

Evaluating Dissolved Organic Carbon Quantity and Character in Lakes with Harmful Algal Blooms

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Abstract

Methylmercury is a notable, bioaccumulating neurotoxin present in many freshwater systems. Concentration of methylmercury is mediated by factors that influence rates of methylation by anaerobic microbes and demethylation, and can be impacted by the amount and relative aromaticity of dissolved organic carbon. Dissolved organic carbon concentrations and chlorophyll a levels were sampled at multiple points over a period from late May to mid July in two lakes noted to have prominent harmful algal blooms, a source of bio-available DOC. DOC concentrations were determined using specific ultraviolet absorbance at 254 nm (SUVA₂₅₄). Correlation between aromatic DOC and HABs was limited, perhaps due to high baseline levels of terrestrial DOC.

Introduction

Methylation of mercury can be influenced by the aromaticity and quantity of dissolved organic carbon (DOC). Aromatic DOC, often derived from terrestrial allochthonous sources of organic carbon high in lignins, is generally considered less bioavailable to methylating microbes, potentially reducing methylating activity. However, aromatic DOC may also be better at forming particle clumps, that break up inorganic mercury particles. As a result, Hg(o) may have a greater presence in nanoparticles, which are more likely to be taken up by methylating microbes. Quantity of DOC can also affect methylation through mechanical measures. Large quantities of DOC can block light penetration into deeper waters. Light is a known abiotic facilitator of

degradation through photodegradation. Aromatic DOC can also adsorb to the cell wall of bacteria, blocking the uptake of mercury.

As a result of these distinct characters, optical measurements have been successful in characterizing the amount and character of dissolved organic carbon. Specific Ultra-Violet Absorbance at 254 nm ($SUVA_{254}$) has been strongly correlated with the degree of aromatic dissolved organic carbon, and is often used as a proxy for complex organic species. Dissolved organic carbon has been shown to have an impact on water treatment and toxic metal complexation. Aromatic DOC, also known as humic-like DOC, is typically derived from terrestrial plants, and is more able to form complexes with toxic metal ions (Pb, Cu) compared to aliphatic DOC.⁵ This complexation can prevent uptake of toxic ions by aquatic fauna and diminish the harmful effects of pollutants.⁷ This effect is diminished for linear, aliphatic DOC prevalent in autochthonous sources.

Aliphatic DOC concentrations are also relevant within bacterial metabolism. Bacterial growth and metabolism is elevated in waters with a higher proportion of aliphatic, autochthonous DOC, contributing to depletion of dissolved oxygen as well as changes in inorganic nutrients, like sulfur and iron. Furthermore, lake bacteria play a key role in the methylation of mercury, which renders it more bioavailable. As a result of rising global temperatures and anthropogenic run-offs, harmful algae blooms have become prevalent in freshwater ecosystems, potentially impacting the character of DOC, and the bioavailability of toxic metals.

Methods

A prior survey conducted in 2025 identified two lakes with notable HAB formation. At each lake, water samples were taken biweekly at two shore points (Shore A and Shore B) as well

as the top and bottom of the lakes at Z_{maz} (top and bottom respectively). Samples were collected on a weekly basis at the lakes inlet and outlet. In the field, water samples were collected in areas that visually appeared clear, though at certain points this was impossible due to dense algal growth. Initially 60 mL of water was collected and filtered through .22 μm Whatman GF/F filters into 60 mL amber glass vials. The used filter was folded and stored in a dark environment and later analyzed using a photospectrophotometer to gauge chlorophyll a and phaeocyanin concentrations.

Samples were stored at cold temperatures until they were analyzed. UVA was analyzed within 48 hours of collection using a Shimadzu spectrophotometer at a wavelength of 254 nanometers with 1 cm thick quartz cuvettes. After analysis, DOC samples were acidified with 200 μL of trace-metal grade HCl and later analyzed on a TOC analyzer. Samples were taken from May 28 to July 17, 2026. Additionally, using a YSI 1200 probe, DO, pH, chlorophyll a and phycocyanin concentrations, and redox conditions were determined. A linear regression line was applied using the Spearman rank test for correlation. Significance was determined at $\alpha = .05$.

RESULTS

Formation of HABs and DOC:

Chlorophyll a concentration was found to have increased at multiple lake points during from mid June to mid July, indicating an increase in algal growth and HAB development. The increase in chlorophyll a levels was most dramatic for samples taken on the surface of stagnant waters, which is consistent with where HABs would be expected to form. Visual field

observations noted that a significant change in chlorophyll a levels was observed at Shore A at Dryden Lake in particular, likely due to the wind's direction.

Despite the confirmed presence of HABs in the time-frame sampled, no significant decrease in SUVA₂₅₄ was observed in either Dryden Lake or Long Ponds (**Figure 1**). There was also no notable relationship between chlorophyll concentration and the amount of aromatic DOC, with the exception of samples from the lakes' bottoms, which had a positive relationship. (**Figure 2**) At Dryden Lake, the most dramatic change in SUVA₂₅₄ readings were increases observed at Dryden's inlet and bottom. A weakly negative correlation between DOC and time was observed at Dryden Lake's top and outlet.

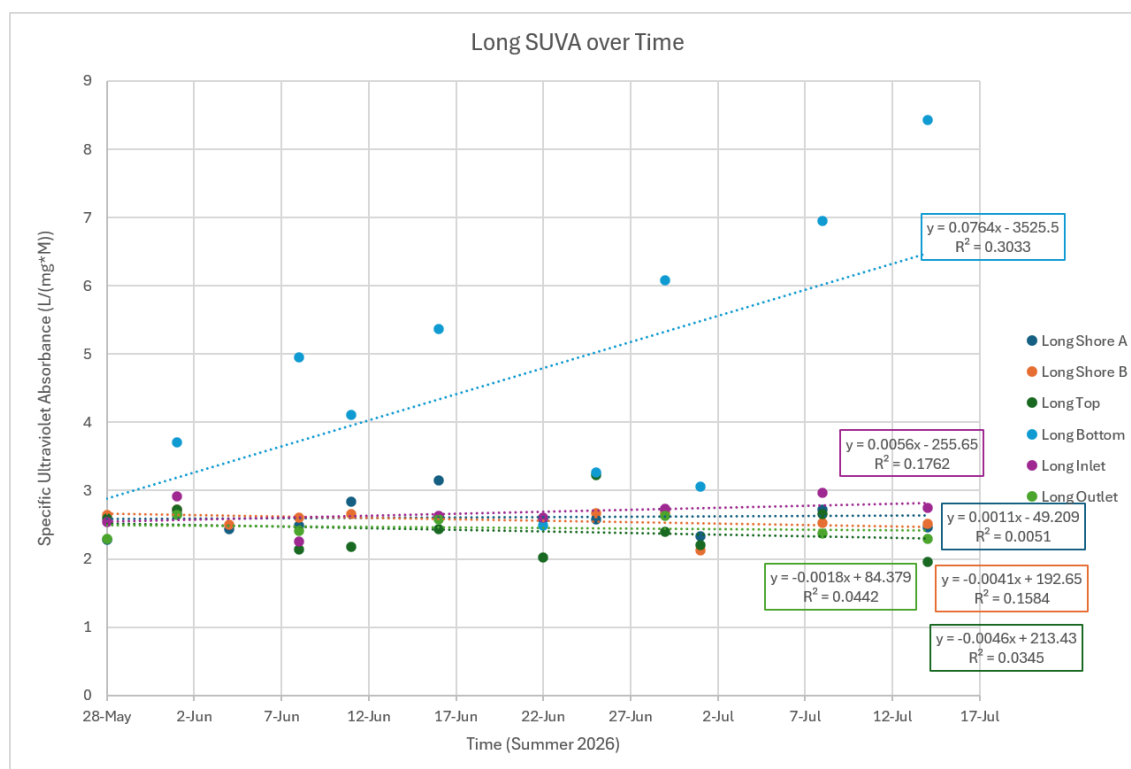
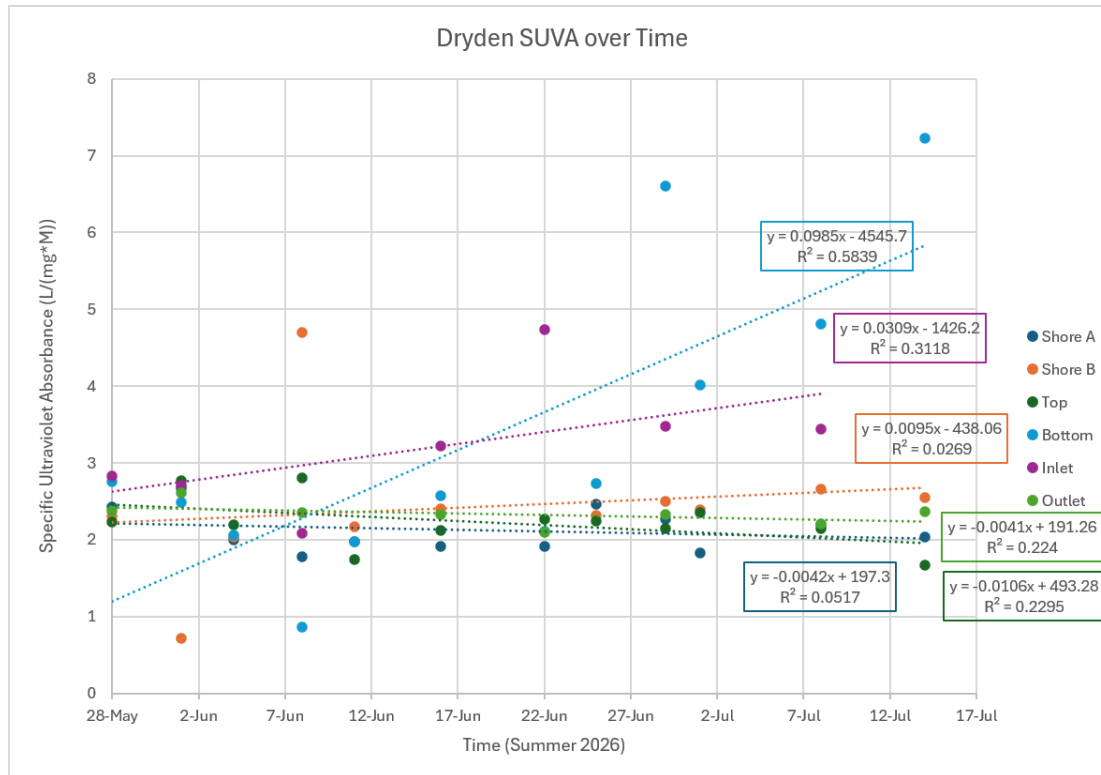
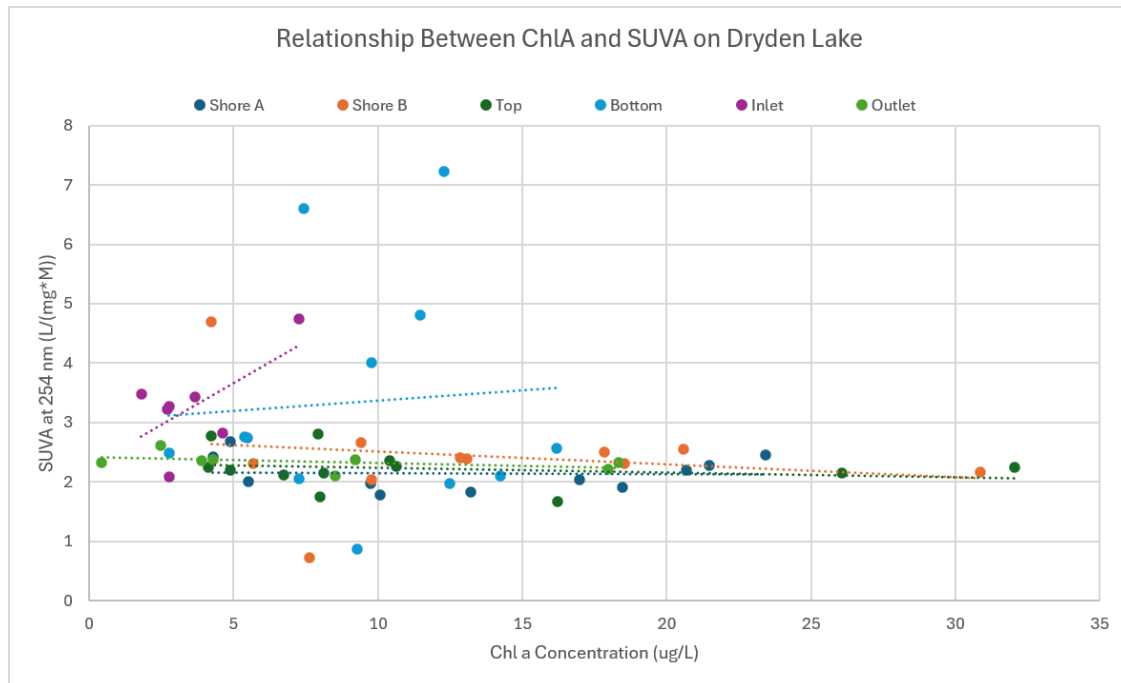


Figure 1: Time series showing SUVA at 254 nm at Dryden and Long Lake over a six week period. Linear trendlines were analyzed for the six locations sampled at each lake. No significant relationship was found between SUVA₂₅₄ over time for all sample points, with the exception of samples taken at Dryden Lake's bottom with $r = 0.5839$ and $p < 0.05$. SUVA₂₅₄ readings were stable for samples taken elsewhere, indicating relatively little change in aromatic character as HABs formed.

A significant positive correlation between SUVA₂₅₄ and time was noted at the bottom of Dryden Lake, indicating that allochthonous DOC increased during the time frame.



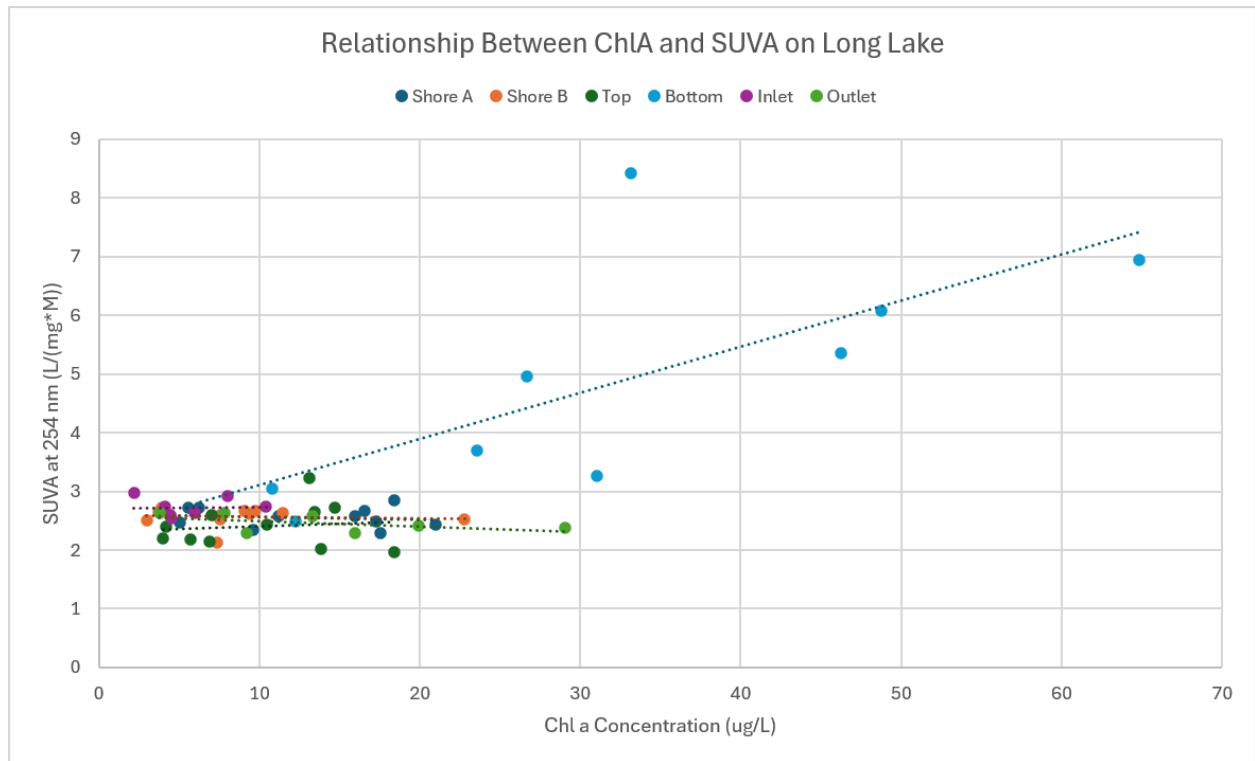


Figure 2: Relationship between chlorophyll concentration and SUVA₂₅₄. Altogether, chlorophyll concentrations did increase over the time samples were taken, indicating greater algal growth over time. However, this did not relate to a significant change in DOC aromaticity.

Discussion:

During the sampled time interval, aliphatic DOC did not appear to increase with the growth of HABs. Prior literature has shown that DOC SUVA₂₅₄ readings decrease further as algal blooms exit the exponential growth stage.⁵ The analyzed points were taken from early in HAB formation, during rapid growth. It is possible that SUVA₂₅₄ will experience more dramatic decreases later in HAB development. The high SUVA₂₅₄ readings at the bottom of the lakes indicate a high proportion of terrestrial plants, perhaps from those growing at the lakes' floors. The samples were taken from the lakes' maximum depths, which were both under five feet. Field observations noted the presence of aquatic plant growth at the bottom of both lakes. Long Ponds

were noted for having high levels of aquatic terrestrial growth, which could explain the higher amount of aromatic DOC present in Long Lake.

DOC concentrations also did not significantly change in this period, regardless of aromaticity, despite the formation of HABs, perhaps as a result of relatively high base levels of DOC, obscuring the small increase from algal blooms. Heavy rains were also observed during the times present, which can further increase allochthonous content through run-off. Future work will focus on analyzing data from later in HAB development, as HABs decompose, releasing intracellular sources of aliphatic DOC.

From this data, it appears that the ability of HABs to DOC content is limited, and may be more prominent in freshwater systems that have lower DOC baselines. Future research is needed to characterize the change in DOC character later in HAB development, as HABs decompose. Microbial activity as a result of changing chlorophyll content can also be directly evaluated, shining light on the impact of HABs on inorganic species and metal complexes.

Citations:

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