



Surfactant control of air-sea gas exchange across contrasting biogeochemical regimes

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Air-sea gas exchange is important to the global partitioning of CO₂. Exchange fluxes are products of an air-sea gas concentration difference, ΔC , and a gas transfer velocity, k_w . The latter is controlled by the rate of turbulent diffusion at the air-sea interface but it cannot be directly measured and has a high uncertainty that is now considered one of the greatest challenges to quantifying net global air-sea CO₂ exchange ... (Takahashi et al., 2009). One important control on k_w is exerted by sea surface surfactants that arise both naturally from biological processes and through anthropogenic activity. They influence gas exchange in two fundamental ways: as a monolayer physical barrier and through modifying sea surface hydrodynamics and hence turbulent energy transfer. These effects have been demonstrated in the laboratory with artificial surfactants ... (Bock et al., 1999; Goldman et al., 1988) and through purposeful surfactant releases in coastal waters ... (Brockmann et al., 1982) and in the open ocean (Salter et al., 2011). Suppression of k_w in these field experiments was $\sim 5\text{--}55\%$. While changes in both total surfactant concentration and the composition of the natural surfactant pool might be expected to impact k_w , the required in-situ studies are lacking.

New data collected from the coastal North Sea in 2012-2013 shows significant spatio-temporal variability in the surfactant activity of organic matter within the sea surface microlayer that ranges from 0.07-0.94 mg/L T-X-100 (AC voltammetry). The surfactant activities show a strong winter/summer seasonal bias and general decrease in concentration with increasing distance from the coastline possibly associated with changing terrestrial vs. phytoplankton sources. Gas exchange experiments of this seawater using a novel laboratory tank and gas tracers (CH₄ and SF₆) demonstrate a 12-45% reduction in k_w compared to surfactant-free water. Seasonally there is higher gas exchange suppression in the summer months likely from primary production and spatially there is less suppression of air-sea gas exchange with increasing distance from the shoreline, which is likely due to riverine inputs.

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