2017 Environmental Chemistry Symposium
University of Alaska

21st April, 2017 (UAF SpringFest) – 9:00 AM to 4:00 PM **UA Museum of the North**
Awards and Posters (and dinner 4:30-7:00 PM) **Akasofu 501**

University of Alaska Museum of the North, 907 Yukon Drive, Fairbanks, AK 99775
The meeting and lunch will take place in the Museum's Auditorium. The evening program is in Akasofu (IARC) Building Room 501.

Organizers:

William R. Simpson, Sarah M. Hayes, Jennifer J. Guerard, Jingqiu Mao

Sponsors:

Department of Chemistry and Biochemistry, UAF
College of Natural Sciences and Mathematics (CNSM), UAF
Geophysical Institute (GI), UAF
IDeA Network for Biomedical Research Excellence (INBRE), UA
Biomedical Learning and Student Training (BLaST), UAF
Undergraduate Research and Scholarly Activities (URSA), UAF

Special Thanks to:

Jessica Armstrong (CNSM Graduate coordinator)

Presentation Schedule

Time	Presenter	Title
9:00 -- 9:15 am	Welcomes and Introduction	
	Session: Keynote Speaker	
9:15 – 10:15 am	Dr. Joel Thornton, University of Washington What happens to air pollution when it is cold and dark?	
	Session: Pollution and Health	
10:15 – 10:35 am	Abdul Kadir	Evaluation of near-roadway ultrafine particulate matter and associated health risk in the Fairbanks North Star Borough (FNSB)
10:35 – 10:55 am	Alyson McPhetres	Validation of MODIS aerosol optical depth (AOD) for prediction of near-ground air quality in Alaska
10:55 – 11:10 am	Break	
	Session: Contaminant Fate & Transport	
11:10 – 11:30 am	Lawrence Itela	Analysis, fate and transport of anti-retroviral drugs in rivers and wastewater treatment plants: study of Nairobi River Basin
11:30 – 11:50 am	Karen Spaleta	Comparison of mineralogy determined by X-ray energy dispersive spectrometry (EDS), X- ray diffraction (XRD), and X-ray fluorescence (XRF) spectrometry
11:50 – 12:10 am	Nicole Knight	Surficial geochemistry, transport, and bioaccessibility of tellurium in semi-arid mine tailings
12:10 -- 12:30 pm	Kyle Milke	Coal ash metal(loid) liberation and association with dissolved organic matter in aquatic boreal systems
12:30 -- 1:30 pm	Lunch	
	Session: Biogeochemical Cycling	
1:30 – 1:50 pm	Kristin Gagne	Alaskan sub-Arctic watershed organic matter: mobilization, characterization, and reactivity
1:50 – 2:10 pm	Bridget Eckhardt	Transport of CH_4 through open-talik lakes in discontinuous permafrost aquifers
2:10 -- 2:30 pm	Nicole Jacobs	Using mobile solar-viewing FTIR spectrometers to detect regional methane fluxes from Tanana Flats and carbon dioxide fluxes from Fairbanks
2:30 – 2:45 pm	Break	

	Session: Marine Systems	
2:45 – 3:05 pm	Kayl Overcast	Reductive attenuation of nitroamine based munitions compounds in anoxic sediments like those found in the Gulf of Alaska
3:05 – 3:25 pm	William Swanson	Seasonal variations in tropospheric reactive bromine over the frozen Arctic Ocean and the coast
3:25 – 3:45 pm	Megan Roberts	The role of iron in marine primary productivity: Inter-annual variability in iron supply to the Gulf of Alaska.
3:45 – 4:05 pm	Taylor Gofstein	Fate and effects of petroleum contamination and chemical dispersants in Arctic marine environments

Poster Presentations

4:30 – 7:00 pm	Presenter	Poster Title
	Sara Ewers	Does natural organic matter redox potential and reactivity in pore water vary between open and closed taliks?
	Brianna Gilmore	Characterization of biofilms related to sub-Arctic drinking water systems
	Kiana Mitchell	Quantifying the metal(loid) bioaccessibility of reacted fly ash in the Arctic.
	Jacob Sterle	Physiological extractions of metal(loid)s from coal ash in interior Alaska
	David Warner	Characterization of solid-phase transformation of boiler slag during leaching
	Roger Vang	Change in haptoglobin concentrations in Steller sea lions (*Eumetopias jubatus*) and environmental exposure to mercury: chemical assay interference?

Abstracts

Oral Presentations

Poster Presentations

Oral presentation:

Transport of CH_4 through open-talik lakes in discontinuous permafrost aquifers

Bridget A. Eckhardt[1], David L. Barnes[1], Ronald P. Daanen[2], Katey Walter Anthony[1]

[1]Water and Environmental Research Center, University of Alaska Fairbanks
[3]Alaska Division of Geological and Geophysical Surveys

As northern regions of the world experience warming climate, scientists look to permafrost, a crucial component of arctic and subarctic ecosystems, as a source and sink of atmospheric carbon. It is well-known that the thawing of permafrost from above as a result of warming climate is a considerable source of greenhouse gases. However, few studies have considered the production of methane, a potent greenhouse gas, beneath the permafrost. A rugged permafrost bottom is proposed to favor the storage of gas in "pockets" that have been formed through permafrost thaw and degradation from below. Sub-permafrost methane can migrate to reach the atmosphere when connections between the sub-permafrost and supra- permafrost (open taliks) form or when changing permafrost morphology opens pathways from the pocket to the bottom of an open-talik lake. We hypothesize that the migration of methane into open-talik lakes from the sub-permafrost can occur through advection and diffusion as a dissolved gas and by movement as an immiscible fluid. Two lakes with varying degrees of talik formation within Goldstream Cr. Basin, Fairbanks, Alaska, serve as the major study sites. To distinguish advection and diffusion of dissolved-phase methane we analyze dissolved methane concentrations, stable isotopes and major ions as tracers and through hydraulic gradient analysis. Monthly collection and analysis of water samples from surface, subsurface, and benthic sources allow for observation of seasonal changes in composition and flow dynamics. Observations and data collected to date indicate the occurrence of multiphase flow. We test the occurrence of immiscible-phase flow through measurement of displacement pressures and aging methane captured in desaturated pore channels beneath the lake bottom. Results to date also bring attention to the complexity of open-talik systems that has previously not been observed. Data obtained in this study will aid in the understanding of greenhouse gas fluxes, and thereby improve research in climate change predictions.
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Oral presentation:

Alaskan sub-Arctic watershed organic matter: mobilization, composition, and reactivity

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

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

Yedoma permafrost is a reservoir for 800 GT of carbon and discontinuous permafrost is dramatically thawing, allowing this carbon organic matter (OM) to be released from the permafrost into the surrounding hydrologic system. This ancient carbon influence on surface water DOM could have a dramatic effect on biogeochemical cycling in the boreal watershed. Characterizing dissolved organic matter (DOM) chemical composition from leached permafrost offers insight into the quality and extent of the permafrost carbon pool that may mobilize and transform upon thaw. The chemical and functional group composition of permafrost organic matter largely remains unknown, especially in discontinuous permafrost. In addition, the heterogeneity of permafrost organic matter with respect to geography is largely unresolved. Permafrost OM was extracted using a variety of media (18 MΩ water at pH = 7, pH = 10, 0.5 M K_2SO_4, and methanol). Cores were leached for seven days at 4°C in the dark to allow for capture of both long and short term kinetic OM. Leaching media was filtered and OM collected via solid phase extraction with PPL cartridges and subsequently freeze-dried. Surface waters collocated to permafrost cores were collected for DOM extraction for comparison to permafrost OM. Further characterization of extracted DOM was conducted via nuclear magnetic resonance (NMR), inductive coupled plasma mass spectrometry (ICP-MS), UV-Vis, and fluorescence excitation emission matrices (EEMs). PARAFAC analysis was also performed to resolve fluorescent component differences between samples. Reactivity of DOM was assessed through addition of reactive oxygen species probes in the presence of a solar simulator.

Oral presentation:

Fate and effects of petroleum contamination and chemical dispersants in Arctic marine environments

Taylor R. Gofstein[1] and Mary Beth Leigh[1]

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

Offshore oil development as well as the shipping of petroleum products carry the risk of spills and the associated hazards to environmental and human health, as evidenced by the Deepwater Horizon and Exxon-Valdez spills. This has become an even greater concern in the Arctic due to increases in exploration and trafficking in recent years. In order to understand the fate of petroleum contaminants and chemical dispersants, their interactions with the environment, and factors that influence their biodegradation by microorganisms, an incubation series of indigenous microorganism in Arctic seawater was conducted to study the Arctic marine ecosystems that can potentially be impacted by petroleum contamination. Seawater was collected from the Chukchi Sea, supplemented with 16 ppm of Bushnell-Haas media, aliquoted 800 milliliters into media bottles, and treated with either 50 ppm of Alaska North Slope crude oil, 5 ppm of Corexit 9500 (1:10 dispersant-oil ratio), or both. Incubations were sampled at 0, 5, 10, 20, and 30 days. An additional incubation of 6 liter aliquots of seawater was also performed and subsampled daily for 7 days in order to study the degradation of the surfactants which compose Corexit. Degradation of the crude oil, including total petroleum hydrocarbons and polycyclic aromatic hydrocarbons, will be measured using GC/MS. Degradation of the surfactants that compose Corexit will be measured using LC/MS/MS techniques. Microbial analyses will be performed for each treatment using 16S rRNA sequencing (Illumina MiSeq) and qPCR and nutrients (NO2-, NO3-, NH4+, $PO4^{-3}$and $SiO4^{-4}$) will be measured flow injection analysis and total iron by atomic absorption spectroscopy. Results from this study will help enable decision-makers to make an informed choice of appropriate response strategies in the event of a spill as well as broaden our general understanding of petroleum biodegradation in the Arctic marine environment.

Oral presentation:

Analysis, fate and transport of anti-retroviral drugs in rivers and wastewater treatment plants: study of Nairobi River Basin

Lawrence O. Itela[1] and Larry K. Duffy[1]

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

Pharmaceutical and Personal Care Products (PPCPs) are emerging contaminants of concern to human and environmental health. These PPCPS can be endocrine disruptors, lead to microbial resistance or can accumulate in biota. Antiretrovirals (ARVs) are a category of drugs widely used in therapeutic management of HIV/AIDS. Due to widespread prevalence of HIV-infected people with low-income settlement areas in Nairobi, government and donor agencies have set up various programs to provide ARVs in these settlements. With limited sanitation and wastewater treatment facilities in these informal settlements, domestic wastewater is disposed directly into the Nairobi River basin. The concentration of these drugs and the possible transformation of these drugs are unknown. Using HPLC and photolysis techniques, this work aims to determine the presence transport and fate of the three most widely used ARV's in the area: lamivudine (3TC), zidovudine(ZDV) and nevirapine(NVP).

Oral presentation:

Using mobile solar-viewing FTIR spectrometers to detect regional methane fluxes from Tanana Flats and carbon dioxide fluxes from Fairbanks

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 a major 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, which is a challenging upscaling problem needing 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 this paucity, 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) vertically integrated through the entire atmosphere. The total atmospheric column includes both local inputs 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 and analyzed the differences between them. We conducted a measurement campaign from 4 August 2016 to 15 October 2016 around the Fairbanks area, during which over 200,000 infrared spectra were collected during over 200 hours of observation time. This was the first project to use EM27/SUNs in the Arctic and the first to attempt regional transects up to 70km. As part of these observations our group and collaborators were on the ground during eight OCO-2 (NASA's Orbiting Carbon Observatory-2) overpasses in target-mode (when the satellite is programed to point at our location) and observed gradients (analyzing the difference between observations at different locations) on 19 days. Using co-located observations, we quantified small (< 0.1%) systematic differences between the two spectrometers. We observe differences of ~2ppb for CH4 and up to 1ppm for CO2 over a transect of just 5km between UAF and downtown Fairbanks on 5 October 2016. Over a 70km transect between UAF and Nenana differences in DMF measurements were insignificant for CO2, but differences of 3-4ppb and up to 5ppb were observed for CH4 on 30 August 2016 and 1 October 2016, respectively, demonstrating the expected CH4 enhancement from fluxes over Tanana Flats. Analysis of these observations will assist in assessing local and regional scale CO2 and CH4 dynamics around Fairbanks and across Tanana Flats, in addition to providing a wealth of validation data for satellite observations at high-latitude, such as those from OCO-2 and the soon to launch European satellite, Sentinel-5p.

Oral presentation:

Evaluation of near-roadway ultrafine particulate matter and associated health risk in the Fairbanks North Star Borough (FNSB)

Kadir Abdul[1] and Srijan Aggarwal[1]

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

Vehicular traffic is a significant contributor of particulate matter in urban airsheds. Thus, time spent on roadways is a major source of exposure to particulates as moving vehicles have high air exchange rates and the cabin air is significantly impacted by ambient air quality. Among various PM size fractions, vehicular emissions represent a major source for ultrafine particulate matter (UFP; aerodynamic diameter < 0.1 µm) and thus UFP concentrations are higher in near-roadway and on-roadway environments. While UFPs have been documented to have serious adverse health impacts, UFPs are not regulated by the United States Environmental Protection Agency (EPA). Since UFPs are not regulated there is a lack information regarding chemical constituents and spatial variation of UFPs, especially in colder environments. Fairbanks North Star Borough (FNSB) is a region of interest not only because of its cold climate conditions, but also because FNSB is a designated non-attainment area for the federal PM2.5 standard. In this work, we seek to measure roadside particle number concentrations of UFPs in the FNSB region, and investigate UFP chemical constituents to estimate the associated health risks. Additionally, the data will be analyzed to understand the correlations between $PM_{2.5}$ and UFPs; and dependence of roadside UFP number concentrations on traffic volume and meteorological parameters (temperature, relative humidity, wind speed).

Oral presentation:

Surficial geochemistry, transport, and bioaccessibility of tellurium in semi-arid mine tailings

Nicole A. Knight[1], Dallon C. Knight[1], and Sarah M. Hayes[1]

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

Tellurium (Te) is a rare metalloid increasingly used in photovoltaics, and the extraction, manufacture, disposal, and recycling of Te and related devices may pose a risk to proximal environments and communities. Few prior studies have examined Te behavior in the surficial environment, despite tellurite (Te^{IV}) being more toxic than arsenite or other Te oxidation states (Te^{-II}, Te^{0}, Te^{VI}). Reduced tellurium (telluride) phases deposited by industrial activities (e.g., mining and photovoltaic production) undergo physicochemical transformation to Te oxyanions, but the identity and bioaccessibility of these secondary phases are unknown. Contradictory thermodynamic data, some of which predict the stability of the toxic tellurite (Te^{IV}), highlights the necessity for direct field observations of Te behavior under a wide range of surficial environmental conditions. Therefore, our overarching goal is to examine geochemical controls of Te behavior using Te-bearing mine tailings to determine the potential ramifications of Te concentration near population centers.

In this study, semi-arid mine tailings with elevated concentrations of Te (up to 319 mg Te kg^{-1}) were collected as a function of depth from the historic Delamar mining district in Lincoln County, NV. Tellurium is enriched at the surface of the tailings, potentially as efflorescent salts, and bulk X-ray absorption spectroscopy (XAS) data indicate the oxidation of Te ore minerals to oxidized tellurate (Te^{VI}) or tellurite (Te^{IV}) species. Further, electron microprobe analyses (EPMA) suggest the predominance of an Fe-rich Te-bearing phase. Physiologically-based extraction tests (PBETs) simulating fasting stomach and lung conditions reveal bioaccessibility of up to 37% Te, indicating that these materials may be toxic if ingested or inhaled. Alluvial and aeolian transport of the Te-bearing tailings is evident at the site, indicated by relatively high concentrations of up to 67 mg Te kg^{-1} in surrounding soil. These findings highlight the importance of understanding the impacts of Te weathering on ecosystems and communities.

Oral presentation:

Validation of MODIS aerosol optical depth (AOD) for prediction of near-ground air quality in Alaska

Alyson McPhetres[1] and Srijan Aggarwal[1]

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

The air quality monitoring network in Alaska is currently limited to urban areas and national parks leaving a large proportion of the state unmonitored. The use of MODIS aerosol optical depth (AOD) to estimate ground-level particulate pollution concentrations has been successfully demonstrated around the world, and could potentially be used in Alaska. In this work MODIS AOD measurements at 550 nm were validated against AOD derived from AERONET ground-based sunphotometers in Barrow and Bonanza Creek to determine if MODIS AOD from the Terra and Aqua satellites could be used to estimate ground-level particulate pollution concentrations. The MODIS AOD was obtained from MODIS collection 6 using the dark target Land and Ocean algorithms from 2000 to 2014. MODIS could only be obtained between the months of April and October, therefore it could only be validated for those months. The MODIS collection 6 products at 10 km resolution for Terra and Aqua combined are not valid over land but are valid over the ocean. The individual Terra and Aqua MODIS collection 6 AOD products at 10 km resolution are valid over land individually but not when combined. Results suggest the MODIS collection 6 AOD products at 3 km resolution are valid over land and ocean and perform better over land than the 10 km product. These findings indicate that MODIS collection 6 AOD products can be used quantitatively in air quality applications in Alaska during the summer months.

Oral presentation:

Coal ash metal(loid) liberation and association with dissolved organic matter in aquatic boreal 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 boiler slag 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. Future work will compare fly ash leaching to boiler slag leaching, and also investigate organic-metal(loid) interactions through leaching with dissolved organic matter solutions.

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:

Reductive attention of nitramine based munitions compounds in anoxic sediments like those found in the Gulf of Alaska

Kayl Overcast[1,2] and Lisa Hoferkamp[2]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks Alaska
[2] Department of Environmental Sciences, University of Alaska Southeast, Juneau, Alaska

The U.S. Navy conducts annual war training exercises off the coast of Kodiak Island in the Gulf of Alaska (GOA). Part of the war training exercise includes an annual expenditure of explosives into deep ocean water which include approximately 400 lbs. of hazard materials. The hazardous materials include a range of nitroamine based explosive chemicals, a class of emerging contaminants. The class of explosive contaminants and their attenuation products, have been identified as toxic carcinogens with long term adverse health effects and have been the focus of groundwater contaminant studies due to high mobility in soils. While the reductive attenuation of these nitroamine based explosive compounds in anaerobic soils is fairly well quantified, there has been almost no research to determine the fate of these compounds in anoxic marine environments like those that would be found in GOA sediments. Understanding the attenuation and fate of these explosive contaminants in GOA sediments is important for determining the potential effects on important fisheries based in the GOA. This study uses sediment slurry reactors to identify sediment reaction rate coefficients for the attenuation of nitroamine based explosives in chemically characterized sediments under anaerobic conditions and investigates how those rate coefficients depend on parameters inherent to the natural system from which the sediments originate. The results from these kinetic studies will further understanding of the natural attenuation of explosive compounds in anaerobic sediments.

Oral presentation:

The role of iron in marine primary productivity: inter-annual variability in iron supply to the Gulf of Alaska

Megan Roberts[1], Ana Aguilar-Islas[2], and Tom Trainor[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska
[2] School of Fish and Ocean Sciences, University of Alaska Fairbanks, Fairbanks, Alaska

The essential micronutrient iron (Fe) limits marine primary production and/or influences the community composition of marine primary producers, thereby it plays a role in the global carbon cycle. The Gulf of Alaska (GOA) is a region where Fe availability creates contrasting ecosystems, i.e. the central GOA displays lower productivity and residual nitrate in surface waters due to low Fe supply, while the highly productive coastal GOA with ample Fe supply becomes limited by nitrate by the end of the summer. The Fe rich shelf waters can exchange with the nitrate rich central GOA waters creating favorable conditions for a phytoplankton bloom. One mechanism of transport is through the movement of eddies that propagate in the southeast and move westerly. Shelf waters in the GOA are subject to glacial runoff and river input that bring in an abundance of both particulate and dissolved Fe species. Additional Fe sources from subsurface waters and the sediment can impact shelf waters. My research investigates the spatial and temporal distribution of Fe over GOA shelf waters and here, I will discuss the inter-annual variability in relation to previous GOA Fe studies.

Oral presentation:

Comparison of Mineralogy Determined by X-ray Energy Dispersive Spectrometry (EDS), X- ray Diffraction (XRD), and X-ray Fluorescence (XRF) Spectrometry

Karen Spaleta[1,2], Sarah Hayes[3], and Rainer Newberry[2]

[1] Advanced Instrumental Laboratory, University of Alaska Fairbanks, Fairbanks, Alaska
[2] Department of Geosciences, University of Alaska Fairbanks, Fairbanks, Alaska

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

Rapid micro-scale elemental mapping with X-ray Energy Dispersive Spectrometry (EDS) has become a routine analytical technique in the earth and environmental sciences to assess grain-scale mineralogy and elemental composition. A complete X-ray spectrum can be generated at each image pixel and statistical algorithms are then applied to identify the spatial distribution of spectrally unique phases. Although the spectral overlaps and electron interaction volumes are well-known limitations of the EDS technique, these have not been fully examined within the context of EDS phase mapping. The results of the Thermo Noran System 7 (NSS) Compass EDS phase identification package were compared with bulk mineralogy results from powder X-ray Diffraction (XRD) and calculated mineralogy from bulk Wavelength Dispersive X-ray Fluorescence (WD-XRF) elemental abundances. Each analytical approach yielded similar results of bulk mineralogical abundances. Prior knowledge of the bulk mineralogical assemblage from XRD analysis was helpful in interpreting both the EDS and XRF results. EDS phase mapping was the most challenging to use for mineral identification as phase differentiation is highly dependent on the electron beam conditions and spectral overlaps can complicate the mineral identification. XRF elemental abundances do not generate a unique mineralogical assemblage and some knowledge of the sample mineralogy is key to correctly assigning elements to minerals. Judiciously setting the EDS phase identification software options and scanning a large sample area allowed the identification of low abundance phases, such as rutile (TiO2) not identified by XRD. NSS's EDS phase identification software is able to identify distinct phases and calculate abundances, but given the limits of EDS quantification, assigning the correct mineral to the phase is simplified by having XRD data. The best correlation between the three methods is when the EDS sample has mineral grains that are uniform in size and larger than the interaction volume of the electron beam.

Oral presentation:

Seasonal variations in tropospheric reactive bromine over the frozen Arctic Ocean and the coast

William Swanson[1] and William R. Simpson[1]

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

Reactive bromine radicals (Br atoms and bromine monoxide, BrO) are produced episodically in the Arctic troposphere, where they deplete ozone, cause mercury deposition, and affect the fate of hydrocarbon species. In situ observations of tropospheric reactive bromine species are necessary to understand this chemistry and its dependence on environmental conditions such as sea ice and temperature. In the Arctic, long-term in-situ measurements are mostly observed at coastal research stations. Little long-term data is available on tropospheric chemical composition over the Arctic Ocean itself. To gather more data on tropospheric composition over the Arctic Ocean, we deployed ocean-borne autonomous buoys (O-BUOYs) from 2009 to present. Multi axis differential absorption spectrometers (MAX-DOAS) mounted on the O-BUOYs gathered spectra during spring, summer and fall, observing high amounts of BrO during the polar spring. These spectra have been translated into vertical column density measurements of the total amount of BrO in the lowest 2000 and 200 meters. While variability between different observation locations and years is high, seasonal variations in BrO have been identified. The BrO vertical column density is high during the early spring, with decreasing vertical column densities observed later in the spring. Near-ground-level (vertically shallow) events are common in early spring, which evolve to be more vertically distributed events later in spring, as the frequency and severity of boundary layer temperature inversions decreases. The O-BUOY dataset is compared to long-term land-based MAX-DOAS observations at Barrow, the most directly comparable coastal research facility. On the O-BUOYs, reactive bromine production continues longer into June. Varying seasonal environmental conditions at different O-BUOY locations are thought to account for many of the discrepancies between coastal and land based observations. Temperature inversions and ice surface area appear to drive many of the observed differences in BrO. Continued study of BrO and meteorological data at both observation sites may allow for future extrapolation of High Arctic tropospheric chemical composition from coastal observations.

Poster presentation:

Does natural organic matter redox potential and reactivity in pore water vary between open and closed taliks?

Sara Ewers[1], Kristin Gagne[1], and Jennifer Guerard[1]

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

Natural organic matter (NOM) within permafrost has important reactive qualities, such as electron transfer and redox reactions when mobilized into the active layer and surface waters. However, this mobilized NOM is not well characterized in literature. As permafrost thaws the permafrost organic matter leaches into the pore water. Pore water is located in the sediment at the bottom of a lake in an anoxic environment. This permafrost organic matter has potential implications on biogeochemical cycling by influencing the chemical composition and reactivity of the NOM. Redox reactivity was determined by analysis before and after oxygen exposure. For this project I obtained pore water samples from two lakes in Goldstream Valley underlain by degrading permafrost zones, called taliks. One is an open talik, where all permafrost is thawed and the other a closed talik, completely underlain by impermeable permafrost. The open site was treated as the control and the closed talik as the test in order to observe chemical composition influence by permafrost. Chemical composition was evaluated by parallel factor analysis (PARAFAC) to determine chemical components found in pore waters. After the samples we collected from each site various chemical analyses including total organic carbon (TOC), nuclear magnetic resonance (NMR), ion chromatography (IC), inductively coupled mass spectrometry (ICP-MS), and fluorescence/UV-vis. Furthermore spectroscopic indices obtained from fluorescence/UV-vis were determined to compare between sampling locations.

Poster presentation:

Characterization of biofilms related to sub-Arctic drinking water systems

Brianna Gilmore[1], Srijan Aggarwal[2], and Jennifer Guerard[1]

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska
[2] Water and Environmental Research Center, University of Alaska Fairbanks

Biofilms are a major concern in both medicine and engineering. In humans these biofilms are estimated to cause 60-80% of microbial infections (7). For instance recurring urinary tract infections and cystic fibrosis pneumonia are both caused by biofilms. Bacteria work with one another to create an extracellular matrix (ECM) to connect to one another in a matrix called a biofilm. This ECM is secreted from the bacteria and can include polysaccharides, lipids, proteins, DNA, and other small molecules. (4). Increasing antibiotic and antimicrobial resistance is becoming more of a problem and part of this is due to the ECM acting as a physical barrier against such assaults (3). Many biological studies of such biofilms have been done, however there is a lack of chemistry based studies. This research will help remedy this by analyzing sampled drinking water cultures without any treatment, and then with a common disinfectant (chlorine). These will then be characterized using NMR and fluorescence spectroscopy to see what kinds of compounds are present and to see how disinfection effects the biofilm composition.

Poster presentation:

Quantifying the metal(loid) bioaccessibility of reacted fly ash in the Arctic

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

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Coal combustion produced 117 megatons of waste globally in 2015. Coal combustion products (CCPs) are used in concrete, cement, structural fills, embankments, and mining applications, but 46% of CCPs remain in stockpiles or landfills. Use of and storage of CCPs may be a mechanism for release of metal(loid)s contained in CCPs to the surficial environment. Boiler slag and fly ash collected from the UAF power plant have been previously characterized as containing potentially toxic arsenic, selenium, mercury, and lead. With coal continuing to be a main energy source around the world, CCPs pose a potential health hazard due to dispersion of potentially toxic metal(loid)s. The overarching goal of this project is to quantify the bioaccessibility of metal(loid)s in boiler slag and fly ash from both unreacted and previously leached solid CCPs in order to determine if leached CCPs represent a health risk.

Physiological based extraction tests (PBETs) were conducted using simulated gastric and alveolar extraction fluids to examine the metal(loid) bioaccessibility through the two major exposure pathways, ingestion and inhalation. Unreacted boiler slag and fly ash, as well as the solid-phase residual of boiler slag leached in 18 MΩ water for one hour, 24 hours, and 3 months were subjected to PBETs. After extraction, ICP-MS was used to analyze the concentrations of various metal(loid)s in the extraction fluid. These results will provide insight into the bioaccessibilty of metal(loid)s in boiler slag and fly ash and be comparable with previous studies conducted with other kinds of coal and in other climates.

Poster presentation:

Physiological extractions of metal(loid)s from coal ash in interior Alaska

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Coal is currently used as a major source of energy worldwide, generating about 40% of global electricity. Coal ash contains several metal(loid)s of physiological concern, such as lead, arsenic, and mercury. Coal ash particles may be released to the environment due to accidental release or uncovered storage, making them susceptible to surface water or aeolian transport, or leaching during precipitation events. This project aims to examine the interaction between coal ash before and after exposure to environmental media and simulated physiological fluids (gastric and alveolar) in order to estimate the potential bioaccessibility of metal(loid)s in ash.

Previous characterization of ash obtained from a local coal-fired power plant identified the presence of toxic metal(loid)s such as arsenic (8.1 + 0.5 mg kg-1), lead (17 + 1 mg kg-1), molybdenum (5.1 + 0.4 mg kg-1), mercury (2 + 1 mg kg-1), manganese (370 + 80 mg kg-1), and selenium (2.0 + 0.5 mg kg-1). Based on these results, gastric and alveolar physiological based extraction tests (PBETs) were performed on unreacted ash and solid phase residuals of ash that had been reacted with either 18MΩ water or simulated rainwater. After agitation at 37° C for times of one week for alveolar or one hour for gastric extractions, filtered supernatants were analyzed by inductively coupled mass spectrometry (ICP-MS) to determine the metal(loid) liberation under physiological conditions. Future work includes characterization of mineralogical transformations during room temperature reactions with the 18MW or simulated rain water and further PBETs after ash reaction with natural aquatic media.

Poster presentation:

Characterization of solid-phase transformation of boiler slag during leaching

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Coal based power plants produce roughly 750 million tons of coal fly ash globally per year, and coal combustion byproducts (CCBs) are often stored in stockpiles and landfills. Although regulations are designed to limit release of CCBs in the environment, dispersion may still occur. Previous studies indicate that CCBs contain potentially toxic elements, which may be released to the environment, but the responsible weathering reactions and the kinetics of these reactions remain poorly understood. In ongoing studies, CCBs from the UAF Power Plant, are being reacted with 18MΩ and acidic rainwater for up to 6 months, with supernatant chemistry analyzed at specific time points. The colloidal size fraction (0.45-0.2 um) was solubilized on the filters by flushing with nitric acid (pH = 2) prior to analysis using ICP-MS. At the same time points, solid-phase samples were harvested and preserved by freeze-drying. These colloidal and bulk solid-phase residuals were characterized electron microscopy to examine mineral transformations that may occur during leaching experiments. In the future, these solids will also be analyzed using infrared spectroscopy and x-ray diffraction to further examine mineral transformation reactions. These analyses will allow us to examine the behavior of metal(loid)-bearing solids over extended weathering times. In conjunction with ongoing analysis and modeling of aqueous chemistry, these results will lend insight into the potential for CCBs release potentially toxic elements into the surficial environment.

Poster presentation:

Change in haptoglobin concentrations in Steller sea lions (*Eumetopias jubatus*) and environmental exposure to mercury: chemical assay interference?

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The Western Distinct Population Segment (WDPS) of Steller sea lions (SSL) have experienced decline, and some regions have yet to recover ("endangered" status). Reasons for the decline are unknown. Some SSL pups from the WDPS have relatively high concentrations of whole blood total mercury ([THg]) compared with the de-listed region. Considering monomethyl mercury ($MeHg^+$) is absorbed and transported through the placenta, developing young may be at risk of adverse effects from mercury. Measurements of the mean acute phase inflammatory protein haptoglobin (Hp) in young SSLs from regions of decline were significantly lower than other regions. Furthermore, individuals with [THg] above clinical effects thresholds as defined by Health Canada (>0.1 ppm) had lower mean Hp than individuals with lower [THg]. The relationship between Hp and [THg] is not well defined. Considering various forms of mercury may interact with proteins similar to Hp, we aimed to test if the addition of various forms of mercury affect the colorimetric Hp assay. We designed three experiments using methyl mercury hydroxide (MeHgOH) and THg to spike the commercial colorimetric Hp assay and test for potential interference. We hypothesized that the addition of MeHgOH and THg to the Hp assay would not affect the determination of Hp concentrations. Our results demonstrated that the addition of MeHgOH and THg did not alter the measurement of Hp concentration from the expected standard concentration. Furthermore, when adding MeHgOH to SSL serum, Hp measurements did not change. This information supports the hypothesis that measurements of Hp are not significantly influenced by the presence of Hg at levels relevant to WDPS SSLs. We conclude that Hp concentrations measured in SSLs over these ranges of mercury concentrations are reliable, and that the relationship of Hp concentrations with THg exposure in SSLs reflects a biological phenomenon rather than an artifact of assay interference.