United States Environmental Protection Agency

Emerging Issues for Source Water

Cyanobacterial Cells and Toxins: Evaluating Source Water Trends and Propagation through Lake Erie Treatment Facilities

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Background

- Harmful algal blooms (HABs), and their associated toxins, in fresh water lakes and reservoirs are drawing the attention of utilities and state regulators nation-wide.

Algal bloom at Grand Lake St. Mary's, Ohio. Photo by Russ Gibson, Ohio EPA.

Background

- Recognizing the potential health and economic consequences, the US Environmental Protection Agency, in partnership with the Ohio Environmental Protection Agency (OEPA) and participating utilities, began sampling the raw water and treatment trains of Lake Erie drinking water treatment facilities:
  - 2013 bloom season: Four (4) western and two (2) eastern
  - 2014 bloom season: Five (5) western and two (2) eastern

Project goals

- Track seasonal bloom development
- Follow the propagation of cyanobacterial cells through the entire treatment process
- Follow the propagation and control of toxins through the treatment process using an enzyme-linked immune substrate (ELISA) assay
- Quantify other dissolved constituents associated with bloom activity, including nitrate, nitrite, ammonia, and phosphate

Sampling

- Monthly sampling
- Six (6) to eight (8) locations per plant:
  - Raw (without permanganate)
  - Post permanganate
  - Post PAC
  - Clarifier effluent
  - Filter effluent prior to chlorination
  - Filter effluent after chlorination
  - Finished water (distribution system entry point)

Sampling

For each sampling event, participating facilities were asked to provide the following information (if available):

- Raw temperature
- Raw pH
- Raw turbidity
- Target permanganate dose (if facility practices permanganate addition)
- Target chlorine dose at all points of application
- Finished water chlorine residual

Core Analyses

- Chlorophyll *a*
  - Proxy for intact cells
- ELISA
  - Total microcystins + nodularin
  - Total (intracellular + extracellular)
  - Extracellular

Chlorophyll A Sample Preparation

Filtration
(0.7 µm nominal pore size glass fiber)

↓

Filter and cell disruption
by bead beating

↓

Solvent extraction
(90% acetone/10% DI water)

↓

Centrifugation

↓

Fluorescence analysis

ELISA Sample Preparation

Raw sample

Left branch:

3 x freeze/thaw
@ -20 ºC

↓

Centrifuge
15 min. @ 3000 x G

↓

Recover supernatant

↓

ELISA analysis

Right branch:

Centrifuge
15 min. @ 3000 x G

↓

Recover supernatant

↓

ELISA analysis

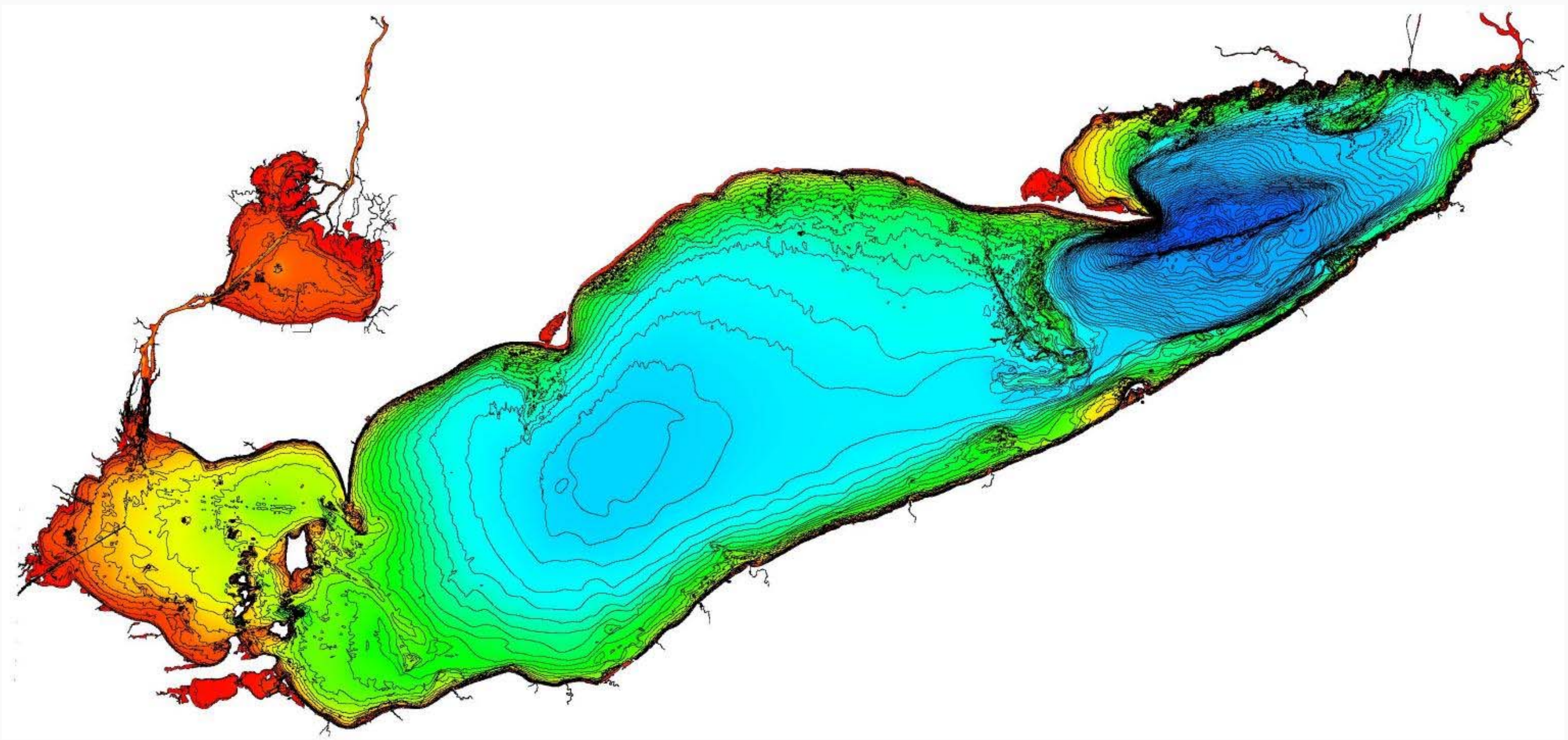
Notes for Chlorophyll and ELISA Data

- Chlorophyll A reporting limit = 0.0044 ppb
  - The chlorophyll A assay, as executed in this study, is a proxy for the concentration of intact cells in suspension.
- Total microcystin & nodularin by ELISA reporting limit = 0.15 ppb
  - The ELISA assay employed in this study reacts with <u>all</u> microcystin congeners.

Naming Conventions

- Treatment facilities assigned a code name
- Western or eastern
- Number based on when they were enrolled in the sampling program, not on their relative geographic position

Study Area

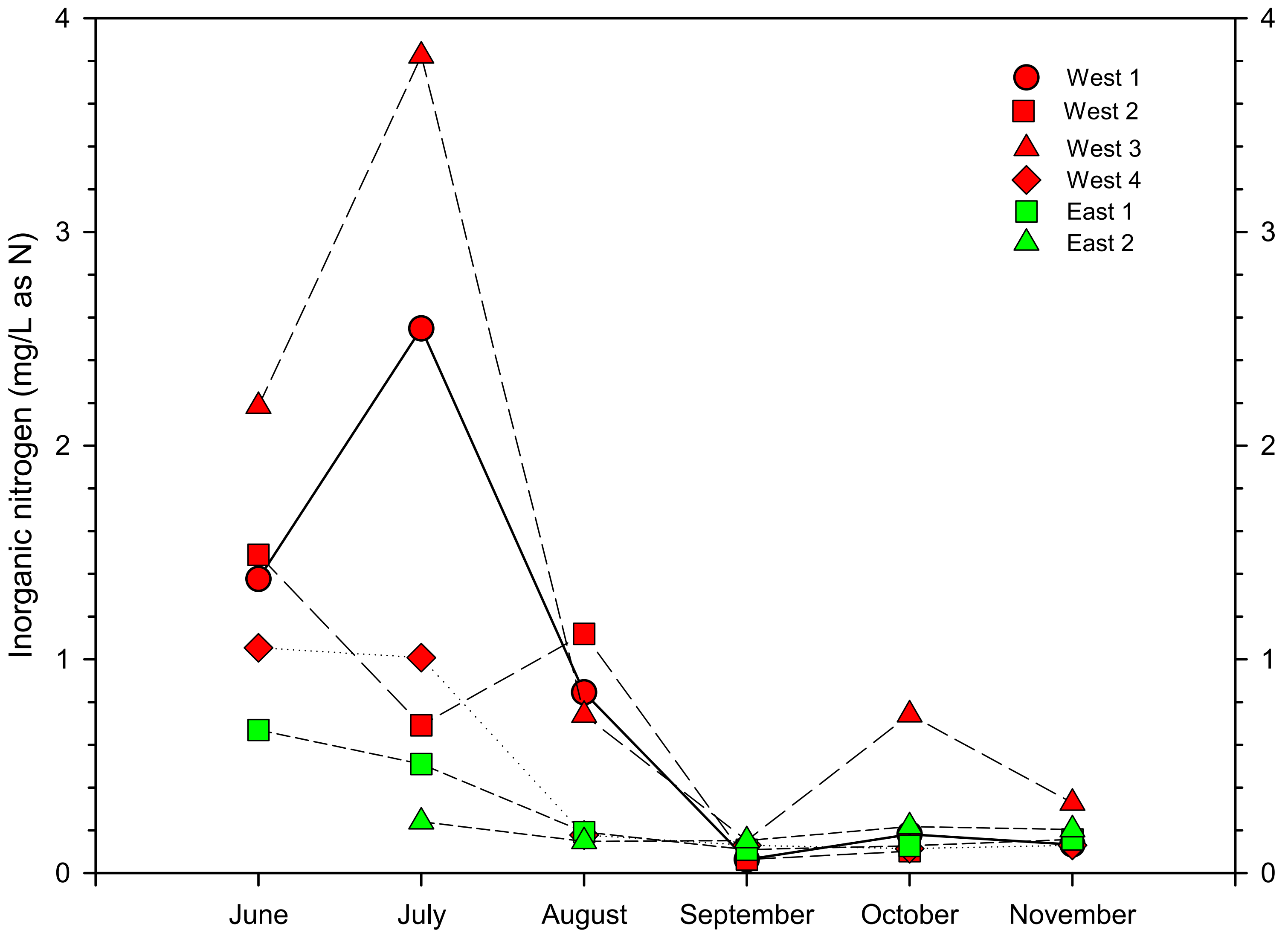


West | East

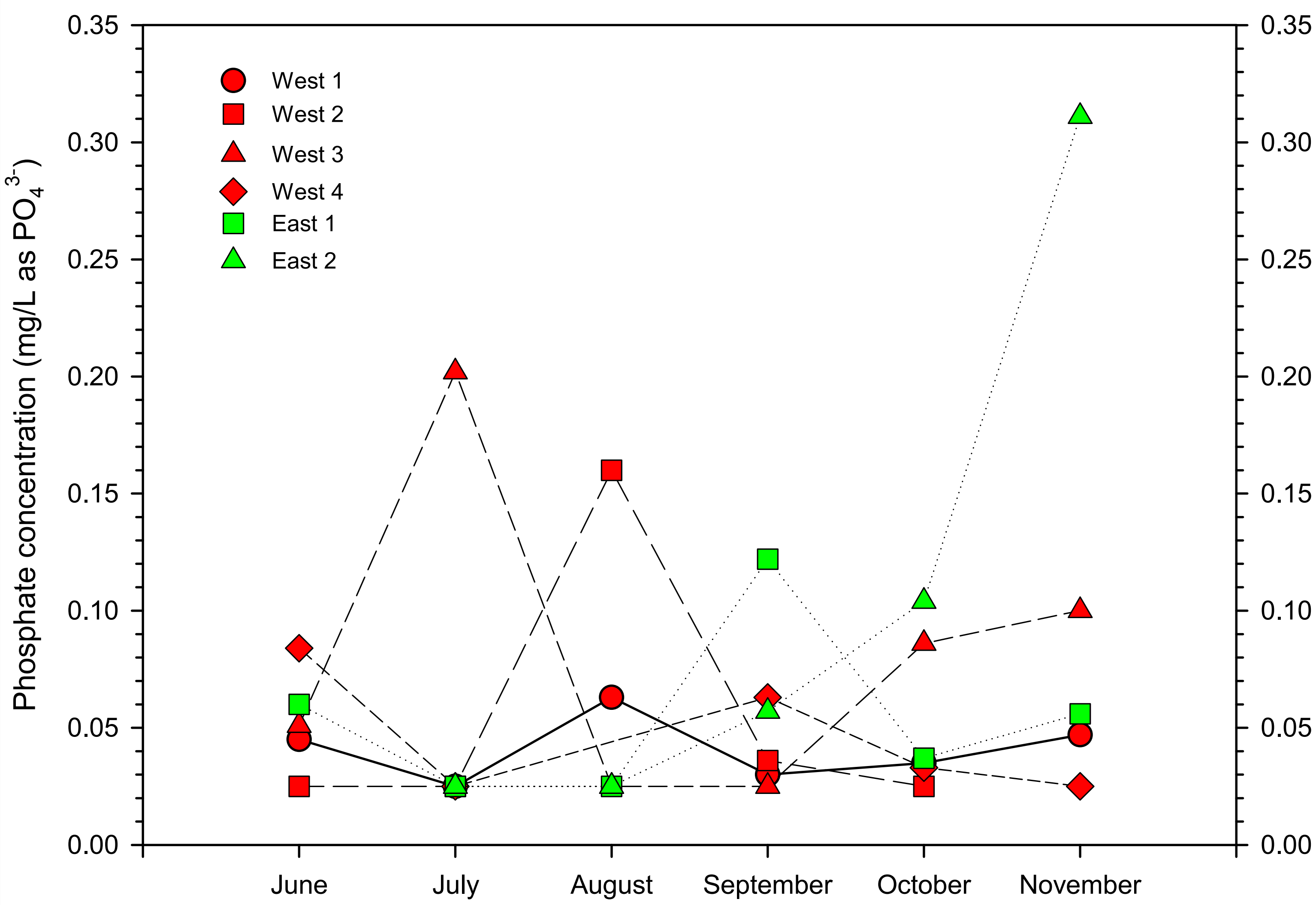
Source: National Oceanic and Atmospheric Administration

Water Quality Indicators Associated with Bloom Development

Lake Erie Bloom Development – 2013 Season
Inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$)



Lake Erie Bloom Development – 2013 Season
Phosphate



Lake Erie Bloom Development
Early 2014 Season

Treatment plant	Mean NH_4^+ (mg/L as N)	Mean inorganic nitrogen $NH_4^+ + NO_2^- + NO_3^-$ (mg/L as N)
West 1	< 0.03	1.6
West 2	0.044	2.5
West 3	0.081	1.7
West 4	0.094	1.3
West 5	0.26	1.0
East 1	0.048	0.43
East 3	< 0.03	0.70

Western basin

Eastern basin

Ammonia Metabolism

- Oxidation of Ammonium to Nitrite

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+$$

- Oxidation of Nitrite to Nitrate

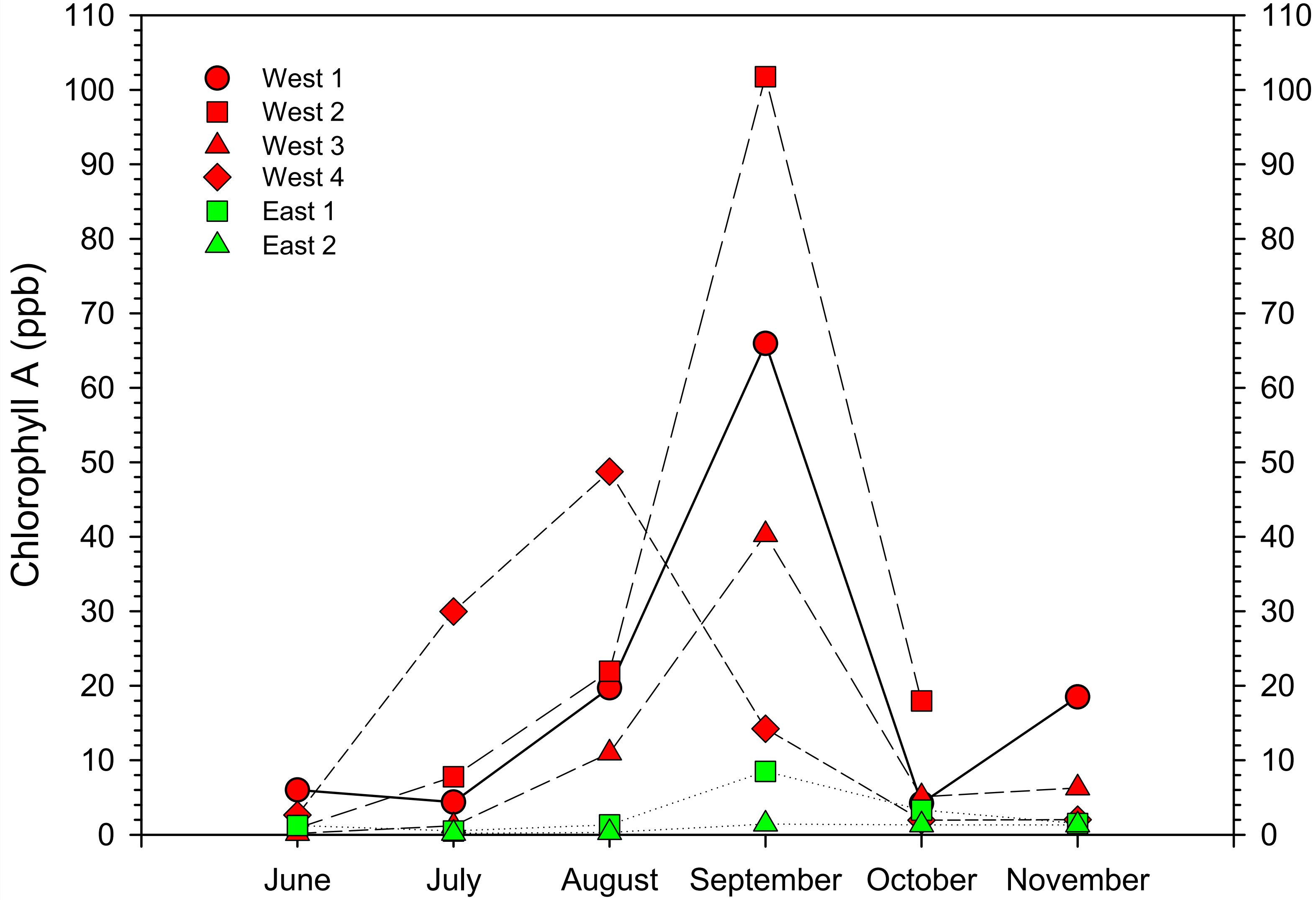
$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$$

- Complete Nitrification Reaction

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O$$

Treatment Plant Influent Chlorophyll Results

Lake Erie Bloom Development – 2013 Season
Chlorophyll A



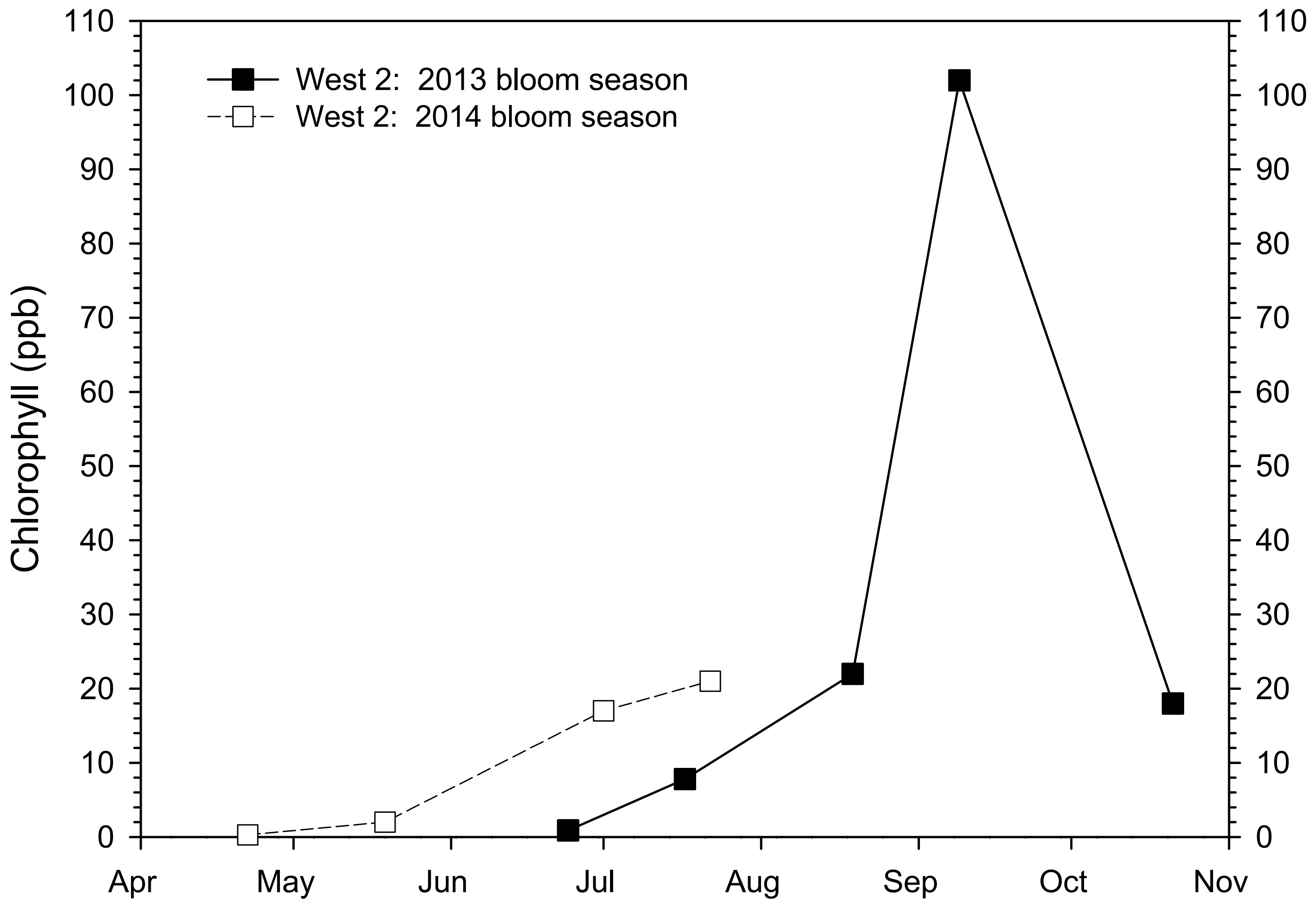
Chlorophyll A Summary - 2013 Bloom Season

Chlorophyll A Treatment plant influent (µg/L)	Mean	Minimum	Maximum
West 1	20	4.2	66
West 2	31	0.89	102
West 3	11	0.17	40
West 4	17	1.9	40
East 1	2.7	0.50	8.5
East 2	0.91	0.19	1.4

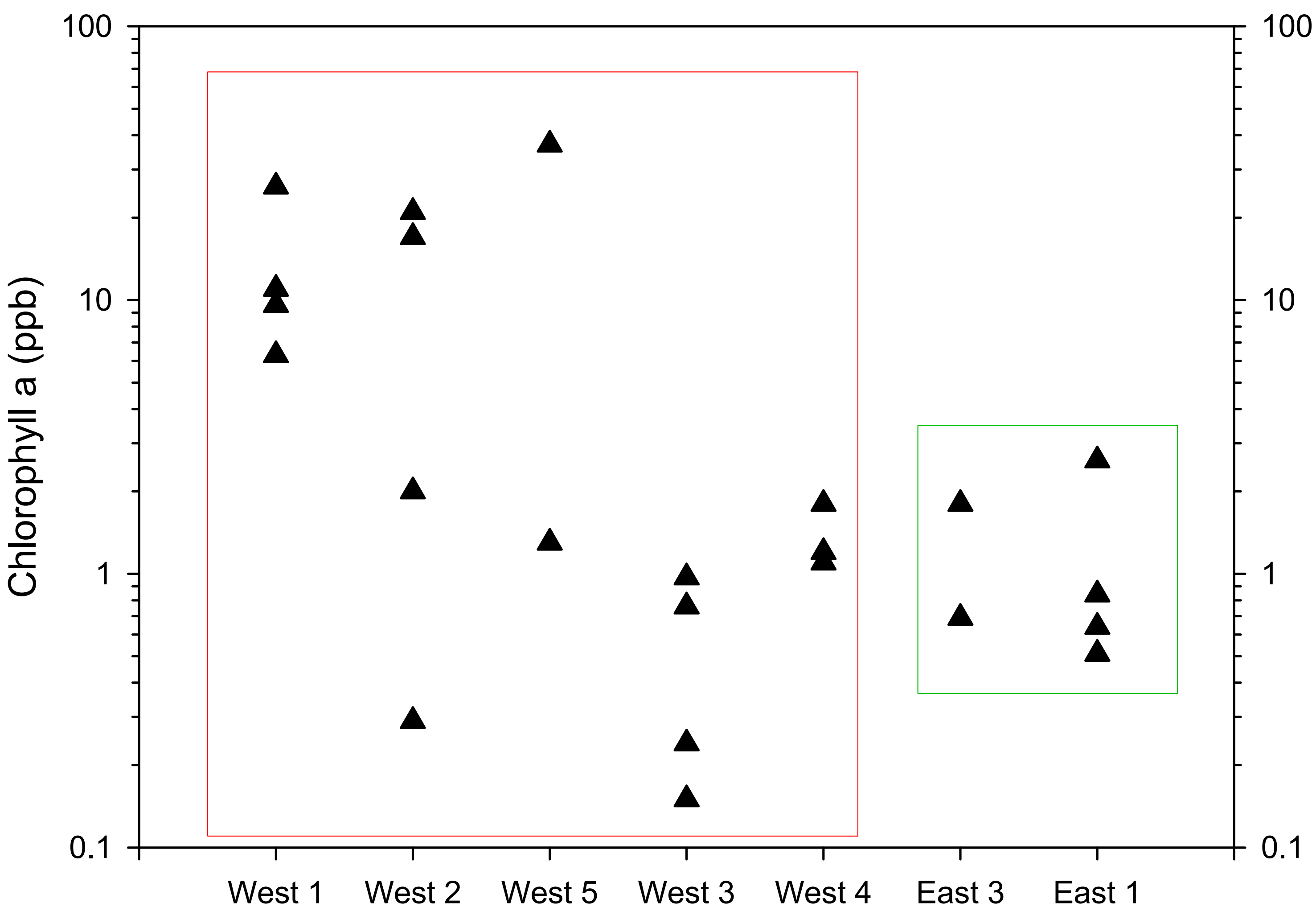
Western basin

Eastern basin

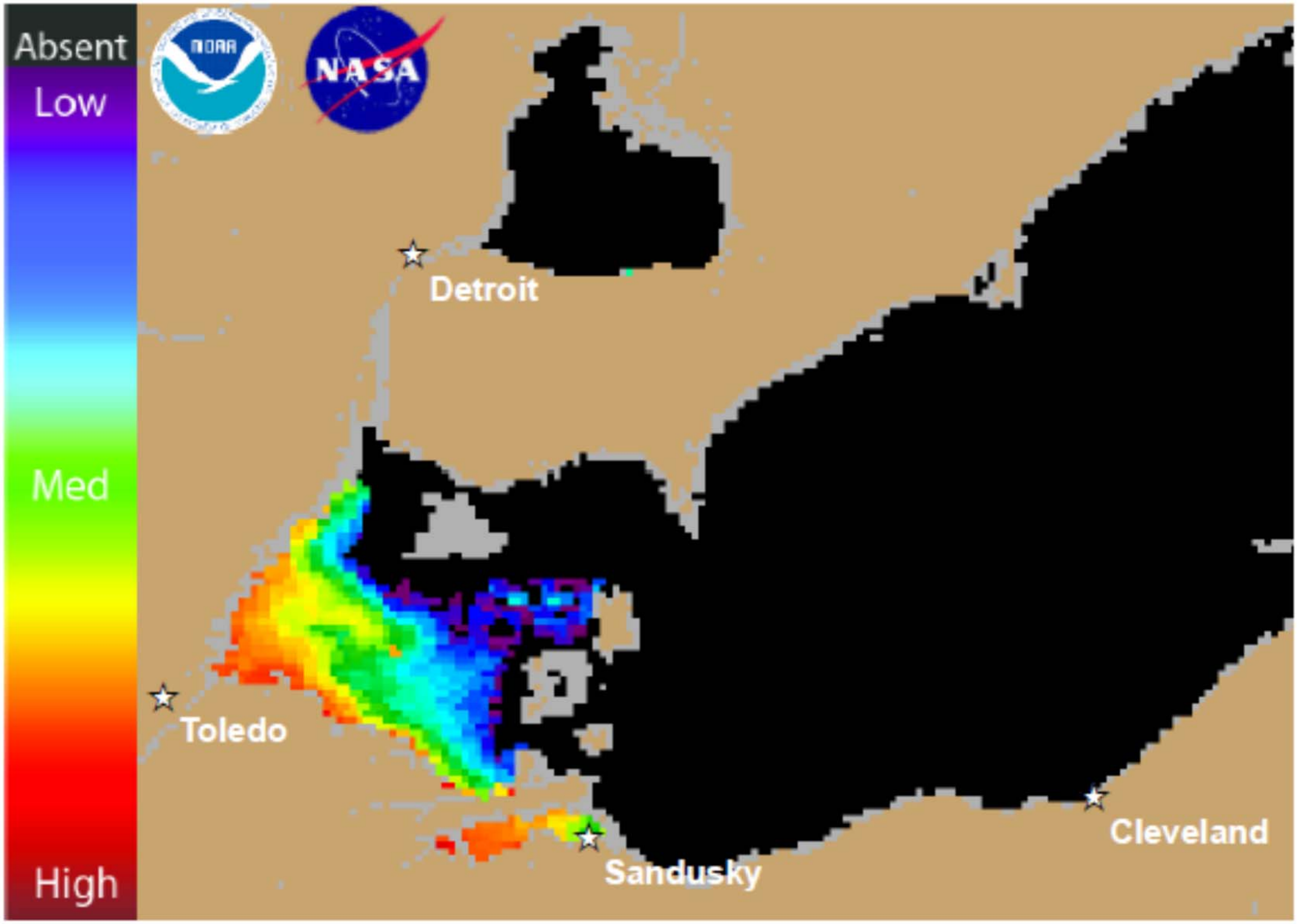
West 2 Raw Chlorophyll: 2013 vs 2014



Chlorophyll A – Early 2014 Bloom Season (West to East)



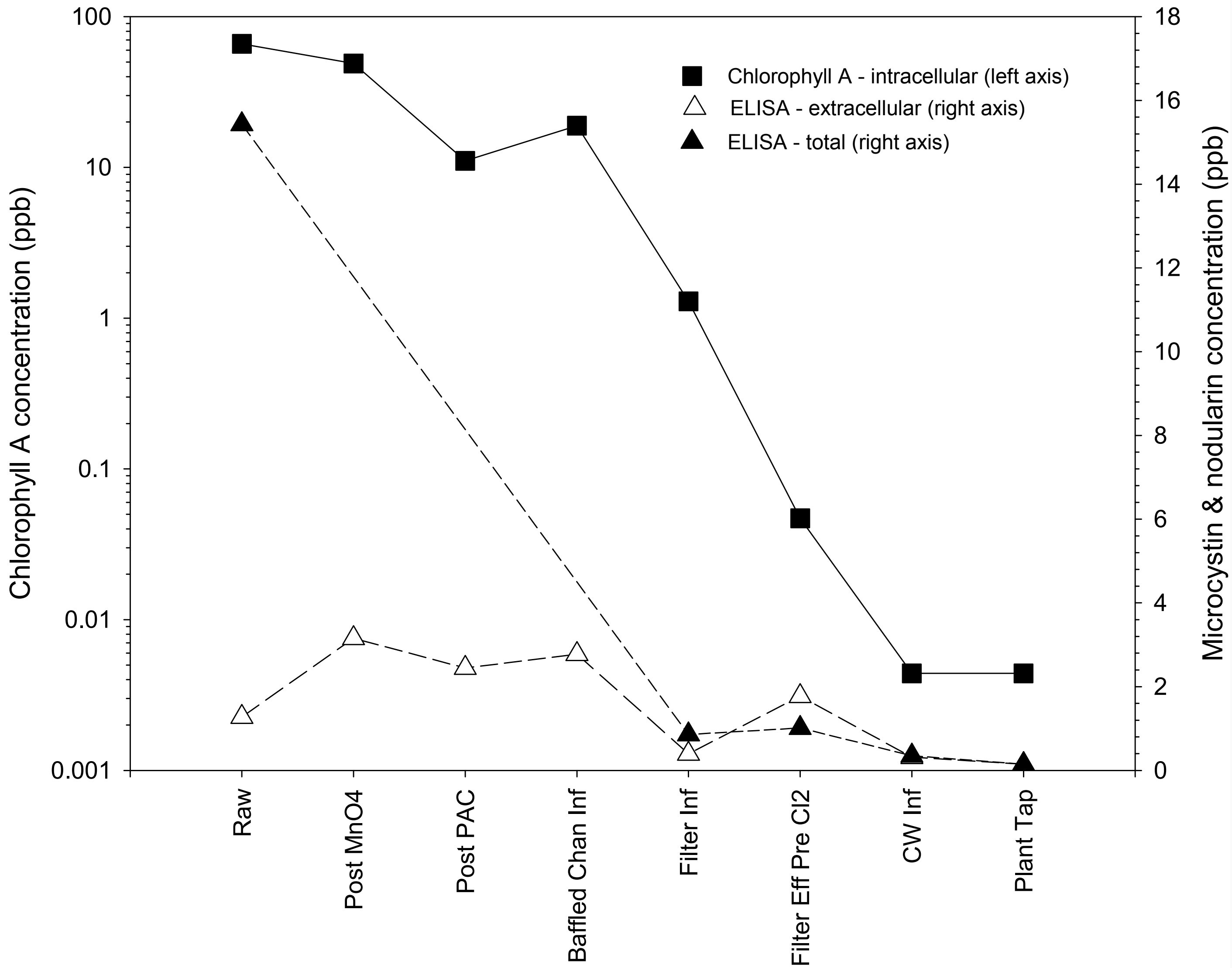
Lake Erie Bloom 6 August 2014



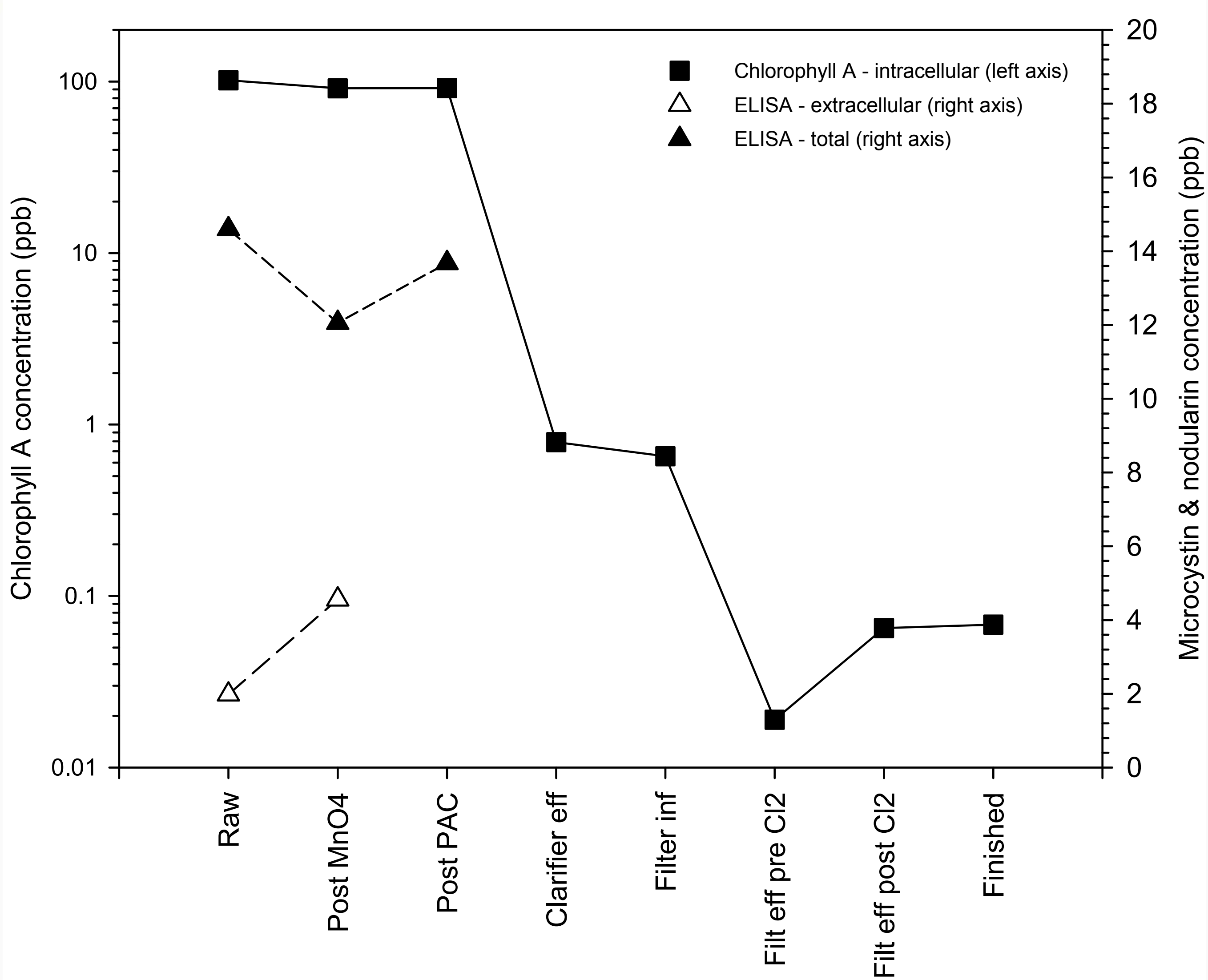
Sources: National Oceanic and Atmospheric Administration; National Aeronautics and Space Administration

Chlorophyll and Toxin Profiles

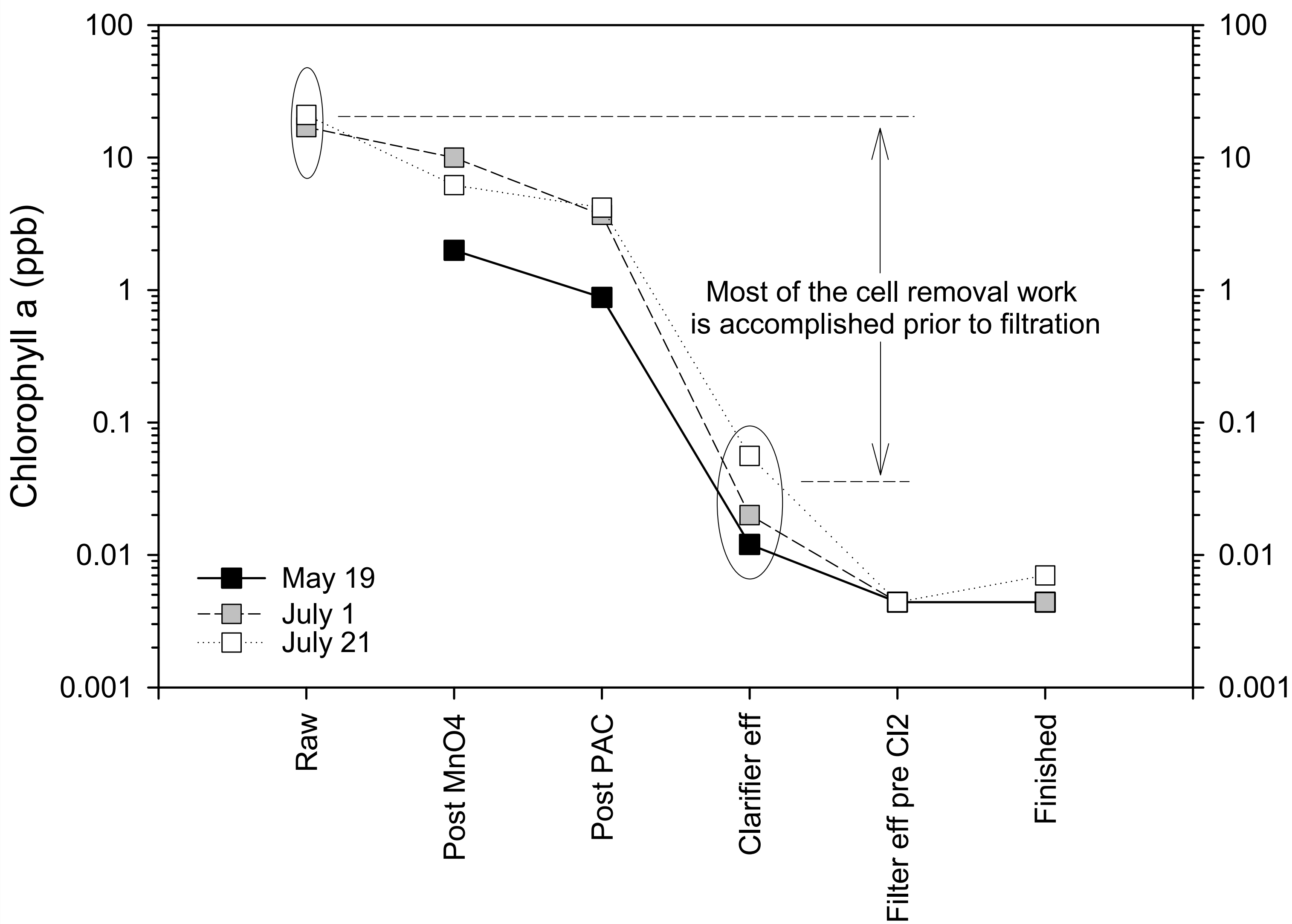
West 1: 9 September 2013



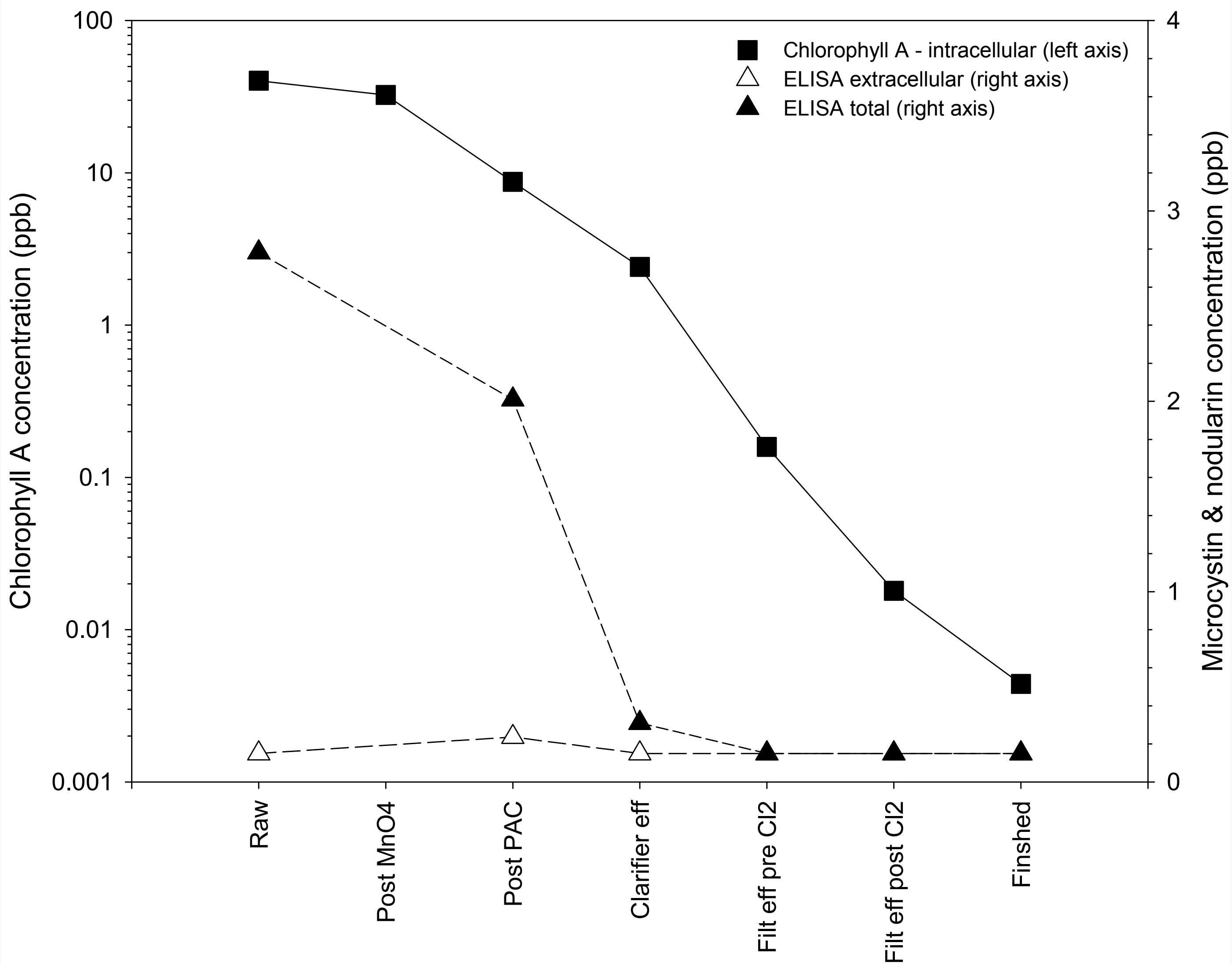
West 2: 9 September 2013



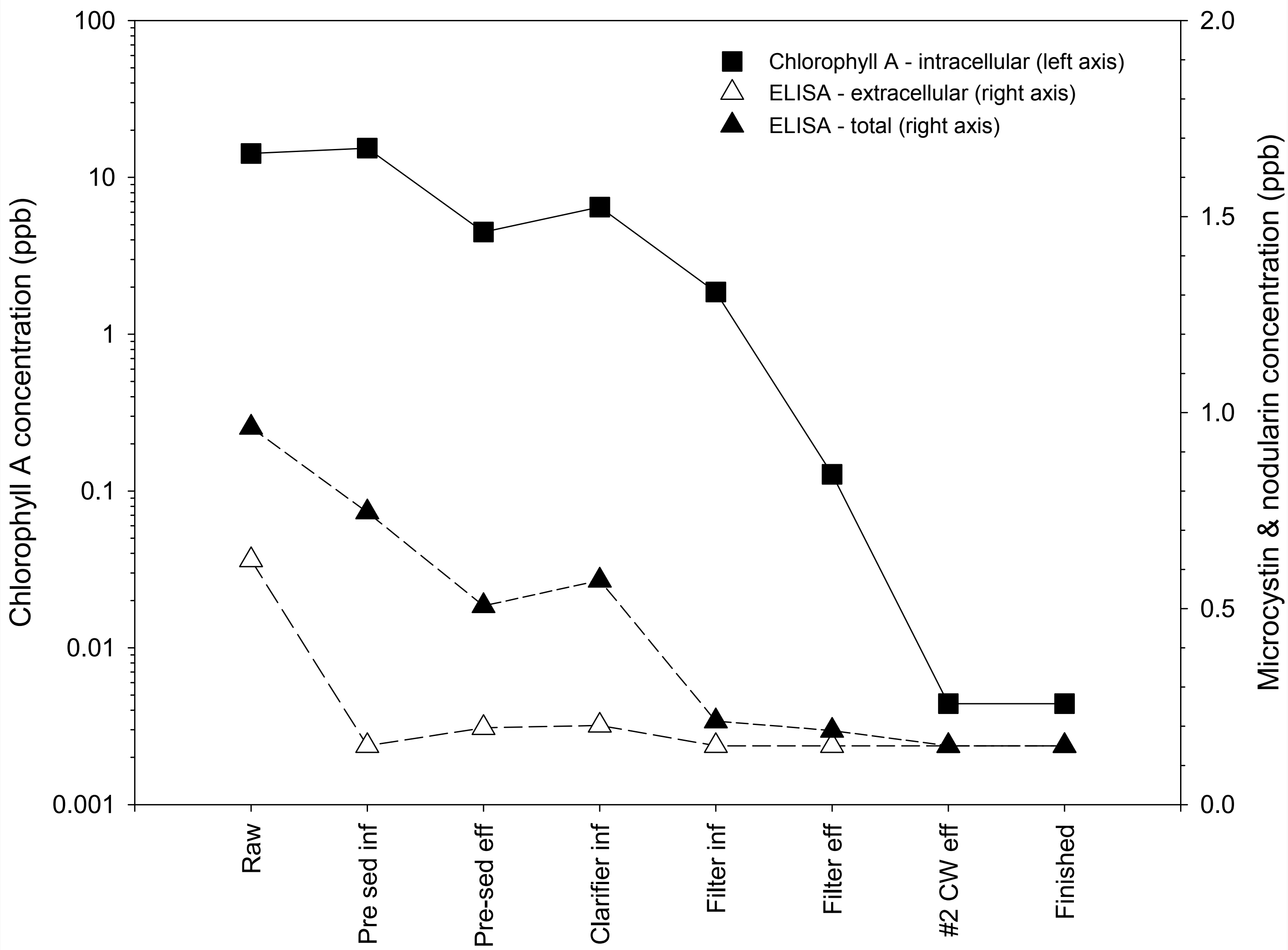
West 2 2014 Chlorophyll a Profiles



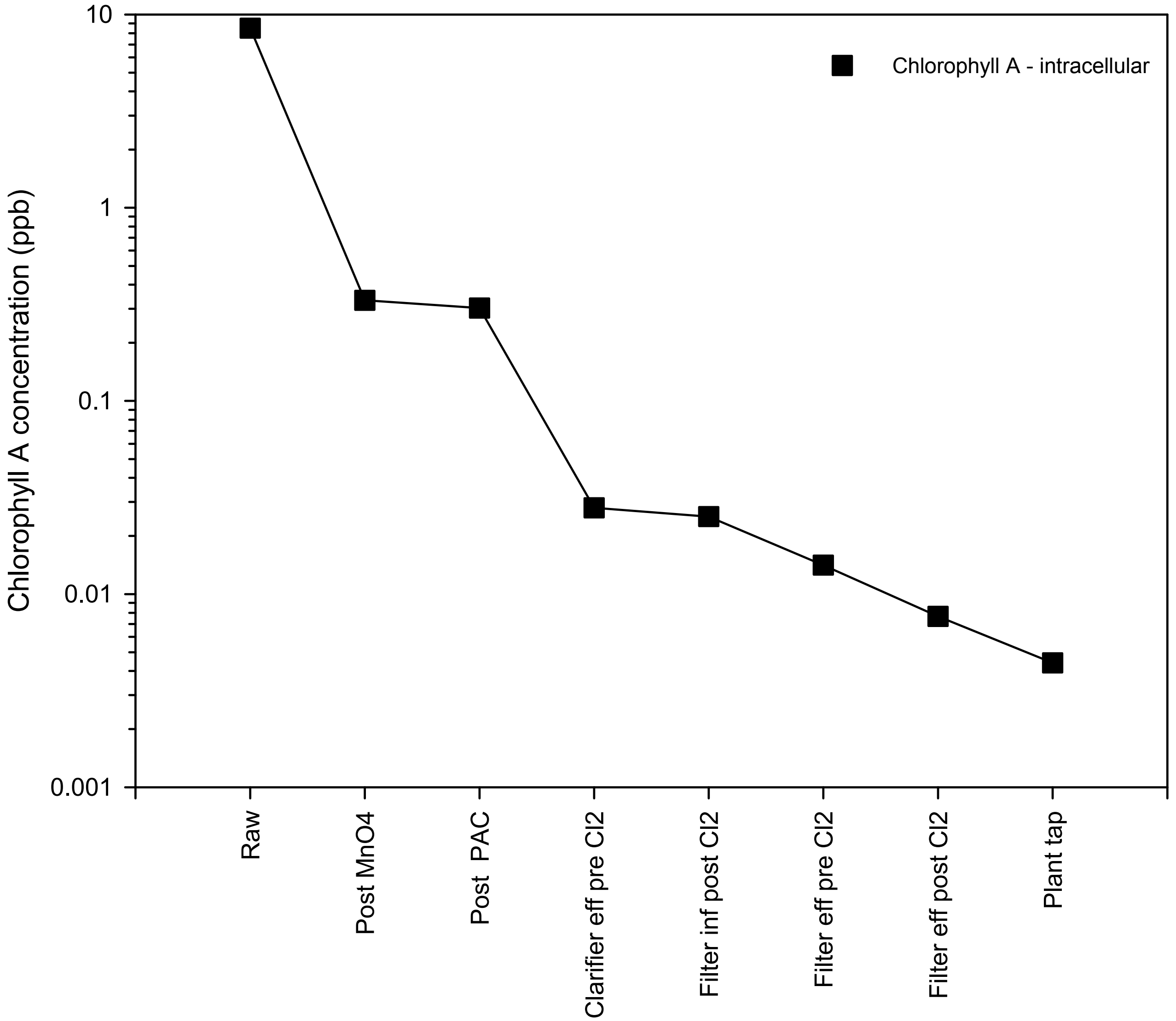
West 3: 9 September 2013



West 4: 9 September 2013



East 1: 9 September 2013



East 2: 2013 Bloom Season

Chlorophyll A – intracellular (ppb)

Sampling Date	Influent	Plant tap
9 July	0.186	< 0.0044
12 August	0.297	< 0.0044
10 September	1.42	< 0.0044
28 October	1.32	< 0.0044
18 November	1.32	< 0.0044

Early treatment stages are critical

Treatment Facility	Cyanobacteria cells removed during bloom peak sampling event[1]- plant influent to clarifier effluent (%)
West 1	98
West 2	99
West 3	94
West 4	11 + 88[2]
East 1	99

[1]Bloom peak sampling event was 9/9/13 for West 1, West 2, West 3, and East 2; 8/14/13 for West 4.
[2]West 4 operates two clarification stages.

Early Summer vs. Late Autumn Chlorophyll A 2013 Season

Chlorophyll A – intracellular (ppb)

Location	June	November
West 1	6.0	19
West 2	0.88	18[A]
West 3	0.17	6.3
West 4	2.7	2.0
East 1	1.2	1.5
East 2	0.19[B]	1.3

[A] West 2 final sample of season collected October 21
[B] East 2 first sample of season collected July 9

Conclusions

- Treatment plant influent water quality significantly degraded in Western basin vs. Eastern basin of Lake Erie.
- Preliminary ELISA evidence indicates that the bulk of toxin in treatment facility influents is intracellular.
- This implies that a facility originally designed for particulate control can, with careful operation, serve as an effective barrier against human exposure.
- High removals of chlorophyll-A (proxy for intact cyanobacteria cells) combined with lack of finished water toxin detections support this hypothesis.

Observations

- ELISA assays are rapid, easy to perform and relatively inexpensive → attractive monitoring option.
- LC/MS assays offer the prospect of increased sensitivity, precision and specificity → long-term the necessary option to support regulatory and enforcement decisions.

Next Steps

- Increase reliability and throughput of LC/MS assay.
- Develop enough data to determine an optimum trade-off between ELISA and LC/MS use.
- Continue evaluating 2014 bloom season samples.
- Bench-scale trials to evaluate relative impacts of permanganate addition, PAC addition, pH and particulate quality.

Notice

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Thank You!

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