Chemical cloud processing impacts abundance of methylamines in the marine atmosphere

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Monomethylamine (MMA), dimethylamine (DMA), and trimethyl amine (TMA) are important organic nitrogen species in the atmosphere emitted from natural as well as anthropogenic sources (Ge et al., 2011). Laboratory and field studies underline their importance in the formation of new aerosol particles as well as secondary organic aerosol (SOA) mass (Qiu and Zhang, 2013; Shen et al., 2023). Further, the atmospheric aerosol acidity is impacted and, thus, key oxidation processes might be as well, such as S(IV) oxidation (Tilgner et al., 2021). To gain a comprehensive understanding of the abundance, sources and processing of MMA, DMA and TMA in the atmosphere, multiphase chemical mechanisms are critical and need to be accounted for in models. However, the complex interactions of MMA, DMA and TMA between atmospheric gas and aqueous phase are to date not studied in a near-explicit manner by atmospheric chemistry models, due to lack of mechanisms.

To this end, a detailed multiphase chemistry mechanism, the CAPRAM Amine module, has been developed to describe the oxidation of ammonia (NH_3), monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) in the atmospheric multiphase system. The development is based published values from laboratory and theoretical works. Moreover, appropriate estimations methods are applied when no data were available. Overall, the mechanism developed contains 537 reactions, thereof 233 gas-phase reactions, 52 phase transfer reactions, and 252 aqueous-phase reactions. After the development, the mechanism module was coupled to the CAPRAM mechanism (Bräuer et al., 2019) for further investigations using the air parcel model SPACCIM (Wolke et al., 2005). Adjunct box model simulations of an idealized pristine marine environment were performed investigating the chemical processing of MMA, DMA, and TMA under cloud and non-cloud conditions in detail.

The simulations indicate that uptake into cloud droplets and further oxidation is important to explain their ambient concentrations. The chemical rates analyses revealed that, during daytime cloud conditions, TMA, DMA and MMA are oxidised effectively to yield into DMA, MMA and NH_3, respectively. The modelled TMA-to-DMA conversion in cloud droplets is about three times higher than the included emission values of TMA.

Further investigations focused on the importance of recently discovered autoxidation processes of DMA and TMA as well as their importance for SOA formation. The simulations verify that autoxidation processes dominate the gas-phase oxidative fate of DMA and TMA. Up to 22% of oxidized DMA and about 69% of oxidized TMA are directly converted into the stable highly oxidized end products. Because of the importance of DMA and TMA for new particle formation, the discovered processes have to be included into atmospheric chemistry models.

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