Aircraft observations of a novel marine sulphur species over the North Atlantic using a HR-ToF-CIMS

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Marine ecosystems are an important component of the climate feedback system. One of the main pathways for ocean-climate interaction is through the atmospheric oxidation of DMS (dimethyl sulphide), a gas released from phytoplankton in the sea surface. DMS derived products are known to be important in marine cloud formation and hence influence the Earth's radiation budget. Aerosol-Cloud interactions currently represent one of the largest uncertainties in climate modelling (IPCC, 2018). Our research focuses on airborne measurements using real-time high resolution instruments to identify and quantify trace oceanic biogenic gases on board the FAAM research aircraft. Here we present aircraft measurements made over the North Atlantic Ocean using an iodide-high resolution time-of-flight chemical ionisation mass spectrometer (HR-ToF-CIMS), across three seasons during the NERC funded ACSIS and ARNA campaigns between 2018 and 2020. These are some of the first observations of an alternative DMS oxidation product, hydroperoxy methylthioformate (HPMTF), that has recently been identified in the atmosphere using a CIMS with iodide reagent ion (Veres et al., 2020), similar to the one used in this study. This new oxidation mechanism involves an intramolecular hydrogen shift in the peroxy radical (MSP, CH3SCH2OO•), a primary product from hydrogen abstraction reaction of DMS oxidation. A further hydrogen shift then forms the stable oxidation product hydroperoxymethyl thioformate (HPMTF, HOOCH2SCHO). Our results greater extend the original atmospheric observations and indicate that HPMTF is most commonly observed just above the sea surface. For the first time we have also shown that under certain conditions, such as those from a jet stream, HPMTF can be transported long distances and throughout the atmosphere. Initial atmospheric observations and laboratory studies suggest that approximately 30-60% of DMS emitted from oceans is oxidised via the formation of HPMTF (Veres et al, 2020; Berdnt, 2019). This has potentially significant climate implications, none of which are currently represented in global climate models. The fate of this newly measured species once in the atmosphere is uncertain but is likely to alter our understanding of the marine sulphur cycle.