2016 Environmental Chemistry Symposium
University of Alaska

22nd April, 2016 (UAF SpringFest) – 9:00 AM to 5:00 PM **UA Museum of the North**
Awards and Posters (and dinner 5:00-8:00 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

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	Various	Welcome and Introduction
	Session: Carbon cycling and emissions	
9:15 -- 9:30	Kristin Gagne	Characterization of permafrost dissolved organic matter composition and reactivity: implications for biogeochemical cycling and contaminant fate in a changing climate
9:30 -- 9:45	Niki Jacobs	Building a model of tropospheric methane fluxes in subarctic interior Alaska by complementing small-sale observations with regional-scale observations: A thesis proposal
9:45 -- 10:00	Bridget Eckhardt	Transport of CH_4 through open-talik lakes in discontinuous permafrost aquifers
10:00 -- 10:15		**Break**
	Session: Snow hydrology and chemistry	
10:15 -- 10:30	Tiffany Gatesman	Hydrograph separation of a sub-arctic glacial watershed, Interior Alaska
10:30 -- 10:45	Justine Burd	Snowpack melt onset ends the reactive halogen season in the Arctic
10:45 -- 11:00	Will Swanson	Investigating the relationship between seasonal bromine monoxide production and arctic sea ice
11:00 -- 11:15		**Break**
	Session: Fate and Transport	
11:15 -- 11:30	Megan Roberts	Transport of iron and copper across glacially influenced estuaries
11:30 -- 11:45	Nicole Knight	Potential environmental implications of tellurium-rich mine tailings as a function of climate
11:45 -- 12:00	Amanda Barker	Speciation of lead and antimony associated with weathering bullets in shooting range soil
12:00 -- 12:15	Kayl Overcast	Sorption and fate of 1,3,5-trinitro-1,3,5-triazine (RDX) in anoxic Gulf of Alaska sediments using batch reactions
12:15 -- 13:15		**Lunch**
	Session: Pollution and Health	
13:15 -- 13:30	Kristian Nattinger	Results from spatial and temporal analysis of the composition of fine particulates in Fairbanks, Alaska
13:30 -- 13:45	Lawrence Itela	Assessment of contaminants in Alaska solid waste and waste water sites
13:45 -- 14:00	Stephanie Kennedy	Assessing the immune status of the endangered Steller sea lion (*Eumetopias jubatus*): update, and demographic and environmental drivers

Presentation Schedule, Cont.

14:00 -- 14:15		Break
	Session: Remediation, extraction, and synthesis	
14:15 -- 14:30	Taylor Gofstein	Biodegradation of petroleum contaminants in Alaskan marine and terrestrial environments
14:30 -- 14:45	Amy Josephson	The behavior of tellurium in copper ore processing at the American Smelting and Refining Company
14:45 -- 15:00	Karen Spaleta	Mineralogical controls of trace metal(loid) behavior during Au and Ag extraction at Golden Sunlight Mine near Whitehall, MT
15:00 -- 15:15	Jamie McKee	Synthesis and characterization of polymer-supported cyclodextrin nanoscaffolds for use in future environmental studies
15:15 -- 15:30		Break
	Session: Undergraduate presentations	
15:30 -- 15:40	Kyle Milke	Coal fly ash metal(loid) liberation and association with dissolved organic matter in aquatic boreal systems
15:40 -- 15:50	Jacob Sterle	Spectroscopic investigation of dissolved organic matter-iron interactions
15:50 -- 16:00	Michael Hooper	Characterization of organic compounds in Interior Alaska particulate matter using NMR spectroscopy
	Session: Careers in Environmental Chemistry	
16:00 -- 16:45	Various	Career symposium

Poster Presentations

17:00 – 20:00	Presenter	Poster Title
	Ruth Osborne	Seasonal variations in composition and photoreactivity of dissolved organic matter isolated from a small sub-Arctic stream
	Sean Egan	Implementation and analysis of an ash aggregation scheme within the Weather Research Forecasting with Chemistry (WRF-Chem) model
	Jennifer Chambers	Determining the composition of aerosols produced through the combustion of different fuel types using FTIR
	Dallon Knight	Bioaccessibility of metal(loid)s in road dust from Fairbanks, Alaska
	Dallon Knight	Climatic control over the bioaccessibility of metal(loid)s in Western United States mine tailings and use of bioaccessibility to prioritize remediation efforts

Abstracts

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Oral presentation:

Speciation of lead and antimony associated with weathering bullets in shooting range soil

Amanda J. Barker[1,2], T.A. Douglas[2], and T.P. Trainor[1]

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[2] U.S. Army Cold Regions Research and Engineering Laboratory, Ft. Wainwright, Alaska

Small arms ranges present a unique opportunity to study the fate of lead (Pb) and antimony (Sb) in various types of soil and soil pore waters, where their fate is largely controlled by microscale morphological and chemical variations exclusive to a particular system. When a small arms round impacts a shooting range berm the bullet is fragmented, exposing fresh metallic surfaces to the environment. Under ambient conditions, these bullet fragments are susceptible to weathering processes and the mobility and extent to which Pb and Sb can migrate depends predominantly on their speciation. Understanding Pb and Sb speciation associated with both the formation and subsequent weathering of secondary mineral phases is essential for identifying the toxicity of a range soil and the potential for mobile species to migrate.

In this study, we analyzed bullet and soil samples from a military shooting range located in the interior of Alaska. Bulk speciation analysis coupled with micro-scale methods show that Sb(V) in octahedral coordination with 5 O and 3 Fe atoms is the predominant Sb species present in the weathering crust. However, trivalent Sb bound to 3 O atoms is likely the initial oxidation product as detected in the weathering bullet alloy and laboratory oxidation samples with metallic Sb. Similar methods show that litharge, cerussite and hydrocerussite comprise the bulk of the Pb concentration in the weathering crust, but cerussite and Pb(II) sorbed to Fe(III) oxides are predominant in the soil fraction distal to the source material. These results highlight differences in speciation between the weathering crust and soil fraction in shooting range samples and showcase a natural association of both Pb and Sb with Fe. In the berm runoff, Sb is more mobilized than Pb in all systems studied, attributable to the overall low solubility of the dominant Pb species present. This result is particularly important to land managers due to the toxic and carcinogenic nature of Sb. Overall, the results stemming from this study are essential for understanding the potential for off-site migration of Pb and Sb at small arms ranges.

Oral presentation:

Snowpack melt onset ends the reactive halogen season in the Arctic

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[2] Department of Chemistry, University of Michigan, Ann Arbor, Michigan
[3] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

Reactive halogen radicals (Br, Cl, I and their oxide forms BrO, ClO, IO) play powerful roles as oxidizers in the troposphere, including removing atmospheric pollutants. In the Arctic, high levels of reactive bromine (up to 40 pptv) are observed episodically during springtime (March-April) due to heterogeneous recycling on snow, ice and/or aerosols surfaces. However, levels of reactive bromine rapidly decrease as spring transitions into summer (late spring, May-June). This study investigated how reactive bromine levels are affected by environmental controls, such as temperature, snow depth and rain, during late spring. Long-term bromine monoxide (BrO) measurements were obtained using a Multi-AXis Differential Optical Absorption Spectrometer (MAX-DOAS) deployed at Barrow, AK (2009 and 2012 – 2014, a part of the Bromine, Ozone, and Mercury EXperiment, BROMEX) and multiple buoys above frozen Arctic Ocean (2011 – 2015, O-Buoy Project). The seasonal end to high BrO levels was objectively determined and found to be strongly correlated to the air-temperature-derived snowpack melt onset (N=11, $R^2 = 0.989$), indicating that the start of the snowpack melt season is the end of the reactive bromine season. Snowpack depth decay and rain precipitation further verified the end of reactive bromine season occurs at the time of melt onset. With future Arctic climate trends potentially leading to longer summer melt seasons due to increasing temperatures, our results suggest future reactive bromine seasons may be shorter, leading to fewer ozone depletion and mercury deposition events overall.

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[3], Anna K. Liljedahl[1], Katey Walter Anthony[1], Vladimir E. Romanovsky[2]

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[2]Geophysical Institute, 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 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 can occur through advection and diffusion as a dissolved gas and by movement as an immiscible fluid. Advection and diffusion of dissolved-phase methane can be characterized through the measurement of environmental chemical and physical tracers; immiscible-phase flow can be characterized through measurements of soil displacement pressures and through the comparison of air sparging and petroleum reservoir literature. We propose to study advection, diffusion and immiscible-phase flow in Doughnut Lake (an open-talik lake) and Goldstream Pond (a closed-talik lake) in Goldstream Creek Basin, Fairbanks, Alaska. Data obtained from these study sites will aid in the understanding of greenhouse gas fluxes, and thereby improve research in climate change predictions.

Oral presentation:

Characterization of permafrost dissolved organic matter composition and reactivity: implications for biogeochemical cycling and contaminant fate in a changing climate

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

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

The northern latitudes encompassing the arctic, subarctic and boreal zones, has an increased susceptibility to global climate shifts, resulting in many dramatic ecosystems from boreal forests to tundra. Permafrost is prominent in Alaska and is a mixture of soil and water frozen for at least two years storing an estimated 750-950 Gt of organic carbon in the upper few meters alone. Thawing of permafrost releases this ancient carbon into the active layer and surface waters above it. The carbon can mobilize as dissolved organic matter (DOM), which is susceptible to photolysis, producing an array of reactive species. These reactive species include radicals and excited state species (peroxides, singlet oxygen, hydroxyl radicals, etc.), which are involved in lower trophic level nutrients, biogeochemical cycling, and contaminant degradation. The production and behavior of reactive species are dependent on the DOM composition, which varies based on its origin through microbial or terrestrial production. Thus, permafrost DOM variation relies heavily on the ecological history and age when it became frozen because it is unchanged due to the lack of photolysis and microbial activity.

The molecular composition of permafrost DOM, its reactivity, and contaminant fate influence are currently unknown. It is critical to elucidate how specific moieties that comprise permafrost organic matter may interact in the environment upon thaw in order to understand the current and future impacts of permafrost DOM as thaw progresses. Therefore, we plan to investigate the following questions in order to determine the future ramifications of permafrost thaw in the sub-arctic with the analysis of samples collected from Caribou Poker Creek, Bonanza Creek Experimental Forest, Toolik Lake, and Goldstream valley.

1. What fraction of permafrost carbon pool mobilizes at environmental pH upon thaw?
2. What is the compositional variability of permafrost, active layer, and surface water DOM in interior AK?
    - How does compositional variability affect the photolytic fate and transformation of mobilized permafrost organic matter?
3. How does permafrost DOM inhibit or promote organic contaminants?

Oral presentation:

Hydrograph separation of a sub-arctic glacial watershed, Interior Alaska

Tiffany A. Gatesman[1], Thomas A. Douglas[2], Anna K. Liljedahl[3], Thomas P. Trainor[1], and Anne Gaedeke[3]

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Glacier melt affects several sub-arctic rivers but the melt contribution to larger-scale watershed runoff has attracted limited attention. Geochemically-based hydrograph separation techniques in combination with glacier mass balance and runoff measurements can help refine our understanding of the contributing sources.

Our study was designed to quantify the contribution of glacier melt, snow melt and rainfall to lowland streamflow of a sub-arctic basin in Interior Alaska. The Jarvis Creek watershed (634 km^2) drains the north-facing Eastern Alaska Range and flows into the Delta and Tanana Rivers. The lower portion of this watershed is dominated by thick deposits of permeable gravel sediments with high hydraulic conductivities and discontinuous permafrost. Jarvis Creek is losing water to the aquifer along its lowland section – a phenomenon that might be common in other headwater streams of the Alaska Range. Glacier contribution estimated from measured glacier melt and lowland runoff account for 26-61% of stream discharge (2012-2015) even though the Jarvis Creek watershed is only 3.3% glacierized by land area.

Daily stable water isotope and dissolved ion samples near the Jarvis Creek outlet have been sampled from 2011-2015. Stable water isotope results show distinct chemical signatures in contributing sources and large seasonal and inter-annual $\delta^{18}O$ variability. For example, $\delta^{18}O$ measurements from 2012 and 2013 show a strong snow melt contribution in late spring whereas 2011 and 2014 lack a major snowmelt period. Unlike 2011 and 2012, 2014 data show high input of rainfall. Measurements of stable water isotopes will constrain an end-member volumetric mixing model, while dissolved ion concentrations will support the differentiation between glacier and groundwater sources. Ultimately, the combination of glacier mass balance, hydrological and geochemical measurements will allow us to refine the quantification of glacier melt from a sub-Arctic headwater stream that provides recharge to the regional groundwater system.

Oral presentation:

Biodegradation of petroleum contaminants in Alaskan marine and terrestrial environments

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

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With the majority of Alaska's economy rooted in its abundant petroleum products, the risk of accidental exposure and contamination to the environment is inevitable. In order to understand the fate of petroleum contaminants, their interactions with the environment, and factors that influence their biodegradation by microorganisms, a thorough investigation of both the marine and terrestrial ecosystems impacted by petroleum contamination within Arctic and subarctic environments is needed. The marine component of this study focuses on the influence of chemical dispersants on crude oil biodegradation by indigenous microorganisms in Arctic seawater through incubation experiments. This includes assessing the degradation of both contaminants and accompanying changes in the microbial community, identifying key hydrocarbon and dispersant degrading organisms and nutrients pivotal to biodegradation, and determining whether significant changes due to seasonal variation exist. The terrestrial component of this study will compare the effectiveness of rhizoremediation of diesel-contaminated soils to traditional landfarming remediation techniques in a field study in the village of Kaltag, Alaska. This study will aim to identify the rhizosphere enhancement factors (i.e., vegetation, nutrients) that drive hydrocarbon degradation processes as well as identify key degrading organisms. Methods of analysis for both marine and terrestrial studies will include GC/MS quantitation of petroleum hydrocarbons including PAHs, microbial community analyses using DNA sequencing, and analyses of nutrients and other environmental parameters. Elucidating the mechanisms underlying petroleum biodegradation will allow for the development of more effective remediation strategies available for use by decision-makers and regulatory agencies in both marine and terrestrial landscapes. This is especially critical in Alaska, where the harsh climate and inaccessibility to a majority of the communities by road systems makes the use of traditional clean-up strategies cost-prohibitive and unfeasible.

Oral presentation:

Assessment of contaminants in Alaska solid waste and wastewater sites

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

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Waste management practices currently carried out by many Alaska communities have immense human and environmental health implications. With limited state and federal funding for operations and maintenance coupled with tough environmental and climactic conditions, most of the waste management practices currently in use are insufficient. Of immense concern is the fact that very little is known about the fate and transport of point source pollutants arising from these wastewater and solid waste sites. These study aims to identify the critical pharmaceutical and heavy metal contaminants present in these sites, which have been shown to be present in previous studies. Understanding the nature and mobility of these contaminants will provide invaluable information on risk of exposure, particularly in the context of climate change.

Oral presentation:

Building a model of tropospheric methane fluxes in subarctic Interior Alaska by complementing small scale observations of arctic methane emissions with regional scale observations: A thesis proposal

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

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Observations of Arctic climate change suggest that warming may increase permafrost degradation with the potential to initiate positive feedback mechanisms. The boundaries of the Boreal Forest of North America may also advance north as the length of the growing season increases. Many areas that were once frozen are becoming wetlands and changes in soil processes have the potential to initiate massive ecological shifts. The possibility of substantial changes in carbon emissions in subarctic environments situated between the Boreal Forest and the Arctic motivate this investigation of trends in tropospheric methane (CH_4) in interior Alaska. Interior Alaska is a diverse and dynamic collection of different types of ecosystems, and in order to develop a broad understanding of climate change mechanisms in this region, small-scale observations of all the different ecosystem types need to be integrated with regional scale observations of fluxes. These regional fluxes are most likely a consequence of meteorological and phenological parameters such as precipitation, temperature, sunlight, length of the growing season, and freeze/thaw cycles that both exist on small scales and pervade ecosystems throughout the region. In a joint US-Japanese project, ground-based direct-sun Fourier Transform Infrared (FTIR) spectra were collected at Poker Flat Research Range, Alaska (65.12°N, 147.43°W) from 2000 to 2010 using a Bruker IFS120HR spectrometer. Using FTIR spectra collected at Poker Flat, vertical profiles of CH 4 volume mixing ratio (VMR), as a function of altitude, were estimated with SFIT4 fitting software. The applicability of a method for calculating VMRs of tropospheric CH 4 proposed by Washenfelder et al. (2003, DOI: 10.1029/2003gl017969) was explored. The proposed method of approximation uses retrievals of HF total column abundance as a proxy for CH_4 oxidation in the stratosphere. Comparative timeseries were constructed relating CH_4 VMR estimated for the surface layer of SFIT4 profiles, tropospheric CH_4 VMR calculated using HF total columns, and in situ data from the NOAA site in Bar- row, Alaska. Preliminary observations suggest possible seasonal trends for each year with maxima in spring and fall. Reactivation of continuous ground-based direct-sun FTIR monitoring in the Fairbanks area would help to advance this research and funding for the installation of a Total Carbon Column Observing Network (TCCON) station is being actively pursued. Attempts are being made to develop a network of collaboration that includes expertise across the spectrum from plot measurements to satellite.

Oral presentation:

The behavior of tellurium in copper ore processing at the American Smelting and Refinery Company

Amy Josephson[1], Karen Spaleta[1], and Sarah Hayes[1]

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Essentially all tellurium (Te), an element used in solar panels and other high technology devices, is recovered as a byproduct of copper mining. Recent increases in demand for Te from the photovoltaic industry have sparked questions of long-term supplies of Te (crustal abundance ~3 μg kg^{-1}). As part of a larger study investigating Te resources, this project examines the behavior of Te during Cu ore mining, smelting, and refining at the American Smelting and Refining Company (Tucson, AZ) as a first step toward optimizing Te recovery and supplying high technology Te-based industries. Mass balance calculations estimate that 90% of Te associated with copper ore is lost during the initial Cu concentration that occurs at mine sites. An additional 6.05% of the Te is lost during smelting (0.76% and 5.29% to slag and dust, respectively). And the overall process recovers only 2.2% of Te. Microprobe data shows the presence of several Te telluride minerals in the concentrate. X-ray absorption spectroscopy, used to examine the extent of Te oxidation in anode slimes indicate that a substantial fraction of Te is present as telluride phases in the smelter dust (56%), and raw and pressed slimes (66%). Refinery dust and slag samples exhibited more oxidation with 48% and 24% reduced Te, respectively. These results demonstrate that little of the Te present in Cu ores is recovered for industrial use and additional optimization studies have the potential to substantially increase the amount of Te available for industrial applications.

Oral presentation:

Assessing the immune status of the endangered Steller sea lion (*Eumetopias jubatus*): update, and demographic and environmental drivers

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Haptoglobin (Hp) is a highly conserved acute phase protein biomarker for inflammation that may be useful for assessing innate immune status of endangered Steller sea lions (*Eumetopias jubatus*). Unlike the eastern distinct population segment (DPS), the western DPS of free-ranging Steller sea lions (SSLs) have been declining since the 1980's. Circulating Hp is mediated by the inflammatory cytokine IL-6 and scavenges free plasma hemoglobin (Hb). The binding of Hp to Hb prevents redox reactions of heme groups from altering other important biomolecules. Once bound, the complex interacts with the CD163 macrophage receptor to facilitate proper elimination of heme groups. Given the role of Hp in innate inflammatory responses, plasma Hp concentrations vary with physical and environmental stressors like trauma, infectious disease, and/or contaminants. Variation in Hp measurements have been observed in free-ranging SSLs between the eastern and western DPS, and significant variation in Hp measurements were previously reported for captive SSLs with confirmed pathologies. Earlier studies were instrumental for demonstrating the use of Hp as a biomarker. However, when these findings are reviewed in the context of changes to the health of SSLs on a population level the results are limited by methodology, sample size, and short duration. Concentration of Hp and other health indices (e.g. hemoglobin, hematocrit, blood cell counts, plasma total protein, contaminants, and body condition) were measured in SSLs in Alaska from the late 1990's to 2013. From this relatively robust, long term data set, age specific ranges in Hp were determined and physiological, demographic, and environmental factors relating to variation in Hp measurements were identified.

Oral presentation:

Potential environmental implications of tellurium-rich mine tailings as a function of climate

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

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

Tellurium-based photovoltaics are contributing to global energy solutions, but the extraction, manufacture, disposal, and recycling of tellurium (Te) and related devices may pose a risk to proximal environments and communities. Although rare, Te^{IV} is more toxic than arsenic or other Te oxidation states (Te^{-II}, Te^{0}, Te^{VI}), and little is known about Te behavior in the surficial environment. 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 most toxic form of Te, 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 in arid to subarctic climates using Te-bearing mine tailings to determine the potential ramifications of Te concentration near population centers.

In this study, mine tailings were collected as a function of depth from a variety of climates present in the western U.S. Tellurium is enriched at the surface of semi-arid tailings, potentially as efflorescent salts or sorbed species. Further, Te bulk XAS data indicate the predominance of Te^{VI}, which is less soluble and toxic than Te^{IV}, and electron microprobe analyses suggest two distinct Te-bearing phases, Te sorbed onto iron (oxy)hydroxides and a Te-rich phase. Physiologically-based extraction tests (PBETs) simulating fasting stomach conditions reveal bioaccessibility of up to 10% Te, indicating that these materials may be toxic if ingested. In contrast, in continental climates, Te enrichment at the tailings surface and homogeneous distribution with depth have both been observed. Bioaccessibility at other sites is variable, with up to 20% bioaccessible Te. Similar to observations for other elements, these results highlight potential climatic control on mineral weathering influencing Te speciation, which controls its mobility and bioaccessibility, and the impacts of Te released to the surficial environment as influenced by climate.

Oral presentation:

Synthesis and characterization of polymer-supported cyclodextrin nanoscaffolds for use in future environmental studies

James McKee[1] and Thomas Green[1]

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The toxicity of transitional and post-transitional metal aqueous species in natural waters is a persistent concern. Macrocyclic coordination complexes impart thermodynamic and kinetic stability beyond their corresponding chelation analogues due to the pre-organized physical constraints of the coordinating ligands. Cyclodextrins are biologically produced and well-studied cyclic glucose macrocycles that possess chemically distinct hydroxyls. We synthetically modified native cyclomaltoheptaose to produce a new amphiphilic cyclodextrin, heptakis (6-O-sulfobutyl-2, 3-dibenzyl) cyclomaltoheptaose. This amphiphile has been shown to form micelles at concentrations near 100 mM and promote the synthesis of nearly monodisperse and colloidally stable polystyrene nanoparticles using emulsion polymerization. We believe these amphiphilic cyclodextrins are non-covalently embedded into polystyrene nanoparticle via the benzyl groups while the particle itself is electrostatically stabilized in solution by the sulfobutyl groups. These particles have been characterized by dynamic light scattering, zeta potential measurements, conductivity titration, and NMR. These highly stable model colloids can be the basis of other nanoparticles, stabilized by amphiphilic cyclodextrins, in which the primary hydroxyls are selectively modified with functional groups other than sulfonates. These polymer-supported cyclodextrin nanoparticles serve as scaffolds upon which functional groups that possess ion-exchange and coordination properties can be anchored and could be subsequently used for environmental investigation and remediation.

Oral presentation:

Results from a spatial and temporal analysis of the composition of fine particulates in Fairbanks, Alaska

Kristian Nattinger[1], Deanna Huff[2], and William R. Simpson[1]

[1] Geophysical Institute and Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, Alaska
[2] Alaska Department of Environmental Conservation, Juneau, Alaska

Fairbanks, AK experiences extreme pollution episodes that result in winter violations of National Ambient Air Quality Standards for fine particulates ($PM_{2.5}$), posing a significant health risk for the inhabitants of the area. Trapping of pollution in a very shallow boundary layer is known to cause these violations, but many aspects of particle formation are not fully understood. Analysis of the $PM_{2.5}$ composition was conducted to provide insight into sources, trends, and possible chemical transformations. Methods were developed to convert particulate carbon measurements from IMPROVE (post-2009 analysis method) to NIOSH (pre-2009 method), and resulted in excellent mass closure between $PM_{2.5}$ mass reconstructed from particulate composition and gravimetric mass. Temporal and inter-site spatial analysis of the $PM_{2.5}$ mass, ambient component concentrations and component/$PM_{2.5}$ ratios was completed for the winters (Nov—end of Feb) when most air quality violations occur. It was determined that the particles consist primarily of organic carbon, with smaller percentages of inorganic components. Ambient concentrations of all $PM_{2.5}$ components correlate well with total $PM_{2.5}$ mass and temperature. The $PM_{2.5}$ mass and composition at the North Pole Fire Station#3 site are significantly different (t-test, 95% conf.) from the other 3 sites. Sulfate and organic carbon show significant differences (t-test, 95% conf.) between the two airsheds, implicating different $PM_{2.5}$ sources. Calculation of average source profile values indicates that the composition difference is likely attributable to more wood burning in North Pole, and more oil combustion in Fairbanks. Inter-annual variability is observed in the mean component/$PM_{2.5}$ ratios, with some years significantly different (t-test, 95% conf.) from the 9 year average. The sulfur oxidation ratio was calculated to be 5%, attributable to primary and possible secondary oxidation of SO_2. Insights from this study regarding spatial differences, interannual variability, and $PM_{2.5}$ production processes can help in identifying effective $PM_{2.5}$ control strategies.

Oral presentation:

Sorption and fate of 1,3,5-trinitro-1,3,5-triazine (RDX) in anoxic Gulf of Alaska sediments using batch reactions

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

[1] Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks Alaska
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In 2013 the Navy began war training exercises off the coast of Kodiak Island in the Gulf of Alaska (GOA). Part of the war training exercise involves an annual expenditure of explosives in deep water with approximately 400 lbs. of hazard materials. The hazardous materials include a range of nitroaromatic explosive chemicals, a class of emerging contaminants. A prominent member of this class of chemicals is 1,3,5-trinitro-1,3,5-triazine (RDX), which has been identified as a carcinogen with long term health effects and has been the focus of many groundwater contaminant studies due to its high mobility in soils. While the reductive attenuation of RDX and other nitro-aromatic 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 deep water GOA sediments. Understanding the attenuation and fate of RDX in GOA sediments is important for determining the effects of the entire class of nitroaromatic explosive chemicals on important fisheries based in the GOA. This project will identify sediment sorption constants and reaction rate coefficients for the degradation of RDX in chemically characterized GOA marine sediments under anaerobic conditions and investigate 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 RDX specifically and nitroaromatic compounds in general, in anaerobic marine sediments.

Oral presentation:

Transport of iron and copper across glacially influenced estuaries

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Iron (Fe) and copper (Cu) are required marine micronutrients, but their different biogeochemical cycles (i.e., biological requirements, sources, and particle reactivity) result in Fe being a limiting nutrient in approximately 40% of the global ocean, and Cu being potentially toxic at low concentrations. River input is an important source of both metals, but estuarine processes remove most of the Fe and Cu from solution. Additional coastal inputs for Cu include anthropogenic sources, such as marine antifouling paints. Organic complexation (binding with organic matter) characterizes Fe and Cu dissolved distribution, and both dissolved metals are > 99 % chelated by organic ligands. In the case of Fe, organic complexation serves to increase is residence time in surface waters, as ferric ions are highly insoluble and particle reactive. On the other hand, Cu is less particle reactive, but organic complexation directly lowers the concentration of the toxic free cupric ion (Cu^{2+}) from the water column. Compared to non-glacial streams, glacial melt waters transport reduced amounts dissolved organic matter and greater sediment loads (glacial flour). The extent of glaciation of a watershed is expected to alter the particle size distribution of these metals through their estuarine transect into coastal waters, which will alter their input into the ocean. Size distribution is of interest, because it affects residence time, lability, and therefore bioavailability. Data on estuarine modification of glacial streams into the Gulf of Alaska are not available, and here I present a project that proposes to investigate the distribution of dissolved and particulate Fe and Cu size classes across transects from streams to coastal waters of Kachemak Bay, Alaska.

Oral presentation:

Mineralogical controls of trace metal(loid) behavior during Au and Ag extraction at Golden Sunlight Mine near Whitehall, MT

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Trace metal(loid) behavior is often ignored during the extraction of economic metals, commonly gold, silver, copper, lead, and zinc. Trace elements, such as Tellurium, co-associated with economic ore deposits are frequently of environmental concern and can be important resources for high technology applications. After the extraction of the target economic metals, the trace element-containing residual waste products are released to the surficial environment, typically at concentrations too low to be economically reprocessed, and may also result in environmental degradation. The overarching goal of this project is to provide a fundamental understanding of trace element behavior during Au extraction to facilitate the development of byproduct recapture of currently unrecovered trace elements, particularly Tellurium. A critical first step in accomplishing this goal is to examine trace metal behavior and mineralogy during current Au and Ag extraction processes.

Golden Sunlight Mine, Whitehall, MT, is a gold-silver telluride deposit with the ore consisting of a complicated telluride mineralogical suite. Previous investigators (e.g., Spry et al.,1997; Spry and Thieben, 2000) have identified 45 minerals, including eight bismuth sulfide and 6 Tellurium phases (Au-, Ag-, Bi-, Hg-, Pb- telluride and native tellurium). Samples from Golden Sunlight were collected from each step in the mine extraction process. We anticipate significant mineralogical changes as the ore goes through the extraction process. Bulk elemental quantification was performed using peroxide sinter dissolution prior to analysis by inductively-coupled plasma mass spectrometry (ICP-MS). So far we see enormous variations in Te concentrations at various steps (>2000 to < 1 ppm) in the operation. Grain-scale petrographic and electron microprobe data will be used to assess grain size, mineral identification and abundance. Together, these results will represent an important step in determining the economic viability of byproduct Te recovery from relatively Te-rich ores.

References:
Spry, P. G., Foster, F., Truckle, J. and Chadwick, T. H. (1997) The mineralogy of the Golden Sunlight gold-silver telluride deposit, Whitehall, Montana. *Mineral. Petrol.,* **53**, 142-64.
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Oral presentation:

Investigating the relationship between seasonal bromine monoxide production and Arctic sea ice

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Arctic sea ice coverage is rapidly receding from its historic seasonal extent. As sea ice recedes and changes in nature, marine boundary layer atmospheric composition is transformed as a result. First year sea ice is becoming the dominant Arctic ice type, from fifty percent in the 1980s to roughly seventy percent as of 2015. First year ice has a much different effect on the formation of halogen radicals than older, multi-year sea ice. Bromine radicals are of particular interest, as they are regularly detected at mixing ratios of up to 41 ppt during seasonal propagation events. Currently, it is thought that first year sea ice is highly effective at releasing bromine radicals into the atmosphere during the Arctic spring. However, as the total ice cover vanishes, the sources of atmospheric halogen will also decrease. Springtime bromine production in the Arctic is dominated by the bromine explosion cycle. In this cycle, one bromine oxide radical can produce two bromine oxide radicals, releasing bromide ions found on ice surfaces into the atmosphere. My doctoral research will focus on the relationship between ice composition and bromine production, and the prediction of future bromine production based upon realistic analysis of changing ice conditions. I will be analyzing data gathered in the Arctic Ocean by the O-BUOY Monitoring Network to determine the nature of this relationship. Halogen propagation may also occur on airborne ice particles, and I plan on investigating changes in atmospheric composition during storms in the troposphere. I hope to collaborate with meteorologists to gain a better understanding of atmospheric composition changes during tropospheric storms. The bromine radicals found in the atmosphere will have uncertain effects, and I intend to look at the oxidative potential of bromine on methane produced by melting permafrost. Additionally, while the potential of bromine to oxidize mercury has been extensively studied, the potential for bromine to oxidize other airborne heavy metals, such as those given off in mining operations in Norilsk, is widely unexplored. I would like to investigate the potential of bromine to oxidize heavy metals in Norilsk and the greater Arctic region.

Poster presentation:

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

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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.

Poster presentation:

Implementation and analysis of an ash aggregation scheme within the Weather Research Forecasting with Chemistry (WRF-Chem) model

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Using simplified versions of well-characterized particle coagulation equations, we detail the implementation of a volcanic ash aggregation scheme into the Weather Research Forecasting with Chemistry (WRF-Chem) model. Forecast output from the 2008 Kasatochi eruption using this new capability are compared to remote sensing retrievals from the Moderate Resolution Imaging Spectroradiometer. These comparisons suggest that by including this aggregation scheme within the WRF-Chem model, forecasted plume heights, mass loadings and particle size distributions better match those with observed, remote sensing data.

Oral presentation:

Characterization of organic compounds in Interior Alaska particulate matter using NMR spectroscopy

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Particulate matter pollution, specifically from particles with a diameter of less than 2.5μm ($PM_{2.5}$), is a significant health concern in Fairbanks and North Pole, Alaska in the winter months when strong atmospheric inversions trap air pollution and frequently lead to $PM_{2.5}$ concentrations that violate the USEPA's National Ambient Air Quality Standards (NAAQS). Previous research using source profiles and chemical mass balance models has shed light on the elemental composition and source of this particulate matter pollution with most of it thought to result from residential wood burning. However, there is still a large degree of uncertainty regarding the source of this particulate matter and no previous research has been done to characterize the organic carbon fraction which makes up 60% of the mass of ambient air $PM_{2.5}$ in Interior Alaska. This research proposes methods to further the characterization and source apportionment of Interior Alaska $PM_{2.5}$ with Nuclear Magnetic Resonance (NMR) Spectroscopy. Ambient air particulate matter samples were collected onto 47mm supported PTFE filters with a vacuum pump. Eight samples were collected for durations between 1 day and 2 weeks at the North Pole Fire Station #3 in February and March 2016. PTFE filters were extracted by sonication in deuterated dimethyl sulfoxide (DMSO-d6) and analyzed on a Bruker AV-600MHz NMR Spectrometer. ^{1}H-NMR spectra were collected for 2048 scans using the NOESY water suppression pulse sequence. Preliminary analysis shows that it is possible to quantify the relative concentrations of organic functional groups through integration of characteristic regions in the ^{1}H NMR spectra. Application of these methods should help further confidence and understanding of the source and chemical composition of fine particulate matter in Interior Alaska with a possible end goal of guiding air pollution regulation and mitigation strategies.

Oral presentation:

Coal fly ash metal(loid) liberation and association with dissolved organic matter in aquatic boreal systems

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Coal plants produce approximately 40% of the power in the U.S., which generates 140 million tons of coal ash waste annually. Coal ash is used for soil stabilization, asphalt, mineral fillers, road base etc., and excess coal ash is stored in stockpiles and coal ash landfills which leads to environmental dispersion of these materials. Coal is expected to continue to serve as a major energy source in the sub-arctic, therefore, it is imperative to understand the impact of coal fly ash on the sub-arctic environment. Previous characterization of fly ash from the UAF power plant revealed elevated levels of toxic metal(loid)s, including arsenic, copper, mercury, and lead at concentrations of 8.1 mg kg^{-1}, 107 mg kg^{-1}, 2 mg kg^{-1}, and 17 mg kg^{-1}, respectively. The overarching goal of this project is to characterize the impact of dissolved organic matter, which is ubiquitous in surface waters, on metal(loid) leaching from coal fly ash. These interactions are hypothesized to affect the rates of mineral weathering and associated liberation of toxic metal(loid)s and examine metal(loid) bioaccessibility. As a preliminary experiment, coal fly ash from the UAF power plant was leached with 18 MΩ water to quantify the rate of metal(loid) liberation as a function of time. Within the first hour pH of the solution rose from neutral to 12.11, reached its peak of 12.29 within 5 days, and steadily declined to 12.10 by day 28. These changes in pH indicate the occurrence of mineral transformations occurring up to one month after the start of the experiment, which will be characterized in future experiments. Examination of metal(loid) concentrations in solution indicate that at 24 hrs, there is already substantial amounts of Ca, Ba, Sb, Te and other toxic elements in solution and these concentrations increase by the 48 hr sampling. The next series of experiments will react the same fly ash material with DOM isolated from boreal wetland water and simulated rain water to examine metal(loid) liberation as a function of time and mineral transformations of solid phase residuals also be examined as part of assessing metal bioaccessibility. These experiments will lend insight into the environmental and human health risks associated with dispersion of fly ash materials in a boreal ecosystem.

Oral presentation:

Dissolved organic matter interaction with fly ash metal(loid)s

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Coal is currently used as a large source of energy worldwide, accounting for about 40% of electricity generation, as well as in interior Alaska where it generates approximately 178,000 tons of fly ash annually. Coal fly ash contains metal(loid)s of concerns (e.g. lead, mercury, and arsenic) which could be released into the environment, through leaching into surface water by mechanisms such as rainfall events. Interactions with dissolved organic matter (DOM), ubiquitous in surface waters, may lead to transformation of speciation or enhanced mobilization of these metal(loid)s. There is a scarcity of literature examining this interaction between DOM and metal(loid)s, particularly in sub-arctic regions. The overall project aims to determine the fate of metal(loid)s from fly ash in the environment in order to further the understanding of DOM-metal(loid) interactions and potential fly ash contamination.

Titrations of increasing concentrations of Fe(II) and Fe(III) were performed on ~10 mg C/L solutions of DOM from Suwannee River, Pony Lake, and a local boreal wetland system in Fairbanks, AK. After each iron addition, ferrozine analysis was used to determine iron speciation/concentration followed by Ultraviolet-visible (UV-Vis) analysis and 3D excitation emission matrix (EEM) fluorescence spectroscopy to determine the effect of the iron addition on DOM. EEMs were corrected for pH and inner filter effects, blank subtracted, and normalized to raman area. Speciation of iron was seen to affect fluorescence of DOM, and Parallel Factor (PARAFAC) analysis will be used to quantify the quenching of fluorophores in DOM due to iron speciation.

Poster presentation:

Climatic control over the bioaccessibility of metal(loid)s in Western United States mine tailings and use of bioaccessibility to prioritize remediation efforts

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Recent studies have underscored concerns regarding health risks associated with wind transport of toxic metal(loid)s sourced from abandoned mine tailings. Efforts are underway to identify the worst sites and costly remediation strategies are mitigating the risk to communities and the environment. In order to evaluate the risk posed by a site, total metal(loid) concentrations are used, which is not well correlated with health risks, leading to inefficient allocation of remediation dollars. One method of getting a more accurate measurement of risk is through the use of bioaccessibility studies.

Bioaccessibility is the fraction of a contaminant that is soluble in physiological conditions. In order to pose a health risk, metal(oid)s from the tailings must enter the body, either by inhalation or ingestion, then solubilize under conditions present in the lung or GI tract. The solubility, and thus toxicity, is determined by speciation, which encompasses composition, oxidation state, molecular structure, and physical form. One contributing factor to speciation is climate. Relative temperatures and precipitation can affect oxidative weathering that occurs within the mine tailings. Climate also has a large control over the potential transport of metal(loid)s away from the tailings. In this study, we report the total metal(loid) content in geomedia as well as the physiologically-soluble fraction from mine tailings from across the Western U.S.

Surficial samples were collected from mine tailings in the southwestern U.S., which represent a range of climates. They were subjected to total elemental analysis and size fractioned by dry sieving to determine the fractions of particles that are small enough for ingestion, wind transport, and inhalation. The smallest and most mobile fraction (< 37 μm) represented 2 to 14% of the bulk sample by mass. Appropriately size fractionated samples were subjected to physiologically based extraction tests (PBETs) simulating interaction of geomedia with lung and stomach fluids prior to supernatant analysis by ICP-MS. Stomach fluids [0-88% bioaccessibility] solubilized a larger fraction of metals in most tailings than the lung PBET [0-25% bioaccessibility]. These results lend insight into evaluating the health risk associated with metal(loid)s from mining activities and current remediation evaluation methods.

Poster presentation:

Bioaccessibility of metal(loid)s in road dust from Fairbanks, Alaska

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Recent studies highlight the health risks associated with toxic metal(loid)s (e.g., As, Zn, and Pb) in mine tailings-derived dusts and near urban and rural roads. Use of potentially toxic metal(loid)-bearing mine wastes as road fill is a common practice in Fairbanks, Alaska and may exacerbate metal(loid) translocation to populated areas. In order to have a deleterious health effect, metal(loid)s must be inhaled or ingested and dissolve under lung or gastrointestinal tract conditions. In this study, we determined total and physiologically-soluble fractions of metal(loid)s in road dust from the Fairbanks area.

Five samples of road dust were collected in Fairbanks using passive samplers and artificial disturbance. Total elemental analysis was performed by peroxide sinter dissolution and inductively-coupled mass spectrometry (ICP-MS). Dry sieving was used to determine the fraction of particles small enough for ingestion (< 250 µm) and inhalation (< 37 µm). Appropriately sized samples were subjected to physiologically based extraction tests, simulating lung and stomach fluids prior to ICP-MS analysis. While some samples contain total Ba, Zn, and Mn concentrations over 100 ppm, the fraction of bioaccessible metal(loid)s varied widely (0-95%). The results lend insight into Fairbanks road dust, but additional studies are needed to quantify the health risk.

Poster presentation:

Seasonal variations in composition and photoreactivity of dissolved organic matter isolated from a small sub-arctic stream

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Dissolved organic matter (DOM) is a complex heterogeneous mixture of organic compounds derived from decomposition products, and ubiquitous to all natural surface waters. Its composition and thus also its chemical reactivity largely depend upon source material inputs from the surrounding system. Elucidating DOM composition and reactivity is complicated by seasonal changes in productivity and source inputs to the water column and variations in solid/liquid phases that affect hydrologic flow. In the arctic and sub-arctic, DOM characterization is especially important to quantify due to the rapid climate-driven changes occurring at high latitudes, and are currently largely unknown. DOM from a small boreal stream in a watershed of discontinuous permafrost in the Goldstream Valley of interior Alaska was isolated by solid-phase extraction (PPL) at three points during the year – winter, spring, and late summer; winter collection occurred during an active overflow event. Compositional characteristics of each of the isolates were characterized by SPR-W5-WATERGATE ^{1}H NMR spectroscopy, UV-Vis absorbance, and 3-D excitation emission (EEM) fluorescence spectroscopy and were compared against end-member reference DOM isolates. Kinetics of photobleaching experiments reveal the influence of compositional differences among the isolated DOMs on their chemical reactivity, and offer insight into potential differences in their source materials and ecological function throughout the year. Photobleaching studies were conducted using a variety of reactive species quenchers in order to assess susceptibility of oxidative and triplet-excited transformation mechanisms on the different DOM isolates, which were then analyzed by ^{1}H NMR, UV-Vis degradation kinetics, and parallel factor analysis (PARAFAC) of fluorescence EEMs.