Overview Of Pesticide Data In Alberta Surface Waters Since 1995

Alberta
Environment

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Prepared by:

Anne-Marie Anderson, Ph.D., P.Biol.

Environmental Monitoring and Evaluation Branch
Alberta Environment

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

Environmental Monitoring and Evaluation Branch
Alberta Environment
10th Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-6278
Fax: (780) 422-6712

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-2700
Fax: (780) 422-4086
Email: env.infocent@gov.ab.ca

EXECUTIVE SUMMARY

Alberta Environment (AENV) has measured pesticides in surface waters since the mid-1980's and reports on pesticide concentrations in surface waters as part of its evaluation and reporting responsibilities. In 1995 the approach to pesticide monitoring was updated to link ambient monitoring to pesticide sale records. Every five years provincial pesticide sales data, information on pesticide behaviour and toxicity, and results of surface water monitoring programs, are reviewed to priorize active ingredients that need to be monitored in surface waters.

The overall objective of this report is to provide an overview of the extent and nature of pesticide contamination in Alberta's surface waters. The overview covers all data from 1995 to 2002 inclusive that are stored on the AENV Water Data System. This includes data from a broad range of water body types (i.e., rivers, creeks, lakes, wetlands, irrigation canals and returns, and urban streams) and from both AENV and Alberta Agriculture, Food, and Rural Development (AAFRD).

The data set consists of 3055 samples from 326 sites, mostly in the 'White Zone' or agricultural area of the province; most agricultural, domestic, municipal and industrial uses of pesticides occur in this zone. Forty active ingredients, breakdown products, and isomers (25 herbicides, 14 insecticides and one fungicide) were monitored consistently in all samples. In 2002, as a follow-up to the second provincial pesticide sales review, an additional 23 active ingredients, and breakdown products (15 herbicides, 3 insecticides and 5 fungicides) were analysed in all samples. From 2000 on, glyphosate, its breakdown product amino-methyl phosphonic acid (AMPA), and glufosinate were analysed in selected monitoring programs.

Pesticide detections in Alberta surface waters are common and widespread. Pesticides were detected in 65% of all samples. Forty-four of the 63 pesticides that were measured were detected. These comprise 33 herbicides, 10 insecticides and one fungicide. Most of the compounds that were not detected were only monitored in 2002. Provincially, 2,4-D was detected most frequently (53 % of samples). Seven compounds were reported in 10 to 50% of the samples (clopyralid, dicamba, glyphosate, MCPA, MCPP, picloram, and triclopyr); 15 were reported in 1 to 10% of the samples (4-chloro-2-methylphenol, 2,4-dichlorophenol, AMPA, atrazine, bentazon, bromacil, bromoxynil, clodinafop-propargyl, diazinon, dichlorprop, triallate, ethofumesate, fluroxypyr, imazamethabenz, imazethapyr, lindane, and quizalofop) and the remaining 19 occurred in less than 1% of the samples (2,4-DB, alpha-BHC, azinphos-methyl, carbathiin, chlorpyrifos, cyanazine, desethyl atrazine, deisopropyl atrazine, dimethoate, diuron, ethalfluralin, malathion, methoxychlor, imazamox, pyridaben, quinclorac, simazine, terbufos, and trifluralin).

Detection patterns are related to sales and use patterns across the province, but they are also influenced by compound-specific behaviour. Generally, pesticides that had the highest sale records were also the most frequently detected. Some notable exceptions include ethalfluralin, trifluralin, and carbathiin which have a high sale volume, but are reported rather infrequently; and picloram which has a relatively low sale volume, but is detected fairly frequently. Pesticide characteristics related to mobility and persistence are believed to override the influence of use patterns in these cases.

There is a distinct north-south pattern in pesticide detection frequency. This is consistent with pesticide use intensity: much lower detection frequencies were recorded in northern basins (Hay, Slave, Peace, Athabasca, and Beaver river basins) than southern basins (North Saskatchewan, Battle, Red Deer, Bow, Oldman, and South Saskatchewan river basins, and Sounding Creek basin).

The pesticide index rates water bodies according to 'poor', 'marginal', 'fair', 'good' or 'excellent', based on the frequency, variety and magnitude of pesticide detections and allows for broad comparisons among water bodies. The detection frequency, number, and concentration of pesticides were highest in irrigation returns and in urban streams; over 75% of these water bodies have a pesticide index score that ranges from 'poor' to 'marginal'. Compared to these water bodies, lakes, rivers, wetlands, creeks and irrigation canals had generally lower pesticide concentrations, frequency of occurrence, and variety. Ninety-four percent of lakes had index scores that ranged from 'good' to 'excellent'; 97% of the rivers ranged from 'fair' to 'excellent'; 97% of wetlands and streams ranged from 'marginal' to 'excellent' and 84% of irrigation canals ranged from 'marginal' to 'excellent'.

Use patterns combined with climatic influences also bring about seasonal and year-to-year changes in the occurrence of pesticides in surface waters. Provincially, there is higher likelihood of pesticide detections from March to September, with June and July being peak months. This is related to the timing of ice break-up and snowmelt runoff (March-April), to the main period of application (May –July), and to peak rainfall periods (June – July) in the province. Typically, highest concentrations are measured following rains that coincide with or follow shortly after the main period of application. Both runoff and atmospheric deposition contribute to the pesticide inputs to surface waters.

In central Alberta streams, the decline in imazamethabenz and increase of clopyralid levels is due to shifts in use patterns. As well, Central Alberta streams, such as Threehills, Ray and Haynes creeks, exhibited lowest total pesticide concentrations in 2002, possibly because of reduced use, low precipitation, and runoff during that severe drought year.

Industrial point sources and urban non-point sources have been associated with changes in pesticide concentrations over time. In the North Saskatchewan River industrial point sources are believed to have been associated with elevated levels of 2,4-D and lindane in the 1970's and early 2000's, respectively**.** Detections declined sharply or were eliminated when remedial actions were taken or when suspected sources disappeared.

Crowfoot Creek supplies irrigation water, which is conveyed via a diversion from the Bow River, to agricultural land in the creek's basin; it also receives irrigation return flows in its lower reaches. Agricultural use of atrazine is mostly on corn crops, a crop of negligible importance in the basin. Atrazine detections in Crowfoot Creek were traced back to urban use of a sterilant in the Calgary area. The decline of detections in the creek is believed to be linked to the decline in sterilant use.

Urban and agricultural use of pesticides results in noticeable patterns of pesticide contamination in surface waters. Pesticide detections downstream of Lethbridge, Calgary, Red

Deer, and Edmonton were generally more diverse and frequent than upstream. Some of the pesticides encountered more frequently downstream included the lawn care herbicides 2,4-D, dicamba, and MCPP, and the insecticides lindane, diazinon, and chlorpyrifos.

Streams draining land where agriculture is intense and pesticide use high, tend to have a greater variety and higher concentration of pesticides than streams that drain land where pesticide use is less intensive. Although agricultural pesticide use prevail in agricultural watersheds, it is recognized that in rural areas domestic, municipal and industrial uses could also contribute pesticides to surface waters. Some pesticides such as methoxychlor, atrazine, cyanazine, and chlorpyrifos were only reported in irrigation systems, which typically are high use areas.

Although surface water quality guidelines are exceeded in less than 30% of samples from Alberta surface waters, the full implications of pesticide occurrence in surface waters remain a complex and largely unresolved issue. Canadian water quality guidelines for the protection of aquatic life, irrigation and drinking water are exceeded in 3.5%, 26.9% and less than 1% of the samples, respectively. Although this frequency is not high, there are uncertainties about how comprehensively pesticide risk in surface waters can be assessed using current guidelines. These uncertainties stem from the unavailability of guidelines for over half of the pesticides detected in Alberta surface waters, the fact that guidelines apply to single compounds, and that many samples have multiple pesticide occurrences or multiple incidences of non-compliance. Because of these uncertainties, the possibility of local chronic effects on aquatic life and some sensitive crops cannot be excluded.

The level of pesticide contamination in Alberta surface waters appears to be similar to that of other jurisdictions with similar use patterns. Pesticide detections in surface waters are reported commonly in other Canadian provinces and the USA and, similar to Alberta, detections tend to be seasonal and related to use patterns. Urban and agricultural uses are identified as primary sources. Incidences of non-compliance with guidelines are reported in other Canadian provinces and in the United States. Uncertainty regarding the actual significance to aquatic ecosystem health of low-level pesticide detections is common to all jurisdictions. More detailed comparisons of pesticide data among jurisdictions are often hampered by differences in scope and design of monitoring programs, and differences in climate, crops, and types of pesticides used.

The report provides general guidance and recommendations to help maintain an effective monitoring program of pesticides in surface waters in Alberta, including the need for regular updates of monitoring programs based on detailed knowledge of provincial pesticide sales. The report also highlights various research needs related to pesticide behaviour and pathways in Alberta's aquatic, terrestrial and atmospheric systems, and the need for further information on urban and rural pesticide contributions. Such information is critical in the development of integrated, holistic beneficial management practices. Finally, the ongoing need for guideline development is emphasized, and, especially, the need to develop sensitive monitoring tools to assess the cumulative effects of man-made pesticides on aquatic ecosystems.

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LIST OF ABBREVIATIONS

AAFRD	Alberta Agriculture Food and Rural Development
AENV	Alberta Environment
AESA	Alberta Environmentally Sustainable Agriculture
ARC	Alberta Research Council
ASWQG	Alberta Surface Water Quality Guidelines
CAESA	Canada Alberta Environmentally Sustainable Agriculture
CCME	Canadian Council Ministers of the Environment
CV	coefficient of variation
MDL	Method Detection Limit
NAWQA	National Water Quality Assessment (USA)
PAL	Protection of Aquatic Life guideline
Irr	Irrigation guideline
QA/QC	Quality Assurance/Quality Control
WDS	Water Data System
µg/L	microgram per liter or ppb (part per billion)

1.0 INTRODUCTION

1.1 Background

Pesticides are man-made chemicals that are introduced intentionally in the environment to control pests that interfere with food production, aesthetic aspects of the human environment, and forestry.

Pesticides can be grouped in a variety of ways (e.g., Byrtus 2000, AAFRD 2004), according to:

- The species groups that they are intended to control: e.g., herbicides (plants), insecticides (insects), fungicides (fungi) and rodenticides (rodents);
- The type of control they offer: biological control (e.g., *Bacillus thuringiensis*) and chemical control (inorganic and organic compounds);
- Their detailed chemical composition: e.g., organophosphates, organochlorines, carbamates, phenoxy acids, sulfonyl ureas, and triazines; and
- Their mode of action: e.g., inhibitors of photosynthesis, lipid synthesis, cell growth and division, or specific enzymes, cell membrane disruptors, synthetic auxins, and acethylcholinesterase inhibitors.

In general, the first grouping has been used in this report.

Pesticide use patterns in Canada tend to differ from those in other developed countries. Canada's total use and average annual application rates of pesticides are lower than those in the USA, Germany, France, the United Kingdom and Japan (AENV 2001). In 1997 herbicides represented 85% of pesticide sales in Canada (SCESD 2000). The lower relative use of insecticides and fungicides compared to many countries is due to the shorter growing season, the predominance of annual crops, and the relatively less intensive nature of agriculture. Based on 1998 pesticide sales records for Alberta, Byrtus (2000) summarized sales by active ingredient (a.i.) for 4 broad sectors: agricultural (i.e., crop production), commercial/industrial (includes forestry, rights of way, landscaping, golf courses and municipal use), domestic (i.e., home and garden, household), livestock and structural. In 1998, the agricultural sector represented 95.8% of the province's sales of pesticide a.i. and relied mostly on herbicides; the commercial /industrial, domestic sector, and livestock and structural sectors accounted for 3.3%, 0.77% and 0.1% of the sales, respectively. It is recognized that some products have multiple uses (e.g. agricultural, landscaping or rights of way maintenance; see also Table 1) and that because sales of such products were lumped under the agricultural sector, that sector's use may be somewhat overestimated (Byrtus 2000). Multiple uses also imply the possibility of multiple sources of surface water contamination. Although the overall amount of active ingredient used in the domestic sector is small, uses are more intense and the use of insecticides and fungicides is proportionately larger than in other sectors (AENV 2001). In Canada, Alberta and British Columbia jointly accounted for 24% of the 1997 pesticide sales compared to 36% for Saskatchewan and 18% for Manitoba (SCESD 2000).

Once applied to the target site (e.g., vegetation, soil) pesticides that are not taken up or absorbed to the target site have a tendency to move off site with runoff and seepage to shallow groundwater. Pesticides can also enter the atmosphere adsorbed to dust particles, or as fine droplets, or as a gas. Once in the atmosphere, contaminants can travel for short or long distances before they are deposited with rain, snow or dust. Work done in Alberta by Hill et al. (2002) on pesticides in rainfall, and by Kumar (2001) on pesticides in air, has shown that pesticides currently used in Alberta can move into the atmosphere and that atmospheric deposition is an important source of pesticide loading to aquatic and terrestrial ecosystems. Pesticides applied in other parts of the world are also transported in the atmosphere and deposited in Alberta and other cold climates through condensation (e.g., Blais et al. 1998). The specific characteristics of the pesticides with respect to volatility, solubility, ability to adsorb to organic matter, and persistence determine which environmental pathways are likely to be most important. These characteristics will influence the partitioning of pesticides to water (surface water, ground water, or rain), air, dust or soil particles, or to biota (SCESD 2000).

1.2 Previous Work on Pesticides in Alberta Surface Waters

In Alberta several studies have been published on persistent organochlorine pesticides, compounds which have been banned for well over 20 years. In the mountain National Parks of Alberta, surface water contamination by persistent organochlorine pesticides (e.g., DDT, DDE, dieldrin, chlordane, and toxaphene) has been the subject of several studies. Organochlorines were manufactured mainly from 1950's to the 1970's and caused considerable concern because of their toxicity, persistence in the environment and their ability to bio-accumulate along food chains. Concentrations of persistent organochlorine pesticides have been shown to increase at high latitude and altitude as a result of long-range transport and preferential deposition in cold climates (e.g., Gregor 1990, Blais et al. 1998, Donald et al. 1994). Blais et al. (2001) showed that glacial melt contributed substantially to the organochlorine inputs to alpine surface waters and that about 10% of the melt water originated from ice deposited in the 1950-1970's when it was contaminated with organochlorines. Furthermore, Blais et al. (2003) documented the concentration of semi-volatile organochlorine compounds in *Gammarus lacustris* at high altitudes. Several studies have dealt with organochlorine contamination in aquatic biota and sediments. Stern et al. (1996) documented the persistence of two toxaphene congeners (chlorobornanes) in sediments from a mountain lake. Further studies on 13 mountain lakes in Alberta and British Columbia confirmed the presence of chlorobornanes (toxaphene breakdown product) in sediments and fish tissue 30 to 40 years after these lakes had been treated (Donald et al. 1997). These contaminants were also detected in untreated lakes, but generally at lower levels.

In a study of PCB and pesticide levels in Alberta fish (Alberta Research Council 1984) traces of DDE, DDD and chlordane were detected in most fish samples taken from 11 major lakes and rivers. Methoxychlor was also detected, but only in goldeye from the North Saskatchewan River. Rosenberg (1975) documented the absence of dieldrin in water, sediment and aquatic plants one year after the experimental application of the insecticide to a slough in central Alberta. However, the insecticide was still detectable in aquatic invertebrate tissue.

Comparatively fewer studies have been published on currently used pesticides in Alberta surface waters. Gummer (1978) provided an overview of the pesticide monitoring conducted by Environment Canada in the Prairies of Western Canada for the period 1971 to 1977. The review focussed on 2,4-D, 2,4,5-T, lindane, dichlorprop, aldrin and beta-endosulfan. It revealed that the chlorophenoxy acid herbicides 2,4-D, dichlorprop, and 2,4,5-T as well as organochlorine pesticides lindane and its isomer alpha BHC, were frequently detected. The review also highlighted the importance of contributions from urban, industrial, agricultural and atmospheric sources. Wayland (1991) found that in a series of enclosures placed in an alkaline pond, carbofuran, an insecticide used to control grasshopper infestations, had no measurable effects on invertebrates at concentrations of 5 µg/L. However, at concentrations of 25 µg/L, *Gammarus lacustris* and Chironomidae abundance and biomass declined significantly. Anderson et al. (1998) established baseline information for currently used pesticides in agricultural streams and described broad relationships between level of contamination, use intensity, and climate. Lindeman and Shaw (1997) examined trends in 2,4-D and 2,4,5-T at Prairie Provinces Water Board monitoring sites on the Alberta-Saskatchewan border. Crosley et al. (1998) reported on trends in gamma and alpha BHC at Environment Canada long-term monitoring sites. Ontkean et al. (2000) reported on pesticide contamination of Crowfoot Creek following a 4-year study of this agricultural stream.

1.3 Objectives

The overall objective of this document is to assess and report on the extent and nature of current-use pesticide contamination in Alberta's surface waters based on data collected during the period 1995-2002.

Specific objectives are to:

- Provide a broad provincial overview of pesticide occurrence and concentrations;
- Compare observed concentrations with Canadian Water Quality Guidelines;
- Present a composite depiction of pesticide contamination with a pesticide index;
- Evaluate temporal (seasonal and year-to-year) patterns of pesticide occurrences; and
- Depict broad-scale urban influences, and influences in watersheds that are primarily agricultural.

2.0 BACKGROUND ON PESTICIDE MONITORING OF SURFACE WATERS IN ALBERTA

Pesticides were monitored in Alberta surface waters from the mid-1970' to the mid-1980's by Environment Canada. In the mid-1980's Environment Canada's sampling was greatly reduced and mostly confined to mountain National Parks. At that time, the province took over the monitoring of major rivers in the rest of the province.

In 1995, three data reviews set the stage for a more comprehensive approach to pesticide monitoring in Alberta.

1. A detailed review of pesticide sales records in Alberta was carried out in 1994 to determine which pesticides were being sold in the province, where, and in what quantities (Cotton and Byrtus 1995). This review made it possible to evaluate spatial and temporal patterns of pesticide sales and use across the province.
2. A review of pesticide characteristics led to a process which allowed the rating of the theoretical risk posed by pesticides to the aquatic environment (Cotton 1995). Risk was defined in terms of likelihood of pesticides entering surface waters (i.e., based on their solubility in water, half-life in soils, volatility and ability to adsorb to organic particles) and the likelihood that, if pesticides entered surface waters, they would represent a risk to aquatic life (based on aquatic and mammalian toxicity). Sales records and information on risk for aquatic environments were used to prioritize the pesticides for the monitoring in surface waters.
3. The third review was a critical assessment of the provincial and federal pesticide databases for Alberta surface waters (Anderson 1995). It pointed to the fact that the list of pesticides that was being monitored had been established in the early 1970's and focussed on organochlorines and organophosphates, which had been of particular concern at the time. However, this list had not been adjusted to reflect market changes. Many of the compounds analyzed were not in use anymore and had seldom been detected in surface waters. Many high use products were not monitored at all. Analytical methods had detection limits above the environmental concentration range. Finally, most data were from larger rivers and little work had been done on smaller streams, wetlands, or lakes.

These reviews led to significant modifications in pesticide monitoring programs in Alberta. The list of pesticides analyzed was changed substantially to reflect current use patterns even though issues regarding analytical cost and availability of analytical methods precluded the analysis of some important high-sale products of monitoring interest listed in Cotton (1995) (e.g., glyphosate). The periodic review of pesticide sale records was recognised as a critical component in pesticide monitoring activities.

Coincident to the above-mentioned reviews, the Alberta Research Council (ARC, and formerly Alberta Environmental Centre), Vegreville, acquired a gas chromatograph mass spectrometer that made it possible to adopt analytical methods with considerably lower detection limits.

As a result of these changes, 40 pesticides became part of routine monitoring programs of pesticides in Alberta surface waters in 1995. A second major sales review in 1998 (Byrtus 2000) led to the inclusion, in 2002, of 23 additional compounds to the monitoring list. In 1999 ARC developed the methodology to analyse glyphosate, glufosinate and the glyphosate breakdown product amino methyl phosphonic acid (AMPA). These compounds have been analyzed as part of specialized studies on wetlands and streams in agricultural areas since 2000.

Since the initial review of the Alberta surface water pesticide database, increased emphasis has been placed on pesticide monitoring by Alberta Environment and Alberta Agriculture, Food, and Rural Development (AAFRD). In addition to continued monitoring of major rivers, samples have been collected from a variety of water bodies such as agricultural streams, wetlands, lakes, irrigation canals and return flows, and urban streams and storm sewers. This monitoring has been conducted as part of AENV's Long Term River Network (LTRN), shorter-term lake and river surveys, and research projects, as well as part of AAFRD's program of monitoring streams in agricultural areas.

Most of the pesticides currently monitored in surface waters are herbicides, followed by insecticides and fungicides. Most of these compounds are registered for use in agriculture, although some have municipal, industrial or domestic registered uses (Table 1). AAFRD (2004) updates information about registered agricultural use, chemical and toxicological characteristics on an annual basis. Cotton (1995) provides a summary of chemical and physical characteristics and toxicity to various test organisms for many compounds used in Alberta. Further toxicological information can be obtained by searching online databases such as ECOTOX.

Table 1 Trade names and registered uses for pesticides monitored in Alberta surface waters (1995- 2002)

Active Ingredient	Trade Name	Start Monitoring	Registered Uses			
			Agricultural	Municipal	Industrial	Domestic
43 HERBICIDES						
2,4-D	Amine 500, LV Ester 500, 600, 700	1995	●	●	●	●
2,4-DB	Embutox, Cobutox, Butyric 400	1995	●			
2,4-DICHLOROPHENOL (*)	Degradation product of 2,4-D, 2,4-DB and 2,4-DP	2002				
4-CHLORO-2-METHYLPHENOL(*)	Degradation product of MCPA, MCPB and MCPP	2002				
ATRAZINE	Aatrex, Atra-pell, Primextra	1995	●		●	
AMPA(*)	Degradation product of glyphosate	2000				
BENTAZON	Basagran, Laddok	2002	●			
BROMACIL	Calmix, Hybor-D, Hyvar,Krovar	1995			●	
BROMOXYNIL	Buctril M, Compas, Mextrol, Pardner, Thumper, Unity	1995	●			
CLODINAFOP-PROPARGYL	Horizon	2002	●			
CLODINAFOP-PROPARGYL acid (*)	Acid metabolite	2002				
CLOPYRALID	Lontrel, Curtail M, Eclipse, Transline	1995	●			
CYANAZINE	Bladex	1995	●			
DESETHYL ATRAZINE (*)	Degradation product of atrazine	1995				
DEISOPROPYL ATRAZINE (*)	Degradation product of atrazine	1995				
DICAMBA	Banvel, Dyvel, Dycleer	1995	●	●	●	●
DICHLORPROP (2,4-DP)	Diphenoprop, Estaprop	1995	●	●	●	
DICLOFOP-METHYL	Hoegrass II, Hoegrass 284	1995	●			
DIURON	Karmex	1995	●		●	
ETHALFLURALIN	Edge	1995	●			
ETHOFUMESATE	Nortron	2002	●			
FENOXAPROP-P(*)	Degradation product of fenoxaprop-p-ethyl	2002	●			
FENOXAPROP-P-ETHYL	Champion, Excel Super, Laser DF, Triumph Plus	1995	●			
FLUAZIFOP	Fusion, Venture	2002	●			
FLUROXYPYR	Attain, Prestige	2002	●			
GLYPHOSATE	Roundup, Touchdown, Vantage, Glyphos, Maverick, Renegade, Factor, Victor, Credit	2000	●	●	●	●
GLUFOSINATE	Liberty	2000	●			●
IMAZAMETHABENZ	Assert	1995	●			
IMAZAMOX	Odyssey	1995	●			
IMAZETHAPYR	Pursuit, Odyssey	1995	●			
LINURON	Afolan	2002	●			
MCPA	MCPA Amine, Ester, K-salt, Na-salt	1995	●	●	●	
MCPB	Tropotox, Clovitox	1995	●			
MCPP (MECOPROP)	Compitox	1995	●	●		●
METOLACHLOR	Dual II Magnum, Primextra	2002	●			
METRIBUZIN	Crossfire, Sencor	2002	●			

Table 1 Trade names and registered uses for pesticides monitored in Alberta surface waters (1995- 2002) (continued)

Active Ingredient	Trade Name	Start Monitoring	Registered Uses			
			Agricultural	Municipal	Industrial	Domestic
PICLORAM	Tordon, Grazon	1995	●	●	●	
QUINCLORAC	Accord	1995	●			
QUIZALOFOP	Assure II, Freedom Gold	2002	●			
SIMAZINE	Princep Nine-T	2002	●			
TRIALLATE	Avadex BW, Fortress	1995	●			
TRICLOPYR	Garlon, Remedy	2002	●	●	●	
TRIFLURALIN	Advance, Bonanza, Fortress, Rival, Treflan	1995	●			●
17 INSECTICIDES						
ALDRIN	No longer registered	2002				
ALPHA-BHC(*)	Isomer of technical lindane; no insecticidal properties	1995				
ALPHA-ENDOSULFAN (*)	Degradation product of endosulfan (endosulfan, thiodan)	1995	●			
AZINPHOS-METHYL	Guthion, Azinphos-methyl, Sniper	1995	●			
CHLORPYRIFOS	Lorsban, Pyrinex, Dursban, domestic uses discontinued	1995	●	●	●	
DIAZINON	Diazinon, Diazol, Basudin, domestic uses discontinued	1995	●			
DIELDRIN	No longer registered	2002				
DIMETHOATE	Lagon, Cygon, Dimethoate, domestic uses discontinued	1995	●			
DISULFOTON	Di-Syston	1995	●			
ETHION	Ethion	1995	●			●
GAMMA-BHC (lindane)	Vitavax Dual, Vitavax RS (registration discontinued)	1995	●			
MALATHION	Malathion, Cythion	1995	●	●	●	●
METHOXYCHLOR	Moxy, Methoxyl, Methoxychlor	1995	●			●
PARATHION	Plant-Fume, Parathion	2002	●			
PHORATE	Thimet	1995	●			
PYRIDABEN	Sanmite, Pyramite, (greenhouse use)	1995	●			
TERBUFOS	Counter	1995	●			
6 FUNGICIDES						
CARBATHIIN	Vitavax Single, Vitavax Powder, Vitavax Dual	1995	●			
CHLOROTHALONIL	Bravo, Daconil	2002	●	●		
HEXACONAZOLE	Proseed	2002	●			
IPRODIONE	Foundation, Rovral	2002	●	●		
METALAXYL-M	Ridomil	2002	●			
PROPICONAZOLE	Tilt, Banner	2002	●	●		

(*) degradation product or isomer

3.0 METHODS

3.1 Pesticide Data on the Water Data System

The data set examined in this report includes all surface water pesticide data on the Alberta Environment Water Data System (WDS) that were generated at the lower detection limits implemented by ARC in 1995. The period of record runs from January 1, 1995 to and including December 31, 2002. The data set consists of an aggregation of pesticide data from all surface water quality projects managed by Alberta Environment and comprises pesticide information for a broad range of water bodies across the major river basins. It includes data on rivers, creeks, lakes, wetlands, irrigation canals, irrigation return flows, and urban streams or drains. Also included in the data set are pesticide data generated under the Environmentally Sustainable Agriculture Agreement (AESA), a program which focuses on agricultural streams and is managed by Alberta Agriculture Food and Rural Development (AAFRD). Pesticide data from the Oldman River Basin Initiative are also included (this program is managed as a partnership among numerous stakeholders in the basin (Oldman Water Council).

Data on WDS that have not been included in this review are the data generated under the Canada Alberta Environmentally Sustainable Agriculture Agreement (CAESA) or under some Water Research User Group (Alberta Environment) projects. These data concerned a limited number of pesticides and were generated at different detection limits than the rest of the database. Results of these projects have been published elsewhere (Anderson et al. 1998 a and b, Byrtus et al. 2002).

Pesticide data generated as part of some watershed initiatives (e.g., detailed watershed studies coordinated by AAFRD on Crowfoot Creek, Battersea Drain and the Little Bow River) have not been entered on WDS and are not part of this analysis.

3.2 Projects and Design

The data originate from 35 different sampling programs across Alberta (Table 2). These programs differ in scope and objectives and as a result have different sampling frequencies and intensities. The sampling designs include fixed-date, flow-weighted (covering a range of flows, but emphasizing runoff events), or event-based sampling (targeting runoff events), and sampling frequencies ranging from the collection of a single sample to the collection of several samples per year over many years. Sampling sites are depicted in Figure 1 and listed in Appendix A.

The sampling design can influence the result of pesticide monitoring programs (e.g., Capel et al. 1996, Battaglin and Hay 1996). Typically, repeated sampling of runoff events during the main period of pesticide application is likely to result in more frequent detections and higher concentrations than a fixed-date (e.g., monthly or quarterly) program. Study designs need to be taken into account in the interpretation of data sets, as they could influence spatial and temporal patterns of detection and ultimately the perceived degree of contamination.

Table 2 Surface water quality projects involving pesticide sampling (1995 - 2002)

Project Number	Project Name	Number of Samples	Sampling Design
ABP001	Tributary Network	161	Fixed date
ABP007	WID Canal Inflows	12	Fixed date
ABP009	Turf Herbicides (describes screen, not specific project)	9	Event based
ABS001	River Monitoring	210	Fixed date
ABS002	Lake Monitoring	7	Fixed date
ABS008	Elbow River	5	Fixed date
ABS009	Highwood / Little Bow	12	Event based
ABS012	Northern MTRN	1	Fixed date
ABS014	NSR Excursions	7	Event based
ABS021	Pine Lake	4	Fixed date
ABS022	Lake WQ Plans (Survey Lakes)	76	Fixed date
ABS026	Pakowki Lake	7	Fixed date
ABS027	Buffalo Lake	3	Fixed date
ABS032	AESA Stream Survey	1034	Flow weighted
ABS034	LTRN-Long Term River Network	580	Fixed dates
ABS042	Lac St Cyr Diversion at NSR	7	Fixed dates
ABS049	Tyrell Lake Assessment	1	Fixed dates
ABS050	AB/NWT Transboundary Pesticides	22	Fixed dates
ABS052	Willow Creek / Pine Coulee	29	Fixed dates
ABS054	Oldman River Basin Overview	184	Fixed dates + event based
ABS056	Dogpound Creek	2	Fixed dates
ABS057	Oldman River - Irrigation District Monitoring (LNID)	29	Fixed dates
ABS059	Cold Lake Survey and Area Lakes	14	Fixed dates
ABS065	Central MTRN	105	Event based
ABS066	ALMS Support - Lake Inflows	25	Event based
ABS068	Six Mile Coulee Study (OMR)	66	Fixed dates + event based
ABS081	ACA Upper Little Red Deer River	10	Fixed dates
ABS082	Pipestone Longitudinal Study	40	Fixed dates + event based
ABS085	Wetlands Project	124	Fixed dates + event based
ABS087	Lethbridge Stormwater Project (Oldman River)	145	Event based
ABS090	North Saskatchewan River Loading Study	35	Fixed dates + event based
ABS094	Nose Creek Watershed Study	68	Fixed dates + event based
ABS101	Glyphosate in Alberta	19	Fixed dates + event based
ABS109	Wabamun Lake Extensive	4	Fixed dates

Notes:
Fixed date: timing of sampling is predetermined
Flow weighted: sampling occur for a range of flow conditions, but particularly following runoff events
Event based: sampling follows runoff events

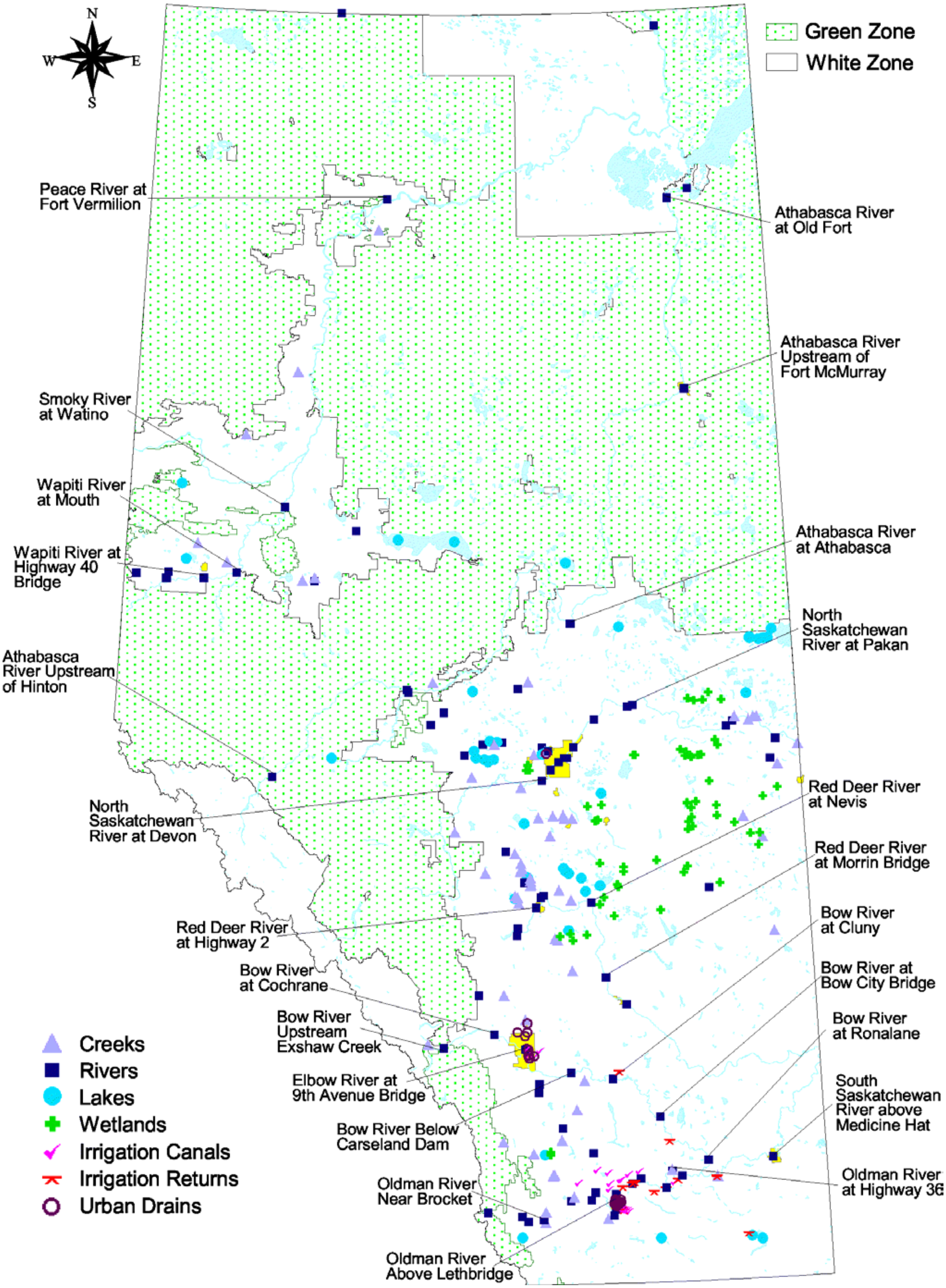


Figure 1 Pesticide sampling sites (1995 – 2002)
Named sites are long-term river monitoring sites.

The aggregated data set provides a general indication of pesticide contamination of surface waters across Alberta and can be used to depict broad distribution patterns of pesticide detection, detection frequency, and compliance with guidelines. However, data from some programs only lend themselves to the analysis of temporal trends or to the assessment of effects from various anthropogenic activities.

3.3 Sampling Methods

Although projects differ in sampling design, they share the same sampling and analytical methods.

The majority of samples are surface grab samples or depth integrated samples, taken at a specific location. In some cases (wetland and lake sampling) samples are composites of grab samples taken from different locations in the water body.

Sampling and sample handling procedures followed methods outlined in AENV (2002). This includes the use of clean sample bottles and the use of clean stainless steel equipment in the preparation of composite and split samples. Pesticide samples were stored in amber 1L glass jars, except for glyphosate, AMPA and glufosinate samples, which were stored in 250 mL plastic bottles.

The sampling programs involve the collection of field blanks, trip blanks, split samples, and spiked samples for the purpose of evaluating the quality of the data. These data were extracted from the database and are evaluated and discussed in Appendix B.

3.4 Pesticide Analyses

3.4.1 List of Pesticides

Most samples were consistently analyzed for the same suite of pesticides, although that suite evolved due to the addition of pesticides in 2002. There were two exceptions: Project ABP009 (Table 2) which involved the analysis of 2,4-D, MCPA, dicamba and MCPP in urban runoff samples, and a study on glyphosate (project ABS101, Table 2) where some samples were only analyzed for glyphosate, AMPA, and glufosinate. The pesticides and their detection limits are shown in Table 3. Forty compounds were analysed routinely from 1995 to 2002. In 2001, the detection limit for dicamba was lowered from L0.02 to L0.005 µg/L and in 2002, twenty-three additional compounds were added to the list of compounds routinely analysed. All pesticide analyses were carried out at the Pesticides and Trace Organics Laboratory, ARC, Vegreville under the supervision of Dave Humphries.

3.4.2 Analytical Methods

3.4.2.1 Routinely Analysed Compounds

One litre, unfiltered water samples were extracted with dichloromethane (DCM) at a pH below 2 (acidified with phosphoric acid) and with the addition of sodium chloride in a separator funnel.

Table 3 Summary of pesticide analyses for the period 1995-2002

Method Code	Compounds Analyzed	Date Analysis Started	Method Detection Limit (µg/L)	Total Number of Samples	Number of Samples w/o Detections	Number of Samples with Detections	Detection Frequency (%)	Median of Measurable Concentration (µg/L)	Maximum Concentration (µg/L)
	HERBICIDES								
100667	2,4-D	1995	L0.005	3061	1435	1626	53.12	0.043	439.000
100668	2,4-DB	1995	L0.005	3052	3048	4	0.13	0.026	0.665
100669	DICHLORPROP (2,4-DP)	1995	L0.005	3053	2891	162	5.31	0.013	0.657
99888	2,4-DICHLOROPHENOL	2002	L0.01	250	244	6	2.40	0.01	1.58
99887	4-CHLORO-2-METHYLPHENOL	2002	L0.01	250	247	3	1.20	0.02	0.43
103453	AMINOMETHYL PHOSPHONIC ACID (AMPA)	2000	L1	110	103	7	6.36	1	4
100674	ATRAZINE	1995	L0.005	3054	2939	115	3.77	0.020	2.617
99897	BENTAZON	2002	L0.005	42	41	1	2.38	NA	0.034
100675	BROMACIL	1995	L0.03	3052	3020	32	1.05	0.25	2.70
100676	BROMOXYNIL	1995	L0.005	3053	2760	293	9.60	0.011	4.710
99881	CLODINAFOP-PROPARGYL	2002	L0.02	22	22	0	0.00	NA	NA
99880	CLODINAFOP ACID METABOLITE	2002	L0.04	23	22	1	4.34	NA	0.11
100688	CLOPYRALID	1995	L0.02	3053	2705	332	10.93	0.05	2.72
100678	CYANAZINE	1995	L0.05	3053	3037	16	0.52	0.07	0.21
102610	DEISOPROPYL ATRAZINE	1995	L0.05	2480	2479	1	0.04	NA	0.48
102609	DESETHYL ATRAZINE	1995	L0.05	2480	2479	1	0.04	NA	0.01
100680	DICAMBA	1995	L0.02	2221	1902	319	14.36	0.03	14.42
103639	DICAMBA	2001	L0.005	838	557	281	33.53	0.027	21.000
100669	DICHLORPROP (2,4-DP)	1995	L0.005	3053	2891	162	5.31	0.013	0.657
100681	DICLOFOP-METHYL	1995	L0.02	3053	3053	0	0.00	NA	NA
100683	DIURON	1995	L0.2	3052	3028	24	0.78	0.3	2.8
100685	ETHALFLURALIN	1995	L0.005	3053	3032	21	0.69	0.007	0.184
99898	ETHOFUMESATE	2002	L0.005	42	39	3	7.14	0.072	0.115
102613	FENOXAPROP-P-ETHYL	1995	L0.04	2481	2481	0	0.00	NA	NA
99894	FLUAZIFOP	2002	L0.01	42	42	0	0.00	NA	NA
99895	FLUROXYPYR	2002	L0.01	42	40	2	4.76	0.10	0.18
103626	GLUFOSINATE	2002	L1	75	75	0	0.00	NA	NA
103452	GLYPHOSATE	2000	L0.2	110	82	28	25.45	0.3	6.1
102088	IMAZAMETHABENZ	1995	L0.05	2741	2565	176	6.42	0.11	9.01
103141	IMAZAMOX	1999	L0.02	2109	2107	2	0.09	4.56	9.09
102612	IMAZETHAPYR	1995	L0.02	2436	2409	27	1.11	0.08	0.41
99899	LINURON	2002	L0.02	42	42	0	0.00	NA	NA
96000 + 100690	MCPA	1995	L0.005	3062	1912	1150	37.56	0.019	8.490
100691	MCPB	1995	L0.02	3052	3052	0	0.00	NA	NA
100692	MCPP (MECOPROP)	1995	L0.005	3061	2346	715	23.36	0.023	586.000

Table 3 Summary of pesticide analyses for the period 1995-2002 (continued)

Method Code	Compounds Analyzed	Date Analysis Started	Method Detection Limit (µg/L)	Total Number of Samples	Number of Samples w/o Detections	Number of Samples with Detections	Detection Frequency (%)	Median of Measurable Concentration (µg/L)	Maximum Concentration (µg/L)
102935	METOLACHLOR	2002	L0.005	42	42	0	0.00	NA	NA
103631	METRIBUZIN	2002	L0.01	42	42	0	0.00	NA	NA
93039 + 100693	PICLORAM	1995	L0.005	3053	2558	495	16.21	0.053	13.407
102611	QUINCLORAC	1995	L0.005	2481	2480	1	0.04	NA	0.024
99896	QUIZALOFOP	2002	L0.03	42	41	1	2.38	NA	0.01
103824	SIMAZINE	2002	L0.01	433	430	3	0.69	0.37	0.76
100696	TRIALLATE	1995	L0.005	3052	2935	117	3.83	0.011	0.464
103825	TRICLOPYR	2002	L0.01	433	387	46	10.62	0.03	3.05
100697	TRIFLURALIN	1995	L0.005	3053	3024	29	0.95	0.004	0.187
	INSECTICIDES								
102929	ALDRIN	2002	L0.005	42	42	0	0.00	NA	NA
100670	ALPHA-BENZENEHEXACHLORIDE (alpha-BHC)	1995	L0.005	3052	3049	3	0.10	0.008	0.091
100671	ALPHA-ENDOSULFAN	1995	L0.005	3053	3053	0	0.00	NA	NA
100687	AZINPHOS-METHYL	1995	L0.2	3053	3052	1	0.03	NA	0.012
100684	CHLORPYRIFOS	1995	L0.005	3052	3030	22	0.72	0.010	0.781
100679	DIAZINON	1995	L0.005	3053	2971	82	2.69	0.014	1.440
102930	DIELDRIN	2002	L0.005	42	42	0	0.00	NA	NA
102618	DIMETHOATE	1995	L0.05	2480	2476	4	0.16	0.09	0.23
100682	DISULFOTON	1995	L0.2	3053	3053	0	0.00	NA	NA
100686	ETHION	1995	L0.1	3053	3053	0	0.00	NA	NA
100672	GAMMA-BENZENEHEXACHLORIDE (LINDANE)	1995	L0.005	3052	2955	97	3.18	0.011	1.315
94013 + 100689	MALATHION	1995	L0.05	3053	3042	11	0.36	0.03	0.22
100673	METHOXYCHLOR	1995	L0.03	3053	3048	5	0.16	0.01	0.22
103630	PARATHION	2002	L0.01	42	42	0	0.00	NA	NA
94020 + 100694	PHORATE	1995	L0.005	3053	3053	0	0.00	NA	NA
102614	PYRIDABEN	1995	L0.02	2481	2480	1	0.04	NA	0.03
100695	TERBUFOS	1995	L0.03	3052	3050	2	0.07	0.02	0.03
	FUNGICIDES								
100677	CARBATHIIN (CARBOXIN)	1995	L0.1	3053	3050	3	0.10	0.04	0.14
99889	CHLOROTHALONIL	2002	L0.005	42	42	0	0.00	NA	NA
99892	HEXACONAZOLE	2002	L0.05	42	42	0	0.00	NA	NA
99890	IPRODIONE	2002	L0.02	42	42	0	0.00	NA	NA
99893	METALAXYL-M	2002	L0.01	42	42	0	0.00	NA	NA
99891	PROPICONAZOLE	2002	L0.05	42	42	0	0.00	NA	NA

NA: not applicable (i.e., no detections, or single detection only)

Sample bottles were rinsed with DCM. Deuterated surrogates were added prior to the extraction to monitor sample-handling procedures and to minimize the possibility of false negative results. The organic extract was dried with acidified sodium sulphate, concentrated with nitrogen, and derivatized with diazomethane. Internal standards were added to the extract immediately prior to analysis by Gas Chromatography/Mass Spectrometry/Iontrap. Qualitative analysis was performed using the relative retention time and relative abundances of two or more characteristic ions (deuterated surrogates). Quantitative analysis was performed using a multi-internal standards technique and extracted areas of characteristic ions.

Water samples were analysed in batches of 12 with one sample being a distilled water/reagent blank that included all steps applied to samples including addition of surrogates.

Mass spectrometer calibration was checked against decafluorotriphenylphosphine (DFTPP). The method was calibrated with a four point calibration curve using certified standards. Ions used for pesticide quantification and qualification were selected from individual standards that represent each compound and are free of matrix interferences.

The percent recoveries of the deuterated surrogate compounds (2,4-D, dicamba, atrazine, lindane) within each batch were evaluated to determine if they were within method specifications.

Results, expressed in µg active ingredient per litre, are not adjusted for recoveries.

3.4.2.2 Glyphosate Analyses

In spring of 2000, ARC implemented an analytical method for glyphosate, AMPA and glufosinate in water samples. The analysis relied on in-situ derivatization in water followed by analysis by gas chromatography/mass spectrometry/Iontrap. Water samples were analysed in batches of nine with one sample being a distilled water/reagent blank that includes all steps applied to samples. Mass spectrometer calibration was checked against DFTPP. The method was calibrated with a three-point calibration curve. Ions used for pesticide qualification and quantification were selected from individual standards that represent each standard and are free of matrix interferences. Results are not adjusted for recoveries. Results are expressed in µg active ingredient per litre. Method detection limits are listed in Table 3.

3.5 Data Analysis

Analyses were performed on the aggregated data set, on data from specific projects, or on data segregated by river basins and water bodies. Pesticide concentrations, pesticide detection frequency and total pesticide concentration were used to describe spatial and temporal trends in the data set. In this report:

- *Pesticide concentration* refers to the actual concentration reported by the analytical laboratory for individual compounds. Statistics such as median and percentiles that are provided for pesticide concentrations apply to *measurable* concentrations; and need to be evaluated in conjunction with detection frequencies to assess the extent of pesticide contamination (e.g., extent and duration of contamination).

- *Total pesticide concentration* per sample is the sum of concentrations reported for individual compounds in that sample.
- *Pesticide detection frequency* is the number of samples with at least one pesticide detection per sample, divided by the number of samples analysed. Pesticide detection frequency was used to represent the frequency of detection of individual compounds as well as the frequency of pesticide detection (e.g., occurrence of samples with at least one detection).
- *Number of detections per sample* is the number of individual pesticides per sample, for which a measurable concentration is reported.

Censored data (i.e., values < MDL) are common in pesticide data sets and were handled in different ways in this review depending on the purpose and nature of the data analysis (e.g., Capel et al. 1996, Adams 1998, Helsel 1990). In this report:

- Statistics such as medians and percentiles for 'measurable concentrations' do not include censored data.
- In the calculation of 'total pesticide concentration', censored data were replaced by 'zero'.
- In statistical analyses, censored values were replaced by 1/10th the MDL (e.g., Donald et al. 2001).
- For the calculation of the pesticide index, censored data were replaced by 1/10th the MDL. The choice of the fraction below the MDL does not influence the resulting index values, however, the inclusion of censored values influences the F1 factor of the index formulation (i.e., the percentage of samples that comply with set objectives).
- For the calculation of mass load, censored data were replaced by 1/10th the MDL.

Comparisons with surface water quality guidelines of Alberta Environment (1999), CCME (1999, 1987), and USEPA (2002) for the protection of aquatic life (PAL), and Alberta Environment (1999) and CCME (1999, 1987) guidelines for irrigation (IRR), drinking water (Drinking), and livestock watering (Livestock) provide a basis to evaluate the significance of reported concentrations. The application of guidelines does not imply that water bodies support specific uses such as irrigation, source of drinking water for human consumption or livestock watering. However, all water bodies would be expected to support aquatic life. Concentrations that were above the guideline were said to be non-compliant; those at or below the guidelines were said to be compliant.

Index

The calculation of the pesticide index relied on the formulation of the Canadian Water Quality Index (CCME 2001). It considers three criteria: the compliance with a set objective, the frequency with which this objective is not met, and the amount by which it is exceeded. In the index calculation, objectives for the pesticides were set at the method detection limit. This is the same approach as for the Alberta River Water Quality Index (Alberta Environment Water Quality Web Page http://www3.gov.ab.ca/env/water/SWQ/resources01.cfm). The use of CCME guidelines as objectives was not an option because the guidelines are only available for some of the pesticides detected in Alberta. In the case of dicamba where the method detection limit was lowered during the record period of interest, the lowest detection limit was applied to the entire data set.

The pesticide index as presented in this report is a relative indicator of pesticide contamination; it does not provide any indication of risk. Index results from various jurisdictions should only be compared if calculations use the same formulation, same variables and same objectives.

Statistical analyses were carried out using S- PLUS (Insightful Corporation 2002). The Kruskal Wallis test was applied to test the significance of differences in median values and as an alternative to the parametric ANOVA (Helsel and Hirsch 1992). Similarly, the Wilcoxon signed rank test was used as a non-parametric alternative to the paired T-test to compare the significance of differences between paired measurements. Maps were produced using ArcView (Environmental Systems Research Institute Inc. 2003).

4.0 RESULTS AND DISCUSSION

4.1 General Overview of the Database

This section provides an overview of the aggregated data set for pesticides monitored in Alberta surface waters during the period 1995 to and including 2002. It discusses which pesticides were detected, how often they were detected, at what concentrations and how concentrations compared with surface water quality guidelines.

4.1.1 Quality Assurance

Quality assurance/quality control (QA/QC) data are presented and evaluated in Appendix B. The evaluation demonstrates that the quality of the pesticide database is similar to, or better than that of other databases with respect to sample contamination, false positives, precision, and accuracy (Martin et al. 1999 and Martin 2002). Recovery rates are generally less than 100% and the likelihood of false negatives is greater than false positives. Hence reported concentrations and detection frequencies could be biased low, a point which is of particular relevance in the interpretation of the data set. These findings are taken into account in the interpretation of the data that follows in this report.

4.1.2 Comparison of Pesticides Detected in Surface Waters and Pesticide Use

Figure 2 provides a comparison of pesticide sales (Byrtus 2000), active ingredients that are monitored, and active ingredients that have been detected in surface waters, between 1995 and 2002. This figure captures the eighty top-selling compounds; well over 100 pesticides of lesser importance in terms of sales volumes are not shown. Among these, azinphos methyl, methoxychlor, parathion, pyridaben, endosulfan, fenoxaprop ethyl, and ethion were monitored, but only the first four were detected in surface waters. This figure does not capture breakdown products and isomers, which are not sold (alpha-BHC, AMPA, 2,4-dichlorophenol, 4-chloro-2-methylphenol, desethyl atrazine, deisopropyl atrazine, fenoxaprop-p), products that are not sold anymore (aldrin, dieldrin, and disulfoton), or were not sold yet in 1998 (hexaconazole). This list does not capture a rather large list of chemical groups that enhance pesticide properties or have pesticidal properties themselves (e.g., adjuvants, surfactants, wood preservatives, disinfectants, anti-microbials).

Overall, Figure 2 shows that pesticides being monitored in surface waters provide a reasonable coverage of the products that are sold in highest volume (47 of the top-selling 70 pesticides are monitored, and so are 7 additional pesticides with much lower sale volumes). Including glyphosate, the target compounds account for 93% of the mass of active ingredients sold in 1998; excluding glyphosate, the target compounds account for 59% of the sales only. There are some notable omissions from the routine monitoring list. Glyphosate has by far the highest sale volume in the province; it has been monitored as part of special studies and detected in surface waters, but it is not part of the routine monitoring because of budgetary reasons. Tralkoxydim, sethoxydim, mancozeb, EPTC, trichlorfon, vinclozolin, and thiram are other examples of pesticides with relatively high sale volumes that are not part of routine monitoring, because of analytical difficulties, or budgetary reasons.

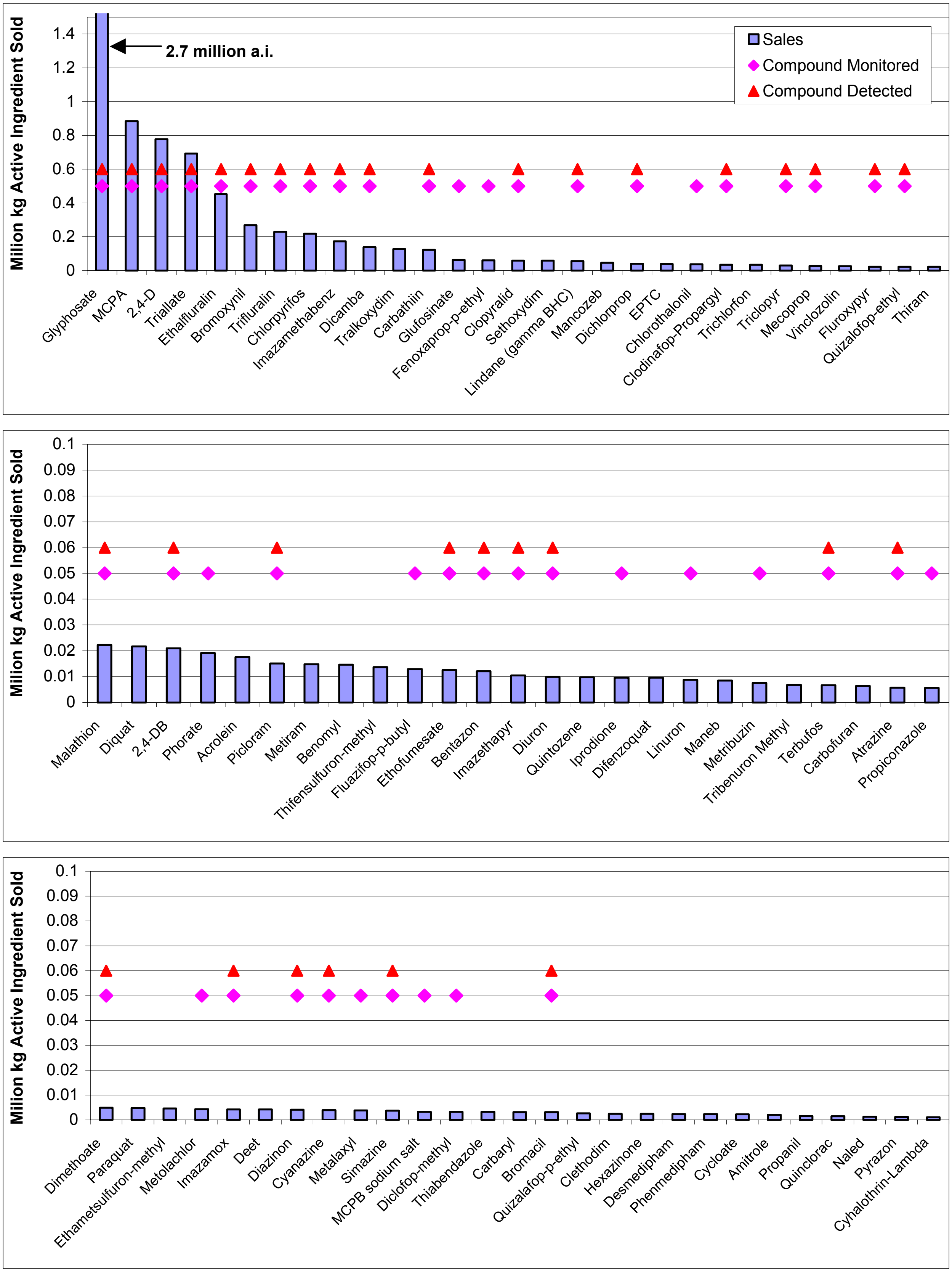


Figure 2 **Comparison of the 1998 pesticide sale volume (Byrtus 2000) of 80 pesticides with the highest sale volume, and pesticides monitored and detected in surface waters (1995-2002). Diamonds and triangles indicate that compound was monitored and detected, respectively.**

4.1.3 Compounds Detected in Surface Waters

Of the 63 pesticides that were analyzed in Alberta surface water during the period 1995 - 2002, 44 were detected in at least one sample (Table 3). These comprise 33 of the 43 herbicides, 10 out of the 17 insecticides and one of the six fungicides. It is worth pointing to differences in the period of record and number of samples processed among pesticides because the duration of monitoring could influence which pesticides were detected. Of the pesticides that were not detected one (alpha-endosulfan) had been monitored since 1995. Glufosinate has been monitored in selected programs since 2000. The others, four herbicides (clodinafop acid metabolite, linuron, metolachlor, metribuzin, fluazifop), three insecticides (aldrin, dieldrin, parathion) and five fungicides (chlorothalonil, iprodione, propiconazole, hexaconazole, metalaxyl-M) were all monitored only for one year (2002). It is expected that some of these compounds will be detected as more samples are analyzed. The likelihood of detecting aldrin and dieldrin is low since these products have not been registered for use in Canada since 1990 (Pesticide Directorate 1990).

4.1.4 Pesticide Detection Frequency and Distribution in Surface Waters

At least one pesticide residue was reported in 65% of the 3055 pesticide samples analyzed between 1995 and 2002. There were pronounced differences in detection frequencies among the various pesticide residues, including isomers and breakdown products (Figure 3 and Table 3). Overall 2,4-D was the compound detected most frequently and the only one that occurred in more than half of the samples (53.12% of samples). Seven compounds were reported in 10 to 50% of the samples (MCPA, glyphosate, MCPP, dicamba, picloram, clopyralid and triclopyr); 15 were reported in 1 to 10% of the samples (dichlorprop, lindane, atrazine, bromacil, bromoxynil, diazinon, triallate, imazamethabenz, imazethapyr, AMPA, 4-chloro-2-methylphenol, 2,4-dichlorophenol, clodinafop-propargyl, fluroxypyr, quizalofop, bentazon, and ethofumesate) and the remaining 19 occurred in less than 1% of the samples (2,4-DB, alpha-BHC, methoxychlor, carbathiin, cyanazine, diuron, chlorpyrifos, ethalfluralin, azinphos-methyl, malathion, terbufos, trifluralin, desethyl atrazine, deisopropyl atrazine, quinclorac, pyridaben, dimethoate, imazamox, simazine).

For many pesticides, patterns of pesticide detections in surface waters are closely related to sales and use patterns as shown in Byrtus (2000), and Cotton and Byrtus (1995). For example, 2,4-D, MCPA, bromoxynil, imazamethabenz, dicamba, triallate, MCPP, triclopyr, and clopyralid (Figure 4) were detected in many surface waters across Alberta. These herbicides are among the most widely sold herbicides in the province, they have broad uses and they are sold across the entire White Zone or agricultural area in the province (Figure 1).

Some herbicides with high sales and broad use patterns have a much more restricted distribution in surface waters. Despite their high sale volume and widespread use, ethalfluralin and trifluralin have been reported from only limited number of surface water sites, mostly along the north-south transportation corridor (Figure 4 U and V). This pattern in detections is believed to be the result of high use and overall higher moisture conditions than further into the east-central part of the province. Similarly, although it is widely used across Alberta, the fungicide carbathiin has only been detected at a few surface water sites (Figure 4Y).

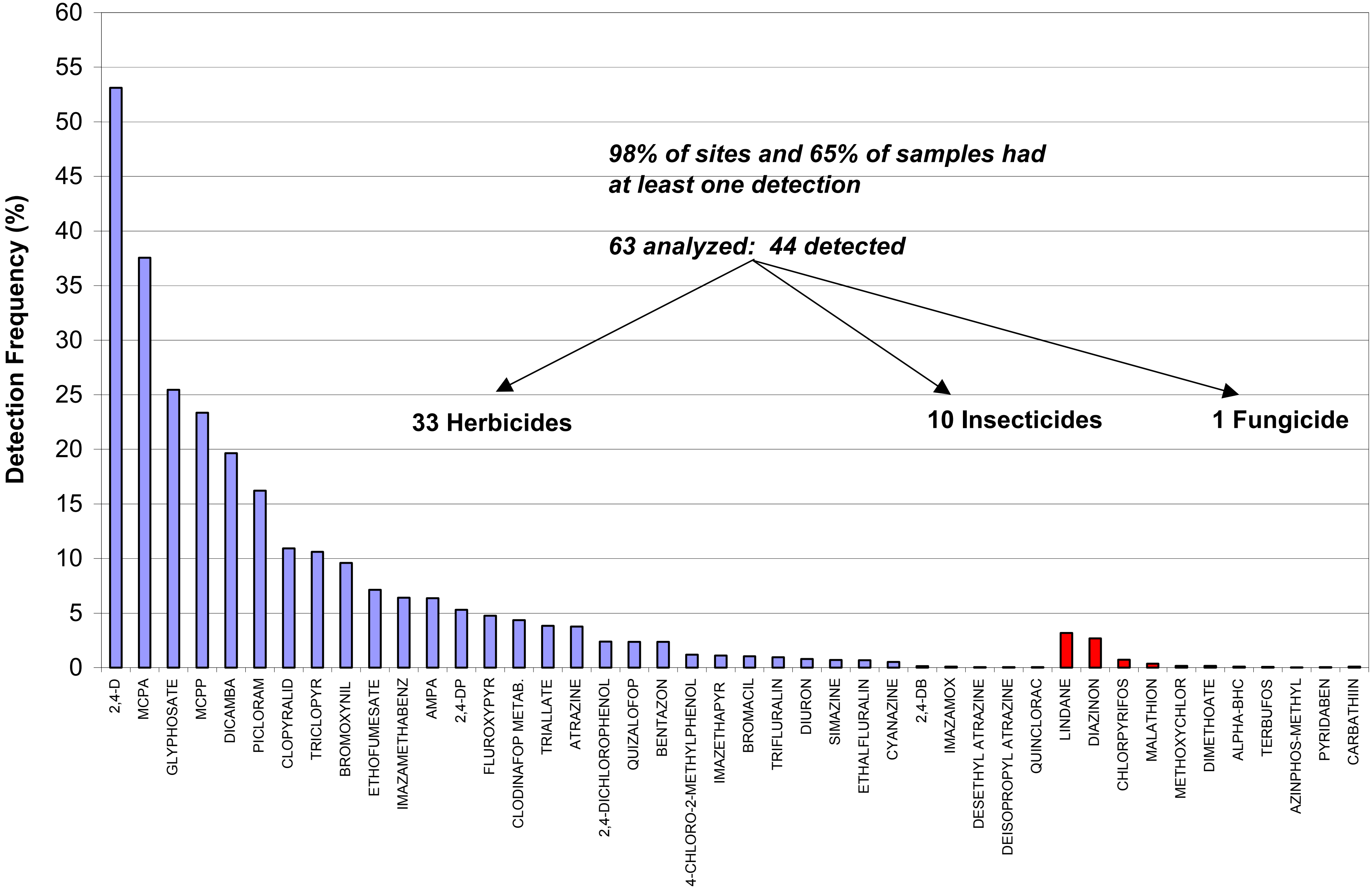


Figure 3 **Pesticides detection frequency in Alberta surface waters (1995-2002)**

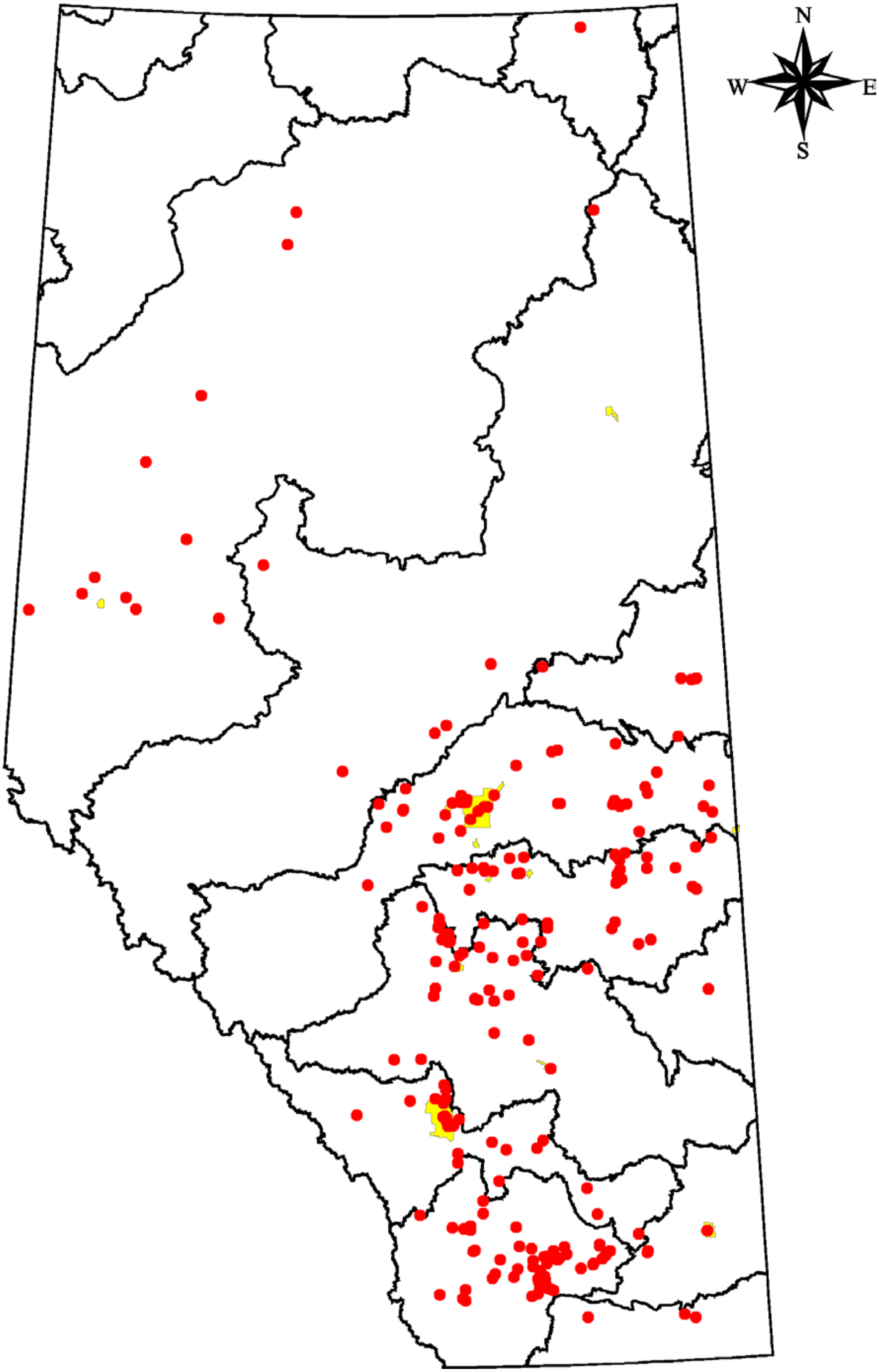


Figure 4a Distribution of 2,4-D detections in Alberta from 1995 to and including 2002

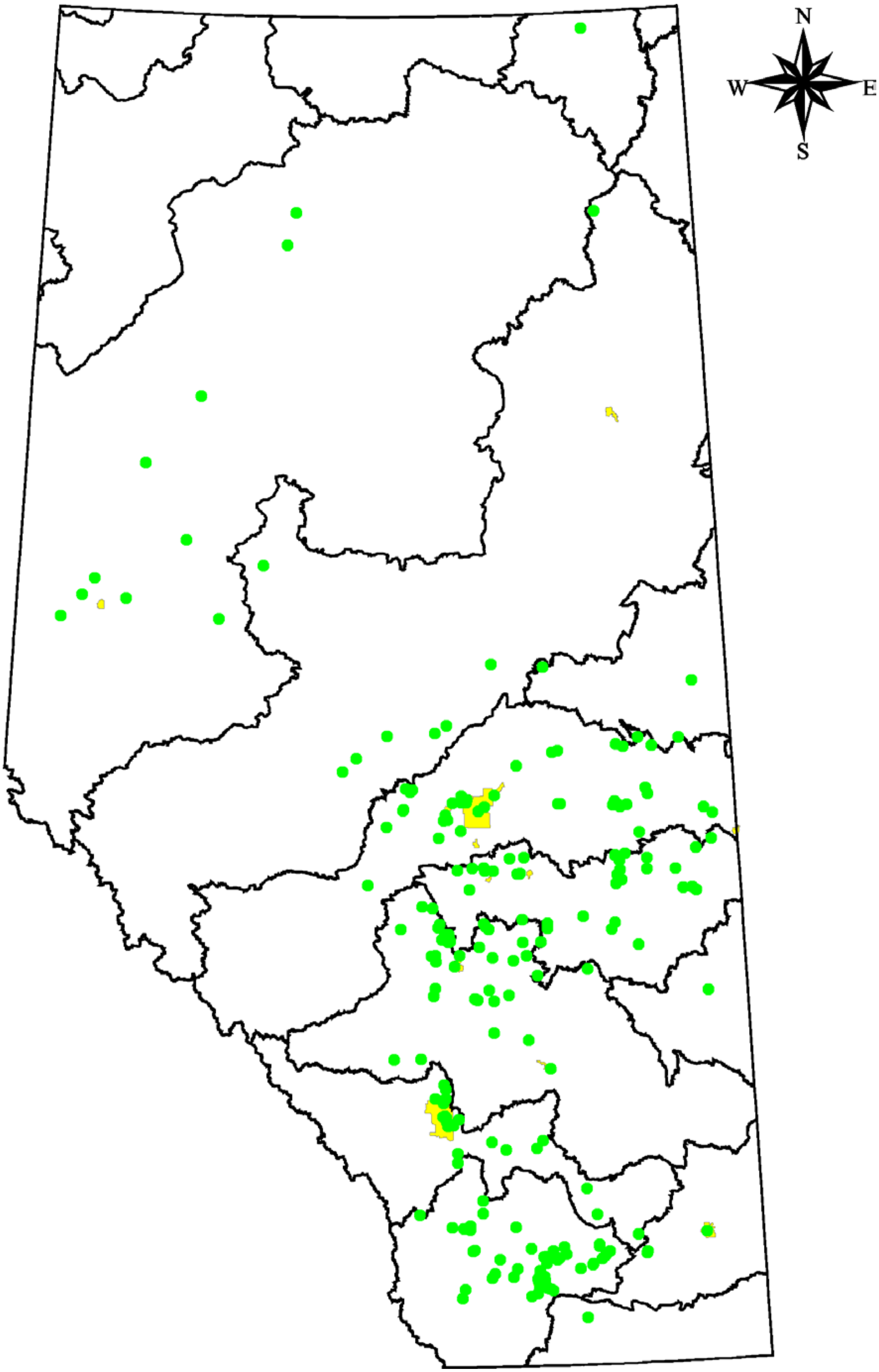


Figure 4b Distribution of MCPA detections in Alberta from 1995 to and including 2002

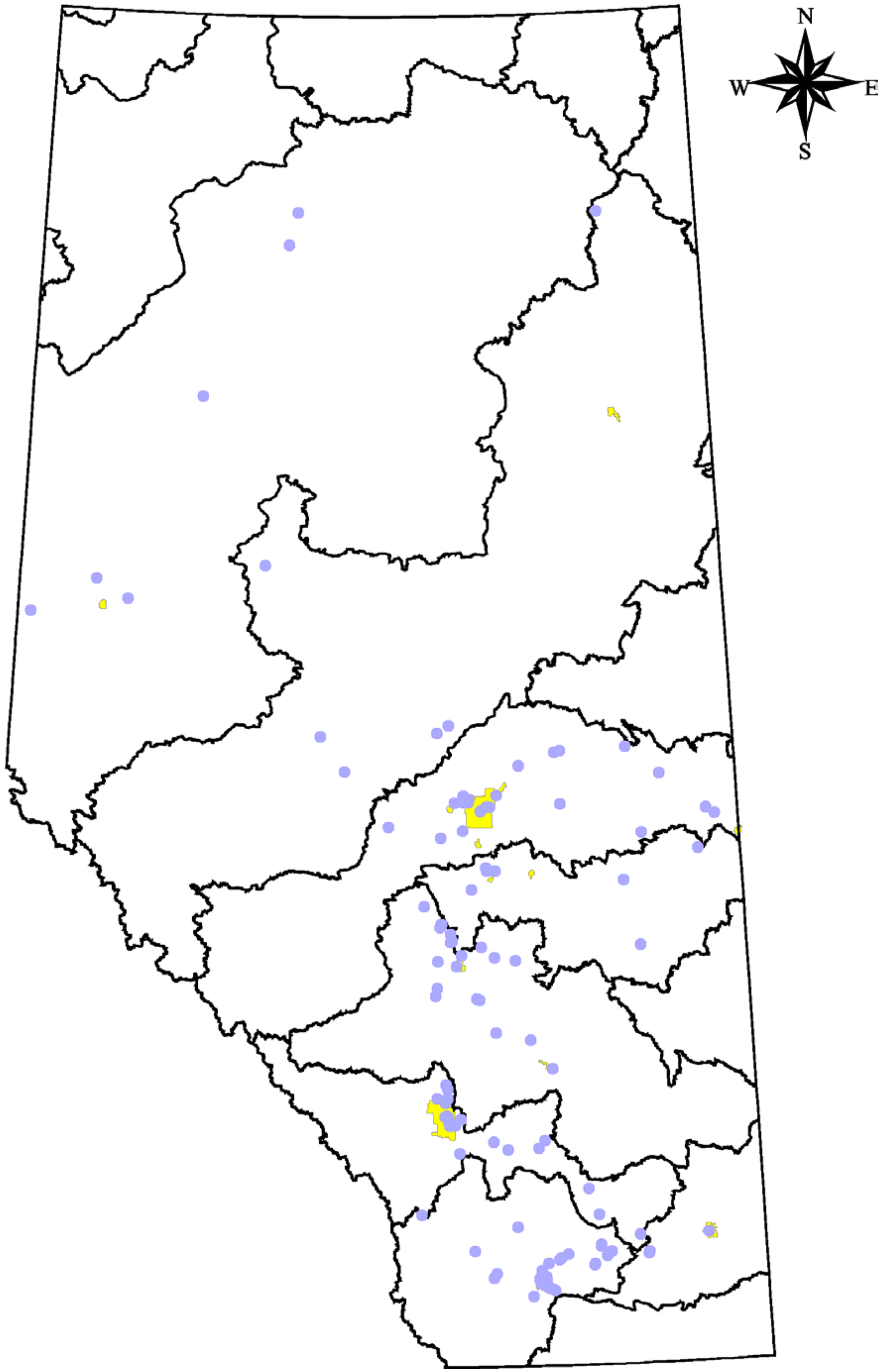


Figure 4c Distribution of MCPP detections in Alberta from 1995 to and including 2002

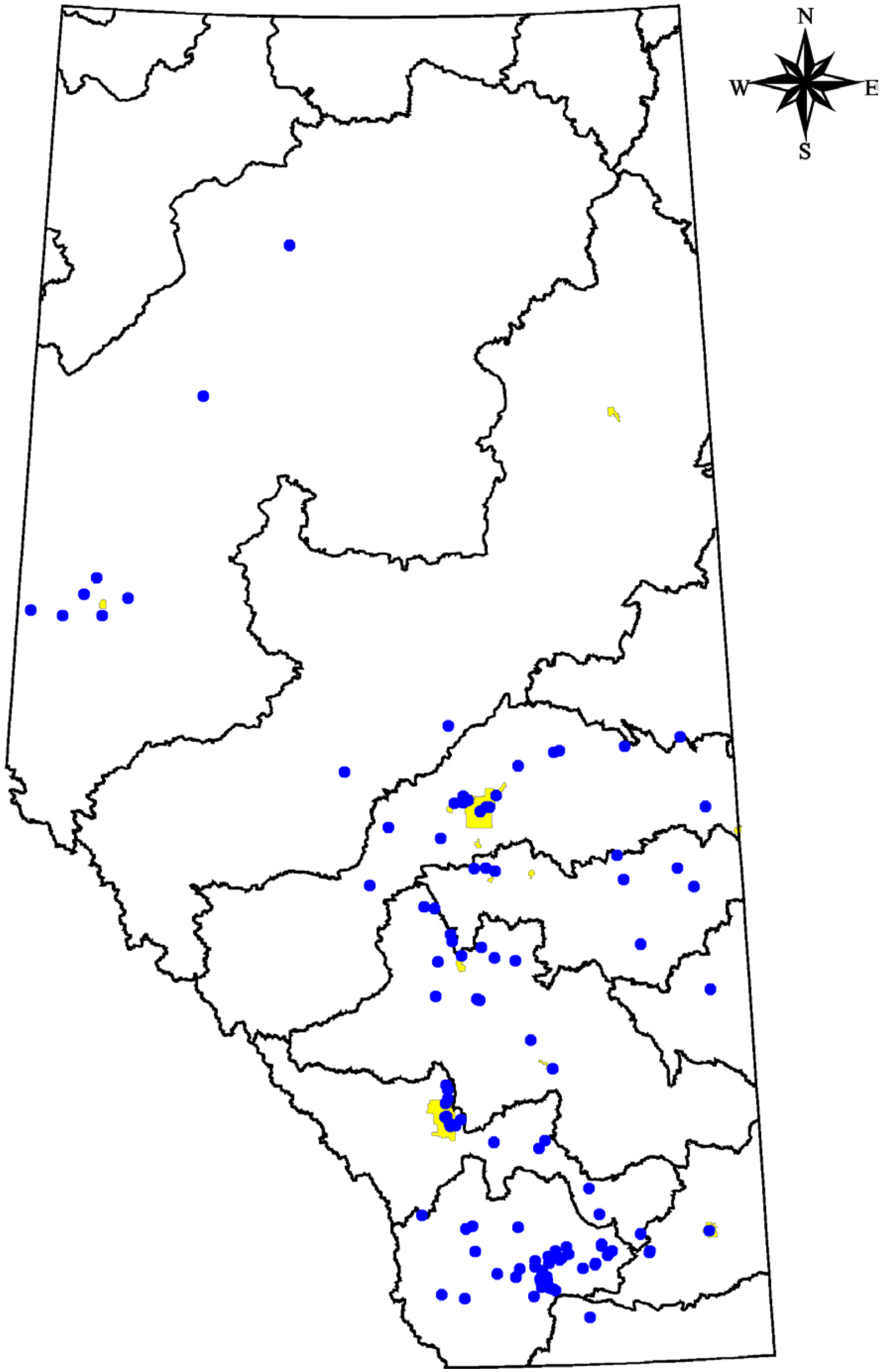


Figure 4d Distribution of dicamba detections in Alberta from 1995 to and including 2002

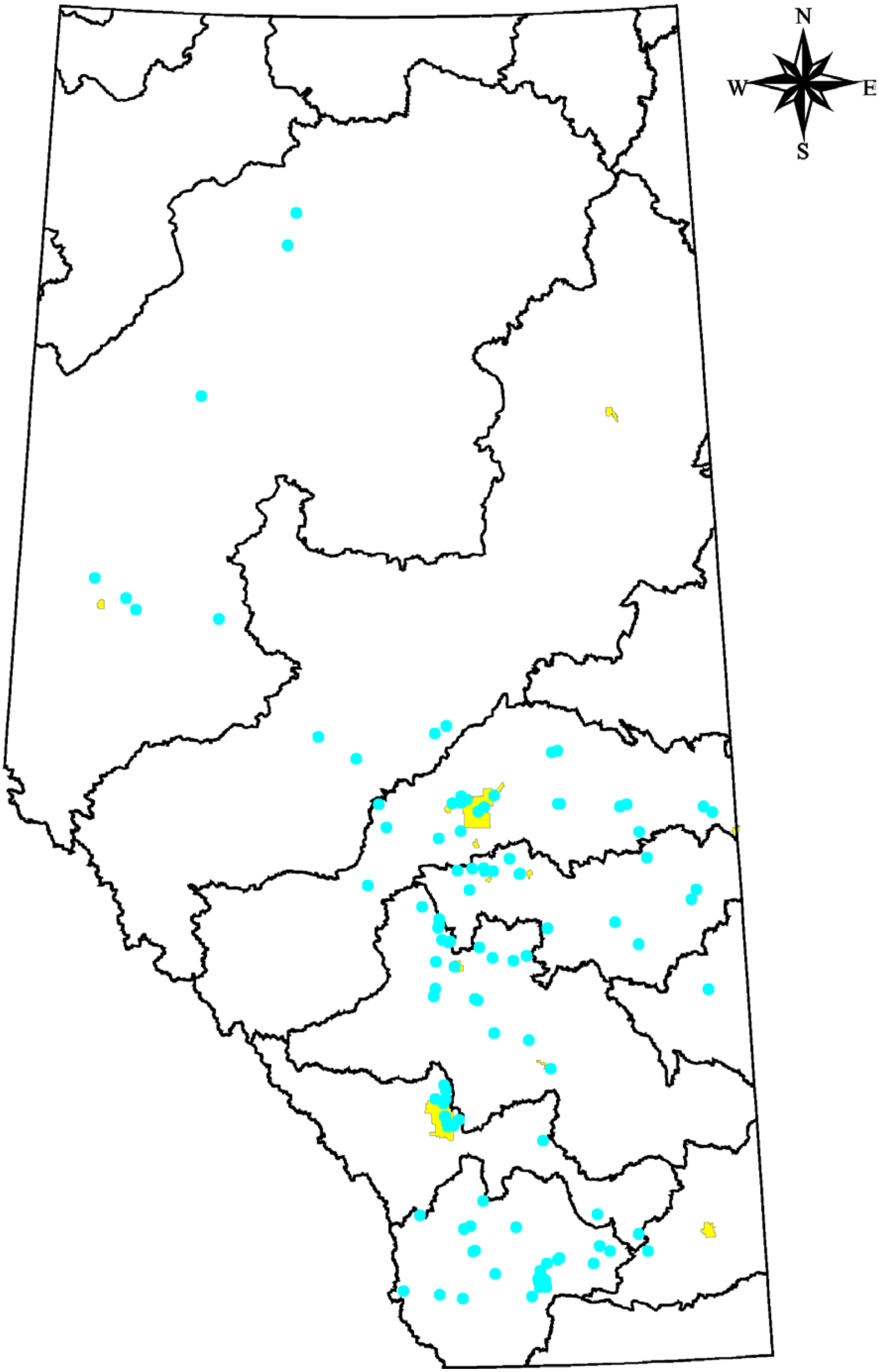


Figure 4e Distribution of picloram detections in Alberta from 1995 to and including 2002

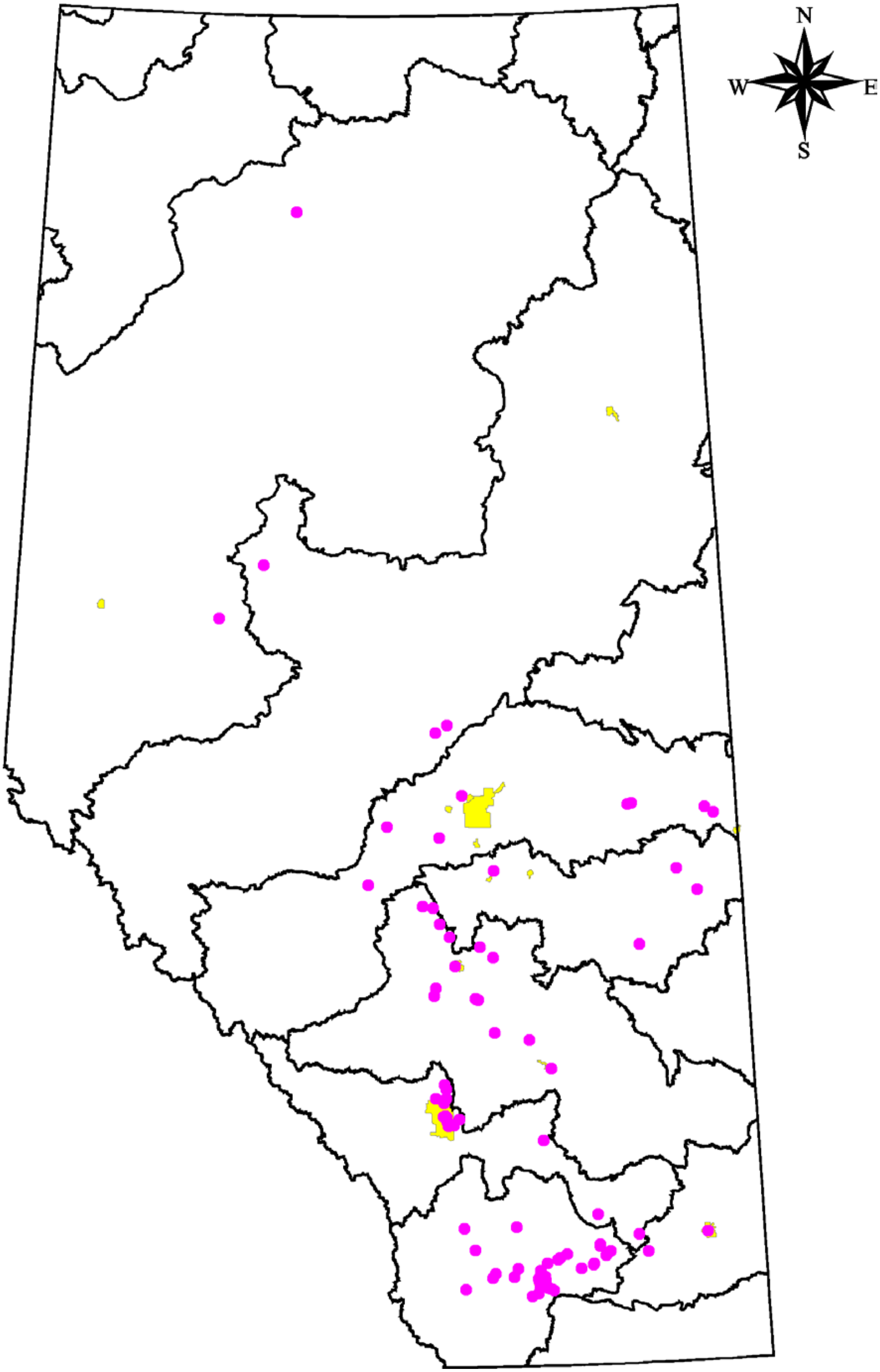


Figure 4f Distribution of bromoxynil detections in Alberta from 1995 to and including 2002

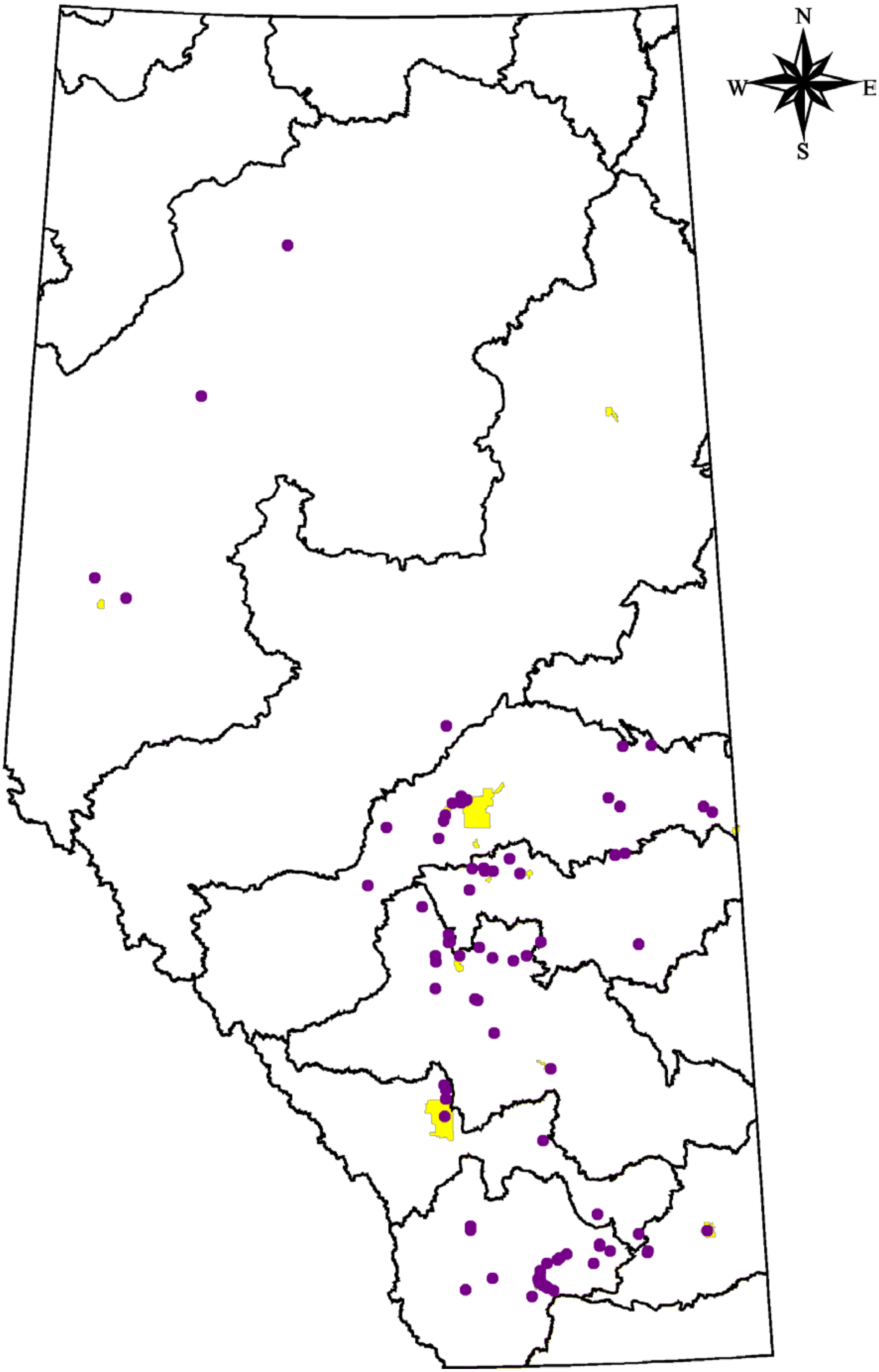


Figure 4g **Distribution of clopyralid detections in Alberta from 1995 to and including 2002**

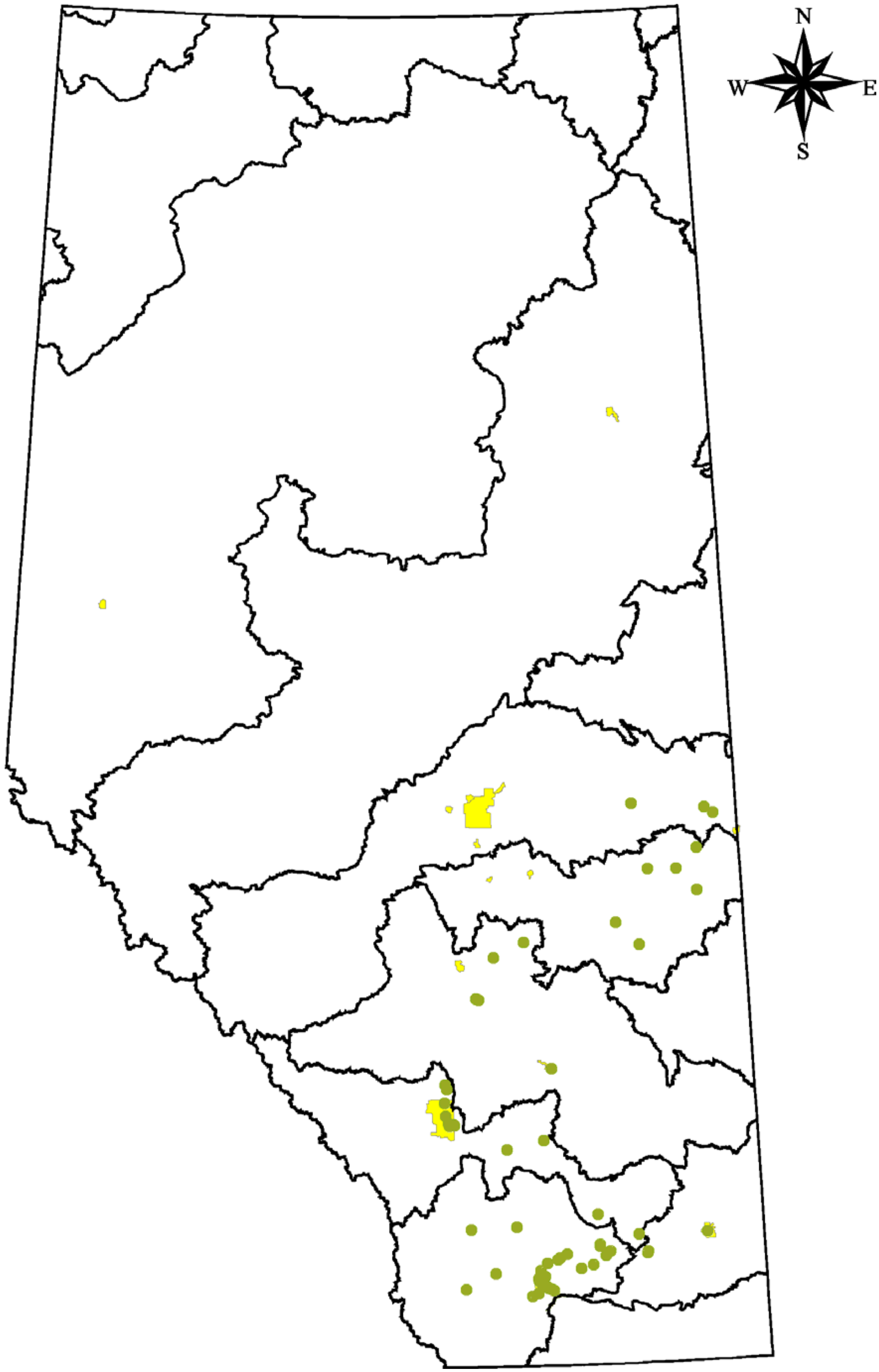


Figure 4h Distribution of dichlorprop detections in Alberta from 1995 to and including 2002

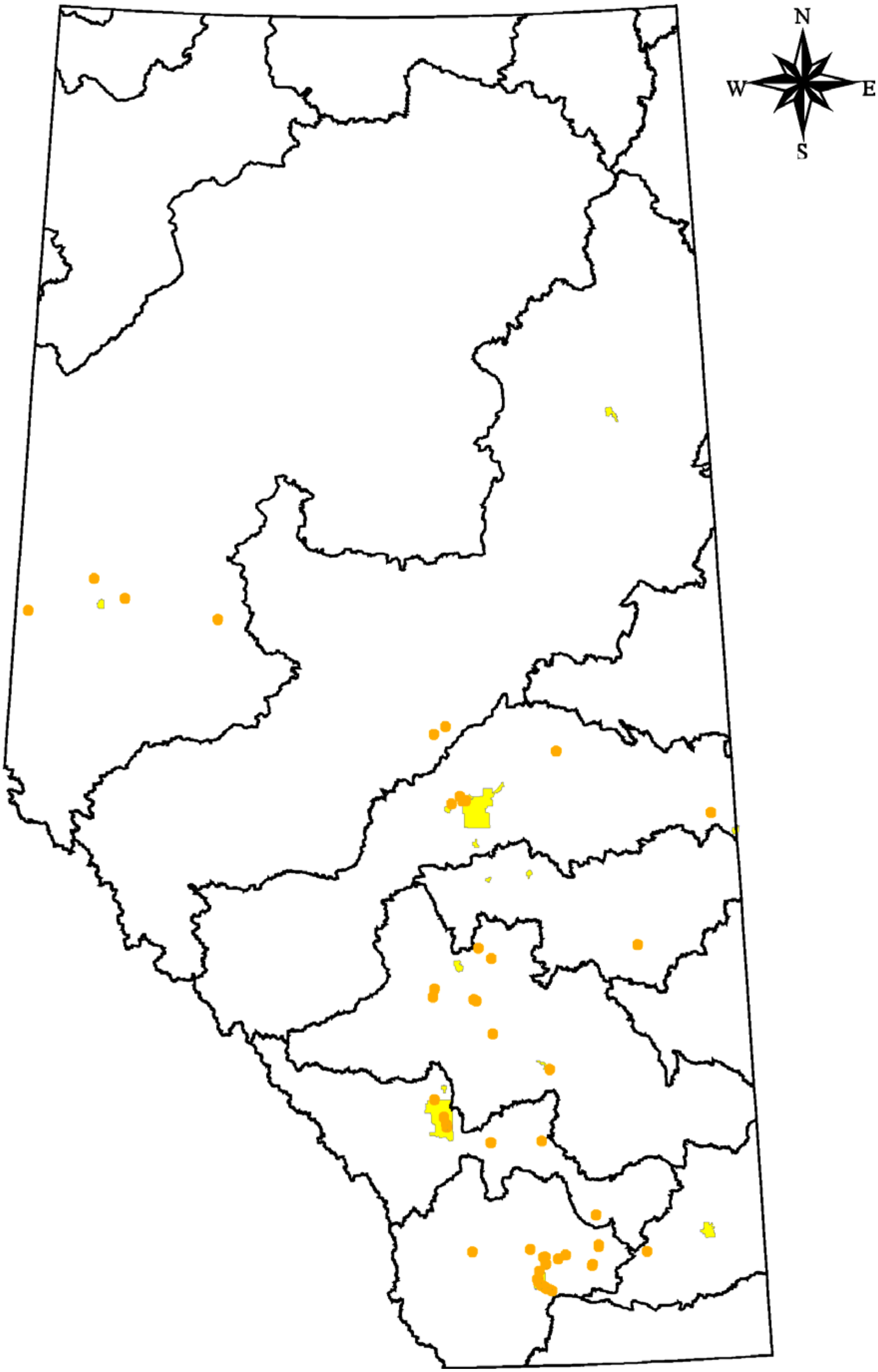


Figure 4i **Distribution of triallate detections in Alberta from 1995 to and including 2002**

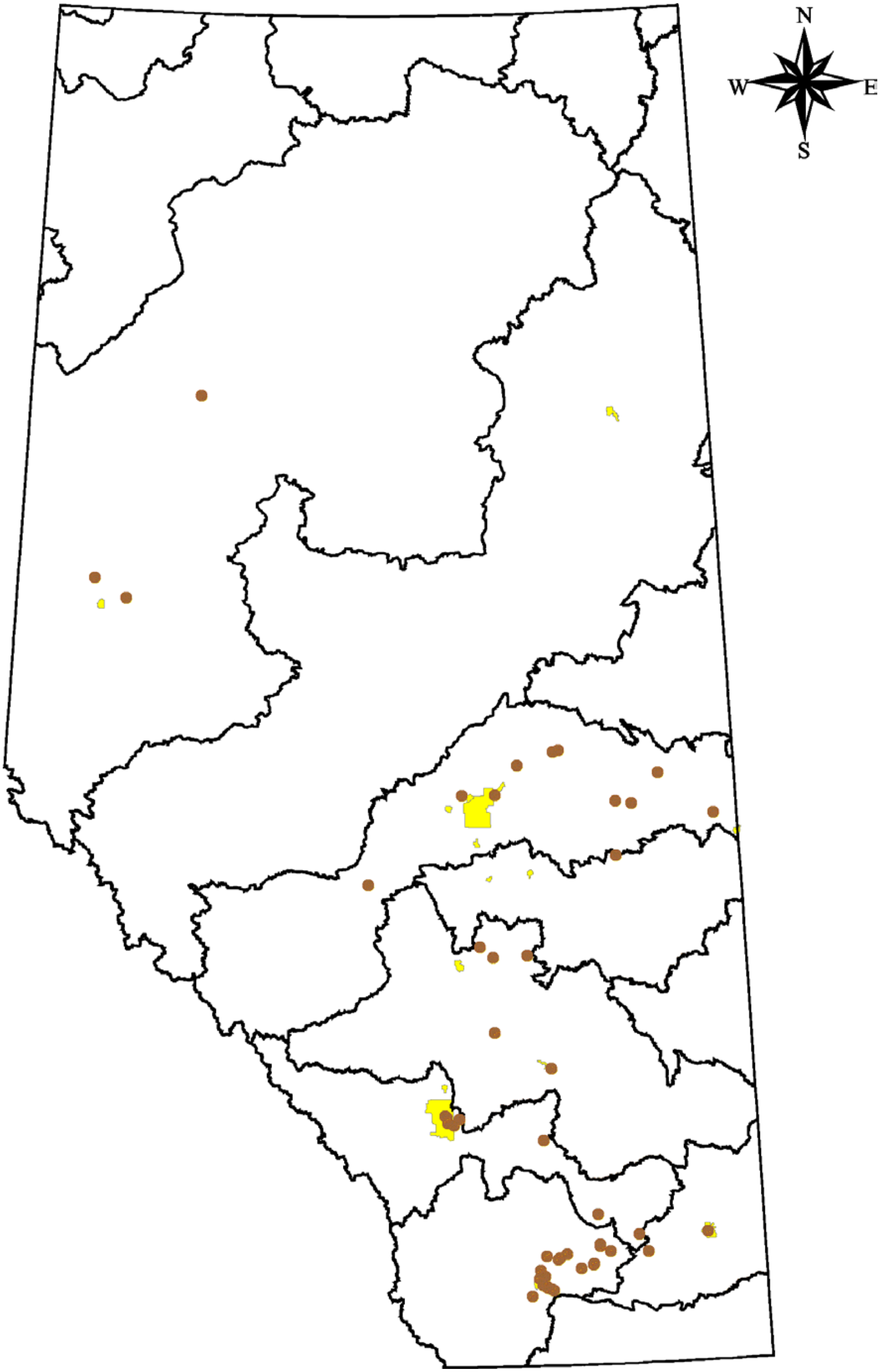


Figure 4j **Distribution of gamma-BHC (lindane) detections in Alberta from 1995 to and including 2002**

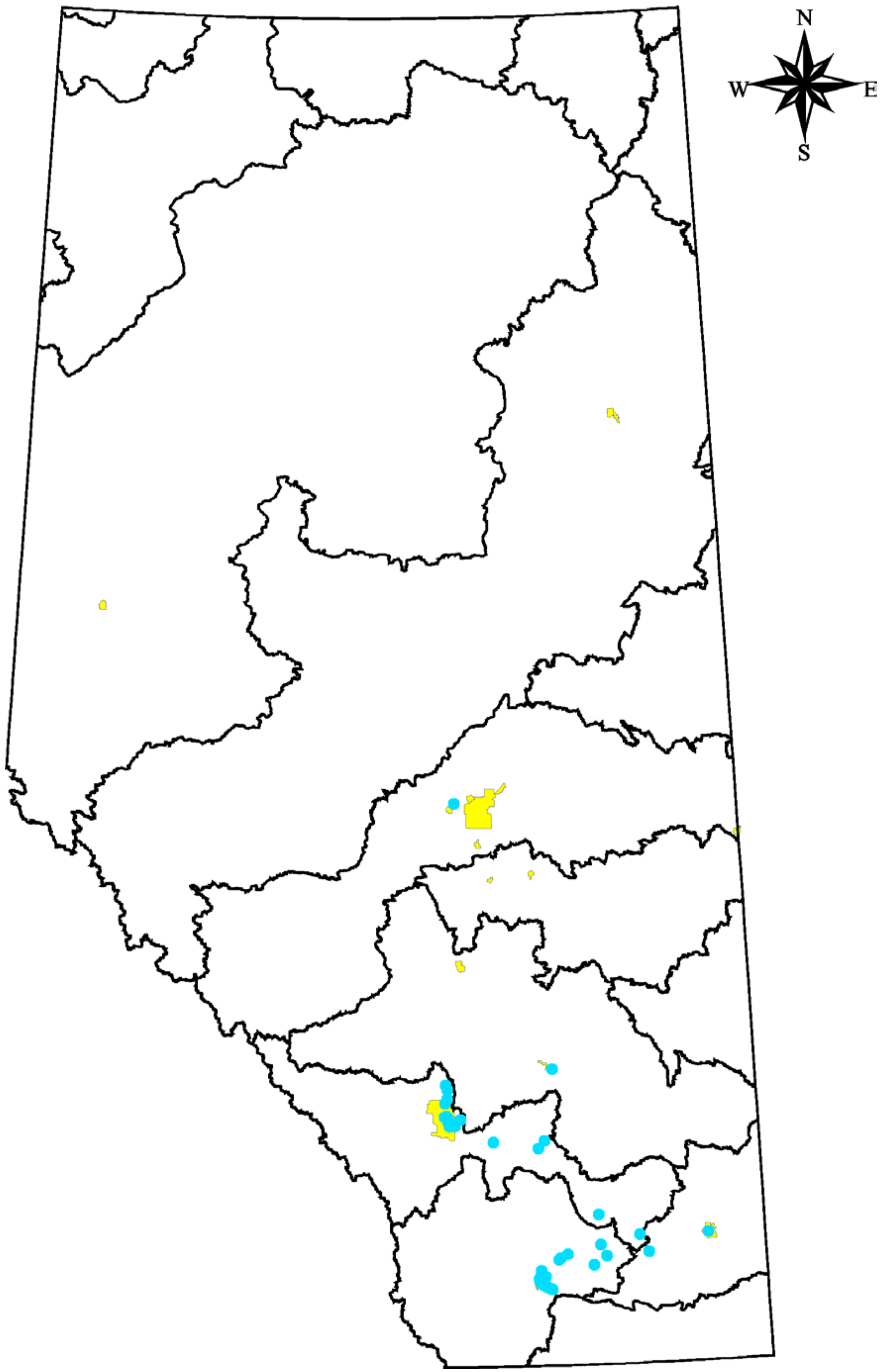


Figure 4k Distribution of atrazine detections in Alberta from 1995 to and including 2002

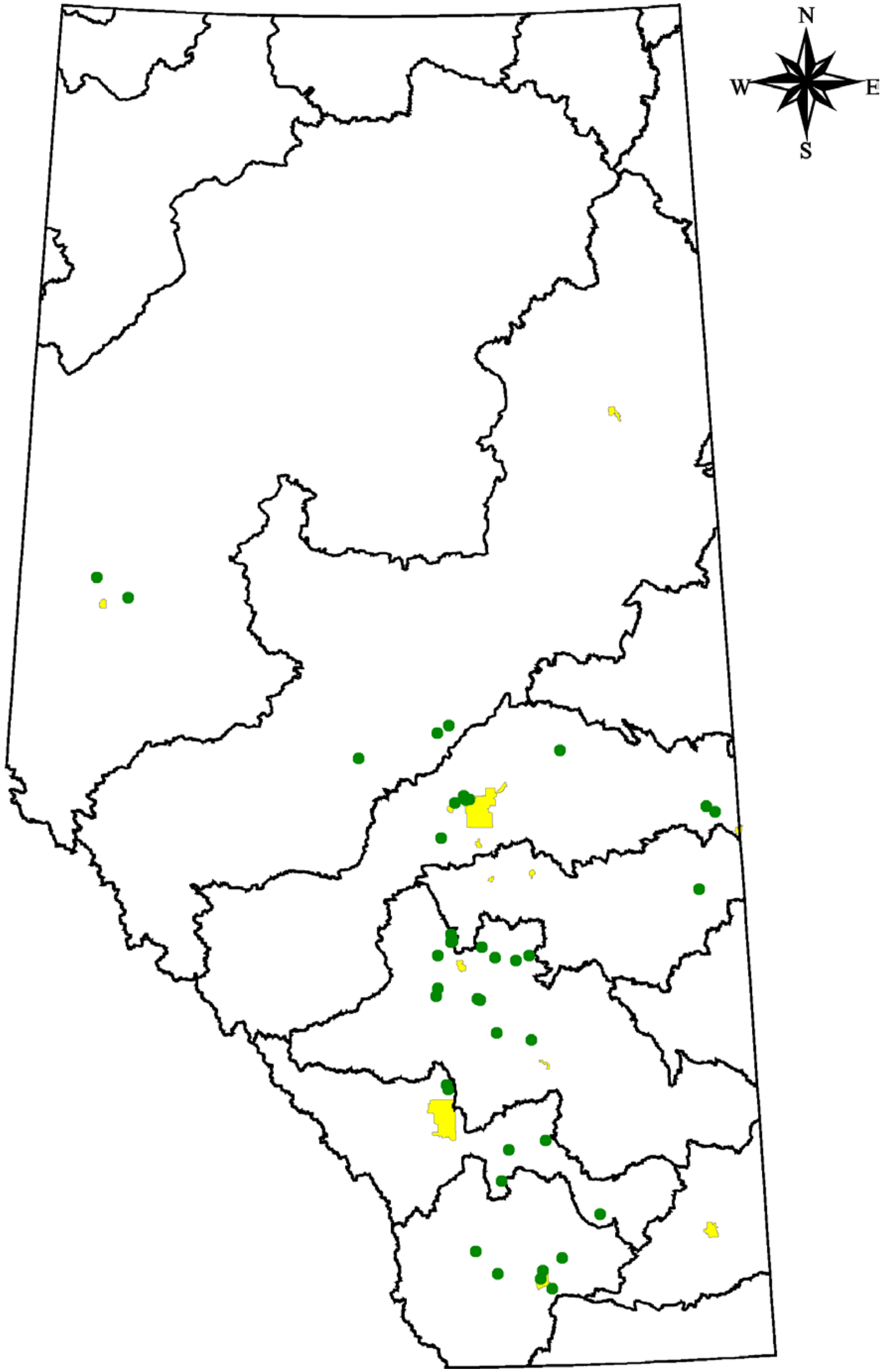


Figure 4l Distribution of imazamethabenz detections in Alberta from 1995 to and including 2002

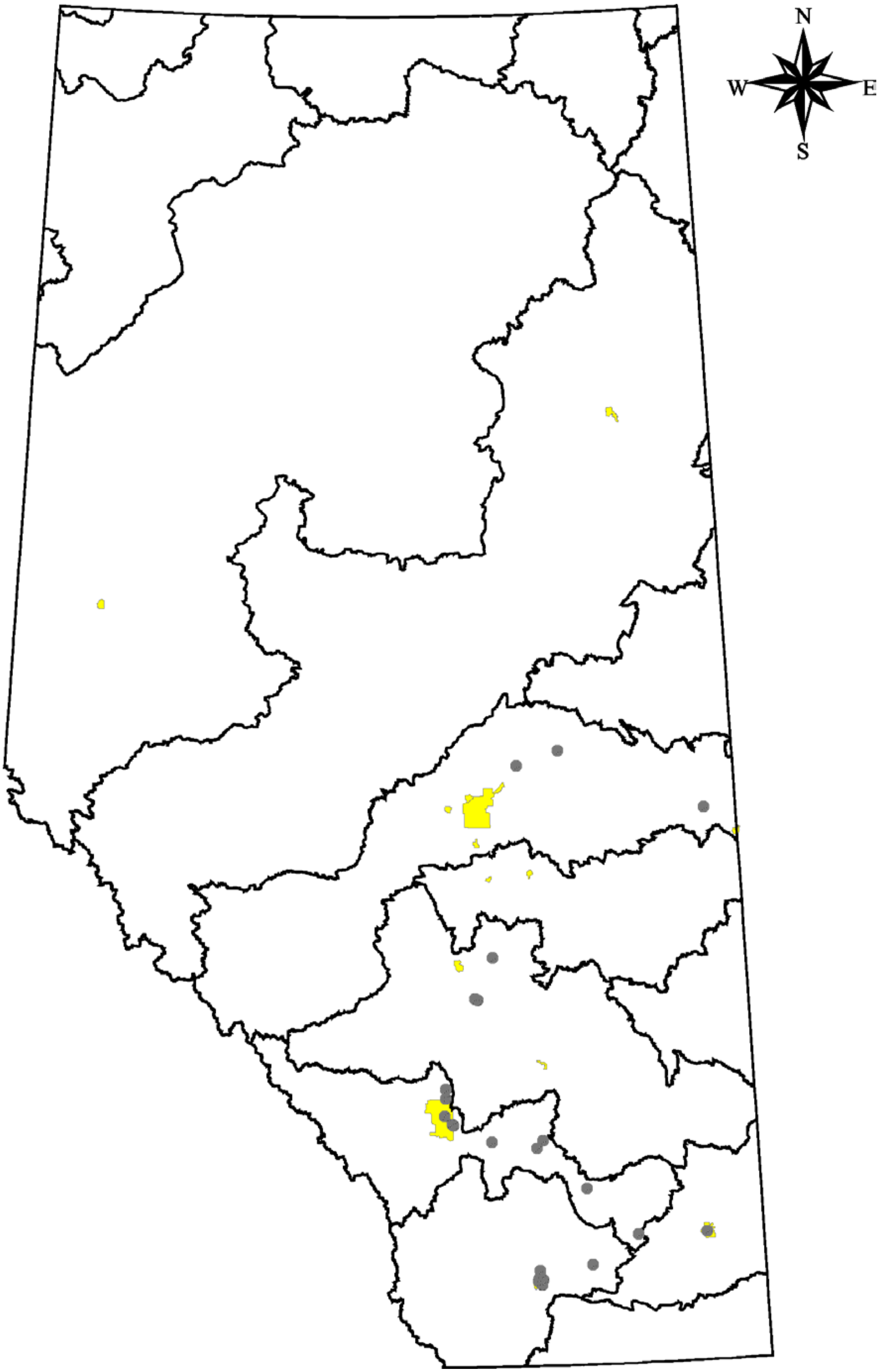


Figure 4m Distribution of diazinon detections in Alberta from 1995 to and including 2002

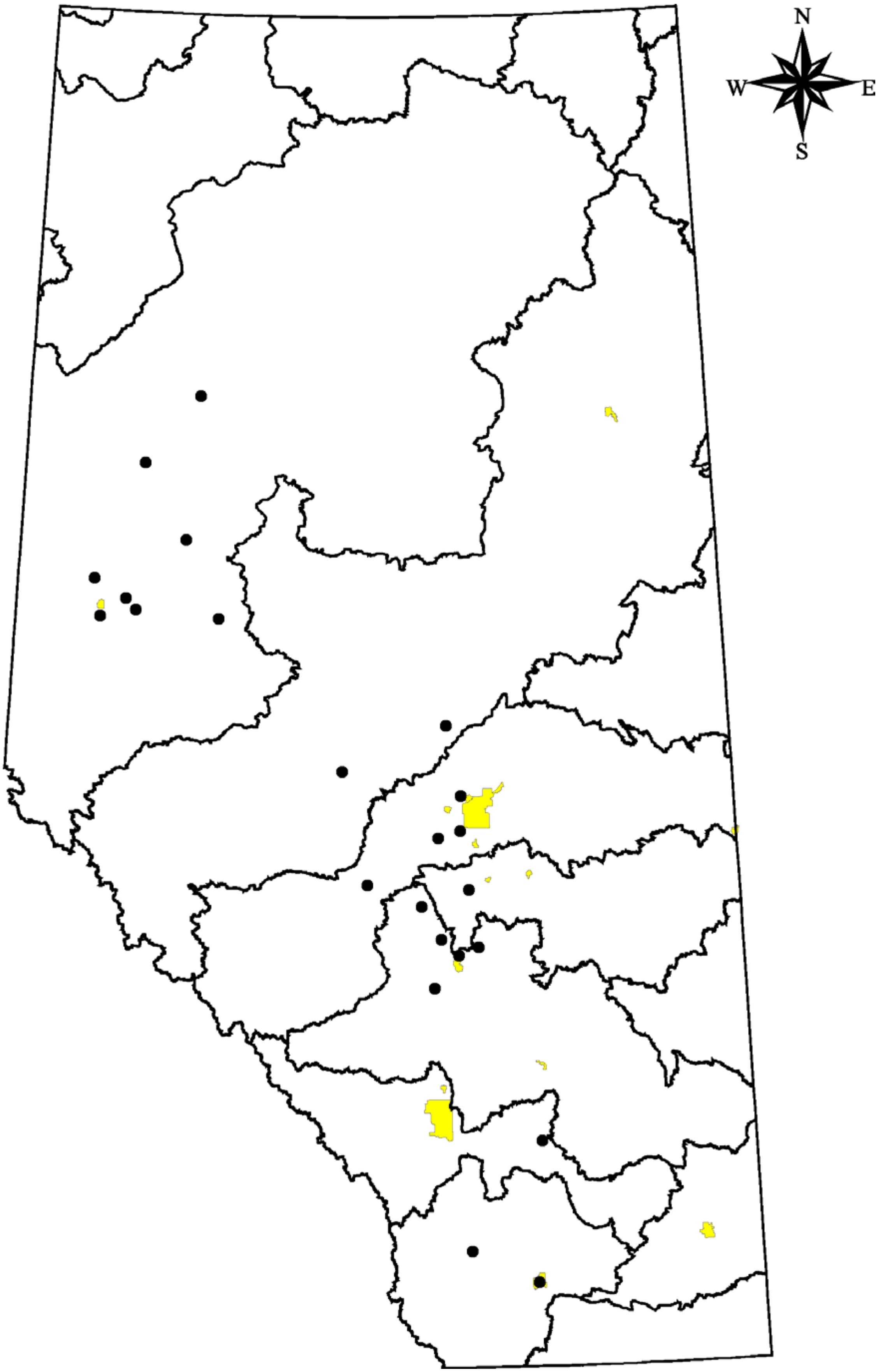


Figure 4n Distribution of triclopyr detections in Alberta from 1995 to and including 2002

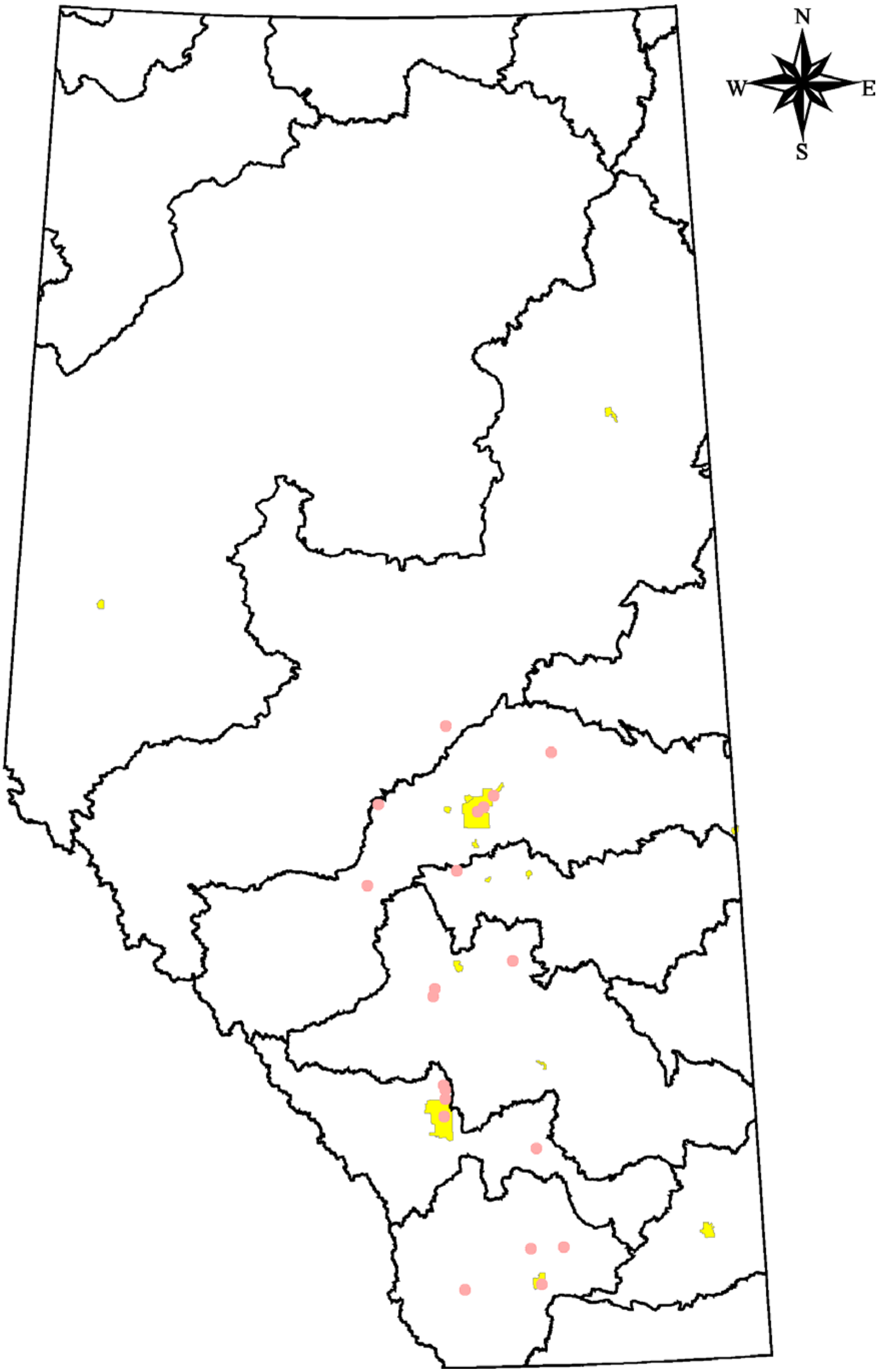


Figure 4o Distribution of diuron detections in Alberta from 1995 to and including 2002

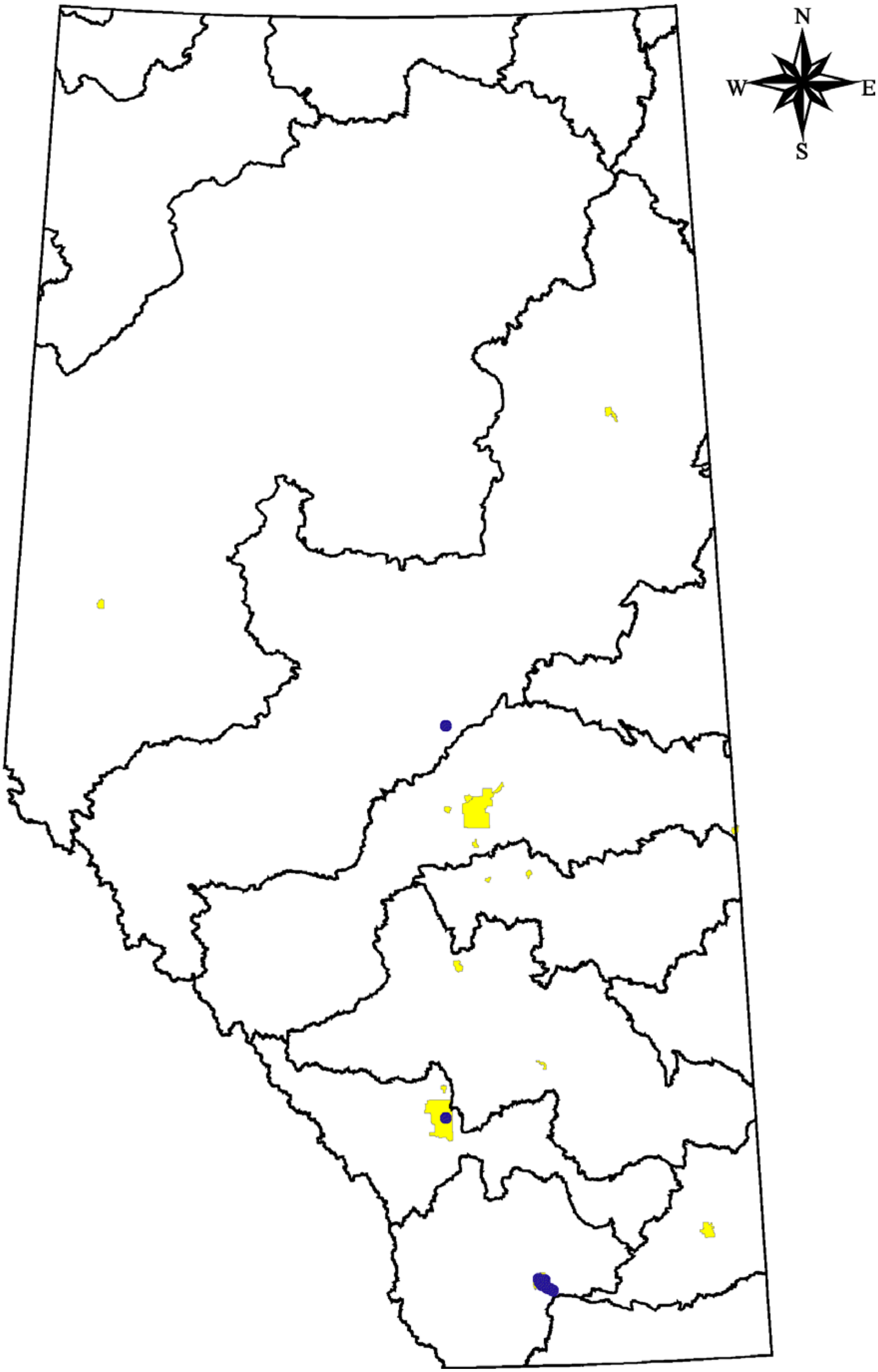


Figure 4p Distribution of bromacil detections in Alberta from 1995 to and including 2002

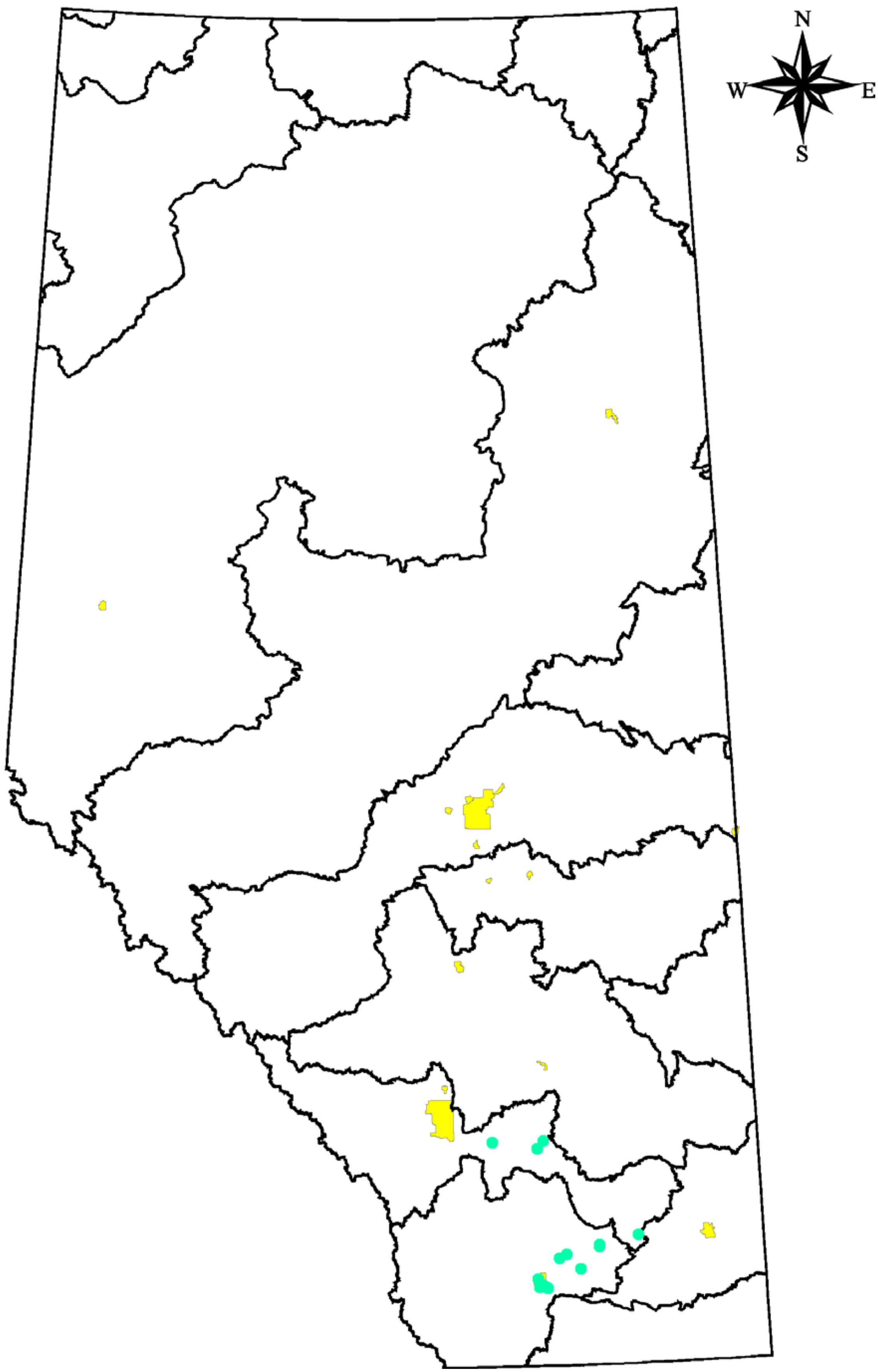


Figure 4q Distribution of clorpyrifos detections in Alberta from 1995 to and including 2002

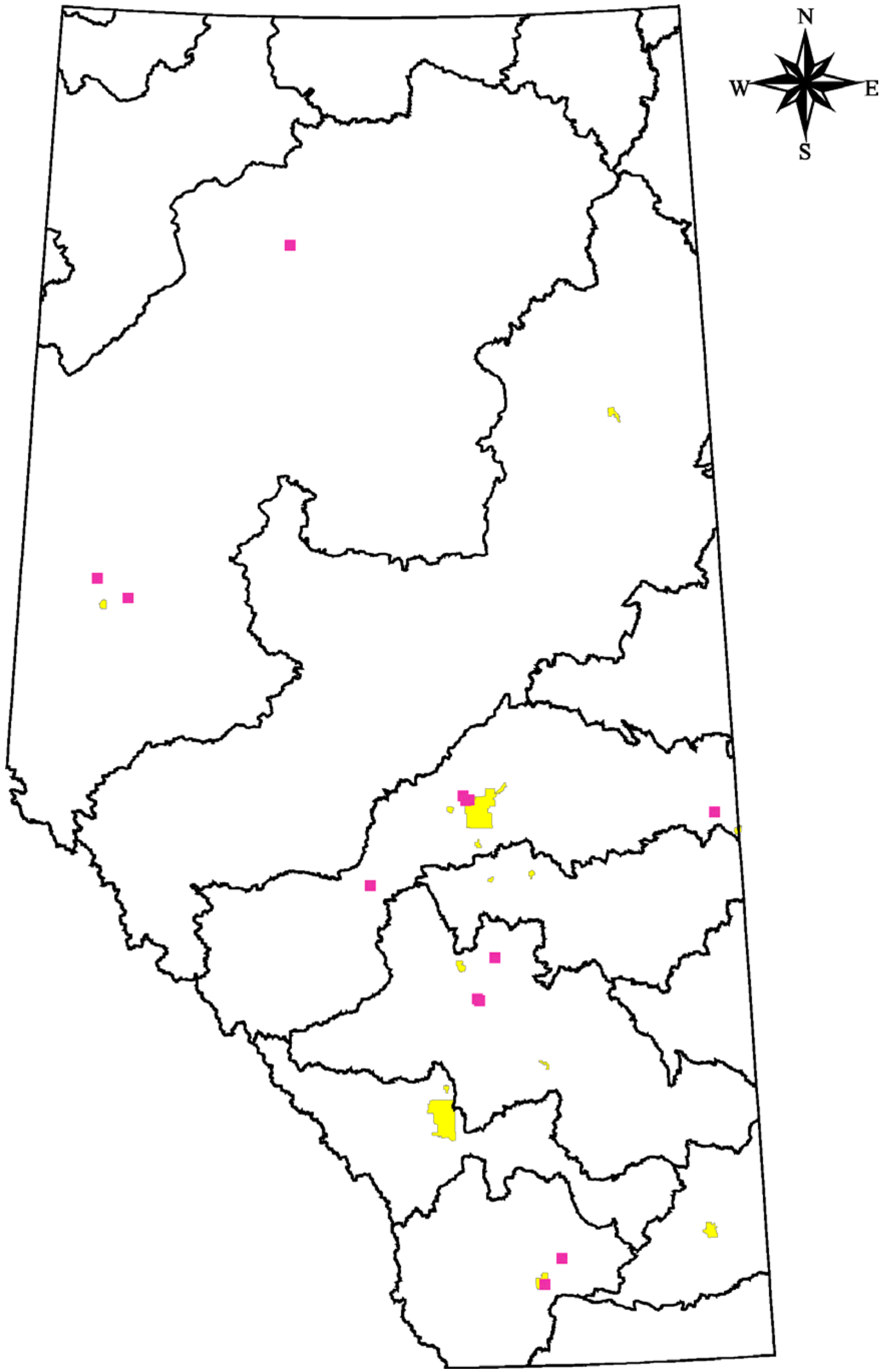


Figure 4r Distribution of imazethapyr detections in Alberta from 1995 to and including 2002

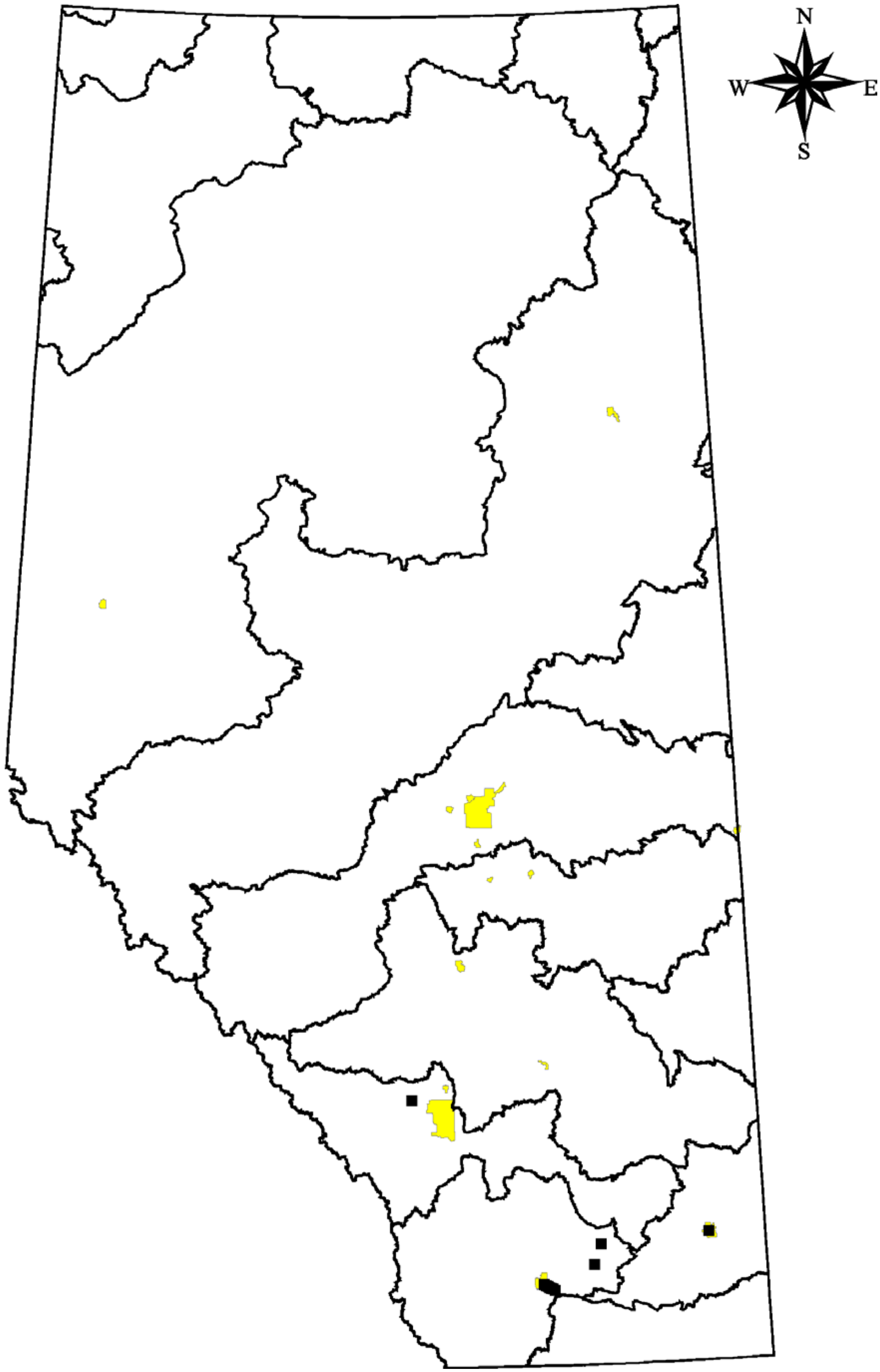


Figure 4s Distribution of cyanazine detections in Alberta from 1995 to and including 2002

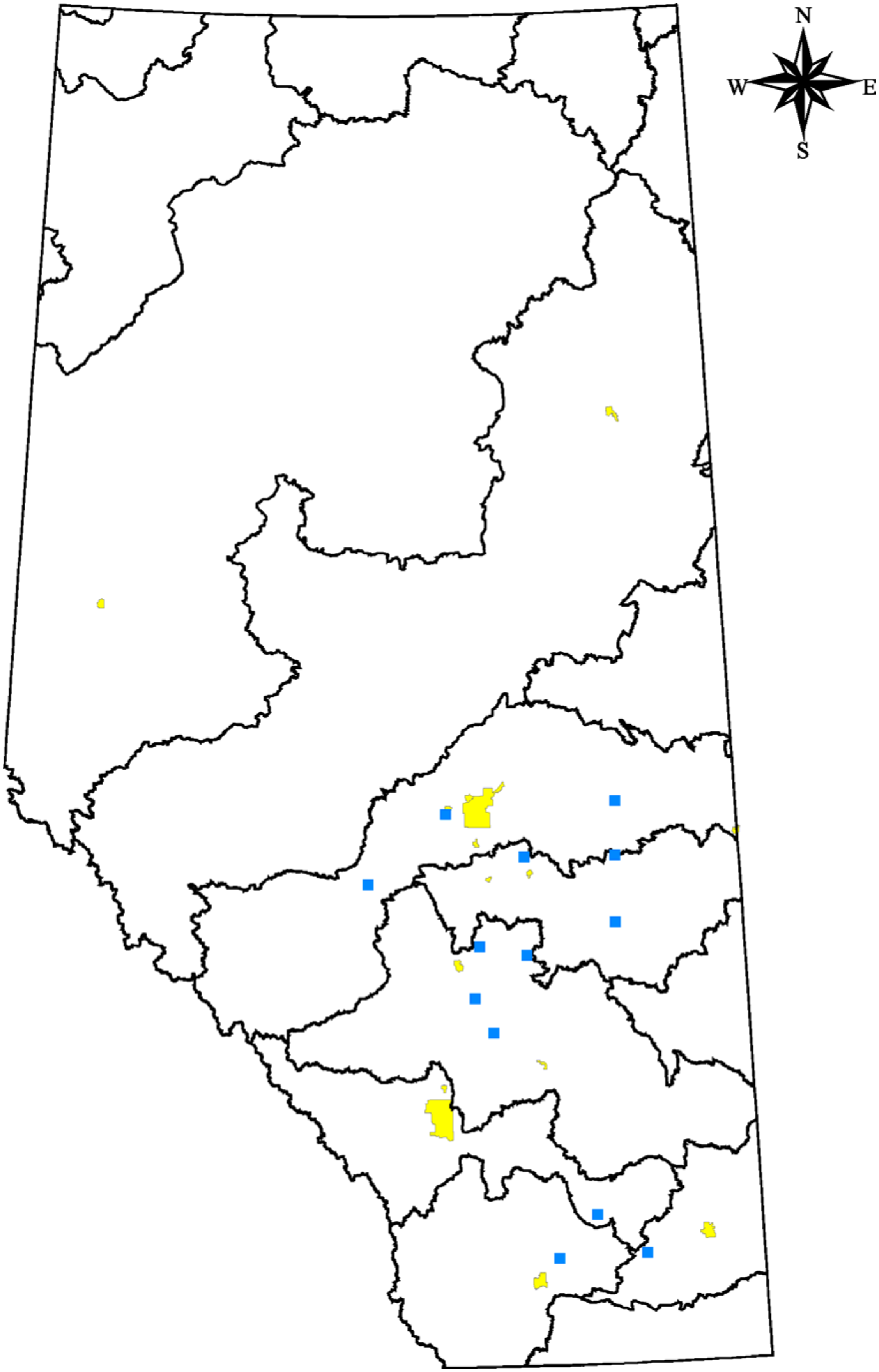


Figure 4t **Distribution of glyphosate detections in Alberta from 1995 to and including 2002**
(Note: glyphosate was measured at selected sites and detected at all these sites)

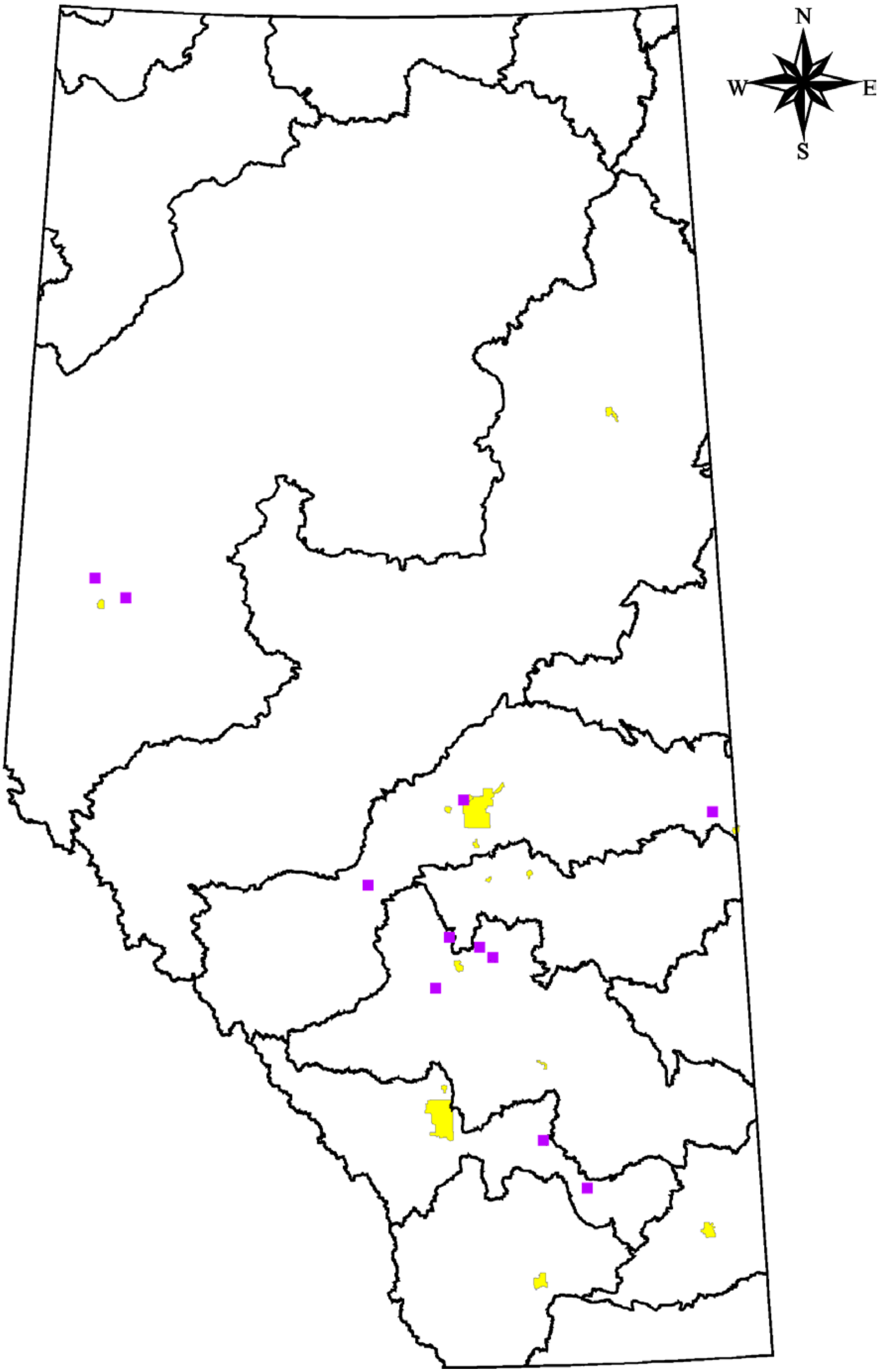


Figure 4u Distribution of trifluralin detections in Alberta from 1995 to and including 2002

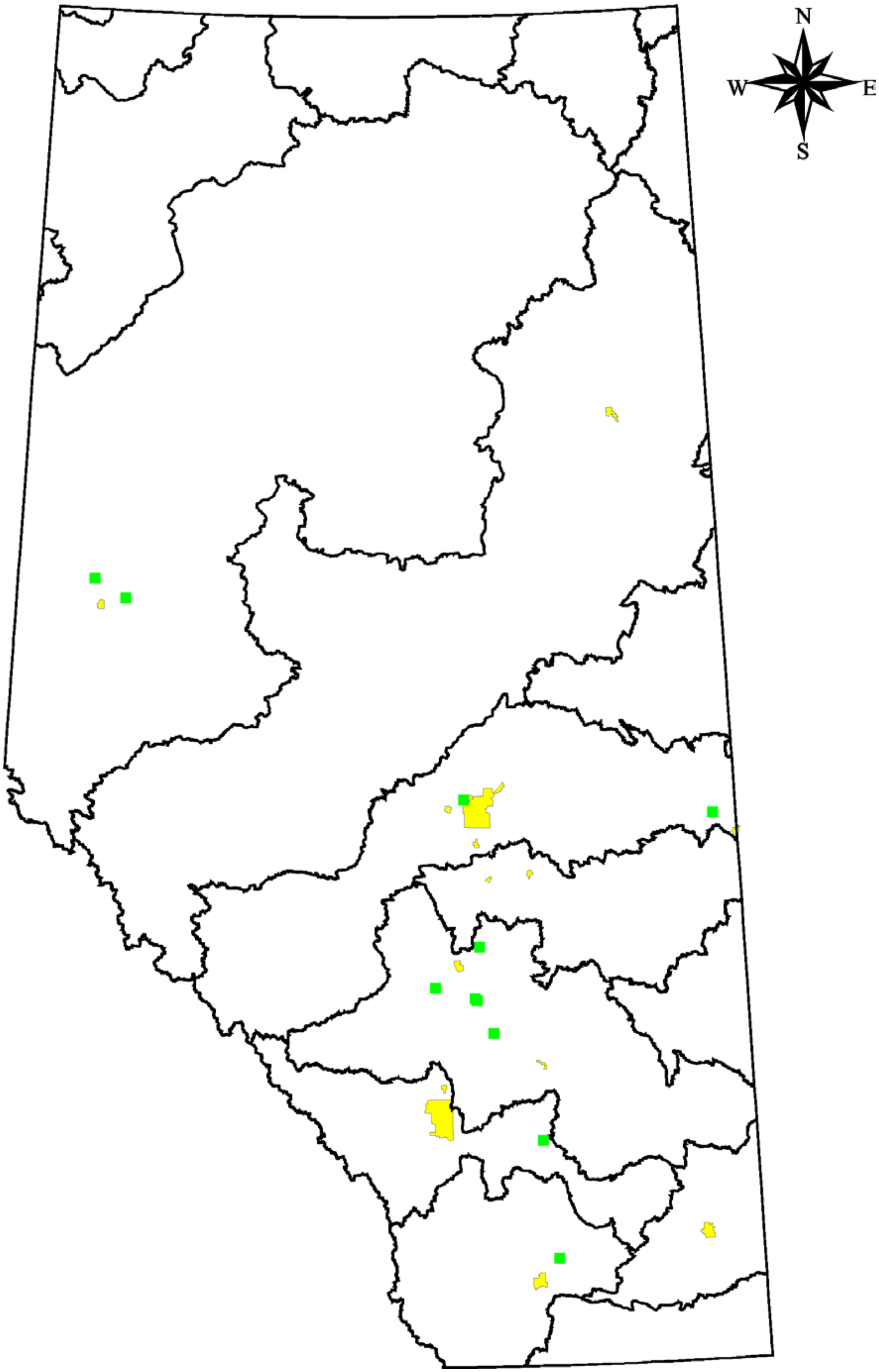


Figure 4v Distribution of ethalfluralin detections in Alberta from 1995 to and including 2002

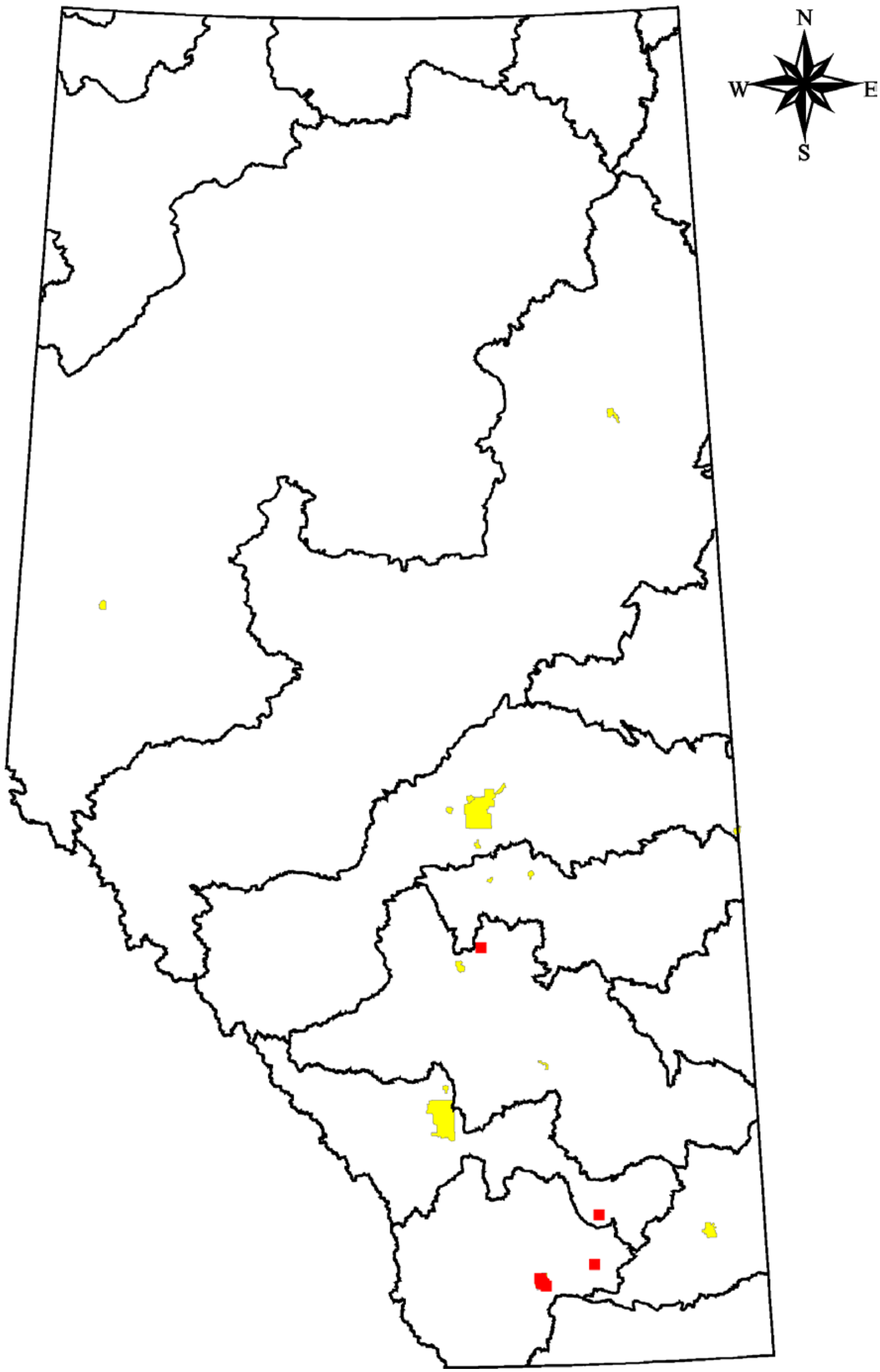


Figure 4w Distribution of malathion detections in Alberta from 1995 to and including 2002

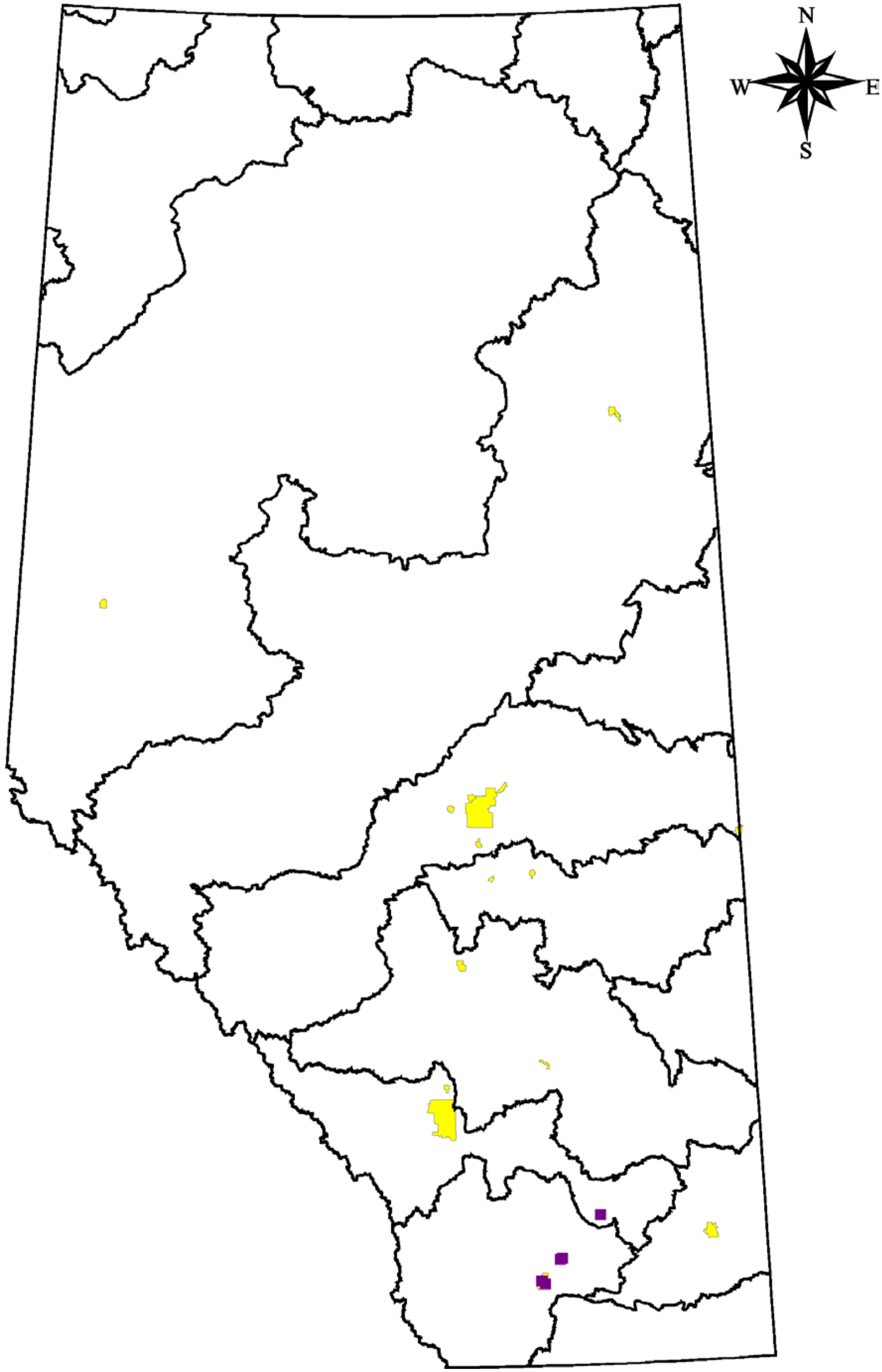


Figure 4x Distribution of 2,4-dichlorophenol detections in Alberta from 1995 to and including 2002

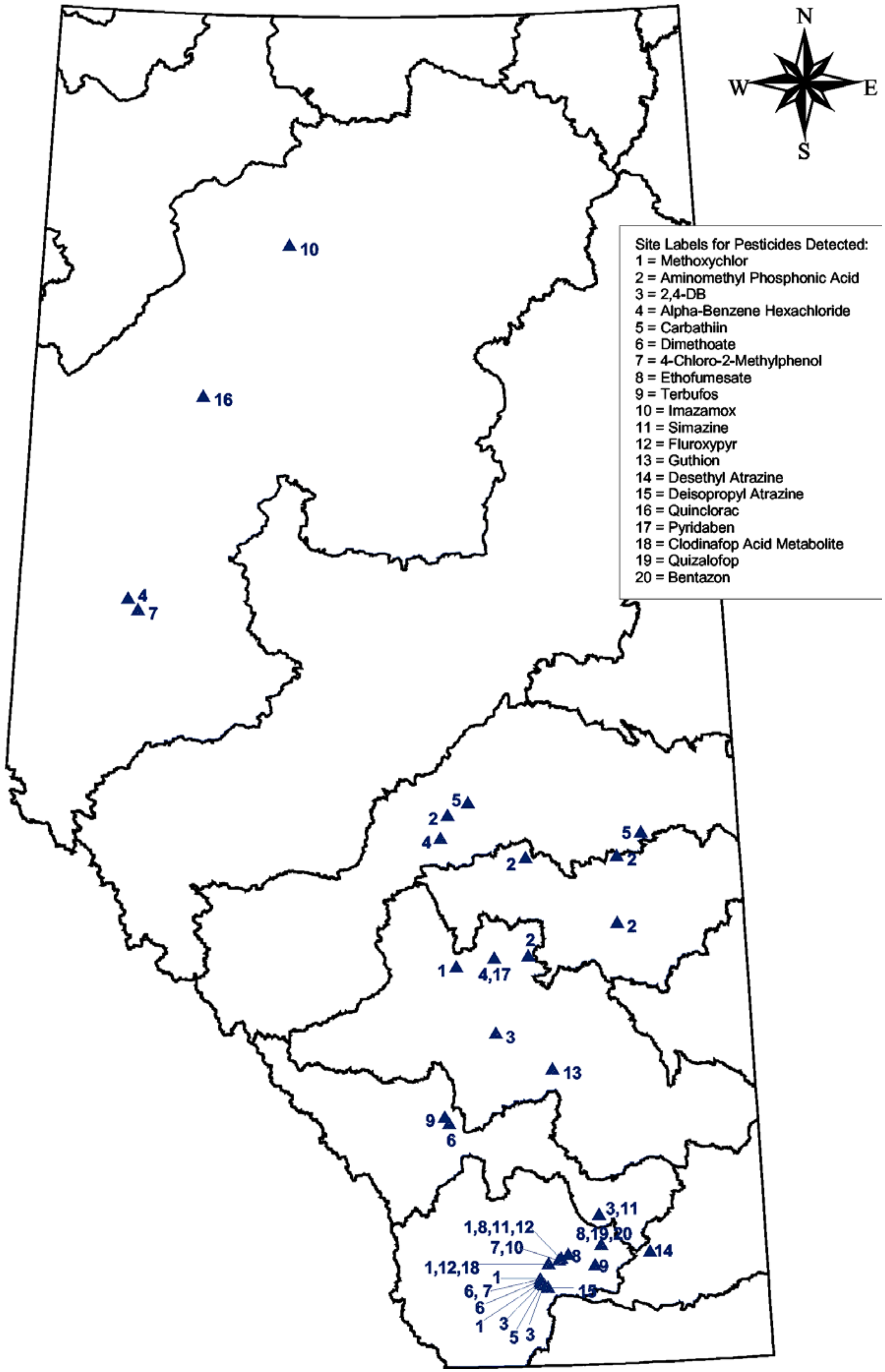


Figure 4y Distribution of pesticides with five or less detections in Alberta from 1995 to and including 2002

Glyphosate is by far the most widely used herbicide in Alberta and it is important to note that Figure 4 T does not provide a representative provincial picture of its distribution in surface waters. Glyphosate is not routinely analyzed; so far it has been analyzed at only a fraction of the sites that have been analyzed for other pesticides (Anderson et al. 2002 and Humphries et al. draft).

Picloram, which has a relatively low sale volume, is detected quite commonly in surface waters (Figure 4 E). Picloram is used to control broad leaf weeds and brush on pasture, rangeland and along roads and rights-of-way. It persists in soils for up to 5 years after application, and it is very soluble and can move away from the target site with runoff (AAFRD 2004). The persistence and mobility of this herbicide, coupled with the fact that roads and some rights of way often drain directly to surface waters, are a likely explanation for its widespread detections in surface waters.

Some herbicides such as dichlorprop, atrazine, bromacil, diuron and cyanazine and the insecticides diazinon and chlorpyrifos have a more regional use and, accordingly, tend to have a more restricted distribution pattern in surface waters.

- Dichlorprop (Figure 4H) detections occur mainly in southern and east central Alberta and correspond with the main areas where barley, spring wheat and winter wheat are grown and where this herbicide is used to control a variety of broad leaf weeds. A dichlorprop and 2,4-D mix is also used to control brush and a variety of broad leaf weeds in industrial areas, non-crop areas, right-of-ways and roadsides (AAFRD 2004).
- Atrazine (Figure 4 K) is used on sweet corn and field corn and is mainly detected in the Oldman River Basin where these crops are grown on irrigated land. However, atrazine has also been used as a sterilant in industrial and domestic settings and it is suspected that the detections in the Calgary area are related to such uses (G. Byrtus, pers. comm.; see also Section 4.2.2.2.3).
- Diazinon (Figure 4 M) is mostly used to control insect pests on ornamental vegetation and fruit trees. Its occurrence in surface waters is closely linked to major urban centers, especially Lethbridge and Calgary.
- Diuron (Figure 4 O) is found mostly along the Lethbridge-Calgary-Edmonton corridor. It is registered for weed control on asparagus and for weed control along non-crop areas, drainage and irrigation ditches, ponds and dugouts (AAFRD 2004).
- Bromacil (Figure 4 P) has been detected at a few sites, most of which are in the Lethbridge area. This herbicide is registered for non-crop use only (AAFRD 2004).
- Chlorpyrifos (Figure 4 Q) and malathion (Figure 4 W) have domestic applications and tend to be found downstream of urban centers, but these insecticides are also used to control various insect pests on a variety of crops some of which include crops typically grown on irrigated land (i.e., corn and sugar beets), hence the detections in southern Alberta.

Several pesticides have monitoring data for 2002 only (i.e., 2,4-dichlorophenol, bentazon, clodinafop-propargil and its acid metabolyte, fluroxypyr, quizalofop and simazine) and they have been detected at only a few locations (Figure 4 X and Y). The relationship between sales, use and detections in surface waters may become clearer as more data for these products become available.

4.1.5 Concentrations

Detected pesticides also exhibit a wide concentration range in surface samples (Figure 5 and Table 3). In general, pesticides detected most frequently also tended to be among those that had the largest concentration range. Imazamox appears to be an exception to this; it was only detected twice, but one of the samples had a high concentration (9.09 µg/L).

Medians of measurable herbicide concentrations of bromacil, diuron, imazamethabenz, deisopropyl atrazine, glyphosate, AMPA, simazine and clodinafop-acid metabolyte were in the 0.1 to 1 µg/L range. Medians for all other herbicides were between the MDL and 0.1 µg/L. Maximum recorded concentration of most herbicides was well below 5 µg/L, but for two compounds, concentration maxima were much higher (439 and 586 µg/L for 2,4-D and MCPP, respectively, were recorded in urban drains).

Insecticide concentrations were generally lower than herbicide concentrations. Terbufos had the highest median concentration (0.016 µg/L), but peak concentrations for some insecticides were as high as 1.44 µg/L for diazinon and 1.315 µg/L for lindane.

Carbathiin, the only fungicide detected, had a median measurable concentration of 0.038 µg/L and a maximum of 0.142 µg/L.

4.1.6 Compliance with Surface Water Quality Guidelines

An initial assessment of the significance of pesticide detections in surface waters can be made by comparing concentrations with Surface Water Quality Guidelines for use in Alberta (Alberta Environment 1999) (Table 4). These guidelines are based primarily on the Canadian Water Quality Guidelines for the protection of various uses (CCME 1999), although they also include USEPA Criteria which are often less stringent. Recently updated USEPA guidelines (USEPA 2002) are listed in Table 4. As indicated earlier, application of guidelines does not necessarily imply that the water body from which samples were drawn is used as a source of drinking water for livestock, or for irrigation. It is noted that drinking water guidelines apply to treated water, not raw water. However, all water bodies would be of direct or indirect (e.g., some urban drains) significance to aquatic life.

The results of the comparison of the pesticide database with CCME guidelines are presented in Table 4. Although 28 of the 62 pesticides monitored have a guideline for at least one use, few have guidelines for the 4 designated uses (only atrazine, bromoxynil, cyanazine, dicamba, diclofop-methyl and simazine). Of the 44 pesticides detected in Alberta surface waters 21, 7, 12 and 14 have a guideline for drinking water, irrigation water, livestock watering and protection of aquatic life, respectively. However, 22 do not have guidelines for any of these uses; this

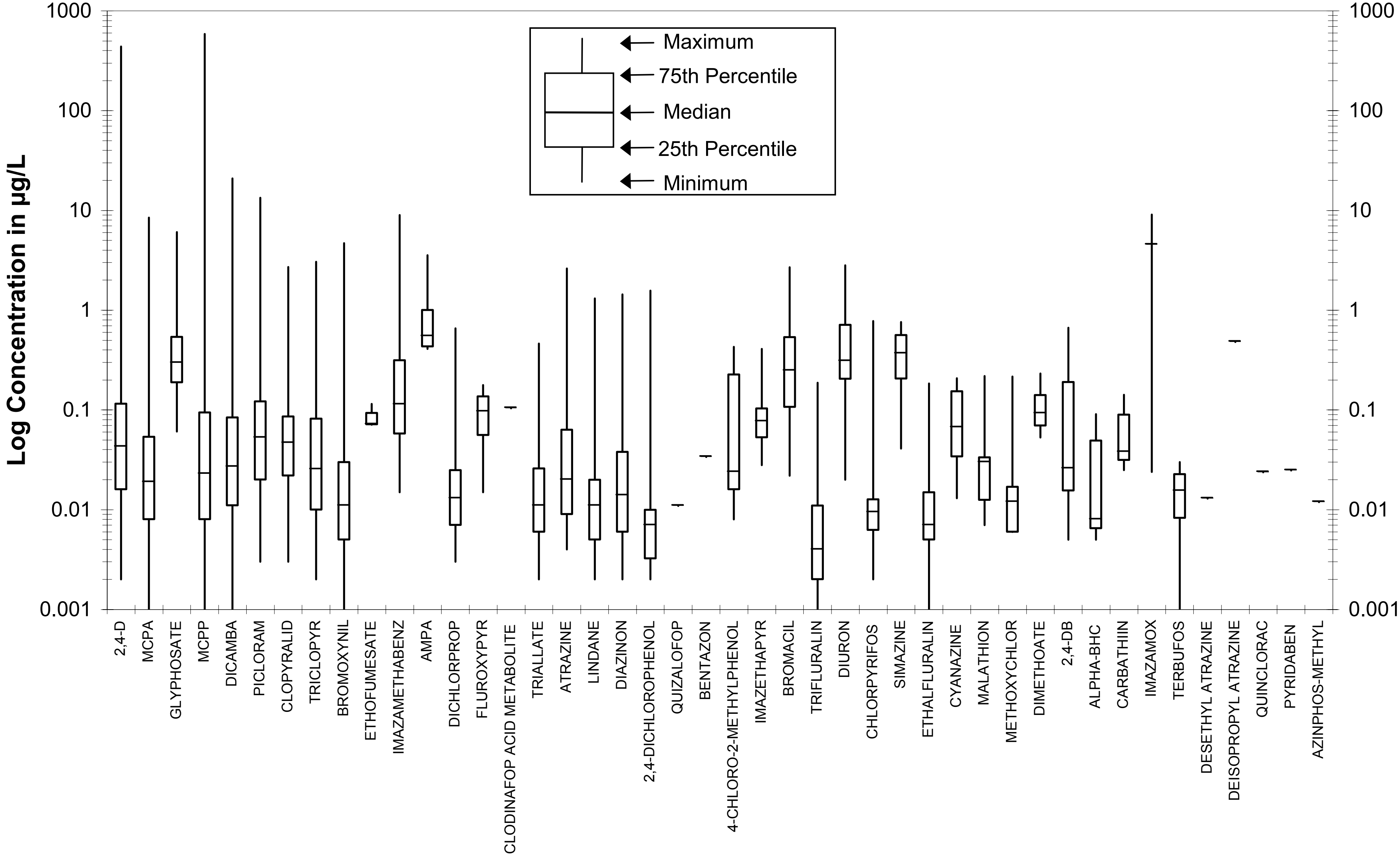


Figure 5 **Range of measurable pesticide concentrations in surface waters (1995 - 2002)**

Table 4a Comparison of pesticide concentrations measured in Alberta surface waters (1995 - 2002) with Surface Water Quality Guidelines for use in Alberta (AENV 1999), Canadian Water Quality Guidelines (CWQG), and USEPA Criteria (2002)

Compounds Analyzed	No. Samples Analyzed	No. Samples with Detections	ASWQG (AENV 1999)/CWQG (CCME 1999) in µg/L				USEPA (2002) in µg/L	Number of Samples Exceeding Guideline				USEPA(2002)
			Drinking	Irrigation	Livestock	Freshwater Aquatic Life	Aquatic Life Criteria	Drinking	Irrigation	Livestock	Freshwater Aquatic Life	Aquatic Life Criteria
HERBICIDES												
4-CHLORO-2-METHYLPHENOL	250	3	NA*	NA	NA	NA	NA					
2,4-D	3061	1626	100	NA	NA	4	NA	**1**			**28**	
2,4-DB	3052	4	NA	NA	NA	NA	NA					
2,4-DICHLOROPHENOL	250	6	900	NA	NA	NA	NA	0				
AMPA	110	7	NA	NA	NA	NA	NA					
ATRAZINE	3054	115	5	10	5	1.8	NA	0	0	0	**1**	
BENTAZON	42	1	NA	NA	NA	NA	NA					
BROMACIL	3052	32	NA	0.2	1100	5	NA		**17**	0	0	
BROMOXYNIL	3053	293	5	0.33	11	5	NA	0	**8**	0	0	
CLODINAFOP ACID METABOLITE	23	1	NA	NA	NA	NA	NA					
CLODINAFOP-PROPARGYL	23	0	NA	NA	NA	NA	NA					
CLOPYRALID	3053	332	NA	NA	NA	NA	NA					
CYANAZINE	3053	16	10	0.5	10	2	NA	0	0	0	0	
DESETHYL ATRAZINE	2480	1	NA	NA	NA	NA	NA					
DEISOPROPYL ATRAZINE	2480	1	NA	NA	NA	NA	NA					
DICAMBA	2221	600	120	0.006	122	10	NA	0	**526**	0	**4**	
DICHLORPROP (2,4-DP)	3053	162	NA	NA	NA	NA	NA					
DICLOFOP-METHYL	3053	0	9	0.18	9	6.1	NA					
DIURON	3052	24	150	NA	NA	NA	NA	0				
ETHALFLURALIN	3053	21	NA	NA	NA	NA	NA					
ETHOFUMESATE	42	3	NA	NA	NA	NA	NA					
FENOXAPROP-P-ETHYL	2481	0	NA	NA	NA	NA	NA					
FLUAZIFOP	42	0	NA	NA	NA	NA	NA					
FLUROXYPYR	42	2	NA	NA	NA	NA	NA					
GLUFOSINATE	75	0	NA	NA	NA	NA	NA					
GLYPHOSATE	110	28	280	NA	280	65	NA	0		0	0	
IMAZAMETHABENZ	2741	176	NA	NA	NA	NA	NA					
IMAZAMOX	2109	2	NA	NA	NA	NA	NA					
IMAZETHAPYR	2436	27	NA	NA	NA	NA	NA					
LINURON	42	0	NA	0.071	NA	7	NA					
MCPA	3062	1150	NA	0.025	25	2.6	NA		**484**	0	**6**	
MCPB	3052	0	NA	NA	NA	NA	NA					
MCPP (MECOPROP)	3061	715	NA	NA	NA	NA	NA					
METOLACHLOR	42	0	50	28	50	7.8	NA					
METRIBUZIN	42	0	80	0.5	80	1	NA					

Table 4a Comparison of pesticide concentrations measured in Alberta surface waters (1995 - 2002) with Surface Water Quality Guidelines for use in Alberta (AENV 1999), Canadian Water Quality Guidelines (CWQG), and USEPA Criteria (2002) (continued)

Compounds Analyzed	No. Samples Analyzed	No. Samples with Detections	ASWQG (AENV 1999)/CWQG (CCME 1999) in µg/L				USEPA (2002) in µg/L	Number of Samples Exceeding Guideline				USEPA(2002)
			Drinking	Irrigation	Livestock	Freshwater Aquatic Life	Aquatic Life Criteria	Drinking	Irrigation	Livestock	Freshwater Aquatic Life	Aquatic Life Criteria
PICLORAM	3053	495	190	NA	190	29	NA	0		0	0	
QUINCLORAC	2481	1	NA	NA	NA	NA	NA					
QUIZALOFOP	42	1	NA	NA	NA	NA	NA					
SIMAZINE	433	3	10	0.5	10	10	NA	0	0	0	0	
TRIALLATE	3052	117	NA	NA	230	0.24	NA			0	4	
TRICLOPYR	433	46	NA	NA	NA	NA	NA					
TRIFLURALIN	3053	29	45	NA	45	0.2	NA	0		0	0	
INSECTICIDES												
ALDRIN	42	0	0.7	NA	NA	NA	3					
ALPHA-BHC	3052	3	NA	NA	NA	NA	NA					
ALPHA-ENDOSULFAN	3053	0	NA	NA	NA	NA	0.22					
AZINPHOS-METHYL	3053	1	20	NA	NA	NA	NA	0				
CHLORPYRIFOS	3052	22	90	NA	24	0.0035	0.083	0		0	19	1
DIAZINON	3053	82	20	NA	NA	NA	NA	0				
DIELDRIN	42	0	0.7	NA	NA	NA	0.24					
DIMETHOATE	2480	4	20	NA	NA	NA	NA	0				
DISULFOTON	3053	0	NA	NA	NA	NA	NA					
ETHION	3053	0	NA	NA	NA	NA	NA					
GAMMA-BHC (LINDANE)	3052	97	NA	NA	4	0.01	0.95			0	49	1
MALATHION	3053	11	190	NA	NA	NA	NA	0				1
METHOXYCHLOR	3053	5	900	NA	NA	NA	0.1	0				1
PARATHION	42	0	50	NA	NA	NA	0.03					
PHORATE	3053	0	2	NA	NA	NA	0.013					
PYRIDABEN	2481	1	NA	NA	NA	NA	NA					
TERBUFOS	3052	2	1	NA	NA	NA	NA	0				
FUNGICIDES												
CARBATHIIN	3053	3	NA	NA	NA	NA	NA					
CHLOROTHALONIL	42	0	NA	NA	NA	NA	NA					
HEXACONAZOLE	42	0	NA	NA	NA	NA	NA					
IPRODIONE	42	0	NA	NA	NA	NA	NA					
METALAXYL-M	42	0	NA	NA	NA	NA	NA					
PROPICONAZOLE	42	0	NA	NA	NA	NA	NA					

NA: not available

includes some of the most frequently detected compounds, which also tend to have the widest concentration range. Some examples of pesticides with no or partial guidelines (Table 4), but with frequent detections in Alberta surface waters include 2,4-D, glyphosate, and picloram, which have no irrigation guidelines, and clopyralid, and MCPP, which have no guidelines at all. USEPA aquatic life criteria exist for several insecticides analyzed in Alberta (i.e., aldrin, alpha endosulfan, chlorpyrifos, dieldrin, lindane, malathion, methoxychlor and parathion); only lindane and chlorpyrifos have CCME guidelines and in both cases the CCME guideline is more protective. In accordance with the philosophy outlined in Alberta Environment (1999), the most stringent guidelines override.

2,4-D was the only pesticide that exceeded Canadian Drinking Water guidelines; this incidence of non-compliance occurred in an urban drain sample and has no direct implication on the quality of drinking water. Unlike Canadian Drinking Water Guidelines which are compound-specific, European drinking water guidelines specify two guidelines for pesticides: 0.5 µg/L as the maximum acceptable total pesticide concentration and 0.1µg/L as a maximum for individual compounds (European Union 1998). If these guidelines were applied to surface waters in Alberta, 383 samples or 12.5% of the samples would have exceeded the total pesticide guideline, and 1423 or 22.7% of measurable concentrations for 35 different pesticides would have exceeded the guideline for individual compounds. The compliance level for raw surface waters has no direct implication on the quality of treated drinking water; however, it identifies a general concern and potential risk for drinking water treatment plants that rely on surface waters (SCESD 2000). Byrtus et al. (2004) recently completed a review of pesticides in treated drinking water in Alberta and found that in 1788 samples taken from 1995 to 2003 not one measurement exceeded pesticide drinking water guidelines. However, similarly to the situation in surface waters, many samples had multiple pesticide detections, and some pesticides detected do not have guidelines.

Pesticides exceeded irrigation guidelines in 26.9% of the samples. In the samples with detectable dicamba, bromacil, MCPA, and bromoxynil, non-compliance amounted to 88%, 53%, 47%, and 2.7%, respectively. As a consequence of their intended toxicity to plants, herbicides tend to have irrigation guidelines that are lower than guidelines for other uses. Irrigation guidelines are designed to protect sensitive crops, and while non-compliance with guidelines may not be of direct concern to some irrigated crops that are grown on a broad scale in Alberta, they could be of concern for specialty crops and produce that are irrigated with contaminated water, particularly if exposure is continuous over the growing season.

All recorded pesticide concentrations complied with available guidelines for livestock watering.

Pesticides exceeded available guidelines for the protection of aquatic life (PAL) in 3.5% of the samples. In the samples with measurable concentrations of chlorpyrifos, lindane, triallate, 2,4-D, atrazine, dicamba, and MCPA, non-compliance with PAL guidelines amounted to 95.5%, 50.5%, 3.4%, 1.7%, 0.9%, 0.7%, and 0.5% respectively. In general, CCME guidelines incorporate a safety factor of an order of magnitude for the protection of aquatic life. Even when that factor is considered there would be incidences of non-compliance for 2,4-D, chlorpyrifos and lindane. Four insecticides with USEPA criteria for aquatic life were detected in Alberta surface waters (chlorpyrifos, lindane, malathion, and methoxychlor); the criteria were exceeded once for each of these 4 insecticides (i.e., in <1% of the samples).

Based on the assessment of spiked samples, pesticide recovery is generally well below 100% (see Appendix B), and in light of the fact that concentrations are not adjusted for recovery it is possible that the reported incidence of non-compliance is biased low.

Overall, of the 3055 samples collected from 1995 to and including 2002, 103 (3.4% of total), 825 (26.9%) and 1 (0.03%) exceeded guidelines for the protection of aquatic life, irrigation and drinking water, respectively. Guidelines were exceeded at 50 sites (PAL), 186 sites (IRR) and 1 site (Drinking water).

Figure 6 provides an indication of the geographic distribution of sites with non-compliant samples. Sites with pesticide levels above the guidelines are distributed over the entire province, but, not surprisingly, they tend to occur more frequently in the White Zone of the province where high agricultural, domestic, and commercial/industrial pesticide uses are combined. This is also illustrated in Tables 4b and 4c which provide a summary of the distribution of non-compliant samples by type of water body and by drainage basin. The distribution of sites where guidelines exceed both PAL and IRR guidelines coincides with the areas of highest pesticide use in the province (Byrtus 2000), thus establishing an association between high use on land and elevated concentrations in water.

The occurrence of several pesticides in a sample is common in Alberta surface waters. Pesticides were detected in 65% (2011 samples) of the samples collected; of these more than 75% contained two or more pesticides, and about 200 samples contained 6 or more pesticides (Figure 7a). In some samples several pesticide residues exceeded available guidelines for the protection of aquatic life or irrigation. CCME guidelines apply to single compounds not mixtures. The presence of multiple pesticides raises the level of uncertainly about implications on uses, particularly when several of these compounds are above their respective guideline (Figure 7b and c). Further uncertainty arises from the fact that many pesticides in mixtures do not have guidelines and hence are not included in Figure 7b or c despite their co-occurrence.

4.1.7 Breakdown of Data Set by Basin and by Water Body Type

The previous description of the aggregated pesticide data yields only a general indication of pesticide contamination at the provincial scale. This section provides further insights about spatial patterns in pesticide contamination across the province by breaking the data set down according to major river basins and types of water bodies.

Table 5 illustrates differences among basins and water body types with respect to the number of pesticide samples collected and the number of sites sampled. The distribution of sampling efforts across the province is a direct result of initiatives undertaken to address regional issues. The Oldman River Basin has been sampled more intensively than any other basin and it has the largest number of samples collected from the largest number of sites and diversity of water body types. In contrast, the Hay and Slave River basins have been sampled the least. Most of the

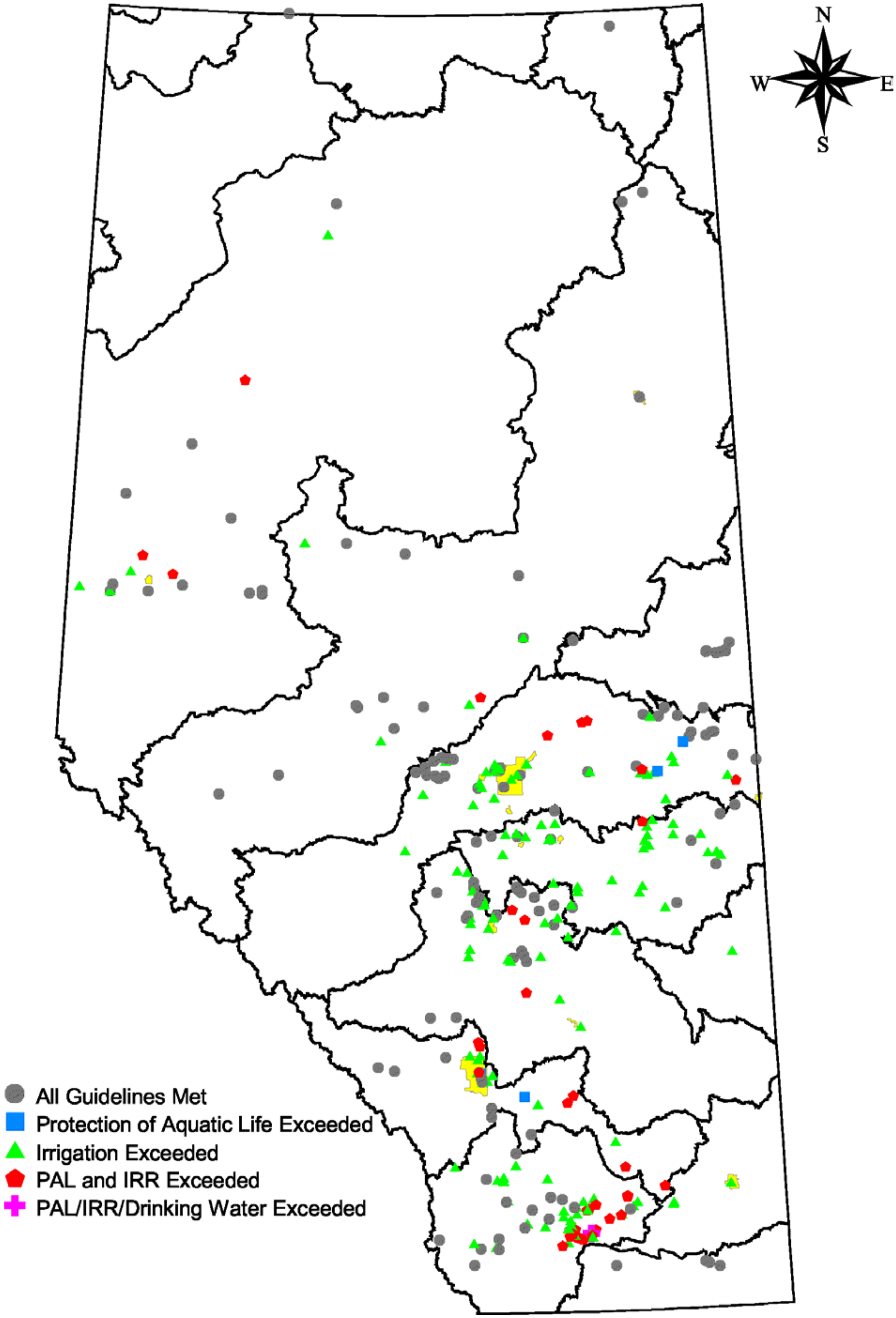


Figure 6 **Comparison of pesticide concentrations with CCME surface water quality guidelines**

Table 4b Summary by water body type of the number of pesticide measurements that exceeded surface water quality guidelines (1995 to 2002)

	2,4-D	ATRAZINE	BROMACIL	BROMOXYNIL	CYANAZINE	DICAMBA	DIURON	GLYPHOSATE	MCPA	PICLORAM	SIMAZINE	TRIALLATE	TRIFLURALIN	AZINPHOS-METHYL	CHLORPYRIFOS-ETHYL	DIAZINON	LINDANE	MALATHION	METHOXYCHLOR	TERBUFOS
All Data	*(326 sites and 3055 samples)*																			
Drinking	1	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	17	8	0	526			484		0									
Livestock	1	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	28	1	0	0	0	4		0	6	0	0	4	0		20		49	1[1]	1[1]	
Lakes	*(49 sites and 115 samples)*																			
Drinking	0	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	0	0	0	6			4		0									
Livestock	0	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	0	0	0	0	0	0		0	0	0	0	0	0		0		0	0	0	
Rivers	*(86 sites and 1289 samples)*																			
Drinking	0	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	0	0	0	97			88		0									
Livestock	0	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	0	0	0	0	0	0		0	1	0	0	0	0		7		13	0	0	
Creeks	*(64 sites and 963 samples)*																			
Drinking	0	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	1	1	0	82			170		0									
Livestock	0	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	3	0	0	0	0	0		0	0	0	0	3	0		1		16	0	0	
Wetlands	*(58 sites and 151 samples)*																			
Drinking	0	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	0	0	0	4			58		0									
Livestock	0	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	0	0	0	0	0	0		0	0	0	0	0	0		0		4	0	0	
Irrigation Canal/Drain	*(35 sites and 326 samples)*																			
Drinking	0	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	11	6	0	163			90		0									
Livestock	0	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	12	0	0	0	0	3		0	4	0	0	1	0		12		5	0	0	
Urban Creeks	*(34 sites and 211 samples)*																			
Drinking	1	0		0	0	0	0	0		0	0		0	0	0	0		0	0	0
Irrigation		0	5	1	0	174			74		0									
Livestock	1	0	0	0	0	0		0	0	0	0	0	0		0		0			
Freshwater Aquatic Life	13	1	0	0	0	1		0	1	0	0	0	0		0		11	1[1]	1[1]	

Notes:

Guidelines used are Alberta/CCME guidelines unless otherwise stated

[1] USEPA (2002) criteria

Only pesticides that were detected and have guidelines are listed here

The number of sites and samples applied to the water body type sampled and may underestimate the number of samples analyzed for some pesticides

Table 4c Summary by basin of the number of pesticide measurements that exceeded surface water quality guidelines (1995 to 2002)

	2,4-D	ATRAZINE	BROMACIL	BROMOXYNIL	CARBATHIIN	CYANAZINE	DICAMBA	DIURON	GLYPHOSATE	MCPA	PICLORAM	SIMAZINE	TRIALLATE	TRIFLURALIN	AZINPHOS-METHYL	CHLORPYRIFOS-ETHYL	DIAZINON	LINDANE	MALATHION	METHOXYCHLOR	TERBUFOS
Hay River	*(1 site, 12 samples*)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	0			0											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		0			
Slave	*(1 site, 10 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	0			0											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		0			
Peace	*(17 sites, 262 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	**17**			**12**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		**2**	0		0		**8**			
Athabasca	*(20 site, 223 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	**1**	0		0	**11**			**13**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		**1**	0		0		0			
Beaver	*(12 sites, 20 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	0			0											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		0			
North Saskatchewan River	*(78 site, 515 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	**32**			**60**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		**16**			
Battle	*(36 sites, 188 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	**4**			**53**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		**2**			
Red Deer River	*(49 site, 552 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	**1**		0	**18**			**114**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	**2**	0	0	0		0	0		0	**1**	0		0	0		0		**6**			

Table 4c Summary by basin of the number of pesticide measurements that exceeded surface water quality guidelines (1995 to 2002) (continued)

	2,4-D	ATRAZINE	BROMACIL	BROMOXYNIL	CARBATHIIN	CYANAZINE	DICAMBA	DIURON	GLYPHOSATE	MCPA	PICLORAM	SIMAZINE	TRIALLATE	TRIFLURALIN	AZINPHOS-METHYL	CHLORPYRIFOS-ETHYL	DIAZINON	LINDANE	MALATHION	METHOXYCHLOR	TERBUFOS
Sounding	*(2 sites, 15 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	**1**			**1**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		0			
Bow	*(30 site, 406 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	**1**	**1**		0	**113**			**65**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	**4**	0	0	0		0	0		0	0	0		**1**	0		**4**		**3**			
Oldman River	*(74 sites, 781 samples)*																				
Drinking	1	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	**15**	**6**		0	**309**			**157**											
Livestock	1	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	**22**	1	0	0		0	**4**		0	**5**	0		0	0		**16**		**14**	**1** [1]	**1** [1]	
South Saskatchewan River	*(2 site, 65 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	**21**			**9**											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		0			
Milk River	*(4 sites, 6 samples)*																				
Drinking	0	0		0		0	0	0	0		0			0	0	0	0		0	0	0
Irrigation		0	0	0		0	0			0											
Livestock	0	0	0	0		0	0		0	0	0		0	0		0		0			
Freshwater Aquatic Life	0	0	0	0		0	0		0	0	0		0	0		0		0			

Notes:
Guidelines used are Alberta/CCME guidelines unless otherwise stated
[1] USEPA (2002) criteria
Only pesticides that were detected and have guidelines are listed here
Number of sites and samples applies to the basin as a whole and may, in some cases, be larger than the number of samples analyzed for a given pesticide

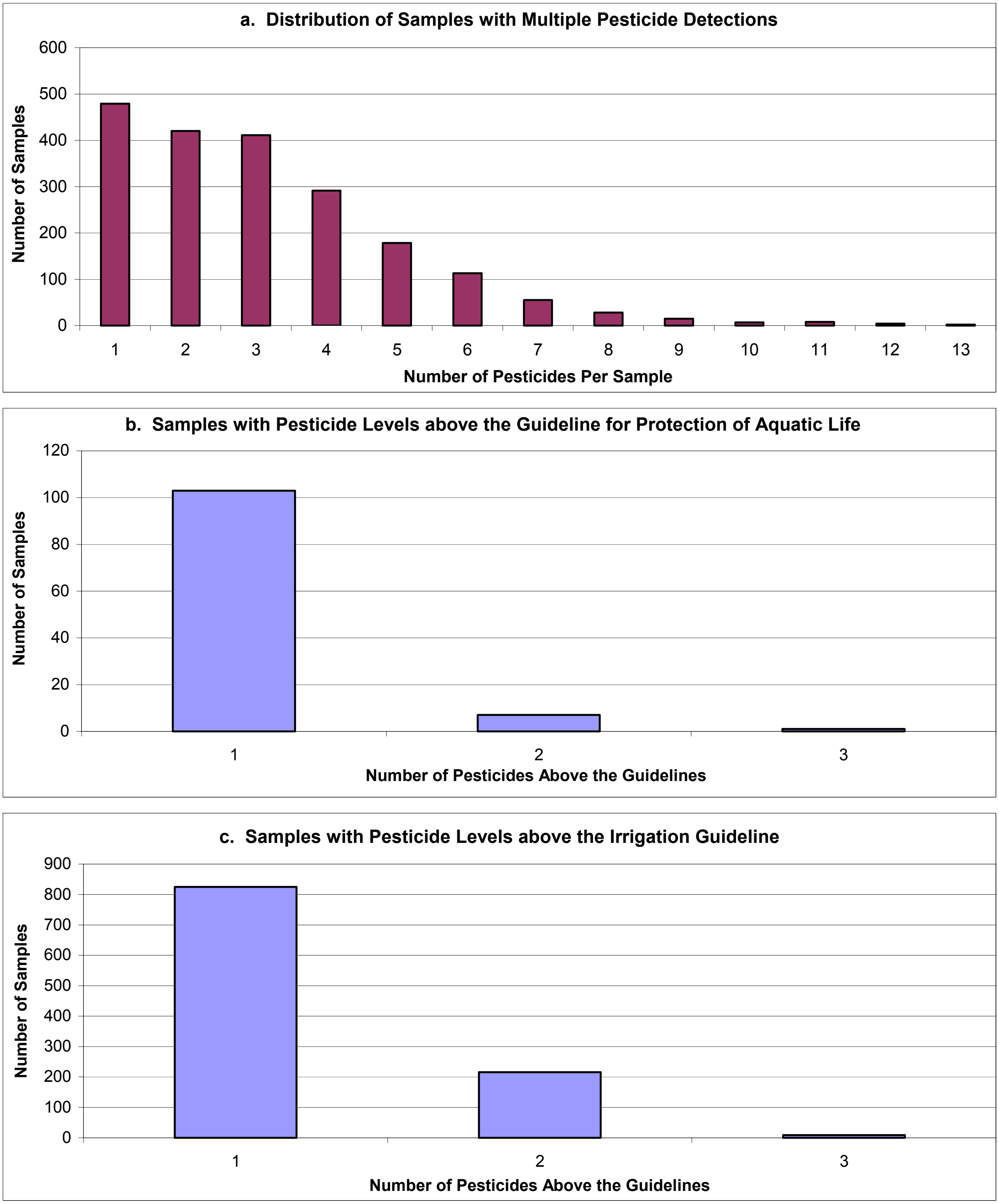


Figure 7 Multiple pesticide detections and non-compliances in the same sample

Table 5 Distribution of pesticide sampling sites according to major drainage basins and types of water bodies

Drainage Basins	Types of Waterbodies														Total No. Sites	Total No. Samples
	Lakes		Creeks		Rivers		Wetlands		Irrigation Canals		Irrigation Return Flows		Urban Storm Drains and Creeks			
	No. Sites	No. Samples	No. Sites	No. Samples	No. Sites	No. Samples	No. Sites	No. Samples	No. Sites	No. Samples	No. Sites	No. Samples	No. Sites	No. Samples		
Hay River					1	12									**1**	**12**
Slave River					1	10									**1**	**10**
Peace River	2	6	6	111	9	145									**17**	**262**
Athabasca River	5	13	2	23	13	187									**20**	**223**
Beaver River	11	19	1	1											**12**	**20**
North Saskatchewan River	15	34	12	210	21	200	20	57					10	14	**78**	**515**
Battle River	1	1	8	105	1	25	26	57							**36**	**188**
Red Deer River	9	24	19	254	11	244	10	30							**49**	**552**
Sounding Creek			1	9							1	6			**2**	**15**
Bow River			4	16	9	234			5	5	2	89	10	62	**30**	**406**
Oldman River	2	12	10	202	19	199	2	7	14	50	13	176	14	135	**74**	**781**
South Saskatchewan River			1	32	1	33									**2**	**65**
Milk River	4	6													**4**	**6**
Total	**49**	**115**	**64**	**963**	**86**	**1289**	**58**	**151**	**19**	**55**	**16**	**271**	**34**	**211**	**326**	**3055**

provincial samples have been taken from rivers and streams; lakes and wetlands have been sampled less frequently and with a narrow regional focus. By the nature of the distribution of irrigation across the province, irrigation return data are available only for the southern basins. Urban drain sampling has been limited to major cities in the Oldman, Bow and North Saskatchewan basins.

Pearson's correlations between number of samples collected (sample intensity) and number of samples with detections (indicator of detection frequency) were calculated for the data set aggregated by drainage basin, then for the data set aggregated by water body type. The rather weak correlation coefficients (basin r = 0.42; and water body type r = 0.39) suggest that sampling intensity influences pesticide detection frequency, but not to a large degree.

Figure 8 a,b,c compares pesticide data broken down by water body type. Pesticide detection frequency, detected concentrations and number of pesticides detected per sample were highest in irrigation streams and urban streams, and lowest in lakes. Hence, when data are aggregated by basin, the proportion of samples contributed from various water bodies could influence the perception of pesticide contamination of drainage basins or other spatial units used to aggregate the data (e.g., municipal district, ecoregion).

Figure 9 compares pesticide data aggregated by major drainage basin. Although some basins (e.g., Oldman River) have been sampled much more intensively than others (e.g., Hay and Milk rivers and Sounding Creek), there is a distinct North-South pattern in detection frequency which is not always consistent with the sampling effort: much lower detection frequencies were recorded in northern basins (Hay, Slave, Peace, Athabasca, and Beaver river basins) than southern basins (North Saskatchewan, Battle, Red Deer, Bow, Oldman, South Saskatchewan and Milk River basins and Sounding Creek basins) (Figure 9 a). Similarly, there are significant differences among basins with respect to total pesticide concentration (Figure 9 b) and number of different compounds encountered per sample (Figure 9 c) (Kruskal Wallis, $P<0.05$). In contrast to patterns in detection frequency, these differences appear to be influenced more by the type of water body sampled and the number of samples taken than by North-South differences. For example, the Oldman and Battle river basins have comparable detection frequencies, but because the Oldman River basin includes data from urban drains and irrigation return flows its total pesticide concentrations are much higher than in the Battle River basin, which only includes data from rivers, creeks, lakes and wetlands.

4.1.8 Pesticide Index

Large, complex, multidimensional data sets are often cumbersome to summarize. Indices are descriptive tools that offer a means of summarizing such information efficiently and in a way that can be 'grasped at a glance'.

The pesticide index is used here to summarize all the data collected from 1995 to and including 2002 and to allow broad, spatial comparisons of pesticide contamination among sampling sites across Alberta. The index rates sites based on how many pesticides were detected, how often, and at what concentration, and is therefore a 'relative index of pesticide contamination'. Index values can range between 0 and 100. Similarly to other water quality indices used by Alberta

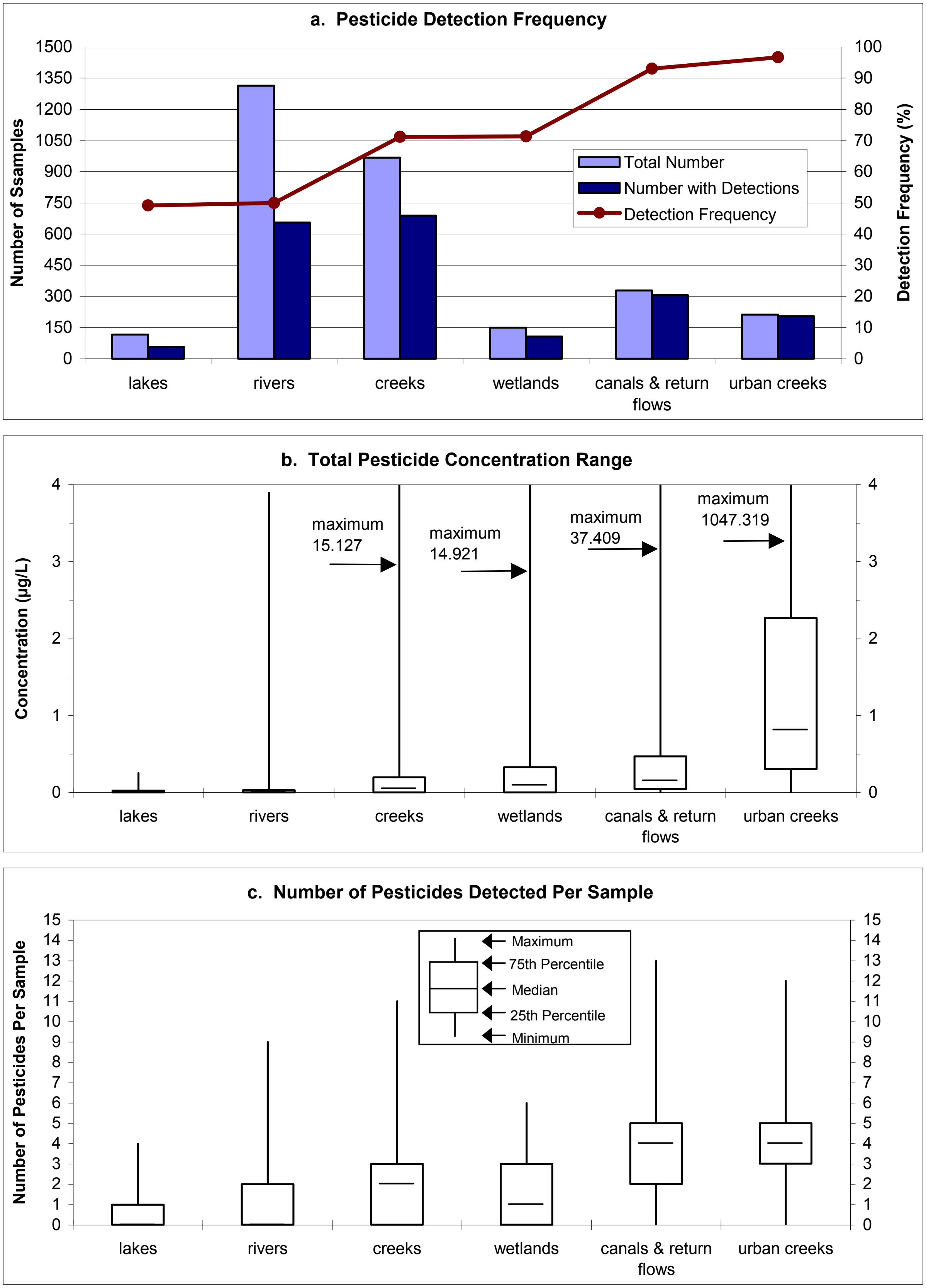


Figure 8 Pesticide data summarized by water body type (1995 - 2002)

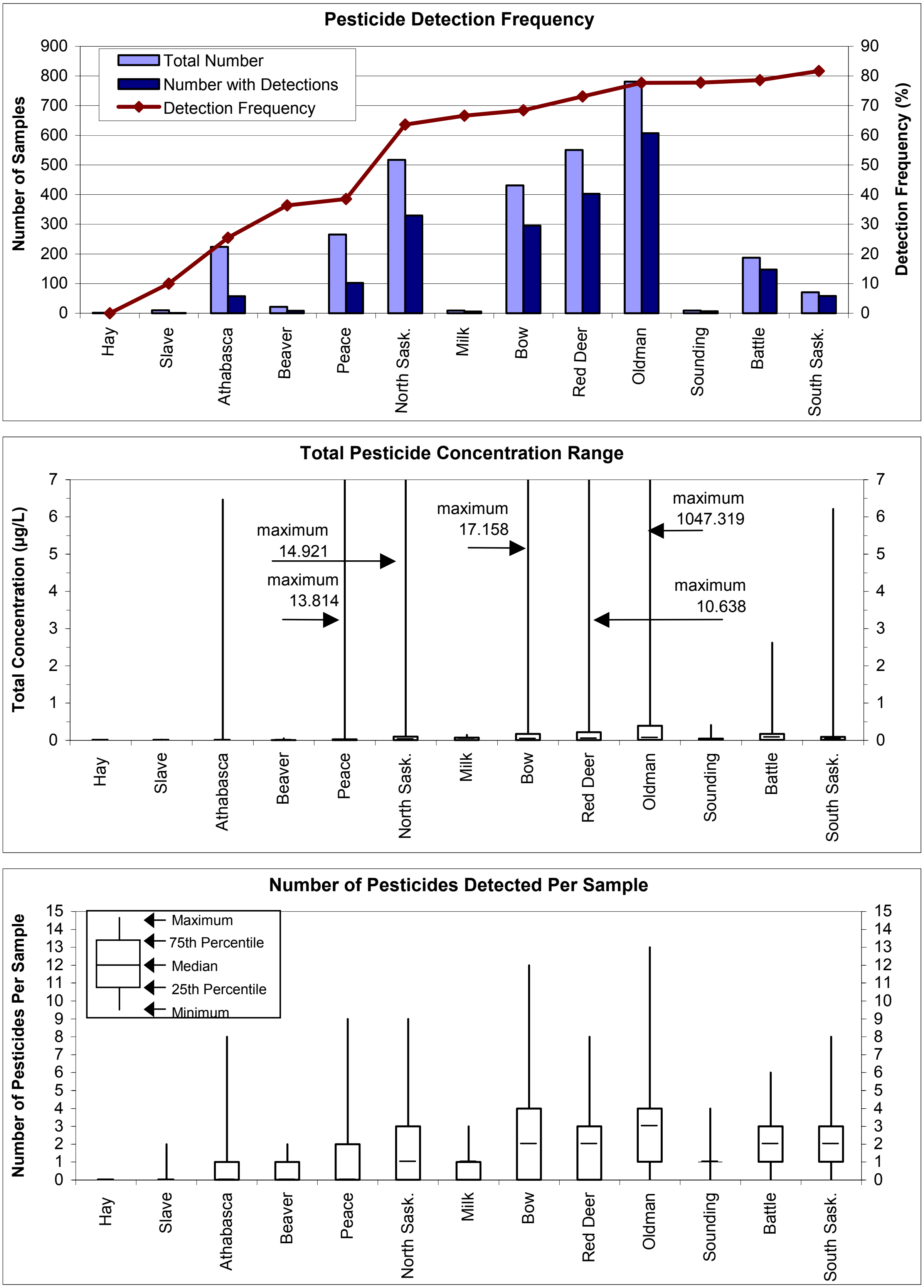


Figure 9 Pesticide data summarized by major drainage basin (1995 – 2002)

Environment (Alberta Environment Surface Water Quality Web Page), and to further simplify the data presentation, index values were ranked according to 5 main categories: ‘poor’ (index value ranging from 0 to 45), ‘marginal’ (46-65), ‘fair’ (66 to 80), ‘good’ (81 to 95) and ‘excellent’ (96 to 100). Because guidelines are not available for all pesticides detected in Alberta, method detection limit values were used as objectives in the index calculation. This implies that even very low-level pesticide detections will result in index values that depart from 100. It is therefore important to stress that the index does not provide an indication of risk to specific users of the water.

The index ratings for all sites are presented in Figure 10 and illustrate a general relationship between index values and use patterns: sites that rate from ‘fair’ to ‘poor’ are located in the White Zone in areas of highest pesticide use (e.g., Byrtus 2002). Figure 11 shows that not all sites had the four or more samples that are conventionally considered as a minimum requirement for index calculation (CCME 2003), and sites with fewer samples may have an unstable index value. However, these sites represent over half the number of sites sampled in Alberta and they contribute to the definition and understanding of spatial patterns and differences among water body types. Table 6 shows that regardless of whether the complete or reduced data set are used more than 50% of creek, river, lake, and wetland sites receive a rating that ranges from ‘fair’ to ‘excellent’. However, more than 50% of irrigation returns and urban drain sites rate ‘marginal’ to ‘poor’. The rating of irrigation canals is biased towards ‘poor’ and ‘marginal’ when only the small number of sites with 4 or more samples is considered. When all sites are considered, more than 50% of the irrigation canals rank from ‘fair’ to ‘excellent’ this differs from the rating based on the much larger number of samples.

A noteworthy attempt has been made by the USGS to build a pesticide index that describes ‘potential toxicity’ for freshwater aquatic life (Munn and Gilliom 2001). This index relies on threshold values defined by toxicity testing (e.g., LC50, EC50). While the index does not indicate whether sampled water is toxic, it can be used to rank and compare the toxicity of samples or sites on a relative basis. It may also be useful as a basis for comparing the potential significance of pesticides among water bodies, on a common basis. Endpoints for pesticides detected in Alberta, but not listed in Munn and Gilliom (2001), are currently being assembled with the intent of testing the value of this index on Alberta surface waters.

4.2 Temporal Trends

4.2.1 Seasonal Trends

Provincially (Figure 12), there is a tendency towards a higher detection frequency, higher total concentration and higher number of pesticides per sample, from March to September, with June and July being peak months. The seasonal pattern of pesticide occurrence in surface waters corresponds broadly with the timing of ice break-up and snowmelt runoff (March-April), the main period of pesticide application (May –July) and the greatest likelihood of significant rainfall (June- July) in the province. Most of Alberta’s water bodies are ice-bound from November to early March. Even under ice-cover, pesticides are detected relatively frequently (one pesticide or more occurs in 20 to 50% of the samples), although concentrations are generally lower than during the open water season. Pesticides that are detected in snowmelt

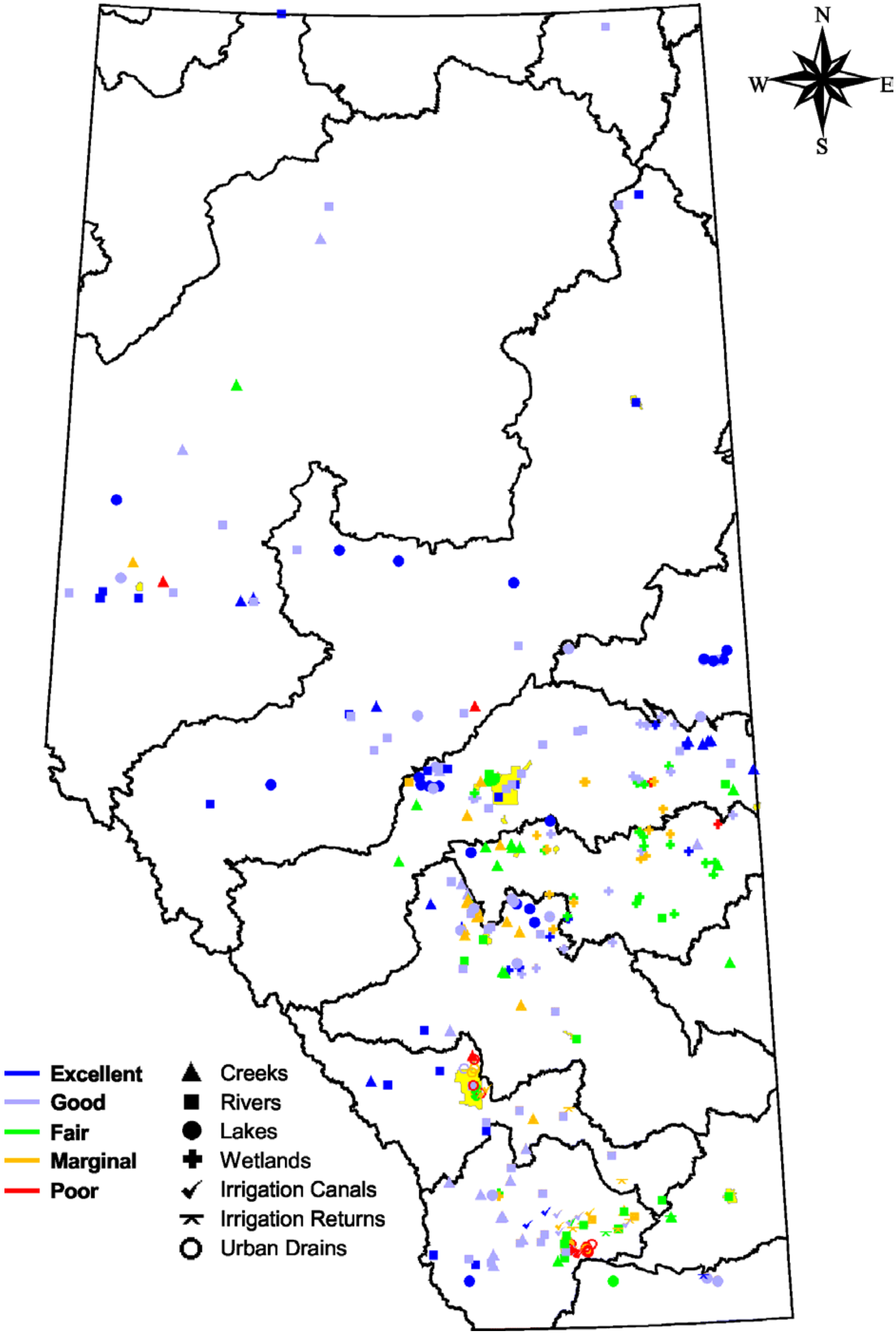


Figure 10 Pesticide index for all sites sampled from 1995 to and including 2002

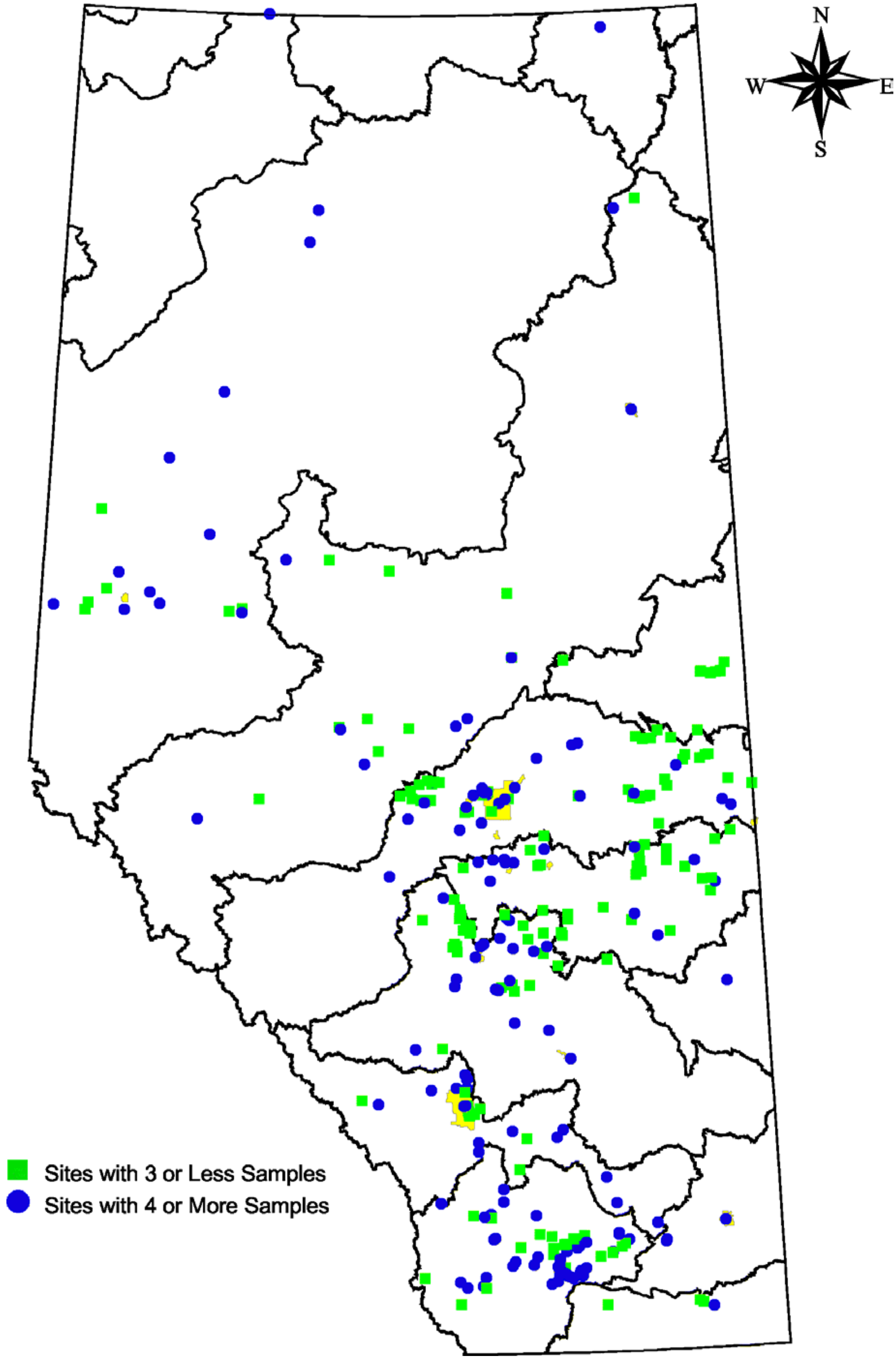


Figure 11 Pesticide sites sampled in Alberta from 1995 to and including 2002

Table 6 Summary of pesticide index for different water bodies across Alberta

All Sites											
Type	Total Number of Sites	Poor		Marginal		Fair		Good		Excellent	
		No. Sites	%	No. Sites	%	No. Sites	%	No. Sites	%	No. Sites	%
Creeks	65	2	3.1	19	29.2	16	24.6	14	21.5	14	21.5
Rivers	85	0	0.0	3	3.5	16	18.8	43	50.6	23	27.1
Lakes	46	0	0.0	0	0.0	3	6.5	21	45.7	22	47.8
Wetlands	61	2	3.3	15	24.6	19	31.1	19	31.1	6	9.8
Irrigation Canals	19	3	15.8	5	26.3	4	21.1	5	26.3	2	10.5
Irrigation Returns	17	6	35.3	7	41.2	2	11.8	0	0.0	2	11.8
Urban Drains	24	11	45.8	9	37.5	2	8.3	2	8.3	0	0.0

Sites With More Than Four Samples											
Type	Total Number of Sites	Poor		Marginal		Fair		Good		Excellent	
		No. Sites	%	No. Sites	%	No. Sites	%	No. Sites	%	No. Sites	%
Creeks	35	3	8.6	9	25.7	14	40.0	9	25.7	0	0.0
Rivers	66	0	0.0	3	4.5	14	21.2	40	60.6	9	13.6
Lakes	9	0	0.0	0	0.0	1	11.1	6	66.7	2	22.2
Wetlands	9	0	0.0	3	33.3	4	44.4	2	22.2	0	0.0
Irrigation Canals	4	3	75.0	1	25.0	0	0.0	0	0.0	0	0.0
Irrigation Returns	12	6	50.0	5	41.7	1	8.3	0	0.0	0	0.0
Urban Drains	14	9	64.3	3	21.4	1	7.1	1	7.1	0	0.0

Index period: 1995 to and including 2002

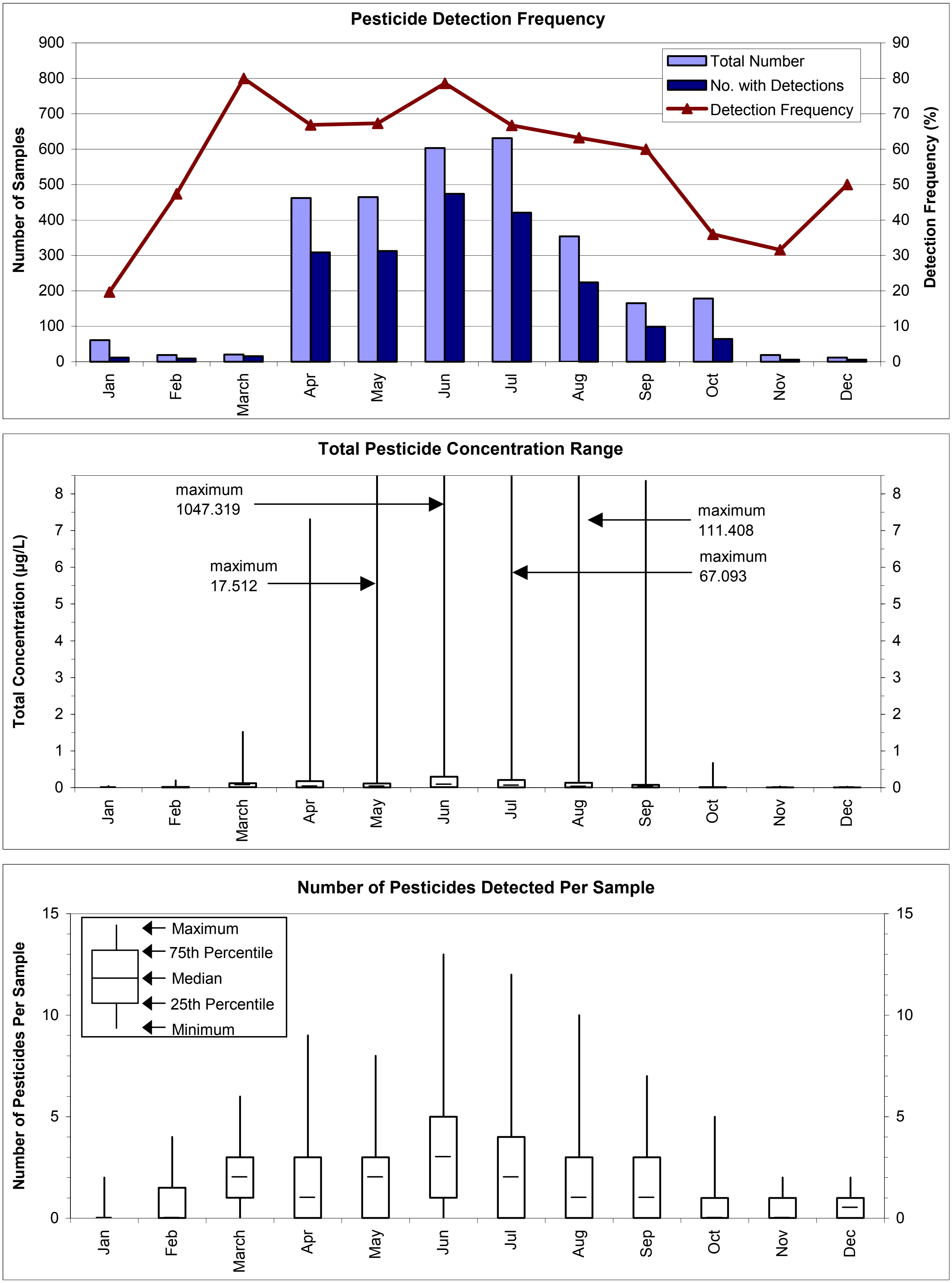


Figure 12 Seasonality of pesticide detection in the provincial data set (1995 - 2002)

runoff originate from the previous application year(s). Their occurrence in snowmelt runoff is indicative of the year-round presence of pesticides in the environment and suggests that degradation of some residues in areas with prolonged periods of deep frost and snow cover may be slower than expected. The detection frequency of some of the most commonly encountered herbicides and insecticides (Figure 13) follows the same broad pattern although some compounds deviate substantially (e.g., highest detection frequency for clopyralid in November, lindane in February and diazinon in December).

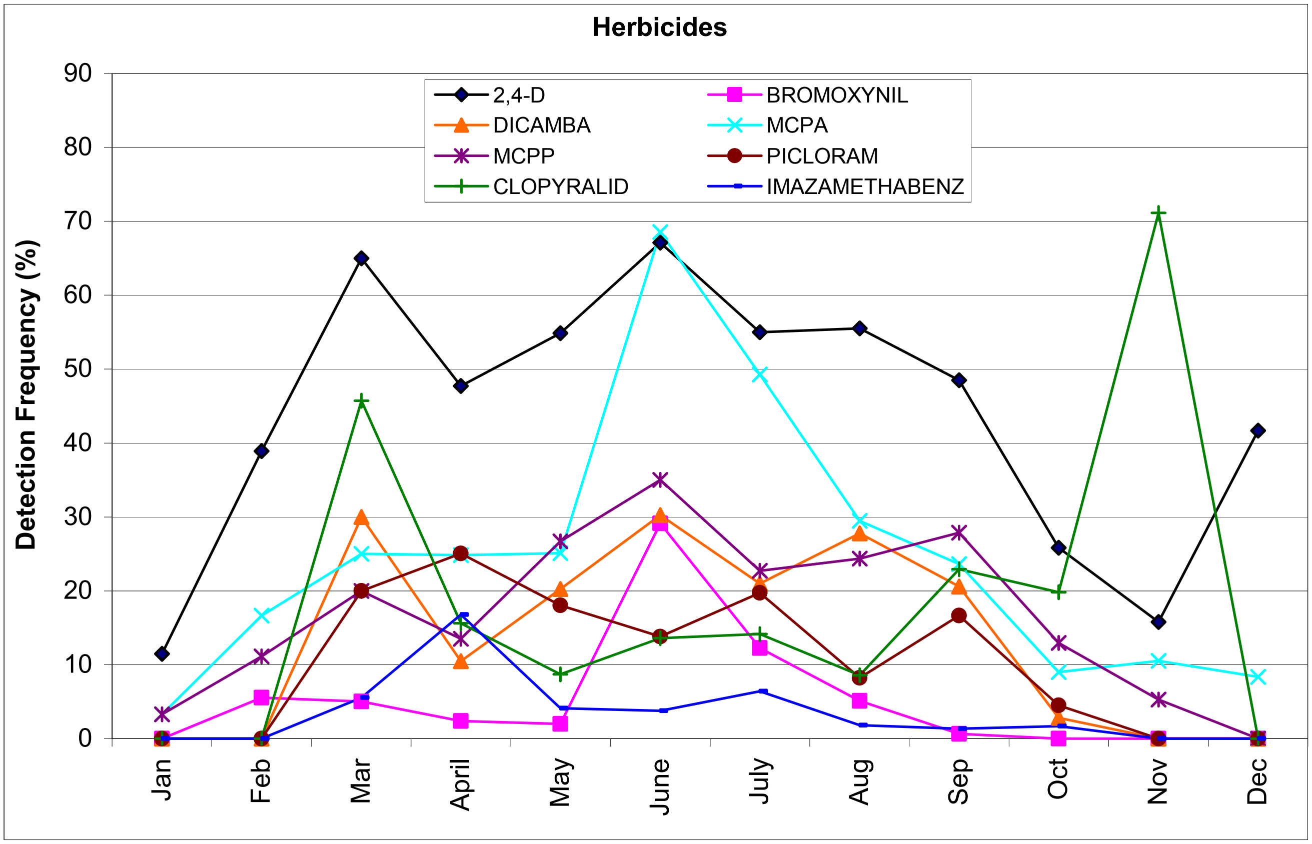
Climatic differences in Alberta result in north-south differences across the province in the timing of spring runoff, the growth of crops, and the timing of pesticide application; these in turn could result in spatial differences in seasonal patterns in pesticide contamination. The stream data set, which consists for a large part of AESA stream data obtained on a flow-weighted basis during the entire open water season, lends itself well to the examination of spatial variability in seasonality. Seasonal patterns in detection frequency and number of pesticides detected per sample are not always clearly defined (Figures 14a to 14f). This could be because in some basins (e.g., Bow and Athabasca) the number of samples per month is too low to discern trends, or because there is little temporal variability (e.g., Red Deer and North Saskatchewan basins). In contrast, concentrations fluctuate more noticeably and tend to be highest in June (Oldman River) or July (all other basins).

The occurrence of seasonal patterns in pesticides poses an additional challenge to long-term monitoring programs, which for budgetary reasons must limit sampling to select months of the year. Pesticide sampling at long-term river monitoring sites (LTRN project, Table 2) was initiated in the 1970's by Environment Canada. Most sites were sampled on a quarterly basis (January, March or April, July and October). This sampling schedule was maintained when Alberta Environment took over the monitoring program in 1987 until 1999. In 1999 pesticide sampling at these sites was changed from quarterly to four consecutive months with a high likelihood of detection (i.e., May, June, July and August); 1999 was a transition year in that some sites still have winter and fall samples. Some sites such as the North Saskatchewan River at Pakan had been sampled nearly monthly from 1995 to and including 1999, and the monthly data were used to depict month-to-month variability in Figure 15 and to illustrate the implications that the shift in sampling schedule may have on the long-term data set. The shift may have little influence on overall pesticide detection frequency, but it increases the likelihood of measuring higher concentrations. While the change in sampling design will yield a better understanding of the degree of pesticide contamination at Long-Term River Network (LTRN) sites, it could result in an artificial step trend in pesticide concentrations and it eliminates the ability to keep track of trends over time in months where contamination has typically been low.

4.2.2 Long-term Trends

4.2.2.1 Trends 1970's – 2002

A few pesticides such as 2,4-D, lindane and MCPA have a continuous data set that spans over three decades. Although the high incidence of censored data coupled with an uneven sampling frequency and significant changes in method detection limits precludes statistical trend analysis,



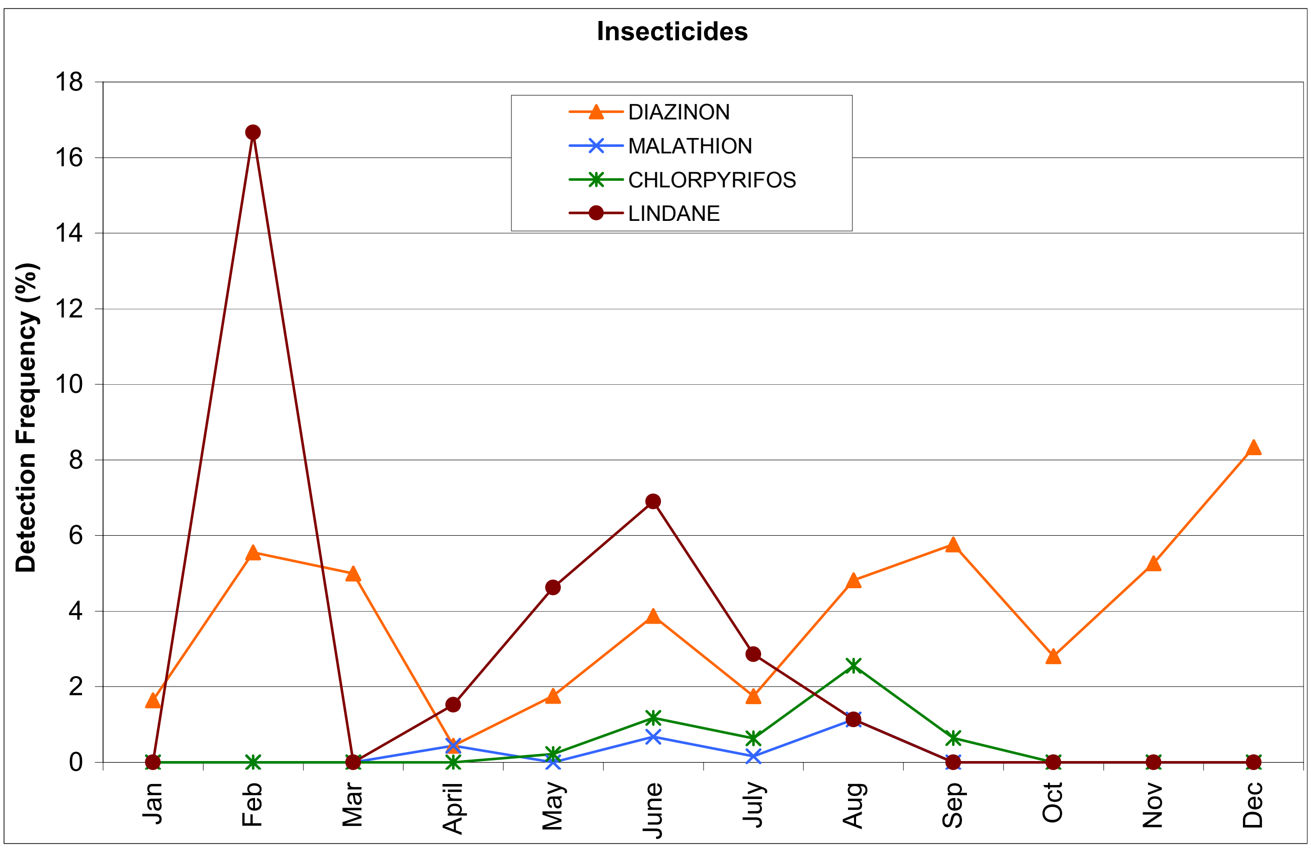


Figure 13 **Seasonal patterns in detection frequency of selected pesticides in the provincial database (1995 – 2002)**

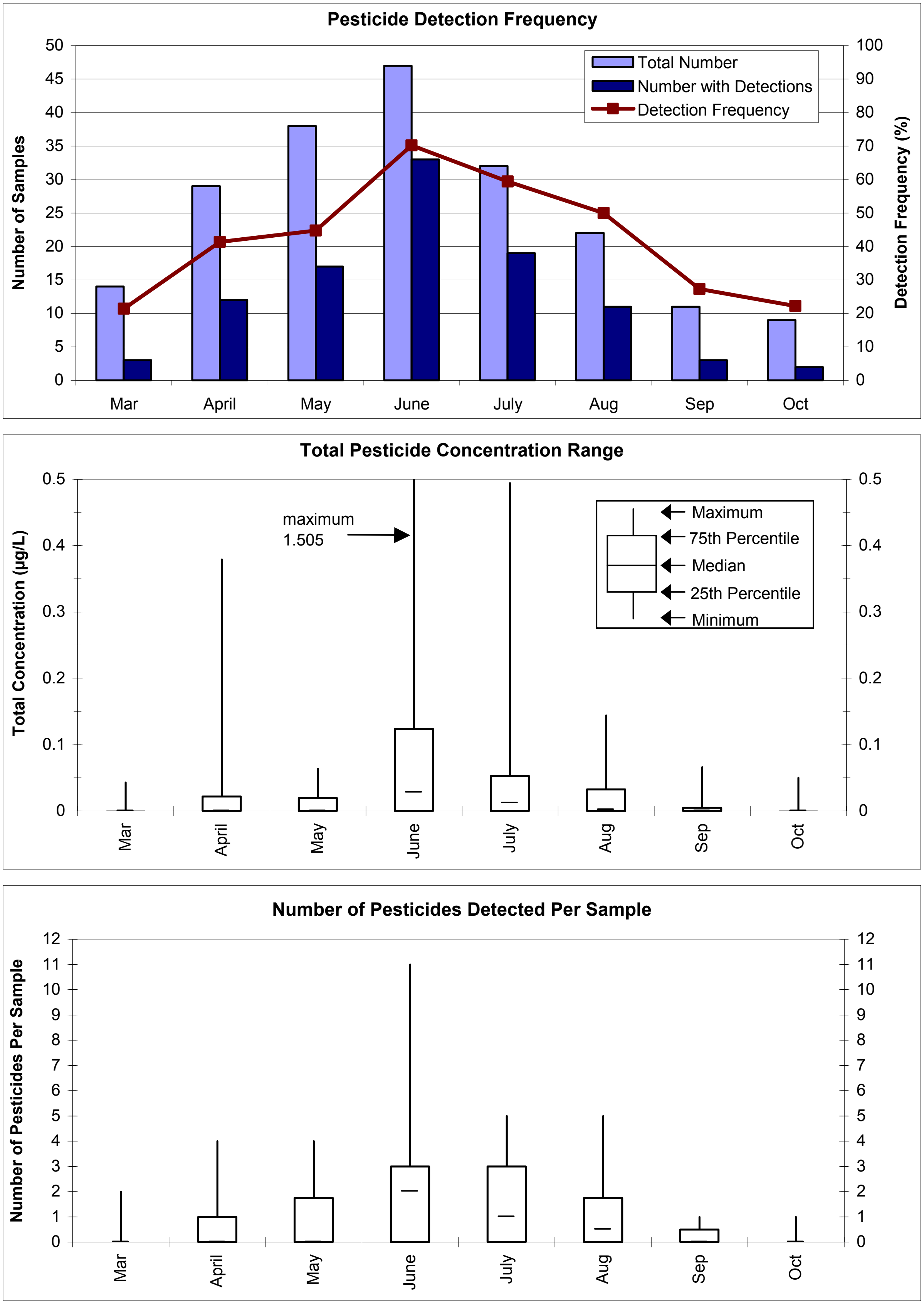
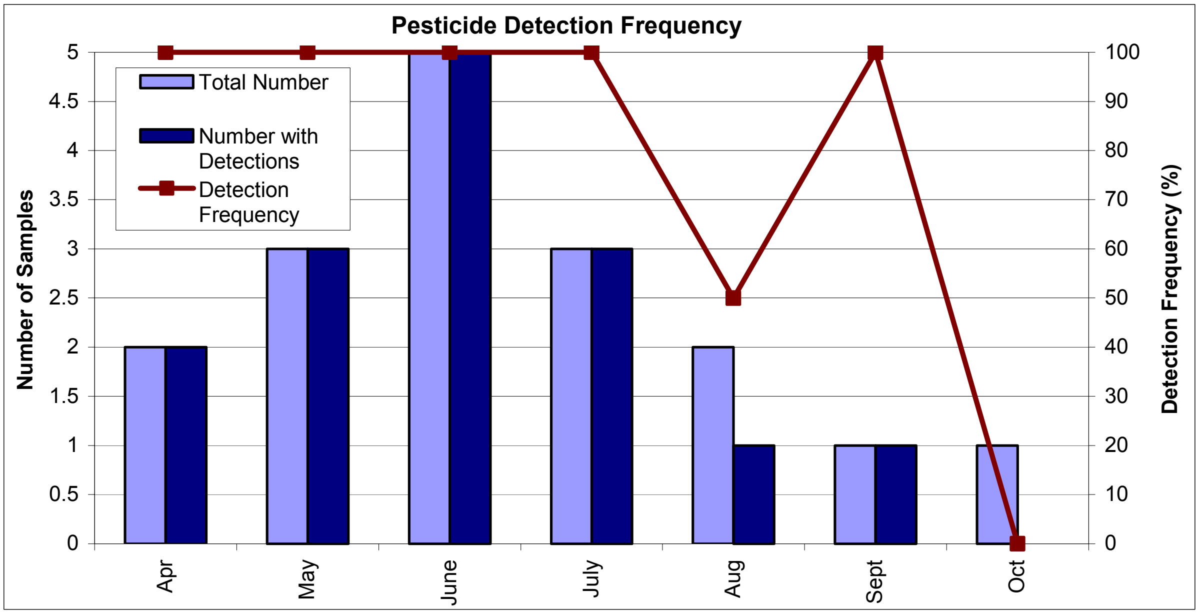
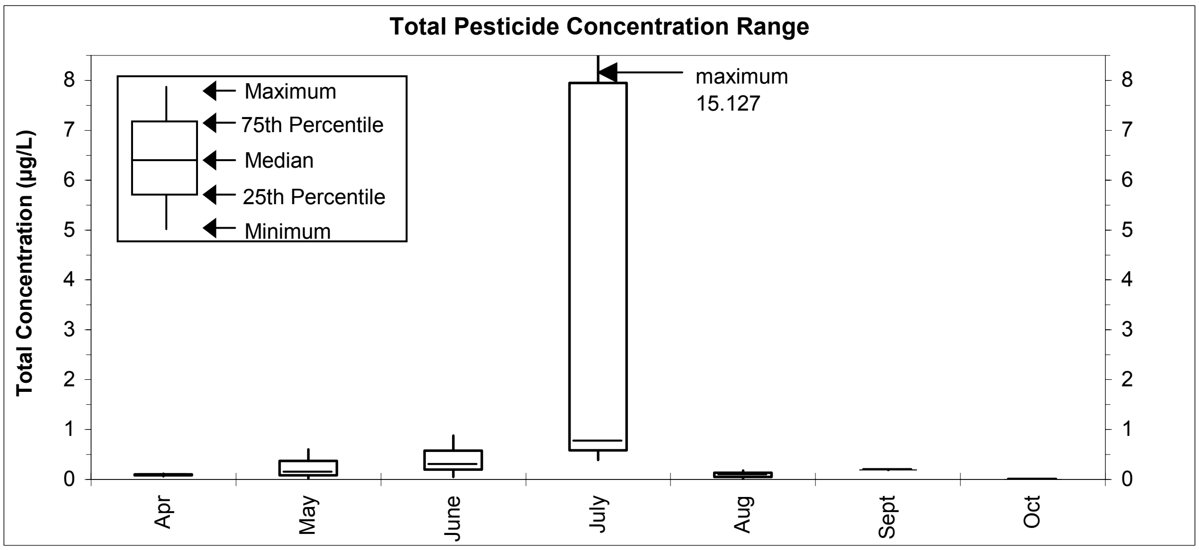


Figure 14a Seasonal pattern of pesticide detections in creeks of the Oldman River drainage basin (1995 – 2002)





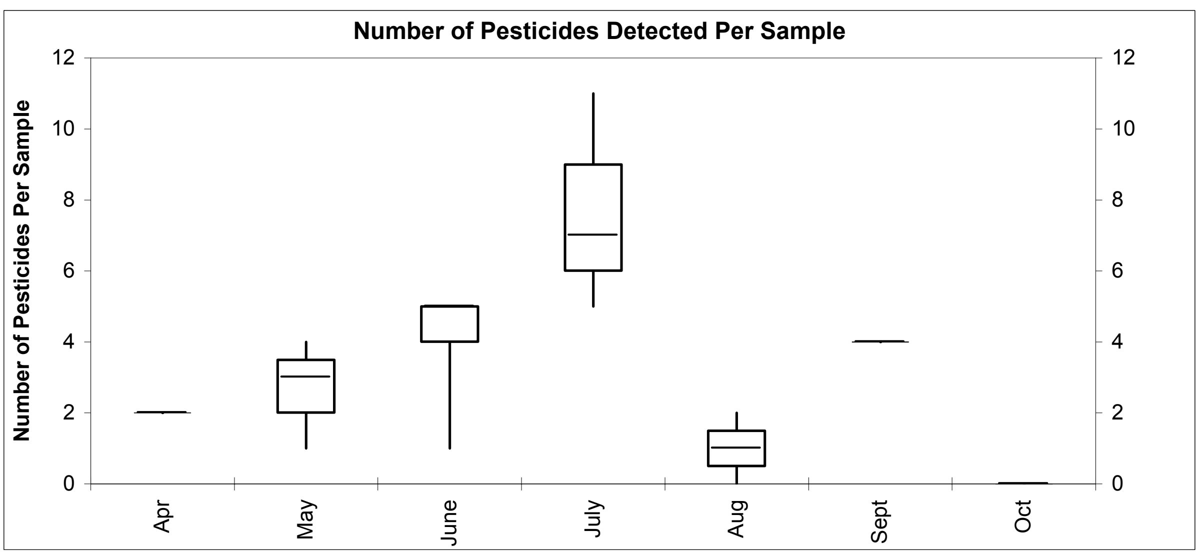


Figure 14b Seasonal pattern of pesticide detections in creeks of the Bow River drainage basin (1995 – 2002)

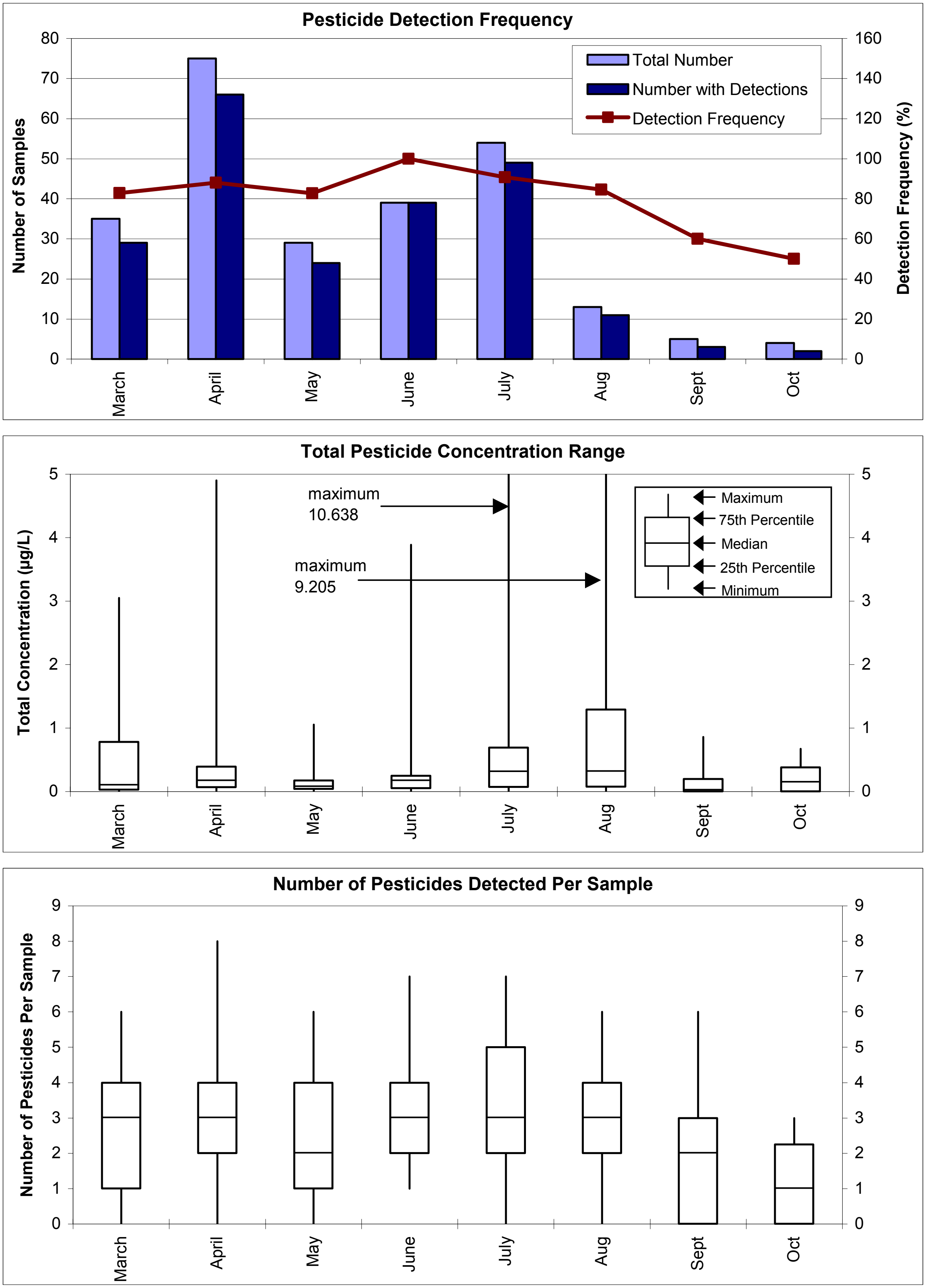


Figure 14c **Seasonal pattern of pesticide detections in creeks of the Red Deer River drainage basin (1995 – 2002)**

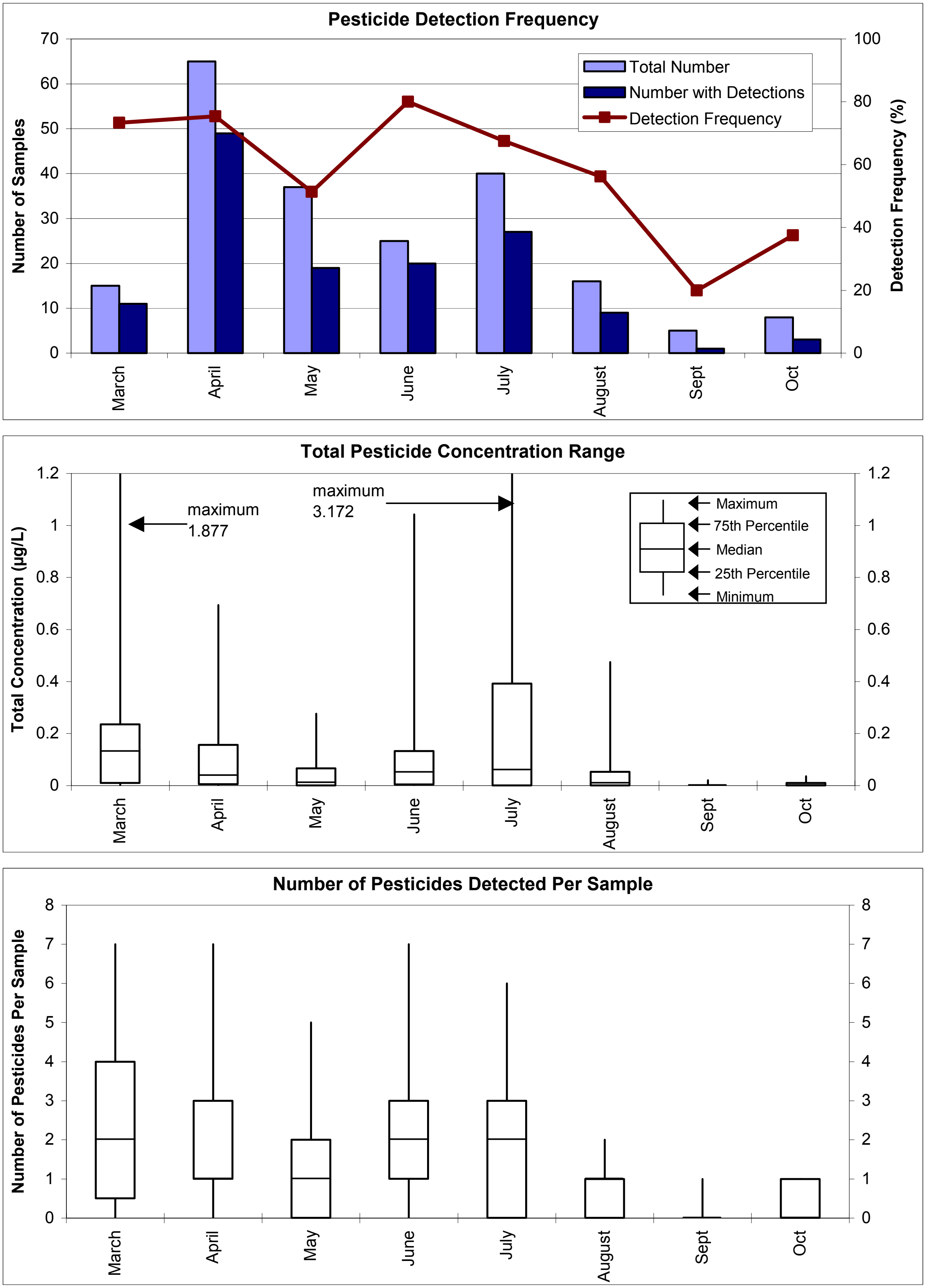


Figure 14d **Seasonal pattern of pesticide detections in creeks of the North Saskatchewan River drainage basin (1995 – 2002)**

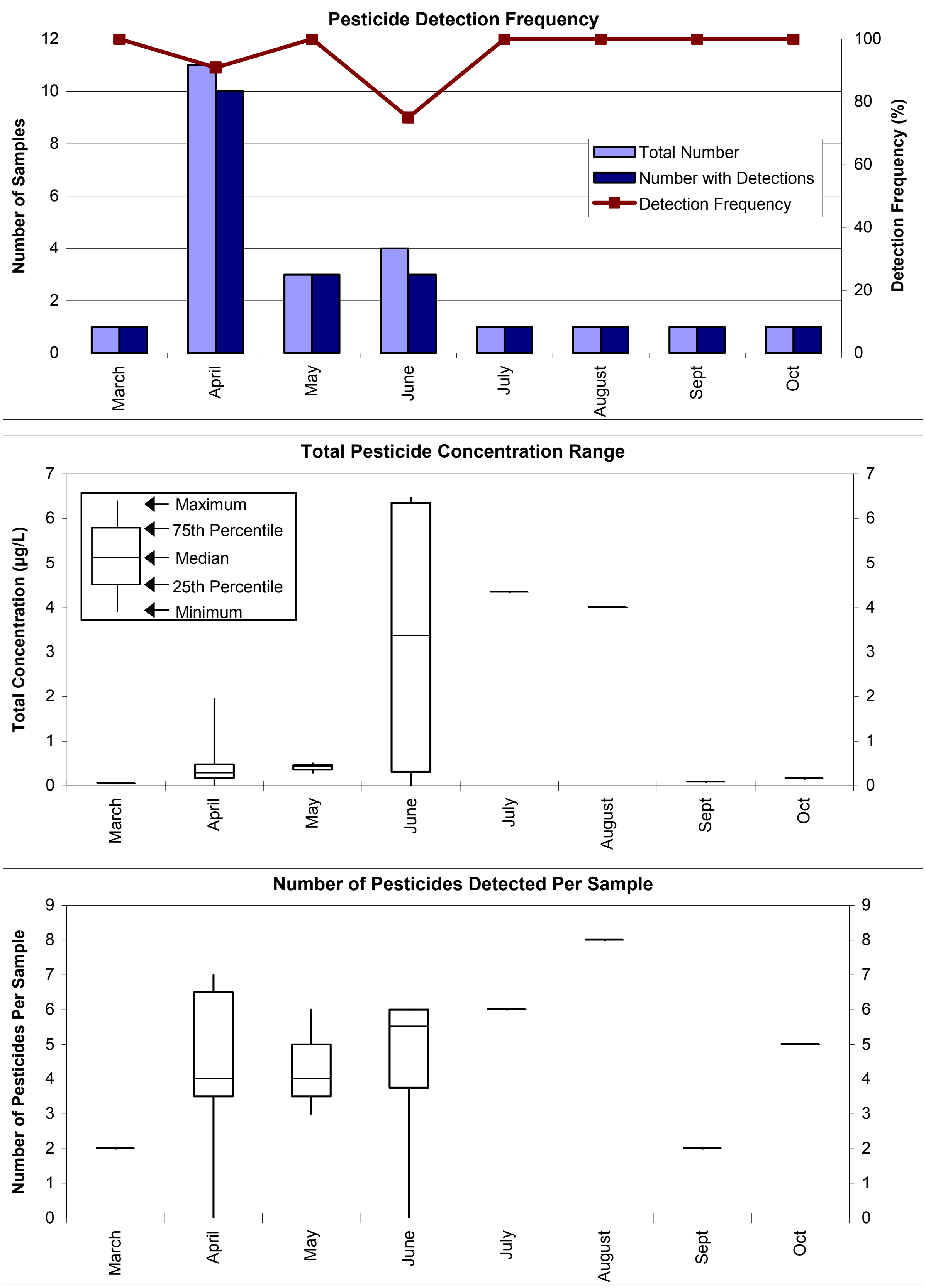


Figure 14e **Seasonal pattern of pesticide detections in creeks of the Athabasca River drainage basin (1995 – 2002)**

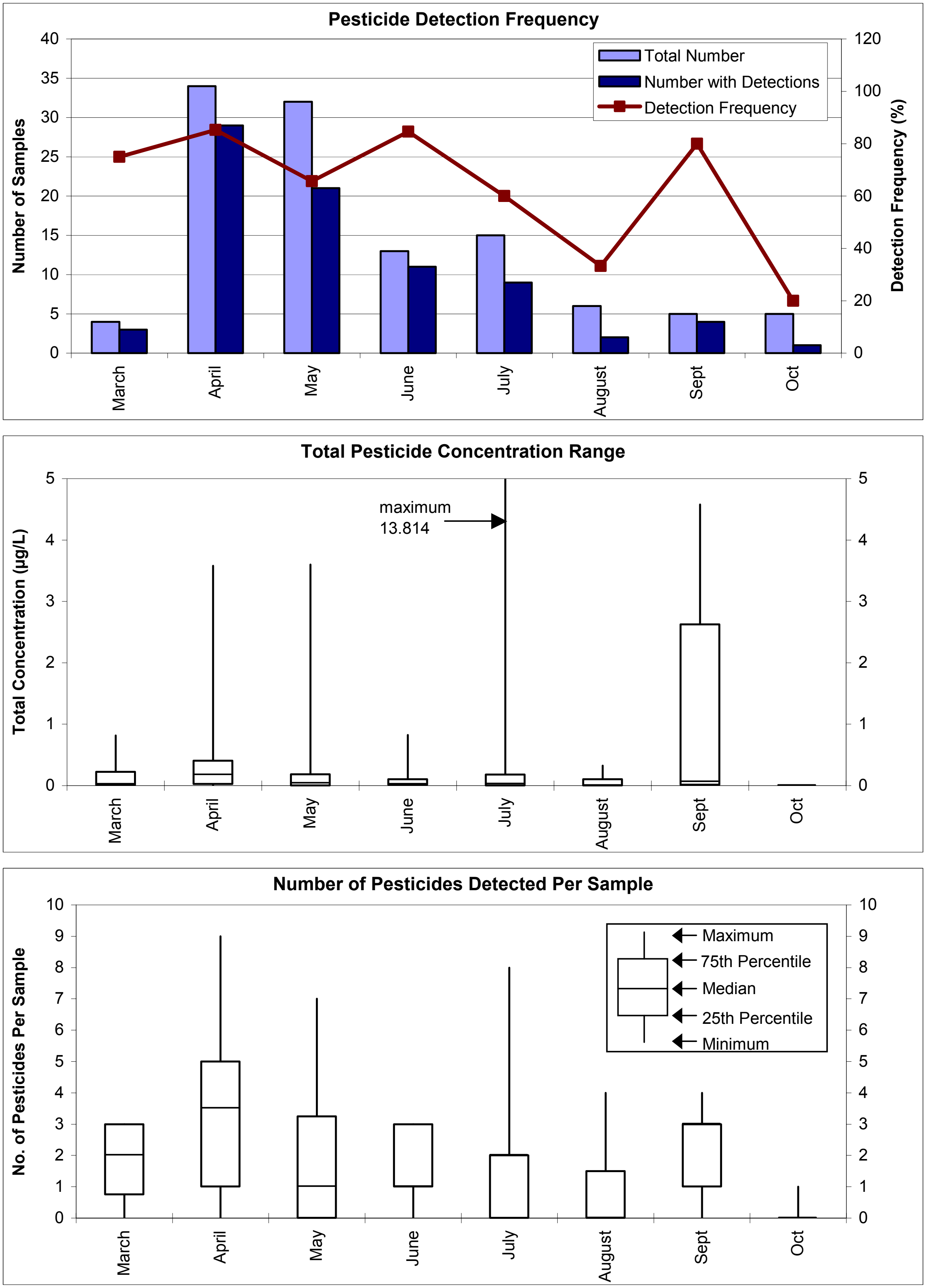


Figure 14f **Seasonal pattern of pesticide detections in creeks of the Peace River drainage basin (1995 – 2002)**

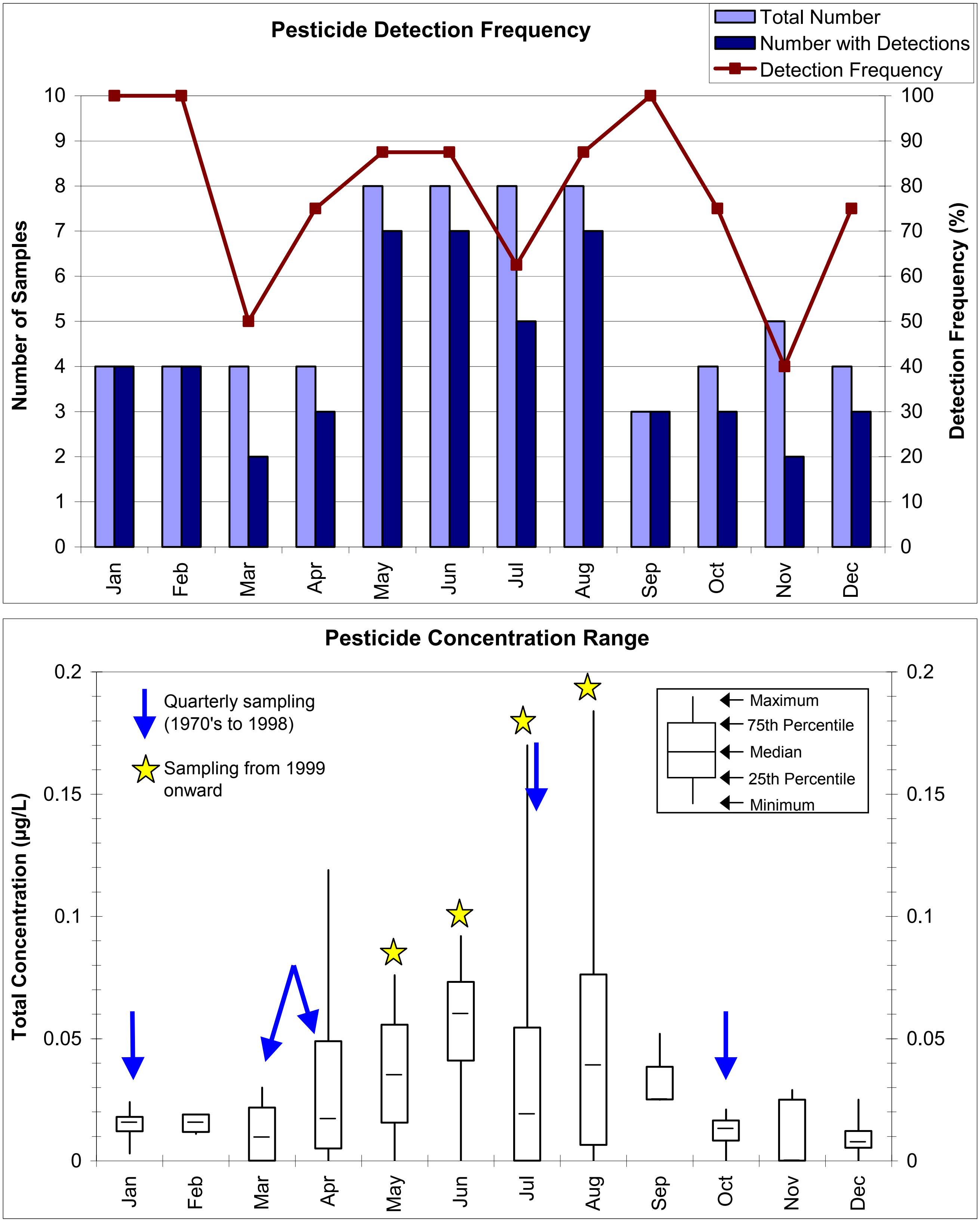


Figure 15 **Seasonality of pesticide detections and concentrations in the North Saskatchewan River at Pakan (1995 - 2002). Data from monthly sampling (1995-1999) illustrate implications of shifting from seasonal sampling regime to sampling in 4 consecutive months with a high likelihood of pesticide contamination.**

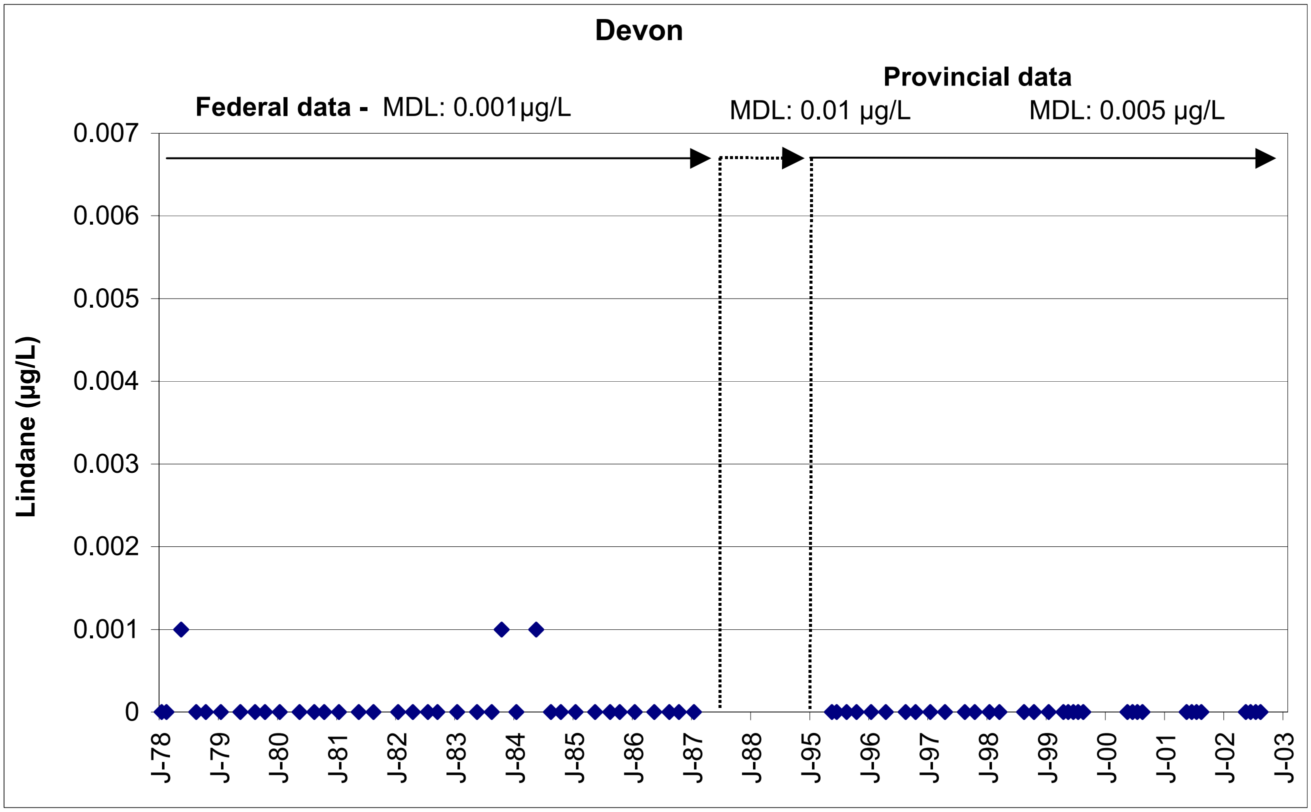
the visual examination of time series graphs provides some valuable insights regarding temporal variability in pesticide detections.

Data from the North Saskatchewan, Bow and Oldman river long-term sampling sites are presented here because they offered the most consistent data set and had regular incidences of measurable concentrations (Figures 16 to 22). Sampling locations are shown in Figure 1.

The data sets consist of federal data (1970's to 1986) and provincial data (1987 to 2002); the provincial data comprise two sets of data (pre- and post- 1995). The most noticeable trends over time are the result of differences in method detection limits between the federal and provincial data set. For the period 1987 to and including 1995, method detection limits were higher than ambient levels at most sites, consequently no detections were reported. From 1995 on, provincial and historical federal detection limits were similar thereby allowing meaningful comparisons.

Concentration patterns for the three pesticides tend to vary among sites.

- In the Bow and Oldman rivers and at Devon on the North Saskatchewan River, lindane is reported frequently in the federal data set (Figures 16, 18, and 20), but usually at concentrations that range between 0.001µg/L (the federal method detection limit) and 0.005µg/L, the post-1995 provincial method detection limit. Hence the rarity of lindane detections in the provincial database is not indicative of a downward trend. The situation is different in the North Saskatchewan River at Pakan (Figure 16) where lindane was recorded more frequently and at higher concentrations after 1995. This situation is believed to have been related to the activities in an Edmonton area seed treatment plant now out of production (G. Byrtus, personal communication). Lindane was a major insecticide used to treat canola seed. Seed treatment has evolved since the advent of "Roundup-ready canola". Previously farmers or local seed treatment plants carried out most of the seed treatment on producer-grown seed. Now most of the Roundup-ready canola is grown and treated by the seed producing industry. Products most commonly used for commercial seed treatment are Helix and Goucho, which combine insecticide and fungicide treatment. Alberta Environment does not track sales of treated seed and several ingredients of Helix (i.e., thiamethoxan, difenoconazole, and fludioxonil) are currently not monitored in surface waters (G. Byrtus, personal communication). This points to an area where the tracking of sales records and ambient monitoring do not capture potential environmental contaminants.
- In the Oldman and Bow rivers there was generally a slightly higher incidence of 2,4-D detections in the historical federal data than in the provincial data (Figures 19 and 21). However, even though the method detection limits differ slightly (federal: 0.004; provincial 0.005 µg/L), concentration ranges are well above these limits. Sampling frequency or timing may be an issue in the Oldman River, but it is possible that a declining trend is occurring here that is related to use patterns. In the North Saskatchewan River, historical federal data indicate that relatively high concentrations of 2,4-D were common at Pakan in the 80's (Figure 17). An increase in 2,4-D river concentration was noted as early as 1977 in the federal database at the



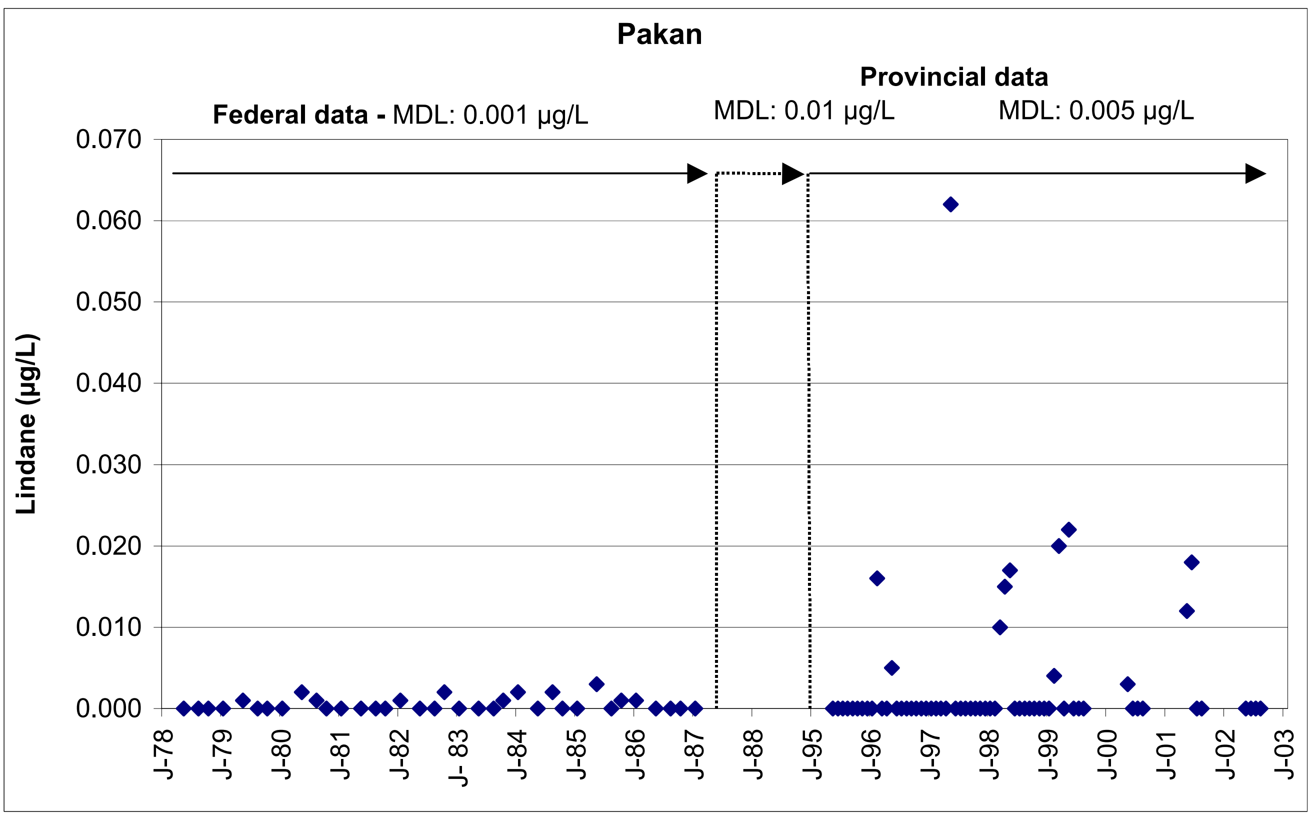
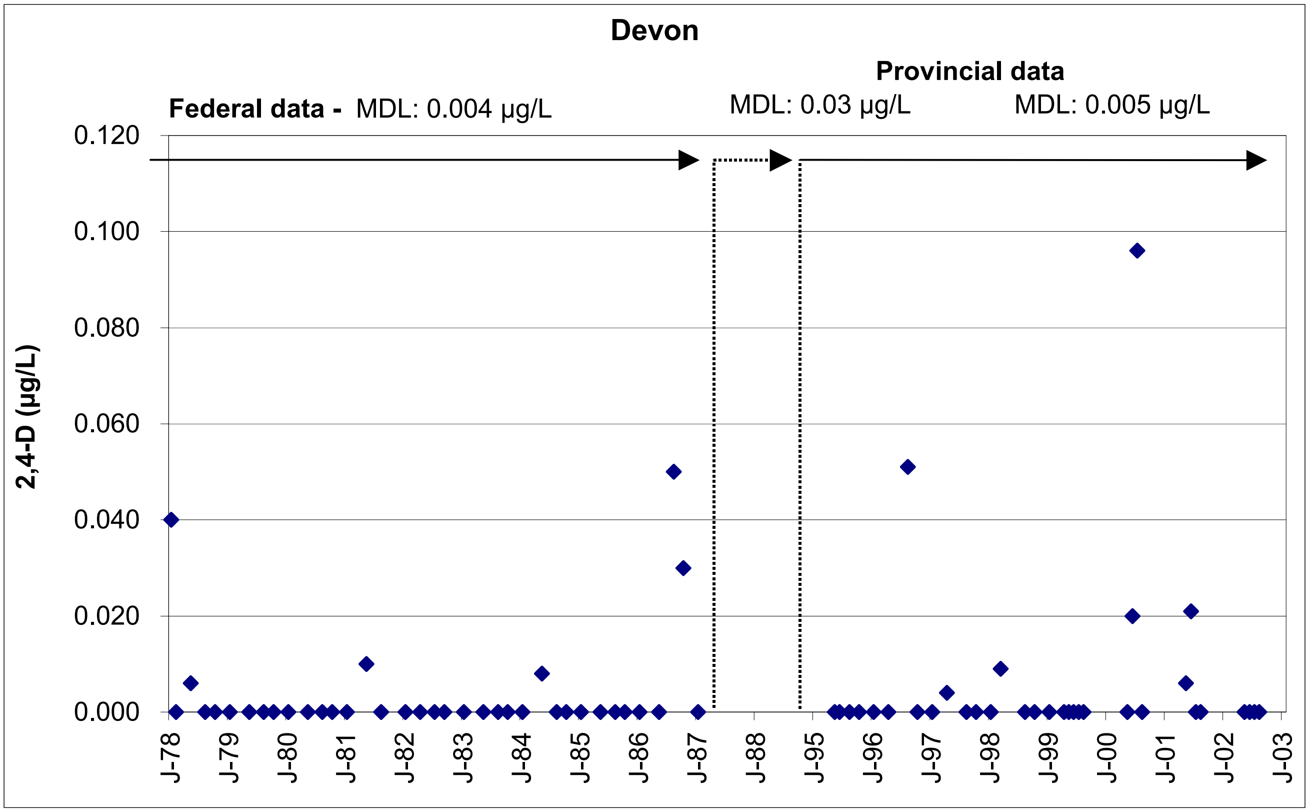


Figure 16 Changes over time in lindane (gamma BHC) concentrations at long-term monitoring sites in the North Saskatchewan River
(Note: from 1987 to and including 1994, absence of detections due to higher MDL)



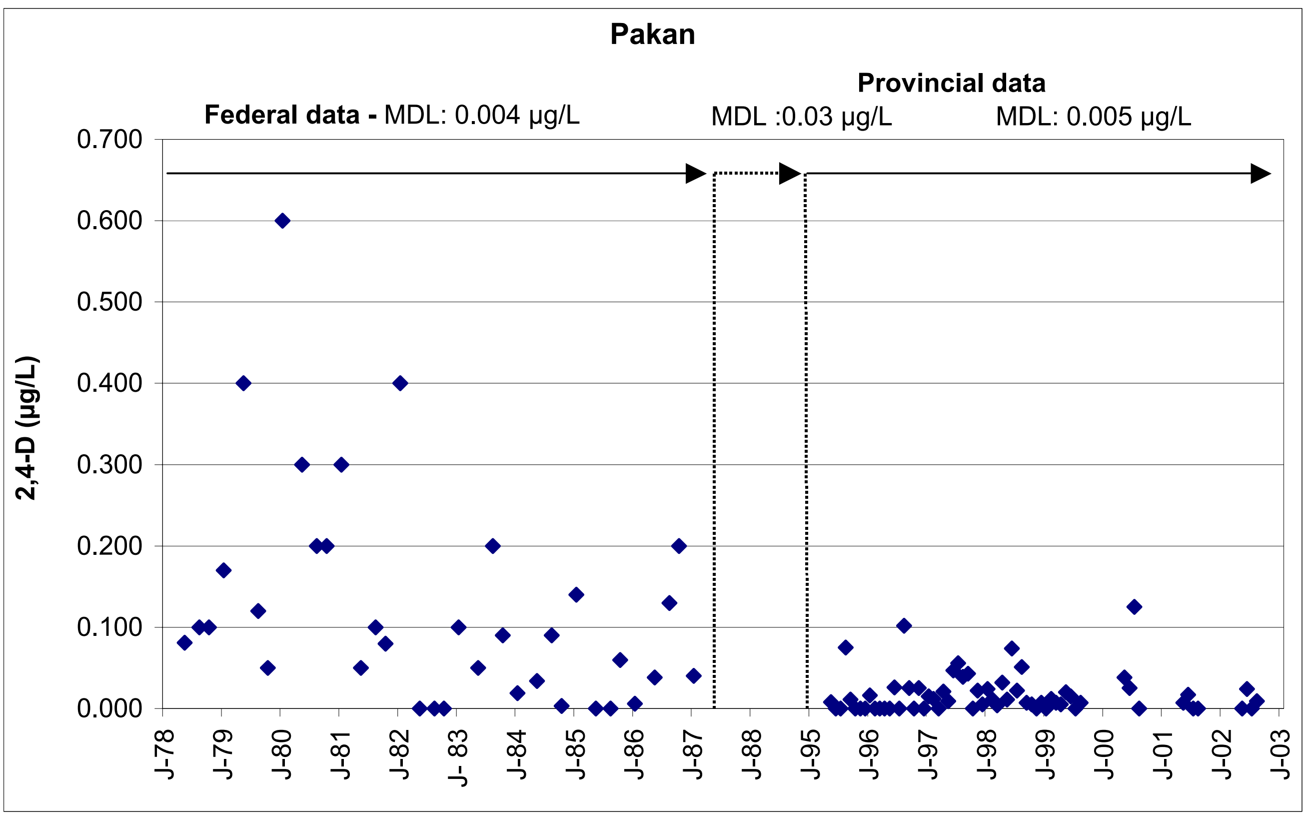


Figure 17 **Changes over time in 2,4-D concentrations at long-term monitoring sites in the North Saskatchewan River**
(Note: from 1987 to and including 1994, absence of detections due to higher MDL)

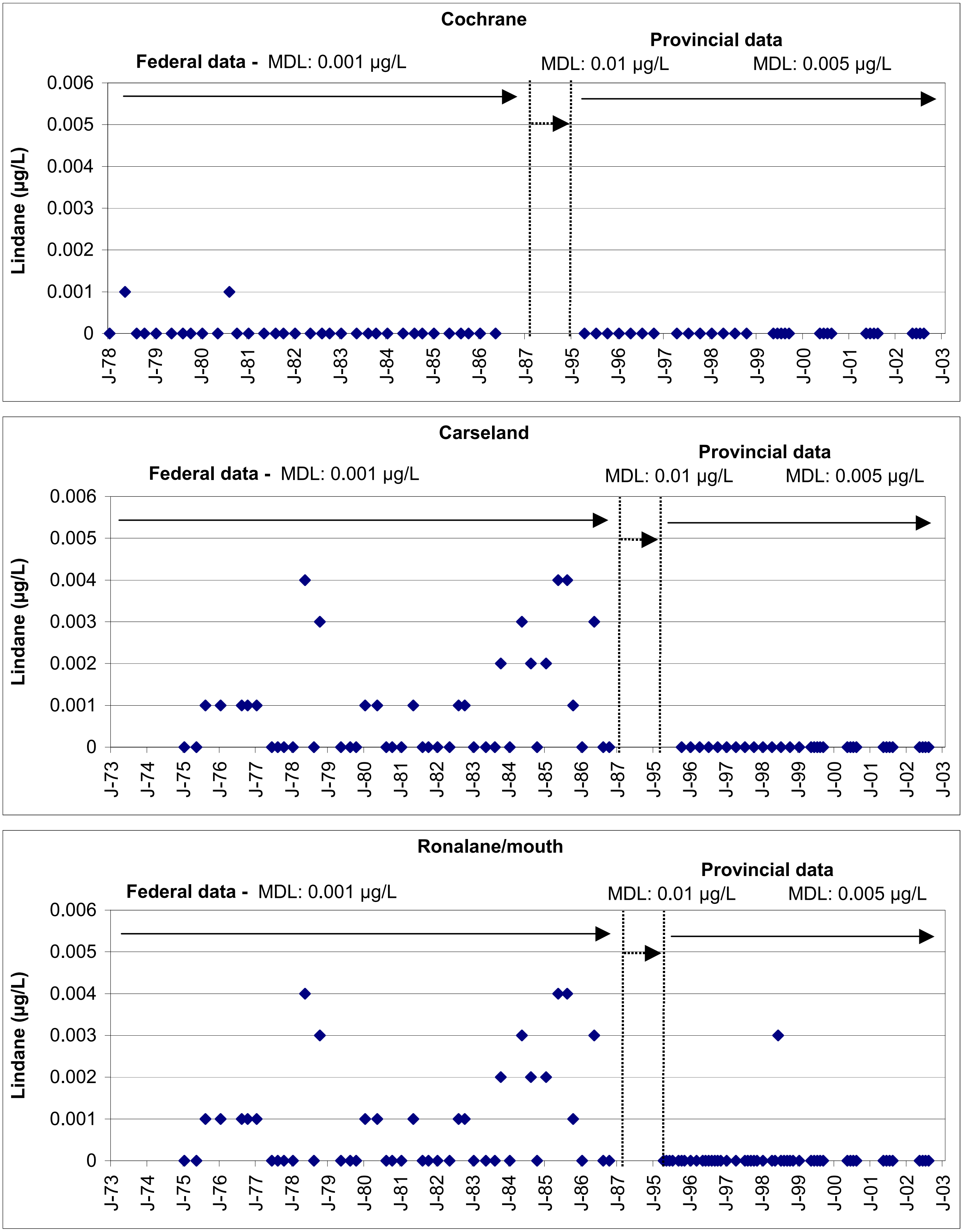


Figure 18 Changes over time in lindane concentrations at long-term monitoring sites in the Bow River
(Note: from 1987 to and including 1994, absence of detections due to higher MDL)

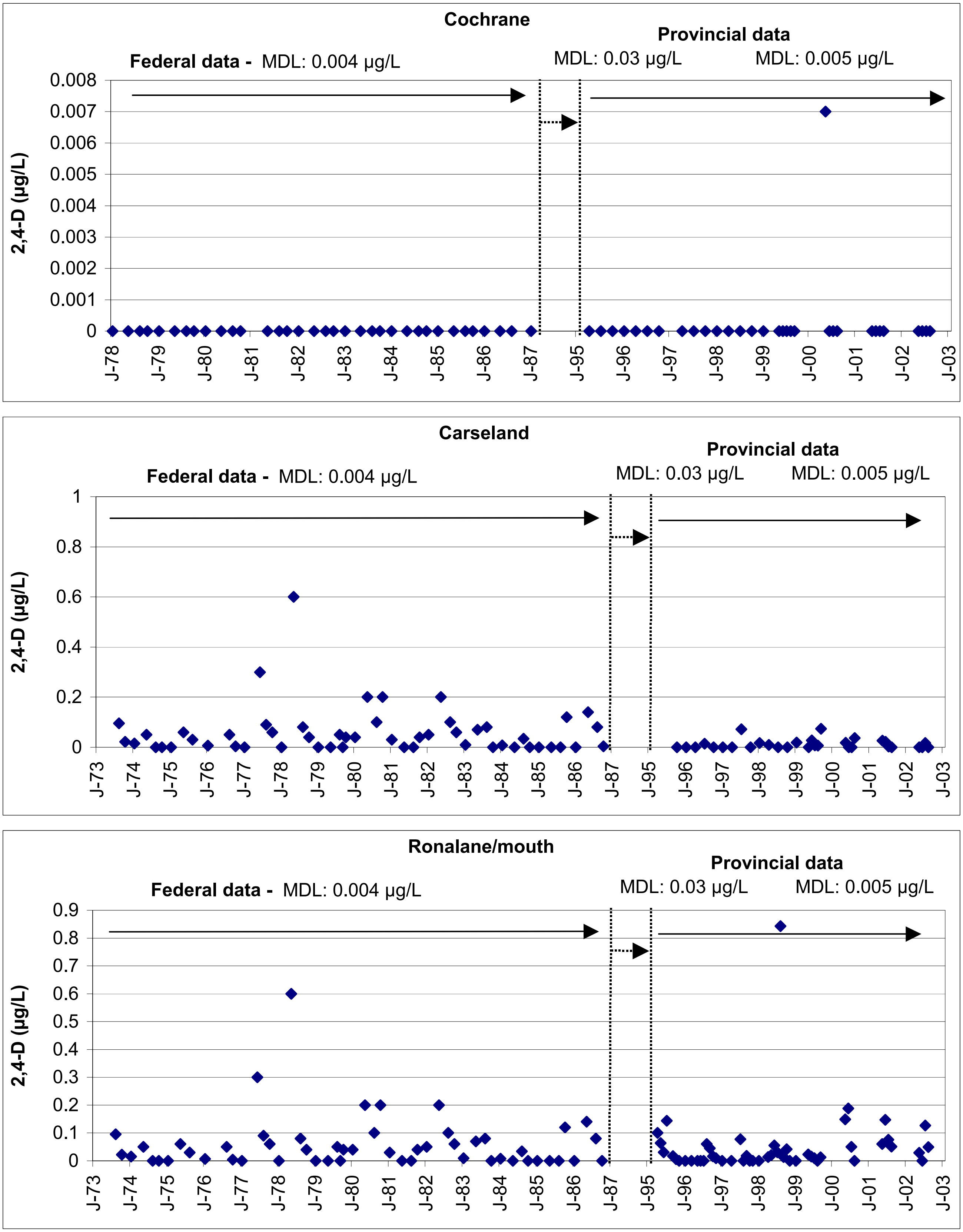
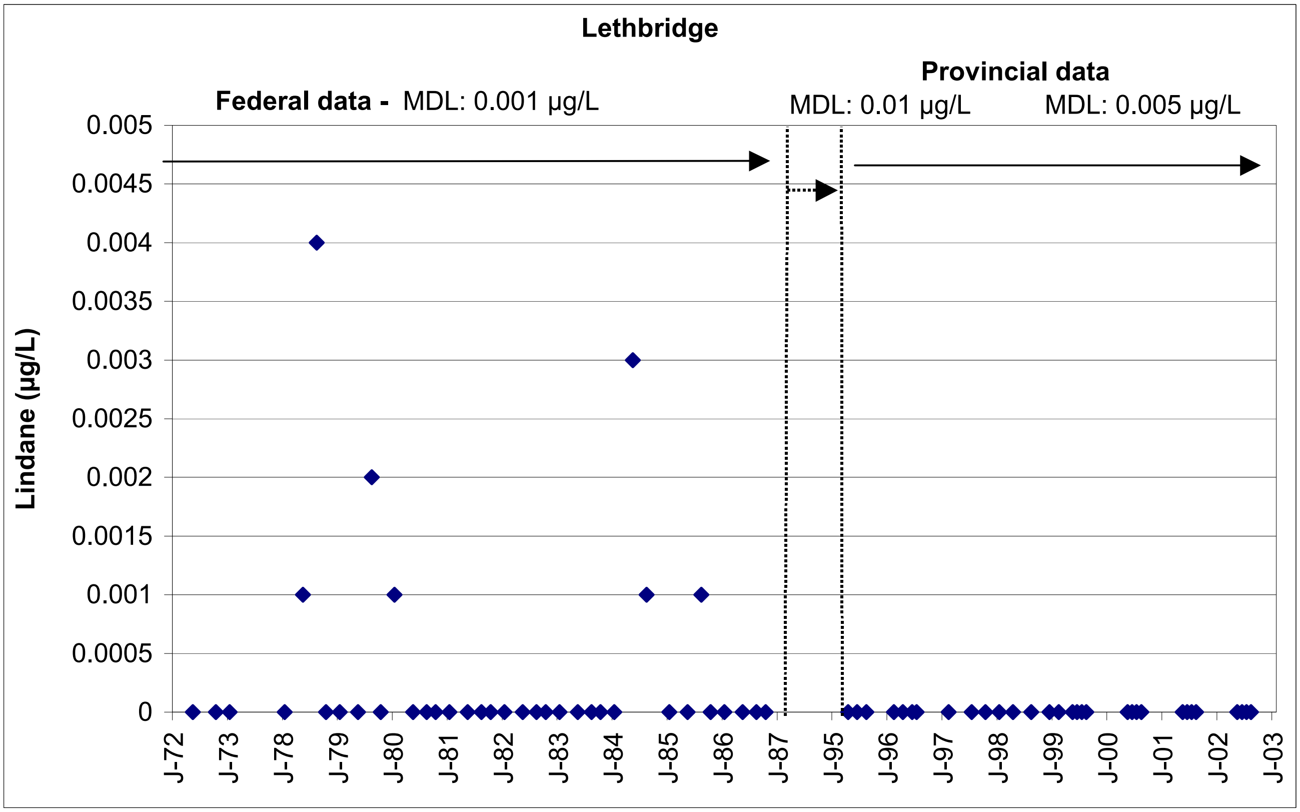


Figure 19 **Changes over time in 2,4-D concentrations at long-term monitoring sites in the Bow River**
(Note: from 1987 to and including 1994, absence of detections due to higher MDL)



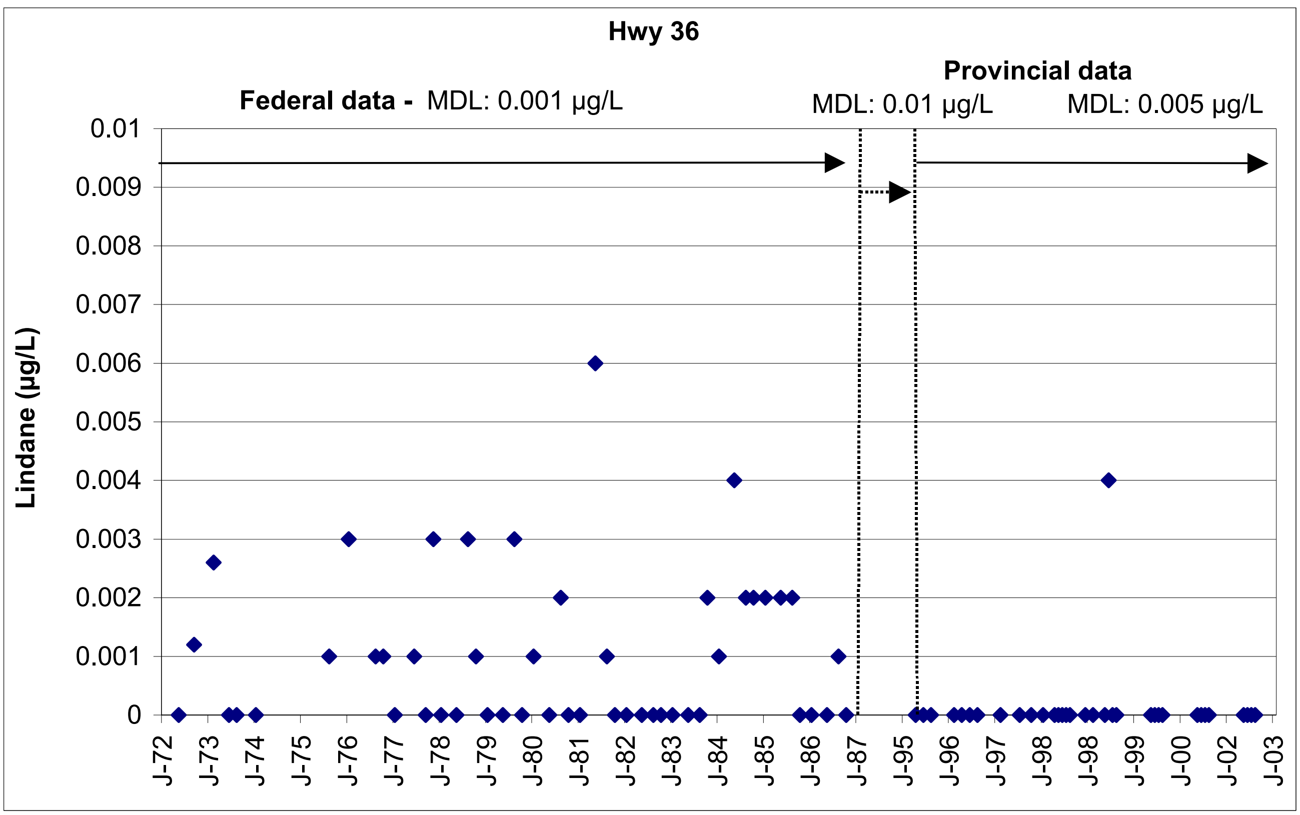
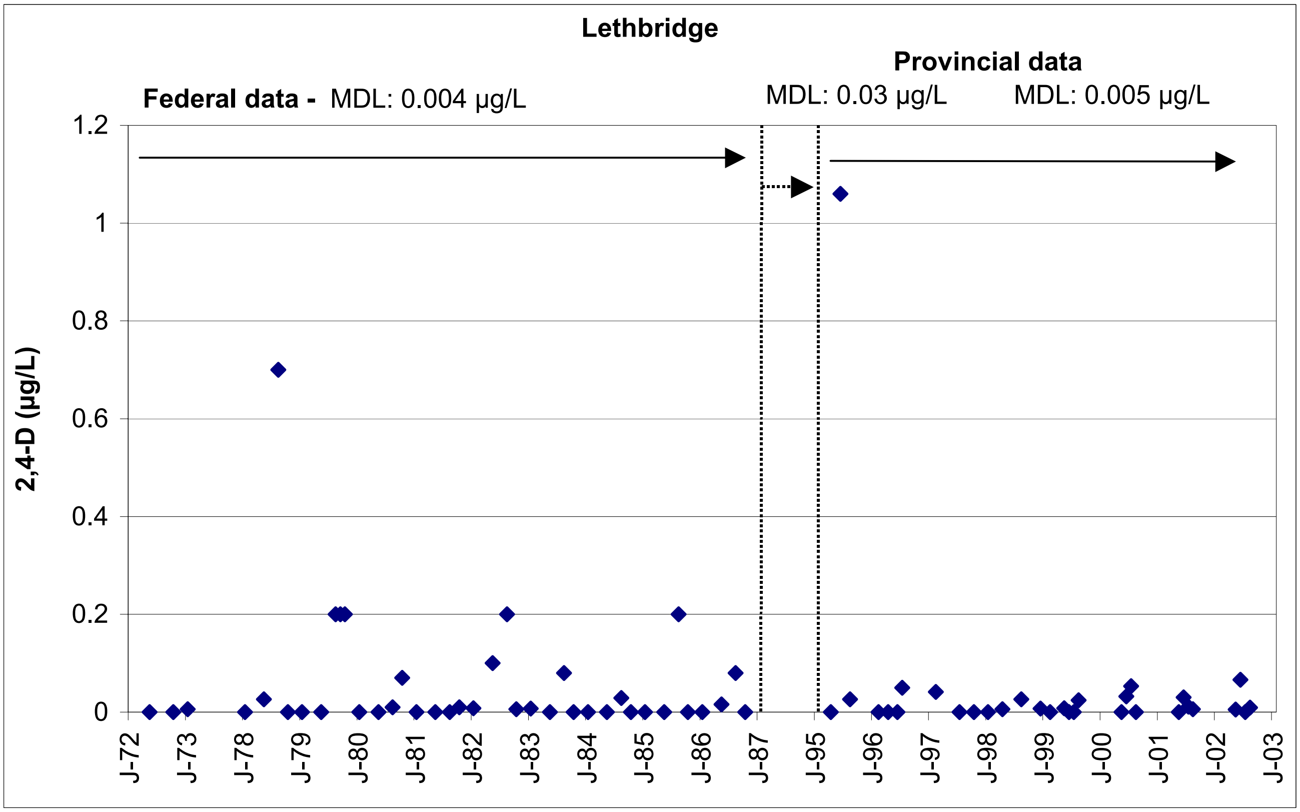


Figure 20 Changes over time in lindane concentrations at long-term monitoring sites in the Oldman River

(Note: from 1987 to and including 1994, absence of detections due to higher MDL)



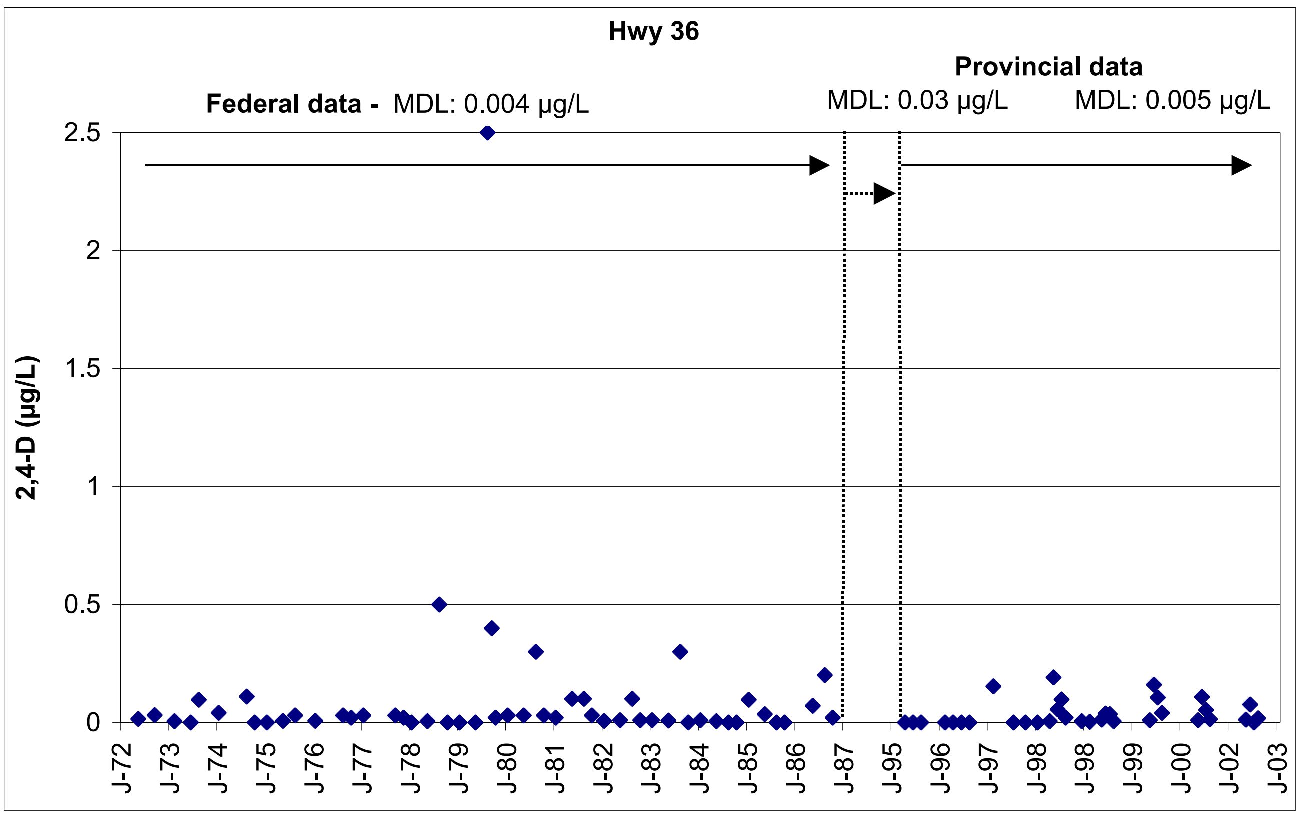
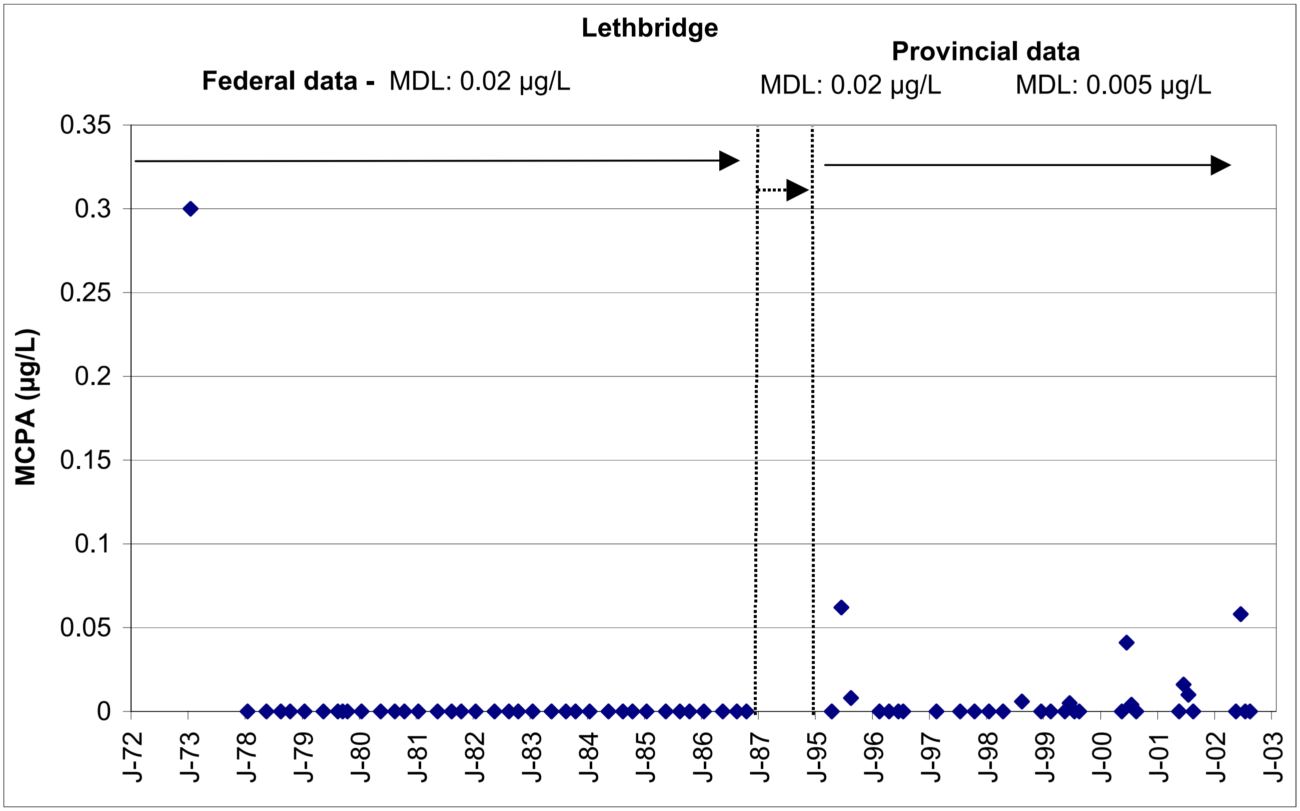


Figure 21 Changes over time in 2,4-D concentrations at long-term monitoring sites in the Oldman River
(Note: from 1987 to and including 1994, absence of detections due to higher MDL)



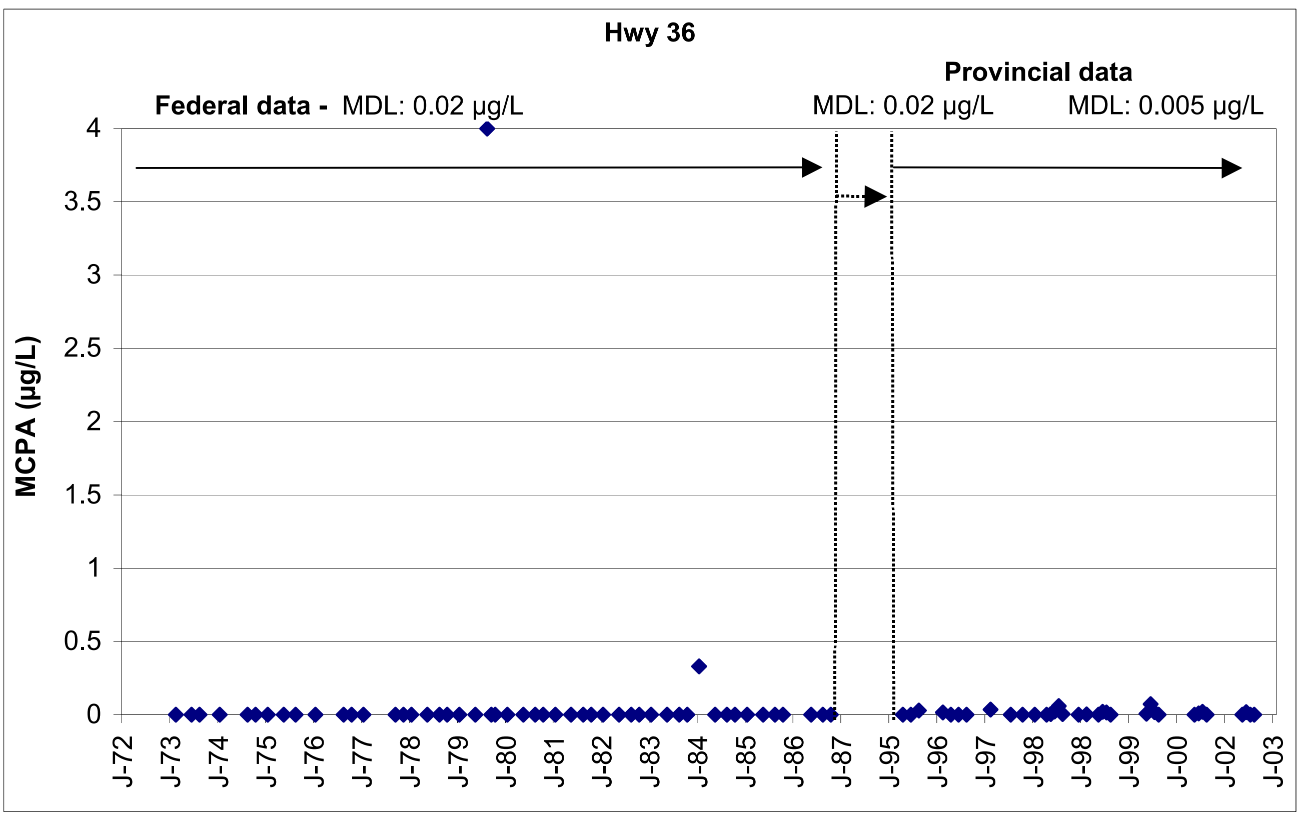


Figure 22 **Changes over time in MCPA concentrations at long-term monitoring sites in the Oldman River**
(Note: from 1987 to and including 1994, absence of detections due to higher MDL)

Alberta-Saskatchewan Border (Gummer 1979). A survey conducted by the Alberta Department of the Environment in 1977 revealed concentrations as high as 4.34 mg 2,4-D/L in the Uniroyal Chemical Co. effluent discharge to the North Saskatchewan River within the eastern part of Edmonton. This plant manufactured 2,4-D from 1963 to 1980 and was decommissioned in 1985. Remediation activity started in compliance with a 1982 Water Quality Control Order and Uniroyal has voluntarily continued remediation (Tony Fernandez, pers. comm. AENV, Waste Specialist). Surface water contamination problems were also encountered at the Dow Chemical plant site, a second plant which manufactured 2,4-D in Fort Saskatchewan, east of Edmonton. The site has been decommissioned, it is still contaminated with 2,4-D and although remedial efforts and monitoring are in place, relatively low amounts of the herbicide could still enter the North Saskatchewan River via a pipeline system (S. Pollard pers. comm. AENV Approvals Coordinator). More recently, 2,4-D is still detected on a regular basis in the North Saskatchewan River, but at lower concentrations. Some of the recent peak detections at Pakan correspond with peak concentrations at Devon, which indicates the influence of unknown sources upstream of Devon.

- The Oldman River was the only one of the three rivers to have a consistent dataset for MCPA (Figure 22). Detections have become more frequent after 1995, which is related to the fact that MCPA is one of the few pesticides where the historical detection limit was higher than provincial detection limit.

4.2.2.2 Trends 1995 – 2002

Year-to-year variability in the aggregated pesticide dataset assembled from 1995 to and including 2002 is depicted in Figure 23. Over the 8-year period there have been some notable changes. The number of pesticide samples increased significantly after 1996 to reach a peak in 2000; coincidently there was an increase in detection frequency and pesticide variety per sample. These changes are not related to an increase in ambient pesticide contamination over the years, but to changes in emphasis of the monitoring programs.

In 1997 and as a follow-up to the surface water monitoring carried out under the CAESA program, 23 agricultural streams distributed in the White Zone were monitored for pesticides under the AESA program. Their inclusion explains the first increase in sample numbers and detection frequency (Figure 23). In 1998, as a result of the Oldman River Basin Water Quality initiative, intensive monitoring was carried out on the Oldman River and some of its major tributaries. This work continued in 1999 where sampling efforts were extended to irrigation return flows and, at a scoping level, to urban drains in the Lethbridge area. The storm drain work was intensified in subsequent years and storm drains account for the elevated concentrations recorded from 1999 on. The higher number of pesticide samples collected in 2000 is due to samples collected from wetlands in the Aspen Parkland.

Since pesticide-monitoring programs have an evolving focus from year-to-year, temporal trends in pesticides could be highly biased at the level of the aggregated data set. Temporal trends are best examined in sampling programs that have been carried out consistently over the years.

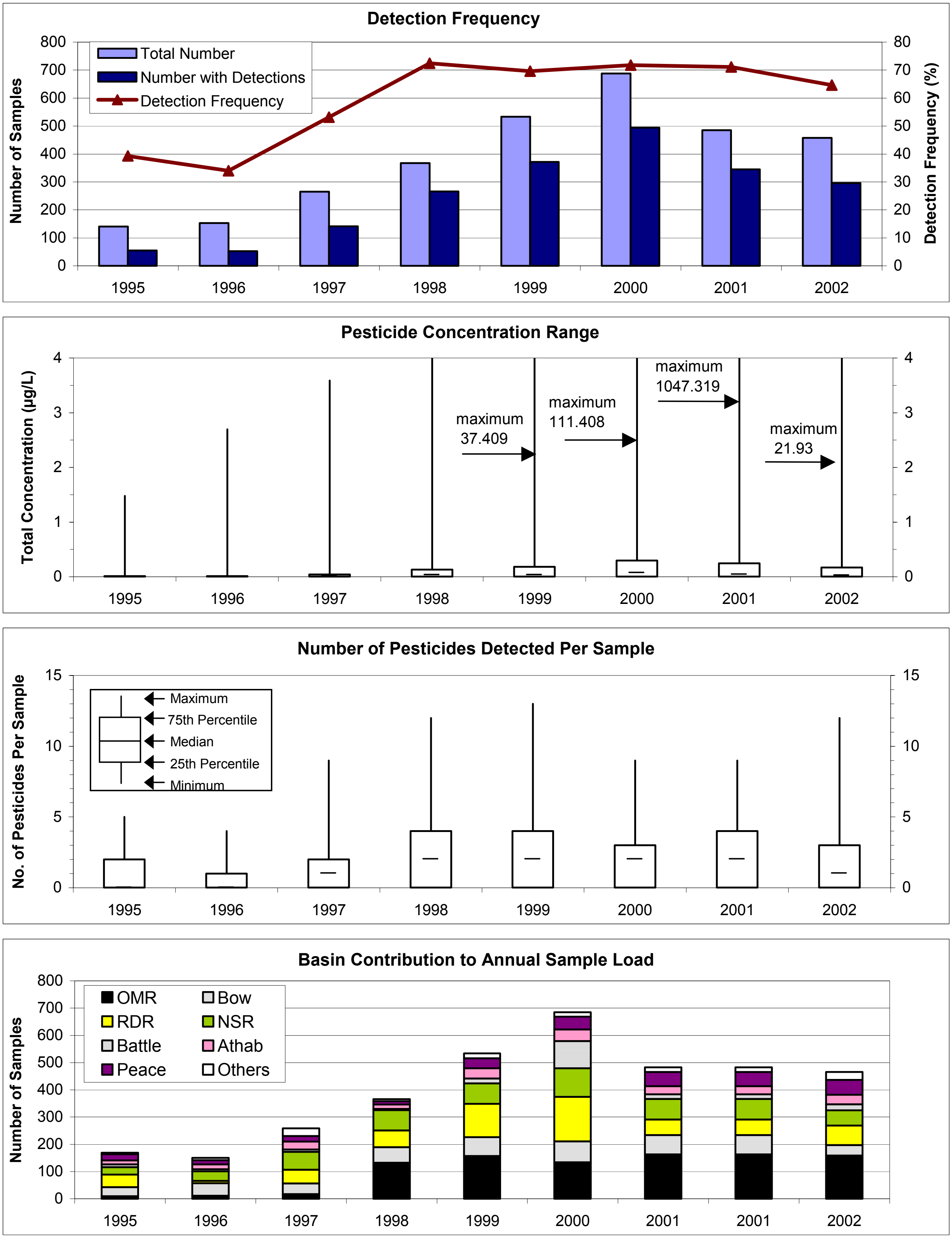


Figure 23 Temporal trends in the provincial pesticide database (1995 - 2002)

These include the LTRN network, the Tributary Network and the AESA stream monitoring program.

4.2.2.2.1 Temporal Trends at Long-term River Monitoring Sites

Alberta Environment monitors pesticides at 22 long-term monitoring sites (LTRN) sites (Figure 1). Initially the sampling was carried out on a seasonal basis; in 1999 a review of the network indicated that a more accurate picture of peak pesticide contamination would be obtained by targeting the sampling to May, June, July and August when concentrations and detection frequencies are highest. The switch in the timing of sample collection was initiated in 1999 and completed in 2000. Although such change was justified, there is a risk that it could have induced artificial trends in the long-term data set. For example, a sudden increase in concentration could be due to the fact that sampling now occurs at a time of year where contamination is high, rather than to the fact that environmental concentrations have increased. Such possibilities need to be considered in the examination of year-to-year differences.

Year-to-year differences in pesticide concentrations were evaluated with the Kruskal Wallis test and results are summarized in Table 7. Significant differences were detected at three sites on the Bow River and one on the Red Deer River. No differences were detected at other sites.

In the Bow River, significant year-to-year differences were detected at Ronalane for 2,4-D, dichlorprop, diazinon, MCPA, and MCPP: concentrations were generally higher in more recent years. (Table 7 and Figures 24 to 29). Total pesticide concentration and number of pesticides detected also differed among the years. Median concentrations of 2,4-D, MCPA, and total concentrations tend to be higher in 2000, 2001 and less so in 2002. This trend appears to be indicative of a real environmental change. Ronalane is one of several LTRN sites that were sampled monthly during the open water season prior to 1999. Data for the months of May, June, July and August are available for the entire period of record and it is only in the last three years that higher concentrations were recorded consistently. The reason for this is unclear.

Significant year-to-year differences in 2,4-D levels were also observed in the Bow River at Bow City upstream of Ronalane (Figure 24). This site was only sampled four times per year throughout the period of record. Higher concentrations in 2000 and 2001 are consistent with observations at Ronalane, although higher concentrations in 1999 are specific to the Bow City site. Increases in 2,4-D levels at Bow City would have been largely missed by the seasonal sampling design previously in place as most elevated concentrations were recorded in May and June.

Significant year-to-year differences in median diazinon concentrations were identified at three sites monitored downstream of Calgary (Figure 27). Most of the detections occurred in 1999 at these three sites, with the median concentrations declining from upstream to downstream sites. In that year, diazinon was detected in five of the six samples taken at Carseland, where concentrations were also highest, suggesting an urban source. The reasons for these frequent detections in 1999, but not other years, are unclear.

Table 7 Comparison among years of pesticide concentrations at LTRN sites (1995 – 2002)

Station Name	Station No.	2,4-D	DICHLORPROP	LINDANE	P,P'-METHOXYCHLOR	ATRAZINE	BROMOXYNIL	CYANAZINE	DIAZINON	DICAMBA	DIURON
Oldman River at Brocket	AB05AB0070	NS	-	-	-	-	-	-	-	-	-
Oldman River upstream of Lethbridge	AB05AD0010	NS	NS	-	NS	-	NS	-	-	?	-
Oldman River at Taber	AB05AG0010	NS	NS	NS	-	-	NS	-	-	?	-
South Saskatchewan River u/s Medicine Hat	AB05AK0020	NS	NS	NS	-	NS	NS	NS	NS	?	-
Bow River at Exshaw	AB05BE0190	NS	-	-	-	-	-	-	-	-	-
Bow River at Cochrane	AB05BH0010	NS	-	-	-	-	-	NS			-
Bow River at Carseland	AB05BM0010	NS	-	-	-	NS	-	-	S	-	-
Bow River at Cluny	AB05BM0590	NS	-	-	-	NS	-	-	NS	?	NS
Bow River at Ronalane	AB05BN0010	S	S	NS	-	NS	NS	-	S	?	-
Bow River at Bow City Bridge	AB05BN0080	S			-	-	-	-	S	-	-
Red Deer River at Hwy 2 above Red Deer	AB05CC0010	NS	-	-	NS	-	NS	-	-	-	-
Red Deer River at Morrin Bridge	AB05CE0010	S	-	-	-	-	NS	-	-	-	-
North Saskatchewan River at Devon	AB05DF0010	NS	-	-	-	-	-	-	-	-	-
North Saskatchewan River at Pakan	AB05EC0010	NS	-	NS	-	-	-	-	NS	?	-
Athabasca River at Hinton	AB07AD0110	-	-	-	-	-	-	-	-	-	-
Athabasca River at Athabasca	AB07BE0010	NS	-	-	-	-	-	-	-	-	-
Athabasca River at Old Fort	AB07DD0010	NS	-	-	-	-	-	-	-	-	-
Wapiti River upstream Hwy 40	AB07GE0020	-	-	-	-	-	-	-	-	?	-
Wapiti River downstream Hwy 40	AB07GE0030	NS	-	-	-	-	-	-	-	?	-
Smoky River at Watino	AB07GJ0010	NS	-	-	-	-	-	-	-	-	-
Wapiti River above confluence with Smoky	AB07GJ0030	NS	-	-	-	-	-	-	-	-	-
Peace River at Fort Vermillion	AB07HF0010	NS	-	-	-	-	NS	-	-	-	-

Station Name	Station No.	CHLORPYRIFOS	CLOPYRALID	MCPA	MCPP	PICLORAM	TRIFLURALIN	TRIALLATE	Total Conc. per Samples	No. of Pesticides per Sample
Oldman River at Brocket	AB05AB0070	-	-	NS	-	NS		-	NS	NS
Oldman River upstream of Lethbridge	AB05AD0010	NS	NS	NS	NS	NS		-	NS	NS
Oldman River at Taber	AB05AG0010	NS	NS	NS	NS	NS		NS	NS	NS
South Saskatchewan River u/s Medicine Hat	AB05AK0020	-	NS	NS	NS	-		-	NS	NS
Bow River at Exshaw	AB05BE0190	-	-	-	-	-		-	NS	NS
Bow River at Cochrane	AB05BH0010	-	-	-	-	-		-	NS	NS
Bow River at Carseland	AB05BM0010	NS	-	NS	NS	-		NS	NS	NS
Bow River at Cluny	AB05BM0590	NS	-	NS	-	-		-	NS	NS
Bow River at Ronalane	AB05BN0010	NS	NS	S	S	NS		-	S	S
Bow River at Bow City Bridge	AB05BN0080	-	-	NS	NS	NS	NS	-	NS	S
Red Deer River at Hwy 2 above Red Deer	AB05CC0010	-	-	NS	NS	NS	-	-	NS	NS
Red Deer River at Morrin Bridge	AB05CE0010	-	-	NS	S	NS	-	-	S	S
North Saskatchewan River at Devon	AB05DF0010	-	-	NS	NS	-	-	-	NS	NS
North Saskatchewan River at Pakan	AB05EC0010	-	-	NS	NS	NS	-	NS	NS	NS
Athabasca River at Hinton	AB07AD0110	-	-	-	-	-	-	-	-	-
Athabasca River at Athabasca	AB07BE0010	-	-	NS		-	-	-	NS	NS
Athabasca River at Old Fort	AB07DD0010	-	-	NS	NS	-	-	-	NS	NS
Wapiti River upstream Hwy 40	AB07GE0020	-	-	-	-	-	-	-	NS	NS
Wapiti River downstream Hwy 40	AB07GE0030	-	-		NS	-	-	NS	NS	NS
Smoky River at Watino	AB07GJ0010	-	-	-	-	-	-	-	NS	NS
Wapiti River above confluence with Smoky	AB07GJ0030	-	-	-	-	-	-	-	NS	NS
Peace River at Fort Vermillion	AB07HF0010	-	-	NS	NS	NS	-	-	NS	NS

Notes: S = Kruskal-Wallis test significant at p<0.05

NS = Kruskal-Walis test not significant at p<0.05 (in some cases no. of detections is very small

- = no detections

? = Significance of year-to-year differences cannot be established because of change in DL

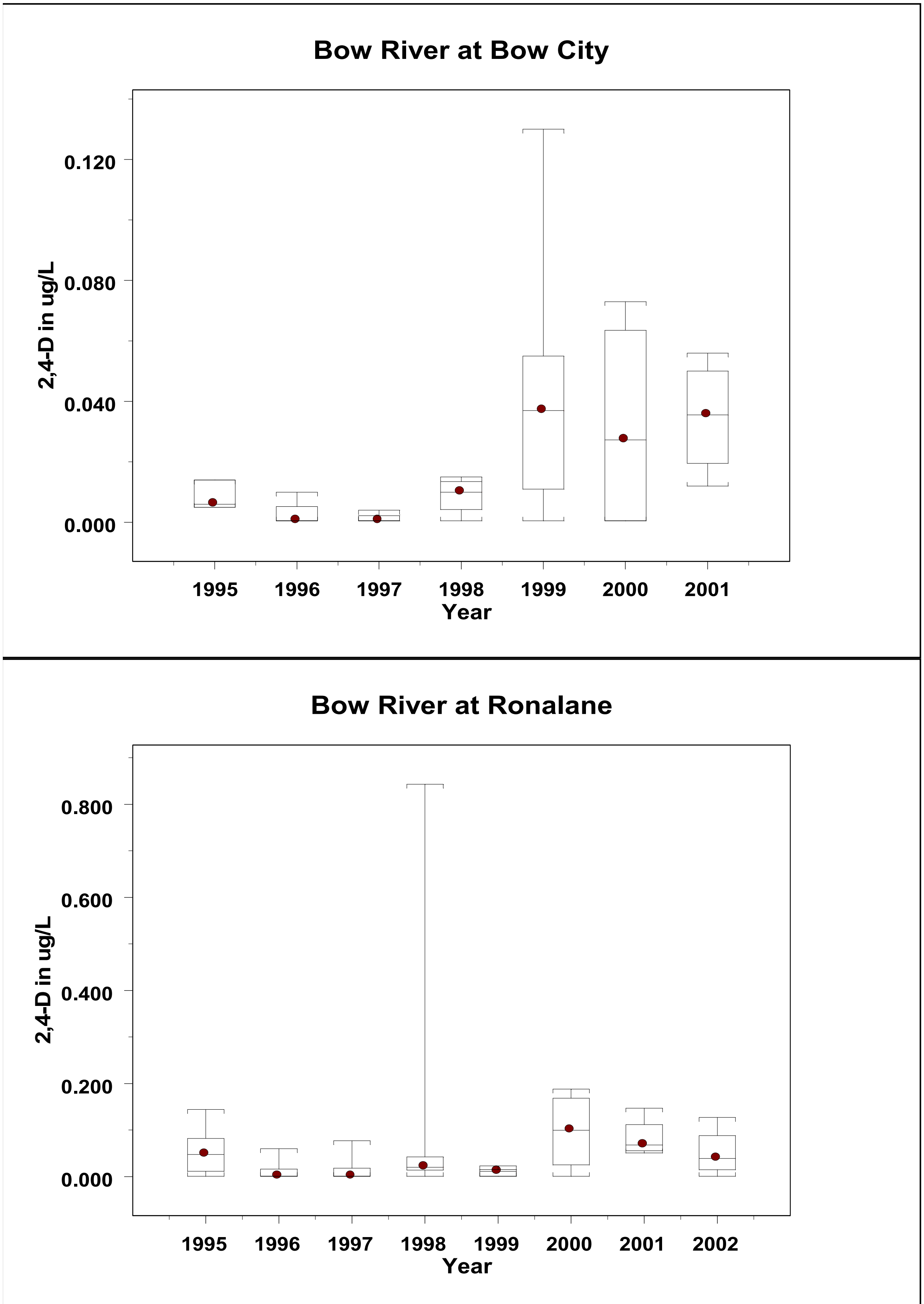


Figure 24 Year-to-year fluctuations in 2,4-D levels at long-term river monitoring sites

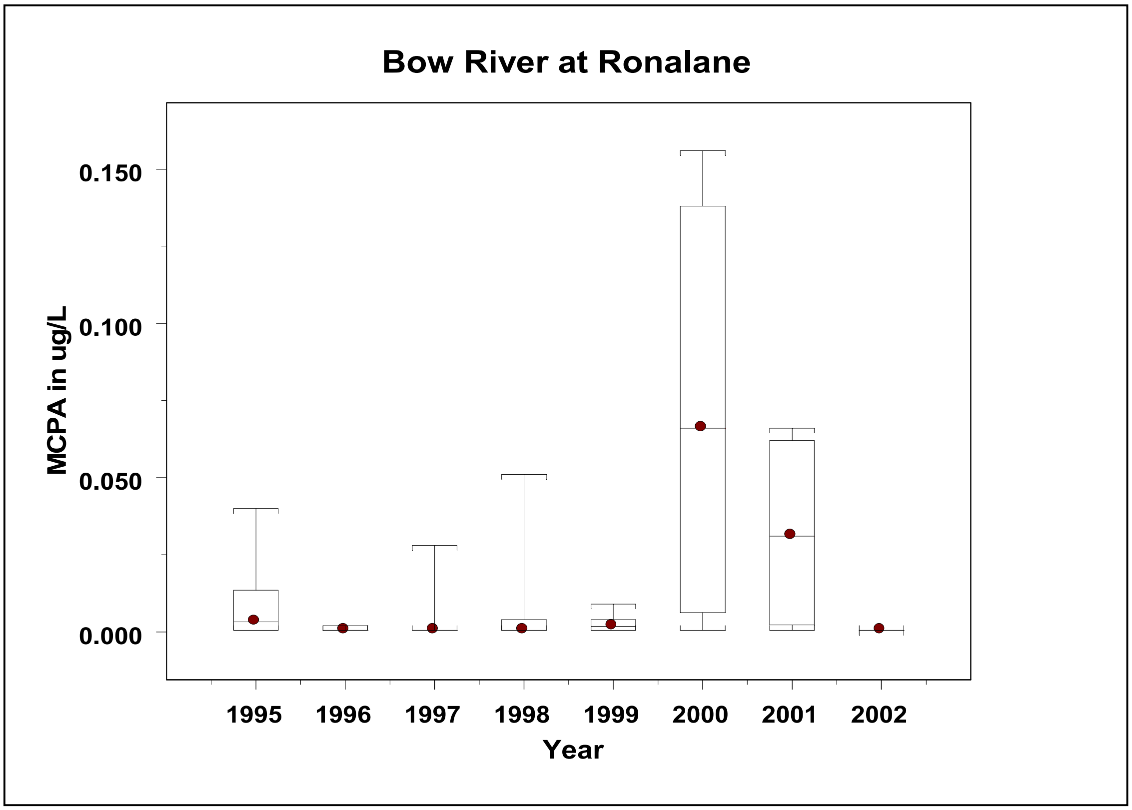


Figure 25 Year-to-year fluctuations in MCPA levels at long-term river monitoring sites

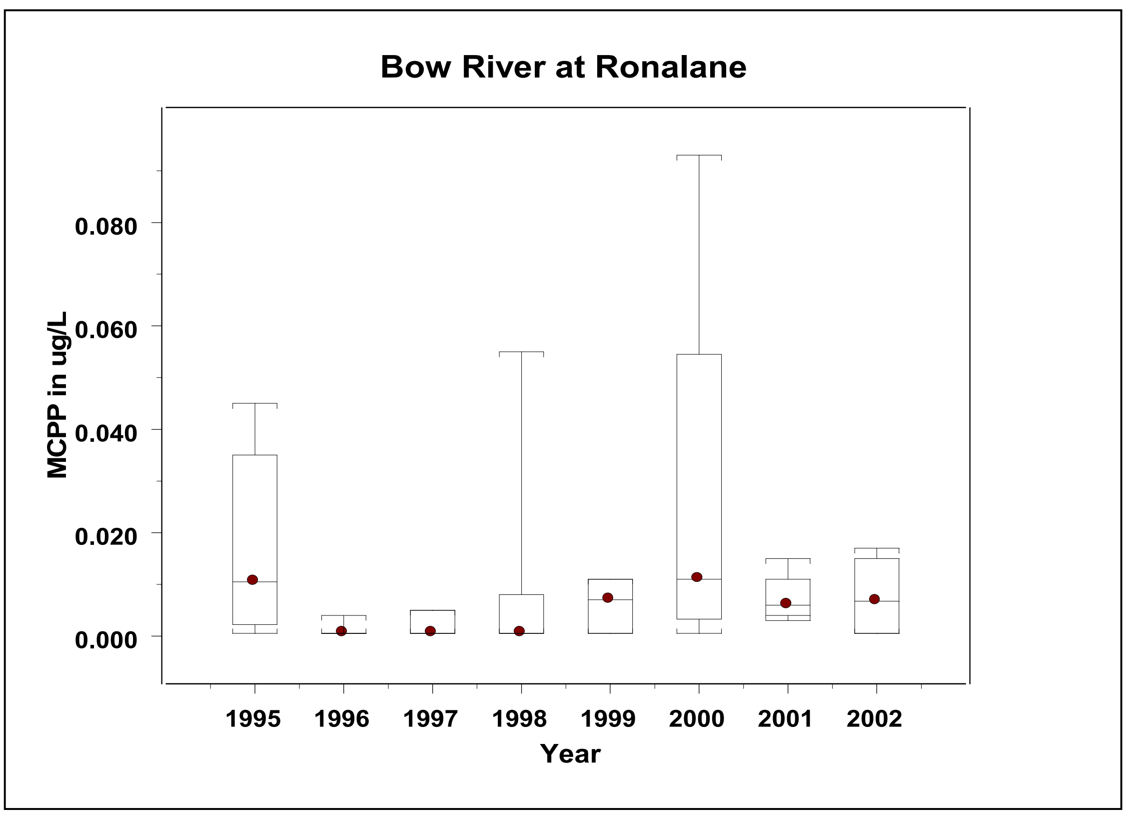


Figure 26 Year-to-year fluctuations in MCPP levels at long-term river monitoring sites

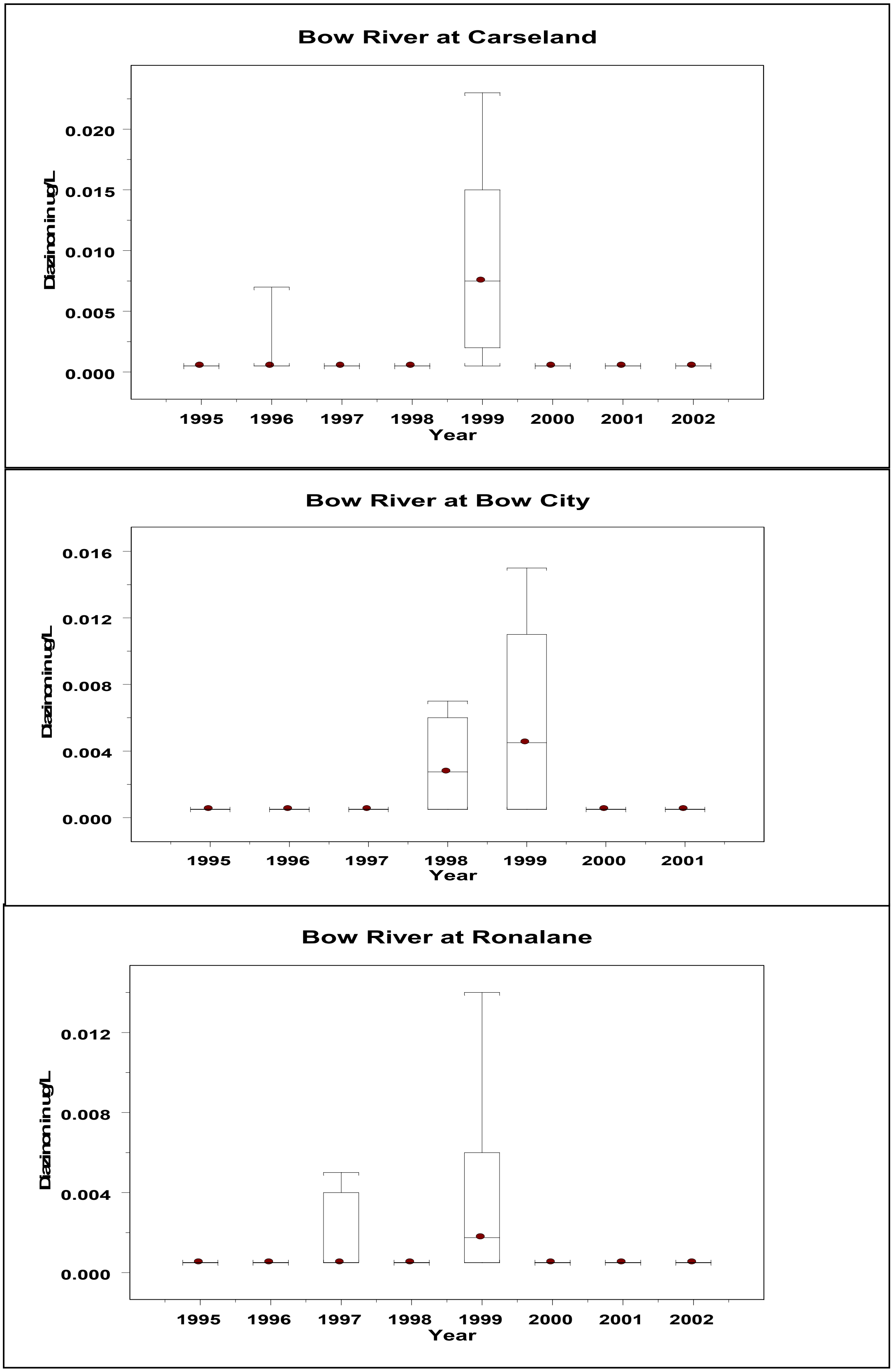


Figure 27 Year-to-year fluctuations in diazinon levels at long-term river monitoring sites

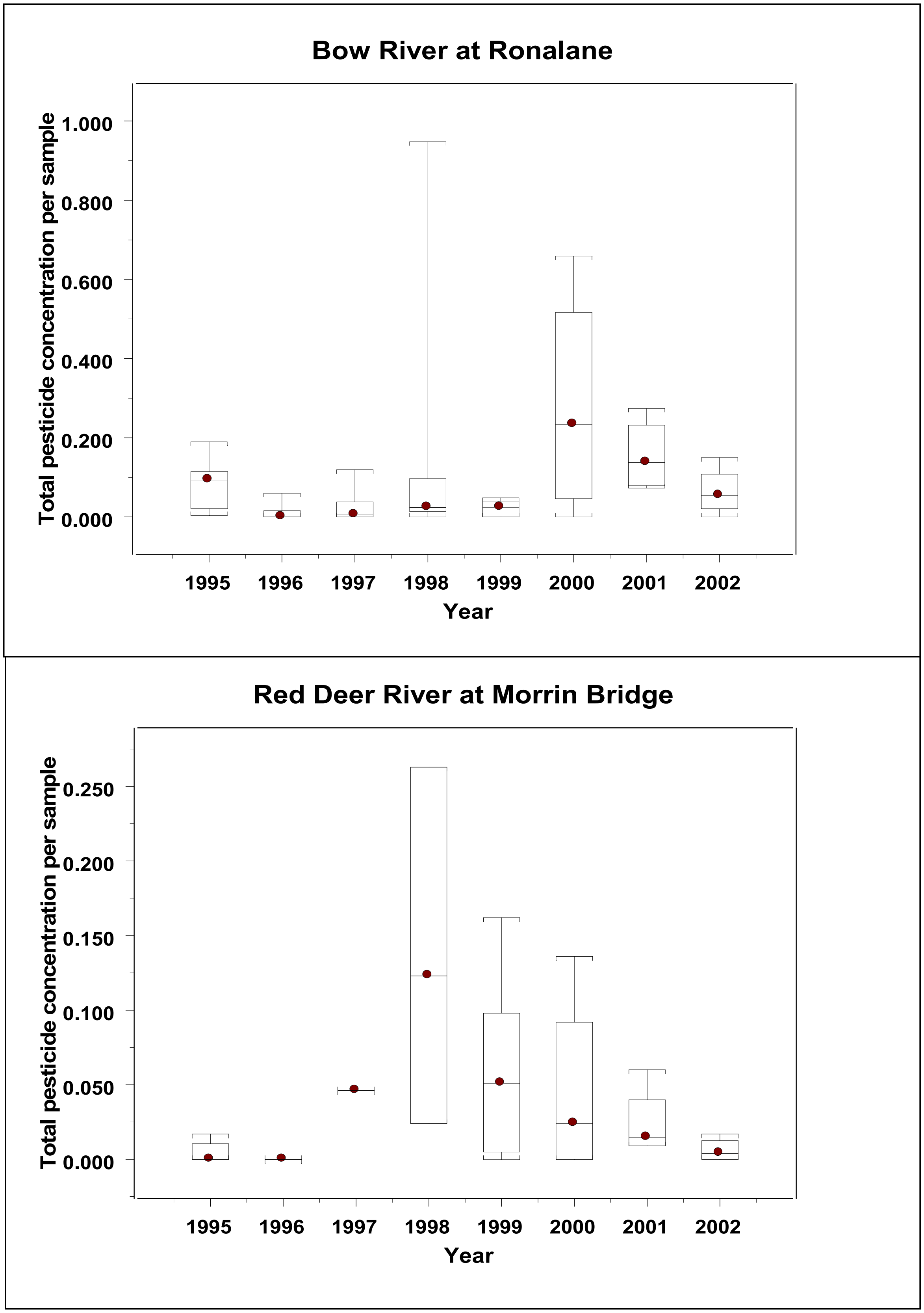


Figure 28 **Year-to-year fluctuations in total pesticide concentration per sample at long-term river monitoring sites**

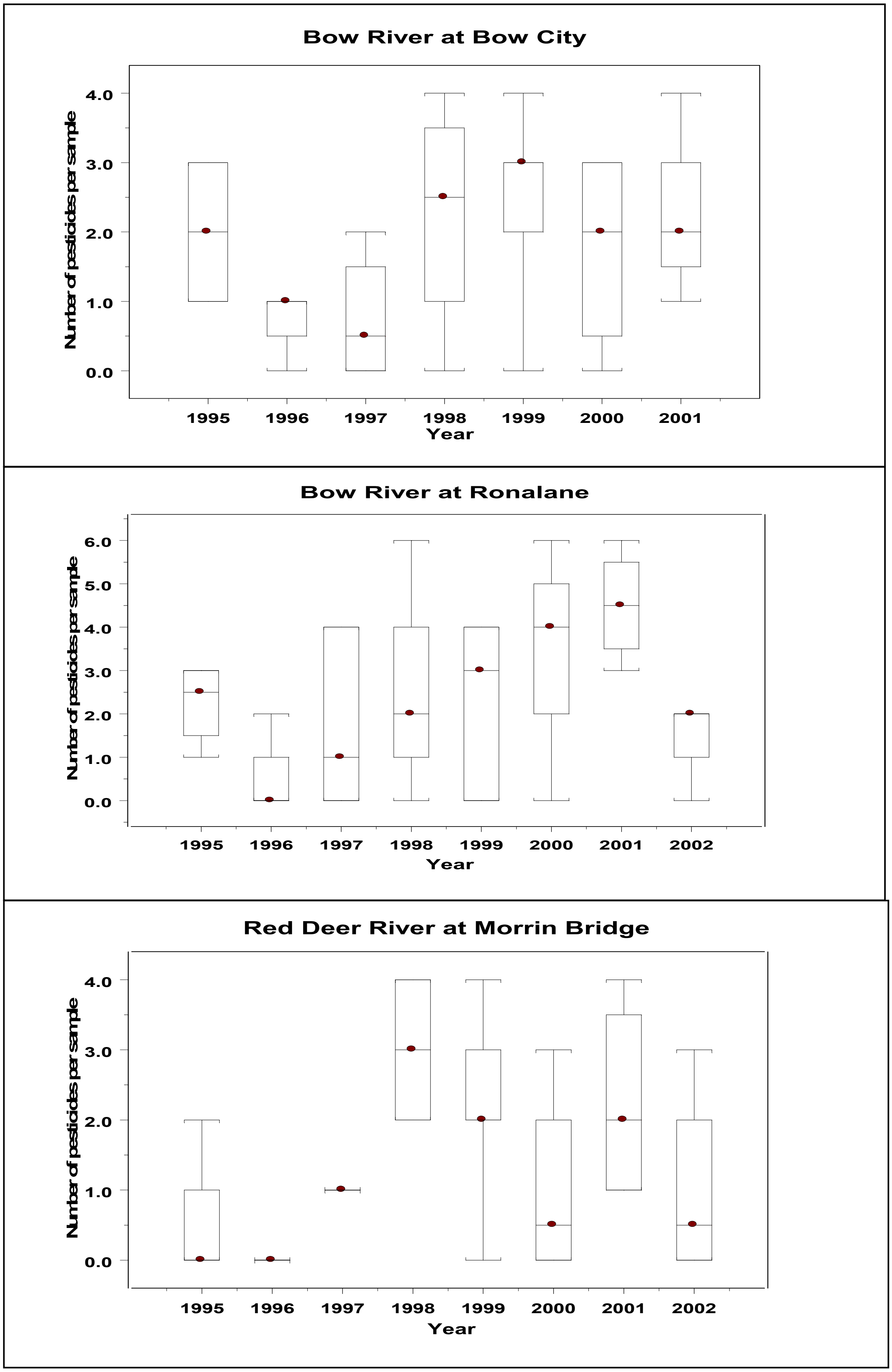


Figure 29 Year-to-year fluctuations in number of pesticides per sample at long-term river monitoring sites

Significant year-to-year differences in median total pesticide concentrations and the number of pesticide detections (Figures 28 and 29) occurred at Morrin Bridge in the Red Deer River. This site was sampled at an irregular frequency over the years (i.e., 8, 5, 1, 3, 6, 4, 4, and 4 times in 1995, ’96, ’97, ’98, ’99, ’00, ’01, and 02, respectively). In 1995 samples were collected in May, June, July and August, and data from that year are directly comparable to ’99 and post-‘99 data. Relative to 1995, concentration ranges were widest in 1998 and 1999 and they declined thereafter. This pattern may be related to general weather conditions in central Alberta. Water Survey of Canada records for tributary streams such as Threehills, and Haynes creeks show declining flows from 1999 on. This suggests that dry conditions could have influenced the incidence of weed growth, herbicide use, and runoff, particularly in 2002, a year of severe drought in central Alberta.

Although there are differences in the number of pesticides detected from one year to the next at some sites, these differences do not follow a consistent pattern and are difficult to interpret (Figure 29).

4.2.2.2.2 Temporal Trends at Tributary Network Sites

The tributary network comprises 13 creek and river sites and was sampled from 1996 to and including 2002. Most of these streams drain land that is primarily agricultural. Sample collection was scheduled in early spring (April), late spring (June) and fall (October), but at several sites only one or 2 samples were collected per year.

Comparisons of pesticide data among years were only attempted for sites which had data in each year of the 7-year sampling period (Table 8). Sampling was discontinued at some sites after only two or three years (i.e., Little Bow, Highwood, Sheep and McLeod rivers); very dry conditions precluded the sampling of Sounding Creek in several years; consequently there were insufficient data for a meaningful analysis.

2,4-D in the Pembina River and clopyralid in the Vermilion River were the only two pesticides for which significant differences in median concentrations were detected among years. 2,4-D was only detected in 1997 and 1998 and clopyralid was detected once in 2002.

4.2.2.2.3 Temporal Trends in Agricultural Streams (AESA streams)

The AESA network comprises 23 streams distributed across Alberta’s White Zone. Pesticide samples are collected in the period from spring runoff to October, on a flow-weighted basis, and as frequently as once per week during periods of high flow. Outside of runoff periods (low flow), samples are collected monthly.

Year-to-year comparisons of pesticide data were carried out on 17 streams which all had a 6-year period of record (Table 9). In many instances the Kruskal Wallis test indicated significant differences in pesticide detections among years for pesticides which were detected in only one or two years. Such differences may be due to a combination of pesticide use patterns and climate conditions, but cause and effect relationships are difficult to establish with available data (e.g.,

Table 8 Comparison among years of pesticide concentrations at Tributary Network sites (1995 – 2002)

Station Name	Station No.	2,4-D	DICHLOR PROP	LINDANE	BROMOXYNIL	DIAZINON	DICAMBA	CLOPYRALID	MCPA
Battle River at Hwy 872 Bridge	AB05FC0150	NS	NS	-	NS	-	?	NS	NS
Little Smoky River at Valleyview	AB07GH0020	NS	-	-		-	-	-	NS
Pembina River at Rossington	AB07BC0010	S	-	-	NS	-	-	-	NS
Ribstone Creek near Heath	AB05FD0011	NS	NS	-	NS	-	-	-	NS
South Heart River at High Prairie	AB07BF0020	NS	-	-	NS	-	-	-	NS
Sturgeon River near Villeneuve	AB05EA0040	NS	-	NS	NS	-	-	NS	NS
Vermillion River West of Marwayne	AB05EE0480	NS	NS	-	NS	NS	?	S	NS
Wapiti River d/s Hwy 40 Bridge	AB07GE0030	-	-	-	-	-	-	-	-
Little Bow River at Carmangay	AB05AC0180	insufficient data							
Highwood River at Aldersyde	AB05BL0380	insufficient data							
Sheep River u/s Highwood River	AB05BL0480	insufficient data							
McLeod River at Whitecourt	AB07AG0400	insufficient data							
Sounding Creek at Monitor	AB05GA0130	insufficient data							

Station Name	Station No.	MCPP	PICLORAM	TRIALLATE	IMAZAMETH ABENZ	IMAZETH APYR	Total Conc. per Sample	No. Pesticides per Sample
Battle River at Hwy 872 Bridge	AB05FC0150	NS	NS	-	-	-	NS	NS
Little Smoky River at Valleyview	AB07GH0020	-	NS	NS	-	-	NS	NS
Pembina River at Rossington	AB07BC0010	NS	NS	NS	NS	-	NS	NS
Ribstone Creek near Heath	AB05FD0011	-	NS	-	NS	-	NS	NS
South Heart River at High Prairie	AB07BF0020	NS	-	-	-	-	NS	NS
Sturgeon River near Villeneuve	AB05EA0040	NS	NS	NS	NS	NS	NS	NS
Vermillion River West of Marwayne	AB05EE0480	NS	NS	-	NS	NS	NS	NS
Wapiti River d/s Hwy 40 Bridge	AB07GE0030	-	-	-	-	-	-	-
Little Bow River at Carmangay	AB05AC0180	insufficient data						
Highwood River at Aldersyde	AB05BL0380	insufficient data						
Sheep River u/s Highwood River	AB05BL0480	insufficient data						
McLeod River at Whitecourt	AB07AG0400	insufficient data						
Sounding Creek at Monitor	AB05GA0130	insufficient data						

Notes:
S = Kruskal-Wallis test significant at p<0.05
NS = Kruskal-Walis test not significant at p<0.05 (in some cases number of detections is very small)
- = no detections
? = Significance of year-to-year differences cannot be established because of change in DL

Table 9 Comparison among years of pesticide concentrations at agricultural stream sites (AESA Program)(1995 – 2002)

Station Name	Station No.	2,4-D	2,4-DB	DICHLO RPROP	ALPHA-BHC	LINDANE	ATRAZINE	BRO MOXY NIL	DIAZINON	DICAMBA	DIURON	CHLORPY RIFOS	ETHAL FLURALIN	CLOPY RALID
Willow Creek at Hwy 811	AB05AB0260	S	-	NS	-	-	-	NS	NS	?	-	-	-	-
Meadow Creek Near the Mouth	AB05AB0240	NS	-	-	-	-	-	NS	-	?	-	-	-	-
Trout Creek Near the Mouth	AB05AB0230	NS	-	-	-	-	-	-	-	?	-	-	-	-
Prairie Blood Coulee Near Lethbridge	AB05AD0290	NS	-	NS	-	NS	-	NS	-	?	-	-	-	NS
Battersea Drain East of Picture Butte	AB05AG0030	NS	-	NS	-	-	S	NS	-	?	-	NS	-	S
Drain S6 Near Bow Island	AB05AJ0410	NS	-	NS	-	NS	-	NS	-	?	-	-	-	NS
Crowfoot Creek on Hwy 1	AB05BM0620	NS	-	NS	NS	NS	S	NS	NS	?	-	NS	NS	NS
Haynes Creek (M1) at Hwy 815	AB05CD0520	NS	-	-	-	NS	-	NS	-	?	-	-	-	S
Haynes Creek (M6) at Gauge	AB05CD0600	S	-	-	NS	S	-	S	NS	?	-	-	-	S
Threehills Creek Below Ray Creek	AB05CE0730	NS	-	NS	-	-	-	NS	NS	?	-	-	S	S
Ray Creek Near Innisfail	AB05CE0710	S	-	NS	-	-	-	NS	NS	?	-	-	S	S
Renwick Creek Near Three Hills	AB05CE0720	S	NS	-	-	NS	-	NS	-	?	-	-	S	NS
Buffalo Creek at Hwy 41	AB05FE0060	S	-	NS	-	-	-	NS	-	?	-	-	-	-
Strawberry Creek Near the Mouth	AB05DF0020	NS	-	-	NS	-	-	NS	-	?	-	-	-	NS
Tomahawk Creek North of Tomahawk	AB05DE0550	NS	-	-	-	-	-	NS	-	?	-	-	-	NS
Rose Creek West of Alderflats	AB05DE0010	NS	-	-	-	NS	-	NS	-	?	NS	-	-	NS
Paddle River Near Anselmo	AB07BB0060	NS	-	-	-	-	-	-	-	?	-	-	-	-

Station Name	Station No.	MALAT HION	MCPA	MCPP	PIC LORAM	TRIAL LATE	TRIFLUR ALIN	IMAZ AMETH ABENZ	DESETHYL ATRAZINE	IMAZETH APYR	PYRID ABEN	Total Conc. per Sample	No. of Pesticides per Sample
Willow Creek at Hwy 811	AB05AB0260	-	NS	NS	NS	-	-	-	-	-	-	S	S
Meadow Creek Near the Mouth	AB05AB0240	-	NS	-	NS	-	-	-	-	-	-	NS	NS
Trout Creek Near the Mouth	AB05AB0230	-	-	NS	NS	NS	-	-	-	-	-	NS	NS
Prairie Blood Coulee Near Lethbridge	AB05AD0290	-	NS	NS	NS	-	-	NS	-	-	-	NS	NS
Battersea Drain East of Picture Butte	AB05AG0030	-	NS	NS	-	S	-	-	-	-	-	NS	NS
Drain S6 Near Bow Island	AB05AJ0410	-	NS	NS	NS	NS	-	-	NS	-	-	NS	NS
Crowfoot Creek on Hwy 1	AB05BM0620	-	NS	NS	S	S	S	NS	-	-	-	NS	S
Haynes Creek (M1) at Hwy 815	AB05CD0520	NS	NS	NS	NS	NS	-	S	-	-	-	NS	NS
Haynes Creek (M6) at Gauge	AB05CD0600	-	NS	NS	S	NS	S	NS	-	NS	NS	S	NS
Threehills Creek Below Ray Creek	AB05CE0730	-	NS	NS	S	NS	-	S	-	NS	-	S	S
Ray Creek Near Innisfail	AB05CE0710	-	NS	NS	NS	S	-	S	-	NS	-	S	NS
Renwick Creek Near Three Hills	AB05CE0720	-	NS	NS	NS	NS	-	NS	-	-	-	NS	NS
Buffalo Creek at Hwy 41	AB05FE0060	-	NS	-	-	-	-	-	-	-	-	NS	NS
Strawberry Creek Near the Mouth	AB05DF0020	-	NS	NS	NS	-	-	NS	-	-	-	NS	NS
Tomahawk Creek North of Tomahawk	AB05DE0550	-	NS	NS	S	-	-	-	-	-	-	S	S
Rose Creek West of Alderflats	AB05DE0010	-	NS	-	S	-	NS	-	-	NS	-	NS	NS
Paddle River Near Anselmo	AB07BB0060	-	S	NS	-	-	-	-	-	-	-	NS	NS

Notes:
S = Kruskal-Wallis test significant at $p<0.05$
NS = Kruskal-Walis test not significant at $p<0.05$ (in some cases number of detections is very small)
- = no detections
?= Significance of year-to-year differences cannot be established because of change in DL

bromoxynil detected in Haynes Creek at M6 only in 1998 and 1999; ethalfluralin detected in Threehills, Ray, and Renwick creeks only in 1997).

In other instances, more consistent trends emerged. Atrazine in Crowfoot Creek exhibits a gradual, but consistent decline over the period of record (Figure 30). Agricultural use of atrazine is primarily restricted to corn, a crop that is of very little importance in the watershed. The report of atrazine in Crowfoot Creek (Buckland 1998) prompted AENV to investigate possible upstream sources (Byrtus 1998). Crowfoot Creek receives return flows from the WID. The WID diversion is located in Calgary, just downstream of where Nose Creek enters the Bow River. The WID canal flows into Chestermere Lake. There are two drains from Chestermere Lake which supply irrigation water to the WID irrigation users. Return flows are to Rosebud Creek and Crowfoot Creek. The source of atrazine appears to link back to a domestic product used for total vegetation control. Urban runoff in the Calgary area appears to be the origin of atrazine detections in Crowfoot Creek. The domestic sterilant is still registered, but its use appears to be declining (Gary Byrtus, personal communication).

Clopyralid is used for broadleaf weed control in cereal, canola and flax seed crops (AAFRD 2004). Because of its very high water solubility and low Koc (measure of adsorption to soils), clopyralid is very mobile, but moderately persistent in soils (Cotton 1995). Clopyralid was first detected in Alberta agricultural streams in 1998 and has been detected fairly regularly since. Several AESA sites in central Alberta exhibit an increasing trend in clopyralid concentrations over time (Figure 31). It is noteworthy that the highest median concentration in these streams was observed in 2002. This was a year of severe drought in that part of the province, where surface runoff did not occur to move this soluble herbicide from land to water. Other pathways may account for the transport of this pesticide.

Imazamethabenz is used to control stinkweed, wild mustard, wild oats and buckwheat in barley, wheat and sunflower crops (AAFRD 2004). Because of its high solubility in water and low Koc value (Cotton 1995) it is mobile and would be expected in surface waters. It is moderately persistent in soils. Imazamethabenz has been primarily detected in central Alberta and highest concentrations were recorded in 1999 and 2000 (Figure 32), lower concentrations in 2001 and 2002. Although the latter two years were dry in central Alberta, drought alone does not explain the decline in imazamethabenz levels recorded in central Alberta surface waters since other pesticides, such as clopyralid, with similar water solubility and Koc exhibited an increase in concentration over time (see above). It is possible that a decline in use is the main factor governing the decline of this pesticide in surface waters.

Picloram was registered in Canada 40 years ago. It is available only to authorized pesticide applicators and is used to control a variety of weeds (e.g., camomile, knapweed, Canada thistle, toadflax, and clover) and brush (e.g., alder, birch, maple, poplar and spruce) on permanent grass pastures, rangeland and utility rights-of-way. Picloram has a very high water solubility and low Koc and is very mobile and persistent (Cotton 1995, AAFRD 2004). Picloram is encountered commonly in surface waters. Although there are year-to-year differences in median concentrations these differences are not consistent among streams, suggesting that use may vary among basins and from year-to-year depending on the need (Figure 33). In general, higher

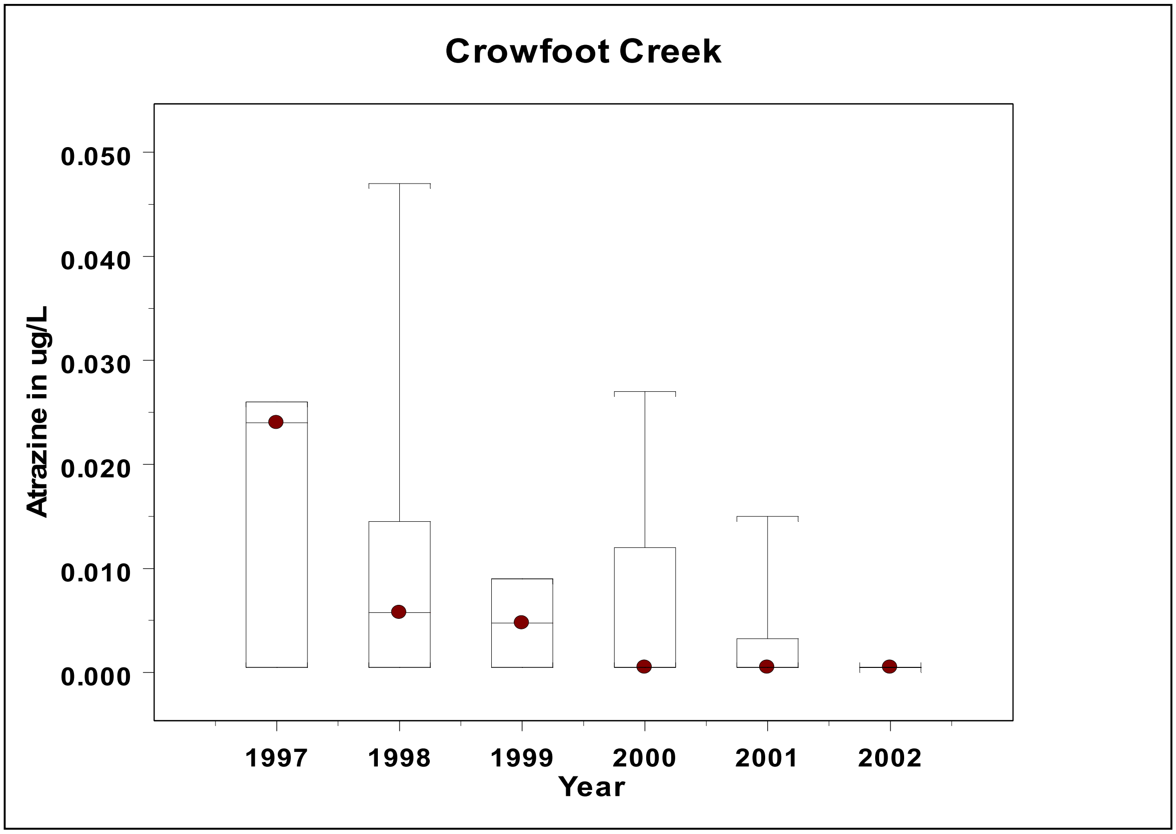


Figure 30 Year-to-year fluctuations in atrazine levels in agricultural streams

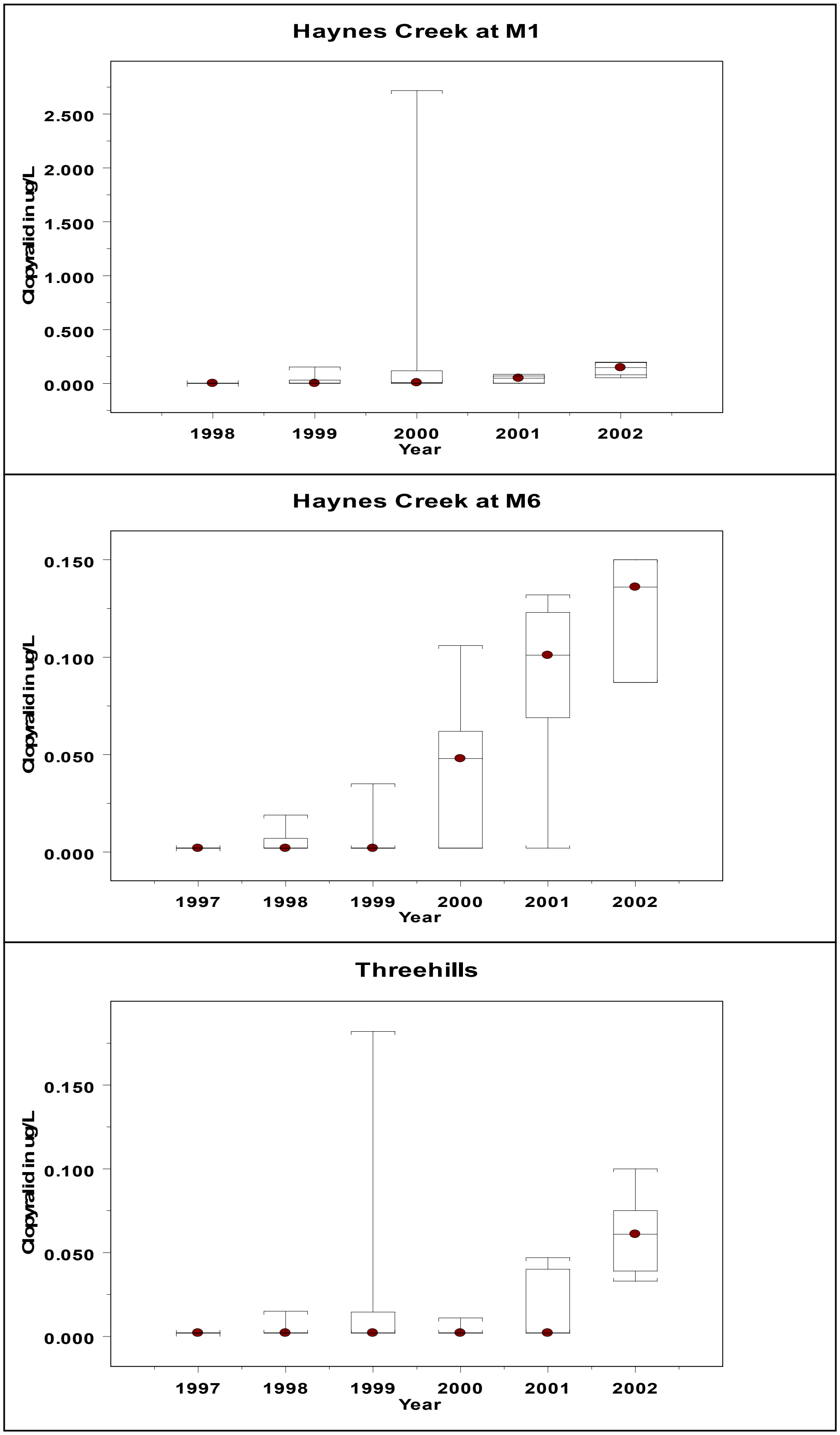


Figure 31 Year-to-year fluctuations in clopyralid levels in agricultural streams

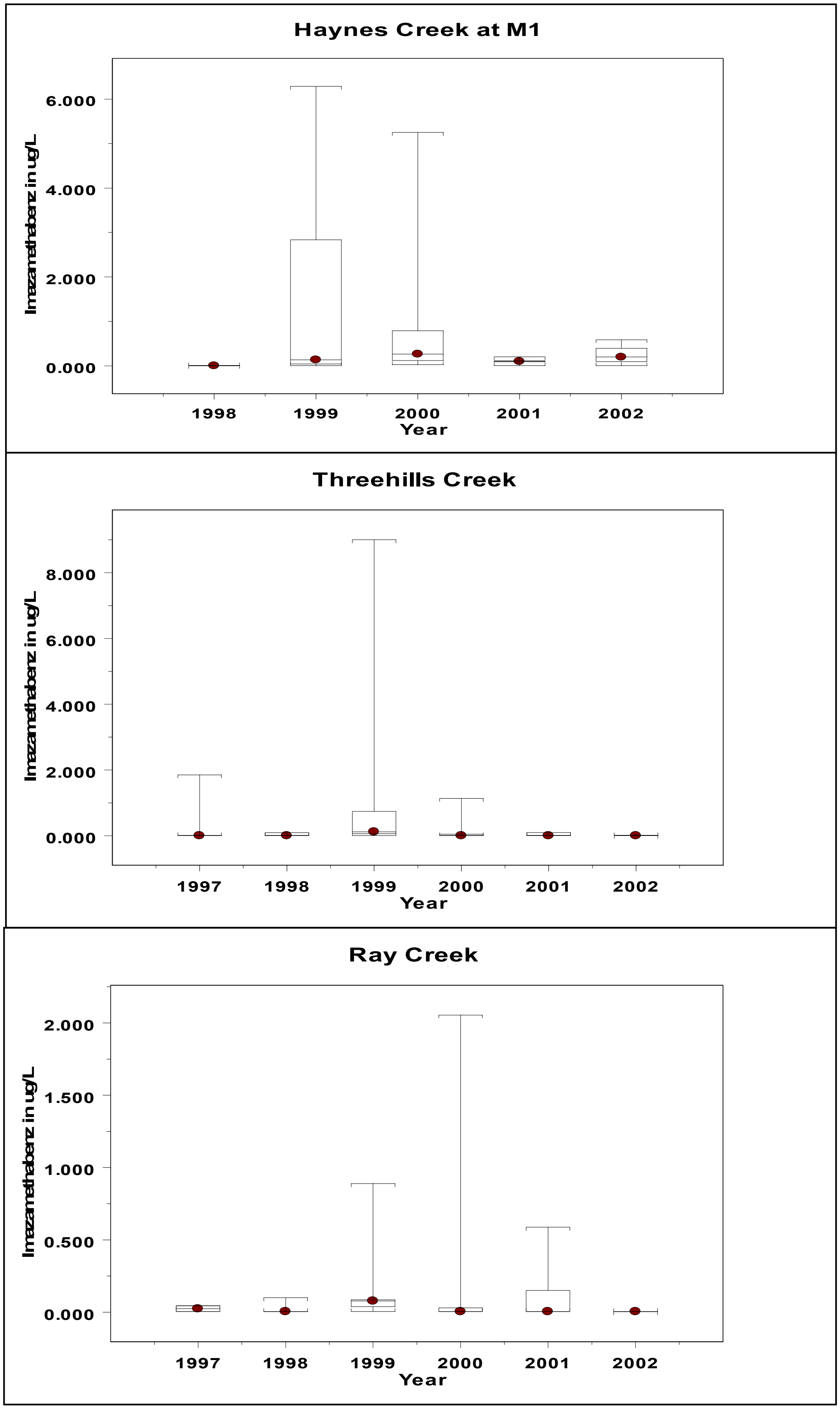


Figure 32 Year-to-year fluctuations in imazamethabenz levels in agricultural streams

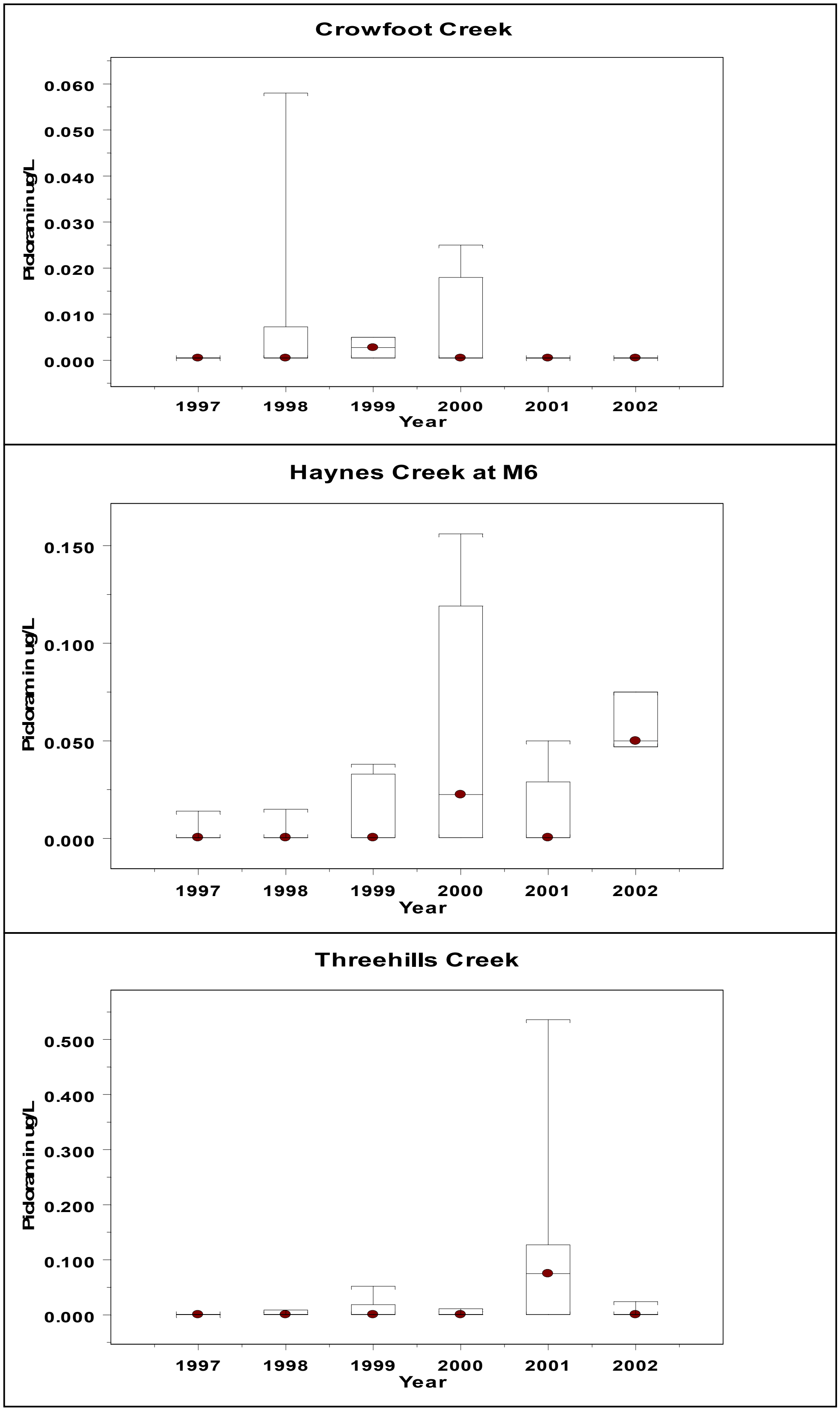


Figure 33 Year-to-year fluctuations in picloram levels in agricultural streams

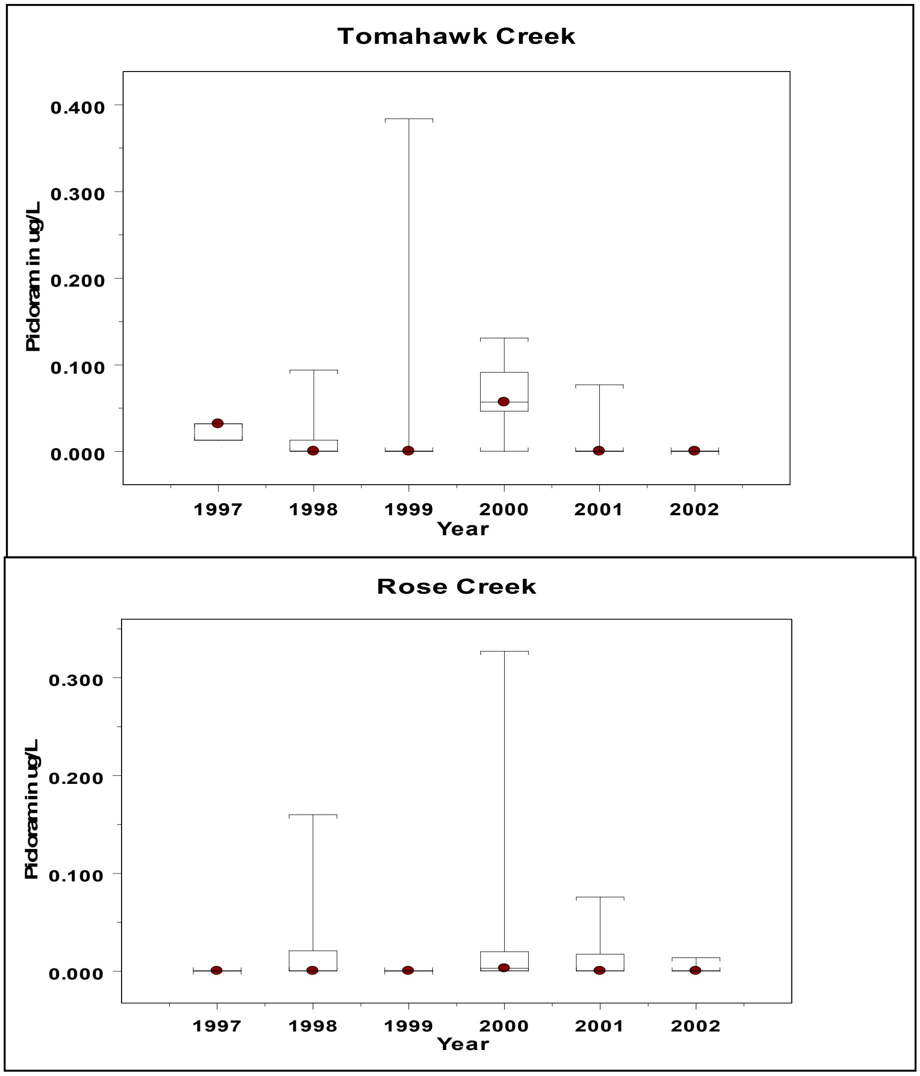


Figure 33 Year-to-year fluctuations in picloram levels in agricultural streams (continued)

concentrations were recorded from 1998 to and including 2001 with lower concentrations detected in 2002. The relatively high concentration measured in Haynes Creek (M6) in the year of severe drought is noteworthy and not readily explainable.

Crowfoot Creek is the only stream for which a gradual, but significant decline in the number of pesticides recorded per site has been noted (Figure 34), although no decline was observed in total concentrations.

In central Alberta Haynes, Threehills and Ray creeks, exhibit significant year-to-year differences in median total concentration (Figure 35). Highest concentration ranges were recorded in 1999 and 2000, the lowest concentration ranges during the drought year of 2002.

4.3 Urban and Agricultural Influences

4.3.1 Urban Influences

Urban influences are reflected by differences in pesticide occurrence at long-term monitoring sites on the Oldman, Bow, Red Deer and North Saskatchewan rivers, above and below Lethbridge, Calgary, Red Deer and Edmonton, respectively. This includes the number and types of pesticides, their detection frequency, and the statistical significance of concentration differences. For pesticides that exhibited significant concentration increases below the cities, differences in mass load (derived from instantaneous pesticide concentration measurements and average daily flows) provide a measure of urban contributions. The small number of data points per year, combined with the high incidence of censored data precludes more detailed calculations of mass loading.

Pesticide detections downstream of major urban centers were generally more diverse and frequent than upstream (Figure 36). Some of the pesticides encountered more frequently downstream of urban centers include the herbicides 2,4-D, MCPP, MCPA, and dicamba and the insecticides lindane, diazinon and chlorpyrifos. These products are registered for agricultural, municipal, industrial and domestic use, but MCPA is only registered for agricultural uses. Consequently, the occurrence of some pesticides below cities may not result solely from urban uses. Some downstream sites are located rather far downstream of the urban areas and could be influenced by non-urban uses (e.g., Morrin Bridge on the Red Deer River is located about 150 km below the City of Red Deer).

Several pesticides occurred at higher concentrations downstream of three of the four urban centers: 2,4-D and bromoxynil below Lethbridge; 2,4-D, MCPP and diazinon below Calgary; and 2,4-D, MCPP and lindane below Edmonton (Table 10, Figures 36, 37, 38, and 39). The association of lindane with the LTRN site downstream of Edmonton is discussed in section 4.2.2.1. Correspondingly, there were significant increases in overall herbicide, insecticide and total pesticide concentrations. In the Oldman (Figure 37; sites 2 and 3), Bow River (Figure 38, sites 2 and 3) North Saskatchewan (Figure 39), and Red Deer (Table 10) rivers the number of pesticides per sample was also higher downstream. In addition to urban influences incremental effects of agricultural contributions are noticeable along the Bow River

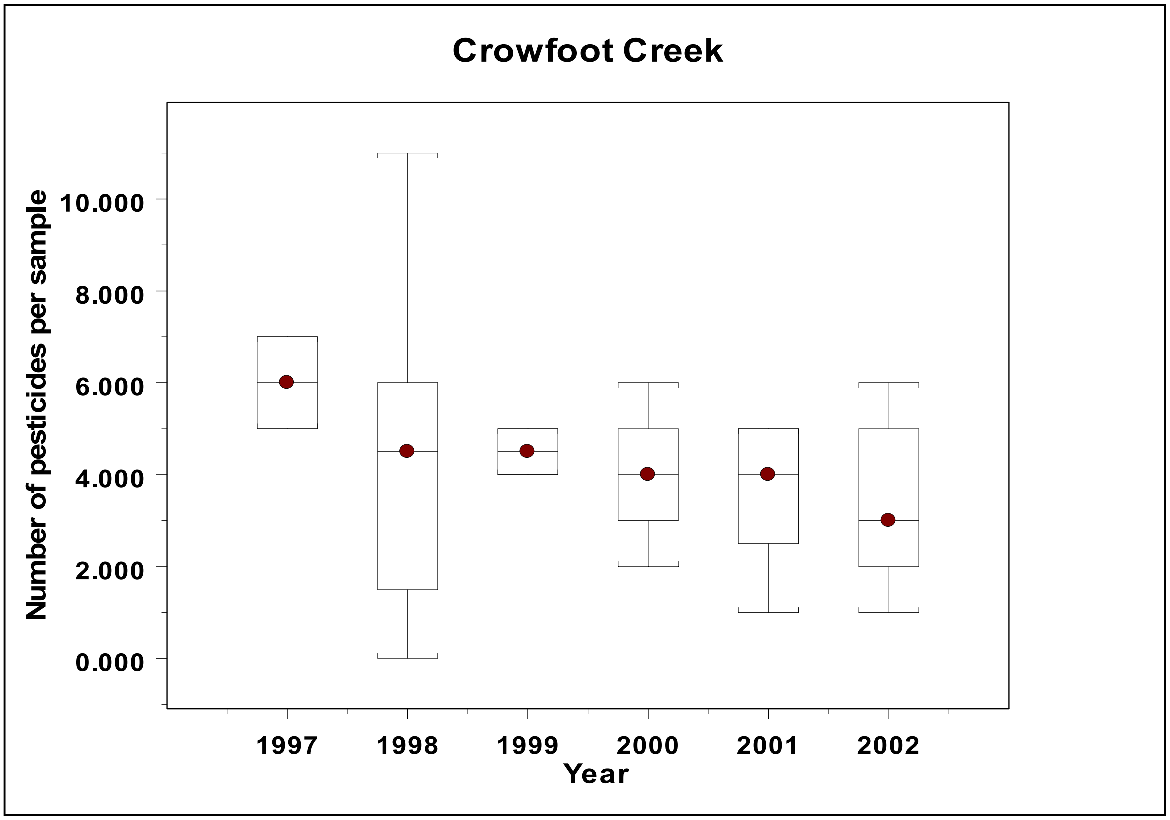


Figure 34 **Year-to-year fluctuations in number of pesticides detected per sample in agricultural streams**

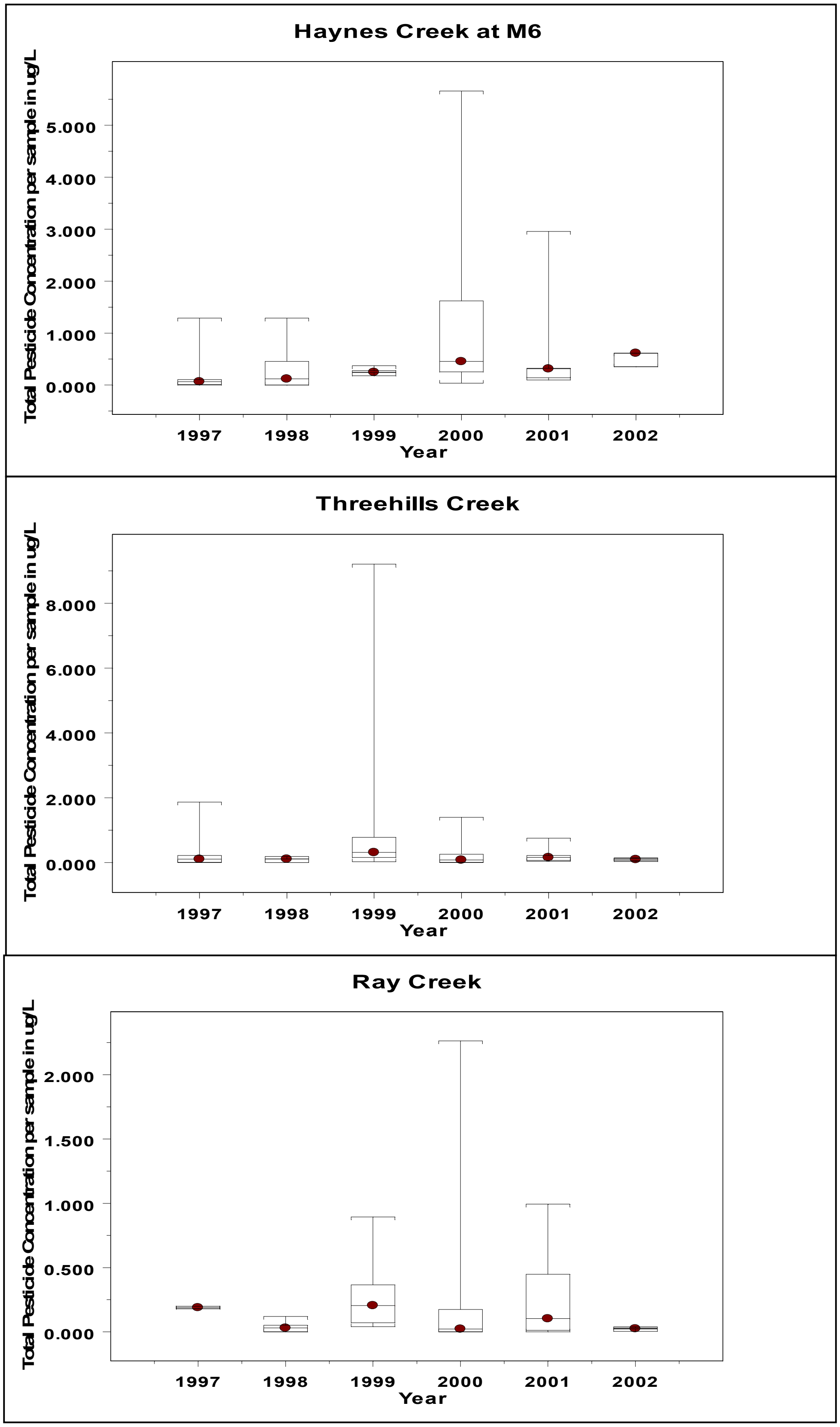


Figure 35 Year-to-year fluctuations in total pesticide concentration detected per sample in agricultural streams

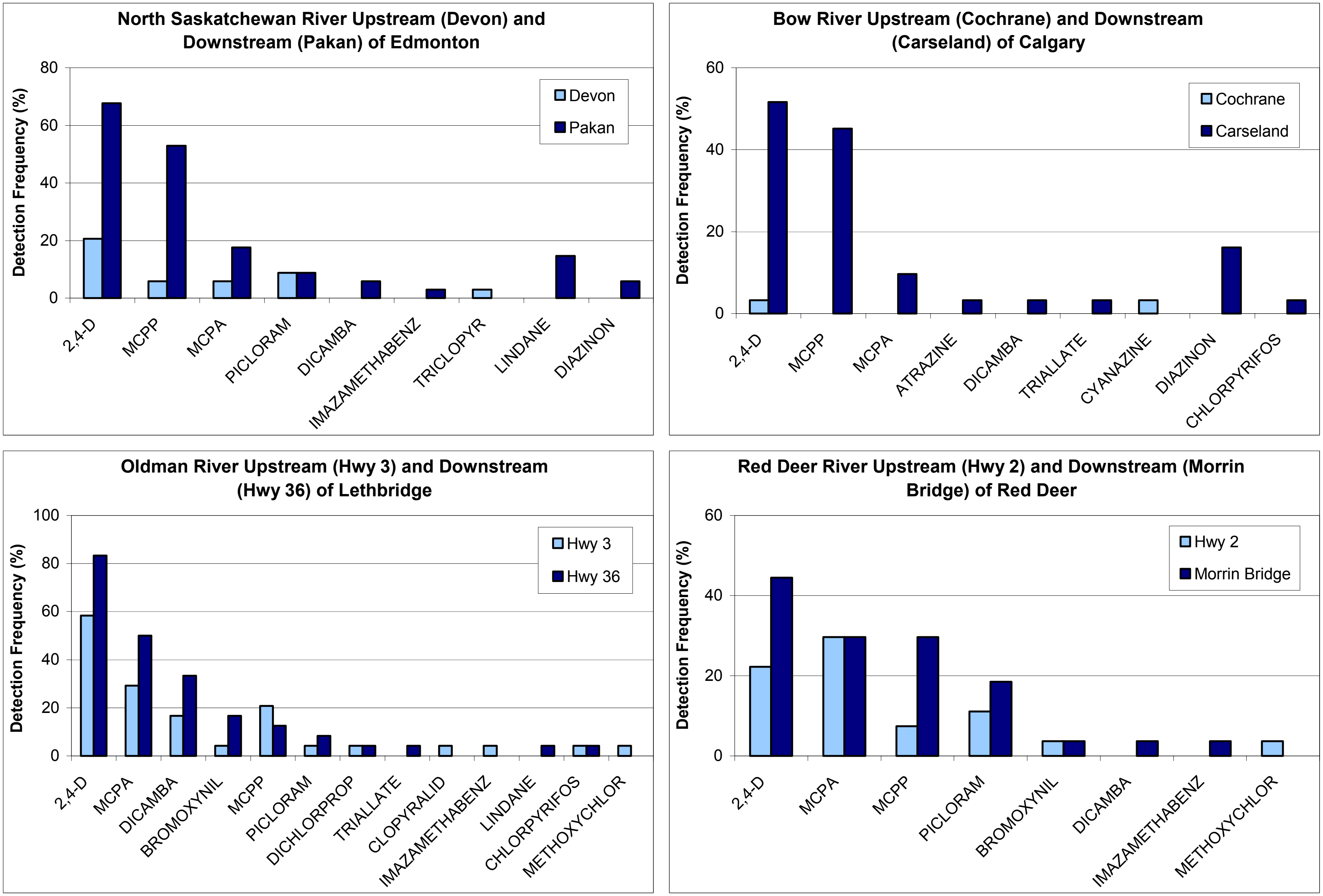


Figure 36 **Detection frequency of pesticides at long-term monitoring sites upstream and downstream of major urban centres (1995 - 2002)**

Table 10 Summary of comparisons of pesticide data at LTRN sites upstream and downstream of major cities, 1995-2002

City:	Lethbridge		Calgary		Red Deer	Edmonton	
Sites Compared:	Oldman River Above Lethbridge at Hwy 3 At Hwy 36		Bow River At Cochrane At Carseland		Red Deer River At Hwy 2 At Morrin Bridge	North Saskatchewan River At Devon At Pakan	
Pesticide Measure:	Significance of Concentration Difference	Range of Incremental Daily Loading in kg a.i..day^{-1}	Significance of Concentration Difference	Range of Incremental Daily Loading in kg a.i..day^{-1}	Significance of Concentration Difference	Significance of Concentration Difference	Range of Incremental Daily Loading in kg a.i..day^{-1}
2,4-D	**S**	-0.7[1]-1.6	**S**	0.00 - 0.53	NS	**S**	-0.04[1] - 2.16
Atrazine	-		NS		-	-	
Bromoxynil	**S**	0.00 - 0.55	-		NS	-	
Chlorpyrifos	NS		NS		-	-	
Clopyralid	NS		-		-	-	
Cyanazine	NS		NS		-	-	
Dicamba	NS		NS		NS	NS	
Dichlorprop	NS		-		-	-	
Imazamethabenz	NS		-		NS	NS	
MCPA	NS		NS		NS	NS	
MCPP	NS		**S**	0.00 -0.37	NS	**S**	0.00 - 0.91
Picloram	NS		-		NS	NS	
Triallate	NS		NS		-	-	
Triclopyr	-		-		-	NS	
Diazinon	NS		**S**	0.00 -0.18	-	NS	
Lindane	NS		-		-	**S**	0.00 -0.57
Methoxychlor	NS		-		NS	-	
Total Herbicide Concentration	**S**	-9.75[1] - 2.51	**S**	-0.66[1] - 0.87	NS	**S**	-2.38[1] - 3.11
Total Insecticide Concentration	NS		**S**	0.00 - 0.19	NS	**S**	0.00 -0.57
Total Concentration	**S**	-9.75[1] - 2.68	**S**	-0.66[1] - 0.87	NS	**S**	-2.38[1] - 3.11
No. Pesticides per Sample	**S**		NS		**S**	**S**	

Notes:
S = significant difference in concentration upstream and downstream of city detected with Wilcoxon Signed Rank Test (<0.05)
NS = no significant difference detected with Wilcoxon Signed Rank Test (<0.05)
- = no detections
[1] = Negative values indicate instances where concentrations upstream were higher than downstream
a.i. = active ingredient

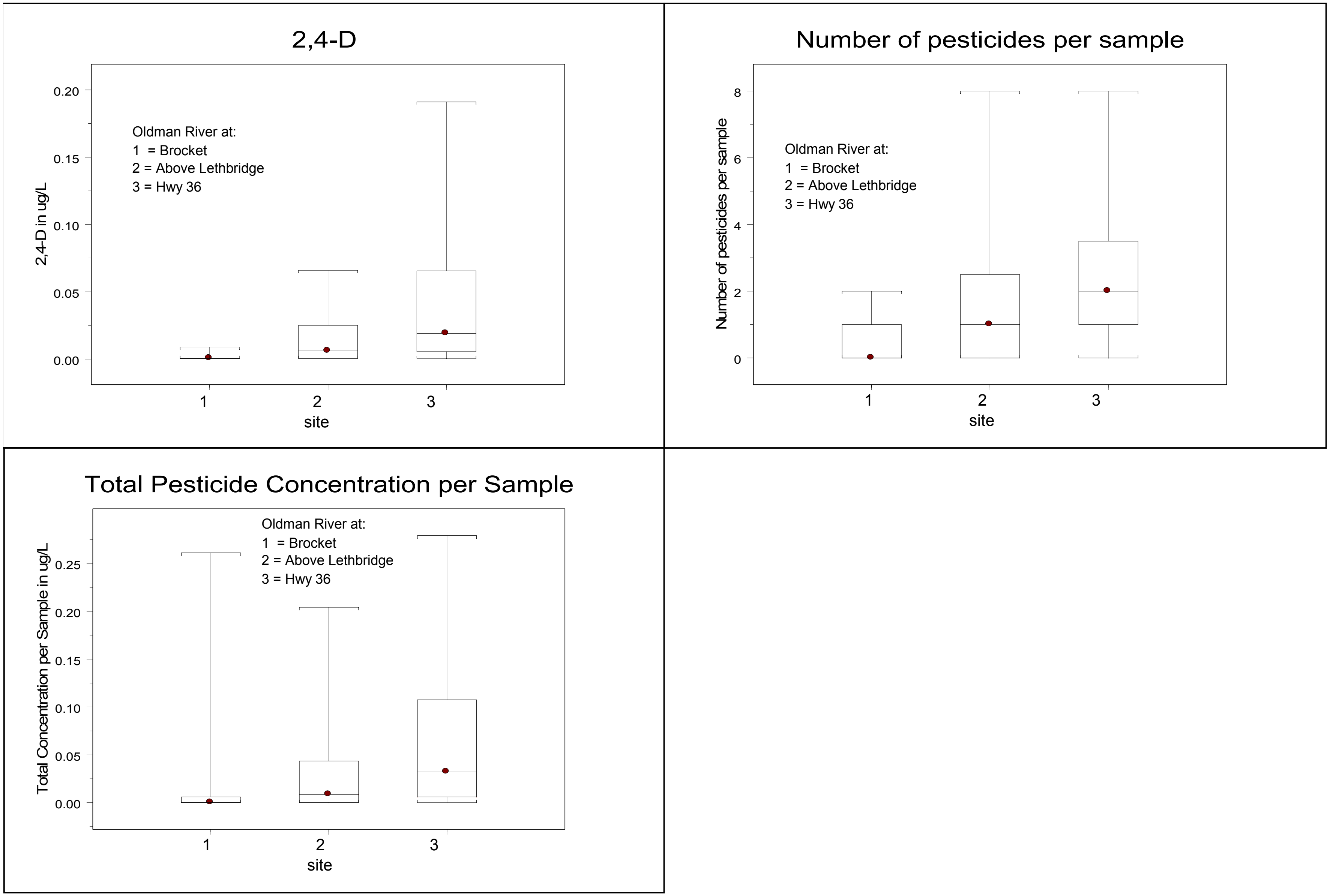


Figure 37 Longitudinal trends in pesticides along the Oldman River (1995 - 2000). Refer to Figure 1 for site location

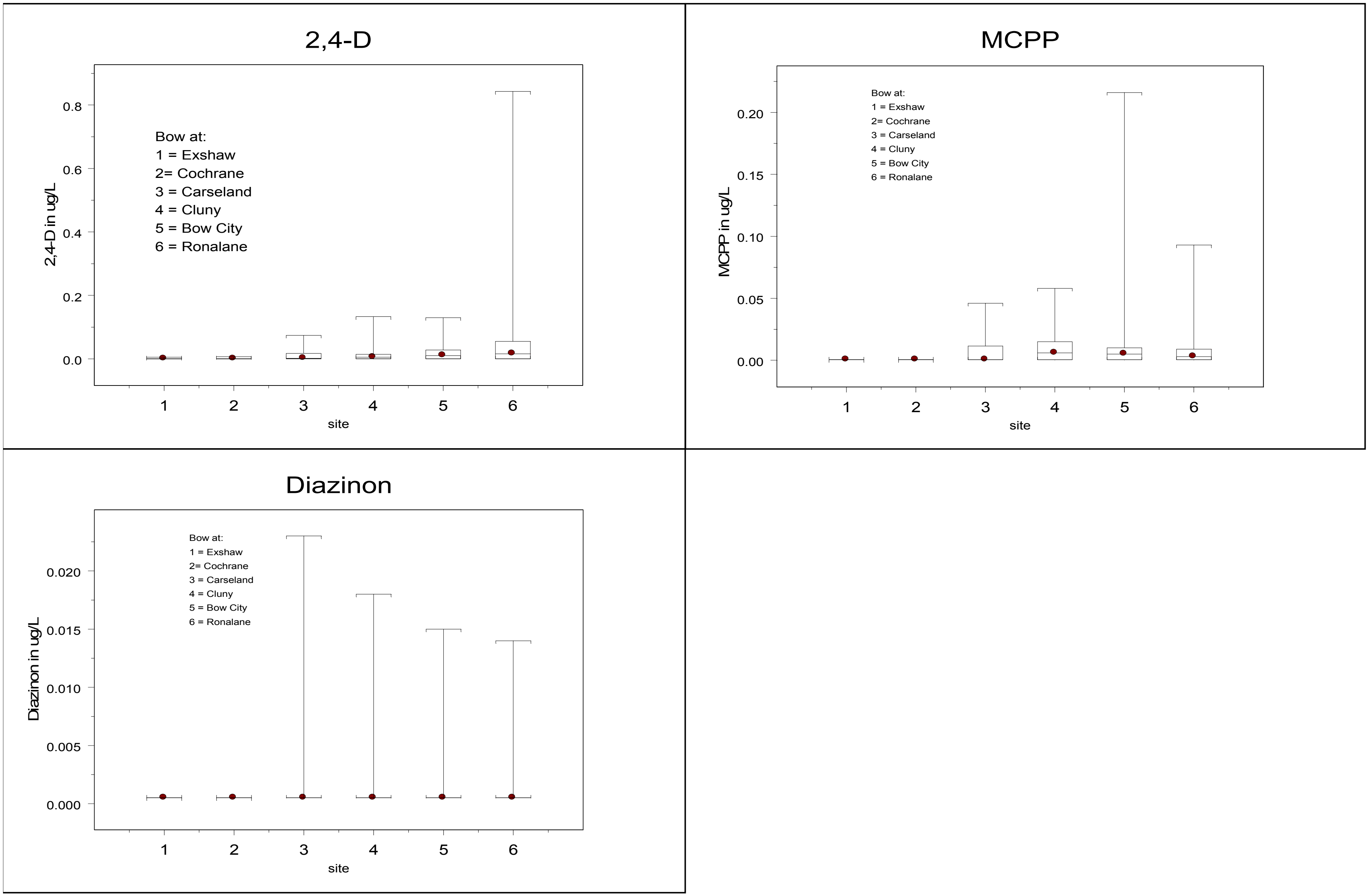


Figure 38 Longitudinal trends in pesticides along the Bow River (1995 - 2002). Refer to Figure 1 for site location

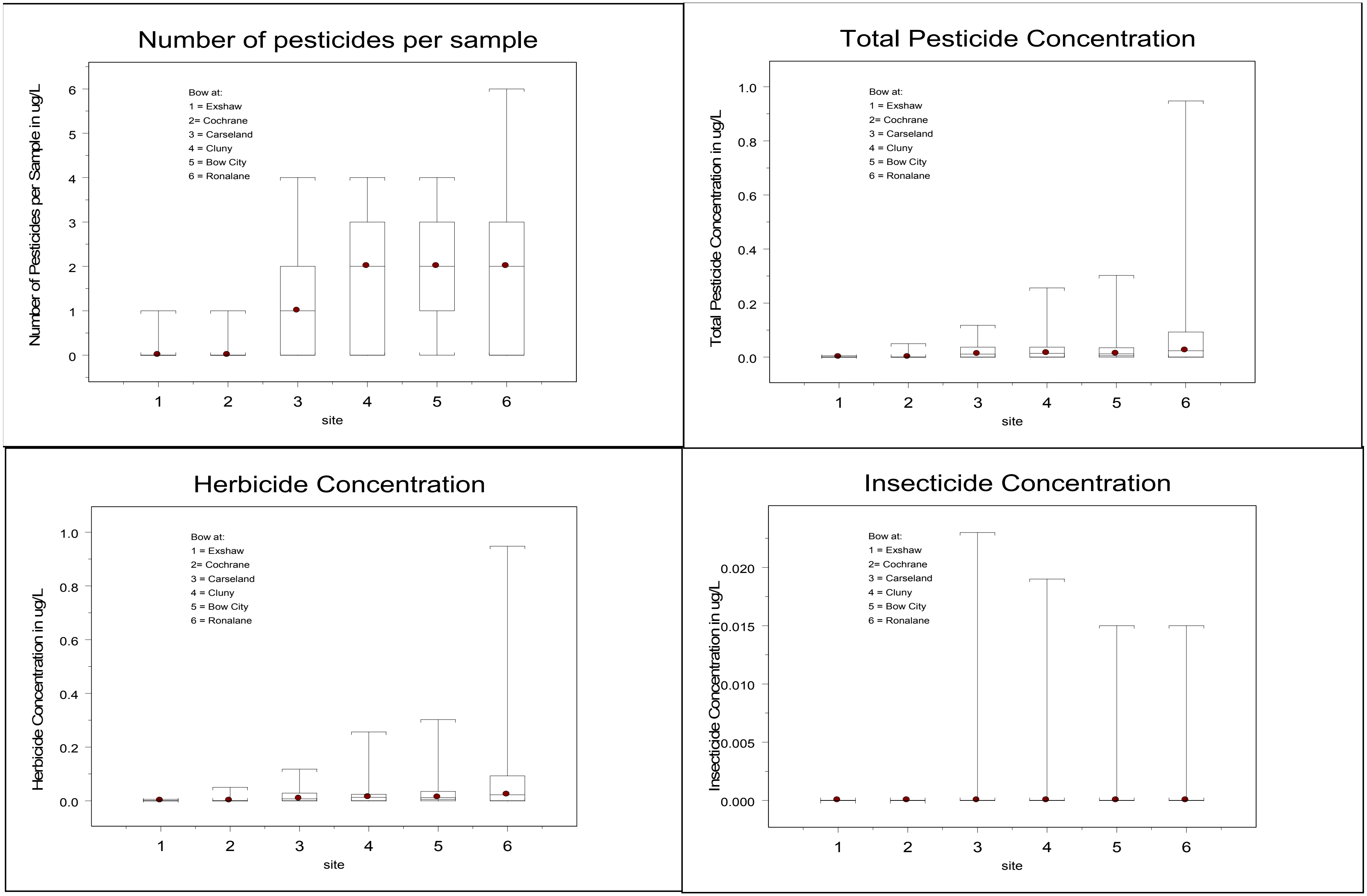


Figure 38 Longitudinal trends in pesticides along the Bow River (1995 - 2002) continued

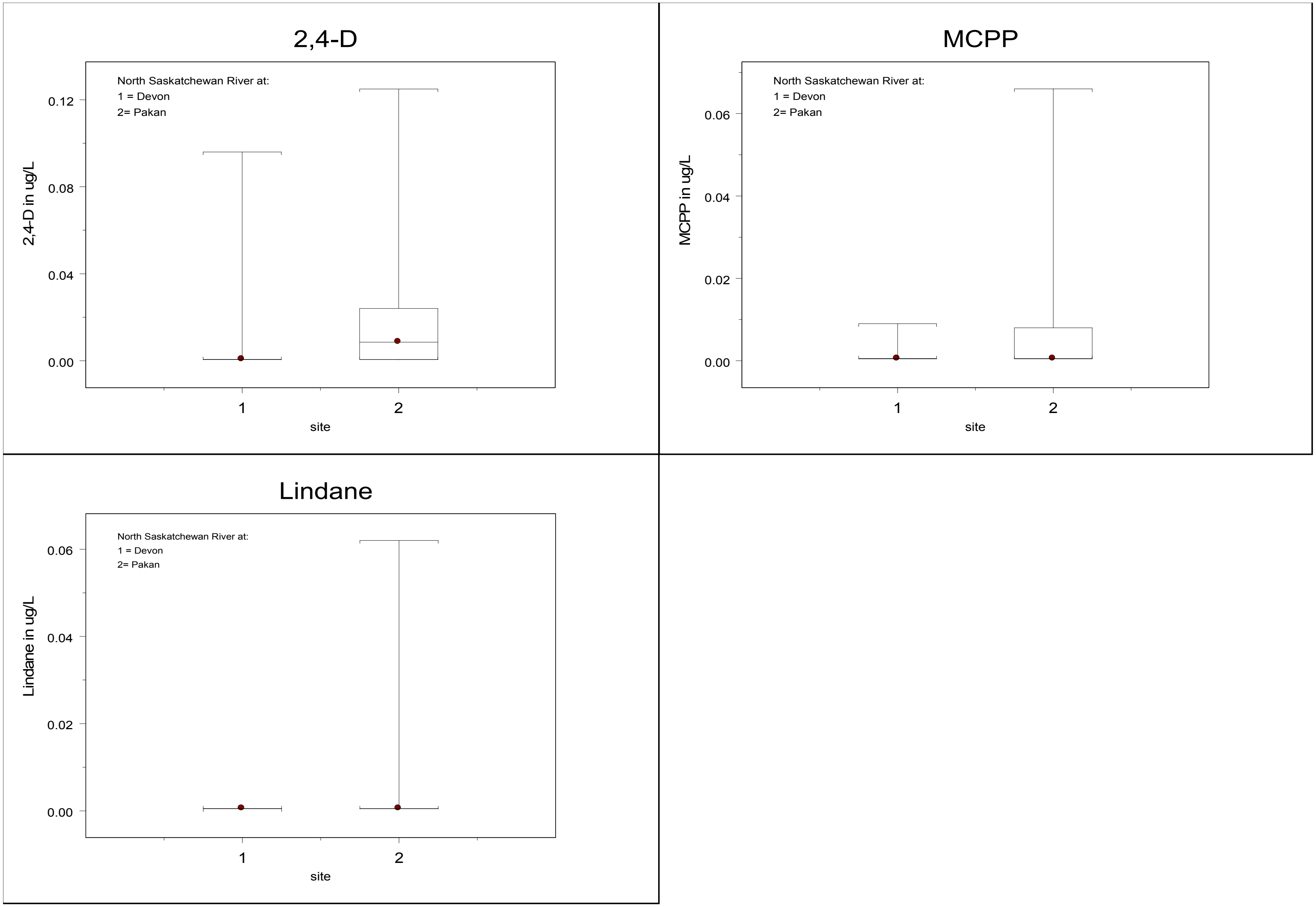


Figure 39 Longitudinal trends in pesticides in the North Saskatchewan River (1995- 2002). Refer to Figure 1 for site location

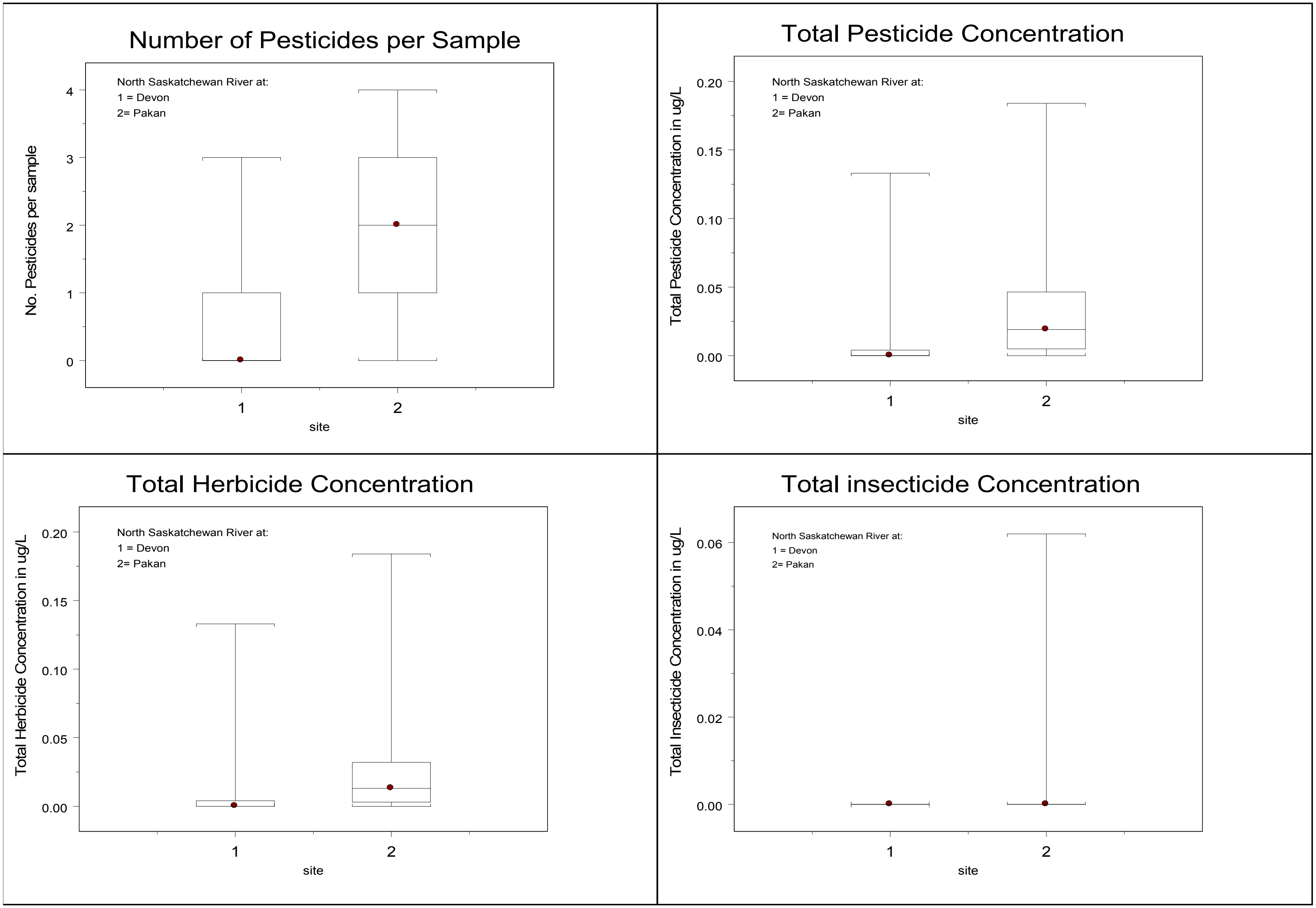


Figure 39 Longitudinal trends in pesticides in the North Saskatchewan River (1995- 2002) continued

(Figure 38). In the Red Deer River this last variable was the only pesticide measure to exhibit a significant increase downstream of Red Deer.

Differences in mass load between LTRN sites upstream and downstream of urban centers indicate that up to 2.16, 0.91, and 0.55 kg active ingredient per day of 2,4-D, MCPP, and bromoxynil, respectively were contributed between the two sites (Table 10). 2,4-D and MCPP are ingredients of lawn care products and some of the noted increases are likely related to such use, but bromoxynil is only registered for agricultural uses and its increased loading in the Oldman River is likely unrelated to urban use.

Insecticide loading was as high as 0.18 kg diazinon per day below Calgary and 0.57 kg lindane per day in the Edmonton area (Table 10). Increases in diazinon loading are particularly noticeable in 1999 in the Bow River (see also section 3.2.2.2). Increases in lindane are typical for the North Saskatchewan River below Edmonton and may have been related to the operation of a seed treatment plant as discussed earlier (section 3.2.2.1).

Overall, the largest relative changes in pesticide contamination were encountered downstream of Calgary and Edmonton; changes below Lethbridge and Red Deer were comparatively smaller. Population density and size of the urban area, as well as the range of municipal and industrial uses may account for the higher relative increase in pesticide contamination downstream of Calgary and Edmonton. In addition, and probably because of the more intense agricultural use, the level of pesticide contamination above Lethbridge and Red Deer is relatively higher than above Calgary and Edmonton and works towards reducing apparent upstream-downstream differences.

Negative loading estimates from urban centers are artifacts of instantaneous daily loading estimates that are based on single paired measurements; they result from situations where concentrations upstream (e.g., low level detection) are higher than downstream (e.g., concentration reported as <MDL). Increased sampling frequency and inclusion of runoff sampling could improve urban loading estimates and allow the calculation of seasonal or annual loading.

4.3.2 Agricultural Influences

Influences of agriculture on pesticide contamination of surface waters are best described by pesticide data obtained from agricultural streams as part of the AESA and CAESA programs. The AESA program and its precursor, the CAESA program, rely on a standardized study design that involved a GIS-based approach to the selection of monitoring sites. Streams drain similar soils and landscapes, but they are distributed across the province's White Zone and cover the variety and intensity of agriculture typical for Alberta. Statistics Canada data were used to define agricultural intensity, based on fertilizer and pesticide expenses, and manure production. Agricultural intensity of monitoring streams was rated low, medium or high based on the streams' rank relative to the provincial distribution. Irrigation streams (return flows) rank among high intensity streams, but they are considered separately because of their managed hydrology. Further details of the site selection process are presented in Anderson et al. (1996) and Anderson and Cooke (1999). Water quality sampling of agricultural streams occurs on a flow-weighted basis at or near a federally- or provincially-maintained, continuous flow gauging station. The total number of pesticide samples collected per year seldom exceeds 10 samples per site and is considerably less than sample numbers for nutrients and bacteria also monitored at these sites.

Although the present program was formalized for 23 streams in 1999, several additional streams have been sampled consistently since 1997. The present analysis relies on data from 32 streams and covering the period 1997 to 2002 inclusive. Not all streams have the same period of record.

The relationship between pesticide contamination and agricultural intensity was evaluated by comparing pesticide detection frequency, concentrations, and mass loads (i.e., product of instantaneous concentration and daily flow) among four groups of streams (irrigation return flows, streams draining land farmed at high, medium and low intensity). In loading calculations, censored data were replaced by 1/10th the MDL and flow records reported as 0.000 cms were replaced by 0.0001 cubic meter per second (cms). The frequency of censored data combined with the relatively small number of data points per year precluded a more detailed calculation of mass transport of individual pesticides. Data summaries and Kruskal Wallis test results are presented in Table 11.

Overall, the total number of pesticides detected in a stream group and the number of pesticides detected per sample was highest in irrigation return flows and declined with agricultural intensity (Figure 40). Some pesticides such as methoxychlor, atrazine, cyanazine, and chlorpyrifos were only reported in irrigation return flows. Significant differences occurred also in total pesticide concentrations with highest median concentrations occurring in irrigation return flows and high intensity streams (Figure 41). Similar patterns in pesticide contamination of agricultural streams in Alberta have been reported previously (Anderson et al. 1998b, Anderson 1998 and 2000, Carle 2001, Depoe and Westbrook 2001, Donahue 2001). These patterns illustrate the influence that pesticide use intensity in a watershed has on pesticide contamination of surface waters. Similar influences are apparent in standing waters across the province (Anderson et al. 1998 and Anderson 1998). Although agricultural uses prevail, it is recognized that pesticides may be used for non-agricultural applications in these watersheds (e.g., domestic, municipal and industrial). These uses are not quantified; hence relative contributions to surface water contamination cannot be estimated at this time.

Stream discharge varies considerably over the course of the open water season, among years, and also among streams. There were significant differences in discharge among the four stream groups (Table 11). Streams in the high agricultural intensity group had flows that were nearly an order of magnitude lower than those in the other groups, respectively. Despite these differences, the median instantaneous load for total pesticides was highest for irrigation return flows followed by the high, medium and low intensity groups in that order. Although median loads follow a pattern that matches that of concentrations, maximum loads are highly influenced by episodes of peak discharge. As a result of high flows, some streams in areas of low agricultural intensity occasionally had a much greater maximum pesticide load than streams draining more intense agricultural land.

Some individual pesticide residues also have significantly higher median concentrations and loads in irrigation return flows and high intensity streams (e.g., 2,4-D, MCPP and

Table 11 Summary of comparisons of pesticide concentrations and instantaneous daily loads in agricultural streams

Pesticide	Significance of Differences		Irrigation Return Flows					Streams in Areas of High Intensity Agriculture				
	Concen-tration	Instantaneous Daily Load	Detection Frequency (%)	Concentration in µg/L		Instantaneous Load in mg/d (1),(2)		Detection Frequency (%)	Concentration in µg/L		Instantaneous Load in mg/d(1)	
				Median	Maximum	Median	Maximum		Median	Maximum	Median	Maximum
2,4-D	S	S	93.53	0.069	7.24	3.097	401.708	65.49	0.0435	4.933	0.048	1410.696
2,4-DB	NS	(S)	0.59	0.665	0.665	0.027	190.754	0.29	0.005	0.005	0.003	4.031
Alpha-BHC	NS	(S)	0.00	0	0	0.000	0.000	0.59	0.048	0.091	0.003	16.286
Lindane	NS	(S)	2.94	0.0075	0.023	0.029	24.797	2.95	0.0115	0.025	0.003	4.031
Methoxychlor	NS	(S)	0.59	0.006	0.006	0.165	7.439	ND	-	-	-	-
Atrazine	S	S	14.12	0.014	0.142	0.030	9.979	ND	-	-	-	-
Bromacyl	NS	(S)	ND	-	-	-	-	1.18	0.1575	0.297	0.016	24.183
Bromoxynil	S	S	17.06	0.011	0.522	0.032	98.771	12.98	0.0085	0.082	0.004	31.726
Cyanazine	NS	(S)	0.59	0.17	0.17	0.275	12.398	ND	-	-	-	-
Diazinon	NS	(S)	0.59	0.041	0.041	0.029	1.240	0.88	0.008	0.012	0.003	4.031
Dicamba	S	S	58.24	0.0195	0.97	0.206	69.193	8.55	0.014	0.381	0.010	16.122
Dichlorprop	S	S	16.47	0.012	0.314	0.038	65.116	3.83	0.013	0.235	0.003	4.031
Diuron	NS	(S)	ND	-	-	-	-	0.29	0.616	0.616	0.109	161.222
Chlorpyrifos	S	S	4.71	0.0065	0.781	0.030	32.483	ND	-	-	-	-
Ethalfluralin	S	S	2.35	0.008	0.184	0.029	14.878	3.83	0.008	0.039	0.003	6.234
Clopyralid	S	S	15.29	0.038	0.237	0.151	45.049	26.25	0.049	2.717	0.030	196.163
Malathion	NS	(S)	0.59	0.007	0.007	0.275	12.398	0.29	0.011	0.011	0.027	40.306
MCPA	S	S	61.76	0.017	7.279	0.193	264.694	55.46	0.0295	1.878	0.022	1773.446
MCPP	S	S	38.82	0.016	0.133	0.038	22.753	12.98	0.0235	2.068	0.004	11.257
Picloram	S	S	8.24	0.019	0.64	0.030	52.618	41.00	0.059	1.355	0.014	1217.229
Triallate	S	S	15.29	0.011	0.407	0.038	1009.230	6.49	0.024	0.34	0.003	93.709
Trifluralin	S	S	0.59	0.007	0.007	0.027	17.358	4.72	0.005	0.187	0.003	10.938
Imazamethabenz	S	S	1.76	0.07	0.074	0.275	12.398	33.14	0.1415	9.005	0.094	1309.104
Imazethapyr	NS	(S)	0.61	0.11	0.11	0.099	1.814	3.77	0.053	0.409	0.006	16.122
Number of pesticides per sample	S			3	12				3	8		
Total concentration per sample	S	S		0.101	9.05	4.871	1480.369		0.14	10.638	0.562	4498.105
Instantaneous discharge in cms	S			0.636	28.7				0.063	93.3		
Number pesticide samples				203					340			

Notes:
S = significant differences among the four stream groups were detected with the Kruskal Wallis test ($p<0.05$)
NS = no significant differences detected
ND = not detected
(S) = significance among sites of difference in loading is due to the influence of discharge.
(1) In loading calculations concentrations less than the detection limit were replaced by 1/10th the method detection limit; and flows reported as 0.000 cms were replaced by 0.0001 cms
(2) As a result of many missing flow data, instantaneous daily loading could not be calculated for all pesticide samples

Streams involved in comparisons:
Irrigation return flows: New West Coulee, Crowfoot Cr., Battersea Drain, Expanse Coulee, Drain S6
High Intensity: Buffalo, Haynes (M1, M6), Ray, Renwick, Strawberry, Stretton,Threehills, Wabash, and West Arrowwood (2 sites) creeks
Moderate Intensity: Blindman River, Trout, Tomahawk, Meadow, Lloyd, Grande Prairie and Block creeks, and KleskunHills Main Drain
Low Intensity: Paddle, Sakwatamau, and Little Paddle rivers, and Willow, Rose, Hines and Christmas creeks and Prairie Blood Coulee

Table 11 Summary of comparisons of pesticide concentrations and instantaneous daily loads in agricultural streams (continued)

Pesticide	Streams in Areas of Moderate Intensity Agriculture					Streams in Areas of Low Intensity Agriculture				
	Detection Frequency (%)	Concentration in µg/L		Instantaneous Load in mg/d[(1)]		Detection Frequency (%)	Concentration in µg/L		Instantaneous Load in mg/d[(1)]	
		Median	Maximum	Median	Maximum		Median	Maximum	Median	Maximum
2,4-D	34.66	0.023	1.972	0.033	330.653	16.75	0.013	0.128	0.045	155.995
2,4-DB	ND	-	-	-	-	ND	-	-	-	-
Alpha-BHC	0.40	0.008	0.008	0.011	4.622	ND	-	-	-	-
Lindane	1.99	0.027	0.03	0.011	7.893	0.96	0.0110	0.0120	0.030	10.109
p,p-methoxychlor	ND	-	-	-	-	ND	-	-	-	-
Atrazine	ND	-	-	-	-	ND	-	-	-	-
Bromacyl	ND	-	-	-	-	ND	-	-	-	-
Bromoxynil	1.99	0.006	0.011	0.011	40.712	3.35	0.0080	0.2670	0.030	4.203
Cyanazine	ND	-	-	-	-	ND	-	-	-	-
Diazinon	ND	-	-	-	-	ND	-	-	-	-
Dicamba	6.37	0.025	0.213	0.031	18.490	5.74	0.0080	0.2450	0.079	16.813
Dichlorprop	ND	-	-	-	-	0.48	0.007	0.007	0.030	4.203
Diuron	ND	-	-	-	-	0.48	0.3870	0.3870	1.206	176.212
Chlorpyrifos	ND	-	-	-	-	ND	-	-	-	-
Ethalfluralin	0.80	0.0025	0.004	0.011	4.622	ND	-	-	-	-
Clopyralid	12.35	0.052	1.79	0.059	80.732	2.88	0.0210	0.0490	0.121	49.533
Malathion	ND	-	-	-	-	ND	-	-	-	-
MCPA	23.90	0.009	0.187	0.018	142.491	14.35	0.0145	1.0050	0.032	4010.757
MCPP	5.18	0.022	0.051	0.013	8.165	2.87	0.0080	0.0170	0.031	4.203
Picloram	26.29	0.0665	13.407	0.023	479.002	10.53	0.0200	0.3270	0.032	443.750
Triallate	4.78	0.0315	0.464	0.012	207.885	ND	-	-	-	-
Trifluralin	2.79	0.007	0.013	0.011	4.622	0.48	0.0040	0.0040	0.030	4.203
Imazamethabenz	6.37	0.112	1.521	0.118	73.668	0.48	0.0260	0.0260	0.302	89.856
Imazethapyr	2.14	0.107	0.182	0.030	29.152	0.52	0.0790	0.0790	0.067	79.860
Number of pesticides per sample		1	9				0	7		
Total concentration per sample		0.009	13.814	0.032	764.433		0	1.46	0.000	4098.712
Instantaneous discharge in cms		0.268	107				0.7	97.3		
Number pesticide samples		251					211			

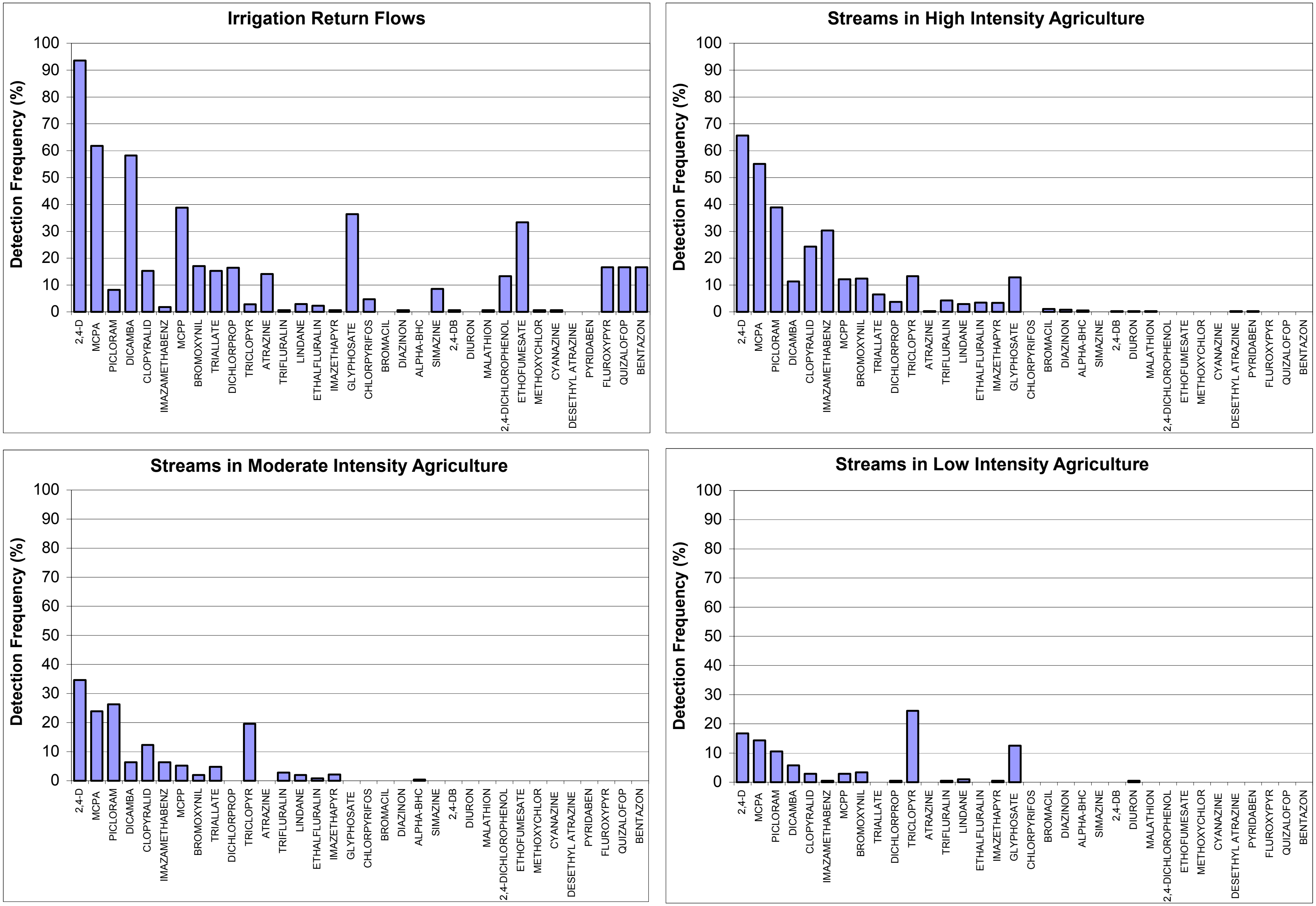
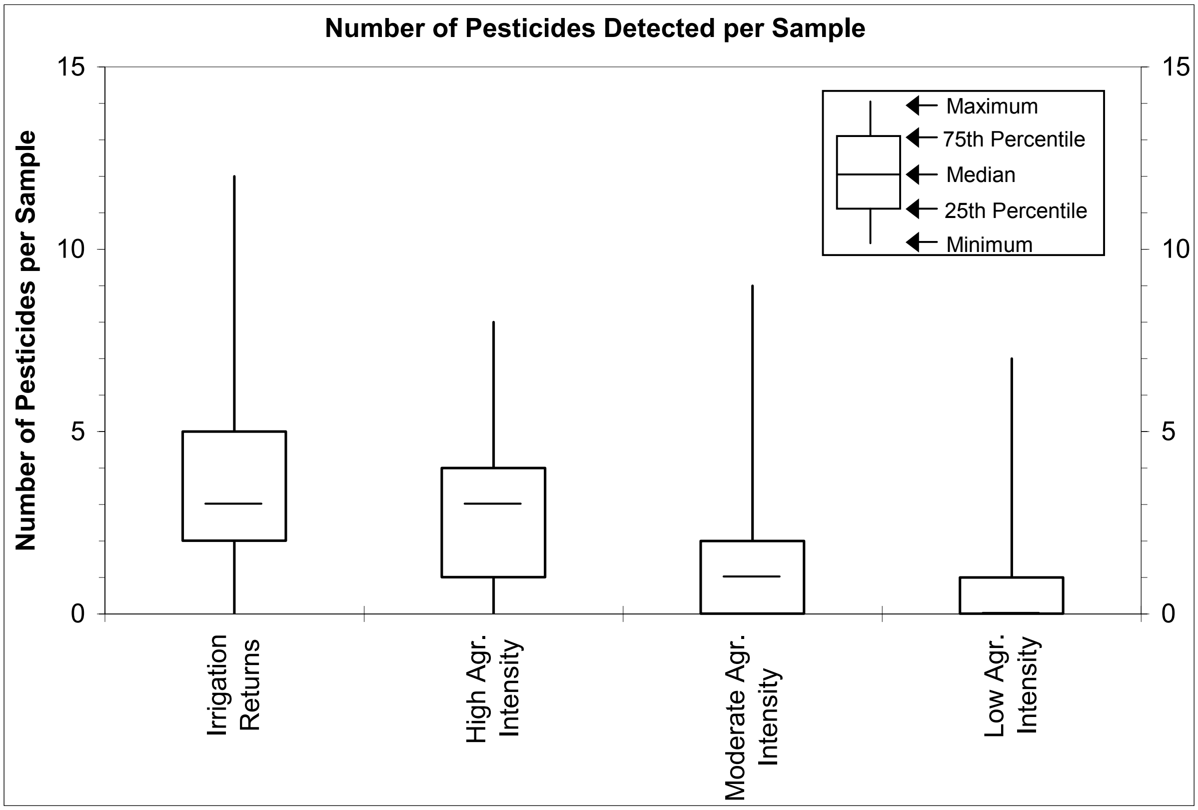


Figure 40 Comparison of pesticide detection frequency in irrigation return flows and streams draining land farmed with different intensity



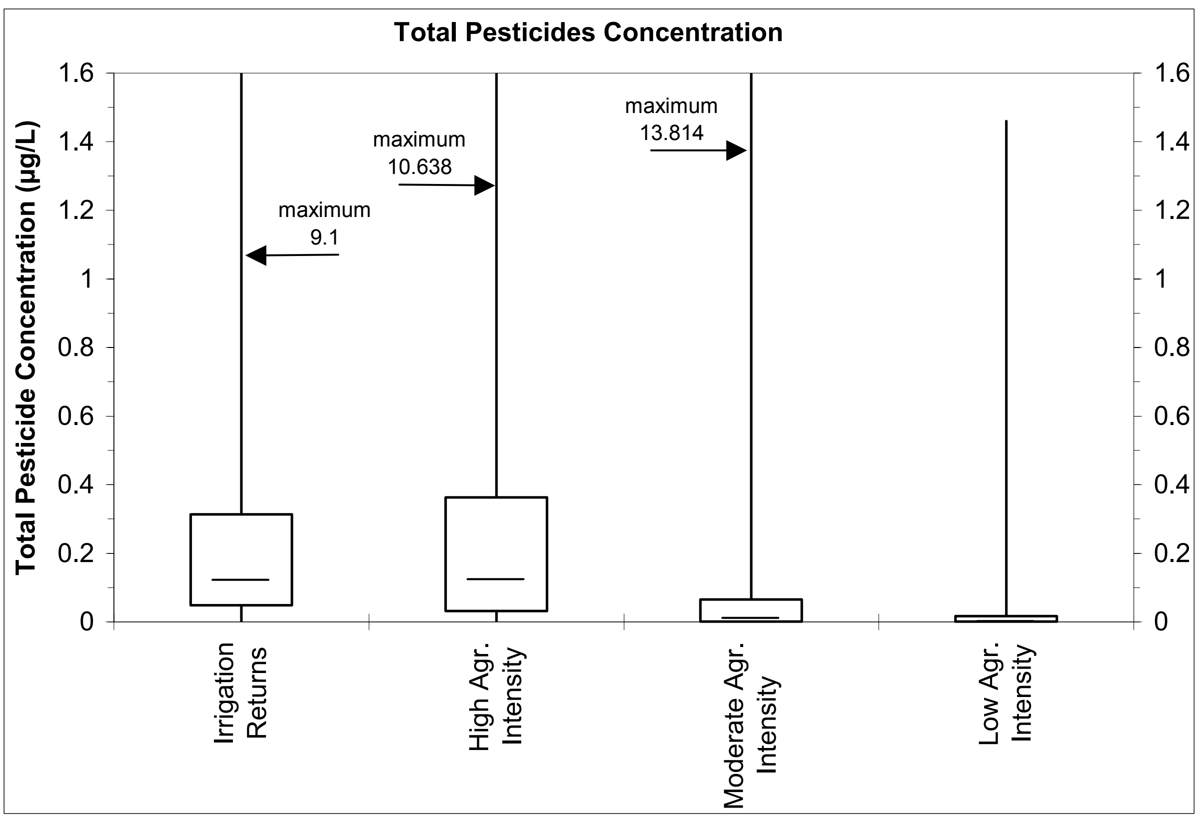


Figure 41 Comparison of pesticide variety and concentrations in irrigation canals and return flows and streams draining land farmed at different intensity

imazamethabenz) compared to medium and low intensity streams (Table 11). However, for pesticides such as dicamba and MCPA, median concentrations and loads are higher in moderate and low intensity streams. These diverging patterns may be the result of a combination of factors such as differences in pesticide use patterns across Alberta due to differences in crops and relative amount of land in crop production, and the influence of differences in hydrologic regime. Much of the runoff in central Alberta, which is mostly intensely farmed (cereal and oils seed production), occurs during spring melt. Pesticides detected at that time are carried over from the previous application year. In the western part of the province where most low and moderate agricultural intensity streams are located (draining some cereal crops and much pasture), intense rain events are more common in late spring and summer and have the potential of moving substantial amounts of pesticides from land to water shortly after the main application period.

5.0 GENERAL DISCUSSION

Our knowledge and understanding of pesticide contamination in Alberta surface waters has evolved considerably from its pre-1995 status described in Anderson (1995). The review of the database maintained by Alberta Environment shows that pesticide detections in Alberta surface waters are common and widespread. Detection patterns are related to sales and use patterns across the province, but they are also influenced by compound-specific characteristics. Influences of localized urban and broad scale agricultural use result in significant spatial differences. Use patterns, combined with climatic influences also bring about seasonal and long-term changes in the prevalence of pesticides in surface waters. Although Canadian Water Quality Guidelines for irrigation and for the protection of aquatic life are exceeded at a relatively low frequency by compounds for which guidelines exist, understanding the full implications of pesticide occurrence and co-occurrence in surface waters remains a complex and largely unresolved issue.

5.1 Sales and Use Patterns and Surface Water Monitoring

Much of the enhanced knowledge of pesticide distribution in surface waters is due to the upgrading of analytical methods and to the structured approach that has been taken to priorize pesticides for monitoring. The regular review of sales records and distribution patterns across Alberta, combined with data on mobility and toxicity, provides an efficient way of determining which pesticides need to be monitored. Ultimately, costs and availability of analytical methods also influence what monitoring takes place. Glyphosate is one of the best examples: it is a top-selling herbicide but has not been widely monitored mainly because of cost considerations. Unlike other top-selling products, the distribution of glyphosate in Alberta surface waters still requires much definition.

Sales records are also important in pesticide-monitoring program design in other jurisdictions. In the USA, sales and usage information provide a foundation to the pesticide monitoring carried out under the National Water Quality Assessment (NAWQA) program (USGS 1999). North South Consulting (2004) indicate that in Canada, Alberta and Quebec are the only provinces to undertake detailed pesticides sales reviews on a regular basis, and to use these reviews in the design of monitoring programs. Other provinces obtain use information from surveys completed by farmers (Ontario) or from information submitted by farmers to crop insurance corporations (Saskatchewan and Manitoba). Although these provinces may conduct site-specific surface water studies, they tend to rely to a large extent on long-term monitoring by Environment Canada.

In contrast, some other countries have taken different approaches. In the Netherlands, local sales or use data describe pesticide contamination in the Rhine and Maas rivers inadequately, because these rivers are influenced by use in several other countries where sales data are often confidential (Faasen 2000). To ensure that all relevant contaminants are being accounted for, broad surveys in which as many substances as possible are examined, are conducted periodically in the Netherlands. Relevant substances are identified in these surveys and they become part of subsequent routine monitoring programs. Such an approach could be applied in Alberta to further validate the list of pesticides monitored in surface waters.

Corresponding patterns between sales and use and prevalence of pesticides in surface waters have been reported elsewhere. Larsen et al (1999) reviewed monitoring data for NAWQA streams and observed that, in general, pesticides that were most used were detected most frequently. In a detailed study of agricultural drainage networks in the Lake Erie Basin, Richards and Baker (1993) also reported that average concentrations were correlated with the amount applied in the basin, although chemical properties of individual compounds and their mode of applications influenced that relationship. In Alberta broad spatial relationships are apparent between pesticide sale distribution patterns, and detection and concentration patterns in surface waters. However, some residues (e.g., triallate, trifluralin) were encountered less often, and others (picloram) more often, than could be expected from their sale volume. This is presumably because these compounds had substantially lower or greater mobility, respectively. Although broad use patterns influence the types and concentrations of pesticides in surface waters, such patterns may be obliterated on a regional scale because some high use pesticides are very volatile and are re-distributed by regional atmospheric transport and distribution patterns. For example, Donald et al. (2001) found no significant differences in 2,4-D and MCPP concentrations in central Saskatchewan wetlands draining land where pesticides were not applied, compared to wetlands where use was moderate or intense.

5.2 Temporal Patterns and Transport Vectors

Seasonal patterns in pesticide contamination of surface waters are commonly reported (e.g., Larsen et al. 1999, Lindeman and Shaw 1997, Richards and Baker 1993, Crosley et al. 1998, Rawn et al. 1999a and b). Typically, higher concentrations and detection frequencies are observed during the open water season and following the main period of application, particularly if it coincides with or is followed by rainstorms. An example of the influence of torrential rains on the mobilization of pesticides has recently been reported by Donald et al (2005). In Alberta, pesticides are typically more prevalent in surface waters in late spring (May-June) and July. Some studies have reported occasional fall peaks presumably related to fall application (Lindeman and Shaw 1997). The occurrence of pesticides in spring runoff is common in Alberta agricultural streams and it is attributed to the carry over of pesticides from the previous growing season. Such initial surge of pesticides in spring is not apparent in data presented for small watersheds in the Lake Erie basin by Richard and Baker (1993), possibly because in that region fall and winter typically have higher stream flow and more runoff events that wash off pesticides and lead to very low stream concentrations in winter and early spring. In Alberta, soils are frozen and often snow-covered for six months of the year essentially immobilizing pesticides and reducing the breakdown rate in soils (e.g., Nicholaichuk and Grover 1983).

Although seasonal patterns are strongly influenced by runoff events which carry contaminants from land to water (Wauchope et al. 1994, Richard and Baker 1993), there are other pathways for surface water contamination. Larney et al. (1999) demonstrated that several herbicides can be transported with eroded soil and warn of potential implications for air and water contamination. In Alberta, it was hypothesized that glyphosate detections in wetlands were due to deposition of dust generated by cultivation of very dry soils (Anderson et al. 2002). Further work on glyphosate confirmed that wind erosion of soil-bound glyphosate was an important transport pathway for this herbicide, especially during dry weather (Humphries et al. draft).

Several studies in Alberta have demonstrated that rain can be a significant contributor of pesticides to surface waters. Byrtus (unpublished) sampled air and precipitation in an urban (Edmonton) and rural (Haynes Creek) area as part of a pilot study in 1997. This study revealed the presence of several herbicides and insecticides in air and rain. Seasonal patterns with peaks in June were pronounced at the rural site where agricultural herbicides were detected most often, but they were much less pronounced at the urban site where turf herbicides (2,4-D and MCPA) were detected most often. These differences may be a reflection of local use patterns. Hill et al. (2002) studied 19 herbicides at 18 locations across Alberta and found the highest herbicide levels associated with small rain events during the agricultural spraying season. They describe spatial patterns in types and concentration of pesticides that are related to use patterns and indicate that some herbicide levels in rain were occasionally higher than drinking water guidelines and often higher than guidelines for the protection of aquatic life. Anderson et al. (2002) estimated that pesticide loading associated with atmospheric deposition was sufficient to explain concentrations of some pesticides detected in central Alberta wetlands, and Donald et al. (1999) related most of the pesticide contamination of Saskatchewan wetlands to rain events. The importance of atmospheric sources of pesticides is also illustrated by Rawn et al. (1999a) who reported high pesticide levels in South Tobacco Creek (Manitoba) at a time when no runoff events were observed, but when pesticide levels in air and rain were high. This led the authors to hypothesize that rain, dry-fall, and gas exchange were the main sources.

The importance of atmospheric deposition to the contamination of surface waters by pesticides raises important questions about the type of beneficial management practices that are required to reduce surface water contamination. Riparian vegetative buffers (e.g., Wenger 1999, USDA 2000), wetlands (e.g., Schulz 2004), and soil incorporation (e.g., Larney et al. 1999) cited for their value at reducing pesticide movement to surface may be less effective for compounds with high water solubility and, or high volatility.

Trends in long-term (multiple years) data can be difficult to establish. In addition to the high and often poorly explained variance in long-term pesticide data there are many factors that can weaken data continuity (e.g., Beard et al. 1999). Changes in study design involving sampling during months with the greatest likelihood of pesticide contamination rather than at quarterly intervals, have been flagged here as a concern for the continuity of the long-term river monitoring data. Step trends appear to be limited to few locations, but may not have been expressed at other sites because of recent drought conditions, which result in lower use and lower movement of pesticides off the application sites. The confounding effect of changes in detection limits on the ability to detect trends was noted earlier (Anderson 1995 and Lindeman and Shaw 1997) and again in this report (MCPA in Oldman River). The major trends which are apparent in over 20 years of monitoring information of major Alberta rivers appear to be related to point source contamination associated with the manufacturing and commercial use of pesticides (i.e., 2,4-D and lindane in the North Saskatchewan River). In a review of the 1976 to 1991 Prairie Provinces pesticide data for 2,4-D, and 2,4,5-T at the Alberta/Saskatchewan border sites Lindeman and Shaw (1997) found that detection frequency had not changed. Crosley et al. (1998) examined lindane (gamma BHC) and alpha BHC data at Prairie Province Water Board sites and other sites in Alberta that had been monitored by Environment Canada and found no change in concentration or detection frequency from 1975 to 1995.

Although the Alberta data set for agricultural streams is relatively short in duration, some trends are apparent. The appearance, peaking and decline of imazamethabenz, and the appearance of clopyralid may be related to changing use patterns in central Alberta (Gary Byrtus, AENV, personal communication). Declines in the number of pesticides detected in Crowfoot Creek may be related to the reduction of atrazine contamination from urban sources (Gary Byrtus, AENV). Although further environmental monitoring is needed to verify these trends over time, the existence of consistent temporal changes in pesticides from some agricultural streams contrasts with the absence of long-term trends in selected pesticides monitored in streams of the Lake Erie Basin (Richard and Baker 1993).

5.3 Urban and Agricultural Influences

In Alberta, the influence of large urban centers on pesticide contamination has not been described as extensively as agricultural influences. One of the main features involved is the higher incidence of insecticides and lawn care herbicides downstream of urban centers (Section 4.3.1). These findings correspond well to those reported by Larsen et al. (1999) for the NAWQA program.

Much of the urban drain or stream data set included in this overview originates from a detailed study of urban drains in the Lethbridge area and a study on Nose Creek, a stream which flows through the north east portion of Calgary. Data for these studies have been summarized by Saffran (draft) and Madawaska Consulting (2002), respectively. During storm events, these urban streams had pesticide levels that were well above peak concentrations recorded in agricultural streams.

Following a survey of urban streams across the USA where insecticides were frequently above aquatic life criteria, Hoffman et al. (2000) concluded that urban areas should not be overlooked when assessing the sources and monitoring for the occurrence of pesticides in surface waters.

Streams draining land where agriculture is intense and pesticide use high, tend to have a greater variety and higher concentrations of pesticides than streams that drain land where pesticide use is less intensive. Such general findings are compatible with those reported in other broad-scale stream surveys (e.g., Larson et al. 1999). Although agricultural uses dominate in our selection of agricultural watersheds, it is recognized that domestic, municipal and industrial uses also occur in most watersheds and could contribute to pesticide contamination of surface waters. The magnitude of such contributions remains to be defined.

5.4 Significance of Pesticides in Surface Waters

Comparison of ambient concentrations with surface water quality guidelines offers a straightforward means for a preliminary assessment of the significance of pesticides in surface waters and the potential for environmental impacts. CCME guidelines, adopted in Alberta, are the most common pesticide guidelines available for the protection of aquatic life and irrigation water. Guidelines for the protection of aquatic life define safe levels for various contaminants and have a built in safety factor of an order of magnitude (Environment Canada 2004a); guidelines for irrigation water define the maximum acceptable toxicant concentration and above these limits harm may result to sensitive crops (Environment Canada 2004 b). In Alberta, non-compliance with guidelines for the protection of aquatic life are relatively infrequent, but the fact that in some instances, 2,4-D, chlorpyrifos and lindane exceed the guidelines by an order of magnitude is cause for concern because, since the built-in safety margin is exceeded, chronic effects are likely to occur. Some herbicides such as dicamba and MCPA exceed irrigation guidelines chronically, although, in general, the amount by which guidelines are exceeded is relatively small, injuries to sensitive crops may occur.

Non-compliance with pesticide guidelines is not unique to Alberta; studies in Canada, the USA, and other parts of the world have reported similar incidences. Following a 5-year study of Saskatchewan wetlands, Donald et al. (1999) reported pesticide levels that exceeded guidelines for the protection of aquatic life in 9 to 24% of the wetlands. Lindane and triallate exceeded the guidelines most frequently, but non-compliance was also reported for 2,4-D and MCPA. In streams that are part of the NAWQA program in the USA, Larsen et al. (1999) reported exceedences of USEPA standards and criteria for drinking water (i.e., alachlor, atrazine, cyanazine, simazine, diazinon, dieldrin, and alpha HCH). However, Gilliom et al. (1999) are careful to point out that annual average concentrations in streams – upon which drinking water criteria are based- are only exceeded for atrazine and cyanazine in no more than two agricultural streams. Nevertheless, aquatic life criteria are exceeded in many samples and at 70% of the sites (Larsen et al. 1999, Gilliom et al. 1999) for pesticides such as atrazine, azinphos-methyl, chlorpyrifos, cyanazine and malathion. The occurrence of two or more compounds exceeding aquatic life criteria in the same sample or at the same site was flagged as cause for concern in these streams. In a review of the worldwide primary literature on aquatic non-point source insecticide pollution, Schulz (2004), reported over 20 insecticides with numerous exceedences of published CCME, USEPA and California guidelines or criteria.

Because guidelines are often incomplete or unavailable for pesticides detected in Alberta, and because guidelines apply to single compounds, assessing the significance to aquatic life or irrigation of pesticide residues in surface waters is complex, especially when multiple contaminants co-occur. Toxicity testing on single species, mesocosm studies, and field studies have been carried out to try and understand the effects of pesticides.

Laboratory testing of single test species generally involves acute (survival) or relatively short-term chronic (growth, and reproduction) tests. Such studies typically reveal a great deal of variability in the toxicity of single pesticides to different test species (e.g., Delorenzo et al. 2002, and Peterson et al. 1994). Because the potential for synergistic effects among contaminants is a concern, numerous laboratory studies have attempted to define the effects of pesticide mixtures on aquatic organisms (e.g., Faust et al. 2000, Deneer 2000, Geest et al. 2000, Delorenzo and Serano 2003 and Goudey 2001). Deneer (2000) reviewed results of 26 aquatic toxicity studies dealing with 202 mixtures and concluded that, when dealing with mixtures with similar modes of action, the joint effect can be predicted by a model referred to as “concentration addition” in more than 90% of the cases. According to this model, overall effective concentration can be calculated by adding up all effective concentrations (expressed as fraction of effect concentration, or toxicity units). Deviations from the model predictions were noted most frequently for combinations of an organophosphorus ester or a carbamate with either another organophosphorus ester or a synthetic pyrethroid. Depending on the nature of the compounds and test organisms, deviations included either increases or reduction in effects. Faust et al. (2000) are of the opinion that concentration addition provides a reasonable worst-case estimation of effects to be considered for regulatory purposes. Furthermore, and in accordance with Deneer's findings, they believe that the occurrence of combined effects that are much stronger or weaker than expected from the concept of concentration addition, or independent action, are exceptions. Yet such exceptions are reported in the literature. Results from Delorenzo and Serrano (2003) who tested the toxicity of atrazine, chlorpyrifos and chlorothalonil on a phytoplankter showed both additive (atrazine + chlorpyrifos) and synergistic (atrazine and chlorothalonil) responses. Goudey (2001) tested acute and chronic responses of mixtures of pesticides which are common in Alberta surface waters of a range of test organisms. No synergistic effects were reported. Effects for herbicide mixtures were observed at concentrations that were much higher than ambient concentrations, but effects for insecticide mixtures involving diazinon were recorded in the range of maximum concentrations observed in Alberta surface waters. This suggests that detrimental effects may occur in some Alberta surface waters.

Single species toxicity studies provide useful initial information on potential toxicity to aquatic species, but they are generally too short in duration and under conditions too simplified to be representative of natural ecosystems. In recent years mesocosm studies have gained popularity in the assessment of effects of pesticides on aquatic systems (Lythe and Lythe 2002, Solomon et al. 1996, Forsyth et al. 1997, Groenendijk et al. 1994, Traas et al. 2004). However, Maund et al. 1997 caution that interpreting the ecological significance of effects measured in these studies can be difficult because ecological factors can influence the outcome of perturbations in the real world. Schindler (1998) further points out that small-scale experiments often give highly replicable, but spurious answers; appropriate spatial scales to include all communities and appropriate temporal scales to account for slow-responding organisms and biogeochemical processes are necessary to understand ecosystem responses to stressors.

Ultimately, assessments of actual aquatic ecosystem responses are needed to define the effects of chemical exposure. Considering species diversity, diverging responses and interferences with uncontrolled variables, convincing conclusions are elusive. In a review of field studies on exposure, effects and risk mitigation of aquatic non-point source insecticide pollution, Schulz (2004) found that only 15 of 42 field studies conducted to determine effects of ordinary farming practices revealed a clear relationship between quantified, non-experimental exposure and observed effects *in situ* on organism abundance, drift, community structure or dynamics. Azinphos-methyl, chlorpyrifos and endosulfan were most frequently found at concentrations above those shown to reveal effects *in situ*. Schultz (2004) provides field effect concentrations for 9 insecticides. Two of these, azinphos-methyl and chlorpyrifos have been monitored and detected in Alberta, but at concentrations well below those shown to induce effects under field conditions.

5.5 Data Gaps and Emerging Issues

Although many efforts have been expended in the monitoring of pesticides in Alberta surface waters, other aquatic ecosystem components such as sediments or aquatic biota have received little attention. In general, current use pesticides are less likely to concentrate in sediments or living organisms than historically used organochlorine compounds, but some may. The USGS

(2000) identified hydrophobicity and persistence as two key features that control the accumulation in sediment and aquatic biota. Pesticides that have a potential to accumulate in sediments and aquatic biota have a water solubility of less than 1 mg/L or an octanol-water partitioning coefficient (Kow) greater than 1,000 and a soil half-life greater than 30 days. Chlorpyrifos, lindane, methoxychlor and trifluralin are compounds that have these characteristics and have been detected in sediment and biota in the USA; they are also compounds that are or have been used extensively in Alberta.

Much of the monitoring of surface waters has concentrated on the major rivers and on smaller streams in agricultural areas. Wetlands are underrepresented. Knowledge on contributions from large urban centers, and non-agricultural uses in rural areas needs to be expanded. There is also a need to improve our understanding of the behaviour of pesticides under Alberta conditions, particularly as it pertains to persistence in soils, water and sediment. Critical to the development of holistic BMP's is the need to better understand the relative importance of atmospheric deposition and surface runoff as vectors of pesticides to surface waters.

Anticipating the effects of pesticides on aquatic life and other water uses is likely to remain difficult. As science advances, unexpected effects are discovered. Eagle (1988) reviewed possible effects of pesticides in current use in the 80's, and concluded that these should have no environmental effects. However, as more information has become available it has become apparent that acute and chronic toxicity can be an issue. More recently, several pesticides have been identified as having endocrine disrupting properties (SCESD 2000, Choi et al. 2004).

In a recent review of emerging contaminants and current issues Richardson (2003) flags several issues pertaining to pesticides. These include the identification and characterization of effects of break down products, chiral pesticides, and the potential effects of various additives.

5.6 Comparisons With Other Jurisdictions

Meaningful comparisons of surface water pesticide data among jurisdictions are difficult because crops and pest species vary with geographic and climatic gradients and may require different suites of pesticides. Even when the variety of pesticides in use is rather similar, use intensity may differ, and the mobility and persistence of pesticides may be influenced by climatic differences. Finally the scope and intensity of pesticide monitoring programs can significantly influence the reported level of contamination. For example, the reported level of contamination can be influenced considerably by detection limits, the number of compounds analysed and how well they represent pesticides in current use, the timing of the sampling relative to use patterns and climatic seasonality.

Despite these limitations, there are commonalities among results reported in various Canadian provinces (e.g., North/South Consulting 2003, 2004, Environnement Quebec web site) and broad-scale monitoring programs in the United States (Gilliom et al. 1999; Larson et al. 1999):

- Pesticides are commonly reported in surface waters from agricultural and urban areas;
- The degree of surface water contamination is related to pesticide use intensity;

- Seasonal patterns in pesticide contamination are commonly reported and are linked to use patterns and climate;
- Exceedences of guidelines for the protection of aquatic life, and to a lesser extent, of drinking water guidelines are reported, and in some cases several pesticides in one sample or at one site exceed guidelines;
- Assessing the actual significance of low-level pesticides in aquatic ecosystems is recognized as a challenge by all.

More detailed data comparisons among Canadian provinces are hampered by differences in scope among provincial monitoring programs. Some of these difficulties are illustrated for the Prairie Provinces, which based on their similar climate and crops should be reasonably comparable with respect to pesticide contamination of surface waters. Based on a recent review by North/South Consulting (2004) on pesticide monitoring activities in Canada it would appear that Alberta has one of the most comprehensive approaches to monitoring pesticide sales and surface water contamination in the country. Overall use intensities tend to be comparable among the three Prairie Provinces, yet a review of provincial pesticide data for surface waters carried out by North/South Consulting (2003, 2004) suggests that the level of contamination in Alberta is considerably higher than in the two other provinces. A closer examination of provincial data used in these comparisons indicates that provincial monitoring programs differ considerably in scope and intensity. They range from a few sites on major rivers in Saskatchewan, to a larger number of sites, primarily on large rivers and lakes, in Manitoba, to an even larger number of sites covering a wide range of water bodies in areas of high pesticide use in Alberta. Differences in method detection limits contribute further to differences in reported level of contamination. For example, while 2,4-D detection frequencies reported in Alberta (53.43%) are considerably higher than those reported in Saskatchewan (14.8%) and Manitoba (15.5%), detection limits in Alberta (0.005 µg/L) are considerably lower than in the 2 other provinces (0.04 and 0.05 µg/L in Saskatchewan and Manitoba, respectively) (North/South Consulting 2004). The use of lower detection limits provides a better indication of surface water contamination and improves the ability to notice upward trends at an early stage, but comparisons among provincial databases should not be attempted without prior standardization of the data. If only 2,4-D levels greater than 0.05 µg/L (i.e., Manitoba detection limit) are considered for LTRN sites in Alberta, then the detection frequency for 2,4-D in Alberta is 9%, which is in line with the two other provinces. The overall detection frequency for all 2,4-D detections at LTRN sites is 36%; this indicates that about 27% of 2,4-D detections in Alberta occur at concentrations below the detection limits of the two other provinces. Furthermore, site-specific research studies in Manitoba and Saskatchewan indicate that at least some water bodies have high 2,4-D detection frequencies. Some examples include Grover et al. (1997) who reported a 2,4-D detection frequency of 93 to 100% in farm dugouts; Donald et al. (2001) 88 to 94% in Saskatchewan wetlands; and Rawn et al. (1999) 48 to 64% in the Red River and its tributaries.

The specific implications for aquatic life of surface water contamination by low levels of pesticides are elusive. Effects on aquatic life, though difficult to assess with current guidelines, are believed to be subtle and of a chronic or sub-chronic nature (Gilliom et al. 1999; Larson et al. 1999, Giroux 2002, North South Consulting 2003, 2004). Prince Edwards Island is one of the few jurisdictions in Canada where acute toxicity (fish kills) has been observed, linked to pesticide runoff, and used as a trigger for investigations on pesticides (North South Consulting 2004).

6.0 CONSIDERATIONS FOR FURTHER PESTICIDE MONITORING IN ALBERTA SURFACE WATERS

Following are considerations that would help maintain an effective and efficient pesticide-monitoring program of surface waters in Alberta.

- Continue the regular review of pesticide sales records and distribution patterns across Alberta, and combine this information with theoretical information on mobility and toxicity in order to determine which pesticides should be targeted for monitoring.
- Consider pilot studies to assess pesticide contamination of water, sediment and biota in surface waters at selected locations. Monitoring budgets do not keep pace with costs associated with increasing analytical capabilities. For example, although the capability to monitor 63 pesticides routinely has existed since 2002, such analyses have been restricted to a few of the long-term river network sites because of budgetary constraints. Furthermore, the number of samples collected annually has declined substantially since 2002. Pilot studies, utilizing lowest practical method detection limits, could be conducted at a few selected sites located primarily in high use areas could:
  - involve broad scale pesticide scans to ensure that the routine target list captures all important pesticide contaminants in aquatic environments;
  - assess the presence of high use compounds not on the routine target list (e.g., glyphosate, mancozeb, EPTC, triochlorfon, vinclozolin, and thiram). Although tralkoxydim and sethoxydim are also in high use, there are issues with the analytical methodology and difficulties determining these compounds; and
  - assess the presence and persistence of pesticides in aquatic sediments and biota, soils and atmospheric deposition.
  - assess the presence and persistence of chemicals which are added to active ingredients to facilitate the use or enhance the effectiveness of active ingredients (i.e., formulants and adjuvants).
  - assess actual aquatic ecosystem responses to ambient concentrations of pesticide mixtures, alone and in combination with other man-made environmental contaminants.

  The outcome of these pilot studies would then allow the upgrading of routine programs in a more informed and cost-effective manner than is currently possible by applying blanket changes to the entire monitoring program.
- Maintain a comprehensive QA/QC program to document and support the accuracy and precision of ambient data.
- Exert particular caution not to erode the continuity of data sets from established long-term monitoring programs such as the long-term river monitoring network or the AESA program (e.g., as a result of reductions in pesticides analyzed, increases in detection limits, changes is sampling frequency or timing). Such continuity is

particularly vulnerable to alterations in study design involving changes or reduction in sampling scope and intensity.

- Better information is needed on pesticide transport vectors, such as atmospheric deposition. Such information is key to the validation of the effectiveness of beneficial management practices to reduce off-site movement of pesticides.
- Ongoing information is needed on pesticides in wetlands. In agricultural areas, the drainage basin of wetlands is often completely converted to cultivated land making these water bodies particularly vulnerable to contamination. Wetland data are needed to validate the effectiveness of beneficial management practices to reduce off-site movement of pesticides.
- In addition to continued monitoring, consideration needs to be given to the development of management plans for compounds which often exceed water quality guidelines (e.g., dicamba and MCPA in irrigation return flows).
- Pesticide contamination from urban centers warrants further investigation. Pesticides contributed by drains from the Lethbridge urban area have been described in detail during runoff episodes. Similar work is needed to describe the influence of urban storm water runoff from other major population centers in the province. Such information, in conjunction with detailed urban pesticide use data, is needed to support education, the development of management plans, and the implementation of beneficial management practices.
- Pesticide contamination from non-agricultural uses in rural areas (e.g., domestic uses, spraying along roadsides, pipelines, power lines, and railways rights of way, and irrigation canals) needs to be documented to assess relative contributions from such activities and the need for improvements in management practices.
- There is an ongoing need for surface water quality guideline development of pesticides; currently commonly detected pesticides such as 2,4-D, glyphosate, picloram, MCPP, clodinafop, imazamethabenz, triclopyr and diazinon have only partial guidelines or no guidelines at all. There is also an increasing need for practical, sensitive tools to assess the cumulative environmental significance of pesticides and other man-made chemicals. The utility of using toxic units to evaluate mixtures should be explored further.

7.0 SUMMARY AND CONCLUSIONS

As part of its evaluation and reporting responsibilities, Alberta Environment reports on pesticide concentrations in surface waters on a regular basis.

The overall objective of this report is to provide an overview of the extent and nature of pesticide contamination in Alberta's surface waters based on data obtained from 1995 to 2002.

In 1995 Alberta Environment updated its approach to pesticide monitoring. To maintain currency with use patterns, pesticides to be monitored in surface waters are re-evaluated every five years based on provincial sales reviews, information on environmental behaviour and toxicity and results of surface water monitoring programs. Improved analytical methods, which were also implemented in 1995, allowed the measurement of trace level concentrations that could be expected in surface waters.

Methods

Included in this overview are all pesticide data collected in surface water monitoring programs carried out by Alberta Environment and partners, and stored on Alberta Environment's Water Data Server. Particularly significant partnerships in terms of volume of data contributed include the monitoring of agricultural streams carried out under the Alberta Environmentally Sustainable Agriculture (AESA) program led by Alberta Agriculture, Food and Rural Development, and the Oldman River Water Quality Initiative.

The data set consists of 3055 samples for 326 sites mostly in the 'White Zone' of the province where most agricultural and urban pesticide uses occur. The data set is very heterogeneous because it contains information from many different programs with different study designs. Depending on study objectives rivers, creeks, lakes, wetlands, irrigation streams, and urban streams or drains were sampled on a fixed-time or pre-determined schedule, following a flow-weighted approach, or during runoff events only; sites were sampled once to nearly 100 times over the seven-year period.

The data set is homogeneous with respect to the list of pesticides analysed. From 1995 to and including 2001, 40 active ingredients, breakdown products, and isomers (25 herbicides, 14 insecticides and one fungicide) were monitored consistently in all samples. In 2002, as a follow-up to the second provincial pesticide sales review, an additional 23 active ingredients, and breakdown products (15 herbicides, 3 insecticides and 5 fungicides) were analysed in all samples. From 2000 on, glyphosate, its breakdown product amino-methyl phosphonic acid (AMPA), and glufosinate were analysed in selected projects.

All analyses were by gas chromatography/mass spectrometry (GC/MS)-ion trap. Detection limits for most compounds ranged from 0.005 to 0.05 µg/L; but were higher for azinophos-methyl and glyphosate (both 0.2 µg/L) and AMPA and glufosinate (both 1 µg/L). Concentrations reported in the database are not corrected for recovery.

In addition to routine Quality Assurance/Quality Control (QA/QC) procedures in the laboratory, QA/QC samples were incorporated in individual field programs. They included 48 split samples, 20 duplicates and 5 triplicates, 15 field and 13 trip blanks and 23 spiked samples.

Pesticide contamination is described in terms of pesticide detection frequency, total pesticide concentration, concentration of individual compounds, and number of pesticides detected per site or per sample. A pesticide index, adapted from the CCME formulation, was used to summarise site-specific data sets and conduct relative comparisons of pesticide contamination among sites; index scores are ranked in 5 categories: excellent, good, fair, marginal, poor. The significance of pesticide detections was evaluated using Canadian Water Quality Guidelines.

Results

QA/QC Results and Implications

The analysis of QA/QC samples helps put the accuracy and precision of data into perspective. Pesticide recovery rates are generally less than 100% and the likelihood of false negatives (not reporting a pesticide residue that is actually present) is greater than false positives (erroneously reporting the presence of a residue). This situation is inherent in other pesticide databases for surface waters. It implies that reported concentrations and detection frequencies are probably biased low, and that the exceedence of water quality guidelines could be higher than reported.

Pesticides Detected in Surface Waters

Pesticides were detected in 65% of all samples. Analyses were conducted for 63 pesticides and 44 were detected overall. These comprise 33 herbicides, 10 insecticides and one fungicide. Most of the compounds that were not detected were only monitored in 2002. Provincially, 2,4-D was detected most frequently (53 % of samples). Seven compounds were reported in 10% to 50% of the samples (clopyralid, dicamba, glyphosate, MCPA, MCPP, picloram, and triclopyr); 15 were reported in 1 to 10% of the samples (4-chloro-2-methylphenol, 2,4-dichlorophenol, AMPA, atrazine, bentazon, bromacil, bromoxynil, clodinafop-propargyl, diazinon, dichlorprop, triallate, ethofumesate, fluroxypyr, imazamethabenz, imazethapyr, lindane, and quizalofop) and the remaining 19 occurred in less than 1% of the samples (2,4-DB, alpha-BHC, azinphos-methyl, carbathiin, chlorpyrifos, cyanazine, desethyl atrazine, deisopropyl atrazine, dimethoate, diuron, ethalfluralin, malathion, methoxychlor, imazamox, pyridaben, quinclorac, simazine, terbufos, and trifluralin).

Generally, pesticides that had the highest sale records were also the most frequently detected. Some notable exceptions include ethalfluralin, trifluralin, and carbathiin which have a high sale volume, but are reported rather infrequently, and picloram which has a relatively low sale volume, but is detected fairly frequently. Pesticide characteristics related to mobility and persistence are believed to override the influence of use patterns in these cases.

Pesticides with the highest detection frequency tended to have a wider range of concentrations. Median concentrations for most herbicides were low, ranging from the method detection limit (MDL) to 0.1µg/L, but for bromacil, diuron, imazamethabenz, glyphosate, simazine, and some metabolites, medians were higher (0.1 to 1 µg/L range). Median insecticide and fungicide concentrations ranged between the MDL and 0.04 µg/L.

Spatial Patterns Across the Province

There is a distinct north-south pattern in pesticide detection frequency, which is consistent with pesticide use intensity: much lower detection frequencies were recorded in northern basins (Hay, Slave, Peace, Athabasca, and Beaver river basins) than southern basins (North Saskatchewan, Battle, Red Deer, Bow, Oldman, and South Saskatchewan river basins, and Sounding Creek basin).

The pesticide index rates water bodies according to 'poor', 'marginal', 'fair', 'good' or 'excellent' based on the frequency, variety and magnitude of pesticide detections and allows for broad comparisons among water bodies. Pesticide detection frequency, detected concentrations and number of pesticides detected per sample were highest in irrigation return flows and in urban streams; over 75% of these water bodies have a pesticide index score that ranges from 'marginal' to 'poor'. Compared to these water bodies, lakes, rivers, wetlands, creeks and irrigation canals have generally lower pesticide concentrations, frequency of occurrence and variety. Ninety-four percent of lakes have index scores that range from 'good' to 'excellent'; 97% of the rivers range from 'fair' to 'excellent'; 97% of wetlands and streams range from 'marginal' to 'excellent' and 86% of irrigation canals range from 'good' to 'excellent'.

Seasonal Trends

Provincially there is a tendency towards higher detection frequency, total concentrations and number of pesticides detected per sample from March to September with June and July being peak months. This seasonal pattern corresponds broadly with the timing of ice break-up and snowmelt runoff (March-April), the main period of application (May –July) and the greatest likelihood of significant rainfall (June – July) in the province. Typically, highest concentrations are measured following rains, coinciding with or following shortly after the main period of application. Both runoff and atmospheric deposition contribute to the pesticide load.

Long-term Trends

Long-term trends were evaluated at sites that have been sampled consistently over time (i.e., 22 long-term river network {LTRN} sites, 13 tributary network sites, and 26 agricultural streams).

- Monitoring of 2,4-D, lindane and MCPA at LTRN sites on the North Saskatchewan, Bow, and Oldman rivers was initiated by Environment Canada (EC) in the 1970's. The continuity of the data set was damaged by an increase in detection limits, when AENV took over the monitoring program from Environment Canada (EC) in 1986. As a result only post-1995 AENV data can be compared with EC data. Trends in detection frequency and concentrations were apparent in the North Saskatchewan River below Edmonton for 2,4-D (concentrations reported by EC > AENV) and lindane (concentrations reported by EC < AENV) and were in both cases related to industrial point source problems which have since been rectified.
- Significant year-to-year differences in 2,4-D, MCPP and MCPA have been observed at Bow River sites since 1995. The higher pesticide concentrations at this site since 2000 are due to the switch in 2000 from quarterly sampling to sampling in May, June, July and August. This change in design targets a time of year with higher likelihood

for frequent detections and higher concentrations. LTRN sites on other rivers did not exhibit a similar trend.

- No significant year-to-year differences were observed at tributary network sites.
- Noteworthy significant year-to-year differences were observed in several agricultural streams:
  - A decline in atrazine in Crowfoot Creek, an irrigation stream supplied with water from the Bow River via a diversion in the Calgary area, appears to be related to the decline in use of a domestic sterilant in the Calgary area.
  - In central Alberta streams, the decline in imazamethabenz and increase of clopyralid levels may be due to changing use patterns.
  - Threehills, Ray and Haynes creeks exhibited lowest ranges in total pesticide concentrations in 2002, possibly because of reduced use and absence of precipitation and runoff during this severe drought year.

Urban and Agricultural Influences

Urban influences from Lethbridge, Calgary, Red Deer, and Edmonton were evaluated by comparing pesticide records at LTRN sites upstream and downstream of the cities. Pesticide detections downstream of the cities were generally more diverse and frequent than upstream. Some of the pesticides encountered more frequently downstream included the lawn care herbicides 2,4-D, dicamba, and MCPP and the insecticides lindane, diazinon, and chlorpyrifos. Several pesticides occurred at significantly higher concentrations downstream of three of the four cities: 2,4-D, and bromoxynil below Lethbridge; 2,4-D, MCPP and diazinon below Calgary; and lindane below Edmonton. Although total pesticide concentration was significantly higher downstream of Red Deer, the concentration of single pesticides did not increase significantly downstream of the city.

Agricultural influences were evaluated by comparing groups of streams with different pesticide use intensity (i.e., irrigation return flows, high, medium and low intensity streams). The total number of pesticides detected in each stream group, and the number of pesticides detected per sample were highest in irrigation return flows and declined with pesticide use intensity. Some pesticides such as methoxychlor, atrazine, cyanazine, and chlorpyrifos were only reported in irrigation return flows. Significant differences also occurred in total pesticide concentrations with the highest median concentrations in irrigation return flows and high agricultural intensity streams. Although the amount of active ingredient used for agricultural purposes in agricultural watersheds generally exceeds other uses, it is recognized that most agricultural watersheds also have domestic, municipal and industrial pesticide uses which could contribute to surface water contamination.

Significance of Detections Related to Guidelines

An assessment of the significance of pesticide detections in surface waters was made by comparing concentrations with Canadian Water Quality Guidelines for the protection of various uses. 2,4-D was the only pesticide that exceeded the drinking water guidelines. This single incidence of non-compliance occurred in a Lethbridge urban drain and, therefore, has no direct implication to treated drinking water. Irrigation guidelines were exceeded in 26.9% of the samples by dicamba, MCPA, bromacil or bromoxynil. Guidelines for the protection of aquatic life were exceeded in 3.5% of the samples by some detections of chlorpyrifos, lindane, triallate, 2,4-D, atrazine, dicamba, or MCPA, and some of the detections of 2,4-D, chlorpyrifos, and lindane exceeded the guidelines by more than the built-in safety factor of an order of magnitude. This level of exceedence implies a possibility of chronic effects in sensitive species. Four insecticides (chlorpyrifos, lindane, malathion and methoxychlor) with USEPA criteria for aquatic life exceeded these criteria in one sample each. Although guidelines are unquestionably useful they are not available for 22 of the 44 pesticides detected in Alberta and many of the remaining pesticides have only a partial set of guidelines. Furthermore, guidelines apply to single compounds and 50% of the samples in this data set had multiple pesticide occurrences or multiple incidences of non-compliance. These limitations create uncertainties about how comprehensively pesticide risk in surface waters can be assessed using current guidelines.

Comparison to Other Jurisdictions

The level of pesticide contamination in Alberta surface waters appears to be comparable to that of other jurisdictions with similar use patterns. Actual comparisons of pesticide data among jurisdictions can be seriously biased by differences in study design, climate, and types of pesticides used. Nevertheless, other jurisdictions commonly report the detection of pesticides in surface waters that drain land where pesticides have been applied. Detections tend to exhibit seasonal patterns and relationships with use patterns and use intensity. Incidences of non-compliance with guidelines are reported in other Canadian provinces and in the United States.

Conclusions

The review of the database maintained by Alberta Environment shows that pesticide detections in Alberta surface waters are common and widespread. Detection patterns are related to sales and use patterns across the province, but they are also influenced by compound-specific characteristics. Influences of localized urban and broad scale agricultural use result in significant spatial differences. Use patterns, combined with climatic influences also bring about seasonal and long-term changes in the prevalence of pesticides in surface waters. Although Canadian Water Quality Guidelines for irrigation and for the protection of aquatic life are exceeded at a relatively low frequency by some compounds, understanding the full implications of pesticide occurrence and co-occurrence in surface waters remains a complex and largely unresolved issue.

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Appendix A Listing of sites sampled from 1995 to and including 2002

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
ATHABASCA RIVER DRAINAGE BASIN					
3	AB07AF1180	Lake	Lake	BLACKMUD LAKE	EUPHOTIC COMPOSITE
1	AB07CB0780	Lake	Lake	CALLING LAKE	EUPHOTIC COMPOSITE
3	AB07BG0030	Lake	Lake	LESSER SLAVE LAKE	WEST BASIN EUPHOTIC COMPOSITE
3	AB07BJ0040	Lake	Lake	LESSER SLAVE LAKE	EAST BASIN EUPHOTIC COMPOSITE
3	AB07BB0250	Lake	Lake (AESA)	THUNDER LAKE	EUPHOTIC COMPOSITE
2	AB07AH0840	Creek	Agric. Creek (AESA)	CHRISTMAS CREEK	AT ATHABASCA RIVER BRIDGE ON HWY #658 (NEAR BLUE RIDGE)
21	AB07BC0540	Creek	Agric. Creek (AESA)	WABASH CREEK	NEAR PIBROCH NW OF WESTLOCK
3	AB07GH0120	Creek	Creek	STURGEON CREEK	U/S OF VALLEYVIEW
16	AB07AD0110	River	LTRN	ATHABASCA RIVER	U/S OF HINTON, 0.2 KM U/S OF MUSKUTA CREEK - CENTRE CHANNEL GRAB
37	AB07BE0010	River	LTRN	ATHABASCA RIVER	AT TOWN OF ATHABASCA
4	AB07CC0030	River	LTRN	ATHABASCA RIVER	U/S FORT MCMURRAY, 100 M ABOVE THE CONFLUENCE WITH HORSE RIVER - LEFT BANK ARC KM 297.6
25	AB07DD0010	River	LTRN	ATHABASCA RIVER	AT OLD FORT - RIGHT BANK
2	AB07DD0105	River	LTRN	ATHABASCA RIVER	D/S OF DEVILS ELBOW AT WINTER ROAD CROSSING
1	AB07BD0070	River	River	ATHABASCA RIVER	ABOVE TOWN OF SMITH AT HWY #2 BRIDGE - RIGHT BANK
2	AB07BE0340	River	River	ATHABASCA RIVER	AT TOWN OF ATHABASCA 1 KM U/S OF HWY #813 BRIDGE - CENTRE ARC KM 687.0
2	AB07BB0050	River	River (AESA)	LITTLE PADDLE RIVER	AT BRIDGE ON HWY #43 (NEAR MAYERTHORPE)
43	AB07BB0060	River	River (AESA)	PADDLE RIVER	AT BRIDGE (NEAR ANSELMO)
2	AB07AH0010	River	River (AESA)	SAKWATAMAU RIVER	NEAR THE CONFLUENCE WITH ATHABASCA RIVER (NEAR HWY #43)
11	AB07AG0400	River	Tributary Network	MCLEOD RIVER	AT WHITECOURT RIGHT BANK ABOUT 100 M D/S OF HWY #43 BRIDGE
21	AB07BC0010	River	Tributary Network	PEMBINA RIVER	AT ROSSINGTON LEFT BANK APPROX 10 M D/S OF HWY #18 BRIDGE
21	AB07BF0020	River	Tributary Network	SOUTH HEART RIVER	AT HIGH PRAIRIE - RIGHT BANK 5 METERS D/S OF SECONDARY ROAD #749
BATTLE RIVER DRAINAGE BASIN					
1	AB05FA0480	Lake	Lake (AESA)	PIGEON LAKE	EUPHOTIC COMPOSITE
25	AB05FE0060	Creek	Agric. Creek (AESA)	BUFFALO CREEK	AT HWY 41
24	AB05FA0265	Creek	Creek	PIPESTONE CREEK	NEAR WETASKIWIN
5	AB05FA1820	Creek	Creek	PIPESTONE CREEK	AT HWY 795
10	AB05FA1830	Creek	Creek	PIPESTONE CREEK	AT HWY 2
9	AB05FA1860	Creek	Creek	PIPESTONE CREEK	AT LARCH TREE PARK, D/S OF HWY 2A
10	AB05FA1870	Creek	Creek	BIGSTONE CREEK	AT HWY 2
5	AB05FA1880	Creek	Creek	BIGSTONE CREEK	AT HWY 2A, NEAR WETASKIWIN
17	AB05FD0011	Creek	Tributary Network	RIBSTONE CREEK	NEAR HEATH AT SEC HWY 610 OUTLFOW OF CULVERT-CENTRE
25	AB05FC0150	River	Tributary Network	BATTLE RIVER	AT SEC HWY 872 BRIDGE
6	AB05FA0015	Wetland	Wetland	WETLAND #31	WETLAND #31 SOUTH OF HWY 623 AT JUNCTION WITH HWY 617
2	AB05FA1930	Wetland	Wetland	WETLAND #32	WETLAND #32 NORTH OF HWY 13 AT HWY 21 JUNCTION NEAR CAMROSE
1	AB05FA1940	Wetland	Wetland	WETLAND #34	WETLAND #34 NORTH OF HWY 13 - 2.5 KM WEST OF HWY 21
2	AB05FA1950	Wetland	Wetland	WETLAND #35	WETLAND #35 NORTH OF HWY 616, NORTH EAST OF ROMAN CATHOLIC CHURCH, EAST OF COAL LAKE
1	AB05FA1960	Wetland	Wetland	WETLAND #59	WETLAND #59 NEAR BASHAW
1	AB05FA1970	Wetland	Wetland	WETLAND #33	WETLAND #33 SOUTH OF HWY 13, 2KM WEST OF HWY 21 JUNCTION
8	AB05FB0005	Wetland	Wetland	WETLAND #40	WETLAND #40 EAST OF NORTH END OF THOMAS LAKE, NE OF VIKING
8	AB05FB0015	Wetland	Wetland	WETLAND #20	WETLAND #20 - 1 KM NORTH OF HWY 608 AND 4 KM WEST OF HWY 869
2	AB05FB0611	Wetland	Wetland	WETLAND #38	WETLAND #38 EAST OF HWY 870, NORTH OF CAMP LAKE, EAST OF VIKING
1	AB05FB0621	Wetland	Wetland	WETLAND #39	WETLAND #39 NORTH OF HWY 619, DIRECTLY EAST OF VIKING 11KM

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
2	AB05FB0631	Wetland	Wetland	WETLAND #41	WETLAND #41 ON TWP RD 482 EAST OF HWY 36, NORTH OF VIKING
2	AB05FB0641	Wetland	Wetland	WETLAND #42	WETLAND #42 SOUTH OF HWY 615, SOUTHEAST OF VIKING
1	AB05FB0651	Wetland	Wetland	WETLAND #43	WETLAND #43 WEST OF HATTIE LAKE, NORTH OF SEDGEWICK
1	AB05FB0661	Wetland	Wetland	WETLAND #44	WETLAND # 44 - 14 KM NORTH OF SEDGEWICK
1	AB05FB0671	Wetland	Wetland	WETLAND #56	WETLAND #56 SOUTH OF HATTIE LAKE AND 5 KM WEST OF HWY 870
2	AB05FB0681	Wetland	Wetland	WETLAND #18	WETLAND #18 5 KM SOUTH OF OIL REFINERY NEAR TOWN OF HARDISTY
1	AB05FB0701	Wetland	Wetland	WETLAND #22	WETLAND #22 6KM EAST OF TOWN OF HEISLER AND 2KM SOUTH
1	AB05FB0711	Wetland	Wetland	WETLAND #23	WETLAND #23 WEST OF TOWN OF GALAHAD
1	AB05FC1020	Wetland	Wetland	WETLAND #19	WETLAND #19 EAST OF BROWNFIELD
2	AB05FC1030	Wetland	Wetland	WETLAND #50	NORHWEST OF LOWDEN LAKE NEAR BIG VALLEY
1	AB05FC1040	Wetland	Wetland	WETLAND #53	4KM WEST OF DONALDA AND 2KM SOUTH OF HWY 953
2	AB05FC1050	Wetland	Wetland	WETLAND #54	NORTHWEST OF DONALDA
1	AB05FD0360	Wetland	Wetland	WETLAND #25	WETLAND #25 SOUTHEAST OF RIBSTONE LAKE NEAR WAINRIGHT
1	AB05FE0480	Wetland	Wetland	WETLAND #16	WETLAND # 16 ON HWY 619, 2KM WEST OF HWY 893
1	AB05FE0490	Wetland	Wetland	WETLAND #17	WETLAND #17 NORTH OF PARADISE VALLEY
2	AB05FE0500	Wetland	Wetland	WETLAND #26	WETLAND #26 14 KM EAST OF WAINRIGHT ON HWY 14
1	AB05FE0510	Wetland	Wetland	WETLAND # 27	WETLAND #27 11 KM NORTH OF TOWN OF IRMA
1	AB05FE0520	Wetland	Wetland	WETLAND #28	WETLAND #28 2KM WEST OF HWY 881 ON HWY 619
1	AB05FE0540	Wetland	Wetland	WETLAND #30	WETLAND #30 NORTH OF HWY 883 NEAR TOWN OF WAINRIGHT
BEAVER RIVER DRAINAGE BASIN					
3	AB06AC0290	Lake	Lake	MURIEL LAKE	MURIEL LAKE WHOLE LAKE EUPHOTIC COMPOSITE
2	AB06AC0550	Lake	Lake	MOORE LAKE EPILIMNETIC COMPOSITE	MOORE LAKE EPILIMNETIC COMPOSITE
2	AB06AC0580	Lake	Lake	HILDA LAKE EPILIMNETIC COMPOSITE	HILDA LAKE EPILIMNETIC COMPOSITE
1	AB06AC0610	Lake	Lake	ETHEL LAKE	ETHEL LAKE PROFILE SAMPLING SITE #1
2	AB06AC0620	Lake	Lake	ETHEL LAKE EPILIMNETIC COMPOSITE	ETHEL LAKE EPILIMNETIC COMPOSITE LONG TERM MONITORING PROGRAM
2	AB06AC0670	Lake	Lake	MARIE LAKE EPILIMNETIC COMPOSITE	MARIE LAKE EPILIMNETIC COMPOSITE
2	AB06AC0705	Lake	Lake	JACKFISH CREEK UPSTREAM OF TUCKER LAKE	JACKFISH CREEK, APPROXIMATELY 1KM UPSTREAM OF TUCKER LAKE AT NORTH END OF LAKE.
2	AB06AC0740	Lake	Lake	TUCKER LAKE EPILIMNETIC COMPOSITE	TUCKER LAKE EPILIMNETIC COMPOSITE
3	AB06AA0340	Lake	Lake (AESA)	NORTH BUCK LAKE	NORTH BUCK LAKE COMPOSITE
1	AB06AC0160	Creek	Creek	INLET TO ETHEL LAKE FROM MARIE LAKE	INLET TO ETHEL LAKE FROM MARIE LAKE
BOW RIVER DRAINAGE BASIN					
2	AB05BM0560	Creek	Agric. Creek (AESA)	WEST ARROWWOOD CREEK	NEAR ENSIGN
1	AB05BM0570	Creek	Agric. Creek (AESA)	WEST ARROWWOOD CREEK	NEAR ARROWWOOD
1	AB05BC0020	Creek	Creek	SPRAY DIVERSION CANAL	AT CANMORE
12	AB05BH0300	Creek	Creek	NOSE CREEK	ABOVE AIRDRIE
30	AB05BE0190	River	LTRN	BOW RIVER	U/S OF EXSHAW CREEK-LEFT BANK
33	AB05BH0010	River	LTRN	BOW RIVER	AT COCHRANE
25	AB05BJ0450	River	LTRN	ELBOW RIVER	AT 9TH AVE BRIDGE
34	AB05BM0010	River	LTRN	BOW RIVER	BELOW CARSELAND DAM
30	AB05BM0590	River	LTRN	BOW RIVER	AT CLUNY
53	AB05BN0010	River	LTRN	BOW RIVER	NEAR RONALANE BRIDGE
29	AB05BN0080	River	LTRN	BOW RIVER	AT BOW CITY BRIDGE
12	AB05BL0380	River	Tributary Network	HIGHWOOD RIVER	AT ALDERSYDE RIGHT SHORELINE UNDER HWY 2 BRIDGE (NE-6-20-29-W4)

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
11	AB05BL0480	River	Tributary Network	SHEEP RIVER	U/S OF CONLUENCE WITH THE HIGHWOOD RIVER
1	AB05BM0220	Irrigation Canal	Irrigation Canal	W.I.D. AT MAX BELL ARENA	ABOVE STO 001
1	AB05BM0235	Irrigation Canal	Irrigation Canal	W.I.D. CANAL	AT 61 AVE S.E., UNDER BRIDGE
1	AB05BM0236	Irrigation Canal	Irrigation Canal	W.I.D.	AT BARLOW TRAIL, ABOVE IC-21 OUTFALL
1	AB05BM0240	Irrigation Canal	Irrigation Canal	W.I.D.	AT 84 ST SOUTHEAST SHEPARD RD
1	AB05BM0250	Irrigation Canal	Irrigation Canal	W.I.D.	AT 132 ST
59	AB05BM0620	Irrigaton Return	Agric. Creek (AESA)	CROWFOOT CREEK	ON HWY 1
30	AB05BN0970	Irrigaton Return	Irrigaton Return (AESA)	NEW WEST COULEE	NEAR MOUTH
13	AB05BH0310	Urban Creek/Drain	Urban Creek/Drain	NOSE CREEK	BELOW AIRDRIE
1	AB05BH0319	Urban Creek/Drain	Urban Creek/Drain	NOSE CREEK	100M U/S COUNTRY HILLS BLVD (112 AVE NE, ALSO HWY#564) AT STORM SEWER PROJECT
15	AB05BH0370	Urban Creek/Drain	Urban Creek/Drain	NOSE CREEK	NEAR THE MOUTH-MEMORIAL DRIVE
14	AB05BH2590	Urban Creek/Drain	Urban Creek/Drain	WEST NOSE CREEK	ON MOUNTAIN VIEW ROAD OFF OF SYMONS VALLEY ROAD
14	AB05BH2600	Urban Creek/Drain	Urban Creek/Drain	EAST NOSE CREEK	NEAR 144 AVENUE
1	AB05BM1036	Urban Creek/Drain	Urban Creek/Drain	STORM OUTFALL IC-08	STORM SEWER OUTFALL IC-08 NEAR CALGARY CANOE CLUB ON WID CANAL
1	AB05BM1045	Urban Creek/Drain	Urban Creek/Drain	STORM OUTFALL IC-17	STORM OUTFALL IC-17 AT 72 AVE AND 30 ST SE
1	AB05BM1048	Urban Creek/Drain	Urban Creek/Drain	STORM OUTFALL IC-21	STORM OUTFALL IC-21 AT BARLOW TRAIL
1	AB05BM1049	Urban Creek/Drain	Urban Creek/Drain	STORM OUTFALL IC-21A	STORM OUTFALL IC-21A AT 40 ST SE
1	AB05BM1060	Urban Creek/Drain	Urban Creek/Drain	STORM SEWER AT 68TH. ST.	STORM SEWER AT 68TH. ST. POND OUTFALL DOWNSTREAM OF GLENMORE TRAIL GRAB SAMPLE
HAY RIVER DRAINAGE BASIN					
12	NT07OB0002	River	River	HAY RIVER AT AB-NWT BORDER (FEDERAL STN)	HAY RIVER AT AB-NWT BORDER (FEDERAL STN)
MILK RIVER DRAINAGE BASIN					
1	AB05AF0010	Lake	Lake	TYRRELL LAKE	COMPOSITE
2	AB05AF0460	Lake	Lake	PAKOWKI LAKE	CENTRAL ZONE COMPOSITE
2	AB05AF0460	Lake	Lake	PAKOWKI LAKE	CENTRAL ZONE COMPOSITE
1	AB05AF0490	Lake	Lake	PAKOWKI LAKE	WEST OF BERM COMPOSITE
1	AB05AF0380	Irrigation Return	Irrigation Return	ETZIKOM COULEE	AT SEC HWY 885
2	AB05AF0520	Irrigation Return	Irrigation Return	ETZIKOM COULEE	U/S OF SEC HWY 885
NORTH SASKATCHEWAN RIVER DRAINAGE BASIN					
4	AB05DE0590	Lake	Lake	WABAMUN LAKE	EAST BASIN PROFILES
1	AB05DE2108	Lake	Lake	WABAMUN GRID 2-3	2 KM EAST OF SEBA BEACH
1	AB05DE2150	Lake	Lake	WABAMUN GRID 10-4	3.5 KM EAST OF FALLIS POINT
1	AB05DE2175	Lake	Lake	WABAMUN GRID 14-7	2 KM EAST OF SUNDANCE PLANT
1	AB05DE2203	Lake	Lake	WABAMUN GRID 20-1	MOONLIGHT BAY (PARK)
3	AB05EA0460	Lake	Lake	ISLE LAKE	EUPHOTIC COMPOSITE
2	AB05EA0570	Lake	Lake	LAC STE. ANNE	EAST SIDE EUPHOTIC COMPOSITE
2	AB05EA0580	Lake	Lake	LAC STE. ANNE	WEST SIDE EUPHOTIC COMPOSITE
4	AB05EA0590	Lake	Lake	LAC STE. ANNE	EAST SIDE PROFILE AT GREATEST DEPTH
2	AB05EA0600	Lake	Lake	LAC STE. ANNE	WEST SIDE PROFILE AT GREATEST DEPTH
4	AB05EA1540	Lake	Lake	BIG LAKE NEAR ST ALBERT	EAST PROFILE AT CENTER
1	AB05EA1550	Lake	Lake	BIG LAKE NEAR ST ALBERT	EAST EUPHOTIC COMPOSITE
2	AB05EA1560	Lake	Lake	BIG LAKE NEAR ST ALBERT	WEST PROFILE AT CENTER
4	AB05EA1570	Lake	Lake	BIG LAKE NEAR ST ALBERT	WEST EUPHOTIC COMPOSITE
2	AB05EB1120	Lake	Lake (AESA)	MIQUELON LAKE	EUPHOTIC COMPOSITE

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
73	AB05DE0010	Creek	Agric. Creek (AESA)	ROSE CREEK	3 KM WEST OF ALDERFLATS
55	AB05DE0550	Creek	Agric. Creek (AESA)	TOMAHAWK CREEK	1 KM NORTH OF TOMAHAWK
50	AB05DF0020	Creek	Agric. Creek (AESA)	STRAWBERRY CREEK	NEAR THE MOUTH
17	AB05EE0550	Creek	Agric. Creek (AESA)	STRETTON CREEK	8.4 KM SOUTH OF MARWAYNE ON HWY 897
5	AB05EA0110	Creek	Creek	ATIM CREEK	WEST OF BIG LAKE
1	AB05EA1310	Creek	Creek	MISSION CREEK	AT LAC ST ANNE PILGRIMAGE SITE
4	AB05EA1580	Creek	Creek	CARROT CREEK	U/S BIG LAKE AT MEADOWVIEW ROAD 1KM EAST OF STURGEON RIVER
1	AB05ED0096	Creek	Creek	ATIMOSWE CREEK	NEAR MOUTH
1	AB05ED0136	Creek	Creek	UNNAMED CREEK	NEAR GRATZ 3-5 KM U/S OF MOUTH
1	AB05ED0139	Creek	Creek	MOOSEHILLS CREEK	NEAR MOUTH
1	AB05ED0145	Creek	Creek	MIDDLE CREEK	AT HWY 646
1	AB05EF0079	Creek	Creek	UNNAMED CREEK	AT MOUTH-TRIBUTARY TO NORTH SASKATCHEWAN RIVER NEAR BORDER
34	AB05DF0010	River	LTRN	NORTH SASKATCHEWAN RIVER	AT DEVON
64	AB05EC0010	River	LTRN	NORTH SASKATCHEWAN RIVER	AT PAKAN BRIDGE
1	AB10CA0001	River	LTRN	FIELD BLANK	FIELD BLANK GENERIC STN NUMBER
5	AB05DF0155	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT AT DEVON BRIDGE
3	AB05DF0175	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT - 2 KM U/S E.L. SMITH WTP
5	AB05EA0050	River	River	STURGEON RIVER	ABOVE BIG LAKE AT MEADOWVIEW ROAD(HWY 633)
1	AB05EA0080	River	River	STURGEON RIVER	ALBERTA BEACH BRIDGE
1	AB05EA0090	River	River	STURGEON RIVER	AT DARWELL BRIDGE
1	AB05EA0100	River	River	STURGEON RIVER	AT MAGNOLIA BRIDGE
1	AB05EA1590	River	River	STURGEON RIVER	500 METRES D/S OF OUTLET TO BIG LAKE
5	AB05EB0075	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT AT WALTERDALE (105 ST) BRIDGE
5	AB05EB0215	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT AT 50 STREET FOOT BRIDGE
2	AB05EB0345	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT AT RUNDLE FOOTBRIDGE
6	AB05EB0525	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT D/S OF CAPITAL REGION STP
4	AB05EB0835	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT AT VINCA BRIDGE
5	AB05EC0215	River	River	NORTH SASKATCHEWAN RIVER	TRANSECT AT PAKAN BRIDGE
12	AB05ED0090	River	River	NORTH SASKATCHEWAN RIVER	AT PUMPHOUSE INTAKE TO LAC ST CYR
1	AB05ED0095	River	River	DEATH RIVER	NEAR MOUTH
1	AB05EE0540	River	River	VERMILION RIVER	LEA PARK CONFLUENCE WITH NORTH SASKATCHEWAN RIVER
20	AB05EA0040	River	Tributary Network	STURGEON RIVER	NEAR VILLENEUVE AT RD RD 262
23	AB05EE0480	River	Tributary Network	VERMILION RIVER	WEST OF MARWAYNE AT WSC GAUGE SITE
7	AB05EA0005	Wetland	Wetland	WETLAND #62	WETLAND #62 SOUTH OF STONEY PLAIN ON RANGE ROAD 275
2	AB05EA1700	Wetland	Wetland	WETLAND #63	WETLAND #63 NORTH OF HWY 627 ON RG RD 274 SOUTH OF STONEY PLAIN
2	AB05EA1710	Wetland	Wetland	WETLAND #64	WETLAND # 64 SOUTH OF STONEY PLAIN ON RG RD 280, NORTH OF HWY 627
8	AB05EB0025	Wetland	Wetland	WETLAND #36	WETLAND #36 SOUTH OF HWY 16, WEST OF MUNDARE TURNOFF
1	AB05EC1060	Wetland	Wetland	WETLAND #37	WETLAND #37 ON HWY 16, 5.5 KM WEST OF HWY 855 NEAR MUNDARE
1	AB05ED1410	Wetland	Wetland	WETLAND #1	WETLAND #1 SOUTH EAST OF MYRNAM
1	AB05ED1415	Wetland	Wetland	WETLAND #13	WETLAND #13 ON HWY 881 NEAR VINCENT LAKE
2	AB05ED1420	Wetland	Wetland	WETLAND #2	WETLAND #2 WEST OF FARM YARD AT AGNEMARK KENNELS
1	AB05ED1430	Wetland	Wetland	WETLAND #3	WETLAND #3 NORTH OF ST PAUL ON RG RD 101, SOUTH OF RAILROAD TRACKS
1	AB05ED1440	Wetland	Wetland	WETLAND #4	WETLAND #4 - 2 KM NORTHEAST OF MYRNAM

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
1	AB05ED1450	Wetland	Wetland	WETLAND #14	WETLAND #14 SOUTHSIDE OF LOTTIE LAKE NEAR ASHMONT
1	AB05ED1460	Wetland	Wetland	WETLAND #15	WETLAND #15 SOUTH OF CHICKENHILL LAKE
13	AB05EE0005	Wetland	Wetland	WETLAND #10	WETLAND #10 WEST SIDE OF RG RD 121
8	AB05EE1080	Wetland	Wetland	WETLAND #5	WETLAND #5 SOUTH OF HWY 16 NEAR MINBURN
1	AB05EE1090	Wetland	Wetland	WETLAND #6	WETLAND #6 - 15KM EAST OF HWY 36 AND 1.5 KM SOUTH OF HWY 631
1	AB05EE2000	Wetland	Wetland	WETLAND #7	WETLAND #7 - 3.5 KM EAST OF HWY 870 AND 1.5 KM NORTH OF HWY 631
2	AB05EE2010	Wetland	Wetland	WETLAND #8	WETLAND #8 ON HWY 631 AT RANGE ROAD 122 NEAR TWO HILLS
2	AB05EE2020	Wetland	Wetland	WETLAND #9	WETLAND #9 ON HWY 631 AT RANGE ROAD 115 NEAR TWO HILLS
1	AB05EE2030	Wetland	Wetland	WETLAND #11	WETLAND #11 WEST OF PLAIN LAKE, SOUTHEAST OF TWO HILLS
1	AB05EE2040	Wetland	Wetland	WETLAND #12	WETLAND #12 SOUTH OF HWY 631 AT JUNCTION WITH HWY 870
5	AB05EA1600	Urban Creek/Drain	Urban Creek/Drain	KIRK LAKE CREEK(BIG LAKE TRIBUTARY)	AT 137 AVE 0.5KM EAST OF 199ST AT UNMARKED BRIDGE
1	AB05EB0136	Urban Creek/Drain	Urban Creek/Drain	MILL CREEK UPSTREAM OF NSR OUTFALL	MILL CREEK U/S OF NSR OUTFALL, MILL CREEK RAVINE PARK
1	AB05EB0137	Urban Creek/Drain	Urban Creek/Drain	MILL CREEK AT MILL WOODS GOLF COURSE	MILL CREEK AT MILL WOODS GOLF COURSE
1	AB05EB0138	Urban Creek/Drain	Urban Creek/Drain	MILL CREEK AT 17 ST	MILL CREEK AT 17 ST
1	AB05EB3190	Urban Creek/Drain	Urban Creek/Drain	EDMONTON - QUESNELL STORM SEWER	EDMONTON - QUESNELL STORM SEWER
1	AB05EB3200	Urban Creek/Drain	Urban Creek/Drain	EDMONTON - GROAT ROAD STORM SEWER	EDMONTON - GROAT ROAD STORM SEWER
1	AB05EB3240	Urban Creek/Drain	Urban Creek/Drain	EDMONTON - KENNEDALE STORM SEWER	EDMONTON - KENNEDALE STORM SEWER
1	AB05EB3241	Urban Creek/Drain	Urban Creek/Drain	CLAREVIEW STORM OUTFALL	CLAREVIEW STORM OUTFALL (#75)
1	AB05EB4720	Urban Creek/Drain	Urban Creek/Drain	BEAUMARIS LAKE	BEAUMARIS LAKE - STORMWATER RETENTION POND
1	AB05EB4730	Urban Creek/Drain	Urban Creek/Drain	HOLLICK KENYON LAKE	HOLLICK KENYON LAKE
OLDMAN RIVER DRAINAGE BASIN					
10	AB05AB0910	Lake	Lake	PINE COULEE RESERVOIR	SOUTH COMPOSITE
2	AB05AA0490	Lake	Lake (AESA)	BEAUVAIS LAKE	EUPHOTIC COMPOSITE
2	AB05AB0190	Creek	Agric. Creek (AESA)	WILLOW CREEK	BELOW LANE CREEK
35	AB05AB0230	Creek	Agric. Creek (AESA)	TROUT CREEK	NEAR THE MOUTH
28	AB05AB0240	Creek	Agric. Creek (AESA)	MEADOW CREEK	NEAR THE MOUTH
27	AB05AB0260	Creek	Agric. Creek (AESA)	WILLOW CREEK	AT SEC HWY 811
39	AB05AB0265	Creek	Agric. Creek (AESA)	WILLOW CREEK	12 KM WEST OF HWY 22 ON SEC HWY 532
24	AB05AD0290	Creek	Agric. Creek (AESA)	PRAIRIE BLOOD COULEE	NEAR LETHBRIDGE
28	AB05AG0140	Creek	Agric. Creek (AESA)	EXPANSE COULEE	ADJACENT TO HWY 36 BRIDGE CROSSING OLDMAN RIVER
3	AB05AA0480	Creek	Creek	PINCHER CREEK	AT HWY 3 NEAR THE MOUTH
12	AB05AB0100	Creek	Creek	BEAVER CREEK	WEST OF PEIGAN INDIAN RESERVE
4	AB05AC0160	Creek	Creek	MOSQUITO CREEK	AT HWY 529 EAST OF PARKLAND
12	AB05AB0070	River	LTRN	OLDMAN RIVER	NEAR BROCKET-LEFT BANK
31	AB05AD0010	River	LTRN	OLDMAN RIVER	ABOVE LETHBRIDGE AT HWY 3
12	AB05AD0300	River	LTRN	OLDMAN RIVER	U/S OF LETHBRIDGE AT POPSON PARK-LEFT BANK
35	AB05AG0010	River	LTRN	OLDMAN RIVER	AT HWY 36 BRIDGE NORTH OF TABER
1	AB05AA0090	River	River	CROWSNEST RIVER	ABOVE COLEMAN
4	AB05AA0220	River	River	CROWSNEST RIVER	U/S OF CONNELLY CREEK
8	AB05AA0400	River	River	CASTLE RIVER	AT CASTLE RIVER RECREATION AREA
4	AB05AB0130	River	River	OLDMAN RIVER	AT FORT MACLEOD-RIGHT BANK
4	AB05AC0010	River	River	OLDMAN RIVER	NEAR MONARCH-RIGHT BANK
4	AB05AC0100	River	River	LITTLE BOW RIVER	AT HWY 533 EAST OF NANTON

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
4	AB05AD0240	River	River	BELLY RIVER	NEAR CONFLUENCE WITH OLDMAN RIVER
12	AB05AD0610	River	River	OLDMAN RIVER	SOUTHWEST OF DIAMOND CITY FROM RIGHT BANK-10 METERS
8	AB05AD0790	River	River	OLDMAN RIVER	AT HWY 845-LEFT BANK
4	AB05AE0070	River	River	ST. MARY RIVER	NEAR CONFLUENCE WITH OLDMAN RIVER
8	AB05AG0090	River	River	OLDMAN RIVER	ABOVE TABER(HWY 864)-LEFT BANK
4	AB05AG0160	River	River	OLDMAN RIVER	NEAR PURPLE SPRINGS
29	AB05AC0320	River	River (AESA)	LITTLE BOW RIVER	NR THE MOUTH-APPROX 12 MILES N OF COALDALE ON HWY 845 AND 5.2 MILES EAST OF MUNICIPAL RD
11	AB05AC0180	River	Tributary Network	LITTLE BOW RIVER	AT CARMANGAY LEFT BANK 50 M U/S OF HWY 23 BRIDGE
4	AB05AC0190	River	Tributary Network	LITTLE BOW RIVER	AT CARMANGAY
2	AB05AB0950	Wetland	Wetland	SNETHUN'S SLOUGH	3.3 KM SOUTH OF TWP RD 140 (PUMPHOUSE RD) ON RR 281. EAST OF PINE COULEE RESERVOIR
5	AB05AB0960	Wetland	Wetland	GULKA'S SLOUGH	DUGOUT ON NORTH SIDE OF TWP RD 140 (PUMPHOUSE ROAD) 0.5 KM WEST OF RR 281
3	AB05AB0850	Irrigation Canal	Irrigation Canal	LNID MAIN CANAL	BEFORE BRANCH AT HWY 519,7 MILES EAST OF GRANUM
3	AB05AC1140	Irrigation Canal	Irrigation Canal	LNID CANAL	AT BARONS INTAKE
2	AB05AC1150	Irrigation Canal	Irrigation Canal	LNID CANAL	AT NOBLEFORD INTAKE (SW OF NOBLEFORD)
3	AB05AC1160	Irrigation Canal	Irrigation Canal	LNID CANAL	D/S OF KEHO LAKE OUTLET
3	AB05AC1170	Irrigation Canal	Irrigation Canal	LNID CANAL	AT SHAUGHNESSY INTAKE (3.5 MI. W OF SHAUGHNESSY)
3	AB05AC1180	Irrigation Canal	Irrigation Canal	LNID INLET	TO PICTURE BUTTE RESERVOIR
3	AB05AC1200	Irrigation Canal	Irrigation Canal	LNID CANAL	AT IRON SPRINGS INTAKE
3	AB05AC1210	Irrigation Canal	Irrigation Canal	LNID CANAL	AT TURIN INTAKE (SW OF TURIN)
3	AB05AC1290	Irrigation Canal	Irrigation Canal	PICTURE BUTTE RESERVOIR OUTLET	LNID
3	AB05AD2220	Irrigation Canal	Irrigation Canal	LNID INLET	TO PARK LAKE
4	AB05AD2320	Irrigation Canal	Irrigation Canal	WHOOP-UP SPILLWAY	ENTERING SIX MILE COULEE
5	AB05AD2340	Irrigation Canal	Irrigation Canal	SIX MILE COULEE	AT SANTANGELO FARM, 1.2 KM NORTH OF HWY 508 ON RR 21-0
7	AB05AD2350	Irrigation Canal	Irrigation Canal	SIX MILE COULEE	NORTH OF CARLSON LIVESTOCK, 1.6 KM NORTH OF HWY 508 ON RR 21-1
5	AB05AD2290	Irrigation Canal	Irrigation Return	SIX MILE COULEE	NEAR MAIN BRANCH
15	AB05AD0720	Irrigation Return	Irrigation Return	PIYAMI DRAIN	APPROX 1.5 MILES SOUTH AND 3.5 MILES EAST OF SHAUGHNESSY
7	AB05AD2260	Irrigation Return	Irrigation Return	SIX MILE COULEE	D/S NATURAL DRAIN-U/S OF HWY 5
7	AB05AD2270	Irrigation Return	Irrigation Return	SIX MILE COULEE	D/S OF WHOOP-UP SPILLWAY-OFF RR 8-2 1 KM EAST OF HWY 5
7	AB05AD2280	Irrigation Return	Irrigation Return	SIX MILE COULEE	D/S OF TIFFIN DRAIN
4	AB05AD2330	Irrigation Return	Irrigation Return	TIFFIN DRAIN	ENTERING SIX MILE COULEE
23	AB05AD2360	Irrigation Return	Irrigation Return	SIX MILE COULEE	U/S OF STORM DRAIN 94-S8, BELOW TUDOR ESTATES
12	AB05AD2380	Irrigation Return	Irrigation Return	HANEY DRAIN	U/S OF HWY 845 BRIDGE NEAR THE MOUTH
3	AB05AG0050	Irrigation Return	Irrigation Return	BOUNTIFUL COULEE	APPROX 2 MILES NORTH AND 1/2 MILE EAST OF CRANFORD
3	AB05AG0060	Irrigation Return	Irrigation Return	DRAIN T-2	1 MILE WEST AND 1/4 MILE SOUTH OF PROVINCIAL PARK
3	AB05AG0150	Irrigation Return	Irrigation Return	DRAIN T-11	APPROX 5.3 MILES NORTH OF FINCASTLE
33	AB05AD0360	Irrigation Return	Irrigation Return (AESA)	SIX MILE COULEE SPILLWAY	NEAR SOUTHERN BOUNDARY OF LETHBRIDGE
59	AB05AG0030	Irrigation Return	Irrigation Return (AESA)	BATTERSEA DRAIN	APPROX 8 MILES EAST OF PICTURE BUTTE
20	AB05AD2300	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN 94-S8 ENTERING SIX MILE COULEE	STORM DRAIN 94-S8 ENTERING SIX MILE COULEE, BELOW TUDOR ESTATES
2	AB05AD2310	Urban Creek/Drain	Urban Creek/Drain	NATURAL DRAIN	ENTERING SIX MILE COULEE U/S OF HWY 5
16	AB05AD2400	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN S-7	STORM DRAIN S-7
17	AB05AD2410	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN S-5/6	STORM DRAIN S-5/6
16	AB05AD2420	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN S-3	STORM DRAIN S-3
16	AB05AD2430	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN N-2	STORM DRAIN N-2

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
17	AB05AD2440	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN W-3	STORM DRAIN W-3
13	AB05AD2450	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN D5028418AG1	STORM DRAIN D5028418AG1
4	AB05AD2460	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN D5088820AA3	STORM DRAIN D5088820AA3, AT ENTRY TO CHURCHILL STORM POND
9	AB05AD2470	Urban Creek/Drain	Urban Creek/Drain	OLDMAN RIVER STORM DRAIN N-9	UPLANDS DRAIN 94-N9 OUTFALL INTO THE OLDMAN RIVER
1	AB05AD2480	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN IN THE CITY OF LETHBRIDGE	MANHOLE AT INTERSECTION OF 2 AVE NORTH AND 8 ST
2	AB05AD2490	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN IN THE CITY OF LETHBRIDGE	MANHOLE AT INTERSECTION OF 2 AVE NORTH AND 22 ST
1	AB05AD2520	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN IN THE CITY OF LETHBRIDGE	MANHOLE AT INTERSECTION OF 2 AVE NORTH AND 28 ST
1	AB05AD2530	Urban Creek/Drain	Urban Creek/Drain	STORM DRAIN IN THE CITY OF LETHBRIDGE	MANHOLE AT INTERSECTION OF 2 AVE NORTH AND 36 ST
PEACE RIVER DRAINAGE BASIN					
3	AB07FD0230	Lake	Lake (AESA)	MOONSHINE LAKE	EUPHOTIC COMPOSITE
3	AB07GE0240	Lake	Lake (AESA)	SASKATOON LAKE	EUPHOTIC COMPOSITE
23	AB07FD1390	Creek	Agric. Creek (AESA)	HINES CREEK	ABOVE GERRY LAKE NW OF GRIMSHAW
23	AB07GE0930	Creek	Agric. Creek (AESA)	KLESKUN HILLS MAIN DRAIN	NEAR GRANDE PRAIRIE NEAR HWY 34
32	AB07GE0940	Creek	Agric. Creek (AESA)	GRANDE PRAIRIE CREEK	NW OF SEXSMITH ON HWY 59
17	AB07HC0540	Creek	Agric. Creek (AESA)	BUCHANAN CREEK	NEAR MANNING, 8 KM EAST ON HWY 641, 2 KM SOUTH
13	AB07JD0180	Creek	Agric. Creek (AESA)	TEEPEE CREEK	NEAR LA CRETE, 1.6 KM SOUTH, 8.0 KM EAST, 3.4 KM SOUTH, AND 1.0 KM EAST
3	AB07GH0160	Creek	Creek	STURGEON CREEK	NEAR THE MOUTH
16	AB07GE0020	River	LTRN	WAPITI RIVER	AT HIGHWAY #40 BRIDGE - CENTRE CHANNEL - KM 44
19	AB07GE0030	River	LTRN	WAPITI RIVER	75 M D/S HWY 40 BRIDGE - RIGHT BANK
39	AB07GJ0010	River	LTRN	SMOKY RIVER	AT WATINO
16	AB07GJ0030	River	LTRN	WAPITI RIVER	ABOVE CONFLUENCE WITH SMOKY RIVER - CENTRE - KM 0.5
29	AB07HF0010	River	LTRN	PEACE RIVER	AT FORT VERMILION - CENTRE
2	AB07GD0060	River	River	BEAVERLODGE RIVER	D/S OF HYTHE
2	AB07GD0080	River	River	BEAVERLODGE RIVER	AT THE MOUTH
2	AB07GD0090	River	River	REDWILLOW RIVER	U/S OF BEAVERLODGE RIVER
20	AB07GH0020	River	Tributary Network	LITTLE SMOKY RIVER	AT VALLEYVIEW LEFT SHORELINE ABOUT 5 M D/S OF ROAD 669 BRIDGE
RED DEER RIVER DRAINAGE BASIN					
3	AB05CD0860	Lake	Lake	BUFFALO LAKE	SECONDARY BAY COMPOSITE
3	AB05CD1660	Lake	Lake	HAUNTED LAKE NEAR ALIX	EUPHOTIC COMPOSITE
3	AB05CD2150	Lake	Lake	UPPER CHAIN LAKE NEAR PONOKA	COMPOSITE
4	AB05CD2170	Lake	Lake	MIDDLE CHAIN LAKE NEAR PONOKA	COMPOSITE
4	AB05CD2190	Lake	Lake	LOWER CHAIN LAKE(MAGEE LAKE)NEAR PONOKA	COMPOSITE
4	AB05CE0980	Lake	Lake	PINE LAKE	NORTH SIDE REGION COMPOSITE
1	AB05CC0600	Lake	Lake (AESA)	GULL LAKE	EUPHOTIC COMPOSITE
1	AB05CC0700	Lake	Lake (AESA)	SYLVAN LAKE	EUPHOTIC COMPOSITE
1	AB05CD0670	Lake	Lake (AESA)	UNNAMED LAKE	SOUTH OF GADSBY (H515S1)
3	AB05CC0480	Creek	Agric. Creek (AESA)	BLOCK CREEK	7.6 KM WEST OF LEEDALE
3	AB05CC0490	Creek	Agric. Creek (AESA)	LLOYD CREEK	10 KM EAST & 2KM SOUTH OF BLUFFTON
48	AB05CD0520	Creek	Agric. Creek (AESA)	HAYNES CREEK	MAINSTEM SITE AT HWY 815 U/S END OF ROAD CULVERT CATTLE WINTERING AREA DRAINAGE (M1)
46	AB05CD0600	Creek	Agric. Creek (AESA)	HAYNES CREEK	MAINSTEM SITE AT FEDERAL GAUGE (M6)
47	AB05CE0710	Creek	Agric. Creek (AESA)	RAY CREEK	EAST ON HWY 590 & SOUTH ON HWY 805 TO BR.(NEAR INNISFAIL)
32	AB05CE0720	Creek	Agric. Creek (AESA)	RENWICK CREEK	WEST ON HWY 583 & NORTH ON RG RD 24-4 (NEAR THREE HILLS)
51	AB05CE0730	Creek	Agric. Creek (AESA)	THREEHILLS CREEK	SOUTH ON HWY 805 & 3.2 KM EAST TO BRIDGE (BELOW RAY CREEK)

No. of Samples	Station No.	Type of Waterbody	Details on Waterbody	Station Name	Station Description
2	AB05CB0580	Creek	Creek	DOGPOUND CREEK	AT SEC 582, 7.5 MILES WEST OF DIDSBURY
1	AB05CC0150	Creek	Creek	GOLF COURSE CREEK (SYLVAN LAKE INFLOW)	NEAR SOUTHEAST CORNER MARINA HWY 11
2	AB05CC1750	Creek	Creek	WEISE STREET CREEK (GULL LAKE INFLOW)	AT CORNER OF WEISE ST & LAKEVIEW AVE IN SUMMER VILLAGE OF GULL LAKE
2	AB05CC1800	Creek	Creek	SUCKER CREEK (GULL LAKE INFLOW)	0.2 KM SOUTH OF PAULSEN'S PASTURE SUBDIVISION ENTRANCE
2	AB05CC1810	Creek	Creek	PARKLAND CREEK (GULL LAKE INFLOW)	AT EAST END OF PARKLAND BEACH ROAD
2	AB05CC1815	Creek	Creek	PARKLAND CREEK SOUTH (GULL LAKE INFLOW)	AT CULVERT CROSSING IN SUMMER VILLAGE OF PARKLAND, SW OF STORE
2	AB05CC1820	Creek	Creek	NORTH CREEK (GULL LAKE INFLOW)	CULVERT AT NORTH END OF NORTH MARSH
3	AB05CC1860	Creek	Creek	WILSON CREEK (GULL LAKE INFLOW)	AT NORTH END OF WILSON BEACH
3	AB05CC1870	Creek	Creek	SONRISE CREEK (GULL LAKE INFLOW)	IN BAPTIST CAMP YARD
3	AB05CC1880	Creek	Creek	SAILING CLUB CREEK (GULL LAKE INFLOW)	APPROX 2 KM NORTHEAST OF GULL LAKE STORE ON ROAD TO SAILING CLUB
1	AB05CC1930	Creek	Creek	BIRCHCLIFF CREEK (SYLVAN LAKE INFLOW)	EAST OF SUNNYSIDE CAMP ALONG BIRCHCLIFF ROAD
1	AB05CC1950	Creek	Creek	LAMBE CREEK (SYLVAN LAKE INFLOW)	CROSSING THROUGH PROPERTY OF B. LAMBE (2015-TWP-RD 394)
27	AB05CC0010	River	LTRN	RED DEER RIVER	AT HWY 2 BRIDGE-ABOVE RED DEER
15	AB05CD0250	River	LTRN	RED DEER RIVER	AT NEVIS BRIDGE-RIGHT BANK
35	AB05CE0010	River	LTRN	RED DEER RIVER	AT MORRIN BRIDGE-CENTER
10	AB05CB0110	River	River	LITTLE RED DEER RIVER	AT ANDERSON RANCH WEST OF WATER VALLEY
32	AB05CB0270	River	River	LITTLE RED DEER RIVER	WEST OF INNISFAIL
30	AB05CC0100	River	River	MEDICINE RIVER	AT HWY 54
2	AB05CC0440	River	River	BLINDMAN RIVER	CANAL TO GULL LAKE
6	AB05CC0460	River	River	BLINDMAN RIVER	NEAR THE MOUTH, AT HWY 2A BRIDGE SOUTH OF BLACKFALDS
1	AB05CC1775	River	River	GULL LAKE DIVERSION (GULL LAKE INFLOW)	DURING PUMPING - AT CULVERT 0.5 KM BEFORE LAKE
14	AB05CE0100	River	River	ROSEBUD RIVER	AT HWY 10
72	AB05CC0470	River	River (AESA)	BLINDMAN RIVER	AT BRIDGE NEAR BLUFFTON SCHOOL
15	AB05CD0005	Wetland	Wetland	WETLAND #51	WETLAND #51 NORTH OF ERSKINE
2	AB05CD2210	Wetland	Wetland	WETLAND # 47	WETLAND #47 - 2KM SOUTH OF GOOSEQUILL LAKE
1	AB05CD2220	Wetland	Wetland	WETLAND # 49	WETLAND # 49 SOUTHWEST OF ERSKINE
2	AB05CD2230	Wetland	Wetland	WETLAND # 52	WETLAND #52 - 16 KM NORTH OF STETTLER AND 2 KM WEST OF HWY 56
1	AB05CD2240	Wetland	Wetland	WETLAND # 55	WETLAND # 55 - 14 KM NORTH OF STETTLER ON WEST SIDE OF HWY 56
2	AB05CE2310	Wetland	Wetland	WETLAND #46	WETLAND # 46 SOUTH OF PINE LAKE NEAR GHOSTPINE CREEK
1	AB05CE2320	Wetland	Wetland	WETLAND #48	WETLAND #48 - 30 KM EAST OF INNISFAIL ON HWY 590 AND 1.5 KM SOUTH
1	AB05CE2330	Wetland	Wetland	WETLAND #57	WETLAND #57 - 11 KM WEST OF TOWN OF ELNORA
2	AB05CF0220	Wetland	Wetland	WETLAND #60	WETLAND #60 - 9 KM NORTH OF SULLIVAN LAKE
3	AB05CF0230	Wetland	Wetland	WETLAND #61	WETLAND #61 - 2 KM EAST OF HALKIRK ON HWY 12
SLAVE RIVER DRAINAGE BASIN					
10	AL07NB0001	River	River	SLAVE RIVER AT FITZGERALD, ALBERTA	SLAVE RIVER AT FITZGERALD, ALBERTA
SOUNDING CREEK DRAINAGE BASIN					
9	AB05GA0130	Creek	Tributary Network	SOUNDING CREEK	AT MONITOR 10 M U/S OF HWY 12 BRIDGE(SE-14-35-4-W4)-CENTRE
SOUTH SASKATCHEWAN RIVER DRAINAGE BASIN					
32	AB05AJ0410	Creek	Agric. Creek (AESA)	DRAIN S-6	NEAR BOW ISLAND AT HWY 879
33	AB05AK0020	River	LTRN	SOUTH SASKATCHEWAN RIVER	ABOVE MEDICINE HAT
6	AB05AJ0420	Irrigation Return	Irrigation Return (AESA)	ST MARY IRRIGATION DISTRICT	SITE 21 UPSTREAM OF DRAIN S-6

Appendix B Overview of results of quality assurance and quality control data in the Alberta pesticide database for surface waters (1995 – 2002)

1.0 INTRODUCTION

This section describes quality assurance and quality control (QA/QC) measures for pesticide sampling and analyses that were implemented both in the field and in the laboratory during the period 1995 to 2002, inclusive. Implications of QA/QC results on the overall quality of Alberta's pesticide database for surface waters are evaluated. Specific recommendations that would help enhance the value of the QA/QC program are provided. All analyses of pesticides presented in this section and in the main body of the report were performed at the Alberta Research Centre (ARC) Trace Organics Laboratory.

2.0 METHODS

2.1 Laboratory Procedures

The Alberta Research Centre (ARC) Trace Organics Laboratory is accredited by the Canadian Association for Environmental Laboratories Inc. (CAEL) under the Authority of Standards Council of Canada. Of particular interest here are the procedures implemented in pesticide analyses.

Standards are purchased as certified mixes and they are diluted into the calibration range in the laboratory. Analytical instruments are calibrated using multi-point calibration curves within the linear range. When new standards are purchased, they are checked against the standards in use and they are utilized only if there is agreement between concentration values for the two sets.

ARC analyzes samples in batch mode. These batches consist of a reagent blank plus 11 samples. Every sample, including blanks, is spiked with deuterated surrogates consisting of one organochlorine pesticide {gamma-hexachlorobenzene-d_6}, one nitrogen-containing pesticide {atrazine-d_5} and two phenoxyacid pesticides {2,4-D-d_5 and Dicamba-d_3}. Surrogates are chemicals that are similar in physical and chemical properties to a target analyte, but that are normally not found in environmental samples. Quality control charts are generated for each batch with the acceptance criteria being +/- two standard deviations for each surrogate.

Three deuterated internal standards are used (start of chromatogram, middle and end) which monitor instrumental variances such as instrument sensitivity and injection differences from sample to sample. Quality control charts are generated for each batch with the acceptance criteria being +/- two standard deviations for each internal standard; standard deviations are calculated for each sample batch based on the results of 4 standards.

When a method is developed, validated or revalidated, distilled/deionized water is spiked at two levels (usually 2 times the MDL and 10 times the MDL). Recoveries and relative standard deviations (RSD) are calculated. Methods are validated every five years.

Reported concentrations for pesticide residues in surface water samples are not corrected for surrogate recovery.

2.2 Field Procedures

In addition to standard laboratory QA/QC protocols implemented by the analytical laboratory, quality assurance procedures are incorporated in regular field sampling programs.

Sampling procedures follow methods outlined in AENV (2002) and involve the use of properly cleaned bottles and stainless steel sampling equipment.

Inclusion of QA/QC samples for the period 1995 to 2002 occurred on a project-by-project basis. Splits, blanks (field and trip blanks) and spikes that were collected as part of the various field programs are evaluated in this section. In addition, the spatial variability in pesticide measurements and the relative value of composite and grab samples was assessed, at a scoping level, for standing water bodies.

Figure B1 provides a breakdown of the type and number of quality assurance samples in successive years. No quality assurance samples were taken in 1995; in 1997 and 1998 mainly split samples were collected; and in following years split samples were largely replaced by split/spiked samples, and more blank samples were taken.

3.0 RESULTS

3.1 Split Samples

Split samples (either duplicate or triplicate splits) provide a general indication of the precision in measurements. Split samples were obtained by apportioning sample water from a stainless steel bucket among two (duplicate) or three (triplicate) sample bottles. The content of the bucket was stirred repeatedly during the process and small sample volumes were dispensed sequentially to each bottle. While this procedure yields two or more samples that are very similar, some variability is still possible, particularly if the amount of particulate matter in the sample is large.

A total of 48 split sets comprised of 20 duplicates, 5 triplicates and 23 split/spikes was evaluated. Split/spikes are splits where one sample was spiked for one or more pesticides while the other was left unaltered; pesticides that were not spiked represent ordinary duplicate splits. Only pairs of unspiked pesticides were considered in this analysis.

Of the 47 pesticides that were analyzed in these samples, 16 were detected at least once. Concentration ranges were generally low and relatively few measurements exceeded 0.1µg/L. The largest number of detections occurred for 2,4-D, MCPA, dicamba, MCPP, bromoxynil and picloram; this corresponds broadly with the dominant detection frequency pattern in the provincial database. 2,4-D was the only pesticide in this sample set where the number of detections exceeded the number of non-detections. The split samples provide a representative cross-section of the overall database in terms of which pesticides were detected and at what concentrations.

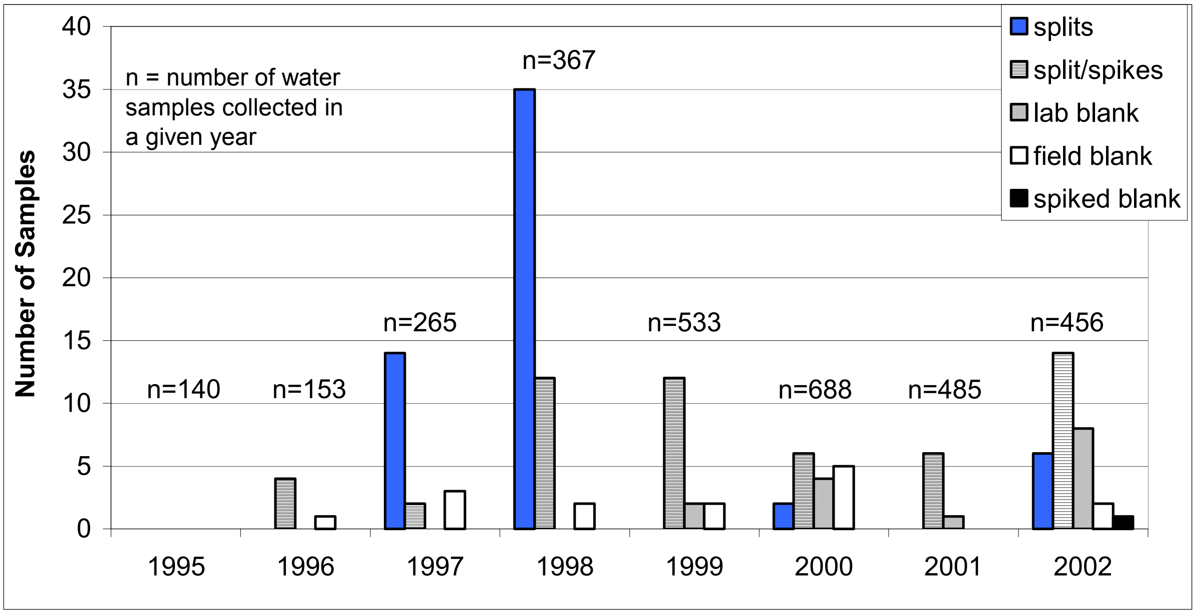

Figure B1 Breakdown of pesticide QA/QC samples collected from 1995 to 2002, inclusive

When dealing with split samples, there are three possible scenarios for the measurements of each pesticide:

1. Consistent non-detections: measurements are reported as less than the method detection limit (<MDL).
2. Consistent detections: measurements are actual concentrations.
3. Inconsistent detections: at least one measurement is reported at concentrations above the MDL, the other(s) as '<MDL'.

The number of split samples belonging to each scenario is reported in Table B1 as an absolute number and as a percent of the total number of split samples.

- For consistent measurements, the coefficient of variation (i.e., CV= SD*100/mean) for each duplicate or triplicate split is used as a measure of precision. The CV is summarized by its range and median for each pesticide with measurable concentrations (Table B1). These statistics are also provided for pesticide concentrations.
- For inconsistent detections, the measured concentration was compared to the MDL and reported in Table B1.

Consistent Detections and Non-Detections

The percentage of paired measurements with consistent detections (6.8%) and non-detections (92.4%) far exceeds the percentage of pairs with inconsistent detections (1.4%) (Table B1). However, for clopyralid, lindane and atrazine the percentage of inconsistent detections exceeded

Table B1 Detections in duplicate and triplicate sets collected during the period 1995 to 2002[1]

Compound	Detection Limit µg/L	No. of Split Sets	Number of replicate sets where pairs of replicates have: Consistent non-detections (2)	Consistent detections (3)	Inconsistent detections (4)	Percentage of split samples where splits have: % Consistent non-detection	% Consistent detection	% Inconsistent detection
2,4-D	L0.005	39	9	29	1	23.1	74.4	2.6
2,4-DB	L0.005	48	48	0	0	100.0	0.0	0.0
2,4-DICHLOROPHENOL	L0.01	3	3	0	0	100.0	0.0	0.0
4-CHLORO-2-METHYLPHENOL	L0.01	3	3	0	0	100.0	0.0	0.0
ALPHA-BENZENEHEXACHLORIDE	L0.005	48	47	1	0	97.9	2.1	0.0
ALPHA-ENDOSULFAN	L0.005	48	48	0	0	100.0	0.0	0.0
AMINOMETHYL PHOSPHONIC ACID	L1	4	4	0	0	100.0	0.0	0.0
ATRAZINE	L0.005	44	42	0	2	95.5	0.0	4.5
ATRAZINE	L0.05	36	36	0	0	100.0	0.0	0.0
AZINPHOS-METHYL	L0.2	48	48	0	0	100.0	0.0	0.0
BROMACIL	L0.03	48	48	0	0	100.0	0.0	0.0
BROMOXYNIL	L0.005	44	33	11	0	75.0	25.0	0.0
CARBATHIIN	L0.1	48	48	0	0	100.0	0.0	0.0
CHLORPYRIFOS	L0.005	47	47	0	0	100.0	0.0	0.0
CLOPYRALID	L0.02	47	42	2	3	89.4	4.3	6.4
CYANAZINE	L0.05	48	48	0	0	100.0	0.0	0.0
DEISOPROPYL ATRAZINE	L0.05	36	36	0	0	100.0	0.0	0.0
DESETHYL ATRAZINE	L0.05	36	36	0	0	100.0	0.0	0.0
DIAZINON	L0.005	44	41	2	1	93.2	4.5	2.3
DICAMBA	L0.02/L0.005	40	27	11	2	67.5	27.5	5.0
DICHLORPROP(2,4-DP)	L0.005	48	40	7	1	83.3	14.6	2.1
DICLOFOP-METHYL	L0.02	47	47	0	0	100.0	0.0	0.0
DIMETHOATE	L0.05	36	36	0	0	100.0	0.0	0.0
DISULFOTON	L0.2	48	48	0	0	100.0	0.0	0.0
DIURON	L0.2	48	48	0	0	100.0	0.0	0.0
ETHALFLURALIN	L0.005	38	38	0	0	100.0	0.0	0.0
ETHION	L0.1	48	48	0	0	100.0	0.0	0.0
FENOXAPROP-P-ETHYL	L0.04	36	36	0	0	100.0	0.0	0.0
GLUFOSINATE	L1	3	3	0	0	100.0	0.0	0.0
GLYPHOSATE	L0.02	1	0	1	0	0.0	100.0	0.0
IMAZAMETHABENZ	L0.05	42	40	1	1	95.2	2.4	2.4
IMAZAMOX	L0.02	13	13	0	0	100.0	0.0	0.0
IMAZETHAPYR	L0.02	36	36	0	0	100.0	0.0	0.0
LINDANE	L0.005	44	41	1	2	93.2	2.3	4.5
MALATHION	L0.05	48	48	0	0	100.0	0.0	0.0
MCPA	L0.005	43	20	21	2	46.5	48.8	4.7
MCPB	L0.02	48	48	0	0	100.0	0.0	0.0
MCPP	L0.005	48	33	11	4	68.8	22.9	8.3
METHOXYCHLOR	L0.03	48	48	0	0	100.0	0.0	0.0
PHORATE	L0.005	48	48	0	0	100.0	0.0	0.0
PICLORAM	L0.005	44	34	6	4	77.3	13.6	9.1
PYRIDABEN	L0.02	36	36	0	0	100.0	0.0	0.0
QUINCLORAC	L0.005	36	36	0	0	100.0	0.0	0.0
SIMAZINE	L0.01	5	5	0	0	100.0	0.0	0.0
TERBUFOS	L0.03	48	48	0	0	100.0	0.0	0.0
TRIALLATE	L0.005	39	36	2	1	92.3	5.1	2.6
TRICLOPYR	L0.01	5	3	2	0	60.0	40.0	0.0
TRIFLURALIN	L0.005	41	41	0	0	100.0	0.0	0.0
Overall			**1652**	**108**	**24**	**92.6**	**6.1**	**1.3**

Notes:

1. Duplicates that contain one spike are eliminated from the counts
2. Consistent non-detections: all measurements of a pesticide are reported as less than the detection limit in each split
3. Consistent detections: all measurements of a pesticide have actual concentration measurements in each split
4. Inconsistent detections: at least one measurement of a pesticide has a measurable concentration or is reported as less than the detection limit in the split samples
5. Measurements greater than 2 times the detection limit are in bold italics and box
6. Measurements less that the detection limit are in bold
7. Concentration range for the average of paired samples
8. RCV: relative coefficient of variation (standard deviation times 100 and divided by mean)

Table B1 Detections in duplicate and triplicate sets collected during the period 1995 to 2002[(1)] (cont'd)

Compound	Inconsistent detections [(4)]	Consistent Detections [(3)]					
		Concentration range consistent detections (µg/L)[(7)]			CV for consistent detections [(8)]		
	Measurable concentration in µg/L [(5,6)]	Minimum	Median	Maximum	Minimum	Median	Maximum
2,4-D	***0.016***	0.006	0.062	1.910	0.0	7.4	80.3
2,4-DB							
2,4-DICHLOROPHENOL							
4-CHLORO-2-METHYLPHENOL							
ALPHA-BENZENEHEXACHLORIDE							
ALPHA-ENDOSULFAN							
AMINOMETHYL PHOSPHONIC ACID							
ATRAZINE	0.009 0.007						
ATRAZINE							
AZINPHOS-METHYL							
BROMACIL							
BROMOXYNIL		0.004	0.017	0.054	0.0	5.2	21.5
CARBATHIIN							
CHLORPYRIFOS							
CLOPYRALID	***0.18*** 0.006 0.005	0.019	0.031	0.043	0.0	30.8	61.6
CYANAZINE							
DEISOPROPYL ATRAZINE							
DESETHYL ATRAZINE							
DIAZINON	0.008	0.015	0.018	0.020	14.1		19.9
DICAMBA	0.007 0.006	0.007	0.037	0.141	0.0	8.1	34.1
DICHLORPROP(2,4-DP)	**0.004**	0.004	0.012	0.108	0.0	12.9	23.6
DICLOFOP-METHYL							
DIMETHOATE							
DISULFOTON							
DIURON							
ETHALFLURALIN							
ETHION							
FENOXAPROP-P-ETHYL							
GLUFOSINATE							
GLYPHOSATE			0.612			44.4	
IMAZAMETHABENZ	***0.11***		0.239			23.4	
IMAZAMOX							
IMAZETHAPYR							
LINDANE	**0.004** 0.005		0.008			9.4	
MALATHION							
MCPA	***0.026*** 0.008	0.001	0.022	0.468	0.0	15.9	38.6
MCPB							
MCPP	0.005 **0.003** 0.008 **0.004**	0.002	0.012	0.352	0.0	6.8	34.6
METHOXYCHLOR							
PHORATE							
PICLORAM	***0.026*** ***0.058*** ***0.018*** ***0.052***	0.009	0.038	0.143	7.4	29.7	48.4
PYRIDABEN							
QUINCLORAC							
SIMAZINE							
TERBUFOS							
TRIALLATE	0.006	0.006	0.009	0.012	6.1	9.5	12.9
TRICLOPYR		0.016	0.018	0.020	14.1		26.5
TRIFLURALIN							

Notes:
1. Duplicates that contain one spike are eliminated from the counts
2. Consistent non-detections: all measurements of a pesticide are reported as less than the detection limit in each split
3. Consistent detections: all measurements of a pesticide have actual concentration measurements in each split
4. Inconsistent detections: at least one measurement of a pesticide has a measurable concentration or is reported as less than the detection limit in the split samples
5. Measurements greater than 2 times the detection limit are in bold italics and boxed
6. Measurements less that the detection limit are in bold
7. Concentration range for the average of paired samples
8. RCV: relative coefficient of variation (standard deviation times 100 and divided by mean)

the percentage of consistent detections slightly (i.e., by 2.1, 2.2, and 4.5%, respectively). These three compounds had low frequencies of detection and occurred at concentrations near the MDL. In contrast, 2,4-D, which was detected in 74.4% (29) of splits, had an inconsistent detection in only a single split (2.6% of splits). Picloram and bromoxynil had the highest (9.1%) and lowest (0%) proportion of inconsistent splits, respectively. These differences are related to the very nature of the two compounds: picloram is typically difficult to extract; in contrast, bromoxynil contains unique ions in its mass spectra and is very easy to identify.

The CV can be used as a measure of precision for pairs of consistent detections. Overall 74% of the splits with consistent detections had a CV that exceeded 20%, a value that has been used as a general and somewhat arbitrary benchmark for assessing precision (e.g., Noton and Saffran 1995). For 2,4-D, MCPA, dicamba, MCPP, bromoxynil, clopyralid and dichlorprop the minimum coefficient of variation was 0, indicating that split measurements were identical (Figure B2 and Table B1). The median CV was below 20% for most pesticides, except for picloram, which was at 23.4%. Median CVs for clopyralid, glyphosate and imazamethabenz were higher than 20%, but these medians were derived from a very small number of splits and may not be representative. The maximum CV was below 50% for most measurements, except for 2,4-D and clopyralid, which had an CV of 80.3 and 61.6, respectively. In both instances, but especially for 2,4-D, these maxima appear to be outliers in the CV distribution.

Inconsistent Detections
In some cases inconsistent detections are the result of a compromise in data reporting.

- In most instances (17 out of 24), measurable concentrations reported in an inconsistent set were within twice the MDL. This is a concentration range where occasionally a compound may appear to be present but due to interferences the lab has difficulties confirming the compound's presence or concentration, and prefers to report a '<MDL' value instead of a possible false positive (D. Humphries personal communication).
- In several (5 out of 24) instances, the reason for the existence of an inconsistent set was due to the fact that some residues were reported at concentrations below the MDL in one of the split samples and as '< MDL' in the other sample(s). In some samples compounds can be identified and quantified with certainty at very low levels (i.e., below the MDL), but in other samples, even as similar as a split sample, they may not. Hence, reporting values that are below the MDL may lead to an increase in frequency of inconsistent detections in QA/QC samples, although the reported concentration still is technically "<MDL". The report of values below the MDL has proven very useful in other areas. For example, data generated below the MDL made it possible to justify the lowering of the detection limit from 0.020 to 0.005 µg/L for dicamba.

In other instances, inconsistent detection can be indicative of some potential problems. In 7 out of 24 instances, the reported concentration of 2,4-D, MCPA, picloram, clopyralid and imazamethabenz was more than twice the MDL. Picloram had measurements that were 10 times greater than the MDL in one split, but '<MDL' in the other(s). Possible explanations for these discrepancies include:

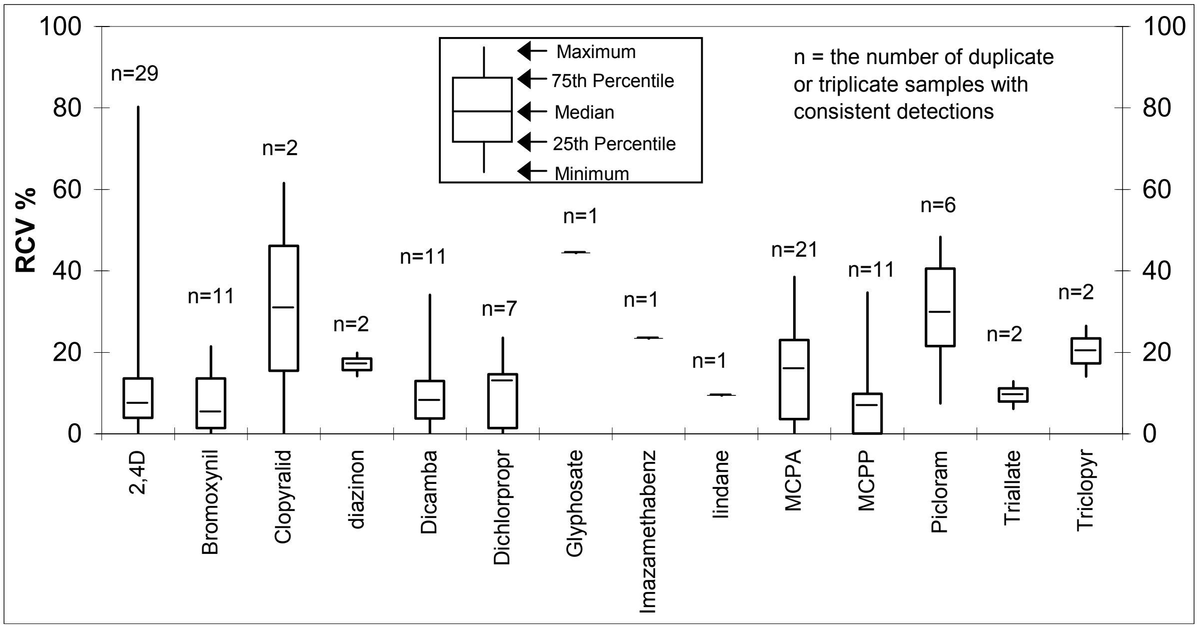

Figure B2 Coefficient of variation for consistent pesticide measurements in split samples

1) Replicate samples not the same,
2) Glassware contamination in lab on one sample and not on other,
3) False positive on one sample, wrongly identified due to interferences,
4) False negative, wrongly dismissed as hit due to interferences, and
5) Possible contamination from previously high sample in a batch run.

Martin (2002) reported on pesticide data for over 25,000 split and replicate sample sets taken across the USA as part of the National Water Quality Assessment Program during the period 1992 to 1997. One-on-one comparisons of results for individual pesticides are difficult between the US and Alberta QA/QC data because of differences in analytical methods and differences in pesticides that are being analyzed. Nevertheless, numbers presented by Martin (2002; Table 2), indicate that consistent detections, consistent non-detections and inconsistent detections represent 6.6, 92.4, and 0.9% of the total number of sample sets. These numbers are very similar to the results for split samples in the Alberta database (i.e., 6.8, 92.4, and 1.4 %, respectively).

Most inconsistent detections are caused by false positive or false negative errors. According to Martin (2002), false positive errors usually are caused by sample contamination, whereas false negative errors usually are caused by water-matrix interference, pesticide degradation or other chemical loss processes. Interference from a compound other that the target compound can also induce false positive errors (D. Humphries, personal communication). Both types of errors are caused by variability inherent to the analytical method, but MDLs are designed to protect against false positive errors.

On the basis of low frequency of detection in our field and laboratory blanks (see below), sample contamination is an unlikely consistent cause of pesticide detections, which would in this case be false positives, in replicate sets. Therefore, inconsistent detections could be caused by variability in analytical method and by water-matrix interferences that cause false negative errors (recognizing that false negatives may be due to lab's bias to not want to report a false positive). The detection frequency is likely biased low because of false negative errors at concentrations near the MDL.

Some pesticides such as picloram and imazamethabenz seem to have a relatively high frequency of inconsistent detections (compared to their respective frequency of consistent detections) and a high relative coefficient of variation. This may be indicative of a higher error associated with the measurements, which can be related to intrinsic difficulties associated with the analysis of some compounds (lower precision). Even among pesticides that are usually measured with high precision, inconsistent detections and elevated CVs occur occasionally.

3.2 Spiked Samples

Spiked samples help evaluate the accuracy of the measurements.

Although some single samples, either blanks or surface water samples, were spiked, most of the spiking program was carried out on split samples. For each split set, one sample was left unaltered, the other was sent to the Quality Control Laboratory, ARC Vegreville, for spiking. Analytical grade 2,4-D, lindane, atrazine, bromoxynil, dicamba, diclofop, chlorpyrifos, ethalfluralin, MCPA, picloram, triallate, imazamethabenz, and trifluralin were used to spike the samples. Spike solutions were prepared once in 1998. EnviroTest Laboratories, in Edmonton, prepared glyphosate spikes in 2002. Spike design concentrations were in the general concentration range for surface water samples in Alberta. Expected spiked sample concentrations are presented in Table B2 and assume the absence of residue in the initial sample. The spiked sample was returned to the Monitoring Branch field office where sample labels were changed to ensure that the sample could not be identified as a spiked sample by the laboratory (i.e., "blind" spike). Both split samples were sent to the Trace Organic Laboratory, ARC Vegreville as part of routine sample batches. A total of 75 samples were spiked from 1995 to 2002, inclusive.

Recovery is defined as the concentration measured in the spiked sample expressed as a percentage of the spike design concentration. The concentration measured in the spiked sample was first adjusted by subtracting the concentration reported in the unspiked sample. If concentrations in the spiked and unspiked sample were "<MDL", spike recovery was described as zero.

Spike recovery exceeded 100% for a few measurements of 2,4-D, lindane, bromoxynil, dicamba, picloram and trifluralin, but on the whole, recoveries tended to be well below 100% (Table B2). Some spikes for ethalfluralin, triallate, and glyphosate went undetected. Average recovery ranged between 58 and 86 %, except for triallate, ethalfluralin and glyphosate which had average recoveries of 42, 39 and 9%, respectively.

Table B2 Spike recovery in split and spiked samples

Unless specified otherwise, spiked samples belong to a split pair where one sample was spiked, the other not

	Unspiked Split	Spiked Split	Spike Design Conc.	% Recovery
2,4-D				
16-Oct-96	L0.005	0.046	0.08	57.5
30-Apr-98	L0.005	0.015	0.2	7.5
10-Jun-98	0.013	0.091	0.08	97.5
22-Jun-98	NS*	0.143	0.143	98.3
21-Apr-99	L0.005	0.143	0.14	102.1
29-Aug-00	L0.005	0.038	0.06	63.3
11-Jul-01	L0.005	0.044	0.06	73.3
15-Jul-02	L0.005	0.057	0.08	71.3
			average	*71.4*
Lindane				
16-Oct-96	L0.005	0.026	0.02	130.0
22-Oct-97	L0.005	0.134	0.16	83.8
14-Jul-98	L0.005	0.044	0.06	73.3
17-Jun-99	L0.005	0.009	0.073	12.3
17-Jun-99	L0.005	0.014	0.073	19.2
28-Jun-99	L0.005	0.005	0.007	71.4
14-Jul-99	L0.005	0.011	0.008	137.5
			average	*75.4*
Atrazine				
15-Jun-98	L0.005	0.19	0.2	95.0
22-Jun-98	NS*	0.044	0.1	41.5
29-Aug-00	L0.005	0.022	0.04	55.0
13-May-02	L0.005	0.03	0.06	50.0
			average	*60.4*
Bromoxynil				
16-Oct-96	L0.005	0.101	0.08	126.3
21-Apr-98	L0.005	0.237	0.3	79.0
26-Aug-98	L0.02	0.059	0.12	40.8
26-May-99	L0.02	0.066	0.12	46.7
27-Aug-01	L0.005	0.036	0.04	90.0
			average	*64.1*
MCPA				
21-Apr-98	L0.005	0.155	0.2	77.5
26-May-99	L0.005	0.096	0.16	60.0
28-Jun-99	L0.005	0.03	0.06	50.0
20-Jul-00	L0.005	0.046	0.06	76.7
27-Aug-01	L0.005	0.082	0.1	82.0
13-May-02	L0.005	0.036	0.08	45.0
			average	*65.2*
Picloram				
10-Jun-98	L0.005	0.119	0.24	49.6
14-Jul-98	L0.005	0.092	0.18	51.1
21-Apr-99	L0.005	0.149	0.18	82.8
23-May-01	L0.005	0.051	0.04	127.5
20-Jun-02	NS**	0.042	0.06	70.0
			average	*76.2*
Triallate				
30-Apr-98	L0.005	0.226	0.24	94.2
26-Aug-98	L0.005	0.126	0.16	78.8
21-Apr-99	L0.005	0.066	0.12	55.0
14-Jul-99	L0.005	L0.005	0.08	0.0
27-Apr-00	L0.005	0.009	0.02	45.0
20-Jul-00	L0.005	0.016	0.04	40.0
23-May-01	L0.005	0.031	0.04	77.5
13-May-02	L0.005	0.01	0.04	25.0
15-Jul-02	L0.005	L0.005	0.04	0.0
			average	*46.2*

	Unspiked Split	Spiked Split	Spike Design Conc.	% Recovery
Dicamba				
30-Apr-98	L0.02	0.376	0.3	125.3
15-Jun-98	L0.02	0.189	0.14	135.0
22-Jun-98	NS*	0.12	0.2	55.0
14-Jul-99	L0.02	0.016	0.04	40.0
27-Apr-00	L0.02	0.046	0.04	115.0
11-Jul-01	L0.005	0.019	0.06	31.7
20-Jun-02	NS**	0.031	0.06	47.5
04-Sep-02	L0.005	0.003	0.02	15.0
			average	*70.6*
Diclofop				
16-Oct-96	L0.02	0.108	0.2	54.0
Chlorpyrifos				
16-Oct-96	L0.005	0.118	0.14	84.3
14-Jul-98	L0.005	0.05	0.1	50.0
26-May-99	L0.005	0.079	0.1	79.0
29-Aug-00	L0.005	0.02	0.07	28.6
			average	*60.5*
Ethalfluralin				
21-Apr-98	L0.005	0.12	0.18	66.7
26-Aug-98	L0.005	0.11	0.12	91.7
27-Apr-00	L0.005	L0.005	0.05	0.0
20-Jul-00	L0.005	L0.005	0.02	0.0
23-May-01	L0.005	0.035	0.06	58.3
27-Aug-01	L0.005	0.017	0.06	28.3
20-Jun-02	NS**	0.006	0.04	8.8
04-Sep-02	L0.005	0.042	0.06	70.0
			average	*40.5*
Imazamethabenz				
22-Oct-97	L0.05	0.164	0.24	68.3
Glyphosate				
12-Jun-02	L0.2	0.048	0.5	9.6
24-Jul-02	0.133	0.506	1	50.6
24-Sep-02	L0.2	L0.2	0.5	0.0
			average	*20.1*
Trifluralin				
16-Oct-96	L0.005	0.204	0.1	204.0
22-Oct-97	L0.005	0.095	0.18	52.8
10-Jun-98	L0.005	0.104	0.12	86.7
15-Jun-98	L0.005	0.145	0.26	55.8
28-Jun-99	L0.005	0.011	0.011	100.0
11-Jul-01	L0.005	0.02	0.04	50.0
			average	*91.5*

Notes:

NS = no sample * single sample spiked by the lab (not blank) ** spiked field blank

Concentrations reported as "< MDL", were assumed to be "zero"

If the spiked and unspiked concentrations were reported as less than the detection limit, then recovery was assumed to be nil

Although recoveries are less than 100%, they are in the general range of recovery expected for the analytical method (D. Humphries, personal communication)(Figure B3). In some samples the presence of organic matter could have reduced recovery rates further. Organic matter can greatly reduce the efficiency of the extraction procedure (by holding on to the pesticides) and can interfere with the identification and quantification of residues. Ethalfluralin and triallate have a low water solubility, but a high vapour pressure. If there was a headspace in the bottles it is quite possible that the compounds volatilized and were released when the bottle was opened. Such explanation is unlikely for glyphosate, which has a lower vapour pressure and a higher affinity to particulate matter (e.g., Cotton 1995).

Figure B4 illustrates changes over time in pesticide recovery rates. Recovery rates for some compounds such as dicamba, atrazine, chlorpyrifos, and triallate and, to some extent, trifluralin and ethalfluralin, appear to show a declining trend over time. Overall, recovery rates for spikes of all pesticides combined indicate a declining trend.

Technically, a decline in spike recoveries could be indicative of analytical problems, or of spike material deterioration. The former would have implications on the quality of the pesticide database; the latter would not.

- A review of recoveries of deuterated surrogates confirmed that there had been no notable changes or trends in recovery over the last eight years (D. Humphries, pers. communication). Such trends, if they had occurred, would have been noticed in recoveries for blank samples.

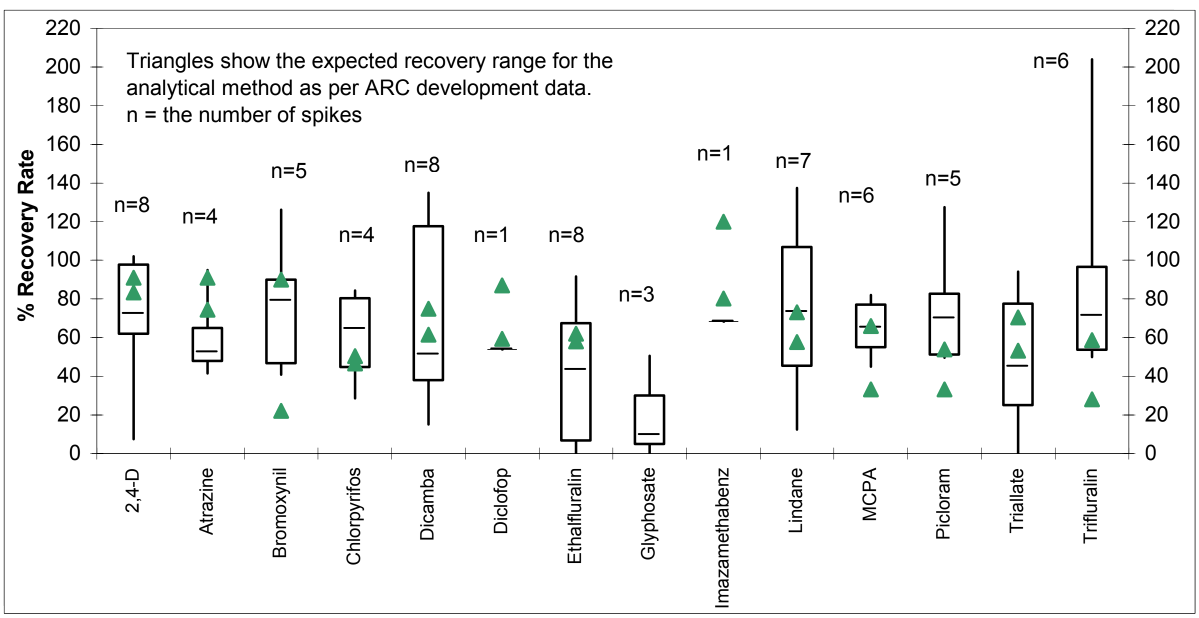

Figure B3 Percent recovery rates of pesticide spikes in surface water samples

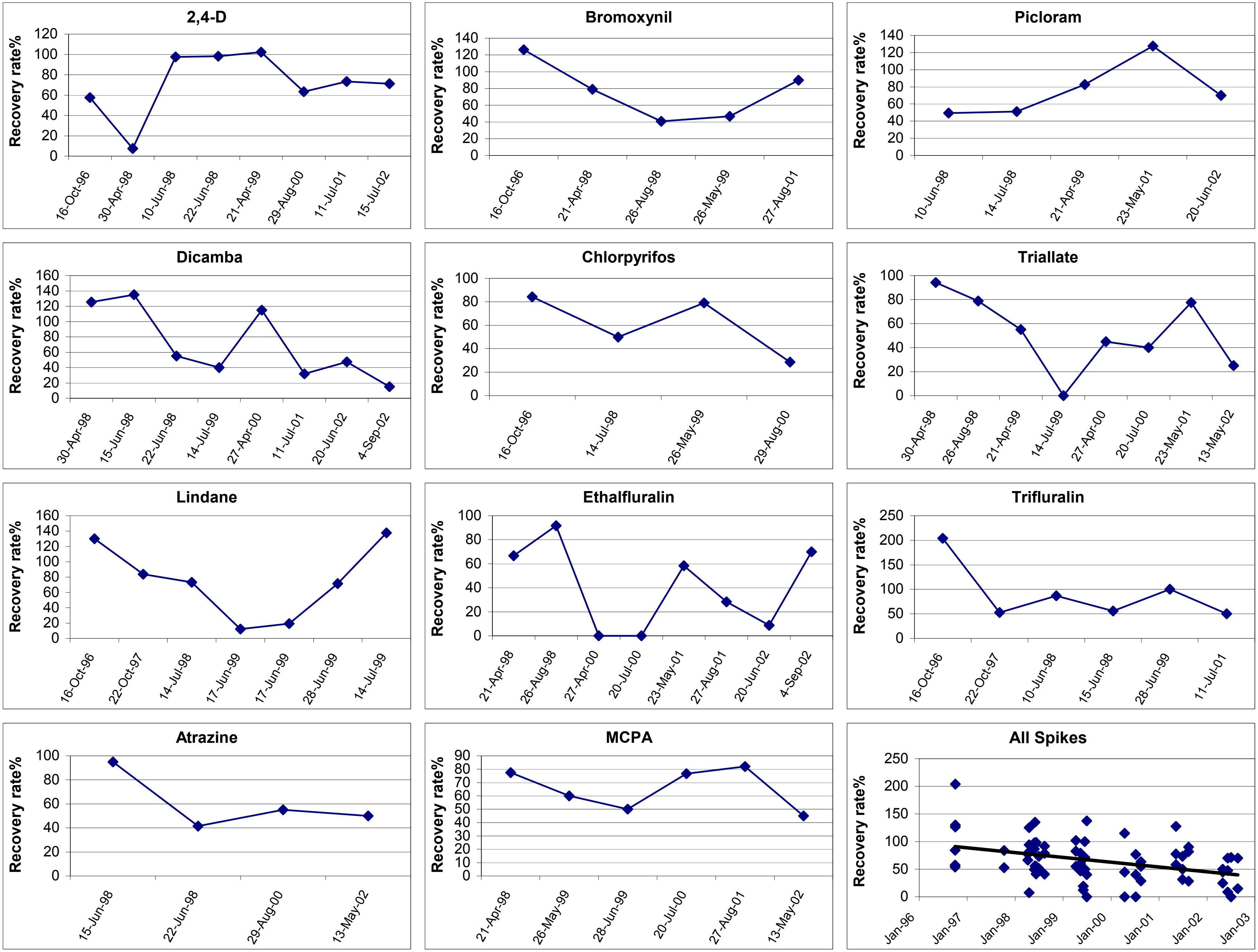

Figure B4 Trends in spike recoveries over time

- Pesticide concentrations in spike stock solutions were determined in February 2004. Table B3 provides a comparison of measured concentration with design concentrations and reveals a significant decline in pesticide levels.

This confirms that degradation of the spike material, rather than declining recoveries in the analysis of ambient samples, was the cause of declining spike recoveries and it alleviates concerns regarding the quality of Alberta Environment's pesticide database.

When design concentrations were adjusted for 2002 spikes (adjustments of spike design concentration based on February 2004 information on spike degradation is more likely to be valid for the most recent spikes in this data set), spike recoveries were considerably higher (Table B3), although usually below 100%. Picloram and ethalfluralin were the only two compounds for which recoveries appeared excessively high (above 100%).

The spiked sample results indicate that the AENV pesticide database is conservative in the sense that for most pesticides, and with the possible exception of some picloram and ethalfluralin measurements, reported concentrations are lower than actual (i.e., spike recovery <100%). In a few instances (some ethalfluralin, triallate and glyphosate measurements), spikes concentrations were not to be reported (false negatives). Furthermore, concentrations for ambient samples are not corrected for surrogate spike recovery, a common practice in dealing with such environmental data (e.g., Capel et al., 1995). It is preferable to continue reporting uncorrected values, as further inherent uncertainty is associated with correcting for recoveries.

3.3 Blank Samples

Trip blanks and field blanks consist of trace organic pure water from the analytical laboratory that is used to fill sample bottles in the laboratory or in the field following routine sample handling procedures. Trip blanks are filled in the laboratory and taken in the field, but bottles are not opened until they reach the analytical laboratory.

Field or trip blank samples make it possible to evaluate the likelihood of contamination.

Blanks were analyzed for 40 to 62 compounds, depending on when they were submitted relative to expansions in the list of pesticides analysed for. A total of 15 field blanks and 13 trip blanks were analyzed from 1995 to 2002, inclusive (Table B4). These samples represent a total of 566 and 562 individual pesticide measurements in field and trip blanks, respectively. Two of these measurements yielded positive detections in field (2,4-D and MCPP measurement), and three in trip blanks (azinophos-methyl, MCPA and glyphosate), representing, 0.4 and 0.5% of the measurements, respectively. In the case of the trip blanks, one reported concentration was below the MDL. In most instances, reported measurements were in a range of 2 to 3 times the MDL (2,4-D, MCPP, and glyphosate), however, the single MCPA detection in a trip blank was 10 times the detection limit. The azinphos-methyl detection in a trip blank was reported at a value less than the MDL.

Table B3 Degradation of spike material and adjusted spike recovery (concentrations in µg/L)

1. Comparison of spike standards with spike design concentrations			
Compound	**Design Concentration**	**Actual Concentration (February 2004)**	**% Decrease in Concentration**
Dicamba	0.250	0.178	-29
2,4-D	0.250	0.192	-23
Ethalfluralin	0.250	0.070	-72
Trifluralin	0.250	0.077	-69
Atrazine	0.250	0.122	-51
Triallate	0.250	0.144	-42
Picloram	0.250	0.145	-42
MCPA	0.250	0.133	-47

2. Recovery rates for 2002 spiked samples, taking decline in spike concentrations into account				
	Unspiked Split	**Spiked Split**	**Adjusted Spike Design Concentrations**	**% Recovery**
2,4-D				
15-Jul-02	L0.005	0.057	0.057	100.0
Atrazine				
13-May-02	L0.005	0.03	0.029	103.4
MCPA				
13-May-02	L0.005	0.036	0.043	83.7
Picloram				
20-Jun-02	NS**	0.042	0.035	120.0
Triallate				
13-May-02	L0.005	0.01	0.023	43.5
15-Jul-02	L0.005	L0.005	0.023	0.0
Ethalfluralin				
20-Jun-02	NS**	0.006	0.011	31.8
04-Sep-02	L0.005	0.042	0.017	247.1
Dicamba				
20-Jun-02	NS**	0.031	0.043	66.3
04-Sep-02	L0.005	0.003	0.014	21.4

Note: Refer to Table 2.2. For unadjusted spike design concentrations

Table B4 Summary of detections in field and laboratory blanks

Pesticide Residue	MDL	Field Blanks			Trip Blanks		
		# Samples	# Samples with Concentration > MDL	Concentration in µg/L	# Samples	# Samples with Concentration > MDL	Concentration in µg/L
2,4-D	L0.005	15	1	0.011	13	0	
2,4-DB	L0.005	15	0		13	0	
DICHLORPROP(2,4-DP)	L0.005	15	0		13	0	
ALPHA-BHC	L0.005	15	0		13	0	
ALPHA-ENDOSULFAN	L0.005	15	0		13	0	
GAMMA-BHC (LINDANE)	L0.005	15	0		13	0	
METHOXYCHLOR	L0.03	15	0		13	0	
ATRAZINE	L0.005	15	0		13	0	
BROMACIL	L0.03	15	0		13	0	
BROMOXYNIL	L0.005	15	0		13	0	
CARBATHIIN	L0.1	15	0		13	0	
CYANAZINE	L0.05	15	0		13	0	
DIAZINON	L0.005	15	0		13	0	
DICAMBA	L0.005 (L0.02)	15	0		13	0	
DICLOFOP-METHYL	L0.02	15	0		13	0	
DISULFOTON	L0.2	15	0		13	0	
DIURON	L0.2	15	0		13	0	
CHLORPYRIFOS	L0.005	15	0		13	0	
ETHALFLURALIN	L0.005	15	0		13	0	
ETHION	L0.1	15	0		13	0	
AZINPHOS-METHYL (GUTHION)	L0.2	15	0		13	1	0.048
CLOPYRALID	L0.02	15	0		13	0	
MALATHION	L0.05	15	0		13	0	
MCPA	L0.005	15	0		13	1	0.048
MCPB	L0.02	15	0		13	0	
MCPP (MECOPROP)	L0.005	15	1	0.014	13	0	
PICLORAM	L0.005	15	0		13	0	
PHORATE (THIMET)	L0.005	15	0		13	0	
TERBUFOS	L0.03	15	0		13	0	
TRIALLATE	L0.005	15	0		13	0	
TRIFLURALIN	L0.005	15	0		13	0	
IMAZAMETHABENZ	L0.05	14	0		13	0	
DESETHYL ATRAZINE	L0.05	11	0		13	0	
DEISOPROPYL ATRAZINE	L0.05	11	0		13	0	
QUINCLORAC	L0.005	11	0		13	0	
IMAZETHAPYR	L0.02	11	0		13	0	
FENOXAPROP-P-ETHYL	L0.04	11	0		13	0	
PYRIDABEN	L0.02	11	0		13	0	
DIMETHOATE	L0.05	11	0		13	0	
IMAZAMOX	L0.02	2	0		13	0	
GLYPHOSATE	L0.2	1	0		4	1	0.228
AMINOMETHYL PHOSPHONIC ACID (AMPA)	L1	1	0		4	0	
GLUFOSINATE	L1	1	0		4	0	
SIMAZINE	L0.01	2	0		5	0	
TRICLOPYR	L0.01	2	0		5	0	
4-CHLORO-2-METHYLPHENOL	L0.01	1	0		2	0	
2,4-DICHLOROPHENOL	L0.01	1	0		2	0	
ALDRIN	L0.005	0	0		1	0	
DIELDRIN	L0.005	0	0		1	0	
METOLACHLOR	L0.005	0	0		1	0	
PARATHION	L0.01	0	0		1	0	
METRIBUZIN	L0.01	0	0		1	0	
CHLOROTHALONIL	L0.005	0	0		1	0	
IPRODIONE	L0.02	0	0		1	0	
PROPICONAZOLE	L0.05	0	0		1	0	
HEXACONAZOLE	L0.05	0	0		1	0	
METALAXYL-M	L0.01	0	0		1	0	
FLUAZIFOP	L0.01	0	0		1	0	
FLUROXYPYR	L0.01	0	0		1	0	
QUIZALOFOP	L0.03	0	0		1	0	
BENTAZON	L0.005	0	0		1	0	
ETHOFUMESATE	L0.005	0	0		1	0	
LINURON	L0.02	0	0		1	0	

The report of five measurable concentrations in these blanks is indicative of false positives or contamination. To date there has been one documented incidence of laboratory contamination. Trifluralin detections in the Drinking Water Survey samples during the winter of 2002-03 were traced back to glassware contamination following the analysis of samples with very high levels of this herbicide. There is no evidence that the detection of the 3 pesticides in the trip blanks was due to laboratory contamination (i.e., laboratory batch blanks were not contaminated, Dave Humphries, personal communication). Hence these detections could represent false positives.

Martin et al. (1999) found that field blanks in the National Water Quality Assessment Program in the USA showed evidence of contamination by some pesticides (15 of the 88 pesticides analyzed were detected in blanks). This contamination did require consideration in the interpretation of detection frequency and concentrations in the pesticide data base for some of the pesticides encountered in blanks (i.e., cis-permethrin, pronamide, p,p'-DDE, pebulate, propargite, ethalfluralin and triallate). In the Alberta database the detection of residues in field blanks is very infrequent relative to the detection frequency in the ambient samples and occurs at concentrations that are low compared to the median ambient concentrations. Contamination of field blanks and trip blanks is believed to have a negligible effect on the reliability of the Alberta surface water pesticide database.

The results of blank analyses suggest that sample contamination, or report of false positives, occurs at a very low frequency, and mostly in a concentration range less than three times the MDL.

3.4 Spatial Variability Of Pesticides In Standing Water Bodies

Samples were collected from standing water bodies in 1997 and 2000 to describe, at a scoping level, the variability that exists on a given day among pesticide residue levels measured in samples taken from various locations in a lake or wetland. The intent was to help define appropriate sampling procedures for standing waters.

Only 6 of the 40 compounds analyzed were detected (Table B5).

In 1997, 10 and 9 samples were taken from different locations in Haunted and Pakowki lakes, respectively. Haunted Lake is a small lake in central Alberta (less than 1km^2); Pakowki Lake is a large shallow lake in southeastern Alberta (approximately 91 km^2, Jim Ames 2004). Each sample consisted of grab samples, taken from 9 to 10 different locations in the lake, that were combined to form a composite sample. No pesticides were detected in any of the Haunted Lake samples, but 2,4-D and MCPA were found at low levels in samples from Pakowki Lake. The coefficient of variation for 2,4-D (17%) was well within the range of variability that can be expected in split samples. Similarly, the variability among the MCPA measurements was low (CV of 47%), particularly considering the very low levels at which concentrations are reported. The absence of detections of other pesticide residues in all replicates is also indicative of low variability in lake samples and of a low incidence of false positives.

In 2002, composite samples were taken from wetlands in the Aspen Parkland to evaluate the incidence of pesticide contamination (Anderson et al. 2002); most of these wetlands were less

Table B5 Pesticide detections in multiple samples from the same water body (concentrations in µg/L)

(40 pesticides analyzed, only those with detections presented here)

	2,4-D	Lindane	Clopyralid	MCPA	Picloram	Imazamethabenz
Haunted Lake near Alix (July 23, 1997)						
Each sample is from a different part of the lake and is a composite of 10 sub-samples						
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.05
*RCV **	*0*	*0*	*0*	*0*	*0*	*0*
Pakowki Lake (July 31, 1997)						
Each sample is from a different part of the lake and is a composite of 10 sub-samples						
	0.054	L0.005	L0.02	L0.005	L0.005	L0.05
	0.034	L0.005	L0.02	0.007	L0.005	L0.05
	0.035	L0.005	L0.02	0.009	L0.005	L0.05
	0.038	L0.005	L0.02	0.008	L0.005	L0.05
	0.048	L0.005	L0.02	0.01	L0.005	L0.05
	0.033	L0.005	L0.02	0.007	L0.005	L0.05
	0.039	L0.005	L0.02	0.008	L0.005	L0.05
	0.041	L0.005	L0.02	L0.005	L0.005	L0.05
	0.037	L0.005	L0.02	L0.005	L0.005	L0.05
RCV	*17*	*0*	*0*	*47*	*0*	*0*
Wetland #62 (June 19, 2000)						
First sample is a composite of 10 subsamples, others are grabs from different parts of the wetland						
	0.472	*L0.005*	*0.066*	*0.036*	*L0.005*	*L0.05*
	0.487	L0.005	0.064	0.035	L0.005	L0.05
	0.508	L0.005	0.064	0.042	L0.005	L0.05
	0.554	L0.005	0.072	0.046	L0.005	L0.05
	0.535	L0.005	0.077	0.04	L0.005	L0.05
	0.413	L0.005	0.057	0.033	L0.005	L0.05
*RCV***	*10*	*0*	*10*	*13*	*0*	*0*
Wetland #10 (June 21, 2000)						
First sample is a composite of 10 subsamples, others are grabs from different parts of the wetland						
	0.005	*0.021*	*L0.02*	*0.075*	*L0.005*	*L0.05*
	0.008	L0.005	L0.02	0.042	L0.005	L0.05
	0.039	L0.005	L0.02	0.109	L0.005	L0.05
	0.033	L0.005	L0.02	0.102	L0.005	L0.05
	0.032	L0.005	L0.02	0.099	L0.005	L0.05
	0.013	0.025	L0.02	0.076	L0.005	L0.05
*RCV***	*54*	*114*	*0*	*32*	*0*	*0*
Wetland #50 (July 6, 2000)						
First sample is a composite of 10 subsamples, others are grabs from different parts of the wetland						
	0.053	*L0.005*	*L0.02*	*0.091*	*L0.005*	*L0.05*
	0.043	L0.005	0.297	0.056	L0.005	0.09
	0.078	L0.005	0.36	0.122	L0.005	0.12
	0.08	L0.005	0.485	0.138	L0.005	0.12
	0.088	L0.005	0.446	0.113	L0.005	0.1
	0.072	L0.005	0.364	0.133	L0.005	0.11
RCV**	24	0	19	29	0	12

Table B5 Pesticide detections in multiple samples from the same water body (cont'd)

	2,4-D	Lindane	Clopyralid	MCPA	Picloram	Imazamethabenz
Wetland #36 (July 18, 2000)						
First sample is a composite of 10 subsamples, others are grabs from different parts of the wetland						
	0.022	*L0.005*	*L0.02*	*L0.005*	*0.899*	*L0.05*
	L0.005	L0.005	0.185	L0.005	1.421	L0.05
	0.035	L0.005	L0.02	L0.005	1.047	L0.05
	L0.005	L0.005	L0.02	L0.005	0.697	L0.05
	L0.005	L0.005	L0.02	L0.005	0.327	L0.05
	L0.005	L0.005	L0.02	L0.005	0.307	L0.05
*RCV***	*161*	*0*	*0*	*0*	*63*	*0*
Wetland #10 (July 18, 2000)						
First sample is a composite of 10 subsamples, others are grabs from different parts of the wetland						
	0.036	*L0.005*	*L0.02*	*0.022*	*L0.005*	*L0.05*
	0.038	L0.005	L0.02	0.018	L0.005	L0.05
	0.042	L0.005	L0.02	0.015	L0.005	L0.05
	0.024	L0.005	L0.02	0.022	L0.005	L0.05
	0.022	L0.005	L0.02	0.018	L0.005	L0.05
	0.024	L0.005	L0.02	0.016	L0.005	L0.05
*RCV***	*31*	*0*	*0*	*15*	*0*	*0*
Wetland #51 (July 27, 2000)						
First sample is a composite of 10 subsamples, others are grabs from different parts of the wetland						
	0.051	*L0.005*	*0.185*	*0.044*	*L0.005*	*0.117*
	0.041	L0.005	0.196	0.025	L0.005	0.085
	0.08	L0.005	0.215	0.035	L0.005	0.185
	L0.005	L0.005	0.05	L0.005	L0.005	0.405
	0.076	L0.005	0.241	0.053	L0.005	0.252
	L0.005	L0.005	L0.02	L0.005	L0.005	L0.005
*RCV***	*94*	*0*	*74*	*92*	*0*	*83*

Notes:

* to calculate the relative coefficient of variation (%CV) concentrations less than the detection limit were replaced by half the detection limit

** RCV calculated on composite and individual grab samples than 5 ha. In June and July, 2002 discrete grab samples were taken from five different locations in each of three wetlands. Pesticide residue levels in these discrete samples were compared to the levels measured in the composite samples. The composite samples were generated from sub-samples taken from the grab sample sites. Six compounds were detected (2,4-D, MCPA, lindane, clopyralid, picloram and imazamethabenz) yielding 19 cases in which measurable levels of pesticides in the composites and the five grab samples could be compared (i.e., at least one pesticide was detected in the composite and/or grab samples). In 12 of these cases a pesticide residue was detected in the composite and in all five grab samples. In two cases a compound was found in the composite and four of the grab samples (wetland 51, July: clopyralid, imazamethabenz); in the composite and three of the grab samples (wetland 51, July: 2,4-D and MCPA); and in the composite and only one of the grab samples (wetland 10, June: lindane and wetland 36, July: 2,4-D). There was one case (wetland 36, July) where clopyralid was detected in one of the replicates, but not in the composite sample. The CV was relatively low in cases where measurable amounts of pesticide residue were found in the composite and all grab samples; it was much higher in instances where concentrations in one or more of the grab samples were "<MDL".

These results suggest that in the majority of cases where pesticides were detected they appeared to be distributed over the entire wetland or lake. Lake samples appeared to be quite uniform in concentrations, which could suggest that the lakes were better mixed. In some wetlands, however, there was an indication of a more patchy distribution. In such cases composite samples had a somewhat better likelihood of detection than individual replicates. For this reason, composite samples are believed to provide a better indication of overall pesticide contamination in standing water bodies. The absence of pesticide detections in the 221 remaining cases of this data set provides further grounds to believe that false positives occur rarely.

4.0 SUMMARY AND CONCLUSIONS

Quality assurance samples that are incorporated in individual field programs include splits, blanks and spikes. The analysis of these samples makes inferences possible about some aspects of the quality of the provincial pesticide database.

- Pesticide detection frequency is likely biased low. Results indicate that there is a greater likelihood of false negatives (not reporting a pesticide residue that is actually present) than false positives (erroneously reporting the presence of a pesticide residue).
- Reported pesticide concentrations are likely biased low. This is based on the fact that recovery rates of spiked samples is usually less than 100%, and on the fact that reported ambient concentrations are not corrected for surrogate recoveries.

Because both pesticide detection frequency and reported concentrations are likely biased low, the pesticide database provides a conservative indication of pesticide contamination in Alberta surface waters. This situation appears to be inherent to pesticide databases for surface waters (e.g., National Water Quality Assessment Program in the USA) and is not regarded as a weakness in the database.

Results of spatial replicate samples from lakes and wetlands indicate that composite samples taken from different locations across the water body offer a somewhat better indication of overall pesticide contamination than do individual single grab samples, especially for wetlands. However, site-specific study design considerations need to enter in the decision to collect discrete or composite samples.

5.0 RECOMMENDATIONS

Inclusion of QA/QC samples is an important component of any sampling program and often needs to be tailored to project-specific needs. However, some aspects of the QA/QC sampling could be coordinated at a provincial level, thereby allowing a more consistent approach and possibly some reductions in cost:

- On a provincial scale, split and spiked surface water samples, field blanks, trip blanks and spiked trip blanks need to be collected at least once a month during the open water season, when most samples are collected. Trip blanks and spiked trip blanks can serve the needs of several projects across the province.
- The spiking program initiated in 1997 focused routinely on 12 of the 32 compounds that were analyzed and that were detected frequently at the time (i.e., 2,4-D, MCPA, dicamba. picloram, bromoxynil, imazamethabenz, triallate, atrazine, lindane, trifluralin, chlorpyrifos, and ethalfluralin). Since then the list of compounds analyzed has increased and patterns of detections have evolved, leading to a need to broaden the spiking program. Consideration should be given to include pesticides which are detected fairly frequently as well as pesticides that have been added recently to the suite of compounds analyzed routinely (e.g., MCPP, clopyralid, dichlorprop, imazethapyr, diuron, simazine, triclopyr, fluazifop, quizalofop, bentazon, ethofumasate, chlorothalonil, iprodione, propiconazole, hexaconazole, and metalaxyl).
- A spiking program also needs to be in place when analyses for glyphosate, aminomethyl phosphonic acid and glufosinate are undertaken.
- Most of the spiking has been done on samples from natural surface waters. There is a need to include spiked trip blanks on a regular basis to determine to what extent matrix interference influences spike recovery rates.
- Concentrations in pesticide spike stock solutions need to be verified on a regular basis (e.g., at the start and the end of the pesticide field program, which goes from March to and including October).

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