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A modelling study of the atmospheric chemistry of DMS using the global model, STOCHEM-CRI

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HIGHLIGHTS

- The lifetime and global burden of DMS is found to be 1.2 days and 98 Gg S yr^{-1}.
- Inclusion of BrO oxidation reduces the lifetime and global burden of DMS by 15%.
- The removal of DMS by Cl_2 is found to be high over the southern hemisphere oceans.
- Model DMS shows a seasonal trend with summer maximum and winter minimum.

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ABSTRACT

The tropospheric chemistry of dimethylsulfide (DMS) is investigated using a global three-dimensional chemical transport model, STOCHEM with the CRIv2-R5 chemistry scheme. The tropospheric distribution of DMS and its removal at the surface by OH abstraction, OH addition, NO_3 oxidation, and BrO oxidation is modelled. The study shows that the lifetime and global burden of DMS is ca. 1.2 days and 98 Gg S, respectively. Inclusion of BrO oxidation resulted in a reduction of the lifetime (1.0 day) and global burden (83 Gg S) of DMS showing that this reaction is important in the DMS budget. The percentage contribution of BrO oxidation to the total removal of DMS is found to be only 7.9% that is considered a lower limit because the study does not include an inorganic source of bromine from sea-salt. BrO oxidation contributed significantly in the high latitudes of the southern hemisphere (SH). Inclusion of DMS removal by Cl_2 showed that potentially a large amount of DMS is removed via this reaction specifically in the remote SH oceans, depending on the flux of Cl_2 from the Southern Ocean. Model DMS levels are evaluated against measurement data from six different sites around the globe. The model predicted the correct seasonal cycle for DMS at all locations and correlated well with measurement data for most of the periods.

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1. Introduction

Dimethylsulfide (DMS) is one of the most abundant sulfur containing compounds present in the Earth's atmosphere which is formed mainly via phytoplankton production (Andreae et al., 1983; Dacey and Wakeham, 1986; Bates et al., 1987; Keller et al., 1989) in the upper surface ocean and then out-gassed to the atmosphere. Other sources of DMS include vegetation, tropical forests and, to a much lesser extent, soils, wetlands, saltmarshes and anthropogenic ones (Watts, 2000). These additional sources are believed to be much smaller and difficult to determine without high uncertainty because they involve direct measurements using enclosure or micro-meteorological techniques (Bates et al., 1992) rather than oceanic flux measurements, which can be determined from oceanic DMS concentrations and an air-sea exchange model (Liss, 1973).

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DMS has a short atmospheric lifetime between 11 min and 46 h due to its fast oxidation processes (Barnes et al., 2006), and thus most DMS resides in the troposphere and indeed in the lower troposphere. The oxidation of DMS contributes to the formation of sulphate aerosols and cloud condensation nuclei (Andreae and Crutzen, 1997) which have a direct (backscattering solar radiation) (Shaw, 1987) and an indirect (cloud albedo) influence on Earth's climate (Charlson et al., 1987).

The main sink of DMS is due to oxidation, specifically the reactions of OH radicals during daytime and NO_3 radicals at nighttime (Wilson and Hirst, 1996). There are two OH oxidation pathways that compete for DMS loss (Hynes et al., 1995).

$$OH + CH_3SCH_3 \rightarrow H_2O + CH_3SCH_2 \text{ (H-abstraction)} \tag{1}$$

$$OH + CH_3SCH_3 \rightarrow CH_3S(OH)CH_3 \text{ (OH-addition)} \tag{2}$$

These two pathways are the starting reactions for a number of oxidised products of DMS including OCS, DMSO, SO_2, H_2SO_4, methanesulfonic acid (MSA) and dimethyl sulfone ($DMSO_2$). The branching ratio for reaction with OH is 0.75 favouring the H-abstraction pathway (Yin et al., 1986) and 0.25 favouring the OH-addition pathway. At low temperatures, the addition reaction can become the major pathway (Wilson and Hirst, 1996). For example, as the temperature decreases from 310 K to 270 K, the branching ratio towards the addition pathway increases from 0.13 to 0.68 (Hynes et al., 1986).

Oxidation by NO_3 occurs at night and proceeds via reaction (3) which occurs exclusively via hydrogen abstraction and produces the same sulfur containing product as reaction (1). In the remote marine troposphere with low concentrations of NO_3, the oxidation via this mechanism can be largely ignored (Andreae et al., 1985; Ferek et al., 1986).

$$NO_3 + CH_3SCH_3 \rightarrow HNO_3 + CH_3SCH_2 \tag{3}$$

Reactions of DMS with halogen oxides (BrO, ClO and IO) are known to occur in the atmosphere (Barnes et al., 1989), but their contributions to the atmospheric DMS budget are poorly understood (Sayin and McKee, 2004). Previous studies suggested that the reaction of IO/BrO with DMS could be a potential sink for DMS (Martin et al., 1987; Toumi, 1994). Sciare et al. (2000) observed that DMS oxidation by OH could not account for the daytime variability of DMS concentrations, suggesting an alternative removal process for DMS with BrO. Breider et al. (2010) showed that DMS removal by BrO oxidation, through reaction (4), could account for approximately 16% of DMS removal in the atmosphere and that inclusion of BrO removal reduces the global DMS burden and lifetime by 18%.

$$BrO + CH_3SCH_3 \rightarrow CH_3S(O)CH_3 + Br \tag{4}$$

This removal process could be especially important in the southern hemisphere (SH) oceans because of low NO_3 concentrations, high sea salt aerosol contributions to BrO concentrations, and high DMS concentrations. This reaction could cause a reduction in the calculated amount of sulfate aerosols as DMS reacts to form DMSO which will reduce the yield of SO_2 (Breider et al., 2014).

Another removal process of DMS is the reaction of DMS with molecular chlorine shown by reaction (5) (Dyke et al., 2005, 2006; Shallcross et al., 2006; Copeland et al., 2014).

$$Cl_2 + CH_3SCH_3 \rightarrow CH_3SCH_2Cl + HCl \tag{5}$$

Analogous to BrO oxidation, the reaction of Cl_2 with DMS could be potentially significant in the regions of the remote marine boundary layer (MBL) where NO_3 concentrations are low and there are high concentrations of Cl_2 derived from large amounts of sea salt spray, particularly in the SH oceans. Cl_2 is produced by the photolysis of O_3 in the presence of sea salt particles (Oum et al., 1998) and the subsequent reaction between DMS and Cl_2 forms HCl and CH_3SCH_2Cl (Dyke et al., 2005, 2006).

The sources of DMS are still a matter of debate (Jardine et al., 2015) and also there are rapid, localised removal processes of DMS (Faloona, 2009) which produce a greater uncertainty in the calculated global budget of DMS. However, there are very few modelling studies (Watts, 2000; Boucher et al., 2003; Berglen et al., 2004; Kloster et al., 2006; Breider et al., 2010) where the global budget and distribution of DMS are shown. However, the contribution of loss of DMS by reaction with Cl_2 to the DMS budget in the atmosphere has not been included in previous model studies. The reaction product, CH_3SCH_2Cl, from the reaction of DMS and Cl_2 could react with OH (Shallcross et al., 2006) or undergo photolysis to yield CH_3S and ultimately SO_2 (Copeland et al., 2014). Including an additional pathway to SO_2 formation from DMS could reconcile discrepancies observed between daytime DMS oxidation rates and SO_2 production rates in remote marine locations (e.g. Chen et al., 2000). In this study, we employ STOCHEM-CRI, a 3-D global chemistry transport model, to evaluate the global budget of DMS in the troposphere and investigate DMS removal processes along with the distribution of DMS in the troposphere and the impact of new DMS removal process by Cl_2.

2. Experimental

2.1. Model description

STOCHEM-CRI is a three dimensional chemistry transport model where 50,000 constant-mass air parcels are advected using a Lagrangian approach allowing the chemistry and transport processes to be uncoupled. The wind fields taken from the UK Meteorological Office are applied to the Lagrangian air parcels at a resolution of 1.25° longitude, 0.833° latitude over 9 unevenly spaced vertical levels from the surface to roughly 100 hPa. The wind fields in the archive are stored as 6 h data sets and contain horizontal winds and vertical winds. The time step used is 3 h so the wind field sets are linearly interpolated with respect to time using a bi-linear interpolation on the horizontal plane and a cubic interpolation in the vertical direction (Collins et al., 2000). A fourth-order Runge-Kutta method is used to determine the new position of the Lagrangian cell after each time-step. The temperature, pressure, and humidity of cells after each advection step are calculated using a 3-dimensional interpolation in a similar way to the wind field calculation. A detailed description of the vertical coordinate, advection scheme, and dispersion processes used in STOCHEM can be found in Collins et al. (1997), with an updated report described by Derwent et al. (2008). The chemical mechanism used in STOCHEM, is the common representative intermediates mechanism version 2 and reduction 5 (CRI v2-R5). The detail of the CRI v2-R5 mechanism is given by Jenkin et al. (2008), Watson et al. (2008), and Utembe et al. (2009) with updates highlighted in Utembe et al. (2010, 2011).

The three types of emissions used in STOCHEM are surface emissions, stratospheric sources and 3-D emissions. Total emission values for CO, NO_x and NMVOCs are obtained from the Precursor of Ozone and their Effects in the Troposphere (POET) inventory (Granier et al., 2005) for the year 1998 with added anthropogenic and biogenic DMS emissions taken from Watts (2000) (See Appendix A for more details). Oceanic emissions are included from Lana et al. (2011). A bromine chemical scheme was incorporated in STOCHEM-CRI v2-R5 (Xiao, 2014; Shallcross et al., 2015). Some of

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