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Water movement and solute transport in permafrost wetlands: implications for inorganic carbon cycling

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Carbon dioxide emissions from thawing permafrost wetlands are an expected consequence of global warming. Addressing the pathways by which carbon is emitted, we investigated the hydrological and geochemical controls on the pore water chemistry of a permafrost wetland, with a shallow geological sequence comprising loam overlain by sphagnum peat, in Ilulissat, Greenland. A 400 m transect parallel to the general flow direction was established, along which water table measurements and slug tests were conducted, and the active layer thickness recorded (typically ~ 0.5 m). Also, in three detailed profiles along the transect, the vertical distributions of stable isotopes of water and major ion chemistry were investigated, by analysis of active layer pore water and water of melted core sections of permafrost. Concentrations of chloride (0.3-0.4 mM) did not show variation with depth, dismissing solute movement by ion freeze-out during fall freeze-up as a main control on the water chemistry. In addition, the observed vertical δ^{18} O distribution did not to any extent conform to modelled Rayleigh distillation curves for the preferential inclusion of $H_2^{18}O$ into ice, which could be a scenario for fall freeze-up. The $\delta^{18}O$ data therefore suggests either a rapid freeze-up or a simultaneous phase transition at all depths of the active layer, which in either case also would minimize potential ion freeze-out effects. Nevertheless, concentrations of major ions generally increased with depth. A conceptual model for water and solute transport was therefore established, according to which solutes are mobilized by weathering reactions in the loam and then transported upwards to the peat by diffusion. In the peat, lateral advective solute transport dominates. We applied the model to observed profiles of Ca, Mg, HCO_3 and the partial CO_2 pressure (P_{CO_2}) . Concentrations of Ca, Mg and HCO_3 increased with depth, reaching \sim 2 mM, \sim 2 mM and \sim 8 meq/L at the bottom of the active layer. Pore water at all depths was of Ca-Mg-HCO₃ type (1:1:4 stoichiometry), and was subsaturated for calcite and dolomite. Immediately below the permafrost table, however, Ca, Mg and HCO $_3$ showed an abrupt decrease. Similarly, highly elevated $P_{\rm CO}_2$ of up to 1.8 atm were observed in the active layer, followed by an abrupt decrease to <0.05 atm below the permafrost table. The combined behavior of Ca, Mg, HCO_3 and P_{CO_2} suggests a mutual control via the carbonate system. Here, the diminutive P_{CO_2} -values below the permafrost table may be an artifact of our method, which allowed loss of CO_2 from the thawing permafrost core samples to the container headspace. We propose that silicate weathering is the primary source of Ca and Mg. Once released, annual cycling of Ca, Mg and inorganic carbon species takes place, via cryogenic carbonate precipitation during fall freeze-up and their re-dissolution during spring thaw. Concomitantly exclusion of CO2 gas to bubble inclusions occurs during freeze-up. CO2 gas liberated during spring thaw may re-enter the cryogenic carbonate cycling. However, the elevated P_{CO_2} of the active layer strongly suggests ebullition of CO₂ to the atmosphere to be a final pathway for the emission of CO₂ from permafrost wetlands to the atmosphere.