

## OCCURRENCE AND FATE OF THE HERBICIDE GLYPHOSATE AND ITS DEGRADATE AMINOMETHYLPHOSPHONIC ACID IN THE ATMOSPHERE

FENG-CHIH CHANG,<sup>†</sup> MATT F. SIMCIK,<sup>\*†</sup> and PAUL D. CAPEL<sup>‡</sup><sup>†</sup>School of Public Health, University of Minnesota, Minneapolis, Minnesota, USA<sup>‡</sup>U.S Geological Survey, Minneapolis, Minnesota

(Submitted 21 April 2010; Returned for Revision 12 June 2010; Accepted 16 September 2010)

**Abstract**—This is the first report on the ambient levels of glyphosate, the most widely used herbicide in the United States, and its major degradation product, aminomethylphosphonic acid (AMPA), in air and rain. Concurrent, weekly integrated air particle and rain samples were collected during two growing seasons in agricultural areas in Mississippi and Iowa. Rain was also collected in Indiana in a preliminary phase of the study. The frequency of glyphosate detection ranged from 60 to 100% in both air and rain. The concentrations of glyphosate ranged from <0.01 to 9.1 ng/m<sup>3</sup> and from <0.1 to 2.5 µg/L in air and rain samples, respectively. The frequency of detection and median and maximum concentrations of glyphosate in air were similar or greater to those of the other high-use herbicides observed in the Mississippi River basin, whereas its concentration in rain was greater than the other herbicides. It is not known what percentage of the applied glyphosate is introduced into the air, but it was estimated that up to 0.7% of application is removed from the air in rainfall. Glyphosate is efficiently removed from the air; it is estimated that an average of 97% of the glyphosate in the air is removed by a weekly rainfall ≥30 mm. Environ. Toxicol. Chem. 2011;30:548–555. © 2011 SETAC

**Keywords**—Atmosphere    Glyphosate    Aminomethylphosphonic acid    Mass budget

## INTRODUCTION

Although the use of pesticides in agriculture has significantly increased crop yields, concerns exist about the environmental occurrence and fate of pesticides [1–3]. Approximately 400 million kilograms of pesticides (AI, active ingredients) was used in the United States in 2001.

The agricultural sector accounted for about 76% of this use. Within U.S. agriculture in 2001, herbicides, insecticides, fungicides, and other pesticides accounted for 64, 11, 6, and 19%, respectively [4].

Some fraction of applied pesticide can move away from the application area. A wide variety of pesticides has been observed in different environmental media, including natural water bodies, soil, and atmosphere [5,6]. Some semivolatile persistent pesticides (dichlorodiphenyltrichloroethane [DDT], hexachlorocyclohexanes [HCHs], trifluralin, and metolachlor) have been observed to be transported regionally and globally in the atmosphere [7–9]. The extent of the pesticide flux from the landscape to the atmosphere is affected by the amount applied, method of application, meteorological conditions, and physical–chemical characteristics of the pesticide. Pesticides can be introduced into the atmosphere through spray drift, volatilization, and wind erosion of soil particles to which they are attached. The removal of pesticides from the local atmosphere include deposition (wet or dry), photochemical reaction, and advective transport [10,11]. In the atmosphere, pesticides are distributed between particle and vapor phases based on the vapor pressure of the chemical, ambient temperature, and concentration of suspended particulate matter [12].

Glyphosate (N-[phosphonomethyl] glycine), a broad-spectrum, nonselective, and postemergence herbicide, is the most

widely used pesticide in the United States [4,13]. It has been used extensively in conjunction with genetically modified crops since 1996 [14,15]. It is estimated that 91% of the soybeans, 22% of the corn, and 23% of the cotton crop hectares in the United States were planted as herbicide-tolerant varieties in 2009 ([16]; <http://www.ers.usda.gov/Data/BiotechCrops/>). Pure glyphosate is a crystalline solid with high water solubility (12 g/L) [17], very low vapor pressure ( $5.7 \times 10^{-8}$  Pa at 25°C) [18], and four pK<sub>a</sub> values (0.31, 2.6, 5.6, and 10.6) [19,20]. From a human health perspective, glyphosate is classified as carcinogenic category E because of evidence of noncarcinogenicity for humans [21]. Some studies have suggested a link between glyphosate exposure and the risk of non-Hodgkin's lymphoma or human placental cell damage [22,23].

The mean half-life of glyphosate in soil has been reported as 32 d in forests and row crops [24,25] but varies considerably as a function of microbial activity, soil pH, and temperature [26]. In the environment, glyphosate is degraded to aminomethylphosphonic acid (AMPA). The half-life of AMPA is largely unknown but is thought to be greater than that of glyphosate, because it has been observed to accumulate in soil. Both glyphosate and AMPA have been detected in natural waters near agricultural areas [27,28]. However, very little work has been done on the atmospheric transport of glyphosate. In one study, it was reported that air concentrations of glyphosate were below 15.7 µg/m<sup>3</sup> during silvicultural spraying periods [29]. Thus, the occurrence and behavior of atmospheric glyphosate are still largely unknown even though glyphosate is the most widely used herbicide in the world [15,30].

Glyphosate and AMPA were quantified in the ambient atmosphere of three agricultural areas in the United States (Mississippi, Iowa, and Indiana). Field sampling and laboratory extraction methods for glyphosate and AMPA in air were developed. Concurrent, weekly integrated air particle and rain samples were collected during two growing seasons in Mississippi and Iowa in 2007 and 2008. Rain was collected only

\* To whom correspondence may be addressed  
(msimcik@umn.edu).

Published online 1 December 2010 in Wiley Online Library  
(wileyonlinelibrary.com).

during one growing season in Indiana in 2004. These field observations were used to quantify the occurrence of glyphosate and AMPA in the atmosphere and to help in elucidating their mechanisms of atmospheric introduction and removal. As a result of the very low vapor pressure of glyphosate, the glyphosate and AMPA concentrations in air are assumed to be equal to their particle-phase concentrations detected on GFFs. The present study offers the first report of glyphosate and AMPA in the ambient air and rain.

## MATERIALS AND METHODS

### Description sampling sites

Air and rainfall samples were collected weekly during the crop-growing seasons near Pace, Mississippi, and Blairsburg, Iowa, in 2007 and 2008. In addition, weekly rainfall samples were also collected near Mohawk, Indiana, in 2004. The major crops grown near the sampling sites in Mississippi, Iowa, and Indiana were soybeans and rice, soybeans and corn, and soybeans and corn, respectively. Typical growing months for major crops were from March to October in Mississippi and April to September in Iowa and Indiana. The meteorological information during sampling periods was acquired from the National Oceanic and Atmospheric Administration, National Weather Service ([31]; <http://cdo.ncdc.noaa.gov/qcld/QCLCD?prior=N>). The summaries of agricultural activities and meteorological data for the three study areas are presented in Table 1.

### Field sampling

Glass-fiber filters (GFFs; 90 mm, GF/F; Whatman), used for collecting atmospheric particle-phase samples, were baked at 550°C for 12 h, cooled to room temperature, and wrapped in aluminum foil before use. High-volume air samplers (Tisch Environmental; Thermo Scientific) were mounted at approximately 1.5 m above ground level at the sampling sites. The air samplers were turned on once each hour for a fixed time period (either 5 or 10 min). Each air sample was an integration of air over a 7-d period. The air samplers were operated at flow rates from 0.15 to 0.37 m<sup>3</sup>/min. The GFFs in the samplers were

replaced every Tuesday during the study period, and both were stored at -15°C until extraction. The flow rates of the air samplers were calibrated with a volumetric air flow meter (Roots meter, Dresser) before and after field season.

The rainfall samples were collected using modified rainfall samplers, which were covered during dry periods and collected wet deposition only. The rainfall was collected in a Teflon<sup>®</sup>-lined container, which drained into a refrigerated, clean, glass carboy. The details of rainfall sampling can be found in Vogel et al. [32]. The weekly-integrated rainfall samples were collected on the same schedule as the air samples.

The GFF samples were slowly pulverized inside a 50-ml polypropylene (PP) tube (mixing tube) with a clean, wide, stainless-steel drill bit. Next, 20 ml of a hydrochloric acid solution (pH 2) was added to this mixing tube, which was then capped and placed on a shaker for 21 h. The free liquid was decanted into another 50 ml PP tube (composite tube). Ten milliliters of a potassium hydroxide solution (pH 11) was then added to the mixing tube, which was again shaken for 24 h. The contents of both tubes were filtered through a cellulose nitrate filter (0.45- $\mu$ m pore diameter, 47-mm filter diameter) under vacuum. The filtered extract was poured into a third, pre-weighed PP tube and weighed again to measure the extract volume. The collected rain sample was filtered through a Supor membrane filter (0.45- $\mu$ m pore diameter; Pall Corporation) and transferred to an amber glass bottle. Because glyphosate and AMPA have extremely high water solubility and have little affinity for the particulate phase in aqueous solution, it was assumed that all of the glyphosate and AMPA that was associated with particles in the atmosphere desorbed into the water in the rain collection vessel before extraction. All of the final extracts from the air and filtered rain samples were shipped on ice to the U.S. Geological Survey Organic Geochemistry Laboratory (Lawrence, KS) for glyphosate and AMPA analysis.

Glyphosate and AMPA were derivitized with 9-fluorenylmethylchloroformate and then analyzed with a Hewlett Packard liquid chromatography/mass spectrometer (HPLC/MS). The HPLC/MS was equipped with automatic online solid-phase extraction (SPE) cartridges. A mobile-phase gradient from 95% of 5 mM ammonium acetate in reagent water to 100%

Table 1. Summary of agricultural activities and environmental characteristics of study watersheds near Pace, Mississippi, Blairsburg, Iowa, and Mohawk, Indiana, USA

	Mississippi	Iowa	Indiana
Area of watershed (ha)	1,383	3,100	1,787
Land in row crops (%)	99	97	87
Major crops	Soybeans, rice	Soybeans, corn	Soybeans, corn
Typical growing season	February–July	April–August	April–August
Month of major glyphosate application	February–July	June–July	May–July
Single glyphosate application rate used on agricultural fields (kg ha <sup>-1</sup> , mean $\pm$ SD)	1.05 $\pm$ 0.21	0.82 $\pm$ 0.10	—
Mean watershed glyphosate application rate during growing season (kg ha <sup>-1</sup> year <sup>-1</sup> )	2.00	0.52	0.58
Total annual glyphosate application <sup>a</sup> (kg) in 2007 or 2004	2,800	1,475	1,040
Total annual glyphosate application <sup>a</sup> (kg) in 2008	2,750	1,719	NA
Method of glyphosate application	Aircraft and ground rig	Ground rig	Ground rig
Mean temperature (°C; April–September in 2007 and 2008 or 2004) <sup>b</sup>	25–26	18–22	22
Accumulative precipitation (mm; April–September in 2007 or 2004) <sup>b</sup>	443	545	661
Accumulative precipitation (mm; April–September in 2008) <sup>b</sup>	716	1,159	NA
Mean surface wind speed (m s <sup>-1</sup> ; April–September in 2007) <sup>b</sup>	2.5	4.0	NA
Mean surface wind speed (m s <sup>-1</sup> ; April–September in 2008) <sup>b</sup>	2.9	3.9	NA

<sup>a</sup> Glyphosate applications are reported for the watersheds of Tommie Bayou near Pace, Mississippi (USGS site No. 07288636), for 2007 and 2008; South Fork of the Iowa River near Blairsburg, Iowa (USGS site 05451080), for 2007 and 2008; and Leary–Weber Ditch near Mohawk, Indiana (USGS site 03361638), for 2004. NA = Not applicable.

<sup>b</sup> NOAA, 2010.

acetonitrile was used for LC column elution. The molecular and fragment ions were 390 and 168 for glyphosate, and 332, 110, and 136 for AMPA. Method detection limits (MDLs) were 0.084 and 0.078  $\mu\text{g/L}$  for glyphosate and AMPA, respectively. More detailed information can be found in Myer et al. ([33]; <http://pubs.usgs.gov/tm/tm5a10/>). The masses (nanograms) of glyphosate and AMPA from extracted air samples were divided by air sampling volume (cubic meters) to obtain the air concentrations.

#### Quality assurance/quality control

A recovery experiment was conducted to validate the efficiency of the extraction procedure for glyphosate and AMPA from the GFFs. Two clean GFFs were fortified with 25  $\mu\text{g}$  glyphosate and 25  $\mu\text{g}$  AMPA in aqueous solution (0.5 mg/ml), and the water was allowed to evaporate. The extraction procedures for GFF were conducted as described above. A recovery experiment was also conducted to validate the efficiency of the sampling procedure for glyphosate and AMPA on the GFFs. Two clean GFFs were fortified with 1  $\mu\text{g}$  glyphosate and 1  $\mu\text{g}$  AMPA in aqueous solution (0.01 mg/ml). The sampler was turned on for 24 h indoors at 25°C (average 186 m<sup>3</sup> of air sampled). The GFFs were removed from the air sampler and extracted as described above.

Several field blanks, laboratory procedural blanks, and fortified matrix were measured in the present study. Air sample volumes ranged from 300 to 1,000 m<sup>3</sup>. A typical GFF extract volume was 50 ml. Because the MDLs for glyphosate and AMPA in aqueous solution were about 0.08  $\mu\text{g/L}$ , the MDLs for glyphosate and AMPA concentrations for air samples were estimated to be in the range of 0.004 to 0.013 ng/m<sup>3</sup>. The laboratory procedural and field blanks for glyphosate and AMPA masses on GFFs and in PUFs were all <0.011  $\mu\text{g}$ . The resulting air concentrations of glyphosate and AMPA in air based on these blanks would be 0.011 to 0.036 ng/m<sup>3</sup>. Therefore, the method reporting limit (MRL) of glyphosate and AMPA in air samples was set at 0.01 ng/m<sup>3</sup>, and the MRL of glyphosate and AMPA in rain samples was 0.1  $\mu\text{g/L}$ . The reported concentrations were not blank corrected.

The extraction efficiency recoveries of glyphosate and AMPA from the GFFs were 83 and 101% and 104 and 122%, respectively. The results indicate that extraction procedures worked acceptably. In the sampling efficiency recovery study, the fortified GFF recoveries after running the air sampler were 76 and 138% and 38 and 42% for glyphosate and AMPA, respectively.

#### Percent AMPA in rain

The percentage AMPA from total atmospheric (air and rain) glyphosate is defined as

AMPA as a percentage of total glyphosate in air

$$= (C_{\text{air AMPA}} / [C_{\text{air glyphosate}} + C_{\text{air AMPA}}]) \times 100$$

AMPA as a percentage of total glyphosate in rain

$$= (C_{\text{rain AMPA}} / [C_{\text{rain glyphosate}} + C_{\text{rain AMPA}}]) \times 100$$

where  $C_{\text{air glyphosate}}$  = concentrations of glyphosate in air (ng m<sup>-3</sup>),  $C_{\text{air AMPA}}$  = concentrations of AMPA in air (ng m<sup>-3</sup>),  $C_{\text{rain glyphosate}}$  = concentrations of glyphosate in rainfall ( $\mu\text{g/L}$ ), and  $C_{\text{rain AMPA}}$  = concentrations of AMPA in rainfall ( $\mu\text{g/L}$ ).

## RESULTS AND DISCUSSION

### Application of glyphosate in Mississippi and Iowa

Based on local interviews with the applicators in the watersheds, glyphosate was applied from February to July in the Mississippi study area and from May to July in the Iowa study area. In both cases, the majority of the fields received applications of glyphosate because of the prevalence of genetically modified crops. The whole-watershed normalized application rates of glyphosate in the Mississippi and Iowa area were 1.97 and 0.52 kg/ha/year, respectively (Table 1). In Mississippi, the timing and seasonal pattern of glyphosate application were similar for 2007 and 2008 (Fig. 1). However, in Iowa, the glyphosate application was extended one month longer in 2008 compared with 2007 because of very large rain events in late May and early June that delayed planting and herbicide application (Fig. 2).

### Detection of glyphosate and AMPA in air and rain

In total 84 air and 80 rainfall samples were collected from three agricultural areas in Mississippi, Iowa, and Indiana during the growing seasons of 2004, 2007, and 2008. Glyphosate was observed in >60% of the air and rain samples in at all three sites. AMPA was also observed in >50% of the air samples and usually >50% of the rain samples at all three sites (Table 2). Both glyphosate and AMPA were detected in 92% of the rain samples in Indiana in 2004. (No air samples were collected during this part of the study.) Both glyphosate and AMPA occurred more frequently in air in Mississippi compared with Iowa (Table 2). Both compounds were detected with about the same frequency in air and rain in Mississippi, whereas, in Iowa, the frequency of detection of glyphosate in rain was similar to that in air, but AMPA was detected less frequently in rain compared with air.

In Mississippi in 2007, glyphosate and AMPA particulate air concentrations ranged from <0.01 to 9.1 ng/m<sup>3</sup> and <0.01 to 0.49 ng/m<sup>3</sup>, respectively (Table 2 and Fig. 1a). The median concentrations of glyphosate and AMPA in air were similar for the two years, but the peak concentrations were much greater in 2007. In 2007, two spikes in glyphosate concentration (6.6 and 9.1 ng/m<sup>3</sup>) occurred in May during the application period. A few much smaller increases over the background concentration occurred in July and August. For AMPA, three small concentration spikes (0.31, 0.39, and 0.49 ng/m<sup>3</sup>) occurred from May to June, and one occurred in August. Both glyphosate and AMPA had lower air concentrations in 2008 compared with 2007 (Table 2 and Fig. 1d).

In contrast to the Mississippi site, the magnitude and pattern of glyphosate and AMPA concentrations in air particles in Iowa were more consistent between 2007 and 2008. In 2007, glyphosate and AMPA in air ranged from <0.01 to 5.4 ng/m<sup>3</sup> and <0.01 to 0.97 ng/m<sup>3</sup>, respectively (Table 2 and Fig. 2a). In 2007, two major spikes in air concentrations for both glyphosate and AMPA occurred in mid-June and mid-July (Fig. 2a) corresponding to the local period of application, just as in Mississippi. After July, glyphosate and AMPA were detected only at very low levels (>0.1 ng/m<sup>3</sup>). The application period in 2008 was shifted to a few weeks later (compared with 2007) because of the large rain events, flooded fields, and saturated soils that occurred from late May into early June. In 2008, a sustained, elevated concentration (>0.5 ng/m<sup>3</sup>) of glyphosate in air was noted from mid-June to mid-July during a sustained dry period. A few smaller concentration

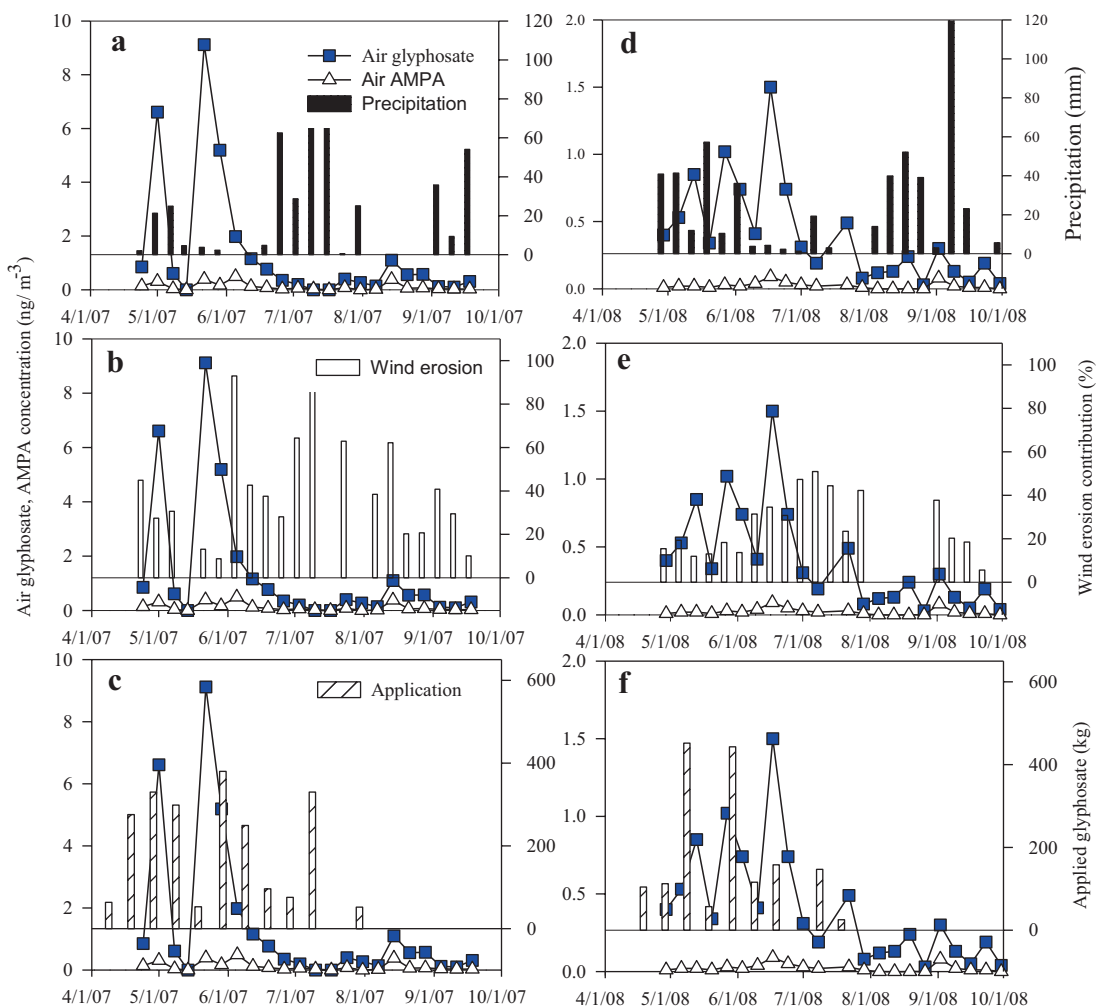


Fig. 1. Time series concentrations of glyphosate and aminomethylphosphonic acid (AMPA) in air ( $\text{ng}/\text{m}^3$ ) compared with weekly rainfall (mm), modeled contribution of atmospheric glyphosate resulting from wind erosion (%) and glyphosate application (kg) for the Tommie Bayou watershed near Pace, Mississippi, USA, in 2007 (a–c) and 2008 (d–f). Note the difference in the scales of the y axes between 2007 and 2008. [Color figure can be seen in the online version of this article, available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

spikes of AMPA in air occurred from mid-June to mid-August. After the end of July, both glyphosate and AMPA in air remained at low concentration levels.

The observations of glyphosate and AMPA in rain were quite similar among the three study areas and the years. The range in concentration was from  $<0.1$  to about  $2 \mu\text{g}/\text{L}$ , whereas the median concentrations were about an order of magnitude less than the maximum (generally  $0.1$ – $0.2 \mu\text{g}/\text{L}$ ). Once or twice a year, the glyphosate rain concentration was much greater than the median. These periods generally occurred during weeks with rainfall following the application period (Table 2 and Fig. 3).

Although AMPA as a fraction of total glyphosate in air ranged from 0 to 1.0, the median fractions ranged from 0.05 to 0.11 for both years at both locations (Table 2). In general, AMPA as a fraction of total glyphosate in air was lower during application seasons and then increased after the last glyphosate applications each year. These changes are due to biodegradation of glyphosate to AMPA in the soil [34], which results in decreasing glyphosate and proportionally increasing AMPA concentrations as the time since last application increases (Fig. 4).

#### Comparison to other herbicides

The detection frequency and median concentrations of glyphosate in both air and rain were not substantially different compared with other current-use herbicides, but maximum glyphosate concentrations were greater. For example, the detection frequency reported here for glyphosate in air (61–100%) is similar to observations for trifluralin (100%), atrazine (67–74%), and metolachlor (81–100%) in the Mississippi River basin [35]. The median glyphosate concentrations in air observed in Mississippi and Iowa ( $0.08$ – $0.48 \text{ ng}/\text{m}^3$ ) were comparable to the median concentrations reported for atrazine ( $0.05 \text{ ng}/\text{m}^3$ ) and metolachlor ( $0.21 \text{ ng}/\text{m}^3$ ) and less than the median concentration of trifluralin ( $0.81 \text{ ng}/\text{m}^3$ ) [35]. The maximum concentrations of glyphosate in air ( $9.1$  and  $7.7 \text{ ng}/\text{m}^3$  in Mississippi and Iowa, respectively) were greater than the maximum concentrations of trifluralin ( $5.5 \text{ ng}/\text{m}^3$ ), atrazine ( $2.8 \text{ ng}/\text{m}^3$ ), and metolachlor ( $1.5 \text{ ng}/\text{m}^3$ ) [35]. Likewise, the detection frequency of glyphosate in rain (63–92%) was similar to that of trifluralin (10–69%), atrazine (75–95%), and metolachlor (94–100%) [32], but the median and maximum concentrations of glyphosate in rain ( $0.10$ – $0.20$ ,  $1.9$ ,

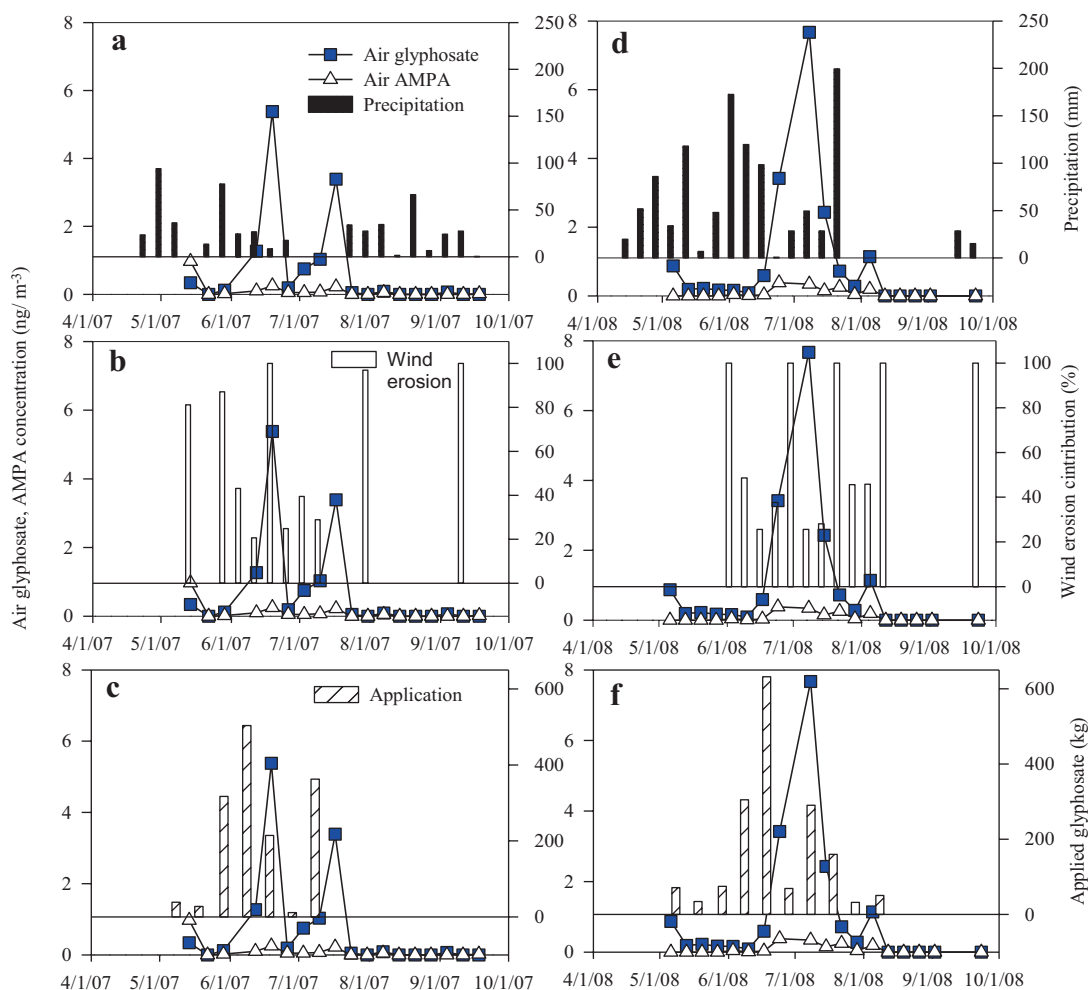


Fig. 2. Time series concentrations of glyphosate and aminomethylphosphonic acid (AMPA) in air ( $\text{ng}/\text{m}^3$ ) compared with weekly rainfall (mm), modeled contribution of atmospheric glyphosate resulting from wind erosion (%) and glyphosate application (kg) for the South Fork of the Iowa River watershed near Blairsburg, Iowa, USA, in 2007 (a–c) and 2008 (d–f). [Color figure can be seen in the online version of this article, available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)]

and  $2.5 \mu\text{g}/\text{L}$ , respectively) were substantially greater than those of atrazine ( $0.02$ ,  $0.83 \mu\text{g}/\text{L}$ ), metolachlor ( $0.02$ ,  $0.25 \mu\text{g}/\text{L}$ ), and trifluralin ( $0.01$ ,  $0.02 \mu\text{g}/\text{L}$ ) in rain [32]. These results are somewhat surprising insofar as the other herbicides are

more volatile than glyphosate. The relatively elevated levels of glyphosate probably are due to its frequent use in these agricultural areas in conjunction with the genetically modified crops.

Table 2. Concentrations of glyphosate and aminomethylphosphonic acid (AMPA) in air and rain and AMPA as a fraction of total glyphosate in air and rain near Pace, Mississippi, Blairsburg, Iowa, and Mohawk, Indiana, USA<sup>a</sup>

Compounds	Statistic	Mississippi: Air		Iowa: Air		Mississippi: Rain		Iowa: Rain		Indiana: Rain
		2007	2008	2007	2008	2007	2008	2007	2008	(2004)
Glyphosate	Median	0.48	0.24	0.08	0.22	0.20	0.15	0.20	0.1	0.14
	Maximum	9.1	1.5	5.4	7.7	1.9	1.6	2.5	1.8	1.1
	Minimum	<0.01	<0.01	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1
	SD	1.8	0.36	1.4	1.9	0.57	0.39	0.72	0.47	0.32
	% of D	86	100	61	72	73	68	71	63	92
	<i>n</i>	22	27	18	18	11	19	14	24	12
AMPA	Median	0.06	0.02	0.02	0.04	0.10	<0.1	<0.1	<0.1	<0.1
	Maximum	0.49	0.09	0.97	0.38	0.30	0.48	0.20	0.24	0.47
	Minimum	<0.01	<0.01	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1
	SD	0.18	0.02	0.23	0.12	2.0	0.14	0.08	0.06	0.13
	% of D	86	70	56	61	73	74	36	50	92
	<i>n</i>	22	27	18	18	11	19	14	24	12
AMPA/total glyphosate	Median	0.11	0.05	0.07	0.10	0.25	0.33	0.00	0.13	0.34
	Maximum	1.00	0.22	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
	SD	0.25	0.07	0.32	0.32	0.32	0.35	0.30	0.31	0.25

<sup>a</sup> Concentration units (air:  $\text{ng}/\text{m}^3$ ; rain:  $\mu\text{g}/\text{L}^{-1}$ ); SD = standard deviation; D = frequency of detection (in percentage); *n* = number of samples.

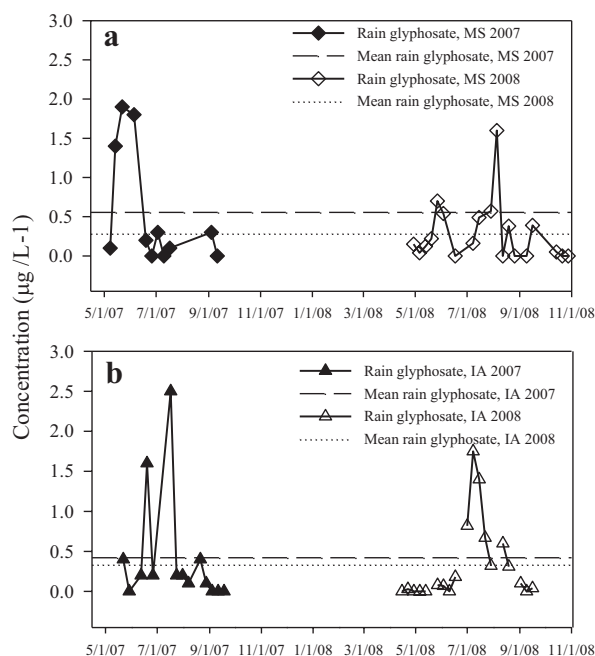


Fig. 3. Time series concentrations of glyphosate in rain in 2007 and 2008 in Mississippi (a) and Iowa (b), USA.

#### Timing of application

The highest concentrations of glyphosate and AMPA in both air and rain were found during the periods of intense glyphosate applications for both Mississippi and Iowa (Figs. 1 and 2). In Iowa, maximum concentration of glyphosate in rain (June and July, 2007: 1.6 and 2.5 µg/L; July, 2008: 1.8 µg/L) occurred during the intense period of application occurred (Fig. 2c,f). In contrast to the application pattern in Iowa, the glyphosate

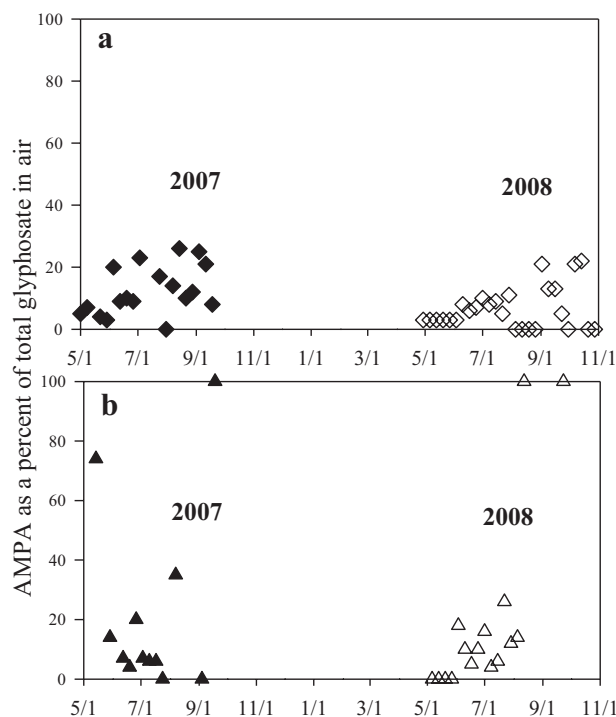


Fig. 4. Aminomethylphosphonic acid (AMPA) as a percentage of total glyphosate in air in Mississippi (a) and Iowa (b), USA.

application in Mississippi was more uniform over a longer period (Fig. 1c,f); the peaks in air and rain concentrations occurred during the intense period of application. At both study locations, the highest air concentrations were observed in the weeks during the application season when little or no rainfall occurred. These conditions gave a strong source of glyphosate to the air but no strong removal mechanism.

#### Estimation of air glyphosate from wind erosion of soil

Given its very low vapor pressure, glyphosate has two important mechanisms for delivery to the atmosphere, spray drift from application and wind erosion of soil particles to which glyphosate is associated. Aminomethylphosphonic acid will be introduced into the atmosphere only by soil erosion processes, because it is formed in the soil after application. Volatilization from the soil will not be an important process for either compound. To estimate the relative contributions of spray drift and wind erosion to glyphosate and AMPA in the air, a simple mass balance model is suggested. The model makes six assumptions: the control volume is a 2,000-m column of well-mixed air with a base of 1 m × 1 m; the only two sources of glyphosate to the air are spray drift and wind erosion; wind erosion is the only source for AMPA; the transformation (biodegradation) of glyphosate to AMPA occurs only in the soil [36]; no or negligible photo-oxidation of glyphosate or AMPA occurred; and the ratio of glyphosate concentration in soil to AMPA concentration in soil ( $S$ ) decreases weekly from 5.1 (first week after application) to 0.1 (twelfth week after application). This is based on the logarithmic fitting of field observations reported by Grunewald et al. [36], and wind erosion produces air particles with the same glyphosate to AMPA ratio as found in the soil.

For any given week, the input of total glyphosate in the air due application and wind erosion is

$$M_{\text{air glyphosate + AMPA}} = M_{\text{application}} + M_{\text{wind}}, \quad (1)$$

where  $M_{\text{air glyphosate + AMPA}}$  is the mass of total glyphosate (glyphosate + AMPA) in the control volume in the air,  $M_{\text{application}}$  is the mass of total glyphosate in the control volume of air contributed by application, and  $M_{\text{wind}}$  is the mass of total glyphosate in the control volume in the air contributed by wind erosion. Therefore,

$$M_{\text{glyphosate + AMPA}} = (C_{\text{air glyphosate}} + C_{\text{air AMPA}}) \times A \times H, \quad (2)$$

where  $C_{\text{air glyphosate}}$  is the concentration of glyphosate in air ( $\text{ng m}^{-3}$ ),  $C_{\text{air AMPA}}$  is the concentration of AMPA in air ( $\text{ng m}^{-3}$ ),  $A$  is the base area of air column ( $1 \text{ m}^2$ ), and  $H$  is the assumed height of the well-mixed air column (2,000 m, corresponding to a low cloud height).

The mass of total glyphosate in air attributed to wind erosion effect is

$$M_{\text{wind}} = (C_{\text{air AMPA}} + [S \times C_{\text{air AMPA}}]) \times A \times H, \quad (3)$$

where  $S$  is the ratio of ( $C_{\text{soil glyphosate}}/C_{\text{soil AMPA}}$ ) in the soil for the specific time step.  $M_{\text{application}}$  is calculated as the difference between  $M_{\text{glyphosate + AMPA}}$  and  $M_{\text{wind}}$ .

The percentage contributions of application spray drift and wind erosion to total mass glyphosate in air are obtained by the following equations:

$$\%_{\text{Application}} = M_{\text{application}} / (M_{\text{application}} + M_{\text{wind}}) \times 100\% \quad (4)$$

$$\%_{\text{Wind}} = M_{\text{wind}} / (M_{\text{application}} + M_{\text{wind}}) \times 100\%. \quad (5)$$

The weekly results from the model are presented in Figures 1b,e and 2b,e for the two sites and two years. For both sites and both years, the majority of the glyphosate in the atmosphere came from application spray drift. The contribution from wind erosion for atmospheric glyphosate was less during the intensive application events (about 20–40%) and greater in weeks without application (50–100%), as would be expected. The estimated seasonal median percentages of glyphosate in the air due to wind erosion in Mississippi were 34% in 2007 and 19% in 2008. For Iowa, these estimated seasonal median values of glyphosate in the air from wind erosion were 41% and 42% for the two years. The greater contribution percentages from wind erosion to the air glyphosate in Iowa may be attributed to a higher wind speed (mean  $\pm$  SD) in Iowa ( $4.0 \pm 1.4$  m/s) than in Mississippi ( $2.7 \pm 0.8$  m/s) during these sampling periods. A high degree of uncertainty exists in this simple model, because it does not explicitly account for the removal of these compounds by rainfall.

#### Removal of glyphosate and AMPA from air by rain

Based on vapor pressures, glyphosate and AMPA are predicted to exist only in the particle phase in the atmosphere, so their removal by rain scavenging is very important [37]. The weekly removal of total glyphosate (glyphosate + AMPA) from air by rain is calculated as

$$M_{\text{rain glyphosate + AMPA}} = (C_{\text{rain glyphosate}} + C_{\text{rain AMPA}}) \times R \times A \times CF_1 \quad (6)$$

where  $C_{\text{rain glyphosate}}$  is the concentration of glyphosate in rainfall ( $\mu\text{g L}^{-1}$ ),  $C_{\text{rain AMPA}}$  is the concentration of AMPA in rainfall ( $\mu\text{g/L}$ ),  $R$  is the total weekly rainfall (mm),  $A$  is the area ( $1 \text{ m}^2$ ), and  $CF_1$  is a unit conversion factor ( $10^3 \text{ ng}/\mu\text{g}$ ). The mass of total glyphosate in the air is the time-weighted average concentration of total glyphosate (which is equal to the concentrations of glyphosate and AMPA measured on air particles in the field) times the control volume (Eqn. 2). From these, the percentage of the weekly mass of total glyphosate in air that is removed by rainfall is

$$WR_{\text{rain}} = M_{\text{rain glyphosate+AMPA}} / (M_{\text{air glyphosate+AMPA}} + M_{\text{rain glyphosate + AMPA}}) \times 100\% \quad (7)$$

The percentage of total glyphosate in air removed by rainfall was grouped into two categories based on weekly rainfall amounts  $<30$  mm or  $\geq 30$  mm (Fig. 5). These calculated median

Table 3. Wet deposition ( $\mu\text{g}/\text{m}^2$ ; mean  $\pm$  SD) of glyphosate and aminomethylphosphonic acid (AMPA) from the atmosphere near Pace, Mississippi, and Blairsburg, Iowa, USA

Year	Mississippi		Iowa	
	Glyphosate	AMPA	Glyphosate	AMPA
2007 <sup>a</sup>	$3.9 \pm 4.1$	$2.1 \pm 3.2$	$5.1 \pm 7.3$	$1.7 \pm 3.9$
2008 <sup>b</sup>	$5.5 \pm 7.6$	$5.2 \pm 11$	$16 \pm 35$	$2.4 \pm 5.0$

<sup>a</sup> Sampling dates in 2007: Mississippi: 4/17–9/18; Iowa: 4/17–9/18.

<sup>b</sup> Sampling dates in 2008: Mississippi: 4/22–10/28; Iowa: 4/8–10/28.

percentages of total glyphosate removed from air by rain were 87 to 92% for the weeks with rainfall  $<30$  mm and 97% for weeks with rainfall  $\geq 30$  mm. The variability in the removal efficiency is less for the category with the higher rainfall. The efficient removal of glyphosate and AMPA from air by rain is not unexpected, because these compounds are in the particle phase in the atmosphere.

The weekly wet deposition ( $\mu\text{g}/\text{m}^2$ ) of glyphosate and AMPA was calculated as the product of the weekly concentration in rain times the weekly rainfall (Table 3). The weekly amounts were summed for the study period to yield their total wet deposition during the growing seasons. In Mississippi, total mass of glyphosate in rainfall was 0.60 and 1.5 kg in 2007 and 2008, respectively, and for AMPA it was 0.52 and 1.3 kg. The sum of total glyphosate (sum of glyphosate and AMPA in wet deposition) was equal to 0.04 and 0.1% of the mass of glyphosate applied in the watershed in 2007 and 2008, respectively. Although the total amount of glyphosate applied to the watershed in Mississippi was about the same in 2007 and 2008 (Table 1), the wet deposition for both compounds was about 2.5 times greater in 2008 compared with 2007 because of greater rainfall.

In Iowa, the total wet deposition of glyphosate during the growing seasons was 2.2 and 9.9 kg in 2007 and 2008, respectively, and for AMPA it was 0.72 and 1.5 kg. The sum of total glyphosate (sum of glyphosate and AMPA in wet deposition) was equal to 0.2 and 0.7% of the mass of glyphosate applied in the watershed in 2007 and 2008, respectively. The total wet deposition was much greater for both glyphosate (4.5-fold) and AMPA (2.0-fold) in 2008 than in 2007. This can be attributed to the substantially greater rainfall and a greater application mass in 2008 compared with 2007 (Table 1).

Glyphosate and its degradate, AMPA, were frequently observed in air particles and rain at all three locations that were studied in the agricultural areas of the midwestern United

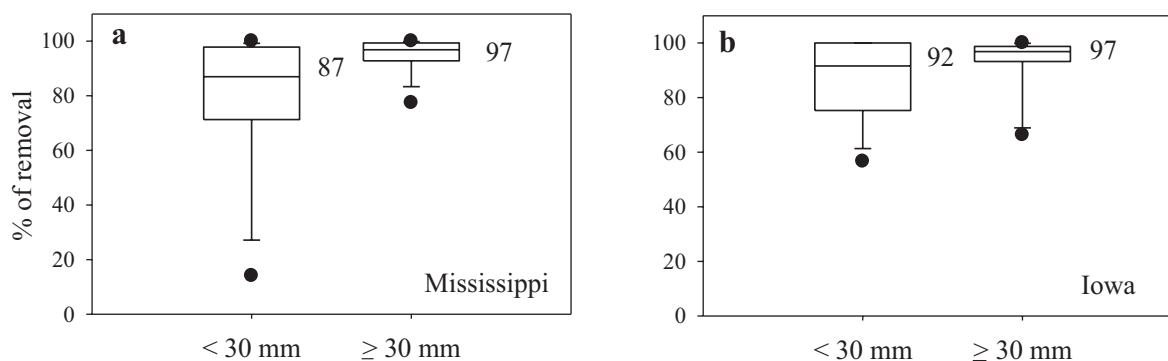


Fig. 5. Box plots showing the relationship between weekly rainfall amount and percentage of total glyphosate in air removed by rain: Mississippi, 2007–2008 (a) Iowa, 2007–2008 (b), USA.

States. Glyphosate occurred at concentrations equal to or greater than the concentrations of other high-use herbicides previously studied in the midwest. The presence of glyphosate in air is due either to spray drift or wind erosion, because it will have no tendency to be volatile because of its low vapor pressure and ionic character in moist soils. The presence of AMPA in air is due to wind erosion, because it is formed in the soil. The maximum concentrations of glyphosate in the air and rain correspond to the period of its application. It is not known what percentage of the applied glyphosate is introduced into the air, but it was estimated that up to 0.7% of application is removed from the air in rainfall. Glyphosate is efficiently removed from the air. It is estimated that an average of 97% of the glyphosate in the air is removed by a weekly rainfall  $\geq 30$  mm.

**Acknowledgement**—The authors thank the members of the U.S. Geological Survey offices in Indiana, Iowa, Mississippi, and Kansas for their support in the field and laboratory. This research was funded by the U.S. Geological Survey, National Water-Quality Assessment (NAWQA) Program. Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

## REFERENCES

- Harner T, Wideman JL, Jantunen LMM, Bidleman TF, Parkhurst MJ. 1999. Residues of organochlorine pesticides in Alabama soils. *Environ Pollut* 106:323–332.
- Tilman D, Cassman KG, Matson PA, Naylor R, Polasky S. 2002. Agricultural sustainability and intensive production practices. *Nature* 418:671–677.
- Juraske R, Anton A, Castells F, Huijbregts MAJ. 2007. PestScreen: A screening approach for scoring and ranking pesticides by their environmental and toxicological concern. *Environ Int* 33:886–893.
- Kiely T, Donaldson D, Grube A. 2004. Pesticide industry sales and usage: 2000 and 2001 market estimates. U.S. Environmental Protection Agency, Washington, DC.
- Coupe RH, Manning MA, Foreman WT, Goolsby DA, Majewski MS. 2000. Occurrence of pesticides in rain and air in urban and agricultural areas of Mississippi, April–September 1995. *Sci Total Environ* 248:227–240.
- Capel PD, McCarthy KA, Barbash JE. 2008. National, holistic, watershed-scale approach to understand the sources, transport, and fate of agricultural chemicals. *J Environ Qual* 37:983–993.
- MacDonald RW, Barrie LA, Bidleman TF, Diamond ML, Gregor DJ, Semkin RG, Strachan WMJ, Li YF, Wania F, Alaee M, Alexeeva LB, Backus SM, Bailey R, Bewers JM, Gobeil C, Halsall CJ, Harner T, Hoff JT, Jantunen LMM, Lockhart WL, Mackay D, Muir DCG, Pudykiewicz J, Reimer KJ, Smith JN, Stern GA, Schroeder WH, Wagemann R, Yunker MB. 2000. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci Total Environ* 254:93–234.
- Waite DT, Bailey P, Sproull JF, Quiring DV, Chau DF, Bailey J, Cessna AJ. 2005. Atmospheric concentrations and dry and wet deposits of some herbicides currently used on the Canadian prairies. *Chemosphere* 58:693–703.
- Yao Y, Tuduri L, Harner T, Blanchard P, Waite D, Poissant L, Murphy C, Belzer W, Aulagnier F, Li YF, Sverko E. 2006. Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. *Atmos Environ* 40:4339–4351.
- Foreman WT, Majewski MS, Goolsby DA, Wiebe FW, Coupe RH. 2000. Pesticides in the atmosphere of the Mississippi River Valley, part II—Air. *Sci Total Environ* 248:213–226.
- Thurman EM, Cromwell AE. 2000. Atmospheric transport, deposition, and fate of triazine herbicides and their metabolites in pristine areas at Isle Royale National Park. *Environ Sci Technol* 34:3079–3085.
- Gioia R, Offenberg JH, Gigliotti CL, Totten LA, Du SY, Eisenreich SJ. 2005. Atmospheric concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. *Atmos Environ* 39:2309–2322.
- Baylis AD. 2000. Why glyphosate is a global herbicide: strengths, weaknesses and prospects. *Pest Manag Sci* 56:299–308.
- James C. 2004. Global Status of Commercialized Biotech/GM Crops: 2004. International Service for the Acquisition of Agri-Biotech Applications (ISAAA) Brief 32. Ithaca, NY, USA, pp 1–12.
- Dill GM, CaJacob CA, Padgett SR. 2008. Glyphosate-resistant crops: Adoption, use and future considerations. *Pest Manag Sci* 64:326–331.
- U.S. Department of Agriculture, National Agricultural Statistics Service. 2009. Acreage. Washington, DC.
- Franz JE, Mao MK, Sikorski JA. 1997. *Glyphosate: A Unique Global Herbicide*. ACS Monograph 189. American Chemical Society, Washington, DC.
- Battaglin WA, Kolpin DW, Scribner EA, Kuivila KM, Sandstrom MW. 2005. Glyphosate, other herbicides, and transformation products in Midwestern streams. *J Am Water Resour Assoc* 41:323–332.
- Smith PH, Raymond KN. 1988. Solid-state and solution chemistry of calcium N-(phosphonomethyl)glycinate. *Inorg Chem* 27:1056–1061.
- Sprankle P, Meggitt WF, Penner D. 1975. Rapid inactivation of glyphosate in soil. *Weed Sci* 23:24–228.
- U.S., Environmental Protection Agency. 1993. Reregistration Eligibility Decision (RED) Glyphosate. PA-738-R-93-014. Washington, DC.
- De Roos AJ, Blair A, Rusiecki JA, Hoppin JA, Svec M, Dosemeci M, Sandler DP, Alavanja MC. 2005. Cancer incidence among glyphosate-exposed pesticide applicators in the agricultural health study. *Environ Health Perspect* 113:49–54.
- Richard S, Moslemi S, Sipahutar H, Benachour N, Seralini GE. 2005. Differential effects of glyphosate and roundup on human placental cells and aromatase. *Environ Health Perspect* 113:716–720.
- Kollman W, Segawa R. 1995. Interim Report of the Pesticide Chemistry Database. Appendix EH 95-04. California Department of Pesticide Regulation, Sacramento, CA, USA.
- Giesy JP, Dobson S, Solomon KR. 2000. Ecotoxicological risk assessment for Roundup<sup>®</sup> herbicide. *Rev Environ Contam T* 167:35–120.
- Mallat E, Barcelo D. 1998. Analysis and degradation study of glyphosate and of aminomethylphosphonic acid in natural waters by means of polymeric and ion-exchange solid-phase extraction columns followed by ion chromatography post-column derivatization with fluorescence detection. *J Chromatogr A* 823:129–136.
- Vereecken H. 2005. Mobility and leaching of glyphosate: A review. *Pest Manag Sci* 61:1139–1151.
- Peruzzo PJ, Porta AA, Ronco AE. 2008. Levels of glyphosate in surface waters, sediments and soils associated with direct sowing soybean cultivation in north pampasic region of Argentina. *Environ Pollut* 156:61–66.
- Jauhiainen A, Rasanen K, Sarantila R, Nuutinen J, Kangas J. 1991. Occupational exposure of forest workers to glyphosate during brush saw spraying work. *Am Indust Hyg Assoc J* 52:61–64.
- Duke SO, Powles SB. 2008. Glyphosate: a once-in-a-century herbicide. *Pest Manag Sci* 64:319–325.
- National Climate and Data Center. 2010. *Quality Controlled Local Climatological Data*. Asheville, NC, USA.
- Vogel JR, Majewski MS, Capel PD. 2008. Pesticides in rain in four agricultural watersheds in the United States. *J Environ Qual* 37:1101–1115.
- Myer MT, Loftin KA, Lee EA, Hinshaw GH, Dietze JE, Scribner EA. 2009. Determination of Glyphosate, its Degradation Product Aminomethylphosphonic Acid, and Glufosinate, in Water by Isotope Dilution and Online Solid-Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. U.S. Geological Survey, Techniques and Methods, Book 5, chapter A10.
- Forlani G, Mangiagalli A, Nielsen E, Suardi CM. 1999. Degradation of the phosphonate herbicide glyphosate in soil: Evidence for a possible involvement of unculturable microorganisms. *Soil Biol Biochem* 31:991–997.
- Majewski MS, Foreman WT, Coupe RH, Goolsby DA, Wiebe FW. 2008. Pesticides in Air and Rainwater in the Midcontinental United States, 1995—Method and Data. Open-File Report 2007-1396. U.S. Geological Survey, Reston, VA.
- Grunewald K, Schmidt W, Unger C, Hanschmann G. 2001. Behavior of glyphosate and aminomethylphosphonic acid (AMPA) in soils and water of reservoir Radeburg II catchment (Saxony/Germany). *J Plant Nutr Soil Sci* 164:65–70.
- Offenberg JH, Baker JE. 1997. Polychlorinated biphenyls in Chicago precipitation: Enhanced wet deposition to near-shore Lake Michigan. *Environ Sci Technol* 31:1534–1538.