Pesticides in Ontario's Treated Municipal Drinking Water

1986-2006

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Pesticides in Ontario's Treated Municipal Drinking Water

1986-2006

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EXECUTIVE SUMMARY

The purpose of this study is to examine the occurrence of pesticides in Ontario's treated (finished) drinking water. The study examines the period 2001-2006 in detail. It also presents trends for the period 1986-2006. The main focus of this study is pesticide detection rates in treated water at surface water systems and groundwater systems.

This study is a review of an existing dataset. Data is from two long-running Ontario Ministry of the Environment (MOE) programs: the Drinking Water Surveillance Program (DWSP) and the Ministry's Drinking Water Inspection/Compliance Program.

104 pesticides and pesticide degradates were included in this study. Samples covered about 90% of Ontario's 697 municipal residential drinking water systems. Over 16,000 treated water pesticide samples were collected, providing 636,000 analytical results. Samples were collected from water treatment plants, well pumphouses, and distribution systems.

The following are important conclusions of this study:

Trends

- From 1986 to 2006 the pesticide detection rate in treated surface water dropped from 86% to 3% due to a decrease in source water pesticide concentrations. Most of the drop was due to decreases in source water concentrations of alpha-HCH and to a lesser degree gamma-HCH (lindane). In the 1970's, Canada and the U.S. banned the main product containing alpha-HCH and started phasing out gamma-HCH.
- Atrazine dominated pesticide detections in treated surface water in most years from 1994 - 2006.
- For most years from 1987 – 2006, the pesticide detection rate in treated groundwater was between 0.0 – 6.7%. The detection rate exceeded 6.7% in three years, reaching as high as 11.7%.

Exceedances of Ontario Drinking Water Quality Standards, 1986-2006

- From 1986 to 2006 there were four exceedances of Ontario drinking water quality standards for pesticides in over 16,000 treated water samples. The samples covered about 90% of Ontario's municipal residential drinking water systems. Two atrazine exceedances occurred at surface water systems and two terbufos exceedances occurred at a groundwater system, in groundwater that is under the direct influence of surface water (GUDI). All exceedances occurred at systems in southwestern Ontario, the region of Ontario with the highest agricultural use of pesticides.

Treated Surface Water, 2001-2006

- Seventeen pesticides and two pesticide degradates were detected in treated surface water.
- Atrazine was the most frequently detected pesticide in treated surface water. It was detected in 11.8% of samples and at 38% of systems. Atrazine and its degradate de-ethylated atrazine together accounted for 66% of pesticide detections in treated surface water.

- The surface water systems with the highest pesticide detection rates were in southwestern Ontario, the southeast corner of Ontario and along the lower Great Lakes and St. Lawrence River. Southwestern Ontario and the southeast corner of Ontario were the areas of highest agricultural pesticide use. High detection rates in drinking water from Lake Erie, Lake Ontario and the St. Lawrence River may have resulted from being downstream of agricultural and urban pesticide inputs into the Great Lakes. They may also have resulted from tributary river discharges in those areas.
- Ninety-five percent of pesticide detections in treated surface water were in the range 1- 840 parts per trillion (1 - 840 ng/L), five percent were above 1 part per billion (1,000 ng/L), and the highest was 9.5 parts per billion (9,500 ng/L).

Treated Groundwater, 2001-2006

- Most groundwater systems had no pesticide detections in treated water.
- Seventeen pesticides and one pesticide degradate were detected in treated groundwater.
- 2,4-D was the most frequently detected pesticide in treated groundwater. It was detected in 1.3% of samples and at 14% of systems.
- Unlike treated surface water, atrazine was rarely found in treated groundwater.
- Eighty-three percent of pesticide detections in treated groundwater were in the range 9 – 580 parts per trillion (9 – 580 ng/L), 17% were above 1 part per billion (1,000 ng/L), and the highest was 19 parts per billion (19,000 ng/L).

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The purpose of this study is to examine the occurrence of pesticides in Ontario's treated (finished) drinking water. The study examines the period 2001-2006 in detail. It also presents trends for the period 1986-2006. The main focus of this study is pesticide detection rates in treated water at surface water systems and groundwater systems.

This study evolved from a project to optimize pesticides monitoring in the Ontario Ministry of the Environment's (MOE) Drinking Water Surveillance Program (DWSP). DWSP is a scientific monitoring program that monitors municipal drinking water quality. One of its focuses is non-regulated drinking water quality parameters, including emerging contaminants. DWSP was initiated by the MOE in 1986. It is a voluntary program operated in partnership with municipalities. DWSP monitors over 250 inorganic, organic and radiological water quality parameters.

In addition to DWSP data, this study uses data from the MOE's Drinking Water Inspection/ Compliance Program. The Drinking Water Inspection/Compliance Program performs annual inspections of municipal water systems to determine compliance with the Safe Drinking Water Act.

104 pesticides and pesticide degradates were included in this study (Table 1). The pesticides included in this study accounted for 68% of the tonnage of pesticide active ingredients used for agriculture in Ontario in 2003 (*1*), and 77% of the tonnage of pesticide active ingredients used by licensed applicators on lawns, golf courses, roadsides, etc. in Ontario in 1993 (*2*). 2003 and 1993 are the years of the most recent Ontario surveys of agricultural and cosmetic pesticide use, respectively.

Table 1. Pesticides in this Study and their Detection Limits from 2001-2006

Pesticide	Detection Limit (ng/L)
2,3,4,6-tetrachlorophenol	20
2,4,5-T	50
2,4-D	100
2,4-DB	200
2,4-DP	100
alachlor	500
aldicarb	2,500
aldrin	1
alpha-HCH	1
alpha-endosulfan	2
ametryne	50
AMPA	5,000
atratone	50
atrazine	50
atrazine, de-ethylated	200
azinphos-methyl	50
barban	2,000
bendiocarb	1,500
beta-HCH	2
beta-endosulfan	5
bromoxynil	50
butachlor	200
butylate	2,000
carbaryl	200
carbofuran	2,000
chlorbromuron	2,000
chlordane, alpha	2
chlordane, gamma	2
chlorpropham	2,000
chlorpyrifos	100
chlorpyrifos-methyl	500
chlortoluron	2,000
cyanazine	100
diallate	2,000
diazinon	200
dicamba	50
dichlorovos	500
diclofop-methyl	100
dieldrin	2
difenoxuron	2,000
dimethoate	500
dinoseb	20
diquat	100
diuron	2,000
methoxychlor	5
endosulfan sulphate	5
endrin	5
eptam	2,000
ethion	200
fluometuron	2,000
gamma-HCH	1
glyphosate	2,000
heptachlor	1
heptachlor epoxide	2
hexachlorobenzene	1
linuron	2,000
malathion	10
malathion	500
MCPA	20
MCPB	20
mecoprop	20
methoprene	5
methoprene acid	20
methoxycitronellal	20
methyl parathion	200
metobromuron	2,000
metolachlor	500
metoxuron	2,000
metribuzin	100
mevinphos	200
mirex	5
monolinuron	2,000
monuron	2,000
neburon	2,000
op-DDT	5
oxychlordane	2
paraquat	100
parathion	100
pentachlorophenol	10
permethrin	100
phorate	100
picloram	100
piperonyl butoxide	100
pp-DDD	5
pp-DDE	2
pp-DDT	5
prometon	50
prometryne	50
propazine	50
propham	2,000
propoxur	2,000
pyrethrin 1	100
pyrethrin 2	100
ronnel	100
siduron	2,000
silvex	20
simazine	50
simazine, de-ethylated	200
temephos	100
terbufos	200
terbutryne	200
toxaphene	500
triallate	1,500
2,4,5-trichlorophenol	100
trifluralin	5

2. METHODS

2.1 Data Source

This study is a review of an existing dataset. Data is from two long-running Ontario Ministry of the Environment (MOE) programs: the Drinking Water Surveillance Program (DWSP) and the Ministry's Drinking Water Inspection/Compliance Program. Drinking water quality data from these programs is stored in the MOE's Drinking Water Information Management System (DWIMS), which is administered by Environmental Monitoring and Reporting Branch. This study uses DWSP data from 1986-2006. It uses Drinking Water Inspection/Compliance Program data from 1997-2006 since Inspection/Compliance Program data was stored in an information system (DWIMS) starting in 1997.

2.2 Sampling

Treated water samples were collected across the province from over 75% of Ontario's 697 municipal residential drinking water systems. Some of these systems supply treated water to other systems and as a result the samples cover about 90% of Ontario's municipal residential systems. Samples were also collected from a few non-municipal year-round residential systems. Source waters for the drinking water systems in this study include the Great Lakes, inland lakes, rivers, creeks and groundwater.

Samples were collected from water treatment plants, well pumphouses, and distribution systems. DWSP samples were collected by water system operators following DWSP protocols. MOE drinking water inspectors collected audit samples following the inspection/compliance program's standard operating procedure. Both DWSP samples and inspection samples were collected using sampling kits from the MOE's Lab Services Branch. The kits were equipped with the necessary bottles and sample preservatives. DWSP kits also contained sampling instructions for the drinking water system operators. Neither program timed sampling to coincide with pesticide application events or rainfall events, both of which can cause large and temporary increases in pesticide concentrations in source waters. Any sampling that captured these events would have occurred by chance.

The inspection/compliance program provided samples from a large number of systems while DWSP provided more frequent sampling at a smaller number of systems. Inspection/compliance program samples from groundwater systems were especially valuable since the program sampled many more groundwater systems than did DWSP (297 systems vs. 36 systems respectively from 2001-2006).

1986-2000

In the period 1986-2000, treated water pesticide samples were collected at 442 drinking water systems. 190 of the systems used surface water and 229 used groundwater. Twenty-three systems were 'mixed' systems that used both surface water and groundwater. For the purposes of this study, aquifer recharge systems were included in the mixed category. DWSP sampled 186 systems and the inspection/compliance program sampled 336 systems. DWSP sampled surface water and groundwater systems from 1 to 10 times per year. Data from the inspection/compliance program was available from 1997 onwards, and from 1997-2000 the program sampled most systems once.

A total of 13,226 treated water pesticide samples were collected by both programs. 10,815 samples were from surface water systems, 1,323 were from groundwater systems and 1,088 were from mixed systems. There were 451,000 analytical results from all samples.

2001-2006

In the period 2001-2006, treated water pesticide samples were collected at 551 drinking water systems. 194 of the systems used surface water, 333 used groundwater and 24 systems were mixed. DWSP sampled 156 systems and the inspection/compliance program sampled 512 systems. DWSP sampled surface water systems 1 to 6 times per year and groundwater systems 1 to 2 times per year. The inspection/compliance program sampled most surface water and groundwater systems once during the six year period.

A total of 2,940 treated water pesticide samples were collected by both programs. 1,983 samples were from surface water systems, 699 were from groundwater systems and 258 were from mixed systems. There were 183,000 analytical results from all samples.

Raw water samples

Though the focus of this report is on treated water, one trend analysis does present raw water pesticides data from surface water systems. DWSP sampling rounds often included raw water pesticide samples. Raw water samples were collected at the same time as treated water samples. Raw water sampling protocols were the same as for treated water samples. From 2001-2006, 1,491 raw water pesticide samples were collected from 101 surface water systems, providing 49,000 analytical results. From 1986-2000, 5,144 raw water pesticide samples were collected from 122 surface water systems, providing 191,000 analytical results. Over 99% of the raw water samples from both time periods were collected by DWSP.

2.3 Sample Analysis

All samples from both programs were analyzed by the MOE's Lab Services Branch.

3. RESULTS AND DISCUSSION

3.1 Trends from 1986-2006

Treated surface water

From 1986 to 2006, the pesticide detection rate in treated surface water dropped from 86% to 3% (Figure 1). The trend in raw surface water was very similar; therefore the drop in the treated water detection rate was due to a decrease in source water pesticide concentrations rather than to improved treatment. In this period the detection limits of some pesticides increased and the detection limits of others decreased. Data was closely checked and it was confirmed that the detection limit changes did not affect the trend significantly.

It is not known why in 2001 the raw water detection rate (4.4%) was about half the treated water detection rate (9.2%). This anomaly does not seem to be due to sample sizes since raw water and treated water sample sizes in 2001 were comparable to those from other years. It is also not known why detection rates in raw and treated surface water were very similar during some periods (1986-1989, 1999-2000 and 2002-2005) and diverged during other periods (1990-1998, 2001 and 2006).

Most of the drop in the treated surface water detection rate occurred from 1986 to 1996, due to the declining detection rate of alpha-HCH, and to a lesser degree gamma-HCH (lindane) (Figure 2). Alpha-HCH dominated detections from 1986-1991.

HCH (hexachlorocyclohexane) is an organochlorine insecticide. Alpha-HCH and gamma-HCH are isomers of HCH. HCH has been commercialized in two predominant products: technical HCH and purified gamma-HCH (lindane). Technical HCH contains 60-70 % alpha-HCH , 10-15% gamma-HCH, and three other isomers. Lindane is almost pure gamma-HCH. Gamma-HCH is the only HCH isomer with insecticidal properties (*3*).

Technical-HCH was used as a pesticide since 1943 (*4*), though its history of use in Ontario could not be found in the literature. It was banned in Canada in 1976 (*5*) and in the U.S. in 1978 (*6*). Lindane was used in Ontario from 1938 (*5*, *7*). Starting in 1970, lindane's use in Canada was increasingly limited (*3*). It was phased out from 1999 to 2004 and finally banned in 2005 for all but pharmaceutical use (*3*, *7*). The history of lindane use in the US is similar to that in Canada (*3*, *5*, *8*) and the USEPA finally banned all agricultural uses of lindane in 2006 (*3*, *8*).

Until at least the late 1990's, HCH residues were among the most widely distributed and frequently detected organochlorine contaminants in the environment (*9*). HCH isomers are persistent organic pollutants (*4*) and can be transported over long distances by air currents (*3*). Their long history of use, persistence, mobility and low detection limit in this study (1 ng/L) probably explain why they dominated pesticide detections long after their use had been banned or restricted in Canada and the U.S.

Atrazine dominated detections in treated surface water from 1994 onwards, with the exception of 2000 and 2001. Including only pesticides that were in use during the period of this study (i.e. excluding alpha-HCH), atrazine dominated detections from 1990 onwards. The Ontario Ministry of Agriculture, Food and Rural Affairs does a survey of agricultural pesticide use every five years. In the 1983 survey, atrazine was the most heavily used pesticide. In 1988 and 1993, it was the second-most heavily used pesticide after metolachlor.

Figure 1. Pesticide Detection Rates in Raw and Treated Surface Water, 1986-2006

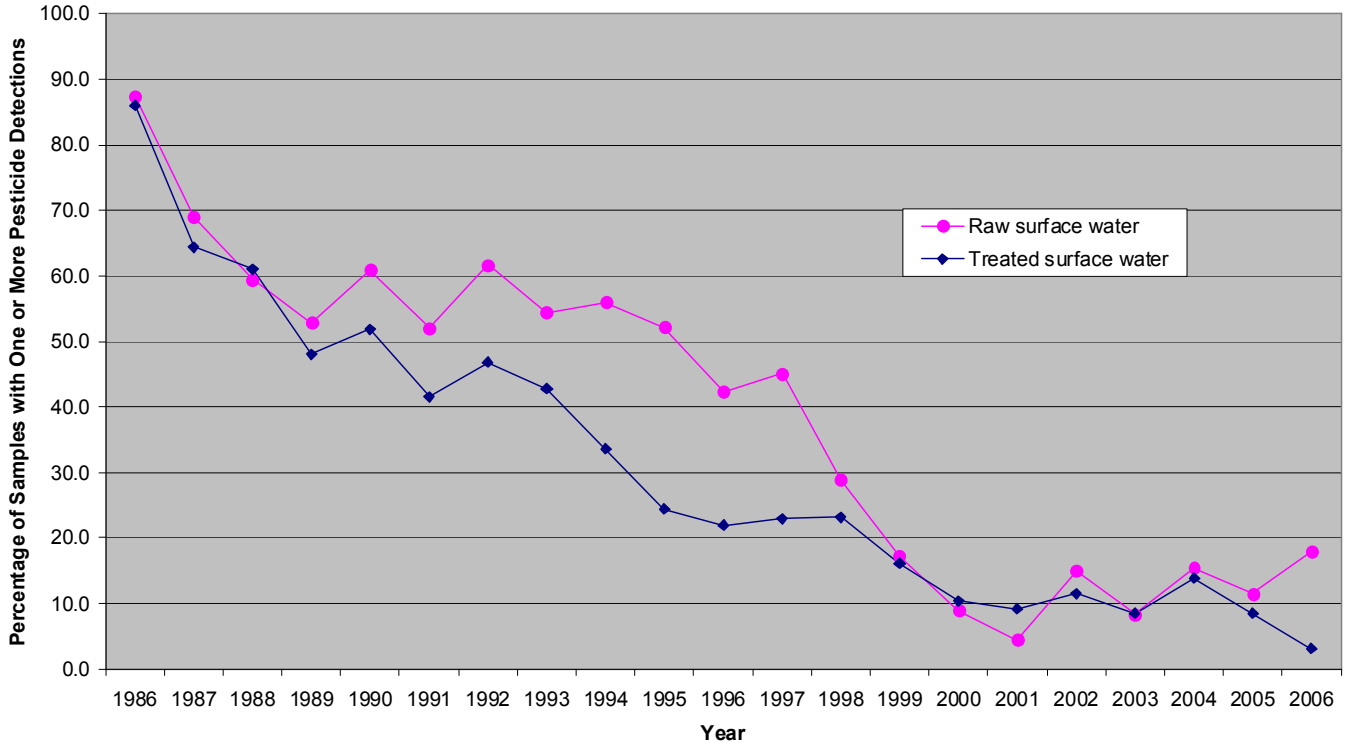
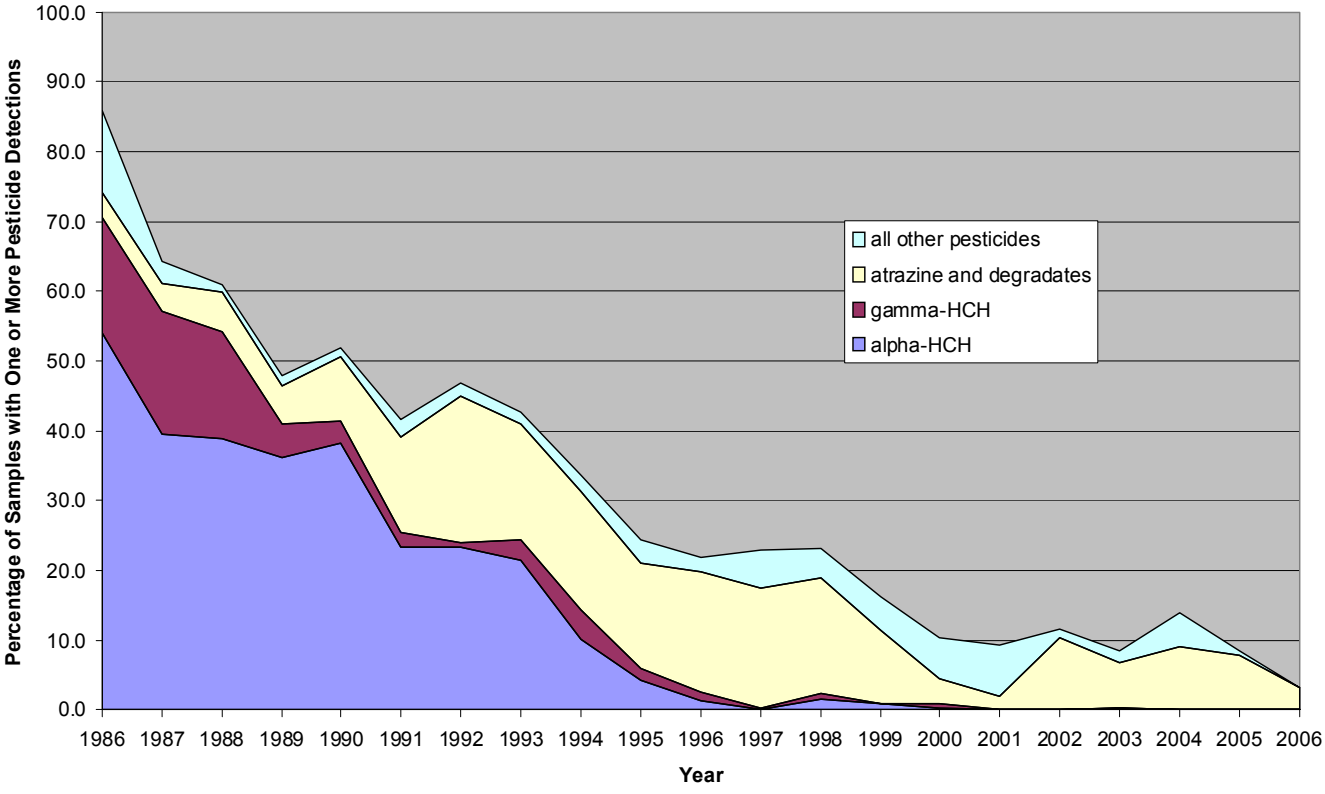


Figure 2. Contribution of Individual Pesticides to Pesticide Detection Rate in Treated Surface Water, 1986-2006



In the 1998 and 2003 surveys, it was the third-most heavily used pesticide. Metolachlor and glyphosate were first and second respectively in 1998 and second and first respectively in 2003.

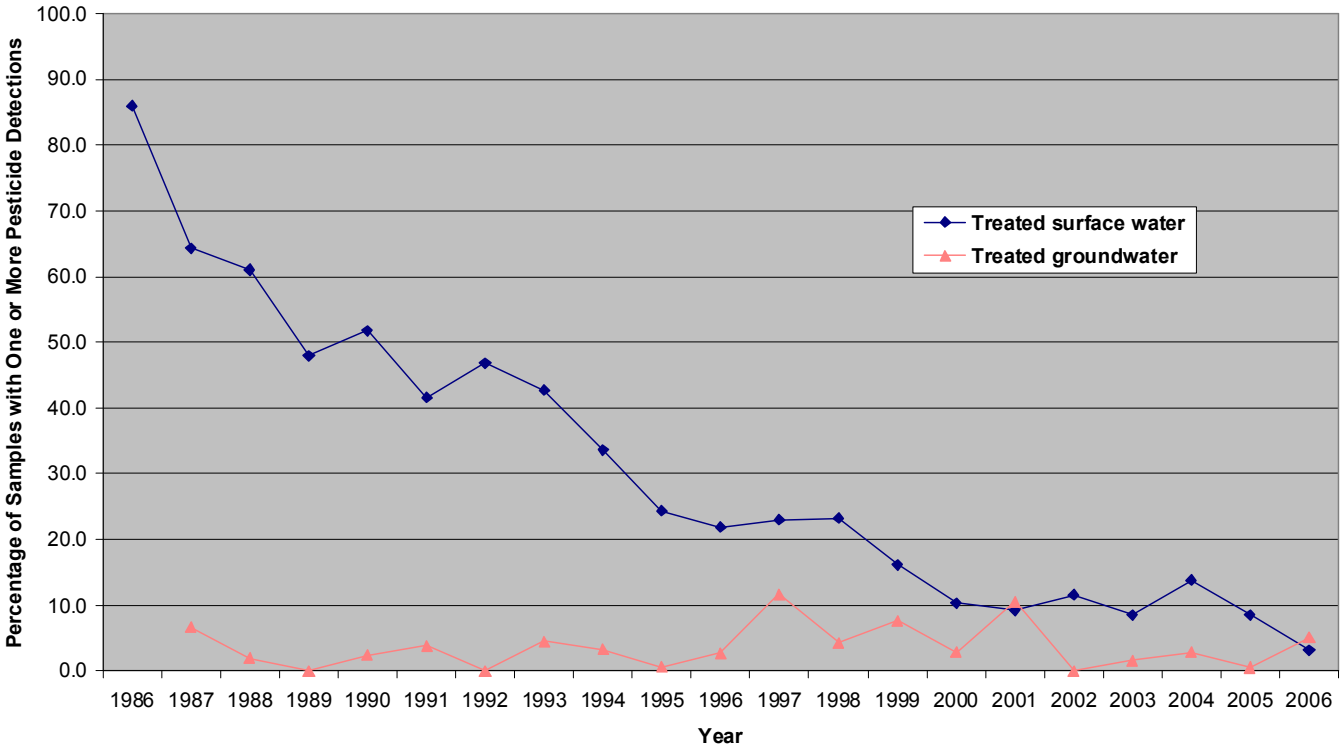
The seven years from 2000-2006 had the lowest detection rates of the entire twenty-one year period. The lowest detection rate occurred in 2006 (3.2%).

Treated groundwater

For most of the period 1987 – 2006, the pesticide detection rate in treated groundwater was between 0.0 – 6.7% (Figure 3). Higher detection rates of 11.7%, 7.7% and 10.6% occurred in 1997, 1999 and 2001 respectively.

From 1987-2006, detection rates in treated groundwater were generally much lower than detection rates in treated surface water, but the gap between them steadily decreased. In 2001 and 2006 detection rates in treated groundwater were slightly higher than those in treated surface water.

Figure 3 . Pesticide Detection Rates in Treated Surface Water and Groundwater, 1986 - 2006



3.2 Exceedances of Drinking Water Quality Standards, 1986 – 2006

From 1986 to 2006, DWSP and the Drinking Water Inspection/Compliance Program collected 16,166 treated water pesticide samples from 675 drinking water systems. Out of the 16,166 samples there were four exceedances of Ontario drinking water quality standards for pesticides (Table 2). The exceedances occurred at three drinking water systems. The two terbufos exceedances were from separate wells at one drinking water system during the same sampling event. Both wells draw groundwater that is under the direct influence of surface water (GUDI). The groundwater system at which the terbufos exceedances occurred is in southwestern Ontario, Ontario's main agricultural area. The atrazine exceedances occurred at two water treatment plants that drew water from the Sydenham River in southwestern Ontario. Much of the river's watershed is agricultural land. The two water treatment plants have since been decommissioned and the communities are now connected to water systems that draw water from the Great Lakes or Great Lakes connecting channels.

Table 2. Exceedances of Ontario Drinking Water Quality Standards for Pesticides, 1986 - 2006

Drinking Water System	Source	Sample Date	Pesticide	Result*	Ontario Standard*
A	Sydenham River	June 15, 1987	atrazine	13.9 ug/L	5 ug/L
B	groundwater	Nov. 12, 1997	terbufos	2.0 ug/L	1 ug/L
B	groundwater	Nov. 12, 1997	terbufos	3.0 ug/L	1 ug/L
C	Sydenham River	June 11, 2001	atrazine+de-ethylated atrazine	9.9 ug/L	5 ug/L

* 1 ug/L = 1,000 ng/L = 1 part per billion

The four exceedances described above were exceedances of Ontario standards. Where a pesticide does not have an Ontario standard, a standard was chosen from other jurisdictions in the the following priority order: USEPA, World Health Organization (WHO), California, Australia, and New Zealand. For example, Ontario does not have a drinking water standard for mecoprop and neither does the USEPA; but the next organization down the list—the WHO—does, so mecoprop results were compared to the WHO drinking water standard. Using this approach, no exceedances were found for pesticides without Ontario standards.

The analysis of drinking water quality standard exceedances is the only analysis in this study that includes results from mixed systems. A mixed system is any system that uses both surface water and groundwater, including aquifer recharge systems.

Table 3 describes the pesticides in this study with the most significant detections. Either there were exceedances of their drinking water quality standards or they were among the most frequently detected pesticides.

Table 3. Descriptions of Pesticides with the Most Significant Detections

Pesticide	Chemical Family	Type of Pesticide	Uses	Where Used
atrazine	triazine	herbicide	control of broadleaf weeds and grassy weeds	agriculture
2,4-D	phenoxy	herbicide	control of broadleaf weeds and brush	agriculture, cosmetic/urban*
dicamba	benzoic acid	herbicide	control of broadleaf weeds and brush	agriculture, cosmetic/urban*
mecoprop	phenoxy	herbicide	control of broadleaf weeds	cosmetic/urban*, some agriculture
pentachlorophenol	chlorophenol	insecticide and fungicide	wood preservative	industry
malathion	organophosphate	insecticide	control of insects on fruits and vegetables, adult mosquito control	agriculture, cosmetic/urban*, public health programs
terbufos	organophosphate	insecticide and nematocide	control of soil-borne insects and nematodes	agriculture

*Refers to uses when the data in this report was collected. The cosmetic use of 2,4-D, dicamba, mecoprop, malathion and many other pesticides was banned in Ontario in April 2009.

3.3 Analysis of 2001-2006 Data

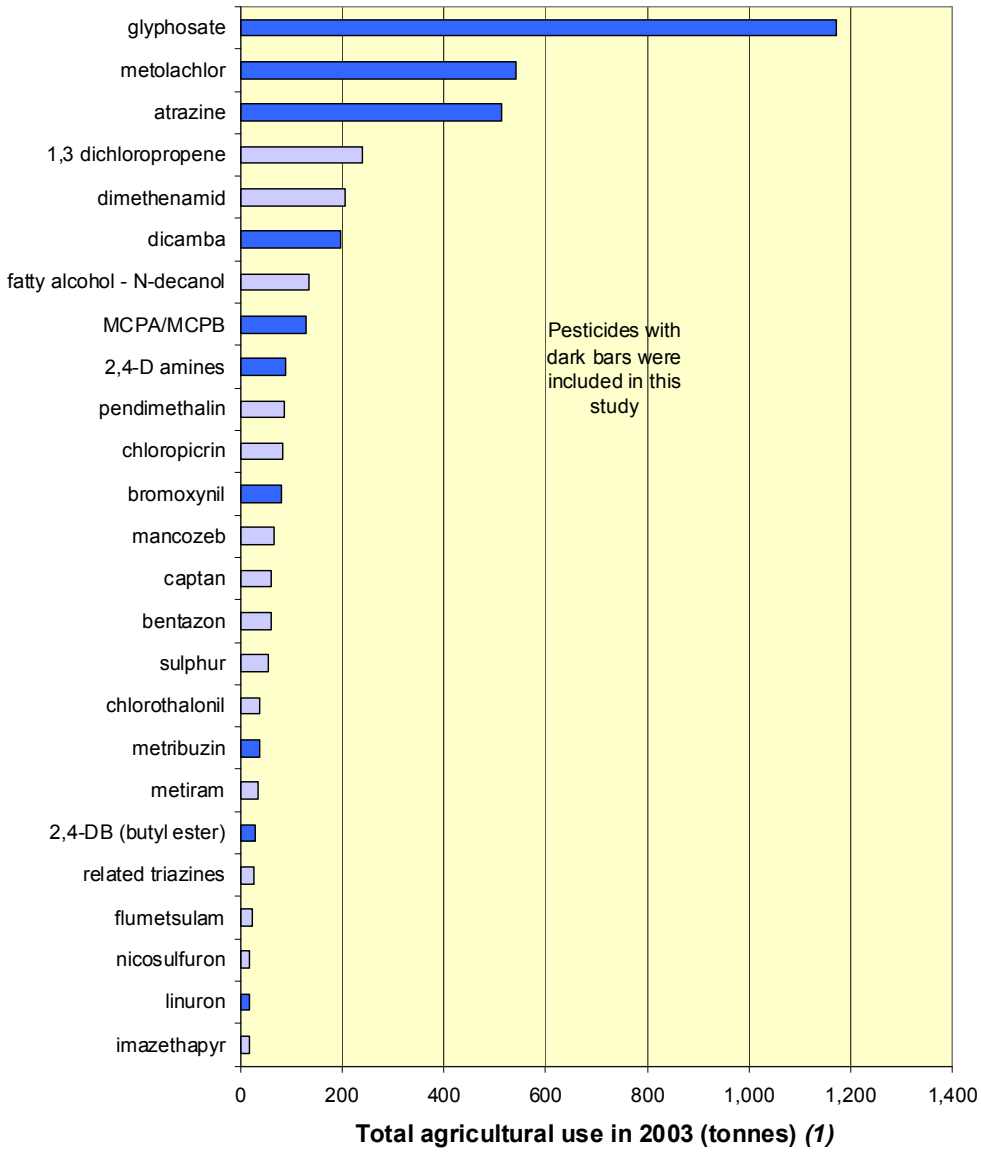
Detection limits

There was a wide range of detection limits in the analytical methods that generated this study's data (Table 1). They ranged from 1 ng/L for some organochlorine pesticides to 5,000 ng/L for AMPA (aminomethylphosphonic acid, a degradate of glyphosate). This study's results must be interpreted with detection limits in mind because detection limits can be the most important factor in determining which pesticides are most often detected. For example, glyphosate was not detected in any samples of raw or treated water even though it was by far the most used pesticide for agricultural purposes. Its degradate AMPA was not detected either. This study's detection limit for glyphosate was 2,000 ng/L. Another study, using a detection limit of 100 ng/L, detected glyphosate in 1/3 of Ontario stream samples *(10)*. In that study the results for almost all the detections were less than 2,000 ng/L.

Pesticide use

Figure 4 shows the 25 most used pesticides in Ontario agriculture in 2003, ranked by weight of active ingredient used. Glyphosate acounted for 28% of agricultural pesticide use. Glyphosate, metolachlor and atrazine together accounted for 53% of agricultural pesticide use.

Figure 4. The 25 Most Used Pesticides in Ontario Agriculture in 2003



The highest agricultural pesticide use occurred in southwestern Ontario, followed by the southeast corner of Ontario (Figure 5). Northern Ontario had the lowest agricultural pesticide use. -

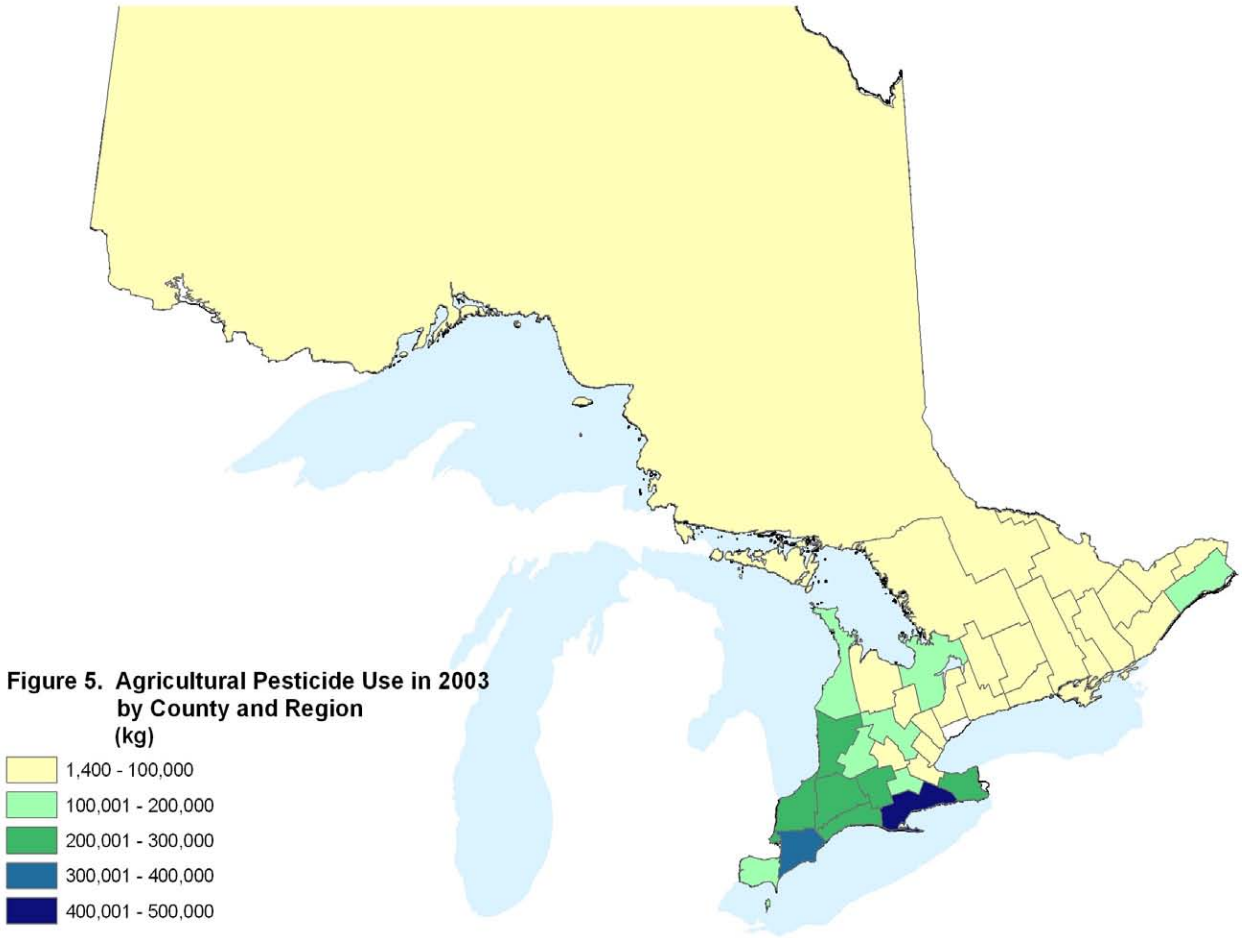


Figure 5. Agricultural Pesticide Use in 2003 by County and Region (kg)

Treated surface water

The surface water systems with the highest pesticide detection rates in treated water were in southwestern Ontario and the southeast corner of Ontario (the areas of highest agricultural use of pesticides) and along the lower Great Lakes and St. Lawrence River (Figure 6). The proportion of systems with pesticide detections was lower in northern Ontario (the area of lowest agricultural pesticide use) than in southern Ontario. In Figure 6 the detection rate is calculated as the percentage of samples with one or more pesticide detections. Of the 102 systems, 97 had eight or more samples and five had from three to seven samples.

High detection rates in drinking water from Lake Erie, Lake Ontario and the St. Lawrence River may have resulted from being downstream of agricultural and urban pesticide inputs into the Great Lakes. They may also have resulted from tributary river discharges in those areas.

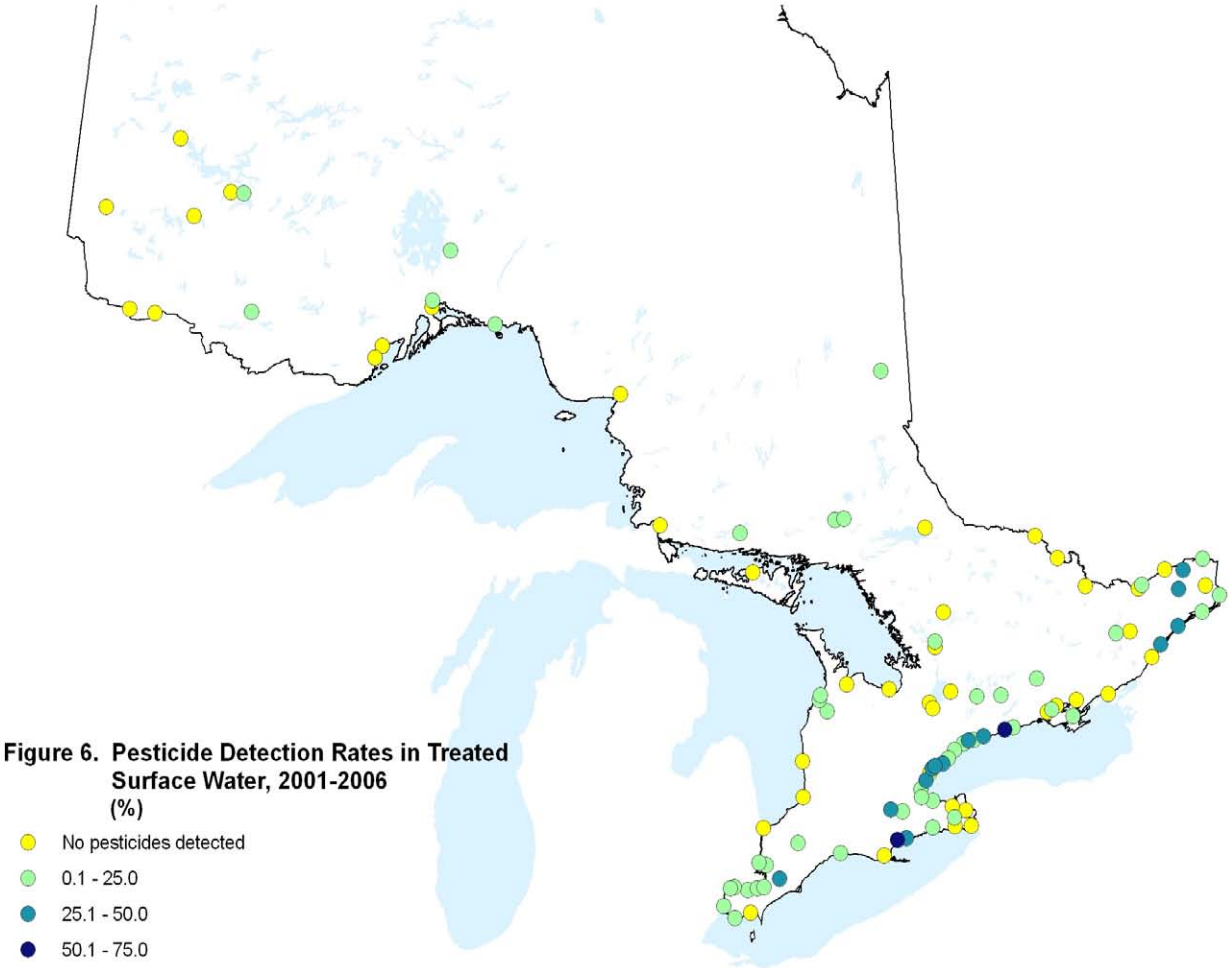


Figure 6. Pesticide Detection Rates in Treated Surface Water, 2001-2006 (%)

Tributary river discharges have been shown to increase the levels of general water quality indicators such as nitrate and conductivity in Great Lakes nearshore areas (*11*). They may have the same effect on pesticide levels. All drinking water intakes in the Great Lakes are in nearshore areas.

Of the 104 pesticides and pesticide degradates included in this study, seventeen pesticides and two degradates were detected in treated surface water (Table 4a). Atrazine and its degradate de-ethylated atrazine together accounted for 66% of detections. Four pesticides—atrazine, 2,4-D, dicamba, and mecoprop—had a detection rate above 1%. Table 4b lists the remaining 85 pesticides and degradates that were not detected in treated surface water.

Table 4a. Pesticide Detection Rates in Treated Surface Water, 2001-2006

Pesticide	# of Samples	# of Samples with Detections	Detection Rate
atrazine	1,200	142	11.8%
2,4-D	1,142	21	1.8%
dicamba	1,152	21	1.8%
mecoprop	580	10	1.7%
paraquat	276	2	0.7%
atrazine, de-ethylated	1,203	7	0.6%
pentachlorophenol	1,153	6	0.5%
diquat	276	1	0.4%
MCPA	579	2	0.3%
metolachlor	1,203	3	0.2%
propham	418	1	0.2%
bromoxynil	1,153	2	0.2%
silvex	1,153	2	0.2%
trichlorophenol 2,4,5	1,150	1	0.1%
propazine	1,193	1	0.1%
alpha-HCH	1,294	1	0.1%
heptachlor	1,294	1	0.1%
oxychlordane	1,294	1	0.1%
pp-DDE	1,294	1	0.1%

Table 4b. Pesticides Not Detected in Treated Surface Water, 2001-2006

Pesticide	# of Samples
2,3,4,6-tetrachlorophenol	1,135
2,4,5-T	1,153
2,4-DB	1,153
2,4-DP	1,153
alachlor	1,203
aldicarb	417
aldrin	1,294
alpha-endosulfan	1,294
ametryne	1,203
AMPA	317
atratone	1,193
azinphos-methyl	458
barban	418
bendiocarb	418
beta-endosulfan	1,294
beta-HCH	1,294
butachlor	951
butylate	418
carbaryl	418
carbofuran	418
chlorbromuron	646
chlordane, alpha	1,294
chlordane, gamma	1,294
chlorpropham	418
chlorpyrifos	458
chlorpyrifos-methyl	458
chlortoluron	646
cyanazine	1,178
diallate	418
diazinon	458
dichlorovos	458
diclofop-methyl	1,133
dieldrin	1,294
difenoxuron	646
dimethoate	458
dinoseb	1,113
diuron	646
endosulfan sulphate	1,294
endrin	1,294
eptam	418
ethion	458
fluometuron	646
gamma-HCH	1,294

Pesticide	# of Samples
glyphosate	314
heptachlor epoxide	1,294
hexachlorobenzene	1,290
linuron	646
malathion	865
MCPB	570
methoprene	443
methoprene acid	443
methoxychlor	1,294
methoxycitronellal	420
methyl parathion	458
metobromuron	646
metoxuron	646
metribuzin	1,203
mevinphos	458
mirex	1,294
monolinuron	646
monuron	646
neburon	646
op-DDT	1,294
parathion	458
permethrin	740
phorate	458
picloram	1,134
piperonyl butoxide	740
pp-DDD	1,294
pp-DDT	1,294
prometon	1,193
prometryne	1,203
propoxur	418
pyrethrin 1	741
pyrethrin 2	740
ronnel	458
siduron	646
simazine	1,199
simazine, de-ethylated	1,199
temephos	458
terbufos	458
terbutryne	951
toxaphene	1,294
triallate	418
trifluralin	1,291

Atrazine was detected in the treated water of 38% of surface water systems, more than twice the rate of the next most-widely occurring pesticide (Table 5). 2,4-D and dicamba were the next most widely occurring pesticides in treated surface water. Only data from DWSP systems were used for the analysis in Table 5 because only DWSP systems had enough samples to make the analysis meaningful.

Table 5. Percentage of Surface Water Systems at which Each Pesticide was Detected in Treated Water, 2001-2006

Pesticide	# of Systems Sampled	# of Systems With Detections	% of Systems With Detections	Average # of Samples per System
atrazine	104	39	38%	12
2,4-D	104	19	18%	11
dicamba	104	18	17%	11
atrazine, de-ethylated	104	7	7%	12
pentachlorophenol	104	6	6%	11
mecoprop	100	4	4%	11
metolachlor	104	3	3%	12
paraquat	99	2	2%	3
MCPA	100	2	2%	11
bromoxynil	104	2	2%	11
silvex	104	2	2%	11
diquat	99	1	1%	3
propham	102	1	1%	4
alpha-HCH	104	1	1%	12
heptachlor	104	1	1%	12
oxychlordane	104	1	1%	12
pp-DDE	104	1	1%	12
propazine	104	1	1%	12
trichlorophenol 2,4,5	104	1	1%	11

The highest atrazine concentrations occurred at systems supplied by rivers in agricultural watersheds in southwestern Ontario and the southeast corner of Ontario (Figure 7). Maximum atrazine concentrations were much lower at systems drawing water from the lower Great Lakes and St. Lawrence River. Systems in Figure 7 each had at least five treated water atrazine samples.

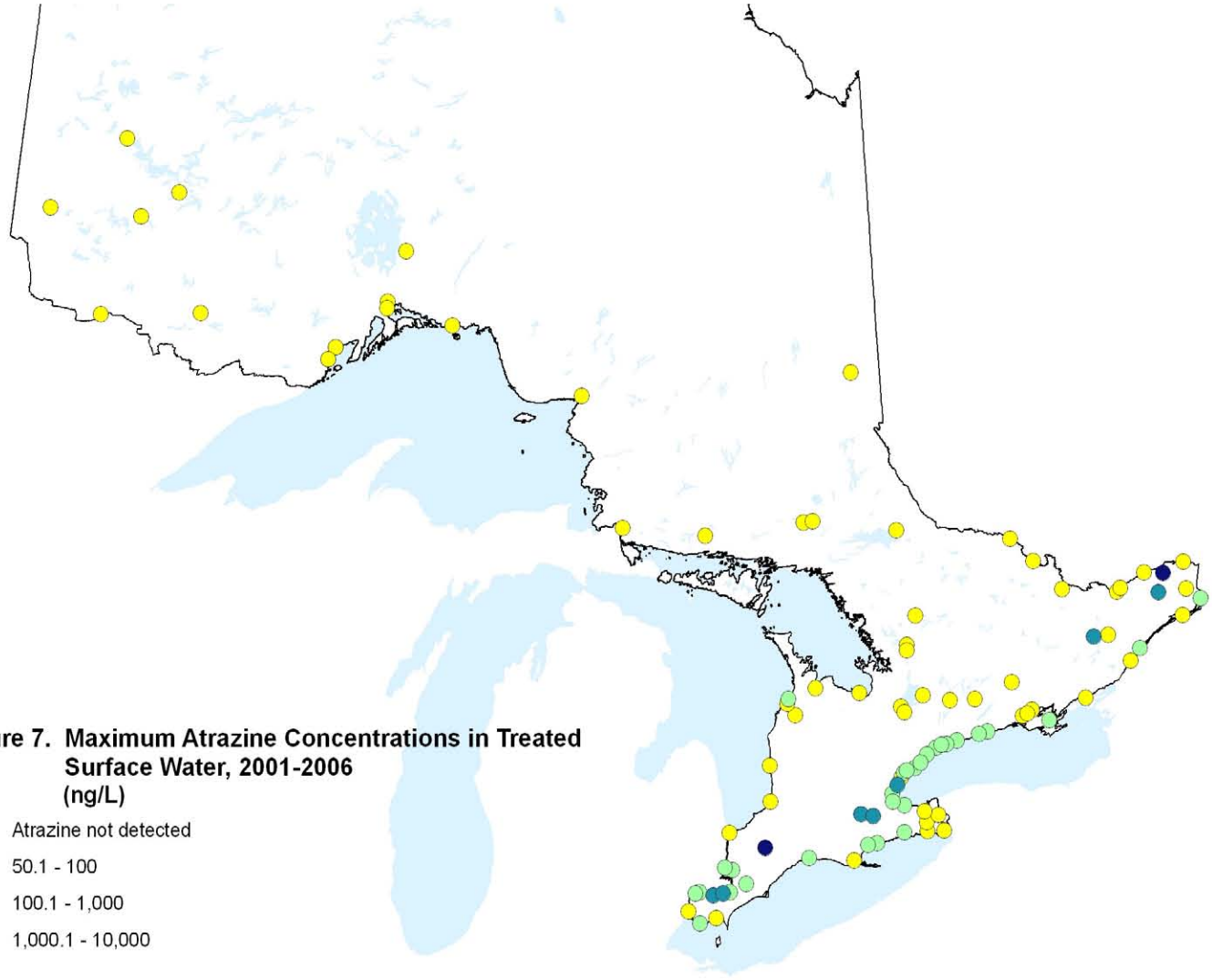
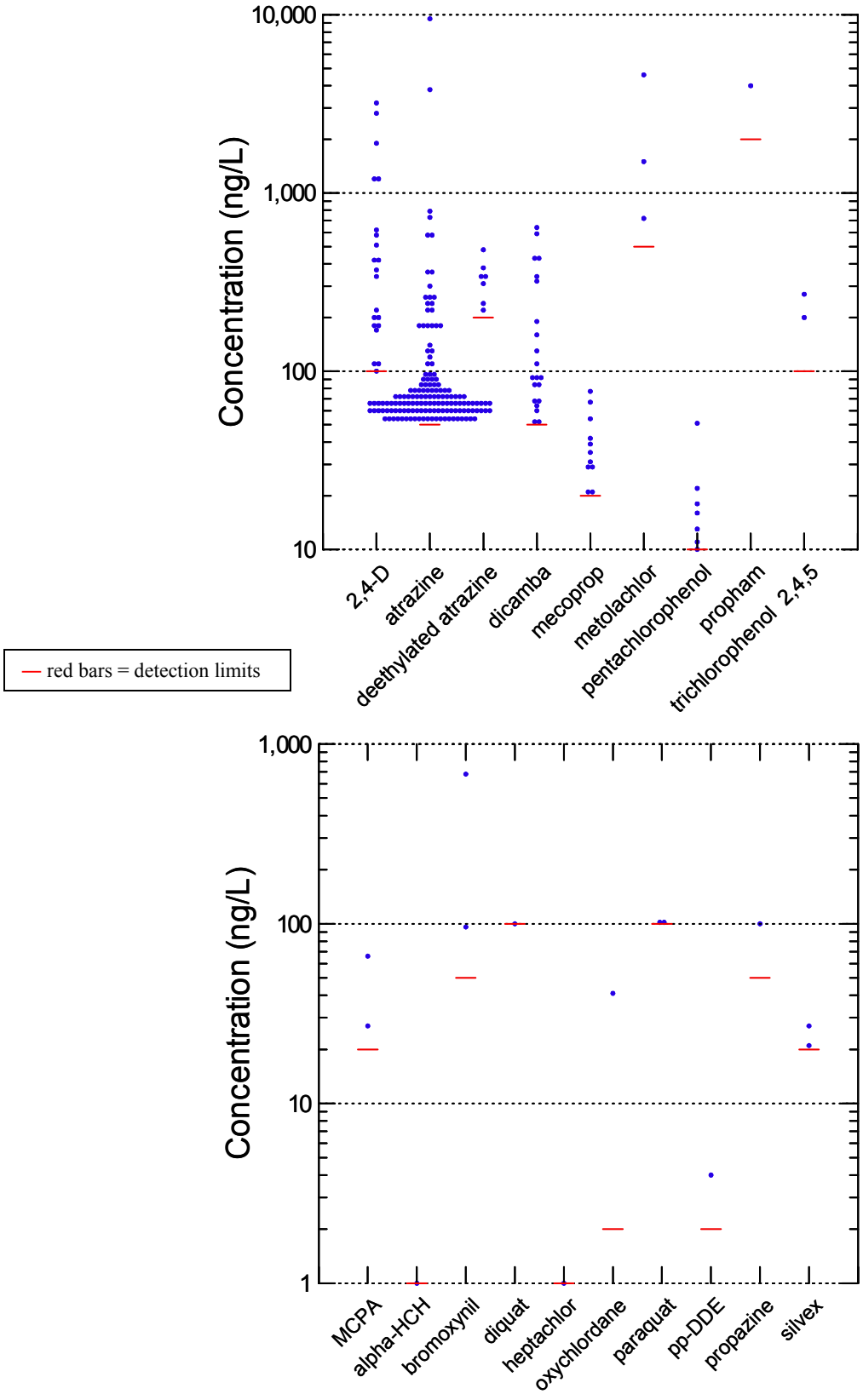


Figure 7. Maximum Atrazine Concentrations in Treated Surface Water, 2001-2006 (ng/L)

Figure 8 presents all pesticide concentrations detected in treated surface water. Each dot represents one detection. Ninety-five percent of pesticide detections in treated surface water were in the range 1- 840 parts per trillion (1 - 840 ng/L) and five percent were above 1 part per billion (1,000 ng/L). Only atrazine, 2,4-D, metolachlor and propham were measured above 1 part per billion. The highest pesticide concentration in treated surface water was an atrazine concentration of 9.5 parts per billion (9,500 ng/L).

Figure 8. Pesticide Concentrations in Treated Surface Water, 2001-2006



Treated groundwater

Most groundwater systems had no pesticide detections in treated water (Figure 9). In Figure 9 the detection rate is calculated as the percentage of samples with one or more pesticide detections. There was a wide range of sample sizes. Systems with no pesticide detections had three or more samples, systems with detection rates from 0.1 – 20% had nine or more samples and systems with detection rates of 33% or more had three or fewer samples. A different set of symbols is used for the systems with one detection and three or fewer samples because the small sample size may have skewed the detection rate upwards.

Detections occurred in true groundwater as well as groundwater under the direct influence of surface water (GUDI).

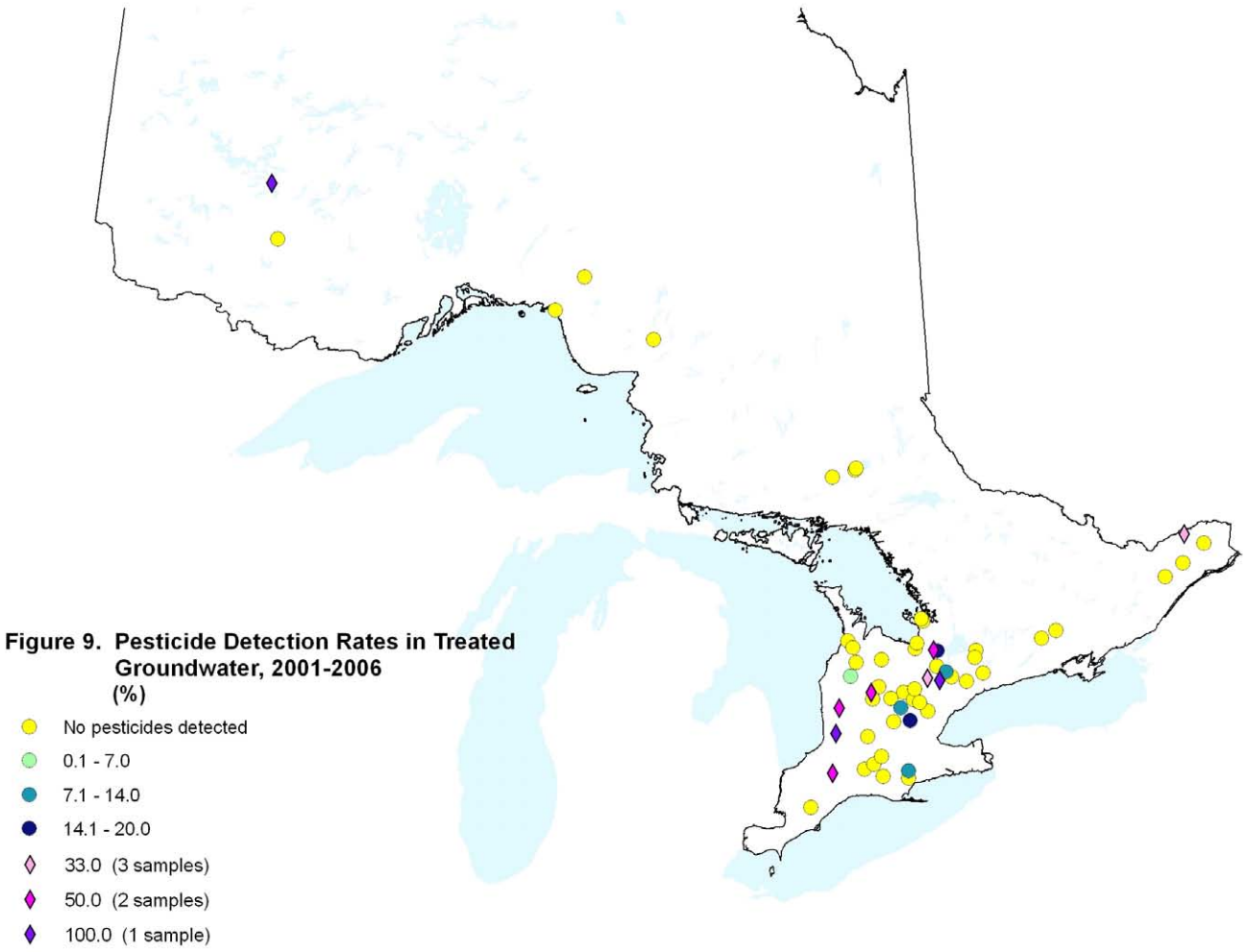


Figure 9. Pesticide Detection Rates in Treated Groundwater, 2001-2006 (%)

Of the 104 pesticides and pesticide degradates included in this study, seventeen pesticides and one degradate were detected in treated groundwater (Table 6a). 2,4-D was the most frequently detected pesticide and the only one with a detection rate above 1%. The 2,4-D detection rate in treated groundwater (1.3%) was similar to that in treated surface water (1.8%). Malathion and mecoprop were the next-most frequently detected pesticides in treated groundwater.

Table 6a. Pesticide Detection Rates in Treated Groundwater, 2001-2006

Pesticide	# of Samples	# of Samples with Detections	Detection Rate
2,4-D	619	8	1.3%
malathion	546	3	0.5%
mecoprop	444	2	0.5%
dicamba	627	2	0.3%
pentachlorophenol	627	2	0.3%
paraquat	491	1	0.2%
diquat	492	1	0.2%
butylate	503	1	0.2%
azinphos-methyl	534	1	0.2%
diazinon	534	1	0.2%
ethion	534	1	0.2%
parathion	534	1	0.2%
temephos	534	1	0.2%
trifluralin	610	1	0.2%
atrazine, de-ethylated	622	1	0.2%
atrazine	623	1	0.2%
2,4-DP	627	1	0.2%
bromoxynil	627	1	0.2%

2,4-D, dicamba and mecoprop were among the most frequently detected pesticides in both treated surface water and treated groundwater. Unlike treated surface water, atrazine was rarely found in treated groundwater. Table 6b lists the remaining 86 pesticides and degradates that were not detected in treated groundwater. -

Table 6b. Pesticides Not Detected in Treated Groundwater, 2001-2006

Pesticide	# of Samples
2,3,4,6-tetrachlorophenol	618
2,4,5-T	627
2,4,5-trichlorophenol	623
2,4-DB	627
alachlor	623
aldicarb	495
aldrin	627
alpha-endosulfan	627
alpha-HCH	627
ametryne	623
AMPA	414
atratone	615
barban	503
bendiocarb	503
beta-endosulfan	627
beta-HCH	627
butachlor	561
carbaryl	503
carbofuran	503
chlorbromuron	621
chlordane, alpha	627
chlordane, gamma	627
chlorpropham	503
chlorpyrifos	534
chlorpyrifos-methyl	534
chlortoluron	621
cyanazine	606
diallate	503
dichlorovos	534
diclofop-methyl	616
dieldrin	627
difenoxuron	621
dimethoate	534
dinoseb	592
diuron	621
endosulfan sulphate	627
endrin	627
eptam	503
fluometuron	621
gamma-HCH	627
glyphosate	395
heptachlor	627
heptachlor epoxide	627

Pesticide	# of Samples
hexachlorobenzene	623
linuron	621
MCPA	438
MCPB	421
methoprene	12
methoprene acid	12
methoxychlor	627
methoxycitronellal	12
methyl parathion	534
metobromuron	621
metolachlor	623
metoxuron	621
metribuzin	623
mevinphos	534
mirex	627
monolinuron	621
monuron	621
neburon	621
op-DDT	627
oxychlordane	627
permethrin	456
phorate	534
picloram	621
piperonyl butoxide	456
pp-DDD	627
pp-DDE	627
pp-DDT	627
prometon	615
prometryne	623
propazine	621
propham	503
propoxur	503
pyrethrin 1	456
pyrethrin 2	456
ronnel	534
siduron	621
silvex	627
simazine	617
simazine, de-ethylated	616
terbufos	534
terbutryne	561
toxaphene	627
triallate	503

2,4-D was detected in the treated drinking water of 14% of groundwater systems, more than twice the rate of the next most widely occurring pesticide (Table 7). Dicamba and pentachlorophenol were the next most widely occurring pesticides in groundwater. 2,4-D was found in groundwater almost as widely as in surface water (14% of systems compared to 18% of systems, respectively). Pentachlorophenol was found equally widely in groundwater and surface water, diquat was found more widely in groundwater, and mecoprop and paraquat were found almost as widely in groundwater as surface water; however with many fewer groundwater systems than surface water systems and only one or two groundwater detections per pesticide, the comparisons for the latter four pesticides are not as conclusive as for 2,4-D.

Table 7. Percentage of Groundwater Systems at which Each Pesticide was Detected in Treated Water, 2001-2006

Pesticide	# of Systems Sampled	# of Systems With Detections	% of Systems With Detections	Average # of Samples per System
2,4-D	36	5	14%	6
dicamba	36	2	6%	6
pentachlorophenol	36	2	6%	6
mecoprop	30	1	3%	4
ethion	34	1	3%	5
azinphos-methyl	34	1	3%	5
malathion	34	1	3%	5
parathion	34	1	3%	5
temephos	34	1	3%	5
2,4-DP	36	1	3%	6
diquat	36	1	3%	4
paraquat	36	1	3%	4
atrazine*	---	1	---	---
atrazine, de-ethylated*	---	1	---	---
bromoxynil*	---	1	---	---
butylate*	---	1	---	---
diazinon*	---	1	---	---
trifluralin*	---	1	---	---

* These pesticides were detected at systems outside the DWSP network. Only data from DWSP systems was used for this table.

Only data from DWSP systems were used for the analysis in Table 7 because only DWSP systems had enough samples to make the analysis meaningful. As a result, six pesticides that were detected at groundwater systems (atrazine, de-ethlayted atrazine, bromoxynil, butylate, diazinon and trifluralin) could not be included in this analysis because they were detected only at systems outside the DWSP network.

Figure 10 presents the locations and concentrations at which 2,4-D was found in treated groundwater. Six groundwater systems had one detection and one system had two detections. Detections may have been due to agricultural or cosmetic use since 2,4-D was used for both purposes during this time. Some detections occurred in agricultural areas. On the other hand, the system with the highest concentration (and two detections) serves a medium-size city, and one of the systems with a detection is in northwestern Ontario where there is little agriculture. Figure 10 presents all groundwater systems that had three or more treated water 2,4-D samples or at least one treated water 2,4-D detection.

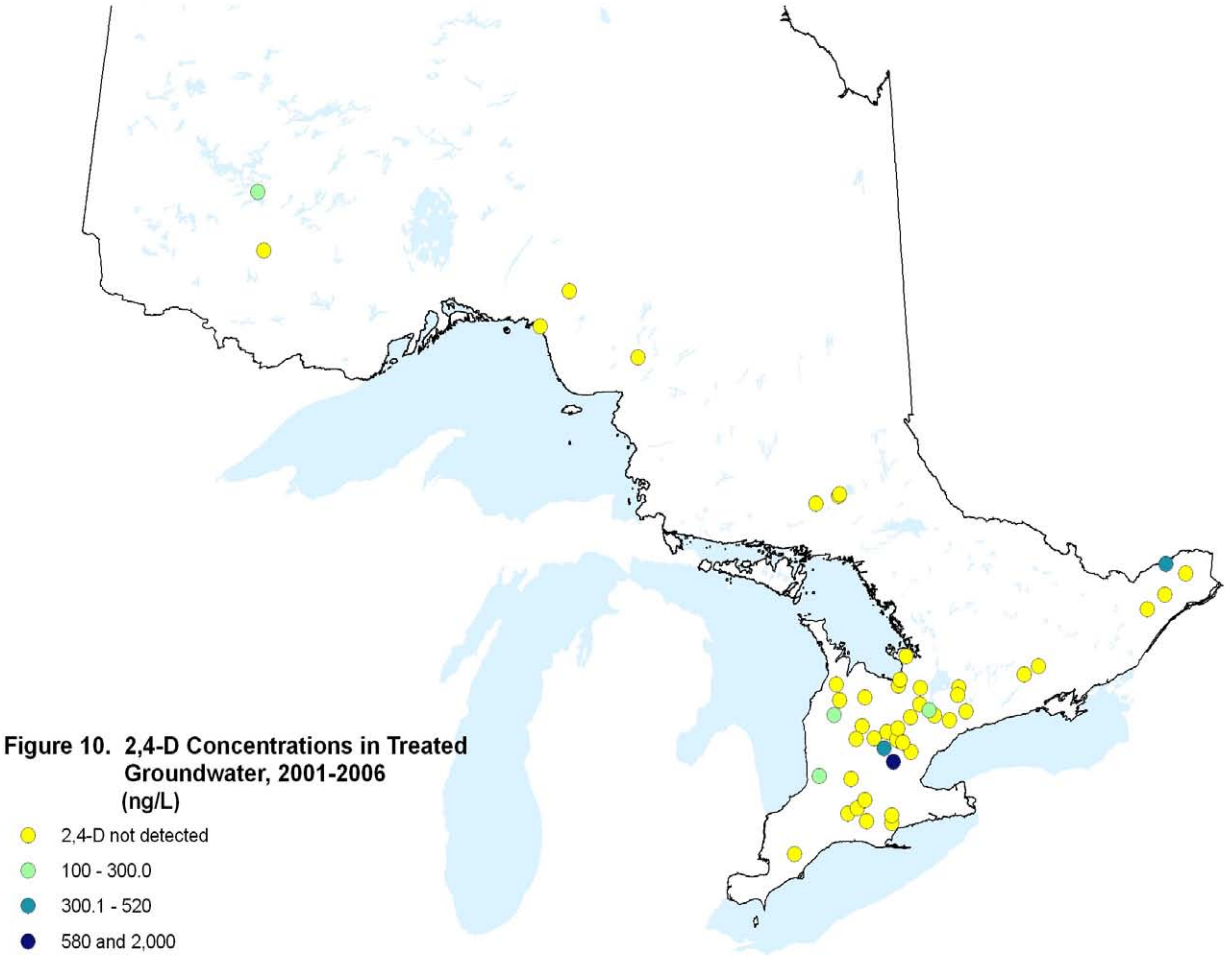
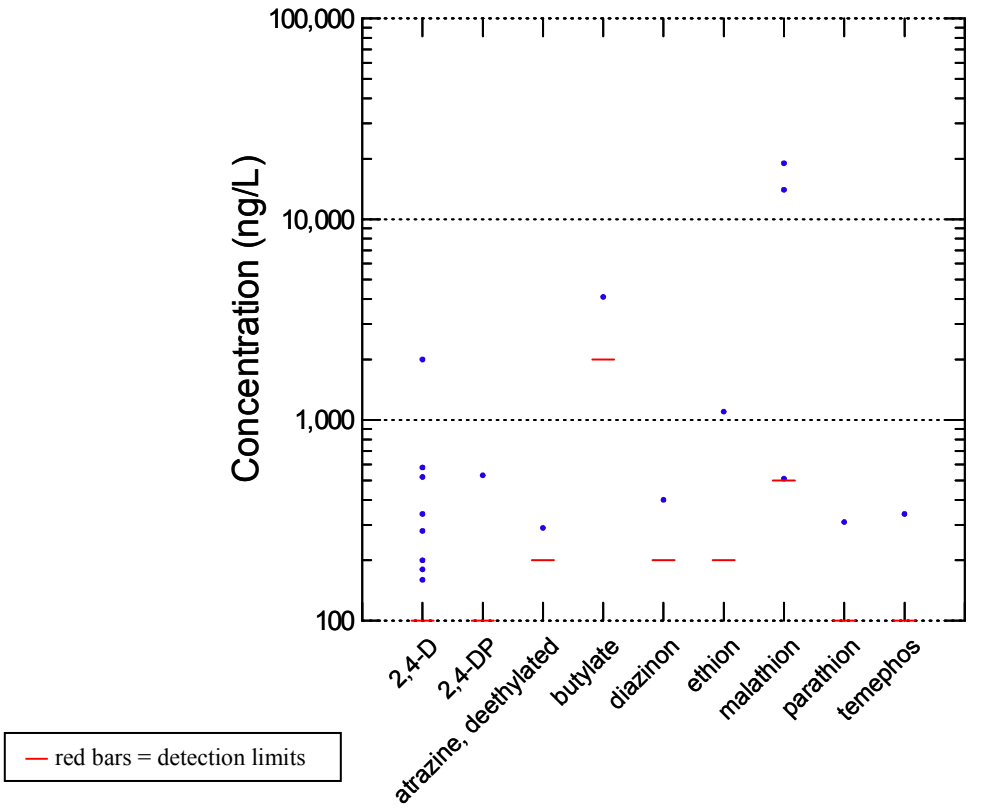
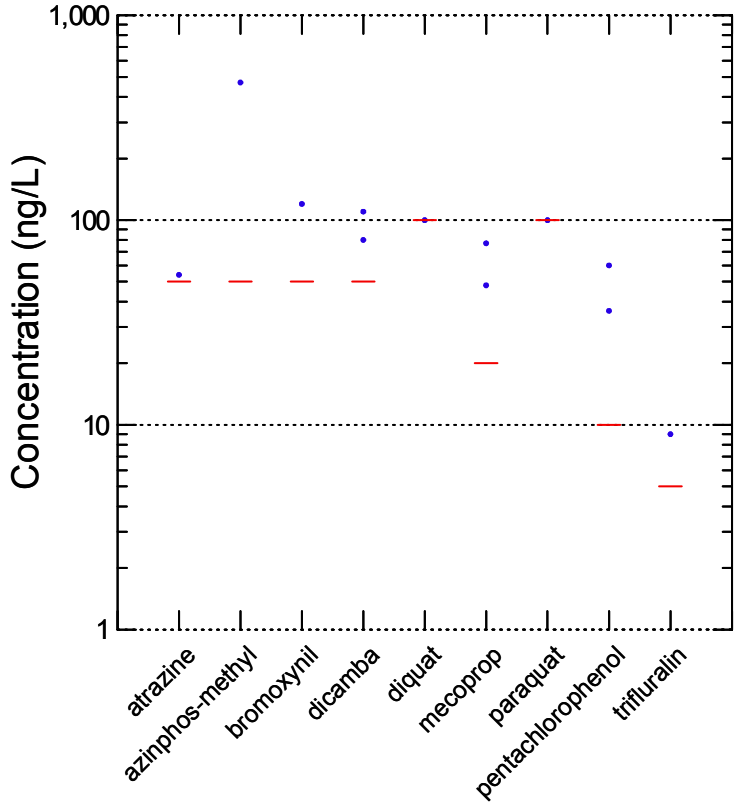


Figure 10. 2,4-D Concentrations in Treated Groundwater, 2001-2006 (ng/L)

Figure 11 presents all pesticide concentrations detected in treated groundwater. Each dot represents one detection. Eighty-three percent of detections were in the range 9 – 580 parts per trillion (9 – 580 ng/L) and 17% were above 1 part per billion (1,000 ng/L). Only malathion, butylate, 2,4-D and ethion were measured above 1 part per billion. The highest measured pesticide concentrations in treated groundwater were malathion concentrations of 19 parts per billion (19,000 ng/L) and 14 parts per billion (14,000 ng/L). The three groundwater malathion detections in this period were from samples collected during a single sampling event from three wells at one groundwater system.

Figure 11. Pesticide Concentrations in Treated Groundwater, 2001-2006





4. CONCLUSIONS

Trends

- From 1986 to 2006, the pesticide detection rate in treated surface water dropped from 86% to 3%. The drop was due to a decrease in source water pesticide concentrations rather than to improved treatment. Most of the drop was due to decreases in source water concentrations of alpha-HCH and to a lesser degree gamma-HCH (lindane). In the 1970's, Canada and the U.S. banned the main product containing alpha-HCH and started phasing out gamma-HCH.
- Atrazine dominated pesticide detections in treated surface water from 1994 - 2006, with the exception of 2000 and 2001.
- For most of the period 1987 – 2006, the pesticide detection rate in treated groundwater was between 0.0 – 6.7%. Higher detection rates of 11.7%, 7.7% and 10.6% occurred in 1997, 1999 and 2001 respectively.
- From 1987-2006 pesticide detection rates in treated groundwater were generally much lower than detection rates in treated surface water, but the gap between them steadily decreased. In 2001 and 2006 detection rates in treated groundwater were slightly higher than those in treated surface water.

Exceedances of drinking water quality standards, 1986-2006

- From 1986 to 2006, DWSP and the Drinking Water Inspection/Compliance Program collected 16,166 treated water pesticide samples covering about 90% of Ontario's municipal residential drinking water systems. Out of the 16,166 samples there were four exceedances of Ontario drinking water quality standards for pesticides. They were for atrazine (and its degradate de-ethylated atrazine) and terbufos. The atrazine exceedances occurred at systems drawing water from a river with a largely agricultural watershed. The terbufos exceedances occurred at a groundwater system, in groundwater that is under the direct influence of surface water (GUDI). The exceedances all occurred at systems in southwestern Ontario, the region of Ontario with the highest agricultural use of pesticides.

Treated surface water, 2001-2006

- Seventeen pesticides and two pesticide degradates were detected in treated surface water.
- Atrazine was the most frequently detected pesticide in treated surface water. It was detected in 11.8% of samples and at 38% of systems. Atrazine and its degradate de-ethylated atrazine together accounted for 66% of pesticide detections in treated surface water.
- The surface water systems with the highest pesticide detection rates were in southwestern Ontario, the southeast corner of Ontario and along the lower Great Lakes and St. Lawrence River. Southwestern Ontario and the southeast corner of Ontario were the areas of highest agricultural pesticide use. High detection rates in drinking water from Lake Erie, Lake Ontario and the St. Lawrence River may have resulted from being downstream of agricultural and urban pesticide inputs into the Great Lakes. They may also have resulted from tributary river discharges in those areas.
- The highest atrazine concentrations in treated surface water occurred at systems supplied by rivers in agricultural watersheds in southwestern Ontario and the southeast corner of Ontario.

- Ninety-five percent of pesticide detections in treated surface water were in the range 1- 840 parts per trillion (1 - 840 ng/L) and five percent were above 1 part per billion (1,000 ng/L). The highest measured pesticide concentration in treated surface water was an atrazine concentration of 9.5 parts per billion (9,500 ng/L).

Treated groundwater, 2001-2006

- Most groundwater systems had no pesticide detections in treated water.
- Seventeen pesticides and one pesticide degradate were detected in treated groundwater.
- 2,4-D was the most frequently detected pesticide in treated groundwater. It was detected in 1.3% of samples and at 14% of systems.
- The 2,4-D detection rate in treated groundwater (1.3%) was similar to that in treated surface water (1.8%). 2,4-D was found in treated groundwater almost as widely as in treated surface water (14% of systems compared to 18% of systems, respectively).
- Unlike treated surface water, atrazine was rarely found in treated groundwater.
- Eighty-three percent of pesticide detections in treated groundwater were in the range 9 – 580 parts per trillion (9 – 580 ng/L) and 17% were above 1 part per billion (1,000 ng/L). The highest measured pesticide concentrations in treated groundwater were malathion concentrations of 19 parts per billion (19,000 ng/L) and 14 parts per billion (14,000 ng/L).

5. ACKNOWLEDGEMENTS

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6. REFERENCES

1. McGee, B.; Berges, H.; Callow, K. Survey of Pesticide Use in Ontario, 2003. Estimates of Pesticides Used on Field Crops, Fruit and Vegetable Crops, and Other Agricultural Crops; Ontario Ministry of Agriculture and Food: Guelph, Ontario, Canada, 2004.
2. Hunter, C; McGee, B. Survey of Pesticide Use in Ontario, 1993. Estimates of Pesticides Used on Field Crops, Fruit and Vegetable Crops, Provincial Highway Roadsides, and by Licensed Pesticide Applicators; Ontario Ministry of Agriculture, Food and Rural Affairs, Policy Analysis Branch: Toronto, Canada, 1994.
3. North American Commission for Environmental Cooperation. The North American Regional Action Plan (NARAP) on Lindane and Other Hexachlorocyclohexane (HCH) Isomers, 2006.
4. Wania, F.; Mackay, D.; Li, Y.F.; Bidleman, T.; Strand, A. Global Chemical Fate of α-Hexachlorocyclohexane. 1. Evaluation of a Global Distribution Model. *Environ. Toxicol. Chem.* **1999,** *18*, 1390-1399.
5. National Round Table on the Environment and the Economy. Managing Potentially Toxic Substances in Canada. Ottawa, Canada, 2001
6. Primbs, T.; Wilson, G.; Schmedding, D.; Higginbotham, C.; Simonich, S.M. Influence of Asian and Western United States Agricultural Areas and Fires on the Atmospheric Transport of Pesticides in the Western United States. *Environ. Sci. Technol.* **2008**, *42*, 6519-6525.
7. Cutten, G. Ontario Ministry of the Environment, Toronto, Canada, personal communication, 2008.
8. USEPA. Addendum to the 2002 Lindane Reregistration Eligibility Decision (RED), EPA 738-R-06-028, 2006.
9. Walker, K.; Vallero, D.; Lewis, R. Factors Influencing the Distribution of Lindane and Other Hexachlorocyclohexanes in the Environment. *Environ. Sci. Technol.* **1999**, *33*, 4373-4378.
10. Byer, J.; Struger, J.; Klawunn, P.; Todd, A.; Sverko, E. Low Cost Monitoring of Glyphosate in Surface Waters Using the ELISA Method: An Evaluation. *Environ. Sci. Technol.* **2008**, *42*, 6052-6057.
11. Howell, T. Challenges to Understanding the Great Lakes Nearshore, Presentation to Great Lakes Source Protection Technical Workshop, Dec. 5, 2008. Ontario Ministry of the Environment, Environmental Monitoring and Reporting Branch.

Pesticides in Ontario's Treated Municipal Drinking Water

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