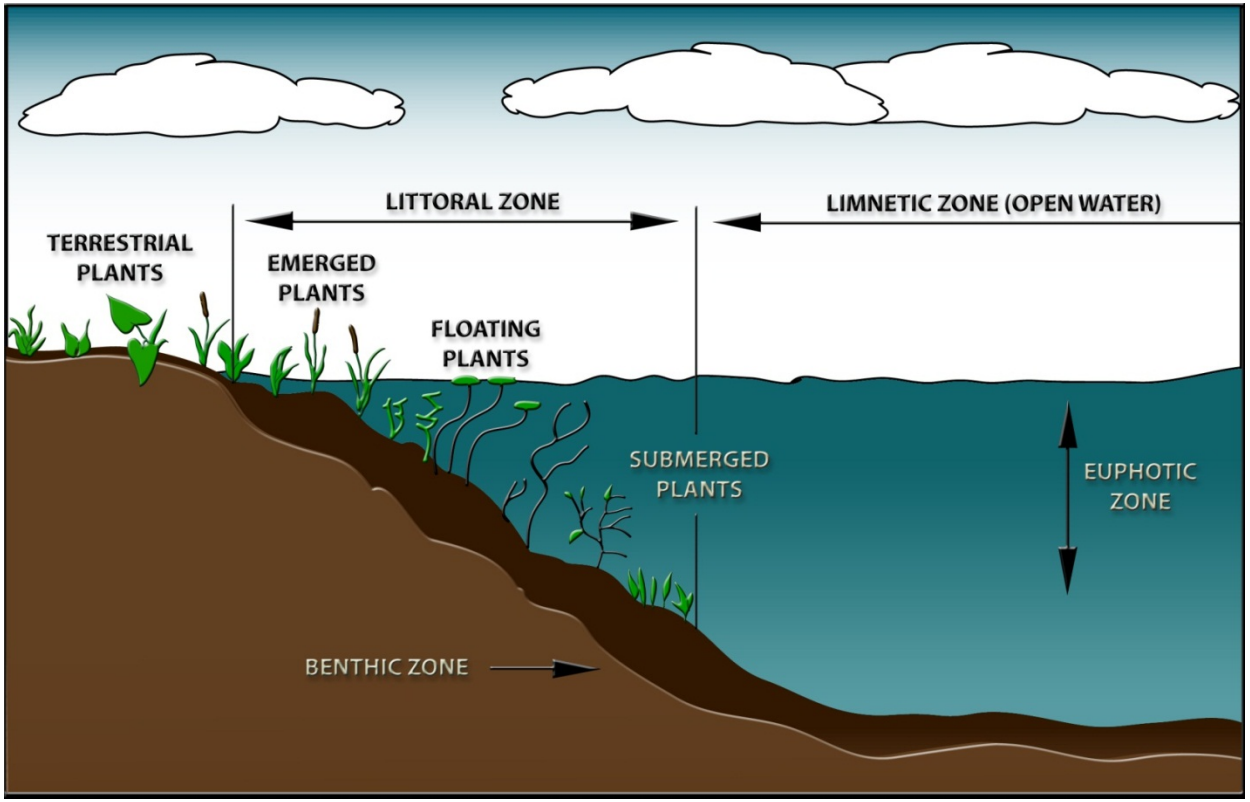
Little St. Germain Lake Sediment Pore Water Sampling for Herbicide Residue

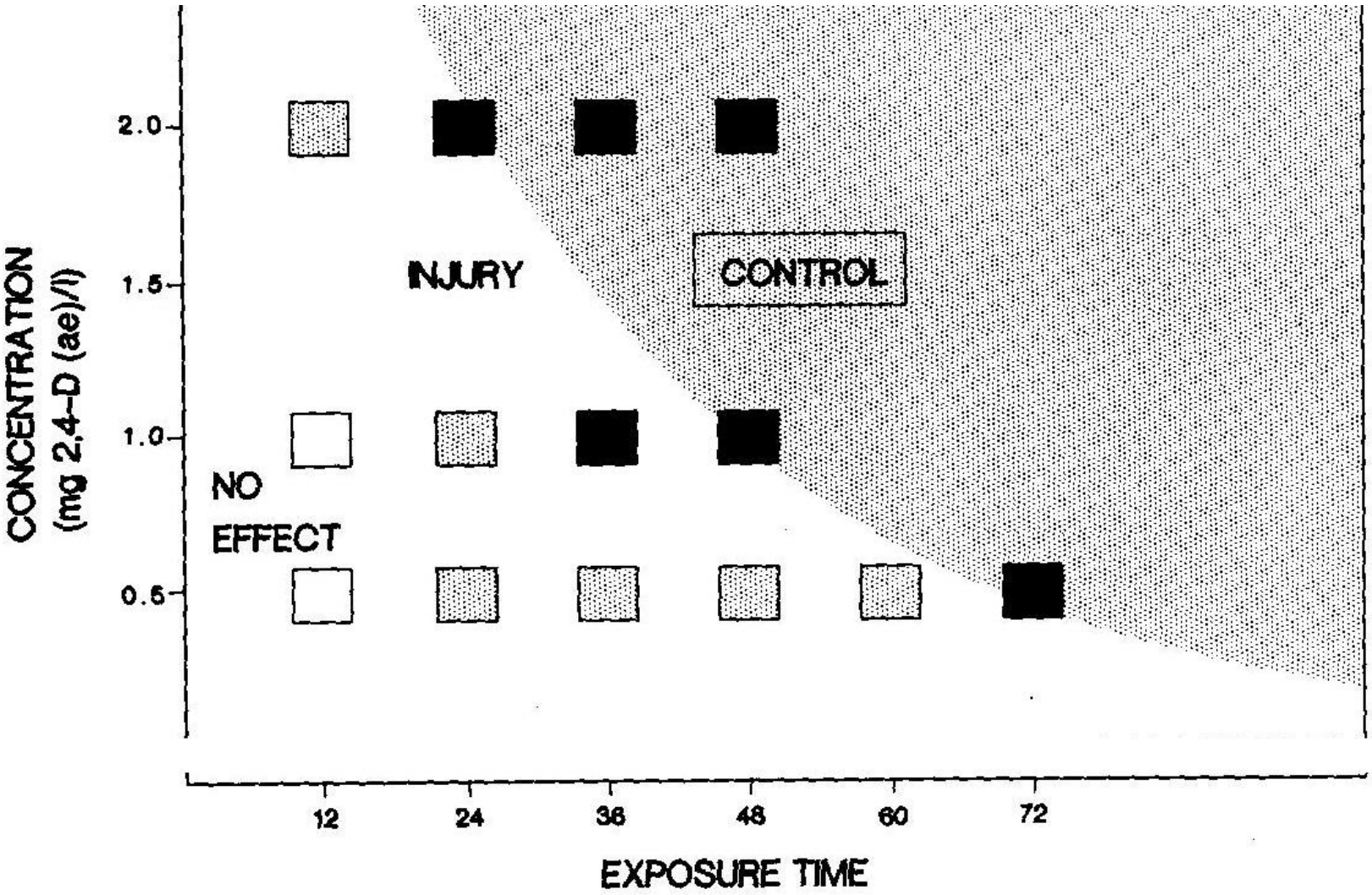
- Where does herbicide end up?
- This presentation will summarize our work conducted in 2011-12
- What we plan to do in 2013



Water Testing (effectiveness of treatments and safety thresholds)

- Advised for large scale and whole-lake scale projects
- Collect samples from multiple sites within treatment areas and mid-lake as a reference point (mid-depth or multiple depths)
- Ideally pre-treatment (0) and 1, 4, 7, 14, 28 DAT
- What are the concentrations and exposure time?

Concentration/Exposure Time Relationship



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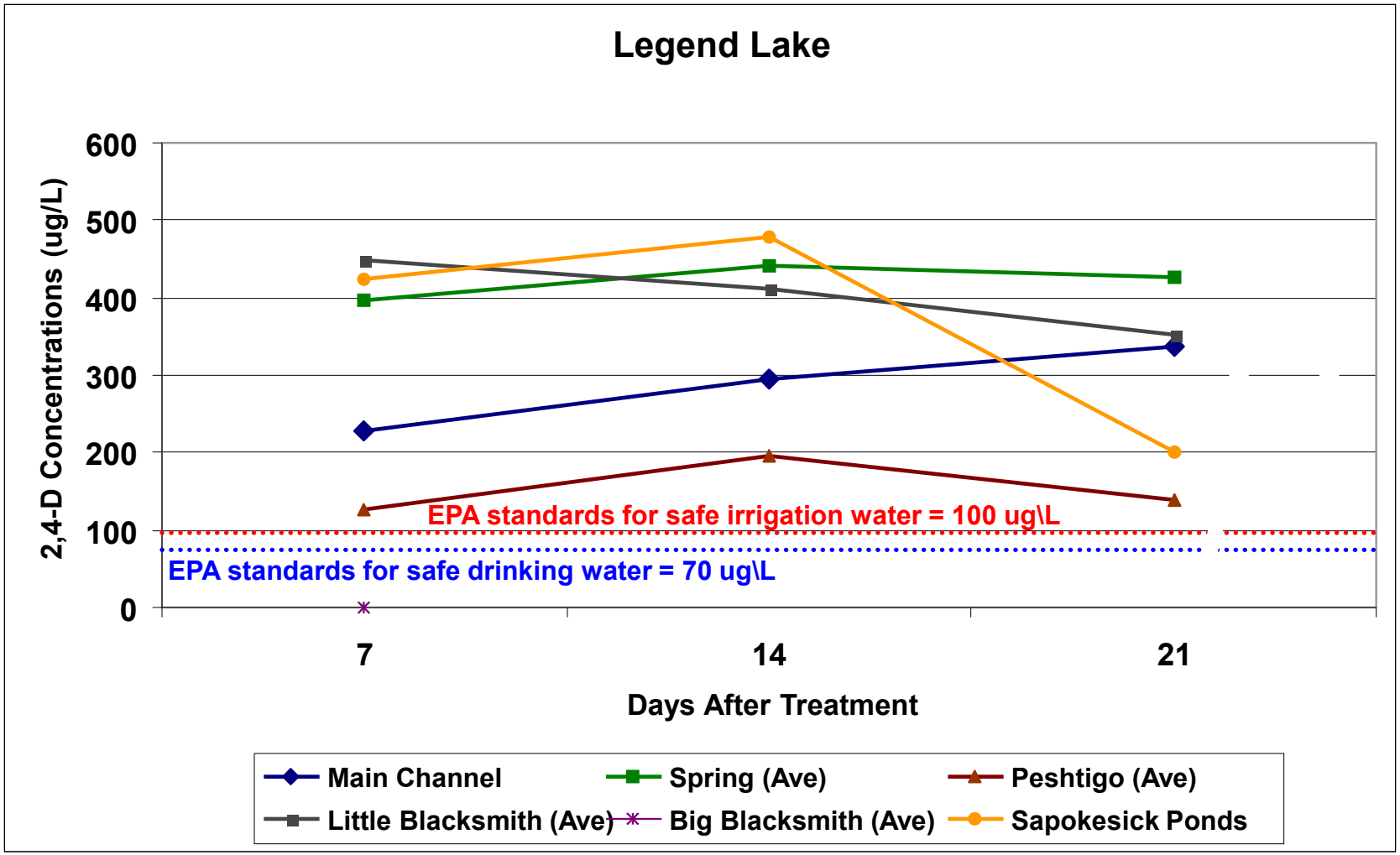
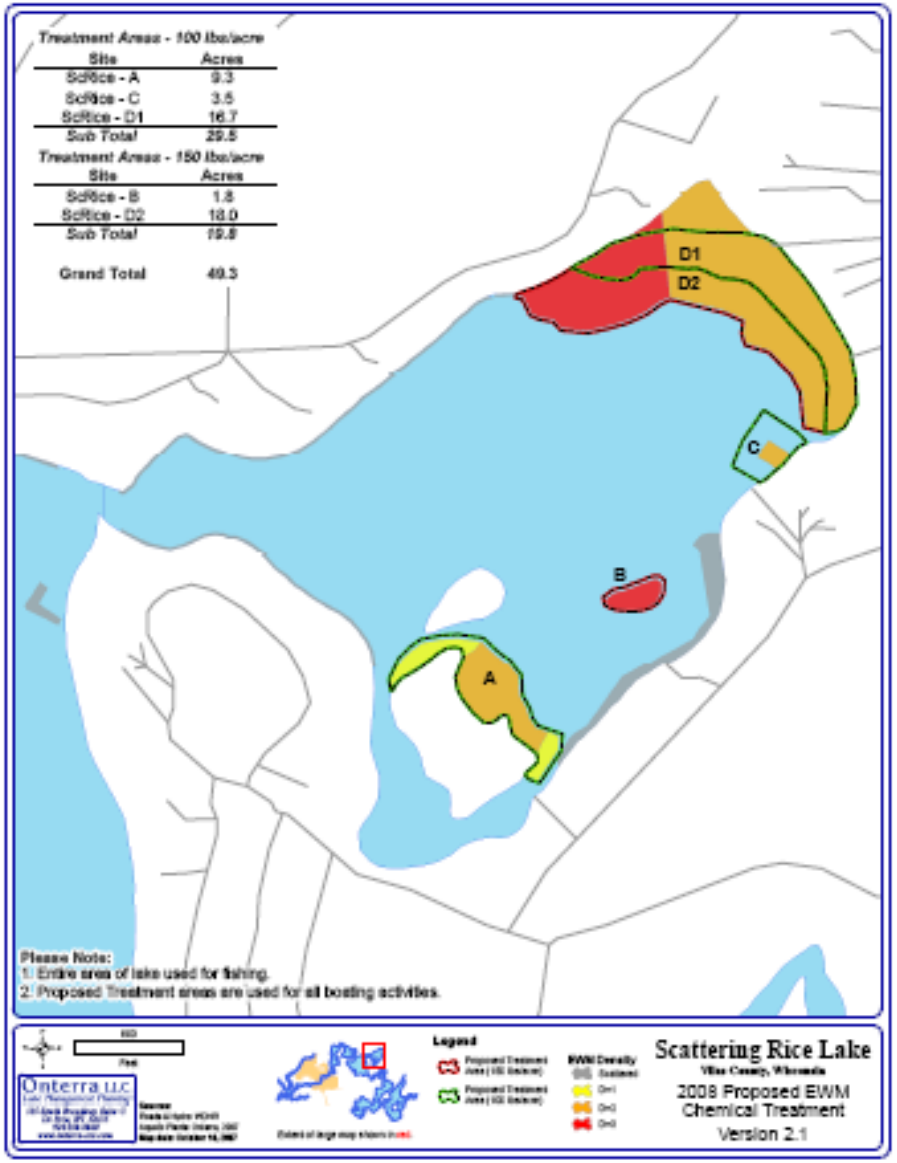
2,4-D residuals from 2007



Treatment Area Monitoring

- Conduct pre and post monitoring
- Was there a reduction in treatment bed size and density?
- Was the frequency of occurrence reduced?

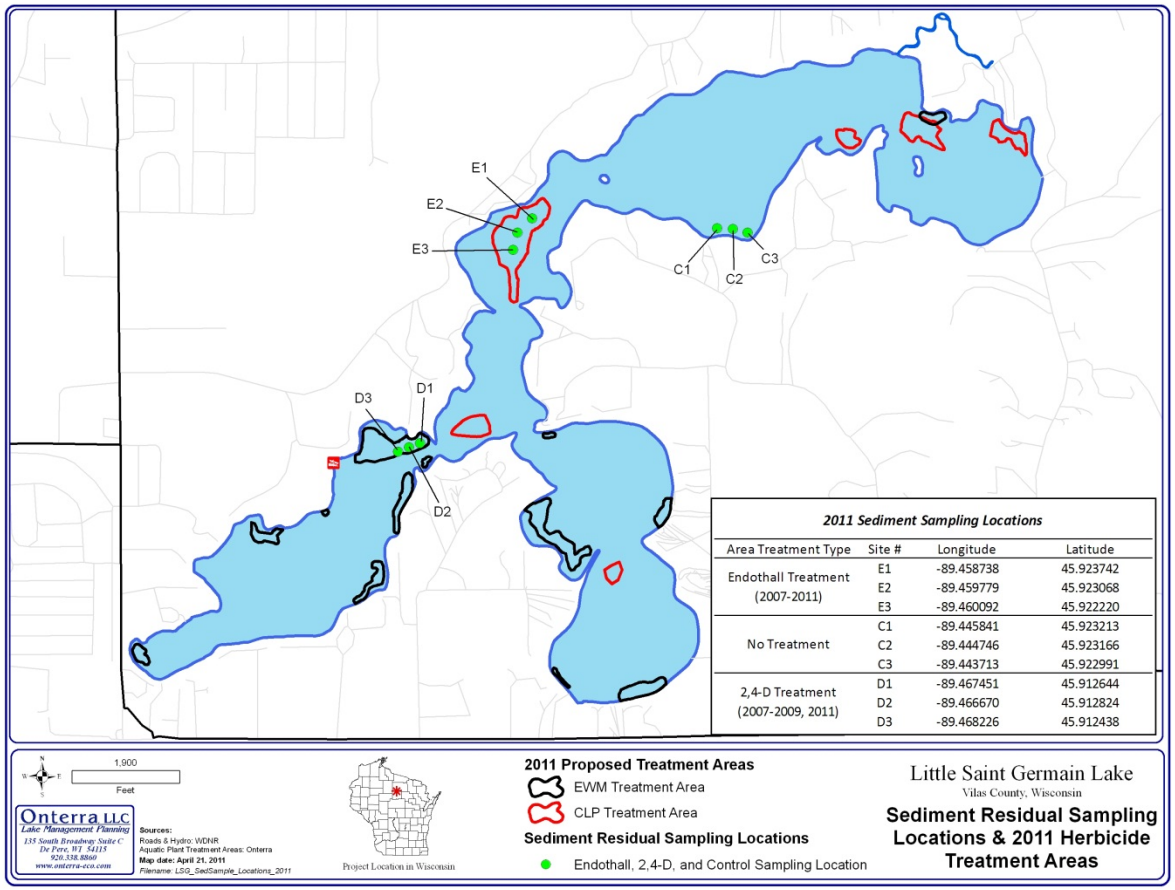


Purpose (Project started in 2011)

- No work has been done in Wisconsin to determine the fate of these herbicides in lake sediment.
- Do these herbicides bio-accumulate in sediment over the long term?
- How quickly to they breakdown or dilute after treatment?
- Do granular herbicides settle in the sediment (sediment pore water) before they dissolve in the water column?
- Are herbicide concentrations high enough in pore water to be another route of exposure through root system (efficacy of treatment).
- Are sediment toxicity problems possible?
- First step was to look at sediment pore water.

Little St. Germain Lake Treatment History

- Contains both Curly Leaf Pondweed (CLP) and Eurasian Water Milfoil (ERW).
- Herbicide treatments (2,4-D and Endothall) have occurred over the last 7- 8 years.
- Both liquid and granular spot treatments have occurred.
- Good candidate for sediment and sediment pore water sampling.

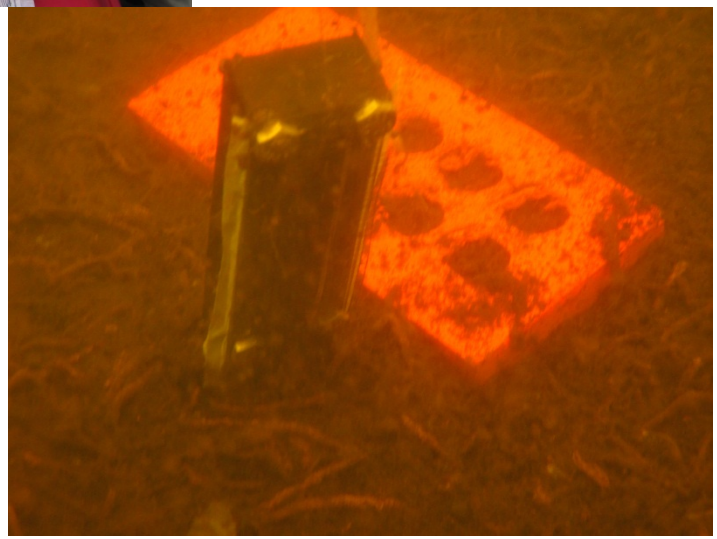


Sediment Pore Water Equilibrators (Peepers)

- Two chambered (allows sampling of the sediment pore water and water at the sediment water interface.
- Chamber wells are filled with distilled water and covered with a 0.2uM membrane held in place by a cover plate.
- A screen cover protects the membrane.
- Herbicides diffuse through the membrane into the distilled water.

Deployment

- Peepers set and retrieved by scuba diver (Kyle McLaughlin)
- One chamber is in the sediment and the other is just above the sediment at the sediment water interface.
- Peepers allowed to equilibrate (10-14 days)



Sampling (Peeper Retrieval)

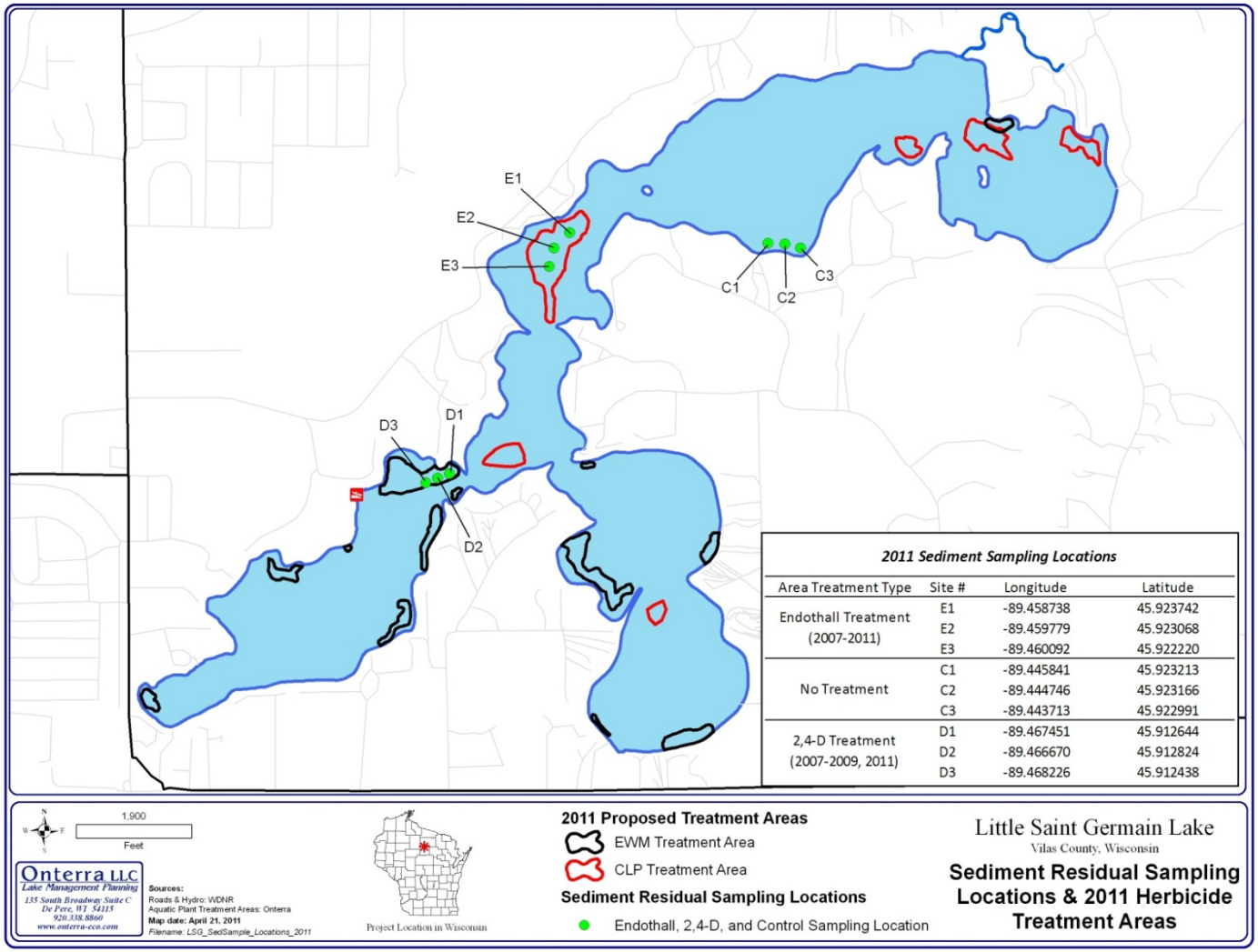
- Peepers retrieved by scuba diving.
- Each chamber sampled with syringe and placed in separate 60 ml bottle.
- Each sample preserved with 3-4 drops of muriatic acid.
- All samples set to the US Army ERDC Lab in Gainesville, Florida under the CRADA agreement.
- Immunoassay laboratory technique used to analyze for 2,4-D and Endothall.

Study Design (2011)

- Three sites (2,4-D/Endothall/Control) were selected for deployment.
- Peepers were originally set on May 18, 2011 and pulled May 24, 2011 (pretreatment sample)
- Herbicide treatment occurred on May 26, 2011.
- Granular 2,4-D (Sculpin G) was used to treat EWM and applied at 2.19-2.43 mg/l acid equivalent.
- Liquid Endothall (Aquathol K) was used to control CLP and applied at 1.5 mg/l active ingredient.
- Samples were collected out to 56 days post treatment (five sampling events).

Sampling Locations

- Sites chosen because of multiple years of treatment
- D sites (2,4-D)/E Sites (Endothall)/C sites (Control)



Endothall Results (ppb)

Target Application concentration 1,500 ppb

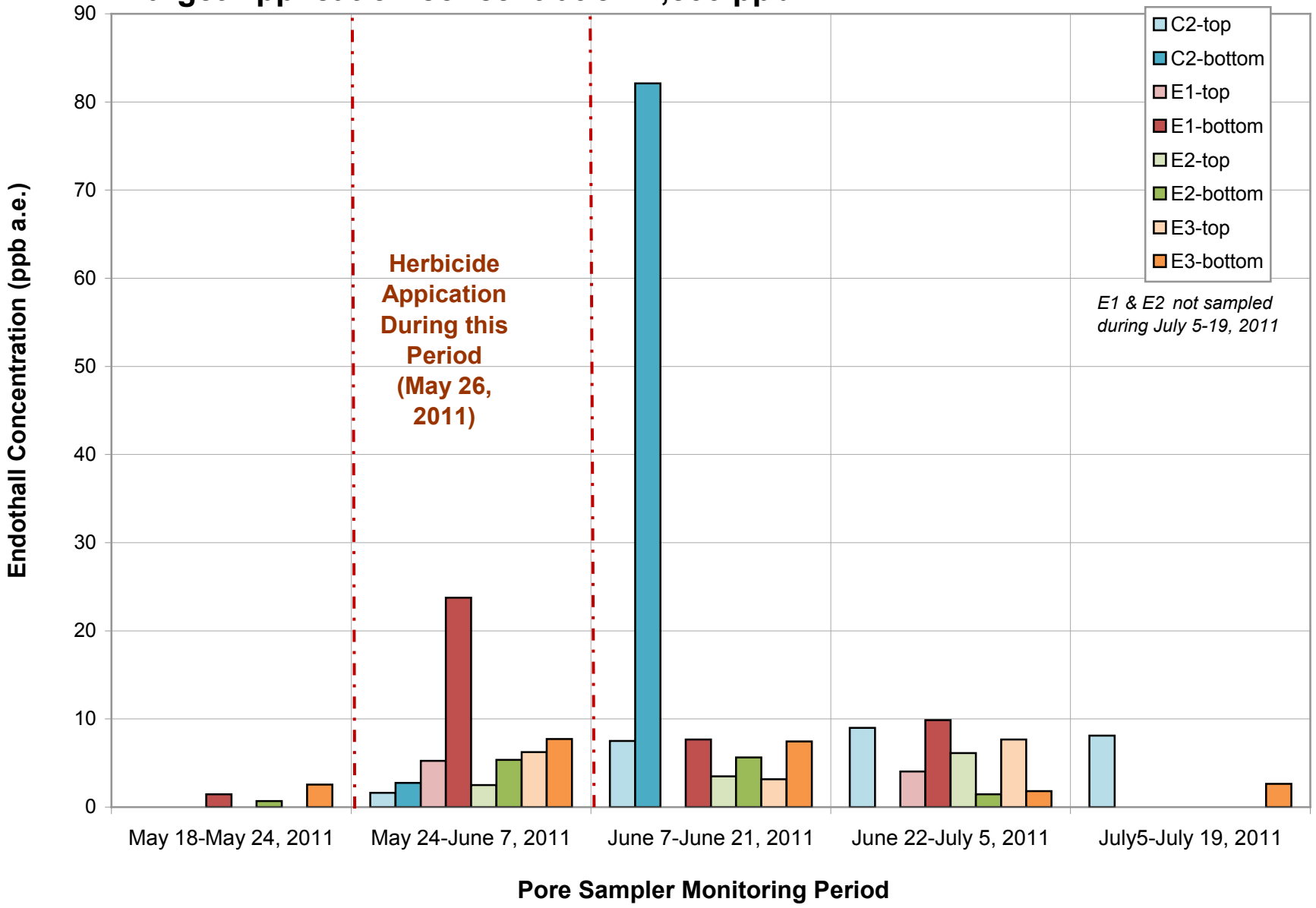


Chart provided by Onterra

Conclusions

Endothall Treatment (liquid)

1. There was very little difference between the top and bottom wells of the peepers.
2. Nearly all off the samples were either no detect (below limit of quantification of 7ppb) or just slightly above.
3. The highest value of 82 ppb was collected from a bottom well at the control site. This could be an outlier or there was some contribution from another treatment site.
4. Bottom line, sampling did not result in the detection of endothall above what might be expected as a typical background interference level.
5. These values do not suggest a short or long-term accumulation of endothall in the sediment pore water either prior to or 2 weeks after treatment.

2,4-D results (ppb)

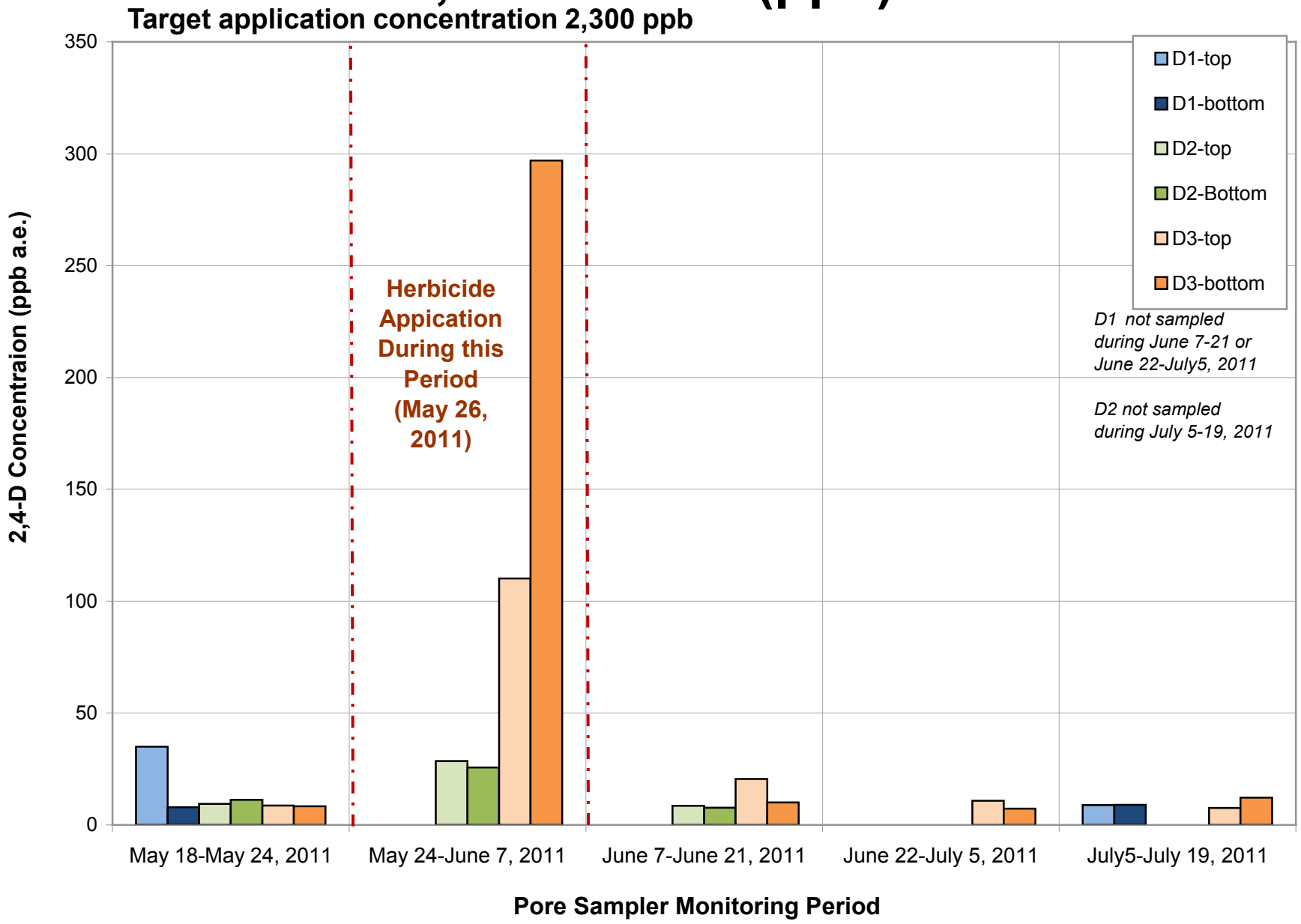
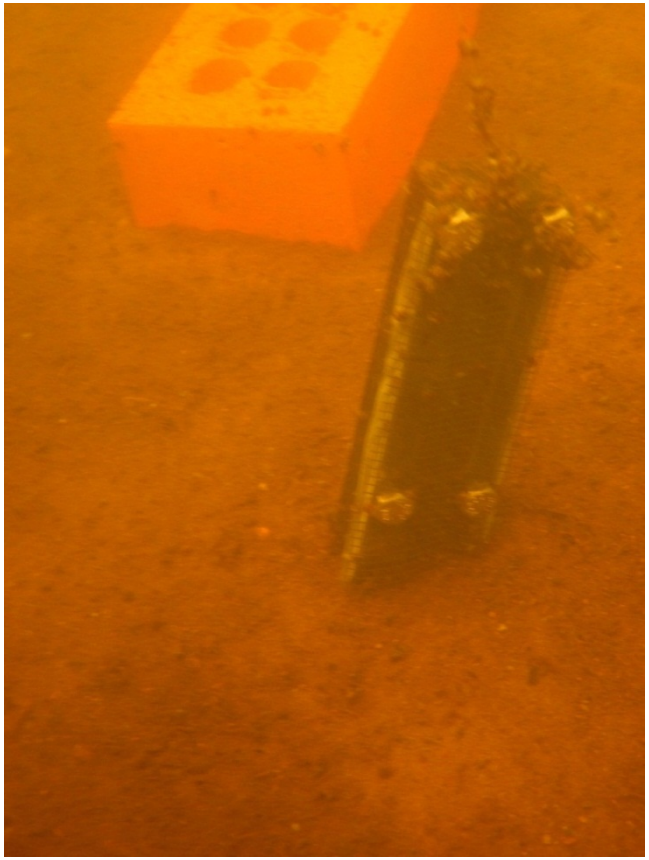


Chart provided by Onterra

Conclusions (continued)

2,4-D granular treatment

1. There was very little difference between the top and bottom wells of the peepers.
2. The 2,4-D sampling also suggests no accumulation prior to or following granular treatment.
3. The only spike (280 ppb) occurred 14 days after treatment (warrants future sampling). **This lead to the 2012 study design.**



Study Design (2012)

Pore Water Sampling

- 4 sites (2,4-D treatment bed only) were selected for deployment.
- 2 peepers were placed at each site i.e. 1 A ,1 B.
- Peepers were originally set on May 21, 2012 the day of herbicide treatment.
- Granular 2,4-D (Sculpin G) was used to treat EWM and applied at 3.0 mg/l acid equivalent.
- Samples were collected 2,4,6 and 8 days after treatment.

Study Design (2012)

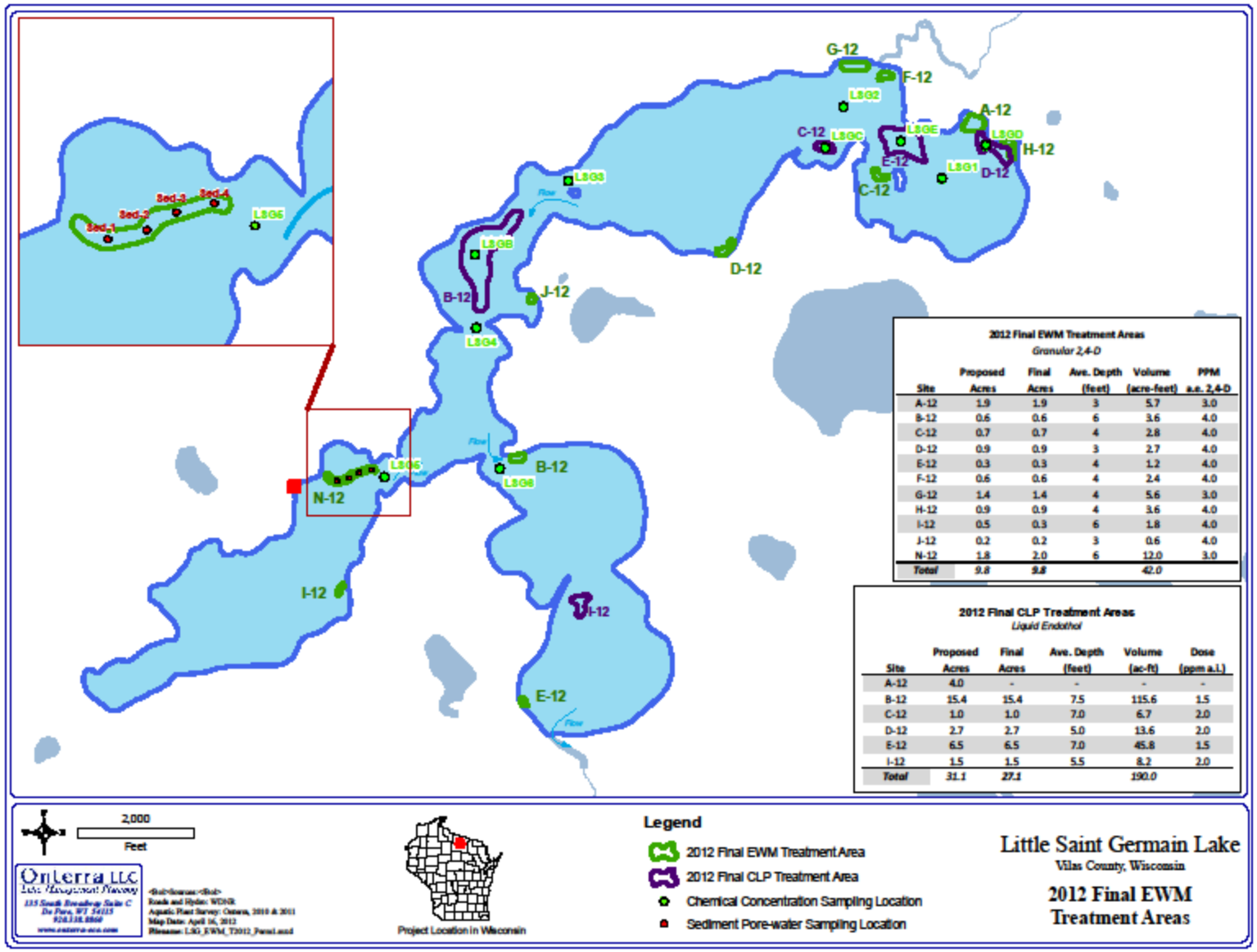
Sediment Sampling

- The half-life of 2,4-D is much longer under anaerobic conditions (4.5 vs.312 days in aqueous solution)
- 2, 4-D is more strongly adsorbed in sediment with higher organic matter content and/or lower pH.

Based on this we proposed:

1. Collecting sediment during the pore water sampling events (top 6 inches) and analyze for total 2,4-D, 2,4-D acid and 2,4-D ester forms.
2. Goal would be to collect highly organic sediment.
3. Particle size analysis would also occur.

LSG Pore Water and Sediment Sampling Location (2012)

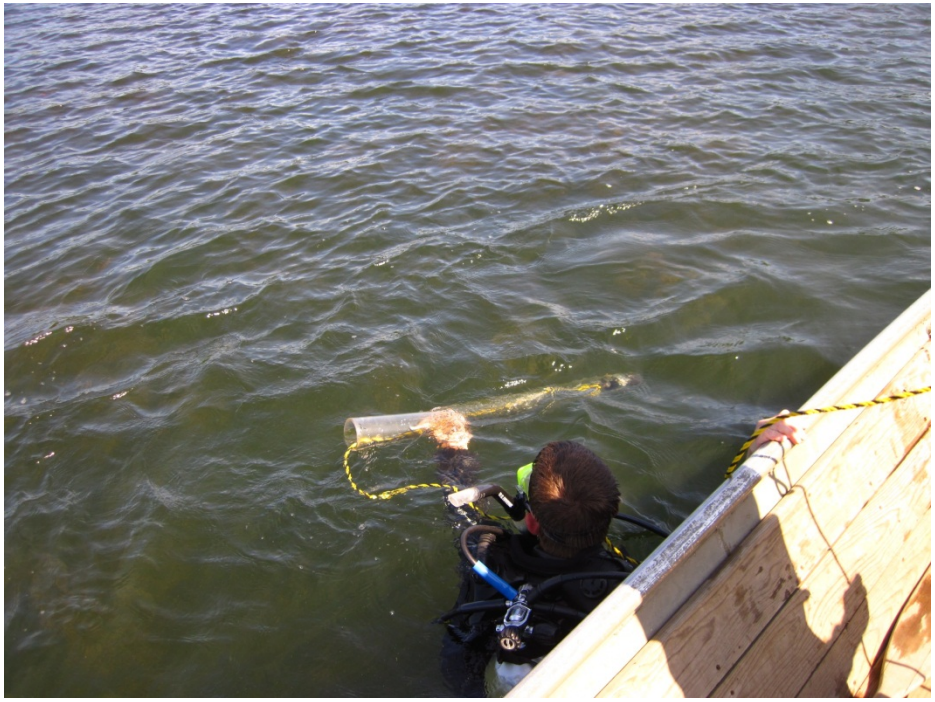


Deployment

- Two Peepers set within one meter square PVC enclosure at each of 4 locations.
- Each site assigned GPS coordinates.
- One chamber is in the sediment and the other is just above the sediment at the sediment water interface.
- DNR Fike net floats and anchors used to mark sites.
- Peepers allowed to equilibrate for 2 days under each sampling event.

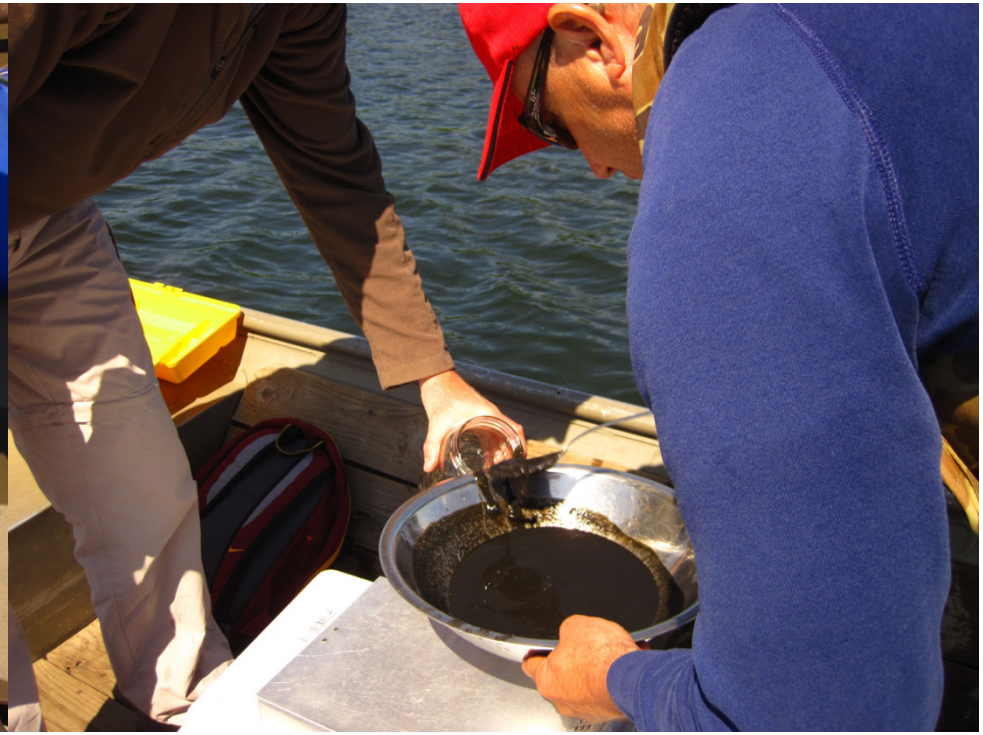
Sediment Sampling

- 3 sediment samples were collected on each sampling date (12 total) using a Plexiglas core tube.
- They were randomly collected within the treatment bed.
- Top 4-6 inches of sediment was collected.

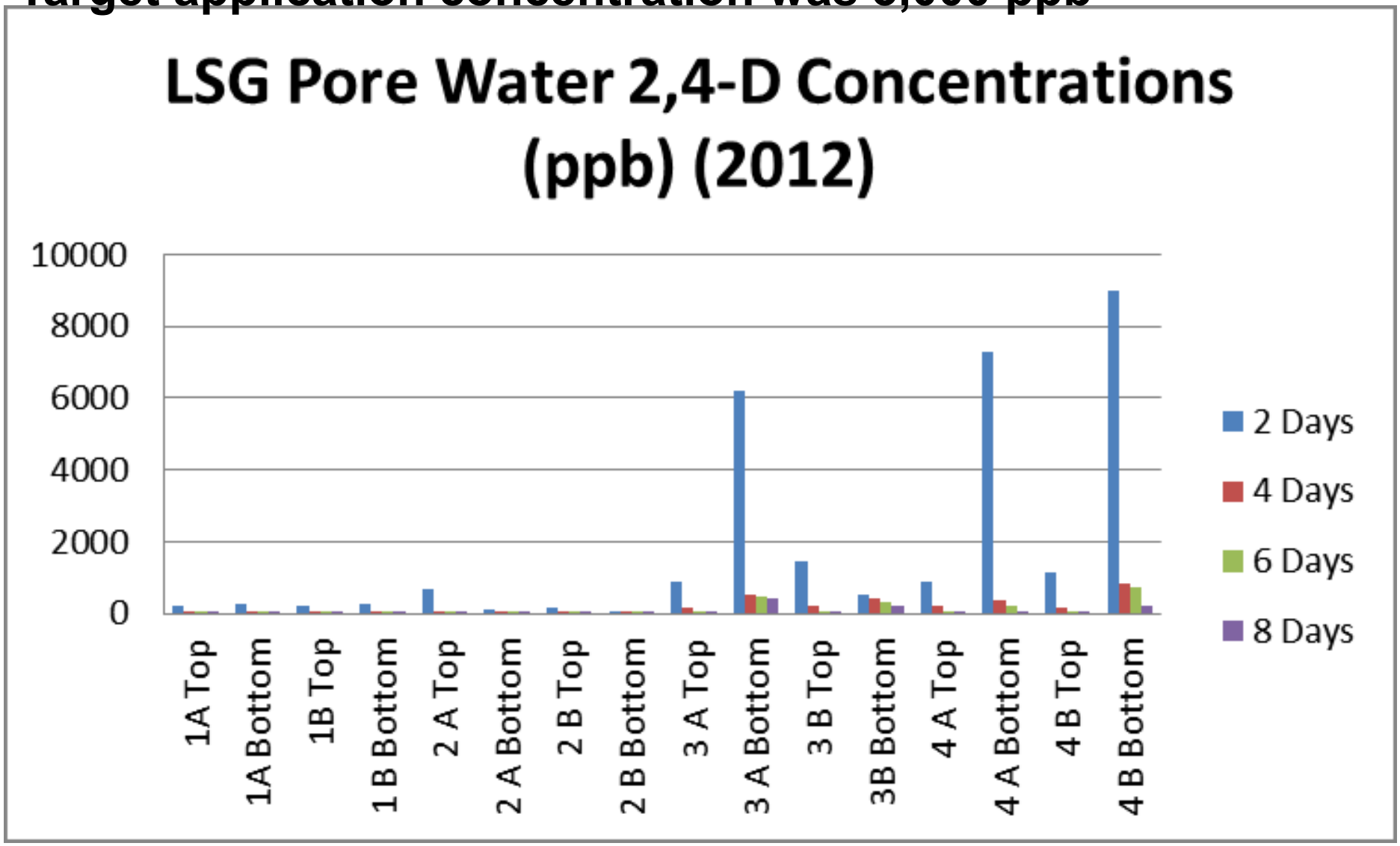


Sediment sampling…

- Each sample was mixed and placed into a mason jar.
- The samples were placed on ice and frozen upon return to office.
- Samples sent frozen to SLOH.
- At the lab the three samples were composited into one (for each sampling date).
- 4 samples were analyzed for Total 2,4-d, 2,4-D acid and 2,4-D ester forms.
- Particle size analysis was also conducted.



Target application concentration was 3,000 ppb



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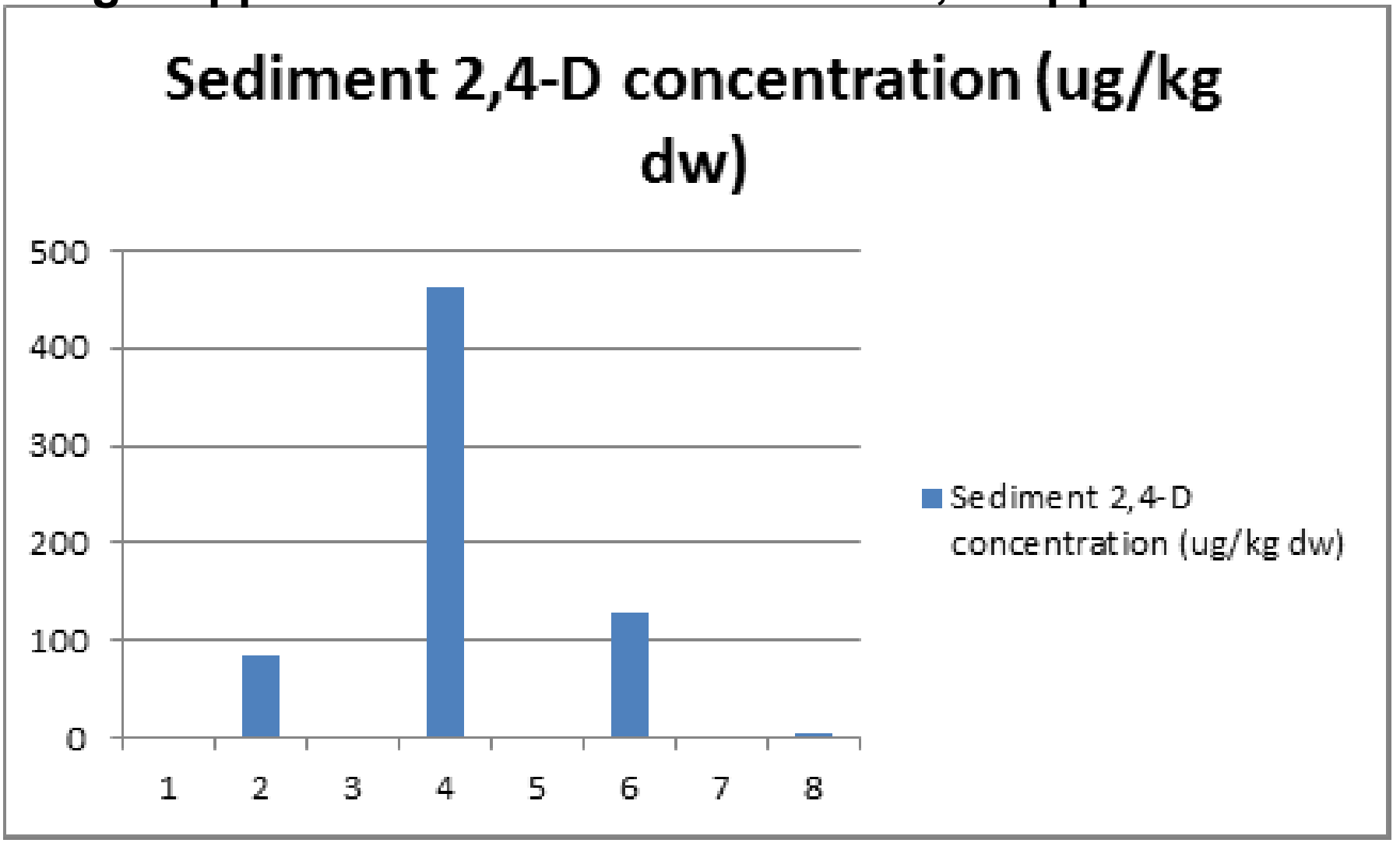

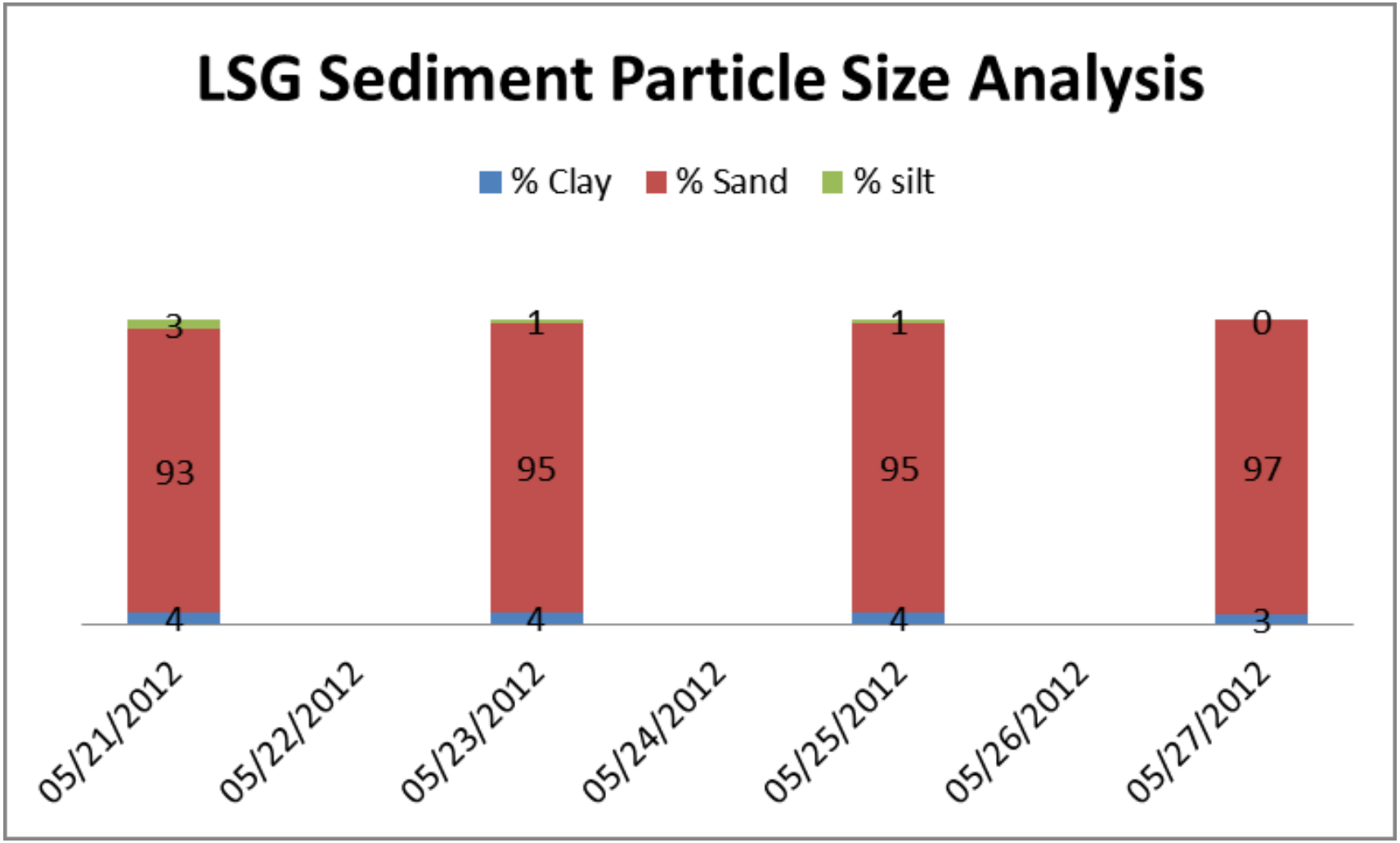
LSG Sediment Particle Size Analysis
% Clay
% Sand
% silt
3
93
4
1
95
4
1
95
4
0
97
3
05/21/2012
05/22/2012
05/23/2012
05/24/2012
05/25/2012
05/26/2012
05/27/2012

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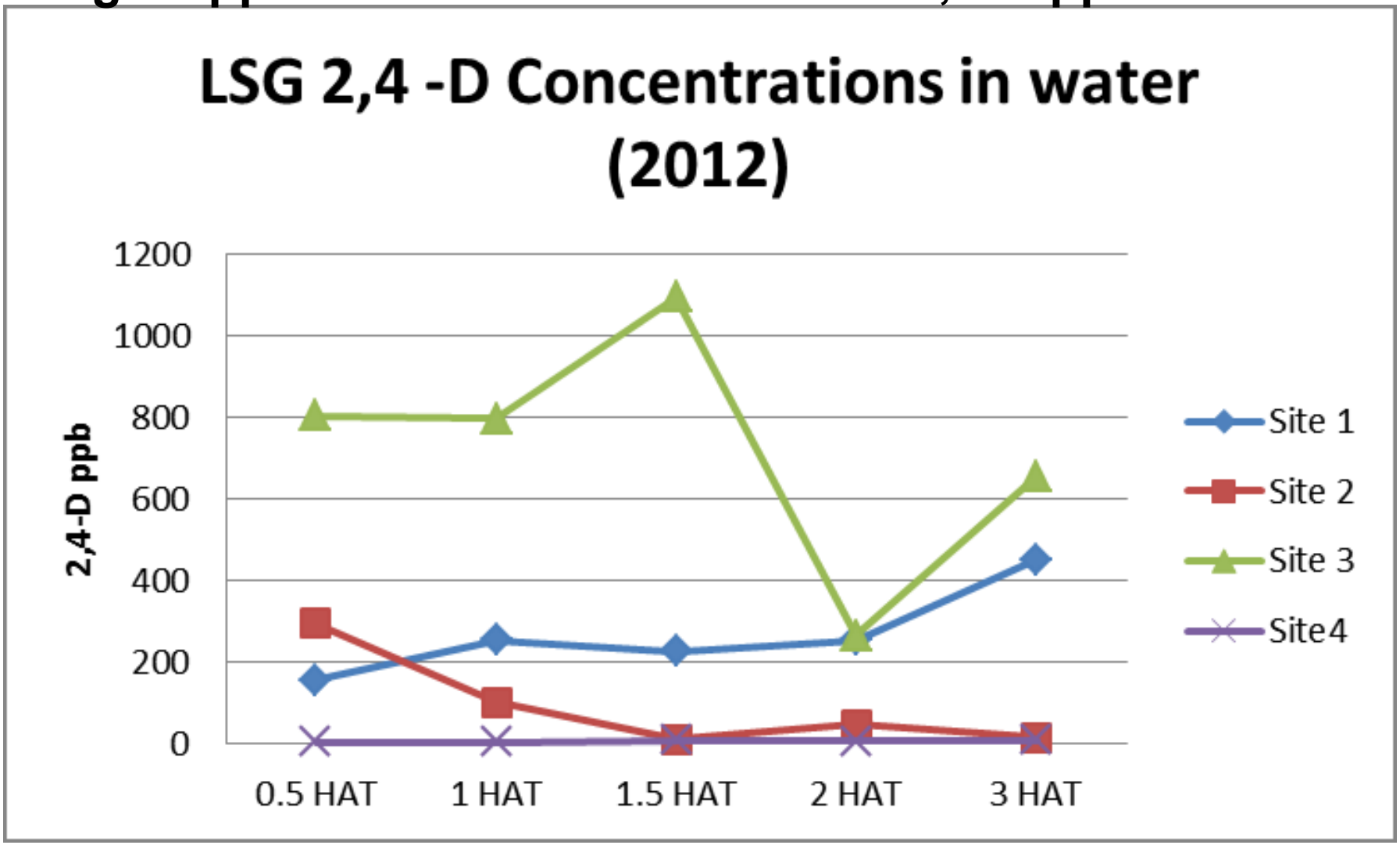
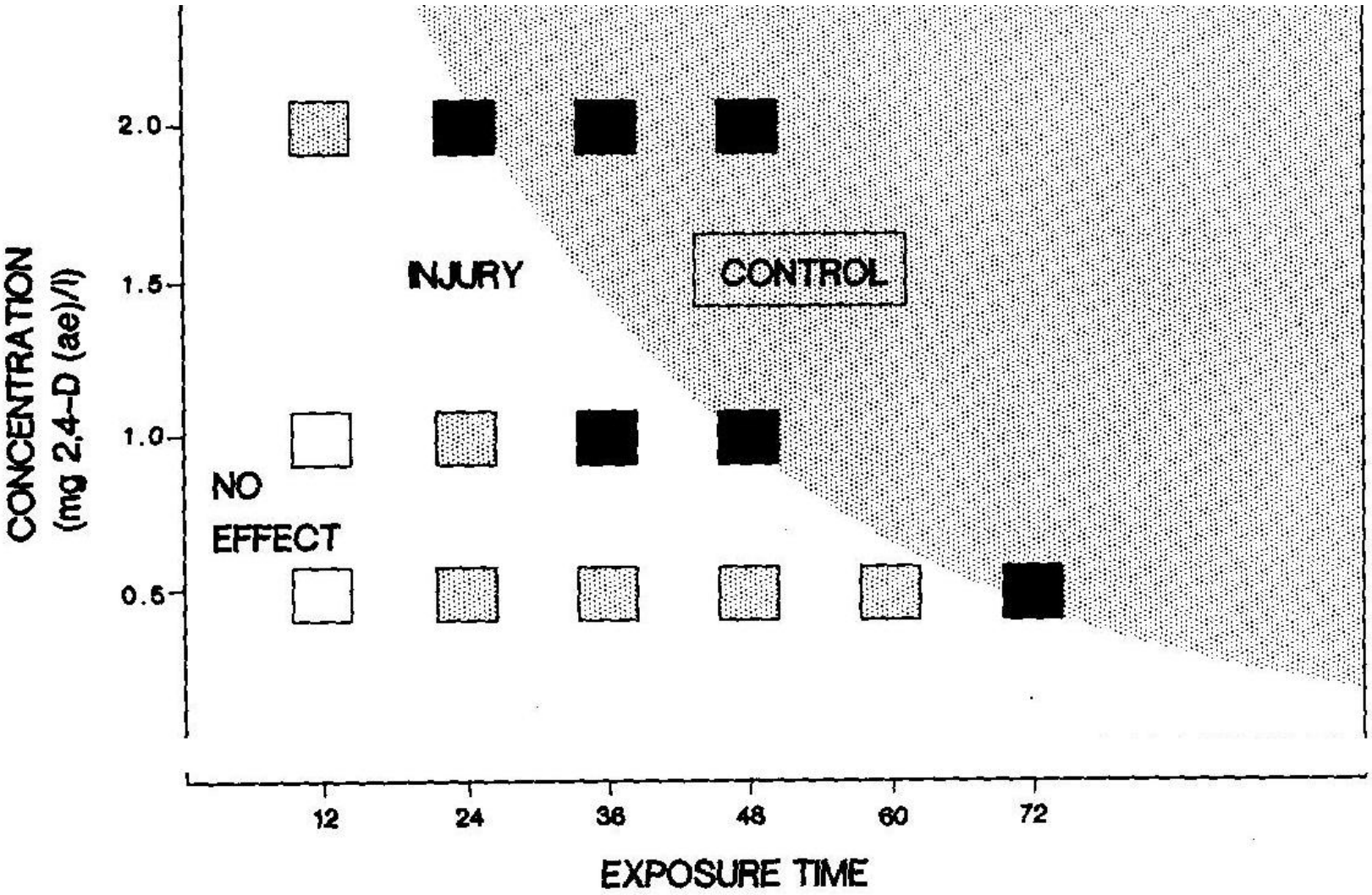


Concentration/Exposure Time Relationship



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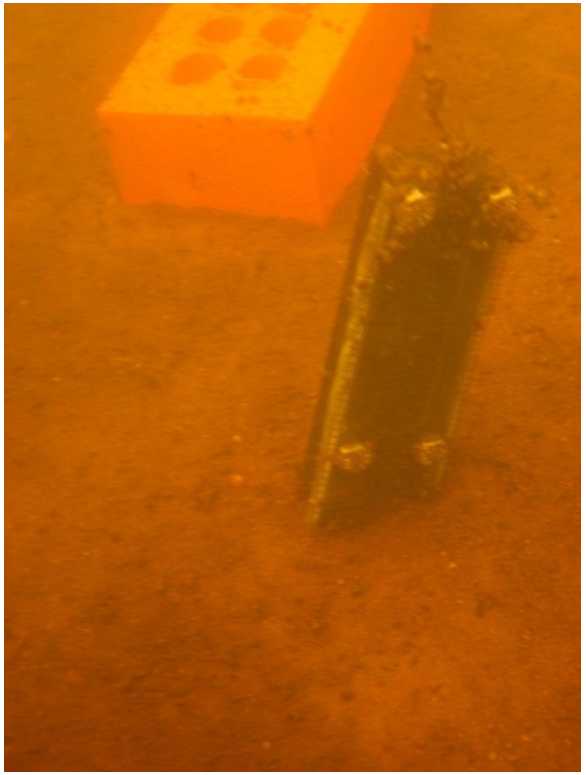
Conclusions

2,4-D granular treatment (pore water analysis)

1. Samples collected at sites 3 and 4 had the highest 2,4-D concentrations in the sediment pore water. Suggests herbicide drift with wind.
2. 2,4-D concentrations were very high (~ 3 times the target application concentration of 3000 ppb) in the bottom well at sites 3 and 4 after two days post treatment.
3. 2,4-D concentrations gradually declined but were as still as high as 410 ppb in a bottom well at site 3 after 8 days post treatment.
4. Could sediment pore water could be another route of exposure?
5. Toxicity to other aquatic life?



Aquakleen Laboratory Toxicity Study

Fish 96hr LC50

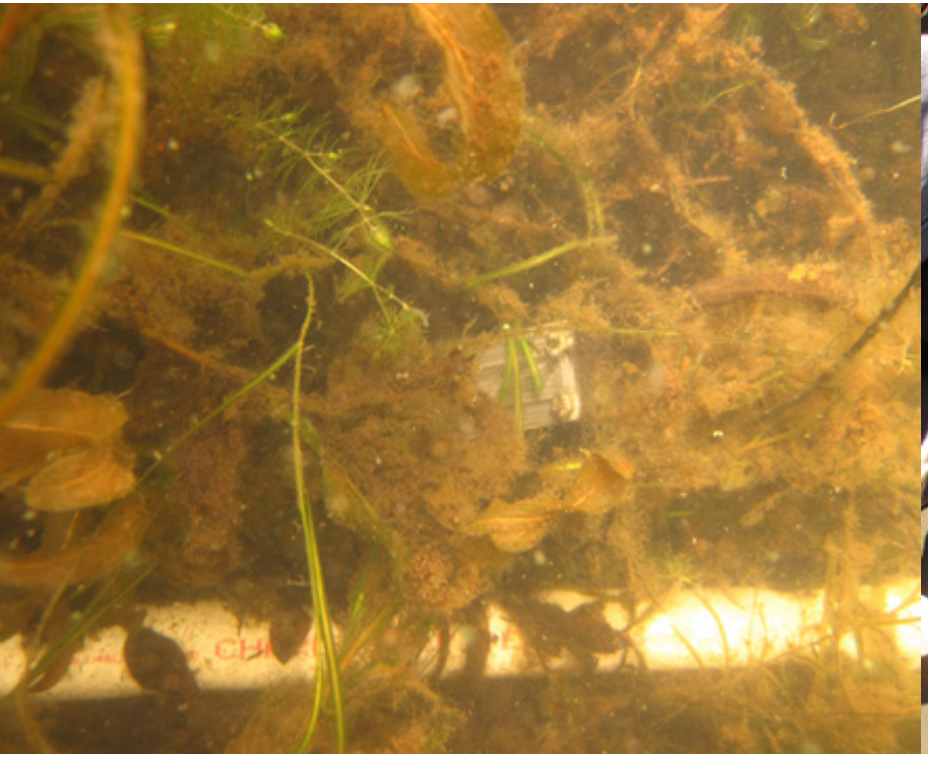
(concentration at which 50% of fish fry were dead after 96 hours)

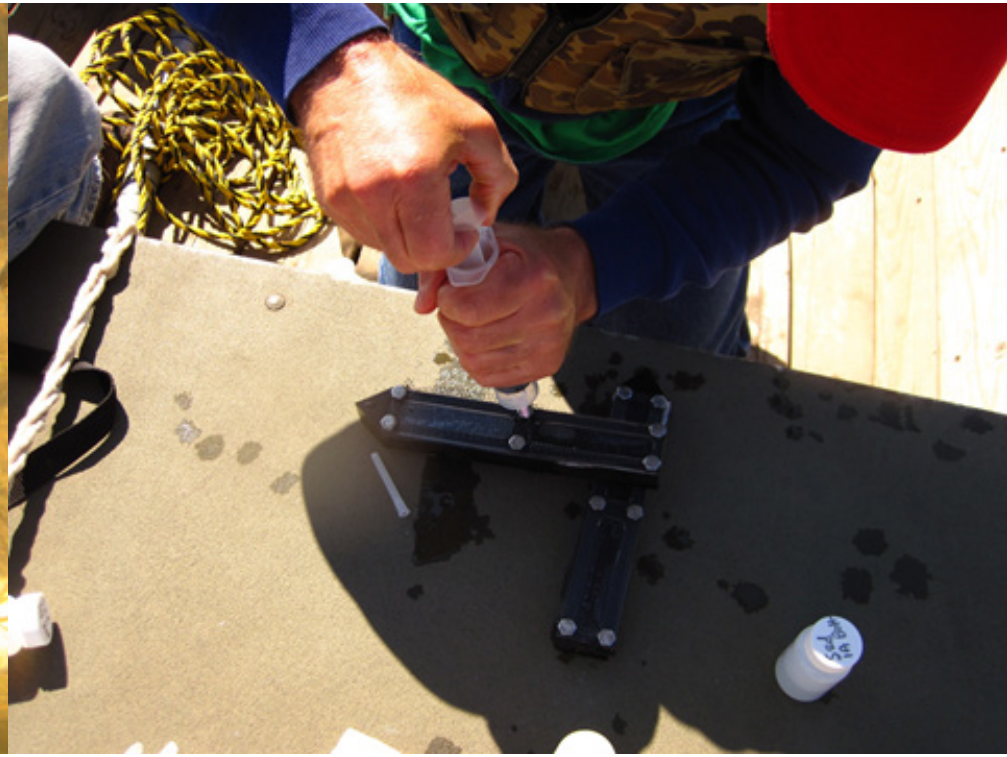
- Brook trout fry - **760 µg/L (ppb)**
- Walleye fry - **660 µg/L (ppb)**
- Fathead minnow - **2220 µg/L (ppb)**
- In addition, the 48-hr LC50 for the amphipod *Hyallela azteca* was determined to be **600 µg/L (ppb).**

Paul, E., Johnson, S, and Skinner, K.M. 2006. Fish and Invertebrate Sensitivity to the Aquatic Herbicide Aquakleen, Journal of Freshwater Ecology, vol 21. 163 - 168.

Future work (Proposed for 2013)

1. Determine sediment pore water (2,4-D) concentration gradient at 0-4 days post treatment (6, 12, 24, 36, 48, 72 and 96 hours after treatment).
2. This may lead to the need to address sediment toxicity issues in the future.
3. We may also sample a couple of additional lakes that have higher organic material in sediment (does that influence sediment pore water concentration?).
4. In a separate study the ACOE evaluate the hypothesis that elevated sediment pore water concentrations can explain efficacy of granular formulations.





Questions?