

Fate and transport of glyphosate and aminomethylphosphonic acid in surface waters of agricultural basins

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Abstract

BACKGROUND: Glyphosate [*N*-(phosphonomethyl)glycine] is a herbicide used widely throughout the world in the production of many crops and is heavily used on soybeans, corn and cotton. Glyphosate is used in almost all agricultural areas of the United States, and the agricultural use of glyphosate has increased from less than 10 000 Mg in 1992 to more than 80 000 Mg in 2007. The greatest intensity of glyphosate use is in the midwestern United States, where applications are predominantly to genetically modified corn and soybeans. In spite of the increase in usage across the United States, the characterization of the transport of glyphosate and its degradate aminomethylphosphonic acid (AMPA) on a watershed scale is lacking.

RESULTS: Glyphosate and AMPA were frequently detected in the surface waters of four agricultural basins. The frequency and magnitude of detections varied across basins, and the load, as a percentage of use, ranged from 0.009 to 0.86% and could be related to three general characteristics: source strength, rainfall runoff and flow route.

CONCLUSIONS: Glyphosate use in a watershed results in some occurrence in surface water; however, the watersheds most at risk for the offsite transport of glyphosate are those with high application rates, rainfall that results in overland runoff and a flow route that does not include transport through the soil.

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Keywords: glyphosate; AMPA; runoff; surface water; subsurface drainage; load

1 INTRODUCTION

Glyphosate [*N*-(phosphonomethyl)glycine] is a herbicide used widely throughout the world in the production of many crops and is heavily used on soybeans, corn and cotton that have been genetically modified (GM) to be tolerant to glyphosate.¹ Glyphosate is used extensively in almost all agricultural areas of the United States. It also has extensive urban use, which has been shown disproportionately to transport glyphosate to surface water.² The agricultural use of glyphosate has increased dramatically since 1992, when the annual use was less than 10 000 Mg (Fig. 1). In 2007, more than 80 000 Mg of glyphosate was used to control unwanted vegetation on cropland. The greatest intensity of glyphosate use is in the midwestern United States, where applications are primarily to GM corn and soybeans (Fig. 2), and in the Mississippi River alluvial flood plain, where applications are to soybeans and cotton and as a 'burn-down' application in preparing fields for planting. More than 90% of the soybeans grown in the United States are glyphosate tolerant, with some states having an even higher percentage, such as South Dakota with 97% and Mississippi with 96% in 2007. In the United States, most of the cotton (72%) and about half of the corn (52%) planted in 2007 were glyphosate tolerant.³ Glyphosate use, particularly on GM crops, has replaced the use of other herbicides in the production of row crops. Glyphosate is considered by some to be more environmentally benign in comparison with other herbicides

because: (1) it strongly sorbs to soil particles, limiting the potential for transport; (2) it has a shorter half-life compared with many other herbicides; (3) the use of glyphosate has resulted in a reduction in the number of herbicide applications to control weeds; (4) the use of glyphosate results in lower fossil fuel usage owing to an increase in conservation tillage; (5) it has a low toxicity to mammals, birds and most aquatic fauna.⁴

The chemical characteristics of glyphosate are strongly dependent on pH owing to the four ionizable hydrogens on its functional groups (pK_a values 2.0, 2.6, 5.6 and 10.6).⁵ The water solubility of glyphosate is 10.1 g L⁻¹ at 20 °C.⁶ The observed K_{oc} values for glyphosate range from 9 to 60 000 L kg⁻¹ and are dependent on the surface characteristics of the solid, the solution pH and the concentration of di- and trivalent cations, but they are not strongly correlated with soil texture or organic matter content.^{7–11}

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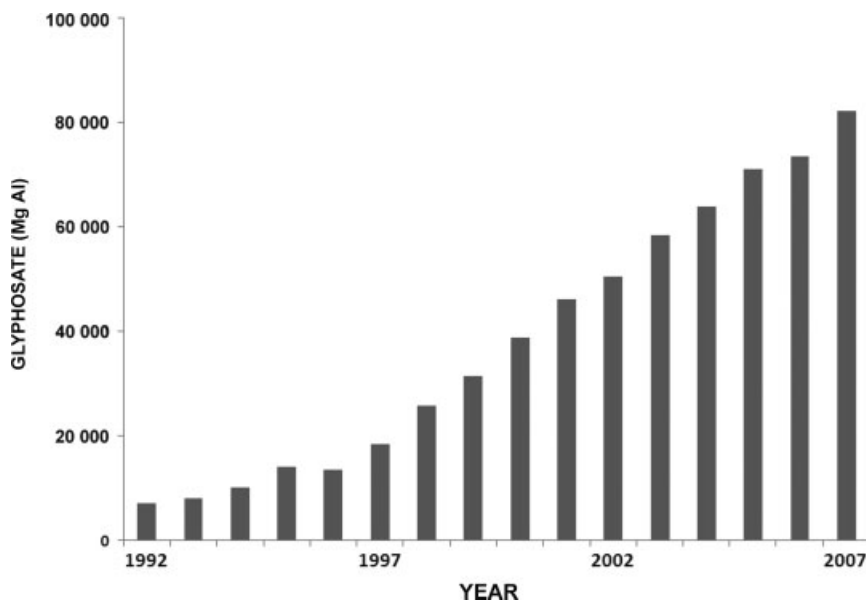


Figure 1. Agricultural use of glyphosate (active ingredient) in the conterminous United States, 1992–2007. Estimates developed using proprietary data (GfK Kynetex, Inc.).

Glyphosate sorption is negatively correlated with phosphate content because it binds to surface sites through its phosphonate group and competes for the same binding sites. The half-life for glyphosate was observed to range from 1.7 to 142 days, with an average of about 40 days.⁷ The variability in half-life is thought to be due to the variability in microbial activity and extent of soil sorption among the various sites that were studied. It has been observed that repeated applications of glyphosate have increased its soil half-life.^{12,13} Less is known about the metabolite of glyphosate, aminomethylphosphonic acid (AMPA). It has a lower water solubility (5.8 g L^{-1} at 25°C) and a longer soil half-life (ranging from 76 to 240 days).⁶

In spite of the reported strong sorption to soils and the short half-life in soil, researchers reported detections of glyphosate in runoff in studies conducted prior to the introduction of GM crops. Edwards *et al.*¹⁴ reported that glyphosate concentrations in runoff from small (0.3–3.1 ha) basins planted in no-till corn or fescue ranged from 2 to $5200 \mu\text{g L}^{-1}$. Glyphosate was detected up to 4 months after application. More recent studies have indicated that glyphosate and its degradate, AMPA, are frequently detected in surface water.^{15–20}

Glyphosate and AMPA have been detected extensively in the Mississippi River basin.^{15,18} In spring 2002, 40% of 51 streams in nine midwestern states had detectable levels ($>0.1 \mu\text{g L}^{-1}$) of glyphosate, and 83% had detectable levels of AMPA.¹⁵ Glyphosate was detected in 32% of 608 surface water samples collected during 2001–2006 as part of the US Geological Survey (USGS) National Water Quality Assessment Program (NAWQA) from streams throughout the United States. AMPA was detected in 52% of the samples.¹⁸ In southern Ontario, the percentage of samples above the reporting level ($5.0 \mu\text{g L}^{-1}$) of glyphosate was 26% in 2004 and 17% in 2005 of more than 500 samples.¹⁹ In Finland, 302 days after application to bare soil, glyphosate loss from runoff was 0.1% of the applied amount. The highest concentration ($4.8 \mu\text{g L}^{-1}$) occurred during the first rainfall event after application. The runoff event moving the most mass occurred 285 days after application; however, the circumstances were somewhat unique in that the snow melt occurring during this

runoff event in April generated runoff volumes 35 times higher than during the previous 200 days.¹⁷

Information on the mechanisms of the movement of glyphosate and AMPA in the environment is scarce; examination of the factors controlling the transport of glyphosate to surface waters on a watershed scale is needed to determine which factors are important in this process, and how those factors may change in importance, both spatially and temporally.

This paper explores the transport of glyphosate and AMPA in seven streams in agricultural basins located in four different environmental settings. Water samples were collected over a 2 year period from two sets of nested basins (Mississippi and Iowa). Water samples were also collected during storm events in Indiana (1 year) and near Rouffach, France (4 years). The concentrations, loads and sources of glyphosate and AMPA in these streams are interpreted using a conceptual model to enhance the understanding of factors controlling their occurrence and transport in agricultural streams.

2 METHODS

2.1 Study sites

The study conducted by the NAWQA Program of the USGS included four basins: the South Fork Iowa River, Iowa; Sugar Creek, Indiana; Bogue Phalia, Mississippi (Fig. 2); Rouffach, France. The Bogue Phalia basin in Mississippi and the South Fork Iowa River basin in Iowa were paired basins of similar land use ($>80\%$ row crop) but located in areas with differing climates and soils. Each of these basins had one or two nested subbasins that were studied in more detail (Table 1, Fig. 2). Results from the paired basins were compared with the more limited datasets from Sugar Creek, Indiana, and Rouffach, France.

2.1.1 Bogue Phalia, Mississippi

The Bogue Phalia basin is located in the low, relatively flat alluvial plain of the Mississippi River in the northwestern part of Mississippi, a slightly undulating area of little topographic relief and an average basin slope of about 0.25 m km^{-1} (Table 1, Fig. 2). Agriculture in

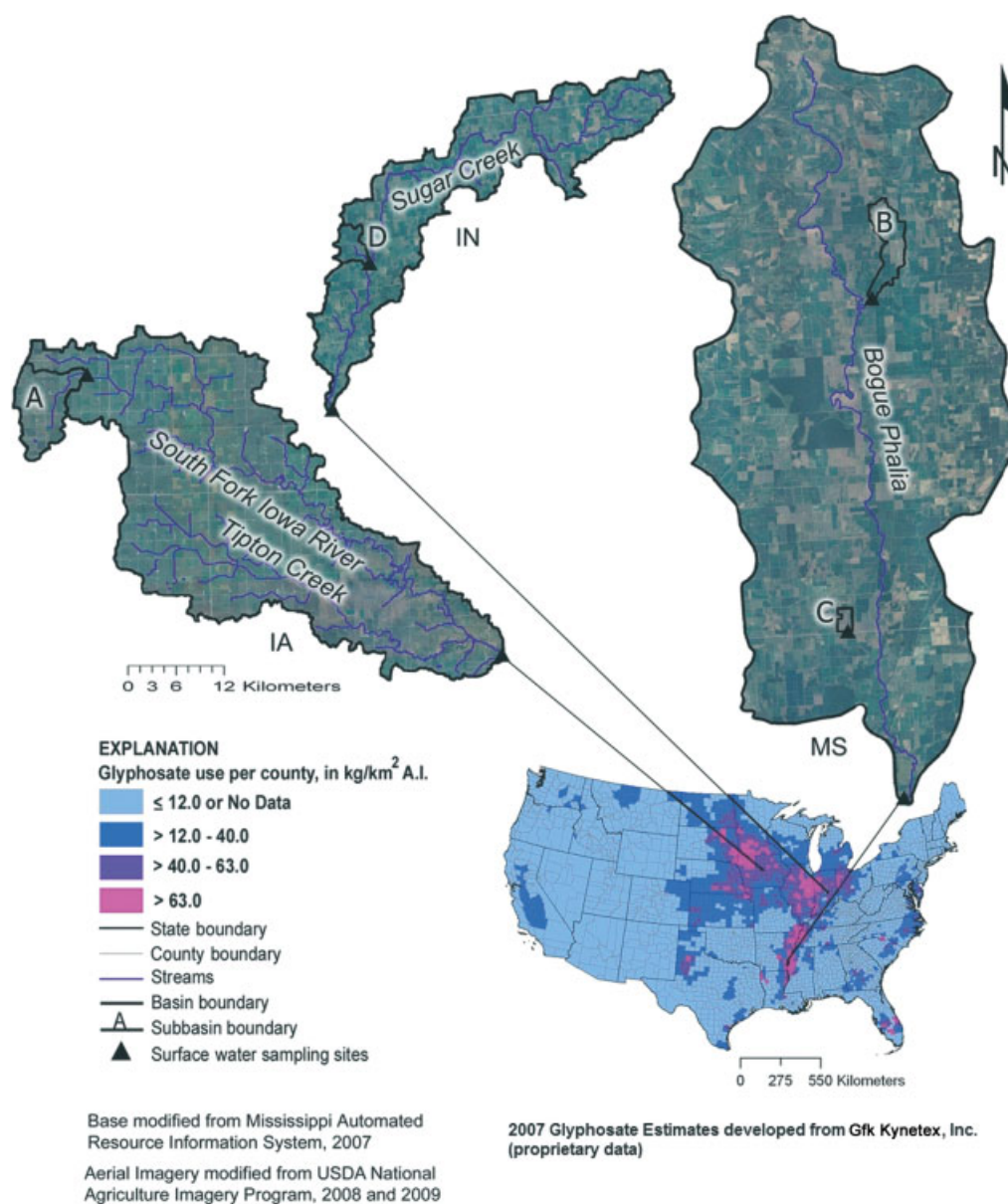


Figure 2. The South Fork Iowa River Basin in Iowa, the Sugar Creek Basin in Indiana, and the Bogue Phalia Basin in Mississippi and subbasins; (A) South Fork Iowa River near Blairsburg, IA, (B) Tommie Bayou near Pace, MS, (C) Unnamed tributary near Napanee, MS and (D) Leary Weber Ditch at Mohawk, IN. Map of agriculture use of glyphosate in the conterminous U.S., in 2007.

the basin is dominated by soybean [*Glycine max* (L.) Merr.], with lesser amounts of cotton (*Gossypium hirsutum* L.), rice (*Oryza sativa* L.) and corn (*Zea mays* L.).²¹ Subbasin sampling sites in the Bogue Phalia basin included Tommie Bayou and an unnamed tributary to Clear Creek near Napanee (Napanee), Mississippi (Table 1, Fig. 2).

The climate is subtropical, with maximum daily summer temperatures nearing 37 °C and an average annual rainfall exceeding 120 cm. Most of the soils in the Bogue Phalia basin are heavy clay soils and are classified into the Natural Resource Conservation Service (NRCS) Hydrologic Soil Groups C and D, indicating high runoff potential.²² The Bogue Phalia basin is a surface-water-driven system, with most of the precipitation running off the land surface into streams and rivers, with little drainage through or penetration into the underlying aquifer.²³ Hydrograph separation analyses (Coupe RC, unpublished) for 10 years of streamflow at the Bogue Phalia gaging station indicate

that the percentage of the total flow in the stream that was contributed by groundwater ranged from 23 to 39% and averaged 28% annually.

2.1.2 South Fork of the Iowa River, Iowa

The South Fork Iowa River (SFIR) basin is located in north-central Iowa²⁴ and flows in a southeasterly direction to its confluence with the Iowa River (Table 1, Fig 2). The area is characterized by low relief, with some distinct ridges as well as some depressions that form lakes, ponds and swamps. Poorly draining glacial till is the dominant surficial material.²⁵ The basin that contains the headwater section of the SFIR at Blairsburg, Iowa, is the nested subbasin in the SFIR.

In addition to the samples collected in the SFIR basin and nested subbasin, water samples were also collected from a 20 cm diameter subsurface drain near the SFIR Blairsburg gage

Table 1. Study basins and subbasins with basic hydrological and agricultural characteristics, data collection period, basin size, mean daily streamflow for 2007 and 2008 and 1997–2006 mean daily streamflow

Location	Basin ^a	Subbasin ^a	Data collection period	Basin size (km ²)	Mean daily flow		Water yield	Basin in agriculture (%)	Percentage of agriculture by major crop type (2007) (2008)					
					(m ³ s ⁻¹) (2007) (2008) ^b	1997–2006 mean daily flow (m ³ s ⁻¹) ^b			Soybean	Corn	Cotton	Rice	Grapes	
Mississippi, USA	Bogue Phalia		January 2007–November 2008	1250	9.71	21.58	27.5	>80	45	11	13	13	0	
					22.94				51	12	4	16	0	
		Tommie Bayou	April 2007–September 2008	15.2	0.18	n/a			32	0	0	64	0	
Iowa, USA	SFIR New Providence		February 2007–September 2008	570	11.13	3.82	25.1	>85	29	70	0	0	0	
					11.33				34	64	0	0	0	
		SFIR Blairsburg	April 2007–September 2008	31.1	0.48	n/a			32	68	0	0	0	
Indiana, USA	Sugar Creek		Two storm events in May 2004	249	n/a	n/a	34.5	75	~50	~50	0	0	0	
					7.22	n/a	n/a		87	47	39	0	0	0
		Leary Weber Ditch Overland Flow Site		0.42	n/a	n/a		~100	100	0	0	0	0	
France	Rouffach		58 storm events March–September 2003–2006	0.42	n/a	n/a	1.48	68	0	0	0	0	100	

^a SFIR: South Fork Iowa River.^b n/a: not applicable.

(Subsurface Drain). The exact size and shape of the area drained by this subsurface drain is unknown. Flow data were not collected from the Subsurface Drain.

Temperatures in the basin are moderate and range from a daily mean of 23.1 °C in July to -8 °C in January. Annual rainfall averages about 80 cm, but most of the rainfall occurs in April–October. The soils in the SFIR basin are highly productive and are mostly classified as NRCS Hydrologic Soil Group B, indicating a moderate infiltration rate that requires artificial subsurface drainage to maximize crop production potential. Over the last 100 years, subsurface drainage has been installed throughout as much as 80% of the basin. Green *et al.*²⁶ estimated that the source of about 71% of the annual streamflow was from subsurface drains, and only 6% of that total was from groundwater. Hydrograph separation indicated that 65% of the total annual flow was from groundwater which includes subsurface drainage.²⁷

2.1.3 Sugar Creek, Indiana

The Sugar Creek basin is located in central Indiana within the White River basin approximately 25 km east of Indianapolis (Table 1, Fig. 2). Within the Sugar Creek basin, the nested subbasin is Leary Weber Ditch at Mohawk, Indiana. Within the Leary Weber Ditch basin there is a 0.014 km² depression, instrumented with a flume and automatic sampler to collect water samples that are representative of overland flow (Overland Flow Site).²⁸

Temperatures in the basin are moderate and range from a daily mean of 24 °C in July to -4 °C in January, and with an average annual rainfall of about 100 cm. Most (>79%) of the basin has soils in the NRCS Hydrologic Soil Group C, with much of the remainder in Soil Group B (>18.5%). The runoff potential for both of these soils is relatively high. Subsurface drainage is used extensively throughout the basin to lower the water table and improve crop yields. It is estimated that >71% of the Sugar Creek basin is artificially drained.^{29,30}

2.1.4 Rouffach, France

The Rouffach basin is located in eastern France in the Alsace region south of Strasbourg on the slopes overlooking the Rhine River Valley.²⁰ The Rouffach basin is small in size, about 0.42 km², with an average slope of about 150 m km⁻¹. Streamflow is ephemeral, occurring only during rainfall events. Generally, when rainfall was less than 4 mm, only the dense road network contributed to the streamflow, whereas, when rainfall was more than 4 mm, streamflow originated from both roads and vineyards. Only rainfall events that generated a runoff volume greater than 8 m³ were monitored. Land use for about 68% of the contributing basin is vineyard.

2.2 Data collection, analysis and quality assurance

Water samples from the larger basins in the United States (the Bogue Phalia near Leland, Mississippi; the SFIR near New Providence, Iowa; Sugar Creek at New Palestine, Indiana) were collected using depth-, width- and velocity-integrating procedures.³¹ Samples were collected on a regular schedule, bimonthly during most of the year but weekly during the growing season (May–August); additional samples were collected during selected storm events.

Water samples from the smaller subbasins and the Rouffach basin were collected using an automatic sampler. With the exception of the Rouffach site, automatic samplers were triggered by a data logger connected to a pressure transducer that measured

water depth in the stream. A predetermined rise in stream level initiated the automatic samplers to collect samples on a time-dependent basis, which varied from site to site depending upon the hydrologic characteristics of the site. At the Rouffach basin, sampling was triggered by flow volume, and a sample was collected every 8 m³ of discharge volume throughout the hydrograph. Most samples from the smaller subbasins were collected from April to August in the United States and from March to October in France, with multiple samples collected over a storm hydrograph.

Water sample collection and processing in the United States followed USGS protocols.³¹ Water samples were filtered and analyzed for glyphosate and AMPA using online solid-phase extraction and analysis by HPLC/MS.^{32,33} Both compounds had a reporting level of 0.02 µg L⁻¹. Water samples collected from the Rouffach basin in France were filtered and analyzed using similar methods, with a reporting level of 0.1 µg L⁻¹.²⁰ The results presented here will only represent the portion of glyphosate and AMPA that is dissolved in water, and not the portion attached to sediment.

During 2007 and 2008 at the US sites, six field blanks and 11 replicates were analyzed for glyphosate and AMPA for quality assurance purposes. None of the blanks had values above the reporting level of 0.02 µg L⁻¹. When the water samples had glyphosate (nine samples) and AMPA (eight samples) concentrations below 1.0 µg L⁻¹, the average differences between replicate samples were 0.02 and 0.03 µg L⁻¹ respectively. For those samples with glyphosate (two samples) and AMPA (three samples) concentrations at or above 1.0 µg L⁻¹, the average differences were 0.2 and 0.1 µg L⁻¹ respectively. There were 143 laboratory duplicates, with an average percentage difference of 7.8% for glyphosate and 8.7% for AMPA.

The mean daily discharge for the US sites was calculated and reported by the USGS according to standard procedures.³⁴ For the Rouffach basin, flow was calculated according to Gregoire *et al.*²⁰

2.3 Glyphosate application and loads

Information on glyphosate application came from two sources. For the two larger basins (Bogue Phalia and the SFIR), estimates of the annual agricultural use of glyphosate were developed using proprietary data (GfK Kynetec, Inc.) on the mass of glyphosate applied to agricultural crops and data on county-harvested crop acreage. Glyphosate use estimates, which were based on surveys of major row crops and specialty crops, were reported for multicounty areas referred to as crop-reporting districts (CRDs). The CRD-level use estimates were converted to basin-level application rates by multiplying the total glyphosate application to the CRD by the percentage of the basin in that CRD. Information on glyphosate application for the smaller subbasins in Mississippi and Iowa was based on interviews with farmers in each of the subbasins. These data were used to calculate a mass loading to the basin. For the Rouffach basin, annual surveys were sent to the 28 farmers in the basin, asking for information on pesticide application methods, timing and amounts.

When glyphosate or AMPA concentrations were reported as less than the reporting limit, the concentrations were set to zero for percentage detection values and load calculations. This was only an issue for the data from Iowa streams, because in the other study areas 99% or more of the water samples had detections of glyphosate and AMPA. Setting the concentrations to zero could bias the load estimates to be low because the actual concentrations

of pesticides reported as less than the detection limit may have ranged up to the detection limit without being observed.

To gain a better understanding of the fate and transport of pesticides, it is often insightful to examine the relation between pesticide degradates and the parent compound. Here, the %AMPA as a percentage of total glyphosate (glyphosate + AMPA) was calculated:

$$\% \text{ AMPA} = \frac{[\text{AMPA}]}{[\text{Glyphosate}] + [\text{AMPA}]} \times 100 \quad (1)$$

where [AMPA] and [Glyphosate] are their respective molar concentrations in water. A %AMPA equal to zero indicated either that both AMPA and glyphosate were below their reporting levels or glyphosate was above its reporting level, but not AMPA (this occurred in 2.5% of the samples from Iowa). If %AMPA was equal to 100, then only AMPA was observed in the water sample.

Linear interpolation was used to estimate the annual loads of glyphosate and AMPA for the sites in Iowa and Mississippi.^{9,35,36} Concentrations on non-sampled days were estimated by interpolating between concentrations measured on sampled days. Measured or interpolated daily concentrations were multiplied by the mean daily discharge to estimate a daily load. Daily loads were summed to estimate annual load. For the site in France, because the stream flowed only after rain events, a load was calculated for each event by multiplying the concentration (using linear interpolation between measured concentrations) by the instantaneous flow for each minute and then summing over the entire event. The annual load was calculated by summing the individual event loads for each year. Annual loads could not be calculated for the site in Indiana because only two storm events were sampled.

The accuracy of the annual load estimates depends upon how well the daily concentration distribution is represented and the accuracy of the daily discharge. The most important component and fortunately the component with the most accurate (typically $\pm 5\%$) measurement is discharge. Discharge is measured continuously, and therefore extrapolation to a missing data point is not necessary. Accurately representing the concentration distribution is more difficult because it is measured discretely, with measurements on the larger basins sometimes days or weeks apart. Because the concentration in the water is seasonally dependent and varies according to the weather conditions, sample collection, especially on the smaller basins, must have a component that is targeted to conditions when high concentrations are expected. In this study, the smaller basins were instrumented with automatic samplers to facilitate the collection of water samples during runoff events, and, for the larger basins with slower response times, high flow samples were collected to augment fixed-interval sampling.

The annual load as a percentage of use (LAPU) was calculated for each of the basins and subbasins (with the exception of Indiana) to compare the behavior of glyphosate across scales and between study areas. It was calculated thus:

$$\text{LAPU} = \frac{\text{annual stream load of glyphosate from that basin (kg year}^{-1}\text{)}}{\text{annual glyphosate use in that basin (kg year}^{-1}\text{)}} \times 100 \quad (2)$$

Additionally, for proper quantification of the total glyphosate load as a percentage of use (TGLAPU), the concentrations of all glyphosate-derived compounds (in this instance, only AMPA) must be expressed on a glyphosate mass equivalent basis. The

total mass equivalent load of glyphosate (MEL_{gly}) was calculated in the following manner (Barbash J, private communication, 2010):

$$\text{MEL}_{\text{gly}} = \text{glyphosate load (kg year}^{-1}\text{)} + \{ \text{AMPA load (kg year}^{-1}\text{)} \times [\text{MW}_{\text{gly}}/\text{MW}_{\text{AMPA}}] \}$$

where

$$\text{MW}_{\text{gly}} = \text{molecular weight of glyphosate (0.16907 kg mol}^{-1}\text{)} \quad (3)$$

and

$$\text{MW}_{\text{AMPA}} = \text{molecular weight of AMPA (0.11104 kg mol}^{-1}\text{)} \quad (4)$$

Inserting the above expression for MEL into equation (2) yields the following:

$$\text{TGLAPU} (\%) = \frac{\text{MEL}_{\text{gly}}(\text{kg year}^{-1})}{\text{annual glyphosate use in basin (kg year}^{-1}\text{)}} \times 100 \quad (5)$$

2.4 Conceptual model

A conceptual model of processes influencing glyphosate transport to surface waters provides a framework for comparing the study basins. The occurrence of glyphosate and AMPA in surface waters of the four watersheds can be described in terms of the following function:

$$\text{Glyphosate or AMPA occurrence or LAPU} = A(S_s)t + B(\text{RRF})t + (\text{FR})$$

where the source strength S_s , which varies with time t , is related to when (in time) glyphosate was applied and to how much was applied, and also to the physical and chemical characteristics of the compound. The rainfall runoff factor (RRF) is related to the amount, frequency and duration of rainfall events or irrigation, but only those events generating flow that reaches the local streams either through the subsurface drainage system or by overland flow, and it also varies with time. The flow route (FR) is either overland flow or subsurface drainage and refers to whether the majority of the rainfall reaches the stream by overland flow or by subsurface drainage. This term includes many factors such as antecedent soil moisture conditions, geology, soils and other factors that affect the movement of water. [In some systems (Iowa and Indiana), the FR can vary over time, depending on the RRF, such as when precipitation exceeds infiltration and overland runoff occurs]. The interaction of these three factors – S_s , RRF and FR – can be used to explain the differences in glyphosate and AMPA occurrence in the surface waters of the four basins.

3 RESULTS

3.1 Mississippi

Water samples collected from the three sites in the Bogue Phalia basin in 2007 and 2008 all had measurable concentrations of glyphosate and AMPA (Table 2, Fig. 3). Concentrations of glyphosate for the Bogue Phalia, Tommie Bayou and Napanee ranged from 0.08 to 73 $\mu\text{g L}^{-1}$, from 0.04 to 6.2 $\mu\text{g L}^{-1}$ and from 0.03 to 41 $\mu\text{g L}^{-1}$ respectively. The highest median glyphosate concentration (1.2 $\mu\text{g L}^{-1}$) was in Napanee, followed by the Bogue Phalia (0.96 $\mu\text{g L}^{-1}$) and Tommie Bayou (0.82 $\mu\text{g L}^{-1}$). Seasonal concentrations of glyphosate and AMPA in the Bogue Phalia

Table 2. The sampling period, number of samples collected, maximum, minimum and median concentrations of glyphosate, AMPA and %AMPA at each sampling site and the percentage of samples below the reporting limit

Basin	Subbasin ^a	Sampling period	Constituent ^b	Units	Number of samples	Maximum	Minimum	Median	Percent of samples below reporting level (0.02 µg L ⁻¹) ^c
Bogue Phalia, MS		October 2006–November 2008	Glyphosate	µg L ⁻¹	62	73	0.08	0.96	0
			AMPA			28	0.48	2.6	0
			%AMPA	%		96	14	72	n/a
	Tommie Bayou	April 2007–September 2008	Glyphosate	µg L ⁻¹	74	6.2	0.04	0.82	0
			AMPA			5.9	0.12	1.5	0
			%AMPA	%		94	20	67	n/a
	Napanee	April 2007–September 2008	Glyphosate	µg L ⁻¹	73	41	0.03	1.2	0
			AMPA			9.7	0.27	1.6	0
			%AMPA	%		94	18	53	n/a
SFIR New Providence, IA		February 2007–September 2008	Glyphosate	µg L ⁻¹	34	1.6	<0.02	0.07	41
			AMPA			1.2	<0.02	0.15	3
			%AMPA	%		100	0	76	n/a
	Subsurface Drain	February 2007–November 2008	Glyphosate	µg L ⁻¹	64	290	<0.02	0.87	19
			AMPA			400	<0.02	0.58	1.6
			%AMPA	%		100	0	52	n/a
	SFIR Blairsburg	February 2007–November 2008	Glyphosate	µg L ⁻¹	79	5.7	<0.02	0.18	28
			AMPA			2.9	<0.02	0.32	8
			%AMPA	%		100	0	57	n/a
Sugar Creek, IN		19–21 May 2004	Glyphosate	µg L ⁻¹	5	1.0	0.15	0.32	0
			AMPA			0.36	0.07	0.14	0
			%AMPA	%		48	9	38	n/a
		30 May–2 June 2004	Glyphosate	µg L ⁻¹	6	1.6	0.37	0.66	0
			AMPA			0.74	0.19	0.39	0
			%AMPA	%		59	12	35	n/a

Table 2. (Continued)

Basin	Subbasin ^a	Sampling period	Constituent ^b	Units	Number of samples	Maximum	Minimum	Median	Percent of samples below reporting level (0.02 µg L ⁻¹) ^c
	Leary Weber Ditch	19–21 May 2004	Glyphosate	µg L ⁻¹	6	2.1	0.16	0.90	0
			AMPA			0.23	0.08	0.19	0
			%AMPA	%		47	10	10	n/a
		30 May–2 June 2004	Glyphosate	µg L ⁻¹	7	5.5	0.47	1.1	0
			AMPA			0.62	0.07	0.31	0
			%AMPA	%		37	6	16	n/a
	Overland Flow Site	19–21 May 2004	Glyphosate	µg L ⁻¹	6	430	21.5	380	0
			AMPA			29.0	24.0	26.0	0
			%AMPA	%		8	6	7	n/a
		30 May–2 June 2004	Glyphosate	µg L ⁻¹	7	49.0	22.0	34.0	0
			AMPA			16.0	3.7	8.2	0
%AMPA	%	18	15	17	n/a				
Rouffach, France	March–September: 2003–2006	Glyphosate	µg L ⁻¹	303	86	<0.1	4.7	0.3 ^d	
		AMPA			44	0.2	1.9	0	
		%AMPA	%		60	6	31	n/a	

^a SFIR: South Fork Iowa River.^b AMPA: aminomethylphosphonic acid; %AMPA: {[AMPA]/([AMPA] + [Glyphosate])} × 100.^c n/a: not applicable.^d A reporting level of 0.1 µg L⁻¹ was used for data from Rouffach.

have a distinct pattern, in that concentrations are lowest in winter and show a steady increase until late fall, coincident with glyphosate application patterns (Figs 3 and 4). The highest median concentration of AMPA ($2.6 \mu\text{g L}^{-1}$) was in the largest stream, the Bogue Phalia. AMPA concentrations were greater than glyphosate concentrations in more than 75% of the samples for all sampling sites in Mississippi. For the Bogue Phalia and Tommie Bayou, AMPA concentrations were higher than glyphosate concentrations in more than 90% of the samples. Glyphosate concentrations were equal to or greater than AMPA concentrations in 41% of the samples collected at Napanee, the smallest subbasin in Mississippi.

Glyphosate and AMPA loads in the Bogue Phalia basin were substantially greater at all sites in 2008 compared with 2007 (Table 3), corresponding to higher rainfall and subsequent discharge as well as higher glyphosate application amounts in 2008 (Figs 3 and 4, Table 3). The AMPA loads were much greater than the glyphosate loads for Tommie Bayou and Bogue Phalia, but the opposite was true for Napanee. The LAPU ranged from 0.14% in 2007 in the Tommie Bayou to 0.86% in Napanee in 2008. The LAPU for the Bogue Phalia for 2007 and 2008 was 0.33 and 0.56% respectively. The TGLAPU was substantially higher, especially for the Bogue Phalia and Tommie Bayou basins (about 70% greater than the LAPU), demonstrating that much of the TGLAPU is in the form of AMPA. For the Napanee basin, the TGLAPU only increased about 50% over the LAPU because of a smaller contribution of AMPA to the TGLAPU.

3.2 Iowa

Fifty-nine percent of water samples collected from the SFIR New Providence site had measurable levels of glyphosate, and 97% had measurable levels of AMPA (Table 2). The SFIR Blairsburg site had measurable levels of glyphosate and AMPA in 72 and 92% of water samples respectively. The range of glyphosate concentrations for SFIR New Providence and SFIR Blairsburg was <0.02 – 1.6 and <0.02 – $5.7 \mu\text{g L}^{-1}$ respectively. Concentrations of glyphosate and AMPA for both SFIR sites increased through the late spring and then decreased in early fall, coincident with glyphosate application (Fig. 3, Table 3). Forty percent of the samples from both sites had higher glyphosate concentrations than AMPA concentrations, although the median %AMPA for SFIR New Providence (76%) was higher than the median for SFIR Blairsburg (57%).

Maximum glyphosate and AMPA concentrations from the Subsurface Drain exceeded $250 \mu\text{g L}^{-1}$ (Table 2), but the median concentrations were 0.87 and $0.58 \mu\text{g L}^{-1}$ respectively, higher than the concentrations at the surface-water sampling sites. Glyphosate was reported in 81% and AMPA in over 98% of the water samples from the Subsurface Drain. Glyphosate concentrations were higher during the application period, but AMPA concentrations were higher at other times.

The glyphosate load from the SFIR New Providence was more than 3 times greater in 2007 than in 2008 (Table 3), in spite of similar annual discharges and 22% more glyphosate applied in 2008. The SFIR Blairsburg glyphosate loads were similar in 2007 and 2008. The LAPU was 0.24 and 0.06 for SFIR New Providence in 2007 and 2008 respectively. The SFIR Blairsburg LAPU was 0.18 and 0.19 for 2007 and 2008 respectively.

3.3 Indiana

The glyphosate and AMPA data from Indiana were limited to two storm events (19 and 30 May 2004).³⁷ These two storms varied greatly in total rainfall (2.6 and 5.7 cm respectively) and

intensity (1.1 and 4.5 cm h^{-1} respectively). The percentages of total streamflow attributed to overland flow were 5 and 32% respectively. Applications of glyphosate occurred in mid-May. The glyphosate median concentration from the Overland Flow Site was 10 times higher during the 19 May storm compared with the 30 May storm: 380 and $34 \mu\text{g L}^{-1}$ respectively. The highest glyphosate concentration ($430 \mu\text{g L}^{-1}$) measured at any site in this study was from a water sample from the Overland Flow Site during the 19 May storm (Table 2). However, there was less glyphosate being transported in overland flow, and the median concentrations in Leary Weber Ditch and Sugar Creek were higher during the 30 May storm, which indicates that there was some difference in the transport mechanism between the two storms.

3.4 France

Fifty-eight runoff events from March to September 2003–2006 were sampled, and 303 samples were collected from the Rouffach basin. All but one sample had concentrations of glyphosate above the reporting level of $0.1 \mu\text{g L}^{-1}$ (Table 2). Every sample had detectable levels of AMPA.²⁰ The maximum concentrations of glyphosate and AMPA (86 and $44 \mu\text{g L}^{-1}$ respectively), as well as the median concentrations (4.7 and $1.9 \mu\text{g L}^{-1}$ respectively) were higher than at any other site, except for the Overland Flow Site in Indiana and the Subsurface Drain in Iowa. The median value for the %AMPA was 31%, which indicates that in most samples the glyphosate concentration was higher than the AMPA concentration. Generally, the LAPU values for glyphosate (0.009–0.029%) for the Rouffach basin were an order of magnitude less than at the other sites (Table 3). The TGLAPU averaged about 24% higher than the glyphosate LAPU, much less of an increase than from the Bogue Phalia or SFIR basins, reflecting the lower concentrations and loads of AMPA from the Rouffach basin.

4 DISCUSSION

4.1 Source strength

The source strength S_s varies by constituent (decreases for glyphosate but increases for AMPA), with time since application, owing to degradation and other loss mechanisms. It will also vary spatially, as not every field will receive glyphosate application. For example, the increase between 2007 and 2008 in the total amount of glyphosate applied in the Napanee basin was the result of the different cropping pattern in the basin. In 2008 the entire basin was planted in GM soybean, in contrast to 2007, when the basin was planted equally in rice and soybeans. Rice is not a GM crop, and glyphosate is used only before rice is planted. The application of glyphosate began much earlier in Mississippi (January in 2007 and February in 2008) than in Iowa (May). The total amount and the duration of glyphosate applications were much higher in Mississippi compared with Iowa (Tommie Bayou and SFIR Blairsburg are shown in Fig. 4). The amounts of glyphosate applied per unit area were as much as 4 times greater in Mississippi than in Iowa, especially when comparing the smaller basins. In both years, nearly 50% of the total application in Mississippi had been completed before application in Iowa began (Fig. 4). In 2008, the Napanee basin had application amounts per unit area that were almost 6 times as much as those in the SFIR basin (Table 3). Although both Mississippi and Iowa basins have much of their agricultural land in GM crops, the difference in S_s is substantial between the basins and explains the differences in detection rates and magnitude of glyphosate concentrations between Mississippi

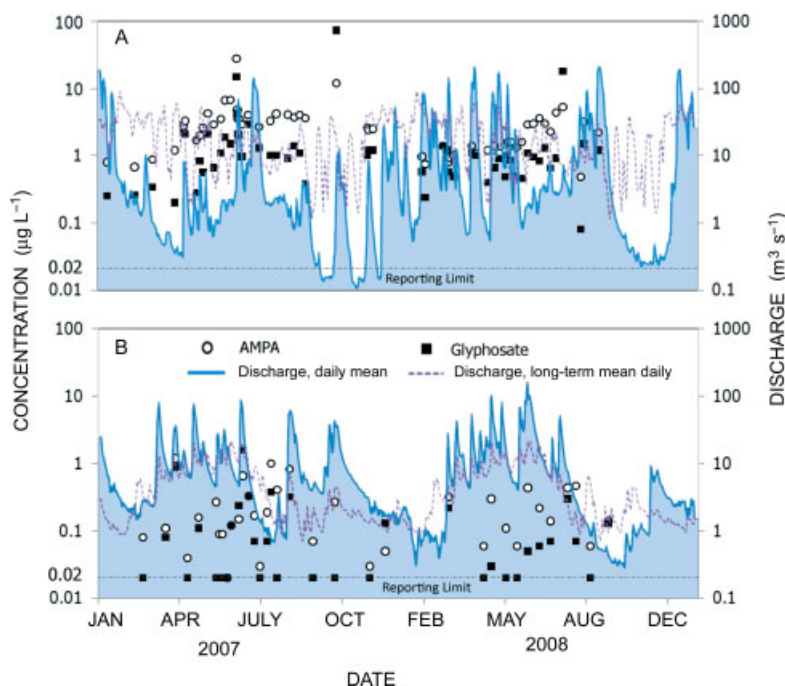


Figure 3. Glyphosate and AMPA concentrations in stream samples, mean daily discharge and the long-term mean daily discharge in the Bogue Phalia near Leland, MS (A) and the South Fork Iowa River near New Providence, IA (B) 2007 thru 2008.

and Iowa, because Mississippi has nearly a continuous application of glyphosate for 9 months, whereas glyphosate applications in Iowa are limited to a few months in the spring and summer.

Cyclical patterns of concentrations of glyphosate in streams are associated with new applications of glyphosate to agricultural fields, followed by higher glyphosate concentrations in surface water by way of runoff from fields (Figs 3 and 4). However, as the most recent application degrades, the amount of glyphosate available for transport during runoff events decreases, and the amount of AMPA available for transport increases. As with other pesticides, the highest concentrations of glyphosate in streams will occur during the first runoff event following application. If the runoff event occurs immediately after application, the AMPA concentration should be small, but, the longer the time lag between application and runoff, the higher the AMPA concentration will be in comparison with the glyphosate. The distribution and occurrence of the AMPA provides insight into how the S_5 influences the transport of glyphosate, because the other two controlling factors (RRF and FR) will be the same. Both compounds (glyphosate and AMPA) have similar solubility, and their affinity for soil is about the same, but the half-life of AMPA is somewhat greater than that of glyphosate.^{6,7} After the first application, glyphosate concentrations are elevated and AMPA concentrations are low. Over time, after repeated applications of glyphosate, AMPA accumulates in the soil because of the slower degradation rate of AMPA and becomes available for transport to streams.

The maximum glyphosate concentration in streams is usually higher than the maximum AMPA concentration (Table 2), which indicates that, immediately after application, there is a large reservoir of glyphosate available for transport. However, the median AMPA concentration is usually higher than the median glyphosate concentration for sampling sites in Iowa and Mississippi, which indicates that the glyphosate reservoir becomes depleted following application, although some level of AMPA generally is available for

transport. The %AMPA in surface water will be dependent upon where in the application/degradation cycle the rainfall runoff event occurs and the amount of AMPA in the soil reservoir from previous applications. The AMPA concentration was almost always higher than the glyphosate concentration for larger basins like the Bogue Phalia and the SFIR New Providence. This is because the spatial variation in the timing of the applications tends to increase with basin size. The longer travel times and flow routes in larger basins provide an opportunity for more glyphosate to degrade. Conversely, more often than the larger basins, the smaller basins (Napane, Tommie Bayou and SFIR Blairsburg) have higher concentrations of glyphosate compared with AMPA. More glyphosate is available for transport during a runoff event following applications to smaller basins because glyphosate applications in smaller basins generally occur over a large percentage of the basin close together in time. For example, glyphosate concentrations were higher than AMPA concentrations (lower %AMPA) in the SFIR near Blairsburg (Fig. 5) only following the major application period of late June and July in 2007 and 2008 (Fig. 4).

Although there is much variability in the %AMPA, there is a slight propensity for the smaller drainage basins to have a lower %AMPA. The median %AMPA for the Bogue Phalia, Tommie Bayou and Napane basins was 72, 67 and 53% respectively, and the median %AMPA for the SFIR at New Providence and near Blairsburg was 76 and 57% respectively (Table 2). These data suggest that there might be some loss of glyphosate because the ratio of AMPA to glyphosate increases with drainage size (a surrogate for time of travel), which indicates that glyphosate may be lost through some process such as degradation or sorption to sediment.

4.2 Rainfall runoff factor

In general, the influence of the rainfall runoff factor (RRF) on LAPU values would be expected to be relatively greater in the Bogue Phalia basin compared with the SFIR basin. The Bogue

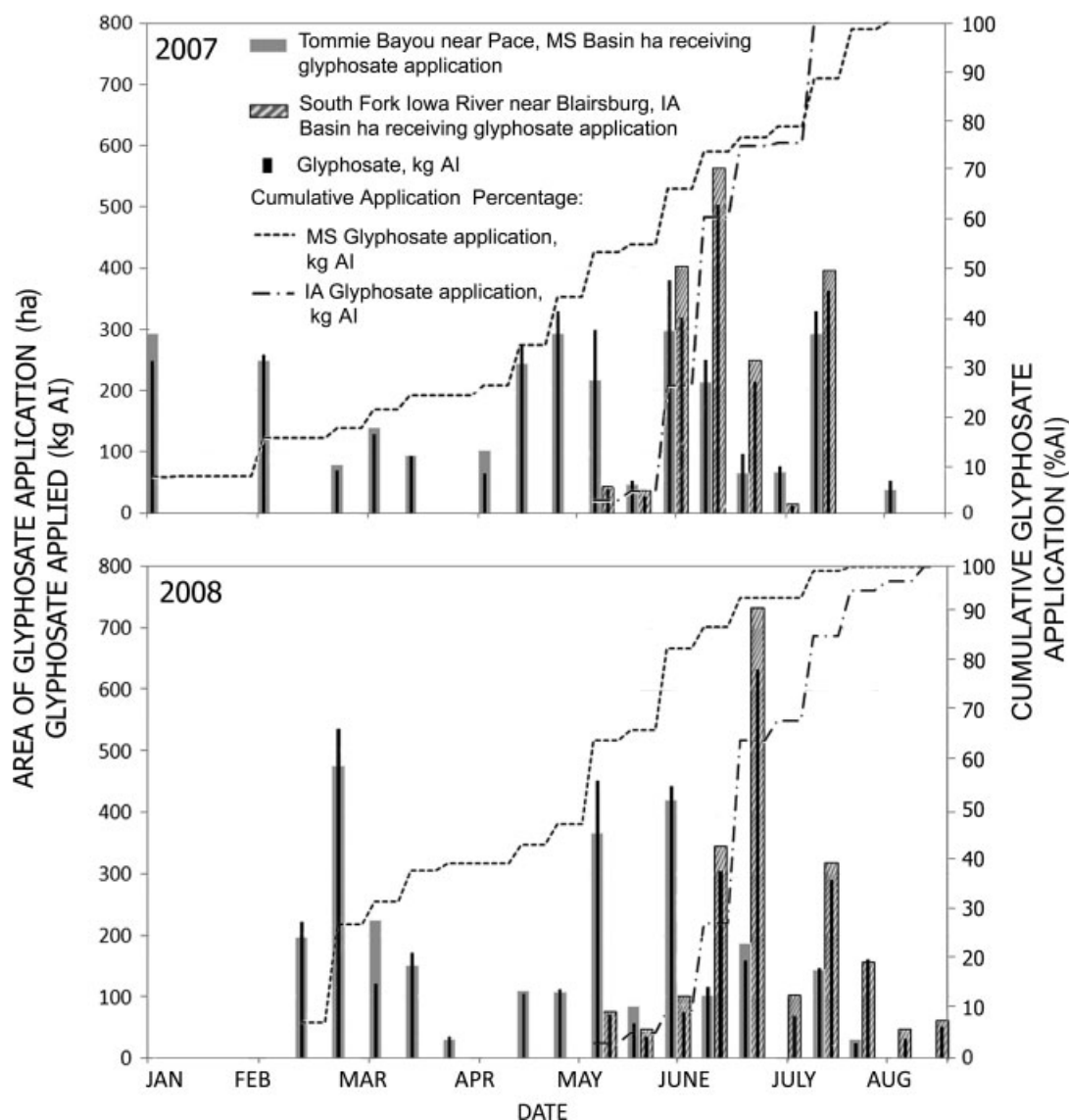


Figure 4. Application of glyphosate to the Tommie Bayou basin in Mississippi and the SFIR near Blairsburg, IA basin. Data are shown for 10 day periods (11 days during the last period for months with 31 days) beginning with and plotted on the first day of the month.

Phalia had an average annual runoff from 1996 to 2008 of 51 cm, which is more than twice the SFIR basin average annual runoff of 23.6 cm for the same time period.³⁸ This might explain the higher LAPU values in the Bogue Phalia basin than those in the SFIR basin. However, 2007 and 2008 were extraordinarily wet years for the SFIR basin (Table 1). The mean daily streamflow was almost 3 times the long-term mean daily streamflow, whereas, for the Bogue Phalia, the mean daily streamflow for 2007 was less than half the long-term mean daily streamflow, and the mean daily streamflow for 2008 was nearly the same as the long-term mean daily streamflow. Streamflows in the Bogue Phalia were well below normal from May to August of both 2007 and 2008 (Fig. 3). In the SFIR basin, streamflows in 2007 were about average for the first part of the growing season (May to mid-July), but were then well above average for the rest of the year, and in 2008 the streamflows were well above average for the spring and early summer months. In this instance, the RRF does not explain the larger LAPU values from the Mississippi basins.

For the Rouffach basin in France, the predominant factor that explains the very low LAPU values is the RRF. The Rouffach basin had the lowest LAPU values among the basins owing to the small percentage of water (1.48%), in terms of total rainfall, that left the basin. The other factors, FR and S_s , contributed to the high detection rate and high concentrations of glyphosate and AMPA. The FR during storm events was predominantly overland flow, and the basin had a high S_s with continuous application of glyphosate from March to October and application rates that were similar to the application rates in the SFIR basin.²⁰ Hence, 302 of the 303 samples collected had concentrations of glyphosate above the reporting level of $0.1 \mu\text{g L}^{-1}$. The highest median and maximum concentrations for glyphosate and AMPA, with the exception of the Overland Flow Site in Indiana, were measured here. The combination of high S_s , a predominant overland FR but low annual runoff leads to episodically high concentrations in the stream but to low total annual offsite movement of glyphosate by comparison with the Iowa and Mississippi basins.

Table 3. Comparison of glyphosate application and glyphosate and AMPA loads, glyphosate LAPU values and the mass equivalent total glyphosate LAPU between the basins studied

Sampling site ^a	Year	Glyphosate			AMPA ^c load as AMPA (kg year ⁻¹ , except where noted)	TGLAPU ^d (%)
		Total mass applied to watershed (kg km ⁻² year ⁻¹)	Load (kg year ⁻¹ , except where noted)	LAPU ^b (%)		
Bogue Phalia, MS	2007	78	319	0.33	726	1.5
	2008	105	739	0.56	1025	1.8
Tommie Bayou, MS	2007	199	4.2	0.14	7.1	0.49
	2008	185	10.6	0.37	20.5	1.5
Napanee, MS	2007	188	2.3	0.56	1.3	1.0
	2008	301	5.7	0.86	4.9	2.0
SFIR New Providence, IA	2007	51.7	70	0.24	100	0.75
	2008	63.4	22.7	0.06	89.8	0.44
SFIR Blairsburg, IA	2007	47.6	2.6	0.18	4.0	0.59
	2008	55.3	3.3	0.19	5.8	0.70
Rouffach, France	2003	54.3	6.6 g year ⁻¹	0.029	2.5 g year ⁻¹	0.046
	2004	66.9	9.4 g year ⁻¹	0.033	2.7 g year ⁻¹	0.048
	2005	43.9	4.7 g year ⁻¹	0.026	1.1 g year ⁻¹	0.034
	2006	146	5.7 g year ⁻¹	0.009	1.2 g year ⁻¹	0.012

^a SFIR: South Fork Iowa River.

^b LAPU: load as a percentage of use.

^c AMPA: aminomethylphosphonic acid.

^d TGLAPU: mass equivalent total glyphosate LAPU.

4.3 Flow route

The flow routes (FRs) are substantially different in the Bogue Phalia, SFIR, Sugar Creek and Rouffach basins. Many parts of the SFIR and Sugar Creek basins have been modified with subsurface drainage, and there is little overland runoff. Much of the water in the streams of these basins is transported through the subsurface drainage system after infiltrating through about 1 m of soil. This process can slow the transport of glyphosate to the stream, resulting in opportunities for degradation and loss by physical factors such as sorption to soil particles. This process was noted in the Sugar Creek basin by Domagalski *et al.*,³⁹ who found that transport of metolachlor to a subsurface drain was less favored because of greater sorption to the sediments relative to the degradation products. There are important exceptions: Stone and Wilson³⁷ reported concentrations of glyphosate in hundreds of $\mu\text{g L}^{-1}$ in water from subsurface drains in the Sugar Creek basin, and glyphosate reportedly can move through preferential flow paths into the unsaturated zone. Concentrations in the Subsurface Drain in the SFIR Blairsburg basin (Fig. 6) of glyphosate and AMPA were higher than in the receiving stream (SFIR Blairsburg), and concentrations in the Subsurface Drain could be as high as hundreds of $\mu\text{g L}^{-1}$ (Table 2). This would indicate that this subsurface drain is influenced by preferential flow, or possibly that it is connected to a surface drain. The important observation here is that subsurface drains can contribute significant substantial amounts of glyphosate to surface water. In contrast, because of the heavy clay soils in the Bogue Phalia basin, there is little infiltration of rainfall, and most water reaches the stream by overland runoff without infiltrating into the soil.

The FR and RRF are important in understanding the difference in the transport of glyphosate between the two storms sampled in the Sugar Creek basin in Indiana (Table 2). The concentration pattern between sampling sites follows the normal pattern of higher median concentrations in the smaller basins. The smallest basin,

the Overland Flow Site, which represents the source signature, had a median concentration of glyphosate at least several orders of magnitude higher than the stream sampling sites (Table 2). Compared with the 19 May storm, the 30 May storm resulted in the opposite effect: higher concentrations of glyphosate in Leary Weber Ditch and in the receiving stream, Sugar Creek. However, at the Overland Flow Site, the glyphosate concentrations were an order of magnitude less for the 30 May storm (median concentration $34 \mu\text{g L}^{-1}$) than for the previous storm (median concentration $380 \mu\text{g L}^{-1}$). There had been no other applications of glyphosate to the Overland Flow Site basin between storms. The decrease in concentration at the Overland Flow Site is probably due to glyphosate degradation and loss from the 19 May storm. The percentage of flow attributed to overland runoff in Leary Weber Ditch was much higher in the May 30 storm (32%) than in the May 19 storm (5%), leading to higher concentrations in the receiving stream because of less opportunity for sorption to soil. The RRF manifested as higher rainfall intensity in the second storm, which triggered a higher percentage of water reaching the stream by overland flow and overwhelmed the influence of diminished S_s , resulting in higher concentrations in the receiving stream.

The higher LAPU values for the sites in the Bogue Phalia basin compared with the SFIR basin (Table 3) are a result of the FR factor overwhelming the relatively larger RRF component of the SFIR basin. The increase in the LAPU value for Tommie Bayou and Napanee between 2007 and 2008 can be explained by the RRF factor. The S_s and the FR are the same between the 2 years for Tommie Bayou, but rainfall was less in 2007 than in 2008 and resulted in a larger LAPU value in 2008. The S_s increased substantially in the Napanee basin, as the entire basin was planted in glyphosate-resistant soybeans in 2008, compared with just about half the basin in 2007, and rainfall was greater in 2008 than in 2007, resulting in a higher LAPU value for 2008.

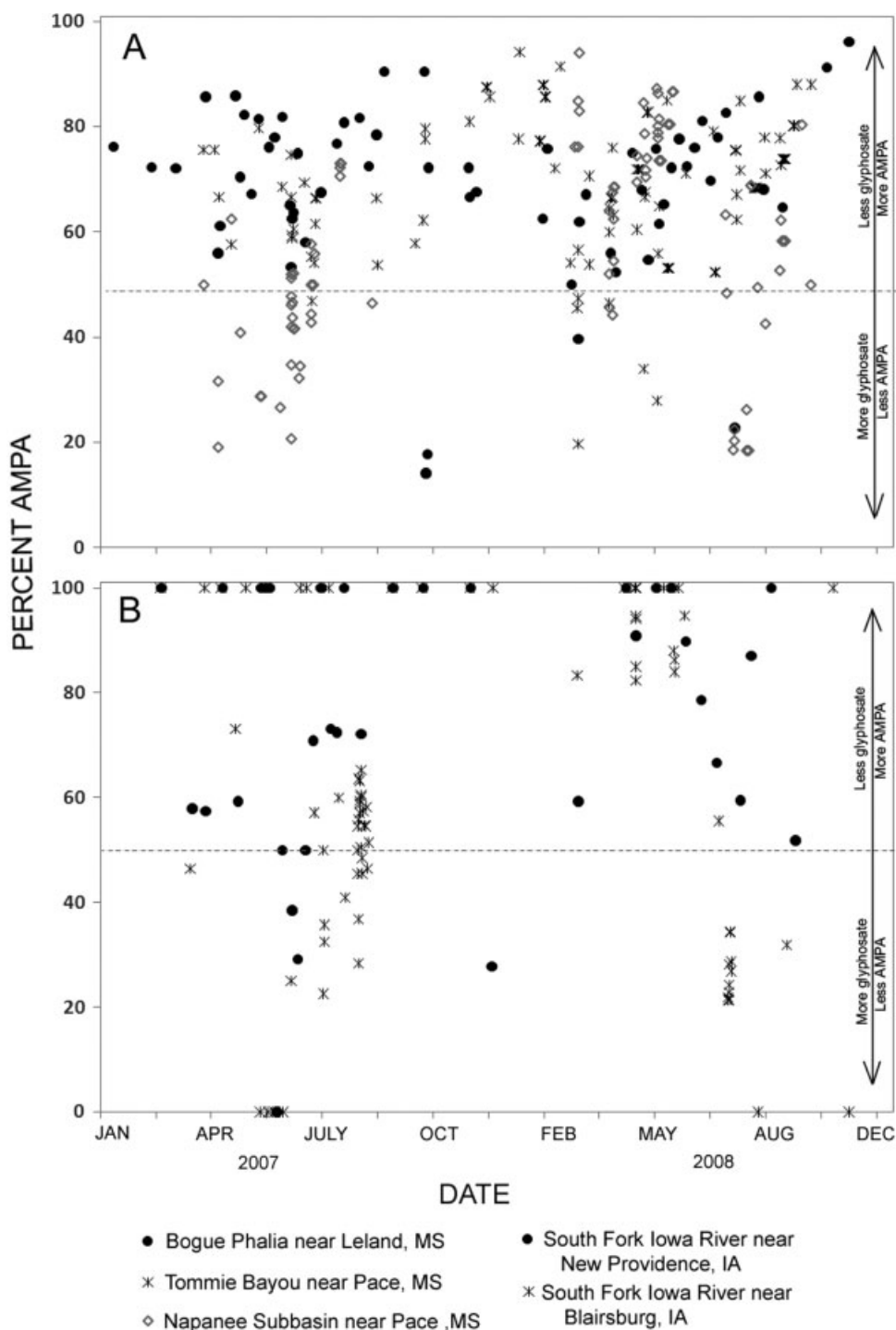


Figure 5. AMPA as a percent of total glyphosate in the Napanee, Tommie Bayou, and Bogue Phalia, MS basins (A), and in the South Fork Iowa River near Blairsburg, IA and the South Fork Iowa River near New Providence, IA basins (B) during January 2007 thru December 2008.

Using edge-of-field data from hundreds of studies to spring 1977 on more than 40 compounds, Wauchope⁴⁰ suggested that the LAPU values of surface-applied herbicides, soil-incorporated herbicides and insecticides would be about 2, 0.5 and 0.5% respectively. More than 20 years later, in an updated review of 39 pesticides and additional data, Capel reported general agreement for the same groups with mean LAPU values of 1.8, 0.23 and 0.84% respectively.⁹ The LAPU values for glyphosate for the Bogue

Phalia basin and the SFIR basin from this study ranged from 0.14 to 0.86%. The Rouffach basin LAPU values were an order of magnitude lower than the LAPU values for the Bogue Phalia and SFIR basins (0.01–0.03%). The mass equivalent total glyphosate LAPU in the SFIR and Bogue Phalia basins ranged from 0.44 to 2.0% respectively (Table 3). From these data it appears, at least for the US basins, that the loss rate for glyphosate is about the same for many other pesticides used in the United States.

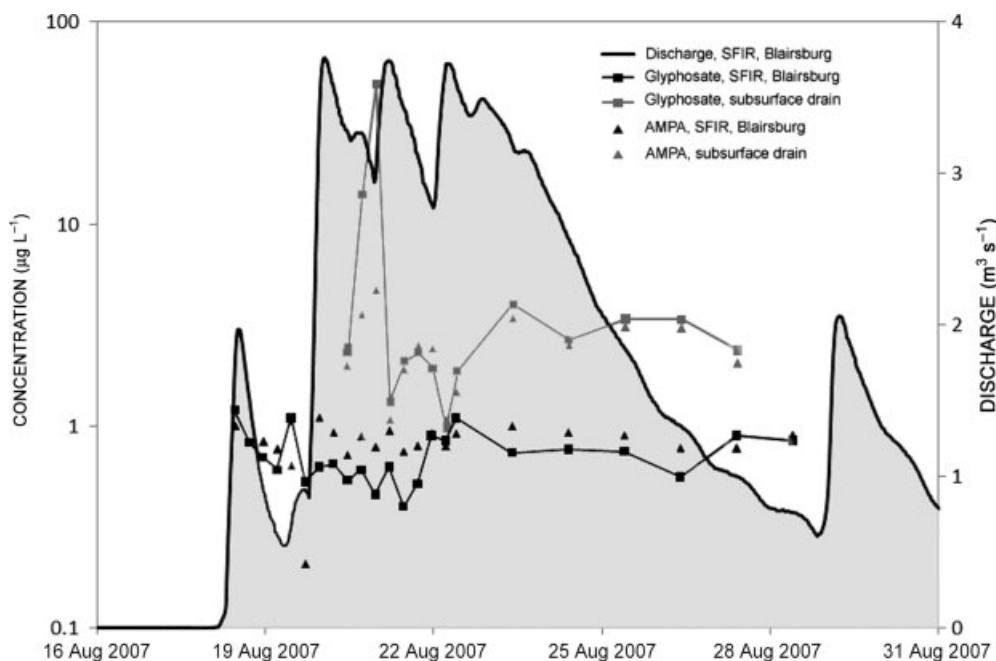


Figure 6. Glyphosate and AMPA concentrations in the South Fork Iowa River near Blairsburg, IA and in a representative subsurface drain during a storm event in August 2007.

Because glyphosate is not soil applied, it would not be expected to have the type of losses predicted by Wauchope and confirmed by Capel for surface-applied herbicides, but rather less, as its application method is more like that of an insecticide than a soil-applied herbicide.^{9,40} Glyphosate is applied to existing vegetation, and much of the herbicide is intercepted by vegetation before reaching the soil surface. To be effective, glyphosate has to be sorbed into the plant, and, once in the plant, it is unavailable to be transported off site by runoff.

These data suggest that glyphosate will be detected in surface water in agricultural basins where it is used. In the four systems that were studied, about 1% or less of the applied glyphosate moves into surface water. The frequencies of detection, concentrations and loads of glyphosate and AMPA are influenced by interrelated factors: source, hydrology and water movement pathways. Because glyphosate degrades, its frequency of occurrence is dependent upon the timeframe of its local application. In Mississippi and France, where the use is almost continuous, glyphosate and AMPA were detected in almost every sample, whereas in Iowa, where the use of glyphosate is more temporally restricted, glyphosate and AMPA are not as frequently detected. Water movement to the stream is required for glyphosate transport. The magnitude and pathways of water movement control the mass of glyphosate and AMPA that is moved off the field. The annual stream load of glyphosate as a percentage of annual use was much greater in Mississippi and Iowa than in France, even though the French site had detections in almost every sample at relatively high concentrations, because the amount of water that leaves this basin is small compared with the others. The pathway of the water from the field to the stream is also a control on the transport of glyphosate. Those basins in which the majority of the water arrives at the stream having passed through the soil transports less glyphosate because of its high affinity for sorption to soil particles. Each of these factors plays an important role in determining the amount of glyphosate that moves off site.

The factors need to be considered together to understand the fate and transport of glyphosate to agricultural streams.

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