

Introduction: High latitude permafrost soils contain vast reserves of organic carbon (C) that, with warming, may become a significant source of greenhouse gases (GHGs) due to increased microbial activity. Current climate model predictions for C storage and fluxes in these ecosystems depend heavily on the rate at which soil organic matter (SOM) is broken down.¹ At present, there are significant uncertainties regarding how the varying chemical and physical differences among these SOM pools and their interactions with the surrounding environment will affect the rates at which they are being degraded by the local biological community.

It has been shown that organic C molecules sorbed to sediment mineral surfaces tend to decompose more slowly, and to a lesser extent than dissolved organic matter (OM).² This may be due to the physical occlusion of the OM by minerals, reducing its susceptibility to microbial attack, thereby changing its long-term accumulation and translocation in the soil profile.³ Recent radiocarbon ($\Delta^{14}\text{C}$) values taken from Alaskan permafrost soils indicate that the carbon dioxide (CO_2) and methane (CH_4) being released to the atmosphere are derived from older C buried deeper in the soil profile.⁴ Mineral phases and complexation mechanisms responsible for the stabilization of permafrost SOM are largely unknown and the role of these C-mineral interactions in the Arctic ecosystem and global C budgets is not well understood.

Research Objectives: The following research questions will be investigated to better quantify and predict GHG emissions from thawing permafrost in response to climate change:

- R1) What are the major mineral species present in Arctic permafrost soils, and how do they affect SOM distribution in the soil profile?
- R2) What are the key chemical bonding mechanisms between soil organic C and mineral phases in these systems?
- R3) How does topographical variation impact C-mineral associations and, in turn, SOM stabilization and GHG emissions?

Hypotheses:

- H1) The major mineral elements I expect to find in these systems are Fe, Ca, and Al. Fe oxides will prove to be an important sorbent in the spatial distribution of SOM-mineral complex formation because of their strong selectivity for aromatic compounds and high molecular weight fractions,² qualities commonly associated with permafrost soils.
- H2) OM preservation will largely be controlled by electrostatic interactions and sorption of minerals into micropores along the soil profile.
- H3) Concentrations of Fe oxides and the relative proportion of OM bound to mineral surfaces will increase at lower topographic regions. Greater portions of OM will be physically protected from the microbial community leading to increased recalcitrance and decreased fluxes of CO_2 and CH_4 to the atmosphere.

Preliminary Results: Addressing these questions will require close monitoring of permafrost soil dynamics throughout seasonal thaw and at different depths along the soil profile. Working with the NGEE-Arctic biogeochemistry team at Oak Ridge National Lab (ORNL), I have helped design and test a large, temperature-controlled soil column apparatus for intact soil cores. Using a two-stage cooling mechanism, this system successfully mimics or accelerates seasonal thaw patterns in the lab.⁵ Access ports for the collection of gas and liquid samples allow for continuous, nondestructive monitoring of biogeochemical properties and their changes over time and space, on the order of days to weeks and cm to m, respectively.

Study Site: Field observations will take place at the Barrow Environmental Observatory (BEO), located at the northernmost point of the Arctic coastal plain, near the remote, native Iñupiaq village of Barrow, Alaska. This high-latitude ecosystem is characterized by a dynamic landscape

dominated by distinct morphological subunits: ice-rich polygonal tundra and drained thaw lake basins (DTLB). The site consists of continuous permafrost with the active layer reaching ~20-55 cm deep. Frozen soil cores (~7.7 cm diameter by 1m depth) will be obtained from low- and high-centered polygons from DTLBs of varying age using a SIPRE auger⁶ and a hydraulic drill.

Experimental Approach: Using cores obtained in the field, **(R1)** I will first physically and chemically fractionate samples from the organic, mineral, and permafrost horizons and then characterize the mineralogical components with energy-dispersive x-ray (EDX) spectroscopy. Intact soil grains will be examined with micro-Raman and Fourier-transform IR spectroscopies to obtain compositional information, including the relative proportions of polysaccharides, amino sugars, phenols, lignin, and lipids to estimate the mineral interactions with different OM functional groups. **(R2)** The stability of these interactions will be tested using batch equilibrium techniques, while the aggregate surface area and soil micropore volumes will be determined by scanning electron microscopy (SEM). **(R3)** Using the soil column mesocosms, I will monitor changes in temperature, moisture, pH, redox potential, and concentrations of gases and solutes throughout a controlled thaw, helping to identify where CO₂, CH₄, and dissolved organic C are being generated. During my summer field campaigns, I will continuously measure land-surface fluxes of CO₂ and CH₄ using chamber measurements and laser-based infrared gas analyses. The isotopic composition and age of mineralized C and SOM C from each core will be determined at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Lab.

Intellectual Merit: Collectively, this research will provide a deeper mechanistic understanding of the physical and chemical controls on SOM stabilization in permafrost soils, while advancing our fundamental knowledge of the role of C-mineral chemistry in the Arctic ecosystem. These data will help provide a firmer empirical foundation for predicting the most important drivers of C degradation and GHG emissions in these high-latitude regions. As a graduate student at UTK working with researchers at ORNL, I will have full access to the extensive resources provided by both, including all instrumentation mentioned, and the support of expert faculty and scientists who specialize in terrestrial biogeochemistry and can help optimize any necessary techniques.

Broader Impacts: Given the importance of climate change to all sectors of society, these results will provide critical data for improving global climate models. Various researchers from a variety of disciplines may use this data to better interpret Arctic systems chemistry and make more informed decisions on current and future governmental policies. My continued involvement with the ACS local section and my tutoring efforts will allow me to actively recruit high school and undergraduate students from underrepresented groups to gain valuable research experience on this project. The interdisciplinary nature of this research will significantly broaden their scientific experience and enhance their understanding of the importance of chemistry in the Arctic to global climate change. I will encourage them to apply for REU support to join me in the field where they will participate in weekly public scientific discussions with native Iñupiaq community members. I am applying to host a PolarTREC teacher, who has recently contacted me from the East Tennessee area, during a summer field campaign where we will connect with her students to share our experiences from the field. Given the close proximity, we will be able to connect more directly with her students through class presentations and scientific demonstrations. On a more regular basis, I am able to share the importance of environmental research, Arctic biogeochemistry, and their impacts on public policy and education, to the broader public, via my website and blog “*Think Like a Postdoc*” (www.malloryladd.com).

References: [1] Jenkinson et al. (2008) *Euro. J. of Soil Sci.*, 59, 400 [2] Gu et al. (1994) *Env. Sci. & Tech.* 28, 38 [3] Mikutta et al. (2006) *Biogeochemistry*, 77, 25 [4] Vogel et al. (2009) *J of Geophys. Res.*, 114 [5] Ladd et al. (2013) ORNL Ann WIS Poster Session: <http://malloryladd.com/> [6] Bockheim et al. (2007) *Soil Soc. of Am. J.*, 71, 1889