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# Pesticides Concentrations in the Lake Erie Watershed and Great Lakes Basin

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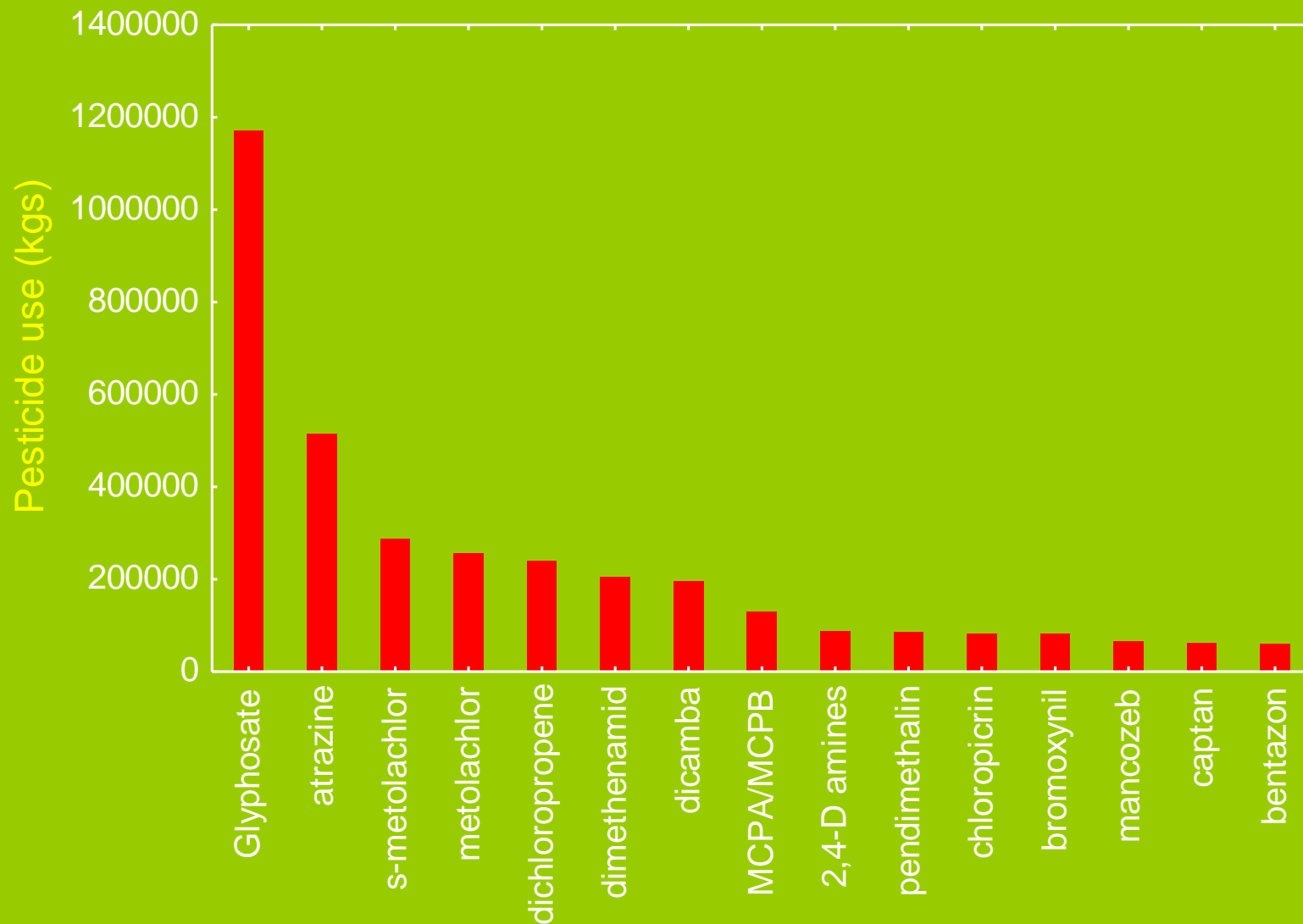
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# Introduction

- Pesticides are heavily used in agricultural and until recently in urban areas of southern Ontario
- In 2003, approximately 4,218,000 kg of A.I. used on agricultural crops in Ontario-more than 120 compounds used
- Our monitoring program is part of a regional and a national EC Pesticide Science Fund initiative to sample various pesticides in the Great Lakes basin and across the country in surface waters
- Program started in 2002 and has evolved from sampling current use pesticides(CUPs) such as neutral and herbicides, and organophosphorous insecticides to include sulfonyl urea and carbamate pesticides
- Program has focused on major pesticides used in row crop and fruit production and urban settings



# Pesticide use in Ontario, 2003





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# Sample Collection

- Water samples collected in 1L sample bottles
- Locations include primarily streams; ponds and some Great Lakes connecting channels
- Samples collected every 10 days or so during the application/growing season
- Over 90 sites sampled during the period from 2002-2008
- Over 900 samples collected, approximately 150 samples/year
- QA/QC samples collected as well (duplicates and field blanks)





# Pesticide Sampling Locations



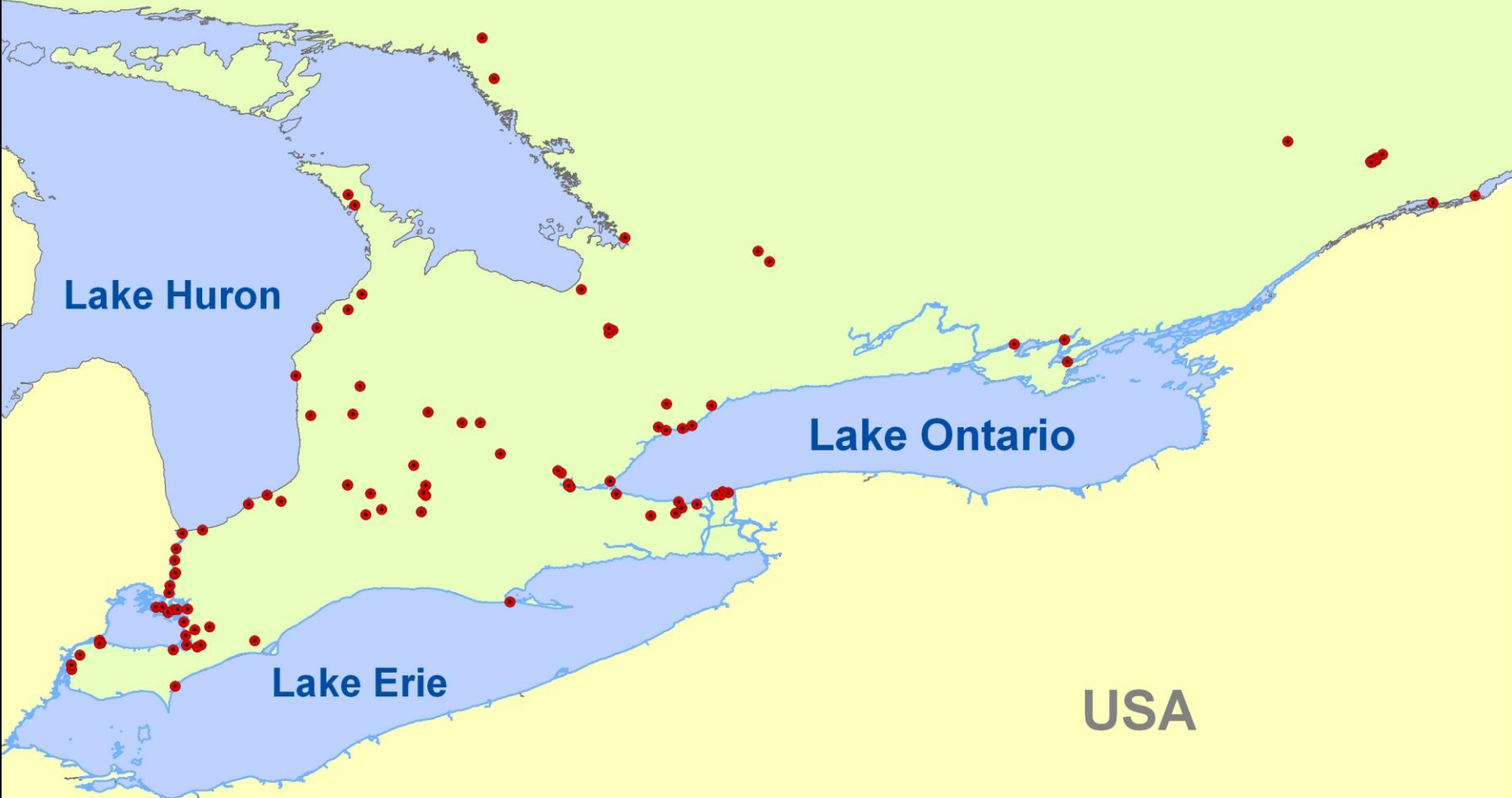
Ontario

Lake Huron

Lake Ontario

Lake Erie

USA







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# Neutral Herbicides (ng/L)



|                          | Number of  | Number of  |               |                |              |              |                 | DL           | GL        |
|--------------------------|------------|------------|---------------|----------------|--------------|--------------|-----------------|--------------|-----------|
|                          | Samples    | Detects    | Mean          | SD             | Median       | Min          | Max             |              |           |
| <b>Atrazine</b>          | <b>924</b> | <b>859</b> | <b>261.70</b> | <b>1060.68</b> | <b>60.85</b> | <b>2.87</b>  | <b>18600.00</b> | <b>2.35</b>  | <b>22</b> |
| Benzoylprop - ethyl      | 924        | 2          | .             | .              | .            | 39.10        | 159.00          | 4.96         | .         |
| Butylate                 | 924        | 0          | .             | .              | .            | .            | .               | 9.57         | .         |
| <b>Desethyl Atrazine</b> | <b>924</b> | <b>573</b> | <b>73.65</b>  | <b>146.01</b>  | <b>37.80</b> | <b>11.30</b> | <b>2470.00</b>  | <b>12.54</b> | <b>.</b>  |
| Desethyl Simazine        | 924        | 22         | .             | .              | .            | 29.60        | 581.00          | 36.44        | .         |
| Diallate I               | 924        | 1          | .             | .              | .            | 67.10        | 67.10           | 11.44        | .         |
| Diclofop-methyl          | 924        | 2          | .             | .              | .            | 88.60        | 351.00          | 11.72        | .         |
| Ethafluralin             | 242        | 0          | .             | .              | .            | .            | .               | 14.38        | 0         |
| <b>Metolachlor</b>       | <b>924</b> | <b>479</b> | <b>157.82</b> | <b>558.74</b>  | <b>24.25</b> | <b>3.82</b>  | <b>9190.00</b>  | <b>4.48</b>  | <b>1</b>  |
| Metribuzin               | 924        | 78         | .             | .              | .            | 13.80        | 1230.00         | 7.98         | 3         |
| Simazine                 | 924        | 177        | .             | .              | .            | 5.36         | 2050.00         | 6.51         | .         |
| Triallate                | 924        | 0          | .             | .              | .            | .            | .               | 2.46         | 0         |
| Trifluralin              | 924        | 3          | .             | .              | .            | 5.21         | 11.80           | 2.97         | 0         |



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# Acid Herbicides (ng/L)

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|                          | Number of  |            | Mean          | SD             | Median       | Min         | Max              | DL          | GL       |
|--------------------------|------------|------------|---------------|----------------|--------------|-------------|------------------|-------------|----------|
|                          | Samples    | Detects    |               |                |              |             |                  |             |          |
| 2,4,5-T                  | 941        | 58         | .             | .              | .            | 0.47        | 241.00           | 1.72        | .        |
| <b>2,4-D</b>             | <b>939</b> | <b>770</b> | <b>158.97</b> | <b>551.10</b>  | <b>14.00</b> | <b>0.71</b> | <b>8240.00</b>   | <b>1.73</b> | <b>4</b> |
| 2,4-DB                   | 941        | 2          | .             | .              | .            | 19.10       | 365.00           | 1.35        | .        |
| 2,4-DP                   | 941        | 270        | .             | .              | .            | 0.42        | 809.00           | 1.07        | .        |
| 236-TBA                  | 941        | 24         | .             | .              | .            | 1.43        | 11.40            | 1.54        | .        |
| Bromoxynil               | 941        | 189        | .             | .              | .            | 1.00        | 692.00           | 1.33        | 0        |
| Clopyralid               | 941        | 267        | .             | .              | .            | 0.60        | 132.00           | 1.06        | .        |
| <b>Dicamba</b>           | <b>940</b> | <b>682</b> | <b>192.51</b> | <b>3473.85</b> | <b>5.98</b>  | <b>0.73</b> | <b>105000.00</b> | <b>0.89</b> | <b>2</b> |
| Imazamethabenz-methyl(A) | 653        | 8          | .             | .              | .            | 0.71        | 5.97             | 0.14        | .        |
| Imazamethabenz-methyl(B) | 653        | 5          | .             | .              | .            | 0.75        | 9.31             | 0.09        | .        |
| Imazethapyr              | 653        | 55         | .             | .              | .            | 1.27        | 146.00           | 1.20        | .        |
| MCPA                     | 941        | 371        | .             | .              | .            | 0.58        | 1230.00          | 1.32        | 0        |
| MCPB                     | 941        | 7          | .             | .              | .            | 1.22        | 7.97             | 1.45        | .        |
| <b>Mecoprop</b>          | <b>665</b> | <b>422</b> | <b>261.61</b> | <b>4009.66</b> | <b>4.75</b>  | <b>0.58</b> | <b>103000.00</b> | <b>1.02</b> | <b>.</b> |
| Picloram                 | 941        | 6          | .             | .              | .            | 7.92        | 40.60            | 2.17        | 0        |
| Silvex                   | 941        | 35         | .             | .              | .            | 0.42        | 3.80             | 1.17        | .        |



# Organophosphorous Insecticides (ng/L)

|                   | Number of | Number of |      |    |        |       |          | DL    | GL |
|-------------------|-----------|-----------|------|----|--------|-------|----------|-------|----|
|                   | Samples   | Detects   | Mean | SD | Median | Min   | Max      |       |    |
| Azinphos - methyl | 847       | 27        | .    | .  | .      | 17.40 | 12200.00 | 16.20 | .  |
| Chlorpyrifos      | 847       | 39        | .    | .  | .      | 2.40  | 349.00   | 2.61  | 37 |
| Diazinon          | 847       | 83        | .    | .  | .      | 16.00 | 8290.00  | 13.20 | .  |
| Dimethoate        | 847       | 38        | .    | .  | .      | 20.40 | 175.00   | 19.80 | 0  |
| Disulfoton        | 847       | 3         | .    | .  | .      | 50.00 | 58.60    | 12.40 | .  |
| Ethion            | 847       | 0         | .    | .  | .      | .     | .        | 2.32  | .  |
| Fonofos           | 847       | 3         | .    | .  | .      | 20.50 | 41.40    | 5.77  | .  |
| Malathion         | 847       | 11        | .    | .  | .      | 10.40 | 611.00   | 3.99  | .  |
| Naled             | 846       | 2         | .    | .  | .      | 89.20 | 122.00   | 33.20 | .  |
| Parathion         | 847       | 0         | .    | .  | .      | .     | .        | 5.50  | .  |
| Phorate           | 846       | 1         | .    | .  | .      | 40.10 | 40.10    | 11.30 | .  |
| Phosmet           | 847       | 0         | .    | .  | .      | .     | .        | 3.66  | .  |
| Terbufos          | 847       | 3         | .    | .  | .      | 11.50 | 49.00    | 9.48  | .  |



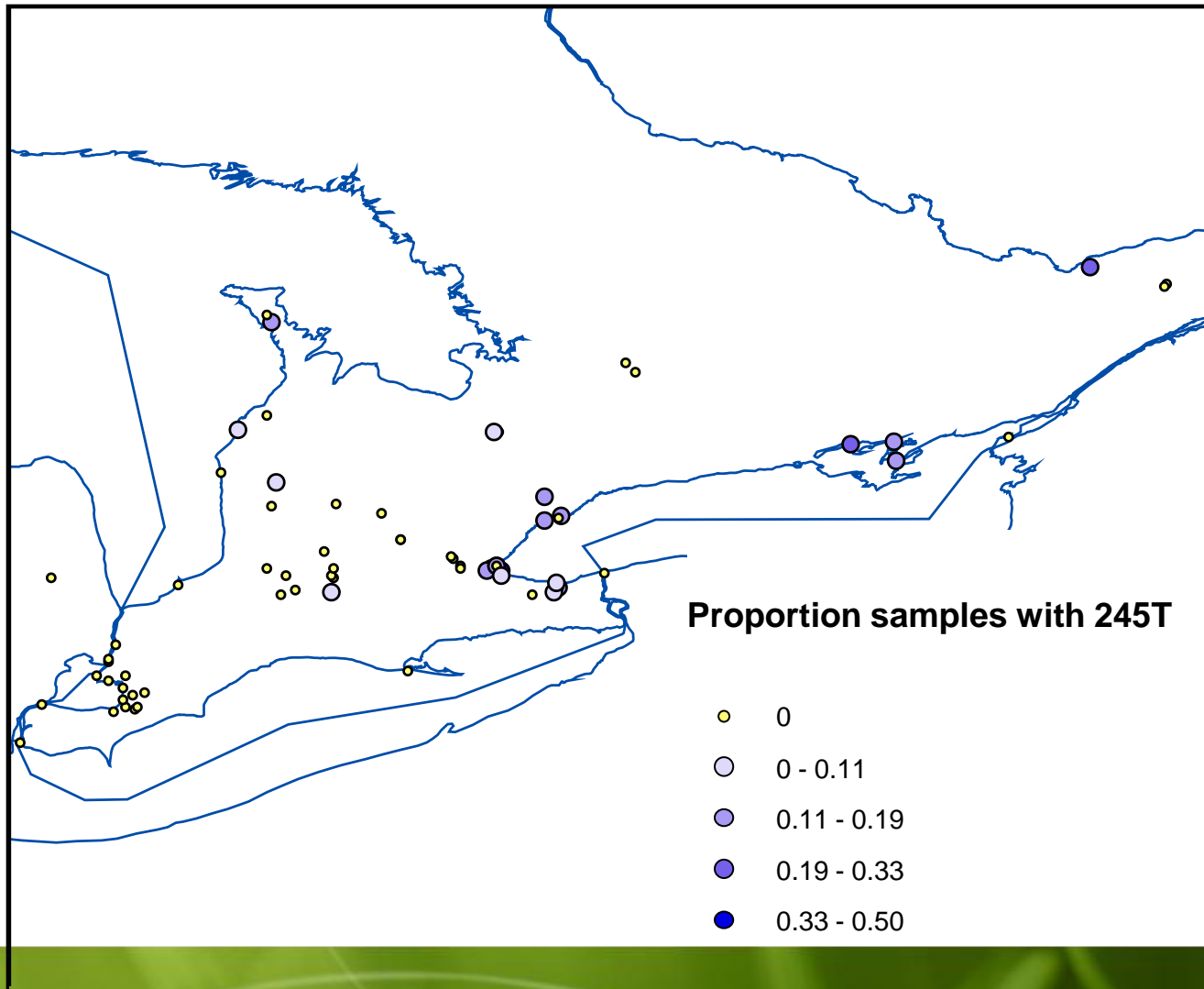
# Carbamate Pesticides (ng/L)

| Compound         | Number of  | Number of  |              |              |             |             |               | DL          | GL       |
|------------------|------------|------------|--------------|--------------|-------------|-------------|---------------|-------------|----------|
|                  | Samples    | Detects    | Mean         | SD           | Median      | Min         | Max           |             |          |
| Aldicarb         | 164        | 0          | .            | .            | .           | 0.35        | 0.35          | 0.70        | .        |
| <b>Carbaryl</b>  | <b>164</b> | <b>121</b> | <b>28.03</b> | <b>94.48</b> | <b>6.39</b> | <b>0.08</b> | <b>948.51</b> | <b>0.16</b> | <b>3</b> |
| Carbofuran       | 164        | 25         | .            | .            | .           | 0.12        | 286.27        | 0.24        | 0        |
| <b>Metalaxyl</b> | <b>164</b> | <b>136</b> | <b>15.20</b> | <b>32.59</b> | <b>2.64</b> | <b>0.21</b> | <b>176.41</b> | <b>0.42</b> | .        |
| <b>Methomyl</b>  | <b>164</b> | <b>23</b>  | <b>.</b>     | <b>.</b>     | <b>.</b>    | <b>0.15</b> | <b>899.01</b> | <b>0.30</b> | <b>.</b> |
| Oxamyl           | 164        | 20         | .            | .            | .           | 0.09        | 292.00        | 0.18        | .        |
| Primicarb        | 100        | 53         | .            | .            | .           | 0.12        | 9.69          | 0.24        | .        |



# Sulfonyl Urea & Related Herbicides(ng/L)

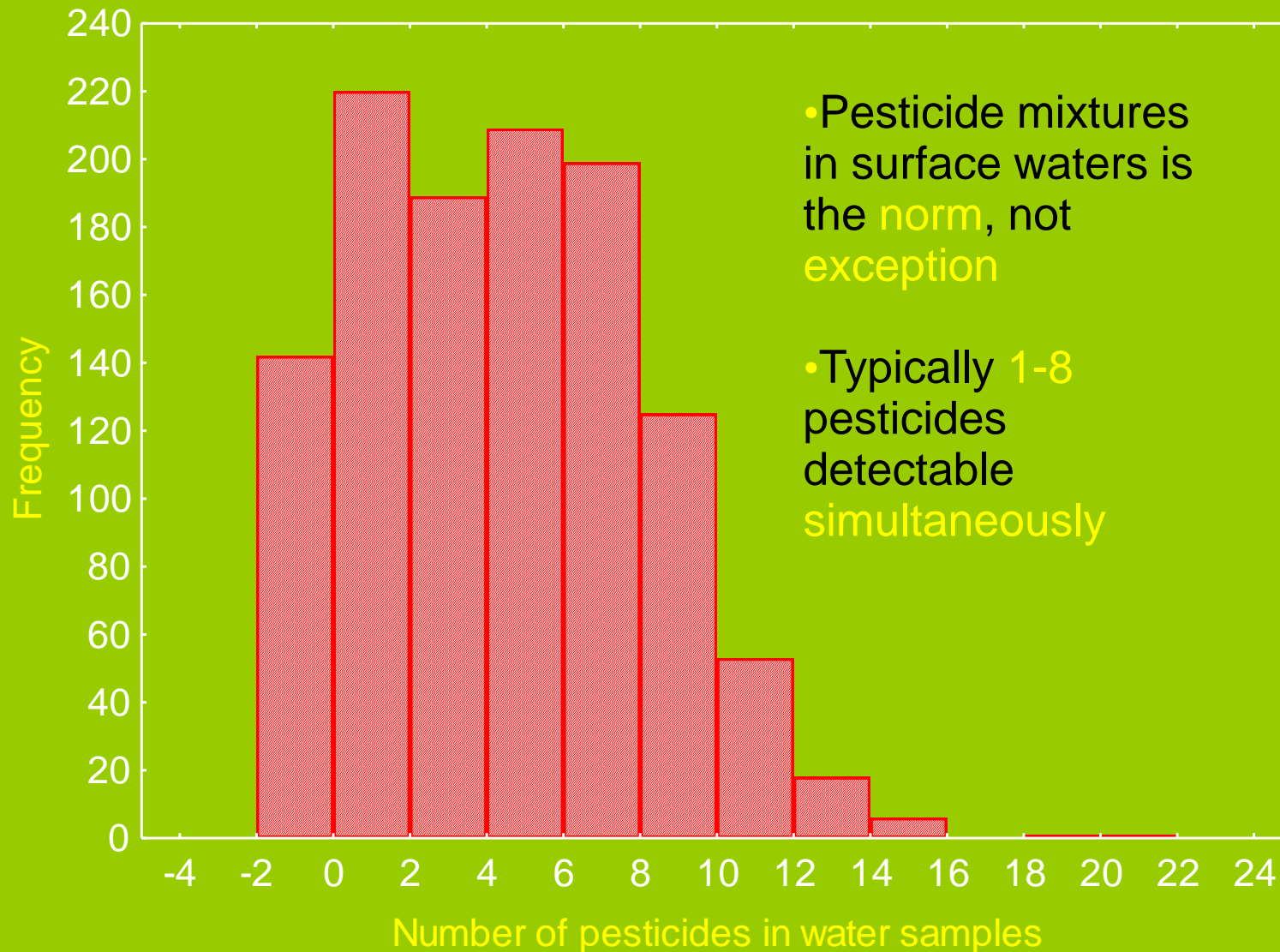
|                         | Number of  | Number of |          |          |          |             |               | DL          | GL       |
|-------------------------|------------|-----------|----------|----------|----------|-------------|---------------|-------------|----------|
|                         | Samples    | Detects   | Mean     | SD       | Median   | Min         | Max           |             |          |
| Acifluorfen             | 249        | 1         | .        | .        | .        | 10.04       | 10.04         | 5.27        | .        |
| Bensulfuron - methyl    | 249        | 0         | .        | .        | .        | .           | .             | 2.80        | .        |
| Chlorimuron - ethyl     | 227        | 25        | .        | .        | .        | 1.46        | 13.83         | 1.44        | .        |
| Chlorsulfuron           | 249        | 0         | .        | .        | .        | .           | .             | 8.37        | .        |
| Clomazone               | 249        | 1         | .        | .        | .        | 2.83        | 2.83          | 0.94        | .        |
| <b>Diurion</b>          | <b>250</b> | <b>88</b> | <b>↓</b> | <b>↓</b> | <b>↓</b> | <b>2.66</b> | <b>872.84</b> | <b>3.99</b> | <b>↓</b> |
| <b>Flumetsulam</b>      | <b>249</b> | <b>61</b> | <b>↓</b> | <b>↓</b> | <b>↓</b> | <b>.67</b>  | <b>232.50</b> | <b>0.66</b> | <b>↓</b> |
| <b>Fomesafen</b>        | <b>249</b> | <b>83</b> | <b>↓</b> | <b>↓</b> | <b>↓</b> | <b>2.75</b> | <b>873.70</b> | <b>2.54</b> | <b>↓</b> |
| <b>Linuron</b>          | <b>254</b> | <b>11</b> | <b>↓</b> | <b>↓</b> | <b>↓</b> | <b>3.10</b> | <b>857.97</b> | <b>9.99</b> | <b>0</b> |
| Metsulfuron - methyl    | 249        | 5         | .        | .        | .        | 4.38        | 6.10          | 3.45        | .        |
| Nicosulfuron            | 249        | 12        | .        | .        | .        | 5.07        | 33.02         | 7.57        | .        |
| Primisulfuron - methyl  | 249        | 11        | .        | .        | .        | 2.22        | 20.99         | 2.14        | .        |
| Prosulfuron             | 249        | 3         | .        | .        | .        | 2.48        | 6.32          | 4.15        | .        |
| Rimsulfuron             | 249        | 1         | .        | .        | .        | 48.92       | 48.92         | 6.25        | .        |
| Thifensulfuron - methyl | 249        | 2         | .        | .        | .        | 2.04        | 3.10          | 1.72        | .        |



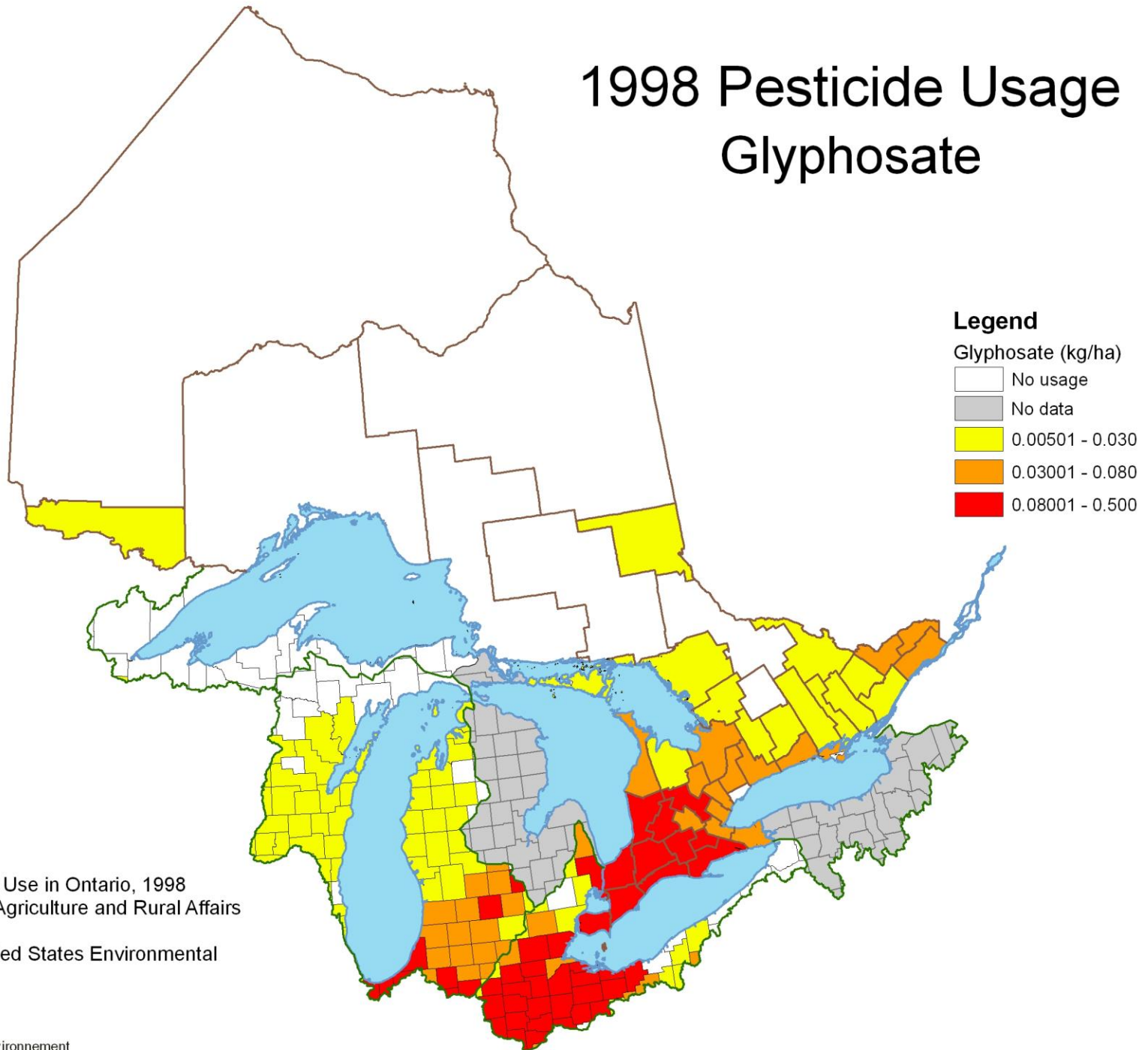




# Pesticide mixtures in surface waters



# 1998 Pesticide Usage Glyphosate



## Data sources:

Survey of Pesticide Use in Ontario, 1998  
Ontario Ministry of Agriculture and Rural Affairs

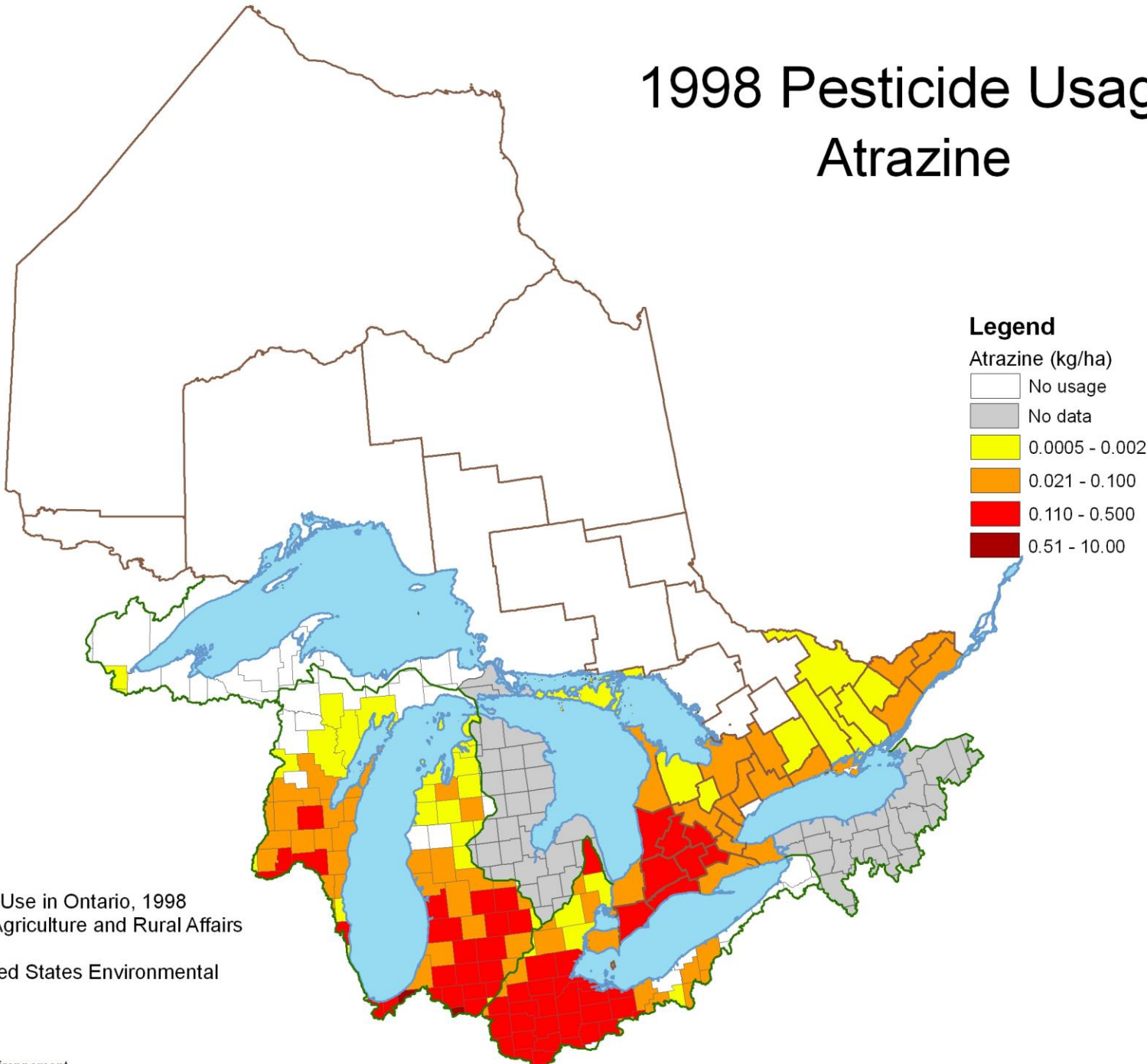
U.S. Data from United States Environmental  
Protection Agency



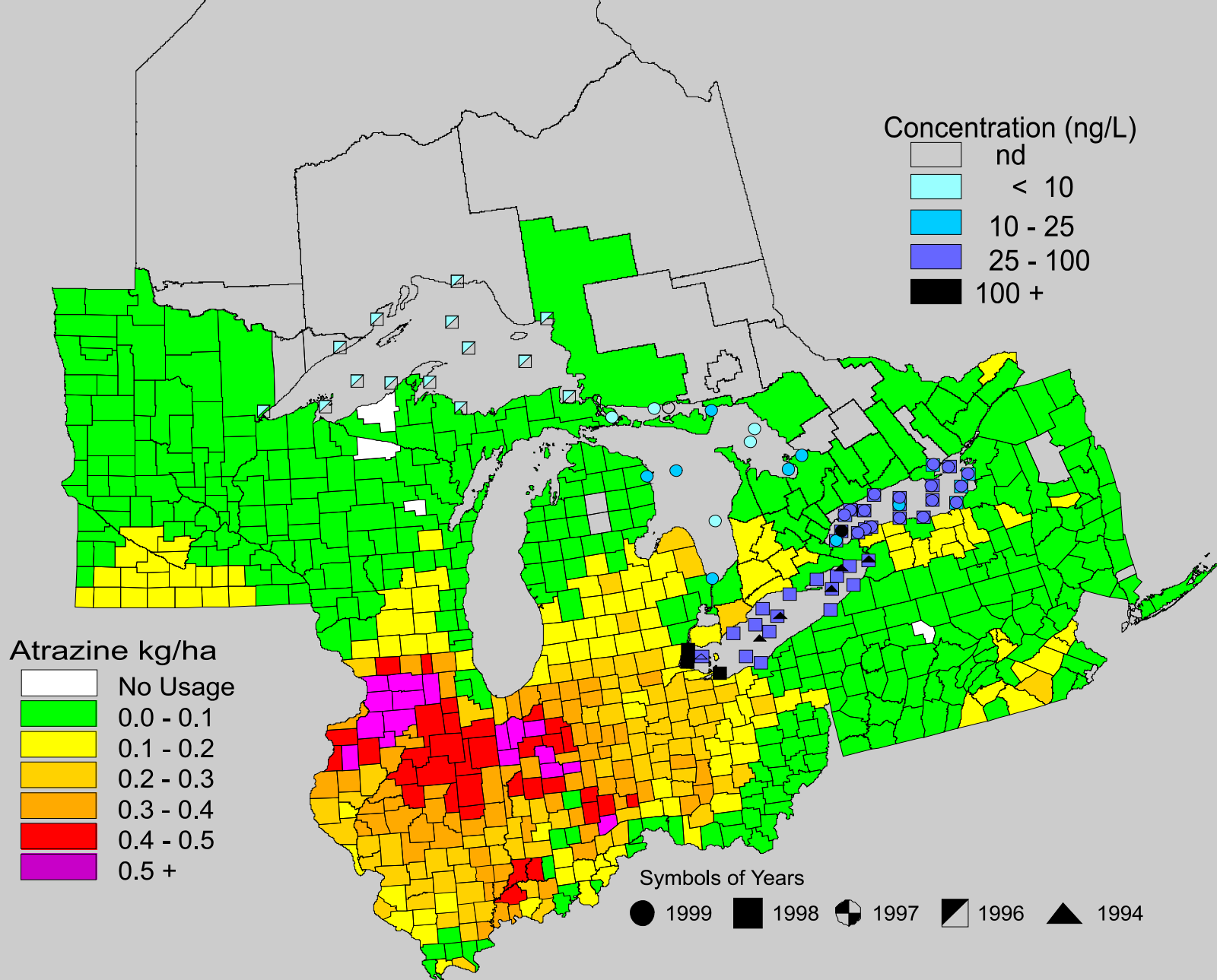




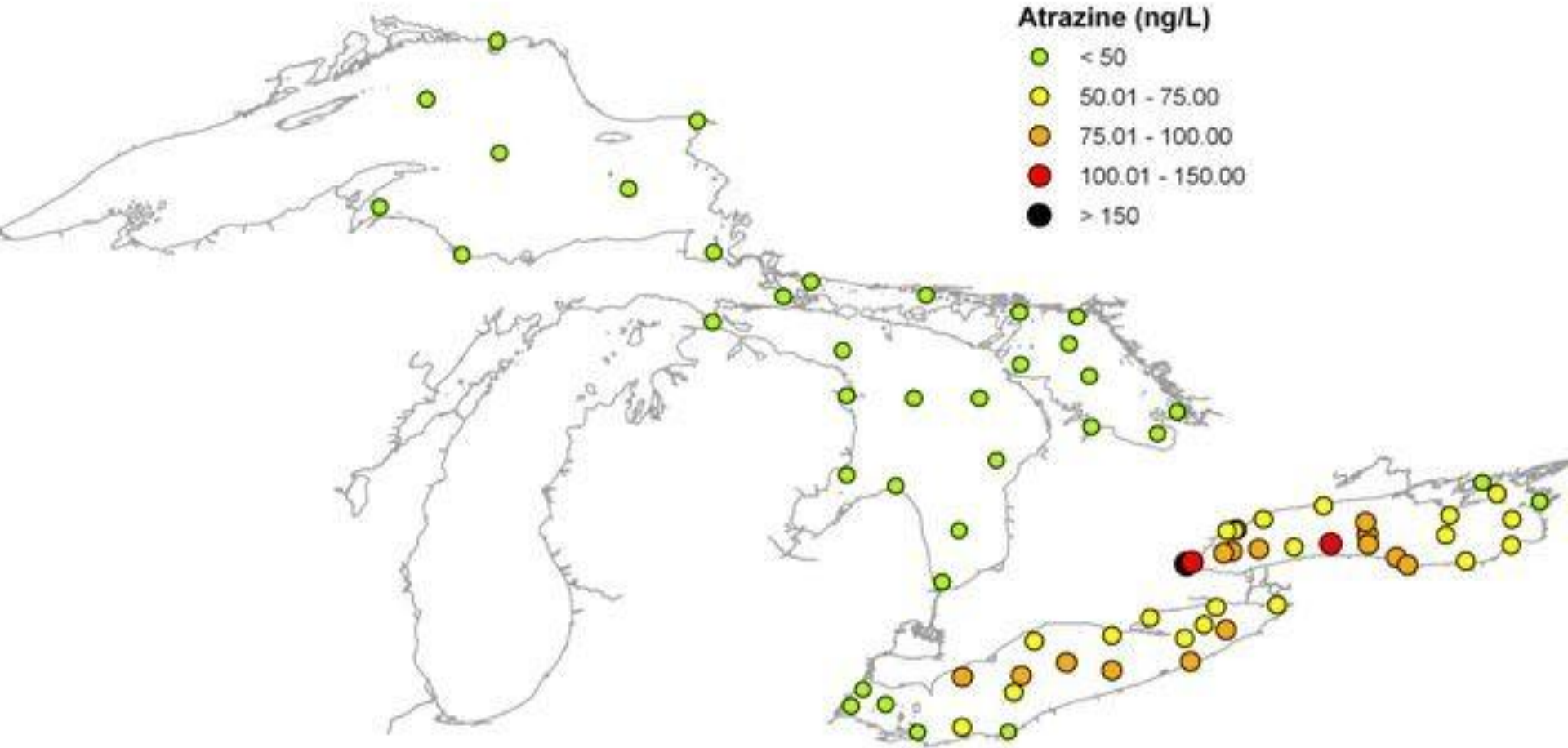
# 1998 Pesticide Usage Atrazine



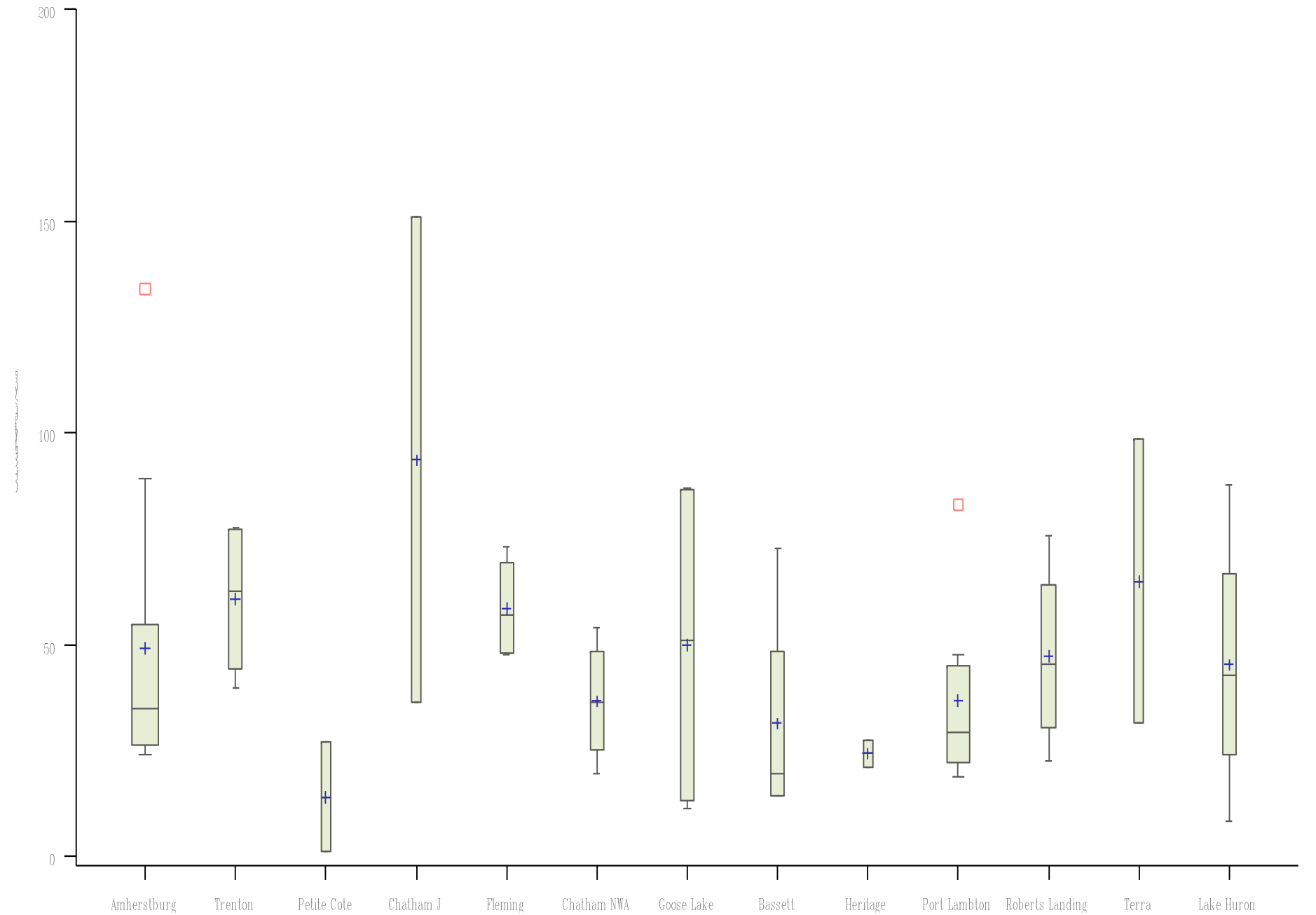
**Data sources:**  
Survey of Pesticide Use in Ontario, 1998  
Ontario Ministry of Agriculture and Rural Affairs  
U.S. Data from United States Environmental  
Protection Agency



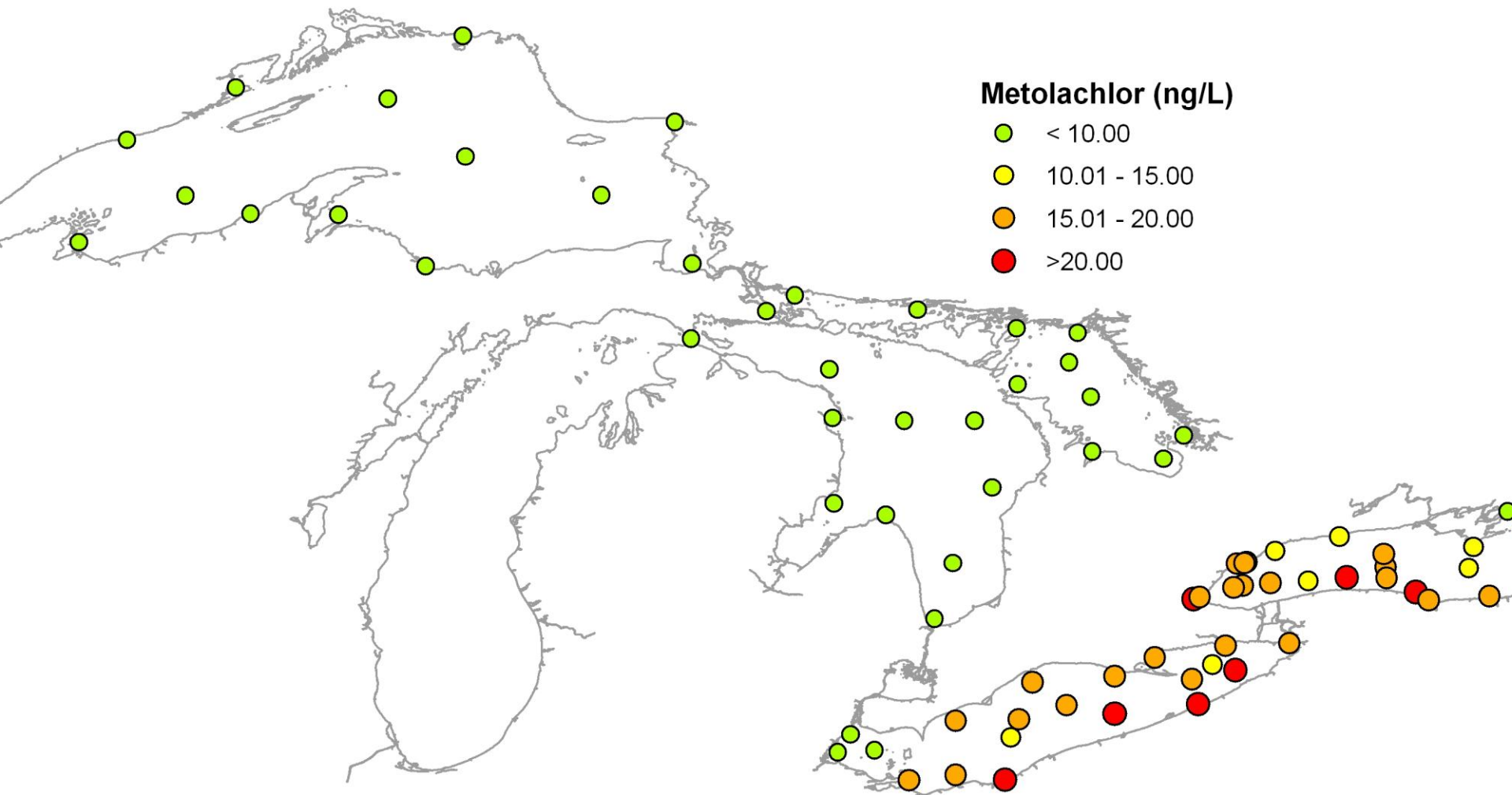
Atrazine usage and Great Lakes concentrations



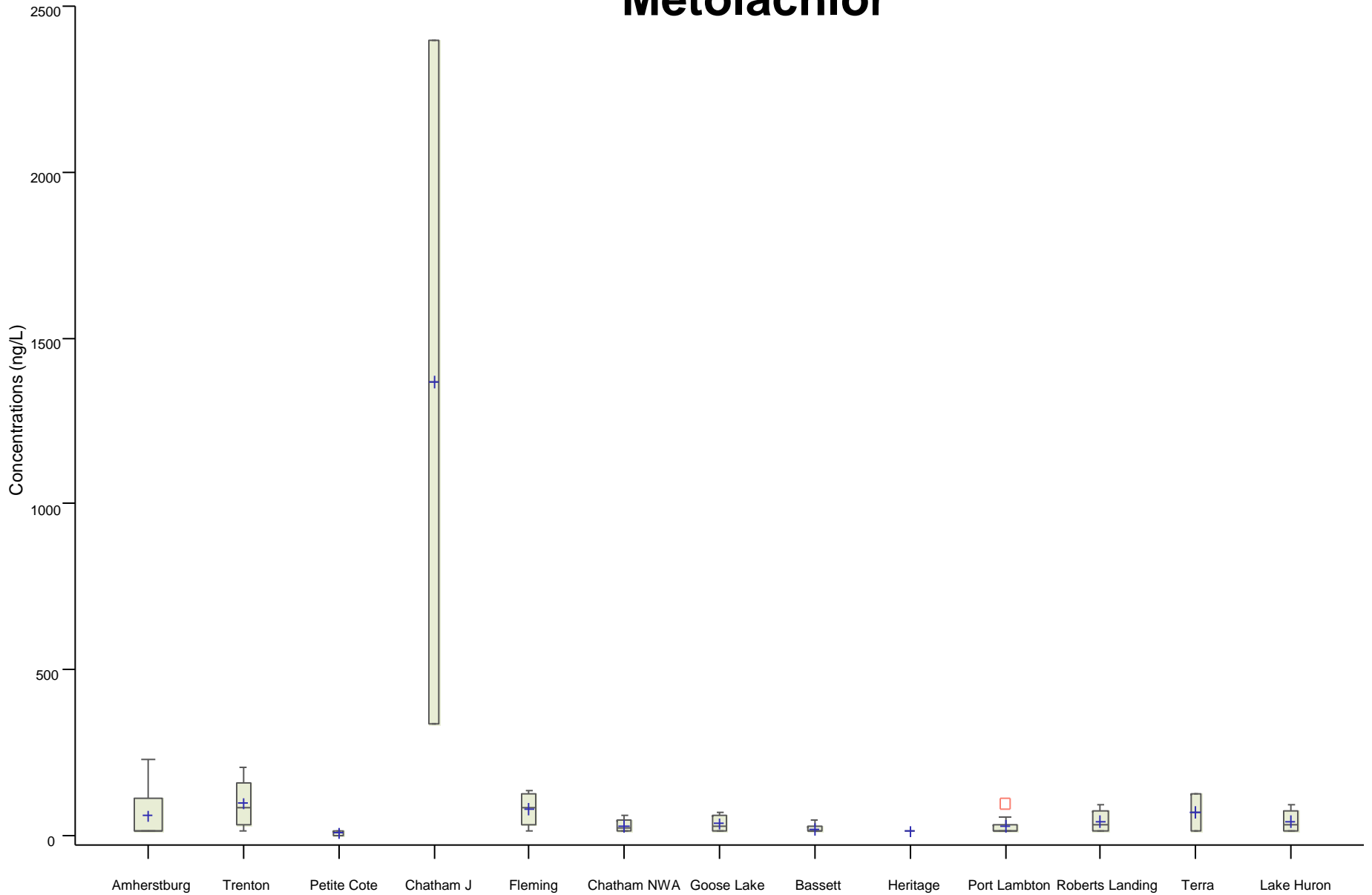
Compound=Atrazine



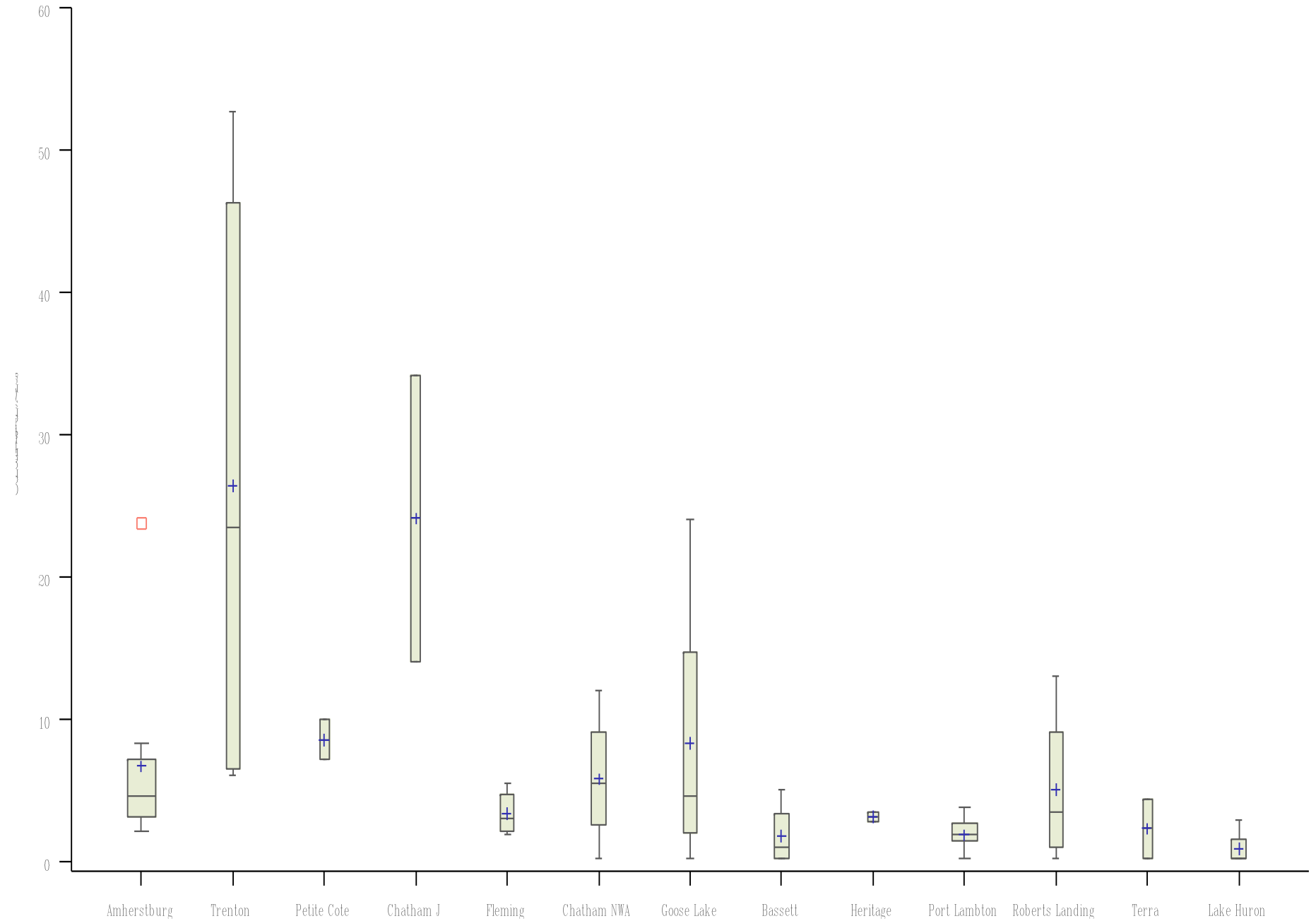




# Metolachlor



Compound=2,4-D





# Results-Watershed monitoring

- Many detections of more commonly used pesticides such as atrazine, metolachlor, 2,4-D, dicamba, mecoprop, diazinon, chlorpyrifos, and azinphos methyl
- Compounds detected in surface waters representative of the land-use (ie row crop, fruit and urban areas)
- frequently detected new classes of compounds such as sulfonyls and carbamate pesticides
- CCME freshwater aquatic guidelines were occasionally exceeded for atrazine, metolachlor, metribuzin, 2,4-D, dicamba, chlorpyrifos and carbaryl-note many pesticides do not have established guidelines

- The suite of pesticides analyzed in this study are fairly indicative of the major herbicides used to control grasses and broad-leaved weeds use in corn, soybean, grain and turf production in Ontario
- The suite of insecticides and fungicides was moderately indicative of the insecticides and fungicides used in fruit, vegetable and turf production.

- Develop methods for pyrethroid insecticides in sediment
- Expand the carbamate pesticide scan to include more dithiocarbamate fungicides
- Continue sampling at our long-term monitoring sites (4 sites) to determine possible changes or trends