Geophysical Research Abstracts, Vol. 9, 08940, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-08940

Geochemical constraints on anaerobic organic matter decomposition in a northern peatland

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Rates of anaerobic respiration are of central importance for the long-term sequestration of carbon in peatlands, which are a relevant sink in the global carbon cycle. However, our current knowledge on in situ decomposition rates and the factors controlling them in deep peat deposits are largely unknown to date. To identify constraints on anaerobic peat decomposition, we determined detailed concentration depth profiles of the decomposition end-products CH_4 and CO_2, along with concentrations of relevant decomposition intermediates, at an ombrotrophic peat bog. We estimated the magnitude of CO_2 and CH_4 production by inverse pore-water modeling, and calculated Gibbs free energy of key processes.

Highest anaerobic decomposition rates occurred near the water table (decomposition constant $k_d = 10^{-3}$ to 10^{-4} a^{-1}) whereas in the deep peat deposit decomposition proceeded very slowly ($k_d = 10^{-7}$ a^{-1}). We hypothesize that this pattern can be related to thermodynamic and transport constraints. Due to slow, diffusion-based transport, metabolic end-products accumulated deeper into the peat (ca. 5500 μmol L^{-1} CO_2 and 500 μmol L^{-1} CH_4). This concentration increase subsequently lead to an accumulation of the methanogenic precursor acetate (up to 150 μmol L^1), which did not compensate for a diminished *in situ* energy yield for acetoclastic methanogenesis close to the threshold for microbially mediated processes (20 to 25 kJ mol^{-1} CH_4). In line with these results, CH_4 formation was dominated by hydrogenotrophic methanogenesis, as indicated by isotopic fractionation. This process ultimately occurred at a Gibbs free energy of only 35 to 40 kJ mol^{-1} CH_4 in larger depths. Furthermore, fermentative degradation of acetate, propionate and butyrate attained Gibbs free energies close to the thermodynamic limit. Based on theoretical consideration, these conditions likely

constrained the methanogenic decay and can thus explain the overall strong slow-down of anaerobic peat decomposition in deep peat deposit.