

Supporting Information

Geospatial Assessment of Trace-Level Benzophenone-3 in a Fish Bearing River using Direct Mass Spectrometry

Authors

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Preparation of benzophenone-3 standards and natural water sample collection

Benzophenone-3 (2-hydroxy-4-methoxybenzophenone; 98%, Aldrich, Oakville, ON, Canada) stock solutions were made using methanol (HPLC grade; VWR International, Edmonton, AB, Canada). Aqueous BP-3 standards (50, 100, 250 ng/L) were prepared by volumetric dilution of the stock solution in deionized water (18.4 MΩ-cm, Facility Scale Reverse Osmosis/Ion Exchange Water Purification System, Applied Membranes Inc., Vista CA, USA) such that final methanol concentrations were kept below 0.2% v/v. Collection of natural water samples, including information on sampling location, time, weather, number of swimmers, and water temperature, is described in Table S1.

Table S1: Additional information for samples collected on September 6, 2020 from Cowichan Lake and the Cowichan River (British Columbia, Canada). Sunny conditions were noted for all sampled locations. Number of swimmers is the total of those in water.

| Sampling Coordinates | | Time | Number of Swimmers | Water Temperature (°C) |
|----------------------|-------------------|----------|--------------------|------------------------|
| 48° 49' 24.39" N | 124° 03' 36.12" W | 1:30 PM | 33 | 20.5 |
| 48° 49' 33.88" N | 124° 03' 28.88" W | 1:50 PM | 16 | 19.5 |
| 48° 49' 32.42" N | 124° 03' 14.07" W | 4:25 PM | 36 | 19.8 |
| 48° 49' 42.57" N | 124° 02' 46.80" W | 3:45 PM | 12 | 18.6 |
| 48° 49' 53.18" N | 124° 01' 56.96" W | 2:55 PM | 35 | 18.4 |
| 48° 49' 48.68" N | 124° 02' 04.92" W | 3:05 PM | 20 | 20.6 |
| 48° 49' 39.46" N | 124° 01' 37.53" W | 3:15 PM | 0 | 22.4 |
| 48° 49' 39.88" N | 124° 01' 41.10" W | 2:25 PM | 0 | 22.2 |
| 48° 49' 32.59" N | 124° 01' 28.86" W | 2:00 PM | 0 | 22.0 |
| 48° 48' 13.48" N | 124° 00' 12.63" W | 1:15 PM | 0 | 22.0 |
| 48° 46' 53.02" N | 123° 56' 54.86" W | 12:30 PM | 11 | 21.0 |
| 48° 47' 01.57" N | 123° 57' 10.66" W | 12:45 PM | 0 | 20.8 |
| 48° 46' 10.29" N | 123° 53' 35.93" W | 12:15 PM | 0 | 20.0 |
| 48° 45' 45.54" N | 123° 51' 09.00" W | 1:56 PM | 0 | 20.6 |
| 48° 45' 28.13" N | 123° 49' 53.64" W | 2:25 PM | 11 | 20.9 |
| 48° 45' 29.34" N | 123° 50' 16.08" W | 2:20 PM | 7 | 20.9 |
| 48° 45' 29.48" N | 123° 49' 44.04" W | 2:30 PM | 4 | 20.9 |
| 48° 45' 39.08" N | 123° 46' 21.13" W | 2:45 PM | 15 | 20.5 |
| 48° 46' 26.06" N | 123° 42' 51.07" W | 1:18 PM | 0 | 19.5 |
| 48° 46' 20.42" N | 123° 41' 53.23" W | 1:31 PM | 0 | 19.8 |
| 48° 46' 37.05" N | 123° 40' 26.40" W | 3:30 PM | 0 | 18.6 |
| 48° 46' 39.50" N | 123° 40' 27.48" W | 3:35 PM | 0 | 18.4 |
| 48° 46' 40.53" N | 123° 40' 21.29" W | 3:20 PM | 0 | 20.6 |
| 48° 45' 57.99" N | 123° 38' 38.40" W | 12:10 PM | 0 | 19.0 |
| 48° 45' 36.75" N | 123° 39' 05.03" W | 12:58 PM | 0 | 18.5 |
| 48° 44' 35.12" N | 123° 37' 25.88" W | 12:46 PM | 0 | 16.9 |
| 48° 47' 55.65" N | 123° 42' 03.83" W | 3:00 PM | 0 | 24.4 |
| 48° 47' 19.39" N | 123° 40' 15.95" W | 3:45 PM | 0 | 24.1 |
| 48° 52' 21.81" N | 124° 13' 00.56" W | 2:50 PM | 58 | 21.8 |
| 48° 50' 40.15" N | 124° 07' 03.34" W | 2:20 PM | 13 | 22.7 |
| 48° 50' 13.63" N | 124° 11' 47.26" W | 12:13 PM | 50 | 22.0 |
| 48° 49' 15.55" N | 124° 10' 32.94" W | 12:35 PM | 10 | 22.0 |
| 48° 48' 40.93" N | 124° 07' 29.04" W | 1:07 PM | 3 | 21.6 |

Samples from the Cowichan River and Cowichan Lake (Vancouver Island, BC, Canada) were collected on July 5, July 19, August 3, August 16, August 29, and September 6, 2020. Those who collected the samples did not apply any form of sunscreen or cosmetics and wore nitrile gloves. An uncapped amber glass sample container was inverted, submerged 30 cm below the water's surface facing an upstream direction, and then righted to allow water below the surface to fill the bottle. Bottles were rinsed three times in this fashion before a final sample was collected. Samples were then immediately capped (PTFE-lined polypropylene; Cole-Parmer Canada, Montreal, QC) and kept in a dark, ice-filled cooler until eventual storage in a laboratory refrigerator at 4°C until analysis. For each sample, data was collected pertaining to sampling location, time, weather, number of swimmers, and water temperature (Table S1). For sample collection between July 5 and August 29, 2020, 4 locations were sampled in 950 mL amber glass bottles, and analyzed by both LC-MS/MS and CP-MIMS-LEI/CI (August 29 only) four days after sample collection. The delay in immediate analysis was due to transit time required for the LC-MS/MS samples. For the sake of method comparison studies, CP-MIMS-LEI/CI analysis was therefore similarly delayed by four days to match sample transit/storage conditions. For sample collection on September 6, 2020, 33 locations were sampled in 50 mL amber glass vials and analyzed by CP-MIMS-LEI/CI within four days of sample collection.

Construction of miniaturized CP-MIMS direct immersion probe

5.5 cm of PDMS hollow fibre membrane (HFM; 190 μm i.d., 300 μm o.d., PermSelect, Ann Arbor, MI, USA) was mounted on two 15 cm pieces of deactivated silica capillary (50 μm i.d., 180 μm o.d.) such that ~ 0.25 cm overlapped on each end of the HFM. Next, two 5 cm pieces of 23 gauge stainless steel (SS) thin wall hypodermic tubing were pierced through a piece of general purpose PDMS septum (3 mm thick) that was cut to a rectangular block (6 by 15 mm), where the SS tubing insertions were spaced ~ 1.5 mm apart. The two pieces of silica tubing were inserted through the SS tubing, such that the overlap between the silica and HFM was contained within the PDMS block, and that 5 cm of HFM was exposed as a loop outside of the PDMS block. The SS tubing was then removed, allowing the PDMS block to constrict, forming a tight seal between the HFM, silica capillary, and PDMS block. A piece of 22 gauge wire, fixed to the sides of the PDMS block, was loosely coiled around the exposed HFM loop and fixed to the PDMS block, allowing the HFM to overcome surface tension when directly inserted into an aqueous sample. All exposed PDMS from the rectangular block was wrapped in Teflon tape to mitigate exposure to the sample. The PDMS block was perpendicularly inserted into the cutout centre of a Teflon-lined PDMS septum.

Additional CP-MIMS-LEI/CI coupling details

Briefly, a syringe pump with a 250 μL glass syringe (Hamilton Company, Reno, NV, USA) was used to flow an 85:15 methanol/heptane v/v solvent mixture at 2 $\mu\text{L}/\text{min}$ through the HFM lumen. The flowrate was measured to be 1000 nL/min post-membrane using a calibrated nanoflow sensor (Sensirion flow meter, model SLG-0150; Stäfa, ZH, Switzerland), where the lower measured flowrate is due, in part, to solvent permeation through the membrane counter to the direction of the analyte. The enhanced permeability afforded by the mixed solvent system is discussed elsewhere.¹⁻² Post-CP-MIMS probe, the flow was coupled to a silica capillary (30 μm i.d., 150 μm o.d., 30 cm long) that was inserted 3 mm inside the MS transfer line (400°C) of what would otherwise be a conventional GC-MS system. The CP-MIMS-LEI/CI coupling is schematically described in Figure S1.

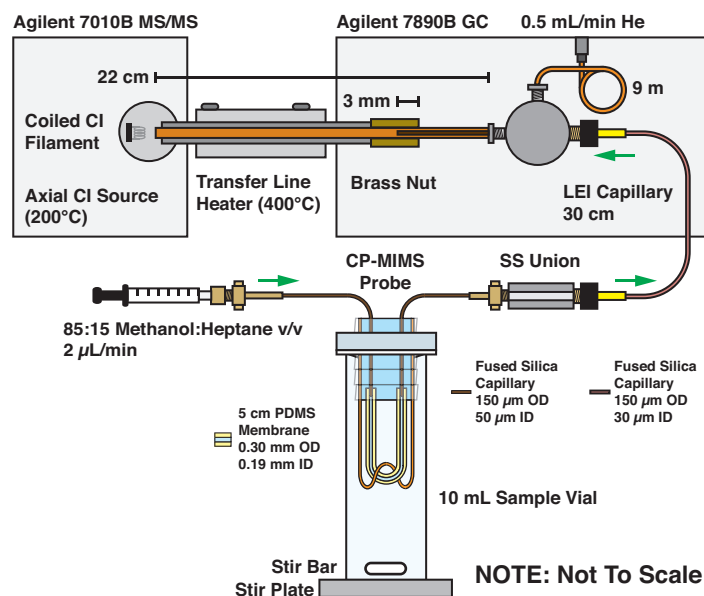


Figure S1: Schematic diagram of the CP-MIMS-LEI/CI experimental apparatus used for this study.

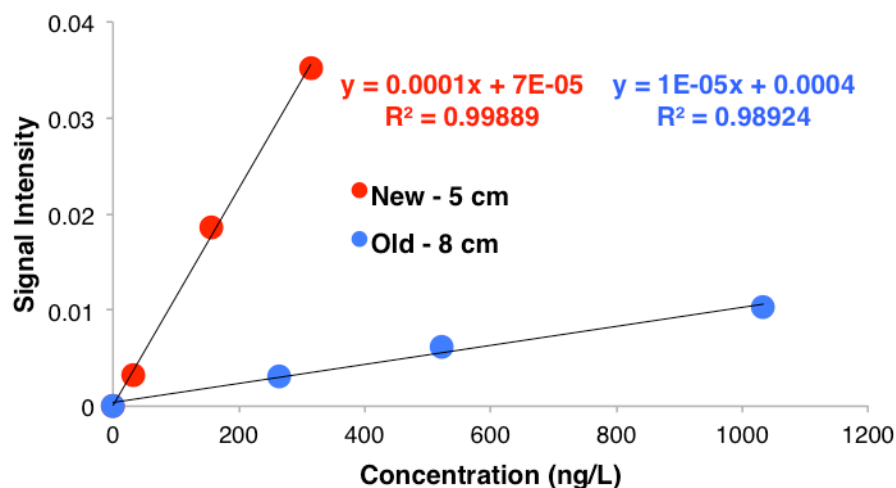


Figure S2: Analytical performance improvement for measurement of aqueous benzophenone-3 of the new generation CP-MIMS probe (labeled as 'New – 5 cm') verses an older generation probe ('Old – 8 cm').^{1,3-5}

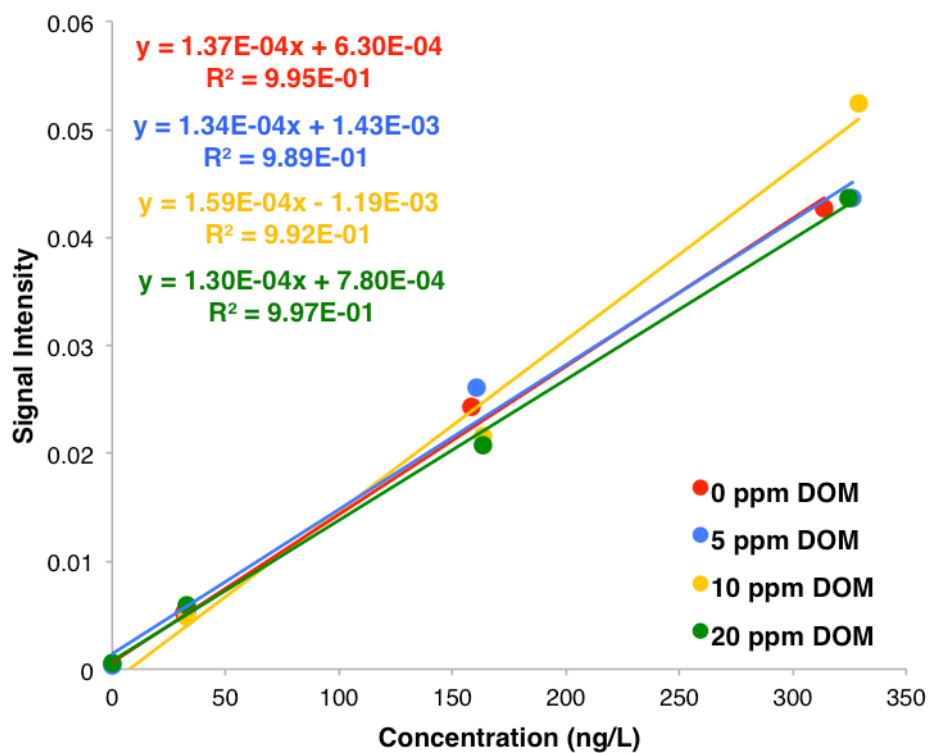


Figure S3: Comparable calibrations for aqueous benzophenone-3 with various loading levels of dissolved organic matter (DOM), using the sodium salt of humic acid (technical grade, Sigma-Aldrich, Oakville, ON, Canada) for these studies.

Table S2: Spike recovery information for CP-MIMS-LEI/CI measurement of aqueous benzophenone-3

| [Spike] ng/L | Percent Recovery |
|--------------------|------------------|
| 163 | 114 |
| 159 | 89 |
| 162 | 98 |
| 161 | 89 |
| <hr/> | |
| Average | 97 |
| Standard Deviation | 12 |

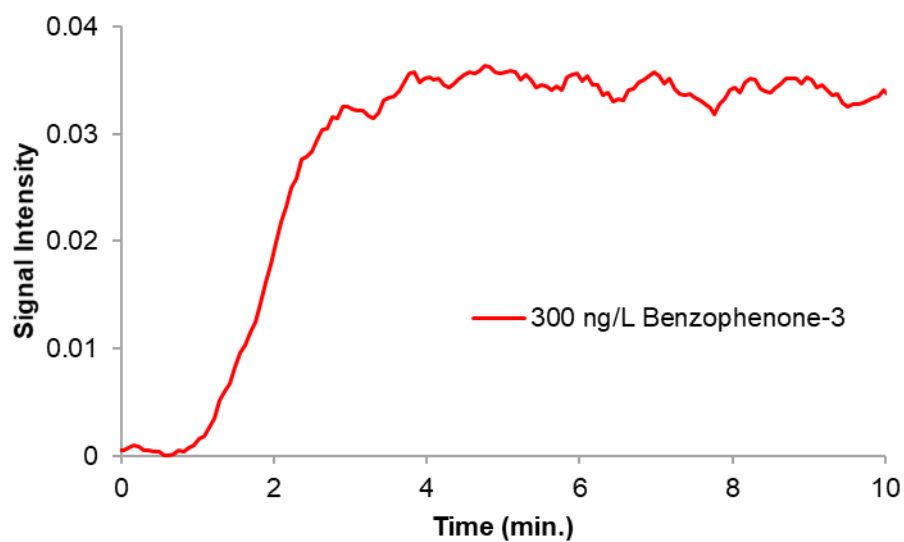
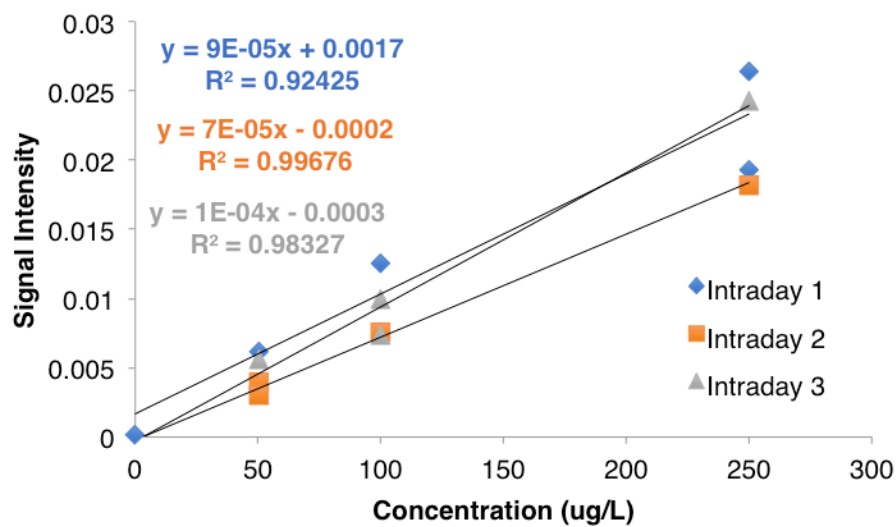


Figure S4: Signal stability (>9 min) for the online measurement of 300 ng/L benzophenone-3 in water obtained using CP-MIMS-LEI/CI.

A.



B.

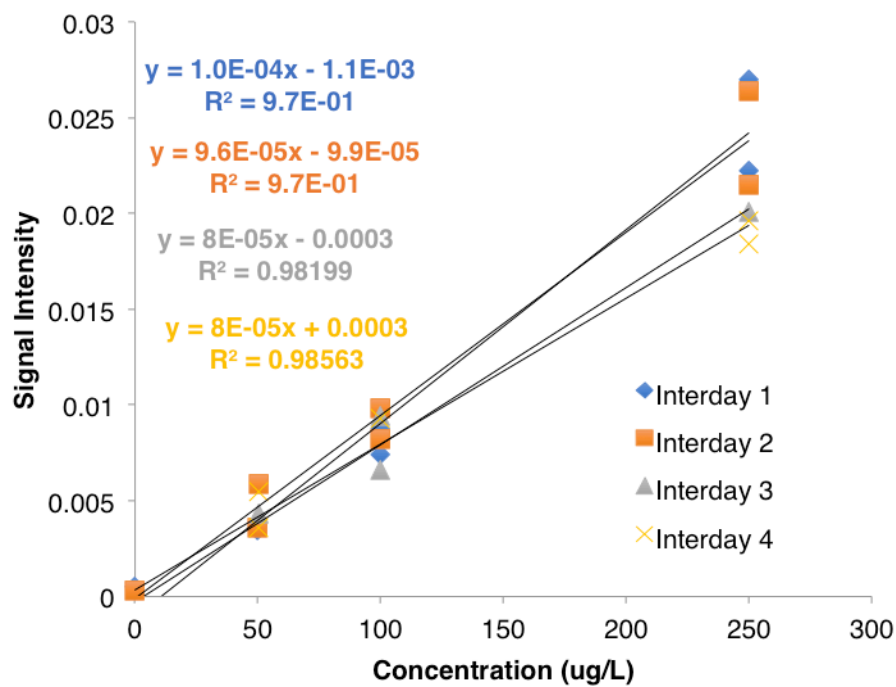


Figure S5: Intra (A) and inter (B) day calibration curves for aqueous benzophenone-3 using CP-MIMS-LEI/CI.

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