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Residues of the herbicide glyphosate in riparian groundwater in urban catchments

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HIGHLIGHTS

- Addresses gap in information about glyphosate and AMPA in urban riparian groundwater.
- Glyphosate and AMPA detected at most sites, 1 in 10 samples overall.
- Detection frequency varied between sites – from none to found in most samples.
- AMPA was correlated with glyphosate, not acesulfame, suggesting a glyphosate source.

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ABSTRACT

The herbicide glyphosate and its putative metabolite aminomethylphosphonic acid (AMPA) have been found in urban streams, but limited information is available on their presence in urban riparian groundwater. Information is also lacking regarding the source of AMPA in these urban settings (glyphosate metabolite or wastewater), and whether, if present, glyphosate residues in urban riparian groundwater contribute significantly to urban streams. Glyphosate and AMPA were detected in shallow riparian groundwater at 4 of 5 stream sites in urban catchments in Canada and each were found in approximately 1 in 10 of the samples overall. Frequency of observations of glyphosate and AMPA varied substantially between sites, from no observations in a National Park near the Town of Jasper Alberta, to observations of both glyphosate and AMPA in more than half of the samples along two short reaches of streams in Burlington, Ontario. In these two catchments, AMPA was correlated with glyphosate, rather than the artificial sweetener acesulfame, suggesting that the AMPA is derived mainly from glyphosate degradation rather than from wastewater sources. Land use, localized dosage history, depth below ground and other factors likely control the occurrence of detectable glyphosate residues in groundwater.

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1. Introduction

Glyphosate ($C_3H_8NO_5P$) was introduced as a nonselective herbicide in the 1970s, and it has become one of the most widely used herbicides worldwide (Vereecken, 2005; Kolpin et al., 2006; Borggaard, 2011; Coupe et al., 2012). It is commonly used to control weed growth in agriculture, silvaculture, along roadways, railways and utility corridors, as well as in urban areas (streets, sidewalks, paved areas, gardens). Aminomethylphosphonic acid (AMPA) is an important metabolite produced during microbial degradation of glyphosate (e.g., Borggaard and Gimsing, 2008). However, AMPA also forms as a residual metabolite during the degradation of other phosphonate compounds, including detergents, and therefore it is not diagnostic as a residue of glyphosate (Horth and Blackmore, 2009; Botta et al., 2009; Hanke et al., 2010). Generally the concentrations of glyphosate and AMPA that have been detected in environmental waters have been below the relevant standards or objectives for protection of the environment, though significant proportions of surface water samples in Europe have glyphosate concentrations that exceed the European Union's objective for drinking water, which is 0.1 μg L^{-1} (Horth and Blackmore, 2009).

Following its application, glyphosate has a strong tendency to sorb to soil particles and to undergo degradation by microorganisms (Giesy et al., 2000; Borggaard and Gimsing, 2008). There is some evidence that AMPA is more persistent than glyphosate in soils (Kjær et al., 2005; Mamy et al., 2008), and, in different soils, AMPA was found to sorb less (Mamy et al., 2008) or more (Bergström et al., 2011) than glyphosate. Given the above properties in soil, both glyphosate and AMPA are generally considered to have a low potential to leach downward through soils to groundwater (Vereecken, 2005; Borggaard and Gimsing, 2008; Giesy et al.,

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2000). However, experimental field studies have shown that applications of glyphosate can result in detectable glyphosate residues in groundwater in the vicinity (Smith et al., 1996; Börjesson and Torstensson, 2000; Kjær et al., 2004, 2011; Crowe et al., 2011), although in one of these studies (Börjesson and Torstensson, 2000) glyphosate and AMPA were detected only at locations with above-normal glyphosate application rates.

Until the past decade, there were very few published reports of the occurrence of glyphosate and AMPA in groundwater. The frequency of detection of glyphosate in groundwater determined from several large data sets (Table 1) ranged from 1.3% to 7.8%, while that of AMPA was 1.7% to 14%. Detections were less frequent in Europe than in the United States and were less common in groundwater than in surface waters. However, temporal changes in the analytical limits of detection make direct comparisons difficult. The majority of the monitoring and surveillance data regarding the occurrence of glyphosate and AMPA in surface water and groundwater has focused on agricultural areas (e.g., Scribner et al., 2007; Van Stempvoort et al., 2008; Horth and Blackmore, 2009; Sanchís et al., 2012), reflecting the widespread, global use of glyphosate as a herbicide in agriculture. Similarly, site-specific process-focused studies of the fate of glyphosate in soil and groundwater have typically also addressed agricultural landscapes (Kjær et al., 2004, 2011; Landry et al., 2005). A few studies have shown that urban areas also contribute significant proportions of glyphosate and AMPA to surface waters (Blanchoud et al., 2007; Botta et al., 2009; Hanke et al., 2010; Struger et al., 2013). In contrast, there is a lack of information about glyphosate residues in groundwater in urban areas. The presence of glyphosate residues in groundwater may differ for urban areas compared to agricultural areas because urban applications tend to be more spatially focused by a larger number of users. Also, urban areas and rural areas have different influences on infiltration and runoff (e.g. irrigation practices, diversion of runoff, tile drains vs. storm sewers, etc.; presence/absence of paved areas and other surfaces, differences in vegetation, etc.). Given such differences, Blanchoud et al. (2007) estimated that much larger portions of pesticides used in urban areas were lost to surface water than those used in agricultural areas (catchment in France).

Here we report on the detection of glyphosate and AMPA in shallow groundwater collected at five streams in Canada (Fig. 1), including urban streams in two cities (Fig. 2) and along the shoreline of a river near a town (Fig. 3). Shallow groundwater sampling occurred along predominantly gaining stream sections (i.e. they receive groundwater discharge).These data were collected as a part of several screening-level investigations of groundwater contaminants potentially impacting urban streams (Van Stempvoort et al., 2011; Roy and Bickerton, 2012), but for which pesticides were not a primary focus. Together the data from these five stream sites provide insight into whether riparian groundwater in urban environments tends to have measureable quantities of glyphosate and/or AMPA, which has implications for gauging the potential impacts on riparian and stream ecosystems, as well as mass loadings to urban streams. The focus on urban riparian groundwater in Canada is especially relevant given the concurrent study by Struger et al. (2013), which reports a high frequency of detection of glyphosate residuals in both urban and rural streams in Ontario, Canada (Table 1).

Our data also provide the opportunity to assess the source of any AMPA found in the near-stream groundwater, i.e. whether it is derived from glyphosate or is associated with wastewater. Some researchers have stated that the relative importance of these two sources that contribute AMPA to surface waters remains uncertain (e.g., Kolpin et al., 2006). Parallel to our study, Struger et al. (2013) report evidence that AMPA found in both urban and rural streams in southern Ontario Canada is mainly derived from glyphosate. With Struger et al. (2013), we examine the correlation of concentrations of glyphosate, AMPA and those of a useful wastewater tracer, the artificial sweetener acesulame (Buerge et al., 2009; Van Stempvoort et al., 2011, 2013) to address the source of AMPA.

2. Study sites

2.1. Burlington, Ontario

At Burlington there are many small streams that drain through urban areas into Lake Ontario. Groundwater was sampled in June 2009 along two of these streams: Tuck Creek and Shoreacres Creek (Fig. 2). The sizes of the catchments for these two streams are 11.8 km^2 and 14.1 km^2 respectively. Their headwaters flow from the Niagara Escarpment, an outcropping ridge of dolostone bedrock (also sandstone, limestone, shale), and over a plain that lies between the Escarpment and the shore of Lake Ontario. In these catchments this plain generally has a thin cover of unconsolidated sediments, mostly glacial till (largely silt, locally clay-rich) and

Table 1
Comparison of the results of this study to earlier summaries for both groundwater and surface water.

Location	Glyphosate			AMPA			
	# Samples	% Detections (det. limit, ng L^{-1})	Maximum concentration, ng L^{-1}	# Samples	% Detections (det. limit, ng L^{-1})	Maximum concentration, ng L^{-1}	Source
Groundwater							
United States	873	7.8% (20–100)	4700	873	9.7% (20–100)	2600	Scribner et al. (2007)
United States	Not reported	6% (20–100)	Not reported	Not reported	14% (20–100)	Not reported	Battaglin et al. (2011)
Europe	⩾36298	~1.3% (3–200)	24000	⩾28254	~1.7% (50–500)	19000	Horth and Blackmore (2009)
Canada (riparian)	281	13.2% (1–10)	42	281	11.7% (50–60)	2870	This study
Surface water							
United States	1262	39% (20–100)	427000	1262	57% (20–100)	41000	Scribner et al. (2007)
United States	Not reported	22% – lakes; 51% – streams (20–100)	Not reported	Not reported	22% – lakes; 87% – large rivers (20–100)	Not reported	Battaglin et al. (2011)
Europe	⩾50805	~29% (10–400)	50000	⩾33612	~50% (10–100)	48900	Horth and Blackmore (2009)
Ontario, Canada	222	76% (10–20)	41881	222	76% (10–60)	14781	Struger et al. (2013)

Fig. 1. Map of Canada showing the locations of the study sites.

glacial lake sediments (sand, silt), over bedrock. Here the bedrock is predominantly shale, which outcrops locally along/near these streams (Source Water Protection Halton–Hamilton Region, 2008). Within this plain, Tuck Creek and Shoreacres Creek are 'warmwater' streams (Source Water Protection Halton–Hamilton Region, 2008), suggesting relatively low influx of groundwater seepage. Along the sampled section of Tuck Creek the urban land use is largely commercial, with some residential, with streets and a railway in the immediate vicinity. In the area of sampling at Shoreacres Creek the urban land uses include both commercial and industrial, with local streets (see Roy and Bickerton, 2012 and Van Stempvoort et al., 2011 for further information about these stream sampling sites).

2.2. Barrie, Ontario

Groundwater samples were collected in the catchments of two streams in the City of Barrie that drain into Lake Simcoe: along Dyment's Creek in September 2009 and along Hewitt's Creek in October 2009 (Fig. 2). Here the Lake Simcoe watershed is underlain by a thick sequence of unconsolidated sediments, mainly glacial tills and glacial lake sediments (sand, silt, clay) (Blackport and Associates, 2012).

Land use in the Hewitts Creek catchment (17.5 km^2 in area) is dominated by agricultural (60%) and forest (20%), but includes 12% urban development, mainly as intensive residential (Louis Berger Group and Greenland International Inc., 2006). Riparian groundwater was sampled within the northernmost urban portion of this catchment, within a residential neighborhood (Fig. 2), including some homes that have septic beds (Van Stempvoort et al., 2013). In the riparian area of the stream much of the land is undeveloped open space and land under environmental protection. Some land is used for municipal services and utilities (Fig. 2).

The Dyment's Creek catchment (approx. 4.5 km^2 in area) includes a wide range of urban uses, mainly a mix of industrial, commercial and residential. Groundwater was sampled along two reaches, an upper reach, which is surrounded largely by industrial developments, but with several areas left undeveloped, and a lower reach, where the land developments are largely residential and commercial (Fig. 2), with several undeveloped or park areas underlain by old landfill materials.

2.3. Jasper, Alberta

Groundwater was collected along two reaches of the Athabasca River in Jasper National Park in August 2009. Here, 100 km from its headwaters, the river spans up to 200 m. These reaches are within a few hundred meters of the Town of Jasper (Fig. 3). Developed land outside of the Town of Jasper include tourist cabins, a municipal wastewater treatment plant for the Town, roads, a railway; the rest is undeveloped forest and wetlands. The surficial geology (uppermost 10 m of subsurface) in this area is dominated by fluvial deposits, mostly sand, gravel and cobbles, though there are also

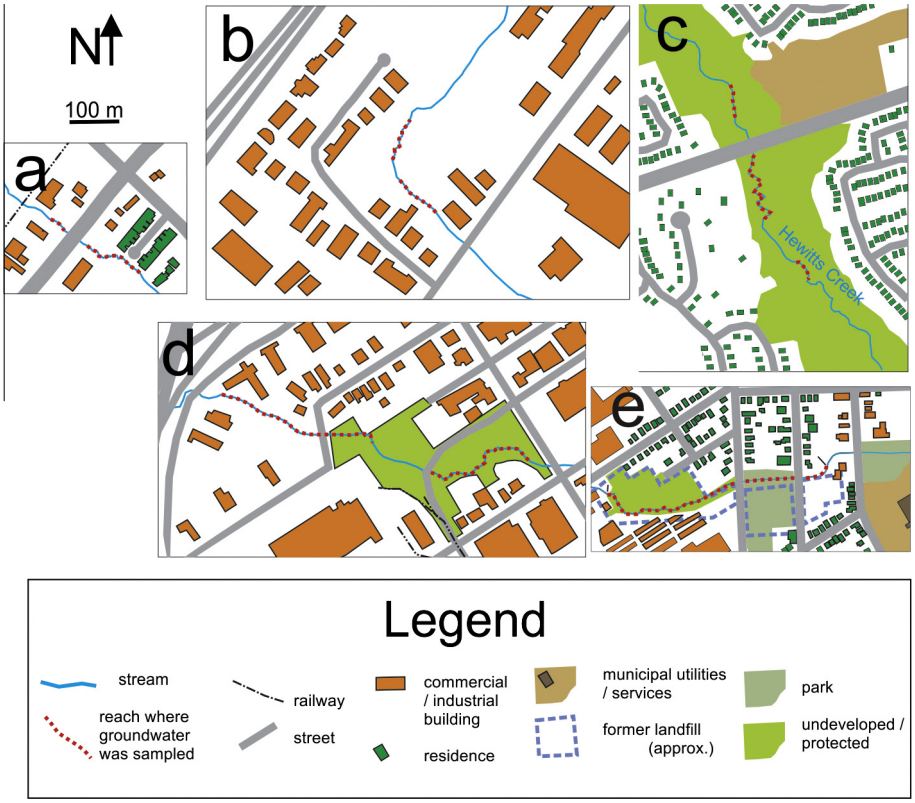

Fig. 2. Plans of the urban study sites (a) Tuck Creek; streamflow is from NW to SE; (b) Shoreacres Creek, streamflow from N to S; (c) Hewitts Creek, streamflow from S to N; (d) upper and (e) lower Dyment's Creek, streamflow from W to E. Scale and compass direction shown in upper left apply to all sites.

layers of silt and silty clay (EBA Engineering Consultants Ltd., 2003).

3. Methods

3.1. Collection of samples

All of the groundwater samples from this study were collected at shallow depths within 2 m of the edge of the streams, usually within the streambed but occasionally on the shore. Groundwater samples were collected from depths of generally 0.25–1.0 m below the ground or streambed surface using a drive-point miniprofiler connected to a peristaltic pump (see Roy and Bickerton, 2010). This consisted of coupled hollow steel-rods (1.6 cm diameter) attached to a stainless steel drive-point which had sampling ports over a vertical interval of 12.7 cm. These ports were internally connected to polyethylene tubing (0.6 cm diameter). The profiler was driven into the sediments using a hammer-drill or pushed in by hand in rare cases. Spacing between samples along the stream reaches was typically 10–20 m. On rare occasions a sample of water seeping directly from the bank was collected as a grab sample. During sampling at each site, one or two stream samples were also collected as grab samples. All samples were filtered in the field (membrane pores $\leqslant$0.45 μm) and collected in HDPE (high density polyethylene) containers. Samples were kept in a cooler with ice packs in the field and during transport to Canada Centre for Inland Waters for analyses.

All field-filtered samples were stored under refrigerated conditions prior to analysis. The majority of the groundwater and stream samples were stored for less than 10 d; samples for Shoreacres Creek were stored for 14–17 d, and those from Jasper were stored for 27–34 d. Our unpublished stability tests with both groundwater and surface water samples indicated that glyphosate and AMPA in filtered and refrigerated samples showed losses of less than 25% over 28 d.

3.2. Laboratory analyses

An ion chromatography electrospray ionization triple quadruple mass spectrometry (IC/MS/MS) was used to analyze glyphosate and aminomethylphosphonic acid (AMPA). Method details are provided in the Supplementary information. The artificial sweetener acesulfame (as a wastewater indicator) was analyzed using the IC/MS/MS method described by Van Stempvoort et al. (2011).

The analytical results, together with other field parameters and laboratory analyses not reported here, were examined to test whether some detections of glyphosate and AMPA in groundwater could be artifacts of our sampling methodology, specifically inadvertent short-circuit flow of surface water along our drive points to our sample intakes. We concluded that for at least the large majority of our samples, this does not appear to be an issue, which is in agreement with Roy and Bickerton (2010), who developed the drive-point sampling method we used in this study (see Section 3.1). However, it is possible, though not certain, that up to three samples from each of the Burlington sites may have been affected by short-circuiting. These samples were excluded from the data set that is reported here.

3.3. Statistical analysis

In this study, we encountered many non-detections of both glyphosate and AMPA. For this reason, we restricted our statistical analyses to the Burlington datasets where the paired analytes were both present in the majority of the samples. For correlation analyses of these compounds, we used Minitab®16 (Minitab Inc., State College, PA, USA) to calculate Spearman rank correlation coefficients (ρ). The standard approach could be used because for

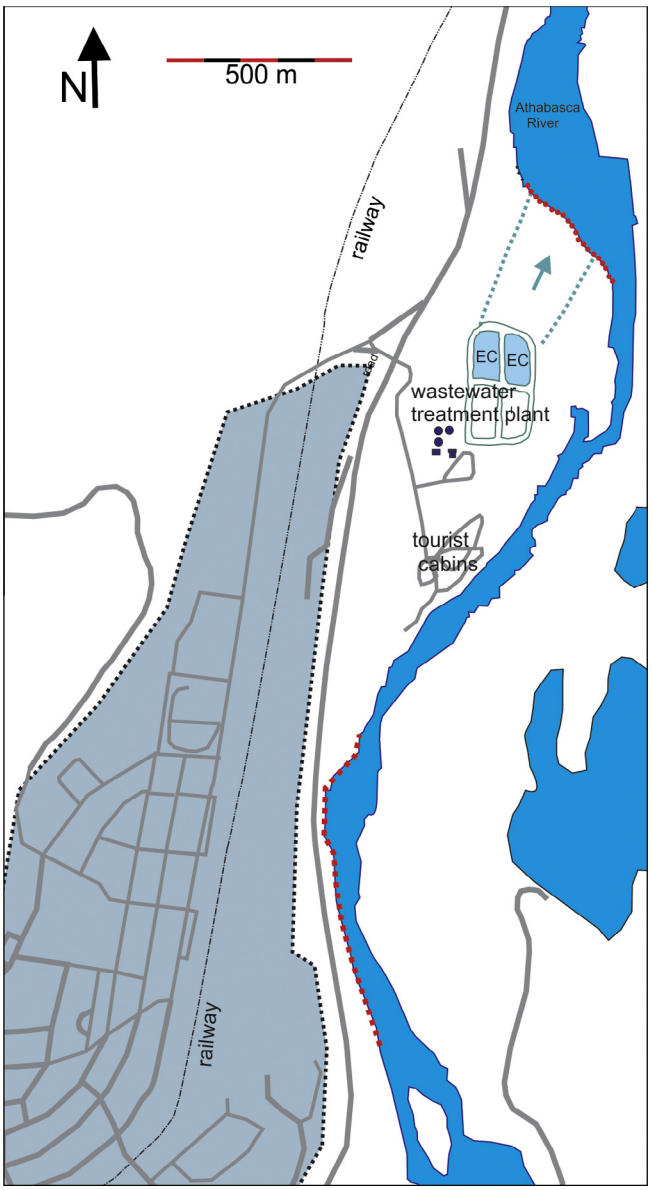

Fig. 3. Plan of the Jasper site, which all lies within Jasper National Park. Roadways and driveways are shown as grey lines; bodies of water are blue. The grey shaded area in lower left is the Town of Jasper which has primarily commercial and residential land uses. Outside of the Town, besides the developments shown, the land is undeveloped wilderness. The groundwater sampling transects along the Athabasca River are shown as red dashed lines. The estimated trajectory of the wastewater plume detected by Van Stempvoort et al. (2013) is outlined with green dashed lines. Two wastewater exfiltration cells are labeled "EC".

each test, each analyte had a single detection (reporting) limit: all non-detections were given the same rank, and all non-quantifiable trace detections were ranked together immediately above the non-detections.

4. Results and discussion

4.1. Glyphosate and AMPA in near-stream (riparian) groundwater

Both glyphosate and AMPA were detected in at least two samples of riparian groundwater at 4 of the 5 urban stream sites. This site-to-site comparison, which does not take into account the number of samples or length of stream reach surveyed, indicates a high frequency of detections. Considering the combined survey results, 13.2% of the 281 samples of riparian groundwater had detectable concentrations of glyphosate, while 11.7% of them had detectable AMPA (Tables 1 and 2).

To further facilitate comparison between sites, we plotted all results as frequencies of observations, using the same reporting limit (highest overall detection limit) for both glyphosate and AMPA (Fig. 4). This figure illustrates that the frequencies of observations of glyphosate were strongly correlated to those of AMPA ($R^2 = 0.878$). AMPA tended to be more prevalent than glyphosate at these sites. If the analytical detection limits for the analyses of glyphosate were the same as the higher ones for AMPA (Table 2), there would be no detections of glyphosate, while nearly 1 in 10 samples would have detections of AMPA. For individual sites, the frequencies of detections varied substantially. For instance, groundwater samples from the two Burlington catchments had observations of both glyphosate and AMPA in nearly half or more of the samples, while there were no observations of either compound in samples from the Jasper site (Fig. 4).

The reaches in Burlington were in areas of dense transportation corridors and commercial development, which may have played a role in the high frequencies of detections of the glyphosate and AMPA in the riparian groundwater. However, some of the groundwater samples from the Burlington sites may have been affected by infiltration of stream water (note – samples potentially affected by short-circuiting were removed from this data set: see Section 3.2), which also had elevated concentrations of both glyphosate and AMPA (Fig. 5). This infiltration may have occurred as bank storage (following some high water event, although we have no information on whether such an event actually occurred in these cases) or hyporheic flow (Winter et al., 1998). However, several samples with high concentrations of glyphosate and/or AMPA were not similar to stream water in their geochemistry or dissolved oxygen (not shown), suggesting the stream is not the sole source of glyphosate residues to this riparian groundwater. Almost all of the groundwater samples at Burlington had higher ratios of AMPA/glyphosate compared to stream samples from the same site (Fig. 5). If the AMPA is derived from glyphosate (see Section 4.3), then this observed pattern may correspond to longer residence times for glyphosate residues in the subsurface compared to the streams. Previous studies have shown that when glyphosate degrades in soils, the ratio of AMPA/glyphosate increases over time because AMPA tends to be more persistent, though AMPA is also transient (e.g., Feng and Thompson, 1990; Simonsen et al., 2008).

There was no apparent influence from the stream as a source of glyphosate residues for the samples from the Barrie sites. Each site had several spatially-sporadic detections, which is suggestive of impacts from multiple localized sources. In a few cases, we found high concentrations of glyphosate (and/or AMPA, see Section 4.3) in samples closest to roads/bridges that cross the stream, but this pattern was not consistent. Similarly, some of our detections were very close to the boundaries of commercial, industrial or residential properties, but again inconsistently. Thus, the determination of specific sources was not possible for these sites. The lack of consistent patterns of detections relative to land uses in the immediate vicinity is not surprising given that not only land use type, but also different herbicide use practices, dosages, and timing of such applications are important, as documented in previous studies (see Section 1), as are other factors such as geology (Kjær et al., 2004).

For the Jasper site, herbicide use is severely restricted because it is in a National Park, which may explain the lack of any detection there, even though some of the samples were located close to a roadway and within 100 m of the town limits (Fig. 3). Low to minimal use of herbicides is characteristic of this community, as reflected in a policy D-002 adopted by the Municipality (town) of Jasper in 2010 to "not use herbicides on any lands for which the Municipality has responsibility." (Municipality of Jasper, 2010).

Table 2
Detections of glyphosate and AMPA in samples of riparian groundwater (2009).

Catchment (s)	Glyphosate				AMPA		
	# Samples	mdl[a]	# With detections (%)	Maximum conc. (ng L^{-1})	mdl[a]	# With detections (%)	Maximum conc. (ng L^{-1})
Burlington, Ontario							
Tuck Creek	18	1	14[b] (77.8%)	42	50	16[b] (88.9%)	547
Shoreacres Creek	16	1	11[b] (68.8%)	20	50	8[b] (50.0%)	176
Barrie, Ontario							
Dyment's Creek – upper	52	10	8 (15.4%)	30	60	0 (0.0%)	n.d.
Dyment's Creek –lower	47	10	2 (4.2%)	14	60	7 (14.9%)	2870
Hewitts Creek	41	10	2 (4.9%)	34	60	2 (4.9%)	125
Jasper, Alberta							
Athabasca River	107	10	0 (0.0%)	n.d.	60	0 (0.0%)	n.d.
All data	281		37 (13.2%)	42		33 (11.7%)	2870

[a] Method detection limit. See Supporting information for an explanation for the differences in mdls for different datasets.
[b] For consistent comparison of the data from all sites, we note at Burlington, the glyphosate detections >10 ng L^{-1}: Tuck Creek, 8 (44%); Shoreacres, 5 (31.3%). The Burlington AMPA detections >60 ng L^{-1}: Tuck Creek, 13 (72%); Shoreacres Creek, 7 (43.8%).

Furthermore, though urban development within the Municipality of Jasper appears to be, in part, upgradient (with respect to groundwater flow) of our sample locations along the Athabasca River, the distance between such development and our sampling points was typically >100 m (Fig. 3), which is much greater than for many of the sampling points at the Burlington and Barrie sites (Fig. 2). In fact, at Burlington, there is no gap of undeveloped land between the sampling points and the adjacent urban properties.

The highest concentrations observed at our sites were 42 ng L^{-1} of glyphosate and 2870 ng L^{-1} of AMPA (Tables 1 and 2). In general, the maximum concentrations of AMPA at each reach that we sampled were notably higher than those of glyphosate (Table 2). This may reflect the fact that AMPA tends to be more persistent than glyphosate in the environment (e.g., Giesy et al., 2000; Coupe et al., 2012). However, it could also be related to the potential for AMPA to be sourced from wastewater; this is discussed below (Section 4.3).

In riparian zones, short, shallow pathways of groundwater flow from soils to streams may be important (e.g., Winter et al., 1998). Given this, and the potential for sorption and degradation of these compounds, it is most likely that the glyphosate residues that we detected are associated with shallow groundwater flow paths (except those few possibly linked to stream inputs), though contributions from deeper flow paths cannot be discounted. The main pathway for glyphosate transport to surface waters is generally inferred to be runoff from soils, either directly (surface runoff) or indirectly, via flow in soil macropores or subsurface (tile) drains (Coupe et al., 2012). Groundwater fluxes of glyphosate and associated AMPA from soils to surface water have generally been considered negligible, likely in large part due to perceptions of high retention and degradation in the soil, and the relatively low levels of detection in groundwater at most sites (Table 1). The results of this study indicate that there may be potential for some contributions of these residues from groundwater to urban streams.

4.2. Comparison of results to past studies

On the basis of these results, we cannot infer whether groundwater in urban areas is more or less prone to glyphosate contamination than in agricultural areas. Comparison between our study and previous studies (e.g., Table 1) is fraught with many difficulties, of which the most obvious is differences in analytical detection limits (see Sanchís et al., 2012), but which also includes non-random selection of sampling locations (all studies), differences in sampling devices (short drive points vs. long well screens, varying depths of samples (sometimes not reported), and perhaps

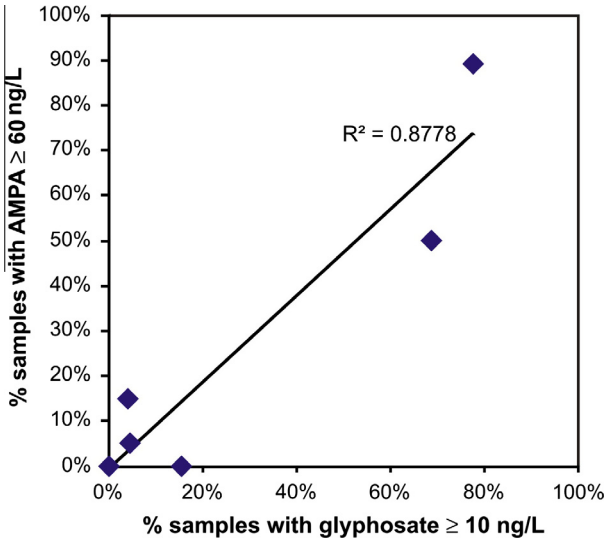

Fig. 4. Comparison of frequencies of glyphosate and AMPA observations at all sites. The lower bound criteria ($\geqslant$10 and 60 ng L^{-1}) were the highest applicable detection limits for all sites collectively for each compound (Table 2).

other factors that have not yet been investigated. However, in this section we attempt to gain broader insight of the relevance of our results by a brief comparison to previous studies.

Our study is not the first to show much variability in frequencies of detections for different subsets of data. For example, Scribner et al. (2007) reported that groundwater sampled in a agricultural catchment in Indiana had detections of 34% and 73% for glyphosate and AMPA, respectively, while 271 samples obtained in "state cooperative studies" had no detections of glyphosate and only one detection of AMPA. These findings suggest that despite widespread use of glyphosate, only certain sites or areas or times (e.g., relative to herbicide application events) may result in noticeable groundwater contamination by this herbicide. A closer look at the Scribner et al. (2007) Indiana dataset, which has the highest frequency of groundwater detections, reveals that in that catchment the monitoring wells were very shallow, most apparently <5 m depth (Baker et al., 2006; Lathrop, 2006). Perhaps the shallow depth of these samples was one of the key factors that resulted in the high frequency of glyphosate and AMPA detections.

The survey-based summary of Horth and Blackmore (2009) and other surveillance-based studies (e.g., Van Stempvoort et al., 2008; Thorling et al., 2010; Hoogeveen et al., 2010) also reported that

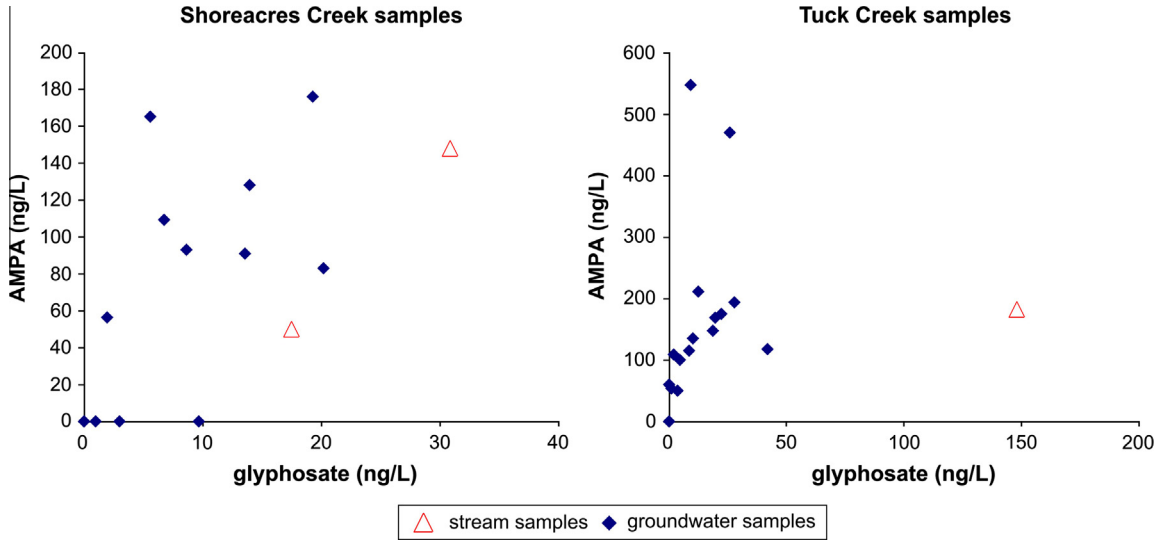

Fig. 5. Paired glyphosate and AMPA concentrations at the Burlington sites.

many or all of their detections in groundwater were from shallow wells or springs, whereas detections for deeper wells were generally rare. Furthermore, for the experimental field-studies in which monitoring depths have been reported, the groundwater in which glyphosate was detected was consistently shallow (Börjesson and Torstensson, 2000; Kjær et al., 2004, 2011). Collectively, the evidence from earlier studies indicates that detections of glyphosate residues in groundwater tend to be at (and are possibly restricted to) shallow depths, and our study indicates that only some sites have high frequency detections of glyphosate residues in shallow groundwater. This model, sporadic occurrence in shallow groundwater, is consistent with previous evidence that glyphosate residues tend to be attenuated by both microbial degradation and sorption in the subsurface, thus less likely to be found at greater depths.

Finally, our highest concentration of glyphosate was much lower than the maximum reported in both groundwater and surface in the earlier summaries that are shown in Table 1. This could be due to the relatively small number of samples and sample locations in our study compared to some others, or it may reflect a greater capacity for degradation within the commonly organic-rich riparian sediments. In contrast, the highest concentration of AMPA in our study was similar to the maximum reported for groundwater by Scribner et al. (2007).

4.3. Evidence for glyphosate as a source of AMPA in riparian groundwater

As discussed above, on a site-by-site comparative basis, the frequencies of observations of glyphosate and AMPA were strongly correlated (R^2 = 0.878) (Fig. 4), which suggests a direct relationship between these compounds. The groundwater samples from the two Burlington subcatchments have the highest percentages of samples with detections of glyphosate and AMPA, and thus were suitable for more detailed correlation analysis. This analysis was used to probe whether there is evidence that AMPA detected in these samples was derived from glyphosate or from various wastewater sources, such as detergents and other phosphonates. For this test, Spearman rank correlation coefficients (ρ) were determined for two different pairs: AMPA with glyphosate, and AMPA with the wastewater tracer acesulfame. Acesulfame was chosen as a suitable wastewater tracer given that it was found in all riparian groundwater samples in these two subcatchments. At both Shoreacres and Tuck Creek, the glyphosate and AMPA concentrations in groundwater were strongly correlated (ρ = 0.754, 0.749 respectively), whereas AMPA correlation with the wastewater tracer acesulfame at these sites was negligible (ρ = −0.258, 0.201 respectively). These results indicate that, in these catchments where AMPA is abundant in groundwater, it appears to be predominantly derived from glyphosate rather than wastewater sources.

In the Hewitts Creek catchment, the two detections of AMPA had no obvious relationship to acesulfame concentrations (not shown), which were substantial and related to the nearby septic systems (Van Stempvoort et al., 2013). But AMPA was present in the two samples that had the highest glyphosate concentrations, suggesting a directrelationship, consistent with the above results for Burlington. Evidence for the source of the AMPA at the other sites is limited. The scattered data for Dyment's Creek show no obvious relationship between AMPA and either glyphosate or acesulfame. The non-detections of both glyphosate and AMPA at Jasper support indirectly the above interpretation that AMPA in riparian groundwater is derived from glyphosate rather than wastewater. At Jasper some of the groundwater samples had elevated concentrations of acesulfame, up to 3490 ng L^{-1}, which were associated with a wastewater plume derived from the municipal wastewater treatment plant (Van Stempvoort et al., 2011, 2013). Given that AMPA is often strongly attenuated in soils (e.g., Bergström et al., 2011), it is likely less mobile in the subsurface than acesulfame. But, if wastewater was an important source of AMPA in the groundwater at Jasper, we might anticipate observing AMPA in association with the elevated concentrations of wastewater indicators (sweeteners and pharmaceuticals) reported by Van Stempvoort et al. (2013). But none of the samples with elevated acesulfame at Jasper had detections of AMPA.

5. Conclusions

The majority of the previous survey-type investigations on glyphosate residues in groundwater have focused on agricultural areas. This is the first survey study to focus on glyphosate residues in urban areas, and more specifically on riparian groundwater along urban streams. In this study, glyphosate and AMPA were detected in near-stream groundwater samples at 4 of 5 stream sites and in slightly more than 10% of the total 281 samples. This suggests that riparian groundwater containing glyphosate and AMPA may be common in some areas along urban streams and, thus,

may contribute to the pesticide load of the stream. Comparison to past studies is complicated by several factors, such that we cannot determine if urban riparian areas are more or less prone to glyphosate contamination than agricultural or other areas. However, the results of this study, in which glyphosate residues were found in shallow groundwater at most sites, are consistent with the results of some earlier studies that have indicated that glyphosate residues tend to be found in shallow groundwater. This interpretation fits with the conceptual model of limited transport of glyphosate and AMPA in the subsurface.

Much variation in the frequency of detection of glyphosate residues in riparian groundwater was observed between sites, from no detections (Jasper) to $\geqslant$60% detections (Burlington sites). Although the controls on glyphosate residue detections at these sites was not a focus of this study, some of this variation appears to be affected by pesticide application restrictions (Jasper National Park). Detection in riparian groundwater could also be affected by infiltration of stream water with elevated concentrations (Burlington sites). The location and levels of other detections did not fit consistently any obvious patterns associated with land-use. Follow-up detailed research would be required to examine the relationships between occurrences and concentrations of glyphosate and AMPA in riparian groundwater and (i) localized patterns in the timing and dosage of glyphosate applications in the immediate vicinity of the sampling locations, (ii) land-use (i.e. commercial vs. industrial vs. residential), and (iii) hydrogeological factors.

Based on consideration of a wastewater tracer (acesufame), there is no evidence for AMPA derived from wastewater sources in this study. Generally the presence of AMPA in riparian groundwater appears to be as a metabolite residue of glyphosate.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.09.095.

References

Baker N.T., Stone W.W., Wilson J.T., Meyer M.T., 2006. Occurrence and transport of agricultural chemicals in Leary Weber Ditch basin, Hancock County, Indiana, 2003–04. US Geological Survey Scientific Investigations Report 2006–5262, 44 p.

Battaglin, W.A., Meyer, M.T., Dietze, J.E., 2011. Widespread occurrence of glyphosate and its degradation product (AMPA) in US Soils, Surface Water, Groundwater, and Precipitation, 2001–2009. American Geophysical Union, Fall Meeting 2011, abstract #H44A-08.

Bergström, L., Börjesson, E., Stenström, J., 2011. Laboratory and lysimeter studies of glyphosate and aminomethylphosphonic acid in a sand and a clay soil. J. Environ. Qual. 40, 98–108.

Blackport and Associates, 2012. Hydrogeologic Framework Technical Memorandum #1, Draft to The City of Barrie, Ontario, Canada; 2012. (Submitted for publication).

Blanchoud, H., Moreau-Guigon, E., Farrugia, F., Chevreuil, M., Mouchel, J.M., 2007. Contribution by urban and agricultural pesticide uses to water contamination at the scale of the Marne watershed. Sci. Total Environ. 375, 168–179.

Borggaard, O.K., 2011. Does phosphate affect soil sorption and degradation of glyphosate? – a review. Trends Soil Sci. Plant Nutr. 2, 17–27.

Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching to ground water and surface waters: a review. Pest Manage. Sci. 64, 441–456.

Börjesson, E., Torstensson, L., 2000. New methods for determination of glyphosate and (aminomethyl)-phosphonic acid in water and soil. J. Chromatogr. A 886, 207–216.

Botta, F., Lavison, G., Couturier, G., Alliot, F., Moreau-Guigon, E., Fauchon, N., Guery, B., Chevreuil, M., Blanchoud, H., 2009. Transfer of glyphosate and its degradate AMPA to surface waters through urban sewerage systems. Chemosphere 77, 133–139.

Buerge, I.J., Buser, H.R., Kahle, M., Müller, M.D., Poiger, T., 2009. Ubiquitous occurrence of the artificial sweetener acesulfame in the aquatic environment: an ideal chemical marker of domestic wastewater in groundwater. Environ. Sci. Technol. 43, 4381–4385.

Coupe, R.H., Kalkhoff, S.J., Capel, P.D., Gregoire, C., 2012. Fate and transport of glyphosate and aminomethylphosphonic acid in surface waters of agricultural basins. Pest Manage. Sci. 68, 16–30.

Crowe, A.S., Leclerc, N., Struger, J., Brown, S., 2011. Application of a glyphosate-based herbicide to Phragmites australis: impact on groundwater and near-shore lake water at a beach on Georgian Bay. J. Great Lakes Res. 37, 616–624.

EBA Engineering Consultants Ltd., 2003. Preliminary Hydrogeological Study, Wastewater Treatment Plant, Jasper, Alberta. Draft report to Earth Tech (Canada) Inc., January 2003. Edmonton, Alberta, Canada.

Feng, J.C., Thompson, D.G., 1990. Fate of glyphosate in a Canadian forest watershed. 2. Persistence in foliage and soils. J. Agric. Food Chem. 1990 (38), 1118–1125.

Giesy, J.P., Dobson, S., Solomon, K.R., 2000. Ecotoxicological risk assessment for roundup® herbicide. Rev. Environ. Contam. Toxicol. 167, 35–120.

Hanke, I., Wittmer, I., Bischofberger, S., Stamm, C., Singer, H., 2010. Relevance of urban glyphosate use for surface water quality. Chemosphere 81, 422–429.

Hoogeveen, R.J.A., Visser, A., Raat, K.J., 2010. PESTO, a risk assessment of pesticide use on groundwater quality in the Chalk aquifer in the province of Limburg, the Netherlands. Abstract no. 339, Groundwater Quality Sustainability, XXXVIII International Congress of the International Association of Hydrogeologists, Krakow, Poland, 12–17 September 12–17, 2010.

Horth, H., Blackmore, K., 2009. Survey of Glyphosate and AMPA in Groundwaters and Surface Waters in Europe. Report by WRc plc, Swindon, Swindon, Wiltshire, United Kingdom. No.: UC8073.02, November 2009.

Kjær, J., Olsen, P., Barlebo, H.C., Juhler, R.K., Plauborg, F., Grant, R., Gudmundsson, L., Brüsch, W., The Danish Pesticide Leaching Assessment Programme. Monitoring results May 1999–June 2003, 2004. Geological Survey of Denmark and Greenland, Copenhagen, Denmark.

Kjær, J., Olsen, P., Ullum, M., Grant, R., 2005. Leaching of glyphosate and aminomethylphosphonic acid from Danish agricultural field sites. J. Environ. Qual. 34, 608–620.

Kjær, J., Ernsten, V., Jacobsen, O.H., Hansen, N., de Jonge, L.W., Olsen, P., 2011. Transport modes and pathways of the strongly sorbing pesticides glyphosate and pendimethalin through structured drained soils. Chemosphere 84, 471–479.

Kolpin, D.W., Thurman, E.M., Lee, E.A., Meyer, M.T., Furlong, E.T., Glassmeyer, S.T., 2006. Urban contributions of glyphosate and its degradate AMPA to streams in the United States. Sci. Total Environ. 354, 191–197.

Landry, D., Dousset, S., Fournier, J.-C., Andreux, F., 2005. Leaching of glyphosate and AMPA under two soil management practices in Burgundy vineyards (Vosne-Romanée, 21-France). Environ. Pollut. 138, 191–200.

Lathrop T.R., 2006. Environmental setting of the Sugar Creek and Leary Weber Ditch basins, Indiana, 2002–04.US Geological Survey Scientific Investigations Report 2006–5170, 27 p.

Louis Berger Group and Greenland International, Inc., 2006. Pollutant Target Loads: Lake Simco and Nottawasaga River Basins Report, June 2006. <http://www.lsrca.on.ca/reports/acs.php>.

Mamy, L., Gabrielle, B., Barriuso, E., 2008. Measurement and modelling of glyphosate fate compared with that of herbicides replaced as a result of the introduction of glyphosate-resistant oilseed rape. Pest Manage. Sci. 64, 262–275.

Municipality of Jasper. 2010. Use of Herbicides Policy, D-002. Adopted June 8, 2010. <http://jasper-alberta.com/default.aspx?pageid=477>.

Roy, J.W., Bickerton, G., 2010. Proactive screening approach for detecting groundwater contaminants along urban streams at the reach-scale. Environ. Sci. Technol. 44, 6088–6094.

Roy, J.W., Bickerton, G., 2012. Toxic groundwater contaminants: an overlooked contributor to urban stream syndrome? Environ. Sci. Technol. 46, 729–736.

Sanchís, J., Kantiani, L., Llorca, M., Rubio, F., Ginebreda, A., Fraile, J., Garrido, T., Farré, M., 2012. Determination of glyphosate in groundwater samples using an ultrasensitive immunoassay and confirmation by on-line solid-phase extraction followed by liquid chromatography coupled to tandem mass spectrometry. Anal. Bioanal. Chem. 402, 2335–2345.

Scribner, E.A., Battaglin, W.A., Gilliom, R.J., Meyer, M.T., 2007. Concentrations of glyphosate, its degradation product, aminomethylphosphonic acid, and glufosinate in ground- and surface-water, rainfall, and soil samples collected in the United States, 2001–06: US Geological Survey Scientific Investigations Report 2007–5122, 111 p.

Simonsen, L., Fomsgaard, I.S., Svensmark, B., Spliid, N.H., 2008. Fate and availability of glyphosate and AMPA in agricultural soil. J. Environ. Sci. Health B 43, 365–375.

Smith, N.J., Martin, R.C., Croix, R.G., 1996. Levels of herbicide glyphosate in well water. Bull. Environ. Contam. Toxicol. 57, 759–765.

Source Water Protection Halton–Hamilton Region, 2008. Report on Conceptual Understanding of Water Budget, Conservation Halton Watershed. Draft Final, Version 3.96, April 7, 2008.

Struger, J., Van Stempvoort, D.R., Brown, S.J., 2013. Sources of aminomethylphosphonic acid (AMPA) in urban and rural catchments in Ontario: glyphosate or other phosphonates in wastewater. Water Qual. Res. J. Can. (in preparation).

Thorling, L., Hansen, B., Langtofte, C., Brüsch, W., Møller, R.R., Mielby, S. og Højberg, A.L., 2010. Grundvand. Status og udvikling 1989–2009. Techical report, De Nationale Geologiske Undersøgelser for Danmark og Grønland (GEUS) 2010. (in Danish).

Van Stempvoort, D.R., Brown, S, Graham, G., Jiang, Y., Spoelstra, J., 2008. Glyphosate in shallow groundwater in Canada. In: Proceedings, GeoEdmonton'08, 61st Canadian Geotechnical Conference and 9th Joint CGS/IAH-CNC Groundwater Conference, Edmonton, AB, Sept. 21–24, 2008, pp. 1541–1547.

Van Stempvoort, D.R., Roy, J.W., Brown, S.J., Bickerton, G., 2011. Artificial sweeteners as potential tracers in groundwater in urban environments. J. Hydrol. 401, 126–133.

Van Stempvoort, D.R., Roy, J.W., Grabuski, J., Brown, S.J., Bickerton, G., Sverko, E., 2013. An artificial sweetener and pharmaceutical compounds as co-tracers of urban wastewater in groundwater. Sci. Total Environ. 461–462, 348–359.

Vereecken, H., 2005. Mobility and leaching of glyphosate: a review. Pest Manage. Sci. 61, 1139–1151.

Winter, T.C., Harvey, J.W., Franke, O.L., Alley, W.M., 1998. Ground water and surface water – a single resource. US Geological Survey Circular 1139, 79 p.