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Occurrence of Glyphosate in Surface Waters of Southern Ontario

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Abstract Glyphosate in surface waters of southern Ontario (Canada) was studied over a 2-year period. A small percentage of samples exhibited glyphosate concentrations greater than the analytical limit of quantitation (17 μg a.e./L), and the maximum concentration of glyphosate measured was 40.8 μg/L. No samples of roughly 500 analyzed exceeded the Canadian Water Quality Guideline of 65 μg a.e./L considered protective of aquatic life. Typical concentrations of glyphosate in amphibian habitats were well below a range of toxicity thresholds for aquatic organisms, and were thus judged to be unlikely to pose a substantial risk to either sensitive amphibian larvae or other aquatic biota.

Keywords Glyphosate · Surface water · Amphibians · Guidelines

Glyphosate (*N*-[phosphonomethyl]glycine; CAS#1071-83-6) is a weak organic acid that inhibits the shikimic acid biosynthesis pathway in plants. It has become the most widely used herbicide worldwide with various formulations applied in agriculture, forestry, industrial rights-of-way, and home-use sectors. In southern Ontario, the dominant use pattern is for weed control in production of glyphosate tolerant agricultural crops including soybeans and corn. Glyphosate is also the dominant herbicide used for vegetation control in forestry, both in Ontario and nationwide (Thompson et al. 2006). In 2003, total usage of glyphosate in Ontario agriculture was roughly 1,200,000 kg, which represented a 60% increase in usage since 1998 (OMAF 2004).

Montgomery (1993) reported physical and chemical properties of glyphosate including water solubility (11.6–12 g/L), log Kow (−3.22 to −2.77), log Koc (3.43–3.69), water half-life (7–10 weeks in natural waters) and soil half-life (<60 days).

The human health and environmental risks associated with the use of glyphosate have been recently reviewed (Giesy et al. 2000; Solomon and Thompson 2003). Although previously classified as moderately toxic to amphibians (Giesy et al. 2000), more recent findings published by Relyea (2005a, b, c) suggest that glyphosate may pose a significant direct toxic threat to native amphibian species. Given the widespread use of glyphosate and concerns regarding its environmental fate and potential effects in aquatic ecosystems, researchers from Environment Canada and the Canadian Forest Service undertook a collaborative two-year study to determine glyphosate concentrations in representative aquatic systems of southern Ontario, including known amphibian habitats in areas of intensive agricultural production, as well as to assess potential spatial distributions and temporal trends in concentrations. The analytical scheme in the current study also included aminomethylphosphonic acid (AMPA), which is the primary degradation product of glyphosate in soils, plants, and water. According to the World Health Organization (WHO), AMPA is only slightly toxic to rats (LD50 8,300 mg/kg, WHO 1996), and is considered to be of no greater toxicological concern than glyphosate (IPCS 1997).

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Materials and Methods

Surface water grab samples (1 L) were taken from more than 30 different sites including rivers, small streams, and low-flow wetlands across southern Ontario in 2004 and 2005 (Fig. 1). Sampling generally occurred biweekly during ice-free periods (April–November). Samples were stored in high density polyethylene bottles on ice following collection in the field; upon return to the laboratory (within 6 h) they were frozen immediately and stored in the dark at $<-10°C$.

Glyphosate residues were quantified using a validated analytical technique involving gas chromatography with nitrogen-phosphorous detection. Known amounts of glufosinate ammonium were added as an internal standard to 50 mL aliquots of aqueous samples. Following addition of the internal standard, the samples were rotary evaporated to dryness (water bath at 60°C), and the flask was subsequently held in an oven at 135°C for 3 min to ensure complete dryness. Glacial acetic acid (3 mL) and trimethylorthoacetate (6 mL) were added sequentially to each flask and the reaction mixture was heated under reflux at 110°C to 135°C for a period of 3 h. The derivatization reaction converts amino, hydroxyl and carboxyl functional groups to volatile less-polar acetyl or methyl moieties yielding a glyphosate derivate amenable to gas chromatographic analysis. Excess derivatization reagent was removed from samples by repetitive rotary evaporation in ethyl acetate (3×15 mL) and final samples were brought to a constant volume of 10 mL in ethyl acetate. Chromatographic analysis were performed on an HP5890 Series II GC equipped with an autosampler set to deliver 3 μL aliquots via splitless injection to a DB17 capillary column (15 m $\times$ 0.53 mm i.d.; 1.0 μM film thickness; J&W Scientific). Concentrations of glyphosate and AMPA were calculated based on relative peak area response of the nitrogen-phosphorous detector in comparison to the internal standard (glufosinate) and reported in units of μg/L. Glyphosate, which occurs as various salts in formulated products, is reported by convention in terms of acid equivalents (μg a.e./L).

Quality control check samples, prepared by fortifying blank natural surface water samples with known levels of glyphosate, AMPA and the internal standard were run concurrently with each set of field samples. Quality control samples were fortified, mixed and stored under dark refrigerated conditions for a period of approximately 18 h prior to analysis. Blank matrix samples were also included in the quality control program to assess the potential for co-extractive interference or cross-contamination. In conjunction with glyphosate field sampling conducted over the two-year period, a total of 80 quality control check samples were prepared and analyzed. Analysis of 11 different blank samples showed low levels of co-extractive interferences for either glyphosate or AMPA analytes. Results from fortified samples showed good average recovery efficiency

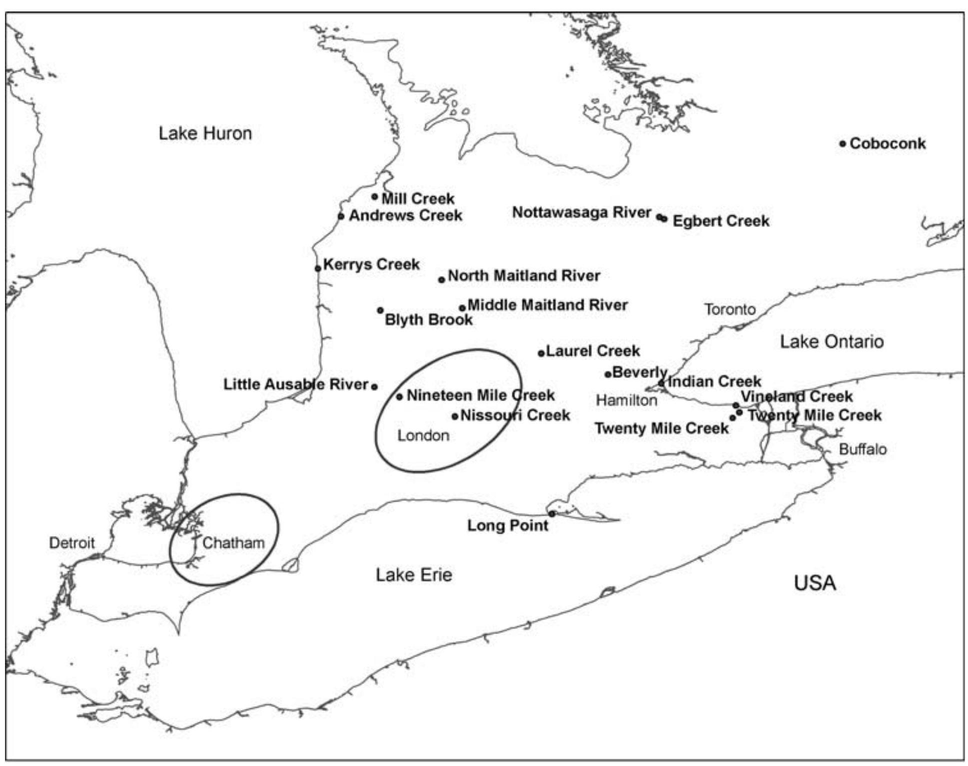


Fig. 1 Surface water sampling sites including rivers, small streams, agricultural drainage ditches and low-flow wetland sites across southern Ontario in 2004 and 2005. The ellipses represent groups of amphibian habitat sites as detailed in Table 1

(>90%) and precision (cv < 14%) for glyphosate analysis in both years. AMPA results also showed high recovery efficiency (>82%) with slightly greater variation (cv ~ 17%). Based on conventional calculations of 3× and 10× the standard deviation in blank baseline noise from representative surface water samples (n = 20) taken from these sites, analytical limits of detection (LOD) and limits of quantitation (LOQ) for glyphosate were estimated as 5 and 17 µg a.e./L, respectively. In these samples, no measurable peaks occurred within the AMPA retention window and thus detection and quantitation limits could not be estimated from the same samples. Based on a separate analysis of n = 9 samples taken from 2005 sites, LOD and LOQ for AMPA were estimated as 20 and 66 µg/L, respectively. Higher values for AMPA reflect the higher variability of baseline noise in this region of the chromatograms.

Results and Discussion

In 2004, a total of 203 surface water samples from 26 different field sites were collected and analyzed for glyphosate and AMPA (Table 1). Samples were taken between May and mid-December, with frequency varying from 1-to-4 times per month. Only 11, or approximately 5%, of the samples exhibited levels of glyphosate above the limit of quantitation. Sites with multiple detections of glyphosate (detected in roughly 50% or greater of samples), and with the highest mean and maximum glyphosate levels, included some sites on the 20 Mile Creek as well as at Blyth Brook, Indian Creek, and Vineland Creek sites (Fig. 1). Trace level detections ($5< X <17$ µg/L) for glyphosate were observed in 42 (21%) of the total samples analyzed in 2004. Overall mean glyphosate concentrations were typically in the low µg/L range (Table 1); typical maximum observed concentrations were in the 10–20 µg/L range. It should be noted that Table 1 includes only sites for which there was at least one trace detection, and therefore does not represent the full geographic scope of the study. In 2004, 16 sites had trace detections of glyphosate. The maximum glyphosate concentration observed was 41 µg/L in a sample taken from the Blyth Brook site in May; other sites exhibiting relatively high maximum concentrations included Indian Creek (39.8 µg/L), Kerrys Creek (37.4 µg/L), and Nissouri Creek (35.1 µg/L). Detectable residues occurred more frequently in spring and fall as compared to mid-summer.

In 2005, a total of 299 surface water samples from 58 different sites were collected and analyzed for glyphosate and AMPA (Table 1). Samples were taken between April and November, with varying frequencies per month. Only 6, or approximately 2%, of total samples contained levels of glyphosate above the limit of quantitation. Trace level detections ($5< X <17$ µg a.e./L) for glyphosate were observed in 45 (15%) of total samples analyzed. In 2005, 45 sites had trace detections of glyphosate. Sites with multiple occurrences of glyphosate, and with highest average and maximal glyphosate levels included Laurel Creek, Middle Maitland River, Nissouri Creek, Mill Creek, Nottawasaga River, West Don River, and 20 Mile Creek. The maximum glyphosate residue (30.5 µg/L) observed in 2005 occurred in the April sample at the 20 Mile-Cherry site. Trace level detections of AMPA were observed in 16 (5.4%) samples, but above the limit of quantitation at one site. Results were similar to 2004 in that typical mean glyphosate concentrations were in the low µg/L range. Among these samples, maximum concentrations were typically in the 20–30 µg/L range. The sample with the maximum AMPA concentration (66 µg/L) was observed at Andrews Creek in April. Almost all of the detectable residues of glyphosate and AMPA were observed in early spring, but positive detections for the two analytes were very poorly correlated.

Overall results of this study are derived based on analysis of a total of 502 surface water samples collected throughout the ice-free period of April to December from sites considered typical of agricultural and urban drainages in southern Ontario where applications of glyphosate are common. Aqueous environmental exposure concentrations for glyphosate residues as observed in this study were very similar to other surface water concentration values published in monitoring studies in the USA and in various European countries. For example, 8.7 and 3.6 µg a.e./L for glyphosate and AMPA, respectively, were observed in agricultural drainages of the mid-western US (Battaglin et al. 2005). In a major study (ZHEW 2002; as cited in Horth et al. 2004) investigating glyphosate concentrations over a 5-year period in surface waters associated with 21 orchard sites, the maximum concentration observed was 23 µg a.e./L, while typical concentrations were less than 10 µg a.e./L. Other European monitoring studies (Bechmann et al. 1999; Soppe 1991 also cited in Horth et al. 2004) showed typical concentrations of glyphosate in surface waters associated with cereal or other agricultural crop production in the Netherlands and Norway of <1 µg a.e./L.

A subset (N = 30) of the sampling sites selected in 2005 (Table 1, Fig. 1), were identified as amphibian habitat by the Canadian Wildlife Service; this assessment was typically based on direct observation and capture of anuran amphibians at the site. In all, 23 wetland sites had trace detections of glyphosate. A conservative assessment was conducted using the 45 samples (out of a total of 112) which showed aqueous glyphosate concentrations greater than analytical detection limits (5 µg a.e./L). The mean value calculated for this data subset was 15.2 µg a.e./L with an upper 99% confidence limit (99% CL) bound of

Table 1 Number of detections (>5 μg a.e./L) and maximum concentrations (μg a.e./L) of glyphosate and its major metabolite AMPA in water collected from water bodies throughout southern Ontario in 2004 and 2005

Location	Year	Glyphosate			AMPA		
		N	Number of detections	Maximum concentration	N	Number of detections	Maximum concentration
20 Mile Creek-Bailey	2004	15	9	12.2	15	0	NA
20 Mile Creek-Bailey	2005	7	3	10.6	7	0	NA
20 Mile Creek-Cherry	2004	19	8	22.9	19	0	NA
20 Mile Creek-Cherry	2005	13	5	30.5	13	0	NA
20 Mile Cr.- Smithville	2005	13	5	17.5	11	1	31.2
Andrews Creek	2005	7	1	15.1	7	1	66.0
Blyth Brook	2004	8	5	40.8	8	0	NA
Blyth Brook	2005	7	3	8.27	7	1	41.9
Chatham A*	2005	4	2	12.2	4	0	NA
Chatham B*	2005	5	3	5.57	5	0	NA
Chatham C*	2005	4	1	5.25	4	0	NA
Chatham H*	2005	4	2	3.66	4	0	NA
Chatham J*	2005	4	1	3.12	4	0	NA
Chatham K*	2005	3	1	1.17	3	0	NA
Chatham NWA*	2005	5	2	9.42	5	0	NA
Chatham O*	2005	5	2	11.9	5	0	NA
Chatham P*	2005	4	1	4.95	4	0	NA
Chatham W*	2005	3	2	6.48	3	1	29.8
Chatham X*	2005	3	3	1.89	3	0	NA
Egbert Creek	2004	8	3	6.40	8	0	NA
Egbert Creek	2005	11	7	4.38	11	1	26.3
Head Lake*	2005	5	3	3.17	5	0	NA
Indian Creek†	2004	18	10	39.8	18	0	NA
Indian Creek†	2005	7	1	10.3	7	1	43.3
Kerrys Creek	2004	9	3	37.4	9	0	NA
Kerrys Creek	2005	7	3	15.0	7	0	NA
Laurel Creek†	2004	7	2	10.6	7	0	NA
Laurel Creek†	2005	6	3	23.4	6	1	28.2
Little Ausable River	2004	8	3	24.6	8	0	NA
Little Ausable River	2005	8	5	9.09	8	1	18.4
Little Ausable Tile	2005	2	1	3.83	2	0	NA
London #5*	2004	1	1	11.7	1	0	NA
London #5*	2005	5	4	5.69	5	0	NA
London #6*	2005	4	2	3.80	1	0	NA
London #11*	2005	4	2	2.77	4	0	NA
London #19*	2005	4	2	4.98	4	0	NA
London #23*	2005	4	2	2.38	4	0	NA
London #25*	2005	3	1	4.08	3	0	NA
London #27*	2005	3	2	10.3	3	0	NA
London #28*	2005	4	2	7.00	4	0	NA
Little Castor River	2005	4	1	2.25	4	0	NA
McFarlane Drain*	2005	4	3	9.14	4	0	NA
Middle Maitland River	2004	7	1	13.0	7	0	NA
Middle Maitland River	2005	7	4	18.6	7	1	21.6
Mill Creek	2004	8	2	13.9	8	0	NA
Mill Creek	2005	7	5	12.4	7	1	20.0

Table 1 continued

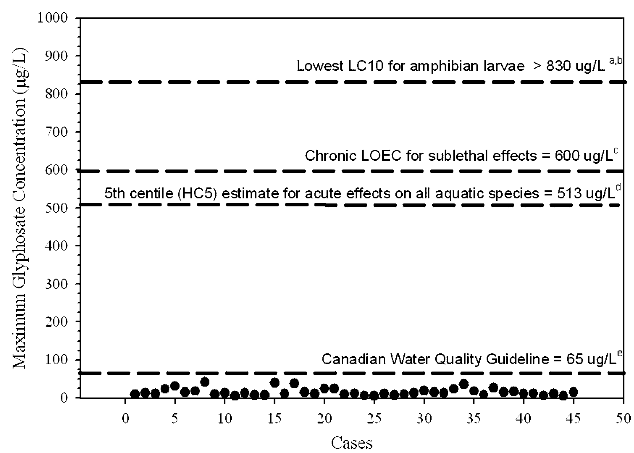
Location	Year	Glyphosate			AMPA		
		N	Number of detections	Maximum concentration	N	Number of detections	Maximum concentration
Nineteen Mile Creek	2004	8	2	23.2	8	0	NA
Nineteen Mile Creek	2005	7	5	9.52	7	1	25.2
Nineteen Mile Tile	2005	2	1	4.66	2	0	NA
Nissouri Creek	2004	7	2	35.1	7	0	NA
Nissouri Creek	2005	7	5	17.1	7	1	28.8
North Maitland River	2004	8	3	7.97	8	0	NA
North Maitland River	2005	7	4	25.8	7	1	31.1
Nottawasaga River	2004	8	1	3.55	8	0	NA
Nottawasaga River	2005	7	6	15.1	7	1	21.4
Vineland Creek	2004	19	7	15.6	19	0	NA
Vineland Creek	2005	14	5	10.3	14	1	48.4
Spring Creek	2005	8	5	5.67	8	0	NA
Stokes River	2005	8	5	10.2	8	0	NA
Town Line Drain*	2005	2	2	5.45	2	0	NA
West Don River†	2005	11	7	14.9	11	1	29.8

Analytical limits of detection (LOD) and limits of quantitation (LOQ) for glyphosate were estimated as 5 and 17 µg a.e./L, respectively. Only sites at which at least one trace detection occurred were included in the table. Sites marked with asterisks (*) correspond to proven amphibian habitat. †Sites corresponding exclusively to urban land use. NA denotes "not applicable"

21 µg a.e./L No detectable residues of AMPA were observed in any case. This result suggests that aqueous glyphosate concentrations in amphibian wetland habitats typical of agricultural or municipal sites in southern Ontario during the period April to September, would typically be below the upper 99th centile bound of 21 µg a.e./L.

The estimate of maximal environmental exposure concentrations is below published toxicity thresholds for amphibians and other aquatic species (Fig. 2). The maximal environmental exposure estimate is substantially lower than the lowest 96 h LC_{10} values reported for amphibian larvae exposed under laboratory (Edginton et al. 2004) or in situ enclosure test conditions (1200 µg a.e./L; Wojtaszek et al. 2004), respectively. The estimate is roughly 25-fold lower than the 5th centile value (513 µg a.e./L) as estimated based on species sensitivity distribution analysis for all aquatic species (Solomon and Thompson in prep) and roughly 30-fold less than the chronic sub-lethal lowest observable effect levels reported by Howe et al. (2004).

Our estimate of maximal environmental exposure concentrations is also approximately 50-fold less than the lowest LC_{50} value (equivalent to 980 µg a.e/L) reported for larvae of six different amphibian species exposed to glyphosate over a period of 16 days (Relyea 2005b). In the latter study, wood frog (*Rana sylvatica*) larvae exposed to both glyphosate formulation and predatory stress cues, resulted in a substantially lower LC_{50} value equivalent to 490 µg a.e./L. However, even under this multiple stressor



[a] Wojtaszek et al. 2004 lowest LC10 estimate from in situ enclosure studies was 1200 ug/L
[b] Edginton et al. 2004 lowest estimate of LC10 from lab studies was 830 ug/L
[c] Howe et al. 2004
[d] Solomon and Thompson 2007 (in prep)
[e] Trotter et al. 1990.

Fig. 2 Relationships between maximum observed glyphosate concentrations in surface waters of southern Ontario (n = 53 over 2 years of monitoring) and various estimates of toxicity threshold values for aquatic organisms

scenario, and relatively long exposure duration, the differential between our maximal observed environmental exposure concentration and observed toxicity estimates suggests a 30-fold safety factor. All observations in this sub-study were below the Canadian Water Quality Guideline of 65 µg a.e./L (Trotter et al. 1990). This guideline is based on toxicity data for the most sensitive species of plants and animals found in Canadian waters and is considered the science-based benchmark for the protection of aquatic life in Canada (Environment Canada, Canadian Water Quality Guidelines Overview; http://www.ec.gc.ca/CEQG-RCQE/English/Ceqg/Water/default.cfm#aqu). The overall mean (N = 45 samples) was 15.2 μg/L with an upper 99% CL of 19 μg/L, the latter of which is 3-fold below the CWQG (Fig. 2).

It has been shown that the surfactant typically used in combination with glyphosate, polyethoxylated tallowamine (POEA), is the primary toxic component of the most commonly used formulation, Roundup® (Monsanto, St. Louis, MO, USA) in both acute (Geisy et al. 2000; Mann and Bidwell 1999; Perkins et al. 2000) and longer term chronic exposures (Howe et al. 2004). Although both POEA and glyphosate are readily sorbed to organic matter and sediments and both are relatively non-persistent in aqueous phase, the assumption of relativity between glyphosate and POEA exposure concentrations under a variety of natural environment scenarios remains incompletely validated. Under some test conditions POEA has been shown to have an estimated half-life of 21–42 days, whereas that of glyphosate is only 2–14 days (Geisy et al. 2000). Of particular interest for future studies is potential exposure of organisms to POEA and glyphosate via sediments or through ingestion of contaminated periphytic biofilms. Glyphosate residues often increase in sediment during a growing season, sometimes reaching concentrations of about 1 μg/g, and may persist for several months (Newton et al. 1994; Goldsborough and Brown 1993). Howe et al. (2004) found that tadpoles chronically exposed to two different glyphosate formulations and POEA by itself, were smaller, suffered from tail damage, were slower to transform into frogs; as well significant numbers of male frogs exhibited intersex gonads at transformation, an abnormal condition in which oocytes develop within testes, suggesting feminization. However, all of these observations occurred following aqueous glyphosate exposure concentrations ranging from 600 to 18,000 μg a.e./L which are far above the maximal environmental exposure concentration of 21 μg a.e./L as estimated in this study.

Given that glyphosate has a short half life in the water column (Geisy et al. 2000) and that our sampling regime was partially based on a calendar schedule and was not timed to spray or run-off events, there is a possibility that sampling was not conducted during periods of peak concentrations of glyphosate in surface waters. However, the data as presented represent glyphosate and AMPA concentrations typical of both base-flow and higher flows due to rain events. Relyea (2005c) demonstrated that roundup can be acutely lethal to amphibians, within a 24 h exposure period, so that short spikes in glyphosate concentrations may be of toxicological concern. Measurements of glyphosate drift in ponds adjacent to agricultural fields suggests that resulting glyphosate concentrations in the water are below levels of concern for amphibian toxicology. Martin et al. (unpublished data) found that glyphosate concentrations taken from ponds adjacent to agricultural fields 24 h after field applications of Roundup were typically low, ranging from below detection limits (1 μg/L) to 13 μg/L. Since glyphosate readily binds to soil particles, glyphosate is likely to enter surface waters sorbed onto water borne particles during runoff events (Takacs et al. 2005). Future surveys of glyphosate residues in surface waters might therefore be focused on runoff events where high magnitude, short duration pulses may occur, such as where storm sewers from municipal sites drain directly into wetlands.

In conclusion, overall results of this study indicate that only 2% to 5% of the total number of samples collected through two years of study showed glyphosate concentrations greater than the analytical limit of quantitation (17 μg a.e./L) and no samples out of a total of 502 samples showed concentrations exceeding the Canadian Water Quality Guideline for glyphosate of 65 μg a.e./L which is considered protective of aquatic life. Typical surface water concentrations of glyphosate as measured in amphibian habitats in this study (99% CL <21 μg a.e./L) are well below a variety of toxicity thresholds for aquatic organisms and thus unlikely to pose a substantial risk to either sensitive amphibian larvae or other aquatic biota in these systems. To complement existing programs focusing primarily on the agricultural sector, we recommend that future research and monitoring related to glyphosate should consider municipal and domestic use scenarios where frequency of occurrence of glyphosate and POEA, and the magnitude and duration of exposures in drainage water receiving environments, is relatively unknown.

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