Treatment Protocol For Cyanotoxins (Microcystins) in a Lake Water Source.

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Presentation Outline.

- Definition of Cyanobacteria and Cyanotoxins.
- Health effects associated with Cyanotoxins.
- How are Cyanotoxins Regulated?
- How Cyanobacteria and Cyanotoxins are Source Controlled and WTP Conditioned.
- Case Study – St. Mary Lake, Salt Spring Island.

Definition of Cyanobacteria and Cyanotoxins

- Cyanobacteria are photosynthetic bacteria that are common in all freshwater and marine environments. They are often called blue-green algae but their structure, genetics and physiology identify them as bacteria.
- Global climate change is allowing cyanobacteria colonies to bloom more frequent/extensively in temperate waters and become a more widespread concern.
- 1% of cyanobacterial species have the ability to generate one or more of the toxic metabolites (i.e., microcystin) in water supplies. This has increased the potential for negative health effects in humans and in the food chain.

Definition of Cyanobacteria and Cyanotoxins.

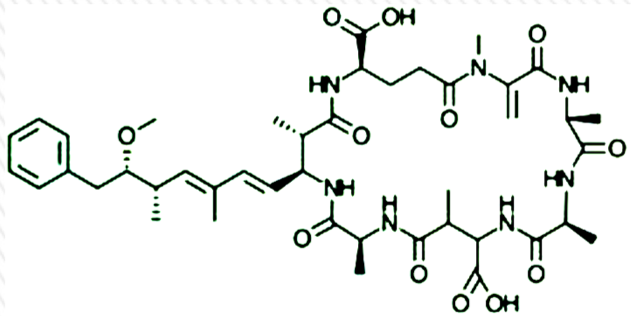
- Cyanobacteria tend to have gas-filled vesicles that allow them to regulate their buoyancy. They can float to the surface of a water body or find different levels below the surface, depending on light conditions, temperature and nutrient levels. This can cause cyanobacteria to concentrate on the water surface, causing a pea-soup green colour or blue-green "scum."
- Factors that affect cyanobacterial bloom formation and persistence include, but are not limited to, light intensity and total sunlight duration, nutrient availability (especially phosphorus and nitrogen), water temperature, pH, an increase in precipitation events, water flow and water column stability.

Definition of Cyanobacteria and Cyanotoxins.

- 3,000 genetic strains of cyanobacteria can exist in a single bloom, but not all are necessarily toxic. Species belonging to genera that can produce the cyanotoxins which cause health risks (e.g. *Microcystis, Cylindrospermopsis, Oscillatoria, Anabaena, Planktothrix, Aphanizomenon, Nodularia, and Lyngbya*) do not always do so. The ability to produce cyanotoxins is controlled by genes which can be activated by local environmental conditions.
- The exact conditions that inhibit or trigger the production of cyanotoxins remain poorly understood.

Definition of Cyanobacteria and Cyanotoxins.

- The most commonly occurring and well-studied of the cyanotoxins are the microcystins; they are of the peptide class with at least 160 reported molecular variants.



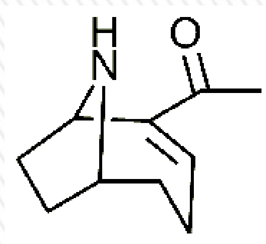
- These microcystins are water-soluble and stable; they are degraded by aquatic microbes only. They do not break down on their own, even with boiling. In fact, boiling works only to further concentrate microcystins in a given water sample.

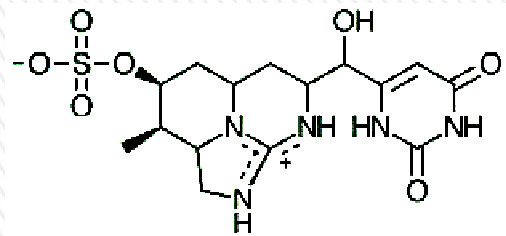
Definition of Cyanobacteria and Cyanotoxins.

- Microcystin-LR and Microcystin-LA, considered hepatotoxins, (i.e. liver toxins) are of particular concern because they are taken up by liver cells, causing weakness and anorexia/gastrointestinal issues.

Definition of Cyanobacteria and Cyanotoxins.

- Anatoxin-a, a potent neurotoxin, is typically found in its cationic form in natural waters, though changes in pH during drinking water treatment will impact the speed at which the compound is oxidized.





- Cylindrospermopsin can also damage the liver and kidneys and is a possible carcinogen.

Health Effects Associated with Cyanotoxins.

Human exposure to cyanotoxins can occur in several ways:

- Ingesting contaminated food (fish or shellfish);
- Dermal contact with water containing cyanotoxins;
- Inhaling or ingesting aerosolized toxins when recreating in waters when cyanotoxins are present;
- Consuming drinking water impacted by a toxic cyanobacterial bloom.

Health Effects Associated with Cyanotoxins.

- Health effects of cyanotoxins can be acute or chronic and have been observed in the liver, nervous system and gastrointestinal system.
- Liver cyanotoxins (i.e., microcystins) are the most commonly found in cyanobacteria blooms and the most frequently studied.
- Microcystin-LR poisoning is associated with abdominal pain, vomiting and diarrhea, liver inflammation and hemorrhage, acute pneumonia, acute dermatitis, kidney damage, potential tumor growth promotion.

Health Effects Associated with Cyanotoxins.

- Anatoxin-a targets the nervous system and at very high levels of exposure can induce paralysis and death by respiratory failure.
- Other symptoms include tingling, burning, numbness, drowsiness, incoherent speech, salivation and respiratory paralysis leading to death.
- Other non-lethal cyanotoxins can trigger fevers, headaches, muscle and joint pain, diarrhea, vomiting or allergic skin reactions.

How are Cyanotoxins Regulated?

- The absolute concentration of cyanobacteria and cyanotoxins is minute (NOM is often present at thousands of times the concentration of cyanotoxins). However, this very low concentration is nonetheless significant.
- St Mary Lake TOC 4.5 mg/L

  Microcystin 0.25 – 5.0 µg/L
- The US EPA has included cyanotoxins on their Contaminant Candidate List.
- No firm MCL has been established but there are worldwide guidelines, including some in Canada.

How are Cyanotoxins Regulated?

- Heath Canada has an Advisory Level for Microcystin LR of 1.5 µg/L. Quebec, in addition to Microcystin LR, also regulates Anatoxin a to 3.7 µg/L.
- The US Environmental Protection Agency (USEPA) developed 10-day Health Advisory Levels (HALs) for two the cyanotoxins of concern, microcystins and cylindrospermopsin.
- Total USEPA microcystins advisory levels are 0.3 µg/L for children younger than school age (<6 years old) and 1.6 µg/L for all other age groups. Cylindrospermopsin advisory levels are 0.7 µg/L for children younger than school age and 3.0 µg/L for all other age groups.

How are Cyanotoxins Regulated?

Specific drinking water advisory levels for microcystin and other cyanotoxins as of January 2016.

Agency	Microcystins (µg/L)	Anatoxin-A (µg/L)	Cylindrospermopsin (µg/L)	Saxitoxin (µg/L)
USEPA Children	0.3	None	0.7	None
USEPA (2015) All Other age groups	1.6	None	3.0	None
WHO (LR only)	1	None	None	None
Health Canada (LR only)	1.5	None	None	None
Quebec (LR only)	1.5	3.7	None	None

Cyanotoxin Source Water Treatment Protocols.

- Many factors come into play when controlling a cyanobacteria boom in a lake water source. Some blooms develop when the water reaches a warm enough temperature. Others form when the lake turns over in late summer or early fall. Blooms may occur either after a substantial rain event or after a series of sunny days.
- Operator observations, based on historical knowledge, are important as are more quantitative and qualitative monitoring options.

Cyanotoxin Source Water Treatment Protocols.

Buck Lake – Pender Island.

Quatse Lake – Van Island.

Cyanotoxin Source Water Treatment Protocols.

St Mary Lake – Salt Spring Island.

Cyanotoxin Source Water Treatment Protocols.

St Mary Lake – Salt Spring Island.

Cyanotoxin Source Water Treatment Protocols.

- During the warm summer months, sampling frequency might need to be increased; also sample immediately following wet weather events, especially if the source water is impacted by nutrient loading from runoff.
- The time of day when samples are collected can be important as buoyant cyanobacteria may accumulate near or at the water surface at night, therefore sampling later in the day and maintaining consistent sampling times for each sampling location is preferred.
- A combination of environmental factors (including but not necessarily limited to temperature, pH, turbidity, nutrient concentrations, and dissolved oxygen) can influence the formation of cyanobacteria blooms.

Cyanotoxin Source Water Treatment Protocols.

- Proactive source water control options include aeration and sonication, riparian buffers, wetlands to attenuate nutrient transport to lakes/reservoirs, or even the use of shade covers.
- High capital investment and labour costs.
- Reactive measures include the use of algaecides (not recommended), artificial mixing, phosphorus (nutrient) control by sequestration (ppt out P with alum) or hypolimnetic aeration, and dredging.
- Less effective and just as expensive.

Cyanotoxin WTP Conditioning Protocols.

- Not all cyanobacteria are capable of cyanotoxin production. Those that are capable do not necessarily produce cyanotoxins at all times; toxin production can vary both between and within blooms.
- The toxin release activation triggers are not known or well understood.
- Intracellular cyanotoxins are contained within whole and intact cells and are relatively easy to remove as long as the cells are not lysed (dissolution, damage, or destruction of cells) prior to or during the treatment process.

Cyanotoxin WTP Conditioning Protocols.

- Cyanotoxins can be released naturally at low concentrations from intact cells, but are more often released from stressed, damaged or otherwise lysed cells.
- These released cyanotoxins dissolve into the surrounding water to become extracellular cyanotoxin. Extracellular cyanotoxins are far more challenging to treat and remove than intracellular cyanotoxins.

Cyanotoxin WTP Conditioning Protocols.

- "Do it Right" – If cyanobacteria-laden water is properly managed, 95% – 98% of all cyanotoxins will remain internal to intact cells as intracellular toxin and will be readily removed by coagulation and filtration.
- "Do it Wrong" – If the cyanobacteria are improperly managed, (i.e. killed, stressed, or otherwise damaged to lysis) then the purveyor has to treat for extracellular cyanotoxins, and the protocols become far more sophisticated. Treatment options/protocols will include physical removal with NF, adsorption onto PAC/GAC, or oxidization/deactivation.

Cyanotoxin WTP Conditioning Protocols.

- Pre-oxidation, and especially pre-chlorination is not recommended. Chlorination and most other pre-oxidation processes may lyse cells, causing the cyanotoxins contained within to be released. Ozone may be an exception because it both lyses cells and oxidizes the cyanotoxins.
- If pre-oxidation is required for other reasons, such as improved coagulation efficiency, or T & O (Taste and Odour) issues, then potassium permanganate ($KMnO_4$) can be considered in low dosages as it is an effective oxidizing agent against microcystins and anatoxins. $KMnO_4$ is generally not effective against cylindrospermopsin.

Cyanotoxin WTP Conditioning Protocols.

- For intracellular cyanotoxins, conventional coagulation, flocculation and filtration are recommended.
- Many cyanobacteria have gas vesicles and tend to be buoyant. DAF is therefore a far more effective option than conventional sedimentation treatment.
- Sedimentation : 70 – 90% removal rate.
- Dissolved Air Floatation : 92 – 98% removal rate.
- Consider pre-treatment with Powdered Activated Carbon (PAC) at 20 mg/L - 30 mg/L if significant extracellular cyanotoxins are thought to be present.

Cyanotoxin WTP Conditioning Protocols.

- The strategy is to limit toxin release and maximize cyanobacterial cell removal through the WTP.
- Coagulant dosage should be tied to the NOM and DOC (dissolved organic carbon) loadings in the raw water as cyanotoxin contribution is small, maybe only 1/1000th of the total organic content.

St Mary Lake	TOC	4.5 mg/L
	Microcystin	0.25 – 5.0 µg/L
Treated Water	TOC	2.0 mg/L
	Microcystin	BDL < 0.1 µg/L

Cyanotoxin WTP Conditioning Protocols.

- The pH within the treatment process should be maintained above 6.0 to reduce the potential for cell lysis in the WTP.
- Conventional filtration, or better yet, microfiltration (MF), or ultrafiltration (UF) membranes, is recommended after the DAF process. However, anthracite, MF or UF are not effective against extracellular cyanotoxins.
- One recommended membrane configuration is coagulation – MF – NF – UV/H_2O_2 – Cl.

Cyanotoxin WTP Conditioning Protocols.

- Cyanobacterial cells containing cyanotoxins (including microcystin) can be remain viable, and even reproduce, for 2–3 weeks within a WTP sludge. However, within 24 hours cells can lyse and release toxin extracellularly. It is therefore paramount to decrease sludge age by increasing the frequency of both filter backwash and clarifier sludge removal.
- Sludge can also concentrate cyanobacterial cells, and become a reservoir for any toxic metabolites contained within those cells. The cells can lyse and cyanotoxins subsequently released extracellularly.
- Do not recycle backwash water to the front of the plant for re-treatment.

Cyanotoxin WTP Conditioning Protocols.

- Activated Carbon, (AC) either PAC (for pre-treatment) or GAC (post treatment – pressure filter) is a proven treatment option for all volatile organic substances. In combination with coagulation and filtration, AC is very effective against cyanotoxins.
- The amount and nature of NOM in the water greatly influences the adsorption and capacity of AC for cyanotoxin removal.
- AC, as a consequence of its source, is somewhat selective in its ability to remove contaminants, so careful selection of the best AC is required.

Cyanotoxin WTP Conditioning Protocols.

- The optimum PAC dosage is variable, but in general 20 - 30 mg/L is a reasonable starting point. Since multiple factors play into removal efficiency with PAC, it is recommended that jar testing be conducted to determine optimal dose and PAC type and to determine likely removal efficiency.
- Wood-based PAC, with mesopores between 2-50 nm, have been found to be most effective for extracellular microcystins as a short term fix.

Cyanotoxin WTP Conditioning Protocols.

- Extracellular cyanotoxins are dissolved organic molecules that will pass through coagulation, sedimentation/DAF and filtration.
- When used as a post-filter adsorption vessel, GAC can be a highly effective barrier for microcystin but must be replaced or regenerated with sufficient frequency to minimize breakthrough (defined as the effluent NOM concentration around 50 to 60% of the influent concentration.)
- Empty Bed Contact Times reported in the literature typically range from 5 to 15 minutes, although some carbon vendors recommend at least a 10 minute EBCT.

Cyanotoxin WTP Conditioning Protocols.

Cyanotoxin WTP Conditioning Protocols.

- Nano-filtration (NF) with membranes and reverse osmosis can be effective in physically removing extracellular cyanotoxins from a treated water source.
- Inactivation of the cyanotoxins is also an important treatment protocol; chlorine is effective against microcystin. However, DBP are an issue.
- Chloramines and chlorine dioxide are ineffective.
- Ozone and $KMnO_4$ are effective against microcystins and anatoxins, and do not generate DBP. However, residual tracking is not possible.

Cyanotoxin WTP Conditioning Protocols.

- UV disinfection is effective, however, the energy required (between 1,530 and 20,000 mJ/cm^2) is orders of magnitude greater than the energy required for normal disinfection, 10 and 40 mJ/cm^2.
- Advanced Oxidization, a combination of UV irradiation and hydrogen peroxide, required to generate the hydroxyl radical (OH^-), is very effective. Energy requirements are still greater than for normal disinfection, but at 400 mJ/cm^2 is manageable. Significant gains in T & O control are possible with this protocol.

Cyanotoxin WTP Conditioning Protocols.

- Best Practice – “belt and suspender approach.”
- Maintain intact cyanobacteria cells
  - Source water control.
  - Wood based PAC pre-treatment.
  - Coagulation.
  - DAF clarification (98% removal).
  - Multimedia filtration.
  - GAC adsorption vessel
  - Advanced hydroxyl radical oxidation (UV and H_2O_2)
  - Trace chlorination.

Case Study – St. Mary Lake, Salt Spring Isld.

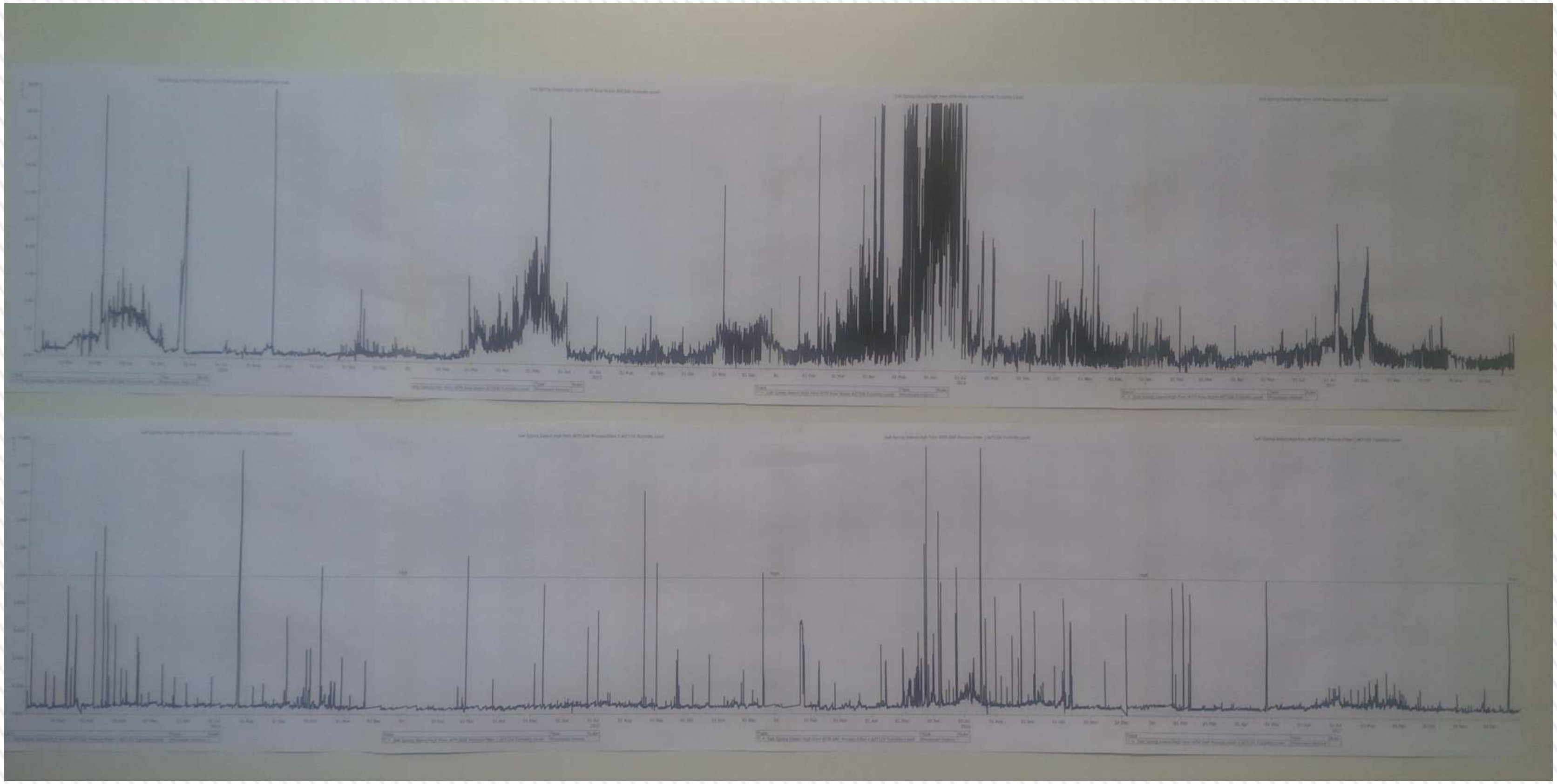
- St Mary Lake on Salt Spring Island is a shallow water body with ample sunshine and nutrients.
- Blue/green algae (cyanobacterial) blooms were historically an issue, and it was their occurrence that required a packaged DAF and UV facility to be built to replace the previous chlorination-only WTP. DBP were the obvious concern at the time.
- Prior to the 2016/17 cyanobacteria bloom, that tested positive for microcystins, the typical PACl coagulant dosage was 20 mg/L.
- Sludge, from the DAF float and backwash water, is hauled off-site for processing.

Case Study – St. Mary Lake, Salt Spring Isld.

- TOC loading in St. Mary Lake doubled from 2.17 mg/L to 4.72 mg/L between March and May of 2016. Some of this gain was expected/normal, however the operator had trouble finding the "coagulant sweet spot."
- Concurrent with the TOC increase, was an obvious cyanobacterial bloom in the Lake and a change in colour in the DAF sludge float.
- Total Algal Concentration (Natural Units or NU/ml) rose from approximately 500 to in excess of 20,000 counts. In July 2017 a count of 139,000 NU/ml was recorded.
- Raw water turbidity also rose to exceptional levels, peaking in June 2016.

Case Study – St. Mary Lake, Salt Spring Isld.

Raw and Treated Turbidity – Jan. 2014 to Dec. 2017.



Case Study – St. Mary Lake, Salt Spring Isld.

- PACl dosage had remained stable at 20 mg/L from 21 August 2014 until 29 March 2016.
- PACl dosage was at 35 mg/L by 13 April 2016, and after some experimentation, the operator settled in between 28 – 35 mg/L until 31 October 2017.
- Some $KMnO_4$ was purchased, and its use contemplated, but fortunately the decision was made to use vigilant control of the coagulation process rather than oxidation. A good choice!
- There was clearly "something different happening" and early on the CRD Aquatic Ecology Laboratory determined it was a significant enough cyanobacterial bloom to be considered a Harmful Algal Bloom (HAB).

Case Study – St. Mary Lake, Salt Spring Isld.

Magic Lake Estate – Pender Island.

Case Study – St. Mary Lake, Salt Spring Isld.

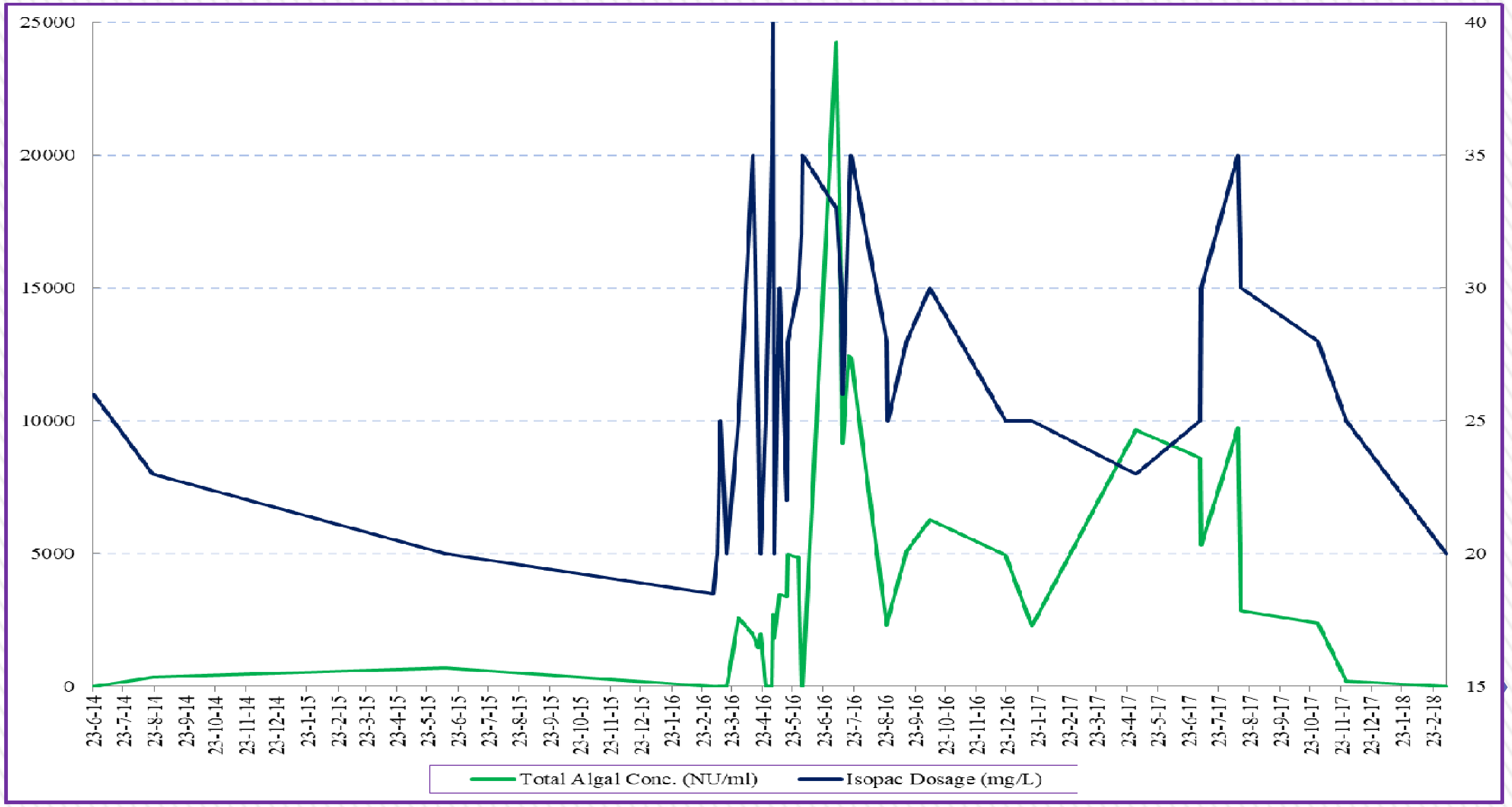
Quatse Lake – Vancouver Island.

Case Study – St. Mary Lake, Salt Spring Isld.

St Mary Lake – Salt Spring Island.

Case Study – St. Mary Lake, Salt Spring Isld.

Total Algal Concentrations vs. Coagulant Dosage.



Case Study – St. Mary Lake, Salt Spring Isld.

- During an extended 20 month period, from April 2016 to November 2017, the cyanobacterial bloom population in St. Mary Lake source water produced a measurable concentration of microcystins.
- In-house CRD testing initially confirmed the presence of microcystins. These results were verified by the Northeast Ohio Regional Sewer District who employed both the ELISA (Enzyme-Linked Immunosorbent Assay) and USEPA 544 (based on Liquid Chromatography and tandem Mass Spectrometry or LC-MS/MS) methods.
- All test methods indicated results of either Non-Detect (ND) or Below Detection Limit (BDL) on all the treated water samples.

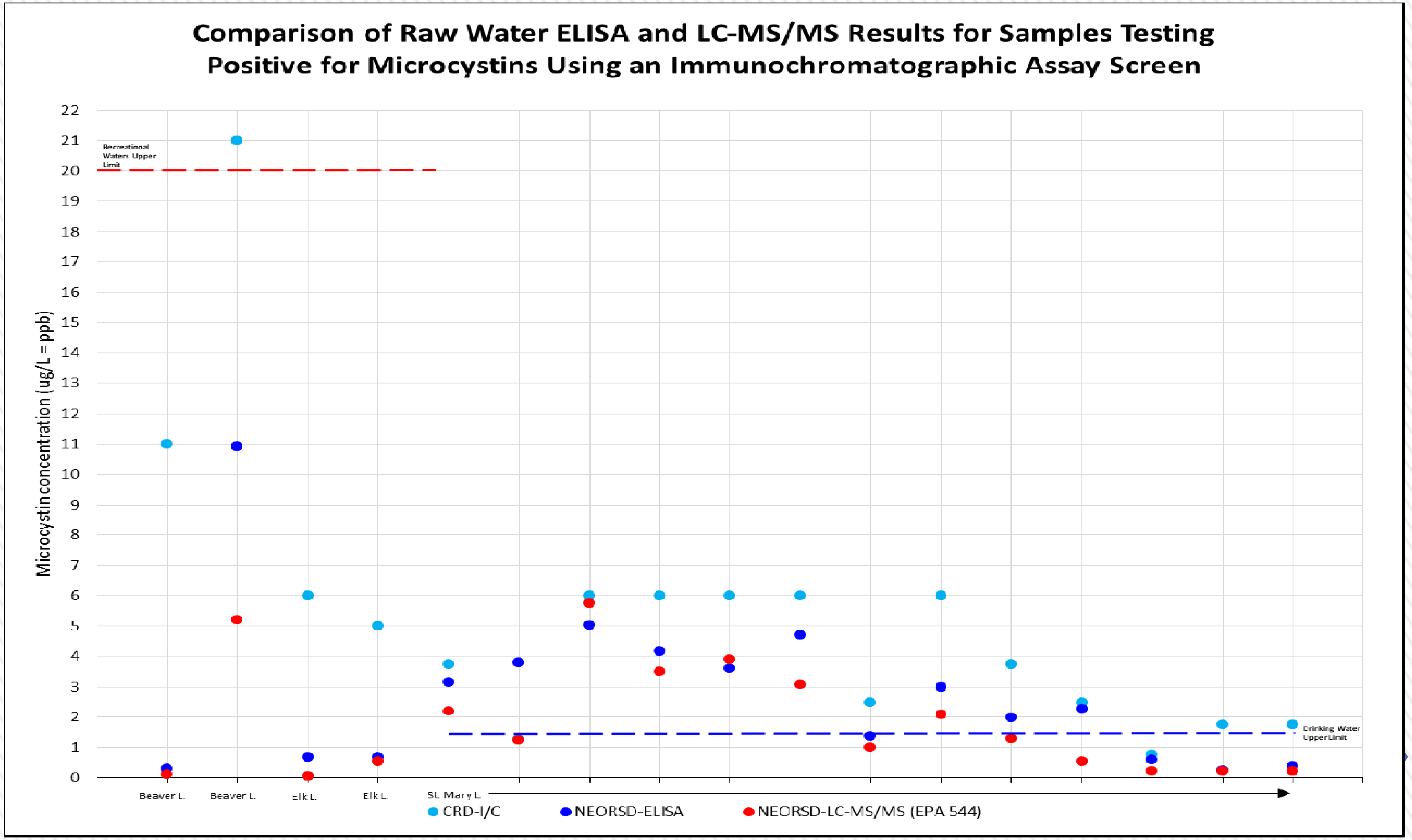
Case Study – St. Mary Lake, Salt Spring Isld.

- Quantitative analytical methods such as LC-MS/MS require rigorous preparation as well as sophisticated and expensive laboratory equipment and do not provide immediate results.
- The CRD analytical protocol used for both the raw and finished water is a Presence/Absence screening test based on an immunochromatographic (IC) assay (similar to ELISA). However, results can be obtained within 1.5 hours of sample receipt.
- External 3rd party testing from September 2016 to the end of January 2017 indicated raw water microcystin levels to be between

  0.25 – 5.0 µg/L (ELISA) and

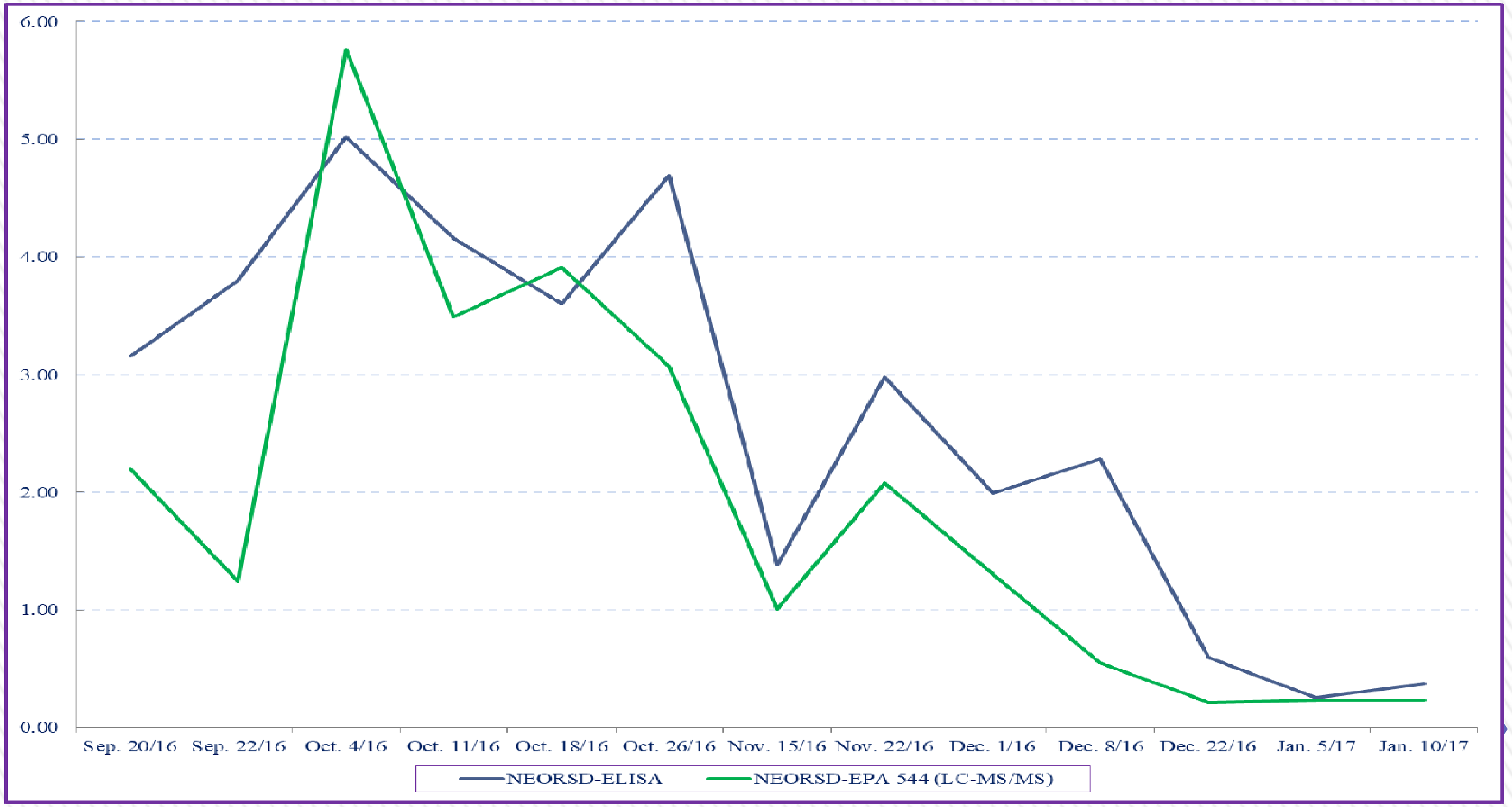
  0.21 – 5.72 µg/L EPA 544 (LC-MS/MS)

Case Study – St. Mary Lake, Salt Spring Isld.



Case Study – St. Mary Lake, Salt Spring Isld.

Validation of Microcystin Analytical Methods.



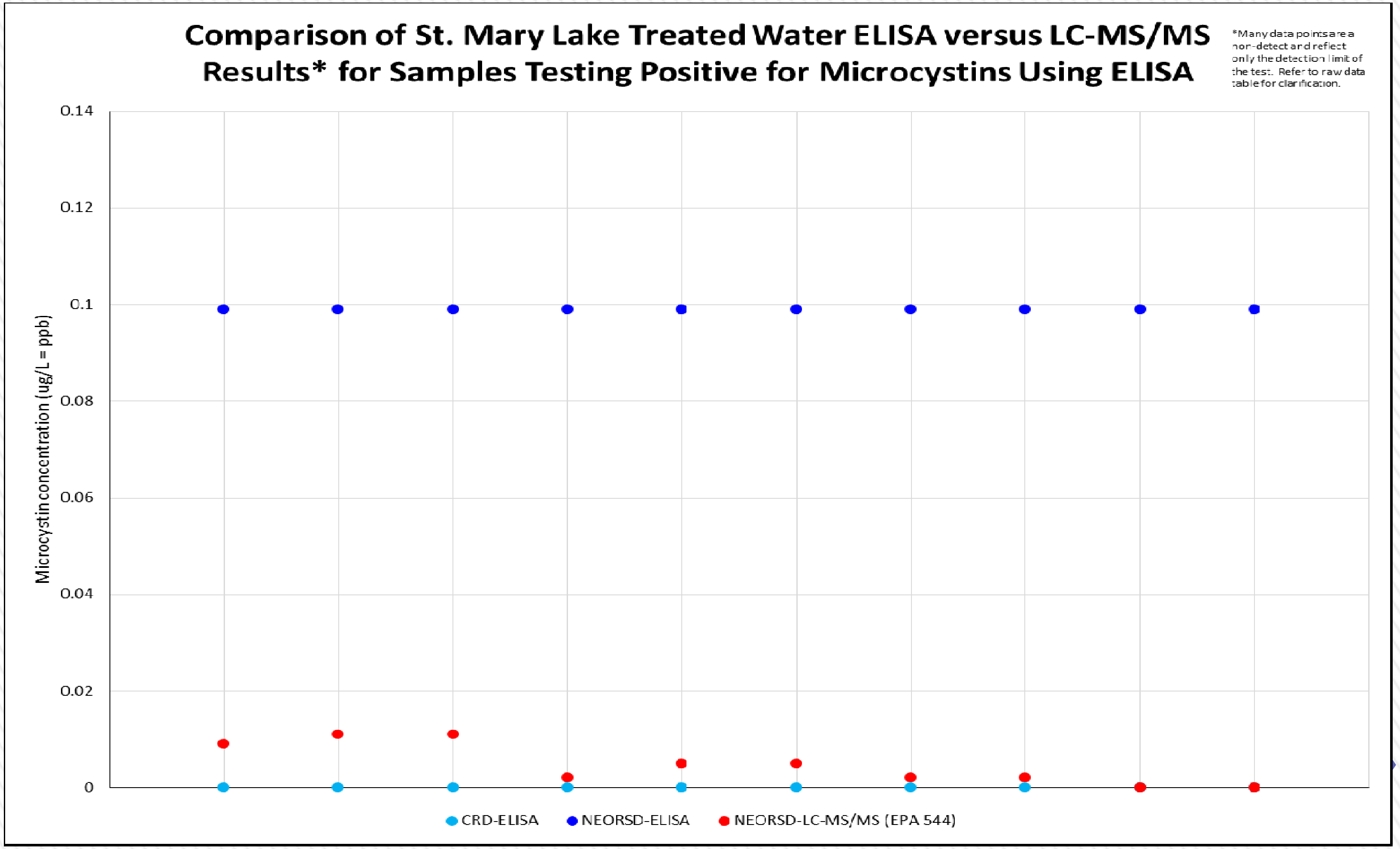
Case Study – St. Mary Lake, Salt Spring Isld.

- Extensive testing was also carried out on the treated water in 2016 and early 2017. For a 6 month period the CRD performed in-house IC Screenings and always determined the result to be BDL.
- External testing in Ohio confirmed the CRD results,

  < 0.1 µg/L (ELISA) and

  ND – 0.011 µg/L EPA 544 (LC-MS/MS)
- The CRD was confident in their analytical test protocols and the results obtained, so they continued with their weekly in-house analytical schedule.

Case Study – St. Mary Lake, Salt Spring Isld.



Case Study – St. Mary Lake, Salt Spring Isld.

- In reality this is a “good news story.”
- Local operators, local field management and the laboratory staff worked closely and employed the technical knowledge of regular suppliers to understand the observations and address them in the best way possible.
- The “Right Decisions” were made; the cyanotoxin bloom was effectively managed.
- Measured treated water microcystin levels were at BDL and Presence/Absence tests always Absent.

Case Study – St. Mary Lake, Salt Spring Isld.

- The “Right Decisions” included,
  - The initial installation of DAF and UV on St Mary Lake
  - Regular lake sampling and analyses allowing for prompt recognition of the cyanobacterial bloom.
  - Utilizing all CRD resources (both main and aquatic ecology laboratories).
  - Extra resources applied to increased monitoring of microcystin concentrations.
  - Extra resources (operator time) applied to operating the WTP.
  - Decision made not to oxidize with $KMnO_4$.
  - Willingness and capacity to accommodate a significant increase in coagulant expenditures.
  - Responsible care and increased disposal frequency for DAF sludge.
  - Maintained the course for the extended 20 month cyanobacterial boom.

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