

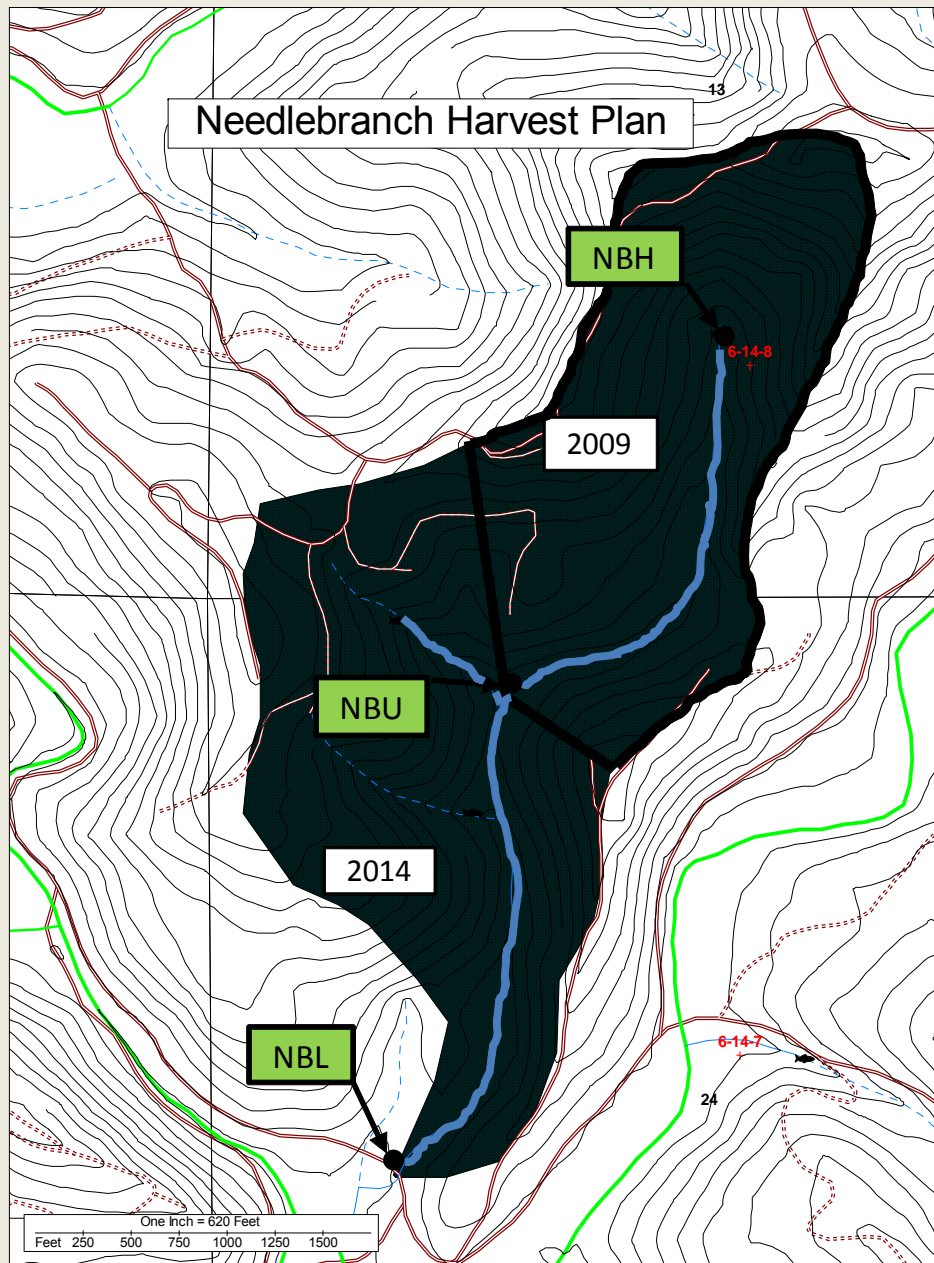
Herbicides in Needle Branch Streamwater

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Needle Branch Watershed with Sampling Stations



Application of Herbicides

- aerial application of herbicides to harvest unit (above NBU) on 8/22/10
- all herbicides applied in single tank mix

<u>Commercial Products</u>		<u>Active Ingredients</u>	
Formulation	oz/ac	Name	g/ac
Accord® XRT II	48	glyphosate	681 (a.e.)
Chopper® Gen II	12	imazapyr	85 (a.e.)
Sulfomet® Extra	4	sulfometuron methyl	64 (a.i.)
Sulfomet® Extra	4	metsulfuron methyl	17 (a.i.)

a.e. is acid equivalent and a.i. is active ingredient

Analytical Overview

- dissolved glyphosate (a.e.) and AMPA calibrated to 15 ng/L (**ppt**)
- dissolved imazapyr (a.e.), sulfometuron methyl (a.i.), and metsulfuron methyl (a.i.) calibrated to 0.6 µg/L (**ppb**)

- glyphosate and AMPA on suspended sediment calibrated to 0.1 µg/g (ppm on dry solids)

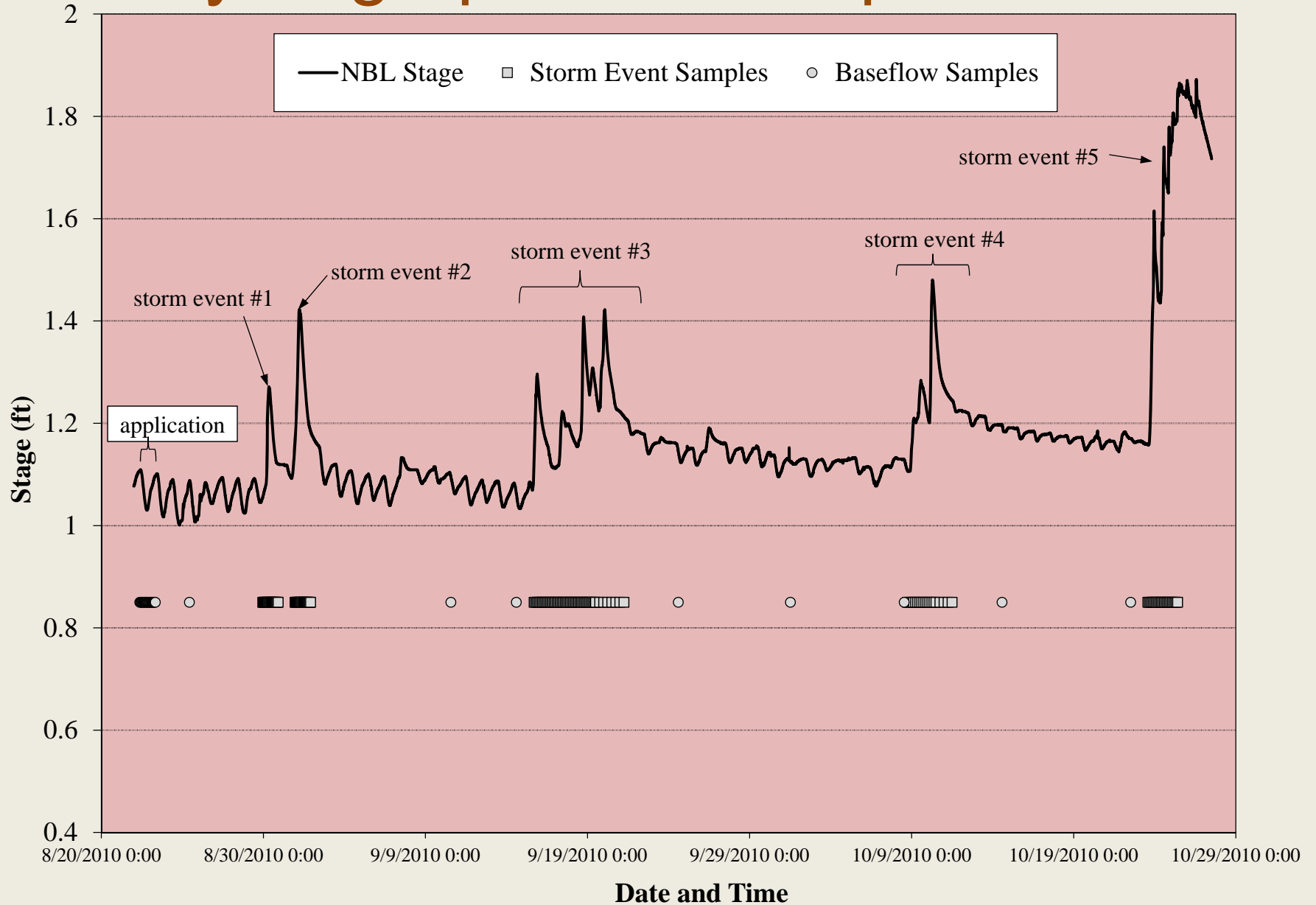
Analytical Caveat

- background interference from sample constituents impacted all analytes and varied sample-to-sample

WHAT DOES THIS MEAN?

- detection levels varied sample-to-sample
- all measured concentrations carry high-bias
- magnitude of high-bias in any given sample is unknown unless sample subjected to alternate confirmatory analysis
- glyphosate and AMPA (only) confirmed in outside laboratory (LC/MS-MS confirmation)

NBL Hydrograph and Sample Collection



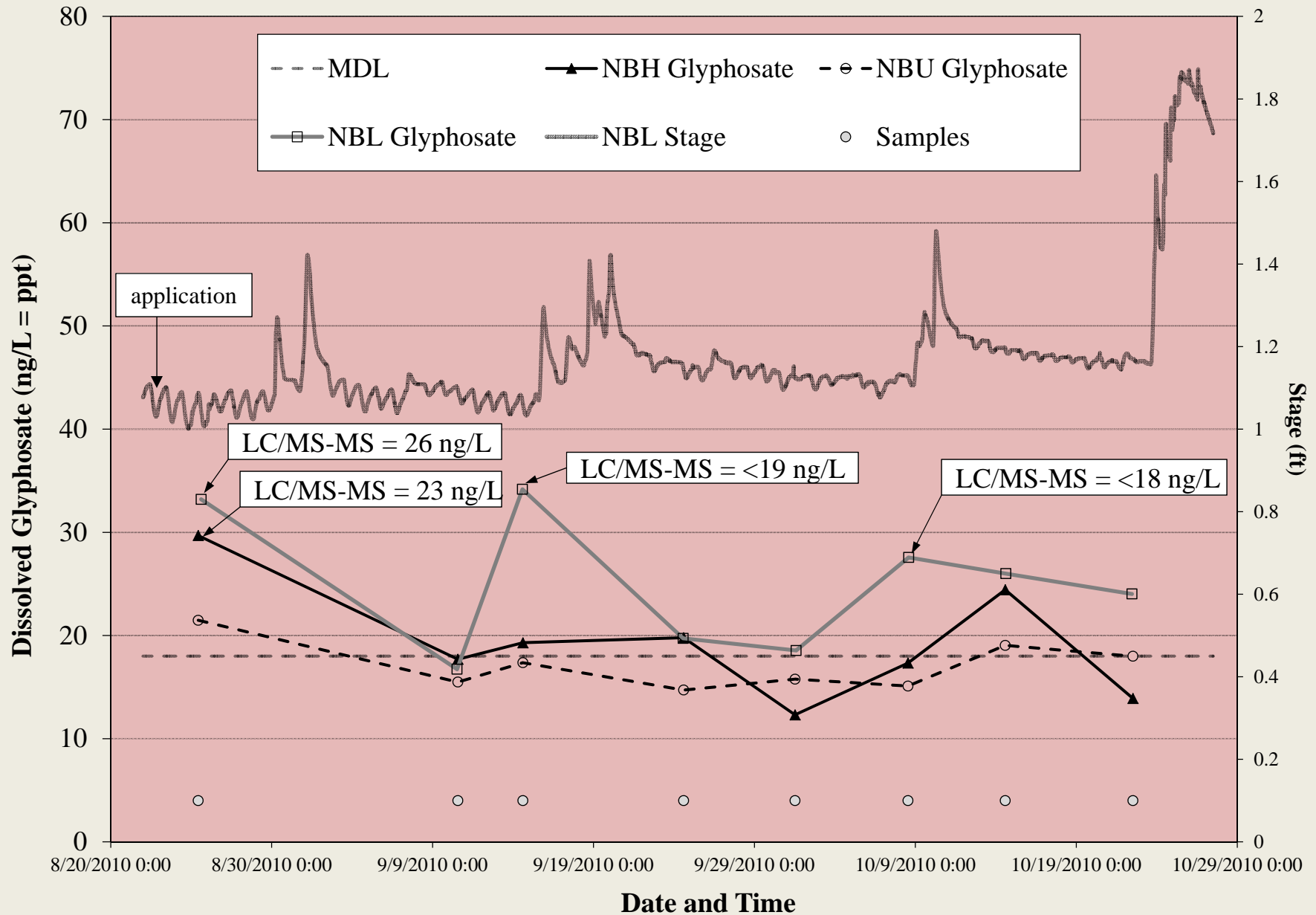
Results

Lots of “Non-Detects” (NDs)

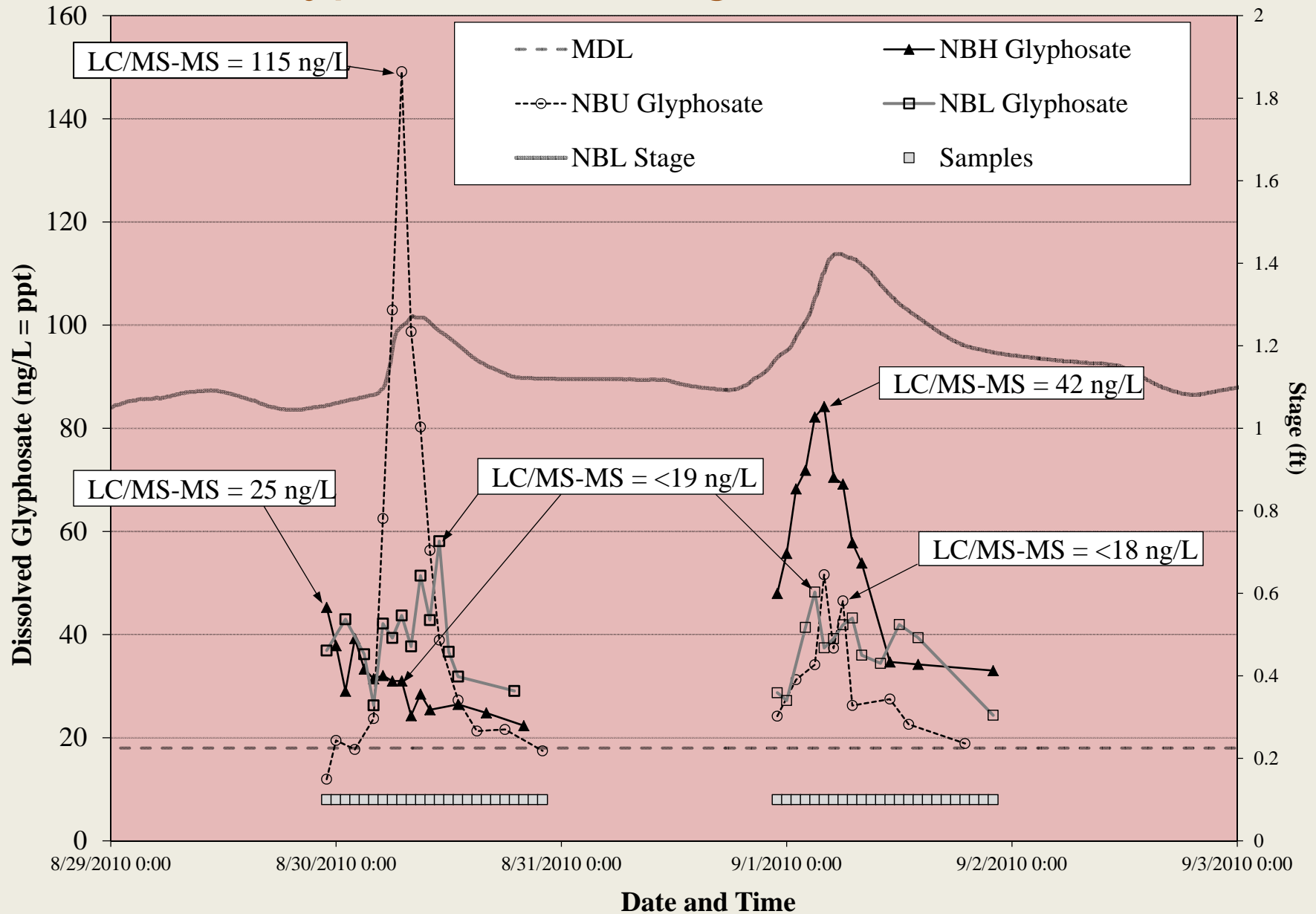
- dissolved AMPA not found in any sample at >15 ng/L (ppt)
- AMPA not found on suspended sediments (very low SS)
- glyphosate not found on suspended sediments (very low SS)
- dissolved imazapyr not found in any sample at >0.6 $\mu\text{g/L}$ (ppb)
- dissolved sulfometuron methyl not found in any sample at >0.5 $\mu\text{g/L}$ (ppb)
- dissolved metsulfuron methyl not found in any sample at >1.0 $\mu\text{g/L}$ (ppb)

Dissolved Glyphosate was the only Analyte Found in any Sample

Dissolved Glyphosate in Baseflow



Dissolved Glyphosate During First Two Storm Events



Summary

Lots of “Non-Detects”

Dissolved Glyphosate was the only Analyte Found in any Sample

- ≈ 4 h pulse during application maximized at ≈ 40 ng/L (ppt)
- ≈ 25 ng/L in baseflow 3 days after treatment (DAT), then to < 20 ng/L by 19 DAT (no intermediate samples)
- 6-8 h pulse at NBU during first storm event (8 DAT) maximized at ≈ 115 ng/L; < 20 ng/L at NBU during subsequent storms
- 9-10 h pulse at NBH during second storm event (10 DAT) maximized at ≈ 42 ng/L; < 20 ng/L at NBH during subsequent storms
- no pulse observed at NBL during any storm
- no glyphosate detected on suspended sediment

(all concentrations from LC/MS-MS confirmatory analysis)

Putting Glyphosate in Perspective

Scenario	Exposure Conditions		Resulting "Dose"	
	Conc. (ng/L = ppt)	Duration (h)	Absolute (ppt-h)	Relative
Needle Branch:				
Needle Branch Storm Pulse 1 (measured)	115	8	920	1
Needle Branch Storm Pulse 2 (measured)	42	10	420	0.5
Needle Branch Baseflow 1 (measured to 3 DAT)	25	72	1800	2
Lowest reported No Observed Effect Concentrations (NOEC) for various aquatic species:				
Aquatic Macrophytes (Giesy et al. 2000)	80000	336	26880000	29217
Aquatic Microorganisms (Giesy et al. 2000)	280000	168	47040000	51130
Larval Amphibians (Fuentes et al. 2011)	680000	2304	1566720000	1702957
Aquatic Invertebrates (Giesy et al. 2000)	50000000	504	25200000000	27391304
Aquatic Vertebrates (Giesy et al. 2000)	26000000	1248	32448000000	35269565
Regulatory Limits:				
Canadian Guideline for protection of aquatic life	800000	ongoing		

Giesy, J.P., Dobson, S. and Solomon, K.R. 2000. *Review of Environmental Contamination Toxicology* 167:35-120.

Fuentes, L., Moore, L.J., Rodgers, J.H., Bowerman, W.W., Yarrow, G.K., Chao, W.Y. 2011. *Environmental Toxicology and Chemistry* 30(12): 2756-2761.