Ozone for the Removal of Harmful Algal Bloom Toxins and Geosmin & MIB

Dr. Saad Y. Jasim, P.Eng.
Manager, Utilities, Engineering and Municipal Operation
White Rock, BC, Canada
HARMFUL ALGAL BLOOMS, CYANOBACTERIA

• Cyanobacteria are photosynthetic bacteria that share some properties with algae and are found naturally in lakes, streams, ponds, and other surface waters.

• Similar to other types of algae, when conditions are favorable, cyanobacteria can rapidly multiply in surface water and cause "blooms."

• *Cyanobacterial toxins* are the naturally produced poisons stored in the cells of certain species of cyanobacteria. These toxins fall into various categories.
LAKE ERIE AND THE ALGAE BLOOM
Lake Erie is once again severely threatened. It is the shallowest of the Great Lakes, the warmest and the most susceptible to eutrophication and the effects of climate change.
• In 2014, the residents of the City of Toledo, Ohio were advised not drink the water due to the elevated levels of Cyanotoxins (*Microsystin*)

• What are they:

  *Cyanotoxin* (algal toxin): Toxin produced by cyanobacteria.

  These toxins include liver toxins, nerve toxins and skin toxins.

  *Microsystin*: A liver toxin produced by a number of cyanobacteria. More than 80 congeners (forms) of these toxins exist. *Microcystin-LR* is the most toxic congener.
August, 2014
Volunteers unload drinking water outside Waite High School in Toledo. About 500,000 residents in and around the Ohio city were without safe drinking water for a few days while local water supplies were being tested after the discovery of high toxin levels from algae on Lake Erie. (Joshua Lott/Reuters),
ALGAL BLOOM TOXINS?

- *Cyanobacterial toxins* are the naturally produced poisons stored in the cells of certain species of cyanobacteria. These toxins fall into various categories.
- Some are known to attack the liver *(hepatotoxins)* or the nervous system *(neurotoxins)*; others simply irritate the skin.
- These toxins are usually released into water when the algae cells rupture or die. Increases in cyanobacterial blooms are driven by a number of factors, including excess nutrient loading from anthropogenic sources and climate change that produces conditions that favor bloom formation.
ARE CYANOBACTERIAL BLOOMS A NEW PROBLEM?

• The toxic effects of cyanobacteria on livestock have been recognized for more than 100 years.

• Since cyanobacterial bloom formation seems to be linked to nutrient-rich water bodies (for example, water that contains a lot of phosphates from detergents and phosphate fertilizers), or wastewater contains organics, the problem is not likely to go away in the near future.
WHAT ARE MICROCYSTINS?

• One group of toxins produced and released by cyanobacteria are called *microcystins* because they were isolated from a cyanobacterium called *Microcystis aeruginosa*.

• Microcystins are the most common of the cyanobacterial toxins found in water, as well as being the ones most often responsible for poisoning animals and humans who come into contact with toxic blooms.
• If the water, fish or blue-green algal products is ingested containing elevated levels of toxins, you may experience headaches, fever, diarrhea, abdominal pain, nausea and vomiting.

• Swimming in contaminated water, may cause itchy and irritated eyes and skin, as well as other hay fever-like allergic reactions.

• If you have come into contact with cyanobacterial toxins and are experiencing any of these symptoms, rinse any scum off your body and consult your physician immediately.
Although many people have become ill from exposure to freshwater cyanobacterial toxins, death from algal-contaminated drinking water is unlikely to occur if water resources are effectively treated to control taste, odour and other algae-related problems.

It's possible that extended exposure to low levels of cyanobacterial hepatotoxins could have long-term or chronic effects in humans.

Children are at greater risk for developing serious liver damage should they ingest high levels of microcystins, because of their comparatively lower body weight.
• Microcystins are extremely stable in water because of their chemical structure, which means they can survive in both warm and cold water and can tolerate radical changes in water chemistry, including pH. So far, scientists have found about 50 different kinds of microcystins.

• One of them, microcystin-LR, appears to be one of the microcystins most commonly found in water supplies around the world. For this reason, most research in this area has focused on this particular toxin.
The US Environmental Protection Agency (EPA) publish a list of unregulated contaminants that are known or expected to occur in public water systems in the US that may pose a risk in drinking water.

Cyanotoxins has been identified by the EPA as: Toxins naturally produced and released by cyanobacteria ("blue-green algae"). Various studies suggest three cyanotoxins for consideration: Anatoxin-a, Microcystin-LR, & Cylindrospermopsin
• More than a dozen countries (including Canada, Brazil, New Zealand, and Australia) have developed regulations or guidelines for microcystins in drinking water and recreational waters.

• Most of the drinking water guidelines are based on the World Health Organization provisional value for drinking waters of 1.0 μg/L microcystin-LR.
WHY DO BLOOMS SOMETIMES APPEAR OVERNIGHT?

Even if you can't see a cyanobacterial bloom floating on the surface of the water, that doesn't mean one isn't present in the water - the bloom could be suspended at various depths in the water where you can't see it.

The depth at which cyanobacterial blooms float depends on a number of factors.
Cyanobacterial blooms can be harmful to the environment, animals, and human health. The bloom decay consumes oxygen, creating hypoxic conditions which result in plant and animal die-off.

Under favorable conditions of light and nutrients, some species of cyanobacteria produce toxic secondary metabolites, known as cyanotoxins.
## Cyanotoxins on the Contaminant Candidate List (CCL)

<table>
<thead>
<tr>
<th>Cyanotoxin</th>
<th>Number of known variants or analogues</th>
<th>Primary organ affected</th>
<th>Health Effects(^1)</th>
<th>Most common Cyanobacteria producing toxin(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcystin-LR</td>
<td>80–90</td>
<td>Liver</td>
<td>Abdominal pain&lt;br&gt;Vomiting and diarrhea&lt;br&gt;Liver inflammation and hemorrhage</td>
<td><em>Microcystis</em>, <em>Anabaena</em>, <em>Planktothrix</em>, <em>Anabaenopsis</em>, <em>Aphanizomenon</em></td>
</tr>
<tr>
<td>Cylindrospermopsin</td>
<td>3</td>
<td>Liver</td>
<td>Acute pneumonia&lt;br&gt;Acute dermatitis&lt;br&gt;Kidney damage&lt;br&gt;Potential tumor growth promotion</td>
<td><em>Cylindrospermopsis</em>, <em>Aphanizomenon</em>, <em>Anabaena</em>, <em>Lyngbya</em>, <em>Rhaphidiopsis</em>, <em>Umezakia</em></td>
</tr>
<tr>
<td>Anatoxin-a group(^3)</td>
<td>2-6</td>
<td>Nervous System</td>
<td>Tingling, burning, numbness, drowsiness, incoherent speech, salivation, respiratory paralysis leading to death</td>
<td><em>Anabaena</em>, <em>Planktothrix</em>, <em>Aphanizomenon</em>, <em>Cylindrospermopsis</em>, <em>Oscillatoria</em></td>
</tr>
</tbody>
</table>

\(^1\)Source: *Harmful Algal Research and Response National Environmental Science Strategy (HARRNESS)*

\(^2\)Not all species of the listed genera produce toxin; in addition, listed genera are not equally as important in producing cyanotoxins.

\(^3\)The anatoxin-a group does not include the organophosphate toxin anatoxin-a(S) as it is a separate group. In the US, the most common member is thought to be anatoxin-a, and thus this toxin is listed specifically.
OZONE & ADVANCED OXIDATION PROCESSES

• Ozone reacts more quickly with microcystins, anatoxin-a and cylindrospermopsin than other common oxidants.

• Saxitoxin is the least susceptible to ozone destruction. Under comparable conditions where microcystins would be adequately destroyed, only 20% of saxitoxins present would be destroyed.

• Although hydrogen peroxide alone does little to remove toxins, ozone with hydrogen peroxide is even more effective than ozone alone.
• Preoxidation (the application of an oxidant at any point in the treatment process prior to filtration) need to be evaluated because most oxidants will lyse the blue-green algal cells present and release their toxins (i.e., extracellular toxin).

• If at all possible, blue-green algae cells should be removed through the coagulation process prior to adding an oxidant to keep the cell structure intact and the toxins contained (i.e., intracellular).
A study conducted by the Water Research Foundation (WRF, Denver, CO, USA) indicated that Ozone applications to destruct the Cyanotoxins depended significantly on Ozone dose and pH. With pH less than 7, ozone is more effective. 97% of m-LR was reduced at acidic conditions (pH lower than 6) and at low ozone dose of 0.4 mg/L.
• The study was conducted on two different water sources to determine the impact of ozone on m-LR removal:

i- a moderately hard water with elevated TOC, Lake Washington in Florida

ii- a soft water with low TOC concentration, Willamette River in Oregon.

There were significant differences in the TOC concentration and in the general characterization of their organic matter as in indicated by the SUVA values
OZONE DOSE IMPACT ON MICROCYSTIN REMOVAL IN LAKE WASHINGTON WATER SOURCE
H$_2$O$_2$ DOSE IMPACT ON MICROCYSTIN REMOVAL IN LAKE WASHINGTON WATER SOURCE
EFFECT OF PH ON M-LR REMOVAL IN LAKE WASHINGTON SOURCE WATER
IMPACT ON TEMPERATURE ON M-LR REMOVAL IN LAKE WASHINGTON SOURCE WATER
ALKALINITY EFFECT ON M-LR REMOVAL, LAKE WASHINGTON SOURCE WATER
INTERACTION EFFECT OF OZONE DOSE AND PH ON M-LR REMOVAL-LAKE WASHINGTON

EFFECT OF INTERACTION OF H₂O₂ DOSE AND PH ON M-LR REMOVAL-LAKE WASHINGTON
• The study found that algal toxins oxidation is achieved almost instantaneously once the entire ozone dose has been transferred to the water.

• If the ozone system has been designed for algal toxins treatment only, the detention time in the reactor will be equal to the time to transfer the required ozone dose plus the time required to allow the ozone residual to decay. The decay information can be used to determine if more time is needed for the ozone residual to decay to very low concentration.
• That study indicated that; neither Total Organic Carbon (TOC), or the difference in general character matter of the organic matter, as characterized by source water Specific Ultraviolet Absorbance (SUVA) affected m-LR removal.

• That contrasts with previous studies that TOC competes with m-LR for the reaction with ozone.
TASTE & ODOR IN WATER SOURCES

- Naturally occurring taste and odour causing compounds in raw water sources are known to be a seasonal concern for drinking water treatment plants using surface water as a raw water source.
- Removal of geosmin and MIB could be accomplished using ozone & ozone based advanced oxidation processes (AOPs).
- The effectiveness of ozone depends on ozone/TOC ratio, pH and alkalinity.
Summary of Odorant Oxidation

- Ozone is the most reliable tool to mitigate the drinking water T&O problems; suitable for frequent and long duration episodes.
- Highest Geosmin, MIB removal capability when compared to carbon adsorption or other oxidants.
- Peroxide addition may enhance removals.
- Fast reaction - short (5 to 10 minutes) contact time can be used.
A STUDY IN WALKERTON, ONTARIO, CANADA

• Water was collected from a lake south west of Ontario and transported to the Walkerton Clean Water Centre using a 16,000 liter truck tanker

• The experiments were conducted using the conventional dual train pilot plant at the Walkerton Clean Water Centre, Ontario, Canada

• Ozone was applied at train #2 only
Dual train conventional treatment pilot plant
Ozone System Schematic
RAW WATER QUALITY

- The tested water had high levels of alkalinity (241-252 mg/L) and hardness (283-300 mg/L); also relatively high dissolved organic carbon (2.5 to 3.2 mg/L)
- Natural geosmin concentration of up to 41 ng/L was measured in the raw water
- Raw water matrix was hard to treat; enhanced jar testing was conducted to estimate the optimum alum dosages to meet treatment objective of ≤ 0.1 NTU
CHEMICALS & OPERATING CONDITIONS

• Several runs were conducted during the period from June 9 until October 8, 2009
• Alum (15 mg/L) was used as the main coagulant; while liquipam (0.032 mg/L) used as a coagulant aid
• Pre-coagulation ozonation and post sedimentation ozonation were applied
• Treatment of both spiked geosmin and MIB, as well as naturally occurring in the raw water were experimented
• Reduced pH conditions were experimented using CO₂
RESULTS AND DISCUSSION

• The early runs were conducted to adjust operating conditions to meet treatment objective of around 0.1 NTU as well as to have a reasonable MIB and geosmin percentage removal.

• The ozone was injected for the first 3 runs at a dosage rate of 2 mg/L.

• In Run #4, 4 mg/L of gaseous ozone. This is due to the high hardness level of the raw water, as well as the relatively high DOC levels, approximately 2.7-2.8 mg/L. The run was successful in terms of meeting treatment objective of 0.1 NTU.
• Run # 6 was conducted to treat naturally occurring geosmin and MIB in the raw water and without adding any artificial geosmin and MIB
• Ozone dosage applied was 4 mg/L
• Test results showed that geosmin levels dropped from 32 ng/L in raw water down to 20 ng/L in train 2 treated water (ozonated side), compared to 26 ng/L in train 1
• The percentage removal of geosmin was about 37% on the ozonated side.
• MIB was below the detection level of 3 ng/L, both in raw and treated water
• In Run# 7, ozone based Advanced Oxidation Process (AOP) using ozone and H2O2; applied to only naturally occurring geosmin and MIB

• Geosmin dropped from 22 ng/L in raw water down to less than 3 ng/L of ozonated treated water. MIB analysis showed concentration less than the detection limit of 3 ng/L.

• MIB was below the detection level of 3 ng/L in the raw water. Using an advanced oxidation process (AOP) showed a substantial effect on geosmin removal of about 86% on the ozonated side

• In Run #8, similar operating conditions were applied, except that post sedimentation ozonation was conducted, Geosmin removal was 88%
Geosmin-Run 7, July 14 & 15, 2009

Geosmin-Run 8, July 21 & 22, 2009
• Generally, natural occurring MIB concentration in the lake raw water was relatively low compared to geosmin. Natural geosmin reached 41 ng/L
• Applying a gaseous ozone dosage of 4-5 mg/L could result in removing from 25% and up to 37% of geosmin content in the raw water source used in this study
• Applying ozone based advanced oxidation (AOP) resulted in the removal of 43 -88% of geosmin content in the raw water.
CONCLUSIONS

In conclusion, the use of ozone and ozone based advanced oxidation processes is effective for the blue-green algal toxin, and Geosmin & MIB removal, and it would be more effective if used as part of a more comprehensive, multi-barrier treatment strategy. When used alone, oxidation effectiveness can range from very effective to detrimental depending upon the process used and the toxins being treated.
THANK YOU

QUESTIONS???