

PROBING THE CHEMODIVERSITY OF SOUTHERN PEATLANDS USING HIGH-RESOLUTION MASS SPECTROMETRY

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Peatlands cover only 3% of the land on Earth but store 24% of global soil carbon. Organic carbon decomposition is slow in peatland ecosystems and thus allows peatlands to become stable and significant carbon reservoirs over millennia. However, the relative contribution of carbon preservation mechanisms over millennial timescales (e.g. soil saturation, mineral protection, inherent stability based on molecular structure) within peatlands are poorly understood. This project aims to develop a deeper understanding of how peat stores carbon for long timescales by studying its molecular-level chemical composition. Prior research has suggested that peat retains organohalides that may be resistant to microbial degradation. Samples from multiple peat cores that were collected in southern Patagonia (~ 52°S) were probed for bromine speciation and concentration using X-ray Absorption Near Edge Structure (XANES) spectroscopy. The peat cores are several meters deep and thousands of years old. The XANES data show that organobromine becomes progressively enriched downcore in one of the coastal peat cores, suggesting organobromine may be biogeochemically stable in this location. To shed light on the molecular-level chemical characterization of these samples, we also analyzed a subset of the peat samples using high-resolution mass spectrometry. The peat samples were freeze-dried, homogenized, and extracted with 1:1 v:v methanol:dichloromethane through sonication. A Bray-Curtis dissimilarity test was performed for all chemical features, revealing that the chemodiversity of these samples is driven by age. Specifically, surface, i.e., younger, samples show higher variability in chemical composition, while deeper core samples, i.e., older than 4000 years, showed lower variability. These findings suggest that organic carbon biogeochemical processes, such as humification, may play a role in the convergence of chemical similarity in older samples. Two organohalides were putatively annotated via high-resolution mass spectrometry. Although the bulk organic carbon concentration is stable downcore and through time, variabilities in chemodiversity and increases in brominated organic carbon indicate that underlying reactions continue to transform peat organic matter throughout burial.