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Bromination of peat organic matter confers millennial-scale stability

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Peatlands serve as essential terrestrial reservoirs of carbon (530–600 Pg). The stability of organic matter (OM) in peat depends on its organic composition, with carbohydrate content more labile than aromatic structures. Peat is also rich in halogens, which bond to OM and are retained over unknown timescales. Although halogens are generally thought to render organic molecules resistant to degradation, their role in peat OM dynamics is poorly understood. We have examined bromine (Br) and organic carbon dynamics along four long (>400-cm) peat cores from coastal sites in southern Chile and Argentina. We use Br K-edge XANES spectroscopy to quantify organically bound Br in particulate peat core material and ATR-FTIR spectroscopy to track changes in organic composition, including aromatic carbon, organic acids/esters, and polysaccharides, along the cores. Our results show that all Br in the peat material is bonded to aromatic polymers and that organo-Br and the aromatic portion of peat OM co-vary over the first eight millennia of the record. The electron-rich Br atoms likely shield aromatic carbon from degradation, contributing to the well documented recalcitrance of the aromatic fraction in peat OM. In our efforts to establish longer-term stability of brominated organic matter in peat, we found evidence that bromide is not released through downcore debromination, suggesting bromide source limitation as a controlling factor for organobromine levels. This finding links organobromine production in terrestrial OM with rising sea levels through the early Holocene, with organically bound Br in peat serving as a geochemical marker of past depositional processes. It further suggests that increasing sea levels could stimulate natural organobromine production in coastal peatlands, enhancing long-term preservation of aromatic carbon in peat ecosystems.