxyl	2015	0.6	7 (1220)	0.075	0.000	0.038	0.025	0.185
Trifloxystrobin	2015	0.5	6 (1220)	0.136	0.001	0.063	0.025	0.434
Pyraclostrobin	2015	0.4	5 (1220)	0.050	0.000	0.046	0.031	0.156
Picoxystrobin	2016	0.3	3 (903)	0.049	0.000	0.044	0.025	0.069
Azoxystrobin	2015	0.3	4 (1220)	0.411	0.001	0.248	0.025	1.013
Iprodione	2015	0.3	4 (1220)	0.040	0.000	0.032	0.025	0.069
Propiconazole	2014	0.3	5 (1539)	0.571	0.002	0.199	0.071	1.620
Chlorothalonil	2015	0.1	1 (1220)	0.033	0.000	0.033	0.025	0.052

Table 3.3 Summary of insecticides detected (2006–2007, 2011–2018) at sites monitored for at least seven years in southern Alberta irrigation districts.

Pesticide	Year added	Detection frequency (%)	No. of detections (No. Of samples)	Detected average (µg/L)	Total average (µg/L)	Detected median (µg/L)	Detected min. (µg/L)	Detected max. (µg/L)
Azinphos-methyl	2015	0.4	5 (1220)	0.927	0.004	0.916	0.511	1.283
Bifenthrin	2011	0.2	6 (2464)	8.610	0.021	0.089	0.025	49.881
Diazinon	2011	0.2	5 (2464)	0.136	0.000	0.080	0.025	0.415
β-HCH	2011	0.1	3 (2464)	0.059	0.000	0.062	0.023	0.083
Cyhalothrin lambda	2015	0.1	1 (1220)	0.072	0.000	0.072	0.024	0.072
Deltamethrin	2015	0.1	1 (1220)	0.051	0.000	0.051	0.025	0.051
Methoxychlor	2006	0.1	2 (3000)	0.105	0.000	0.105	0.025	0.137
Chlorpyrifos-methyl	2011	0.0	1 (2464)	0.067	0.000	0.067	0.040	0.067
Ethion	2011	0.0	1 (2464)	0.065	0.000	0.065	0.040	0.065
Dieldrin	2006	0.0	1 (3000)	0.072	0.000	0.072	0.024	0.072

Most water samples contained at least one or two pesticides, with 2,4-D and MCPA being the most common. Up to 13 pesticides were detected in a single sample (Figure 3.1). Herbicides 2,4-D and MCPA are sold in southern Alberta (Alberta Environment and Parks 2015) and are used in agriculture and residential settings. Despite the great variability in the number of pesticides detected within and among irrigation districts, samples containing a greater number of pesticides were usually collected from irrigation districts with greater area under cultivation, and in particular, a greater percentage of land cover attributed to specialty crops (primarily TID, BRID, and SMRID) (Table D.1, Table D.2). The detection of four pesticides or more per sample was sporadic, occurring in roughly 10% of the samples, and was found in all irrigation districts apart from MVID and AID, which are closest to the Rocky Mountains–the source of southern Alberta's irrigation water (i.e., mountain snowpack runoff).

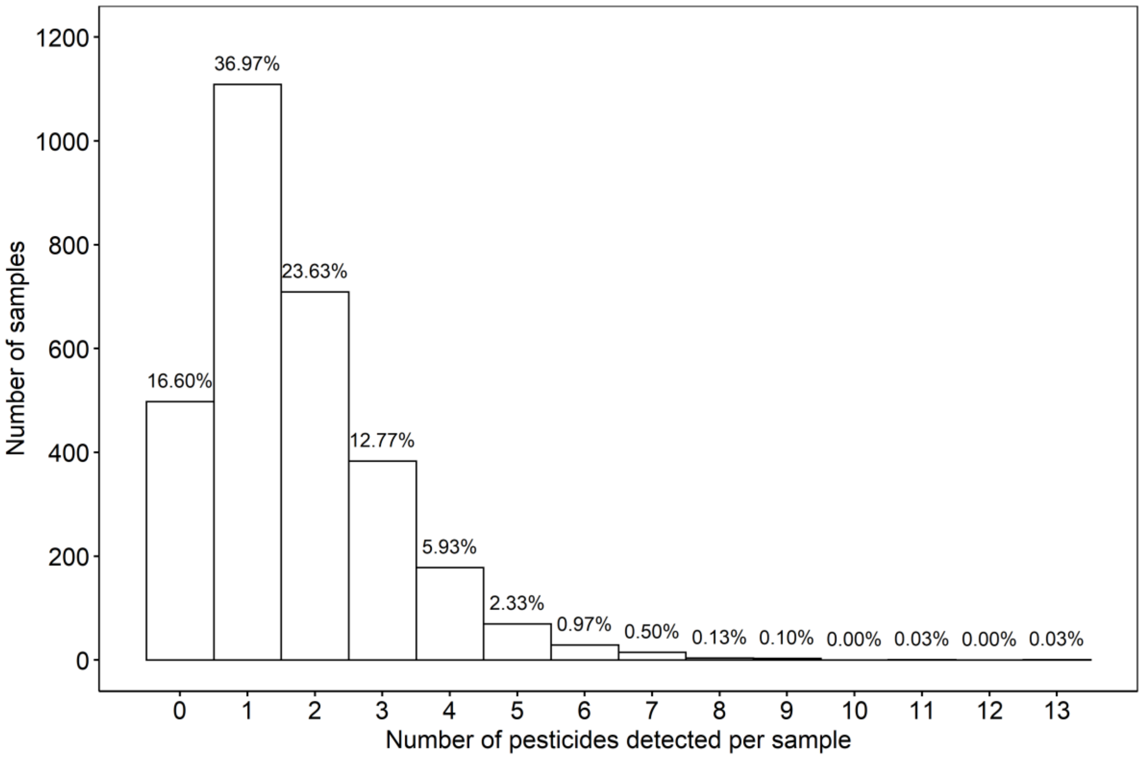

Figure 3.1 The number of pesticides detected simultaneously per individual water sample for all samples collected at sites monitored for at least seven years from 2006 and 2007 and 2011 to 2018 (3000 samples). Percentages represent the number of samples that contained a specific number of pesticides detected.

The physico-chemical properties of pesticides, including half-life of compounds in soils and water solubility, are often used for inferring pesticide fate and transport (e.g., Bannwarth et al. 2014). Figure 3.2 depicts the detection frequency for each pesticide in relation to physical and chemical properties. The soil adsorption coefficient, K_{oc}, represents the adherence of a chemical to soil corrected for the soil organic carbon content, and therefore the likelihood of binding to particulate matter rather than remaining dissolved in water. The aerobic half-life of a pesticide in soil (DT50) represents the time in days it takes for half of the pesticide to degrade in soil under aerobic conditions. DT50 can vary greatly depending on soil type, pH, and temperature (Kah et al. 2007). The pesticides with greater detection frequencies have high water solubility but span a range of half-lives (3–34 days) in soil, and have relatively low K_{oc} values (5 to 74). This suggests that pesticide detections are associated with greater solubility, while pesticide persistence in soil is less directly related to detections. Physico-chemical properties of pesticides cannot exclusively explain detections. For instance, 2,4-D, MCPA, dicamba, and hexazinone have similar water solubility values, yet very different detection frequencies (i.e., 78, 25, 23, and 3% detection frequencies for all samples, respectively). The latter is likely partially due to pesticide usage, as the 2013 pesticide sales data for Alberta show MCPA and 2,4-D in the top five active ingredients sold, while dicamba sales were less than 10% of 2,4-D by weight, and hexazinone sales were less than 5% of 2,4-D by weight (Alberta Environment and Parks 2015). Pesticides with similar physico-chemical properties were detected at different frequencies highlighting the role of other factors (e.g., usage, soil properties, crop requirements, climate, hydrological variability) on presence or absence in irrigation water.

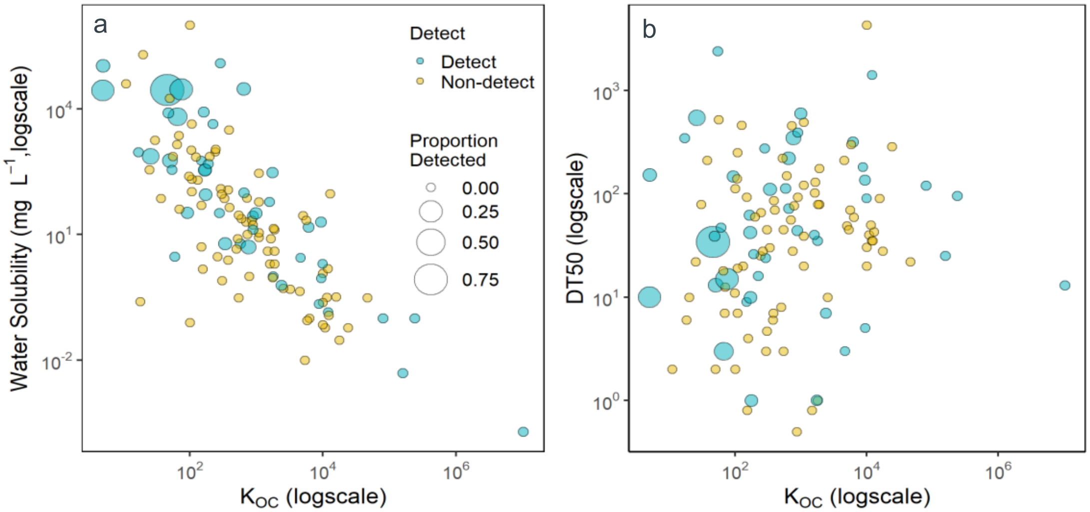

Figure 3.2 Scatterplots of each pesticide's physico-chemical properties relative to pesticide detections using properties from the PAN database (PAN 2019) a) Water solubility vs. absorption coefficient (K_{OC}) and b) Half-life in aerobic soil (DT50) vs. $K_{OC.}$ The colour of points represents the detects or non-detects and the size of points represent the proportion of detections.

The average concentrations of pesticides with at least a 20% detection frequency calculated using only positive detections, zero-substitution, and ROS methods, as described in Section 2.8, are presented in Table 3.4. Median and standard deviations calculated using the ROS methods are also shown in Table 3.4. A clear overestimation of pesticide concentrations are observed when only positive detections were averaged, whereas substituting zeroes for the samples with concentrations below the method detection limits tended to underestimate the pesticide concentrations. These results are expected given that the ROS method would include all samples in the analysis, thus not focusing on those above the detection limit, and inputs positive, non-zero concentration values for the samples below the detection limit. On average, the most frequently detected pesticides were present at low concentrations, with all calculated averages less than 0.6 µg/L. Due to the sampling protocol conducted in the irrigation districts (monthly grab samples), it is difficult to assess the maximal exposures that may have occurred (Hageman et al. 2019; Spycher et al. 2018). Bundschuh et al. (2014) found that maximum concentrations of pesticides in streams were 6- to 7-times greater for samples collected by flow-event triggered sampling compared to time-proportional sampling. It is unclear if the same processes occur in irrigation canals as increased flows in irrigation canals during precipitation events may partially be due to increased runoff; however, higher flows are also a result of a reduced amount of water being used for irrigation as systems are shut down prematurely during or in anticipation of rain. The unused irrigation water remains in the canals. Moreover, irrigation canals, unlike natural systems (rivers, streams), often have bermed banks to minimize overland flow. Concentrations of pesticides measured suggest high quality irrigation water; however, sampling protocols could be underestimating pesticide presence in irrigation districts due to low sampling frequency.

Table 3.4 Non-detects statistical measures of median, average, and standard deviation (SD), using a Regression on Order Statistics (ROS) technique, for pesticides with detection frequencies of at least 20%**,** compared to average concentrations where only detected values were included and the average concentrations where non-detects were substituted with zeroes.

Pesticide	ROS median (µg/L)	ROS average (µg/L)	ROS SD (µg/L)	Average of detects only (µg/L)	Average including zero-substitution (µg/L)
2,4-D	0.065	0.164	0.853	0.206	0.161
MCPA	0.005	0.148	3.100	0.573	0.144
Dicamba	0.015	0.060	0.401	0.217	0.050
Glyphosate	0.073	0.136	0.290	0.427	0.074

3.2 Water Quality Guidelines

The concentrations of pesticides were compared against the Environmental Quality Guidelines for Alberta Surface Waters (Government of Alberta 2018) for the protection of aquatic life, irrigation, and livestock watering uses. Overall, the quality of irrigation water in southern Alberta from a pesticide perspective was high with few guideline exceedances. However, there are a limited number of water quality guidelines for pesticides available. Table 3.5 shows the three groups of provincial environmental quality guidelines with the number of exceedances for the range of pesticides detected throughout the study. The pesticides exceeding available guidelines were 2,4-D, MCPA, dicamba, simazine, diazinon, deltamethrin, and trifluralin. The herbicides MCPA and dicamba exceed the guidelines for irrigation uses in at least 17% and 23% of all samples, respectively. Since the guideline for dicamba is less than the detection limit, all detects are in exceedance, as well as possibly some of the samples with values below the detection limit. Since these values are impossible to know, guideline exceedances were calculated only for values above the detection limit. The herbicides MCPA and dicamba rarely exceeded guidelines for the protection of aquatic life (PAL) and livestock watering. Only in 10 samples did 2,4-D exceed PAL guidelines despite being frequently detected. The exceedances of 2,4-D occurred in most years, half of which occurred in WID. Ten detections of MCPA were above the PAL guideline; all occurred in different irrigation districts (except TID, MVID, and EID) and in one AEP canal (the highest of all detections in 2015). Six of these detections occurred in 2016, three in 2015, and one in 2014. Dicamba exceeded its PAL guideline once in the EID in August 2013. Four detections of simazine exceeded its irrigation water quality guideline and all occurred in BRID in 2011. Lastly, diazinon exceeded its PAL guideline once in WID in September 2014. Dicamba and MCPA exceeded guidelines in approximately 25% of samples, with most other pesticides rarely exceeding guidelines with exceedances usually clustered in space or time. However, as previously mentioned, it is quite possible that peak concentrations may have been missed due to the sampling strategy, as has been suggested by others for river systems (Hageman et al. 2019; Spycher et al. 2018).

Table 3.5 Environmental Quality Guidelines for Alberta Surface Waters (Government of Alberta 2018) of pesticides detected and number of exceedances at sites monitored for at least seven years. Grey cells do not have a guideline specified.

Pesticide	Environmental Quality Guidelines (µg/L)			Number of exceedances			No. of detections (No. of samples)
	PAL[z]	Irrigation	Livestock watering	PAL[z]	Irrigation	Livestock watering	
2,4-D	4		100	10		0	2342 (3000)
2,4-DB	25			0			4 (3000)
Atrazine	1.8	10	5	0	0	0	45 (3000)
Azinphos-methyl	0.01			4			4 (1220)
Bromacil	5	0.2	1100	0	0	0	2 (3000)
Bromoxynil	5	0.44	11	0	5	0	50 (3000)
Chlorothalonil	0.18	9.3	170	0	0	0	1 (1220)
Deltamethrin	0.0004		2.5	DL[y]		0	1 (1220)
Diazinon	0.17			1			5 (2464)
Dicamba	10	0.008	122	1	DL[y]	0	686 (3000)
Glyphosate[x]	800		280	0		0	77 (443)
Hexachlorocyclohexane	0.01[w]			3			3 (2464)
MCPA	2.6	0.04	25	10	501	3	755 (3000)
Mecoprop	13			0			235 (3000)
Methoxychlor	0.03			2			2 (3000)
Metolachlor	7.8	28	50	0	0	0	6 (2464)
Picloram	29		190	0		0	15 (3000)
Simazine	10	0.5	10	0	4	0	56 (2464)
Triallate	0.24		230	0		0	6 (3000)
Trifluralin	0.2		45	0		0	1 (3000)

[z]PAL refers to the protection of aquatic life. The Government of Alberta provides values for long-term (chronic) and short-term (acute) exposure. This tables uses the long-term (chronic) values which are levels of the substance or condition that should result in negligible risk of adverse effects on growth, reproduction, or survival of aquatic biota, for an indefinite period (Government of Alberta 2018).
[y]DL indicates that the guideline is below the detection limit/all detections are exceedances of the guideline.
[x]Glyphosate monitored for 5 years with less frequent samplings.
[w]PAL guideline is for all Hexachlorocyclohexane isomers.

3.3 Pesticide Trends in Alberta's Irrigation Districts

The percentage of pesticide detections differed by pesticide and irrigation district (Table 3.6, Table D.2), emphasizing the complexity of pesticide dynamics and their spatial variability. Taber Irrigation District had some of the highest detection frequencies of 2,4-D, bentazon, dicamba, fluroxypyr, and MCPA, and also had the greatest variety of crops grown (Table D.1). In contrast to TID, some of the lowest detection frequencies of the most commonly detected pesticides occurred in the districts nearest to the Rocky Mountains where Alberta's irrigation water originates as mountain snowpack runoff (e.g., MVID). Additionally, MVID has less crop diversity, as the district primarily cultivates forages (Table D.1). When comparing irrigation districts, it is important to recognize that the number of sampling locations and their type (primary, secondary, and return sites) vary, and can influence the observed patterns (Table D.3). Higher pesticide detection frequencies occurred in districts growing specialty crops, such as TID, SMRID, and BRID (Table D.1).

Urban areas are considered sources of 2,4-D and dicamba, which are used for lawn care and maintenance. Alberta Environment and Sustainable Resource Development (2015) reports usage of 2,4-D and dicamba in the large urban centre of the City of Calgary. Higher detection frequencies for 2,4-D, dicamba, and mecoprop were observed in WID, which is in close proximity to the City of Calgary, and also has a golf course on one of WID's primary reservoirs (upstream of W-P2). Studies have shown that golf courses can be a significant source of pesticides (Metcalfe et al. 2016; Phillips and Bode, 2004; Rice et al. 2010). While 2,4-D was commonly detected in WID, dicamba had higher detection frequencies in primary (particularly W-P2) and secondary sites relative to return sites The most frequently detected pesticides were 2,4-D, MCPA, dicamba, and glyphosate, all of which were reported to be used on canal banks by most districts (Personal communication, April 2020). While the presence of pesticides in irrigation waters are likely a reflection of the types and diversity of crops, other practices such as weed management of irrigation canals likely influences detection frequencies of pesticides.

Table 3.6 Pesticide detection frequency (%) for the eight most frequently detected compounds by irrigation district during the study period (2006-2007; 2011-2018)[z].

Irrigation district	2,4-D	AMPA	Bentazon	Dicamba	Fluroxypr	Glyphosate	MCPA	Mecoprop
AEP	60.2	0.0	0.0	12.0	5.7	12.5	7.2	21.7
AID	78.9	10.0	0.0	18.4	0.0	0.0	10.5	0.0
BRID	88.8	8.5	6.4	15.1	18.7	4.2	24.2	1.4
EID	61.0	5.6	3.1	36.8	3.9	15.3	11.0	6.3
LNID	67.6	10.9	2.5	12.5	5.5	12.7	30.5	2.4
MID	58.9	0.0	2.8	13.4	12.5	10.0	20.5	0.0
MVID	36.7	6.3	0.0	2.5	2.1	0.0	5.1	0.0
RID	80.7	27.8	4.2	18.5	22.5	27.8	22.7	0.8
SMRID	95.3	13.3	6.4	11.5	27.0	29.6	35.5	2.3
TID	98.3	10.5	15.3	36.2	26.4	18.4	44.0	4.3
UID	36.7	10.0	4.2	48.3	8.3	60.0	13.3	0.8
WID	96.1	5.4	3.7	36.8	5.3	18.9	30.3	46.1

[z] for n size per district, see Table D.4

3.4 Influence of Crops on Pesticide Detections

In order to assess the influence of crop types on pesticide detection frequencies, the annual percent cover of crop types in the irrigation districts were clustered into seven groups, as described in Section 2.8, and the frequency of pesticide detections were evaluated within these groupings (Figure 3.3 and Table 3.7). Differences in the type and frequency of pesticides detected were observed for the different crop-type groups (Figure 3.4, Table D.5), suggesting that cropping patterns influence pesticide transport dynamics. For instance, Group 1 contains the most specialty crops and had relatively high detection frequencies for the eight most frequently detected pesticides and metabolites.

A greater average number and maximum number of pesticides detected per sample were observed in Groups 1 and 4 (Table 3.8). Group 1 had the largest percent crop cover of specialty crops and was exclusively in TID, BRID and SMRID, while Group 4 included a mix of forage, cereal, oilseed, specialty crops, and other(Table 3.7), and were exclusively in WID. Group 4 (WID) had the highest frequency of mecoprop, which is likely an urban influence as previously mentioned. Group 6 (UID, MID, RID) also had a mix of crops, with the largest percentage of oilseed crops of all groups, and relatively high detection frequencies of glyphosate and fluroxypyr were observed. Similarly, Group 5 had a diverse mix of cereals, forages, oilseeds and specialty crops and had similar pesticide detections as Group 6, either in similar frequencies or lower with the exception of dicamba which was higher. Group 5 is exclusively in EID, which is one of the largest districts spanning approximately 123,202 ha and with more monitoring sites than the other districts. This explains the variability of detection frequencies among sites, and therefore, the lower overall detection frequencies of Group 5. Overall, urban sources, specialty crop types, and variety of crop types seem to influence the type of pesticide detected and frequency of detections.

Some pesticides did not show clear patterns in terms of crop management, such as fluroxypyr and glyphosate. Bürger et al. (2012) highlights the role of crop management on pesticide use, suggesting that agricultural practices and crop rotations will influence pesticide application rates. Further, agricultural practices such as crop-cover mulches have been observed with slower degradation of glyphosate (Cassigneul et al. 2016), and can complicate patterns of pesticide fate in the environment. While the percentage of specialty crops and urban influences within an irrigation district can help elucidate pesticide dynamics, there are a plethora of other factors that may contribute to pesticide fate and transport including crop-specific pest management, soil properties, tillage practices, and microbial activities (Arias-Estévez et al. 2008; García-Delgado et al. 2019; Gavrilescu 2005; Kah et al. 2007; Larson et al. 1997; Reedich et al. 2017).

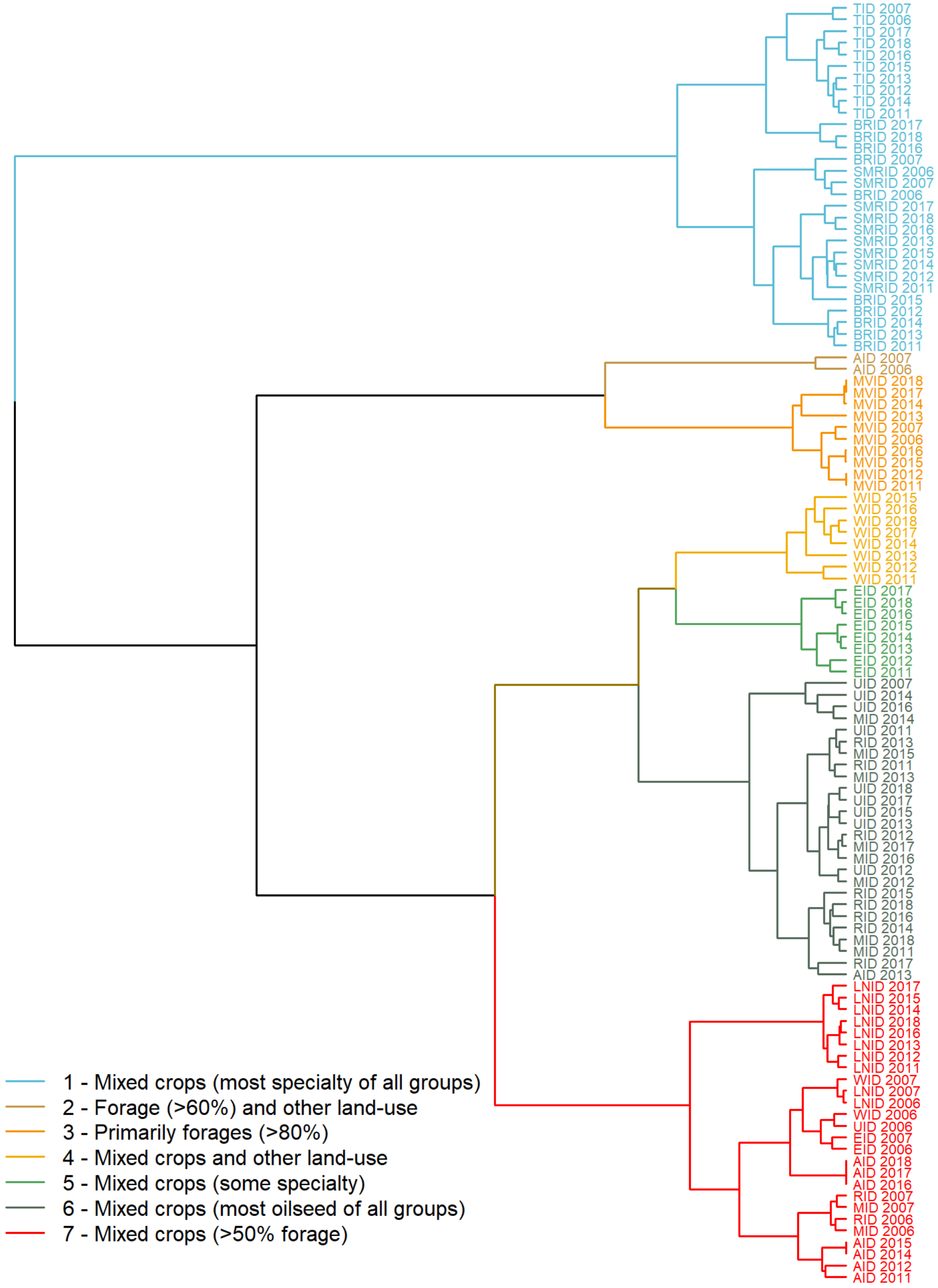

Figure 3.3 Hierarchical clustering (using Ward's agglomeration on Euclidean distances) classifying the percentage of crops per year for the irrigation districts.

Table 3.7 Average percent crop cover (%) for each hierarchical Ward cluster crop group.

Crop group	Cereals	Forages	Oilseeds	Specialty	Other
1	35.0	22.5	9.2	29.7	3.6
2	3.0	61.7	0.0	0.0	35.4
3	10.7	84.9	1.3	2.1	1.0
4	26.6	34.3	16.5	6.4	15.3
5	28.6	40.9	13.7	16.3	0.5
6	34.8	43.6	18.1	2.9	0.5
7	28.9	58.5	8.4	2.8	1.5

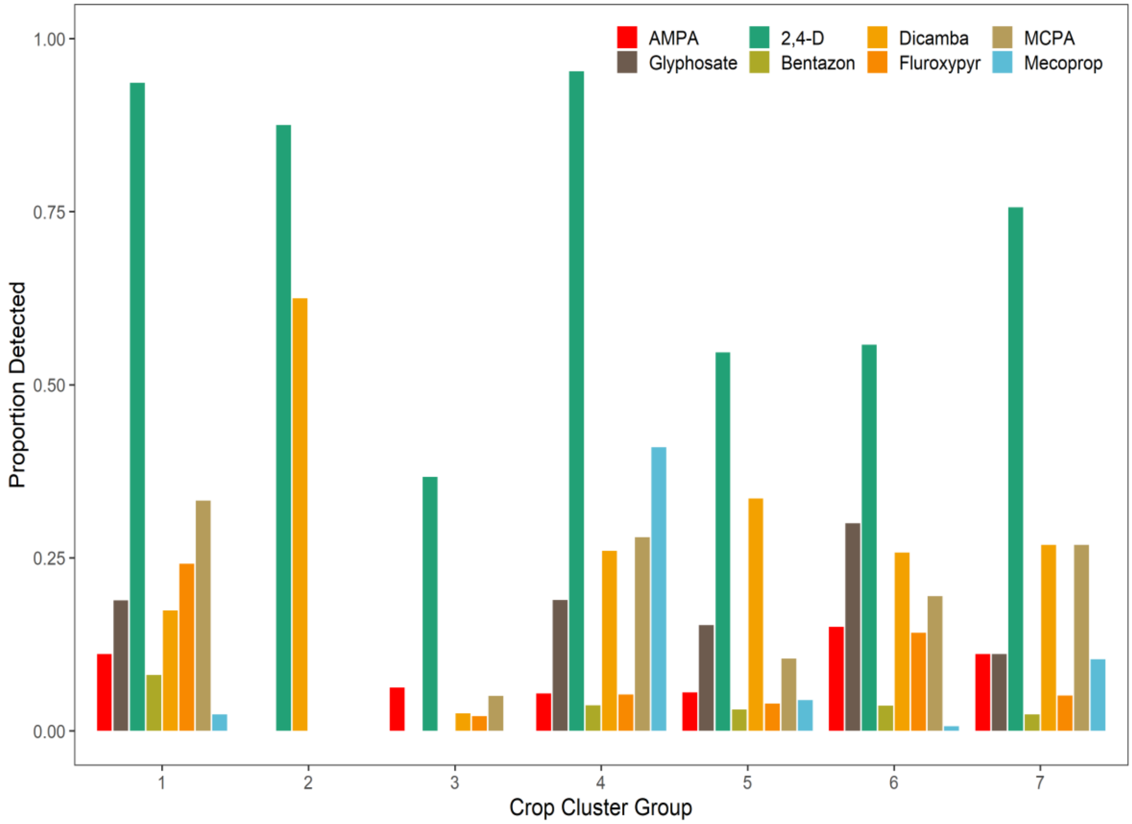

Figure 3.4 Proportion of detections for the eight most frequently detected compounds by seven crop cluster groups, determined by Ward's agglomerative hierarchical clustering. Group 2 results included one district, AID, for only two years (2006 and 2007) with only two sites. Fewer pesticides were analyzed in these early years. See Table D.6 for sample sizes.

Table 3.8 Average and maximum number of pesticide detected among all samples by hierarchical clusters of crop cover.

Crop group	Crop cover	Average no. of pesticide detected per sample	Max. no. of pesticide detected per sample
1	Mixed crops (most specialty of all groups)	2.0	11.0
2[z]	Forage (>60%) and other land-use	1.5	2.0
3	Primarily forages (>80% forage)	0.5	2.0
4	Mixed crops and other land-use	2.1	13.0
5	Mixed crops (some specialty)	1.2	8.0
6	Mixed crops (most oilseed of all groups)	1.3	7.0
7	Mixed crops (>50% forage)	1.6	9.0

[z] Group 2 results included one district, AID, for only two years (2006 and 2007) with only two sites. Fewer pesticides were analyzed in the early years than in later years when the analytical suite was expanded.

3.5 Site-specific Trends

During the 10-year period of the study, the varying pesticide detection frequencies observed at the sampling sites were associated with irrigation district and site type (Figures 3.5 to 3.9). Detections at primary sites appeared to differ based on site surroundings, in addition to the source of the water. Some irrigation districts draw water directly from rivers, while others draw water from storage reservoirs or from main canals. Primary sites of districts such as LNID and UID that source water directly from rivers (LN-P1 and U-P1) generally had lower detection frequencies (Figures 3.11 to 3.13). Detection frequencies varied for districts that draw source water from reservoirs. For example, primary sites receiving water from reservoirs in MVID (MV-P1), MID (M-P1), and EID (E-P1) had a lower detection frequency of 2,4-D and MCPA, while primary sites receiving water from reservoirs in BRID (BR-P1) and SMRID East Block (SME-P1) showed a higher detection frequency of 2,4-D and MCPA. The range of pesticide detection frequencies in primary sites demonstrate how variability can be driven by many factors, such as land-use, soil properties, slope, vegetation strips, agricultural practices, proximity to sources, or climatic variation (Alletto et al. 2011; Arias-Estévez et al. 2008; Fox et al. 2010; Kah et al. 2007). Two sites located nearest to Calgary, an AEP site (AEP-P2) and a WID primary site (W-P2), had relatively high detection frequencies of mecoprop (42.9 and 66.7% respectively) and dicamba (32.1 and 46.2% respectively) compared to other sites in the district and other primary sites overall – highlighting the role of urban sources of pesticides even in primary canals. Most primary sites had lower detections of pesticides than secondary and return sites within their own districts, with some exceptions, including SMRID (SMC-P1 had elevated detection frequencies of bentazon, clopyralid and MCPA) and WID (W-P2 had elevated detection frequencies of dicamba, mecoprop and glyphosate).Two other primary sites from TID (T-P2) and SMRID (SMC-P1) had relatively high detection frequencies of 2,4-D, MCPA, fluroxypyr, and bentazon compared to their respective secondary and return sites. WID primary site (W-P1) had the highest detection frequencies of mecoprop in WID, and a primary site in the UID (U-P1) had the highest detection frequency of dicamba of all sites in UID. Finally, a return site in LNID (LN-R4) (Figure 3.5a) was located in a suburb of Lethbridge and was observed to have had the highest detection frequencies of dicamba, glyphosate, MCPA, and mecoprop within LNID.

Identifying patterns of detected pesticides between site types and locations will allow the irrigation districts to identify areas of concern which will benefit their management planning. In order to do this, a PCA (Figure 3.6) was used to represent and maximize the explained variability of the six most commonly detected pesticides among sampling locations. The PCA is depicted in a biplot, which reduces the six pesticides (6-dimensions) to two-dimensions using linear combinations of pesticide detection frequencies. The arrows represent the pesticides that contribute to each axis, with the length of the arrow indicating the strength of the linear relationship between the compound and the axes and the arrows point in the direction of higher frequencies of detection. Primary sites in LNID, MID, MVID, and UID all had lower pesticide detections compared to the secondary and return site types within those districts, while all other districts showed variable primary site responses where detection frequencies varied between different primary sites. Specifically, primary sites in RID, TID (T-P2), and SMRID (SMC-P1) had detections that were similar to secondary and return sites in their respective districts while some primary sites, such as those in BRID and WID (W-P2), had the highest frequency of pesticide detection of all site types.

Pesticide detection frequencies in secondary sites were variable with some clustering within districts, likely reflecting proximity to areas with recent pesticide applications, variation in flows, and pesticide transport.

Similar to other types of sites, return sites varied with regard to pesticide detection frequency, with differences among irrigation districts. Site-specific pesticide detection frequencies (Table D.2) confound the patterns of pesticide occurrence in southern Alberta’s irrigation districts. Generally, districts closer to the source water (mountain snowpack), such as MVID (Figure 3.5b) and AID had lower detections and areas with intensive speciality crops (e.g., TID, SMRID, BRID) had higher frequency of detections of 2,4-D, MCPA, bentazon, and fluroxypyr (Figures 3.6 to 3.9).

Figure 3.5 Site locations related to pesticide detections such as a) near urban influences; LN-R4 or b) geographically closer to the mountains and source of southern Alberta's irrigation water; MV-P1**.**

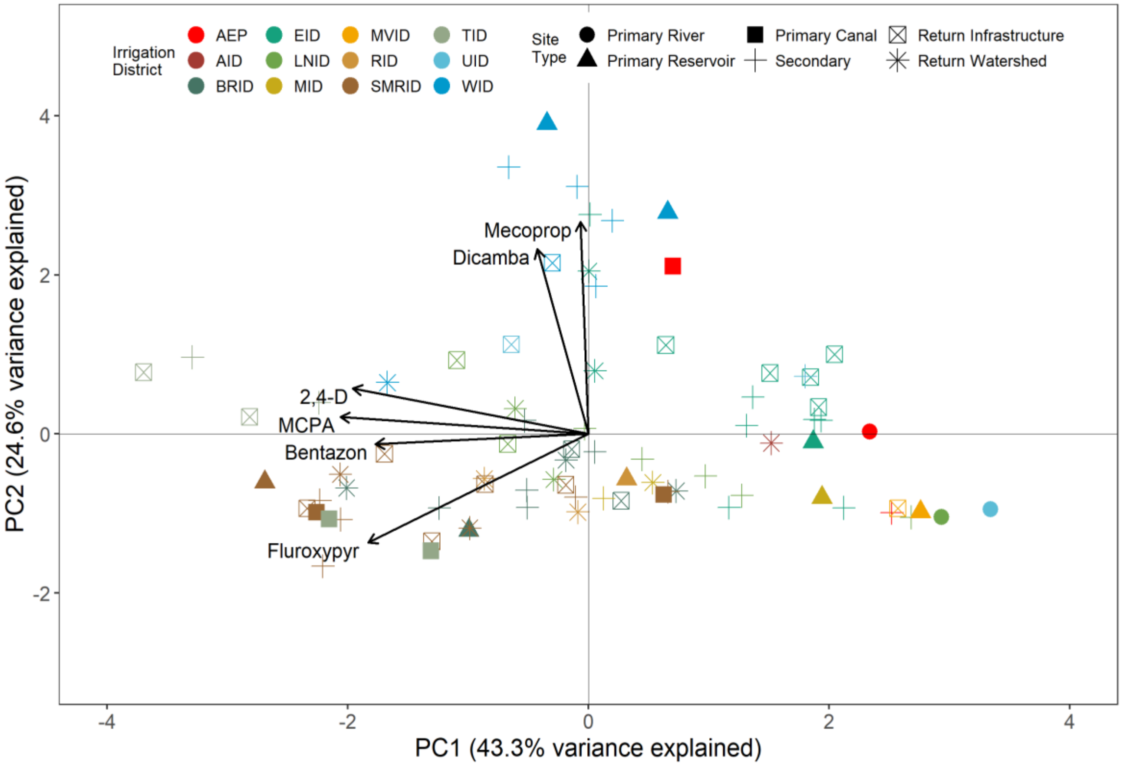

Figure 3.6 Principal component analysis plot showing the multivariate detection frequency of the six most commonly detected pesticides among all sites with at least 7 years of data from 2006 to 2018. Vectors (arrows) indicate the direction and strength of each pesticide detection frequency to the coordinate axes, which explain 67.9% of the variance**.**

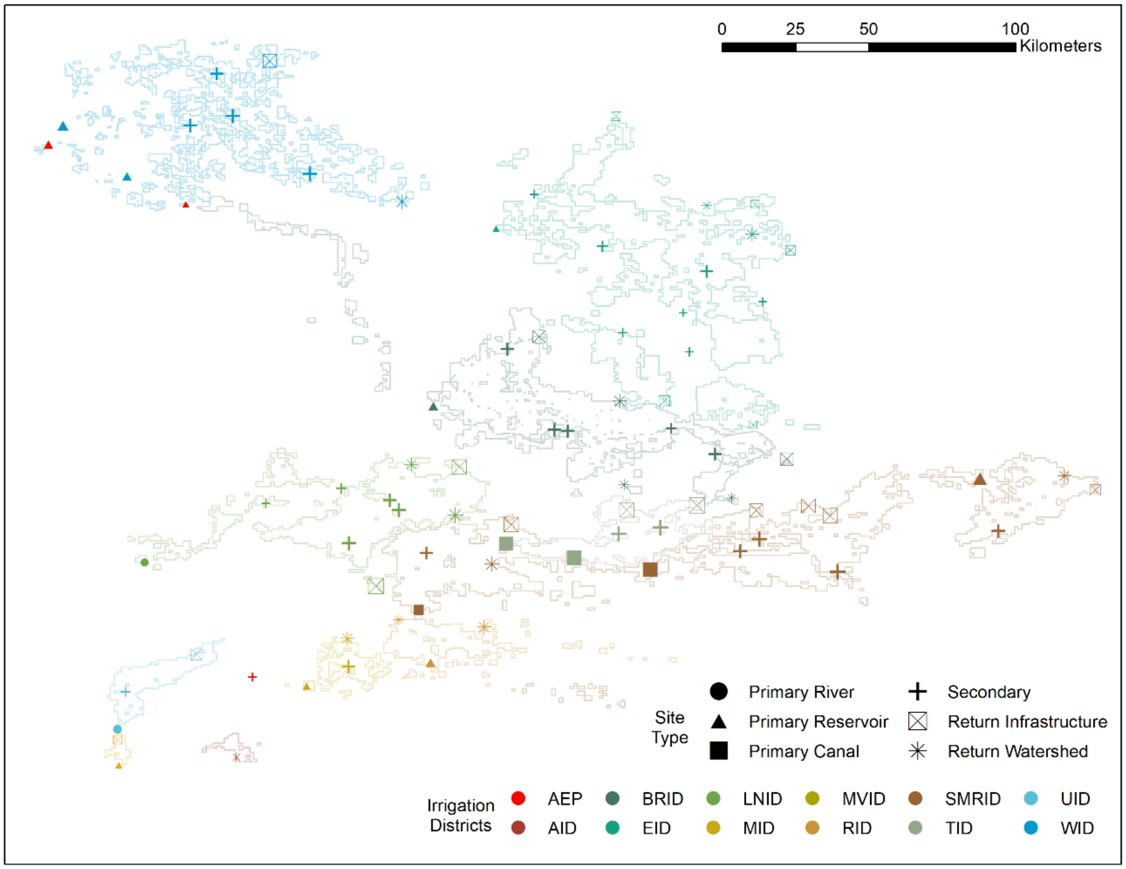

Figure 3.7 Map of 2,4-D frequency detections with shapes representing different site types and the size of points representing the frequency of detections.

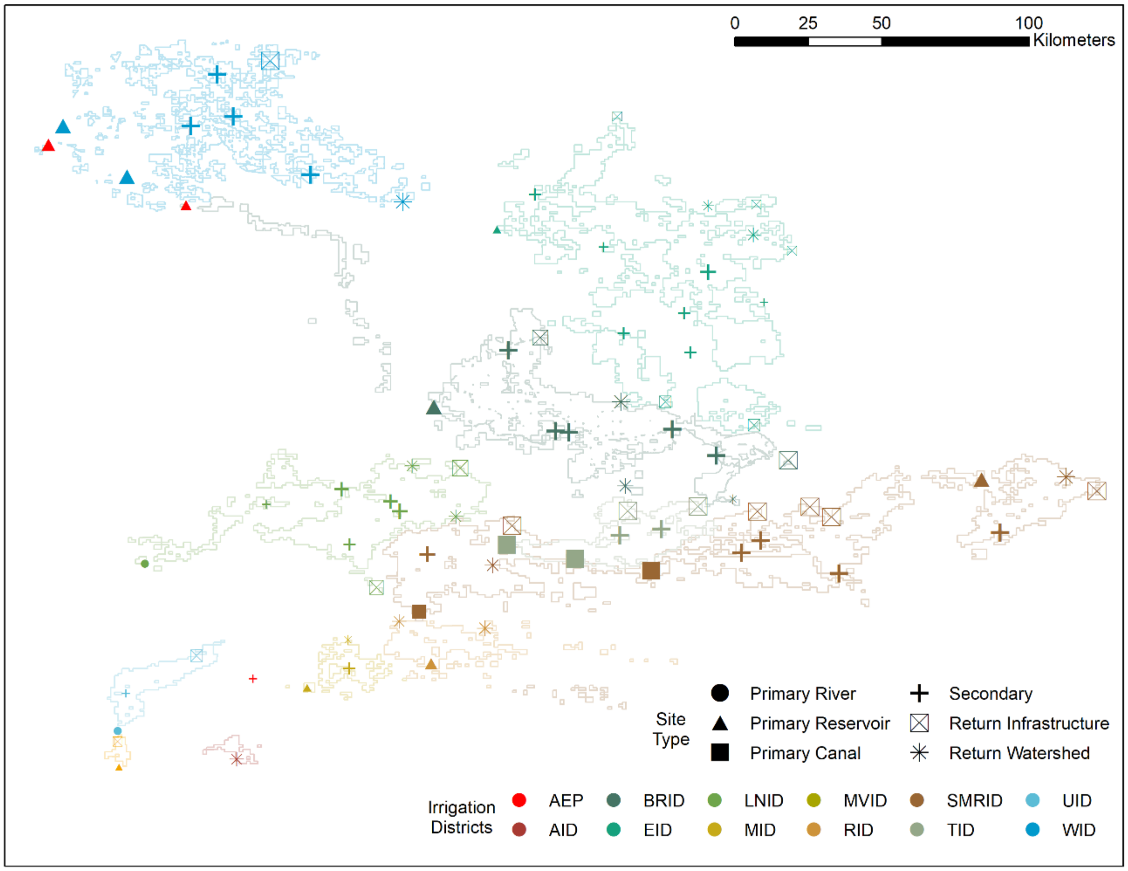

Figure 3.8 Map of dicamba frequency detections with shapes representing different site types, and the size of points representing the frequency of detections.

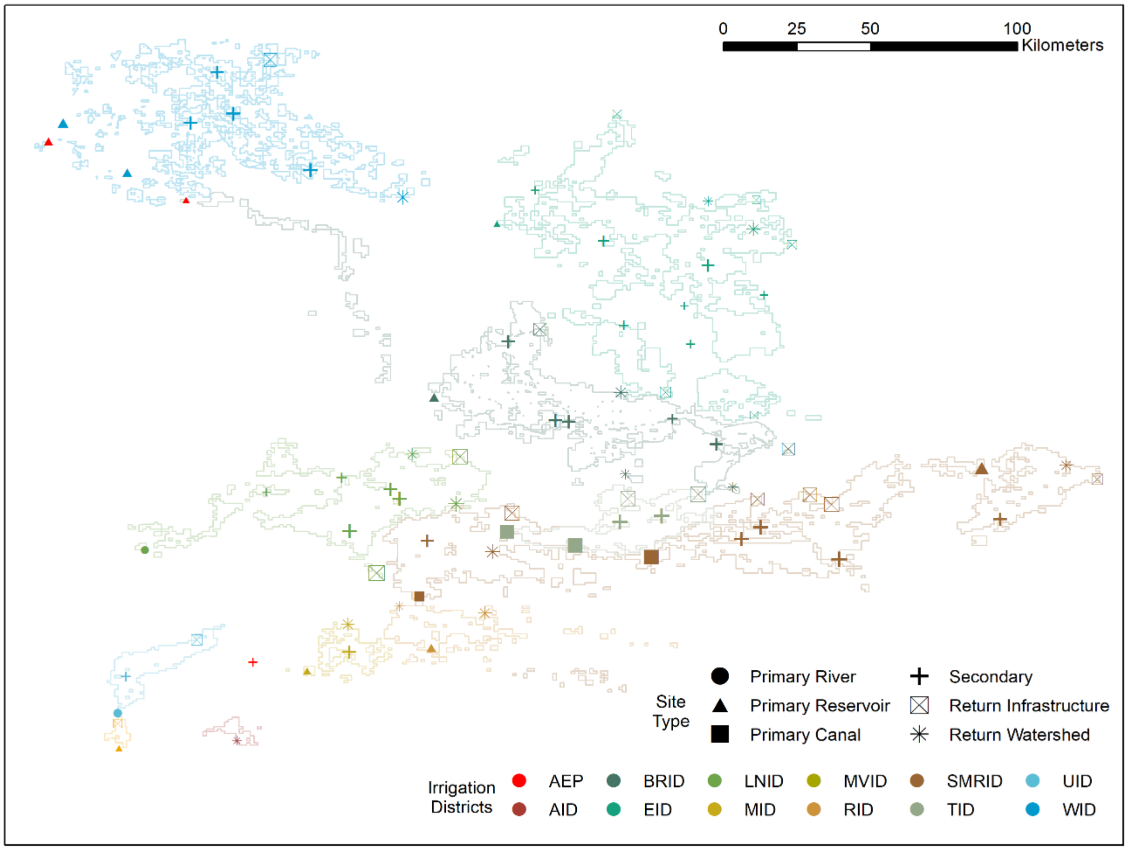

Figure 3.9 Map of MCPA frequency detections with shapes representing different site types and the size of points representing the frequency of detections.

3.6 Annual Pesticide Detections

No consistent year-to-year detection frequencies were observed for the eight most frequently detected pesticides (Table 3.9) except for 2,4-D which had the greatest proportion of detections in each year. Growing season precipitation was variable among years and locations. For example, in 2015, 2017, and 2018, the growing season was drier than other years in most districts due to low amounts of precipitation, while precipitation during the growing season in 2016 was comparably higher (Figure 3.10). The detection frequencies of 2,4-D, bentazon, dicamba, MCPA, and mecoprop were higher in 2016 compared to drier years (2015, 2017, 2018), indicating that precipitation influences the movement of pesticides to irrigation waters. Pesticide loading in other prairie provinces has been attributed to annual variation of winter precipitation, runoff events, and timing of pesticide applications (Challis et al. 2018). However, despite differences observed with growing season precipitation, this pattern is not consistent for all pesticides, indicating that precipitation is not the sole driving force behind pesticide movement into irrigation water. Annually fluctuating pesticide concentrations and detection frequencies may be due in part to; climatic variability, including rapidly changing microclimates throughout southern Alberta; the artificial nature of irrigation water conveyance networks; field and canal management practices; crop cover; and changes in pesticide and irrigation needs.

Table 3.9 Annual detection frequencies (% of samples) for the eight most frequently detected compounds. For n size per year see Table D.7. Grey cells represent years where a pesticide was not measured.

Year	2,4-D	AMPA	Bentazon	Dicamba	Fluroxypyr	Glyphosate	MCPA	Mecoprop
2006	91.0			59.0			35.4	18.3
2007	88.8			34.7			38.1	8.6
2011	90.4			31.3			21.0	16.5
2012	81.4	31.3		16.4		29.2	14.2	5.3
2013	82.0	2.1	1.9	22.5	3.8	2.1	19.9	9.2
2014	82.1	7.1	13.8	22.6	19.7	30.6	31.0	6.3
2015	64.4	1.1	2.2	13.9	16.4	9.6	30.6	5.4
2016	81.7	5.1	10.3	18.3	15.3	13.6	43.5	7.6
2017	56.5		0.3	6.6	0.3		14.6	1.3
2018	65.4		1.3	10.0	26.2		6.0	1.7

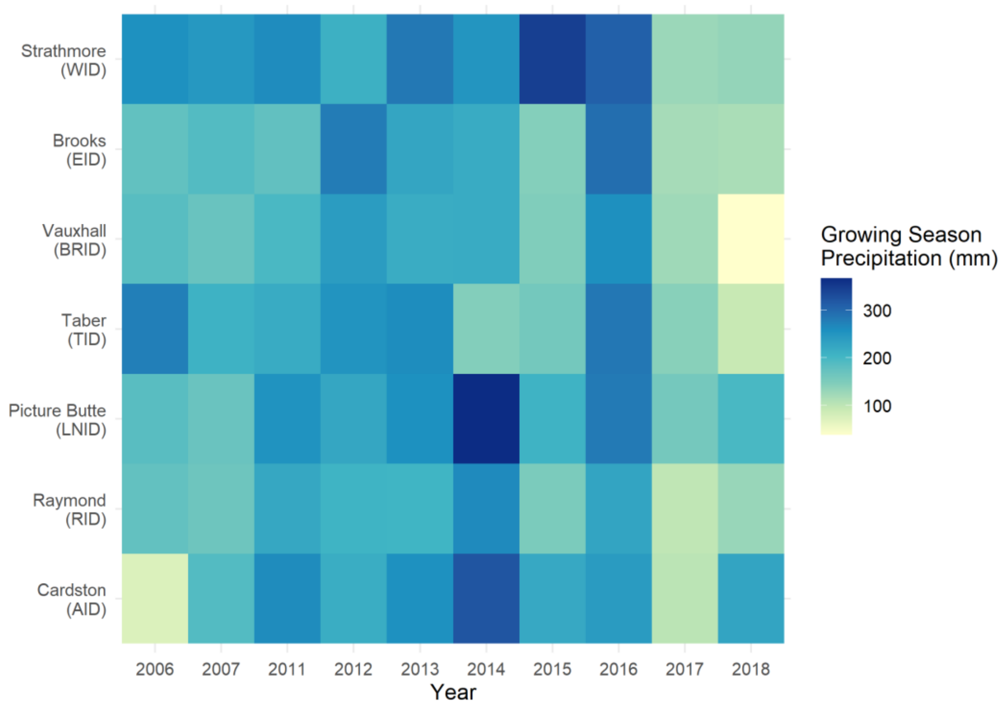

Figure 3.10 Heatmap of growing season (May to September) precipitation (mm) by location and year of study. Daily precipitation data obtained through Environment and Climate Change Canada was summed from May to September for each year of the study.

As mentioned, pesticide sales data can be used as a proxy for pesticide usage (Sheedy et al. 2019). Glyphosate, MCPA, glufosinate, and 2,4-D are the most frequently sold active ingredients in Alberta. Specifically, in 2013, glyphosate sales (8.6 million kg) were an order of magnitude greater than MCPA (0.9 million kg) which had the second highest number of sales (Alberta Environment and Parks 2015). Notably, 2,4-D and MCPA had the highest overall detection frequencies. There were relatively lower detection frequencies for glyphosate and no detections of glufosinate. As indicated, there was an increase in glyphosate sales from 2008 to 2013 (41.5%) (Alberta Environment and Parks 2015); but this was not reflected in the detection frequencies during this project. This could be due to the compound's physical/chemical properties, as glyphosate binds readily to soil particles and degrades quickly (Mamy and Barriuso 2005). Pesticide sales may partially explain some frequencies of detection, since 2,4-D and MCPA were the most commonly sold pesticides in 2013; however, factors such as affinity to soil, degradation rates, pesticide transport, and differences in pesticide use spatially and temporally likely confound interpretation of pesticide occurrence in irrigation waters.

When southern Alberta is divided using the four sub-basin boundaries (Bow, Red Deer, Oldman, and South Saskatchewan), the Bow River sub-basin had the greatest amount of pesticide sales in 2013 which was the most recent year with reported data (Table 3.10, Alberta Environment and Parks 2015). Year-to-year detection frequencies by sub-basin (Table D.8) did not relate directly to greater total sales, and that may be a result of the variability observed at sites and the complexity of water movement between irrigation districts, which does not adhere to watershed boundaries. Likewise, pesticides purchased within an area may be transported and used elsewhere. As previously discussed, variation in the climate among sub-basins, soil properties, microbial communities, crop requirements, and proximity to the source of irrigation water could complicate our ability to detect and ascribe causes to patterns of pesticide detection frequencies.

Table 3.10 Total kilograms of pesticides sold as active ingredient (ai) in the province of Alberta by river sub-basins (Alberta Environment and Parks 2015).

River sub-basin	Districts in basins	2003 kg ai	2008 kg ai	2013 kg ai
Bow River	BRID, EID, WID	10652.4	20276.6	124567.4
Red Deer River	EID, WID	3710.2	7208.1	30942.9
South Saskatchewan River	SMRID	1602.0	2816.8	17763.7
Oldman River	AID, BRID, LNID, MID, MVID, RID SMRID, TID, UID	2638.9	5106.9	16619.6

3.7 Seasonal Patterns of Pesticide Detections

Pesticides detections for the three most frequently detected pesticides (2,4-D, MCPA, and dicamba) were variable for the different seasons and site types (Figures 3.11 to 3.13). Studies have found patterns of increased pesticide concentrations, or peak concentrations, during crop pre-emergence and after spring pesticide applications (e.g., Holten et al. 2018; Lerch et al. 2011) Yet, in this study inter-year variability was greater than any seasonal (early, mid, late) detection frequency pattern (Table 3.11), with seasonal patterns changing for districts and pesticides. This suggests that annual variability due to changing management practices, climatic conditions, annual crop changes, and changes in annual pesticide use, as described in previous sections, are likely drivers of pesticide detections, as suggested by others (Malaj et al. 2019). Detection frequencies for 2,4-D, dicamba, and MCPA by district, season, and site type showed that often, samples collected from primary sites had detection frequencies lower than those collected from secondary and return sites (Figures 3.11 to 3.13). However, there are some exceptions, including a decrease in dicamba from primary to return sites in WID. Another exception is where detection frequencies of 2,4-D were relatively similar among site types in BRID, TID, SMRID, and WID.

Differences were also observed within site types. For example, infrastructure and watershed returns had pesticides that had different detection frequencies and seasonal patterns in BRID, EID, LNID, and WID (Figures 3.11 to 3.13). When comparing site types among districts it is important to remember that some districts do not have certain site types and the number of sites monitored varied among districts (Table D.3). The timing of peak detection frequency differed among pesticides, districts, site types, and years, highlighting the variability of pesticide detection in irrigation water.

Table 3.11 Detection frequency (%) by year and season for the eight most frequently detected compounds. For n size per year and season, see Table D.9.

Season	Year	2,4-D	AMPA	Bentazon	Dicamba	Fluroxypyr	Glyphosate	MCPA	Mecoprop
Early (May 28th to Jun 15th)	2012	92.4	6.3	0.0	17.7	0.0	35.4	21.5	3.8
	2013	87.3	2.1	0.0	19.0	2.5	2.1	40.5	13.9
	2014	83.8	0.0	1.3	12.5	1.3	16.3	15.0	3.8
	2015	67.9	2.1	1.3	10.3	5.1	8.3	5.1	2.6
	2016	70.7	0.0	1.3	14.7	0.0	0.0	10.7	2.7
	2017	64.9	0.0	0.0	10.8	0.0	0.0	5.4	1.4
	2018	53.9	0.0	2.6	5.3	39.5	0.0	1.3	0.0
Mid (Jun 16th to Aug 3rd)	2006	95.5	0.0	0.0	66.4	0.0	0.0	47.8	21.6
	2007	94.8	0.0	0.0	48.5	0.0	0.0	52.2	17.2
	2011	95.2	0.0	0.0	41.1	0.0	0.0	26.7	17.8
	2012	87.7	0.0	0.0	18.4	0.0	0.0	20.2	7.0
	2013	82.0	0.0	4.5	27.8	1.9	0.0	21.8	7.5
	2014	90.0	0.0	17.5	27.5	18.2	0.0	55.0	10.0
	2015	62.5	0.0	3.8	19.4	0.0	0.0	53.8	6.3
	2016	88.2	0.0	22.4	13.2	24.7	0.0	42.1	3.9
	2017	58.6	0.0	0.7	6.6	0.0	0.0	15.1	1.3
	2018	72.0	0.0	1.3	15.3	9.3	0.0	10.7	2.7
Late (Aug 4th to Sept 4th)	2006	86.6	0.0	0.0	51.5	0.0	0.0	23.1	14.9
	2007	82.8	0.0	0.0	20.9	0.0	0.0	23.9	0.0
	2011	85.5	0.0	0.0	21.4	0.0	0.0	15.2	15.2
	2012	68.8	56.3	0.0	13.6	0.0	35.4	4.0	4.8
	2013	77.9	2.0	0.0	18.3	6.0	2.1	1.9	7.7
	2014	77.4	14.3	18.2	25.2	41.3	16.3	27.0	5.7
	2015	64.6	0.0	0.0	6.3	30.0	8.3	8.9	6.3
	2016	84.0	5.1	8.7	22.7	11.8	13.6	60.7	12.0
	2017	44.0	0.0	0.0	2.7	0.7	0.0	22.7	1.3
	2018	64.0	0.0	0.0	4.0	28.0	0.0	1.3	1.3

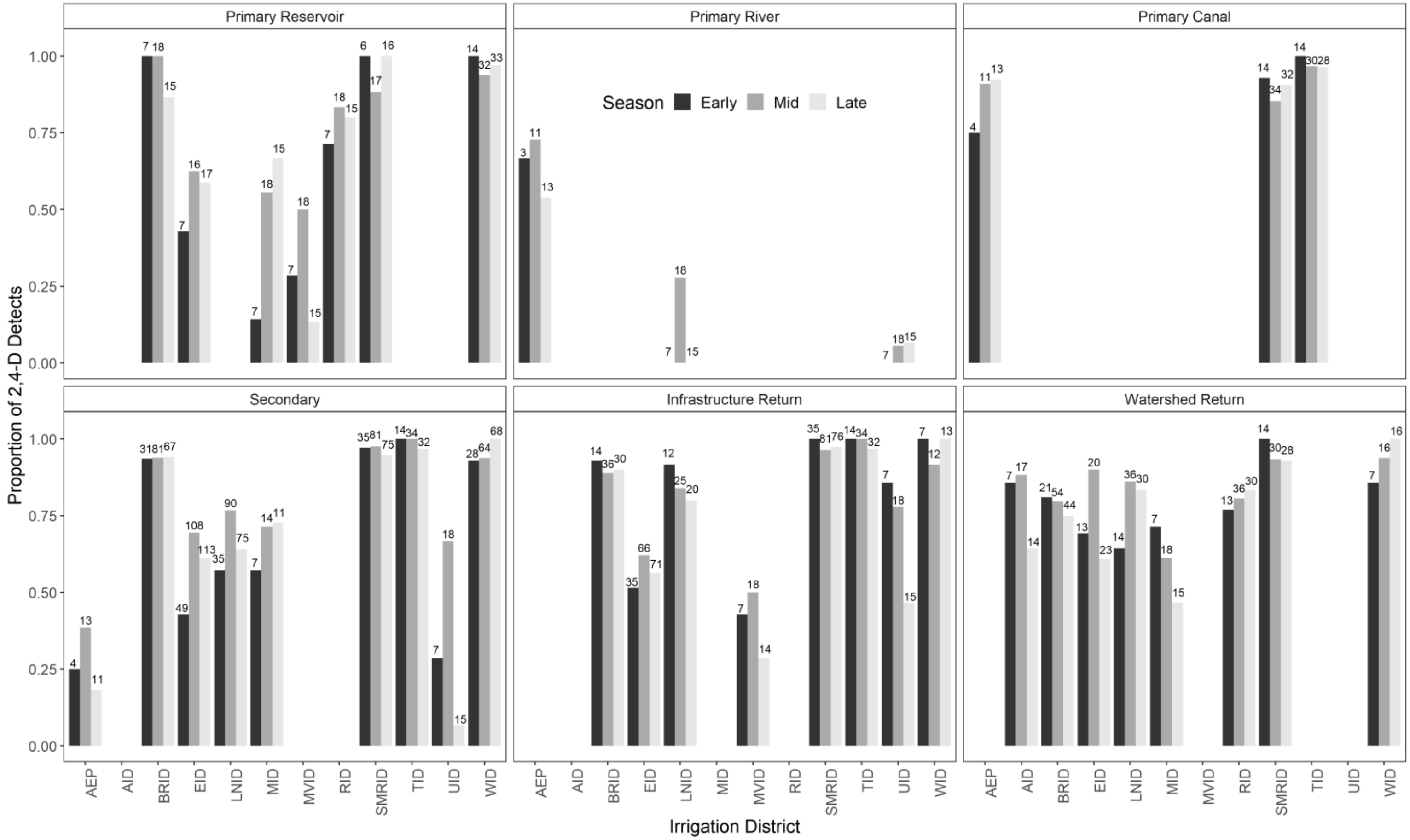

Figure 3.11 Detection frequency of 2,4-D for each season, irrigation district, and site type (primary, secondary, return). Number above the bars represent the number of samples.

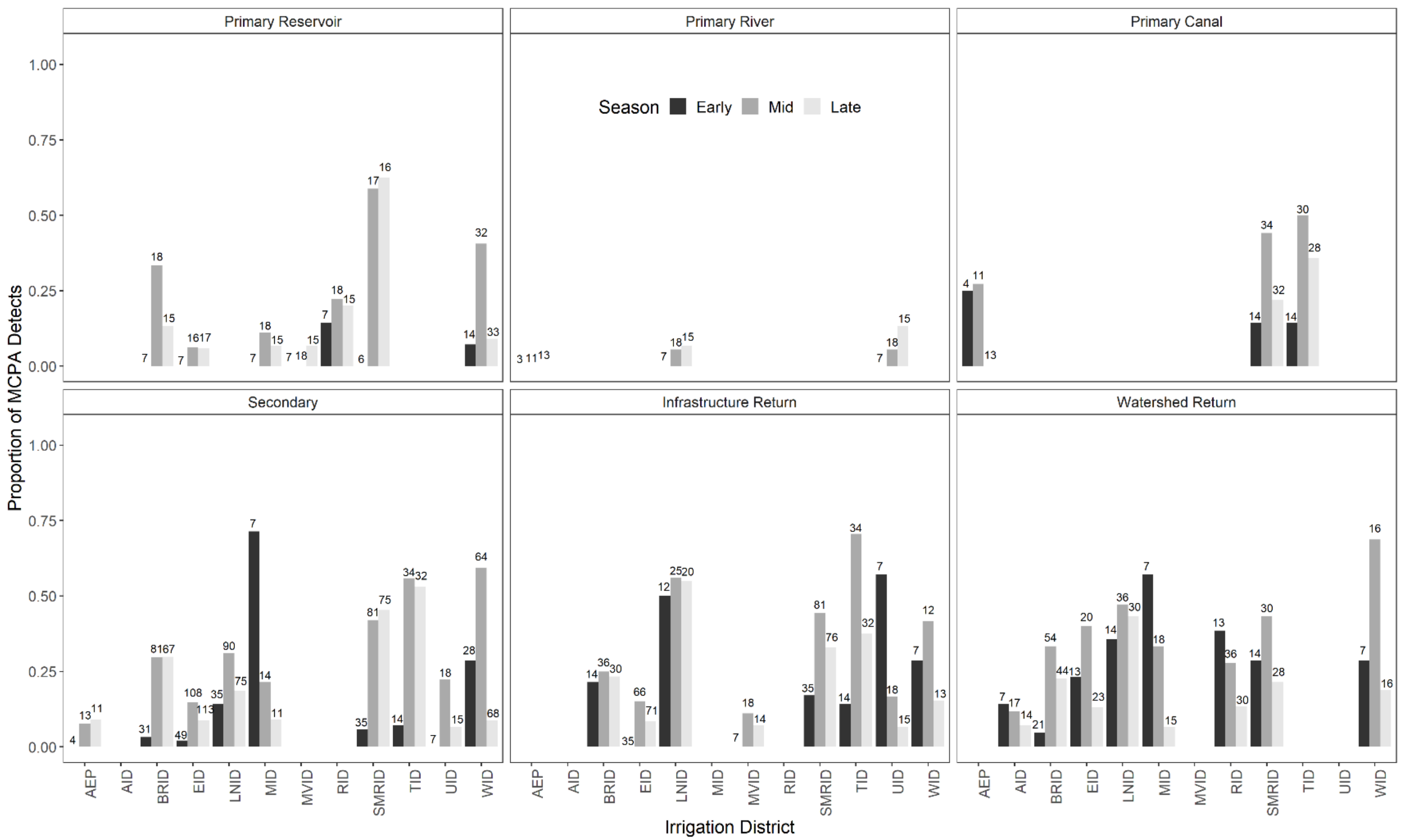

Figure 3.12 Detection frequency of MCPA for each season, irrigation district, and site type (primary, secondary, return). Number above the bars represent the number of samples

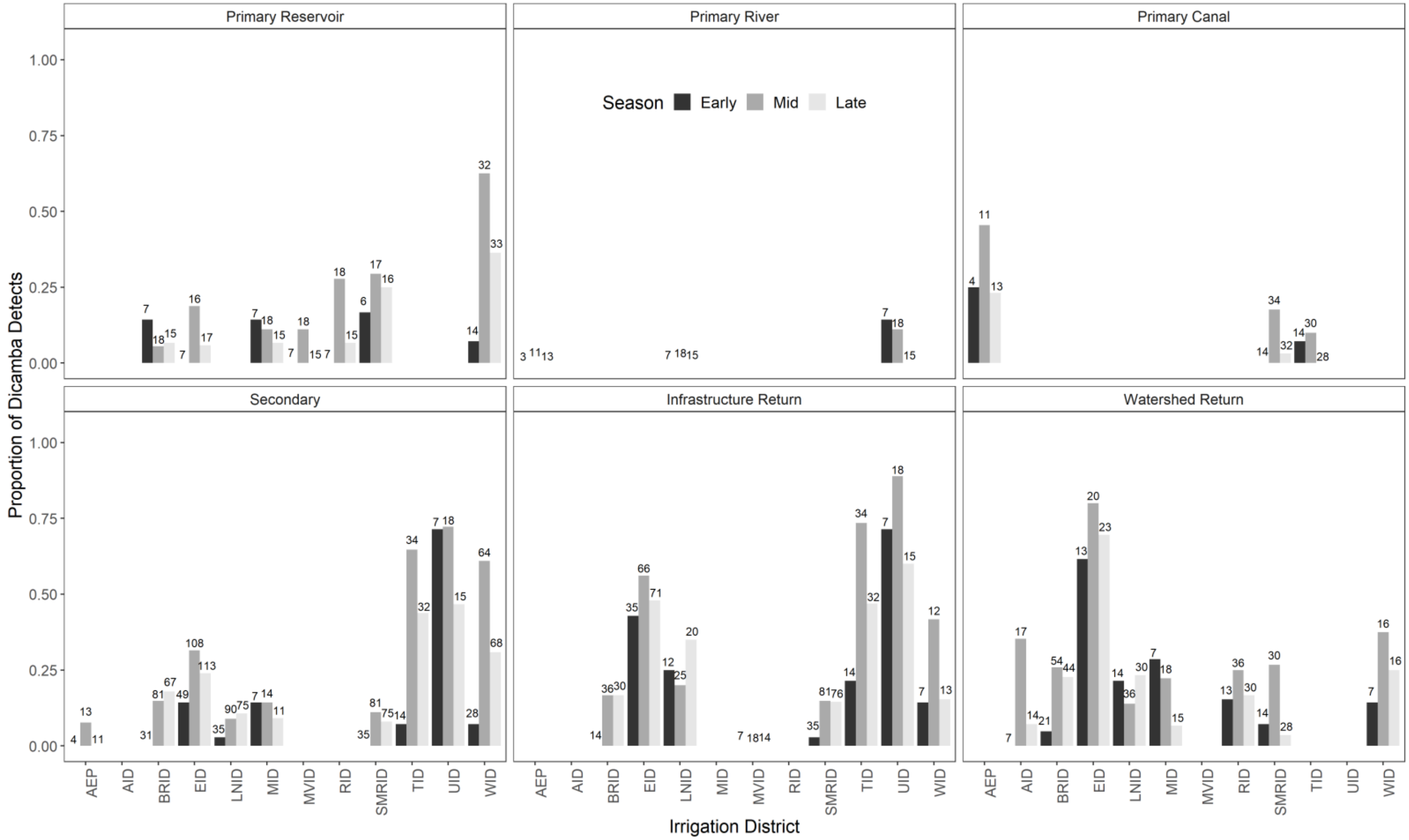

Figure 3.13 Detection frequency of dicamba for each season, irrigation district, and site type (primary, secondary, return). Number above the bars represent the number of samples.

4 Conclusions

Overall, pesticides in irrigation water pose little risk to water quality, with a low proportion of samples exceeding irrigation water quality guidelines. The most commonly detected pesticides were herbicides, which included 2,4-D, MCPA, dicamba, glyphosate, fluroxypyr, AMPA (a herbicide metabolite), mecoprop, and bentazon. It is possible that peak concentrations and detections were not captured because of the monthly sampling interval used, and because sampling events avoided precipitation events. Variability in pesticide properties (e.g., affinity to soil) can influence how frequently certain pesticides are observed. In this study, commonly sold pesticides with high water solubility and with a low affinity for soils (i.e., lower K_{oc} values) had higher frequencies of detections. However, not all pesticides with similar K_{oc} properties were detected, which likely reflects variability in application rates, crop-specific pest requirements, and crop management (e.g., spray timing).

Spatial variability among districts, crops, and sampling sites found in this study demonstrates the complexity of pesticide movement into irrigation water. There was no single driver to explain differences among irrigation districts, with different pesticides exhibiting different patterns in different irrigation districts. When irrigation districts were grouped by crop cover, it was apparent that groups with specialty crops (e.g., potato and sugar beet) and greater variety of crop types (e.g., cereals, forages, oilseeds, specialty, and other land-use) had greater numbers of pesticides detected per sample, as well as groups with urban influences. Sampling locations had inconsistent results among site types and within districts with respect to the frequency of pesticide detections. Variation among sites suggests that geospatial factors, such as canal management, distance to field with active pesticide use, and soil type could influence observations.

The most commonly detected pesticides (2,4-D, MCPA, and dicamba) exhibited year-to-year variations and seasonal patterns of detection rates. Growing season precipitation varied annually, as well as spatially, and may have contributed to the variability in pesticide detections. Annually changing environmental conditions, crop rotations, and pesticide use means seasonal patterns were difficult to assess. Temporal variations were also difficult to parse out due to the spatial heterogeneity of sampling locations among and within irrigation districts, although year-to-year variations were evident with regard to annual pesticide detection frequencies. While these variations may be related to climate, other factors such as changes in pesticide use with crop rotations or other management practices may also play a role. Although pesticides do not currently pose a concern to irrigation water quality in southern Alberta, it is important to continue to monitor patterns of pesticide detections and the mechanisms of pesticide movement into irrigation water. This will ensure proper management and protection of this valuable resource.

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Appendix A. List of Pesticides Analyzed and Detection Limits

Table A.1 Suite of pesticides and detection limits of pesticides (µg/L), by year. Grey cells represent years where a pesticide was not measured, typically due to an expansion of the suite in later years.

Pesticide	2006	2007	2011	2012	2013	2014	2015	2016	2017	2018
AMPA			10.000	1.000	0.100	0.300	0.300	0.300		
Glufosinate				1.000	1.000	0.400	0.400	0.400		
Glyphosate			10.000	0.200	0.100	0.100	0.100	0.100		
2,4-D	0.025	0.025	0.025	0.025	0.027	0.025	0.025	0.024	0.026	0.025
2,4-DB	0.025	0.025	0.025	0.025	0.023	0.025	0.025	0.026	0.025	0.025
2,4-Dichlorophenol					0.034	0.140	0.139	0.143	0.148	0.152
Alachlor			0.026	0.025	0.025	0.025	0.025	0.026	0.024	0.025
Aldrin	0.025	0.025	0.025	0.025	0.029	0.025	0.026	0.025	0.022	0.026
Allidochlor			0.025	0.025	0.028	0.025	0.026	0.025	0.025	0.026
Atrazine	0.025	0.025	0.025	0.025	0.023	0.025	0.024	0.025	0.025	0.025
Azinphos-methyl							0.637	0.627	0.517	0.511
Azoxystrobin							0.025	0.106	0.108	0.113
Benalaxyl			0.025	0.025	0.025	0.025	0.024	0.026	0.025	0.025
Benfluralin			0.025	0.025	0.026	0.025	0.025	0.014	0.014	0.025
Bentazon					0.031	0.025	0.025	0.026	0.024	0.025
Benzoylprop-ethyl			0.030	0.030	0.032	0.025	0.025	0.027	0.025	0.026
Bifenazate								0.144	0.131	0.131
Bifenthrin			0.025	0.025	0.025	0.025	0.025	0.026	0.025	0.026
Bromacil	0.025	0.025	0.025	0.025	0.030	0.025	0.025	0.025	0.025	0.026
Bromophos-ethyl			0.025	0.025	0.026	0.026	0.025	0.025	0.025	0.026
Bromopropylate			0.050	0.050	0.053	0.052	0.051	0.051	0.053	0.050
Bromoxynil	0.025	0.025	0.025	0.025	0.024	0.024	0.025	0.024	0.025	0.025
Boscalid							0.025	0.026	0.026	0.025
Bupirimate			0.025	0.025	0.025	0.025	0.025	0.027	0.025	0.025
Butachlor			0.040	0.080	0.080	0.079	0.084	0.083	0.081	0.082
Butralin			0.030	0.040	0.038	0.025	0.025	0.025	0.025	0.025
Butylate			0.025	0.025	0.024	0.026	0.025	0.026	0.025	0.026
Captan							0.031	0.134	0.113	0.059
Carbaryl							0.032	0.067	0.056	0.051
Carbofuran							0.025	0.031	0.025	0.025
Carfentrazone-ethyl							0.025	0.026	0.025	0.025
cis-Chlordane			0.025	0.025	0.020	0.025	0.027	0.025	0.026	0.025
t-Chlordane			0.025	0.025	0.024	0.025	0.025	0.026	0.025	0.026
Chlormephos			0.025	0.025	0.022	0.026	0.025	0.026	0.025	0.025

Table A.1 *continued*.

Pesticide	2006	2007	2011	2012	2013	2014	2015	2016	2017	2018
Chloroneb			0.025	0.025	0.025	0.026	0.025	0.025	0.025	0.025
Chlorothalonil							0.025	0.050	0.048	0.052
Chlorpyrifos	0.025	0.026	0.025	0.040	0.033	0.025	0.025	0.027	0.025	0.025
Chlorpyrifos-methyl			0.040	0.040	0.049	0.050	0.046	0.050	0.050	0.053
Chlorthal-dimethyl			0.025	0.025	0.026	0.025	0.026	0.027	0.025	0.025
Chlorthiamid			0.030	0.030	0.028	0.026	0.026	0.026	0.025	0.025
Clodinafop-propargyl						0.150	0.150	0.144	0.145	0.152
Clomazone			0.025	0.025	0.024	0.025	0.026	0.025	0.025	0.026
Clopyralid	0.025	0.025	0.026	0.025	0.031	0.025	0.026	0.024	0.025	0.026
Cycloate			0.025	0.025	0.025	0.025	0.026	0.024	0.026	0.026
Cyfluthrin								0.074	0.077	0.073
Cypermethrin-beta								0.074	0.075	0.071
Cypermethrin-zeta								0.074	0.073	0.072
Cyhalothrin lambda							0.025	0.024	0.025	0.026
Cyprodinil								0.026	0.025	0.025
o,p-DDD			0.025	0.025	0.024	0.025	0.025	0.258	0.024	0.025
p,p-DDD			0.025	0.025	0.025	0.025	0.026	0.025	0.025	0.026
o,p-DDD	0.025	0.025	0.025	0.025	0.025	0.050	0.051	0.051	0.052	0.055
p,p-DDD	0.025	0.026	0.025	0.025	0.028	0.025	0.025	0.024	0.025	0.025
o,p-DDT			0.025	0.035	0.032	0.025	0.025	0.024	0.025	0.025
p,p-DD			0.025	0.050	0.059	0.059	0.059	0.061	0.063	0.062
Deltamethrin							0.025	0.027	0.025	0.025
Desmetryn			0.025	0.025	0.023	0.026	0.025	0.026	0.025	0.026
Diazinon			0.025	0.025	0.027	0.025	0.025	0.025	0.025	0.025
Dicamba	0.025	0.025	0.025	0.025	0.026	0.024	0.025	0.026	0.025	0.025
Dichlobenil			0.030	0.030	0.032	0.025	0.025	0.026	0.024	0.025
Dichlorprop	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
Dichlorvos			0.050	0.060	0.064	0.068	0.050	0.052	0.052	0.054
Dichlofenthion			0.030	0.030	0.030	0.025	0.026	0.026	0.028	0.025
Diclofop	0.025	0.025	0.025	0.025	0.023	0.026	0.025	0.026	0.026	0.025
Dieldrin	0.025	0.025	0.025	0.025	0.027	0.025	0.025	0.025	0.024	0.026
Difenoconazole							0.025	0.100	0.102	0.102
Dimethachlor			0.025	0.025	0.024	0.026	0.025	0.027	0.025	0.025
Dimethoate	0.025	0.122	0.500	1.000	1.098	0.967	0.251	0.255	0.248	0.255
Dioxathion			0.050	0.150	0.145	0.145	0.143	0.142	0.156	0.154
Diphenamid			0.025	0.025	0.026	0.026	0.025	0.026	0.026	0.025
alpha-Endosulfan			0.050	0.080	0.086	0.085	0.081	0.088	0.080	0.085
Endrin			0.025	0.025	0.028	0.025	0.025	0.025	0.025	0.025
EPTC			0.035	0.035	0.034	0.025	0.025	0.025	0.025	0.025

Table A.1 *continued.*

Pesticide	2006	2007	2011	2012	2013	2014	2015	2016	2017	2018
Ethalfluralin	0.126	0.126	0.120	0.120	0.135	0.120	0.117	0.114	0.119	0.125
Ethion			0.040	0.040	0.045	0.045	0.046	0.047	0.049	0.054
Ethofumesate			0.025	0.025	0.026	0.025	0.026	0.025	0.025	0.025
Etradiazole			0.025	0.035	0.036	0.025	0.026	0.025	0.025	0.025
Etrimphos			0.025	0.025	0.023	0.026	0.025	0.026	0.026	0.071
Famoxadone								0.140	0.147	0.154
Fenamidone								0.026	0.025	0.026
Fenchlorphos			0.025	0.025	0.029	0.025	0.025	0.025	0.026	0.026
Fenoxaprop	0.126	0.126	0.200	0.300	0.312	0.368	0.050	0.052	0.053	0.052
Fenthion			0.030	0.030	0.029	0.026	0.026	0.026	0.026	0.025
Flamprop-isopropyl			0.025	0.025	0.025	0.025	0.025	0.024	0.026	0.025
Flamprop-methyl			0.025	0.025	0.027	0.025	0.025	0.025	0.025	0.025
Fluazifop-p-butyl							0.025	0.026	0.026	0.025
Fludioxonil							0.025	0.025	0.025	0.025
Flumetralin			0.030	0.045	0.052	0.025	0.026	0.028	0.026	0.026
Flumioxazin								0.069	0.071	0.073
Fluroxypyr					0.039	0.025	0.025	0.026	0.024	0.026
Folpet							0.025	0.204	0.211	0.212
Fonofos			0.025	0.025	0.031	0.026	0.025	0.025	0.025	0.026
Hexachlorocyclohexane-α			0.025	0.025	0.024	0.025	0.025	0.025	0.025	0.025
Hexachlorocyclohexane-ß			0.025	0.025	0.023	0.025	0.025	0.026	0.025	0.025
Hexachlorocyclohexane- δ			0.121	0.150	0.177	0.154	0.158	0.154	0.149	0.153
Hexachlorocyclohexane-Γ	0.025	0.026	0.025	0.025	0.033	0.025	0.026	0.027	0.025	0.025
Heptachlor	0.025	0.025	0.025	0.025	0.026	0.025	0.025	0.026	0.025	0.026
trans-Heptachlor epoxide	0.025	0.025	0.030	0.060	0.071	0.071	0.070	0.072	0.080	0.082
Hexazinone							0.025	0.053	0.050	0.051
Imazamethabenz							0.151	0.412	0.478	0.050
Imazethapyr	0.127	0.127	0.121	0.120	0.119	0.115	0.104	0.107	0.105	0.108
Ipconazole								0.025	0.025	0.025
Iprodione							0.025	0.025	0.025	0.025
Isofenphos			0.050	0.050	0.052	0.051	0.051	0.050	0.051	0.051
Malathion							0.025	0.026	0.025	0.025
MCPA	0.025	0.026	0.025	0.025	0.023	0.025	0.025	0.026	0.025	0.025
MCPA-EHE									0.024	0.026
MCPB-methyl							0.025	0.026	0.025	0.025
Mecoprop	0.025	0.025	0.025	0.025	0.024	0.025	0.025	0.026	0.025	0.025
Metalaxyl							0.026	0.026	0.025	0.025
Metconazole								0.144	0.142	0.152
Methoprene							0.076	0.076	0.076	0.071

Table A.1 *continued*.

Pesticide	2006	2007	2011	2012	2013	2014	2015	2016	2017	2018
Methoxychlor	0.025	0.025	0.025	0.025	0.029	0.025	0.025	0.026	0.025	0.025
Metolachlor			0.025	0.025	0.023	0.025	0.025	0.026	0.025	0.025
Metribuzin							0.631			
Mirex			0.025	0.025	0.026	0.025	0.025	0.025	0.025	0.025
Monolinuron							0.627	0.662	0.622	0.610
Myclobutanil								0.026	0.025	0.025
Naled							0.032	0.151	0.150	0.151
Napropamide							0.025	0.024	0.025	0.025
Nicotine							1.375			
Nitrapyrin			0.030	0.030	0.033	0.026	0.025	0.027	0.025	0.025
Oxycarboxin							0.152	0.609	0.000	0.025
Oxyfluorfen							0.025	0.124	0.117	0.123
Pendimethalin							0.025	0.025	0.025	0.025
cis-Permethrin			0.025	0.025	0.025	0.024	0.025	0.025	0.025	0.025
trans-Permethrin			0.025	0.025	0.027	0.025	0.026	0.025	0.025	0.025
Phorate			0.030	0.040	0.044	0.041	0.042	0.022	0.024	0.026
Picloram	0.025	0.025	0.025	0.025	0.027	0.025	0.060	0.064	0.070	0.072
Picoxystrobin								0.026	0.026	0.025
Piperonyl butoxide							0.025	0.025	0.024	0.025
Pirimicarb			0.025	0.025	0.024	0.026	0.026	0.025	0.026	0.026
Pirimiphos-ethyl			0.030	0.050	0.059	0.059	0.049	0.048	0.051	0.052
Pirimiphos-methyl			0.025	0.025	0.031	0.025	0.025	0.027	0.025	0.025
Procymidone			0.040	0.040	0.037	0.024	0.026	0.025	0.025	0.025
Prometon			0.025	0.025	0.023	0.025	0.025	0.027	0.025	0.026
Prometryn							0.025	0.026	0.025	0.026
Propetamphos								0.027	0.026	0.026
Propham			0.025	0.025	0.024	0.026	0.025	0.029	0.024	0.025
Propiconazole						0.074	0.074	0.076	0.075	0.071
Propoxur							0.025	0.025	0.026	0.025
Propyzamide			0.025	0.025	0.023	0.025	0.026	0.027	0.026	0.025
Prothioconazole-desthio							0.025	0.025	0.025	0.025
Pymetrozine							0.196	0.846		
Pyraclostrobin							0.031	0.142	0.145	0.156
Pyridaben								0.025	0.026	0.025
Pyrimethanil								0.048	0.049	0.053
Quinclorac	0.025	0.025	0.025	0.025	0.027	0.026	0.025	0.025	0.025	0.026
Quintozene			0.025	0.040	0.040	0.041	0.045	0.044	0.046	0.053
Quizalofop-ethyl							0.025	0.026	0.027	0.025
Simazine			0.035	0.040	0.034	0.025	0.052	0.073	0.074	0.075

Table A.1 *continued*.

Pesticide	2006	2007	2011	2012	2013	2014	2015	2016	2017	2018
Spiromesifen								0.026	0.026	0.025
Sulfentrazone								0.483	0.477	0.504
Sulfotep			0.025	0.025	0.025	0.026	0.025	0.025	0.025	0.026
Sulprophos			0.040	0.040	0.038	0.025	0.024	0.026	0.025	0.025
Tebuconazole							0.025	0.052	0.053	0.051
Terbacil			0.050	0.050	0.081	0.092	0.090	0.091	0.103	0.107
Terbufos			0.025	0.035	0.042	0.044	0.048	0.048	0.050	0.053
Terbutryn			0.025	0.025	0.030	0.025	0.025	0.027	0.025	0.025
Tetradifon			0.025	0.025	0.022	0.026	0.025	0.025	0.026	0.025
Tetramethrin I								0.025	0.026	0.025
Tetrasul			0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.026
Triallate	0.026	0.025	0.025	0.025	0.031	0.025	0.025	0.024	0.025	0.025
Triclopyr					0.024	0.025	0.025	0.025	0.025	0.025
Trifloxystrobin							0.026	0.025	0.025	0.026
Trifluralin	0.025	0.025	0.025	0.025	0.028	0.026	0.025	0.026	0.025	0.025
Triticonazole							0.025	0.143	0.151	0.154
Vinclozolin							0.025	0.027	0.025	0.026
Zoxamide								0.491	0.471	0.502

Appendix B. Supplemental Information for AMPA, Glufosinate and Glyphosate Analysis

Table B.1 Sites and number of samples collected for AMPA, glufosinate and glyphosate analyses. Grey cells indicate no samples.

Site	2012	2013	2014	2015	2016	Total
AEP-P2	2	2	2	2		8
A-R1	2	2	2	2	2	10
BR-P1	2	2	2	2	2	10
BR-S2	2	1[z]	2	2		7
BR-S5	2	2	2	2	2	10
BR-R1	2	2	2	2		8
BR-R2	2	2	2	2		8
BR-R3	2	2	2	2	2	10
BR-R4	2	2	2	2		8
BR-R5	2	2	2	2	2	10
BR-R7	2	2	2	2		8
E-P1	2	2	2	2	2	10
E-S7	2	2	2	2		8
E-R1	2	2	2	2		8
E-R1a	2	2	2	2		8
E-R2	2	2	2	2		8
E-R2a	2	2	2	2	2	10
E-R3	2	2	2	2	2	10
E-R3a	2	2	2	2		8
E-R4a	2	2	2	2		8
-E-R5	2	2	2	2	2	10
E-R5a	2	2	2	2		8
E-R6	2	2	2	2		8
E-R7	2	2	2	2		8
E-R8a	2	2	2	2		8
LN-P1	2	2	2	2	2	10
LN-S4	2	2	2	2	2	10
LN-R1	2	2	2	2	2	10
LN-R2	2	2	2	2		8
LN-R3	2	2	2	1[z]		7
LN-R4	2	2	2	2	2	10
M-R1	2	2	2	2	2	10

Table B.1 continued.

Site	2012	2013	2014	2015	2016	Total
MV-P1	1[z]	2	2	2	2	9
MV-R1	2	2	2	1[z]		7
R-R1	2	2	2	2	2	10
R-R2	2	2	2	2		8
SMW-S2	2	2	2	2	2	10
SMW-R1	2	2	2	2		8
SMW-R2	2	2	2	2	2	10
SMC-S2	2	2	2	2		8
SMC-S3	2	2	2	2	2	10
SMC-R1	2	2	2	2	2	10
SMC-R3	2	2	2	2		8
SMC-R4	2	2	2	2		8
SME-P1	2	2	2	2	2	10
SME-R1a	2	2	2	2	2	10
SME-R2	2	2	2	2		8
T-P1a	2	2	2	2	2	10
T-S3	2	2	2	2	2	11
T-R1	2	2	2	2	2	10
T-R2	2	2	2	2	2	10
U-R2	2	2	2	2	2	9
U-R3	2	2	2	2		8
U-R4	2	2	1[z]	2		7
W-P1	2	2	2	2	2	10
W-P2	2	2	2	2	2	10
W-R1a	2	2	2	2	2	10
W-R2	2	2	2	2		8
Total samples	115	115	115	114	60	519

[z] Sample missed due to sampler error, no access or no flow

Appendix C. Concordance Statistics

Table C.1 Concordance statistics of *a posteriori* Kendall tests on the crop covers contributing to seven crop groups identified by Ward's cluster analysis. W = Kendall's coefficient of concordance. Irrigation districts by year are significant in a group at α = 0.05.

Group	Irrigation district by year	Spearman mean	W	Permutation probability
1	BRID 2006	0.97	0.97	0.00
1	BRID 2007	0.96	0.97	0.00
1	BRID 2011	0.95	0.95	0.00
1	BRID 2012	0.95	0.95	0.00
1	BRID 2013	0.97	0.97	0.00
1	BRID 2014	0.97	0.97	0.00
1	BRID 2015	0.97	0.97	0.00
1	BRID 2016	0.97	0.97	0.00
1	BRID 2017	0.97	0.97	0.00
1	BRID 2018	0.97	0.97	0.00
1	SMRID 2006	0.97	0.97	0.00
1	SMRID 2007	0.96	0.96	0.00
1	SMRID 2011	0.97	0.97	0.00
1	SMRID 2012	0.97	0.97	0.00
1	SMRID 2013	0.90	0.90	0.00
1	SMRID 2014	0.88	0.89	0.00
1	SMRID 2015	0.96	0.96	0.00
1	SMRID 2016	0.97	0.97	0.00
1	SMRID 2017	0.97	0.97	0.00
1	SMRID 2018	0.97	0.97	0.00
1	TID 2006	0.97	0.97	0.00
1	TID 2007	0.96	0.97	0.00
1	TID 2011	0.97	0.97	0.00
1	TID 2012	0.97	0.98	0.00
1	TID 2013	0.97	0.97	0.00
1	TID 2014	0.97	0.97	0.00
1	TID 2015	0.94	0.94	0.00
1	TID 2016	0.95	0.96	0.00
1	TID 2017	0.97	0.97	0.00
1	TID 2018	0.97	0.97	0.00
2	AID 2006	0.96	0.98	0.00
2	AID 2007	0.96	0.98	0.00
3	MVID 2006	1.00	1.00	0.00
3	MVID 2007	1.00	1.00	0.00
3	MVID 2011	1.00	1.00	0.00
3	MVID 2012	1.00	1.00	0.00
3	MVID 2013	1.00	1.00	0.00
3	MVID 2014	1.00	1.00	0.00
3	MVID 2015	0.99	0.99	0.00
3	MVID 2016	1.00	1.00	0.00
3	MVID 2017	1.00	1.00	0.00
3	MVID 2018	1.00	1.00	0.00
3	MVID 2014	1.00	1.00	0.00
3	MVID 2015	0.99	0.99	0.00
3	MVID 2016	1.00	1.00	0.00

Table C.1 *continued*.

Group	Irrigation district by year	Spearman mean	W	Permutation probability
3	MVID 2014	1.00	1.00	0.00
3	MVID 2015	0.99	0.99	0.00
3	MVID 2016	1.00	1.00	0.00
3	MVID 2017	1.00	1.00	0.00
3	MVID 2018	1.00	1.00	0.00
4	WID 2011	0.96	0.97	0.00
4	WID 2012	0.96	0.96	0.00
4	WID 2013	0.90	0.91	0.00
4	WID 2014	0.97	0.97	0.00
4	WID 2015	0.92	0.93	0.00
4	WID 2016	0.96	0.96	0.00
4	WID 2017	0.97	0.97	0.00
4	WID 2018	0.97	0.97	0.00
5	EID 2011	0.87	0.88	0.00
5	EID 2012	0.93	0.94	0.00
5	EID 2013	0.95	0.96	0.00
5	EID 2014	0.96	0.96	0.00
5	EID 2015	0.96	0.96	0.00
5	EID 2016	0.93	0.94	0.00
5	EID 2017	0.89	0.91	0.00
5	EID 2018	0.94	0.95	0.00
6	AID 2013	0.95	0.95	0.00
6	MID 2011	0.96	0.96	0.00
6	MID 2012	0.96	0.96	0.00
6	MID 2013	0.96	0.96	0.00
6	MID 2014	0.95	0.95	0.00
6	MID 2015	0.97	0.97	0.00
6	MID 2016	0.97	0.97	0.00
6	MID 2017	0.97	0.97	0.00
6	MID 2018	0.96	0.96	0.00
6	RID 2011	0.97	0.97	0.00
6	RID 2012	0.97	0.97	0.00
6	RID 2013	0.97	0.97	0.00
6	RID 2014	0.95	0.96	0.00
6	RID 2015	0.93	0.93	0.00
6	RID 2016	0.96	0.96	0.00
6	RID 2017	0.93	0.93	0.00
6	RID 2018	0.91	0.91	0.00
6	UID 2007	0.97	0.97	0.00
6	UID 2011	0.88	0.88	0.00
6	UID 2012	0.97	0.97	0.00
6	UID 2014	0.96	0.97	0.00
6	UID 2015	0.92	0.92	0.00
6	UID 2016	0.96	0.96	0.00
6	UID 2017	0.91	0.92	0.00
6	UID 2018	0.96	0.97	0.00

***Table C.1** continued.*

Group	Irrigation district by year	Spearman mean	W	Permutation probability
7	AID 2011	0.90	0.90	0.00
7	AID 2012	0.93	0.93	0.00
7	AID 2014	0.92	0.92	0.00
7	AID 2015	0.92	0.92	0.00
7	AID 2016	0.92	0.93	0.00
7	AID 2017	0.92	0.93	0.00
7	AID 2018	0.92	0.93	0.00
7	EID 2006	0.90	0.90	0.00
7	EID 2007	0.93	0.93	0.00
7	LNID 2006	0.93	0.93	0.00
7	LNID 2007	0.87	0.88	0.00
7	LNID 2011	0.95	0.95	0.00
7	LNID 2012	0.94	0.94	0.00
7	LNID 2013	0.91	0.91	0.00
7	LNID 2014	0.92	0.92	0.00
7	LNID 2015	0.93	0.93	0.00
7	LNID 2016	0.94	0.94	0.00
7	LNID 2017	0.93	0.93	0.00
7	LNID 2018	0.91	0.91	0.00
7	MID 2006	0.92	0.92	0.00
7	MID 2007	0.95	0.95	0.00
7	RID 2006	0.91	0.92	0.00
7	RID 2007	0.95	0.96	0.00
7	UID 2006	0.92	0.93	0.00
7	WID 2006	0.87	0.87	0.00
7	WID 2007	0.90	0.90	0.00

Table C.2 Concordance statistics of global Kendall tests on seven crop groups identified by Ward's cluster analysis. W = Kendall's coefficient of concordance. All seven groups are significant at $\alpha = 0.05$, using permutation tests.

Group	1	2	3	4	5	6	7
W	0.96	0.98	1.00	0.96	0.94	0.95	0.92
F	738.43	44.15	2710.12	153.53	103.88	506.46	299.16
Probability of F	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chi-squared	3146.43	213.17	1086.39	833.98	816.95	2700.69	2615.44
Permutation Probability	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix D. Crop and Land Cover of Irrigation Districts, Pesticide Detection Frequencies and Sample Sizes

Table D.1 Average crop cover (km^2) and percentage of total land cover by irrigation district for the years monitored (2006, 2007, 2011–2018) (Alberta Agriculture and Food 2007; Alberta Agriculture and Forestry 2015-2019; Alberta Agriculture and Rural Development 2008-2014).

Irrigation district	Cereals		Forage		Oilseeds		Specialty		Other	
	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%
AID	1275	28	2552	59	142	3	24	1	369	10
BRID	90095	38	43573	18	24957	10	69101	29	11705	5
EID	83801	28	12982 7	44	37070	13	43171	15	1,800	1
LNID	39800	22	10632 7	59	24750	14	5886	3	3004	2
MID	6385	35	8310	45	3063	17	497	3	36	0
MVID	389	11	3096	85	48	1	76	2	37	1
RID	16004	34	22298	48	7312	16	1104	2	76	0
SMRID	137907	36	93854	24	51515	13	96224	25	4998	1
TID	26182	32	20523	25	3165	4	29473	36	3713	4
UID	12362	36	14784	43	4960	17	1206	4	190	1
WID	25187	27	37942	40	13760	15	6525	6	11589	12

Table D.2 Most common pesticide detection frequencies (%) by site (2006, 2007, 2011–2018).

Irrigation district	Site	Glyphosate	2,4-D	Bentazon	Bromoxynil	Boscalid	Clopyralid	Dicamba	Dichlorprop	EPTC	Fluroxypyr	Hexazinone	MCPA	Mecoprop	Simazine
AEP	AEP-P2	12.5	89.3	0.0	7.1	0.0	7.1	32.1	3.6	0.0	8.3	0.0	14.3	42.9	0.0
	AEP-P3	0.0	63.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18.5	0.0
	AEP-S2	0.0	28.6	0.0	0.0	25.0	3.6	3.6	0.0	0.0	8.3	0.0	7.1	3.6	0.0
AID	A-R1	0.0	78.9	0.0	2.6	0.0	0.0	18.4	0.0	0.0	0.0	0.0	10.5	0.0	0.0
BRID	BR-P1	0.0	95.0	8.3	0.0	0.0	5.0	7.5	0.0	0.0	29.2	0.0	20.0	0.0	0.0
	BR-R1	0.0	85.0	0.0	0.0	0.0	2.5	7.5	0.0	0.0	16.7	0.0	25.0	0.0	6.3
	BR-R2	12.5	92.5	8.3	12.5	25.0	7.5	27.5	15.0	0.0	37.5	56.3	37.5	2.5	21.9
	BR-R3	10.0	89.7	8.7	0.0	6.7	2.6	17.9	5.1	12.9	8.7	20.0	20.5	0.0	16.1
	BR-R4	0.0	52.5	8.3	5.0	0.0	5.0	17.5	5.0	3.1	12.5	25.0	15.0	0.0	12.5
	BR-R5	0.0	95.0	4.2	0.0	12.5	5.0	20.0	0.0	3.1	12.5	18.8	22.5	2.5	18.8
	BR-S1	0.0	95.0	4.2	2.5	0.0	5.0	10.0	0.0	0.0	16.7	0.0	30.0	0.0	0.0
	BR-S2	14.3	92.9	8.3	0.0	0.0	10.7	21.4	7.1	0.0	8.3	100.0	28.6	7.1	55.0
	BR-S3	0.0	92.5	8.3	0.0	6.3	2.5	12.5	0.0	0.0	29.2	6.3	27.5	2.5	15.6
	BR-S4a	0.0	93.5	8.3	0.0	6.3	0.0	9.7	0.0	0.0	20.8	6.3	16.1	0.0	9.7
	BR-S5	0.0	95.0	4.2	0.0	12.5	0.0	15.0	5.0	3.1	8.3	18.8	22.5	2.5	18.8
EID	E-P1	0.0	57.5	4.2	0.0	0.0	0.0	10.0	0.0	0.0	0.0	0.0	5.0	10.0	0.0
	E-R1	0.0	44.4	0.0	0.0	0.0	0.0	52.8	0.0	0.0	8.3	0.0	8.3	5.6	0.0
	E-R2	37.5	52.8	0.0	2.8	0.0	0.0	61.1	2.8	0.0	0.0	0.0	5.6	0.0	0.0
	E-R2a	30.0	67.9	9.5	3.6	0.0	3.6	60.7	0.0	0.0	9.5	13.3	17.9	0.0	0.0
	E-R3	10.0	72.2	4.2	2.8	0.0	0.0	47.2	0.0	3.6	4.2	0.0	19.4	11.1	0.0
	E-R4a	0.0	46.4	4.2	3.6	0.0	0.0	53.6	0.0	0.0	4.2	0.0	10.7	3.6	0.0
	E-R5	10.0	69.4	0.0	2.8	0.0	2.8	36.1	0.0	0.0	0.0	0.0	2.8	0.0	0.0
	E-R8a	37.5	78.6	4.3	3.6	6.7	7.1	82.1	0.0	0.0	0.0	0.0	32.1	3.6	3.6
	E-S1	0.0	62.5	0.0	0.0	0.0	0.0	25.0	0.0	0.0	4.2	0.0	5.0	7.5	0.0
	E-S2	0.0	55.3	4.3	2.6	6.3	2.6	10.5	0.0	0.0	0.0	0.0	21.1	13.2	0.0
	E-S3	0.0	60.0	4.2	0.0	0.0	0.0	27.5	0.0	0.0	4.2	6.3	10.0	12.5	0.0
	E-S4	0.0	62.5	0.0	0.0	0.0	0.0	32.5	0.0	0.0	4.2	0.0	2.5	2.5	0.0
	E-S5	0.0	72.5	4.2	0.0	0.0	0.0	2.5	0.0	0.0	8.3	0.0	7.5	0.0	0.0

***Table D.2** continued.*

Irrigation district	Site	Glyphosate	2,4-D	Bentazon	Bromoxynil	Boscalid	Clopyralid	Dicamba	Dichlorprop	EPTC	Fluroxypyr	Hexazinone	MCPA	Mecoprop	Simazine
EID	E-S6	0.0	32.5	4.2	0.0	0.0	0.0	7.5	0.0	0.0	8.3	0.0	5.0	2.5	0.0
	E-S8	0.0	87.5	4.2	0.0	6.3	3.1	81.3	0.0	0.0	4.2	6.3	21.9	21.9	3.1
LNID	LN-P1	0.0	12.5	4.2	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	5.0	2.5	0.0
	LN-R1	10.0	82.5	12.5	0.0	0.0	0.0	7.5	0.0	0.0	4.2	0.0	25.0	0.0	0.0
	LN-R2	0.0	80.0	0.0	5.0	6.3	2.5	30.0	2.5	0.0	4.2	0.0	62.5	0.0	0.0
	LN-R3	28.6	86.2	4.8	3.4	0.0	6.9	17.2	0.0	0.0	9.5	0.0	44.8	3.4	0.0
	LN-R4	40.0	82.1	0.0	3.6	0.0	7.1	35.7	0.0	0.0	12.5	0.0	64.3	14.3	0.0
	LN-S1	0.0	32.5	0.0	0.0	0.0	5.0	2.5	0.0	0.0	4.2	0.0	5.0	0.0	0.0
	LN-S2	0.0	80.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.2	0.0	15.0	0.0	0.0
	LN-S3	0.0	65.0	0.0	2.5	0.0	2.5	20.0	0.0	0.0	12.5	0.0	35.0	2.5	0.0
	LN-S4	0.0	80.0	0.0	0.0	0.0	5.0	2.5	0.0	0.0	0.0	0.0	27.5	0.0	3.1
	LN-S5	0.0	85.0	4.2	0.0	0.0	0.0	17.5	0.0	3.1	4.2	0.0	35.0	5.0	0.0
MID	M-P1	0.0	52.5	0.0	0.0	0.0	2.5	10.0	0.0	0.0	8.3	0.0	7.5	0.0	0.0
	M-R1	10.0	57.5	4.2	5.0	0.0	5.0	17.5	5.0	0.0	12.5	0.0	27.5	0.0	3.1
	M-S1	0.0	68.8	4.2	3.1	0.0	6.3	12.5	0.0	0.0	16.7	0.0	28.1	0.0	0.0
MVID	MV-P1	0.0	32.5	0.0	0.0	0.0	2.5	5.0	0.0	0.0	4.2	0.0	2.5	0.0	0.0
	MV-R1	0.0	41.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	7.7	0.0	0.0
RID	R-P1	0.0	80.0	4.2	0.0	0.0	2.5	15.0	0.0	0.0	12.5	0.0	20.0	0.0	0.0
	R-R1	30.0	85.0	4.2	0.0	6.3	2.5	25.0	2.5	0.0	29.2	0.0	30.0	2.5	3.1
	R-R2	25.0	76.9	4.3	0.0	13.3	7.7	15.4	2.6	0.0	26.1	0.0	17.9	0.0	0.0
SMRID	SMC-P1	0.0	97.5	12.5	0.0	0.0	7.5	12.5	5.0	0.0	29.2	0.0	42.5	0.0	0.0
	SMC-R1	20.0	95.0	4.2	0.0	12.5	2.5	5.0	2.5	21.9	37.5	0.0	30.0	2.5	0.0
	SMC-R3	25.0	100.0	0.0	0.0	18.8	2.5	10.0	0.0	9.4	25.0	0.0	37.5	5.0	0.0
	SMC-R4	12.5	97.5	12.5	2.5	6.3	0.0	10.0	5.0	0.0	29.2	0.0	45.0	2.5	0.0
	SMC-S1	0.0	100.0	4.2	2.5	12.5	0.0	12.5	0.0	12.5	45.8	0.0	37.5	7.5	0.0
	SMC-S2	12.5	97.5	4.2	2.5	12.5	5.0	5.0	2.5	15.6	50.0	0.0	40.0	2.5	0.0
	SMC-S3	30.0	100.0	8.3	0.0	6.3	2.5	15.0	5.0	9.4	29.2	0.0	50.0	0.0	0.0

Table D.2 *continued.*

Irrigation district	Site	Glyphosate	2,4-D	Bentazon	Bromoxynil	Boscalid	Clopyralid	Dicamba	Dichlorprop	EPTC	Fluroxypyr	Hexazinone	MCPA	Mecoprop	Simazine
SMRID	SME-P1	33.3	94.9	13.0	0.0	18.8	2.6	25.6	7.7	0.0	30.4	0.0	51.3	0.0	0.0
	SME-R1a	50.0	100.0	4.2	0.0	31.3	3.1	3.1	0.0	0.0	16.7	0.0	18.8	6.3	0.0
	SME-R2	25.0	100.0	8.3	0.0	18.8	3.1	3.1	0.0	0.0	25.0	6.3	21.9	0.0	0.0
	SME-S1	0.0	95.0	0.0	0.0	18.8	0.0	2.5	2.5	0.0	16.7	6.3	30.0	2.5	0.0
	SMW-P1	0.0	80.0	4.2	2.5	0.0	2.5	5.0	2.5	0.0	8.3	0.0	17.5	0.0	0.0
	SMW-R1	37.5	90.0	12.5	2.5	0.0	7.5	22.5	2.5	0.0	29.2	0.0	40.0	5.0	0.0
	SMW-R2	50.0	95.0	8.3	0.0	6.3	2.5	32.5	2.5	6.3	25.0	0.0	40.0	0.0	0.0
	SMW-S2	22.2	87.1	0.0	3.2	0.0	3.2	3.2	0.0	0.0	8.3	0.0	22.6	0.0	0.0
TID	T-P1a	20.0	96.9	4.2	0.0	0.0	9.4	0.0	0.0	0.0	33.3	0.0	34.4	0.0	0.0
	T-P2	0.0	97.5	12.5	7.5	6.3	5.0	10.0	5.0	3.1	29.2	0.0	40.0	0.0	0.0
	T-R1	11.1	97.5	16.7	2.5	18.8	7.5	45.0	5.0	21.9	29.2	0.0	42.5	5.0	0.0
	T-R2	22.2	100.0	20.8	5.0	18.8	2.5	62.5	5.0	21.9	29.2	0.0	52.5	5.0	0.0
	T-S2	0.0	100.0	16.7	0.0	12.5	7.5	35.0	10.0	18.8	16.7	0.0	40.0	7.5	0.0
	T-S3	20.0	97.5	20.8	2.5	12.5	2.5	57.5	10.0	21.9	20.8	0.0	52.5	7.5	0.0
UID	U-P1	0.0	5.0	0.0	2.5	0.0	0.0	7.5	0.0	0.0	0.0	0.0	7.5	0.0	3.1
	U-R2	60.0	67.5	12.5	0.0	0.0	0.0	75.0	0.0	0.0	16.7	0.0	20.0	2.5	0.0
	U-S1	0.0	37.5	0.0	2.5	0.0	2.5	62.5	0.0	0.0	8.3	0.0	12.5	0.0	3.1
WID	W-P1	0.0	95.0	0.0	0.0	0.0	0.0	37.5	2.5	0.0	0.0	0.0	20.0	47.5	0.0
	W-P2	33.3	97.4	8.7	0.0	0.0	2.6	46.2	0.0	0.0	0.0	0.0	23.1	66.7	0.0
	W-R1a	0.0	96.9	4.2	3.1	0.0	3.1	25.0	0.0	0.0	8.3	0.0	28.1	46.9	0.0
	W-R2	50.0	94.9	13.0	12.8	6.7	7.7	28.2	5.1	0.0	13.0	0.0	41.0	15.4	0.0
	W-S1	0.0	95.0	0.0	2.5	0.0	2.5	40.0	5.0	0.0	0.0	0.0	32.5	42.5	0.0
	W-S2	0.0	95.0	0.0	0.0	0.0	2.5	35.0	0.0	0.0	0.0	0.0	37.5	27.5	0.0
	W-S3	0.0	97.5	4.2	2.5	0.0	5.0	40.0	2.5	0.0	8.3	0.0	35.0	62.5	0.0
	W-S4	0.0	97.5	0.0	2.5	0.0	12.5	40.0	2.5	0.0	12.5	0.0	25.0	60.0	0.0

Table D.3 Number of site types by irrigation district with at least seven years of data.

Irrigation district	Primary			Secondary	Return	
	Reservoir	River	Canal		Infrastructure	Watershed
AEP	0	1	1	0	0	0
AID	0	0	0	0	0	1
BRID	1	0	0	5	2	3
EID	1	0	0	7	5	2
LNID	0	1	0	5	2	2
MID	1	0	0	1	0	1
MVID	1	0	0	0	1	0
RID	1	0	0	0	0	2
SMRID	1	0	2	5	5	2
TID	0	0	2	2	2	0
UID	0	1	0	1	1	0
WID	2	0	0	4	1	1

Table D.4 Sample size (n) for detection frequencies of the eight most frequently detected pesticides (grouped into three columns) for each irrigation district.

Irrigation District	AMPA/ Glyphosate	2,4-D/ Dicamba/ MCPA/mecoprop	Bentazon/ Fluroxypr
AEP	8	83	35
AID	10	38	22
BRID	71	418	251
EID	72	538	355
LNID	55	377	237
MID	10	112	72
MVID	16	79	47
RID	18	119	71
SMRID	98	574	359
TID	38	232	144
UID	10	120	72
WID	37	310	190

Table D.5 Detection frequencies (%) for the eight most frequently detected pesticides by hierarchical clusters of crop cover.[z] Grey cells represent samples where pesticides were not measured.

Group	Crop covers	2,4-D	AMPA	Bentazon	Dicamba	Fluroxypyr	Glyphosate	MCPA	Meco-prop
1	Mixed crops, most specialty	93.6	11.1	8.1	17.4	24.1	18.8	33.3	2.4
2[z]	>60% forage (AID 2006-7)	87.5			62.5			0.0	0.0
3	>80% forage (MVID)	36.7	6.3	0.0	2.5	2.1	0.0	5.1	0.0
4	Mixed crops, other (WID)	95.3	5.4	3.7	26.0	5.3	18.9	28.0	40.9
5	Mixed crops, some specialty (EID)	54.7	5.6	3.1	33.6	3.9	15.3	10.4	4.4
6	Mixed crops, most oilseed	55.8	15.0	3.7	25.7	14.2	30.0	19.5	0.7
7	Mixed crops, >50% forage	75.6	11.1	2.4	26.9	5.1	11.1	26.9	10.4

[z]Group 2 results included one district, AID, for only two years (2006 and 2007) with only two sites. Fewer pesticides were analyzed in these early years than in later years when the analysis suite was expanded.

Table D.6 Sample size (n) for detection frequencies of the eight most frequently detected pesticides by crop groups determined from Ward's agglomerative hierarchical clustering on Euclidean distances of crop cover per district and year.

Group	2,4-D	AMPA	Bentazon	Dicamba	Fluroxypyr	Glyphosate	MCPA	Mecoprop	Meco-prop
1	Mixed crops, most specialty	93.6	11.1	8.1	17.4	24.1	18.8	33.3	2.4
2[z]	>60% forage (AID 2006-7)	87.5			62.5			0.0	0.0
3	>80% forage (MVID)	36.7	6.3	0.0	2.5	2.1	0.0	5.1	0.0
4	Mixed crops, other (WID)	95.3	5.4	3.7	26.0	5.3	18.9	28.0	40.9
5	Mixed crops, some specialty (EID)	54.7	5.6	3.1	33.6	3.9	15.3	10.4	4.4
6	Mixed crops, most oilseed	55.8	15.0	3.7	25.7	14.2	30.0	19.5	0.7
7	Mixed crops, >50% forage	75.6	11.1	2.4	26.9	5.1	11.1	26.9	10.4

[z]Group 2 results included one district, AID, for only two years (2006 and 2007) with only two sites. Fewer pesticides were analyzed in these early years than in later years when the analysis suite was expanded.

Table D.7 Sample size (n) by year for the eight most frequently detected pesticides (grouped into three columns).

Year	AMPA/ Glyphosate	2,4-D/ Dicamba/ MCPA/Mecoprop	Bentazon/ Fluroxypyr
2006	0	268	0
2007	0	268	0
2011	0	291	0
2012	96	318	0
2013	96	316	316
2014	98	319	319
2015	94	317	317
2016	59	301	301
2017	0	301	301
2018	0	301	301

Table D.8 Annual detection frequencies (%) per river sub-basin for the eight most frequently detected pesticides. BR= Bow River; OMR= Oldman River; RDR= Red Deer River; SSR= South Saskatchewan River. Grey cells represent years were pesticides were not measured.

Pesticide	Sub-basin	2006	2007	2011	2012	2013	2014	2015	2016	2017	2018
2,4-D	BR	98.3	91.7	92.3	73.3	83.3	83.3	64.4	86.3	38.5	65.4
	OMR	82.0	82.8	84.5	77.3	79.5	80.3	50.0	77.8	56.0	61.3
	RDR	100.0	94.4	97.4	85.7	81.5	70.9	76.8	75.9	41.1	49.1
	SSR	100.0	100.0	100.0	100.0	89.7	100.0	100.0	95.0	97.5	97.5
MCPA	BR	33.3	28.3	3.8	5.0	8.3	13.3	33.9	41.2	9.6	7.7
	OMR	29.7	29.7	22.3	19.3	27.2	34.9	32.7	47.9	14.9	4.9
	RDR	16.7	33.3	5.1	14.3	18.5	18.2	21.4	42.6	14.3	7.3
	SSR	81.3	100.0	52.5	5.0	10.3	52.5	27.5	30.0	22.5	7.5
Dicamba	BR	71.7	38.3	26.9	11.7	13.3	16.7	13.6	13.7	1.9	9.6
	OMR	45.3	28.1	26.4	10.7	23.2	28.3	8.7	10.4	7.1	11.3
	RDR	91.7	55.6	74.4	48.2	48.1	32.7	41.1	55.6	16.1	14.5
	SSR	59.4	34.4	10.0	0.0	0.0	0.0	0.0	2.5	0.0	2.5
Glyphosate	BR				20.0	5.0	10.0	5.0	0.0		
	OMR				25.0	2.2	34.8	9.5	9.4		
	RDR				28.6	0.0	28.6	14.3	40.0		
	SSR				56.3	0.0	43.8	6.3	25.0		
Fluroxypyr	BR					3.3	1.7	16.9	9.8	1.9	17.3
	OMR					4.6	19.7	14.0	16.7	0.0	26.8
	RDR					1.9	3.6	7.1	14.8	0.0	0.0
	SSR					5.1	60.0	35.0	15.0	0.0	67.5
AMPA	BR				15.0	5.0	0.0	5.0	0.0		
	OMR				38.6	2.2	6.5	0.0	0.0		
	RDR				14.3	0.0	7.1	0.0	20.0		
	SSR				43.8	0.0	12.5	0.0	12.5		
Mecoprop	BR	35.0	21.7	19.2	8.3	6.7	8.3	8.5	13.7	0.0	0.0
	OMR	6.3	0.0	6.8	0.7	3.3	1.3	0.0	0.0	0.0	0.0
	RDR	52.8	27.8	56.4	19.6	31.5	23.6	21.4	27.8	5.4	9.1
	SSR	3.1	0.0	15.0	0.0	7.7	0.0	0.0	2.5	0.0	0.0
Bentazon	BR					0.0	6.7	3.4	7.8	1.9	1.9
	OMR					2.0	19.1	1.3	10.4	0.0	2.1
	RDR					0.0	1.8	3.6	13.0	0.0	0.0
	SSR					5.1	20.0	0.0	10.0	0.0	0.0

Table D.9 Sample size (n) by year and season for the eight most frequently detected pesticides (grouped into three columns)

Season	Year	AMPA/ Glyphosate	2,4-D/ Dicamba/ MCPA/Mecoprop	Bentazon/ Fluroxypr
Early (May 28th to June 15th)	2007	48	79	0
	2012	47	79	79
	2013	49	80	80
	2014	48	78	78
	2015	0	75	75
	2016	0	74	74
	2017	0	76	76
	2018	0	134	0
Mid (June 16th to August 3rd)	2006	0	134	0
	2007	0	146	0
	2011	0	114	0
	2012	0	133	133
	2013	0	80	80
	2014	0	160	160
	2015	0	76	76
	2016	0	152	152
	2017	0	150	150
	2018	0	134	0
Late (August 4th to September 4th)	2006	0	134	0
	2007	0	145	0
	2011	48	125	0
	2012	49	104	104
	2013	49	159	159
	2014	46	79	79
	2015	59	150	150
	2016	0	75	75
	2017	0	75	75
	2018	48	79	0