Contributions of organic matter and organic sulfur redox processes to electron flow in anoxic incubations of peat

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Anaerobic decomposition of peat soils involves a number of interdependent microbial processes that ultimately generate CO$_2$ and CH$_4$. In many peat soils, a high ratio of CO$_2$:CH$_4$ was reported, which presumably results from a direct or indirect role of soil organic matter serving as an electron acceptor. Therefore, in this study we intended to test the hypothesis that organic matter (OM) suppresses methanogenesis and sustains anaerobic CO$_2$ production, serving as i) direct electron acceptor or ii) via supporting internal sulfur cycling to maintain CO$_2$ production through bacterial sulfate reduction (BSR). We incubated peat samples of commercial bog peat, inoculated with a small amount of fresh peat to introduce an active microbial community. Samples were amended with sulfate or sulfide and incubated under anoxic conditions for 6 weeks at 30 °C. Upon anaerobic incubation of peat virtually devoid of inorganic electron acceptors, CO$_2$ and CH$_4$ were produced at a ratio of 3.2. According to the electron budget, the calculated electron accepting capacity (EAC) of OM was 2.36 µeq cm$^{-3}$ d$^{-1}$. Addition of sulfate significantly increased CO$_2$ production and effectively suppressed CH$_4$ production. After subtracting the EAC provided though sulfate addition (0.97~2.81 µeq cm$^{-3}$ d$^{-1}$), EACs supplied by OM reached 3.88 to 4.85 µeq cm$^{-3}$ d$^{-1}$. The contribution of organic sulfur was further evaluated by XANES spectroscopy and using natural abundance of $\delta^{34}$S as a tracer. Results demonstrated that BSR involved both addition of H$_2$S and sulfate to OM leading to a formation of reduced organic sulfur and partial changes of oxidized organic sulfur species. The original peat prior to incubation contained 70.5% reduced organic S (R-S-H, R-S-R, R-S-S-R), and 25.9% oxidized S (R-SO$_3$, R-SO$_2$-R, R-SO$_4$-R), whereas the treatment with H$_2$S or sulfate addition comprised 75.7~81.1% reduced organic S, and only 21.1~18.9 % oxidized S. Our results imply that that organic matter contributes to anaerobic respiration i) directly by electron accepting capacity of redox active functional groups ii) directly by oxidized organic sulfur and iii) indirectly by recycling of sulfide to maintain BSR. Moreover, investigating the stability of organic sulfur compounds in peat soil towards abiotic and biotic reduction and oxidation is essential for the understanding of environmental sulfur cycling in anaerobic systems.

Keywords: Methanogenesis; Electron transfer; organic sulfur; Redox processes; Freshwater systems;