Available online at www.sciencedirect.com

SCIENCE DIRECT®

Science of the Total Environment 354 (2006) 191–197

Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Urban contributions of glyphosate and its degradate AMPA to streams in the United States

Dana W. Kolpin[a,*], E. Michael Thurman[b], Edward A. Lee[b], Michael T. Meyer[b], Edward T. Furlong[c], Susan T. Glassmeyer[d]

[a]U.S. Geological Survey, 400 S. Clinton Street, Iowa City, Iowa 52244, USA
[b]U.S. Geological Survey, 4821 Quail Crest Place, Lawrence, Kansas 66049, USA
[c]U.S. Geological Survey, Box 25406, MS407, Denver, Colorado 80225, USA
[d]U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, 26 W. Martin Luther King Dr., Cincinnati, OH 45268

Received 28 October 2004; accepted 31 January 2005
Available online 16 March 2005

Abstract

Glyphosate is the most widely used herbicide in the world, being routinely applied to control weeds in both agricultural and urban settings. Microbial degradation of glyphosate produces aminomethyl phosphonic acid (AMPA). The high polarity and water-solubility of glyphosate and AMPA has, until recently, made their analysis in water samples problematic. Thus, compared to other herbicides (e.g. atrazine) there are relatively few studies on the environmental occurrence of glyphosate and AMPA. In 2002, treated effluent samples were collected from 10 wastewater treatment plants (WWTPs) to study the occurrence of glyphosate and AMPA. Stream samples were collected upstream and downstream of the 10 WWTPs. Two reference streams were also sampled. The results document the apparent contribution of WWTP effluent to stream concentrations of glyphosate and AMPA, with roughly a two-fold increase in their frequencies of detection between stream samples collected upstream and those collected downstream of the WWTPs. Thus, urban use of glyphosate contributes to glyphosate and AMPA concentrations in streams in the United States. Overall, AMPA was detected much more frequently (67.5%) compared to glyphosate (17.5%).

Keywords: Glyphosate; Streams; United States

1. Introduction

Glyphosate (*N*-Phosphonomethyl glycine) is a non-selective, broad spectrum herbicide that is the most widely used herbicide in the world (Baylis, 2000; Woodburn, 2000). Dramatic increases in the agricultural use of glyphosate occurred in 1997

* Corresponding author. Tel.: +1 319 358 3614; fax: +1 319 358 3606.
E-mail address: dwkolpin@usgs.gov (D.W. Kolpin).

0048-9697/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2005.01.028

corresponding to the introduction of genetically altered glyphosate-resistant crops (such as corn, cotton, and soybeans) through a glyphosate-resistant protein product isolated from a naturally occurring gene that was cloned and expressed in the target crops (Padgette et al., 1995; Giesy et al., 2000; Pline et al., 2001). Microbial degradation of glyphosate produces aminomethyl phosphonic acid (AMPA), the primary glyphosate transformation product (Rueppel et al., 1977; Forlani et al., 1999). AMPA, however, is also formed by the degradation of phosphonic acids in detergents (Skark et al., 1998). The chemical and toxicological properties of glyphosate appear to be well documented (Carlisle and Trevors, 1988; Duke, 1988; Malik et al., 1989; Tate et al., 1997; WHO, 1994; Giesy et al., 2000), with multiple studies finding that glyphosate-based formulations are more toxic to aquatic organisms than glyphosate itself (Folmar et al., 1979; Mann and Bidwell, 1999; Servizi et al., 1987; Tsui and Chu, 2003; Tsui and Chu, 2004) due to surfactants present in the technical formulations. AMPA is thought to be equal or less toxic than glyphosate (Carlisle and Trevors, 1988; Giesy et al., 2000). Research has shown that low levels of glyphosate are frequently detected in the urine of farm workers shortly after a glyphosate application (Acquavella et al., 2004).

The high polarity and water-solubility of glyphosate and AMPA (Rubio et al., 2003; Skark et al., 1998; Veiga et al., 2001) makes their analysis in water samples problematic. Thus, compared to other herbicides (e.g. atrazine) there are relatively few studies on the environmental occurrence of glyphosate and AMPA, particularly given its extensive worldwide use. Recent research, however, has documented the environmental occurrence of glyphosate and AMPA associated with use on crops (Araujo et al., 2003; Battaglin et al., 2005; Fomsgaard et al., 2003; Scribner et al., 2003), forests (Veiga et al., 2001; Thompson et al., 2004), and railway tracks (Skark et al., 1998). Little data appears to exist on the environmental occurrence of glyphosate and AMPA derived from the extensive urban use of glyphosate.

The purpose of this study was to provide a better understanding of the potential contribution of glyphosate and AMPA to streams derived from the urban use of this herbicide. This paper describes the analytical results of 29 stream samples and 11 treated effluent samples collected across the United States during 2002.

2. Methods

This study focused on 10 WWTPs across the United States (Fig. 1). Site selection was primarily based on results of previous research activities (Kolpin et al., 2002, 2004b). Most sample sets consisted of one upstream, one effluent, and two downstream samples (DS1=sites proximal to WWTP discharge and DS2=sites more distal from WWTP discharge) (Glassmeyer et al., 2003). The network consisted of 40 sampling sites: eight upstream samples (one site had no upstream sampling point and one sample at an upstream site was not able to be analyzed), 11 WWTP effluent samples (one site had two WWTP discharge points), 19 downstream samples (one sample at a downstream site was not able to be analyzed). In addition, two reference sites were sampled (Fig. 1) in areas anticipated to have little glyphosate use because of limited human activity. The 10 WWTP locations represent a variety of climatic conditions, population densities, stream sizes, and treatment practices (Table 1). The distances from the treatment plants to the upstream and downstream locations vary, due to sampling accessibility.

All samples were collected by U.S. Geological Survey personnel using consistent protocols and procedures designed to obtain a representative water sample using standard depth and width integrating

Fig. 1. Sample collection locations. Circles indicate the 10 wastewater treatment plants being investigated; triangles designate the two reference locations.

Table 1
Select ancillary information on the wastewater-treatment plants investigated

Location	Population served	Number of hospitals served	Treatment level	Disinfectant	Volume treated on sample day (MGD)	Maximum flow (MGD)	Distance from up-stream to WWTP (m)	Distance from WWTP to DS1[c](m)	Distance from WWTP to DS2[d](m)	Flow at upstream sample (m^3/s)	Flow of effluent (m^3/s)	Flow at DS 1 (m^3/s)	Flow at DS 2 (m^3/s)
Arizona	419000	5	Secondary	Chlorine	37	50	NA	NA	NA	NA	1.40	NA	NA
	320278	2	Secondary	Chlorine	25	33	NA	2330	13780	NA	1.42	2.32	1.21
Colorado	1500000	40	Secondary	Chlorine	130	227	7242	14484	96561	5.97	4.81	15.0	2.07
Georgia	800000	15	Secondary[1]	UV	80	186	48753	2736	64372	26.0	4.50	36.2	32.0
Iowa	29700	0	Secondary	UV	3	10	6.1	393	8441	0.0028	0.13[b]	0.14	0.10
Kansas	115000	1	Secondary	UV	10.5	15	457	1067	1372	0.025	0.40	0.42	0.45
Minnesota	90000	4	Secondary	Chlorine	14	19.1	91.4	305	1067	3.96	0.61	4.58	4.58
Nevada	625000	4	Tertiary	Chlorine/UV	85	110	3219	1609	9656	0.32	3.72[b]	6.42	4.53
New Jersey	65000	0	Secondary	Chlorine	10	16	1175	96	3584	0.17	0.44[b]	0.48	0.62
New York	10000	0	Tertiary	Chlorine	1	1.5	100	100	805	0.39	0.044[b]	0.42	0.71
South Dakota	134000	6	Tertiary	Chlorine	17	19.7	11265	1609	6437	2.83	0.82	2.55	2.09

[MGD, million gallons per day; max, maximum; DS1, downstream sampling site 1; DS2, downstream sampling site 2; NA, not applicable; UV, ultraviolet].
[1]Incudes ammonia and biological phosphorus removal; [a]With ammonia and biological phosphorus removal; [b]Flows estimated based on volume treated on sample day (MGD*0.0438=m^3/s); [c]DS1=first downstream sample; [d]DS2=second downstream sample.

techniques (Shelton, 1994). At each stream site, a composite water sample was collected from about 4 to 6 vertical profiles through a stream cross section. This composite sample was subsequently split into pre-cleaned, amber, glass bottles and prepared in duplicate. The duplicate samples were used for backup purposes (in case of breakage of the primary sample) and for laboratory replicates. Samples were passed through a 0.7 μm, baked, glass-fiber filter. After filtration, all samples were immediately chilled and shipped to the laboratory for analysis. Samples were collected between July and November of 2002. Streamflow significantly increased between the sites upstream of the WWTP (median flow=0.39 m^3/s) and those downstream (median flow=2.44 m^3/s). Discharge from the WWTPs contributed roughly between 10% and 95% of the flow at the DS1 sites.

All samples were analyzed for glyphosate and AMPA using a precolumn derivatization with 9-fluorenylmethylchloroformate followed by an automated online solid-phase extraction and direct injection into a liquid chromatograph/mass spectrometer (Lee et al., 2002). The analytical reporting limit was 0.1 μg/L for both compounds.

Five field blanks were collected during this study to determine if field conditions were introducing target analytes to the environmental samples. These blanks were prepared from laboratory-grade organic-free water and were subject to the same sample processing, handling, and equipment as the stream samples. There were no detections of either glyphosate or AMPA in these field blanks.

3. Results

Glyphosate or its degradate AMPA were commonly detected in the stream and WWTP effluent samples, being present in 67.5% of the 40 samples collected. Concentrations were generally low, although nine detections of AMPA (maximum concentration=3.9 μg/L) and three detections of glyphosate (maximum concentration=2.2 μg/L) exceeded 1 μg/L. AMPA was detected much more frequently (67.5%) than glyphosate (17.5%). Previous research has shown that herbicide degradates are often detected more frequently than their parent compounds in both streams (Battaglin et al., 2003) and ground water (Kolpin et al.,

2004a). Results of this study are similar to a study of herbicide concentrations in 51 Midwestern streams during three runoff events where AMPA was detected in 69% and glyphosate in 36% of the samples (Scribner et al., 2003; Battaglin et al., 2005).

Both AMPA (Fig. 2) and glyphosate (Fig. 3) had the greatest frequency of detection in the WWTP effluent samples, with roughly a two-fold increase in the frequency of detection for both AMPA and glyphosate between stream samples located upstream and those located downstream of the WWTPs. These results suggest an apparent contribution of WWTP effluent to both AMPA and glyphosate concentrations in streams. AMPA concentrations found in the WWTP effluent samples were significantly greater (P=0.03, Kruskal–Wallis test) than those measured in stream samples collected upstream of the WWTPs studied, but not significantly different (P=0.56, Kruskal–Wallis test) than those measured in stream samples collected downstream of the WWTPs studied. To our knowledge, this is the first time that it has been documented that the urban use of glyphosate contributes to glyphosate and AMPA concentrations in streams. It should be noted, however, that AMPA can also be derived from the degradation of phosphonic acids (such as EDTMP and DTPMP) in detergents (Skark et al., 1998). About 18.1 million kg of phosphonates are used in the United States annually (Nowack and Stone, 1999). Thus, part of the AMPA detections from this study could be derived from a detergent source. Other components of detergents, such as 4-nonylphenol diethoxylate and 4-nonylphenol monoethoxylate were also measured in the samples collected for this study (Glassmeyer et al., 2003) and were both found to be present in 22% of the upstream, 91% of the WWTP effluent, 70% of the first downstream and 60% of the second downstream samples. Detergent compounds also have been frequently detected in streams containing WWTP discharge (Kolpin et al., 2002; Lye et al., 1999; Rice et al., 2003). However, AMPA was always present in samples that had detections of glyphosate, which suggests that at least part of the AMPA concentrations in this study were derived from the degradation of glyphosate.

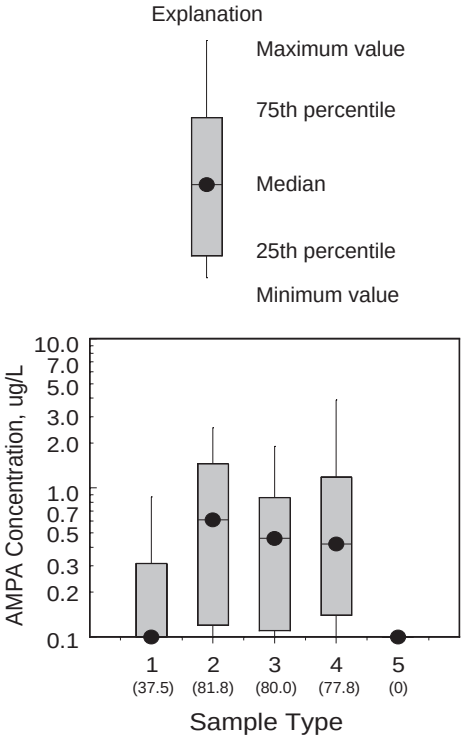

Fig. 2. AMPA concentrations by sample type (1=stream samples upstream of wastewater treatment plants, 2=treated effluent, 3=first stream sample downstream of wastewater treatment plants, 4=second stream sample downstream of wastewater treatment plants, 5=reference samples). Number in parentheses is the frequency of detection for each sample type.

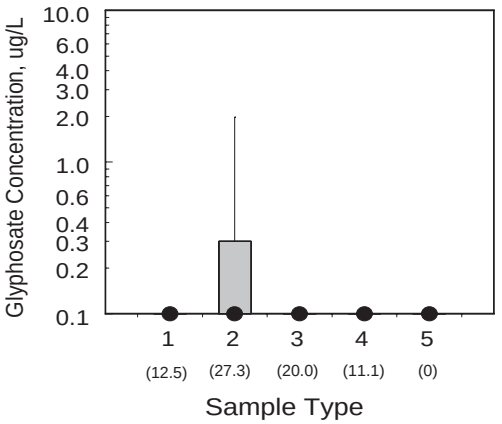

Fig. 3. Glyphosate concentrations by sample type (1=stream samples upstream of wastewater treatment plants, 2=treated effluent, 3=first stream sample downstream of wastewater treatment plants, 4=second stream sample downstream of wastewater treatment plants, 5=reference samples). Number in parentheses is the frequency of detection for each sample type. An explanation of a boxplot is provided in Fig. 2.

Diazinon (a common urban insecticide) and atrazine (a common agricultural herbicide) were examined for supporting evidence that the urban use of glyphosate contributes to stream concentrations. The trends for diazinon (Fig. 4) were similar to that of glyphosate (Fig. 3) and AMPA (Fig. 2) in that WWTP effluent had the most detections (72.7%), with much greater detections in samples located downstream (50.0%) of the WWTPs than in samples located upstream (37.5%) of the WWTPs. Previous research has shown that the urban use of diazinon contributes to diazinon concentrations in streams (Hoffman et al., 2000). Conversely, atrazine (Fig. 5) displayed a much different pattern compared to both diazinon (Fig. 4) and the glyphosate compounds (Figs. 2 and 3) in that detections in the WWTP effluent (27.2%) were less common than in the stream samples, with greater detections found in samples located upstream (62.5%) of the WWTPs than in samples located downstream (50.0%) of the WWTPs.

Even though travel time was not taken into account when collecting the stream samples for this study, the data may give a crude idea of spatial concentration patterns as water is transported downstream. As water moved from the first to the second downstream sampling sites, glyphosate detections decreased about

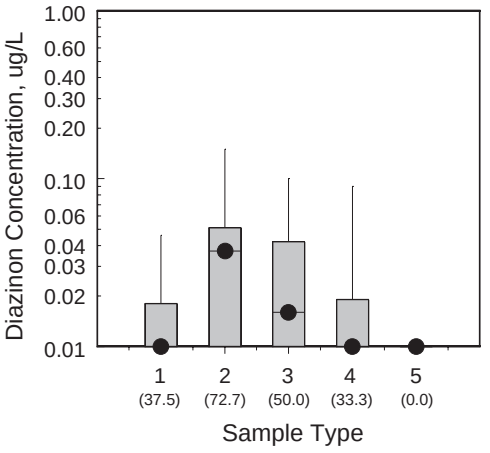

Fig. 4. Diazinon concentrations by sample type (1=stream samples upstream of wastewater treatment plants, 2=treated effluent, 3=first stream sample downstream of wastewater treatment plants, 4=second stream sample downstream of wastewater treatment plants, 5=reference samples). Number in parentheses is the frequency of detection for each sample type. An explanation of a boxplot is provided in Fig. 2.

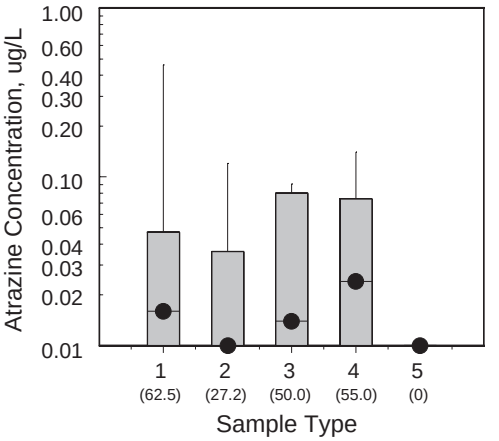

Fig. 5. Atrazine concentrations by sample type (1=stream samples upstream of wastewater treatment plants, 2=treated effluent, 3=first stream sample downstream of wastewater treatment plants, 4=second stream sample downstream of wastewater treatment plants, 5=reference samples). Number in parentheses is the frequency of detection for each sample type. An explanation of a boxplot is provided in Fig. 2.

45% (Fig. 3), whereas AMPA detections only decreased about 3% (Fig. 2). This suggests that AMPA is more mobile than glyphosate (as indicated by its greater frequency of detection compared to glyphosate), and may be more persistent (as indicated by downstream concentration patterns). The overall results of this study suggests that glyphosate and AMPA are more mobile and persistent in aquatic environments that earlier research has indicated (Giesy et al., 2000).

Acknowledgements

The authors would like to thank USGS personnel Bob Boyd, Gail Cordy, Betsy Frick, Sheridan Haack, John Lambing, Kathy Lee, David Mau, Pat Phillips, Steve Sando, Doug Schnoebelen, and Paul Stackelberg for their efforts in arranging the sample collection for this study. The United States Environmental Protection Agency through its Office of Research and Development partially funded and collaborated in the research described here under DW-14-93940201 to the United States Geological Survey. It has been subjected to Agency review and approved for publication. The use of trade, firm, or brand names in this paper is for identification

purposes only and does not constitute endorsement by the United States Environmental Protection Agency, or the United States Geological Survey.

References

Acquavella JF, Alexanders BH, Mandel JS, Gustin C, Baker B, Chapman P, et al. Glyphosate biomonitoring for farmers and their families: results from the farm family exposure study. Environ Health Perspect 2004;112:321–6.

Araujo ASF, Monterio RTR, Abarkeli RB. Effect of glyphosate on the microbial activity of two Brazilian soils. Chemosphere 2003;52:799–804.

Battaglin WA, Thurman EM, Kalkhoff SJ, Porter SD. Herbicides and transformation products in surface waters of the midwestern United States. J Am Water Resour Assoc 2003;39:743–56.

Battaglin WA, Kolpin DW, Scribner EA, Kuivila KM, Sandstrom MW. Glyphosate, its transformation product AMPA, and other herbicides in midwestern streams, 2002. J Am Water Resour Assoc 2005;41: (in press).

Baylis AD. Why glyphosate is a global herbicide: strengths, weaknesses and prospects. Pest Manag Sci 2000;56:299–308.

Carlisle SM, Trevors JT. Glyphosate in the environment. Water, Air, & Soil Pollution 1988;39:409–20.

Duke SD. Glyphosate. In: Kearnery PC, Daufman DD, editors. Herbicides: Chemistry, Degradation, and Model of Action. New York: Marcel Dekker; 1988. p. 1–70.

Folmar LC, Sanders HO, Julin AM. Toxicity of the herbicide glyphosate and several of its formulations to fish and aquatic invertebrates. Arch Environ Contam Toxicol 1979;8: 269–78.

Fomsgaard IS, Spliid NH, Felding G. Leaching of pesticides through normal-tillage and low-tillage soil—a lysimeter study: II Glyphosate. J Environ Sci Health, Part B, Pestic Food Contam Agric Wastes 2003;B38:19–35.

Forlani G, Mangiacalli A, Nielsen E, Suardi CM. Degradation of the phosphonate herbicide glyphosate in soil: evidence for a possible involvement of unculturable microorganism. Soil Biol Biochem 1999;31:991–7.

Giesy JP, Dobson S, Solomon KR. Ecotoxicological risk assessment for roundup herbicide. Rev of Environ Contam Toxicol 2000; 167:35–120.

Glassmeyer ST, Ferrer I, Furlong ET, Cahill JD, Zaugg SD, Werner SL, et al. Transport of chemical and microbial contaminants from known wastewater discharges [abs]. Proceedings of the 3rd International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, Minneapolis, Minn., National Ground Water Association, 2003.

Hoffman RS, Capel PD, Larson SJ. Comparison of pesticides in eight US urban streams. Environ Toxicol Chem 2000;19:2249–58.

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environ Sci Technol 2002;36:1202–11.

Kolpin DW, Schnoebelen DJ, Thurman EM. Degradates provide insight to spatial and temporal trends of herbicides in ground water. Ground Water 2004a;42:601–8.

Kolpin DW, Skopec M, Meyer MT, Furlong ET, Zaugg SD. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Sci Total Environ 2004b;328:119–30.

Lee EA, Strahan AP, Thurman EM, 2002. Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—determination of glyphosate, aminomethylphosphonic acid, and glufosinate in water using online solid-phase extraction and high-performance liquid chromatography/mass spectrometry. U.S. Geological Survey Open-File Report 01-454.

Lye CM, Frid CLJ, Gill ME, Cooper DW, Jones DM. Estrogenic alkylphenols in fish tissues, sediments, and waters from the UK Tyne and Tees Estruaries. Environ Sci Technol 1999; 33:1009–14.

Malik J, Barry G, Kishore G. The herbicide glyphosate. BioFactors 1989;2:17–25.

Mann RM, Bidwell JR. The toxicity of glyphosate and several glyphosate formulations to four species of southwestern Australian frogs. Arch Environ Contam Toxicol 1999;36: 193–9.

Nowack B, Stone AT. Adsorption of phosphonates onto the goethite–water interface. J Colloid Interface Sci 1999;214:20–30.

Padgette SR, Kolacz KH, Delannay X. Development, identification, and characterization of a glyphosate-tolerant soybean line. Crop Sci 1995;35:1451–61.

Pline WA, Price AJ, Wilcut JW, Edmisten KL, Wells R. Adsorption and translocation of glyphosate in glyphosate-resistant cotton as influenced by application method and growth stage. Weed Sci 2001;49:460–7.

Rice CP, Schmitz-Afonso I, Loyo-Rosales JE, Link E, Thoma R, Fay L, et al. Alkylphenol and alkylphenol-ethoxylates in carp, water, and sediment from the Cuyahoga River, Ohio. Environ Sci Technol 2003;37:3747–54.

Rubio F, Velduis LJ, Clegg BS, Fleeker JR, Hall JC. Comparison of a direct ELISA and an HPLC method for glyphosate determinations in water. J Agric Food Chem 2003;51:691–6.

Rueppel ML, Brightwell BB, Schaefer J, Marvel TT. Metabolism and degradation of glyphosate in soil and water. J Agric Food Chem 1977;25:517–28.

Scribner EA, Battaglin WA, Dietze JE, Thurman EM, 2003. Reconnaissance data for glyphosate, other selected herbicides, their degradation products, and antibiotics in 51 streams in nine Midwestern states, 2002. U.S. Geological Survey Open-File Report 03-217.

Servizi JA, Gordon RW, Martens DW. Acute toxicity of garlon 4 and roundup herbicides to salmon, *Daphnia*, and trout. Bull Environ Contam Toxicol 1987;39:15–22.

Shelton, L.R., 1994 Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program. U.S. Geological Suvey Open-File Report 94-455.

Skark C, Zullei-Seibert N, Schottler U, Schlett C. The occurrence of glyphosate in surface water. Int J Environ Anal Chem 1998;70:93–104.

Tate TM, Spurlock JO, Christian FA. Effect of glyphosate on the development of *Pseudosuccinea columella* snails. Arch Environ Contam Toxicol 1997;33:286–9.

Thompson DG, Wojtaszek BF, Staznik B, Chartband DT, Stephenson GR. Chemical and biomonitoring to assess potential acute effects of Vison® herbicide on native amphibian larvae in forest wetlands. Environ Toxicol Chem 2004;23:843–9.

Tsui MTK, Chu LM. Aquatic toxicity of glyphosate-based formulations: comparison between different organisms and the effects of environmental factors. Chemosphere 2003;52: 1189–97.

Tsui MTK, Chu LM. Comparative toxicity of glyphosate-based herbicides: aqueous and sediment porewater exposures. Arch Environ Contam Toxicol 2004;46:316–23.

WHO. Environmental Heal Criteria: Glyphosate. Geneva: World Health Organization; 1994.

Veiga F, Zapata JM, Fernandez Marcos ML, Alvarez E. Dynamics of glyphosate and aminomethylphosphonic acid in a forest soil in Galicia, North-west Spain. Sci Total Environ 2001;271:135–44.

Woodburn A. Glyphosate: production, pricing and use worldwide. Pest Manag Sci 2000;56:309–12.