A Summary of Pesticide Residue Data from the Alberta Treated Water Survey, 1995-2003

Alberta Environment

A Summary of Pesticide Residue Data from the Alberta Treated Water Survey, 1995-2003

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SUMMARY

Pesticide residues in aquatic environments in Alberta were relatively poorly documented until recently. Although pesticides had been analyzed for in environmental samples since the early 1970's, and in treated water supplies since 1978, detection limits were high and few pesticides were detected. Recently, new analytical instrumentation has enabled a 1-2 order of magnitude reduction in detection levels, resulting in information on pesticides in treated water supplies that was not available before.

Because very few detections of pesticides had been made previously, no reviews had been done on pesticides in treated water supplies. Since 1995, when the new analytical instrumentation came on line, a pesticide residue database for treated water supplies in Alberta was established. A review of this database was timely as it coincided with an increased focus on treated water quality following incidents with bacterial contamination in Ontario and Saskatchewan, and with an incident in eastern Alberta with significant herbicide contamination of a treated water supply (Village of Chauvin). Further focus on water quality issues in Alberta has come about with the recent release of Water for Life: Alberta's Strategy for Sustainability, a provincial water strategy which has protection of water quality for all uses as one of its major components.

During the period of 1995-2003, 1788 water samples were collected for pesticide residue analysis through the Treated Water Survey Program. Pesticides were detected in 26.6% of all samples; with 2,4-D (18.1%) and MCPA (10.6%) being the two most commonly detected pesticides. Other pesticides (mecoprop – 3.6%; clopyralid – 3.6%, picloram – 3.4% and dicamba – 2.8%) were detected less frequently. Thirteen other pesticides were detected infrequently (<2%).

Analysis of the data showed that there was no overall trend over the nine years in detection frequency, or concentration.

Although it was anticipated that higher detection frequencies and concentrations would be observed in the May – July period when the majority of pesticides are applied in Alberta, no seasonality in either detection frequency or magnitude of concentration was observed ($p > 0.05$). This indicated that pesticides could be detected in treated water supplies year round.

Extensive analysis was done to determine if the water source (groundwater or surface water) was a contributing factor to pesticide detections. The highest rate of detection frequency was observed at facilities utilizing surface water (32.3%), followed by facilities utilizing shallow groundwater (16.7%), and by facilities utilizing deep groundwater (5.8%). For the most part, maximum concentrations found were also higher in surface water sourced facilities.

A preliminary analysis of this data (up to 2001) highlighted the fact that only limited sampling had been done at groundwater sourced facilities, as over 75% of the samples had been collected at surface water facilities. This was brought to the attention of the

regional staff, and a greater sampling intensity of groundwater sourced facilities occurred in 2002 and 2003.

A small project to assess the effect of current water treatment processes on pesticide removal was conducted in 2001 at Lethbridge and Carmangay, approximately 55 km north of Lethbridge. Raw and treated water samples were collected weekly for five weeks in June and July. The paired results from these two facilities were assessed along with paired samples collected in 1995 from seven other facilities in Alberta. No statistically significant differences in overall raw and treated water results were observed at either facility individually, or at all facilities combined, although some significant reductions (though slight) in MCPA concentrations were observed. These results confirm other findings and suggest that water treatment processes do not effectively reduce pesticide concentrations, hence they point out the need for watershed protection to minimize pesticide contamination of surface waters.

The analytical results were also assessed for differences in spatial distribution of detections across the province. As many of the facilities sampled utilize surface water, river basins were used as one of the spatial units to summarize the data. Facilities in the South Saskatchewan River and the Oldman River basins displayed the highest frequency of pesticide detections (55.7% and 46.9%, respectively). Water treatment facilities in the Battle River basin also had relatively high frequencies of pesticide detections (40.3%). Facilities in the Athabasca River basin had the lowest detection frequency (6.8%). Differences observed between the basins are related to pesticide usage patterns and intensity in those basins.

Water quality guidelines for drinking water, livestock watering, protection of fresh water aquatic life (FAL) and irrigation have been established for a number of the pesticides detected in treated water supplies. All of the pesticides detected were in compliance with the available Canadian Drinking Water Guideline, with the maximum levels detected being approximately 1-2% of the guideline(s). Similarly, guidelines for livestock watering were also met. The FAL and Irrigation guidelines are generally lower than the Drinking Water Guidelines. One insecticide (lindane) exceeded the FAL guideline in three samples, while the herbicides dicamba and MCPA exceeded the Irrigation guideline in 38 and 34 samples, respectively.

This report does not suggest that pesticide residue levels have compromised drinking water quality, but the information contained in the report will be of use in further development of water strategy initiatives relating to watershed protection and aquatic ecosystem protection. Land activities (such as pesticide application) can have significant impacts upon water systems (surface and groundwater), and the information in this report highlights the potential effects of these land-based activities on water treatment systems within the watershed.

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ACKNOWLEDGEMENTS

The efforts of Alberta Environment regional staff, who carry out the Treated Water Survey, made it possible to prepare this review of a small portion of the data that is generated on an annual basis from the Treated Water Survey Program. Their assistance is gratefully acknowledged.

Karen Saffran assisted with the utilization of WQHYDRO, while Carol Thurston and Ted Bolseng assisted with report formatting and preparation.

This report has benefited from the reviews of Janet Mclean and Anne-Marie Anderson.

This report is dedicated to the memory of Garry Halina, who undertook the first Treated Water Survey in 1978, and was responsible for ensuring that the program was sustained over the years.

1.0 INTRODUCTION

Alberta Environment undertook the routine sampling of treated water supplies back in 1978, as part of its initiative to enhance and protect the quality of water being supplied to municipal residents. Although all treated water facilities are required to conduct their own routine sampling for common inorganic parameters, only two facilities (Edmonton and Calgary) are required to conduct routine pesticide analyses. As part of its quality assurance program, Alberta Environment carries out a treated water survey program. Under that program, a wide range of parameters are measured at a number of water treatment facilities each year to verify the data collected by the facility, to check on the facility's operation, and to identify any areas for improvement. These parameters include routine inorganic chemistry, extractable and volatile priority pollutants, and pesticides.

Prior to 1995, very few pesticides were ever detected in treated water supplies. In 1995 however, the Alberta Research Council, who does the priority pollutants and pesticides analyses for Alberta Environment for this program, obtained a new analytical instrument. They were able to lower their pesticide detection levels[1] from 0.2 µg/L to 0.005 µg/L (5 parts per trillion) for many of the commonly used pesticides in Alberta.

As a consequence of lowering the detection limits, reports of low-level pesticide detections have become common in a wide range of water samples collected by Alberta Environment after January of 1995. Data from 1995 to March of 2003 were summarized and analyzed for trends, so that recommendations for possible treatment process or regulatory changes could be made.

The objectives to this report were to:

- summarize the pesticide data collected under the Treated Water Survey Program, looking at various attributes such as pesticide detection frequencies, trends, seasonality, and spatial distributions;
- compare groundwater and surface water supplies with regards to pesticide detections;
- evaluate the results for compliance with Canadian Drinking Water Guidelines and other water quality guidelines; and
- on a preliminary scale, evaluate the effectiveness of current water treatment technologies on pesticide removal.

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[1] Detection level as used in this report is the laboratory's method detection level, which is actually the "quantification level", or the level at which the analytical laboratory can quantify the level of pesticide in a sample. This is based upon the ability of the laboratory to statistically reproduce the analytical value. The laboratory would, on occasion, identify the presence of a compound through the presence of qualifying ions, and would report a value that would be less than the detection (or quantification) level, as an estimated value.

2.0 TREATED WATER SURVEY

The Treated Water Survey commenced in 1978, with a two year survey of the treated water of Edmonton, Red Deer, Calgary and Lethbridge (Halina 1980). Samples were collected on a monthly basis, and were analyzed for a wide range of parameters, including pesticides. Analysis was done by the Pollution Control Laboratory of Alberta Environment. This laboratory eventually became the Alberta Research Council laboratory in Vegreville, which still does the majority of the organic analyses for the Treated Water Survey.

The report on the first survey recommended that the monitoring program should be an ongoing one and that it should be expanded to include additional cities (Medicine Hat, Grande Prairie and Drumheller). A second survey was conducted during 1980 at all of the municipalities listed above (Halina 1982).

Since then, the program continued to grow and expand. However, the focus changed from monthly sampling at large urban centre water treatment plants to sampling 2-3 times/year at water treatment plants with surface water sources, and at least once every five years for water treatment facilities utilizing ground water (Beier 2002). The selection of facilities to be sampled was influenced by routine inspection schedules, and facilities undergoing source and/or process changes. The Treated Water Survey is supplemental to the routine water quality monitoring conducted by municipalities as part of their approval requirements for their water treatment plant.

Annual data reports were prepared until 1996. Li (1997) was the last report to be prepared and released.

It should be noted that the Treated Water Survey was not systematically or statistically designed to provide a detailed provincial assessment and overview of treated water quality. It is a supplement to routine inspections. The sampling was merely intended to identify any serious problems with water quality that might be present at a facility. It was a program that evolved over the years, and focussed on facility inspections, population served, and quality of source water. It was also constrained by budget and staff limitations. As such, the current overview does not provide a complete province-wide assessment of treated water quality with respect to pesticides, which is why only 440 facilities were sampled over the time period under review.

Another aspect of the Treated Water Survey that has not been addressed is a QA/QC (Quality Assurance/Quality Control) program. The program has depended upon internal laboratory QC protocol to ensure quality data. However, the data is reviewed upon receipt for obvious errors or missing data.

Pesticides are only one component of treated water analysis and, based on current concentrations, represent a lower risk than bacterial contamination or other parameters that can often be near, or exceed the Drinking Water Guidelines. However, a review of the pesticide data was undertaken to identify issues at a provincial scale and to provide guidance in the future management of pesticides in Alberta.

3.0 METHODS

3.1 Sampling

Regional technicians from Alberta Environment conduct routine inspections of water and wastewater treatment facilities as part of the regulatory assurance process. During these inspections, water samples were often collected for a wide range of parameters. Treated water samples for pesticides were usually collected right at the water treatment plant, but they have also been collected at various municipal buildings (town office, town shop), as well as retail establishments. A 1 L brown amber bottle, certified to trace organic standards, was filled to the top (with no head space), placed in a cooler, and shipped to the Alberta Research Council (ARC) laboratory in Vegreville for analysis.

Sampling was conducted throughout the year. Approximately 200 samples were collected each year, with samples being collected in each month of the year. Over the slightly more than eight years of data under review, 1788 samples were collected for the Treated Water Survey and analyzed for pesticide residues. It should be noted that only three months of data from 2003 (January, February and March) were included in the data review.

3.2 Sample Analysis

Water samples for pesticide analysis were logged in upon arrival at ARC, and kept refrigerated until extraction. Samples were acidified below pH 2 with concentrated H_3PO_4 and salted out with 200g NaCl per 1 L sample. Extraction involved adding 50 ml of dichloromethane, repeated three times. The extract was dried with acidified sodium sulphate, and concentrated to approximately 500 µL.

The extracts were derivatized using about 1 ml of diazomethane per sample/tube. The dichloromethane was exchanged with n-hexane, which was reduced to 200 µL (using fume hood air flow) and transferred to 200 µL autosampler vial inserts. Extracts were spiked with an internal standard mix (naphthalene-d_8, phenanthracene-d_{10}, and benzo(a)anthracene-d_{12}) and analyzed using a Varian 3400 GC/MS (Ion trap). The GC was brought up to 65^{o}C, then ramped up to 115^{o}C at 10^{o}C/minute. It was taken from 115-220^{o}C at 3.5^{o}C/minute, from 220-300^{o}C at 8^{o}C/minute, and held at 300^{o}C for 4.9 minutes. A 30 metre, 0.25 mm internal diameter DB-5MSITD fused silica column with a 25 µm film thickness was used.

Samples were injected using an 8200 Autosampler, with 2 µL injection. The Varian Saturn 3 Iontrap used for the mass spectrometry covers a full scan of ions (79-399 m/z). Two to three extracted ions were used for identification: 1 for quantification, and 1 or 2 ions as qualifier ions. A four-point calibration curve was utilized for calibration.

Analysis of 32 parameters was conducted in 1995, with quantification (detection) levels ranging from 0.2 to 0.005 µg/L. Additional parameters were added in 1998 and 1999, and 40 parameters were included in the analytical screen by 2000 (Appendix 1). More parameters were added in 2003-2003 following a review of Alberta pesticide usage and analytical capabilities, resulting in 44 parameters in the basic screen, and 62 parameters in the extended screen. Only a small number of samples have been analyzed to date with the extended screen.

3.3 Data Analysis

Initial analysis of the data involved pesticide detection frequency and mean pesticide concentrations.

Pesticide detection frequency was based upon the number of samples with at least one pesticide detection, divided by the total number of samples analyzed (for that particular parameter). It was expressed as a percentage. Although the number of samples varied from sampling period to sampling period, the detection level for most parameters was consistent over the period under review. The only exception was for dicamba, where the detection level was lowered from 0.02 µg/L to 0.005 µg/L in 2001.

Mean pesticide concentrations were used to determine the relative magnitude of pesticide concentrations found in treated water supplies. Some studies (e.g., Cross 1999) have used total pesticide concentrations (summation of the concentrations of all pesticides detected), however that analysis is best used for comparisons involving similar sample sizes. In this study, sample sizes were not the same, therefore it was felt that a mean concentration would better represent the magnitude of the pesticide detection's, as a comparison to the frequency of pesticide detections.

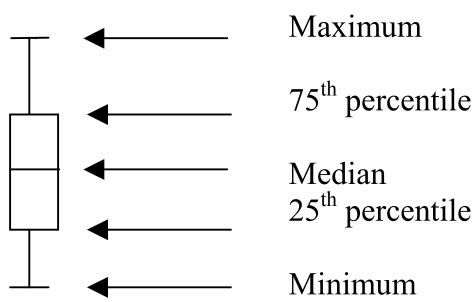
Concentrations for parameters reported as non-detected were not included in frequency of detections, mean pesticide concentrations, or number of pesticides detected per sample. In statistical analyses, these records were replaced by values that represented 1/10 of the detection level (Donald et al. 2001).

Non-parametric statistical tests were applied to the data to determine features of interest such as seasonality and trends. The Spearmans rho correlation (Hollander and Wolfe 1973) was applied to the annual frequency of detections of selected pesticides to determine if a statistically significant trend in annual detection frequencies could be observed.

Testing for seasonality was done on raw pesticide concentration data and frequency of detection data for selected parameters using the Kruskal-Wallis Test for Seasonality (Aroner 1994). The Seasonal Kendall Test (Aroner 1994) was also applied to the data to test for trends in pesticide concentrations.

Box and whisker plots using WQHYDRO (Aroner 1994) were prepared for selected parameters for monthly detection frequency and for mean pesticide concentrations (summation of monthly concentrations divided by number of monthly samples).

Box and whisker plots provide a visual display of basic summary statistics associated with a group or range of samples. The top and bottom endpoints (whiskers) show the maximum and minimum values in a group of samples. The top line of the box is the 75th percentile, and the bottom line of the box is the 25th percentile. The line bisecting the box is the median value of the group of samples.



The Wilcoxon Matched Pair Sign Test (Steel and Torrie 1980) was applied to paired samples (raw and treated water) collected from two water treatment facilities, to compare the influence of water treatment processes on pesticide concentrations.

4.0 RESULTS

4.1 Temporal Trends

4.1.1 Annual Trends

There were 1788 treated water samples collected and analyzed for pesticides between January of 1995 and March of 2003. A summary, by year, of the compounds detected, frequency of detection, maximum levels detected, and number of samples with single and multiple detection's is in Table 1. Nineteen compounds were detected over the period of record. The predominant compounds found in treated water are 2,4-D (18.1% of all samples) and MCPA (10.6% of all samples). Other compounds found regularly, but at a lower frequency include mecoprop (MCPP) (3.6%), clopyralid (3.6%), picloram (3.4%) and dicamba (2.8%). Forty-three of the 62 parameters analyzed for were not detected during the period of sampling.

There were 476 samples with at least one pesticide detected or 26.6% of all samples (Table 2). Between 1995 and 2001, there did not appear to be any specific year that was worse or better for number of detections in the samples, with the detection frequency fluctuating around 25%. The lower detection frequency reported for 2003 may be related to the limited number of samples collected in January – March of that year (data from only these three months of 2003 are included in this report).

Another component of the data is the number (and percentage) of samples with multiple pesticides detected (more than one pesticide). Within the dataset, pesticide detection's ranged from one to as many as six pesticide detections per sample. From 1995 to 2001, a slight trend appeared in that more pesticides were detected in a small number of samples (from 3 to 6 detections/sample), but that trend dropped off in 2002 and 2003.

Of the 1788 samples analyzed, and 476 samples with one or more detections, over 260 (14.5 %) samples had a single pesticide detection. Samples with two pesticide detections represented 7.0% (125) of the total number of samples analyzed. Three pesticide detections were found in 3.3% (59) of samples. Four pesticide detections were found in a total of 24 samples (1.3%). Samples with five to six detections were relatively infrequent, with usually only one sample per year showing up, in only four of the years under review.

The annual detection frequency for six of the most frequently detected compounds was plotted (Figure 1). Although 2,4-D detections fluctuated between 12 and 31%, there is no apparent trend. MCPA, on the other hand, showed a consistent increase over the first seven years from a 5.4% to a 15.8% detection frequency, but dropped below 5% in 2002 and 2003. Clopyralid also showed a slight increase in detections, from 0.6 to 6.1% detections until 2001, then also declined. Mecoprop and picloram were consistent, fluctuating from 1% to just over 7%. Dicamba was consistent from 1% to around 3%

detection frequency, until 2001, when it jumped to almost 10%. It dropped back to previously observed levels in 2002 and 2003. Further analysis on this data was done using the Spearmans rho correlation (Hollander and Wolfe 1973). There was no significant increase in frequency of detection for the six compounds ($p>0.05$).

The concentration data for these six pesticides was first tested for seasonality with the Kruskal-Wallis Test for Seasonality using WQHYDRO (Aroner 1994). None of the parameters exhibited any seasonality ($p>0.05$). The Seasonal Kendall test, using WQHYDRO, was subsequently applied to the data for the six parameters, and there was no significant increase in concentrations over the study period ($p>0.05$) for the compounds.

The data analysis indicates that the frequency of detection is not increasing for the six compounds, nor are the concentrations increasing over the time period involved. There was an increasing trend in selected compounds up to 2001, but declines in detection frequency and concentrations in 2002 and 2003 negated the trend.

Table 1 Summary by year of pesticide active ingredients detected in treated water samples – January 1995 - March 2003

		2,4-D	MCPA	Mecoprop	Clopyralid	Picloram	Dicamba	Bromoxynil	Atrazine	Lindane	Triallate	Triclopyr	Diazinon	Imazamethab-enz	Dichlorprop	MCPB	Imazethapyr	Diclofop	Azinphos-methyl	Methoxychlor
1995	# Det'ns	29	9	10	1	5	2		2											1
(n=166)	% Det'ns	17.5%	5.4%	6.0%	0.6%	3.0%	1.2%		1.2%											0.6%
	Max (µg/L)	0.199	0.085	0.027	0.027	0.086	0.072		0.057											0.031
1996	# Det'ns	25	12	2	4	8	1		2				2							
(n=212)	% Det'ns	11.8%	5.7%	0.9%	1.9%	3.8%	0.5%		0.9%				0.9%							
	Max (µg/L)	1.235	0.07	0.016	0.351	0.085	0.057		0.038				0.057							
1997	# Det'ns	46	23	2	9	3	7	2	2				1							
(n=219)	% Det'ns	21.0%	10.5%	0.9%	4.1%	1.4%	3.2%	0.9%	0.9%				0.5%							
	Max (µg/L)	0.443	0.571	0.007	0.158	0.044	0.049	0.005	0.01				0.014							
1998	# Det'ns	51	40	10	8	9	4	10	2	4				1				1		
(n=243)	% Det'ns	21.0%	16.5%	4.1%	3.3%	3.7%	1.6%	4.1%	0.8%	1.6%				0.4%				0.4%		
	Max (µg/L)	0.108	0.076	0.069	0.183	0.49	0.052	0.014	0.013	0.015				0.11				0.08		
1999	# Det'ns	34	25	9	10	8	6	2	2	2	1			1	1	1			1	
(n=191)	% Det'ns	17.8%	13.1%	4.7%	5.2%	4.2%	3.1%	1.0%	1.0%	1.0%	0.5%			0.5%	0.5%	0.5%			0.5%	
	Max (µg/L)	0.174	0.052	0.059	0.34	0.064	0.085	0.003	0.009	0.008	0.008			0.075	0.009	0.017			0.123	
2000	# Det'ns	39	34	11	10	7	5			2	2						1			
(n=238)	% Det'ns	16.4%	14.3%	4.6%	4.2%	2.9%	2.1%			0.8%	0.8%						0.4%			
	Max (µg/L)	0.649	0.045	0.024	0.245	0.089	0.284			0.026	0.011						0.055			
2001	# Det'ns	60	31	14	12	8	19		4	1	2				1					
(n=196)	% Det'ns	30.6%	15.8%	7.1%	6.1%	4.1%	9.7%		2.0%	0.5%	1.0%				0.5%					
	Max (µg/L)	0.48	0.18	0.03	0.22	4.07	0.11		0.01	0.004	0.014				0.008					
2002	# Det'ns	24	10	3	9	11	4	7				4								
(n=212)	% Det'ns	11.3%	4.7%	1.4%	4.2%	5.2%	1.9%	3.3%				1.9%								
	Max (µg/L)	0.031	0.024	0.01	0.127	0.353	0.008	0.008				0.185								
2003	# Det'ns	15	6	1	1	1	3	4				1								
(n=111)	% Det'ns	13.5%	5.4%	0.9%	0.9%	0.9%	2.7%	3.6%				0.9%								
(Jan-Mar)	Max (µg/L)	0.155	0.079	0.006	0.037	0.106	0.015	0.199				2.405								
Overall	**# Det'ns**	**323**	**190**	**64**	**64**	**60**	**50**	**25**	**14**	**9**	**5**	**5**	**3**	**2**	**2**	**1**	**1**	**1**	**1**	**1**
(n=1788)	**% Det'ns**	**18.1%**	**10.6%**	**3.6%**	**3.6%**	**3.4%**	**2.8%**	**1.4%**	**0.8%**	**0.5%**	**0.3%**	**0.3%**	**0.2%**	**0.11%**	**0.11%**	**0.06%**	**0.06%**	**0.06%**	**0.06%**	**0.06%**
	Max (µg/L)	**1.235**	**0.571**	**0.069**	**0.351**	**4.07**	**0.284**	**0.199**	**0.057**	**0.026**	**0.014**	**2.405**	**0.057**	**0.11**	**0.009**	**0.017**	**0.055**	**0.08**	**0.123**	**0.031**

Table 2 Annual pesticide detections summarized by the number of pesticides detected per sample and the detection frequency (January 1995 – March 2003)

Year (no of samples)	Number and percentage of samples with pesticides detected						
	Number of pesticides detected per sample						
	1	2	3	4	5	6	All
1995 (n=166)	28 16.9%	11 6.6%	3 1.8%				42 25.3%
1996 (n=212)	30 14.2%	6 2.8%	3 1.4%	1 0.5%			40 18.9%
1997 (n=219)	37 16.9%	15 6.8%	8 3.7%	1 0.5%			61 27.8%
1998 (n=243)	45 18.5%	18 7.4%	10 4.1%	6 2.5%	1 0.4%		80 32.9%
1999 (n=191)	27 14.1%	9 4.7%	9 4.7%	5 2.6%	1 0.5%	1 0.5%	52 27.2%
2000 (n=238)	24 10.1%	22 9.2%	8 3.4%	2 0.8%	1 0.4%	1 0.4%	58 24.4%
2001 (n=196)	31 15.8%	25 12.8%	13 6.6%	4 2.0%	2 1.0%	1 0.5%	76 38.8%
2002 (n=212)	24 11.3%	13 6.1%	4 1.9%	3 1.4%			44 20.8%
2003 (n=111)	11 9.9%	5 4.5%	1 0.9%	2 1.8%			19 17.1%
Overall (n=1788)	**260 14.5%**	**125 7.0%**	**59 3.3%**	**24 1.3%**	**5 0.3%**	**3 0.2%**	**476 26.6%**

A different perspective is displayed in Figure 2, which shows the percentage of samples with pesticides detected, based upon the monthly detection frequencies. 2003 had the lowest percentage of samples with pesticide detections, at just over 17%, however this set of data was limited to the first three months of the year. The highest percentage of detection's was observed in 2001, at 38.8%.

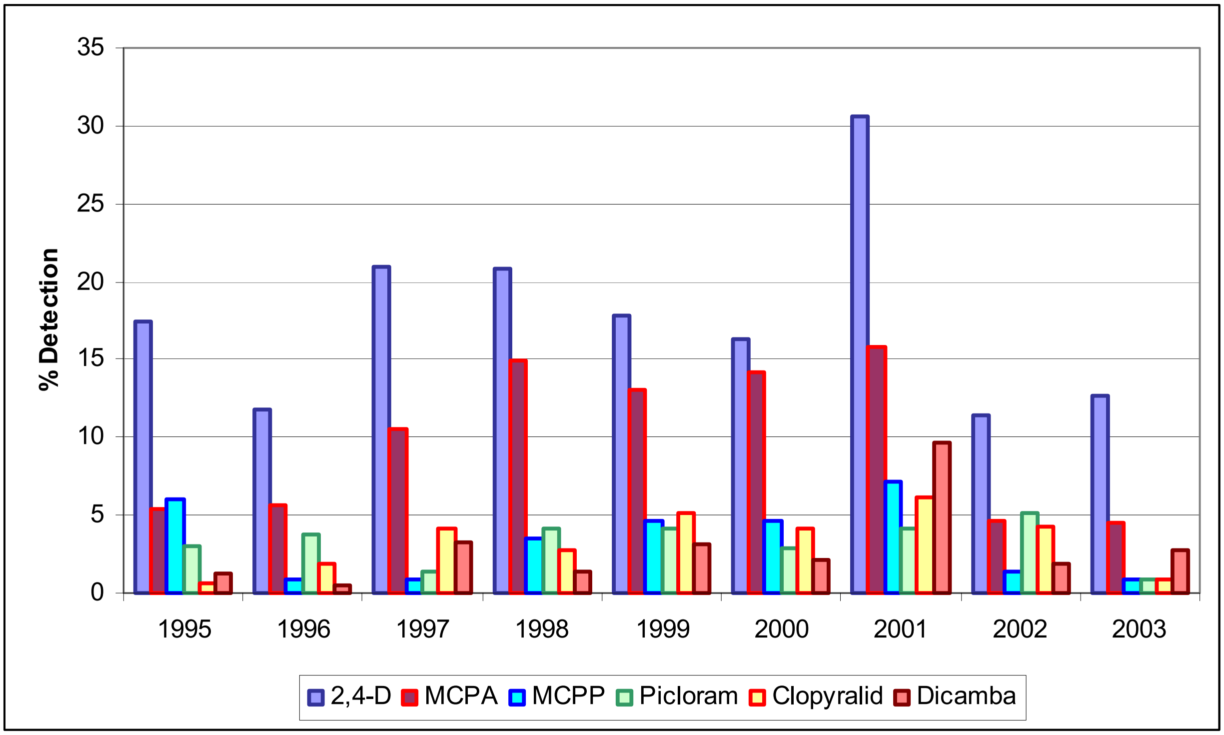


Figure 1 Detection frequencies in treated water for selected active ingredients

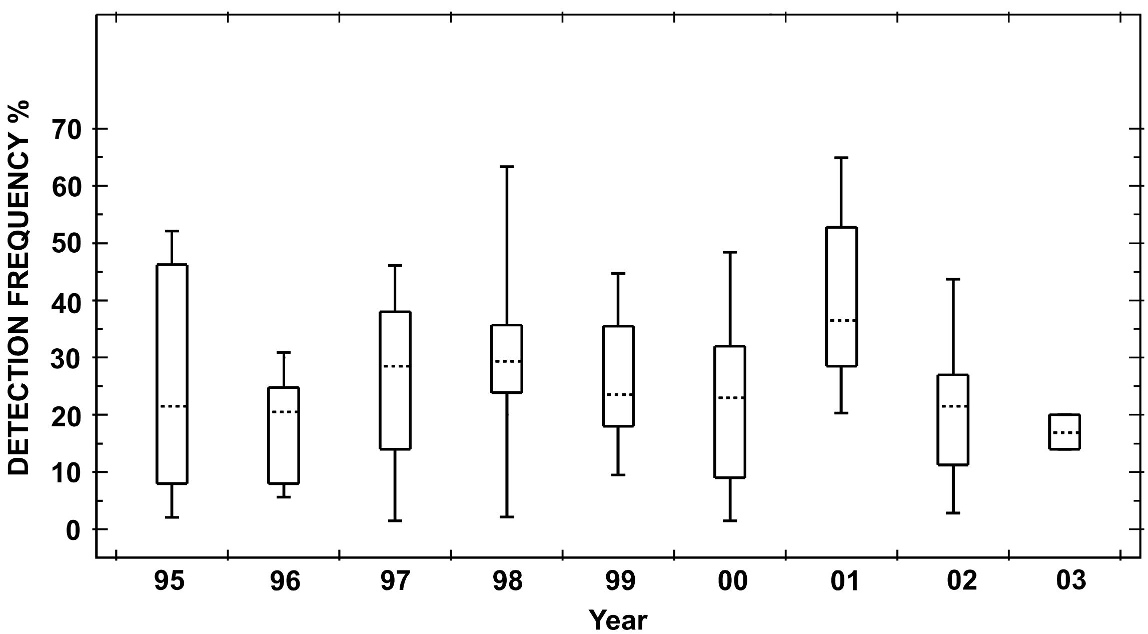


Figure 2 Box and whisker plot – Annual detection frequencies for all pesticides (based upon monthly detection frequencies)

4.1.2 Monthly Trends

A detailed review of the monthly detection frequency by compound is provided in Appendix 3. Since the pesticides analyzed for in the Treated Water Survey are field applied during the months of April through October, with the majority being applied from May through July, some seasonality in detection frequency, or in concentrations was observed.

From 1995-2003, the total number of samples collected by month ranged from 99 (November) to 162 (July). The percentage of detections ranged from an average of 19.7% in October to 42.7% in June. The monthly detection frequencies for all parameters were tested for seasonality using the Kruskal-Wallis Test for Seasonality in WQHYDRO (Aroner 1994). As well, monthly detection frequencies for 2,4-D and MCPA, the two most commonly detected pesticides, were also tested for seasonality using the Kruskal-Wallis Test. No seasonal trends in detection frequency ($p>0.05$) were observed for all parameters combined, or for 2,4-D or MCPA alone. Box and whisker plots that illustrate the monthly distribution of detection frequency for all parameters combined, and 2,4-D and MCPA separately are shown in Figures 3 – 5. The box and whisker plots illustrate that there are no apparent seasonal trends in detection frequencies for pesticides in treated water.

Further analysis was conducted to determine if the concentrations found in the water samples showed a seasonal distribution. Total average monthly pesticide concentrations were tested for seasonality using the Kruskal-Wallis Test for Seasonality. This procedure was also carried out for 2,4-D and MCPA separately.

Seasonal trends were not observed for concentrations of all parameters combined, 2,4-D or MCPA ($p> 0.05$), however, at a lower level of significance, seasonal trends were observed for MCPA ($p<0.1$). In this case, a single high value appears to have resulted in a lower level of significance, partly because there were fewer observations for this parameter than for all parameters combined. MCPA displayed a higher concentration level in October, well after the major application period for this compound.

Overall, there are no seasonal trends in pesticide detection frequency or concentration in treated water supplies. In other words, pesticides can be found year-round in treated water supplies. Data from Alberta surface waters often shows seasonality in the presence of pesticides (Anderson et al. 2004). Further examination of the data on a facility by facility basis in comparison with routine surface water monitoring data should be undertaken to determine what factors might influence the attenuation of pesticide residues in treated water supplies.

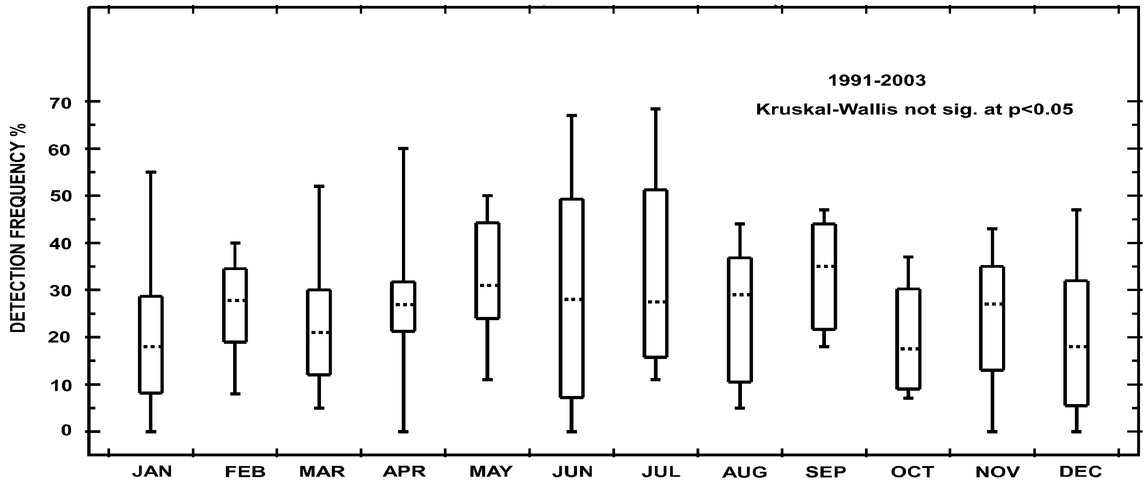


Figure 3 Box and whisker plot – Monthly detection frequencies for all parameters.

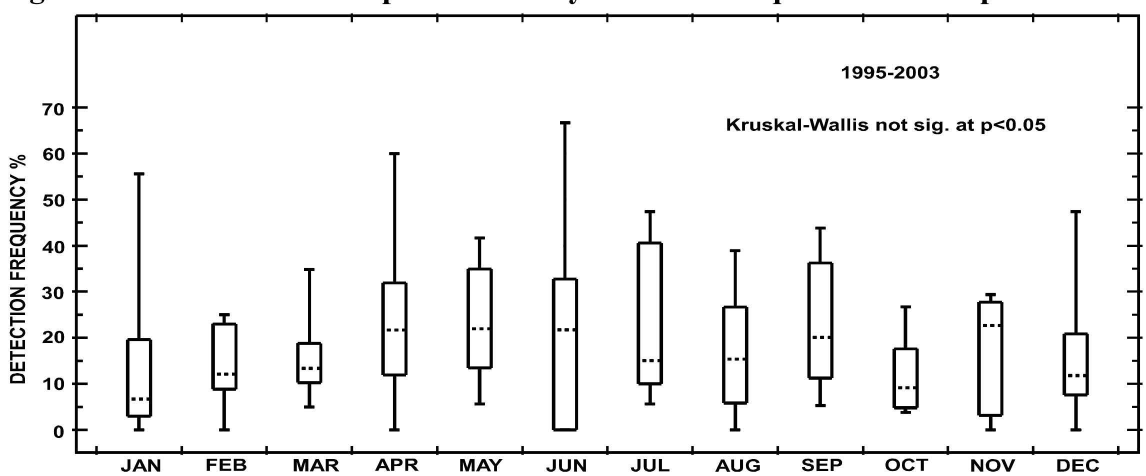


Figure 4 Box and whisker plot – Monthly detection frequencies for 2,4-D

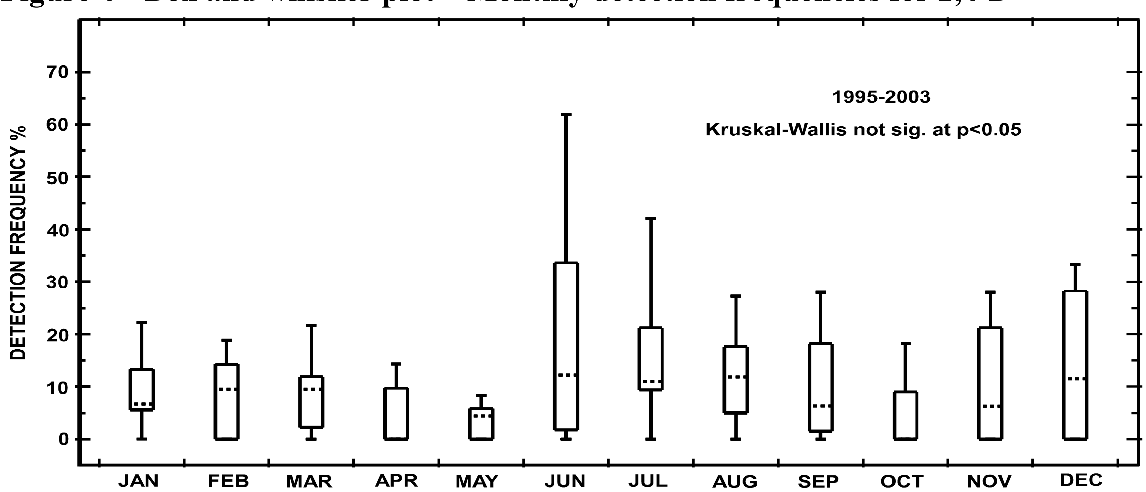


Figure 5 Box and whisker plot – Monthly detection frequencies for MCPA

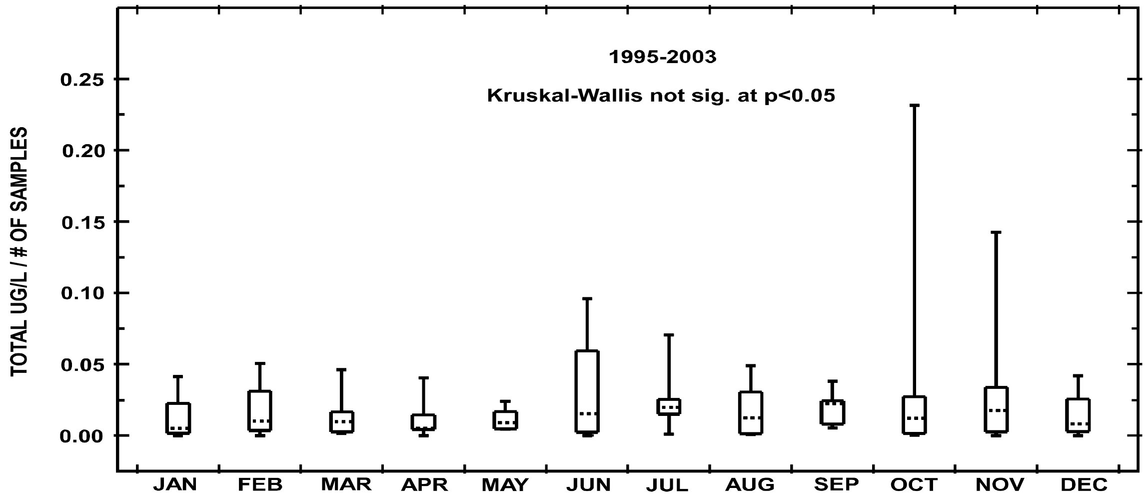


Figure 6 Box and whisker plot – Monthly mean concentrations for all parameters

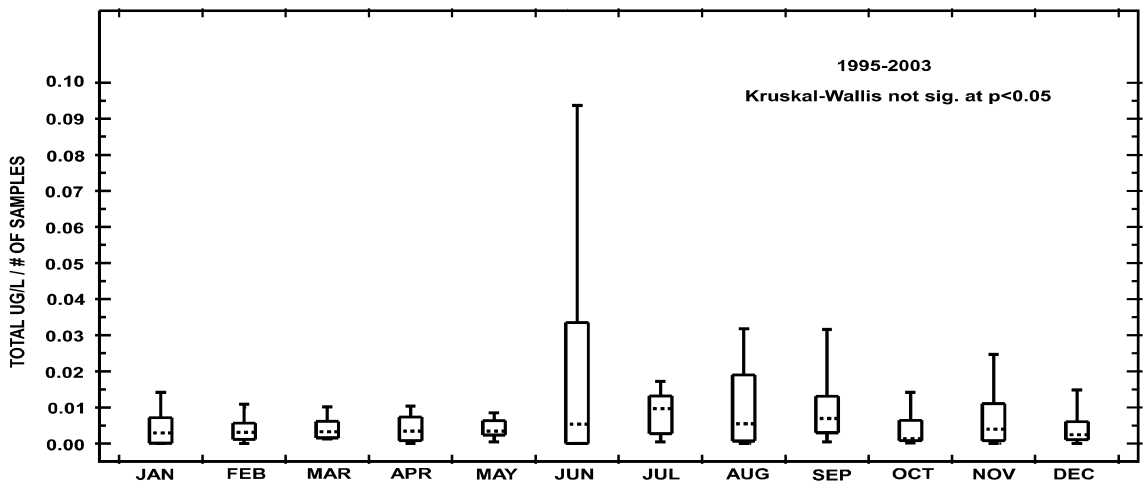


Figure 7 Box and whisker plot – Monthly mean concentrations for 2,4-D

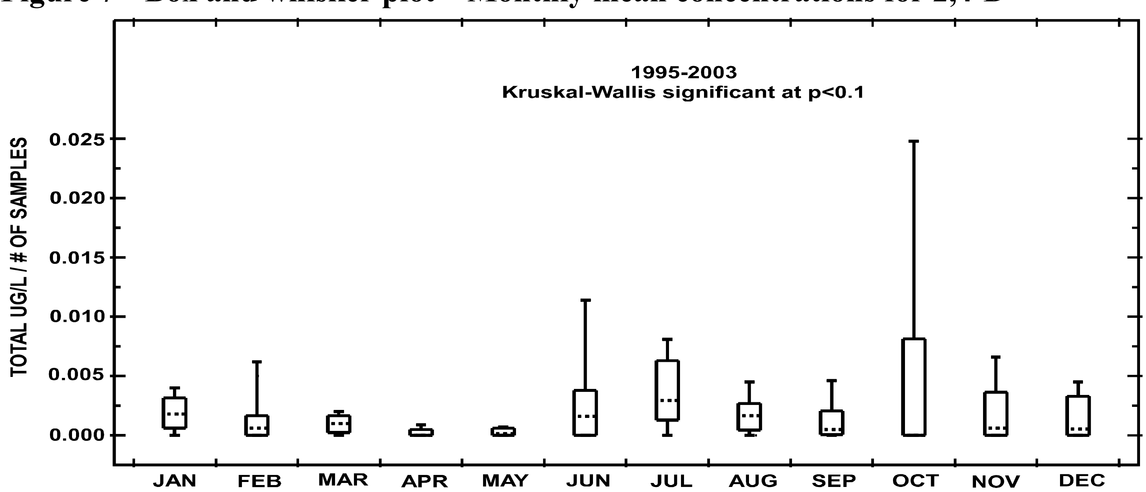


Figure 8 Box and whisker plot – Monthly mean concentrations for MCPA

4.2 Water Source

The data were summarized by source of the water (i.e., surface water, shallow or deep groundwater), as listed in the approval associated with each facility (Table 3). Four categories of source water were used: shallow groundwater, deep groundwater, surface water (includes rivers and lakes), and a combination of surface and groundwater. Water treatment facilities that used surface water as a source provided the majority of samples (1354 or 75.7%), while the next largest sample category (deep groundwater) consisted of 329 samples, or 18.4% of the total. Facilities that use shallow groundwater, or both surface and groundwater comprised only 60 (3.4%) and 45 (2.5%) samples each, respectively. Further assessment of those facilities that utilize both surface and groundwater was not done for this section.

Samples from surface water sources have the highest rate of detection of most compounds (32.3% compared to 16.7% for shallow groundwater and 5.8% for deep groundwater). It would be anticipated that shallow groundwater would be more susceptible to pesticide contamination than deep groundwater, and this trend is apparent in the data. However, there are relatively few samples collected from shallow groundwater-sourced facilities. Reliable comparisons are difficult to make because of the large number of surface water samples in the dataset compared to the groundwater samples. More extensive sampling of groundwater-sourced facilities would be required to better characterize pesticide detections from facilities utilizing groundwater.

The compounds that were predominantly found at facilities with groundwater sources (2,4-D, picloram) are also extensively found at facilities with surface water sources. Clopyralid was found in almost 5% of samples from surface water facilities, but no detections were reported in groundwater facilities. MCPA was also detected extensively at facilities with surface water sources, but only once at facilities with groundwater sources.

The number of multiple pesticide detections is also greater for the surface water sources (Table 4), in that samples with 4, 5 and 6 pesticide detections were only from facilities with surface water sources. Again, this is likely related to the larger number of samples from these facilities.

A closer look was taken at the facilities that utilize groundwater and that had pesticide detections. The location of these facilities was overlaid on an Alberta map outlining the areas that are potentially vulnerable to groundwater contamination from pesticides (McCrae 1989). Of the 25 facilities that utilized groundwater and recorded pesticide detections over the period of record, only three facilities were in an area that was identified as being potentially vulnerable to groundwater contamination by pesticides. One facility was at a provincial park, and its approval indicated that the groundwater source was shallow, and influenced by surface water (a nearby lake). However, no current pesticide data is available for this lake. The second facility was a small village south of Edmonton that utilizes deep groundwater as its water supply. The third facility utilized deep groundwater, however the local soils were very sandy. While the data do not suggest that the use of vulnerability maps is a good indicator of specific facilities where pesticides might be found, it does provide a tool to focus monitoring efforts on. It would appear that the use of vulnerability maps requires further assessment and fine-tuning before they can be considered a good guide to areas of the province vulnerable to pesticide contamination of groundwater. The further development of groundwater vulnerability maps, along with the utilization of pesticide leaching indices, would assist future assessments.

Table 3 Summary of pesticide detection frequency by type of water supply source, with maximum concentrations found

	Surface Water (n=1354)		Shallow Groundwater <15m (n=60)		Deep Groundwater (n=329)	
	% Detections (n)	Max (µg/L)	% Detections (n)	Max (µg/L)	% Detections (n)	Max (µg/L)
2,4-D	23.0 % (312)	1.235	3.3 % (2)	0.018	1.5 % (5)	0.11
MCPA	13.7 % (185)	0.571	1.7 % (1)	0.005	0.3 % (1)	0.004
Mecoprop (MCPP)	4.4 % (59)	0.056	3.3 % (2)	0.069	0.9 % (3)	0.03
Dicamba	3.5 % (47)	0.284	(0)		0.9 % (3)	0.005
Bromoxynil	1.5 % (20)	0.199	3.3 % (2)	0.029	0.9% (3)	0.011
Picloram	4.0 % (54)	0.95	1.7 % (1)	0.009	1.5 % (5)	4.07
Clopyralid	4.7 % (64)	0.351	(0)		(0)	
Others	2.8 % (38)	2.405	8.3 % (5)	0.057	0.6 % (2)	0.031
At least one pesticide per sample detected	32.3% (438)	2.405	16.7% (10)	0.069	5.8% (19)	4.07

Table 4 Summary of pesticide detection frequency by number of compounds detected per sample, by water source type

	Surface Water (n=1354)		Shallow Groundwater <15m (n=60)		Deep Groundwater (n=329)	
No. of Detections per sample	% Detections	N	% Detections	N	% Detections	N
1	16.9 %	229	11.7 %	7	5.2 %	17
2	8.8 %	119	5.0 %	3	0.3 %	1
3	4.3 %	58			0.3%	1
4	1.8%	24				
5	0.4%	5				
6	0.2%	3				
Total	32.3%	438	16.7%	10	5.8%	19

A breakdown of the 440 facilities sampled, by water source, was also done (Table 5). The breakdown was done by surface water sources, deep groundwater, shallow groundwater, and surface water and groundwater sources. The breakdown shows that sampling of the groundwater-sourced facilities was equivalent or slightly greater than the surface water-sourced facilities, however the sampling intensity (# of samples/# of facilities sampled) for groundwater facilities was quite a bit less frequent than for surface water facilities (2.0 and 3.2 compared to 5.5).

Table 5 Summary of facilities sampled, by type of water source and facility sampling intensity (1995-2003)

	Surface Water	Deep Groundwater	Shallow Groundwater	Surface Water/ Groundwater	Totals
Facilities Sampled	246	163	19	12	440
Total Facilities	329	209	26	18	582
Percent Sampled	74.8	78.0	73.1	66.7	75.6
No. of samples	1354	329	60	45	1788
Samples/ facilities sampled	5.5	2.0	3.2	3.8	4.0

4.3 Raw Water compared to Treated Water

An area of discussion has been whether the water treatment processes used in Alberta reduce the amounts of pesticide detected in treated water. A small number of samples were collected from raw and treated water from seven water treatment facilities in central and northern Alberta in 1995, but the sample size was not large enough to do a valid comparison at the time.

In 2001, a slightly more comprehensive project looking at pesticide residues in raw and treated water was undertaken at two different facilities in southern Alberta, which are typical of many other water treatment facilities throughout Alberta. The first facility was the Lethbridge water treatment plant, which services just under 70,000 residents, and draws its raw water from the Oldman River. The water treatment process consists of prechlorination, flocculation with poly-aluminium salts, clarification (settling), filtration (sand and anthracite media), followed by chlorination.

The second facility was at the Village of Carmangay, which obtains its raw water from the Little Bow River and services 258 residents. The water treatment process consists of flocculation with an inorganic coagulant, prechlorination, direct filtration (no clarifier), and chlorination after the filter.

Samples were collected from the raw inflow water, and treated outflow water on a weekly basis for five weeks, starting in mid June and going through until mid-July. Samples were sent to ARC in Vegreville, and analyzed for four parameters commonly found in Alberta surface waters: 2,4-D, MCPA, dicamba and mecoprop. Detection levels for all four parameters were 0.005 μg/L.

A summary of the results is in Table 5. In most cases, there was little difference between the raw and treated sample results. The data from this table, along with the paired samples from seven facilities in 1995, was analyzed using the Wilcoxon Matched Pair Sign Test (Steel and Torrie 1980) to determine whether it could be statistically concluded that the water treatment process had an effect on pesticide residue levels ($H_{\text{Ø}}$ – there is no significant difference in pesticide residues between raw water and treated water samples). Non-detections for parameters from both raw and treated samples were not included in the data set, only positive detections for either raw, treated or both. If one of the paired sample parameters was non-detected, the assumed value was $1/10^{th}$ of the detection level, to enable numerical analysis. If both samples had exactly the same concentration for a parameter, that pair was not included.

A total of 40 paired samples were utilized in the analysis, with the differences ranging from 0.001 μg/l to 0.045 μg/L between raw and treated water samples. The results of the Wilcoxon Matched Pair Sign Test for all available data combined showed that there was no significant difference between the raw and treated water data ($p>0.01$).

As 2,4-D and MCPA detections made up the bulk of the data set, these two parameters were analyzed separately. There were 8 usable pairs of 2,4-D data (no matches), and 9 usable pairs of MCPA data. There was no significant difference between the raw and treated data for 2,4-D ($p>0.05$), however for MCPA, there was a significant difference between raw and treated water ($p<0.01$), in that the treated water had slightly lower concentrations.

Overall, there is no significant difference in pesticide residue levels between raw and treated water samples. However, for MCPA, there does appear to be a reduction in residue concentrations from some water treatment processes. MCPA levels were reduced by over ½ at the Lethbridge water treatment plant, but no reduction in levels was observed in the data from the Carmangay plant. The conclusion is that there is limited or insignificant reduction in pesticide residues using current water treatment technologies in place at these two facilities.

Table 6 Analytical results from raw and treated water samples collected from Lethbridge and Carmangay water treatment facilities, 2001 (µg/L)

Date	Parameter	Lethbridge		Carmangay	
		Raw Water	Treated Water	Raw Water	Treated Water
June 19	2,4-D	0.030	0.032	0.042	0.047
	MCPA	0.027	0.014	0.030	0.029
	Dicamba	0.003x	0.004x	0.003x	0.004x
	Mecoprop	0.002x	<0.005	0.003x	0.004x
June 26	2,4-D	0.050	0.061	0.035	0.036
	MCPA	0.017	0.007	0.057	0.045
	Dicamba	0.009	0.014	0.005	0.026
	Mecoprop	<0.005	<0.005	<0.005	<0.005
July 3	2,4-D	0.019	0.024	0.044	0.044
	MCPA	0.073	0.033	0.054	0.040
	Dicamba	0.016	0.013	0.004x	0.009
	Mecoprop	<0.005	<0.005	0.004x	<0.005
July 10	2,4-D	0.021	0.019	0.037	0.038
	MCPA	0.018	0.008	0.034	0.031
	Dicamba	0.103	0.058	0.004x	0.006
	Mecoprop	<0.005	<0.005	<0.005	<0.005
July 17	2,4-D	0.016	0.016	0.011	0.016
	MCPA	0.020	<0.005	0.006	0.006
	Dicamba	0.013	0.014	0.005	<0.005
	Mecoprop	<0.005	<0.005	<0.005	<0.005

x – Estimated Value. The target compound meets the identification criteria, but is less than the method detection level.

The Wilcoxon Matched Pair Sign Test was also run on Lethbridge and Carmangay results independently, and no significant difference was observed between the overall residue levels of the raw and treated water samples for the individual facilities.

An initial assessment of relationship between pesticide concentration in treated waters and current water treatment processes was also carried out. Activated carbon is considered to be an effective way of removing pesticides from treated water, and is used by a small number of water treatment facilities in Alberta, mainly for taste and odour control, or to clarify water with high organic loading. Water treatment facilities that utilize activated carbon, or water distribution facilities that obtain water from facilities that utilize activated carbon, carbon adsorption filtration, powdered activated carbon (taste and odour control), or activated carbon filtration were listed (Li, 1996) and compared to the sampling data.

216 samples were collected over the period of sampling from the 13 facilities that had carbon filtration listed in 1996, and again in 2003. 2,4-D was detected in 32 of 216 samples, or 14.8%. MCPA was detected in 13 samples (6.0%), mecoprop in 8 samples (3.7%), clopyralid in 4 samples (1.8%), dicamba in 3 samples (1.4%), picloram and triallate in 2 samples (0.9%), and bromoxynil in one sample (0.5%). Although the sample size from these facilities is a subset of the overall data, it would appear that there is only a slight difference in the detection frequencies for these facilities compared to the overall data set. These water treatment processes utilizing some form of activated carbon were not efficient in removing pesticides. It could be that the activated carbon was only on-line for seasonal usage when taste and odour problems were an issue (i.e. spring runoff), or that the water treatment process and the activated carbon used were not optimized for trace organic removals such as pesticides.

Since 1996, an additional 27 water treatment plants in Alberta have installed carbon filtration. As information on when these process changes were made is not tracked, it was not possible to determine if there were changes in pesticide detection frequencies at these facilities after the carbon filtration was installed.

4.3.1 QA/QC Summary

In conjunction with the Lethbridge and Carmangay sampling, a small QA/QC (Quality Assurance/Quality Control) project was undertaken to validate the results of the sampling and analytical work done for the project. A spiked sample using distilled water was prepared by Enviro-Test Laboratories in Edmonton on June 14, and shipped to Lethbridge along with a trip blank sample containing Type 1 reagent grade water (reverse osmosis purified and E-Pure™ polished). The spike sample was intended to assess recovery rates, while the trip blank was intended to assess field and lab sample handling procedures. These samples were submitted, unknown to the lab, with the samples collected on June 26. On July 17, a temporal replicate (sequential) sample (two bottles filled one after the other – not a true split sample) of Lethbridge treated water were submitted to the lab to assess reproducibility. The results of the QA/QC assessment are summarized in Table 6.

Table 7 QA/QC Summary

Sample type	Details	2,4-D	Mecoprop	Dicamba	MCPA
Spike	Actual spike levels (µg/L)	0.100	0.100	0.000	0.000
	Reported levels (µg/L)	0.075	0.080	0.002x	0.000
	% Recovery	75%	80%	+	--
Trip blank	Reported levels (µg/L)	0.000	0.000	0.000	0.000
Sequential samples	Labelled sample (µg/L)	0.016	0.000	0.014	0.000
	Replicate Sample (µg/L)	0.019	0.005	0.016	0.003x
	± %	+18.8%	+	+14.3%	+

x- below MDL, estimated value.

The results of the spike sample indicate that the recovery rates for 2,4-D and mecoprop were slightly below 100%, although within the window of 70-130% of recovery's that would be expected at this concentration. A trace of dicamba was reported in the spike sample, and while this would be considered a false positive, it is well below the detection level, and may have originated from cross contamination in one of the labs, or in the preparation of the spike standards. The trip blank came back with no pesticides detected, which indicated that there was no sample contamination during the handling or transportation, or in the lab analysis process.

Reproducibility of analytical results was assessed in the sequential sample. The blind sequential sample came back higher in all parameters than the labelled sample. A review of the analytical process indicated that the two samples were extracted and analyzed on the same date, eliminating inter-day sample handling and analytical equipment differences as a possible reason. Although the percentage differences between the samples for 2,4-D and dicamba are substantial, at 18.8% and 14.3% respectively, the numerical differences are slight (only 0.003 and 0.002 µg/L [ppb], respectively). At such low concentrations relative to the method detection level, differences of 0.002 or 0.003 µg/L are insignificant. Trace levels of mecoprop and MCPA were also detected in the blind sequential sample (one at detection level and one below detection level), but not the labelled sample. Slight differences in concentrations from the tap are also possible. The sample bottles were filled in sequence, and it is possible slight differences in concentrations occurred as the tap was flowing.

Daily differences were also observed at the Lethbridge water treatment plant in 2001, when a routine TWS sample was collected on June 25, and 0.489 µg/L of 2,4-D and 0.159 µg/L of dicamba were reported. A sample collected on the following day (June 26) showed 2,4-D levels of 0.061 µg/L and dicamba of 0.014 µg/L, a substantial reduction over 24 hours. These differences are likely associated with variability in the source water (Oldman River), although little information is available on day-to-day variability in pesticide concentrations in larger Alberta rivers. The laboratory data were reviewed, and there was no indication of problems from that aspect, leaving source water variations as the primary source.

4.4 Spatial Patterns

4.4.1 Comparisons among River Basin

The treated water data were sorted according to major river basin (Figure 9), and a summary of the commonly found compounds is presented in Table 8. Several pesticides with infrequent detections were summarized into the ‘Others’ column. Not all basins were sampled evenly, as over the nine years the North Saskatchewan, Athabasca and Peace river basins had over 250 samples each, while the South Saskatchewan, Oldman, Bow, Red Deer and Battle river basins had less than 200 samples per basin. This is partly a reflection of the size of the basins and the number of water treatment facilities present in each basin. Data from basins with only a handful of samples (e.g. Beaver, Slave Hay and Milk river basins) were not included. These smaller basins also have only a small number of water treatment facilities.

The treated water from facilities in the South Saskatchewan River basin had the highest frequency of pesticide detections (55.7 % of samples analysed). The Oldman and Battle basins were next highest, with a detection frequency of 46.9% and 40.3%, respectively. Detection frequency in the remaining basins ranged from 18.9% to 33.3%. The Athabasca basin had the lowest frequency of pesticide detections for the major river basins (6.8%).

In the South Saskatchewan and Oldman basin, 2,4-D was detected in almost half of the treated water samples. In most basins, 2,4-D and MCPA dominated the pesticides detected, however in the Battle, picloram was found in over 17% of the samples. Another regional detection was clopyralid, which was not detected at all in the Oldman or Bow basins, yet was found in over 12% of samples collected in the Peace River basin. Over half of the 44 samples with clopyralid from the Peace River basin had concentrations greater than 0.1 ug/L. Although clopyralid was found in water samples from 12 facilities in the basin, four of these facilities accounted for 20 of the 23 clopyralid detections above 0.1 µg/L.

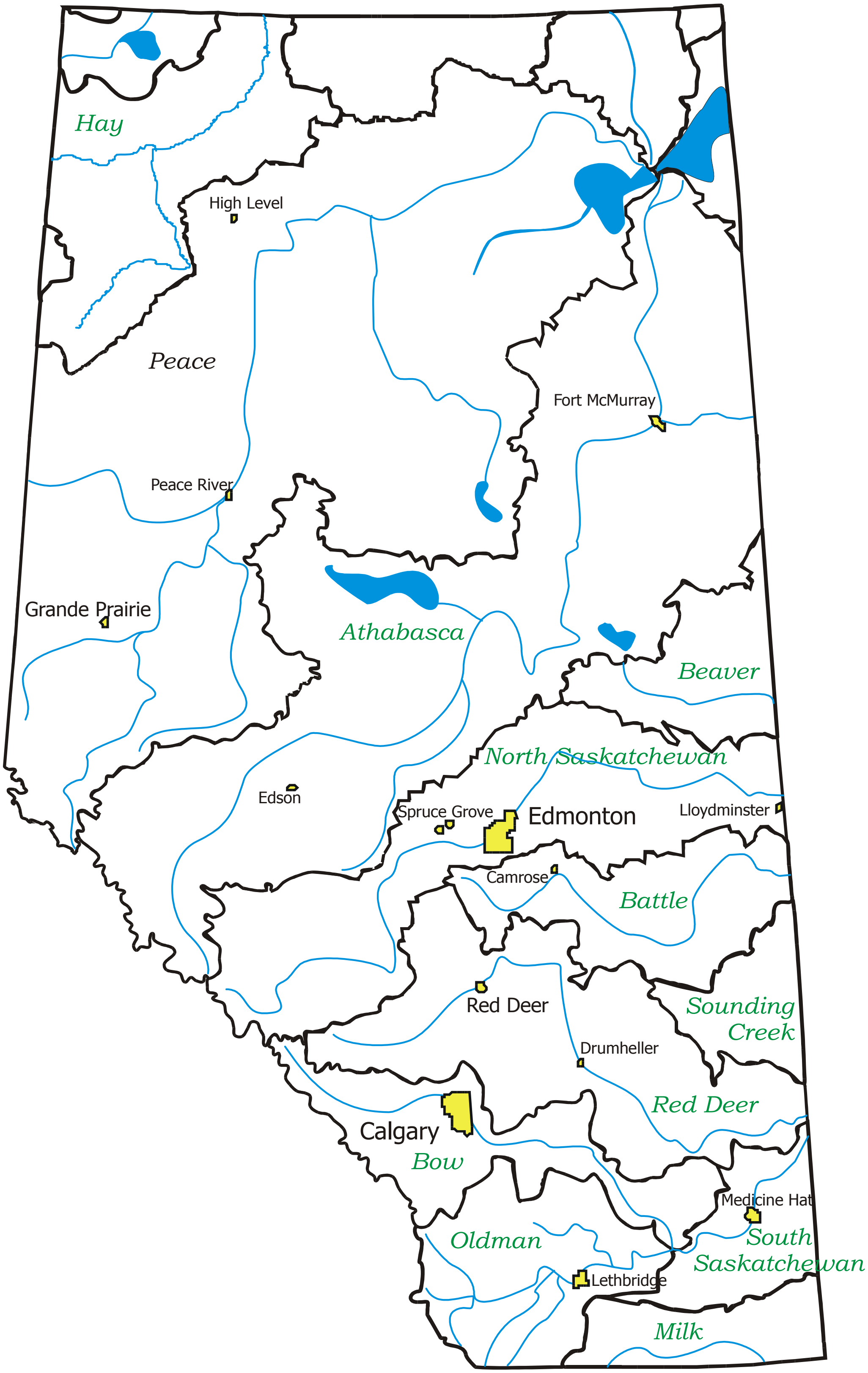


Figure 9 River basins in Alberta

Table 8 Summary of pesticide detections and concentrations in treated water samples by basin, along with the number of pesticide detections per sample

		2,4-D	MCPA	Mecoprop	Dicamba	Atrazine	Picloram	Bromoxynil	Clopyralid	Others	Number of detections per sample						
											1	2	3	4	5	6	1-6
South Sask.	# Det'ns	30	12	5	6			1	1		18	12	3	1			34
(n=61)	% Det'ns	49.2%	19.7%	8.2%	9.8%			1.6%	1.6%		29.5%	19.7%	4.9%	1.6%			55.7%
	Max (µg/L)	0.230	0.032	0.016	0.027			0.003	0.051								
Oldman	# Det'ns	70	30	7	10	1	2	7		7	39	26	5	7			77
(n=164)	% Det'ns	42.7%	18.3%	4.3%	6.1%	0.6%	1.2%	4.3%		4.3%	23.8%	15.8%	3.0%	4.3%			46.9%
	Max (µg/L)	0.480	0.052	0.013	0.036	0.005	0.015	0.014		0.017							
Bow	# Det'ns	35	16	14	15	5	1	1		1	14	13	9	4	1		41
(n=191)	% Det'ns	18.3%	8.4%	7.3%	7.8%	2.6%	0.5%	0.5%		0.5%	7.3%	6.8%	4.7%	2.1%	0.5%		21.5%
	Max (µg/L)	0.649	0.070	0.056	0.284	0.013	0.009	0.029		0.010							
Red Deer	# Det'ns	44	24	12	7	3	4	2	2	2	35	10	7	3		2	57
(n=171)	% Det'ns	25.7%	14.6%	7.0%	4.1%	1.8%	2.3%	1.2%	1.2%	1.2%	20.5%	5.8%	4.1%	1.8%		1.2%	33.3%
	Max (µg/L)	0.199	0.030	0.030	0.085	0.010	0.012	0.007	0.033	0.020							
Battle	# Det'ns	33	24	3			23		10	4	28	14	8	3	1		54
(n=134)	% Det'ns	24.6%	17.9%	2.2%			17.2%		7.5%	3.0%	20.9%	10.4%	6.0%	2.2%	0.7%		40.3%
	Max (µg/L)	0.077	0.571	0.008			4.070		0.051	2.405							
North Sask.	# Det'ns	32	18	11	1	4	3	2	4	4	36	16	2		1		55
(n=291)	% Det'ns	11.0%	6.2%	3.8%	0.3%	1.4%	1.0%	0.7%	1.4%	1.4%	12.4%	5.5%	0.7%		0.3%		18.9%
	Max (µg/L)	1.235	0.180	0.059	0.028	0.057	0.054	0.004	0.110	0.031							
Athabasca	# Det'ns	11	9		1		1	5	3		18	3	2				23
(n=342)	% Det'ns	3.2%	2.6%		0.3%		0.3%	1.5%	0.9%		5.3%	0.9%	0.6%				6.8%
	Max (µg/L)	0.155	0.079		0.005		0.016	0.199	0.046								
Peace	# Det'ns	53	56	7	9		26	5	44	13	55	26	22	6	2	1	112
(n=351)	% Det'ns	15.1%	16.0%	2.0%	2.6%		7.4%	1.4%	12.5%	3.7%	15.5%	7.3%	6.2%	1.7%	0.6%	0.3%	31.6%
	Max (µg/L)	0.104	0.076	0.011	0.072		0.950	0.012	0.351	0.185							

4.5 Comparison with Health Canada and CCME Water Quality Guidelines

There are two agencies in Canada involved in establishing water quality guidelines: Health Canada, which establishes drinking water quality guidelines (Health Canada 1996) and the Canadian Council of Ministers of the Environment (CCME 1999), who establish surface water quality guidelines. The drinking water guidelines set by Health Canada focus on human health, while the CCME guidelines are established for the protection of freshwater aquatic life, for use in irrigation, and for use as water supplies for livestock. There are also recreation guidelines established for surface water contact, but those are not applicable for pesticides.

Not all pesticides have drinking water or CCME guidelines. Some pesticides will have a drinking water guideline, but no CCME guideline, and others will have one or more CCME guideline values, but no drinking water guideline. Guidelines are also established for a wide range of parameters (metals, nutrients, trace organics, ions and physical and biological characteristics), and the priorities for guideline development are constantly being reviewed.

A list of the parameters analyzed for in the treated water samples, along with their respective water quality guidelines, is in Table 9.

4.5.1 Drinking Water Guidelines

No drinking water guidelines were exceeded for any of the parameters that were detected in treated water. However, there were 9 parameters with detections that do not have drinking water guidelines, including some of the more commonly found pesticides such as MCPA and mecoprop. In 2002, clopyralid was assigned an interim emergency drinking water guideline (Emergency Health Advisory) of 700 µg/L (Giddings 2002).

4.5.2 Guidelines for the Protection of Aquatic Life

Only one parameter exceeded a guideline value for the Protection of Aquatic Life. Lindane was observed in 0.2% of samples (3 of 1788) at levels that exceeded the freshwater aquatic life guideline of 0.01 µg/L.

4.5.3 Guidelines for Agriculture (Irrigation and Livestock)

Of the CCME Irrigation Guidelines, two parameters were detected at levels that exceeded their respective irrigation guideline. Dicamba was observed in 38 samples (2.1% of all samples) at levels that exceeded the irrigation guideline of 0.006 µg/L. MCPA was also observed in 34 samples (1.9% of the total) at levels that exceeded the irrigation guideline of 0.025 µg/L for this parameter. No parameters exceeded the Livestock Watering Guidelines.

As with the drinking water guidelines, some pesticides were detected that do not have a CCME guideline. A total of 14 pesticides detected do not have values for one or more of the CCME guidelines. Some of these compounds (e.g., picloram, clopyralid, 2,4-D) are known to affect sensitive vegetation at low concentrations, and would be candidates for irrigation guideline development.

Table 9 Parameters analyzed for in treated water samples collected between 1995 and 2003, with maximum concentrations detected, water quality guidelines (µg/L) and percentage of samples with guideline exceedences, where applicable (in brackets)

			Guidelines			
Parameter (# of samples)	**# Detections**	**Maximum concentration detected (µg/L)**	**Drinking Water (µg/L) (a)**	**Freshwater Aquatic Life (µg/L)(b)**	**Irrigation (µg/L) (b)**	**Livestock (µg/L) (b)**
HERBICIDES						
2,4-D (1788)	323	1.235	100	4		
2,4-DB (1788)	*0*	*ND*				
2,4-Dichlorophenol (174)	*0*	*ND*	900			
2,4-DP (dichlorprop) (1788)	2	0.009				
4-chloro-2-methylphenol (174)	*0*	*ND*				
Atrazine (1788)	14	0.057	5	1.8	10	5
Bentazon (13)	*0*	*ND*				
Bromacil (1788)	*0*	*ND*		5	0.2	1100
Bromoxynil (1788)	25	0.199	5	5	0.33	11
Clodinafop acid (10)	*0*	*ND*				
Clodinafop-propargyl (10)	*0*	*ND*				
Clopyralid (1788)	64	0.351	700 (c)			
Cyanazine (1788)	*0*	*ND*		2	0.5	10
Des-ethyl atrazine (1004)	*0*	*ND*				
De-isopropyl atrazine (1003)	*0*	*ND*				
Dicamba (1788)	50	0.284	120	10	0.006 **(2.1%)**	122
Diclofop-methyl (1788)	1	0.08	9	6.1	0.2	9
Diuron (1788)	*0*	*ND*	150			
Ethalfluralin (1788)	*0*	*ND*				
Ethofumesate (6)	*0*	*ND*				
Fenoxaprop-p-ethyl (1003)	*0*	*ND*				
Fluazifop (13)	*0*	*ND*				
Fluroxypyr (8)	*0*	*ND*				
Imazamethabenz (1191)	2	0.11				
Imazamox (911)	*0*	*ND*				
Imazethapyr (1004)	1	0.055				
Linuron (13)	*0*	*ND*		7.0	0.071	
MCPA (1788)	190	0.571		2.6	0.025 **(1.9%)**	25
MCPB (1788)	1	0.017				
Mecoprop (1788)	64	0.069				
Metolachlor (13)	*0*	*ND*	50	7.8	28	50
Metribuzin (13)	*0*	*ND*	80	1	0.5	80
Picloram (1788)	60	4.07	190	29	Insuff. Data	190

			Guidelines			
Parameter (# of samples)	**# Detections**	**Maximum concentration detected (µg/L)**	**Drinking Water (µg/L) (a)**	**Freshwater Aquatic Life (µg/L)(b)**	**Irrigation (µg/L) (b)**	**Livestock (µg/L) (b)**
Quinclorac (1004)	*0*	*ND*				
Quizalofop (13)	*0*	*ND*				
Simazine (279)	*0*	*ND*	10	10	0.5	10
Triallate (1788)	5	0.014		0.24	Insuff. Data	230
Triclopyr (278)	5	2.405				
Trifluralin (1788)	*0*	*ND*	45	0.2	Insuff. Data	45
INSECTICIDES						
Aldrin (91)	*0*	*ND*	+dieldrin 0.7			
Alpha-BHC (1788)	*0*	*ND*				
Alpha-Endosulfan (1788)	*0*	*ND*		0.02		
Azinphos-methyl (1788)	1	0.123	20			
Chlorpyrifos (1788)	*0*	*ND*	90	0.0035	Insuff. data	24
Diazinon (1788)	3	0.057	20			
Dieldrin (91)	*0*	*ND*	+aldrin 0.7			
Dimethoate (1004)	*0*	*ND*	20	6.2	Insuff. Data	3
Disulfoton (1788)	*0*	*ND*				
Ethion (1788)	*0*	*ND*				
gamma-BHC (lindane) (1788)	9	0.026		0.01 **(0.2%)**		No guideline recomme-nded (d)
Malathion (1788)	*0*	*ND*	190			
Methoxychlor (1788)	1	0.031	900			
Parathion (13)	*0*	*ND*	50			
Phorate (1788)	*0*	*ND*	2			
Pyridaben (1004)	*0*	*ND*				
Terbufos (1788)	*0*	*ND*	1			
FUNGICIDES						
Carbathiin (1788)	*0*	*ND*				
Chlorothalonil (13)	*0*	*ND*		0.18	5.8	170
Hexaconazole (13)	*0*	*ND*				
Iprodione (13)	*0*	*ND*				
Metalaxyl-M (6)	*0*	*ND*				
Propiconazole (13)	*0*	*ND*				

ND - Not detected
(a) - Health Canada (1996)
(b) - CCME (1999)
(c) - Emergency Health Advisory for clopyralid (Giddings 2002)
(d) - Environmental exposure is predominantly via sediment, soil, and/or tissue, therefore refer to the respective guidelines for these media (CCME 2000)

5.0 DISCUSSION

5.1 Temporal

It is difficult to draw any definite conclusions on overall temporal trends of pesticide detections based upon monitoring data from only slightly over eight years of sampling treated water supplies, especially when a wide range and variety of facilities are being sampled on an irregular basis. However, the data do provide an insight into specific compounds and possibly water treatment facilities that should be examined in more detail. The data also provides an extensive set of baseline information that can be used for future evaluations, including trend assessments.

The available data showed increasing temporal trends for pesticide detections for only three compounds (MCPA, dicamba and clopyralid). Although 2,4-D was more frequently detected, and detections of this compound were more widespread, the frequency of detections for 2,4-D remained fairly constant overall over the period, at around 17-18%, until 2001 when it jumped to over 30%. It dropped to below 15% in 2002 and 2003. 2,4-D is sold in the same magnitude province-wide as MCPA (766 tonnes vs. 885 tonnes of MCPA, Byrtus 2000). Dicamba sales are much less than 2,4-D or MCPA, (138 tonnes) but its use has been constant over time. Clopyralid, although not sold or used to the same extent as MCPA or 2,4-D (only 59 tonnes), also shows an increasing trend in detections. Clopyralid came on the market in 1984, and has only recently been detected in environmental samples. The first detection of clopyralid in a routine sampling program was from groundwater near Edmonton in 1992. It was added to the routine monitoring analytical screen in 1995, and the frequency of detections of this compound has been increasing in recent years.

Trends in overall pesticide detections showed that the highest percentage of detections occurred in 1998, and 2001. 1998 corresponded to the peak year of agricultural chemical sales for western Canada (CPI, 2001). Monitoring results for 2002 and the early portion of 2003 showed a decline in pesticide detections. This may be related to the drought experienced throughout a large part of Alberta during late 2001 and 2002, which reduced both the amount of pesticides applied (less weed growth and less economic incentive to spray because of lower crop yield), and reduced pesticide loading from runoff and precipitation to surface water bodies. Figure 10 illustrates the drop in precipitation throughout most of the province starting in 2001, and continuing through 2002, although Lethbridge (and other areas of southern Alberta) had received more normal levels of precipitation during 2002.

As pesticides are used on a seasonal basis, it was expected to see concentrations and frequency of pesticide detections during the primary pesticide application season (May-August). A slight increase was observed in detection frequencies in June for 2,4-D and MCPA, but the expected decline during the winter months was not observed. Most water treatment systems in Alberta are dependent upon surface water sources, however, surface water monitoring done in Alberta shows few pesticides detected in the winter period.

Water treatment facilities not situated close to major rivers use raw water reservoirs to store water from normally low flow sources during seasonal high flow periods (spring-summer), which results in retention of pesticide residues in the water treatment system. Degradation of phenoxy herbicides (2,4-D, MCPA) is limited in surface waters, especially during periods of cold weather and low light, resulting in limited degradation from microbial processes and ultraviolet light. This results in a potential for chronic exposures to low levels of pesticides in treated water, rather than seasonal exposures.

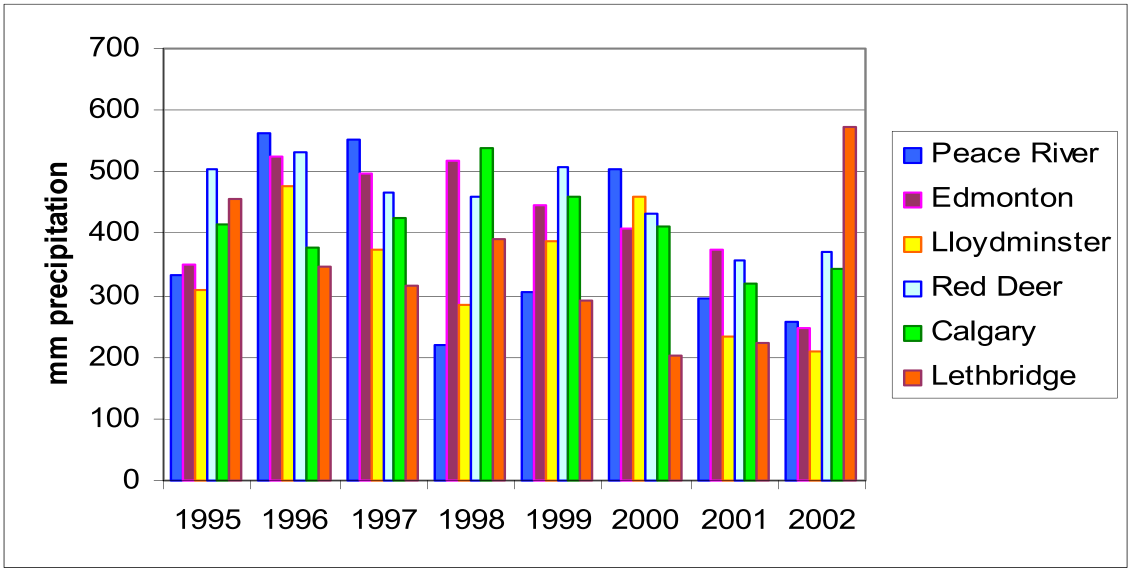


Figure 10 Annual precipitation amounts for selected meteorological stations throughout Alberta from 1995-2002

Further analysis using site-specific detailed analysis (monthly sampling) for selected water treatment facilities would be required to determine typical seasonal fluctuations, rather than using overview data based upon data from a wide range of water treatment facilities.

5.2 Water Source

Alberta's water treatment plants utilize surface water as their prime source of water (rivers, lakes, reservoirs, irrigation canals, etc). As a result, pesticide detections reported here are mainly from facilities utilizing surface water sources. Comparison of the limited data from groundwater sources to the surface water sources suggested that groundwater is less susceptible to pesticide contamination, as the frequency of detection is much less in the groundwater-supplied water treatment facilities.

The ability to utilize ambient monitoring data as an indicator of specific issues and concerns related to pesticides is limited by the lack of ambient groundwater monitoring data. Ambient pesticide monitoring in surface waters has been carried out for approximately 30 years and an extensive dataset has been developed. From 1995-2002, over 2800 surface water samples have been analyzed for pesticides at low detection levels, which provides a rich dataset to compare the treated water dataset to (Anderson, et al. in prep). On the other hand, there is no ongoing ambient groundwater monitoring being carried out in the province, limiting the pesticide data from groundwater to the small number of samples collected for the Treated Water Survey, as well as small, site-specific research projects or small monitoring programs.

The only major project that has looked at ambient groundwater quality, including pesticides, was a farm well survey that was carried out under the direction of Alberta Agriculture, Food and Rural Development in 1995-1996 (Fitzgerald et al. 1997). A total of 824 samples were collected from 824 wells situated on agricultural farmsteads, and a wide range of parameters, including nitrates, metals, microbiological parameters, and pesticides, were analyzed. Only 27 samples (3%) had detections of pesticides, although two samples contained 2,4-D above the Drinking Water Guideline of 100 μg/L, and one sample contained bromoxynil above the Drinking Water Guideline of 5 μg/L. The project, although of a large size and wide geographic distribution, was restricted to the analysis of eight pesticides at higher detection levels (0.05 μg/L) than is used for comparable parameters in the analytical screen for treated water, and in only one sample from each well.

More extensive use of groundwater as a water source would be a potential option for municipalities; however good quality groundwater at economically recoverable depths and quantities is limited in Alberta. As a result, larger municipalities in the province utilize surface water. Surface water is a dynamic environment, subject to rapid inflows (precipitation, runoff, local and mountain snowmelt), and exposure to a wide range of environmental conditions that expose the surface water supply to pesticide contamination (precipitation, runoff from fields, pesticide drift), but also provide some mechanisms for degradation (photolysis, microbial, oxidation/reduction). Groundwater, on the other hand, is more protected from rapid inflows of contaminants, being naturally filtered by the surficial soils, but is also more resistant to natural degradation processes. In most cases, municipalities do not have a choice in their supply source. Either the quantity or quality of groundwater is insufficient for their needs, or the municipality has ready, inexpensive access to a surface water source that offers acceptable quality and sufficient quantity.

5.3 Raw Water compared to Treated Water

The results showed that the water treatment processes used at Lethbridge and Carmangay had little effect on reducing pesticide concentrations in treated water supplies. A water treatment facility in the U.S. has 10 years of weekly raw and treated water pesticide analytical data, which showed no removal of major agricultural herbicides by conventional water treatment processes (SAP 2001).

A more extensive pilot monitoring program was conducted in 1999 and 2000 in the U.S., where the United States Geological Survey (Blomquist et al. 2001) collected water samples from 12 reservoirs supplying water treatment facilities, and treated water samples from those facilities. A wide range of pesticides was detected in both raw and treated water (116 of 186 pesticides and degradation products analyzed for), most at low concentrations. Some of the widely used herbicides were detected in 36-96% of raw water samples, and in 19-96% of treated water samples. For example, atrazine (parent compound) was detected in 95.6% of treated water samples, while 2,4-D was detected in 43.6 % of treated water samples. On the other hand, MCPA was only rarely detected. The data from this study also suggests that current water treatment technology has little effect on removal of commonly detected pesticides.

One means of removing organic compounds such as pesticides is by activated carbon. Although some municipalities in Alberta utilize activated carbon for assistance in reducing total organic carbon levels in highly organic water, it would appear that these processes, as currently set up, have little effect in reducing pesticide concentrations. Further work is required in this area to evaluate currently used activated carbon filters on pesticide removal efficiency under Alberta conditions.

Current basic water treatment processes (coagulation, filtration, sedimentation and conventional filtration) do not facilitate pesticide removal or transformation. Disinfection and softening can facilitate pesticide transformation and in some cases, degradation (EPA 2001). On the other hand, processes such as ozonation and chlorination can create pesticide disinfection by-products. Reaction time and concentration play a major role in the creation of disinfection by-products from chlorine or ozone (SAP 2001).

It can be argued that implementing expensive and technically complex water treatment processes to reduce pesticide concentrations is inefficient. A more proactive approach in watershed protection would potentially reduce pesticide levels in raw water sources and possibly reduce other problem constituents that affect drinking water quality. The problem in this is that pesticides are broadly used in the agricultural areas of Alberta, resulting in non-point sources of pesticide loading to surface and groundwater water supplies. A review of current agricultural management practices to reduce the impact of agriculture on water quality is underway, with an objective to reduce the impacts by the transfer of technology and information to agricultural producers (AESA 2000). Other changes will come about as older pesticides are replaced with newer compounds that are used at lower rates, are less mobile, and are less persistent. The process of identifying compounds that are increasing in frequency of detection (MCPA, dicamba and clopyralid) will focus attention on the need for short-term management of these compounds.

5.4 Basin-wide Trends

The most frequently found pesticide in southern Alberta (South Saskatchewan River (SSR) and Oldman River (OMR) basins) was 2,4-D. This compares to the results of research on pesticides in precipitation by Agriculture and Agri-Food Canada, which found that 2,4-D was the predominant compound found in rainfall in southern Alberta, while MCPA is found in precipitation more in central and north central Alberta (Hill, 2001). The fact that 2,4-D dominated detections in treated water and precipitation is probably not a coincidence, but a reflection of its extensive use in southern Alberta.

In the treated water survey, 2,4-D dominated the detections in most samples, double the detection frequency of MCPA in the SSR, OMR and Bow River basins, with the proportion declining further north. In the Peace River basin, a higher frequency of MCPA compared to 2,4-D was observed.

Water treatment facilities in the SSR, OMR and Battle River basins had the highest overall frequency of detections (almost 56% for the SSR, almost 47% for the OMR and over 40% for the Battle). The most intensive agricultural production and pesticide use is in these basins. An assessment of pesticide use intensity by basin for 1998 was reported in Byrtus (2000), and the OMR, SSR and Battle River basins were among the highest in pesticide use, ranging from 0.35 to 0.69 kg of total active ingredient/hectare. These basins are also characterized by having high proportions of agricultural land under cultivation, which is more pesticide use intensive than pasture or rangeland.

Of interest are the frequent clopyralid detections in treated water from the Peace River basin. The detection frequency of clopyralid in treated water from the Peace River basin (12.4% of the samples) is higher than in any other basin and approaches the detection frequency for 2,4-D (15.0% of the samples) in that basin. As discussed earlier, clopyralid is showing an increasing trend in detections, and with the detections being concentrated in the Peace River basin, clopyralid may soon surpass 2,4-D and MCPA as the most frequently detected pesticide in this basin. The Peace River basin accounts for just over 10% of total pesticide sales in Alberta, but clopyralid sales in this basin account for almost 22% of the provincial sales for this product (Byrtus 2000), a possible reason for the more frequent detection's of this compound in this basin. However, another perspective on this situation is that only four facilities, which were sampled extensively over the period being assessed, accounted for 25 of the 44 clopyralid detections in this basin. This intensive sampling may have biased the overall results, but does point out the continuity of clopyralid detections in these systems, which should be pursued. It may be that their source water (surface runoff) is affected by clopyralid spraying operations in the area.

5.5 Water Quality Guidelines

All facilities sampled during the period of 1995 to 2003 were in compliance with Health Canada Drinking Water Guidelines. No pesticides exceeded available Drinking Water Guidelines, and most of the highest detections were approximately 1% of the relevant guideline (2,4-D: 1.235 µg/L vs. guideline of 100 µg/L; atrazine 0.057 µg/L vs guideline of 5 µg/L; diclofop-methyl: 0.08 vs. guideline of 9 µg/L). The highest concentration detected of clopyralid (0.351 µg/L) was 0.05% of the Emergency Health Advisory value (700 ug/L) recently obtained for that parameter (Giddings 2002). Picloram was found at approximately 2% of the Drinking Water Guideline (4.07 µg/L vs. guideline of 190 µg/L). Although pesticides with Drinking Water Guidelines were found at concentrations no greater than 2% of those guidelines, which suggests a very low level of concern, several pesticide were detected that do not have Drinking Water Guidelines, and no risk assessments could be made (e.g., MCPA, mecoprop).

Several pesticides were detected at levels that exceeded other guidelines (Protection of Aquatic Life, Irrigation). Drinking Water Guidelines are relatively high compared to other guidelines, as the exposure is lower and tolerances are higher, resulting in lower risk to humans as compared to other organisms. Levels of some herbicides (e.g., picloram and clopyralid) are phytotoxic at very low levels, and can negatively impact sensitive vegetation. Insecticides such as chlorpyrifos can be toxic to aquatic organisms at very low concentrations, and with continuous exposure in an aquatic environment; low levels of insecticides can represent a major risk to vertebrates and invertebrates; however, they would likely have a limited effect on vegetation.

A situation arose in 2001, where the residents of the Village of Chauvin in eastern Alberta were experiencing problems with garden vegetables. A crop specialist recognized the typical symptoms of picloram damage. Subsequent follow-up sampling by Alberta Environment found picloram levels ranging from 3 to 17 ug/L in treated water. The village uses a number of wells, and it appeared the source of the picloram was limited to one well. This well has been taken out of use, and additional monitoring is on going.

The Drinking Water Guideline for picloram is 190 µg/L. There is no Irrigation Guideline, although damage to sensitive vegetation is generally believed to occur at concentrations near 1 µg/L. The damage to the vegetation was likely exacerbated by the lack of rainfall in the area during 2001, which resulted in an increased need for residents to irrigate their gardens. Chauvin was not included in the treated water survey during the period from 1995-2000, but was included in 2001.

6.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Since 1995, when new analytical instrumentation came on line at the Alberta Research Council in Vegreville, pesticides have been detected in routine treated water samples collected from municipal water treatment or water distribution facilities. Over the slightly more than eight years from 1995-2003, 26.6% of all samples collected had at least one pesticide detected. 2,4-D was the most commonly detected pesticide, with an overall detection frequency of 18.0%. This is much less than the detection frequency for 2,4-D in treated water (43.6%) in a study in the U.S. There were no distinct seasonal trends in the detection frequency of any pesticide detected in treated water.

A small project to compare pesticide residues in raw water and treated water supplies was conducted at two water treatment facilities in 2001. Statistical analysis of the data indicated that there was no significant reduction of pesticide residue levels as a result of the water treatment process at either facility.

The majority of samples were collected from facilities using surface water sources, and the majority of pesticide detections were also reported from this type of facility. Relatively few treated water samples were collected from groundwater-sourced water treatment facilities, making a direct comparison between surface water and groundwater sources difficult.

Most of the province's population is supplied by surface water (93% of the population that is served by municipal water treatment facilities). Pesticide detections in treated water are much less frequent than detections in surface water, but do follow the detections of pesticides observed in surface water. There is a well-established surface water monitoring program in Alberta, with which the data from the treated water survey can be compared. On the other hand, there is no ambient groundwater monitoring program currently in place in Alberta, and therefore no ambient groundwater pesticide data. Although the relatively limited sampling from groundwater supplies in the treated water survey provides valuable information on pesticides in ambient groundwater, further assessment of groundwater resources is needed. Although the available samples from the treated water survey indicated that groundwater is associated with less frequent pesticide detections, the discovery in 2001 of picloram contaminated groundwater at the Village of Chauvin highlights the need for further assessment of facilities utilizing groundwater to ensure that a similar situation does not exist elsewhere.

The area of Alberta with the most frequent detections of pesticides was in southern Alberta, particularly water treatment facilities in the South Saskatchewan River and the Oldman River basins. Water treatment facilities in the Battle River basin also experienced relatively higher frequency of pesticide detections. Water treatment facilities in the Athabasca River basin had the lowest frequency of pesticide detection.

The frequency of pesticide detection in treated water supplies appears to be linked to pesticide use in the watershed.

There were no incidents of pesticide non-compliance with Drinking Water Quality Guidelines during the more than eight years of data summarized in this document. The highest concentrations observed were approximately 1-2% of the relevant drinking water guideline. Guidelines for Freshwater Aquatic Life were exceeded in only 3 samples (0.2%) for lindane. Guidelines for Irrigation Water Quality were exceeded for dicamba in 2.1% of samples (38), and also for MCPA in 1.9% of samples (34). Nine pesticides detected in treated water do not have Drinking Water Guidelines.

One objective that could be implemented would be to manage pesticides in treated water supplies to the lowest available guideline value. For pesticides, the lowest guideline values are generally Freshwater Aquatic Life guidelines or Irrigation Water Quality guidelines, not Drinking Water guidelines. As treated water is used for a number of purposes, (household, domestic irrigation, industrial and commercial) besides human consumption, the utilization of other water quality guidelines could be considered. This would be the most conservative and most protective of water quality, however there are cost, process and management implications associated with achieving (or not achieving) compliance with all water quality guidelines. The current priority for treated water in Alberta is to focus on compliance with Drinking Water Guidelines.

The following recommendations are intended to assist in ensuring the continued quality of treated water supplies in Alberta by increasing the available data on water quality, and by improving evaluation measures.

Recommendations

1. Continue monitoring for pesticides in the provincial treated water survey to document detections, assess trends, identify specific pesticides that should be recommended for guideline development, and identify any situations that may be of concern for risk mitigation.

   1(a). Implement more intensive monitoring of pesticides for water treatment facilities that rely on groundwater sources, particularly for areas identified as vulnerable to pesticide entry. The identification of vulnerable areas would require integration of several data sources, such as pesticide use or sales information and province-wide risk assessment of groundwater that is being developed by PFRA, in co-operation with the Alberta Geological Survey.

   1(b). Integrate surface water monitoring data and treated water data from surface water facilities to maximize the use of resources (e.g., QA/QC program) and utilization of information.

2. Develop a Department QA/QC program for all of the parameters in the Treated Water survey, possibly in conjunction with surface and groundwater monitoring programs.

3. Comparable reports should be prepared by Alberta Environment to summarize the presence and trends of other constituents in the treated water survey (e.g., metals, extractable and volatile priority pollutants), or annual data reports summarizing the parameters analyzed from each municipality, similar to the treated water survey reports prepared up to 1996 (Li 1997). This would complement the recently developed on-line reporting system for drinking water.

4. Review the Treated Water Survey program, its objectives, performance, and integration with approval monitoring conditions, guideline compliance or non-compliance identified through the survey, and whether requirements for self-monitoring and reporting by water treatment facilities should be expanded.

5. The following pesticides are recommended for Health Canada Drinking Water Guideline development on the basis of routine detections in treated water: MCPA, MCPP (mecoprop), and lindane (in the event that continued detections occur since it will not be used after 2004). A full guideline (instead of the preliminary Emergency Health Advisory) should be developed for clopyralid. Based upon detections in treated water and risk to vegetation, the following pesticides should be recommended for CCME Irrigation Water Quality Guideline Development: picloram, clopyralid, 2,4-D and MCPP (mecoprop). Based upon detections in treated water and risk to aquatic vegetation, the following pesticides should be recommended for CCME Protection of Aquatic Life Guidelines: clopyralid and MCPP (mecoprop).

6. Review and determine the implications of managing treated water supplies to the most stringent water quality guidelines available (not necessarily the Drinking Water Guidelines). Treated water is utilized for other purposes beside human consumption, and these uses might be compromised by concentrations of pesticides below Drinking Water Guideline values.

7. Integrate watershed management programs with Alberta Environmentally Sustainable Agriculture (AESA), Watershed Protection Groups or Watershed Advisory Councils, rural municipalities and other land managers to minimize all potential agricultural, and industrial inputs (pesticides, nutrients, and microbial contaminants) to Alberta surface water and groundwater resources.

8. Integrate watershed management programs and urban Integrated Pest Management (IPM) programs with urban municipalities to reduce all urban inputs (pesticides, nutrients, metals and microbial contaminants) to Alberta surface water and groundwater resources.

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Appendix 1 Summary of Annual Pesticide Screens Used for Treated Water Survey and Detection Levels (Alberta Research Council - Vegreville) (ug/L)

Parameter	1995-1997	1998	1999-2000	2001	2002-2003
HERBICIDES					
2,4-D	0.005	0.005	0.005	0.005	0.005
2,4-DB	0.005	0.005	0.005	0.005	0.005
2,4-DP (dichlorprop)	0.005	0.005	0.005	0.005	0.005
2,4-Dichlorophenol (metabolite)					0.01
4-chloro-2-methylphenol (metabolite)					0.01
Atrazine	0.005	0.005	0.005	0.005	0.005
Bentazon					0.005
Bromacil	0.03	0.03	0.03	0.03	0.03
Bromoxynil	0.005	0.005	0.005	0.005	0.005
Clodinafop propargyl					0.04
Clodinafop acid (metabolite)					0.02
Clopyralid	0.02	0.02	0.02	0.02	0.02
Cyanazine	0.05	0.05	0.05	0.05	0.05
Des-ethyl atrazine (metabolite)			0.05	0.05	0.05
Deisopropyl atrazine (metabolite)			0.05	0.05	0.05
Dicamba	0.02	0.02	0.02	0.005	0.005
Diclofop-methyl	0.02	0.02	0.02	0.02	0.02
Diuron	0.2	0.2	0.2	0.2	0.2
Ethalfluralin	0.005	0.005	0.005	0.005	0.005
Ethofumesate					0.005
Fenoxaprop-p-ethyl			0.04	0.04	0.04
Fluroxypyr					0.01
Fluazifop					0.01
Imazamethabenz		0.05	0.05	0.05	0.05
Imazamox			0.02	0.02	0.02
Imazethapyr			0.02	0.02	0.02
Linuron					0.005/0.02
MCPA	0.005	0.005	0.005	0.005	0.005
MCPB	0.02	0.02	0.02	0.02	0.02
Mecoprop (MCPP)	0.005	0.005	0.005	0.005	0.005
Metolachlor					0.005
Metribuzin					0.01
Picloram	0.005	0.005	0.005	0.005	0.005
Quinclorac			0.005	0.005	0.005
Quizalofop					0.03
Simazine					0.01
Triallate	0.005	0.005	0.005	0.005	0.005
Triclopyr					0.01
Trifluralin	0.005	0.005	0.005	0.005	0.005

Parameter	1995-1997	1998	1999-2000	2001	2002-2003
INSECTICIDES					
Aldrin					0.005
alpha-BHC	0.005	0.005	0.005	0.005	0.005
alpha-Endosulfan	0.005	0.005	0.005	0.005	0.005
Azinphos-methyl	0.2	0.2	0.2	0.2	0.2
Chlorpyrifos	0.005	0.005	0.005	0.005	0.005
Diazinon	0.005	0.005	0.005	0.005	0.005
Dieldrin					0.005
Dimethoate			0.05	0.05	0.05
Disulfoton	0.2	0.2	0.2	0.2	0.2
Ethion	0.1	0.1	0.1	0.1	0.1
gamma-BHC (lindane)	0.005	0.005	0.005	0.005	0.005
Malathion	0.05	0.05	0.05	0.05	0.05
Methoxychlor	0.03	0.03	0.03	0.03	0.03
Parathion					0.01
Phorate	0.005	0.005	0.005	0.005	0.005
Pyridaben			0.02	0.02	0.02
Terbufos	0.03	0.03	0.03	0.03	0.03
FUNGICIDES					
Carbathiin	0.1	0.1	0.1	0.1	0.1
Chlorothalonil					0.005
Hexaconazole					0.05
Iprodione					0.02
Metalaxyl-M (mefenoxam)					0.01
Propiconazole					0.05

Appendix 2 Summary of pesticide detections and samples collected at water treatment or water distribution facilities in Alberta, 1995-2003 (Regional or treated water supply source in brackets)

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
ACADIA VALLEY	GW	0	3
ACHESON INDUSTRIAL PARK (Edmonton)	SW	0	1
ACME	GW	0	4
AIRDRIE (Calgary)	SW	0	1
ALBERTA HOSPITAL	GW	0	1
ALBIAN SANDS	SW	0	1
ALCOMDALE	GW	0	2
ALDERSYDE (High River)	GW (<15 m)	0	1
ALIX	GW	0	1
ALLIANCE	SW	11	7
AL-PAC CONSTRUCTION CAMP	SW	0	3
AMISK	GW	0	1
ANTHONY HENDAY REGIONAL WTP	SW	0	3
ANZAC	SW	0	7
ARDMORE	GW	0	4
ARROWWOOD	GW	0	1
ASHMONT	SW	2	7
ATHABASCA	SW	0	19
BANFF GATE MOUNTAIN LODGE	GW	0	1
BANFF	GW	0	3
BARNWELL	SW	7	3
BARONS	SW	6	3
BARRHEAD	SW	4	10
BASHAW	GW	0	4
BASSANO	SW	5	5
BATTLE RIVER POWER PLANT	SW	5	1
BAWLF	GW	0	1
BEAR CANYON	SW	7	10
BEARSPAW MEADOWS	SW	0	7
BEARSPAW RIDGE	SW	0	2
BEARSPAW VILLAGE	SW	0	2
BEAVERLODGE	SW	6	9
BEISEKER	GW	0	3
BELLEVUE - CROWSNEST PASS	SW / GW	0	2
BENTLEY	GW	1	2
BERWYN	GW	0	2
BIG LAKE AREA DEVELOPMENT (Edmonton)	SW	0	1
BLACK DIAMOND	GW (<15 m)	1	5
BLACKFALDS	GW	0	3
BLACKFOOT	GW	0	2
BLACKIE	GW	0	1

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
BLAIRMORE - CROWSNEST PASS	GW	1	2
BLOCK 6 WATER COOP	SW	0	1
BLUE RIDGE	GW	0	2
BLUE RIDGE MOUNTAIN	GW	0	1
BLUESKY (Fairview)	SW	0	1
BON ACCORD (Edmonton)	GW	0	5
BONNYVILLE	SW	2	11
BOW ISLAND	SW	7	4
BOWDEN (Anthony Henday)	SW	1	4
BOYLE	SW	0	8
BRETON	GW	0	1
BROOKS	SW	4	6
BROWNVALE	GW	0	4
BRUCE (Edmonton 2002)	SW	2	4
BRULE	SW	0	7
BUFFALO LAKE METIS SETTLEMENT	GW	2	4
BURDETT	SW	4	3
BUSBY	GW	0	1
BYEMOOR	GW	0	1
CADOGAN	GW	0	1
CADOTTE LAKE	SW	1	11
CALAWAY PARK	SW	0	2
CALGARY BEARSPAW	SW	0	8
CALGARY GLENMORE	SW	7	8
CALLING HORSE ESTATES	GW	0	4
CALLING LAKE	SW	0	7
CALLING LAKE PROVINCIAL PARK	SW	0	1
CALMAR (Edmonton)	SW	0	1
CAMROSE	SW	15	13
CANMORE	SW / GW	1	9
CANYON CREEK	SW	0	7
CARBON	GW	3	3
CARDINAL RIVER COAL	SW	0	1
CARDSTON	SW	6	6
CAREFREE RESORTS	SW	0	2
CARMANGAY	SW	1	4
CAROLINE	GW	0	4
CARSELAND	GW	0	2
CARSON-PEGASUS PROVINCIAL PARK	SW	1	4
CARSTAIRS (Anthony Henday)	SW	0	2
CASTOR	SW	11	9
CAYLEY	SW	2	3
CENTRAL PARK	GW	0	1
CENTRE FOR OUTDOOR EDUCATION	GW (<15 m)	0	1
CEREAL	SW	1	1
CESSFORD	SW	7	5
CHAMPION	SW	1	2

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
CHAUVIN	GW	1	1
CIRCLE SQUARE RANCH	SW	3	2
CLAIRMONT	GW	0	2
CLANDONALD	GW	0	1
CLARESHOLM	SW	5	7
CLEARDALE	SW	11	7
CLIVE	GW	0	1
CLYDE	GW	0	5
COALDALE	SW	6	5
COALHURST	SW	2	3
COCHRANE	SW	0	9
COLD LAKE	SW	1	11
COLEMAN - CROWSNEST PASS	GW	0	2
COLINTON	GW	0	1
CONKLIN	SW	0	7
CONSORT	GW	0	2
CORONATION	GW	0	1
COTTONWOOD ESTATES	GW	0	2
COUTTS	SW	0	4
COWLEY	SW	1	5
CRAIGMYLE (Henry Kroeger Regional WTP)	SW	4	3
CROSSFIELD (Anthony Henday)	SW	0	2
CYNTHIA	GW	1	2
CYPRESS HILLS PROVINCIAL PARK	GW	0	2
DAYSLAND	GW	0	3
DEBOLT	GW	0	1
DEERHAVEN ESTATES	GW	0	1
DELBURNE	GW	0	1
DELIA (Henry Kroeger)	SW	4	2
DERWENT	GW	0	1
DESMARAIS	SW	0	11
DEVON	SW	0	8
DIAMOND RIDGE ESTATES	GW	0	2
DIDSBURY (Anthony Henday)	SW	0	1
DINOSAUR PROVINCIAL PARK	GW	0	1
DIXONVILLE	GW	1	3
DONNELLY	SW	1	7
DRAYTON VALLEY	SW	0	11
DRUMHELLER	SW	10	8
DUCHESS	SW	4	2
EAGLESHAM	SW	16	6
EAST PRAIRIE	SW / GW	0	4
ECKVILLE	GW	0	2
EDBERG	GW	0	1
EDGERTON	GW	0	1
EDMONTON E.L. SMITH	SW	6	47
EDMONTON ROSSDALE	SW	11	46

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
EDSON	GW	0	5
ELIZABETH METIS SETTLEMENT	GW	0	4
ELK POINT	SW	13	10
ELKANA RANCHES	SW	0	2
ELNORA	GW	0	1
EMERALD BAY	GW	0	5
EMPRESS	GW	0	1
ENCHANT	SW	0	2
ENILDA (High Prairie)	SW	0	1
ENTWISTLE	GW	0	4
EVANSBURG	GW	0	4
EXCEL (Henry Kroeger)	SW	2	1
FABYAN	GW	0	1
FAIRVIEW	SW	2	6
FALHER	SW	9	7
FAUST	SW	4	8
FAWCETT	GW	0	1
FERINTOSH	SW	3	6
FISHING LAKE METIS SETTLEMENT	GW	0	3
FLATBUSH	GW	0	4
FOLDING MOUNTAIN ESTATES	SW / GW	0	1
FOOTNER LAKE (High Level)	SW	0	1
FOREMOST	GW	1	3
FORESTBURG	GW	0	2
FORT ASSINIBOINE	GW	0	1
FORT CHIPEWYAN	SW	0	7
FORT MACKAY	SW	2	7
FORT MACLEOD	SW	1	7
FORT MCMURRAY	SW	3	20
FORT SASKATCHEWAN (Edmonton)	SW	1	2
FORT VERMILION	SW	5	8
FORTRESS MOUNTAIN	SW	0	3
FOX CREEK	GW	0	6
FRANCHERE BAY MOOSE LAKE	GW (<15 m)	2	1
GADSBY (Stettler)	SW	1	1
GARNER LAKE PROVINCIAL PARK	SW	1	6
GEORGIAN DEL-RICH	GW	0	1
GHOST RIVER CADET CAMP	SW / GW	0	2
GIBBONS (Edmonton)	SW	0	1
GIFT LAKE	SW	1	8
GIROUXVILLE	SW	1	2
GLEICHEN	SW	12	6
GLENCOE	SW	0	2
GLENDON	GW	0	2
GLENWOOD	GW	0	2
GRANDE CACHE	SW	2	6
GRANDE PRAIRIE	SW	6	17

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
GRANUM	SW	2	5
GRASSLAND	SW / GW	2	8
GRASSY LAKE	SW	3	4
GREENSHIELDS	GW	0	2
GREGOIRE LAKE PROVINCIAL PARK	SW	0	5
GRIMSHAW	GW	0	4
GROUARD	SW	3	9
GUNN SOCIAL SERV CENTRE	GW	0	1
GUY	SW	13	5
HALKIRK	GW	0	1
HANNA (Henry Kroeger)	SW	6	7
HARDISTY	GW	0	2
HARMON VALLEY (East Peace Regional)	SW	0	1
HAY LAKES	SW	15	8
HAYS	SW	6	4
HEISLER	GW	0	1
HENRY KROEGER REGIONAL WTP	SW	2	1
HERITAGE POINTE	SW	2	2
HEWITT ESTATES	GW	0	1
HIGH LEVEL	SW	1	7
HIGH PRAIRIE	SW	1	10
HIGH RIVER	GW (<15 m)	0	5
HILDA	GW	0	2
HILL SPRING	GW	0	1
HILLCREST - CROWSNEST PASS	GW	0	2
HILLTOP ESTATES SUBDIVISION	GW	0	1
HINES CREEK	SW	22	8
HINTON	SW	0	8
HOLDEN (Edmonton 2002)	SW	5	5
HUGHENDEN	GW	0	2
HUSSAR	GW	0	1
HUXLEY	GW	0	2
HYTHE	GW	0	1
INNISFAIL (Anthony Henday/Wells)	SW / GW	0	1
INNISFREE	GW	0	3
IRMA	GW	0	1
IRON SPRINGS	SW	0	1
IRRICANA	GW	0	2
IRVINE	GW	0	1
ISLAY	GW	0	1
JANVIER	SW	0	8
JARVIE	GW	0	1
JASPER	SW / GW	0	4
JEAN COTE	SW	11	6
JOSEPHBURG (Edmonton)	SW	1	1
JOUSSARD	SW	0	10
KANANASKIS BARRIER LAKE INFO	GW (<15 m)	0	2

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
CENTER			
KANANASKIS EVAN THOMAS	GW	0	1
KANANASKIS FIELD STATION	SW	0	1
KEG RIVER	SW	0	7
KIKINO	SW	0	4
KILLAM	GW	2	3
KINBROOK ISLAND	SW	4	2
KINSELLA	GW	0	1
KINUSO (Faust)	SW	0	1
KITSCOTY	GW	0	2
LA CRETE	GW	0	2
LAC LA BICHE	SW	0	12
LACOMBE	GW	0	1
LAKE NEWELL RESORT	SW	4	3
LAMONT (Edmonton)	SW	0	1
LAVOY	GW	0	2
LETHBRIDGE	SW	22	29
LIBERTY PARK	GW	0	1
LINDBERGH (CANADIAN SALT MFG PLANT)	SW	2	2
LINDEN	GW	0	2
LITTLE BOW RESORT	SW	2	2
LITTLE BUFFALO (Cadotte Lake)	SW	0	1
LITTLE BURNT RIVER WATER COOP	GW	0	1
LOMOND	SW	4	2
LONGVIEW	GW (<15 m)	1	4
LOON LAKE	SW	0	1
LOTTIE LAKE	GW	0	3
LOUGHEED	SW / GW (<15 m)	0	1
LUNDBRECK	SW / GW	0	1
MAGRATH	SW	1	2
MALLAIG	SW	0	2
MANNING	SW	1	8
MANNVILLE	GW	0	1
MARIE REINE	SW	0	1
MARLBORO	GW	0	3
MARWAYNE	GW	1	1
MAYERTHORPE	GW	0	5
MCLAUGHLIN	GW	0	1
MCLENNAN	SW	4	9
MEDICINE HAT	SW	25	30
METISKOW	GW	0	1
MILK RIVER	SW	1	3
MILLET	GW	1	3
MILO	SW	7	3
MIRROR	SW	9	9
MONARCH	SW	1	2

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
MOON RIVER ESTATES	GW (<15 m)	0	2
MOONSHINE LAKE PROV PARK	SW	0	1
MORRIN	GW	0	3
MOSSLEIGH	GW	0	1
MOUNTAIN MEADOWS ESTATES	GW	1	1
MUNDARE (Edmonton)	SW	0	1
MUNSON (Drumheller)	SW	1	2
MYNARSKI PARK SUBDIVISION	GW	0	1
MYRNAM	GW	0	1
NAKISKA	GW (<15 m)	1	3
NAMPA	SW	12	7
NANTON	SW / GW	2	5
NEERLANDIA	SW	4	8
NEW DAYTON	SW	3	3
NEW NORWAY	GW	0	2
NEW SAREPTA	GW	0	1
NEWBROOK	GW	0	2
NOBLEFORD	SW	5	2
NORDEGG	SW	0	5
NORTH SPRINGBANK WATER CO-OP	GW	1	6
OKOTOKS	GW (<15 m)	0	4
OLDS (Anthony Henday)	SW	5	5
ONOWAY	GW	1	4
OYEN (Henry Kroeger)	SW	0	1
PADDLE PRAIRIE	SW	7	9
PADDLE RIVER	SW	0	1
PARADISE VALLEY	GW	0	1
PARK LAKE PROVINCIAL PARK	SW	2	1
PARKLAND VILLAGE	GW	1	1
PATRICIA	SW	1	2
PEACE RIVER	SW	1	12
PEACE RIVER CORRECTIONAL	SW	0	4
PEAVINE	SW	1	6
PEERLESS LAKE	SW / GW	1	7
PENHOLD	GW	0	1
PEORIA	SW	8	5
PIBROCH	GW	0	2
PICTURE BUTTE	SW	9	7
PINCHER CREEK	SW	3	6
PLAMONDON	SW	0	9
PONOKA	GW	0	4
POPLAR VIEW	SW	0	2
PRIDDIS GREENS	GW (<15 m)	0	1
PRINCE OF PEACE LUTHERAN CHURCH	GW	0	1
PROVOST	GW	0	2
RADWAY (Edmonton)	SW	2	1
RAINBOW LAKE	SW	4	7

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
RAINIER	SW	0	1
RAYMOND	SW	2	3
RED DEER	SW	2	18
RED EARTH	SW	1	11
REDCLIFF	SW	3	4
REDWATER (Edmonton)	SW	1	1
RENO (East Peace Regional)	SW	0	1
RICHDALE (Henry Kroeger)	SW	2	1
RIDGE VALLEY	GW	0	1
RIMBEY	GW	1	2
ROCKY MOUNTAIN HOUSE	SW	2	10
ROCKY RAPIDS	GW	0	1
ROCKY VIEW WATER COOP	SW	2	2
ROCKYFORD	SW	18	6
ROLLING HILLS	SW	4	2
ROSALIND	GW	0	1
ROSEBUD	GW	0	2
ROSEDALE (Drumheller)	SW	2	2
ROSEMARY	SW	8	2
RUMSEY	GW	0	2
RYCROFT	SW	7	8
SAGEBRUSH ESTATES	SW	3	2
SANDSTONE RANCH (SALTBOX COULEE)	GW (<15 m)	0	2
SANDY LAKE	SW	2	10
SANGUDO	GW	1	4
SCANDIA	SW	0	1
SEDGEWICK	GW	0	2
SEEBE	SW	0	4
SENTINEL	SW	0	1
SEVEN PERSONS	SW	10	4
SEXSMITH	GW	0	3
SHAUGHNESSY	SW	0	3
SHAWS POINT RESORT	SW	0	1
SHEERNESS	SW	2	1
SHERWOOD PARK (Edmonton)	SW	0	2
SILVER POINTE VILLAGE	GW	0	1
SILVER WILLOWS ESTATES	GW (<15 m)	4	5
SIR WINSTON CHURCHILL PROV PARK	SW	0	5
SLAVE LAKE	SW	0	11
SLOPES SUBDIVISION	GW	0	1
SMITH	SW	0	8
SMOKY LAKE	GW (<15 m)	3	7
SPIRIT RIVER	SW	16	7
SPRING COULEE	GW	0	1
SPRINGBANK	GW (<15 m)	0	5
SPRUCE GROVE (Edmonton)	SW	0	1
SPRUCE VIEW	GW	0	2

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
SQUARE BUTTE RANCH	GW / GW (<15 m)	0	1
ST. ALBERT (Edmonton)	SW	0	2
ST. ISIDORE (East Peace Regional)	SW	0	1
ST. MICHAEL	GW (<15 m)	0	1
ST. PAUL	SW	6	13
STANDARD	SW	7	2
STAVELY	GW	1	2
STETTLER	SW	0	11
STIRLING	SW	1	3
STONY PLAIN (Edmonton)	SW	0	1
STRATHMORE	SW	13	6
STROME	GW	0	1
SUNCOR	SW	0	3
SUNDANCE	SW	2	1
SUNDRE	GW	0	3
SWALWELL	GW	0	1
SWAN HILLS	SW	0	9
SYLVAN LAKE	GW	0	4
SYNCRUDE AURORA	SW	0	1
SYNCRUDE MILDRED LAKE	SW	0	4
TABER	SW	18	10
TANGENT	SW	19	9
THORHILD (Edmonton)	SW	0	2
THORSBY	SW	2	7
THREE CREEKS (East Peace Regional)	SW	0	1
THREE HILLS	SW	4	6
TILLEY	SW	3	3
TOFIELD (Edmonton)	SW	0	1
TORRINGTON	GW	0	1
TRI-WEST RESORTS	SW	2	3
TROCHU	GW	0	2
TROUT LAKE	GW (<15 m)	0	7
TURIN	SW	1	2
TURNER VALLEY	GW (<15 m)	1	3
TWELVE MILE COULEE	SW	0	2
TWO HILLS	GW	0	1
VALLEYVIEW	SW	0	8
VAUXHALL	SW	3	3
VEGREVILLE (Edmonton)	SW	1	3
VERMILION	GW	0	2
VETERAN	GW	0	2
VIKING (Edmonton 2002)	SW	10	9
VILNA	SW	2	8
VIMY	GW	0	3
VULCAN	SW	9	5
WABAMUN	SW	3	7
WABASCA	SW	1	11

FACILITY NAME (Treated Water Source)	Surface Water or Groundwater Source	Total Number of Pesticide Detections	Total Number of Samples
WAINWRIGHT (CFB Wainwright)	SW	5	4
WALSH	SW	0	3
WANDERING RIVER	SW	1	9
WANHAM	SW	14	6
WARBURG	GW	0	2
WARNER	SW	3	3
WARSPITE	GW	0	1
WASKATENAU	SW	5	6
WEMBLEY	GW	0	4
WESTLOCK	SW	2	9
WESTRIDGE	SW	2	4
WESTVIEW ESTATES	GW (<15 m)	0	1
WETASKIWIN	SW	14	15
WHITECOURT	SW	0	11
WHITELAW	SW	2	3
WILDWOOD	GW	0	4
WILLINGDON	GW	0	1
WIMBORNE	GW	0	2
WINFIELD	GW	0	1
WINTERGREEN WOODS CO-OP	SW	3	2
WOKING	SW	0	8
WORSLEY	SW	1	7
WRENTHAM	SW	5	4
YOUNGSTOWN (Henry Kroeger)	SW	1	1
ZAMA	GW	0	4
Totals		821	1788

SW – Surface Water source
GW (<15) Ground Water source (water level less than 15 m, often considered to be under surface influence)
GW – Deep Groundwater source (well depth/groundwater level >15m)

Appendix 3 Summary by month of pesticides detected in treated water samples (1995-2003)(sample numbers for newer pesticides in brackets under max level)

		2,4-D	MCPA	MCPP	Clopyralid	Picloram	Dicamba	Bromoxynil	Atrazine	Lindane	Triallate	Triclopyr	Diazinon	Imazamethabenz	Dichlorprop	MCPB	Imazethapyr	Diclofop	Azinphos-methyl	Methoxychlor	Samples with Detections
January	# Det'ns	21	15	2	4	3		3	1				1								38
(n=178)	% Det'ns	11.8%	8.4%	1.1%	2.2%	1.7%		1.7%	0.6%				0.6%								21.3%
	Max (ug/L)	0.155	0.079	0.009	0.26	0.198		0.199	0.013				0.057								
February	# Det'ns	28	14	2	8	5	1	2	1		1	1									41
(n=196)	% Det'ns	14.3%	7.1%	1.0%	4.1%	2.6%	0.5%	1.0%	0.5%		0.5%	1.6%									20.9%
	Max (ug/L)	0.142	0.048	0.007	0.125	0.353	0.015	0.007	0.038		0.014	2.405									
												(n=64)									
March	# Det'ns	29	17	10	10	10	4	2		1		1					1				46
(n=184)	% Det'ns	15.8%	9.2%	5.4%	5.4%	5.4%	2.2%	1.1%		0.5%		2.1%.					1.0%				25.0%
	Max (ug/L)	0.089	0.139	0.056	0.227	0.102	0.054	0.004		0.007		0.052					0.055				
												(n=47)					**(n=104)**				
April	# Det'ns	23	4	3	1	2	2	1						1							27
(n=106)	% Det'ns	21.7%	3.8%	2.8%	0.9%	1.9%	1.9%	0.9%						1.7%							25.5%
	Max (ug/L)	0.084	0.008	0.01	0.34	0.044	0.014	0.014						0.11							
														(n=57)							
May	# Det'ns	26	5	6	1	7	6	4	2			1		1					1		35
(n=124)	% Det'ns	21.0%	4.0%	4.8%	0.8%	5.6%	4.8%	3.2%	1.6%			4.8%		1.2%					0.8%		28.2%
	Max (ug/L)	0.08	0.012	0.014	0.03	0.051	0.032	0.005	0.057			0.02		0.075					0.123		
												(n=21)		**(n=86)**							
June	# Det'ns	36	33	8	4	8	7	5	2	2			1		1						48
(n=131)	% Det'ns	27.5%	25.2%	6.1%	3.1%	6.1%	5.3%	3.8%	1.5%	1.5%			0.8%		0.8%						36.6%
	Max (ug/L)	1.235	0.07	0.022	0.127	0.202	0.11	0.007	0.01	0.004			0.006		0.008						

Appendix 3 (continued)

		2,4-D	MCPA	MCPP	Clopyralid	Picloram	Dicamba	Bromoxynil	Atrazine	Lindane	Triallate	Triclopyr	Diazinon	Imazametha-benz	Dichlorprop	MCPB	Imazethapyr	Diclofop	Azinphos-methyl	Methoxychlor	Samples with Detections
July	# Det'ns	39	25	12	6	7	9	3	2	3	1										55
(n=174)	% Det'ns	22.4%	14.4%	6.9%	3.4%	4.0%	5.2%	1.7%	1.1%	1.7%	0.6%										31.6%
	Max (ug/L)	0.182	0.085	0.069	0.351	0.49	0.033	0.009	0.013	0.015	0.008										
August	# Det'ns	30	22	4	3	1	7	3	1						1	1				1	47
(n=174)	% Det'ns	17.2%	12.6%	2.3%	1.7%	0.6%	4.0%	1.7%	0.6%						0.6%	0.6%				0.6%	27.0%
	Max (ug/L)	0.649	0.052	0.024	0.174	0.028	0.284	0.012	0.005						0.009	0.017				0.031	
September	# Det'ns	35	16	9	9	3	9		2	1		2	1								51
(n=155)	% Det'ns	22.6%	10.3%	5.8%	5.8%	1.9%	5.8%		1.3%	0.6%		12.5%	0.6%								32.9%
	Max (ug/L)	0.443	0.045	0.03	0.156	0.085	0.085		0.009	0.002		0.185	0.014								
												(n=16)									
October	# Det'ns	14	5	3	2	3	2	1	1		2		1								25
(n=134)	% Det'ns	10.4%	3.7%	2.2%	1.5%	2.2%	1.5%	0.7%	0.7%		1.5%		0.7%								18.6%
	Max (ug/L)	0.128	0.571	0.006	0.11	4.07	0.049	0.006	0.024		0.011		0.008								
November	# Det'ns	20	15	3	11	7	1	1		1											28
(n=106)	% Det'ns	18.9%	14.1%	2.8%	10.4%	6.6%	0.9%	0.9%		0.9%											26.4%
	Max (ug/L)	0.174	0.075	0.005	0.245	0.95	0.001	0.005		0.008											
December	# Det'ns	22	19	2	5	4	2		2	1	1							1			35
(n=126)	% Det'ns	17.5%	15.1%	1.6%	4.0%	3.2%	1.6%		1.6%	0.8%	0.8%							0.8%			27.8%
	Max (ug/L)	0.088	0.026	0.008	0.158	0.23	0.042		0.01	0.026	0.006							0.08			

Note: sample numbers for recently added parameters are highlighted in brackets below the specific parameter.

Appendix 4 Preliminary Review of Treatment Technologies for Removal of Pesticides from Treated Water

While activated charcoal has been utilized in the past, and continues to be the standard for removing organic contaminants for treated water supplies, the most promising technology for removing pesticides from drinking water is membrane filtration. There are four main types of membrane filtration:

- microfiltration, which is effective in reducing turbidity;
- ultrafiltration, which can remove viruses, protozoan cysts and organisms such as *Giardia* and *Cryptosporidia*;
- nanofiltration, which reduces hardness, sulfate, dissolved organics, pathogens and the precursors to disinfection by-products; and finally
- reverse osmosis, which has the smallest pore size, can remove nearly all salts and dissolved organics (SAWRA 1997).

Because reverse osmosis has the smallest membrane size (10^{-3} to 10^{-4} µm), it has the highest operating cost, and even with extensive pre-treatment, results in a large quantity (15-30% of feed water) of reject water (water not passing through the membrane). This reject water can be difficult and expensive to dispose of because of the high concentration of solutes. Even with reverse osmosis, pesticide removals can vary depending upon membranes used (cellulose acetate, polyamide, or thin film composite) and with the pesticide class involved (EPA, 2001).

There are a small number of membrane filtration processes in use or under development at Alberta water treatment facilities, ranging from microfiltration to reverse osmosis. The facilities currently utilizing reverse osmosis processes use deep groundwater primarily, which is at less risk from pesticide contamination. One of the current directions for development of water treatment processes is directed towards those that can deal with Giardia and *Cryptosporidia*, and the one that shows the most promise is ultraviolet disinfection, possibly combined with membrane filtration (ultrafiltration). Another focus for membrane filtration implementation is for water treatment plants that require upgrades to achieve higher capacity, reduction in turbidity, and to deal with taste and odour problems. This follows the proven multibarrier design approach that has demonstrated the capability of meeting bacterial and microbiological standards for drinking water (raw water storage, chemical addition to precondition water for filtration, filtration and disinfection) (Alberta Environment Working Group on Drinking Water, 2001).

Not all facilities in Alberta would require advanced technology for reducing pesticide concentrations in water supplies. The identification of those facilities with recurrent pesticide detection's and the evaluation of current water treatment processes at these facilities, with an assessment of possible upgrades would be a first step.

Variations in water quality of source waters and variations in plant design and construction affect pesticide removal efficiency. Efficient removal also depends upon the treatment process being tailored to the pesticide of concern (SAP, 2001).

Appendix 5 Selected Pesticide Characteristics

A summary of the characteristics of selected pesticides found in treated water was compiled, to identify similarities that might be used to assist in prediction of pesticide detections in treated water. As well as basic characteristics such as water solubility and Koc (a indication of the adsorption characteristics of the compound), the degradation processes in water and limitations to degradation were also compiled.

Cotton (1995) summarized the relative environmental rankings of a number of pesticides used in Alberta, and developed new or adapted existing ranking systems specific to pesticide characteristics. For water solubility's, 30-300 mg/L indicated moderate mobility, while 300 mg/L and above indicated high pesticide mobility. Most of the pesticide listed below had high water solubility's, and the more frequently detected pesticides had the highest water solubility's.

For Koc values, anything greater than 1000 g/ml indicated high adsorption to organic matter and soil particle, and very immobile (excepting with soil and sediment movement). Koc values from 500-1000 ml/g indicate a concern, depending upon the influence of other factors. Koc values of 300 - 500 ml/g indicated a tendency to move with water, and a potential for leaching. Koc values less than 300 indicated low adsorption to soil and organic matter, and high mobility. It can be seen from the table that aside from bromoxynil and MCPA ester, most of the Koc values are very low. These low values would indicate higher mobility, and partially attribute to the residues found in treated water supplies. Low adsorption factors would also limit the amount of physical removal of the pesticides during the water treatment process.

The half-life of the following pesticides shows a wide range of values. Obviously, the shorter the half-life, the less opportunity that the pesticide has to move into surface or groundwater. Determination of pesticide half-lives is not an exact science, as factors such as temperature, oxygen level, microbial populations, pH, and other factors all play a role in the degradation or transformation of a pesticide (Cotton, 1995). Field and lab determinations of half-life can also be significantly different. Compounds with long half-lives (picloram, clopyralid and atrazine) might be expected to be found in water supplies. However, a compound like 2,4-D, with a reported half-life of 10 days, would not be expected to be the most prevalent pesticide found in treated water supplies. In the case of 2,4-D, other factors such as low adsorption, high water solubility, and high use have a major effect on pesticide residues in water supplies. The value of 10 days for an aquatic half life is somewhat suspect, however, as 2,4-D is detected in treated water supplies year round, while its use is only during the months of April to October. It should be noted that the analysis and lab reports are based upon the 2,4-D and MCPA acid forms, primarily as the ester and amine forms convert to the acid form in the environment.

Appendix 5 Selected Pesticide Characteristics

Compound	Detections in treated water (%)	Water Solubility (mg/L)	Koc (ml/g)	1998 Sales (kg ai)[1]	½ Life in Water	Degradation in Water	Limitations to Degradation
2,4-D (ester)	18.1	100[3]	100[3]	535 068	10 days[2]	Hydrolysis significant at higher pH. Esters also hydrolyzed by microorganisms [6]	Rate of degradation dependent upon pH and availability of humic materials. Biological factors as well as pH, photodegradation and adsorption may affect removal[6]
2,4-D (amine)		796 000[3]	20[3]	138 849	10 days[2]	Photodegradation by UV light is relatively rapid, and is more rapid as pH of water increases[6]	
MCPA (ester)	10.6	5[3]	1000[3]	687 831	20-24 days (photolytic - pH 8.3 and sunlight)[5]	Degraded completely by aquatic organisms in 13 days.[5]	Does not volatilize from aqueous solutions. Residue levels in flooded soil remain unchanged.
MCPA (amine)		66 000[3]	20[3]	142 504			
Mecoprop	3.6	660 000[3]	20[2]	27 264	n/a	Microbial degradation under aerobic conditions[7]	Lag period (42-56 days) required to induce specific enzymes, growth of an initially small degrading microbial population or both[7]
Clopyralid	3.6	7850[9]	0.4-29.8[9]	59 020	261 days @ 25°C[9] (Alberta field studies: 22 days, 40 days in sediment)[9]	Microbial processes[9]	No significant aerobic aquatic metabolism. No significant degradation from sunlight. Resists hydrolysis and photolysis in sterile water at pH 7. Low volatility[9]
Picloram	3.4	400 000[2]	16[3]	15 109	<10% degraded after 300 days in anaerobic aquatic metabolism[4]	Direct photolysis[4]	Stable to hydrolysis in acidic, neutral and basic media. Major role of dissipation from soil is leaching. Not susceptible to abiotic hydrolysis or volatilization[4]

Appendix 5 Selected Pesticide Characteristics continued

Compound	Detections in treated water (%)	Water Solubility (mg/L)	Koc (ml/g)	1998 Sales (kg ai)[1]	½ Life in Water	Degradation in Water	Limitations to Degradation
Dicamba	2.8	5600[2]	2[3]	138 279	<7 days[2]	Microbial processes impact removal process, photolysis may contribute[6]	Aquatic hydrolysis, volatilization, adsorption to sediment and bioconcentration not expected to be significant[6]
Bromoxynil	1.4	27[3]	1079[3]	268 105	4.6 days @ pH 5[8]	Abiotic hydrolysis, aquatic photolysis, microbially mediated metabolism under aerobic and anaerobic conditions[8]	Stable in dark @ pH 5 with 110.7 day half-life[8]
Atrazine	0.8	33[3]	100[3]	5754	742 days[2]	Atrazine degraded in soil by photolysis and microbial processes[5]	Stable in aerobic g/w supplies incubated for 15 mo. in dark at 10°C. Dissipation in aquatic field studies due to leaching and dilution by irrigation water. Residues persisted for 3 yrs in soil[5]

1 Byrtus, 2000
2 Cotton, 1995
3 Wauchope et al., 1992
4 EPA, 1995
5 EPA, 1989
6 Howard, 1991
7 Klint et al., 1993
8 EPA, 1998
9 DowAgroSciences, 1998