

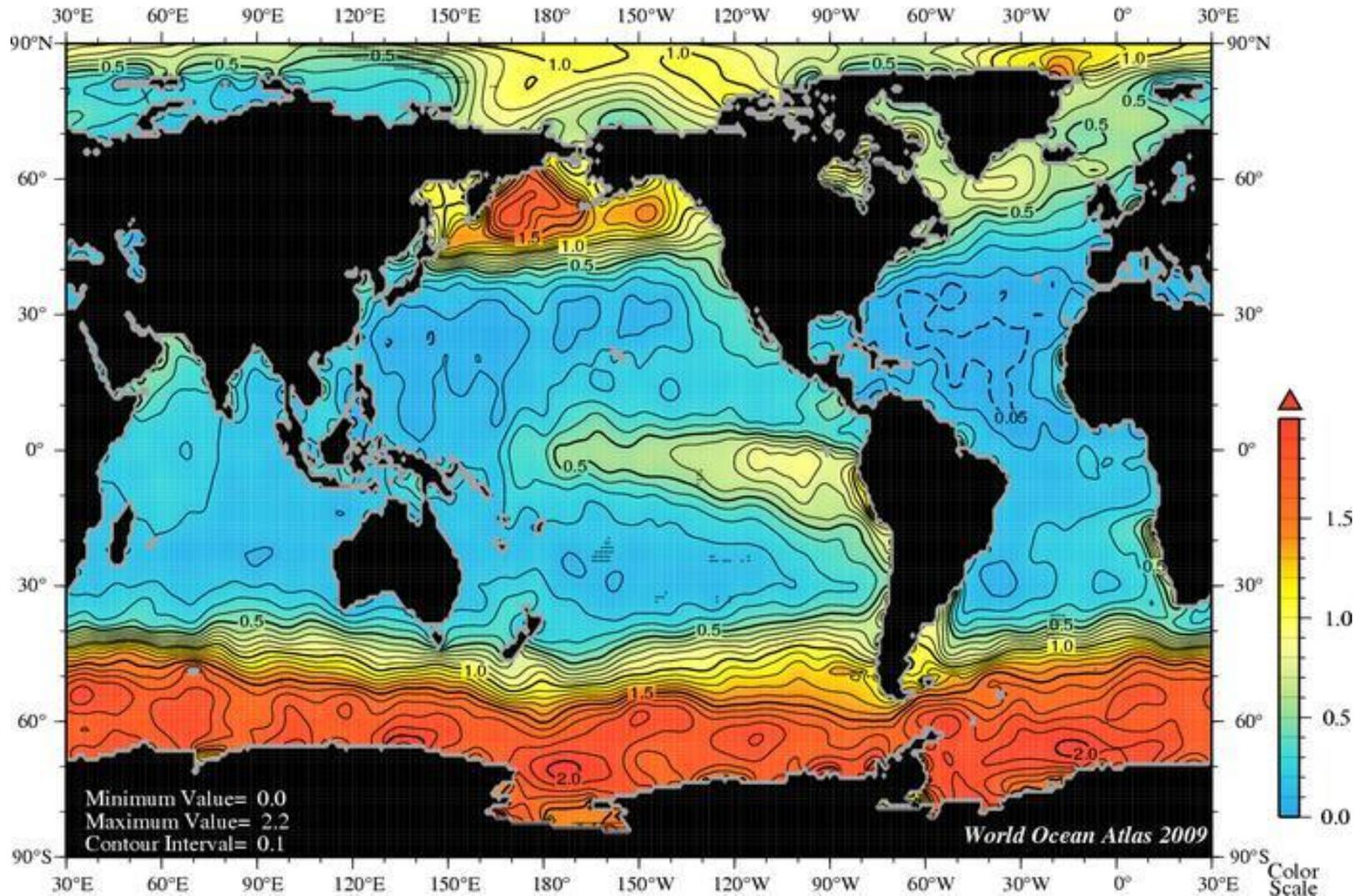
Phosphonates: Their occurrence and utilization by cyanobacteria in Lake Erie and it's watershed

R.M.L. McKay, I. Ilikchyan and G.S. Bullerjahn

Acknowledgements

- Doug Kane, Defiance College
- Joe Conroy, OSU
- Tom Bridgeman, U Toledo
 - Justin Chaffin
- Erica Young, UW-Milwaukee
- Steve Wilhelm, U Tennessee
 - Matt Saxton
- City of Napoleon, OH
 - Water Treatment Plant
- Ohio Sea Grant
 - R/ER-080
- LEPF
 - SG 357-09

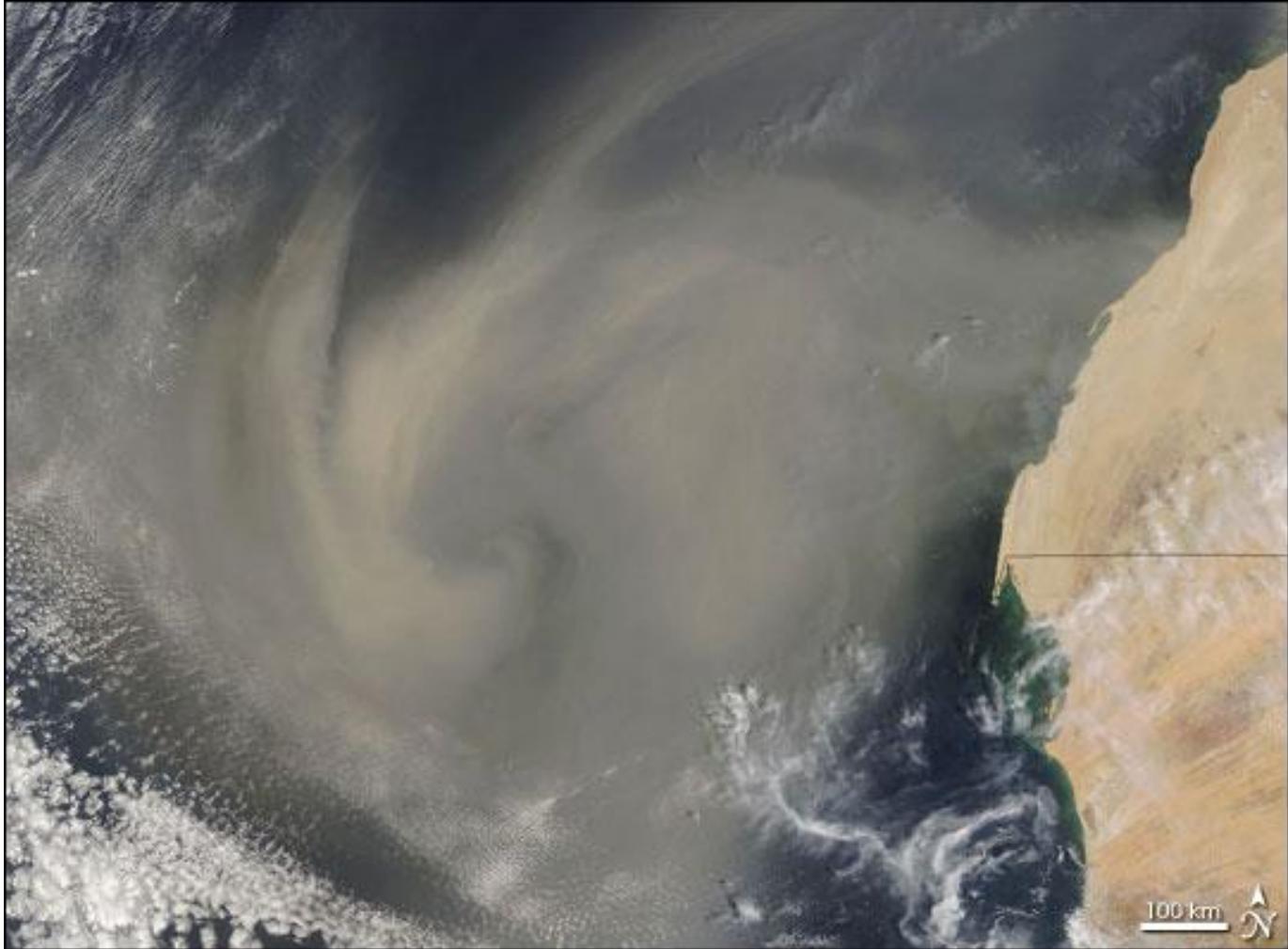
Annual phosphate [$\mu\text{mol/l}$] at the surface.



Source: National Oceanographic Data Center, World Ocean Atlas 2009

http://www.nodc.noaa.gov/OC5/WOA09F/pr_woa09f.html

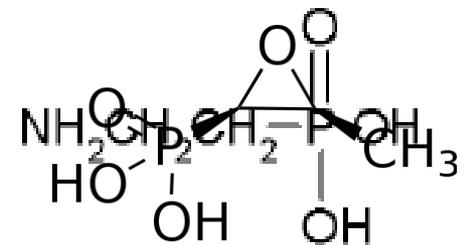
Sargasso Sea



Credit: NASA

Phosphonates

- contribution to HMW oceanic DOP?
 - up to 25%
 - (Clark et al. 1998, Kolowith et al. 2001)
- refractory C-P bond
- naturally occurring phosphonates:
 - phosphonolipids
 - antibiotics

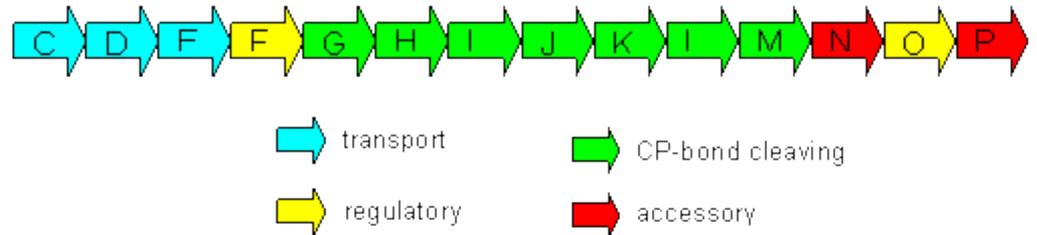


fosfomicin
2-aminoethylphosphonate

Phosphonates in marine habitats

- phosphonate utilization genes

- *phn* operon



- present in cyanobacterial genomes

- *Trichodesmium* spp. (N₂ fixing filamentous genus)

- Dyhrman et al. 2006

- Marine and freshwater *Synechococcus* spp.

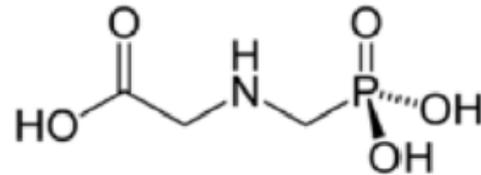
- Palenik et al. 2003; Su et al. 2003; Ilikchyan et al. 2009

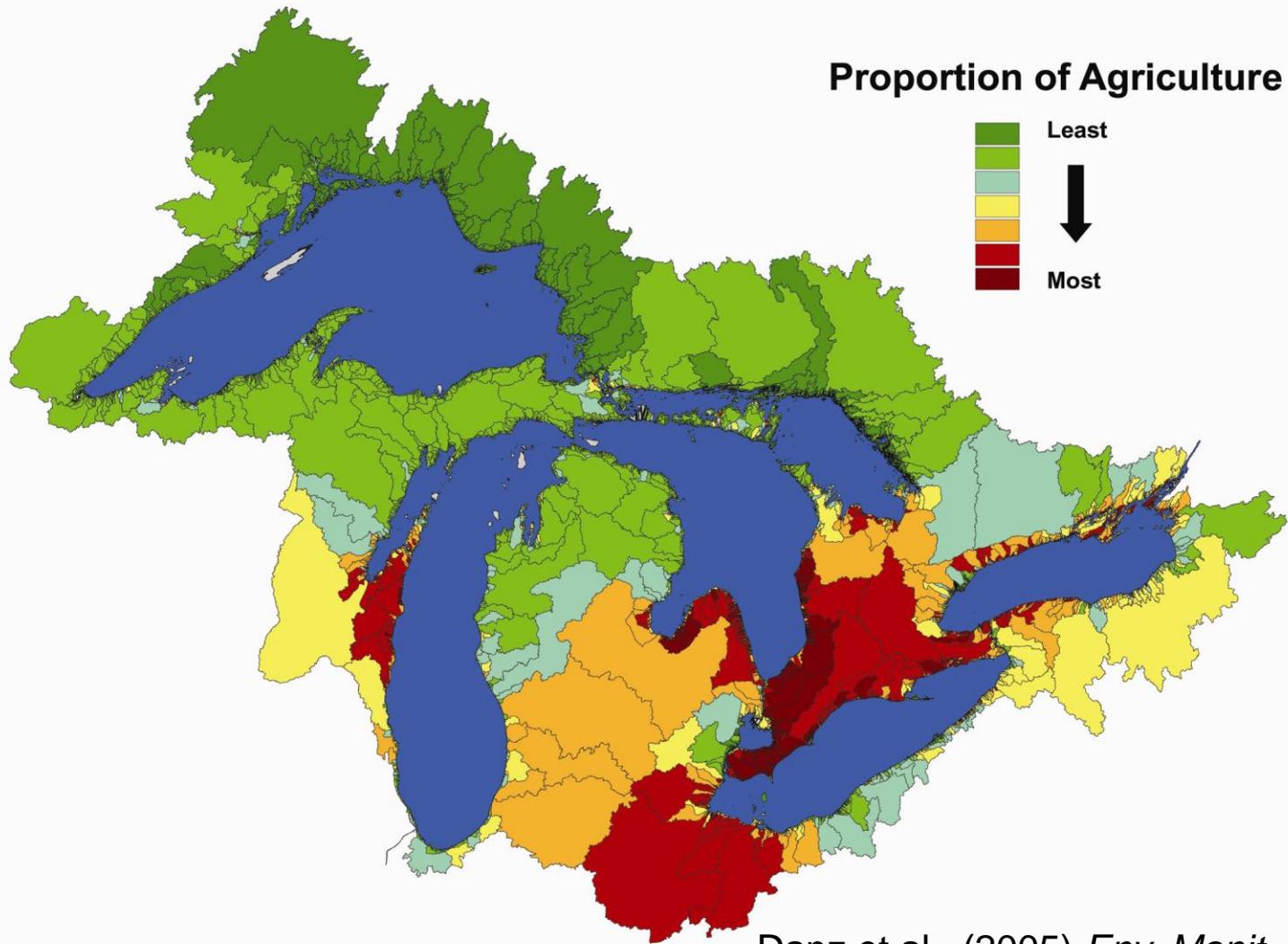
- *Prochlorococcus* spp.

- Ilikchyan et al. 2009

Phosphonates in freshwater

- many lakes are P-limited
 - Lake Superior N:P ~ 8,000
- utilization of phosphonates?
 - naturally occurring?
 - anthropogenic sources?
 - Roundup[®]



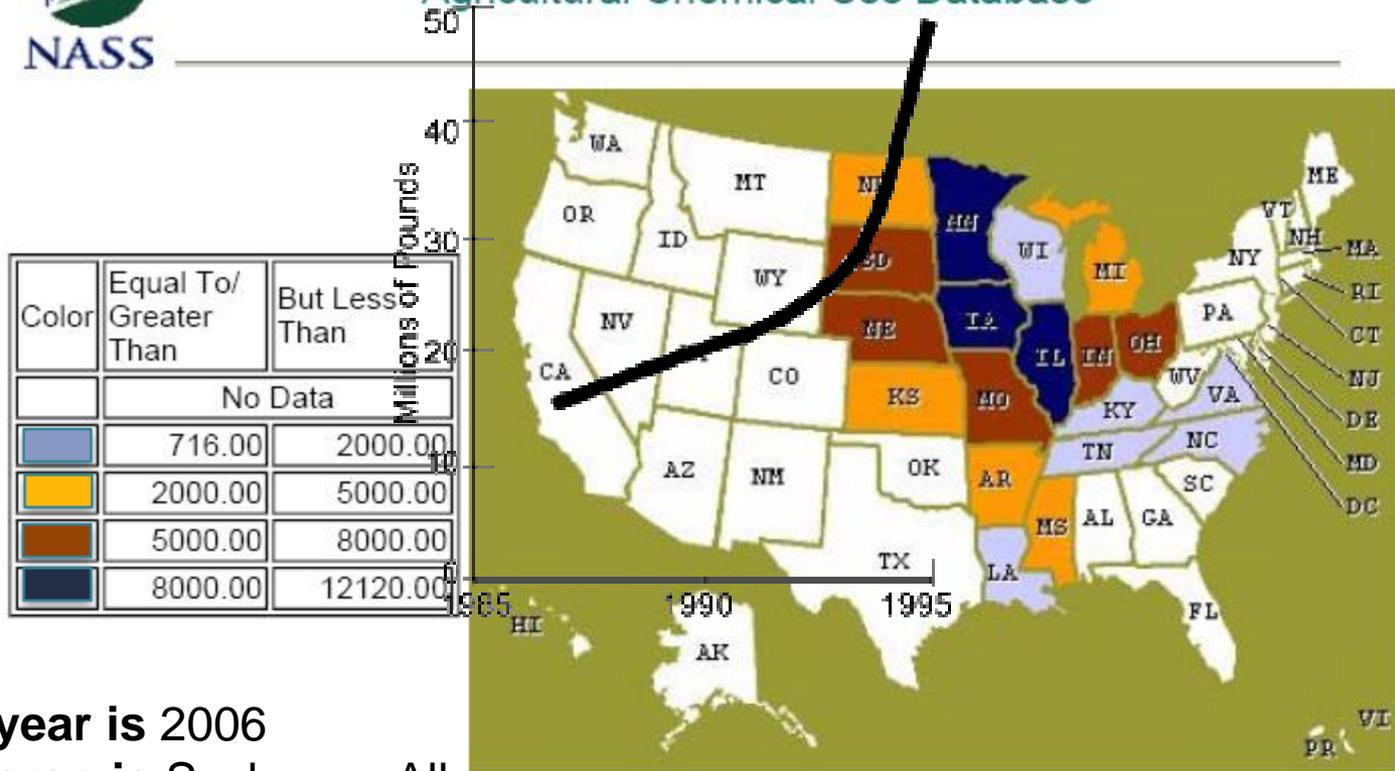


Danz et al., (2005) *Env. Monit. Assess.*

Glyphosate application: Nationwide



National Agricultural Statistics Service (NASS)
Agricultural Chemical Use Database



The year is 2006

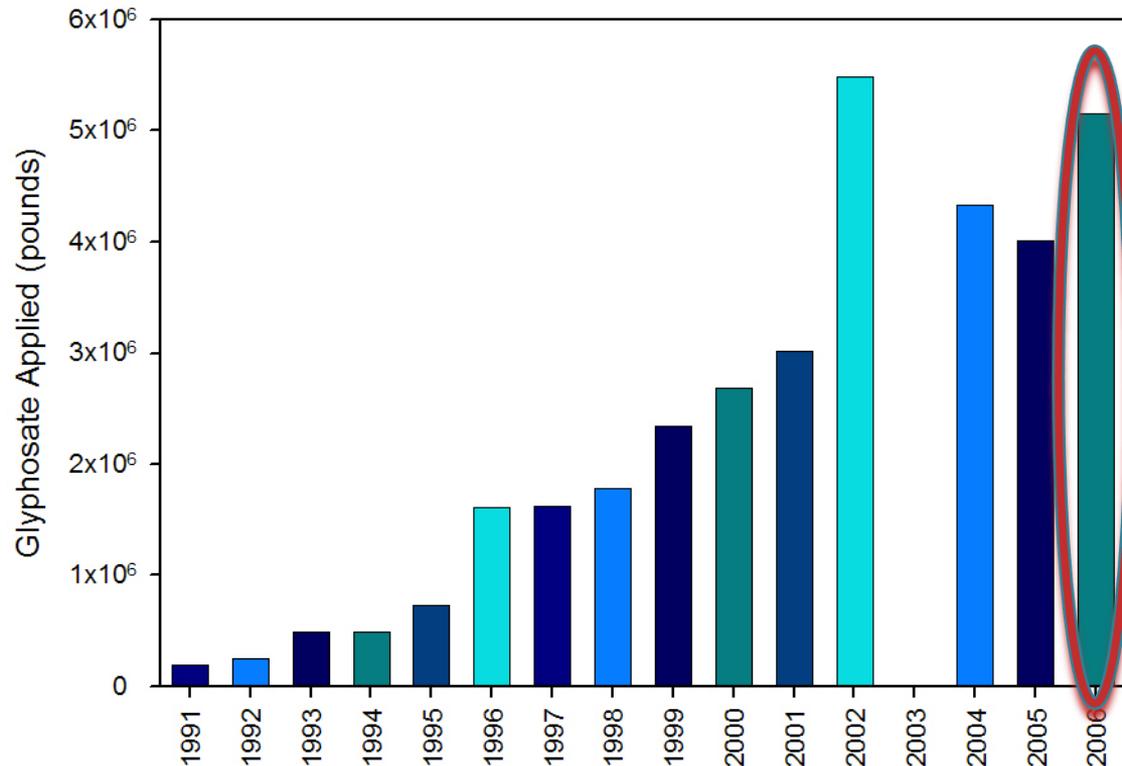
The crop is Soybeans-All

The agricultural chemical is Glyphosate

The statistic is Total Active Ingredient Applied (000lb/year)

Glyphosate application to soybeans in Ohio

- > 2300 tonnes applied



USDA – National Agricultural Statistics Service

Outlook for 2010

Soybeans: Area planted in OH (acres)

2006	2007	2008	2009	2010 ¹
4,650,000	4,150,000	4,500,000	4,550,000	4,600,000

¹ Intended plantings in 2010 as indicated by reports from farmers

Prospective Plantings, 31 March, 2008 & 2010
USDA – National Agricultural Statistics Service

What is the issue being addressed?

- is glyphosate present in Lake Erie and it's watershed?
- can endemic phytoplankton use glyphosate as a P source?

Is glyphosate present in Lake Erie and it's watershed?



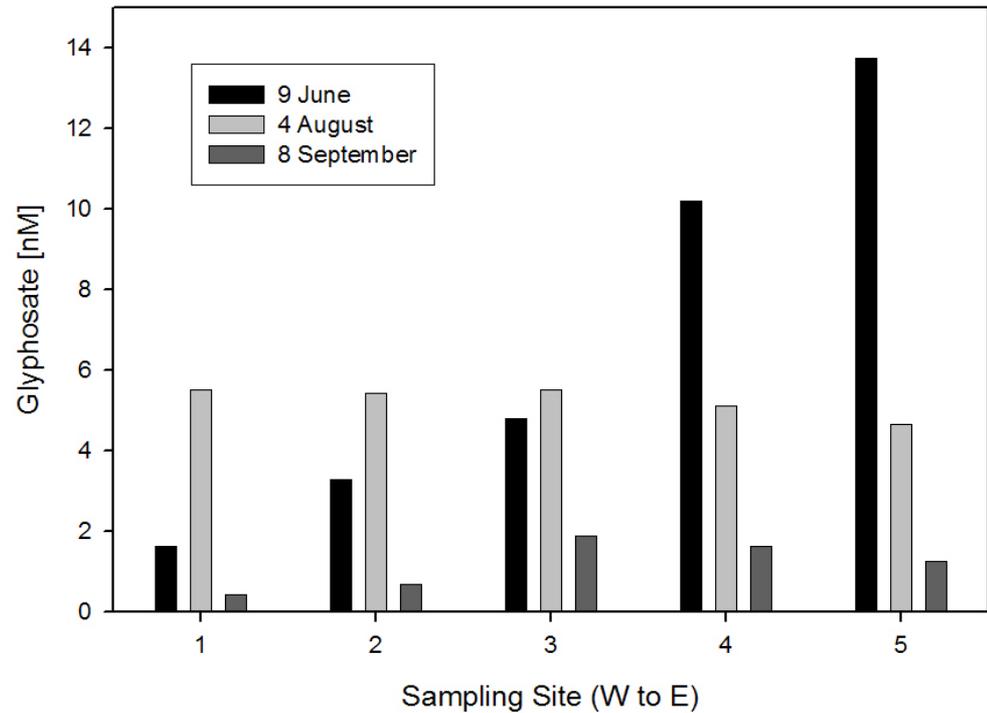
- Environment Canada presentations
 - glyphosate detected in tributaries and nearshore regions
 - Byer et al. 2008, *Environ. Sci. Technol.* 42: 6052
 - Struger et al. 2008, *Bull. Environ. Contam. Toxicol.* 80: 378

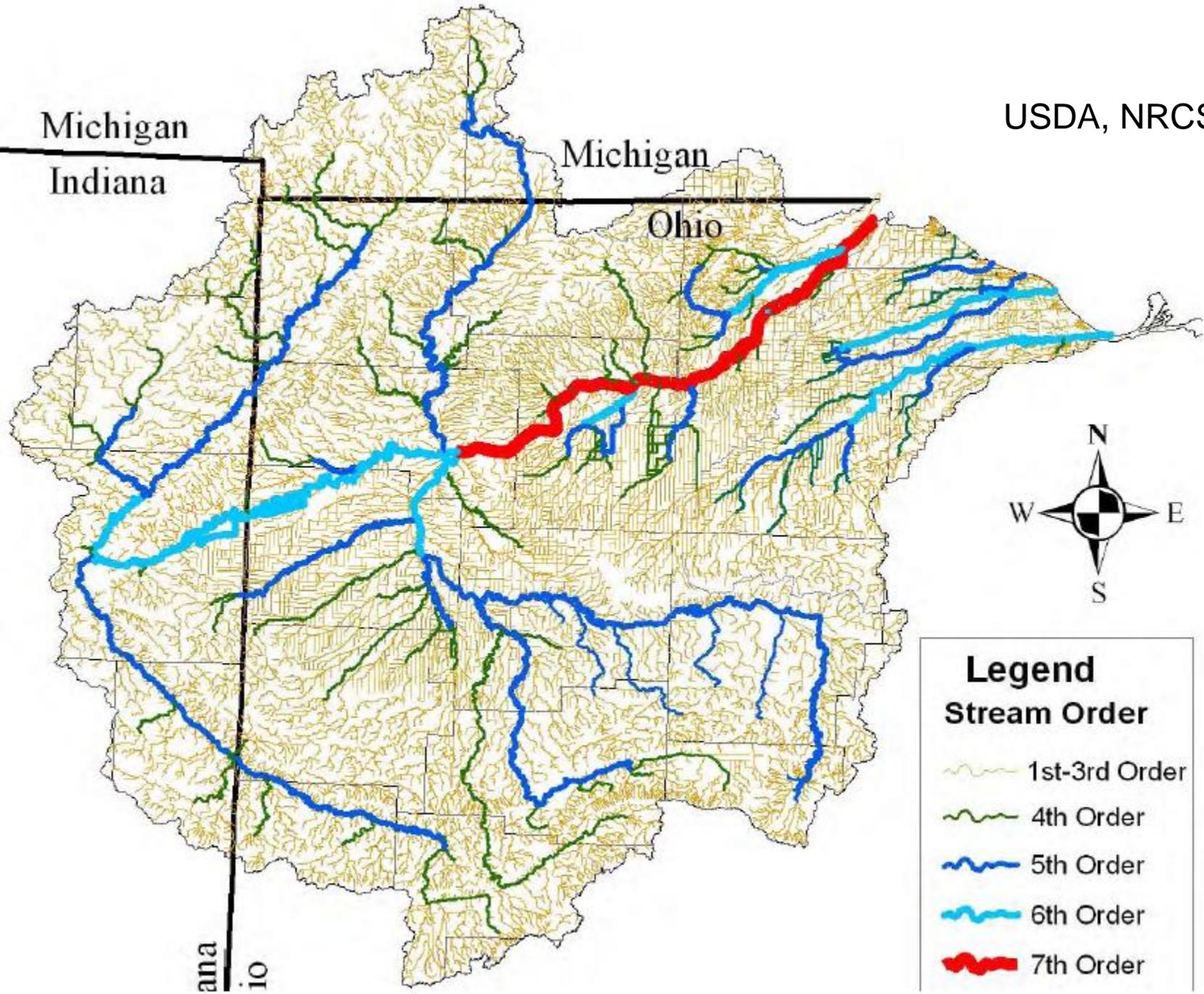
Glyphosate is detectable in Maumee Bay (ELISA)

Station (western basin)	Lat/long	Date (2008)	Phosphate Dissolved/Total ($\mu\text{g L}^{-1}$)	Glyphosate (nM/ng L ⁻¹)
ER 60	41° 53' 31" N 83° 11' 49" W	21 April	4.6/16.9	Below detection
7M	41° 43' 58" N 83° 17' 47" W	5 May	37/ND	Below detection
7M	41° 43' 58" N 83° 17' 47" W	29 May	29/115	0.76 / 128
7M	41° 43' 58" N 83° 17' 47" W	11 June	9/36	1.20 / 203
7M	41° 43' 58" N 83° 17' 47" W	10 July	15/77	1.65 / 276
MB 20	41° 42' 54" N 83° 27' 19" W	11 June	79/186	1.27 / 215
MB 20	41° 42' 54" N 83° 27' 19" W	10 July	66/195	1.72 / 291

- onset of detection is consistent with spring planting in Maumee River valley
 - values comparable to Byer et al. 2008

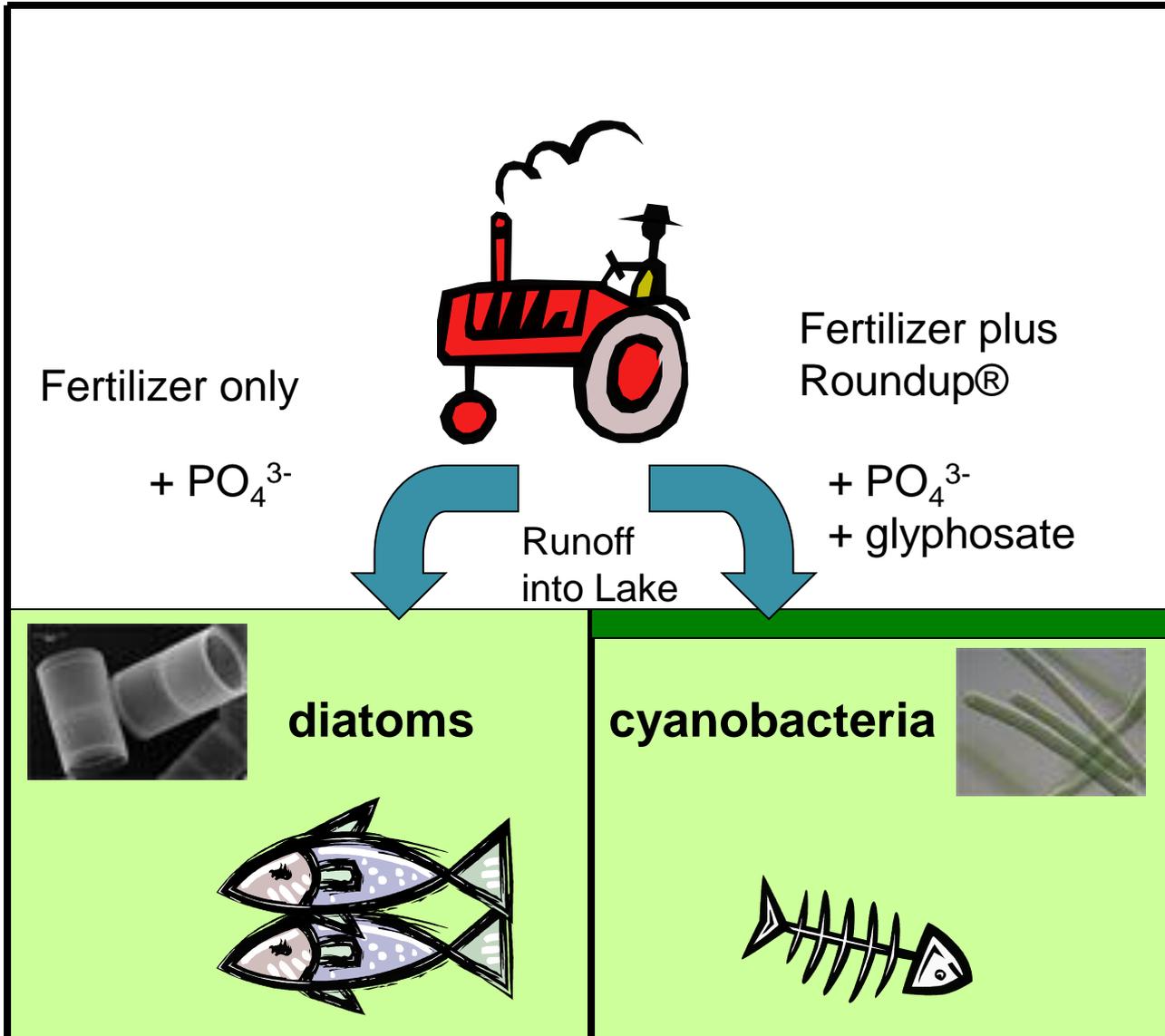
Glyphosate in the Maumee River: 2009





Glyphosate in the Maumee River

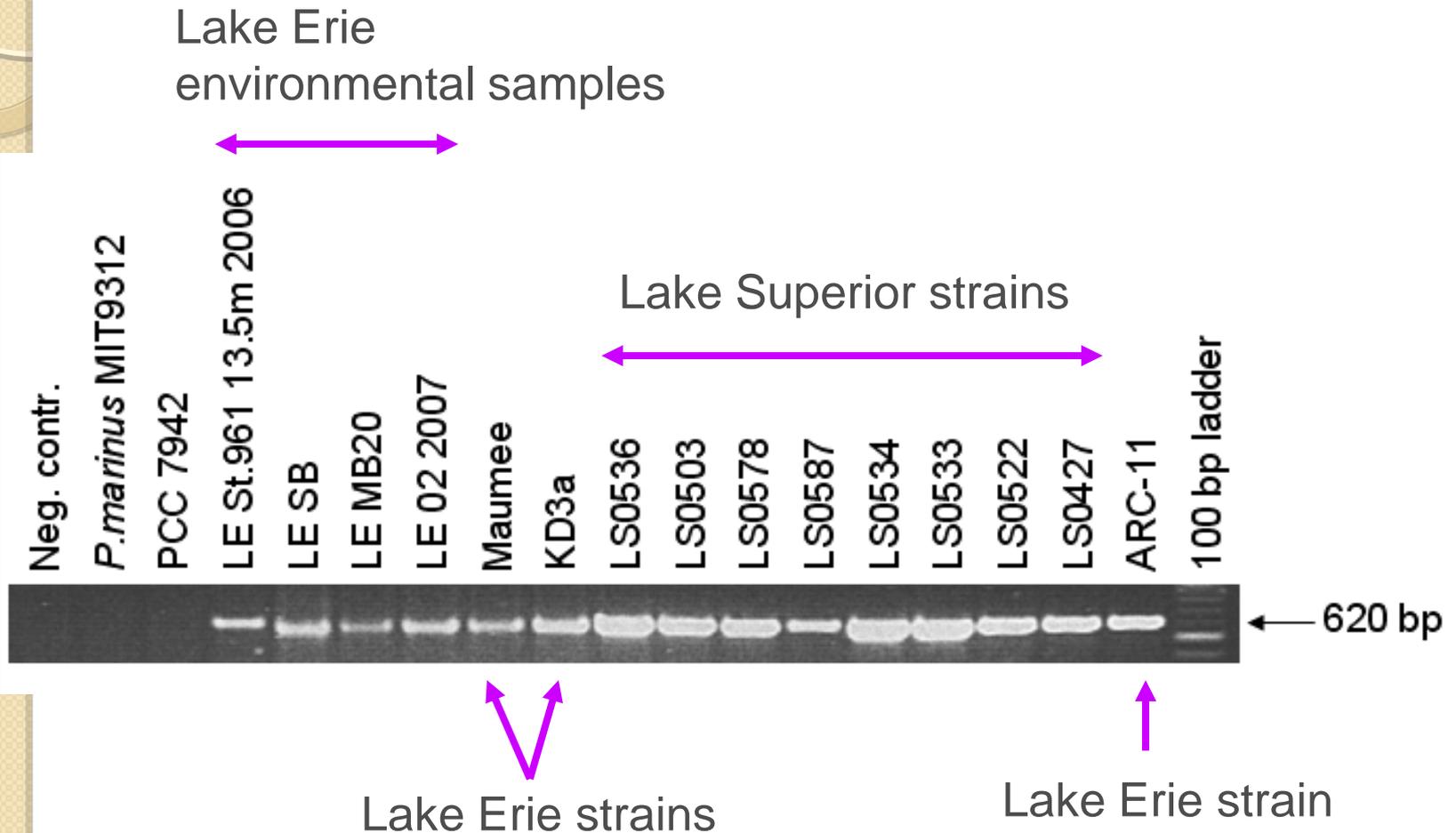
- regulatory considerations?
- EPA guidelines
 - 700 $\mu\text{g L}^{-1}$ (4.1 μM)
- Canadian Water Quality Guideline
 - 65 $\mu\text{g L}^{-1}$ (0.38 μM)
- ecosystem impact?



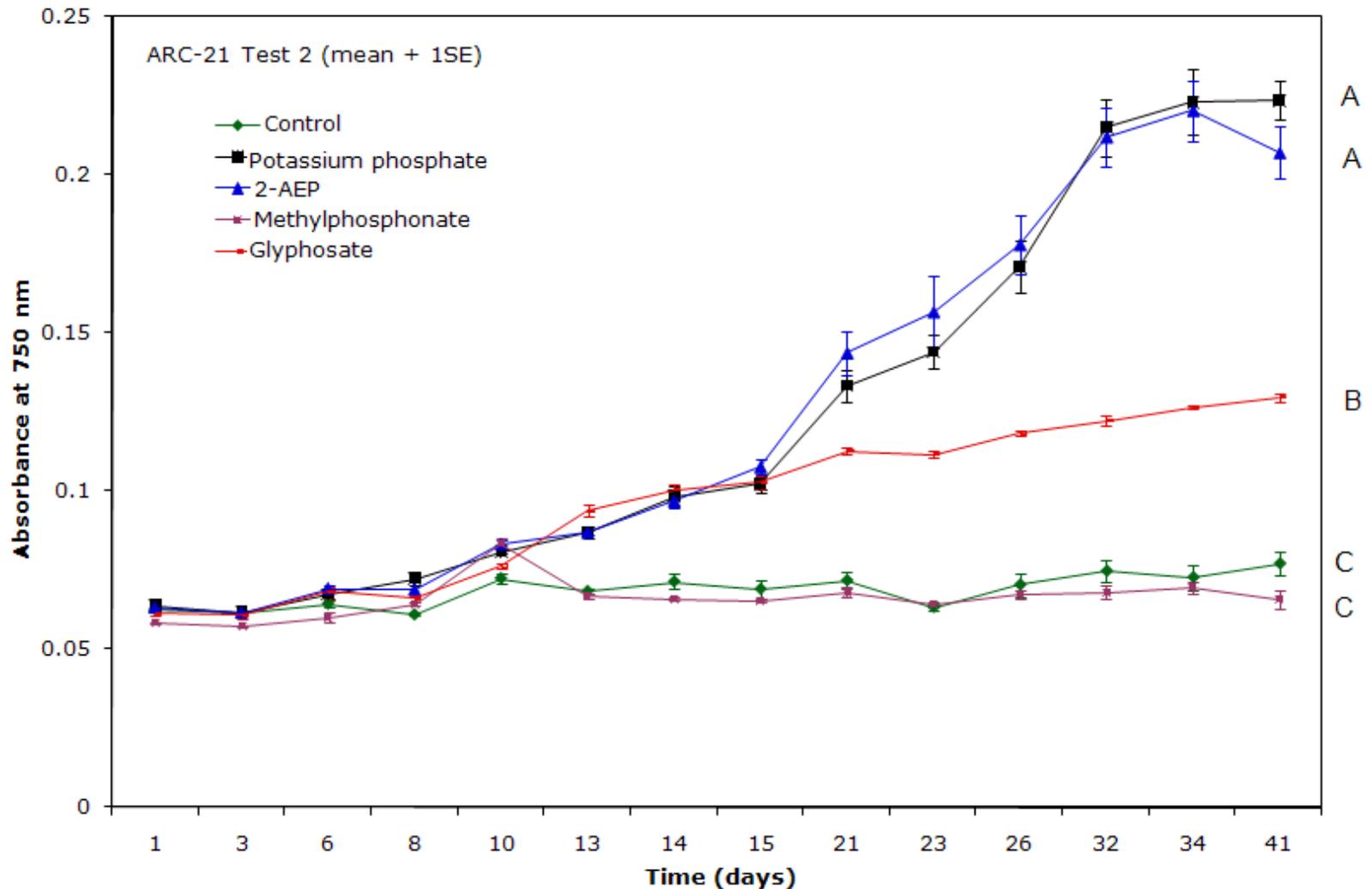
Healthy good algae, no toxic algae
GOOD!

Stimulation of toxic algae?
BAD!

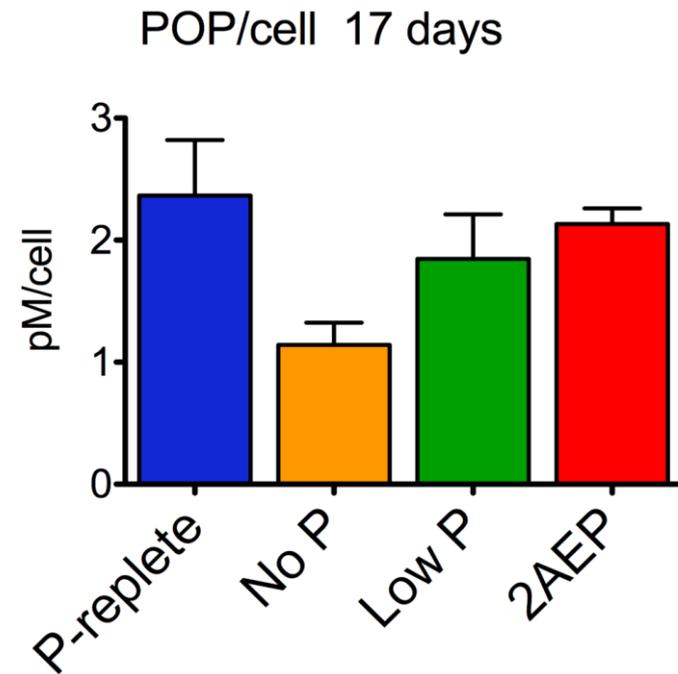
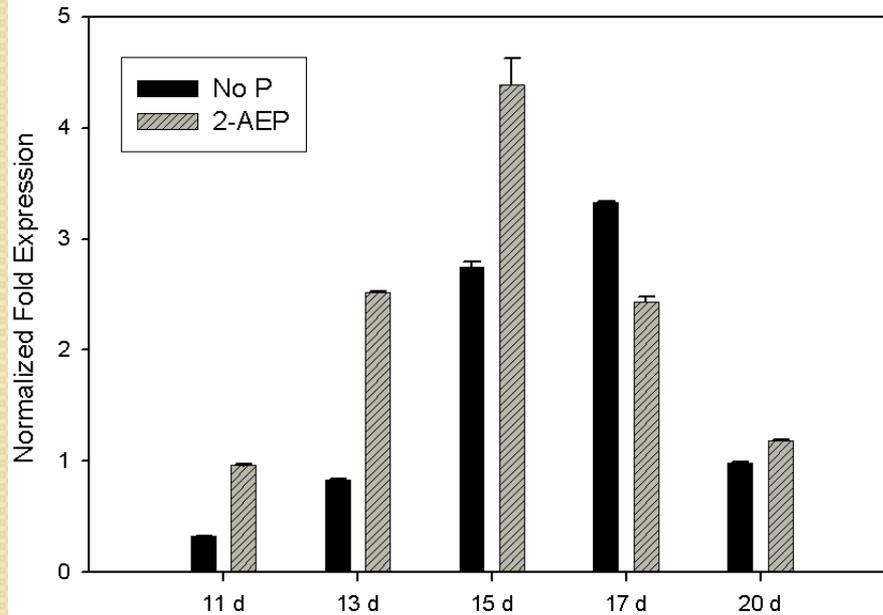
Freshwater *Synechococcus* spp. *phnD*



Growth response: *Synechococcus* sp. ARC-21



ARC-21 *phnD* expression (RT-qPCR) (freshwater)



Is there an impact?



Crop Observation and Recommendation Network
C.O.R.N Newsletter 2009-23
July 21, 2009 - July 28, 2009

Glyphosate and Phosphorus Robert Mullen, Keith Diedrick

There was a recent article in the *Columbus Dispatch* discussing the concerns with glyphosate application, and the risk of phosphorus transport to surface waters specifically in the Lake Erie Basin region of our state (actually they reference a recent publication called *TwineLine* (Brannan, 2009)). In the *TwineLine* article, they report that over 1000 metric tons of glyphosate is applied annually in the Lake Erie Basin that potentially represents a threat to water quality in the region. The original publication in *TwineLine* does report that researchers at Bowling Green State University have discovered that the phosphonate (which is different than phosphate) portion of the glyphosate molecule can be utilized by the blue-green algae found in Lake Erie. Since this issue has been raised as a concern, we thought we would run some calculations to determine the extent of the potential threat.

Is there an impact?

- 1,000 metric tons of glyphosate applied
 - 2.2 million pounds
- 15% as P
 - 330,000 pounds P
- 3.7 million acres corn, soybeans
 - 0.1 pound acre⁻¹
- NE Ohio Regional Sewer District
 - release of 365,000 pounds P
- does this represent a significant threat to water quality?
 - it depends

Fate of glyphosate

- Given the high loadings yet low levels of glyphosate in the Maumee:
 - Glyphosate is assimilated by bacteria upstream and in soil
 - nutrient source for bacteria
 - Converted to phosphates by hydrolysis
 - Enters food web upstream as a new source of phosphate

Questions / future research

- Trend in yearly applications of glyphosate in the Erie watershed?
- What about application in Ontario?
- Research should include mesocosms
 - Lifetime of glyphosate
 - Microbial/algal community shifts after glyphosate addition
- are there naturally-occurring autochthonous phosphonates?
 - test Lake Superior water
 - substrate specificity of pico phosphonatases

Conclusions: Phosphonates in the Great Lakes

- anthropogenic loadings are detected
 - glyphosate and degradation products
- freshwater picocyanobacteria possess *phn* genes
 - both Lake Erie and Superior endemic picos
- some taxa can utilize glyphosate as a sole P source