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The effect of fatty acid surfactants on the uptake of nitric acid to deliquesced NaCl aerosol

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Abstract. Surface active organic compounds have been observed in marine boundary layer aerosol. Here, we investigate the effect such surfactants have on the uptake of nitric acid (HNO_3), an important removal reaction of nitrogen oxides in the marine boundary layer. The uptake of gaseous HNO_3 on deliquesced NaCl aerosol was measured in a flow reactor using HNO_3 labelled with the short-lived radioactive isotope ^{13}N. The uptake coefficient γ on pure deliquesced NaCl aerosol was γ=0.5±0.2 at 60% relative humidity and 30 ppb HNO_3(g). The uptake coefficient was reduced by a factor of 5–50 when the aerosol was coated with saturated linear fatty acids with carbon chain lengths of 18 and 15 atoms in monolayer quantities. In contrast, neither shorter saturated linear fatty acids with 12 and 9 carbon atoms, nor coatings with the unsaturated oleic acid (C18, cis-double bond) had a detectable effect on the rate of HNO_3 uptake. It is concluded that it is the structure of the monolayers formed, which determines their resistance towards HNO_3 uptake. Fatty acids (C18 and C15), which form a highly ordered film in the so-called liquid condensed state, represent a significant barrier towards HNO_3 uptake, while monolayers of shorter-chain fatty acids (C9, C12) and of the unsaturated oleic acid form a less ordered film in the liquid expanded state and do not hinder the uptake. Similarly, high contents of humic acids in the aerosol, a structurally inhomogeneous, quite water soluble mixture of oxidised high molecular weight organic compounds did not affect HNO_3 uptake. As surfactant films on naturally occurring aerosol are expected to be less structured due to their chemical inhomogeneity, it is likely that their inhibitory effect on HNO_3 uptake is smaller than that observed here for the C15 and C18 fatty acid monolayers.

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