Technical Note Glyphosate-1:

Monitoring transient glyphosate concentrations in runoff from recently sprayed agricultural fields: Synopsis for Journal Supplemental Information

Version 1, March 2018

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Cornell University, Biological and Environmental Engineering, Soil and Water Lab

Reflecting the work of dozens of other Cornellians

Cooperating with USGS Organic Geochemistry Research Lab (OGRL), Lawrence Kansas

Glyphosate work sponsored by New York State Department of Environmental Conservation

and Cornell Atkinson Center for a Sustainable Future.

Cornell field site operation funded by USDA.

1.0 Purpose

This document describes selected aspects of environmental sampling, chemical analyses, and data interpretation in a joint Cornell-BEE and USGS-OGRL venture to observe glyphosate moving with water that leaves a sprayed agricultural area. We hope this will help understand how the data were obtained, and most importantly, to help judge their adequacy for reuse.

We also maintain deeper documentation to provide memory so that later work can be consistent with earlier work, minus earlier mistakes. While the deeper documentation is not edited well enough to be fully understandable outside our group, it may be useful to others contemplating similar monitoring. We will entertain requests for copies of the deeper, unedited documentation.

Subsequent sections of this synopsis cover collecting samples, analyzing samples, cross-laboratory and other confidence testing, and adopted results per sample. This is designed to be part of the Cornell eCommons repository of archival documentation. This and later versions will be available at the Cornell eCommons repository, Soil and Water Lab collection: https://ecommons.cornell.edu/handle/1813/34420

Some of this content overlaps with an article submitted to Environmental Science and Technology Letters. Please also note that this is written from the perspective of the Cornell part of the joint venture, thus does not give much coverage to details of the partner USGS group who performed the most important laboratory analyses.

2.0 Sampling approach

Experience with time patterns in solute concentrations near intense chemical sources, such as phosphorus escape from dairy farms (Longabucco & Rafferty, 1998), indicates that water sampling must extend for several days if an early post-spray stormflow event lasts that long. To discern time patterns in concentration, with dynamic range of over two orders of magnitude within a day in the L&R work, requires many separate samples within the multi-day event. Variability and sample protection force robotic autosampling and a team of at least four people to operate the sampler(s) and process the samples after collection.

ISCO model 6700 autosamplers support programmable compositing (several draws into one container) and discretization (up to 24 containers sequentially). Test autosampling in spring 2014 (preceding the collaboration with the USGS – OGRL) showed that autosampling could work in this application. Our sample containers and processing changed in spring 2015 and have been stable since. The 2015-2017 approach is derived from USGS-OGRL advice and the USGS National Field Manual (U.S. Geological Survey, variously dated). Matching USGS fully was not affordable, but setting the bar high was worthwhile, and we believe that the USGS essentials are captured despite the limited resources available. The sampling essentials inspired by USGS traditional rigor and glyphosate experience include:

- Methanol rinsing of sample collection and processing apparatus, especially the filter equipment.
- Minimizing metal and glass contact with liquid during sample collection and processing. Plastic is favored.
- Early separation of particulates from liquid after a sample is drawn, to minimize transfer between particulate and dissolved forms. Done via filtering through GF/F paper that USGS-OGRL demonstrated would pass all dissolved glyphosate.
- Single use sample containers instead of reusable containers.

Ice in the autosampler cores slow biochemical processes until samples are retrieved from an autosampler for filtration, then freezing. A 2014 trial approach of acidifying samples with HCl at collection (Kylin, 2013) was abandoned to be consistent with USGS.

Figure 1 provides an overview of how autosamplers were deployed in four USGS-inspired campaigns between spring 2015 and spring 2017. This and other flow charts in this document omit many details, trying to capture the spirit and most important considerations of the part of the project they cover. (Fully detailed guidance in forms, flowcharts, and other tools was used in practice.)

Each campaign started at the first flow-creating storm after spraying; the spraying was timed based on agricultural considerations. To avoid confusion, the Cornell field site we monitored is not hosting a glyphosate loss experiment; the site has routine glyphosate use, and we monitor losses from that routine use on plots within our biofuel cropping experiment. (An actual glyphosate loss experiment is planned.)

Rain forecasts drove the launch of the autosampler. The first effective sample is when flow rises enough to immerse the autosampler's peristaltic pump intake. We successfully sampled the first flow of each season's first possible glyphosate mobilization event.

We wished to continue sampling for the whole flow event after the rainstorm until flow was zero or a slow trickle. To keep workload -- correlated with the number of samples and number of times having to visit the autosampler – feasible, we lengthened time duration per sample container as a campaign proceeded. 2015 started with 1-hour sample durations and phased toward 4-hour durations by the end of the campaign. A single autosampler sample is an equal-volume composite of 4-16 draws at 15 to 60 minute intervals. A 1L container can hold four 220 mL draws or sixteen 55 mL draws.

As soon as possible after collection of the samples, the solids were separated by vacuum filtration. This could be up to 4 days after collection at the longest sample duration, or an average of 12 hours when using the 1-hour duration. The filtrate and filters containing particles were frozen. In hindsight, since the filters only contain 0.1g or less of trapped sediment, the glyphosate concentration of the particles would have to be very high to be detectable, or for the particle-bound glyphosate mass flux to amount to much. (The highest solids concentration recorded was around 350 mg solids/L, with nearly all samples under 100 mg/L.) We have not been able to attempt extractions from sediment on filters as of early 2018. A different autosampling tactic using >1L containers may be needed to trap enough suspended particles to make this worthwhile at our 100% grass, low-erosion site.

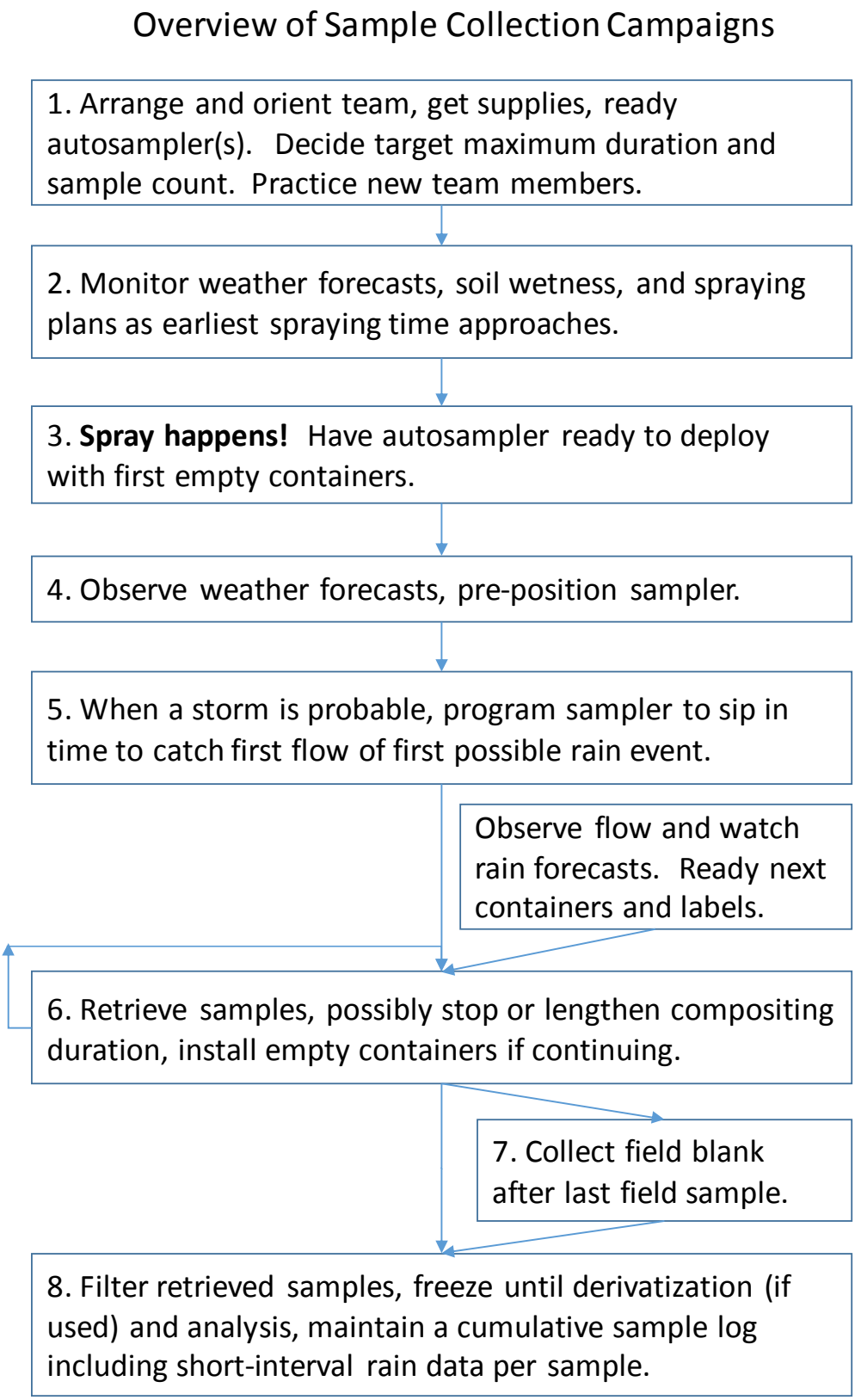

Figure 1: Sampling campaigns

3. Analytical approach

Because of the number of samples, workloads beyond this project in both collaborating groups, comparative inexperience of Cornell personnel in glyphosate analysis, and very limited access to Liquid Chomatograph – Mass Spectrometer (LC-MS) equipment in project principal Ludmilla Aristilde's facilities at Cornell, the samples in the 2015 and 2016 batches were divided across laboratories based on *a priori* sample priority:

- The most important went to the proven USGS lab. This would provide a usable time series regardless of the junior Cornell lab's progress.
- A batch drawing from most important and a few expected low concentration samples went to both USGS and Cornell, to provide strong results against which learner Cornell results could be measured.
- A batch of lower priority samples went to the Cornell lab only.
- The remainder were divided into three batches based on results of earlier batches. These were destined for USGS, destined for Cornell, and "when feasible."

(Note: "LC-MS" and "LC-MSMS" are used interchangeably in this document; the latter refers to tandem mass spectrometry, a specialized form of the general MS.)

There were also "learning" and quality assurance samples included in most of the batches.

The 2015 *a priori* categorization of samples was initially informed by analyses of nine of the 2014 trial samples at a NYS DEC pesticide laboratory, which found (as expected from the Longabucco and Rafferty sampling for phosphorus) a positive correlation between flow rate and concentration. Thus samples near any flow peak (whatever the magnitude) would be highest priority, and samples at a lowest flow trailing edge would be lowest priority. The 2016 spring categorization was informed by the full 2015 results -- we managed to have all reliable samples tested. Each campaign's prioritization built on accumulated knowledge from analyses of earlier campaigns' samples and the current campaign's measured outflow regime. By the 2017 spring sampling round, the USGS lab was having difficulty fitting in more samples and the Cornell lab became better after shifting to accessible and familiar ELISA instead of rarely accessible LC-MS. The highest priority samples were tested at Cornell and lesser priority plus both-lab split samples went to USGS. While the Cornell personnel's ELISA experience has accumulated over a decade, and there have been favorable cross-comparisons between ELISA and LC-MS for glyphosate (Sanchís, et al., 2012; Mahler, et al., 2017), we consider the continuing split-sample checking important.

Figure 2 portrays the preparation of samples prior to LC-MS analysis at either lab. All such preparation was done at Cornell, and when analysis would be done at the USGS lab, Cornell filled liquid chromatography vials to ship (insulated with ice) to USGS, reducing the personnel time needed in the USGS lab. While the senior lab personnel are far more experienced with the analysis via LC-MS, the mostly manual preparation of derivatized samples is very similar to processing of samples during ELISA analysis which is very familiar to the involved Cornell personnel. Also the analytical sequence design

used by USGS was highly familiar from ion chromatography work by the same Cornell personnel. There is just one minor difference in preparation for USGS versus Cornell: for Cornell the samples are filtered through 0.2 micron, plastic syringe filters before analysis, and the samples for USGS were not filtered again after the initial 0.7 micron GF/F filtering done when the samples were collected.

Figure 3 picks up with the Cornell version of LC-MS analysis that was used for many 2015 samples and a few 2014 samples. This was adapted from the LC-MS procedure published by USGS-OGRL (Meyer, et al., 2009). Part of the adaptation was to omit the USGS pre-concentration and cleanup step of Solid Phase Extraction (SPE). The Cornell faculty member controlling the LC-MS device and advising about its operation, Ludmilla Aristilde, prefers not to use SPE, and neither does the current USGS-OGRL procedure use SPE.

Cornell glyphosate project staff proceeded to use the LC-MS via direct injection and it worked well for 2015 calibrators and samples, albeit with a higher base noise level than USGS had. An estimated lower detection limit in matrix water of 0.1 left at least 50-fold dynamic range (up to at least 5.0) which left us surprised that an instrument operated by MS novices could yield results this close to desired on the first try. The second level of positive surprise was the agreement between the results of samples split between the USGS and Cornell labs (section 4 below).

Current USGS-ORGL lab procedure is similar to the Meyer documentation (Meyer, et al., 2009), and may be close to Figure 3 for this project's samples because of the derivatization being done at Cornell without SPE.

Initial Cornell LC-MS results of spring 2016 campaign samples demonstrated that the good 2015 LC-MS results at Cornell were not necessarily repeatable, and the 2016 Cornell LC-MS attempt was terminated after major analytical column clogging, muting of internal standard, and repeat fouling of a MS gas capillary, none of which were observed when testing the 2015 and 2014 samples. There must have been some change in the matrix, probably organic matter that makes it through 0.2 micron syringe filters. The USGS lab did not experience the clogging but noted some carryover of glyphosate into cleanout blanks following field samples. The 2016 Cornell LC-MS attempt also include some samples from road ditches and extracts from animal feeds which may also have contributed to column clogging.

Fortunately, the Abraxis ELISA procedure (Figure 4) proved applicable, had very good agreement with USGS LC-MS results in 2015 and 2016 samples (see section 4), yielded a similar lower detection limit and dynamic range to Cornell 2015 LC-MS, and had considerably lower cost per sample than LC-MS when taking into account the labor costs. USGS-OGRL experience with ELISA was another influence. Finally, Cornell experience with the USGS approach to LC-MS analysis provided insight into the design of ELISA sequences to incorporate data quality checking. Cornell ELISA results for fall 2016 and spring 2017 are temporarily the only ones available, and await USGS analytical work to check again the LC-MS versus ELISA results and coverage of more samples. Pending USGS LC-MS results will later replace Cornell ELISA results for the same samples.

Figure 5 shows how the diverse analytical results are combined to make judgments about detection limits and other aspects of data reporting. The following section reviews details about most formal quality assurance tests made to ensure usable data quality.

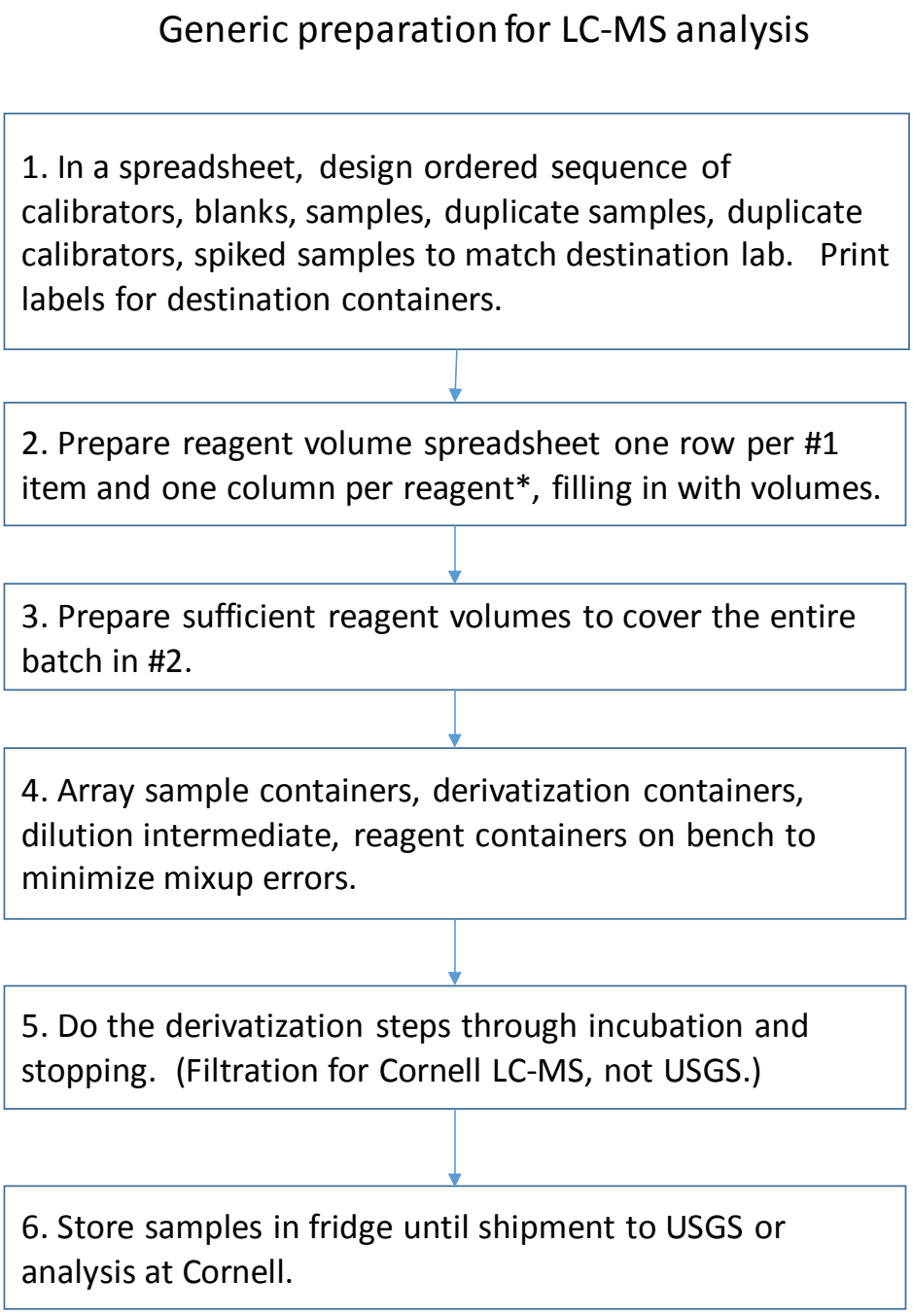

Figure 2: Preparation for LC-MS analysis

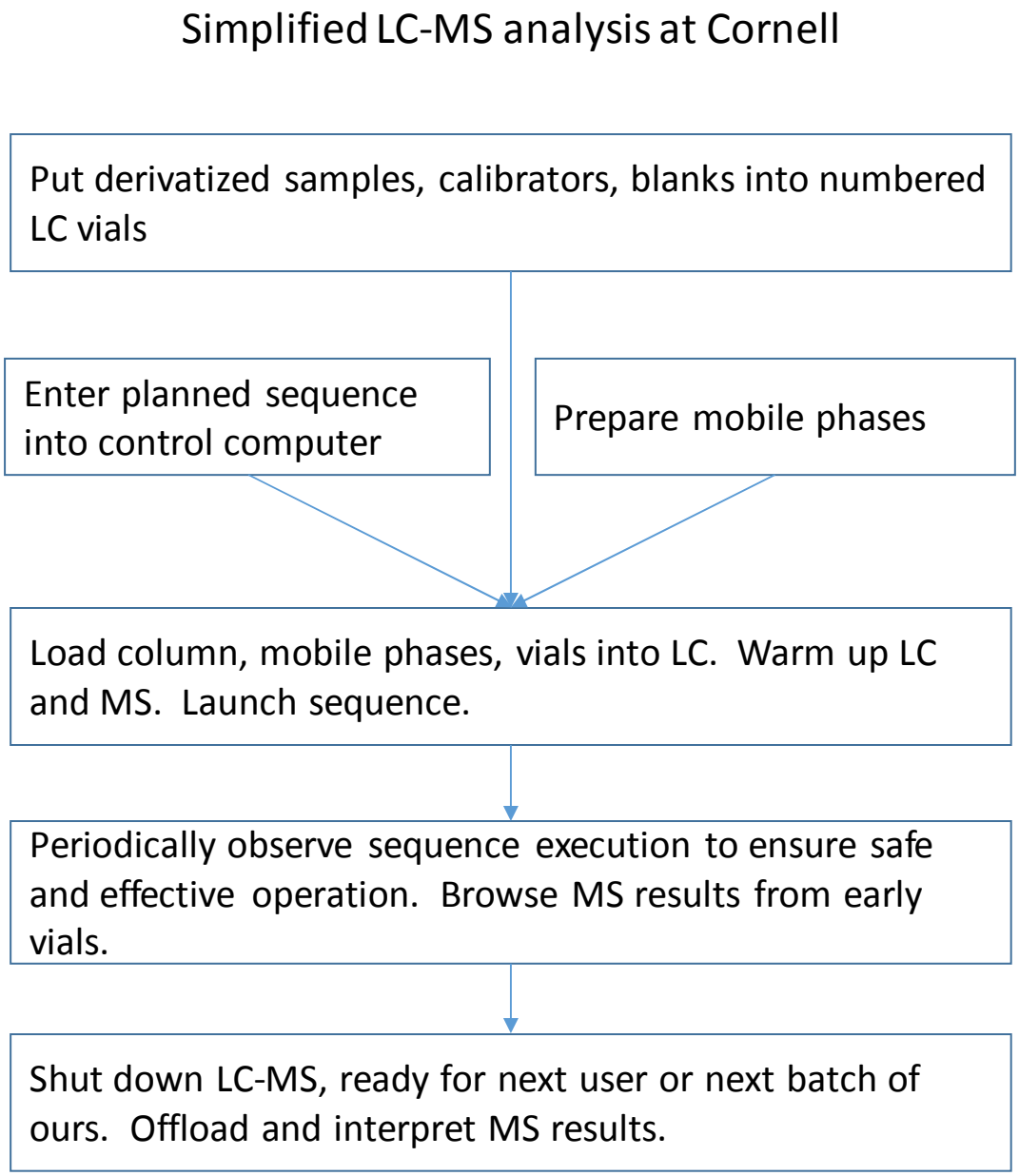

Figure 3: LC-MS procedure at Cornell

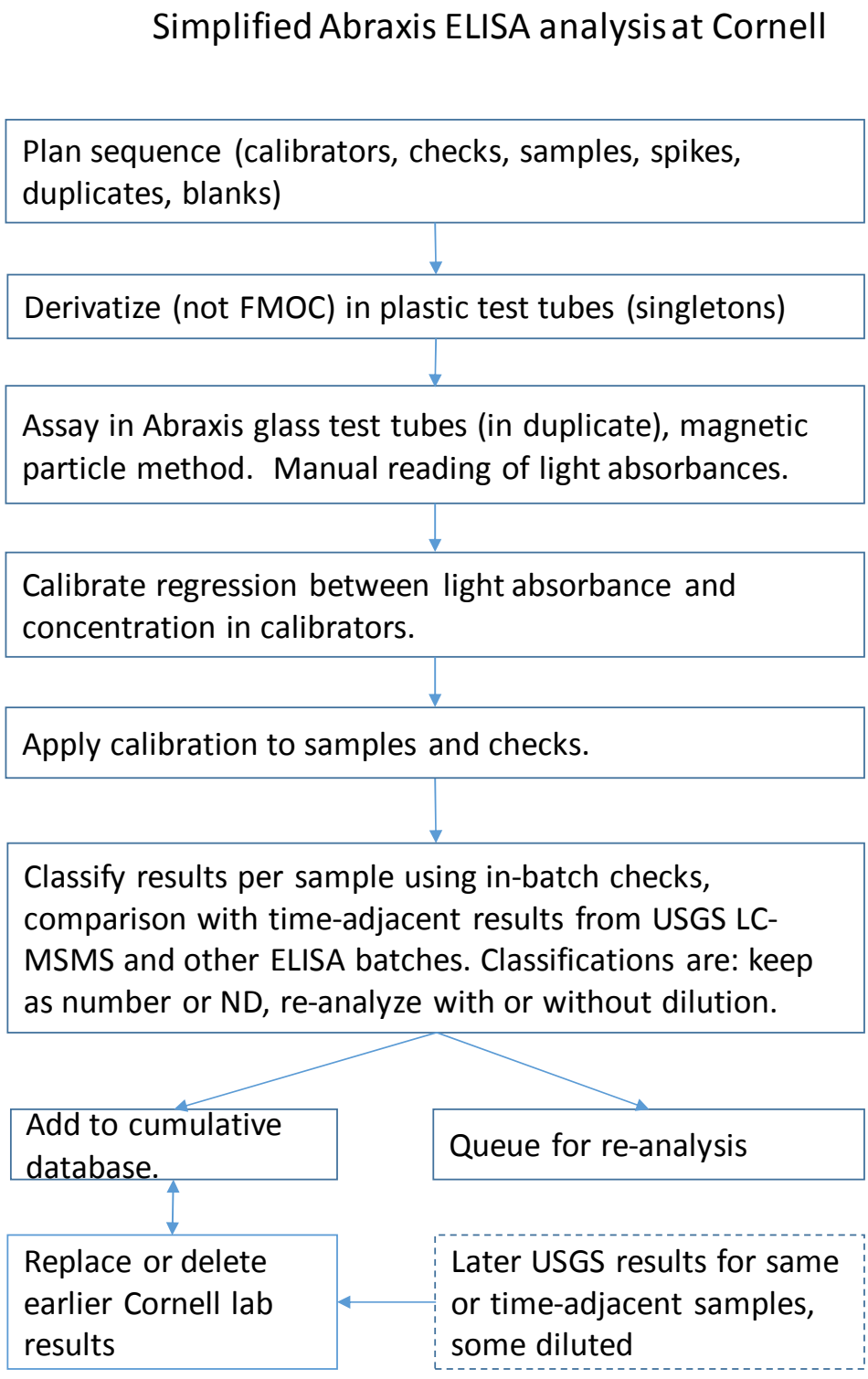

Figure 4:ELISA analysis at Cornell lab

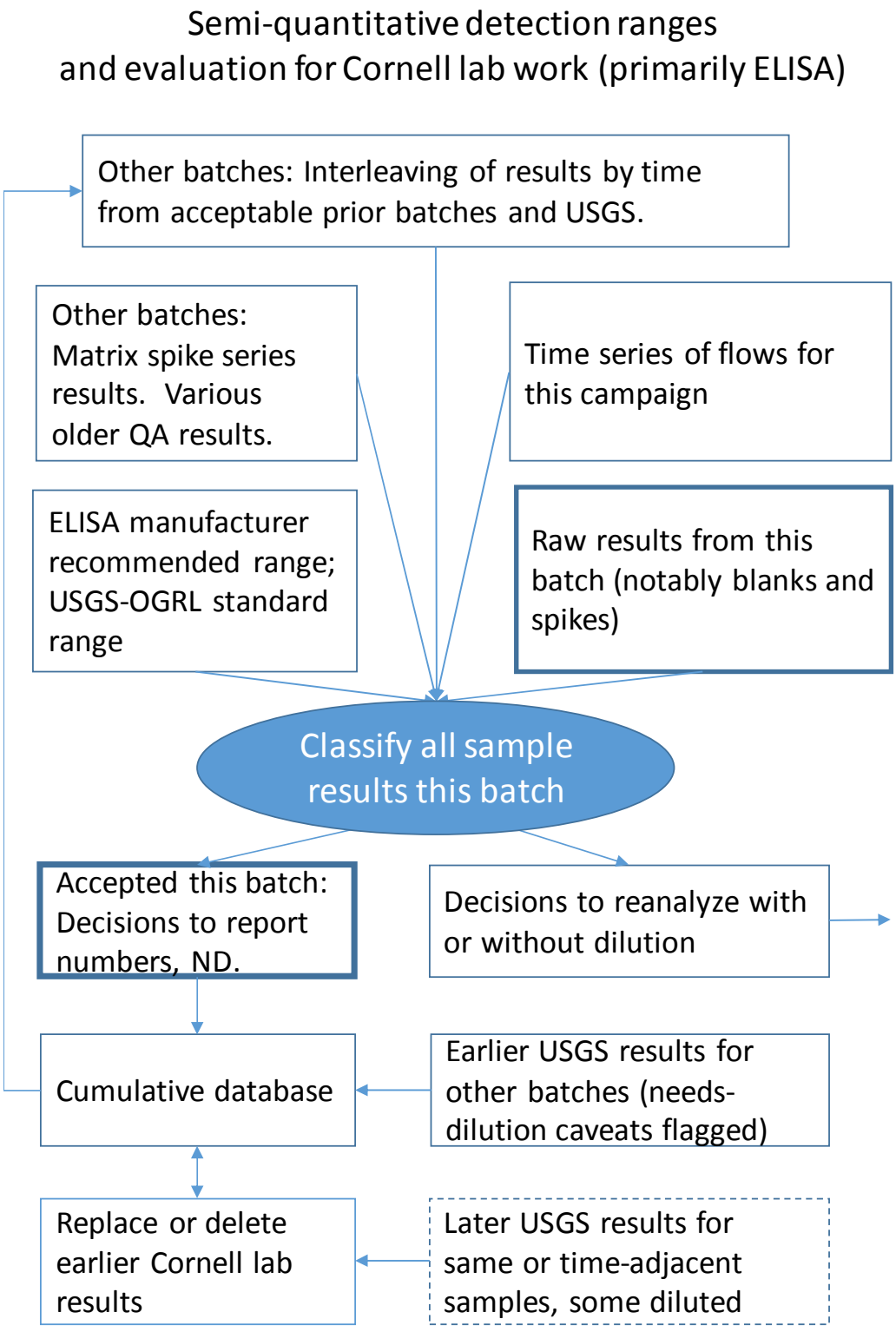

Figure 5: Decision making about analytical results

4. Quality testing and assurance

Note: An excerpt of material in this section appears in Supplemental Information (SI) documents accompanying at least one (submitted) journal paper. This content is provided here for those who do not read the journal papers or who which to examine the whole sample-to-number process. When a reader has access to published Journal SI, they should use that because that narrative was usually edited in response to peer and agency partner reviews.

4.1 Cross-lab and cross-method comparisons

2015 USGS LC-MSMS versus Cornell LC-MS

The most important confidence test for 2015 samples was done by sending 32 samples to USGS and testing them at Cornell as well. These were the highest priority samples of that vintage, selected to reflect peak flow and low flow conditions so that a spectrum of concentrations could be compared. This comparison was between USGS with adjustments based on an internal standard at 1 µg/L (nominally) of isotopically labeled glyphosate, and a calibration at Cornell without using an internal standard. Figure 6 shows that the weir-sample results (the most important subset of the 32) compare well over the range 0.1 to 7.0 µg/L (for the USGS result on the X axis). The slope of the regression was 1.14 and the R^2 of 0.99 indicate that the methods provided similar concentrations. The regression line (dotted blue) is pulled above 1:1 slope by the single highest concentration sample. The percent difference between the samples ranged from 0 to 24%. The mean percent difference was 12.4% (SD +/-10.42%). For this comparison, the USGS LCMS data were censored at 0.1 µg/L to match the censoring of the Cornell data.

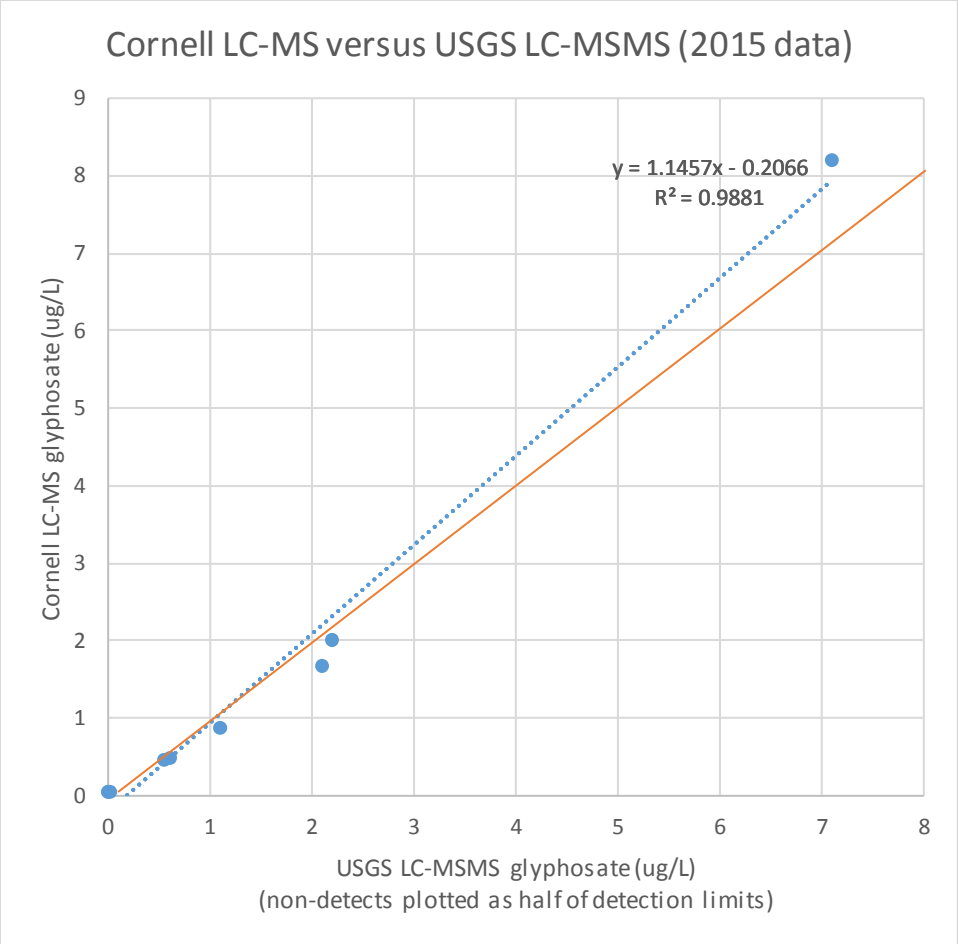

Figure 6: Cornell LC-MS versus USGS LC-MSMS (2015 weir samples)

The second most important comparison was to interleave the respective laboratories' time series of 2015-sample results for all samples. Figures 7 and 8 shows a consistency in the occurrence pattern of glyphosate concentrations provided by both laboratories at weir and tile drains. Thus, the %difference statistics, regression, and the occurrence pattern demonstrate that the interpretation of the data would have been similar whether the Cornell or the USGS laboratories had conducted all of the analyses.

These interleaved plots also demonstrate that the *a priori* basis for dividing samples, to give USGS the most important ones, was effective *a posteriori*.

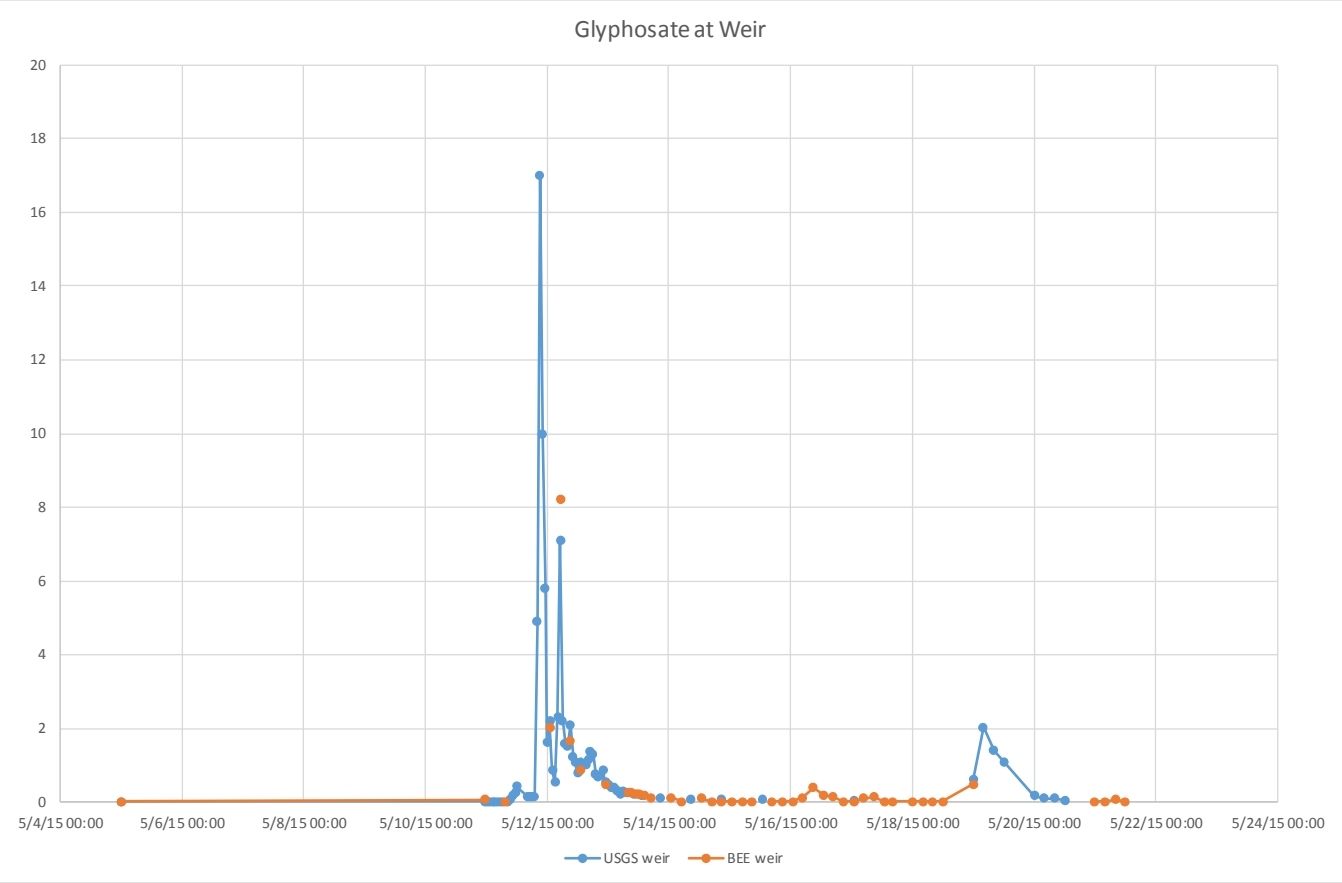

Figure 7: Cornell LC-MS interleaved with USGS LC-MSMS (2015 samples at weir)

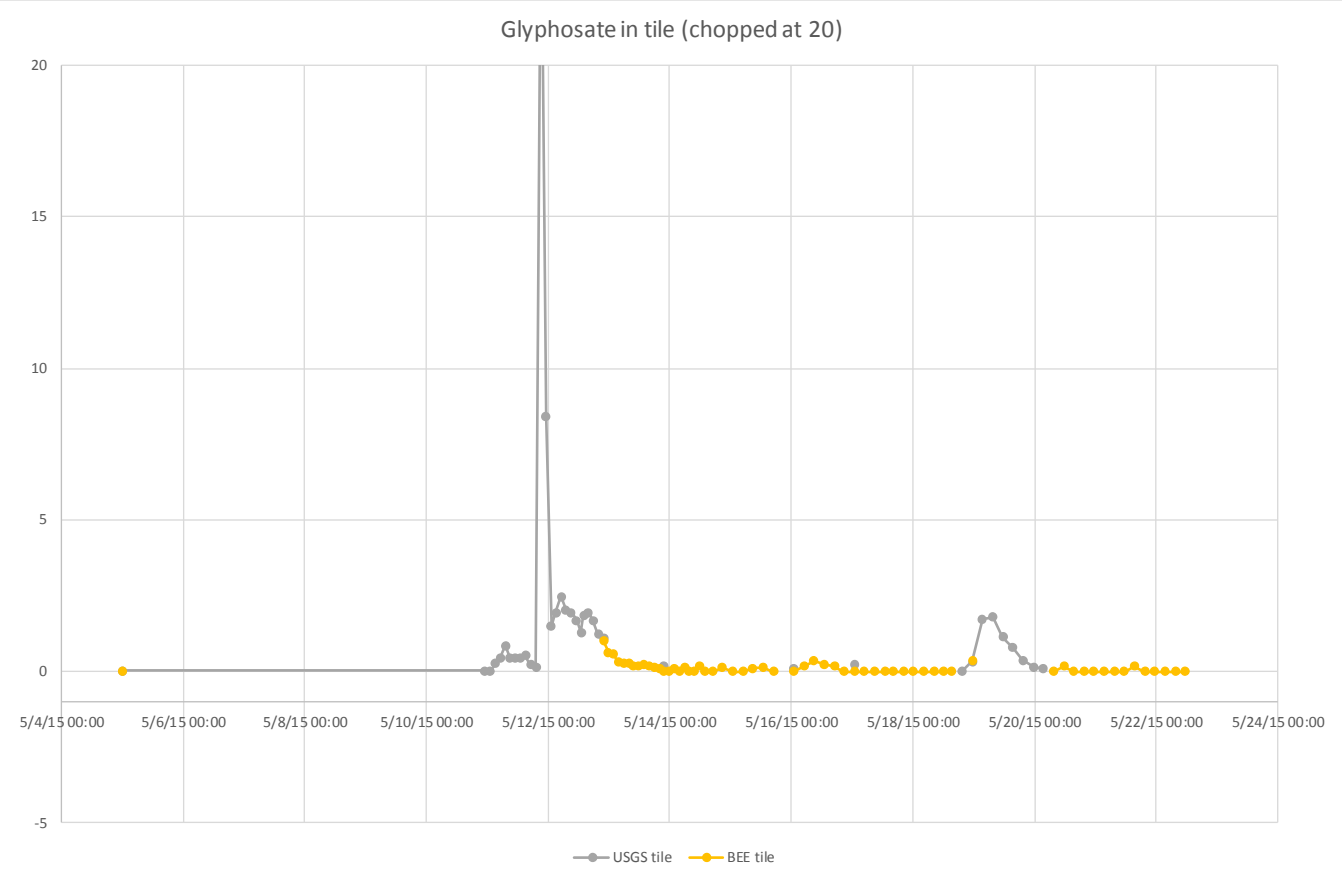

Figure 8: Cornell LC-MS interleaved with USGS LC-MSMS (2015 samples at tile box)

2015-2016 USGS LC-MSMS versus Cornell ELISA

The Cornell ELISA results were consistent with USGS LC-MS analyses of the split samples taken in spring 2015 and spring 2016 (Figure 9). The slope of the regression is 0.99 and the R^2 is 0.93, indicating that the methods yield similar concentrations. There is more scatter in the ELISA versus LC-MSMS than in the previous figure comparing the two 2015 LC-MS series, yet no bias evident in results. Percentage deviations ranged from 0 (with both labs yielding values below the Cornell detection limit 0.1), to 92% in one sample where Cornell found 0.75 and USGS 2.03, and one sample for which USGS returned non-detect and Cornell returned 0.20. The mean percentage difference was 30% (SD +/-30%). Higher values >4 had percentage differences 7.79-30.5, and lower values <4 had percentage differences 35.4-92% (excluding four duals <0.10 and the non-detect/0.20 pair which do not have numeric differences). Thus, the data indicate increasing scatter at lower concentrations, a fortunate direction because of this work's focus on peak concentrations, cumulative loadings, and peak concentration timings.

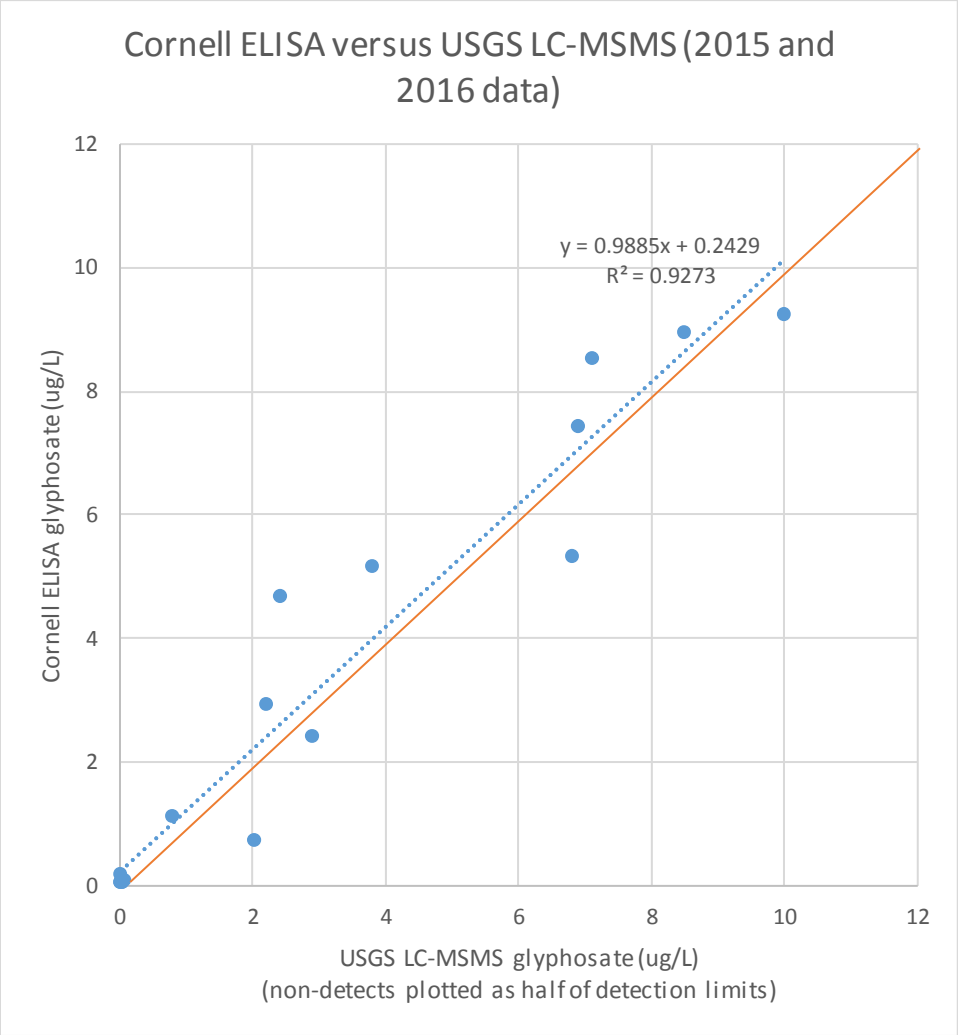

Figure 9: Cornell ELISA vs USGS LC-MSMS (2015 and 2016 at weir)

The regression line (dotted) in unbiased. There is more scatter in the ELISA versus LC-MSMS than in the previous figure comparing the two 2015 LC-MS series.

Figure 10 shows the interleaved Spring 2016 results for USGS LC-MS and Cornell ELISA. As with the 2015 interleaved plot, this is well aligned at the transitions and the ELISA results were considered usable. When USGS and Cornell have both tested the same sample at the same dilution (i.e. a split sample), the USGS results prevailed.

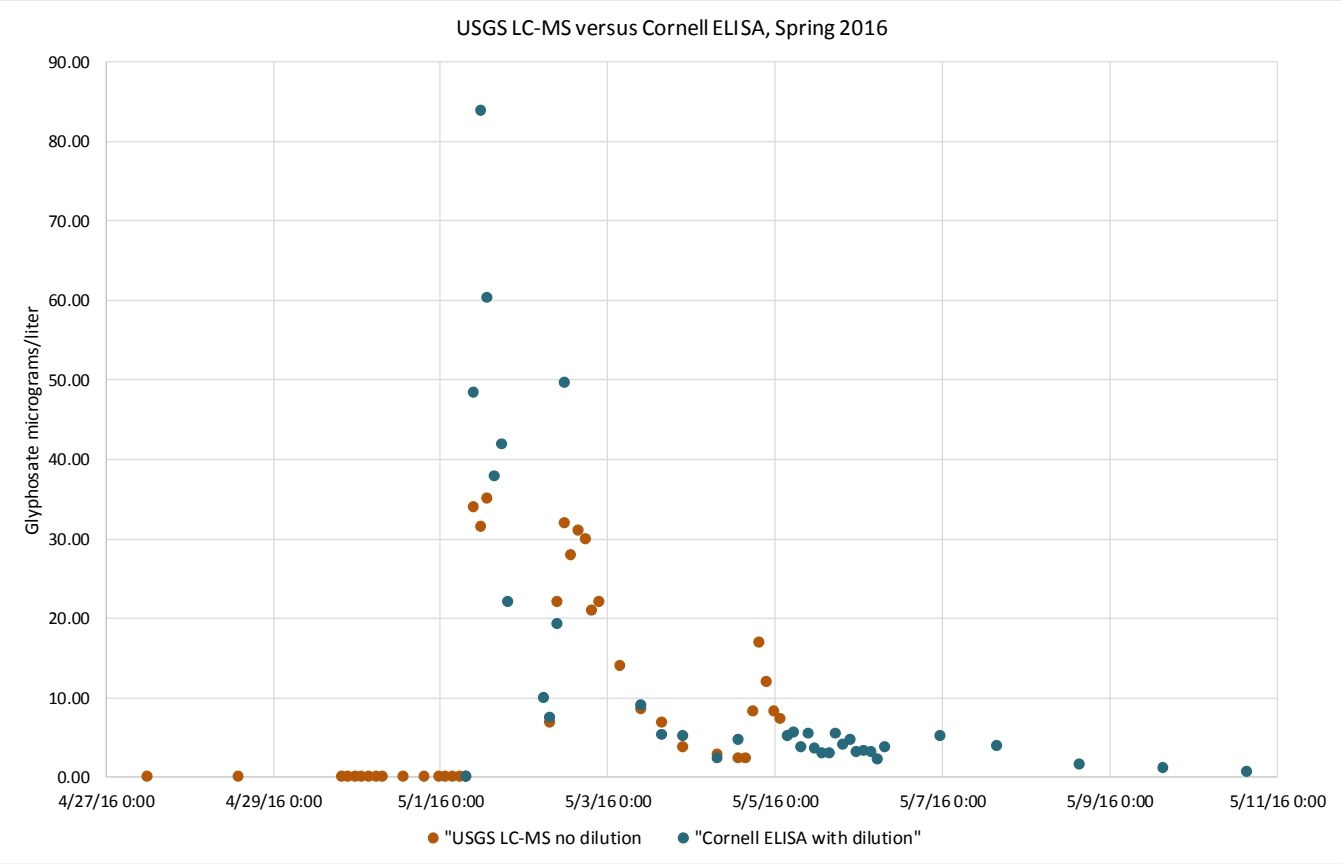

Figure 10: Cornell ELISA interleaved with USGS LC-MSMS (2016 spring samples at weir)

4.2 Artificial samples in MilliQ and LC-MS water

An ELISA test batch included a made concentration series (in MilliQ water) whose results (Figure 11) included scatter less than the comparison between USGS LC-MS and ELISA (previous Figure 9).

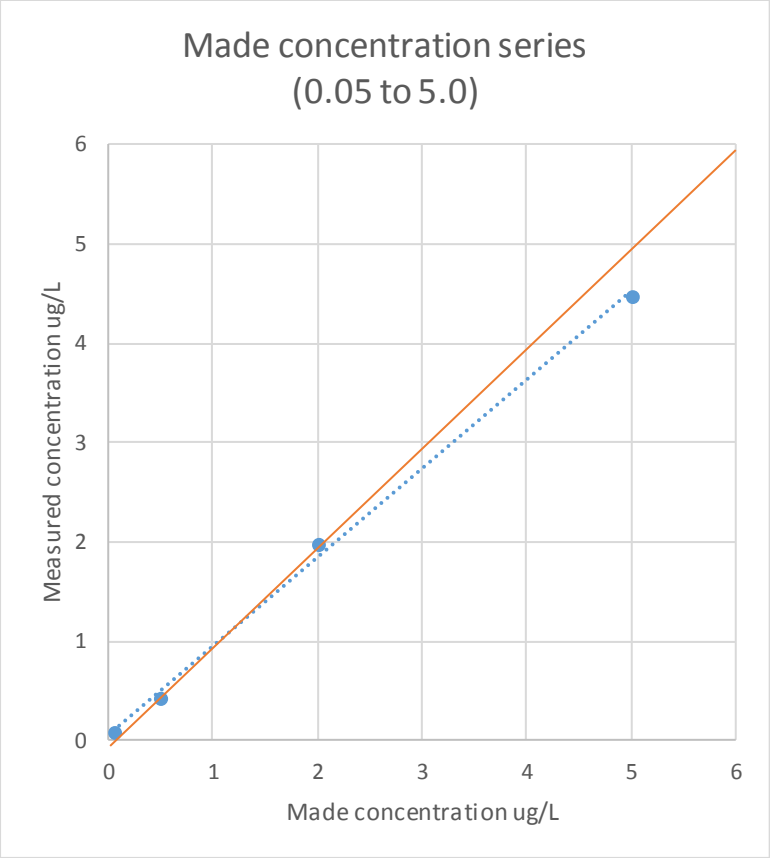

Figure 11: Theoretical and actual ELISA results in artificial samples

4.3 Spiked (fortified) samples

Batches of samples tested by USGS and Cornell in any method all included at least one sample spiked to raise its concentration by 1 µg/L (nominally). This is an indicator of matrix effects on recovery. The results were generally good in LC-MS work and fair to good in ELISA. However a matrix spike series adding 0.25 to 5.0 ug/L to replicates of a sample initially testing at 0.97 µg/L glyphosate came out quite well (Figure 12), indicating little to no matrix interference.

This repeated an approach and acceptable results of a 2015-sample matrix spike series tested via LC-MS at Cornell (no plot shown for brevity).

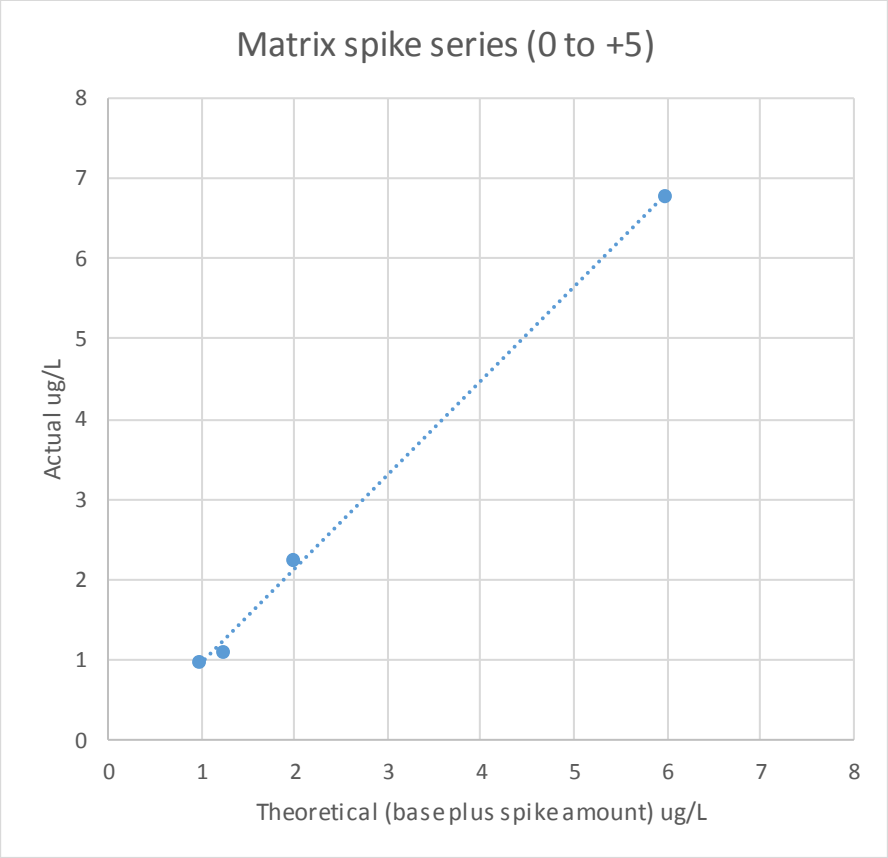

Figure 12: Matrix spike series results from ELISA:

5. Choice of results per sample

5.1 Principles

Because the workload was deliberately divided across two labs, and the Cornell lab used two different methods, some samples were analyzed three times, and quite a few twice. There remained a need to converge on a single number to represent a given sample. We did this using the following principles:

1. USGS results in any year are the best as long as they are under 25 ppb before up-scaling to adjust for dilution. USGS had flagged values >=25 ppb in 2016 as needing retesting with dilution.
2. Cornell LC-MS results for 2015 are second best. This makes Cornell ELISA results for 2015 samples supplementary, for USGS LC-MS versus ELISA confidence testing only.
3. For 2016, Cornell ELISA results (with any necessary dilution) are second best and used for any sample not analyzed by USGS or when the USGS preliminary result was >25 ppb for an undiluted sample which had been flagged for retesting with dilution.
4. USGS results for 10x or greater dilutions will replace the Cornell ELISA results for the same samples when they become available. This includes a few spring 2016 samples and more fall 2016 and spring 2017 samples. USGS results are all pending as of March 2018. It is important to consider the sensitivity of conclusions to using temporary ELISA values instead of final USGS values.
5. Because of the good results from split samples and interleaving, it is not necessary in plotting or computing cumulative loadings to distinguish which lab provided a result for a given sample. However, when presenting individual numbers, such as peak values, it is best to cite the lab and method.

5.2 Results from weir samples chosen as best per sample, divided by batch

All times in this appendix are in Eastern Daylight Time (UTC -4). Sample times in 2015-2017 are accurate to better than 3 minutes (estimated). Timestamps are at the end of the sample compositing interval which has variable length, up to 4 hours.

Spring 2015

Best values shown with green cell background. Results of the style <0.02 mean “not detected with a detection limit 0.02”. Almost all samples were tested thus no interpolated values are shown.

Table 1: Spring 2015 analytical data

Sample Date/Time	USGS LC-MSMS	Cornell LC-MS	Cornell ELISA
5/05/15 grab	<0.02	<0.1	
5/10/15 23:25	<0.02	<0.1	<0.1
5/11/15 00:25	<0.02		
5/11/15 01:25	<0.02		
5/11/15 02:25	<0.02		
5/11/15 03:25	<0.02		
5/11/15 04:25	<0.02		
5/11/15 05:25	<0.02		
5/11/15 06:25	<0.02		
5/11/15 07:25		<0.1	
5/11/15 08:25	0.02		
5/11/15 09:25	0.08		
5/11/15 10:25	0.17		
5/11/15 11:25	0.24		
5/11/15 11:55	0.43		
5/11/15 16:05	0.16		
5/11/15 17:05	0.15		
5/11/15 18:05	0.14		
5/11/15 19:05	0.14		
5/11/15 20:05	4.90		
5/11/15 21:05	17.00		
5/11/15 22:05	10.00		9.25
5/11/15 23:05	5.80		
5/12/15 00:05	1.64		
5/12/15 01:05	2.20	2.02	2.94
5/12/15 02:05	0.87		
5/12/15 03:05	0.54		
5/12/15 04:05	2.32		
5/12/15 05:05	7.10	8.20	8.53
5/12/15 06:05	2.21		
5/12/15 07:05	1.60		
5/12/15 08:05	1.53		
5/12/15 09:05	2.10	1.67	
5/12/15 10:05	1.21		
5/12/15 11:05	1.10		
5/12/15 12:05	0.80		
5/12/15 13:05	1.10	0.88	
5/12/15 15:05	1.02		
5/12/15 16:05	1.16		
5/12/15 17:05	1.36		
5/12/15 18:05	1.31		
5/12/15 19:05	0.77		
5/12/15 20:05	0.68		
5/12/15 21:05	0.72		
5/12/15 22:05	0.86		
5/12/15 23:05	0.56	0.46	
5/13/15 00:05	0.47		
5/13/15 01:05	0.40		
5/13/15 02:05	0.38		
5/13/15 03:05	0.32		
5/13/15 04:05	0.28		
5/13/15 05:05	0.21		
5/13/15 06:05	0.30		
5/13/15 07:05	0.25		
5/13/15 08:05		0.26	
5/13/15 09:05		0.24	

Sample Date/Time	USGS LC-MSMS	Cornell LC-MS	Cornell ELISA
5/13/15 10:05	0.21		
5/13/15 11:05		0.21	
5/13/15 12:05		0.23	
5/13/15 13:05	0.19		
5/13/15 14:05		0.18	
5/13/15 16:50		0.11	
5/13/15 20:50	0.09		
5/14/15 00:50		0.12	
5/14/15 04:50		<0.1	
5/14/15 08:50	0.06		
5/14/15 12:50		0.11	
5/14/15 16:50		<0.1	
5/14/15 20:50	0.06	<0.1	
5/15/15 00:50		<0.1	
5/15/15 04:50		<0.1	
5/15/15 08:50		<0.1	
5/15/15 12:50	0.07		
5/15/15 16:50		<0.1	
5/15/15 20:50		<0.1	0.11
5/16/15 00:50		<0.1	
5/16/15 04:50		0.12	
5/16/15 08:50		0.39	
5/16/15 12:50		0.19	
5/16/15 16:50		0.13	
5/16/15 20:50		<0.1	
5/17/15 00:50	0.03	<0.1	
5/17/15 04:50		0.10	
5/17/15 08:50		0.13	
5/17/15 12:50		<0.1	
5/17/15 16:03		<0.1	
5/18/15 00:03		<0.1	
5/18/15 04:03		<0.1	
5/18/15 08:03		<0.1	
5/18/15 12:03		<0.1	
5/18/15 16:03			
5/18/15 20:03			
5/19/15 00:03	0.61	0.48	
5/19/15 04:03	2.03		0.75
5/19/15 08:03	1.40		
5/19/15 12:03	1.09		
5/19/15 16:03			
5/19/15 20:03			
5/20/15 00:03	0.18		
5/20/15 04:03	0.11		
5/20/15 08:03	0.10		
5/20/15 12:03	0.05		
5/21/15 00:03		<0.1	
5/21/15 04:03		<0.1	
5/21/15 08:03		<0.1	
5/21/15 12:03		<0.1	
5/21/15 13:06			

Spring 2016

Brighter green cells indicate best data, paler green are temporary substitutes for data in yellow cells which are above maximum extrapolation by USGS (25.0). Because some samples were not analyzed by either lab, some interpolation was done taking into account the nearest bracketing analytical results and the flow regime. This is similar to the interpolation automatically done in time plots.

Table 2: Spring 2016 analytical data and interpolations

Sample Date/Time	USGS LC-MSMS	Cornell ELISA	Interpolated for loadings
3/24/16 15:25 grab	<0.02		
4/12/16 grab			0.01
4/21/16 grab			0.01
4/23/16 grab			0.01
4/26/16 12:55			0.01
4/26/16 13:20			0.01
4/27/16 12:00	<0.02		
4/28/16 14:15	0.05		
4/29/16 17:45			0.01
4/29/16 19:45	<0.02		
4/29/16 21:45	<0.02		
4/29/16 23:45	<0.02		
4/30/16 01:45	<0.02		
4/30/16 03:45	<0.02		
4/30/16 05:45	<0.02		
4/30/16 07:45	0.05		
4/30/16 09:45			0.01
4/30/16 11:45			0.01
4/30/16 13:45	<0.02		
4/30/16 15:45			0.01
4/30/16 17:45			0.01
4/30/16 19:45	<0.02		
4/30/16 21:45			0.01
4/30/16 23:45	<0.02		
5/01/16 01:45	<0.02		
5/01/16 03:45	<0.02		
5/01/16 05:45	<0.02		
5/01/16 07:45	0.02	<0.10	
5/01/16 09:45	34.00	48.30	
5/01/16 11:45	31.50	83.90	
5/01/16 13:45	35.00	60.30	
5/01/16 15:45	38.00	37.90	
5/01/16 17:45	36.00	41.90	
5/01/16 19:45	33.00	22.10	
5/01/16 21:45			22.00
5/01/16 23:45			22.00
5/02/16 01:45			15.00
5/02/16 03:45			8.00
5/02/16 05:45		10.02	
5/02/16 07:45	6.90	7.43	
5/02/16 09:45	22.00	19.20	

Sample Date/Time	USGS LC-MSMS	Cornell ELISA	Interpolated for loadings
5/02/16 11:45	32.00	49.60	
5/02/16 13:45	28.00		46.00
5/02/16 15:45	31.00		48.00
5/02/16 17:45	30.00		47.00
5/02/16 19:45	21.00		
5/02/16 21:45	22.00		
5/02/16 23:45			19.70
5/03/16 01:45			17.40
5/03/16 03:45	14.00		
5/03/16 05:45			12.50
5/03/16 07:45			10.50
5/03/16 09:45	8.50	8.96	
5/03/16 11:45			8.00
5/03/16 13:45			7.40
5/03/16 15:45	6.80	5.34	
5/03/16 17:45			5.80
5/03/16 19:45			4.80
5/03/16 21:45	3.80	5.17	
5/03/16 23:45			3.60
5/04/16 01:45	3.30		
5/04/16 03:45			3.00
5/04/16 05:45			3.00
5/04/16 07:45	2.90	2.42	
5/04/16 09:45			2.70
5/04/16 11:45			2.60
5/04/16 13:45	2.40	4.70	
5/04/16 15:45	2.30		
5/04/16 17:45	8.30		
5/04/16 19:45	17.00		
5/04/16 21:45	12.00		
5/04/16 23:45	8.30		
5/05/16 01:45	7.40		
5/05/16 03:45		5.11	
5/05/16 05:45		5.69	
5/05/16 07:45		3.81	
5/05/16 09:45		5.53	
5/05/16 11:45		3.55	
5/05/16 13:45		3.05	
5/05/16 15:45		2.99	
5/05/16 17:45		5.50	
5/05/16 19:45		4.05	
5/05/16 21:45		4.63	
5/05/16 23:45		3.15	
5/06/16 01:45		3.37	
5/06/16 03:45		3.20	
5/06/16 05:45		2.17	
5/06/16 07:45		3.71	
5/06/16 09:45			3.89
5/06/16 11:45			4.07
5/06/16 13:45			4.25
5/06/16 15:45			4.43
5/06/16 17:45			4.61
5/06/16 19:45			4.79
5/06/16 21:45			4.97
5/06/16 23:45		5.14	
5/07/16 01:45			5.03
5/07/16 03:45			4.87
5/07/16 05:45			4.70

Sample Date/Time	USGS LC-MSMS	Cornell ELISA	Interpolated for loadings
5/07/16 07:45			4.53
5/07/16 09:45			4.36
5/07/16 11:45			4.19
5/07/16 13:45			4.02
5/07/16 15:45		3.85	
5/07/16 19:30			3.49
5/07/16 23:30			3.12
5/08/16 03:30			2.75
5/08/16 07:30			2.38
5/08/16 11:30			2.01
5/08/16 15:30		1.64	
5/08/16 19:30			1.54
5/08/16 23:30			1.45
5/09/16 03:30			1.37
5/09/16 07:30			1.29
5/09/16 11:30			1.21
5/09/16 15:30		1.13	
5/09/16 19:30			1.06
5/09/16 23:30			0.98
5/10/16 03:30			0.90
5/10/16 07:30			0.82
5/10/16 11:30			0.74
5/10/16 15:30		0.66	

Fall 2016

USGS results are all pending. They will replace most of the interpolated values and any ELISA value for the same sample.

Table 3: Fall 2016 analytical data and interpolations

Sample Date/Time	Glyphosate ELISA	Interpolated for loadings
10/21/16 01:45	2.50	
10/21/16 03:45	4.30	
10/21/16 05:45	4.40	
10/21/16 07:45	4.90	
10/21/16 09:45	1.60	
10/21/16 11:45	0.60	
10/21/16 13:45	0.80	
10/21/16 15:45	1.60	
10/21/16 17:45	4.10	
10/21/16 19:45	0.20	
10/21/16 21:45	1.80	
10/21/16 23:45	1.60	
10/22/16 01:45		1.40
10/22/16 03:45		1.20
10/22/16 05:45		1.00
10/22/16 07:45		0.80
10/22/16 09:45		0.60
10/22/16 11:45		0.40
10/22/16 13:45		1.00

10/22/16 15:45	1.30	
10/22/16 16:00		1.20
10/22/16 18:00		1.10
10/22/16 20:00	0.97	
10/22/16 22:00		0.91
10/23/16 00:00		0.85
10/23/16 02:00		0.78
10/23/16 04:00		0.71
10/23/16 06:00		0.64
10/23/16 08:00		0.57
10/23/16 10:00		0.50
10/23/16 12:00		0.43
10/23/16 14:00		0.36
10/23/16 16:00		0.29
10/23/16 18:00	0.22	
10/23/16 20:00		0.19
10/23/16 22:00		0.17
10/24/16 00:00		0.15
10/24/16 02:00		0.13
10/24/16 04:00		0.10
10/24/16 06:00		0.08
10/24/16 08:00		0.06
10/24/16 10:00		0.04
10/24/16 12:00		0.02
10/24/16 14:00		0

Spring 2017

USGS results are all pending and are now primarily for cross-checking with Cornell ELISA results for the same samples. USGS results for split samples will replace the Cornell ELISA results. Highest priority samples were tested at Cornell.

Table 4: Spring 2017 analytical data and interpolations

Sample Date/Time	Glyphosate ELISA	Interpolations for loading
4/28/17 01:17	<0.1	
4/28/17 02:17	<0.1	
4/28/17 03:17	<0.1	
4/28/17 04:17	<0.1	
4/28/17 05:17	<0.1	
4/28/17 06:17	<0.1	
4/28/17 07:17	<0.1	
4/28/17 08:17	<0.1	
4/28/17 09:17	<0.1	
4/28/17 10:17	<0.1	
4/28/17 11:17		0
4/28/17 12:17	<0.1	
5/01/17 20:17	27.80	
5/01/17 22:17	47.00	
5/02/17 00:17	31.50	
5/02/17 02:17	18.80	
5/02/17 04:17	9.80	

Sample Date/Time	Glyphosate ELISA	Interpolations for loading
5/02/17 06:17	6.13	
5/02/17 08:17	3.84	
5/02/17 10:17	3.33	
5/02/17 12:17	2.03	
5/02/17 14:17	2.93	
5/02/17 16:17	1.65	
5/02/17 18:17	0.88	
5/02/17 20:17		1.00
5/02/17 22:17		1.00
5/03/17 00:17	1.17	
5/03/17 02:17	0.63	
5/03/17 04:17		0.55
5/03/17 06:17	0.49	
5/03/17 08:17		0.35
5/03/17 10:17	0.19	
5/03/17 12:17		0.20
5/03/17 14:17		0.20
5/03/17 16:17		0.20
5/03/17 18:17	0.36	
5/03/17 20:17		0.20
5/03/17 22:17		0.20
5/04/17 00:17		0.15
5/04/17 02:17	0.17	
5/04/17 04:17		0.16
5/04/17 06:17	0.15	
5/04/17 08:17		0.10
5/04/17 10:17		0.10
5/04/17 12:17		0.10
5/04/17 14:17		0.10
5/04/17 16:17		0.20
5/04/17 18:17		0.30
5/04/17 20:17		0.40
5/04/17 22:17		0.40
5/05/17 00:17		0.40
5/05/17 02:17		0.50
5/05/17 04:17		0.50
5/05/17 06:17	1.02	
5/05/17 08:17	3.65	
5/05/17 10:17	2.98	
5/05/17 12:17	6.21	
5/05/17 16:11	5.80	
5/05/17 20:11	2.09	
5/06/17 00:11	1.12	
5/06/17 04:11	0.56	
5/06/17 08:11	1.88	
5/06/17 12:11	2.15	
5/06/17 16:11	0.56	
5/06/17 20:11	0.87	
5/07/17 00:11	1.04	
5/07/17 04:11	1.00	
5/07/17 08:11	1.51	
5/07/17 12:11		1.30
5/07/17 16:11		1.09
5/07/17 20:11		0.88
5/08/17 00:11		0.67
5/08/17 04:11	0.46	
5/08/17 08:11		0.42
5/08/17 12:11		0.38

Sample Date/Time	Glyphosate ELISA	Interpolations for loading
5/08/17 16:11		0.34
5/08/17 20:11		0.30
5/09/17 00:11		0.25
5/09/17 04:11	0.21	
5/09/17 08:11		0.20
5/09/17 12:11	0.21	

Team

Sample collection work at Cornell by:

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Sample processing and analytical work at Cornell by:

> Steven Pacenka (adaptation of USGS LC-MS procedure, ELISA debugging, filtration design, QA, liaison with USGS lab, LC-MS operation, overall lead), Anna Schatz (ELISA, filtration), Karin Teuffer, Bahar Hassanpoor (filtration), Reid Balkind (derivatization), Zoe Maisel (derivatization), Cedric Mason (filtration), Fasikaw Atanaw (derivatization), Adugnaw Tadesse (derivatization).

Additional data compilation by:

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Glyphosate Project Lead Principals: Brian K. Richards, Tammo S. Steenhuis.

Richards also is lead principal for the project site's Biofuel Cropping experiment. This experiment provides the site infrastructure and applies the glyphosate.

All personnel are affiliated with Cornell University, Dept. of Biological and Environmental Engineering except as noted.

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