



Rapid aqueous phase SO₂ oxidation in winter fog in the Indo-Gangetic Plain

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Sulphate and sulphur dioxide play an important role in environmental chemistry and climate. The majority of anthropogenic sulphur is released directly as SO₂, and a significant fraction of biogenic and natural sulphur emissions are also either directly released as SO₂ or oxidised to SO₂ in the atmosphere (e.g. H₂S, OCS, DMS). Around 50% of global atmospheric sulphur dioxide is then oxidised to sulphate, while the rest is lost through dry and wet deposition. The pathway by which SO₂ is oxidised to sulphate is critical in determining the climate forcing and environmental effects of sulphate. Gas-phase oxidation of SO₂ by OH radicals or criegee intermediates produces H₂SO₄ (g), which plays an important role in controlling new particle formation in the troposphere and also modifies the surface properties of hydrophobic particles such as soot and mineral dust. Heterogeneous oxidation of SO₂ is considered to occur primarily in cloud droplets, although oxidation on sea salt aerosols and mineral dust surfaces are considered to be regionally important. Heterogeneous oxidation leads to the formation of fewer and larger particles with shorter atmospheric lifetime. The major oxidation pathways which are considered to contribute to sulphate formation in the aqueous phase are oxidation by H₂O₂ and oxidation by O₃ and the lifetime of SO₂ with respect to all known loss processes combined is considered to be 1-2 days.

Here we report measurements of SO₂ measurements from IISER Mohali – Ambient Air Quality Station (30.67°N, 76.73°E), a station located at a suburban site in the Indo Gangetic Basin (IGB) during wintertime (10th Dec. 2011 to 29th Feb. 2012). We use a strong point source of SO₂ with known SO₂/CO emission ratio (brick kiln) located 6.5 km east of our measurement site to estimate the loss rate of SO₂ in wintertime fog in the IGB. We consider the transport from the source to the receptor site to be Lagrangian and use the measured CO concentration at the receptors site to account for changes in the emission intensity (activity pattern) and the dilution of the plume during transport. We see a linear correlation between the measured SO₂/CO ratio and the transport time. Binning the data on the basis of relative humidity and applying first order kinetics to SO₂ loss within each humidity bin we find the SO₂ loss rate with respect to aqueous phase oxidation at our sites varies between $> 2.2 \times 10^{-3}$ mol/cm³/s at 96 % RH and 3.8×10^{-4} mol/cm³/s at 47 % RH.

Simple box model calculations reveal that neither oxidation by H₂O₂ nor oxidation by O₃ can account for such rapid SO₂ oxidation in the fog water. Considering the high mineral dust loadings are our station (PM 10 typically $> 300 \mu\text{g}/\text{m}^3$) we propose that transition metal catalysis by TMI leached from natural mineral dust and resuspended road dust may be responsible for the rapid oxidation of SO₂ in the fog water. However, the observed lifetime with respect to aqueous phase oxidation in wintertime fog is a factor 150-800 times shorter than the lifetime of SO₂ with respect to TMI catalyzed oxidation currently implemented in global atmospheric chemistry models.

During 2012-2013 winter season we will measure TMI concentrations in the fog water and verify the rates coefficients estimated from the ambient observation by conducting controlled experiments both using collected fog water and different TMI mixtures. If confirmed through laboratory studies our findings have major implications for the SO₂ lifetime over the IGP (and possibly other regions with high mineral dust loadings) and will significantly alter the regional direct and indirect aerosol forcing estimates due to anthropogenic SO₂ emissions.

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