

Controls on anaerobic methane oxidation coupled to iron reduction in a brackish coastal sediment subject to eutrophication

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Anaerobic oxidation of methane (AOM) is an important process of methane removal from sediments. It has been proposed that AOM coupled to Fe-oxide reduction may complement sulfate driven AOM in methane rich sediments, leading to high dissolved Fe concentrations in porewaters of methane-bearing, non-sulfidic sediments [1, 2]. Additionally, recent incubation experiments have demonstrated that sediments amended with ferrihydrite can support sulfate independent AOM in both brackish and freshwater environments [3,4]; however still very little is known about this process. Here, we use a reactive transport model to describe the sediment biogeochemistry in an oligotrophic coastal marine basin where AOM coupled to Fe-oxide reduction (Fe-AOM) has been postulated to occur [1]. At this site, there has been a recent upward shift of the sulfate methane transition zone (SMTZ). High concentrations of dissolved Fe (>2 mM) are observed in the methane-bearing, Fe-oxide rich sediments below the SMTZ. We test the hypothesis that eutrophication has led to the recent upward shift in the SMTZ, submerging a pool of reactive iron oxides in the methanic zone and away from available hydrogen sulfide. This redox shift has created conditions that allow for AOM coupled to iron reduction. The occurrence of the process is recorded in the accumulation of reduced dissolved iron at depth. We show that the main controls on Fe-AOM in sediments at this site are water column salinity (i.e. low sulfate concentrations), higher organic matter loading (to cause sulfate depletion) and high iron oxide loading. We demonstrate that AOM coupled to iron reduction has the potential to significantly alter iron and phosphorus cycling and that this process is particularly consequential for eutrophic, iron-rich, brackish systems.

[1] Slomp C.P. *et al* (2013) *PLoS ONE* **8**, e62386 [2] Riedinger *et al* (2014) *Geobiology*, DOI: 10.1111/gbi.12077 [3] Beal *et al* (2009) *Science* **325**, 184 – 187 [4] Segarra *et al* (2013) *Geochim. Et Cosmochim. Acta* **115**, 15 – 30