## Atmospheric sulfate formation pathways over the past 60 years constrained by a global chemical transport model

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Since the industrial revolution, the increase of sulfur dioxide (SO<sub>2</sub>) had increased the SO<sub>4</sub><sup>2-</sup> load. The period including the 1950s to 1970s had significant SO<sub>2</sub> emissions, but these emissions decreased after the 1980s across North America (NA) and Western Europe (WE), reducing atmospheric SO<sub>4</sub><sup>2-</sup> burden. However, SO<sub>4</sub><sup>2-</sup> aerosols decreased less rapidly than SO<sub>2</sub> reduction, suggesting the existence of chemical feedback processes.

In the atmosphere,  $SO_4^{2^-}$  is produced from gas-phase  $SO_2$  oxidation by hydroxyl radicals (•OH) and oxidation in aqueous-phase (i.e., in clouds).  $SO_2$ , dissolved in an aqueous-phase, forms S(IV) species (i.e.,  $SO_2 \cdot H_2 O$ ,  $HSO_3^{-}$ , and  $SO_3^{2^-}$ ) that react with hydrogen peroxide ( $H_2O_2$ ), ozone ( $O_3$ ), and molecular oxygen ( $O_2$ ) to form  $SO_4^{2^-}$ . Among these chemical processes, several studies have proposed several mechanisms causing the weakened response of  $SO_4^{2^-}$  to  $SO_2$  decreases.

To obtain quantitative information in sulfate formation pathways, we simulate global tropospheric sulfate chemistry using the version 12.5.0 of the GEOS-Chem chemical transport model. We performed the model simulations with anthropogenic emissions corresponding to the years 1960, 1973, 1986, 1999, and 2013, to investigate the past changes in atmospheric sulfate formation and its efficiency in response to the changes in anthropogenic emission.

Relative contributions of S(IV)+  $O_3$  and  $H_2O_2$  were increased between 1973 and 2013 over the Eastern NA (ENA) and WE, and the proportional increases of S(IV) +  $O_3$  pathway are consistent with our previous observation of triple oxygen isotopic composition of S $O_4^{2-}$  in a Greenland ice core. The increase of S(IV) +  $O_3$  pathway is best explained by an increase in the cloud water pH over the period, and not by  $O_3$  concentration increase.

The promotion of  $S(IV) + O_3$  pathway over the period caused higher  $SO_2$  conversion efficiency for both summertime and wintertime in ENA and WE. On the basis of the GEOS-Chem model outputs, we found two regional characteristics: (i) gradual increase of  $SO_2$  conversion efficiency in WE over the period, and (ii) a small increase of  $SO_2$  conversion efficiency in ENA between 1960 and 1999 and an abrupt increase between 1999 and 2013.

In the presentation, we will discuss several implications including perspective for future sulfate formation by the worldwide reduction of  $SO_2$  and the important role of acidity (defined as cloud pH) in the atmospheric chemistry.

Keywords: Global chemical transport model, Sulfate, Triple oxygen isotopes, Aerosol, Anthropogenic activity