Performance of Vacuum UV (VUV) for the degradation of MC-LR, geosmin, and MIB from cyanobacteria-impacted waters

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Source Water Characteristics

Source water samples from two Canadian cyanobacterial-impacted lakes, identified as Lakes A and B (Table 1) were collected to conduct this work. Lake A is located 40 km west of Montreal (Quebec, Canada) and constitutes a system of two lakes that supplies a bank filtration water system. Pazouki et al. (2016) conducted a study on Lake A and strongly suggested the importance of having a monitoring program to detect possible breakthroughs of cyanobacteria through the bank filtration. They used phycocyanin probes, since phycocyanin is a pigment produced by cyanobacteria and used to monitor its presence in water. They found a strong correlation between cyanobacterial concentrations and phycocyanin in raw and filtered water for this system (1).

Lake B, located 160 km east of Montreal (Quebec, Canada), is a recreational water body currently under consideration to become a source of drinking water for the area. This lake is part of the "Voluntary Lake Monitoring Network" of the Ministry of the Environment and Fight Against Climate Change (Quebec, Canada). In 2011, 656 lakes were part of this program which aims to acquire data to establish the trophic level of lakes and track their evolution over time (2). During the summer of 2017, we observed that Lake B was affected by an intense cyanobacterial bloom (Table 1). The total cell counts for this event showed 220,000 cell mL^{-1} (88% was of the Cyanophyceae class) and 83% of the cyanobacterial cells corresponded to *Planktothrix agardhii*.

Samples were collected from Lake A and Lake B on August 25, 2017 and September 7, 2017, respectively. Source waters were analyzed for total organic carbon (TOC), dissolved organic carbon (DOC), and biodegradable dissolved carbon (BDOC) concentrations using a TOC analyzer (5310C Sievers Instruments Inc., USA). BDOC analysis was performed using the 30-d incubation batch method of Servais et al. (3). The pH was measured using a Fisher Scientific pH-meter (Accumet, Fisher Scientific Instruments, USA), pre-calibrated with pH 4, 7, and 10 standard buffers (BDH VWR Analytical). Turbidity measurements (Hach 2100N turbidimeter) were assessed following Standard Methods #2130B (4). Ions were measured by ionic chromatography ICS 5000 AS-DP DIONEX (Thermo Scientific) with an As18-4µm column. Alkalinity was measured by titration according to Standard Methods #2320 (4).

A YSI 6600 V2-4 water-quality multi-probe (YSI, Yellow Springs, Ohio, USA) equipped with a self-cleaning wiper was used to determine the presence of cyanobacteria (i.e., the phycocyanin measured was higher than 2.4 relative fluorescence units (RFU)) (5). Lugol's iodine preserved the water samples for further taxonomic identification and cell counting.

Targeted Cyanobacterial Metabolites Detection

Our initial intent was to collect waters during bloom events with the hope that cyanobacterial metabolites (GSM, MIB, and cyanotoxin) would be simultaneously present in sufficiently high concentrations to avoid spiking. However, due to their low abundance, we had to resort to spiking the three target compounds in the waters collected from both lakes. The source waters were always spiked with 100 ng L^{-1} of MIB and GSM and 10 µg L^{-1} of MC-LR.

Because microcystin is the most common cyanotoxin and MC-LR the most frequent and one of the most toxic (6, 7), we decided to spike our samples with MC-LR. Also, most studies of cyanotoxin oxidation by AOP are performed using MC-LR (8-10). For this purpose, dry MC-LR was purchased from Alexis Chemical (Cedarlane, Canada). MC-LR was measured by an on-line solid phase extraction coupled with ultra-high performance liquid chromatography, heated electrospray ionization, and high-resolution mass spectrometry detection, Q-Exactive (Thermo Fisher Scientific, Waltham, MA) (UHPLC-HESI-HRMS), as described in Fayad et al. (11). The limit of detection (LOD) of the method was 10 ng L^{-1}, and the limit of quantification (LOQ) was 33 ng L^{-1}.

GSM (purity ≥ 97%), MIB (purity ≥ 98%) and cis-decahydro-1-naphthol, used as an internal standard (IS, purity ≥ 99%), were purchased from Sigma-Aldrich (St. Louis, MO). Individual stock solutions were prepared daily in ultrapure water (Milli-Q™) at a

concentration of 10 mg L^{-1} in HPLC grade methanol (MeOH) from Fisher Scientific (Whitby, ON, Canada). The contribution to carbon concentration in the water by MeOH was 4.12×10^{-7} mg C L^{-1}. This represented a negligible amount of carbon introduced to the samples (0.001% of the lower C concentration measured in our samples). For the MIB and GSM analysis, a GC 3800 coupled to a MS 4000 from Varian (Palo Alto, CA) equipped with a PAL auto sampler (Zwingen, Switzerland) and a Gerstel Twister system (Baltimore, MD) was used. The LOD and LOQ for MIB and GSM were respectively determined as 8/27 ng L^{-1} and 8.5/29 ng L^{-1}.

Vacuum UV Experiments

CRB setup

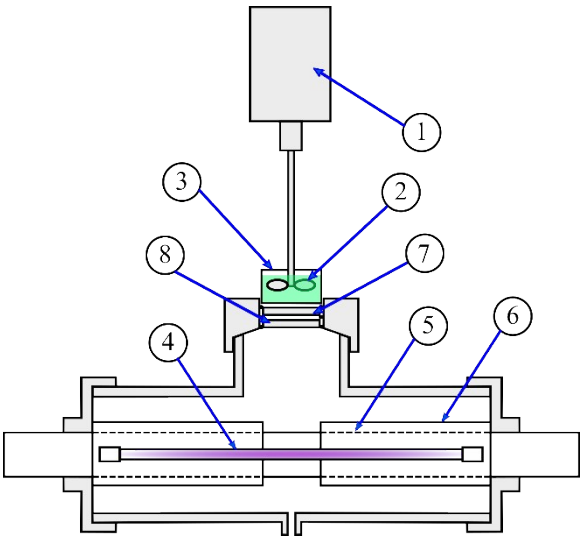

Figure A (SI). Collimated Beam Reactor. (1) motor, (2) stirrer, (3) reaction vessel, (4) vacuum UV lamp, (5) quartz sleeve, (6) Teflon cylinder, (7) optical filter, (8) Suprasil® quartz (12)

FTR setup

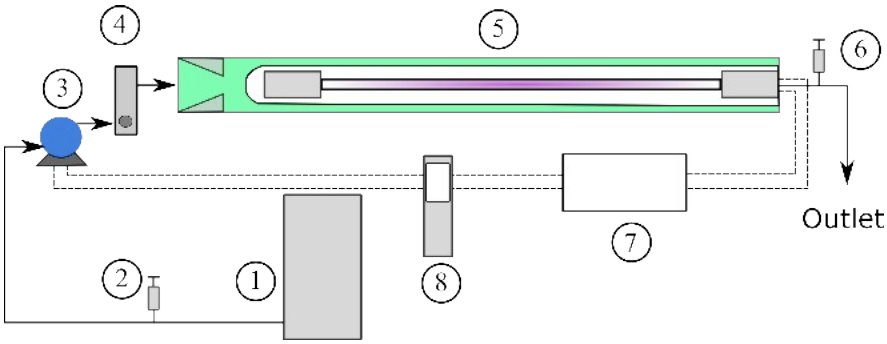

Figure B (SI). Flow-through Reactor. (1) water reservoir, (2) inlet sampling point, (3) pump, (4) flow meter, (5) photoreactor, (6) outlet sampling point (dashed lines = electric connections and solid lines = water connections), (7) ballast, (8) power meter (13)

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