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A study carried out under the Canada-Alberta Environmentally Sustainable Agriculture Agreement (CAESA)

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Introduction

Federal and Provincial agencies have collected pesticide residue data from Alberta surface waters since 1971. Much of the sampling effort has focused on fixed locations in major rivers within the National Parks, at provincial and international boundaries, and at key locations above and below major cities. With the exception of 2,4-D, lindane, and alpha-BHC, which have been detected in at least 20% of these samples, pesticide detections have been infrequent. Generally, reported concentrations have been well below Canadian Water Quality Guidelines (CWQG) for the protection of aquatic life and for irrigation use (CCME 1997). Although the historical database indicates that pesticides have not affected the quality of water for these sensitive uses, it provides an incomplete picture of pesticides in Alberta surface waters. Few sampling sites were located in intensive agricultural areas and no data exist for small streams and lakes. Furthermore, the standard list of pesticides being monitored was outdated.

The purpose of this scoping-level study was to determine if agricultural pesticides currently sold and used in large quantities across Alberta were detectable in small streams and lakes and to compare their concentrations with CWQG for the protection of aquatic life and for irrigation. We hypothesized that the pattern of detections would be influenced by the intensity of pesticide use in the drainage basins and by the median annual runoff. Using data from 1995 and 1996, we tested our hypotheses by examining pesticide detections in streams and lakes draining land where pesticide use differs, and by comparing patterns of detections in lakes located in different runoff zones.

Methods

Site Selection

Census data for pesticide expenditures (Statistics Canada 1991), incorporated in the Soil Landscapes of Canada database (Shields *et al.* 1991), were used to rank soil landscape units in Alberta, thereby providing an indication of pesticide use (MacAlpine *et al.* 1995, Anderson *et al.* 1996). Units which ranked in the upper quartile were considered to have high pesticide use, those which ranked between the 25^{th} and 75^{th} percentiles were labeled as having medium pesticide use, and those in the lower quartile had low pesticide use (Figure 1). High use of pesticides occurs mainly in central and southern Alberta (Lloydminster - Edmonton - Calgary - Lethbridge), but high use areas can also be found in north central (northwest of Edmonton) and northwestern (Grande Prairie - Peace River) Alberta.

Sequential searches in the Soil Landscapes of Canada database were used to identify areas in the province which are similar in terms of soil development (chernozemic, luvisolic, and solenetzic), soil texture (fine-grained loam or clay soils) and local topography (typified by long slopes). By selecting streams and lakes in these areas, we ensured that soil landscape features, which can influence contaminant transport in surface runoff, were comparable among drainage basins.

Alberta is typified by a wide range of climatic zones that receive significantly different amounts of runoff (PFRA 1994). Most areas of central and southern Alberta have very low amounts of runoff (5-20 mm per year); north central Alberta receives 30-75 mm and northwestern Alberta receives more than 75 mm of runoff annually (Figure 1).

Twenty-seven streams with comparable soil landscape features were chosen in areas of high, medium and low pesticide use. Streams draining the appropriate soil landscape types could not be identified in areas of high runoff; therefore, runoff zones were not incorporated in the study design for streams. A total of 25 small lakes were selected in areas of high and low pesticide use; these lakes could also be assigned to zones of high, medium and low runoff (Figure 1).

Selection of Pesticides for Monitoring
A compilation of pesticide sales records from major agricultural chemical distributors in Alberta for the period 1988 – 1993, providing information for 95 active ingredients, was used to identify pesticides which should be monitored (Cotton and Byrtus 1995). For this project, 13 compounds, primarily herbicides, (Table 1) were retained for monitoring because the quantities used in agricultural areas of the province were large or because application rates were such that, based on sales records, a large surface area of the province could be treated. Several pesticides meeting these criteria, such as glyphosate and sulfonylurea compounds, were excluded because of analytical costs and limitations. Although many of these pesticides have been monitored in Alberta previously, this was the first time that imazamethabenz had been analyzed in water.

Sampling Methods
Sampling was carried out during the open water season in 1995 and 1996. Each location was sampled at least twice in 1995: once in early July, then either after a rainstorm during the summer, or in the fall. In 1996, an additional sample was taken from streams during spring runoff and from lakes in June.

Surface grab samples were collected from streams and small lakes, while surface composite samples, consisting of 10 to 15 sub-samples, were collected from larger lakes. The analytical laboratory provided sample bottles that were cleaned to trace organic standards. Sampling equipment was cleaned, then rinsed with hexane and acetone, and wrapped in aluminum foil between sampling sites.

Laboratory Methods
Samples (2 L, unfiltered) were extracted with dichloromethane (DCM and extracts were analyzed by Gas Chromatography-Mass Spectroscopy using Selected Ion Monitoring (GC/MS – SIM) (Bruns *et al.* 1991); the method detection limit was 0.02 ug/L (ppb) for most analyses.

Quality Assurance/Quality Control (QA/QC)
QA/QA samples (26 in total), either splits, spikes, or blanks, were submitted 'blind' with each batch of samples that was sent to the analytical laboratory. The absence of detections in five blank samples indicates that the possibility of false positives is low. Reported concentrations in 11 pairs of split samples varied by up to 25%. This variability suggests that some compounds may not have been detected (*i.e.*, there is a possibility of false negative detections). Twenty-eight spike recoveries from environmental samples were below 100%; recoveries for four spikes, in a blank sample, were higher to much higher than 100%. Therefore, actual concentrations in water may be higher than reported (detection frequency and reported concentrations may be biased low rather than high). In light of these QA/QC data, the database for this study is believed to provide a conservative indication of pesticide contamination in Alberta streams and lakes.

Results

Detection Frequency
At least one pesticide was detected in 44% of the stream samples (n=110) and 51% of the lake samples (n = 123) (Table 2); in many samples, several pesticides were detected (up to six per sample). Of the 13 compounds analyzed, 2,4-D, MCPA, imazamethabenz, triallate, dicamba, bromoxynil, and picloram were detected in both lakes and streams (Table 3). Trifluralin and lindane were detected in streams, diclofop-methyl was detected in lakes, but fenoxaprop-p-ethyl, ethalfluralin, and carbathiin were not detected in either lakes or streams. The four most commonly detected compounds overall were 2,4-D, MCPA, imazamethabenz and triallate.

The most notable difference in detections between 1995 and 1996 was an increase in imazamethabenz detection frequency from 3.4% in 1995 to 16.0% in 1996. Imazamethabenz is used mainly on wheat and barley in Alberta; seeded acreage of these two crops increased by about 15% between 1995 and 1996 (AAFRD 1997).

Influence of Intensity of Pesticide Use

Streams and lakes draining land with high pesticide use had, on average, higher detection frequencies per sample, higher peak concentrations, and a larger number of pesticides detected than those draining basins with low pesticide use (Table 2). Residues of MCPA, bromoxynil, 2,4-D, picloram and triallate were, however, detected in some samples from small lakes in non-agricultural areas (Table 3).

In high use areas, frequency of detection, concentration of pesticides, and number of detections were generally highest in zones of high runoff and lowest in zones of low runoff (Table 2).

Compliance with Canadian Surface Water Quality Guidelines

Currently, Canadian Surface Water Quality Guidelines for the protection of aquatic life are available for nine of the 13 pesticides monitored in this study. One lindane detection (streams) and one triallate detection (lakes), both in areas of high pesticide use, did not comply with guidelines, but all other recorded concentrations were well below guidelines (Table 3).

There are also Canadian Water Quality Guidelines for irrigation for four of the 13 pesticides monitored. These guidelines are more restrictive than those for the protection of aquatic life and were therefore exceeded more frequently. All detections of dicamba in both streams and lakes exceeded the irrigation guideline, which is below the method detection limit used in this study. Most detectable concentrations of MCPA also exceeded the irrigation guideline, as did some of the bromoxynil detections. Most incidences of non-compliance in lakes and streams occurred in areas of high pesticide use.

Discussion and Conclusions

The results of pesticide monitoring conducted on a selection of streams and small lakes across Alberta confirm that several pesticides currently used in the province occur at measurable concentrations in surface waters. There are at least 96 active ingredients in pesticides sold on the Alberta market, and well over 40 of these are in common use. Monitoring of 13 of these compounds can only provide a scoping-level picture of the incidence of pesticide contamination in the province’s surface waters.

Of the nine compounds detected in this survey, all except imazamethabenz and diclofop-methyl had been detected previously in large Alberta rivers (Anderson 1995). Detection frequency in this study was higher than reported previously. However, lindane was detected considerably more frequently in past and usually at concentrations well below the method detection limit for this study. Most compounds detected in this study have also been found in surface waters in Manitoba (Currie and Williamson 1997) and in Saskatchewan lakes and dugouts (Donald and Syrgiannis 1995, Grover and Cessna 1996).

Comparing concentration patterns in small and large streams, Wauchope *et al.* (1994) describe short pulses of high pesticide concentrations in small streams and longer pulses of low pesticide concentrations in larger streams as being most typical. However, the maximum concentrations reported in this study tend to be lower than those reported for large streams in the long-term Alberta database. Several factors related to sampling frequency and climate can account for this situation. Times of peak pesticide concentrations could have easily been missed as a result of the low sampling frequency and the short duration of our sampling program. Furthermore, in 1995 and 1996, heavy rains causing runoff did not occur after the main period of herbicide application in drainage basins where pesticide use is most intense.

Although several pesticides monitored in this study have industrial, municipal, and domestic uses in addition to agricultural applications, our results indicate that there is a positive relationship between the intensity of agricultural pesticide use and the level of pesticide contamination of surface waters, within a drainage basin. Detection frequency, concentration, and non-compliance with surface water quality guidelines tend to be higher in areas of high pesticide use than in areas of low pesticide use. However, local agricultural use patterns do not explain all occurrences of pesticides in this study. In one instance, roadside spraying for weed control was identified as the most likely reason for a picloram detection in a small, remote lake in northwestern Alberta. In other instances, there was no clear explanation for the presence of pesticides. Detections in lakes and streams draining land with little or no use of pesticides suggests that atmospheric transport and deposition may be contributing to the presence of pesticides in Alberta surface waters. Such pathways of pesticide entry to water bodies have been documented in other parts of Canada (Muir and Grift 1995, Waite *et al.* 1995).

Higher frequencies of pesticide detections have been reported in surface waters after rain events (*e.g.*, Senseman *et al.* 1997) and especially when rain occurs shortly after pesticide application (*e.g.*, Wauchope *et al.* 1994). Our results also indicate that for a given level of pesticide use, regional differences in pesticide detections may be related to annual runoff, and therefore to the amount of precipitation. Consequently, streams and lakes in high runoff zones may have a higher risk of becoming contaminated than surface waters in low runoff zones.

Canadian Water Quality Guidelines have yet not been determined for several of the pesticides monitored in this study. Where guidelines exist, compliance was high with guidelines for the protection of aquatic life, but was low with irrigation guidelines. These results suggest that herbicide use could have detrimental effects on sensitive, irrigated crops, although in this study, few of the streams and none of the lakes monitored supply irrigation water.

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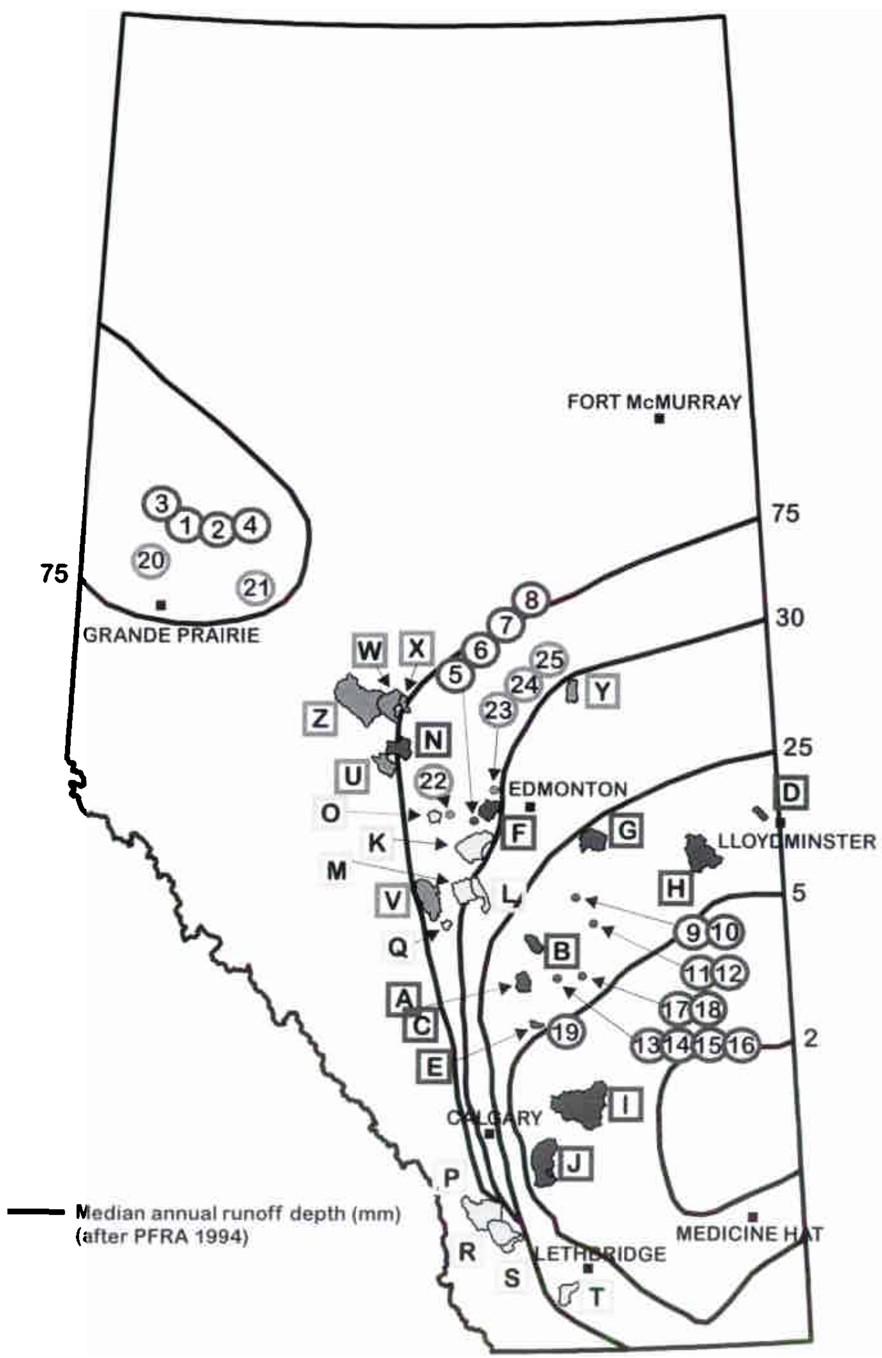
FIGURE 1: Locations of Streams and Lakes



LAKES

HIGH PESTICIDE USE

1 BELLOY RESERVOIR
2 CODESA LAKE
3 LAKE N.E. RYCROFT
4 LAKE NEAR EAGLESHAM
5 LONGHURST LAKE
6 H442S1
7 H442S2
8 H442S3
9 H508S1
10 H508L1
11 H512S1
12 WINDSOR LAKE
13 GADSBY LAKE
14 H515S1
15 H515S2
16 H515S3
17 FOXALL SOUTH
18 H537S1
19 BRACONNIER RESERVOIR

LOW PESTICIDE USE

20 LAKE IN SADDLE HILLS
21 DOLLAR LAKE NORTH
22 L703S1
23 CHICKAKOO LAKE
24 L440S1
25 MUIR LAKE

STREAMS

HIGH PESTICIDE USE

A RAY CREEK
B HAYNES CREEK
C THREEHILLS CREEK
D STRETTON CREEK
E RENWICK CREEK
F ATIM CREEK
G AMISK CREEK
H BUFFALO CREEK
I CROWFOOT CREEK
J WEST ARROWWOOD CREEK
J ARROWWOOD CREEK

MEDIUM PESTICIDE USE

K STRAWBERRY CREEK
L LLOYD CREEK
M BLINDMAN RIVER
N LITTLE PADDLE RIVER
O TOMAHAWK CREEK
P WILLOW CREEK
Q BLOCK CREEK
R TROUT CREEK
S MEADOW CREEK
T PRAIRIE BLOOD CREEK

LOW PESTICIDE USE

U PADDLE RIVER
V ROSE CREEK
W CHRISTMAS CREEK
X GOOSE CREEK
Y FLAT CREEK
Z SAKWATAMAU RIVER

Table 1. List of Pesticides Selected for Monitoring.

	Pesticide	Registered Use in Alberta
Herbicides	Bromoxynil	agricultural
	Fenoxaprop-p-ethyl	agricultural
	Diclofop-methyl	agricultural
	Triallate	agricultural
	Ethalfluralin	agricultural
	Imazamethabenz	agricultural
	Trifluralin	agricultural + domestic (limited)
	Dicamba	agricultural + industrial + domestic + landscape
	MCPA	agricultural + industrial + landscape
	2,4-D	agricultural + industrial + domestic + landscape
	Picloram	industrial + landscape + agricultural (discontinued)
Fungicide	Carbathiin	agricultural + municipal (limited)
Insecticide	Lindane	agricultural

Table 2. Pesticide Detections in Alberta Streams and Lakes which Drain Land Receiving HIGH, MEDIUM and LOW Quantities of Pesticides, and for Lakes in Different Runoff Zones (1995 & 1996).

	Pesticide Use	Runoff Zone (mm per year)	# Samples	# Samples with Detections	% Samples with Detections	Total # of Detections	Average # of Detections per Sample
Streams	HIGH		42	31	73.8%	67	1.6
(27 sites)	MEDIUM		39	9	23.1%	12	0.3
	LOW		29	6	20.7%	8	0.3
	OVERALL		**110**	**46**	**41.8%**	**87**	**0.8**
Lakes	HIGH	> 75	22	20	90.9%	34	1.5
(25 sites)		30 - 75	20	12	60.0%	22	1.1
		5 - 20	50	19	38.0%	33	0.7
	LOW	> 75	9	6	66.7%	9	1.0
		30 - 75	22	6	27.3%	7	0.3
	OVERALL		**123**	**63**	**51.2%**	**105**	**0.9**

Table 3. Maximum Pesticide Concentrations (µg/L) and Non-compliance with Canadian Water Quality Guidelines-CWQG (CCME 1997) for the Protection of Aquatic Life (PAL) and for Irrigation (IRR) in Alberta Streams and Lakes which Drain Land Receiving HIGH, MEDIUM and LOW Quantities of Pesticides, and for Lakes in Different Runoff Zones (1995 & 1996).

		Dicamba	MCPA	Bromo-xynil	Diclofop-methyl	2,4-D	Picloram	Trifluralin	Triallate	Lindane	Ethal-fluralin	Carba-thiin	Fenoxa-prop-p-ethyl	Imaza-metha-benz
IRR (µg/L)		*0.006*	*0.03*	*0.35*	*0.18*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*	*NA*
PAL (µg/L)		*10*	*2.6*	*5*	*6.1*	*4*	*29*	*0.1*	*0.24*	*0.01*	*NA*	*NA*	*NA*	*NA*
27 STREAMS (110 samples)														
						Maximum Concentration (µg/L)								
HIGH PESTICIDE USE		0.08	0.55	0.71	-	0.46	0.65	0.047	0.16	0.051	-	-	-	1.4
MEDIUM PESTICIDE USE		0.092	0.022	-	-	2.1	-	-	0.033	-	-	-	-	0.12
LOW PESTICIDE USE		-	0.026	0.022	-	1.2	0.2	-	0.076	-	-	-	-	-
						Number of Noncompliant Concentrations/Total Detections								
Guideline Exceeded:		*IRR*	*IRR*	*IRR*						*PAL*				
HIGH PESTICIDE USE		4/4	11/13	1/5	NA/0	0/23	0/4	0/2	0/7	1/1	NA/0	NA/0	NA/0	NA/16
MEDIUM PESTICIDE USE		1/1	0/3	0	NA/0	0/6	0/0	0/0	0/1	0/0	NA/0	NA/0	NA/0	NA/1
LOW PESTICIDE USE		0	0/1	0/1	NA/0	0/3	0/1	0/0	0/2	0/0	NA/0	NA/0	NA/0	NA/0
25 LAKES (123 samples)														
						Maximum Concentration (µg/L)								
	Median Annual Runoff													
HIGH PESTICIDE USE	> 75 mm	4.6	1.7	-	-	-	-	-	0.022	-	-	-	-	2.3
	30 - 75 mm	-	0.2	0.39	0.036	0.34	-	-	0.48	-	-	-	-	-
	5 - 20 mm	0.07	0.39	0.39	0.036	0.36	-	-	0.48	-	-	-	-	0.44
LOW PESTICIDE USE	> 75 mm	-	0.039	0.11	-	0.14	0.029	-	0.021	-	-	-	-	-
	30 - 75 mm	-	0.021	-	-	0.073	-	-	0.052	-	-	-	-	-
						Number of Noncompliant Concentrations/Total Detections								
Guideline Exceeded:		*IRR*	*IRR*	*IRR*					*PAL*					
HIGH PESTICIDE USE	>75 mm	6/6	6/6	0/0	0/0	0/0	0/0	0	0/4	NA/0	NA/0	NA/0	NA/0	NA/8
	30-75 mm	0/0	5/5	1/3	0/1	0/5	0/0	0	1/3	NA/0	NA/0	NA/0	NA/0	NA/5
	5-20 mm	2/2	13/13	0/0	0/1	0/16	0/0	0	0/2	NA/0	NA/0	NA/0	NA/0	NA/0
LOW PESTICIDE USE	> 75 mm	0	1/1	0/1	0/0	0/5	0/1	0	0/1	NA/0	NA/0	NA/0	NA/0	NA/0
	30 - 75 mm	0	0/1	0/0	0/0	0/3	0/0	0	0/3	NA/0	NA/0	NA/0	NA/0	NA/0

NA = no guideline available
- = no detections