

Towards explaining excess CO₂ production in wetlands – the roles of solid and dissolved organic matter as electron acceptors and of substrate quality

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To understand carbon storage in water logged, anaerobic peatlands, factors controlling mineralization have been studied for decades. Temperature, substrate quality, water table position and the availability of electron acceptors for oxidation of organic carbon have been identified as major factors. However, many studies reported an excess carbon dioxide (CO₂) production over methane (CH₄) that cannot be explained by available electron acceptors, and peat soils did not reach strictly methanogenic conditions (i.e., a stoichiometric formation ratio of 1:1 of CO₂ to CH₄). It has been hypothesized that peat organic matter (OM) provides a previously unrecognized electron acceptor for microbial respiration, elevating CO₂ to CH₄ ratios. Microbial reduction of dissolved OM has been shown in the mid 90's, but only recently mediated electrochemical techniques opened the possibility to access stocks and changes in electron accepting capacities (EAC) of OM in dissolved and solid form. While it was shown that the EAC of OM follows redox cycles of microbial reduction and O₂ reoxidation, changes in the EAC of OM were so far not related quantitatively to CO₂ production. We therefore tested if CO₂ production in anoxic peat incubations is balanced by the consumption of electron acceptors if EAC of OM is included. We set up anoxic incubations with peat and monitored production of CO₂ and CH₄, and changes in EAC of OM in the dissolved and solid phase over time.

Interestingly, in all incubations, the EAC of dissolved OM was poorly related to CO₂ and CH₄ production. Instead, dissolved OM was rapidly reduced at the onset of the incubations and thereafter remained in reduced form. In contrast, the decrease in the EAC of particulate (i.e. non-dissolved) OM was closely linked to the observed production of non-methanogenic CO₂. Thereby, the total EAC of the solid OM pool by far exceeded the EAC of the dissolved OM pool. Over the course of eight week incubations, measured decreases in the EAC of total NOM could explain 22-38 % of excess CO₂ production in a weakly decomposed peat, 30-67 % of excess CO₂ production in a well decomposed peat, and >100 % of excess CO₂ production in a peat that had been exposed to oxygen for > 1 year. In this latter peat, EAC by OM explained 45-57 % of CO₂ production, while reduction of sulfate available in this material readily explained the remaining fraction.

Despite having considerable uncertainty arising from methodological challenges, the collected data demonstrated that accounting for the EACs of solid and dissolved OM may fully explain excess CO₂ production. As we conservatively assumed a carbon oxidation state of zero for our budget calculations, a higher oxidation state of C in NOM as suggested by elemental analysis would result in electron equivalent budgets between EAC decreases and CO₂ formation even closer to 100 %. A higher oxidation state of mineralized carbon seemed especially likely for weakly decomposed peat, as this material had higher concentrations of oxygen and showed the largest percentage of formed CO₂ that could not be explained based on OM reduction.