



Atmospheric SO₂ oxidation efficiency over a semi-arid region: Seasonal patterns from observations and GEOS-Chem model



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HIGHLIGHTS

- Assess molar ratio of SO₄²⁻ to total SO_x (SO_x = SO₂ + SO₄²⁻) at a high altitude site.
- Observed patterns are validated against GEOS-Chem model simulations.
- The ratios from field measurements as well as simulations exhibit a seasonality.
- Assess contributions from PBL, OH, RH, dust load, transport and dry deposition.

ARTICLE INFO

Article history:

Received 17 February 2015
Received in revised form 2 September 2015
Accepted 4 September 2015
Available online 10 September 2015

Keywords:

Sulphur dioxide
Sulphate
Atmospheric oxidation
GEOS-Chem
OH radical
Dry deposition

ABSTRACT

The oxidation efficiency of atmospheric SO₂, measured as a molar ratio of SO₄²⁻ to total SO_x (SO_x = SO₂ + SO₄²⁻), referred as S-ratio, have been studied from a high altitude site (Gurushikhar, Mt. Abu: 24.6° N, 72.7° E, 1680 m ASL) in a semi-arid region of western India. A global 3-dimensional Chemical Transport Model (CTM), GEOS-Chem (v8-03-01), is employed to interpret the observed patterns. The S-ratios derived from time series SO₂ and SO₄²⁻ measurements exhibited a pronounced seasonality, with relatively low ratios in Feb–Mar 2010, high ratios in Nov–Dec 2009 and intermediate values in Sep–Oct 2009. The lower S-ratios for Feb '10 and Mar '10 (median values 0.10 and 0.08 respectively) have been attributed to the relatively high planetary boundary layer (PBL) heights – to reduce the SO₂ loss from the atmosphere via dry deposition – as well as the lower OH radical levels and low 'aged air mass influx' during these months. On the other hand, low PBL heights and significant long range transport contributions are projected to be the possible causes for the higher S-ratios during Nov '09 and Dec '09 (median values 0.30 and 0.28 respectively). The seasonal patterns for the S-ratios predicted by the CTM for the GEOS-Chem 4° × 5° grid cell containing the sampling site showed highest ratios in Jul–Aug, and the lowest in Apr. The model has been employed further to study the contributions from various parameters to the S-ratios such as PBL, OH, RH, dust load, transport pattern and dry deposition. Sensitivity simulations showed the S-ratios enhancing with dust load with the peak in May (~4.7% (median)). Similarly, the 'dry deposition' is seen to boost the S-ratios with the peak in August (~66.3% (median)). Also, model simulations to assess the 'altitudinal dependence of S-ratios' have revealed a pronounced seasonal behaviour.

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1. Introduction

The aerosol sulphate (SO₄²⁻) formation in the atmosphere is predominantly via the oxidation of its precursor species sulphur dioxide (SO₂) (EPA I, 1996; EPA II, 1996), and proceeds through homogeneous as well as heterogeneous pathways. Studies by earlier

workers (Hidy et al., 1978; Husar and Patterson, 1980) indicated that the molar ratio of SO₄²⁻ to total SO_x (SO_x = SO₂ + SO₄²⁻), termed S-ratio, exhibit a seasonality. Further, Kaneyasu et al. (1995) showed that the S-ratio can be best used as a measure of the formation efficiency of SO₄²⁻ in the atmosphere. Miyakawa et al. (2007) suggested that the seasonal variation of S-ratio is linked to the seasonality in the boundary layer height and photochemical activity. They proposed that the higher planetary boundary layer for summer results in reduced loss rate of SO₂ via dry deposition which in turn causes an efficient oxidation of SO₂ to SO₄²⁻ before loss onto the surface, to enhance the S-ratio.

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Similarly the production rate of OH radical – the major species responsible for the atmospheric oxidation process (Levy, 1971) – is influenced by the incoming solar radiation (insolation) intensity as well as the water vapour content. The seasonal changes in the transport pattern of polluted air and the resulting variability in the aged air mass input also could contribute to a seasonal variability in the S-ratio.

This paper presents a study assessing the seasonal patterns in S-ratios over a semi-arid region in western India. The analysis includes deriving monthly median S-ratios from field measurements of SO₂ and SO₄²⁻ and comparing with those from a global 3D chemical transport model (CTM), GEOS-Chem (v8-03-01).

A remote high altitude site (Gurushikhar, Mount Abu) was opted for the experimental study.

2. Materials and methods

2.1. Site description and meteorological parameters

The sampling site, Gurushikhar, Mt. Abu (24.6° N, 72.7° E, 1680 m ASL) is a remote high altitude mountain site in a semi-arid region of western India, with minimal local emissions. The region has an annual average rainfall of about 600–700 mm spread over Jul–Sep, during SW-monsoon. The site makes occasional entry into the free-tropospheric zone during post-monsoon (Oct–Nov) and winter (Dec–Feb) when the PBL is relatively low over the region (Francis, 2012). During the summer months (Mar–Jun) the site mostly gets accommodated within the PBL. The meteorological parameters during the sampling periods (wind speed, wind direction, relative humidity (RH), and air temperature) were recorded by an automatic weather station at the site (Fig. 1).

2.2. Experimental setup

The experimental set up for the SO₂ measurements are elaborated in Francis (2012) and is briefed here. A primary UV fluorescence SO₂ Monitor (Thermo – 43i TLE) was employed for the ambient SO₂ measurements. The performance evaluations of similar systems are reported elsewhere (Igarashi et al., 2004; Luke, 1997; Luria et al., 1992). The manufacturer claims that the Model 43i-TLE measures SO₂ at levels never before achieved, down to a 0.05 ppb level (300 s averaging time) (see <http://www.thermoscientific.com/content/tfs/en/product/enhanced-trace-level-so-sub-2-sub-analyzer-model-43-i-i-i-tle.html>). Calibrations were performed routinely with a standard SO₂ gas (2 ppmv with N₂ balance gas, Spectra, USA) and zero air, employing a dynamic gas calibrator (Thermo – 146i).

For the SO₄²⁻ measurements, fine mode aerosol samples were collected on Whatman cellulose filters (200 × 250 mm²) employing a high volume air sampler (Thermo) with a flow rate of 1.12 m³/min and a cut off diameter of 2.5 micron (PM_{2.5}) – in general three aerosol samples (sampling duration ~4 h) were collected during daytime and one sample (sampling duration ~12 h) during night time. Table 1 provides relevant details of the aerosol sampling, such as date of sample collection and the number of samples collected. In the analytical procedure for the measurement of sulphate (SO₄²⁻) in the aerosol samples, one-fourth portion of the filter was soaked in 50 mL of Milli-Q water (18.2 MΩ resistivity) for 4 h during which ultrasonication was performed in steps of 5 min to a total of 20 min to extract water soluble ionic species (WSIS). In the water extracts, inorganic anions (Cl⁻, NO₃⁻ and SO₄²⁻) were measured on a Dionex ion chromatograph (Rastogi and Sarin, 2005; Rengarajan and Sarin, 2004). The anions were separated on Ionpac AS14A analytical column and AG14A guard column, in conjunction with an anion self-regenerating suppressor (ASRS), using 8.0 mM Na₂CO₃ – 1.0 mM NaHCO₃ as eluent. The measured

Cl⁻, NO₃⁻ and SO₄²⁻ concentrations were further corrected for procedural blanks (comprising of blank filters and analytical reagents).

2.3. Model description

The global 3-dimensional chemical transport model, GEOS-Chem (v8-03-01; <http://acmg.seas.harvard.edu/geos/>) with GEOS-5 assimilated meteorology was employed for this study. The GEOS-5 data have a temporal resolution of 6-h (3-h resolution for surface fields and mixing depths) and horizontal resolution of 0.5° latitude × 0.667° longitude, with 72 levels in vertical extending from surface to approximately 0.01 hPa. The model simulates HOx-NOx-VOC-ozone chemistry (Bey et al., 2001; Park et al., 2004) and elaborate simulation evaluations can be found elsewhere (Park et al., 2004; Wang et al., 2008; Fairlie et al., 2007; Chen et al., 2009).

The model was spun up for 12 months, from Jan 2008 to Jan 2009, starting from chemical climatology; this effectively removes the influence of initial conditions. The simulations were then conducted for Jan 2009–Apr 2010 at 4° × 5° resolutions. Unless mentioned otherwise, the standard input.geos file distributed with the GEOS-Chem codes (v8-03-01), specifying the various input parameters and emission inventories – EMEP (Vestreng and Klein, 2002), BRAVO (Kuhns et al., 2003), EDGAR (Olivier and Berdowski, 2001), Streets inventory (Streets et al., 2006), CAC (http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), and EPA/NEI05 – have been used, with only the simulation start/end dates and ND49 diagnostics – to generate the time series data – modified. Aerosol sources and processes used in the present simulation are as described by Park et al. (2006), with the addition of dust and sea salt as described by Fairlie et al. (2007) and Alexander et al. (2005). Wet deposition of soluble aerosols and gases follows the scheme of Liu et al. (2001) including contributions from scavenging in convective updrafts, rainout, and washout. Dry deposition follows a standard resistance-in-series model (Wesely, 1989). The model outputs were analysed using global atmospheric model analysis package (GAMAP) (Version 2.15; <http://acmg.seas.harvard.edu/gamap/>).

3. Results and discussions

3.1. S-ratios from experiments

At Mt. Abu, the simultaneous measurements of ambient SO₂ (Francis, 2012) and SO₄²⁻ were made during Sep '09, Oct '09, Nov '09, Dec '09, Feb '10 and Mar '10.

The molar ratio of SO₄²⁻ to total SO_x (SO_x = SO₂ + SO₄²⁻), termed S-ratio, for the different sampling periods were then calculated as:

$$S - \text{ratio} = \frac{[\text{SO}_4^{2-}]}{([\text{SO}_2] + [\text{SO}_4^{2-}])} \quad (1)$$

For this, the sulphate (SO₄²⁻) in the aerosol (PM_{2.5}) samples were measured in the ion chromatograph. The median of the SO₂ concentrations for the corresponding sampling interval also were obtained from the time series SO₂ (Francis, 2012). The monthly median S-ratio is then calculated from the S-ratios for the different sampling intervals.

Fig. 2 shows the S-ratios for the different sampling months, and the median values are given in Table 2. During Feb '10 and Mar '10 the S-ratios were lower compared to Nov '09 and Dec '09. Intermediate between these were the values for Sep '09 and Oct '09.

The lower S-ratios for Feb '10 and Mar '10 (median values 0.10 and 0.08 respectively) may be explained by the higher PBL heights for these months and a resulting dilution of SO₂ in the lower layers of the atmosphere – to reduce the dry deposition losses of SO₂. A detailed discussion on the PBL effect on S-ratio, based on GEOS-Chem simulations, is given in Section 3.4.1. The relatively low

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