SURFACE WATER MONITORING OF GLYPHOSATE USED IN RIGHTS-OF-WAY RAILROAD VEGETATION MANAGEMENT (2005 – 2006)

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- Linda Benevides, Executive Office of Environmental Affairs
- Richard Bonanno, University of Massachusetts
- Donovan Bowley, Massachusetts Department of Environmental Protection
- Michael Hutcheson, Massachusetts Department of Environmental Protection
- Gerard Kennedy, Massachusetts Department of Agricultural Resources
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- Mike McClean, Massachusetts Department of Agricultural Resources
- Ray Putnam, Massachusetts Pesticide Analytical Laboratory, University of Massachusetts
- Joel Zimmerman, Massachusetts Department of Conservation and Recreation.

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EXECUTIVE SUMMARY

In 2005 and 2006, the Pesticide Bureau of the Massachusetts Department of Agricultural Resources ("DAR" or "the Department") undertook a surface water quality monitoring program for the herbicide glyphosate (N-phosphonomethyl-glycine) and its metabolite, AMPA (amino-methylphosphonic acid). The objective of the monitoring program was to determine the effectiveness of a ten-foot no-spray buffer zone around a tributary in protecting stream water quality from glyphosate, when it is applied as a part of a railroad vegetation management program. The results of the study are intended to provide the Massachusetts Pesticide Board with a clear scientific basis for making decisions on proposed changes to no-spray zones in the Rights-of-Way regulations at 333 CMR 11.00. Specific goals of the monitoring program were to:

(1) Determine if herbicides applied to vegetation on railroad ballast and non-ballast areas will migrate into tributaries to public water supplies within 10 feet of the area of application.
(2) Establish how long the herbicides persist in the environment and whether, when and how they move offsite.
(3) Establish if surface water supplies are being impacted by herbicide applications to vegetation along railroad track beds where the railroad tracks are located outside of the Zone A for the surface water supply.

Water quality monitoring studies of the Ten Mile River in Attleboro and of Fort Pond Book Stream in Boxborough, were initiated in July, 2005 and continued for eight months. A limited amount of sediment sampling was included as part of the monitoring program.

Chemical analysis of water samples taken at Attleboro and at Boxborough showed that none contained detectable glyphosate or its metabolite at a detection limit of 1.1 parts per billion. A limited number of sediment samples also showed no detects. The results, along with the DEP modeling study and the chemical profile for glyphosate, indicate that a 10 foot buffer zone around a stream is likely to be sufficient to ensure adequate protection of the stream from herbicide applications to manage railway track vegetation.

A. INTRODUCTION

DAR first proposed changes to the Rights-of-Way Regulations at 333 CMR 11.00 in 2000. During the public comment period, the Department received over 200 oral and written comments on the proposed changes.

Pursuant to Section 5 of the Massachusetts Pesticide Control Act, the Pesticide Board must approve all pesticide regulations before the regulations can take effect. Over a series of meetings in 2001 and 2002, the Pesticide Board reached a consensus on all of the proposed changes with the exception of provisions that address the size of no-spray buffer zones for several sensitive areas.

The regulations require concentric no-spray zone and limited-spray zone protective buffers around environmentally sensitive areas. Within no-spray zones, herbicides are completely prohibited from use. Within the limited-spray zones, only certain herbicides subject to a special joint Department of Environmental Protection (DEP)/ DAR review process can be used.

The major unresolved issue was the size of the no-spray zones intended to protect tributaries to surface water sources of drinking water from herbicides applied to manage vegetation along rights-of-way. The Pesticide Board proposed the following no-spray zones:

> A no spray zone of 100 feet on each side of a tributary, where the tributary runs through the Zone A (a 400 foot distance) of a surface water supply. Outside of the Zone A for the surface water supply, the tributary is protected by a ten foot no-spray zone.

Concerns were raised about the adequacy of a ten-foot no-spray zone to protect the tributary from herbicides migrating offsite. To address those concerns a modeling analysis of glyphosate was undertaken by DEP. The analysis report concluded: "results predict that the majority of the applied glyphosate does not travel more than one-half meter (1.64 feet) from the point of application" (Appendix A). The DEP report also recommended that "a field verification study be conducted to verify the conclusions presented…before ten-foot setbacks are adopted for this particular type of herbicide application." Subsequently, the Office of Commonwealth Development requested that DAR conduct a water quality monitoring program to address the issue of glyphosate migration into sensitive resources.

A technical advisory committee was formed to advise DAR on the study design. The committee agreed on the following goals for the program:

(i) Determine if herbicides containing glyphosate which are applied to vegetation on railroad ballast and non-ballast areas will migrate into streams within 10 feet of the area of application as a result of the following processes:

- Drifting from the site of application during, and immediately after the application.
- Overland flow, in which a pesticide, or a pesticide bound to soil, is carried along in runoff to nearby surface waters.
- Leaching down through the soil to the groundwater table to be discharged to tributaries, wetlands and water bodies.

(ii) Establish if surface water bodies into which the streams flow receive any of the chemical from the streams.

In July 2005, DAR initiated two surface water monitoring programs for glyphosate in Attleboro and Boxborough, respectively. The monitoring programs tested stream water for glyphosate and its main metabolite, AMPA.

B. MATERIALS AND METHODS

At both Attleboro and Boxborough respectively, Round Up-Pro (EPA Registration Number 524-475), which is formulated as 41% Glyphosate, isopropylamine salt, was tank mixed at a dilution rate of 2 quarts/ 30 gallons. Prior to herbicide applications at the Attleboro site, a Pesticide Inspector took a tank sample of the spray mixture directly from the spray tank for analysis later at the Massachusetts Pesticide Analytical Laboratory (MPAL) (Table 1, page 11). No sampling of the spray mixture took place at the Boxborough site. Instead, pesticide application records were inspected to identify the tank mixture and application rates. This was appropriate given that the applicators had no prior knowledge of the sampling program.

In both cases, low pressure herbicide applications were made from a specialized hi-rail truck equipped with a spray boom to the roadbed tracks at a rate of 2 quarts per acre. Round Up-Pro was applied for brush control at a rate of 4 quarts per acre. The trucks shut off the sprayer at a distance of ten feet from the river, as required under current regulations. The truck then continued over the bridge and restarted the sprayer once it passed the ten foot no-spray zone marker which is painted on the track ties.

Ten Mile River, Hebronville, Attleboro: At Hebronville, Amtrak's high-speed trains cross a metal bridge over the Ten Mile River (Figure 1). The bridge runs 15 feet above the river (Figure 2.c. and 2.d.) There are clear no-spray delineations on the track ten feet from the bridge. The river is fast moving, about 35 feet wide with a depth of approximately two feet (Figure 2.d.).

The river overlays a high yield aquifer. Soils in this area are described in the Natural Resource Conservation Service (NRCS) Soils Survey of Bristol County as a mixture of Windsor (WnA) and Hinckley (HfB). Soils of this type are mainly loamy/sand and sand/ loam texture. Both soil types are of "Hydrologic Group A" and are characterized by rapid to very rapid permeability.

Sampling at Hebronville in Attleboro began on July 17, 2005. The day was warm with moderate humidity. The average temperature was 70°F with a high of 84°F and an average dew point of 61.6°F. The average wind speed for the day was 6mph[1]. Sampling commenced at 5.30AM. Vegetation along the riverbank was dense with a large amount of poison ivy present.

The locations for the water and sediment samples were 100 feet upstream of the track (Sampling Location 1), immediately downstream of the bridge (Sampling Location 2) and one half mile downstream (Sampling Location 3) (Figures 2.e. and 2.f.).

Figure 1: Ten Mile River at Hebronville, Attleboro, MA

A total of 191 water samples and three sediment samples (at Sampling Location 3) were taken over a 224 day period. Wet weather sampling was also conducted. Results of the analyses are shown in Tables 1 to 5.

[1] Temperature and humidity data from the National Weather Service website: http://www.nws.noaa.gov/

a. High speed track northbound

b. High speed track southbound

c. Sampling Location 1

d. Bridge from Sampling Location 2

e. Sampling Location 3

f. Sampling Location 3 (Other side of the road)

Figure 2: Attleboro, Sampling Locations

Fort Pond Book Stream, Boxborough: At Sargent Road, in Boxborough the single track Fitchburg commuter rail line passes over Fort Pond Book Stream, a narrow stream about 6 feet wide with a depth of about a foot (Figure 4.). Vegetation at this location was less dense than at the Attleboro location.

Soils in the area consist of a mixture of Scituate Fine Sandy Loam, Freetown Muck and Scarboro Mucky fine Sandy Loam according to NRCS soils data.

Sampling started on July 21st 2005. The day was warm and humid with a light wind of less than 3mph. The average temperature for the day was 74 ° F with a high of 88 ° F. The dew point was 64°. [2]

Water and sediment sampling took place twenty feet upstream of the track, (Sampling Location 1); ten feet from the bridge on the downstream side (Sampling Location 2) and at a point about two tenths of a mile further downstream, where the stream passes under a culvert, Location 3 (see Figures 3 and 4.e. and 4.f.).

A total of 145 water samples were taken over a 224-day period.

Six sediment samples were also taken at Sampling Locations 2 and 3 according to the schedule in Appendix C.

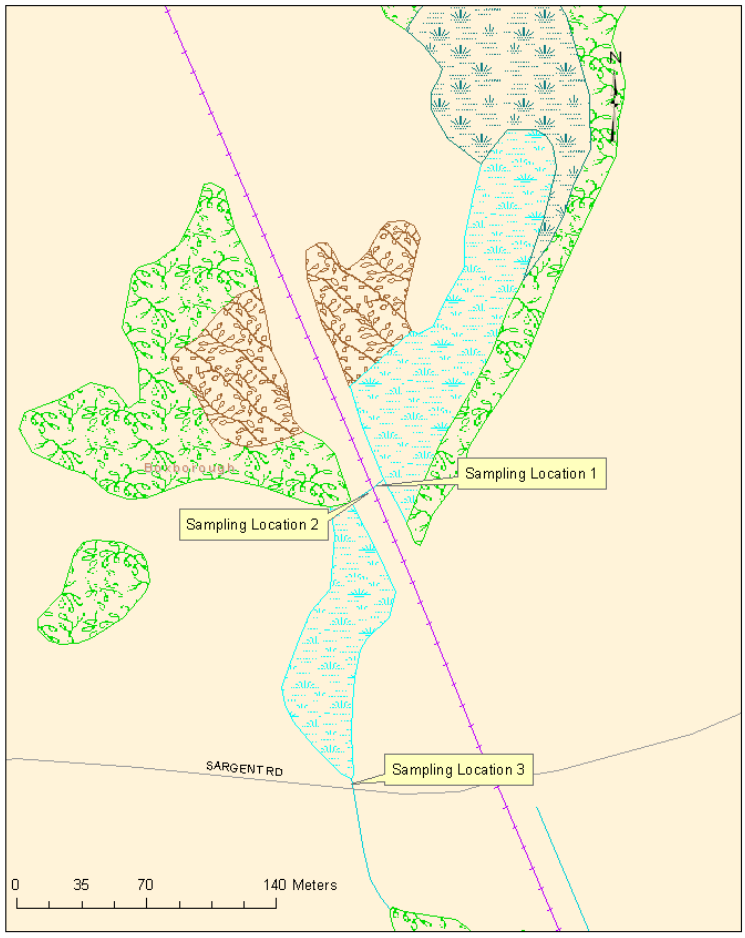

Figure 3: Fort Pond Book, Sargent Road, Boxborough, MA

[2] Temperature and humidity data from the National Weather Service website: http://www.nws.noaa.gov/

a. Commuter Rail

b. Track with Rights-of-Way markers visible

c. Sampling Location 1

d. Sampling Location 2

e. Sampling Location 3

f. Sampling Location 3

Figure 4: Boxborough, Sampling Locations

Sampling Details: At each sampling site, single grab samples of water were collected directly into one-liter amber glass bottles. Grab samples were collected as close to the center channel as possible using a grab pole consisting of the glass bottle at the end of an extendable pole. The bottle was plunged into the water and, with the mouth of the sample bottle facing upstream, water samples were collected by drawing up the bottle from a point midway between the bottom and surface. After the water samples were collected, the bottles were labeled, kept on ice, then transported to MPAL for analysis. Samples generally arrived at MPAL within 24 hours of the time of collection, except where samples were collected on a weekend, in which case they were refrigerated and transported to MPAL as soon as possible. Field documentation consists of standard collection forms.

Water samples were taken according to the following schedule:

- Pre-spray samples were taken prior to the time of application.
- Post application samples were taken according to a regular sampling schedule at each location.
- During the first three significant rainfall events (more than 0.1”per day), after application, one daily sample was taken at each location and for three days after the end of the storm.

Because glyphosate degrades at an exponential rate, DEP recommended a sampling regimen in which samples were collected on a log scale with increasing sampling intervals. To account for variance in sampling, duplicate samples were taken as outlined in the sampling schedule. Details of the sampling regimens for both sites are provided in Appendices B and C.

Sediment samples were collected directly into the sample bottles from the river or stream bed, labeled and kept on ice prior to analysis.

Analytical Details: MPAL analyzed the samples according to the protocol titled “Determination of Glyphosate in Soil and Water” (Appendix D: SOP No. Glyphosate 001). Samples of river water were spiked with glyphosate and AMPA standards and analyzed, according to the SOP (Appendix E). MPAL maintains a Quality Assurance Project Plan with QA/QC protocols for the analysis of samples used in the state and federal pesticide regulations. Only a subset of duplicates was analyzed. To reduce the analysis burden, upstream samples were only to be analyzed if detectable glyphosate residues were found in the downstream samples.

C. RESULTS:

(i) **Hebronville, Attleboro**

Active Ingredient	% Claim in Spray Tank	% Found in Tank	% of Claim
Glyphosate	0.80	0.914	114.2

Table 1: Concentrations of Glyphosate in Tank Mix Sample. Analysis of the Tank Mix Sample shows that the percentage level of glyphosate in the spray tank for application in Attleboro is well within acceptable limits.

	Location 2				Location 3			
Time from Application	**Glyphosate (ppb)**	**AMPA (ppb)**	***Glyphosate (ppb) duplicate***	*AMPA (ppb) duplicate*	**Glyphosate (ppb)**	**AMPA (ppb)**	***Glyphosate (ppb) duplicate***	*AMPA (ppb) duplicate*
Pre-application Sample 1	< 1.1ppb	< 1.1ppb	-	-	< 1.1ppb	< 1.1ppb	-	-
Pre-application Sample 2	< 1.1ppb	< 1.1ppb	-	-	< 1.1ppb	< 1.1ppb	-	-
30 sec	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	-	-	-	-
3 min	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	-	-	-	-
10 min	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb
16 min	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	< 1.1ppb	-	-
30 min	< 1.1ppb	< 1.1ppb	-	-	< 1.1ppb	< 1.1ppb	-	-
1 hr	< 1.1ppb	< 1.1ppb	-	-	< 1.1ppb	< 1.1ppb	-	-
2 hr	< 1.1ppb	< 1.1ppb	-	-	< 1.1ppb	< 1.1ppb	-	-
4 hr	< 1.1ppb	< 1.1ppb	-	-	< 1.1ppb	< 1.1ppb	-	-
				-				
Total # Samples	10		4		8		1	
							Grand Total	**23**

Table 2: Concentrations of Glyphosate and AMPA in Water Quality Samples (Northbound Application). Because there are two tracks, the applicators sprayed the tracks on the northbound side initially, followed by a later spraying of the southbound tracks. Samples were collected for the northbound section up until the time that the spray rig returned on the southbound side at which point the sampling regimen started over. The times for sampling over the long-term study commenced at this point. To reduce the analysis burden, upstream samples were only to be analyzed if detectable glyphosate residues were found in the downstream samples. Two sets of pre-application samples were taken, one set being used for the lab to conduct glyphosate method validation.

	Location 2				Location 3			
Time from Application	**Glyphosate (ppb)**	**AMPA (ppb)**	*Glyphosate (ppb)*	*AMPA (ppb)*	**Glyphosate (ppb)**	**AMPA (ppb)**	*Glyphosate (ppb)*	*AMPA (ppb)*
30 sec	< 1.1	< 1.1	< 1.1	< 1.1	-	-	-	-
3 min	< 1.1	< 1.1	< 1.1	< 1.1	-	-	-	-
10 min	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1
16 min	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	-	-
30 min	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
1 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
2 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
4 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
8 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
12 hr	-	-	-	-	-	-	-	-
24 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
7 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
14 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
28 d	-	-	-	-	-	-	-	-
56 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
112 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
224 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 1	-	-	-	-	-	-	-	-
Rainfall event 1 D1	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 1 D2	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 1 D 3	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2 D1	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2 D2	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2 D3	-	-	-	-	-	-	-	-
Rainfall event 3	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 3 D1	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 3 D2	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 3 D3	-	-	-	-	-	-	-	-
Total # Samples	24		4		22		1	
							GRAND TOTAL	**51**

Table 3: **Concentrations of Glyphosate and AMPA in Water Quality Samples (Southbound Application).** The tracks on the Southbound side were sprayed a few hours after the Northbound side. To reduce the analysis burden, upstream samples were only to be analyzed if detectable glyphosate residues were found in the downstream samples. Samples were not taken at the 12 hour or the 28 day point due to lack of resources.

Time from Application	Location 3	
	Glyphosate (ppb)	AMPA (ppb)
before Northbound Applications	<10.1ppb	< 9ppb
1 hour after Southbound Applications	<10.1ppb	< 9ppb
24 hours after Southbound Applications	<10.1ppb	< 9ppb

Table 4: Concentrations of Glyphosate and AMPA in Sediment Samples (Attleboro): Samples were only taken at Sampling Location 3 because of the difficulty in getting samples at the upstream locations.

(ii) Fort Pond Book Stream, Boxborough

	Location 2				Location 3			
Time from Application	**Glyphosate (ppb)**	**AMPA (ppb)**	**Glyphosate duplicate (ppb)**	**AMPA Duplicate (ppb)**	**Glyphosate (ppb)**	**AMPA (ppb)**	**Glyphosate (duplicate) (ppb)**	**AMPA (duplicate) (ppb)**
Pre-application Sample 1	<1.1	<1.1	-	-	<1.1	<1.1	-	-
30 sec	<1.1	< 1.1	< 1.1	< 1.1	-	-	-	-
3 min	< 1.1	< 1.1	< 1.1	< 1.1	-	-	-	-
10 min	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1
16 min	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	< 1.1	-	-
30 min	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
1 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
2 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
4 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
8 hr	-	-	-	-	-	-	-	-
12 hr	-	-	-	-	-	-	-	-
24 hr	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
7 d	-	-	-	-	-	-	-	-
14 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
28 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
56 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
112 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
224 d	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 1	-	-	-	-	-	-	-	-
Rainfall event 1 D1	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 1 D2	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 1 D3	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2	-	-	-	-	-	-	-	-
Rainfall event 2 D1	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2 D2	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 2 D3	< 1.1	< 1.1	-	-	< 1.1	< 1.1	-	-
Rainfall event 3	-	-	-	-	-	-	-	-
Rainfall event 3 D1	-	-	-	-	-	-	-	-
Rainfall event 3 D2	-	-	-	-	-	-	-	-
Rainfall event 3 D3	-	-	-	-	-	-	-	-
			-					
Total # Samples	21		4		19		1	
							GRAND TOTAL	**45**

Table 5: Concentrations of Glyphosate and AMPA in Water Quality Samples: Only a subset of duplicates was analyzed. To reduce the analysis burden, upstream samples were only to be analyzed if detectable glyphosate residues were found in the downstream samples. No samples were analyzed from Location 1. Samples were not taken at the 8 hour, 12 hour, 7 day points and after the third rainfall event due to lack of resources.

Time from Application	Location 2		Location 3	
	Glyphosate (ppb)	AMPA (ppb)	Glyphosate (ppb)	AMPA (ppb)
before applications	<10.1	<9.1	<10.1	<9.1
1 hour after applications	<10.1	<9.1	<10.1	<9.1
24 hours after applications	-	-	-	-
Total # Samples	2		2	
	GRAND TOTAL		4	

Table 6: Concentrations of Glyphosate and AMPA in Sediment Sampling (Boxborough): No samples were taken 24 hours after the application.

D. DISCUSSION

No detections of glyphosate or its primary metabolite were found in any of the water or sediment samples analyzed over the course of the monitoring program. The laboratory detection limit for glyphosate of 1ppb in water is well below current health and aquatic based criteria for glyphosate. The MCL drinking water standard for glyphosate has been set at 700 ppb by the USEPA. According to the DEP/ DAR Rights-of-Way fact-sheet for glyphosate[3]: (the active ingredient) "glyphosate is considered to be only slightly toxic to fish species (LC50 greater than 10,000 ppb).

The intensive sampling approach attempted to account for migration via drift, run-off and by movement, over the longer term, along groundwater flow paths into a stream. To address concerns about drift, water sampling immediately after the applications was rapid, beginning 30 seconds following the application; then after 3, 10, 16, 30 and 60 minutes. Sampling continued with increasing intervals for 224 days (Appendices B and C). A limited amount of sediment sampling was also conducted to account for the potential for glyphosate accumulation in sediment. However, it was difficult to generate samples at the Attleboro sampling site adjacent to the tracks because of the very hard river bed. While sediment sampling was limited, the long term water quality sampling served to address the potential for the sediment to serve as a constant source of glyphosate.

Runoff issues were addressed by sampling after three significant rainfall events. A significant rainfall event was defined as a rainfall event of greater than 0.1" of rain per day. However, staff were unable to sample from the Attleboro site during the first significant rainfall event which took place overnight on July 20 (three days after the application). Samples were taken immediately afterwards and on the two subsequent days, however. Sampling took place during the two subsequent rain events (on August 15 and August 31, respectively). At Boxborough, no significant rain event took place until July 27 (six days after the application). Field staff were able to sample on the days after the initial rain event, but not during the rain event itself. No sampling took place after the third rain event in Boxborough due to lack of resources. The results of the post rainfall event sampling, showing no detections, are consistent with the results of the modeling analysis conducted by DEP which stated that glyphosate was unlikely to migrate beyond ten feet from the site of application.

To investigate the potential movement of glyphosate through groundwater, the monitoring program was conducted over an eight month period. The results show that, under the conditions of this monitoring program, glyphosate is not expected to move readily from the area of application via groundwater flow paths.

However, soil and hydrologic characteristics do vary statewide. Glyphosate is relatively immobile in most soil environments as a result of its strong adsorption to soil particles. According to the Glyphosate fact-sheet, binding occurs with particular rapidity to clays and organic matter. Clays and organic matter saturated with iron and aluminum (such as in the Northeast) tend to absorb more glyphosate than those saturated with sodium or calcium. The soil phosphate level is the main determinant of the amount of glyphosate adsorbed to soil particles. Soils which are low in phosphates will adsorb higher levels of glyphosate. With little variability in the structure and makeup of railroad ballast, the monitoring program results should be valid statewide for ballast area applications. The high permeability of the soils in the Attleboro monitoring indicate that the program results should be valid for soils with a lower potential for leaching.

Taking into consideration the results of the monitoring, a rigorously reviewed rights-of-way process, the use of sensitive area materials, no-spray zone buffers around sensitive areas, and low pressure selective application of sensitive area material herbicides at the lowest labeled rate, selective application of Round-Up Pro for vegetation management along railroads should not constitute an unreasonable risk to the environment or public health in Massachusetts.

[3] Glyphosate fact-sheet by DEP and DAR. Online at http://www.mass.gov/agr/pesticides/rightofway/Glyphosate2005.pdf

E. RECOMMENDATIONS

The purpose of the monitoring program was to provide the Pesticide Board with a clearer scientific basis for decision making with respect to no-spray zones around tributaries in the proposed Rights-of-Way regulations. The Pesticide Board had reached agreement, at one point, on the following no-spray zone for tributaries:

- No Spray Zone: A no-spray buffer of 100 feet around a tributary in the Zone A of a surface water source which reduces to a buffer of 10 feet around the tributary in the rest of the watershed for that surface water source.

The monitoring program provides a sound basis for the Pesticide Board to finalize its decision making regarding the proposed changes to the Rights-of-Way regulations. The results, along with the DEP modeling analysis, indicate that a 10 foot buffer zone around a stream is likely to be sufficient for glyphosate to ensure adequate protection of the stream from Round-Up applications to railway track ballast and non-ballast areas when conducted according to the risk reduction provisions of 333 CMR 11.00.

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RE: Glyphosate Fate and Transport Modeling
DATE: November 5, 2003

This memo is in response to a request to determine an appropriate "no-pesticide spray" buffer distance from railroad rights-of-way for the pesticide glyphosate (as the formulation Roundup) around tributaries to water supplies and wetlands. The railway passes a number of wetlands and tributaries that connect to water supplies. There is a concern that glyphosate introduced in or migrating to these areas may contaminate these supplies. A range of "no-pesticide spray" setback distances from tributaries and wetlands, the smallest of which is 10 feet, was proposed by the Pesticide Board.

A brief review of fate and transport information and toxicity information for glyphosate was conducted to determine its potential for movement beyond a buffer of this size as well as its potential for toxicity impacts to aquatic organisms and humans. Based on the fate and transport characteristics of glyphosate, it was concluded that glyphosate is not likely to migrate very far in soil to impact groundwater. As such, this information only offered the opportunity to make a qualitative determination, based on professional judgment.

To improve upon this conclusion and offer quantitative support, a groundwater transport model was used to predict the attenuation rate of glyphosate in groundwater and to compare predicted glyphosate concentrations in groundwater to available human health and ecological toxicity information.

Conclusions:

The modeling results predict that the majority of the applied glyphosate does not travel more than one-half meter from the point of application.

A comparison of predicted groundwater concentrations for glyphosate to chronic toxicity values for aquatic invertebrates, fish and humans indicates that predicted values at the ten foot buffer location are well below these criteria.

Based on fate and transport characteristics of the surfactant contained in the Roundup formulation, polyethoxylated tallowamine (POEA), it is not likely that concentrations of this compound will be of concern in

surface waters at the ten foot buffer location. However, it is recommended that modeling of POEA concentrations be done should the appropriate chemical and physical parameter information become available.

The Office of Research and Standards recommends that a field verification study be conducted to verify the conclusions presented above before ten-foot setbacks are adopted for this particular type of herbicide application. The data obtained would go towards addressing any remaining uncertainties on the fate of glyphosate applied with a surfactant in close proximity to water resources.

Discussion:

There are conceivably two ways in which pesticide applied to railroad ballast can impact surface water bodies. The first involves overland flow, in which a pesticide is carried along in runoff to nearby tributaries and wetlands and is then carried into surface waters from there. With glyphosate, it is unlikely that applied pesticide will be carried along in surface runoff as glyphosate binds very tightly to soil. In a situation with heavy runoff which causes erosion of soil, it is possible that glyphosate-bound soil could be washed into tributaries, wetlands or other surface water bodies. Given the affinity of glyphosate for soil and the fact that railroad ballast is largely devoid of finer material which would tend to be moved as surface runoff, it is unlikely that overland flow will pose a significant source of contamination.

The second way in which applied glyphosate can impact surface waters is if it travels down through the soil to the groundwater table, to be discharged to tributaries, wetlands and water bodies. The groundwater sampling model was used to quantitatively predict groundwater concentrations flowing away from the application point that would result after a glyphosate application to the rail bed. Predicted concentrations at the shortest proposed setback distance were then compared to available toxicity information for aquatic organisms and humans.

Modeling Approach:

To answer the question of mobility of the herbicide Glyphosate that is applied to the ballast area of railroad lines, the PHAST Model was selected (PHAST--A Program for Simulating Ground-Water Flow and Multicomponent Geochemical Reactions, By David L. Parkhurst, Kenneth L. Kipp, and Peter Engesgaard). PHAST is a 3-dimensional multicomponent reaction-transport model, which can be used to simulate transient ground-water flow with or without geochemical reactions. In this application the geochemical reactions were simulated.

The model used available chemical data, application rate and generalized soil characteristics to simulate the movement of the herbicide in the ground water. To simplify the modeling process, only the active compound was modeled. For reaction-transport calculations, PHAST needs three data files for execution, the flow and transport data file, the chemical data file, and the thermodynamic database file. These files were created to reflect the characteristics of the herbicide and a typical soil in Massachusetts.

The simulation time frame for the transport of the herbicide within the groundwater is currently set for 400 days. The model run was based upon the typical application rate of 1.5-2 quarts product/acre for Roundup Pro (41% glyphosate) used in applications utilizing a rail mounted spray truck with spray boom height approximately two feet above the rail bed. The model was used to predict the movement of the active ingredient, glyphosate.

The modeling effort determined the probable distance the herbicide will travel based upon the general characteristics of the soil and groundwater movement and the chemical characteristics of the compound to be about 1 meter. Significant attenuation of close to two orders of magnitude was noted within ½ meter.

Toxicity:

To interpret the results of the modeling exercise, toxicity values for the endpoints of concern were identified. The endpoints of concern in this evaluation are invertebrates and fish in surface waters that would potentially be impacted by application of glyphosate to railroad rights of way.

Chronic surface water toxicity criteria for glyphosate were identified for use in assessing the potential for adverse ecological effects to these organisms. The basis for these chronic criteria are no-observed effect concentrations (NOEC) or no-observed adverse effect concentrations (NOAEC) which are the greatest test concentrations that will cause no observed effects or no observed adverse effect in test organisms. Taxa-specific chronic reference values (TRVs) were derived based on a review of chronic toxicity information from a number of studies on the ecological effects of glyphosate (Giesy et al., 2000).

In addition to toxicity criteria for the active ingredient glyphosate, the toxicity data reviewed included data for the formulation Roundup, which is a commercial product which also includes the surfactant, polyethoxylated tallowamine (POEA). POEA is considered to be more toxic to aquatic organisms than is glyphosate. Chronic surface water criteria for invertebrates and fish were also identified for POEA.

Acute surface water toxicity criteria for invertebrates and fish were only identified for the product formulation Roundup. Use of acute criteria to evaluate whole products is based on EPA registration requirements which allow acute toxicity studies to be conducted on the product whereas chronic toxicity studies are required to be conducted on the individual components. The rationale for this approach is that during an acute exposure to Roundup, simultaneous exposure to glyphosate and the surfactant POEA can occur, whereas under chronic conditions, the individual components may be influenced by even minor differences in the fate of the components.

Limited available information was also compiled for the primary metabolite of glyphosate, aminomethylphosphonic acid (AMPA). In the limited results for AMPA presented, little toxicity of AMPA was observed. In addition, AMPA does not bioaccumulate in the environment (Giesy et al., 2000). As a result, no TRVs specific for AMPA were derived in this section.

Table 1. Ecological Reference Values

Organism	Roundup (Acute) (mg/L)	Ref.	Glyphosate (Chronic) (mg/L)	Ref.	POEA (Chronic) (mg/L)	Ref.
Invertebrates	0.8	1	0.7	2	0.1	3
Fish	0.35	1	1	2	0.03	3

1. Acute Toxicity Reference Value for Roundup as recommended in: Giesy, John P., Dobson, Stuart and Solomon, Keith R. 2000. Ecotoxicological Risk Assessment for Roundup Herbicide. Rev Environ Contam Toxicol 167:35-120.
2. Chronic Toxicity Reference Value for Glyphosate as recommended in: Giesy, John P., Dobson, Stuart and Solomon, Keith R. 2000. Ecotoxicological Risk Assessment for Roundup Herbicide. Rev Environ Contam Toxicol 167:35-120.
3. Chronic Toxicity Reference Value for POEA as recommended in: Giesy, John P., Dobson, Stuart and Solomon, Keith.

In addition to ecological effects, a number of criteria are available to evaluate potential human health exposures and effects. The EPA has developed several Drinking Water Health Advisories for glyphosate. Health Advisories are defined as concentrations of a substance in drinking water estimated to have negligible deleterious effects in humans, when ingested for a specified period of time. These values include a ten-day health advisory for a child of 20 mg/l as well as a lifetime health advisory of 1 mg/l for a child and 4 mg/l for a 70 kg adult (USEPA, 1988).

The EPA has also developed a Maximum Contaminant Level Goal (MCLG) for drinking water of 0.7 mg/l and has promulgated this value as a Maximum Contaminant Level (MCL) standard (USEPA, 1993b; USEPA, 1995a). Massachusetts has adopted this value as a drinking water standard, known as a Massachusetts Maximum Contaminant Level (MMCL).

Since the modeling results only predict concentrations of glyphosate, only a quantitative evaluation for chronic exposures to glyphosate could be conducted. A comparison of maximum predicted groundwater concentrations at the ten foot buffer location was done to chronic TRVs as well as to the Health Advisories and MMCLs. Predicted groundwater concentrations at the ten foot buffer location were many orders of magnitude below these criteria.

The effects of the POEA surfactant could not be quantitatively evaluated based on the results of this modeling analysis. Qualitative information on the fate and transport of this compound however, indicates that POEA binds tightly to soil particles, making it practically immobile in most soils. In addition, POEA is relatively non-persistent in soil and is rapidly degraded with a half-life of about seven days. Roundup contains approximately 41% glyphosate and 14.5% of POEA. Thus, the concentration of POEA is approximately 2.8 times less than that of glyphosate. The initial concentration of glyphosate and POEA were estimated to be quite low. The predicted glyphosate concentration dropped very quickly. For an application made to railroad ballast, at the ten foot buffer location, theoretical groundwater concentrations of glyphosate are predicted to be in the concentration range of 1×10^{-8} mg/l. It is likely that under this application scenario, POEA concentrations in water supplies will drop to well below the levels of the toxicity criteria identified. For similar reasons as those given above for POEA, acute exposures to Roundup will likely not be of concern in surface waters at the ten-foot buffer location.

The quantitative fate and transport parameters for POEA have not been identified to allow the modeling exercise to be repeated for POEA. However, once this information becomes available, we propose repeating the modeling exercise with POEA to confirm quantitatively the conclusions that we have reached qualitatively.

References:

Giesy, John P., Dobson, Stuart and Solomon, Keith R.. 2000. Ecotoxicological risk assessment for Roundup herbicide. Rev Environ Contam Toxicol. 167:35-120.

Glyphosate and Environmental Fate Studies, *Backgrounder*, April 2003, Monsanto Company

APPLICATION MANUAL, Glyphosate, Pickering Laboratories, Inc., Mountain View, CA

INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY, ENVIRONMENTAL HEALTH CRITERIA 159 GLYPHOSATE, Published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization, World Health Orgnization, Geneva, 1994

APPENDIX B: HEBRONVILLE, MA: SAMPLING DETAILS FOR GLYPHOSATE

(a) Labeling Northbound Water Quality Samples

(Spraying is expected to commence on the north bound side of the tracks)

LOCATION						
	1		2		3	
Time from Application	50 feet Upstream	*duplicate*	20 feet downstream	*duplicate*	0.5 miles downstream	*duplicate*
before1	1NBPRE1		2NBPRE1		3NBPRE1	
before2	1NBPRE2		2NBPRE2		3NBPRE2	
0	-	-	-	-	-	-
30 sec	1NB1	1NB1D	2NB1	2NB1D	-	-
3 min	1NB2	1NB2D	2NB2	2NB2D	-	-
10 min	1NB3	1NB3D	2NB3	2NB3D	3NB3	3NB3D
16 min	1NB4	1NB4D	2NB4	2NB4D	3NB4	3NB4D
30 min	1NB5		2NB5	2NB5D	3NB5	3NB5D
1 hr	1NB6		2NB6	2NB6D	3NB6	3NB6D
2 hr	1NB7		2NB7	2NB7D	3NB7	3NB7D
4 hr	1NB8		2NB8	2NB8D	3NB8	3NB8D
Total # Samples	10	4	10	8	8	6
					GRAND TOTAL	**46**

KEY:

only to be analyzed where detectable concentrations of lyphosate found in downstream or primary samples.

Field duplicates to be taken and kept in reserve for analysis to corroborate positive results or anomalous results in primary samples.

(b) **Labeling Southbound Water Quality Samples**

(The tracks on the Southbound side will be sprayed a few hours after the Northbound side has been sprayed)

LOCATION						
	1		2		3	
Time from Application	50 feet Upstream	*duplicate*	20 feet downstream	*duplicate*	0.5 miles downstream	*duplicate*
0	-	-	-	-	-	-
30 sec	1SB1	1SB1D	2SB1	2SB1D	-	-
3 min	1SB2	1SB2D	2SB2	2SB2D	-	-
10 min	1SB3	1SB3D	2SB3	2SB3D	3SB3	3SB3D
16 min	1SB4	1SB4D	2SB4	2SB4D	3SB4	3SB4D
30 min	1SB5		2SB5	2SB5D	3SB5	3SB5D
1 hr	1SB6		2SB6	2SB6D	3SB6	3SB6D
2 hr	1SB7		2SB7	2SB7D	3SB7	3SB7D
4 hr	1SB8		2SB8	2SB8D	3SB8	3SB8D
8 hr	1SB9		2SB9	2SB9D	3SB9	3SB9D
12 hr	1SB10		2SB10	2SB10D	3SB10	3SB10D
24 hr	1SB11		2SB11	2SB11D	3SB11	3SB11D
7 d	1SB12		2SB12	2SB12D	3SB12	3SB12D
14 d	1SB13		2SB13	2SB13D	3SB13	3SB13D
28 d	1SB14		2SB14	2SB14D	3SB14	3SB14D
56 d	1SB15		2SB15	2SB15D	3SB15	3SB15D
112 d	1SB16		2SB16	2SB16D	3SB16	3SB16D
224 d	1SB17		2SB17	2SB17D	3SB17	3SB17D
Sig. Rainfall event 1	1R1		2R1	2R1D	3R1	3R1D
Sig. Rainfall event 1 Day 1	1R1Day1		2R1Day1	2R1Day1D	3R1Day1	3R1Day1D
Sig. Rainfall event 1 Day 2	1R1Day2		2R1Day2	2R1Day2D	3R1Day2	3R1Day2D
Sig. Rainfall event 1 Day 3	1R1Day3		2R1Day3	2R1Day3D	3R1Day3	3R1Day3D
Sig. Rainfall event 2	1R2		2R2	2R2D	3R2	3R2D
Sig. Rainfall event 2Day 1	1R2Day1		2R2Day1	2R2Day1D	3R2Day1	3R2Day1D
Sig. Rainfall event 2 Day 2	1R2Day2		2R2Day2	2R2Day2D	3R2Day2	3R2Day2D
Sig. Rainfall event 2 Day 3	1R2Day3		2R2Day3	2R2Day3D	3R2Day3	3R2Day3D
Sig. Rainfall event 3	1R3		2R3	2R3D	3R3	3R3D
Sig. Rainfall event 3 Day 1	1R3Day1		2R3Day1	2R3Day1D	3R3Day1	3R3Day1
Sig. Rainfall event 3 Day 2	1R3Day2		2R3Day2	2R3Day2D	3R3Day2	3R3Day2
Sig. Rainfall event 3 Day 3	1R3Day3		2R3Day3	2R3Day3D	3R3Day3	3R3Day3
Total # Samples	29	4	29	29	27	27
					GRAND TOTAL	**145**

KEY:

only to be analyzed where detectable concentrations of glyphosate are found in downstream or primary samples.

Field duplicates to be taken and kept in reserve for analysis to corroborate positive results or anomalous results in primary samples.

(c) Labeling Sediment Sampling

LOCATION		
	2	3
Time from Application	20 feet *downstream*	0.5 miles *downstream*
before Northbound Applications	2SED1	3SED1
1 hour after Southbound Applications	2SED2	3SED2
24 hours after Southbound Applications	2SED3	3SED3
Total # Samples	3	3
	GRAND TOTAL	**6**

APPENDIX C: BOXBOROUGH MA: SAMPLING DETAILS FOR GLYPHOSATE AND RAILROAD SETBACKS

LOCATION						
	1		2		3	
Time from Application	50 feet Upstream	*duplicate*	20 feet downstream	*duplicate*	0.5 miles downstream	*duplicate*
0	-	-	-	-	-	-
30 sec	1BOX1	1BOX1D	2BOX1	2BOX1D	-	-
3 min	1BOX2	1BOX2D	2BOX2	2BOX2D	-	-
10 min	1BOX3	1BOX3D	2BOX3	2BOX3D	3BOX3	3BOX3D
16 min	1BOX4	1BOX4D	2BOX4	2BOX4D	3BOX4	3BOX4D
30 min	1BOX5		2BOX5	2BOX5D	3BOX5	3BOX5D
1 hr	1BOX6		2BOX6	2BOX6D	3BOX6	3BOX6D
2 hr	1BOX7		2BOX7	2BOX7D	3BOX7	3BOX7D
4 hr	1BOX8		2BOX8	2BOX8D	3BOX8	3BOX8D
8 hr	1BOX9		2BOX9	2BOX9D	3BOX9	3BOX9D
12 hr	1BOX10		2BOX10	2BOX10D	3BOX10	3BOX10D
24 hr	1BOX11		2BOX11	2BOX11D	3BOX11	3BOX11D
7 d	1BOX12		2BOX12	2BOX12D	3BOX12	3BOX12D
14 d	1BOX13		2BOX13	2BOX13D	3BOX13	3BOX13D
28 d	1BOX14		2BOX14	2BOX14D	3BOX14	3BOX14D
56 d	1BOX15		2BOX15	2BOX15D	3BOX15	3BOX15D
112 d	1BOX16		2BOX16	2BOX16D	3BOX16	3BOX16D
224 d	1BOX17		2BOX17	2BOX17D	3BOX17	3BOX17D
Sig. rainfall event 1	1BOXR1		2BOXR1	2BOXR1D	3BOXR1	3BOXR1D
Sig. rainfall event 1 Day 1	1BOXR1Day1		2BOXR1Day1	2BOXR1Day1D	3BOXR1Day1	3BOXR1Day1D
Sig. rainfall event 1 Day 2	1BOXR1Day2		2BOXR1Day2	2BOXR1Day2D	3BOXR1Day2	3BOXR1Day2D
Sig. rainfall event 1 Day 3	1BOXR1Day3		2BOXR1Day3	2BOXR1Day3D	3BOXR1Day3	3BOXR1Day3D
Sig. rainfall event 2	1BOXR2		2BOXR2	2BOXR2D	3BOXR2	3BOXR2D
Sig. rainfall event 2Day 1	1BOXR2Day1		2BOXR2Day1	2BOXR2Day1D	3BOXR2Day1	3BOXR2Day1D
Sig. rainfall event 2 Day 2	1BOXR2Day2		2BOXR2Day2	2BOXR2Day2D	3BOXR2Day2	3BOXR2Day2D
Sig. rainfall event 2 Day 3	1BOXR2Day3		2BOXR2Day3	2BOXR2Day3D	3BOXR2Day3	3BOXR2Day3D
Sig. rainfall event 3	1BOXR3		2BOXR3	2BOXR3D	3BOXR3	3BOXR3D
Sig. rainfall event 3 Day 1	1BOXR3Day1		2BOXR3Day1	2BOXR3Day1D	3BOXR3Day1	3BOXR3Day1
Sig. rainfall event 3 Day 2	1BOXR3Day2		2BOXR3Day2	2BOXR3Day2D	3BOXR3Day2	3BOXR3Day2
Sig. rainfall event 3 Day 3	1BOXR3Day3		2BOXR3Day3	2BOXR3Day3D	3BOXR3Day3	3BOXR3Day3
Total # Samples	29	4	29	29	27	27
					GRAND TOTAL	**145**

KEY:

only to be analyzed where detectable concentrations of glyphosate are found in downstream or primary samples.

field duplicates to be taken and kept in reserve for analysis to corroborate positive results or anomalous results in primary samples.

(c)Labeling Sediment Sampling (Boxborough)

LOCATION		
	2	3
Time from Application	20 feet *downstream*	0.2 miles *downstream*
before Northbound Applications	2BOXSED1	3BOXSED1
1 hour after Southbound Applications	2BOXSED2	3BOXSED2
24 hours after Southbound Applications	2BOXSED3	3BOXSED3
Total # Samples	3	3
	GRAND TOTAL	**6**

BSOP No Glyphosate 001	page 1 of 3
Determination of Glyphosate in Soil and Water	

Purpose

Describes the analysis of soil and water for glyphosate and its metabolite AMPA.

Outline

Compounds are extracted from soil with 0.25M NH_4OH/0.1M KH_2PO_4 and derivatized with 2:1 TFAA:HFB

References

1. Determination of Glyphosate and (Aminomethyl)phosphonic Acid in Soil, Plant, and Animal Matrices and Water by Capillary Gas Chromatography with Mass Selective Detection. Alferness, P. and Iwata, Y. 1994. J. Agric. Food Chem. 42, 2751-2759

Holding time

Soil samples should be stored at -20 ^oC. Water samples can alternatively be held at 4 ^oC and analyzed within 2 weeks.

Soil Extraction

- Allow sample to equilibrate to room temperature
- Weigh 20.0g soil into 120 ml amber glass jar.
- Add 80 ml 0.25M NH_4OH/0.1M KH_2PO_4.
- Teflon tape threads and seal with a teflon lined cap.
- Place in tabletop shaker sideways, and shake for 90 minutes.
- Allow soil to settle for 5 minutes
- Filter supernatant through 0.45µm syringe filter.

Water Extraction

- Transfer 10.0 ml mixed sample to a 15 ml centrifuge tube
- Evaporate to 1.0 ml under N_2 at 80 ^oC.

Derivatization

- Place 1.6 ml of 2:1 TFAA:HFB in clear 4 ml sample vials with teflon caps.
- Place vials in aluminum heating block.
- Place block on bed of dry ice.
- Surround block with more dry ice. (Total of three pounds is adequate).
- Place low temperature thermometer in block.
- When temperature is between **-50 and -60º C** add 36 µl sample with eppendorf pipette.
- Rinse pipette 4 times in derivatizing reagent. **Keep pipette tip under the surface of the chilled reagent at all times.**
- Place heating block in heater.

Page 2 of 3

- React for 1 hour at 90º C.
- Allow to equilibrate to room temperature.
- Reduce to apparent dryness under nitrogen.
- Continue evaporation for 30 minutes after apparent dryness.
- Reconstitute in 200 ц l of 2 ц l/ml citral in ethyl acetate.

Preparation of calibration curve

- Standard curve should include 6 points.
- Standard solutions are made in ddH_2O. 0.005 ug/ml - 1.0 ug/ml. (0.009 – 0.18 ug/ml final volume.
- Standards are derivatized in the same manner as the samples (36 µl aliquot).
- All standards should be derivatized individually along with the samples.

Analysis

At least two samples should be injected before running the first standard curve.
GC-MS with ChemStation
column: 30M DB-5MS (30m x 0.25 mm x 0.25 µm) or equivalent
carrier gas: He @ 0.9 ml/min
Detector 280^{o}C; Injector 250^{o}C
Solvent delay: 6.50 minutes
80^{o}C (1 min) - 200^{o}C (0 min) @ 8^{o} C/min - 300°C (1 min) @ 25°C/min
2.0 µl autosampler inj
SIM mode
Tune File: glytune

Method parameters using 30M DB-5MS

Analyte	**$t_{R\ (min)}$**	**m/z**
AMPA	7.38	446, 502, 571
Glyphosate	9.47	460, 584, 611

Additional QA

- Each sample set should contain:

Soil

- 80 ml extracting solution blank
- 80 ml extracting solution spike. Spike range should be 50-200 ppb.
- Soil blank and soil spike if possible.

Water

- 10.0 ml ddw blank
- 10.0 ml ddw spike (10-20 ppb)

- Limit of detection is based on a signal that is greater than 5 times the background noise contributed by the matrix blank.
- Positive compound identification is based on instrument retention time and the relative ratio of at least three analyte ions (including the molecular ion for AMPA, Glyphosate molecular ion is outside instrument m/z range). Whenever possible, positive samples should be concentrated, along with blanks, and re-analyzed by GC/MSD for full spectra confirmation.

Expected method performance based on initial demonstration of capability

Spike recovery: soil and water

Analyte	% recovery QC limits
AMPA	80-130%
Glyphosate	80-120%

Expected LOD = 20 ppb (soil); 1.0 ppb (water).

APPENDIX E
Quality Assurance Data for Glyphosate Analysis

QA/QC Data

Daily Spike Recovery

Water

	AMPA	Glyphosate
4-Aug	86.60%	86.70%
17-Aug	86.20%	81.80%
18-Aug	95.30%	96.20%
31-Aug	100.50%	95.30%
7-Sep	106.50%	103%
8-Sep	100.60%	104.60%
12-Sep	93.40%	96.30%
13-Sep	93.40%	102.20%
14-Sep	110.50%	100.10%
21-Sep	105.60%	106.30%
22-Sep	105.70%	100.30%
16-Nov	120.10%	114.80%
15-Mar	102.60%	104.50%
	100.54%	99.39%

Sediment

	AMPA	Glyphosate
9-Sep	81.60%	82.70%
22-Sep	89.50%	116.70%
	85.55%	99.70%

Storage Stability Study (Water)

Storage Spikes (prepared 7/19/05)

Analysis date	AMPA	Glyphosate
1-Sep	123.20%	96.20%
2-Sep	158.60%	98.30%
7-Sep	163.60%	104.80%
12-Sep	142.20%	113.30%
12-Sep	121.00%	97.00%
14-Sep	234.10%	100.10%
21-Sep	141.70%	86.60%
22-Sep	122.60%	114.90%
	150.88%	101.40%

Storage data indicate there was no glyphosate degradation over the two month storage stability study conducted concurrently with sample storage. The longest storage of an actual field sample was 32 days.

Samples were analyzed utilizing the following method:
"Determination of Glyphosate and (Aminomethyl)phosphonic Acid in Soil, Plant, and Animal Matrices, and Water by Capillary Gas Chromatography with Mass-Selective Detection"
Alferness, P., and Iawata, Y. J. Agric. Food Chem. 1994. (42) 2751-2759.