

ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND HEAVY METALS IN THE LAKE CHAMPLAIN BASIN

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds containing fused aromatic rings. Some sources of PAHs include gasoline and diesel engine combustion, wood burning, and pavement sealants. Anthropogenic activity is therefore a direct cause of increasing PAH concentration in the environment. A number of PAHs have been determined to be carcinogenic if inhaled or ingested. Another product of anthropogenic activity has been increased heavy metal leaching into the environment. Heavy metals, including mercury, cadmium, and lead, can be found in products such as batteries, industrial waste, cigarettes, and paint. At or above certain concentrations, heavy metals can be carcinogenic or toxic to organisms through direct exposure or by ingesting food products that concentrate these metals.

The aim of this study was to obtain longitudinal data to determine presence of PAHs and heavy metals in various sites in the Lake Champlain Basin. Our hypothesis was that areas of higher PAH contamination would also contain high levels of heavy metals. We report, herein, data obtained from 2018 - 2023 on the presence of PAHs in sediment from sites across the Basin and the concentration of heavy metals in the lake water at those sites. We also discuss several different methods employed for the extraction of PAHs from lake sediment. Qualitative results indicate that PAHs were present at various sites across the lake in 2018 and again in 2022 - 2023. However, quantitative screening results from 2023 show mostly very low or undetectable concentrations of all metals tested.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a family of neutral hydrophobic organic compounds that often contain at least three aromatic fused rings.^{1,2} Some sources of PAHs include gasoline and diesel engine combustion, wood burning, and pavement sealants.³ Many PAHs have been determined to be carcinogenic via exposure or ingestion.⁴ The United States Environmental Protection Agency (U.S. EPA) has included 16 PAHs on its priority pollutants list, and has classified seven PAHs as Group 2, or probable human carcinogens, including chrysene (CHR), benz[a]anthracene (BaA), benzo[k]fluoranthene (BkF), and benzo[a]pyrene (BaP).³ The United States Department of Health and Human Services deems BaA and BaP to be known animal carcinogens. Animal and aquatic life studies have indicated that certain PAHs can affect immune, reproductive, and neurological systems, and can be detrimental to organism development.^{5,6} PAHs that are only slightly mutagenic have the ability to generate biologically active metabolites or derivatives that are potent mutagens.⁷ In addition, studies have shown that the toxicity of these compounds can increase when exposed to UV light.⁸ Due to their high lipophilicity and hydrophobicity, PAHs in aquatic environments tend to be localized in sediment or on suspended particulates,³ although they have also been detected in the water of lakes and other bodies.⁹

Heavy metal contamination plays its own part in negatively affecting the health of humans and other organisms. Threats to human health, in terms of exposure to heavy metals, are due primarily to mercury, lead, cadmium, chromium, and arsenic, as well as other heavy metals at high enough concentrations (specific to each metal).¹⁰ While emission of lead has declined in the United States in recent years due to the phasing out of leaded gasoline, exposure to products such as cigarettes, rechargeable batteries such as the nickel-cadmium battery, industrial and agricultural waste, and cosmetics remain problematic sources for heavy metal exposure. Metals such as copper and zinc can be introduced into bodies of

water through the use of antifouling paints on boats^{11,12} and from heavy-fuel-oil combustion in marine engines.¹³ Heavy metals can induce oxidative stress and affect signal transduction,¹⁰ and can result in damage to internal organs and the skeletal structure as well as skin issues and cancer.¹⁴

Infrastructure development and anthropogenic activity have increased in the Lake Champlain basin area (located in the northeastern part of the United States of America, specifically in the states of New York and Vermont, and the southern portion of the Province of Quebec, Canada) over the past several decades, including increased rates of road-paving and homebuilding near the basin. In addition, with an increase in population (and tourism) comes an increase in use of the lake for boating and recreational activities.

The PAH concentrations in the Lake Champlain Basin have been followed intermittently since 1994, when the Lake Champlain Sediment Toxics Assessment Program found elevated levels of PAHs in surface sediments from Cumberland Bay (Plattsburgh, NY), at the mouth of the Ticonderoga Creek (Ticonderoga, NY), and in the Inner Burlington Harbor (Burlington, VT).¹⁵ In 2001, another study measured PAH concentrations as well as heavy metals and polychlorinated biphenyls (PCBs) in Burlington Harbor sediments that were sampled in 1993. The authors determined that concentrations were highest in areas adjacent to the outlet of the nearby sewage treatment plant and decreased with increasing distance from the plant. PAHs at certain sampling sites were found at levels likely to impact lake biota; the authors also evaluated sediment cores to obtain a proxy record of historical PAH/PCB and heavy metal concentrations. The peak concentration for certain heavy metals, including cadmium and lead, was in the late 1960s after discharges from the sewage treatment plant began, and declined subsequently, most likely due to increased water and air regulations.¹⁶

In 2007, Kreitinger et al.¹⁷ measured the toxicity of PAHs to the test species *Hyaella azteca*, an amphipod crustacean. In their study, sediment samples were collected from four manufactured-gas plants, including one in Plattsburgh, NY, which is located on Lake Champlain. The total PAH concentrations in sediments from Plattsburgh, NY ranged from 6-3,430 mg/kg; most of the PAHs identified at this site were the 2- and 3-ring PAHs. Of the seven samples collected from that site, three samples resulted in a 0 % survival rate of the test species. Interestingly, survival rate was determined not to correlate with total PAH concentration, as a low-concentration sample from Plattsburgh was one of the most lethal to this test species. It is therefore important, the authors stressed, to use the measured bioavailability of PAHs to predict chronic toxicity to *H. azteca* instead of simply considering total PAH concentration.

In 2009, Phillips and Chalmers measured PAH concentrations in water (not sediment) samples collected in 2006 from a variety of bodies of water, such as lake sites, wastewater treatment plants, a combined sewer overflow site, and large rivers and urban streams that empty into Lake Champlain. Of the nine PAHs analyzed, they detected seven, attributing their presence to non-wastewater, broad diffuse urban watershed sources (specifically certain urban streams, a site near an abandoned coal yard, and street runoff that feeds into combined-sewer-overflow sources). PAHs were not detected in the Lake Champlain or large river samples – but again, these samples were of the water itself, not of the sediment.¹⁸

Finally, in 2015, the Vermont Agency of Natural Resources, Department of Environmental Conservation, Waste Management and Prevention Division personnel conducted a statewide study¹⁹ to determine background concentrations (attributed to atmospheric deposition or naturally occurring minerology) of 18 PAHs, arsenic, and lead in soil samples collected between August through November of that same year from locations across Vermont. Locations that were chosen included the largest municipality in each 100-square mile grid across Vermont, as well as municipal parks, greens, building lawns, school lawns, and town forests. Locations with a known release or land use that would have been a source of these contaminants were not analyzed. 130 property samples, of which 17 were duplicates, were collected. Overall PAH concentrations were reported as a Total Equivalency Quotient (TEQ) using the World Health Organization's 2005 Toxicity Equivalence Factor values.²⁰ Higher concentrations of PAHs were found in urban areas as compared to rural areas. These measurements were used to define TEQ PAH background threshold levels for state regulation purposes (580 ppb for urban/commercial/industrial areas and 26 ppb for rural/residential areas). Although none of these sources were located in the lake itself, they did provide useful information on threshold levels for PAHs in soil.¹⁹

The aim of this study was to determine whether detectable levels of PAHs in lake sediment were found in 2018, when our analysis began, and again in 2022 and 2023. In addition, we wanted to examine whether areas of higher PAH contamination also contained high levels of heavy metals, such as lead and cadmium. This hypothesis is bolstered by the findings of other groups such as Egardt et al, who describe a correlation between the use of leisure boats and elevated levels of heavy metals and PAHs.¹² We also wished to explore alternative methods of PAH extraction

that would be more environmentally-friendly than the traditional methods, which rely on heat and solvents.

This study holds significant value in ensuring that the waters of Lake Champlain are safe for both aquatic life and human use. With the increase in population, carbon-based material emissions, lake-based leisure activities, and construction in the area, we expected to observe an increased presence of PAHs in Lake Champlain year-over-year.¹⁵ Knowing where PAH and heavy metal concentrations are the highest – both in the lake sediment and in the water itself – can identify where aquatic and other organisms, including humans, would be most at risk. In addition, longitudinal studies such as this one will help to determine where to focus remediation efforts in the future.

Materials and Methods

Sediment Sample Collection and Preparation:

At each of the selected locations on both the New York and Vermont sides of Lake Champlain, along with one smaller lake in New York and one smaller pond in Vermont (Figures 1 and 2), surface sediment samples were collected in individual 15-mL conical tubes from an area with a 5-meter diameter and a water depth of 0.3 – 0.6 meters. In 2018, eight sites of interest surrounding Lake Champlain were identified and tested (n = 4 from each location) once at the beginning of June (6/1/18 and 6/6/18). In 2022 and again in 2023, these same sites were sampled (n = 2 from each location) in the last week of June and first week of July of each year. Each site was sampled once.

Throughout the study, exposure of the samples to UV light was minimized to avoid photodegradation. Samples were stored in a freezer until they were ready for extraction, where they were allowed to stand at room temperature until completely thawed. Large rocks and pebbles were removed via sieve and by manual removal. 15 g of each sample was massed out, vacuum filtered with a Buchner funnel to remove lake water and placed in an oven at a maximum of 130 °C until dry (for at least 30 minutes). Care was taken not to expose samples to high heat. Approximately 10 g of each sample (known to ± 0.0001 g) was massed out and used for extraction.

Soxhlet Extraction of PAHs:

Several methods for the extraction of PAHs from the lake sediment samples were attempted. The first was a Soxhlet extraction, which



Figure 1. Visual depiction of the sampling sites. a) Map of the United States. The black box highlights the Northeast of the United States, where Lake Champlain is situated. b) Zoomed-in satellite image of the Northeast United States (and the southern portion of the Province of Quebec, Canada). The red box highlights the sampling sites on Lake Champlain and Lake Chateaugay. All pins (blue, red, green, and pink) indicate the specific sites where sediment was sampled. *The map of the United States was generated using Mapchart.net and the satellite map was generated using the pin map feature from alist.com; both are free, open-source map-generating tools.

is commonly used for the extraction of PAHs from sediments and soils.^{3,21,22} Our Soxhlet method paralleled the U.S. EPA method 3540C²³; specifically, a measured sediment sample was placed in a cellulose extraction thimble, which was then inserted into a Soxhlet extractor. 300 mL of acetone/n-hexane mix in a 1:1 volumetric ratio was added to a 500-mL round-bottom flask, which was then attached to the extractor. The temperature of the heating mantle was set to a gentle boil (approximately 60 – 64 °C) and the sample was extracted for 8 - 12 hours at approximately 4 - 6 cycles per hour. The Soxhlet apparatus was then allowed to cool and was disassembled, and the sample was evaporated to near dryness with heat via a heating mantle. The product was then allowed to fully dry overnight at room temperature. The contents were then re-suspended in 1.000 mL of methanol, and the flask was sealed and allowed to settle for approximately 24 hours. The solution was then transferred to a microcentrifuge tube, centrifuged at 14,000 rpm for 2 minutes, and the supernatant was extracted and stored for analysis via gas chromatography – mass spectrometry (GC-MS).

If samples appeared more contaminated (darker color, stronger odor, etc.), the evaporation after extraction was, by necessity, done at a lower temperature to avoid what appeared to be burnt product; additionally, samples evaporated under higher heat sometimes adhered to the round-bottom flask, which made resuspension of the post-extraction product difficult. For these samples especially, but for all samples analyzed in 2023, we tested the use of an aluminum-bead bath coupled with a probe-controlled hotplate. While this method lessened the loss of product and amount of burnt product and helped in re-suspension, the final method for solvent evaporation and Soxhlet extraction used rotary evaporation until final solvent volume was ~ 0.5 - 1.0 mL.

Eucalyptus Oil for the Extraction of PAHs:

Soxhlet extractions are not without their drawbacks, especially because they typically utilize organic solvents in combination with heat. However, as described above, PAHs can be volatilized or de-

graded in the presence of high heat, so this method may not pose as the best choice for their analysis. In addition, the use of large quantities of organic solvent is not environmentally friendly. In 2023, using samples obtained the same year, we tested a second, “greener” extraction method that utilized eucalyptus oil, a method determined to be useful for the extraction of various organic compounds from certain samples.²⁴

The eucalyptus oil procedure used in this study was based on the method developed by the Doran group,²⁵ which was shown to extract 112% of phenanthrene (PHE), 108% of pyrene (PYR), 102% of CHR, and 98% of BaP from spiked soil samples and 90 % of PHE, 111% of PYR, 84% of CHR, and 82% of BaP from spiked sediment samples. Briefly, the method employs the addition of 4 - 6 mL of pure eucalyptus oil to 2 g of soil, followed by mixing via inversion for 3 - 7 days at room temperature, then centrifugation immediately prior to analysis by GC-MS.

Of note, issues with the eucalyptus oil extraction may arise if the samples contain more clay and less organic matter (which was descriptive of many of our samples), as these samples can bind PAHs more tightly, which may restrict the oil’s access.²⁵ Another issue mentioned by the Doran group is that the extraction efficiencies of the various PAHs analyzed were highly dependent on temperature, volume of oil, shaking time, and matrix composition in the oil extraction procedure²⁵, which indicates that appropriate method development and optimization is vital to ensure to usefulness of this method for complete PAH extraction from lake sediment.

The two different variations of the eucalyptus oil extraction method developed in our lab involved either shaking at room temperature or microwave extraction. For room temperature extraction, 2 g of wet sediment from a sample obtained from site 12 (Table 1) was placed in 5 mL of eucalyptus oil. Another 2-g sample from the same site was placed in 5 mL of eucalyptus oil and 1 mL of acetonitrile. Both samples were shaken continuously in an incubator shaker (New Brunswick Science C24) for 7 days. 750 µL of each sample was taken every 24 hours and stored at 4 °C until later analyzed via GC-MS.

Microwave extraction involved 10 g of wet sediment samples from the same sampling site (site 12). This portion of the site 12

Table 1. Location of sample sites indicated by Figure 2 (above).

Site Number (#)	Location
1	St. Albans Town Beach, St. Albans, VT
2	Malletts Bay, Colchester, VT
3	North Beach State Park, Burlington, VT
4	Burlington Harbor, Burlington, VT
5	Oakledge State Park, Burlington, VT
6	Shelburne Town Beach, Shelburne, VT
7	Crown Point State Historic Site, Crown Point, NY
8	Ticonderoga Ferry Launch, Ticonderoga, NY
9	Ausable Point Campground, Peru, NY
10	Wilcox Dock, Plattsburgh, NY
11	Cumberland Bay State Park, Plattsburgh, NY
12	Point Au Roche State Park, Plattsburgh, NY
13	Chateaugay Lake Boat Launch, Merrill, NY
14	Narrows Road Bridge, Chateaugay Lake, Merrill, NY
15	Gilbrook Pond, Colchester, VT

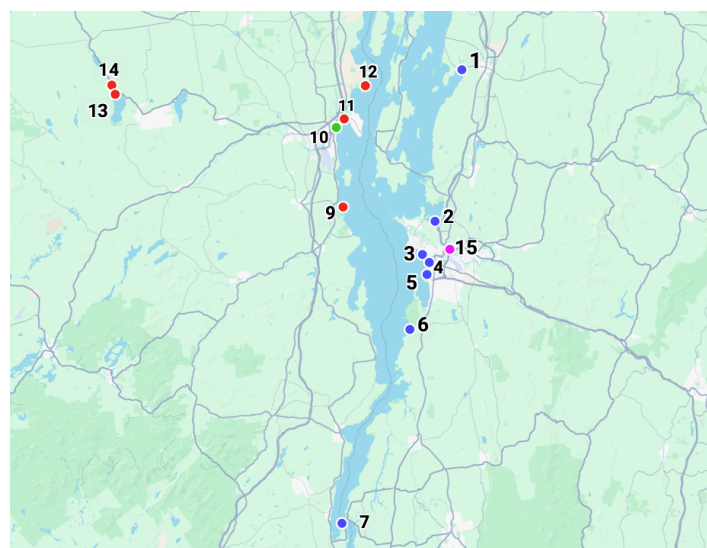


Figure 2. A visual representation of the fifteen sample sites. The blue pins indicate the sites sampled in 2018, and again in 2022. The red pins and pink pin indicate the sites sampled in 2023. The green pin (Wilcox dock, Plattsburgh, NY), was sampled during all three sampling campaigns (2018, 2022, and 2023). The pink pin (Gilbrook Pond, Colchester, VT) was a local site on the St Michael’s College campus that was not sampled for PAHs. See Table 1 for specific locations. *Sample site map was generated using the pin map feature from alist.com, a free, open-source map-generating tool.

sample was dried in an incubator for 48 h at 50 °C. 2 g of dry sediment (times three samples) was spiked with 20 mg/mL of PAH standard (RESTEK EU 15+1 PAH Standard) and volumes of eucalyptus oil and acetone were added at three different ratios (Figure 3). Each formulation was then extracted using a microwave (CEM discovery 2.0) at 120 °C. For each formulation, 2 mL of supernatant was collected after 8, 15, and 25 minutes and stored at 4 °C. Prior to analysis, 1.5 mL of supernatant was transferred to a microcentrifuge tube and centrifuged at 4000 RPM for 5 minutes. If sediment was still suspended, the sample was transferred to another microcentrifuge tube with a filter and recentrifuged at 4500 RPM for 2 minutes. 1 mL of this sample was then placed into a GC-MS vial for later analysis. Both methods deployed a eucalyptus oil-only negative control during analysis.

Qualitative Analysis of PAHs in Lake Sediment Using GC-MS:

GC-MS is a typical instrument deployed for the quantitation of extracted PAHs, especially when a column appropriate for separating the various PAHs is used.²¹ For our 2018 campaign, all samples were analyzed using a Varian GC-MS system with autosampler and Phenomenex Zebron ZB-5 column (30 m, 0.25 mm ID, 1 µm film thickness). 5 µL of each sample was injected under the following conditions: 3-minute solvent delay; 22.5-minute scan in electron ionization (EI) mode, auto from 50 – 650 (m/z); GC oven parameters of an initial temperature of 60 °C for 1 min, ramp at 50 °C/min until 210 °C, ramp at 10 °C/min to 300 °C, hold at 300 °C for 9.5 minutes; inlet conditions were splitless, 280 °C, with the initial split state off, and then split state on at 0.9 min with split ratio of 40.

Under these conditions, the peaks eluted on the chromatogram at the standard retention times for the specified PAH; if the parent ion was visible on the corresponding mass spectrum for that eluted peak, that sample was identified as containing that specified PAH. If, however, the parent ion (or any subsequent product ions for the specified PAH) was not visible, that sample was identified as not containing that PAH. The presence or absence of five PAHs were examined; these were pyrene (PYR), chrysene (CHR), benz[a]anthracene (BaA), benzo[k]fluoranthene (BkF), and benzo[a]pyrene (BaP).

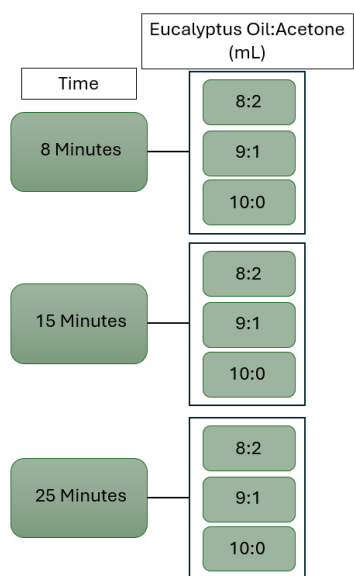


Figure 3. Formulations of site 12 samples for eucalyptus oil/microwave extraction.

For our 2022 and 2023 campaign, selected samples (including the spiked samples extracted using the various eucalyptus oil techniques described above) were analyzed using a Shimadzu GC-MS - QP2010 SE system with a standard C-18 column. Qualitative results were obtained under the same instrument conditions as described above. The presence or absence of six PAHs were determined; these include the same five PAHs listed above, with the addition of phenanthrene (PHE). Quantitative results were not obtained due primarily to issues with complete removal of sticky residue that remained after Soxhlets were complete.

Quantitative Analysis of Heavy Metals in Lake Water Using ICP-OES:

In our 2022 and 2023 campaign, dissolved-phase heavy metal contamination of filtered lake water samples from our selected sites (n = 1, obtained during one visit to each site in late June or early July of each year) was analyzed by inductively coupled plasma – optical emission spectroscopy (ICP-OES) in a procedure mirroring the U.S. EPA method 200.7.²⁶ Collection flasks (100.00-mL volumetric flasks) were washed with a lab detergent solution and soaked in a 20 % nitric acid bath for at least 24 hours, followed by extensive rinsing with ultrapure water. Samples (> 100 mL) were collected in individual acid-washed flasks from an area with a 5-meter diameter. Water samples were stored on ice until returned to the lab, then promptly gravity-filtered to remove sediment/suspended material. Filtered samples were acidified by addition of 5 % (v/v) hydrochloric acid and 4 % (v/v) ICP-grade nitric acid following procedures detailed in U.S. EPA method 3005a²⁷ and published by other researchers.²⁸ Samples were covered, sealed, and kept at 4 °C until ICP-OES analysis.

An Agilent Technologies 5110 ICP-OES was used to quantify select metals in each sample, with appropriate nebulizer and plasma gas flow rates. A blank of ultrapure water (acidified as per the sample procedure described above) was run and the blank subtraction performed by the ICP-OES software. A two-point calibration curve using 1.00 and 0.10 ppm standards of each element under analysis (prepared by dilution of a 10-ppm standard supplied by SPEX CertiPrep) was made (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, and Zn). Ca, K, Na, and Sr analyses were run in the radial plasma view; all other elemental analyses were run in the axial view. Due to procedural and system limitations, this did not include mercury. Samples were then analyzed, and after every 10th sample, three replicates of a procedural blank sample replicate and a control (standard) were run to ensure absence of contamination and verify the analysis. None of these QA/QC checks yielded >10% deviation from expected values. Synthetic controls, where standards were diluted to appropriate concentrations, and spiked samples for percent recovery were not analyzed, so instrument detection limit (IDL) and limit of quantitation (LOQ) values were not calculated.

Results and Discussion

Post-Soxhlet Sample Observations

As mentioned above, samples after Soxhlet frequently appeared burnt (very dark brown, tarry, and sticky), and there was concern as to whether the PAH compounds present were chemically altered to form products that would not be identifiable by GC-MS.

The stickiness of the samples post-Soxhlet also made resuspension of the product difficult, resulting in a significant loss of product, which affected the results. While care was taken to minimize these issues and their impact on the data, true quantification of PAH compounds in sediment post-Soxhlet remained problematic.

Qualitative Analysis of PAHs by Soxhlet/GC-MS (2018):

All samples obtained during this campaign (8 sites, visited once, $n = 4$ for each site) were collected and analyzed following the methods described above. Five PAH-specific retention times were analyzed for all 32 samples (four samples per site). This generated 160 total mass spectra. Of the 160 total spectra analyzed, the parent ion (indicative m/z at specified retention time) was present in 39 spectra (Table 2). Therefore, 24% of all spectra analyzed contained a peak of interest, indicating presence of at least one PAH. Of significance, PYR was present in 53% of all samples. In addition, BaA and CHR were present in 28% and 25% of the 32 samples, respectively; as mentioned above, both PAHs are deemed probable human carcinogens by the U.S. EPA.

Qualitative Analysis of PAHs by Soxhlet/GC-MS (2022 & 2023):

All sites were sampled as above (one visit, $n = 2$ from each site). Site 10 (Wilcox Dock, Plattsburgh, NY) was of specific interest, as this specific sample had the worst odor, highest turbidity, and stickiest sediment of all the samples obtained from the original sampling campaign in 2018; this location was also identified in 1994 as having elevated levels of PAHs in sediment samples.¹⁵ Therefore, both samples from site 10 were analyzed; samples from other sites either yielded no useable extractant due to issues with the Soxhlet method as described earlier or were not analyzed due to time constraints. Then, using the same methodology for analysis via GC-MS, these two samples exhibited the presence of PYR, CHR, BaA, and BkF. BaP was not identified in the samples. However, another PAH compound – PHE – was determined to be present in both samples; however, this was not an analyte examined during the 2018 campaign.

In 2023, sampling and analysis focused mainly on sites located on the New York (western) side of Lake Champlain (Figure 2). Both samples from site 10 and one sample from site 9 (Ausable Point Campground, Peru, NY) were analyzed and showed the presence of all six PAHs. Other samples were obtained as shown in Figure 2, but again, due to issues with extraction or time, they were not analyzed by GC-MS.

Use of Eucalyptus Oil to Extract PAHs:

GC-MS analysis of all spiked samples extracted using eucalyptus oil, whether using the shaken or the microwave extraction meth-

Table 2. Percentage of PAH presence in 32 total sediment samples (4 samples per location) analyzed.

Sample Site (#)	PYR	CHR	BaA	BkF	BaP
1	50%	0%	0%	0%	0%
2	75%	75%	75%	25%	25%
3	25%	0%	0%	0%	0%
4	75%	75%	75%	0%	25%
5	100%	50%	50%	25%	25%
6	75%	0%	0%	0%	0%
7	0%	0%	25%	0%	0%
10	25%	0%	0%	0%	0%
Total presence (of 32 samples)	53%	25%	28%	6%	9%

od, showed no detectable PAHs. As this same sediment sample as extracted by the Soxhlet method was shown to include PAHs, and as the microwave extracted samples had been spiked with a known concentration of PAHs, we believe that our eucalyptus oil extraction methods need significant refinement prior to being used as a replacement for more traditional methods, at least as performed by our lab. It is also possible that the issues with the eucalyptus oil extraction for samples that contain more clay and less organic matter did indeed restrict the oil's access. However, we do believe that the microwave extraction method has potential based on published results from other groups,²⁵ and future aims include optimization of this more environmentally-friendly technique.

Quantitative Analysis of Heavy Metals by ICP-OES:

In 2022 and 2023, we also collected water samples at each of the sediment sampling locations, for analysis of certain heavy metal concentrations by ICP-OES. 2023 results are shown in Figure 4a. The higher concentrations of Ca, Na, K, and Mg shown in Figure 4a are to be expected in lake water. Results after removal of Ca, Na, K, and Mg are shown in Figure 4b for greater visibility, as the concentration of these analytes overwhelm Figure 4a.

Site 6 (Jun 12) and site 15 showed Cd levels of 0.01 ppm for both, in excess of safe concentrations (maximum contaminant level goal, or MCLG) as outlined by the U.S. EPA (0.005 ppm). It is worth mentioning that our calibration used 0.10- and 1.00-ppm standards, so these levels are sub-calibration; however, the comparison between sites is interesting. QC samples containing 0.01 ppm and 10.0 ppm Cd reported at 0.01 and 10.0 ppm respectively, indicating probable high accuracy of sample results. The two sam-

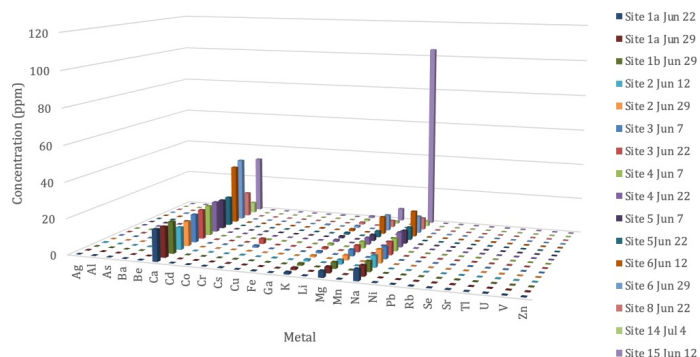


Figure 4a. Concentration (ppm) of all metals analyzed for 2023 samples. See Table 1 for specific site locations. Two samples were gathered from site 1 for ICP-OES analysis; St. Albans Bay is listed as site 1a and St. Albans Dock is listed as site 1b.

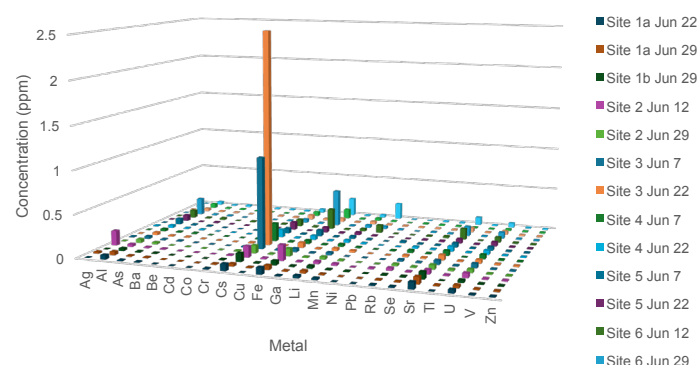


Figure 4b. Concentration (ppm) of all metals analyzed for 2023 samples with the removal of Ca, K, Mg, and Na. See Table 1 for specific site locations. Site 1 samples are listed as described in the Figure 4a legend.

ples from site 3 both showed a concentration of Cs that was more than tenfold higher than the next highest sampled site. However, quality control (QC) samples containing 0.01 and 10.0 ppm Cs reported at 1.32 and 4.31 ppm respectively, calling into question the accuracy of the site 3 results.

Site 5 (Jun 7) showed a Pb level (0.02 ppm) in excess of the MCLG for Pb (0.01 ppm), although the site 5 (Jun 22) detected no Pb present. This concentration is around the detection limit of ICP-OES, however, so it should not be considered truly quantitative. The 0.01 and 10.0 ppm Pb QC samples reported at 0.01 and 9.23 ppm respectively, again indicating probable high accuracy of sample results.

A number of samples showed Tl levels in excess of the MCLG for Tl (ranging from 0.00 - 0.02 ppm; safe concentration is 0.002 ppm), although recommended testing of Tl concentration is ICP-MS or atomic absorption, not ICP-OES, so this exceedance claim is not well supported.²⁹ It is worth noting that 0.01 and 10.0 ppm Tl QC samples reported at 0.02 and 9.91 ppm Tl respectively.

No water samples gathered and tested in 2022 exceeded the U.S. EPA safe concentration limits (data not shown).

The U.S. EPA also provides guidance on secondary maximum contaminant levels (SMCL) for drinking water contaminants that are not enforced but are designed to be guidelines for aesthetic considerations such as taste, color, and odor, but are not considered to present a risk to human health at these levels.³⁰ The SMCL for Al is 0.05 - 0.2 ppm; the site 6 (Jun 29) sample contained 0.2 ppm of Al. 0.01 and 10.0 ppm Al QC samples reported at 0.01 and 12.08 ppm Al respectively. Both site 6 samples (Jun 12 and Jun 29) had the highest Fe levels of all sites sampled (0.24 and 0.43 ppm respectively); the SMCL for Fe is 0.3 ppm. 0.01 and 10.0 ppm Fe QC samples reported at 0.01 and 10.7 ppm. Both site 6 (Jun 12) and site 15 samples had Mn in excess of the 0.05 ppm SMCL (0.09 and 0.19 ppm respectively); 0.01 and 10.0 ppm Mn QC samples reported at 0.01 and 10.45 ppm. Finally, the site 2 (Jun 12) sample had an Ag concentration of 0.17 ppm, which is in excess of the SMCL (0.1 ppm), although the site 2 (Jun 29) sample had no detected Ag present. The 0.01 ppm Ag QC sample did report at 0.01 ppm, but the 10.0 ppm sample yielded values over the calibration range of the instrument for that dataset. This calls into question the accuracy of the Ag results for that sample..

These MCLG/SMCL levels are EPA drinking-water values, and therefore these results should be considered screening benchmarks rather than compliance exceedances.

Conclusions

The two overarching goals of this research were to quantify the concentration of PAHs in sediment samples from both the Vermont and New York sides of Lake Champlain, as well as determine heavy metal concentrations from water samples across the basin. However, due to issues with Soxhlet products and time constraints, the PAH-specific analysis shifted to a qualitative approach. In 2018, when we began collecting samples for analysis, almost 60 % (all extracted by the Soxhlet technique) contained at least one PAH compound out of the five analyzed, including 34% that con-

tained at least one PAH compound that has been determined to be probable human carcinogens by the United States Environmental Protection Agency.

In 2022 and again in 2023, samples from one specific site analyzed in 2018 – the Wilcox Dock site in Plattsburgh, NY - were analyzed for the presence or absence of six different PAHs, again using Soxhlet extraction. In 2022, five of the six PAHs were present at this site; by 2023, all six PAHs were detected. While quantitative data was not obtained (due primarily to issues with the Soxhlet extraction products being difficult to completely remove from the round-bottom flask), this increase in the presence of PAHs between 2018 and 2023 is concerning.

It was originally hypothesized that areas containing detectable levels of PAHs would also contain greater concentrations of heavy metals, due to sources of both forms of contamination being similar. The results did not support this initial hypothesis, as no more than trace amounts of certain dangerous dissolved-phase metals were detected in the shallow water samples, although the concentrations of Cd, Pb, and Tl in certain areas in the lake were slightly higher than the U.S. EPA MCLG values for drinking water. However, further analysis is required before any correlation between PAH presence and heavy metal contamination can be determined with statistical significance.

The initial results from our eucalyptus oil method development, specifically extraction of PAHs from a spiked sediment sample via long-term shaking and microwave methods, were disappointing, but could be due to sample composition; however, since other research groups have shown the shaking method to be useful, method optimization is warranted and is a future goal for our lab. Additional future goals include the determination of more efficient, environmentally-friendly, and less (potentially) damaging methods by which to extract PAHs from sediment, including optimization of the microwave extraction technique using eucalyptus oil.

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ChemRxiv.³¹ Small changes have been made to the article since that publication, focusing on clarification about the comparison to the US EPA drinking water guidelines and the ICP-OES quantitative results. lyzed in 2018 – the Wilcox Dock site in Plattsburgh, NY - were analyzed for the presence or absence of six different PAHs, again using Soxhlet extraction. In 2022, five of the six PAHs were present at this site; by 2023, all six PAHs were detected. While quantitative data was not obtained, this increase in the presence of PAHs between 2018 and 2023 is concerning.

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