2018 Environmental Chemistry Symposium
University of Alaska

7th April 2018 – 9:30 AM to 4:00 PM UAF **Akasofu (IARC) 401**
Awards and Posters (and dinner 4:00 – 6:30 PM) UAF **Akasofu (IARC) 401**

Organizers:
William R. Simpson, Jennifer J. Guerard, Jingqiu Mao

Sponsors:
Department of Chemistry and Biochemistry, UAF
College of Natural Sciences and Mathematics (CNSM), UAF
Geophysical Institute (GI), UAF
Undergraduate Research and Scholarly Activities (URSA), UAF

Symposium Schedule

Time	Presenter	Title
9:30 -- 10:15 am	Breakfast Reception	
10:15 – 10:20	Opening Remarks	
	Session 1: Atmospheric Chemistry & Cycling	
10:20 – 10:40 am	Nicole Jacobs	*A year of regional atmospheric CO2 and CH4 measurements in Fairbanks and other boreal forest sites*
10:40 – 11:00 am	Sujai Banerji	*Pandora - A new UV-Vis spectrometer developed for measurements of vertical column density of NO2*
11:00 – 11:20 am	William Swanson	*Modeling Arctic Reactive Bromine Using Principal Components Analysis*
11:20 – 11:40 am	Coffee Break	
	Session 2: Aquatic Photochemistry	
11:40 – 12:00pm	Kristin Gagné	*A Snapshot into the Past: Permafrost Chemical Composition and Photochemical Reactivity*
12:00 – 12:20pm	Lawrence Itela	*Photolysis of the Anti-Retroviral Drug Nevirapine in Aquatic Waters*
12:30 – 1:45 pm	Lunch	
1:45 – 2:00 pm	Group Photo	
	Session 3: Aerosols & Air Pollution	
2:00 – 2:20 pm	Abdul Kadir	*Investigation of Particulate Air Pollution in Interior Alaska*
2:20 – 2:40 pm	Jennifer Chambers	*Determining the composition of aerosols produced through the combustion of different fuel types using FTIR*
2:40 – 3:00 pm	Ragen Davey	*Characterizing Anion and Metal Aerosol Composition and Formation in Arctic Air*
3:00 – 3:20 pm	Coffee Break	
	Session 4: Contaminant Fate & Transformation	
3:20 – 3:40 pm	Taylor Gofstein	*Fate and Effects of Petroleum Contamination and Chemical Dispersants in Arctic Marine Environments*
3:40 – 4:00 pm	Kyle Milke	*Release of metal(loid)s from coal ash and association with dissolved organic matter in aqueous systems*
4:00 – 5:00 pm	***Undergraduate Poster Session***	
5:00 – 6:30 pm	Dinner and Awards Reception	

Poster Presentations

4:00 – 5:00 pm	Presenter	Poster Title
	Kiersten Johnson	Diurnal ambient aerosol concentration during the Fairbanks Winter
	Kiana Mitchell	Leaching behavior of boiler slag and fly ash in sub-Arctic environmental media.
	David Warner	Diversity of Alaskan boreal DOM: Relationships between DOM composition and molecular size

Abstracts

Oral Presentations

Poster Presentations

Oral presentation:

Pandora - A new UV-Vis spectrometer developed for measurements of vertical column density of NO_2

Sujai Banerji[1] and Jingqiu Mao[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Nitrogen dioxide (NO_2) is one of the major air pollutants released into the troposphere from primarily from burning of fossil-fuel such as the emissions from automobiles, power plants, and oil rigs, which are a major source of contribution for Alaska. In addition to that, the limited satellite data that is available for the subarctic region such as OMI and TROPOMI are largely uncertain and lack ground validation. Therefore, these reasons make Fairbanks a favourable site for testing a new ultraviolet-visible (UV) spectrometer named Pandora that has been loaned to the University of Alaska Fairbanks (UAF) by the Goddard Space Flight Center (GSFC). The first measurements of vertical column density of nitrogen dioxide - C(NO_2), which are available now, have been used to compare the outputs from a global chemical transport model - (GEOS-Chem), for a very small time span to check if the model can successfully capture the pollution profile.

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Oral presentation:

Determining the composition of aerosols produced through the combustion of different fuel types using FTIR

Jennifer Chambers[1] **and Catherine Cahill**[1]

[1] Department of Chemistry and Biochemistry and Geophysical Institute, University of Alaska Fairbanks, Fairbanks, Alaska

Solid particles and liquid droplets suspended in the atmosphere, a.k.a. particulate matter, result in environmental impacts, such as changing the scattering and absorption of light in the atmosphere and decreasing the earth's albedo, and human health concerns, such as increasing the risk of heart attack, asthma, and chronic obstructive pulmonary disease. The sources of particulate matter include sea spray, vehicle emissions, industrial processes, and biomass burning. These sources have unique chemical and spectral signatures that can be used to identify them and quantify their contributions to an ambient air sample. Fourier Transform Infrared Spectroscopy will be utilized to determine the functional group compositions of primary organic aerosols resulting from the combustion of the most common fuel types in Alaska's boreal forest. This information will be used to quantify the impacts of particles from different fuels on the particle concentrations in and impacts of wildfire smoke. Experimental methods and preliminary results will be presented.

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Oral presentation:

Characterizing Anion and Metal Aerosol Composition and Formation in Arctic Air

Ragen Davey[1] and Jingqiu Mao[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Fairbanks, Alaska is classified as a "serious non-attainment zone" due to the exposure of high levels of air pollutants throughout the winter months. This causes the city to violate the Fine Particulate Matter ($PM_{2.5}$) National Ambient Air Quality Standards set in place by the United States Environmental Protection Agency. These fine particulates, with a diameter less than 2.5 μm, are pollutants that cause major health risks to the citizens of Fairbanks. Previous studies have shown the significant amount of sulfate aerosols observed in Fairbanks winters, but the formation mechanism of sulfate aerosols in the atmosphere is still unknown. While sulfate formation is commonly driven by oxidants including OH, H_2O_2 and ozone, these species are limited in Fairbanks winter months. This indicates sulfate formation may occur through a non-traditional pathway, and this project will investigate the mechanism in which transition metals catalyze sulfate formation. Winter air samples will be collected using a Particle into Liquid Sampler (PILS) and analysis of sulfate and metal concentrations will be conducted using Ion Chromatography (IC) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). By establishing a link between the two species, mechanisms of sulfate formation and the sources of the poor winter air quality will be investigated.

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Oral presentation:

A Snapshot into the Past: Permafrost Chemical Composition and Photochemical Reactivity

Kristin R. Gagne[1] and Jennifer J. Guerard[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Permafrost is soil frozen for two or more consecutive years and houses a large carbon pool that is susceptible to thaw. This ancient carbon sequestered in permafrost has the potential to leach into surface waters impacting the biogeochemical cycling of a watershed. The chemical composition and reactivity of permafrost natural organic matter (NOM) is not well understood and thus, the ramifications of permafrost thaw in a changing climate is unknown. NOM composition is dependent on environmental inputs from terrestrial and microbial life in the ecosystem. Permafrost NOM is typically reported to have a decreased aromatic content through observations by nuclear magnetic resonance (NMR), UV-Vis, and fluorescence. Aromatic character is often responsible for light absorption, and thus influences NOM's photoreactivity in sunlit surface waters. Characterization of soil NOM composition was performed through radiocarbon dating, NMR, UV-Vis, and fluorescence excitation-emission matrices (EEMs). Results from NMR analysis showed a decrease in leachable aliphatic and ketone functional groups with depth. This change in ketone content has the potential to influence the chemical reactivity of permafrost NOM in the presence of sunlight. Additionally, ^{13}C solid-state NMR was conducted on soil with paramagnetic metals removed through a washing sequence of hydrofluoric acid. Whole soil NMR did not reflect the same trends and leachable fractions from permafrost NOM. Furthermore, through the analysis of NMR samples it has been determined that leaching of NOM lacks aliphatic carbons present in the soil prior to leaching. Chemical probes were used to determine permafrost NOM's ability for photoproduction of •OH and $^{3}NOM^{*}$. The permafrost NOM photoreactivity was compared to reference microbial and terrestrial NOM isolates to observe reactivity variation with known NOM composition. This research will allow for a better understanding on how water quality and reactivity will be altered through the active thawing of permafrost in a changing sub-Arctic climate.

Oral presentation:

Fate and Effects of Petroleum Contamination and Chemical Dispersants in Arctic Marine Environments

Taylor R. Gofstein[1], Matt Perkins[2], Jennifer Field[2], and Mary Beth Leigh[1]

[1] Department of Chemistry and Biochemistry and Institute of Arctic Biology, University of Alaska Fairbanks, Fairbanks, Alaska
[2]Oregon State University

The potential for oil spills due to offshore oil development and marine shipping of petroleum products have become a major concern in the Arctic in recent years. We are conducting a series of experiments aimed at understanding the fate of petroleum contaminants and chemical dispersants, their interactions with the environment, and factors that influence their biodegradation by microorganisms in an Arctic marine ecosystem likely to be impacted by petroleum contamination. Mesocosms (800 ml) were established using seawater collected from the Chukchi Sea that were then treated with either 50 ppm of Alaska North Slope crude oil, 5 ppm of Corexit 9500 (1:10 dispersant-oil ratio), or both. Mesocosms were incubated on stir plates at environmentally relevant temperatures and replicates were destructively harvested at 0, 5, 10, 20, and 30 days. A series of larger-scale (6 L) incubations was also established and subsampled daily for 7 days in order to study the degradation of the surfactants that comprise Corexit. We then analyzed total petroleum hydrocarbon (TPH) loss using GC/MS, degradation of the surfactants that compose Corexit using LC/MS/MS techniques, and nutrient concentrations (NO_2^-, NO_3^-, NH_4^+, $PO_4^{-3}$and SiO_4^{-4}) using flow injection analysis. Oil biodegradation was quantified over time and we found slight enhancement of oil degradation with the addition of Corexit 9500. Rapid degradation of the nonionic surfactant components (Span 80, Tween 80, and Tween 85) of Corexit was also observed, however, conclusions regarding the degradation of the anionic surfactant DOSS remains unclear at this time and will be the subject of continued analysis. Future analyses will focus on changes to the microbial community over the course of the incubations in order to identify putative oil- and surfactant-degrading microbes and to evaluate their changes in population size, biogeochemical cycling potential, and gene expression during biodegradation. Together, the results will provide new insight into the biodegradation of oil and dispersants in Arctic waters.

Oral presentation:

Photolysis of the Anti-Retroviral Drug Nevirapine in Aquatic Waters

Lawrence Itela, Marcos Toniolo, Lawrence Duffy and Jennifer Guerard

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Antiretroviral drugs (ARVs) are a class of pharmaceutical compounds that are used to manage the Human Immuno-deficiency virus (HIV) and related infections. Recently, there have published reports of measured levels of these drugs (lamivudine, zidovudine and nevirapine) at concentrations of environmental concern. Nevirapine is non-nucleoside reverse transcriptase inhibitor, most effective against HIV-! And primarily used in prevention of mother-to-child transmission. Its prevalent use in low income, endemic areas and its high octanol- water partition coefficient poses a high risk for bioaccumulation. It is relatively resistant to hydrolysis. Despite sun-lit flocculation ponds being the most widely used in wastewater treatment in these regions, the effectiveness of photolysis in elimination of these pharmaceutical compounds has not been investigated. In this study, we seek to determine the photolysis of nevirapine in water, and determine its rate constant and half-life. The analysis includes characterization of aqueous nevirapine followed by timed photolysis experiments and HPLC-UV analysis of the samples. Analysis of nevirapine is hampered by it low aqueous solubility. Calibration curves for UV analysis have been developed for this method to determine it molar absorptivity. These parameters will then be used in study of Dissolved Organic Matter (DOM)- mediated indirect photolysis of Nevirapine. Knowledge of this information will help in managing wastewater treatment processes and tune them to ensure maximum attenuation of drug concentrations.

Oral presentation:

A year of regional atmospheric CO2 and CH4 measurements in Fairbanks and other boreal forest sites

Nicole Jacobs[1] **and William R. Simpson**[1]

[1] Geophysical Institute and Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

The Boreal Forest of North America is one of the world's largest seasonal carbon dioxide (CO2) sinks and northern wetlands are an important ecological source of methane (CH4). High-latitude ecosystems are particularly vulnerable to the effects of rising temperatures and global climate shifts, so understanding the regional dynamics of atmospheric CO2 and CH4 in the sensitive climates of the Boreal forest and northern wetlands is critical for modeling global greenhouse gas fluxes and feedbacks. These fluxes can be measured on small scales (~200m) via eddy covariance methods, but these data need to be extrapolated to a regional scale for use in climate models, posing a challenging upscaling problem that requires observations at larger scales for validation. Regional estimates from these ecosystem models are often compared against aircraft observations, tall-towers, or satellites; however, these regional and global scale observation methods have logistical limitations that restrict their coverage.

To address these challenges, we began the AMIGGO (Arctic Mobile Infrared Greenhouse Gas Observations) campaign to quantify regional-scale atmospheric CO2 and CH4 net fluxes in central Alaska through the use of mobilized solar-viewing Fourier-transform infrared (FTIR) spectrometers. The EM27/SUN spectrometer has been developed by KIT (Karlsruhe Institute of Technology) in collaboration with Bruker Optics (Gisi et al., 2012, doi: 10.5194/amt-5-2969-2012), and it is used to measure a column-averaged dry-air mole fraction (DMF), which is vertically integrated through the entire atmosphere. The total atmospheric column includes both local sources/sinks and variations aloft that have been transported continentally or even globally, so to narrow our focus on local and regional effects we deployed two FTIR instruments to a variety of sites in the Fairbanks area and analyzed the differences between them during late summer/fall 2016. From 11 March 2017 to 3 November 2017 we continued to observe with one EM27/SUN spectrometer on the roof of the Geophysical Institute at UAF and used these observations to evaluate the seasonal cycles of CO2 and CH4 from August 2016 through October 2017. Results from a comparative analysis between our measurements of CO2 columns from the ground in

Fairbanks and those from the NASA satellite OCO-2 (Orbiting Carbon Observatory-2) will be presented. In addition, the full time series of CH4 and CO2 column measurements in Fairbanks will be discussed and compared to similar column measurements observed on the ground at two other boreal sites; Sodankyla, Finland and East Trout Lake, Saskatchewan. Continued observations with two EM27/SUN spectrometers through the spring, summer, and fall of 2018 can be expected to further elucidate seasonal and spatial CO2 and CH4 dynamics in the sub-Arctic Boreal Forest of central Alaska and contribute to ongoing validation efforts for OCO-2 as well as new satellite validation efforts for CH4 and carbon monoxide measured by the European TROPOMI satellite.

Oral presentation:

Investigation of Particulate Air Pollution in Interior Alaska

Abdul Kadir and Srijan Aggarwal[1]

[1] Water and Environmental Research Center, University of Alaska Fairbanks

Fairbanks and North Pole, two cities in the Fairbanks North Star Borough, Interior of Alaska, are well known for their bad ambient air quality. The topography contributes to air temperature inversion and low mixing height in winter. Along with low air temperatures, this city is exposed to high concentration level of $PM_{2.5}$, which is particulate matter with aerodynamic diameter less than or equal to 2.5 micron. The air pollutants are trapped for days, sometimes for weeks. The Environmental Protection Agency (EPA) has declared the Fairbanks North Star Borough as $PM_{2.5}$ non-attainment area in 2009 for not fulfilling 24-h National Ambient Air Quality Standard. Additionally, forest fires in summer can also result in acute conditions of unhealthy air. The polluted air can affect indoor air quality too due to poor ventilation systems. In this seminar I want to present my studies on air quality in Fairbanks and North Pole that include (i) understanding spatial variation of road-side $PM_{2.5}$; (ii) exploring correlation of ultrafine particulates (particles less than 0.1 micron in diameter) with $PM_{2.5}$, meteorology and traffic counts; and (iii) assess the impact of high concentration of outdoor particulates due to forest fires on indoor air quality.

Oral presentation:

Release of metal(loid)s from coal ash and association with dissolved organic matter in aqueous systems

Kyle P. Milke[1], Sarah M. Hayes[1], and Jennifer J. Guerard[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Little is known about the fate and toxicity risk of metal(loid) leaching from coal combustion products (CCPs) into the (sub-)Arctic environment. Coal is expected to continue to serve as a major energy source, therefore it is imperative to understand the potential impact of CCPs on the environment. Several elements in CCPs are enriched relative to the average crustal abundance including calcium oxide, arsenic, chromium, copper, germanium, molybdenum, lead, and antimony. The overarching goal of this project is to examine the release of metal(loid)s from boiler slag and fly ash and identify transformations in the presence of aqueous environmental media. Boiler slag was reacted with 18 MΩ water (control) or simulated rainwater to quantify metal(loid) liberation with time. Leachate pH rose from circumneutral for the control and pH = 4.6 for simulated rainwater and ended at ~pH = 11.9 at 6 months. Changes in pH indicate mineral transformations that may release metal(loid)s. Quantification of metal(loid)s was done by ICP-MS and will be further assessed using electron microscopy and ion chromatography. Some metals such as calcium exhibited initial fast leaching and decreased in concentration for both leachates, which is most likely due to the precipitation of a secondary phase, possibly $CaCO_3$. Other metals such as aluminum exhibited initial fast leaching and rose in concentration, which then began to level off for both leachates. $Al(OH)_4^-$ is expected to be the predominant species. For chromium, there was no evidence of fast release and the concentration remained the same from 1 hr to 1 day for both leachates. At 1 day, chromium concentrations decreased for the simulated rain water and increased for the control. The presence of chromium (III) and chromium (VI) complicate speciation predictions. Fly ash and boiler slag were also reacted with two reference and one Alaskan DOM samples to investigate organic-metal(loid) interactions. Through these experiments, we will obtain a quantitative analysis and an understanding of the kinetic controls of metal(loid) release from coal ash leaching with various aqueous media. Results from these experiments can potentially help to improve storage and remediation processes for CCPs in an effort to protect humans and the ecosystem.

Oral presentation:

Modeling Arctic Reactive Bromine Using Principal Components Analysis

William Swanson[1], William Simpson[1], Kelly Graham[2], Chris Holmes[2], and John Halfacre[3]

[1]Department of Chemistry and Biochemistry, Geophysical Institute, University of Alaska Fairbanks, Fairbanks AK [2]Department of Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee FL [3]Shepson Atmospheric Chemistry Group, Purdue University, West Lafayette IN

Reactive bromine radicals (a family including Br atoms and BrO, bromine monoxide) are produced episodically in the Arctic troposphere, where they deplete ozone, cause mercury deposition, and affect the fate of hydrocarbon species. Field campaigns and laboratory experiments suggest that various meteorological and chemical processes are important in driving reactive bromine production. We sought to test the validity of these sometimes divergent hypothesized factors' role in driving reactive bromine production in the Arctic spring using a large dataset of tropospheric BrO observations. To gather this large dataset, we deployed fifteen ocean-borne autonomous buoys (O-Buoys) in the Arctic Ocean from 2009 until 2017. Multiple axis differential optical absorption spectrometers (MAX-DOAS) mounted on the O-Buoys observed episodic BrO production events over eight springtime seasons. To analyze these variations statistically, principal components analysis was applied to the meteorological and chemical data gathered aboard the O-Buoys, as well as to data from the MERRA-2 meteorological reanalysis product. A predictive model for the observed BrO, consisting of a combination of meteorological and chemical data, was derived from the principal components analysis. The model results in a correlation coefficient (R) of 0.524 between the predicted and observed BrO in the lowest 2000 m above ground level. Explanations of the environmental and chemical factors driving reactive bromine production can be tested with this model to determine their efficacy in explaining observed BrO within the extensive O-Buoy dataset. The hypothesis that BrO mixing ratio in the boundary layer is diluted when the boundary layer height rises is confirmed by the improved model performance when BrO is predicted using the inverse of boundary layer height rather than the height itself. Continued application and training of this model may allow for its implementation in a coupled global chemistry and meteorology model.

Poster presentation:

Diurnal Ambient Aerosol Metal Concentrations During the Fairbanks Winter

Kiersten Johnson[1], Ragen Davey,[1] and Jingqiu Mao[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

The Environmental Protection Agency (EPA) recently designated the Fairbanks North Star Borough (FNSB) in Alaska a nonattainment zone because of the borough's extremely high air pollution levels which exceed EPA standards. The pollution is exacerbated in winter months because of the cold temperatures and an inversion layer. Although FNSB's air is routinely measured, the hourly concentration levels of transition metals in the ambient aerosol is unknown. This research project aims to determine the metal concentrations in FNSB's ambient aerosols and possible sources. Ambient aerosol samples were collected in January and February 2018 on 24 hour cycles of clean and polluted days using a Particle into Liquid Sampler (PILS) at a location next to an EPA National Core (NCore) site in Fairbanks. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine total concentrations of 6 transition metals in polluted and clean day samples. Initial results show different diurnal cycles between clean and polluted days for the tested metals, suggesting a major contribution from local sources. We find our data to be comparable to a study conducted in the winter of 2011 at the same location.

Poster presentation:

Leaching behavior of Boiler Slag and Fly Ash in sub-Arctic Environmental Media

Kiana L. Mitchell[1], Kyle P. Milke[1], Jennifer J. Guerard[1], and Sarah M. Hayes[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Approximately 110 Mt of coal combustion byproducts (CCBs) are produced nationally every year. As coal continues to serve as a main energy source around the world, CCBs pose a potential hazard in the event of environmental exposure. Several large accidental releases have deposited large amounts of CCBs, which have caused substantial impact to the environmental health of adjacent ecosystems and communities. The overarching goals of this project are to provide a detailed characterization of two different CCBs, boiler slag and fly ash, and simulate leaching of boiler slag and fly ash in sub-Arctic environmental media in order to determine the leaching behavior and the effects of CCB metal(loid)-DOM interactions Mineralogical and organic characterization experiments were performed using WD-XRF and CP-MAS NMR, respectively. Leaching experiments will be performed by reacting each CCB in dissolved organic matter (DOM) collected from Goldstream Valley located in Fairbanks, Alaska. The leachate will then be analyzed using ICP-MS and Flame AA. Characterization experiments showed that the major minerals found in both CCBs were CaO, SiO_2, FeO, Al_2O_3, SO_3, and MgO. The organic composition was determined to contain mostly oxygenated aliphatic and aromatic functional groups. The composition of the CCBs provides information on where the particles may associate with DOM in the environment. From the results of the characterization experiments, I hypothesize that the metal(loid)s leached in sub-Arctic DOM will be greater than previous leaching experiments done in 18 MΩ water and rainwater due to the low pH of the DOM solution and high pH of CCBs.

Poster presentation:

Diversity of Alaskan Boreal DOM: Relationships between DOM Composition and Molecular Size

David Warner[1], Kristin Gagne[1], and Jennifer J. Guerard[1]

[1]Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska

Molecular weight is very important to reactivity of Dissolved Organic Matter (DOM) including its ability to complex with metals. This can affect, and be affected by, the formation of DOM-metal nanoparticles (McAdams et al.). We used HPSEC to determine the average molecular weights of different DOM sources of natural waters and soil from Alaskan boreal regions. This strategy was modeled from the McAdams study, using 2016 PSS standards. Values of number average molecular weight and weighted average molecular weight were determined by a log(MW) versus retention time plot. Polydispersity is determined by a ratio of Mw and Mn. Our samples were isolates prepared in mobile phase at 1mg/10ml. Trends in MW are compared across DOM source and type against physical and chemical composition properties.