Geophysical Research Abstracts,
Vol. 10, EGU2008-A-03226, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-03226
EGU General Assembly 2008

Methane cycling and its relationship with DMSP during a phytoplankton bloom

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A methane surplus relative to the atmospheric equilibrium concentration is a persistent feature of most ocean surface water. Although it is evident that microbial *in situ* production within the photic zone generates this supersaturation, the potential of the upper ocean methane cycle remains underestimated because the *in situ* production is masked by a simultaneous and nearly equals *in situ* methane oxidation.

Here we report on an *in situ* methane production/consumption cycle and its potential link to DMSP degradation in Storfjorden (Svalbard Archipelago) - a polar shelf region. The study is based on measurements of $\delta^{13}C_{CH4}$ values, concentrations of methane, chlorophyll-a, particulate and dissolved DMSP, as well as water temperature and salinity along four transects in August 2005.

Freshwater input creates a stable surface layer in Storfjorden during summer and inhibits the sea air flux of biogenic trace gases like methane and DMS. Hence an unusually high methane surplus (up to 55 nM) in relation to the atmospheric equilibrium concentration (about 3.5 nM) is detected in surface water. Also, the carbon isotopic signatures of dissolved methane (-52 to -42‰ PDB) deviate from those of atmospheric methane (-47‰ PDB).

We propose that methane *in situ* production occurs during the summer phytoplankton bloom. The *in situ* production creates a ^{13}C-depleted methane pool relative to the background methane while beyond a threshold value, methane consumptions begins, again reducing the methane concentration. At a reversal point, methane production ceases while consumption continues and then the residual methane becomes more and more enriched in ^{13}C relative to the background level. The formation and conservation of the production-removal cycle is enhanced by the restricted water exchange in the semi-enclosed Storfjorden, while the stratified water column restricts vertical mixing and stabilizes the vertically differentiated horizons where methane production and oxidation occur simultaneously. DMSP is considered to be a precursor of methane, suggesting that methanogenesis occurs via the methylotrophic pathway. DMSP and methane concentrations were inversely correlated up to the threshold value, i.e. prior to incipient methane consumption. When DMSP concentration drops to <5 nM, substrate limitation is attained and methane production slows down or ceases while methane consumption continues, leading to the decoupling of the two processes.