



Glyphosate in shallow groundwater in Canada

Dale R. Van Stempvoort, Susan Brown, Gwyn Graham, Yefang Jiang and John Spoelstra

NWRI RESEARCH SUMMARY

Plain language title

Occurrence of trace levels of the herbicide glyphosate in shallow groundwater in Canada

What is the problem and what do scientists already know about it?

Glyphosate is used widely as a non-selective herbicide world-wide. It's behavior in soil and it's toxicity (generally low) are quite well known; it is considered to have a low potential to leach to groundwater. However it's fate in the environment needs to be monitored. Evidence is emerging that glyphosate can sometimes leach to groundwater, though reported concentrations in groundwater have been low, and the majority of analyses have indicated no detection in groundwater.

Why did NWRI do this study?

To address the information gap on the potential occurrence of glyphosate in shallow groundwater in Canada.

What were the results?

Thirty-two percent of shallow groundwater samples were found to contain low, detectable quantities of glyphosate (0.02-0.05 μ g/L).

How will these results be used?

These results are some of the first available published analyses of glyphosate in groundwater in Canada. It will be useful for researchers and regulators of pesticide use in Canada to review these results with respect to their current conceptual and numerical models of glyphosate leaching in Canada.

Who were our main partners in the study?

Saskatchewan Watershed Authority, Agriculture Canada, Prince Edward Island Department of Environment, Energy and Forestry University of Waterloo.

Abstract

An exploratory investigation was conducted to assess whether the widely-used herbicide glyphosate is present at detectable concentrations in shallow groundwater in Canada. An analytical method that combines ion chromatography with tandem mass spectrometry was developed to measure glyphosate at trace concentrations (< 0.1 μ g/L). Samples of shallow groundwater were collected from readily available rural monitoring sites in British Columbia, Saskatchewan, Ontario, New Brunswick and Prince Edward Island. Thirty-two percent of groundwater samples were found to

contain detectable quantities of glyphosate, at concentrations ranging from 0.02-0.05 $\mu g/L$.

Glyphosate dans les eaux souterraines peu profondes

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Sommaire des recherches de l'INRE

Titre en langage clair

Présence de l'herbicide glyphosate à l'état de trace dans les eaux souterraines peu profondes au Canada.

Quel est le problème et que savent les chercheurs à ce sujet?

L'utilisation du glyphosate, un herbicide non sélectif, est très répandue à l'échelle mondiale. Son action dans le sol et sa toxicité (faible, en général) sont plutôt bien connues. On considère également que son potentiel de lixiviation vers les eaux souterraines est faible. Toutefois, il est nécessaire de surveiller son devenir dans l'environnement. Les analyses tendent à démontrer que le glyphosate peut parfois rejoindre les eaux souterraines, même si les concentrations mesurées demeurent faibles. Néanmoins, dans la majorité des cas, la présence de glyphosate n'a pas été décelée dans ces eaux.

Pourquoi l'INRE a-t-il effectué cette étude?

Pour combler le manque de renseignements sur la présence possible de glyphosate dans les eaux souterraines peu profondes au Canada.

Quels sont les résultats?

Trente-deux pour cent des échantillons prélevés dans les eaux souterraines peu profondes avaient une faible concentration de glyphosate (0.02 à 0.05 µg/L).

Comment ces résultats seront-ils utilisés?

Ces résultats comptent parmi les premières analyses publiées sur le glyphosate dans les eaux souterraines au Canada. L'examen de ces résultats permettra aux chercheurs et aux autorités de réglementation qui s'intéressent à l'utilisation des pesticides au Canada de mettre à jour leurs modèles conceptuels et numériques sur la lixiviation du glyphosate.

Quels étaient nos principaux partenaires dans cette étude?

Saskatchewan Watershed Authority, Agriculture Canada, ministère de l'Environnement, de l'Énergie et des Forêts de l'Île-du-Prince-Édouard, Université de Waterloo.

Résumé

Une phase d'exploration a eu lieu afin d'évaluer si l'herbicide glyphosate, dont l'utilisation est très répandue, était présent à des concentrations détectables dans les eaux souterraines peu profondes au Canada. Une méthode d'analyse combinant la chromatographie d'échange d'ions et la spectrométrie de masse en tandem a été

élaborée afin de mesurer les concentrations de glyphosate à l'état de trace (< 0,1 $\mu g/L$). Des échantillons d'eaux souterraines peu profondes ont été prélevés à des sites de surveillance d'accès facile dans des milieux ruraux de la Colombie-Britannique, de la Saskatchewan, de l'Ontario, du Nouveau-Brunswick et de l'Île-du-Prince-Édouard. Trente-deux pour cent des échantillons prélevés avaient des concentrations détectables de glyphosate, qui variaient de 0,02 à 0,05 $\mu g/L$.

Glyphosate in shallow groundwater in Canada

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ABSTRACT

An exploratory investigation was conducted to assess whether the widely-used herbicide glyphosate is present at detectable concentrations in shallow groundwater in Canada. An analytical method that combines ion chromatography with tandem mass spectrometry was developed to measure glyphosate at trace concentrations (< 0.1 µg/L). Samples of shallow groundwater were collected from readily available rural monitoring sites in British Columbia, Saskatchewan, Ontario, New Brunswick and Prince Edward Island. Thirty-two percent of groundwater samples were found to contain detectable quantities of glyphosate, at concentrations ranging from 0.02-0.05 µg/L.

RÉSUMÉ

Une recherche exploratoire a été conduite pour évaluer si le glyphosate employé couramment d'herbicide est présent aux concentrations discernables en eaux souterraines peu profondes au Canada. Une méthode analytique qui utilise la chromatographie d'ion/spectrométrie de masse tandem a été développée pour mesurer le glyphosate aux concentrations de trace (< 0.1 µg/L). Des échantillons d'eaux souterraines peu profondes ont été rassemblés des emplacements de surveillance ruraux aisément disponibles Colombie britannique, Saskatchewan, Ontario, au Nouveau Brunswick et île de prince Edouard. Trente deux pour cent des échantillons d'eaux souterraines se sont avérés pour contenir des quantités discernables de glyphosate, aux concentrations s'échelonnant de 0.02-0.05 µg/L.

1 INTRODUCTION

Glyphosate (C₃H₈NO₅P) was introduced as a nonselective herbicide in 1974, and it is now widely used in Canada and worldwide (Vereecken 2005; Kolpin et al. 2006). Glyphosate is a weak acid, soluble as an anion in water (Borgaard and Gimsing, 2008). The health-based Guideline for Canadian Drinking Water Quality is 280 μg/L (Health Canada 1987,1995), and the Canadian Water Quality Guideline for Protection of Aquatic Life is 65 µg/L (Trotter et al. 1990). Glyphosate has been reported to be biodegraded readily in soils and surface waters, with reported half lives in soil typically on the order of days to months (World Health Organization 2005). A metabolic product of glyphosate degradation by microorganisms, aminomethylphosphonic acid (AMPA), is sometimes found in environmental samples. The toxicity of AMPA is considered to be similar to that of glyphosate (Borggaard and Gimsing, 2008).

Studies have shown that glyphosate sorbs readily to soils, and that both glyphosate and AMPA sorb to mineral surfaces, such as iron oxides (Borggaard and Girnsing 2008; Barja and dos Santos Afonso 2005). This may result in low to negligible biodegradation of the sorbed glyphosate (Sørensen et al. 2006). Given glyphosate's tendency to be either degraded or sorbed in soils, it has generally been assumed to have a low potential to leach to groundwater (Vereecken 2005; Borggaard and Girnsing 2008). However, some studies have detected glyphosate in shallow groundwater (Vereecken 2005; see Section 1.2).

The purpose of this study was to conduct an exploratory investigation to see whether glyphosate has impacted shallow groundwater at detectable concentrations in various regions of Canada.

1.1 Previous Surveys of Glyphosate in Environmental Samples in Canada

Humphries et al. (2005) reported the detection of glyphosate in most Alberta surface water samples collected from wetlands and streams in 2002. The concentrations were generally close to the detection limit (0.2 \Box g/L), and ranged up to 6.1 \Box g/L. Humphries et al. (2005) also reported detectable glyphosate residues in atmospheric deposition at three locations in Alberta, ranging up to 1.2, 1.6 and 5.6 \Box g/L respectively.

In a recent survey conducted in southern Ontario, Struger et al. (2008) found both glyphosate and AMPA were present in a large percentage of approximately 500 surface water samples. Glyphosate concentrations ranged up to 40.8 µg/L, and AMPA concentrations ranged up to 66 µg/L.

Wan et al. (2006) found that glyphosate was common in surface water sampled from ditches flowing to tributaries of the Lower Fraser River of British Columbia, averaging 6 μ g/L.

1.2 Reports of Glyphosate Detections in Groundwater

Globally, reported detections of glyphosate in groundwater are very sparse. Scribner et al. (2007)

Researchers in Denmark (Kjær et al. 2004) found that glyphosate did not leach readily through a sandy soil profile to groundwater at one site, but that it was mobilized through macropores in fractured clay to tile drains at three of four "loamy soil" sites. At these sites, detectable concentrations of glyphosate in groundwater were less than 0.1 $\Box g/L$ (Kjaer et al. 2004).

Brüsch (2006) reported the detection of glyphosate and AMPA in small private groundwater supply systems in a glacial till-dominated agricultural region in Denmark. These samples were collected in 2001-2002 and the detectable glyphosate and AMPA concentrations ranged between approximately 0.01 and 1 □g/L.

At least one previous study has reported glyphosate in groundwater in Canada. At an electrical substation site in Newfoundland, where glyphosate was used to clear vegetation, it was detected in groundwater at concentrations ranging from 7 to 45 μ g/L (Smith et al. 1996).

2 SAMPLING AND ANALYSIS METHODS

Samples of shallow (< 60 m below ground) groundwater were obtained at readily available sites in various regions of Canada (See following Sections 4 to 8). Peristaltic pumps were used to sample dedicated monitoring wells, following standard techniques. Domestic wells were sampled using the dedicated submersible pumps for these water supplies. Some of these domestic wells had in-well or in-line treatment systems for nitrate or hardness.

Following an earlier study of other pesticides (Wood and Anthony, 1997), groundwater discharging as springs was sampled at selected sites in Saskatchewan. Tile drains were sampled at two farm sites in Ontario.

All samples were collected in high density polyethylene bottles and filtered in the field (0.2µm SFCA/PF syringe filters, Corning Inc., Corning, NY, USA). Headspaces in sample bottles were minimized, and samples were immediately placed on ice or cooler packs and stored at 4°C prior to analysis.

A new method (Brown et al. in prep.) was developed specifically for this study, to analyze glyphosate in

groundwater, together with its degradation product, AMPA. Samples were re-filtered and analyzed using suppressed ion chromatography (IC) coupled to a tandem mass spectrometer (MS/MS). Separation was performed using a Dionex (Sunnyvale, CA, USA) 2500 IC system on a Dionex IONPAC® AS20 analytical column (2 x 250 mm). The IC was interfaced to an API 2000 MS/MS (MDS Sciex, ON, Canada), and operated in the negative electrospray ionization (ESI) mode. Isotope labeled glyphosate (98%, 100 mg/L 1,2-13C,15N) was used as an internal standard (IS) to account for matrix effects. Detection limits were as follows: glyphosate 0.02 µg/L, AMPA 0.2 µg/L.

3 OVERALL RESULTS: GLYPHOSATE DETECTION IN GROUNDWATER

Glyphosate was detected in 32% (23 of 72) of the groundwater samples (combined from all sites, excluding samples from springs and tile drains), at concentrations ranging from 0.02 to 0.05 \Box g/L. Five of the groundwater samples had trace levels of glyphosate, below the method detection limit of 0.02 \Box g/L.

Only trace detections (less than the method detection limit of 0.2 μ g/L) of AMPA were found in two groundwater samples. This may be a reflection of the higher detection limit of AMPA, by an order of magnitude, compared to glyphosate.



Figure 1. Maps showing general locations of sampling sites in British Columbia (BC), Saskatchewan (SK), Ontario (ON), New Brunswick (NB) and Prince Edward Island (PEI).

4 GLYPHOSATE IN THE ABBOTSFORD AQUIFER, BRITISH COLUMBIA

The Abbotsford-Sumas aquifer is a surficial deposit of coarse-grained glaciofluvial sediments that straddles the

international border in southern British Columbia and Washington State. The land-use is largely agricultural. In October 2007, groundwater was sampled at 10 sites and from a total of 20 monitoring wells, all completed in the Abbotsford-Sumas aquifer in British Columbia. This included samples from multilevel nests of 2 or 3 wells at some of these sites.

Glyphosate was observed in groundwater sampled from 4 of the 10 sites, and overall it was found at depth ranges between about 10 to 30 m below ground (Fig. 2). At two multilevel sites, the glyphosate concentrations were observed to decrease with increasing depth (Fig 2). But at two other sites with multilevel wells, glyphosate concentrations increased with depth or it was only non-detectable in the shallowest well (Fig. 2). There were no detections of AMPA.

These initial results appear to indicate that in some zones, glyphosate has penetrated to depths of at least 30 m below ground in the Abbotsford-Sumas aquifer. The nonuniformity of the results suggests that there are various factors that control the distribution of glyphosate in this aquifer. A more detailed analysis should include information on land use, recharge areas and the groundwater flow system in order to discern the distribution of glyphosate concentrations.

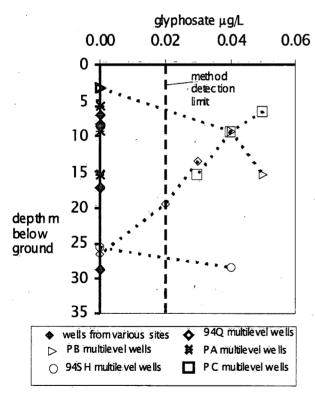


Figure 2. Glyphosate concentrations versus well depths (middle of screen intervals) for October 2007 samples from the Abbotsford aquifer, British Columbia.

GLYPHOSATE IN OBSERVATION WELLS AND SPRINGS IN SASKATCHEWAN

5.1 Observation Wells

Eight shallow groundwater wells that were selected from the provincial monitoring network in Saskatchewan were sampled in October/November 2007. The screens of these wells are installed in surficial sand aquifers (6 wells), in surficial silt (1 well), or beneath stratified silt, clay and sand deposits (1 well).

Of the four deepest wells that were sampled, three had no detectable glyphosate (Fig. 3). In contrast, all four of the wells completed at depths less than 10 m below ground had detectable glyphosate (Fig. 3). These results, though based on a small number of samples at widely scattered sites, suggest that depth is an important factor controlling the presence/absence of glyphosate in shallow groundwater in Saskatchewan.

Trace detections of AMPA (less than the method detection limit of $0.2 \mu g/L$) were found in two wells.

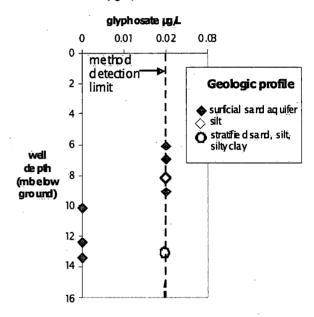


Figure 3. Glyphosate concentrations versus monitoring well depths (middle of screen intervals) for Saskatchewan sites sampled in Oct/Nov 2007.

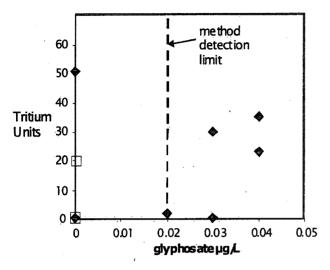


Figure 4: Glyphosate concentrations for Saskatchewan spring samples (Oct-Nov, 2007), versus tritium activities for same springs (1990s) reported by Wood and Anthony (1997). Trace levels below the method detection limit are plotted as open squares.

The deepest well with detectable glyphosate is screened at a depth of approximately 13 m below ground (Fig. 3). The stratified sediments above the screen interval in this well include 8.5 m of sand, 2.5 m of silty clay and 2 m of silt. Perhaps glyphosate has been mobilized through fracture pores in the clay and silt units at this site. As noted in the introduction, such a process was found to be important at some agricultural sites studied recently in Denmark (Kjær et al., 2004).

5.2 Springs

Of nine springs in Saskatchewan that were sampled in October/November 2007, five had measurable detections of glyphosate, two had trace levels (below method detection limit), and two had no detectable glyphosate (Fig. 4). None of the spring samples had detectable concentrations of AMPA. As shown by a comparison to earlier measurements of tritium activities for these springs (Fig. 4), the overall mean ages (i.e. time since recharge) of the water in these springs is variable. Tritium activities do not seem to be strongly correlated with the detection of glyphosate.

5.3 Potential Sources

Based on the observed land uses in the vicinity of the sampling sites, the glyphosate detections in groundwater/discharge from wells and springs in Saskatchewan do not appear to be related only to local sources of the herbicide. Consistent with the observations of Wood and Anthony (1997), who analyzed other herbicides (atrazine, simazine), in a larger array of spring samples in the Saskatchewan in the early 1990s, some of the spring samples that had detectable glyphosate in 2007 were in areas with limited herbicide

use. The same applies to some of the wells sampled in 2007 with detectable glyphosate.

Wood and Anthony (1997) suggested an atmospheric deposition origin to account for herbicide detections in springs discharging from aquifers that were located in areas with limited herbicide use. An atmospheric deposition source is a plausible explanation for at least some of the glyphosate detections in groundwater in Saskatchewan in 2007. Such an interpretation is supported by recent glyphosate detection in atmospheric deposition at three locations in Alberta, which borders Saskatchewan, (Humphries et al., 2005). The atmospheric deposition concentrations ranged up to several □g/L, which is perhaps consistent with sub □g/L levels of glyphosate detected in shallow groundwater in Saskatchewan, derived from atmospheric deposition.

6 GLYPHOSATE IN SHALLOW GROUNDWATER IN ONTARIO

In November 2007, groundwater samples were taken from 7 shallow monitoring wells (0.75 to 2 mbgs) at an agricultural watershed located within the Region of Waterloo in southern Ontario (Site A). Samples of tile drainage water were also collected at this site in January 2008 and at another agricultural site in Wellington County, southern Ontario (Site B), in December 2007 (Table 1). Tile discharge at these sites consists of shallow groundwater that is captured by tiles when the water table is high. Both sites are dominated by silt/clay rich soils derived from glacial till. A Drive-Point Profiler (Solinst Canada Ltd.) was used to collect 4 samples of groundwater from a surficial sand aquifer at a site in Norfolk County in November 2007.

Glyphosate and AMPA were not detected in any of the 7 shallow wells at Site A. However, glyphosate was detected in 6 of 7 samples of tile drainage at the same site in January 2008 (Table 1), sometimes together with AMPA. Both were also found, but more sporadically and at lower concentrations in tile drainage from Site B (Table 1). Although the tile drainage is predominantly composed of shallow groundwater at these sites, we cannot rule out the possibility of a small surface water contribution derived from macropore flow. As a result, some glyphosate detected in tile discharge might be derived from ponded water on the surface of the fields, where glyphosate concentrations are expected to be higher.

Of the 4 Drive-Point Profiler groundwater samples collected in Norfolk County, one had a trace of glyphosate, the others had no detectable glyphosate.

Overall this small suite of samples from Ontario indicated no significant presence of glyphosate in the shallow groundwater, but low levels of glyphosate and AMPA were found in the majority of tile drainage samples at two sites. A larger number of samples would be required to infer any patterns with respect to glyphosate detection in groundwater in Ontario.

Table 1. Concentrations of glyphosate and its metabolite AMPA in samples collected from tile drains at two agricultural sites in southern Ontario.

	glyphosate	AMPA
	μġ/Ĺ	μg/L
Site A		
tile drain	0.13	0.00
tile drain	0.10	n.d.
tile drain	0.06	n.d.
tile drain	n.d.	n.d.
tile drain	6.61	2.80
Site B		
tile drain	n.d.	n.d.
tile drain	n.d.	n.d.
tile drain	n.d.	0.11

7 GLYPHOSATE IN FRACTURED BEDROCK IN NEW BRUNSWICK

In October 2007, samples were taken from 11 domestic wells and 3 monitoring wells in the Black Brook watershed within the potato belt of northwest New Brunswick. The watershed covers an area of 14.5 km². about 38% of which is under potato production every year (Chow et al, 1999). Fields are underlain by 3-5 m of glacial drift (sandy loam or loam) above late Ordovician and early Silurian shale, slate and limestone (Wilson, 1990). The bedrock units are folded and heavily fractured in outcrops in the study area. The domestic wells that were sampled are open boreholes in the fractured bedrock, which forms an aquifer. The reported open hole intervals (below casing) for these domestic wells are typically within the range 6 to 40 m below ground. The 3 monitoring wells are also installed in the bedrock, and they have intake intervals between 24.8 and 29 m below ground.

Glyphosate was detected in at least one sample from 8 of the 11 domestic wells sampled (several were sampled twice). Glyphosate was also detected in all 3 of the monitoring wells. In contrast, there were no detections of AMPA in any of the wells.

7.1 Evidence for Downward Transport of Glyphosate in the Fractured Bedrock

Results specifically for the 3 monitoring wells suggest that the fractured bedrock aquifer in New Brunswick is vulnerable to contamination by low levels of glyphosate, to depths of at least 30 m below ground. Perhaps the downward migration of glyphosate to such depths is facilitated by rapid flow through the fracture network.

Rapid downward transport of glyphosate may be related to the relatively low porosity of this bedrock. In support of this interpretation, recent monitoring data indicated that the water table in the bedrock responded

quickly to snow melt infiltration, rising about 4.4-5.4 m within a day (Y. Jiang, unpublished data).

Overall, the high number of wells with detectable glyphosate (11/14) might imply quick infiltration, short groundwater residence times, or frequent/high-rate uses of glyphosate in this intensively farmed watershed, or a combination of these factors.

8 GLYPHOSATE IN THE SANDSTONE AQUIFER OF PRINCE EDWARD ISLAND

The "sandstone aquifer" in Prince Edward Island is a terrestrial sandstone formation, consisting of a sequence of Permo-Carboniferous red beds of unknown thickness (van de Poll 1981) that underlies the entire province. Sixteen samples of shallow groundwater were collected in November 2007 from domestic wells completed in the sandstone aquifer. Detailed information was not available regarding the well construction, or water treatment in these wells. It appears that all 16 wells were completed as open holes in the bedrock, likely at depth intervals (below casing) ranging between 12 and 60 m below ground.

Glyphosate was detected in only 2 of 16 samples from the sandstone aquifer at concentrations of 0.04 and 0.05 µg/L. There were no detections of AMPA. These preliminary results suggest that glyphosate has a relatively small impact on the sandstone aquifer in Prince Edward Island. This interpretation must be tempered by the fact that details regarding the water producing zones and treatment systems in the wells were not available.

It would be useful to investigate the role of matrix diffusion in the attenuation of glyphosate in the sandstone aquifer. An earlier study reported that this process has played an important role in the attenuation of another pesticide, aldicarb in this aquifer (Jackson et al., 1990). The sorption of glyphosate by iron oxides in this aquifer and in the overlying soil may be significant, given that these minerals are relatively abundant in the reddish soil and "red beds" of Prince Edward Island (c.f., Balsam et al., 1995).

9 SUMMARY AND PRELIMINARY CONCLUSIONS

This exploratory study detected the herbicide glyphosate in shallow groundwater in some regions of Canada, albeit at low concentrations, well below the Canadian guidelines for drinking water and for the protection of aquatic life. Detectable concentrations found in shallow groundwater sampled from wells (0.02 to 0.05 μ g/L) were significantly lower than the maximum concentrations reported in surface water in Canada in recent studies (Humphries et al., 2005; Wan et al., 2006; Struger et al., 2008).

Glyphosate was found in fractured bedrock aquifers and in surficial sand aquifers. In a small number of samples from Saskatchewan detectable glyphosate was largely restricted to the upper 10 m below ground in surficial sand aquifers. In contrast, samples from the Abbotsford-Sumas aquifer in British Columbia indicated

detectable glyphosate to depths of 30 m. Glyphosate was commonly detected and found at depths up to 30 m in a shale/limestone aquifer in New Brunswick, but was rare in samples from a sandstone aquifer in Prince Edward Island.

Nearly all samples had no detectable AMPA, possibly reflecting an order of magnitude higher detection limit for AMPA, compared to glyphosate.

More data is required to identify the factors controlling the occurrence or absence of detectable glyphosate in shallow groundwater in Canada, and to elucidate the potential role of atmospheric deposition as a source of glyphosate in shallow groundwater.

There appear to be no data on temporal trends of glyphosate in shallow groundwater in Canada. This is an important science gap given that (1) glyphosate has only been in use for past few decades, (2) that it tends to sorb to soil/mineral particles, and (3) the half life of glyphosate in various groundwater environments in Canada is unknown.

In order to make conclusive inferences about how land use in recharge areas, attenuation processes and other factors affect the occurrence and concentrations of gylphosate in groundwater, case studies would be required on groundwater flow systems that have detectable glyphosate.

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