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Cut off from supplies - sulfate exhaustion and implications for methane emissions in a brackish rewetted peatland after separation from the coast

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Coastal ecosystems are at the interface between marine and freshwater and exhibit a special geochemistry. We investigate the S and C geochemistry of a coastal, degraded fen peatland. The site has been cut off from the Baltic Sea since 1995 and was rewetted with freshwater from the surrounding catchment in 2010. Despite of locally high pore water sulfate (SO42-) concentrations, the fen turned into a strong source for methane (CH4) with annual budgets up to 0.26$\pm$0.06 kg m-2 (Hahn et al. 2015). To reconcile this apparent contradiction we use concentration patterns and stable isotope signatures of water, SO42-, pyrite, dissolved carbon, and CH4 (δ2H, δ13C, δ18O, δ34S) along a transect with increasing distance to the Baltic coastline (300-1500 m).
The current peatland geochemistry is characterized by a combination of relict signals reflecting former brackish water intrusion events and indicators of recent human activities such as internal eutrophication and increasing freshwater contribution. The shallow peat layer (depth mostly $\leq$ 55 cm) exhibited a pronounced vertical gradient with a freshwater-front lying on top of the brackish water layer. S geochemistry was decoupled from present brackish water distribution as marine SO42- was almost completely biotically reduced and converted to pyrite. The remaining pore water SO42- pool was remarkably 34S-enriched in relation to Baltic Sea SO42- (up to +86.4 and +21‰ respectively) and also δ34S-values of pyrite were comparatively high (+4.8‰, thereby demonstrating a distinct reservoir effect under closed-system conditions. However, one of the profiles situated 1150 m from the Baltic Sea coast line exhibited a contrasting S pattern with pronounced excess of isotopically lighter SO42- at depth (up to 32.8 mM and +22.7‰. We hypothesize, that local groundwater seeps might provide electron acceptors such as NO_3- for the contemporary oxidation of pyrite. δ13C in DIC exhibited a pronounced vertical shift from -23.9‰ in the bottom up to +4.2‰ in the top profile, thereby indicating zones of high CH4 production in the top 30 cm of the peat, whilst non-fractionating C metabolic processes such as SO42- reduction are dominating in the deeper parts.
Our study shows that coastal wetlands can turn to strong sources for CH4 when marine SO42-supply is cut off. Indeed, brackish impact might still be present in form of high salinities, however, the contemporary SO42- pool becomes exhausted. Thus, locally high SO42-concentrations do not inhibit high CH4 emissions on ecosystem scale.

Citation: Hahn J, Köhler S, Glatzel S, Jurasinski G (2015) Methane Exchange in a Coastal Fen in the First Year after Flooding - A Systems Shift. PLoS ONE 10(10): e0140657. doi:10.1371/journal.pone.0140657