DETERMINATION OF NEW PESTICIDES IN ALBERTA'S SURFACE WATERS (1999 – 2000)

Alberta Environment

DETERMINATION OF NEW PESTICIDES IN ALBERTA'S SURFACE WATERS (1999 – 2000)

Prepared for:

The Water Research User Group, Alberta Environment

Prepared by:

Gary Byrtus, Anne-Marie Anderson, and Karen Saffran
Alberta Environment

Gary Bruns and Larry Checknita
EnviroTest Laboratories

November 2002

X0305

Pub No. T/674
ISBN No. 07785-2443-4 (Printed Edition)
ISBN No. 07785-2444-2 (On-line Edition)
Web Site: http://www.gov.ab.ca/env/

Any comments, questions, or suggestions regarding the content of this document may be directed to:

Science and Standards Branch
Alberta Environment
4th Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Fax: (780) 422-4192

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Great West Life Building
9920 – 108th Street
Edmonton, Alberta T5K 2M4
Phone: (780) 944-0313
Fax: (780) 427-4407
Email: env.infocent@gov.ab.ca

SUMMARY

Pesticides have been an issue with regards to widespread environmental contamination for many years, and residues are now commonly encountered in Alberta surface waters.

The pesticide market is very dynamic and diverse, and new pesticides are marketed each year while older ones are being phased out. This requires on-going adjustments of monitoring programs. The complex chemistry of many new active ingredients requires increasingly sophisticated equipment to analyze environmental samples at lower detection levels, which leads to ever increasing analytical costs. This results in particular challenges for monitoring agencies.

Approximately 40 compounds are routinely monitored in Alberta surface waters. Periodic, comprehensive reviews of provincial pesticide sales data are used to identify new compounds on the market, and to describe their relative usage patterns across the province. The need to add these compounds to the monitoring list is evaluated based on sale volumes, pesticide characteristics pertaining to mobility and aquatic toxicity, and availability and cost of analysis.

This two-year project was initiated in 1999 with the following objectives:

- To identify pesticides that are used intensively on locally grown specialty crops (such as corn, sugar beets, potatoes) and have not been monitored, or new pesticides that are used broadly across the province; and

- To implement a sampling program to determine, at a scoping level, the occurrence and concentration of these chemicals in surface waters.

Compounds used on specialty crops are metiram, mancozeb, phorate, chlorothalonil, bentazon, ethofumesate, thiophanate methyl, phenmedipham, desmedipham and thiabendazole. Compounds with a potentially widespread use across the province are imidacloprid, clodinafop-propargyl, cloquintocet-mexyl, fluazifop-p-butyl, quizalofop-ethyl, and EPTC.

EnviroTest Laboratories, Edmonton, were retained to develop or refine analytical methods for the identification and quantification of these compounds in surface water samples. Technology used in sample analysis includes GC/MSD using SIM and LC/MS using SIM.

A sampling program was carried out on four irrigation return flows in southern Alberta and eight dry-land agricultural streams in central Alberta. Specialty crops such as sugar beets, corn, and potatoes along with cereal and oil seed crops are grown in southern Alberta and justified the analysis of all compounds in irrigation return flows sampled in 1999. Specialty crops are generally not important in dry-land farming, and only compounds used on cereal and oil seed crops were analyzed in central Alberta streams sampled in 2000.

In 1999, ethofumesate was detected in three of the 20 samples analyzed; no other compounds were detected. In 2000, the clodinafop metabolite was detected in five streams sampled during spring run-off; fluazifop-p-butyl was identified at the detection limit in one spring sample and quizalofop-ethyl was detected in a June sample.

These results indicate that some of these newly introduced pesticides are sufficiently mobile and persistent to leave the target application site and enter aquatic ecosystems. The compounds that were detected are known to be moderately (fluazifop-p-butyl and quizalofop-ethyl) to highly (clodinafop-propargyl) toxic to rainbow trout. However, no comprehensive guidelines have been developed to evaluate the significance of detections in water to such uses as aquatic ecosystem health protection, irrigation, and drinking water for livestock or humans.

TABLE OF CONTENTS

LIST OF TABLES

ACKNOWLEDGEMENTS

This project was funded by the Water Research User Group (WRUG), Alberta Environment (AENV).

Water samples for pesticide analyses were collected by Ray Walker and Mike Sajjad (Monitoring Branch, AENV).

Bridgette Halbig (Water Quality Section, Air and Water Branch, AENV) assisted in report preparation.

This report has benefited from the review comments of Dave Humphries and Yogesh Kumar (Alberta Research Council, Vegreville) and Dave Trew (Water Quality Section, Air and Water Branch, AENV).

1.0 INTRODUCTION

Pesticides are among the most widespread and commonly used man-made chemicals intentionally released into the environment. It is therefore relevant to track their fate. Their presence in surface waters, for example, can have implications for the value of the water as a source of potable water or irrigation water, and on the health and diversity of aquatic life.

New pesticides appear continuously on the market to control plants, insects or fungi that are regarded as pests in agricultural, industrial, or domestic settings. Although pesticides are applied site-specifically to control or kill specific species, off-target movement is known to occur. Movement away from the application site can occur through dissolution in runoff water and movement to surface and ground waters, movement associated with soil losses, or volatilization into the atmosphere. Once in the atmosphere, pesticides can be transported for some distance before being deposited on land and water with dust or precipitation. Partitioning of pesticides among environmental components such as air, water, soil, or biota depends on characteristics such as volatility, solubility, persistence, and ability to adsorb to organic matter. These characteristics will determine if the compound is more likely to be found in air (high volatility or Henry's Law Constant H), dissolved in water (high water solubility), adsorbed to soil (high organic carbon partitioning coefficient or K_{OC}), or if it is likely to bio-accumulate (high octanol/water partitioning coefficient or K_{OW}).

The highly dynamic and diverse nature of the pesticide market poses continuous challenges to environmental monitoring. As new products appear and old ones are discontinued environmental monitoring programs must evolve. Furthermore, newer active ingredients tend to have a highly complex chemistry. Their chemical identification and quantification in environmental samples becomes more costly as it requires increasingly sophisticated equipment.

Approximately 40 pesticides are currently monitored in surface waters by the Alberta provincial government. The list was initially established in 1995 following an extensive review of sales records (Cotton and Byrtus 1995) and historic data (Anderson 1995). Compound characteristics such as use patterns, likelihood of compounds entering surface waters (Cotton 1995), and availability and cost of analytical methods were other factors considered in the compound selection. Since the initial list was established, several new products have appeared on the market. Some compounds, such as imazamethabenz and imazethapyr, have been added to the list of compounds monitored in surface waters. Others have never been monitored because they have appeared only recently on the market or because the technology was not readily available.

This project was initiated in 1999 with the following objectives:

- To identify pesticides that are used intensively on locally grown specialty crops or new pesticides that are used broadly across the province; and

- To implement a sampling program to determine, at a scoping level, the occurrence and concentration of these chemicals in surface waters.

2.0 METHODS

2.1 Compound Identification

Based on an initial review of 1998 pesticide sales records, later formalized in Byrtus (2000), two lists of new pesticides were compiled:

- Compounds that are applied to sugar beets, corn and potatoes, primarily in irrigated areas in south Alberta.

- Compounds that are applied to control pests on crops with widespread distribution in Alberta.

Pesticides and some of their most common uses are listed in Table 1. This list comprises 16 compounds, including nine herbicides, five fungicides and two insecticides. Compounds used on specialty crops are metiram, mancozeb, phorate, chlorothalonil, bentazon, ethofumesate, thiophanate methyl, thiabendazole, phenmedipham and desmedipham. Compounds with a potentially widespread use across the province are imidacloprid, clodinafop-propargyl, cloquintocet-mexyl, fluazifop-p-butyl, quizalofop-ethyl and EPTC. Chemical characteristics of these compounds are listed in Table 2. Phorate is a herbicide which has been routinely analyzed by AENV, but, so far, has not been detected. Phorate is primarily used in the irrigated area of the province on potato and sugar beet crops. This compound was included in this study because samples were taken from an area where specialty crops were grown and where phorate was likely to have been applied.

By applying a rating system similar to that developed by Cotton and Byrtus (1995), chemicals were rated according to their overall mobility and aquatic toxicity, thereby providing some theoretical measure of the likelihood that they would enter surface waters and cause damage to aquatic ecosystems (Table 3). Results of this ranking indicate that in this list, imidacloprid, bentazon, and EPTC are among the most mobile and that clodinafop-propargyl, phorate and thiabendazole are among the most toxic. No compounds ranked “high” with respect to mobility and toxicity.

2.2 Analytical Capabilities

Enviro-Test Laboratories, Edmonton (ETL) is equipped with GC/MS (Gas Chromatography/Mass Spectrometry) and LC/MS (Liquid Chromatography/Mass Spectrometry) and has the analytical capabilities to analyze most compounds. The Edmonton laboratory has been directly involved in the testing required for registering six of the compounds listed in Table 1. However, most of the registration work involves residue testing on crops and soils; concentrations tend to be much higher in these media than in surface waters. ETL proposed to set up several screens for different groups of compounds. Cost per screen and anticipated method detection limits are listed in Table 4. A total of 14 pesticides were analyzed in surface water samples. In addition, the metabolites for clodinafop and cloquintocet were analyzed in some samples collected in 2000.

Table 1 List of pesticides, trade names and uses

Pesticide	Trade Names	Application Timing	Crop	Crop Type	Type	Pest
Imidacloprid	Gaucho	seed treatment	Seed treatment canola, rape, mustard (for export seed only)	BU	I	flea beetle
Imidacloprid (cont'd)	Admire	foliar or in-furrow	potatoes	SC	I	Colorado potato beetle
Clodinafop-propargyl	Horizon	post emergent	all types of wheat	BU	H	wild oats, foxtail, persian darnel
Cloquintocet-mexyl	Horizon	post emergent	all types of wheat	BU	H	wild oats, foxtail, persian darnel
Fluazifop-p-butyl	Venture 25 DG	post emergent	canola, lentils, flax, descue, creeping red, alfalpha, red clover, bird'sfoot trefoil, linola, mustard, sunflowers	BU	H	barley, corn, darnel, foxtail, barnyard grass, wild oats, wheat, wild proso millet
Quizalofop-ethyl	Muster Gold	post emergent	canola	BU	H	barley, flixweed, foxtail, barnyard grass, hemp-nettle, wild mustard, oats, smartweed, stinkweed, wheat
Quizalofop-ethyl (cont'd)	Assure	post emergent	canola, red fescue, flax, lentils, peas, seed alfalfa,soybeans	BU	H	barley, foxtail, oats, wheat, barnyard grass, quackgrass
Metiram	Polyram	post emergent	potatoes, sugar beets	SC	F	blackleg, cercospora, blight, fusarium, seed-borne common scab
Mancozeb	Ridomil MZ 72WP	postemergent	potatoes	SC	F	late blight, late blight tuber rot, early blight
Mancozeb (cont'd)	Dithane DG/manzate 200/tuberseal/ potatoe seed treatment	post emergent	corn, potatoes, sugar beets, wheat	SC	F	cercospora leaf spot, blight, fusarium decay, leaf rust, root rot, seedling blight, septoria,tan spot
Mancozeb (cont'd)	Acrobat MZ	post emergent	potatoes	SC	F	early and late blight
Phorate	Thimet	postemergent	beans, corn, potatoes	SC	I	aphids, colorado beetle, leafhopper, leafminer, lygus bug, mites, thrips
Chlorothalonil	Bravo 500	post emergent	peas, lentils, vegetables, wheat, potatoes	SC	F	anthracnose, ascochyta, blight, botrytis, tan spot, septoria leaf spot, …

Table 1 List of pesticides, trade names and uses (cont'd)

Pesticide	Trade Names	Application Timing	Crop	Crop Type	Type	Pest
Bentazon	Basagran	post emergent	seedling legumes, grasses, established stands for seed production, corn	SC	H	see below
Bentazon (cont'd)	Laddok	post emergent	corn	SC	H	buttercup, chikweed, coclebur, cudweed, galinsoga, groundsel, lady's thumb, lamb's-quarters,… russian thistle +many others
Ethofumesate	Nortron	post emergent	sugar beets	SC	H	barnyard grass, foxtail, kochia, lady's-thumb, lamb's quarter, redroot pigweed, purslane, shepherd's purse, volunteer barley oats and wheat, wild oats
EPTC	Eptam	post emergent	alfalfa, bird's-foot trefoil, cicer milk vetch, dry beans, snap beans, flax, irish potatoes, sunflowers, turnips, sugar beets, sweet clover	SC	H	barley, barnyard grass, blue grass, chickweed, foxtail, henbit, lamb's-quarter, nightshade, oats, pigweed, purslane, quackgrass, ryegrass, cornspurry, wheat
EPTC	Eradicane 8-E	post emergent	corn	SC	H	many see above
Thiophanate methyl	Easeout PSPT	seed treatment	potatoes	SC	F	fusarium rot, silver scurf, verticillium wilt control of seed piece decay and black leg infections
Thiabendazole	Mertect	storage and post emergent (sugar beets)	potatoes, sugar beets	SC	F	storage rot of potatoes and sugar beets, cercospora leaf spot on sugar beets
Phenmedipham	Betamix and Betanex	post emergent	sugar beets	SC	H	foxtail, kochia, lamb's quarter, mustard, nightshade, ragweed, redroot pigweed, stinkweed, wild buckweat
Desmedipham	Betanex	post emergent	sugar beets	SC	H	foxtail, kochia, lamb's quarter, mustard, nightshade, ragweed, redroot pigweed, stinkweed, wild buckweat

Notes: SC = speciality crops; BU = broad use; I = insecticide; H = herbicide; F = fungicide

Table 2 Chemical characteristics

Chemical Name	CAS #	Molecular Formula	Molec. Wt	Data Temp (°C)	Water sol (mg/L)	VP (Pa)	Log K_{OW} (unit less)	MP (°C)	Water 1/2 life (hr)	Soil 1/2 life (hr)	K_{OC} (mL/g)	LC_{50} (96 hr rainbow trout) (mg/L)	Comments
Imidacloprid	138261-41-3	$C_9H_{10}ClN_5O_2$	255.7	20	510	2×10^{-7}	0.57	143.8	744	4560	1.52*	211	
Clodinafop-propargyl	105512-06-9	$C_{17}H_{13}ClFNO_4$	349.8	25	4	3.19×10^{-6}	3.9	59.4	64	2	1404	0.39	
CGA 194639 (met)	?	$C_{14}H_{11}ClFNO_4$	311.7	?	?	?	2.9	?	?	552	?	?	
Cloquintocet-mexyl	99607-70-2	$C_{18}H_{22}ClNO_3$	335.8	25	590	5.31×10^{-6}	5.03	69.2	4.6	101	99054	>76	
CGA 153433 (met)	?	$C_{11}H_8ClFNO_3$	256.6		?	?	?	?	?	4032	?	?	
Fluazifop-p-butyl	79241-46-6	$C_{19}H_{20}F_3NO_4$	383.4	20	1	0.00054	4.5	5	?	504	5700	1.07	
Quizalofop-ethyl	76578-14-8	$C_{17}H_{13}ClN_2O_4$	344.8	20	0.3	0.866×10^{-9}	4.28	92	?	504	510	10.7	
Metiram	9006-42-2	mixture	1088.7	20	insoluble	<0.00001	2	140	v. rapid to ETU	480	500,000	1.1	metab. to ETU
Mancozeb	8018-01-7	$[C_4H_6N_2S_4Mn]_xZn_y$	200	20	6-20	0	3.69*	192	24-48	144-360	>2000	2.2 (48 hr)	metab. to ETU
Phorate	298-02-2	$C_7H_{17}O_2PS_3$	260.4	25	50	0.085	3.92	<-15	36-504?	48-336	543	0.013	
Chlorothalonil	1897-45-6	$C_8Cl_4N_2$	265.9	25	0.9	7.6×10^{-5}	2.89	250	792-1032	120-864	5000	49	
Bentazon	25057-89-0	$C_{10}H_{12}N_2O_3S$	240.3	20	570	0.00046	0.35	138	24	326	34	>100	
Ethofumesate	26225-79-6	$C_{13}H_{18}O_5S$	286.3	25	50	0.00065	2.7	71	?	720	340	>180	
EPTC	759-94-4	$C_9H_{19}NOS$	189.3	25	375	0.00001	3.2	-30	3696	1008	200	19	
Thiophanate-methyl	23564-05-8	$C_{12}H_{14}N_4O_4S_2$	342.4	25	insoluble	9.5×10^{-6}	1.5	172	864	504-672	1850	7.8 (48 hr)	
Thiabendazole	148-79-8	$C_{10}H_7N_3S$	201.3	20	0.03	0.00046	2.39	197	29	792-2880	2500	0.55	
Desmedipham	13684-56-5	$C_{16}H_{16}N_2O_4$	300.3	25	7	40×10^{-9}	3.39	120	22	816	1500	1.7	
Phenmedipham	13684-63-4	$C_{16}H_{16}N_2O_4$	300.3	25	4.7	1.33×10^{-9}	3.59	144	?	600	2400	1.4-3.0	

Notes:
*Calculated values
CAS# = Chemical Abstracts Service Registry Number (CAS)
Data Temp (°C) = Temperature in °C for which characteristics apply
Vp (Pa) = Vapour pressure at 25°C
Log K_{OW} = Octanol Water partition coefficient
MP (°C) = Melting point in °C
K_{OC} = Organic carbon partition coefficient

Table 3 Preliminary ranking (Low, Medium, High) of pesticides based on relative mobility and toxicity

Pesticide	Water Solubility Rating	Koc 'Mobility'	Half Life in Soils	Overall Mobility Rating	Toxicity Rating (Based on Rainbow Trout LC 50)
Imidacloprid	H	H	H	**H**	L
Clodinafop-propargyl	L	M - L	L	L	**H**
Cloquintocet-mexyl	H	L	L	M	L
Fluazifop-p-butyl	L	L	M	M	M
Quizalofop-ethyl	L	M	M	M	M
Metiram	L	L	L	L	M
Mancozeb	L	L	M	M	M
Phorate	M	M	L	M	**H**
Chlorothalonil	L	L	M	M	L
Bentazon	H	H	L	**H**	L
Ethofumesate	M	M	M	M	L
EPTC	H	M	M	**H**	M
Thiophanate methyl	L	H	M	M	M
Thiabendazole	L	L	M	M	**H**
Phenmedipham	L	L	M	M	M
Desmedipham	L	L	M	M	M
criteria used in ranking:	0 to 30 mg/L = L 30 to 300 mg/L = M 300 to 3000 mg/L = H	<100: H 100-1000:M >1000: L	<20 days: L 20-100 d: M >100 d: H		<1 mg/L: H 1-20 mg/L: M >20 mg/L: L

Table 4 Pesticide scans proposed by ETL for the analysis of the new pesticides

ETL Scans	Compounds/Scan	Anticipated Detection Limit	Cost
LC/MS scan		**20 - 50 ppt**	**$340**
Acid metabolite will be analysed	imidacloprid clodinafop-propargyl cloquintocet-mexyl fluazifop-p-butyl quizalofop-ethyl	(0.02-0.05 µg/L)	
EBDC scan		**100 ppt (0.1 µg/L)**	**$220**
EBDC stands for ethylene bisdithiocarbamate, which is a group of chemically related fungicides, including metiram and mancozeb; scan does not differentiate between the two compounds.	metiram mancozeb		
GC/MS scan		**30 - 60 ppt**	**$290**
	phorate chlorothalonil bentazon ethofumesate EPTC	(0.03-0.06 µg/L)	
MBC scan		**20 ppt**	**$340**
i.e., methyl-2-Benzimidazole carbonate scan	thiophanate methyl thiabendazole	(0.02 µg/L)	
None			**not quoted**
	phenmedipham desmedipham		

Details about analytical methods and laboratory QA/QC procedures that were used in this study are presented in Appendix 1.

2.3 Sampling Program

In designing the sampling program, an attempt was made to select suitable sampling locations from existing pesticide monitoring programs such as the Alberta Environmentally Sustainable Agriculture (AESA) program, the Oldman River Basin Water Quality Initiative (ORBWQI) and the Long-Term Tributary Network (LTTN). This reduced sampling costs and offered the benefit of existing information on land use and dominant crops.

The AESA program and ORBWQI focus on relatively small agricultural streams and irrigation return flows (Anderson et al. 1999; K.A. Saffran, pers. comm.). In selecting watersheds for this study, preference was given to watersheds where cropping intensity, and presumably chemical use, was high. Selected watersheds and the main crops grown in their basin are shown in Table 5. Assumptions about pesticide use were based on the knowledge of the types of crops grown in each basin. There was a reasonable probability for all compounds listed in Table 1 to be used on cropland draining to Drain S6, New West Coulee, Battersea Drain, and Expanse Coulee. However, it was unlikely that chemicals for specialty crops were used in basins where dominant crops are cereals and oilseed crops.

Funding availability required that the sampling program be split over two years. Irrigation return flows were sampled in 1999 and analyzed for compounds listed in Table 4. In 2000, sites sampled were mostly dry-land streams; available funding allowed for the analysis of imidacloprid, clodinafop-propargyl, cloquintocet-mexyl, fluazifop-p-butyl and quizalofop-ethyl.

The sampling schedule in each year was intended to maximize the chances of detecting compounds if they were present in surface waters. In streams receiving irrigation return flows, five samples were collected from mid-June to August; this is the peak irrigation season and the time of year when the likelihood of detection is greatest. In other streams the likelihood of detection is greatest during snowmelt runoff and during rain induced runoff after pesticide application (late June to August). These streams were sampled three times: during spring runoff, and in June and July after rainfall.

At each site, two 2L depth-integrated water samples were collected from the main flow channel. The 2L water trace organic clean bottles were obtained from ETL. Samples were kept in coolers with ice packs and delivered to the laboratory within 24 hours. Only one sample was analyzed; the other was retained as a spare.

Table 5 List of sampling sites

Site	Program	WDS Station Code	Main Crops in Drainage Basin
1999 **IRRIGATION RETURN FLOWS**			
Drain S6 near Bow Island	AESA	AB05AJ0410	beets, potatoes, corn, beans
New West Coulee @ Hwy 36 Crossing	AESA	AB05BN0970	potatoes and alfalfa
Battersea Drain near confluence with Oldman River	ORBWQI	AB05AG0030	beets
Expanse Coulee near Hwy 36	ORBWQI	AB05AG0140	potatoes
2000 **DRY-LAND FARMING STREAMS**			
Stretton Creek near Marwayne	AESA	AB05EE0550	cereal and oil seed crops
Threehills Creek below Ray Creek	AESA	AB05CE0730	cereal and oil seed crops
Ray Creek near Innisfail	AESA	AB05CE0710	cereal and oil seed crops
Renwick Creek near Threehills	AESA	AB05CE0720	cereal and oil seed crops
Haynes Creek (M1)	AESA	AB05CD0520	cereal and oil seed crops
Crowfoot Creek near Cluny*	AESA	AB05BM0620	cereal and oil seed crops
Battle River at Secondary Hwy 872	LTTN	AB05FC0150	cereal and oil seed crops
Vermilion River at Marwayne	LTTN	AB05EE0480	cereal and oil seed crops

Notes:
*Crowfoot Creek receives water from the Western Irrigation District
AESA - Alberta Environmentally Sustainable Agriculture Program
ORBWQI - Oldman River Basin Water Quality Initiative
LTTN - Long-Term Tributary Network

3.0 RESULTS

Results of the 1999 and 2000 sample collection and analysis are presented in Tables 6 and 7, respectively.

ETL refined analytical protocols in an effort to lower method detection limits (MDL) to a likely environmental range for Alberta surface waters. For most compounds rather low detection limits were achieved, ranging between 0.005 and 0.02 µg/L in 1999. However, for some compounds such as metiram and mancozeb, low detection limits could not be achieved (MDL of 10 µg/L). Detection limits achieved in 2000 were generally higher than anticipated (Table 4) or achieved in 1999. This was particularly so for samples collected in July.

Testing was conducted for fourteen compounds in 1999, but ethofumesate was the only pesticide detected. It was found in two samples from New West Coulee (July 7: 0.03 µg/L; and July 27: 0.77 µg/L) and one sample from Battersea Drain (August 18: 0.97 µg/L).

Of the seven compounds analyzed for (i.e., including two metabolites) in 2000, three were detected. The clodinafop metabolite was found in spring runoff samples from several streams (Haynes, Ray, Stretton, and Threehills creeks, and the Vermilion River) at concentrations that ranged from 0.03 to 0.13 µg/L. Fluazifop-p- butyl was identified at the detection limit in a spring runoff sample from Crowfoot Creek (0.01 µg/L). Quizalofop-ethyl was detected in a June sample from the Vermilion River (0.07 µg/L).

Table 6 Analytical results for surface water samples collected in 1999
Concentrations are expressed in µg/L (ppb)

Site	Date	Imidacloprid	Clodinafop-propargyl	Cloquintocet-mexyl	Fluazifop-p-butyl	Quizalofop-ethyl	Metiram	Mancozeb
Battersea Drain	Jun-99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/6/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/20/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/4/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/17/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
Drain S6	Jun-99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/8/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/21/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/5/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/17/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
Expanse Coulee	6/15/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/7/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/21/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/5/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/17/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
New West Coulee	Jun-99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/7/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	7/27/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/5/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10
	8/24/99	<0.02	<0.02	<0.02	<0.005	<0.01	<10	<10

Site	Date	Phorate	Clorothalonil	Bentazon	Ethofumesate	EPTC	Phenmedipham	Desmedipham
Battersea Drain	Jun-99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/6/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/20/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/4/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/17/99	<0.02	<0.05	<0.01	**0.97**	<0.005	<0.02	<0.02
Drain S6	Jun-99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/8/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/21/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/5/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/17/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
Expanse Coulee	6/15/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/7/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/21/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/5/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/17/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
New West Coulee	Jun-99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	7/7/99	<0.02	<0.05	<0.01	**0.03**	<0.005	<0.02	<0.02
	7/27/99	<0.02	<0.05	<0.01	**0.77**	<0.005	<0.02	<0.02
	8/5/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02
	8/24/99	<0.02	<0.05	<0.01	<0.005	<0.005	<0.02	<0.02

Table 7 Analytical results for surface water samples collected in 2000
Concentrations are expressed in µg/L (ppb)

Site	Date	Imidacloprid	Clodinafop-propargyl	Clodinafop metabolite	Cloquintocet-Mexyl	Cloquintocet metabolite	Fluazifop-p-buthyl	Quizalofop-ethyl
Battle River	31/3/00	<0.05	<0.01	<0.01	<0.01	<0.01	<0.05	<0.8
	20/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	<0.05
	21/7/00	<1	<1	NA	<1	NA	<1	<1
Crowfoot Creek	6/4/00	<0.05	<0.01	<0.01	<0.01	<0.01	**<u>0.01</u>**	<0.8
	20/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	<0.05
	18/7/00	<1	<1	NA	<1	NA	<1	<1
Haynes Creek (M1)	5/4/00	<0.05	<0.01	**0.04**	<0.01	<0.01	<0.05	<0.8
	21/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	<0.05
	11/7/00	<1	<1	NA	<1	NA	<1	<1
Ray Creek	5/4/00	<0.05	<0.01	**0.03**	<0.01	<0.01	<0.05	<0.8
	21/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	<0.05
	26/7/00	<1	<1	NA	<1	NA	<1	<1
Renwick Creek	5/4/00	<0.05	<0.01	<0.01	<0.01	<0.01	<0.05	<0.8
Stretton Creek	5/4/00	<0.05	<0.01	**0.13**	<0.01	<0.01	<0.05	<0.8
	20/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	<0.05
	31/7/00	<1	<1	NA	<1	NA	<1	<1
Threehills Creek	5/4/00	<0.05	<0.01	**0.03**	<0.01	<0.01	<0.05	<0.8
	21/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	<0.05
	26/7/00	<1	<1	NA	<1	NA	<1	<1
Vermilion River	31/3/00	<0.05	<0.01	**0.03**	<0.01	<0.01	<0.05	<0.8
	23/6/00	<0.25	<0.01	NA	<0.05	NA	<0.01	**0.07**
	25/7/00	<1	<1	NA	<1	NA	<1	<1

Notes:
NA = not analyzed
- note difference in reported detection limits among sampling dates
- underlined value found at detection level

4.0 DISCUSSION AND CONCLUSIONS

The scoping-level sampling program resulted in the detection of three herbicides (ethofumesate, fluazifop-p-butyl, and quizalofop-ethyl) and one metabolite (clodinafop) in several water bodies sampled in 1999 and 2000. This confirms that at least some of pesticides that are used on specialty crops as well as some newly introduced pesticides are sufficiently mobile to leave the targeted application site and enter aquatic ecosystems.

The most straightforward way to evaluate the significance of these detections for various water uses is to refer to water quality guidelines. However, no guidelines exist, whether for aquatic life, irrigation, livestock, or human consumption, to determine safe levels of any of the compounds tested in this study. This points to a chronic deficiency, which has been identified for some time (e.g., CAESA 1998), in the way new pesticides are regulated. Based on available toxicity information (Table 2 and 3), thiabendazole is considered highly toxic to fish, but fluazifop-p-butyl and quizalofop-ethyl are moderately toxic. Clodinafop-propargyl is highly toxic. However, the toxicity of its metabolite is not documented. Concentrations recorded in this study are well below acute toxicity concentrations for fish (Table2). However, it is important to stress that acute fish toxicity data may not provide an accurate, overall indication of impacts to all components of aquatic ecosystems, neither are they indicative of chronic effects or of effects single compounds have in combination with other environmental contaminants or stressors.

The fact that other pesticides analyzed in this study were not detected could be due to a combination of several reasons.

- The selection of sampling sites was based on the assumption that pesticides were used in the watershed. It is possible that this assumption was incorrect for some watersheds and/or some compounds.

- It is also possible that local conditions at the time of sampling were such that even though the compounds were used, residues had not reached the streams yet.

- While detection limits were as low as could practically be achieved by the analytical laboratory, it is possible that, in the aquatic environment, pesticides occur at concentration below the reported analytical detection limit. This may be of particular relevance for certain compounds (e.g., metiram and mancozeb) and for certain surveys (e.g., 2000 samples, in general and July survey in particular).

- The fairly common detection of the clodinafop metabolite in spring 2000 indicates that residual concentrations from the previous application year can be detected during spring melt. Presumably metabolites could occur more frequently and at higher concentrations shortly after the time of application. Unfortunately, metabolites were not analyzed in June or July and there are no data to document their occurrence shortly after application.

- Imidacloprid is expected to replace lindane, which is currently being phased out as a seed treatment insecticide. Imidacloprid was not used in Alberta as a seed treatment compound at the time the surveys were carried out and there was no expectation that it would be found. Its inclusion was purely for the purpose of analytical method development. The fact that it was not detected indicates the absence of ‘false positives’ (i.e., erroneously reporting the detection of a compound which is not there).

These points all need to be considered carefully when planning or implementing further work on new pesticides.

Several additional compounds have been introduced in Alberta for pest control since 1998. They include cymoxanil, fludioxonil and zoxamide (specialty crops) and florasulam, flucarbazone-sodium, thiamethoxam, azoxystrobin, difenoconazole, triticonazole, tebuconazole and hexaconazole (for a variety of crops grows across Alberta). Occurrence in surface waters may need to be determined for these compounds, once their overall usage has been determined for Alberta. Also, quizalofop-ethyl has recently been replaced by the racemic isomer quizalofop-p-ethyl, however because the analysis looks for the acid form of the compound, it did not make much difference to this project in which form was looked for.

There is an ongoing need to dedicate resources to develop and implement analytical methodology to analyze trace organic contaminants, including pesticides, in environmental samples. This work necessitates a level of consistency and attention to detail that requires coordinated efforts among research and service laboratories, manufacturers, and agencies involved in monitoring.

5.0 LITERATURE CITED

Anderson, A-M., 1995. Overview of pesticides data for Alberta surface waters. In: Madawaska Consulting *et al.* (1995). Selection of landscape units for water quality monitoring. Appendix A4. Prepared for CAESA Committee on Water Quality.

Anderson A.-M., S. Cooke and N. Mac Alpine 1999. Watershed selection for the AESA stream water quality monitoring program. Prepared for Alberta Environmentally Sustainable Agriculture, Water Quality Monitoring. Published by Alberta Agriculture Food and Rural Development.

Byrtus, G. 2000. Overview of 1998 pesticide sales in Alberta. Municipal Program Development Branch, Environmental Science Division, Environmental Service, Alberta Environment. 58 pp.

CAESA. 1998. Agricultural impacts on water quality in Alberta Agreement. Alberta Agriculture, Food and Rural Development, Lethbridge. 95 pp.

Cotton, M. 1995. Pesticide characteristics and a preliminary assessment of the potential environmental significance of pesticides. In: Madawaska Consulting *et al.* (1995). Selection of landscape units for water quality monitoring. Appendix A1. Prepared by Artemis Consulting Ltd. for CAESA Committee on Water Quality.

Cotton, M. and G. Byrtus. 1995. Pesticide sales records for Alberta (1988-93). In: Madawaska Consulting *et al.* (1995). Selection of landscape units for water quality monitoring. Appendix A2. Prepared by Artemis Consulting Ltd. for CAESA Committee on Water Quality.

Saffran, K.A. 2002. Limnologist, Air and Water Branch, Alberta Environment, pers. comm.

Tomlin, C.D.S. 2000. The Pesticide Manual, 12th Edition. British Crop Protection Council, Surrey, United Kingdom. 1250 pp.

Margni, M., O. Jolliet, D. Rossier and P. Crettaz. 2001. Life cycle impact assessment of pesticides on human health and ecosystems. Submitted to Agriculture, Ecosystems and Environment.

U.S. EPA. 2002. REDS (Reregistration Eligibility Documents). *http://www.epa.gov/pesticides*.

6.0 APPENDIX A

THE DETERMINATION OF A SELECT GROUP OF PESTICIDES IN WATER BY GC/MS AND LC/MS

Document prepared by:
Larry Checknita, Senior Analyst, EnviroTest Laboratories

1.0 OVERVIEW

A total of 20 and 22 samples were received at ETL Laboratories, in 1999 and 2000, respectively, for a select group of pesticide analyses, in accordance with contract agreement #000014, assignment #07. All of the samples were received in good condition.

2.0 PROCEDURES

2.1 For Acid/Neutral Herbicides and Pesticides in Water

A portion of the water sample was decanted into a 1 L separatory funnel. NaCl was added and the sample was partitioned two times with ~ 100 mL dichloromethane (DCM). The sample was then acidified to pH <2 and partitioned two times with ~ 100 mL DCM combining all extracts. The extracts were then reduced by rotoevap and brought to a 1 mL final volume. The extract was split with one portion derivatized with diazomethane and a non-derivatized portion. The analysis was by GC/MSD using selected ion monitoring (SIM) and LC/MS using SIM.

2.2 For Mancozeb in Water

An 8 mL portion of sample was placed into a 40 mL vial along with 10% EDTA, and 3% $SnCl_2$/8N HCl solution and capped. The samples were placed in a heating block at 100^{o}C for four hours with shaking at various time intervals. The samples were then analyzed by GC/MSD using SIM.

3.0 REAGENTS

Dichloromethane, diazomethane, ethylene diamine tetra acetic acid (EDTA), hydroclorc acid, sodium chloride, stannous chloride, sulfuric acid.

4.0 EQUIPMENT

Heating block, N_2 evaporator – organomatic, ratovap – Janke & Kunkel RV-06-mL, standard laboratory glassware

5.0 INSTRUMENTATION

5.1 Instrument for Pesticide Analysis

HP 5970E Mass Selective Detector with:
- HP 5890A Gas Chromatograph
- HP 5982A gauge controller
- HP Chem workstation

Conditions:
- Column – DB 1301
- Column, initial – 100^{o}C
- Rate – 10^{o}C/min
- Final – 280^{o}C
- Injector – 250^{o}C
- Initial hold time – one minute
- Voltage – 2400-2600 V
- Detector – 300^{o}C

Flows:
- Split flows – 40
- Head Pressure – 10 psi
- Split valve closure – 0.5 min
- Injector Volume – 3 uL

Ions:
- EPTC- m/z 128, 132, 189
- Phorate – m/z 121, 260, 231
- Bentazon – m/z 212, 105, 254
- Chlorothalonil – m/z 266, 264, 268
- Ethofumesate – m/z 268, 161, 207
- Fluazifop-p-butyl – m/z282, 254, 383
- Quizalofop – m/z 299, 358, 372

5.2 Instrument for Mancozeb Analysis

Detector:
- HP 5971B
- HP 5890 gas chromatograph
- HP 59822 gauge controller

Conditions:
- Column – SPB-1 Sulfur (10174-038)
- Column, initial – 25^{o}C
- Rate – 50^{o}C
- Final temp. – 100^{o}C

Injector – 250°C
Initial hold time – six minutes
Voltage – 400 (Rel)
Detector – 280°C

Flows:
Split flows – 40 mL/min.
Head pressure – 10 psi
Split valve closure – 0.10 min
Injector volume – 50 uL

Ions:
Mancozeb – m/z 76, 78

5.3 Instrument for HPLC/MS Analysis

Detector:
HPLC/MS Sciex API 150 EX
Varian 9012 solvent delivery system
Rainin Al-200 Autosampler
Apple power MAC computer 7300/200

Column:
Symetry C18, 25 cm, 5 um
Column temp. – 35°C

Conditions:
Flow rate: 0.90 mL/min.
Gradient conditions:
A = 0.2% acetic acid in H_2O
B = 0.2% acetic acid in acetonitrite

Time	%A	%B
0 min	80	20
1 min	80	20
6 min	50	50
16 min	20	80
23 min	20	80
23 min	20	80
23.1 min	80	20

Ions:
Imidacloprid – m/z 256.0
Clodinafop – m/z 350.1
Cloquintocet – m/z 336.2

Desmedipham/ – m/z 323.0
Phenmedipham – m/z 323.0

6.0 CALCULATIONS

6.1 Response Factor (R.F.):

$$\text{R.F.} = \frac{\text{Concentration of standard (ppm)}}{\text{Area of standard or peak height}}$$

6.2 Concentration of Analyte (ppb)

$$\text{Conc. (ppb)} = \frac{\text{Area or height of analyte x R.F. x F.V. (mL)}}{\text{L.Extracted}}$$

Where:
R.F. = response factor
F.V.= final volume (mL)
L. Extracted = Litres of samples extracted

6.3 Analyte Recovery

$$\text{\% Recovery} = \frac{\text{Amount found}}{\text{Fortification level}} \text{ x 100}$$

7.0 FORTIFICATION

During analysis, control water samples were fortified at levels of approximately 5 and 0.5 ppb for all compounds

8.0 STANDARDS

Most standards were sent from Agriculture Canada, ChemService or Novartis. Purity stated ranged from 95% - 100%.

9.0 DISCUSSION

The recoveries ranged from 55% to 138% for the majority of the compounds (see Tables A1 and A2). The clodinafop, cloquintocet and imidacloprid low-level spikes had recoveries slightly lower than the others. This is due to the increased difficulty with the analysis of these three compounds.

The desmedipham and phenmedipham co-elute and share the same ions. Therefore, it is impossible to differentiate between the two.

The analysis of phorate showed lower recoveries as this compound typically shows poor recovery values.

There were extra spikes done for ethofumesate due to the positive results obtained on two samples.

All other compounds were not detected at the stated detection limits.

Table A1 Fortification recoveries (1999)

Compound	Fortification Level (ppm)	Level Found (ppm)	% Recovery
EPTC	0.0078	0.0062	79
	0.00078	0.00049	63
	0.0078	0.0079	101
			Average recovery = 81%
BENTAZON	0.0074	0.0052	70
	0.00074	0.00041	55
	0.0074	0.0055	74
	0.00074	0.00075	101
			Average recovery = 75%
CHLOROTHALONIL	0.0063	0.0082	130
	0.00063	0.00076	121
	0.0063	0.0058	92
			Average recovery = 114%
ETHOFUMESATE	0.0069	0.0046	67
	0.00069	0.00039	57
	0.0069	0.009	130
	0.0069	0.0083	120
	0.00069	0.00061	88
	0.0069	0.0076	110
	0.00069	0.00054	78
			Average recovery = 93%
FLUAZIFOP-P-BUTYL	0.0069	0.0048	70
	0.00069	0.00048	70
	0.0069	0.0081	117
	0.0069	0.0055	80
	0.0069	0.0063	91
	0.00069	0.00061	88
			Average recovery = 86%
QUIZALOFOP	0.004	0.0055	138
	0.0004	0.00042	105
	0.004	0.0038	95
	0.0004	0.00049	123
			Average recovery = 115%
IMIDACLOPRID	0.0063	0.0041	65
	0.00063	0.0003	48
	0.0063	0.0044	70
	0.00063	0.00042	67
			Average recovery = 63%
CLOQUINTOCET	0.012	0.0082	68
	0.0061	0.004	66
	0.00061	0.00037	61
			Average recovery = 65%
CLODINAFOP	0.012	0.011	92
	0.0061	0.0039	64
	0.00061	0.00047	77
			Average recovery = 77%
DESMEDIPHAM	0.0063	0.0053	84
	0.00063	0.00049	78
	0.0063	0.0035	56
			Average recovery = 73%
MANCOZEB	0.021	0.021	100
	0.21	0.16	76
			Average recovery = 88%
PHORATE	0.007	0.0039	56
	0.0007	0.00043	61
			Average recovery = 58%

Table A2 Fortification recoveries (2000)

Compound	% Recovery
IMIDACLOPRID	67
CLODINAFOP-PROPARGYL	60
CLOQUINTOCET-MEXYL	67
FLUAZIFOP-P-BUTYL	96
QUIZALOFOP-ETHYL	88