

Occurrence and Distribution of Sulfonylurea and Related Herbicides in Central Canadian Surface Waters 2006–2008

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Received: 15 February 2011 / Accepted: 1 July 2011 / Published online: 27 July 2011
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Abstract Surface water sampling in 2006–2008 measured the occurrence of sulfonylureas and related herbicides (SUs) during base flow conditions and wet weather events. Flumetsulam (29.2%), diuron (36.5%) and fomesafen (25.3%) were most frequently detected over the course of the study. Typical SU concentrations were in the low parts per trillion range; however, maximum concentrations of fomesafen (873 ng/L), linuron (856 ng/L) and diuron (2,900 ng/L) approached or exceeded 1 µg/L. The temporal trend in SUs showed a correlation with application periods. In general, detections of SUs were more frequent where rotation of row crops was more intense. Sampling during wet-weather events indicated potential for a range of SUs to be flushed into surface waters at relatively high concentrations.

Keywords Sulfonylurea herbicides · Surface water · Pesticides

Sulfonylurea (SU) herbicides were introduced in the early 1980s and have become widely-used in many major agronomic crops for control of broadleaf and grass weeds during pre- and post-emergent crop production (E.I. du Pont de Nemours and Company 2005). Sulfonylureas

inhibit acetolactate synthase (ALS), which is involved in the synthesis of branched-chain amino acids in plants. Low application rates (10–40 g/ha) resulting from high biological activity, coupled with reportedly low mammalian toxicities and short half-lives have made SUs popular worldwide. SUs are weak acids with pK_a values ranging from 3 to 5 and are typically found as a mixture of the ionized and non-ionized forms, with the ratio dependent on the pH of the matrix. SUs are highly water soluble with typical $\log K_{ow}$ values less than 3.

There have been substantial increases in sulfonylurea usage in Canada over the last decade (Table 1), but there is currently a lack of information on the distribution and fate in Canadian surface waters. Cessna et al. (2006) studied the persistence of SUs in farm dugouts in the Canadian prairies and determined a relatively long persistence in water. Environment Canada undertook surface water sampling for SUs over the period 2006–2008 in the central Canadian provinces of Ontario and Quebec. The purpose of this study was to measure the occurrence and distribution of SUs, and to compare concentrations with other pesticides during both base flow conditions and wet weather events.

Materials and Methods

Water samples were collected in 1 L amber glass bottles with PTFE lids, and affixed to a fiberglass sampling pole. Bottles and lids were rinsed twice in sample water prior to collection. Whole water samples were collected by submersing the sample bottle at mid-stream where possible to a depth of 10–20 cm below the surface and allowing to fill completely. Samples were generally collected during base flow conditions, but some peak flow (wet weather) sampling was conducted in 2006.

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Table 1 Sulfonylurea herbicide usage in the Province of Ontario (McGee et al. 2004; Ontario Ministry of Agriculture, Food and Rural Affairs 2001)

Herbicide	Crops	Total applied (kg)	Application rate (g/ha)
Flumetsulam	Corn, soybeans	22,807	185–1,022
Fomesafen	Soybeans, other beans	3,077	240
Nicosulfuron	Corn, vegetables	18,360	12.5
Linuron	Corn, soybeans, vegetables	17,634	55–2,225
Rimsulfuron	Corn, vegetables	6,212	15
Prosulfuron	Corn	2,567	10
Clomazone	Vegetables	1,029	
Thifensulfuron-methyl	Winter wheat	613	4.1–6
Diuron	Vegetables, fruit, non-crop	299	1,800–44,000
Primisulfuron-methyl	Corn	285	
Acifluorfen	Soybeans	262	300

Approximately 15 sites were sampled in Southern Ontario consisting mostly of small streams near agricultural areas; two agricultural reservoirs and one urban control site (Indian Creek) were sampled starting May 2006 (Figs. 1, 2). These regions primarily exhibit a rotation of corn, soybean and grain, with more than 73,000 kg of SUs (and related herbicides) applied in 2003 (McGee et al. 2004).

Three sites were sampled from the Yamaska River basin in Quebec beginning in June 2007, where almost one quarter of all agricultural activity in Quebec takes place. Roughly 106,000 ha, or 50% of the cultivated land in the basin, is dedicated to growing corn. Of the 400 tonnes of pesticides applied in this watershed, 143 tonnes can be attributed to corn farming.

1 L water samples were extracted through OASIS HLB (6 cc, 500 mg) SPE cartridges conditioned sequentially with 5 mL acetone, 5 mL methanol and then 5 mL of Type I water. Samples were extracted at a rate of 5 mL/min and the cartridge was subsequently dried for 10 min. The cartridge was eluted with 8 mL of methanol, after which the extract was concentrated to 0.9 mL for analysis. Prior to analysis, 100 μ L of the internal standard (linuron- d_6 and thifensulfuron-methyl- d_3) was added to the extracts.

An Agilent 1100 series HPLC system equipped with an Agilent Zorbax SB-C8 analytical column (3 \times 100 mm i.d., 3.5 μ m particle size) was used at a rate of 350 μ L/min in both positive and negative MS ion mode. A mobile phase of 2 mM formic acid in both water and acetonitrile was used for both positive and negative ion analyses. The

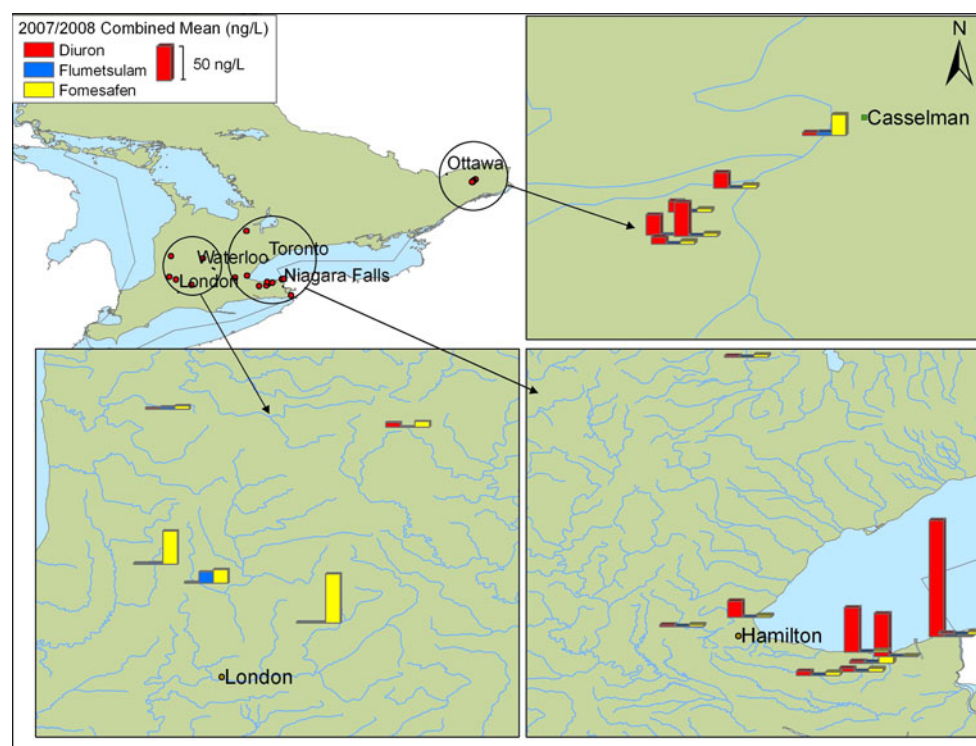
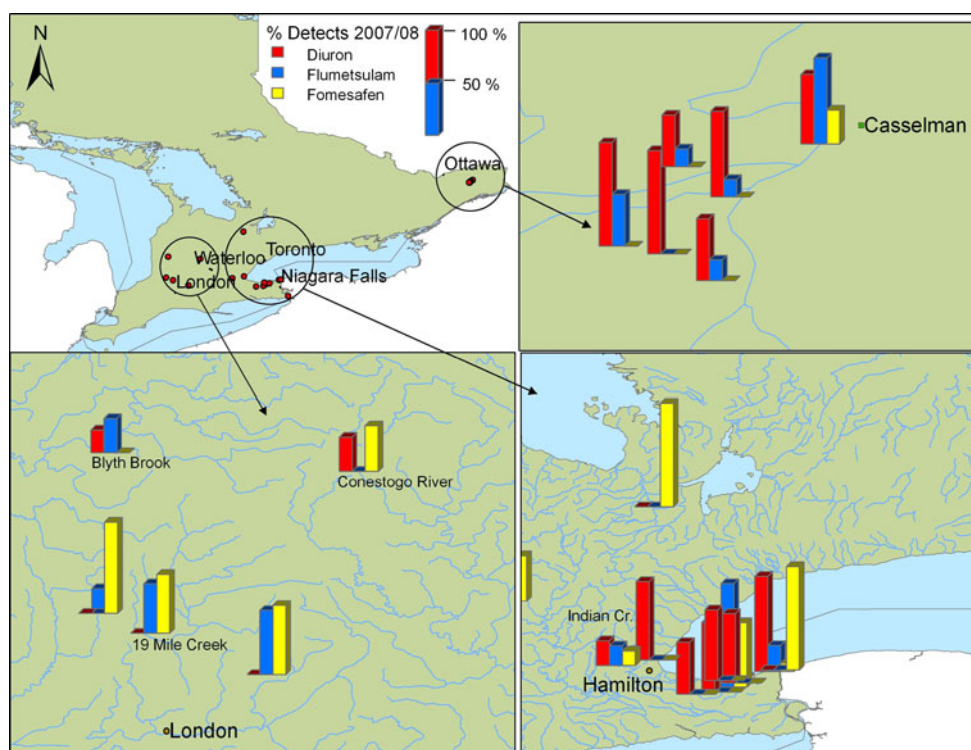
Fig. 1 Spatial distribution of diuron (red bar), flumetsulam (blue bar) and fomesafen (yellow bar) in Ontario surface waters

Fig. 2 Frequency of detections for diuron (red bar), flumetsulam (blue bar) and fomesafen (yellow bar) in Ontario surface waters



injection volume was 5 μL ; all compounds were analysed using a Sciex API 2000 tandem mass spectrometer with an electrospray ionization (ESI) source. Identification was based on one multiple reaction monitoring (MRM) transition per analyte. Analytical standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Surface water concentrations were determined using a multi-point calibration ranging from 16 to 900 $\text{pg}/\mu\text{L}$ with continuing calibration every six samples.

For determination of method detection limits (MDLs), a mixed herbicide standard was spiked into Type I water. A one-sided student's *t* distribution was used at a 95% confidence limit. Recoveries in the spiked Type I water samples were 96% or higher for all compounds except rimsulfuron, which was recovered at 60% ($n = 12$). Extraction efficiency of natural water samples was determined to be greater than 64% using diuron- d_6 and metsulfuron-methyl- d_3 as surrogates. Based on the results of the spiking study, instrument detection limits (IDLs) for SUs ranged from 0.33 to 9.88 pg/L and method detection limits (MDLs) generally ranged from 0.7 to 22.0 ng/L .

Results and Discussion

The identification and quantification of SUs and related herbicides presents an analytical challenge. Based on recommended application rates, expected concentrations of SUs in surface waters would be at low ng/L (parts per

trillion, ppt) levels, and therefore method detection limits should reflect these environmentally relevant concentrations. Previous studies employed liquid chromatography (LC) coupled with mass spectrometry (MS) in electrospray ionization (ESI) mode and gas chromatography–mass spectrometry (GC/MS) to measure SUs in water; examples of these methods exhibited method reporting limits (MRLs) of 10 ng/L for LC/MS (Battaglin et al. 2000; Furlong et al. 2000) and 1 ng/L for GC/MS (Zaugg et al. 1995). These methods employed solid phase extraction (SPE) for initial clean up and pre-concentration of SUs in water samples. In our developed method, use of positive pressure rather than vacuum by the automated SPE unit results in less variability during the extraction and elution steps. This procedure also offers uniform throughput and the ability to extract and analyze samples the same day. Based on the results of the spike studies and application to field samples, our method has proven sensitive and robust, and applicable to the routine determination of SUs in water samples typical of central Canada.

Our survey design and selection of sampling locations over the course of the 3 years of sampling was predicated on a number of factors, including land use, proximity to application zones, potential impacts on agricultural reservoirs, typical application periods, degree of crop rotation, and base flow conditions and peak flow conditions (wet-weather events). A variety of agricultural areas were sampled to determine differences in SU occurrence in areas of row crop farming, compared to fruit orchards. In

addition, an urban control site (Indian Creek, Fig. 2) was sampled.

Over the course of the entire study period from 2006 to 2008, flumetsulam, diuron and fomesafen yielded the greatest percentages of detections for the whole data sets (Tables 2, 3, 4). Other prevalent compounds were chlorimuron-ethyl and nicosulfuron. All of these compounds are routinely applied to row crops including corn and/or soybeans for control of broadleaf weeds. However, diuron is also used on fruits, vegetables and ornamental crops, as well as for non-crop applications including rights-of-way and industrial sites. The application rates can range from 4.1 g/ha for thifensulfuron-methyl to 44,000 g/ha for diuron (Table 1). Most SU concentrations were in the low parts per trillion (ppt) range (~ 1 – 10 ng/L); however, maximum concentrations of compounds such as fomesafen, linuron and diuron approached 1 μ g/L (Tables 2, 3, 4).

The temporal trend in SU detections over the study period showed a strong correlation with typical application periods. In general, sample analysis showed a temporal trend of herbicide concentrations increasing over the growing and application season up to June–July, and subsequently decreasing from August to September.

In 2007 and 2008, sites were sampled in the Yamaska River watershed as part of a cursory Canadian national survey in order to determine baseline levels of SUs, and to provide samples for methods development. In Quebec, samples generally contained low levels of nicosulfuron, diuron, prosulfuron and fomesafen that typically increased over the application period (June–July).

Flumetsulam, diuron and fomesafen were the most widely detected SUs in samples from Ontario (Fig. 1; Tables 2, 3, 4); all three of these compounds were detected in greater than 10% of the total sample set for all 3 years. In some cases, relatively high concentrations of linuron were also detected. In 2006, concentrations of >100 ng/L were also observed for nicosulfuron, chlorimuron-ethyl, primisulfuron-methyl and rimsulfuron. Nicosulfuron was also detected in $>20\%$ of the total sample set for 2006, and chlorimuron-ethyl was detected in roughly 17% of the total sample set for 2008 in Ontario.

In general, detections of SUs at sites in Ontario were more frequent where rotation of corn/soybeans/grain (row crops) was more intense, i.e., in southwestern Ontario (London, Waterloo, Niagara Falls) versus southeastern Ontario (Ottawa area, Fig. 1). This trend was also evident in the comparison of areas of row crop applications with areas of fruit production (Niagara Peninsula). There was an apparent higher prevalence in the detection of fomesafen in the London area, which we attribute to application on bean crops other than soybeans in this area, compared to other areas in the province. Fomesafen and diuron were the only SUs detected at a monitoring station at Fort Erie in the Niagara River. These compounds were only detected occasionally at low concentrations (<4 ng/L) indicating that although these pesticides are widely used in the Lake Erie watershed, they are not entering open lake environments at substantial concentrations.

The study of Battaglin et al. (2000) on the occurrence of sulfonyleurea and other herbicides in rivers, reservoirs and

Table 2 Summary statistics for sulfonyleurea herbicides in 2006 in Ontario

	Number of samples	Number of detects	% of detects	Mean	SD	Min	Max	P25	P75	DL	GL
Acifluorfen	150	0	0.000	–	–	–	–	–	–	21.0	–
Bensulfuron-methyl	150	3	2.00	–	–	1.08	32.6	–	–	2.15	–
Chlorimuron-ethyl	150	10	6.67	–	–	1.07	114	–	–	3.10	–
Chlorsulfuron	150	0	0.000	–	–	–	–	–	–	4.60	–
Clomazone	150	1	0.660	–	–	17.1	17.1	–	–	1.43	–
Diuron	150	58	38.7	55.2	260	4.15	2,900	1.23	22.8	2.46	–
Flumetsulam	150	59	39.4	40.0	158	1.18	1,100	0.66	6.81	1.31	–
Fomesafen	150	16	10.7	8.87	16.8	9.83	132	4.86	4.86	9.71	–
Linuron	150	3	2.00	–	–	107	240	–	–	12.8	0
Metsulfuron-methyl	150	3	2.00	–	–	17.1	57.2	–	–	0.740	–
Nicosulfuron	150	32	21.3	–	–	3.95	525	–	–	4.76	–
Primisulfuron-methyl	150	5	3.33	–	–	5.74	157	–	–	5.01	–
Prosulfuron	150	5	3.33	–	–	1.75	4.13	–	–	1.28	–
Rimsulfuron	150	3	2.00	–	–	36.1	145	–	–	22.0	–
Thifensulfuron-methyl	150	4	2.67	–	–	5.62	47.0	–	–	0.770	–

Minimum value is based on the concentrations that were observed to be greater than the detection limit. Analytes reported in ng/L. GL indicates the number of detections that exceeded the CCME guidelines, while ‘–’ in the GL column indicates that no guidelines were available for these pesticides

Table 3 Summary statistics for sulfonylurea herbicides in 2007 in Ontario

	Number of samples	Number of detects	Percent detects	Mean	SD	Min	Max	P25	P75	DL	GL
Acifluorfen	120	1	0.83	–	–	10.0	10.0	–	–	21.0	–
Bensulfuron-methyl	120	0	0.000	–	–	–	–	–	–	2.15	–
Chlorimuron-ethyl	98	3	3.06	–	–	6.21	7.98	–	–	3.10	–
Chlorsulfuron	120	0	0.000	–	–	–	–	–	–	4.60	–
Clomazone	120	0	0.000	–	–	–	–	–	–	1.43	–
Diuron	121	52	43.0	–	–	2.66	133	–	–	2.46	–
Flumetsulam	120	16	13.3	–	–	1.42	22.4	–	–	1.31	–
Fomesafen	120	15	12.5	–	–	10.6	873	–	–	9.71	–
Linuron	125	4	3.20	–	–	3.10	856	–	–	12.8	0
Metsulfuron-methyl	120	0	0.000	–	–	–	–	–	–	0.74	–
Nicosulfuron	120	9	7.50	–	–	5.07	33.0	–	–	4.76	–
Primisulfuron-methyl	120	4	3.33	–	–	10.1	21.0	–	–	5.01	–
Prosulfuron	120	2	1.67	–	–	2.48	3.72	–	–	1.28	–
Rimsulfuron	120	1	0.83	–	–	48.9	48.9	–	–	22.0	–
Thifensulfuron-methyl	120	1	0.83	–	–	3.10	3.10	–	–	0.77	–

Minimum value is based on the concentrations that were observed to be greater than the detection limit. Analytes reported in ng/L. GL indicates the number of detections that exceeded the CCME guidelines, while ‘–’ in the GL column indicates that no guidelines were available for these pesticides. Summary statistics calculated for only pesticides with greater than 50% detection rates

Table 4 Summary statistics for sulfonylurea herbicides collected in 2008 in Ontario

	Number of samples	Number of detects	Percent detects	Mean	SD	Min	Max	P25	P75	DL	GL
Acifluorfen	129	0	0.000	–	–	–	–	–	–	5.27	–
Bensulfuron-methyl	129	0	0.000	–	–	–	–	–	–	2.80	–
Chlorimuron-ethyl	129	22	17.1	–	–	1.46	13.8	–	–	1.44	–
Chlorsulfuron	129	0	0.000	–	–	–	–	–	–	8.37	–
Clomazone	129	1	0.78	–	–	2.83	2.83	–	–	0.94	–
Diuron	129	36	27.9	–	–	4.35	873	–	–	3.99	–
Ethametsulfuron-methyl	129	0	0.000	–	–	–	–	–	–	177	–
Flumetsulam	129	45	34.9	–	–	0.67	233	–	–	0.66	–
Fomesafen	129	68	52.7	25.7	56.0	2.75	374	1.27	28.8	2.54	–
Foramsulfuron	129	0	0.00	–	–	–	–	–	–	9.44	–
Linuron	129	7	5.43	–	–	11.2	145	–	–	9.99	0
Metsulfuron-methyl	129	5	3.88	–	–	4.38	6.10	–	–	3.45	–
Nicosulfuron	129	3	2.33	–	–	12.6	22.1	–	–	7.57	–
Primisulfuron-methyl	129	7	5.43	–	–	2.22	8.10	–	–	2.14	–
Prosulfuron	129	1	0.78	–	–	6.32	6.32	–	–	4.15	–
Rimsulfuron	129	0	0.000	–	–	–	–	–	–	6.25	–
Thifensulfuron-methyl	129	1	0.78	–	–	2.04	2.04	–	–	1.72	–
Tribenuron-methyl	129	0	0.000	–	–	–	–	–	–	8.49	–

Minimum value is based on the concentrations that were observed to be greater than the detection limit. Analytes reported in ng/L. GL indicates the number of detections that exceeded the CCME guidelines, while ‘–’ in the GL column indicates that no guidelines were available for these pesticides. Summary statistics calculated for only pesticides with greater than 50% detection rates

ground water in the Midwestern United States in the late 1990s affords the best data set for comparison with the present study. Common analytes in both studies included

bensulfuron methyl, chlorimuron ethyl, chlorsulfuron, flumetsulam, nicosulfuron and prosulfuron. In both studies, flumetsulam was widely detected. Another general

similarity between the studies was general detection of SUs in surface waters at low ng/L levels, with maximum concentrations in the hundreds of ng/L. For example, the highest concentration of flumetsulam in the 1998 US study was 358 ng/L, compared to 1,100 ng/L in 2006 in our study. Battaglin et al. (2000) estimated expected maximum concentrations of SUs to range from 10 to 1,000 ng/L based on chemical characteristics, typical application rates and areas treated.

The relatively lower concentrations measured at the Quebec sites, compared to the Ontario sites, reflects the fact that the Yamaska watershed is much larger than any of the Ontario watersheds sampled; therefore, herbicide run-off from application areas in this region can undergo substantial dilution prior to sampling. Concentrations of compounds such as linuron and fomesafen were higher than anticipated given their higher potency, and therefore lower required application rates. In fact, SUs were frequently detected at concentrations approximating those of conventional herbicides including atrazine, metolachlor, mecoprop and 2,4-D (data not shown). However, it should be considered that application rates for some non-crop uses can be quite high, e.g., non-crop application rates for diuron can exceed 44,000 g/ha (Table 1). The Ontario urban control site (Indian Creek, Fig. 1) had consistently detectable (100% detection rate in 2007) concentrations of up to 130 ng/L of diuron. Diuron is also registered for non-crop usage, including control of aquatic weeds and algae, and industrial applications; therefore, its detection was not unexpected in a watercourse discharging an urbanized watershed.

A comparison of SU concentrations at the Ontario sites between 2006 and 2007 showed the presence of more of the target compounds at higher levels in 2006, compared to 2007 (Tables 2, 3); however, this discrepancy could be attributed to the much dryer growing season of 2007, and subsequently less herbicide leaching from agricultural sites into surface waters. Precipitation levels for the 2008 growing season were similar to those for the 2007 season (Tables 3, 4).

During 2006, select Ontario sites were sampled in July during wet weather events (Blyth Brook, 19 Mile Creek and Conestogo River, Fig. 2). Results of analyses of these

samples were dramatic in that most of the target analytes were detected, and at substantially higher concentrations compared to base flow conditions. At these three sites, between 7 and 13 compounds out of 15 target analytes were detected. For example, the mean concentration of nicosulfuron (280 ng/L) detected during the 4 rain events in 2006 was roughly an order of magnitude higher than the maximum concentrations observed during base flow conditions in 2007 and 2008 (22 and 33 ng/L, respectively). These results indicate the potential for a wide range of SUs to be flushed from areas of application into surface waters at relatively high concentrations; we are planning follow up studies to determine temporal trends in SU concentrations subsequent to rain events and national studies to determine the occurrence, distribution and fate of SUs across Canada.

Acknowledgments The authors thank Mr. John Kraft and Mr. Michael Knudson of Environment Canada for technical assistance.

References

- Battaglin WA, Furlong ET, Burkhardt MR, Peter CJ (2000) Occurrence of sulfonyl urea, sulfonamide, imidazolinone, and other herbicides in rivers, reservoirs and ground water in the Midwestern United States, 1998. *Sci Total Environ* 248:123–133
- Cessna AJ, Donald DB, Bailey J, Waiser M, Headley JV (2006) Persistence of the sulfonylurea herbicides thifensulfuron-methyl, ethametsulfuron-methyl, and metsulfuron-methyl in farm dug-outs (ponds). *J Environ Qual* 27:2395–2401
- E.I. du Pont de Nemours and Company (2005) DuPont crop protection sulfonylurea herbicides. DuPont brochure K-05825 (09/05)
- Furlong ET, Burkhardt MR, Gates PM, Werner MG, Battaglin WA (2000) Routine determination of sulfonylurea, imidazolinone, and sulfonamide herbicides at parts per trillion concentrations by solid-phase extraction and liquid chromatography/mass spectrometry. *Sci Total Environ* 248:135–146
- McGee B, Berges H, Callow K (2004) Survey of pesticide use in Ontario, 2003. Ontario Ministry of Agriculture, Food and Rural Affairs, Toronto. ISBN 0-7743-9959-7
- Ontario Ministry of Agriculture, Food and Rural Affairs (2001) Guide to weed control 2001. Publication 75, Toronto. ISSN 0836-1045
- Zaugg SD, Sandstrom MW, Smith SG, Fehlberg KM (1995) Methods of analysis by the US Geological Survey National Water Quality Laboratory – determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. US Geological Survey Open-File Report 95-181