



Variability of atmospheric carbonyl sulfide at a semi-arid urban site in western India



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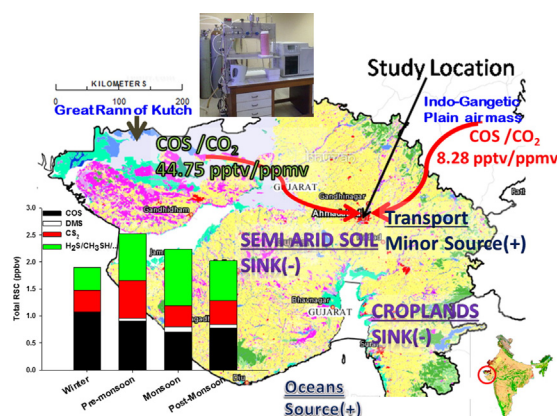
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HIGHLIGHTS

- First time measurements of atmospheric COS over an Indian site
- Vegetation and dry soil act as potential sink of atmospheric COS over Ahmedabad.
- Oceans, marshlands, and transport sector are major COS sources over Ahmedabad.
- COS/CO₂ slopes are very different for marshland and anthropogenic influences.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric carbonyl sulfide (COS) is a major precursor for sulfate aerosols that play a critical role in climate regulation. Recent studies have highlighted the importance of COS measurements as a reliable means to constrain biospheric carbon assimilation. In a scenario of limited availability of COS data around the globe, we present gas-chromatographic measurements of atmospheric COS mixing ratios over Ahmedabad, a semi-arid, urban region in western India. These measurements, being reported for the first time over an Indian site, enable us to understand the diurnal and seasonal variation in atmospheric COS with respect to its natural, anthropogenic and photochemical sources and sinks. The annual mean COS mixing ratio over Ahmedabad is found to be 0.83 ± 0.43 ppbv, which is substantially higher than free tropospheric values for the northern hemisphere. Inverse correlation of COS with soil and skin temperature, suggests that the dry soil of the semi-arid study region is a potential sink for atmospheric COS. Positive correlations of COS with NO₂ and CO during post-monsoon and the COS/CO slope of 0.78 pptv/ppbv reveals influence of diesel combustion and tire wear. The highest concentrations of COS are observed during pre-monsoon; COS/CO₂ slope of 44.75 pptv/ppmv combined with information from air mass back-trajectories reveal marshy wetlands spanning over 7500 km² as an important source of COS in Ahmedabad. COS/CO₂ slopes decrease drastically (8.28 pptv/ppmv) during post-monsoon due to combined impact of biospheric uptake and anthropogenic emissions.

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1. Introduction

Sulfur is ubiquitous in all spheres of the globe. It is emitted from the soil and the oceans into the atmosphere in various states of oxidation. The biogeochemical cycling of various sulfur species between different ecosystems has important implications to the climate, to the pH of rain-water, to the health of human beings, fauna and flora. While the most conspicuous form of sulfur in the atmosphere is sulfur dioxide (SO₂), its several precursors in lower oxidized state called reduced sulfur compounds (RSCs), contribute significantly to the global budget. The major atmospheric RSCs are dimethyl sulfide (DMS, CH₃SCH₃), hydrogen sulfide (H₂S), carbonyl sulfide (COS) and carbon disulfide (CS₂). As per estimates of Watts (2000) and Faloon (2009); DMS, H₂S, COS and CS₂ sources account for 24.5, 7.7, 1.3 and 0.7 TgS per year respectively.

Among the RSCs, the most stable and long lived species is COS. Compared to H₂S, which reacts with OH with a rate constant of 5×10^{-12} cm³ per molecule at 298 K, the value for COS is 0.04×10^{-12} cm³ per molecule (Warneck, 1999). Consequently, the average tropospheric lifetime of atmospheric COS is about 44 years (Warneck, 1999), and it easily penetrates into the upper troposphere and even the stratosphere, where its photolysis at $\lambda < 250$ nm and oxidation lead to formation of SO₂ and ultimately sulfate (SO₄²⁻). COS accounts for about 43% of the stratospheric sulfate aerosol, while the stratospheric SO₂ oxidation and upward-transported tropospheric sulfate account for 27%, and the remaining 30% respectively (Pitari et al., 2002). Thus, COS is a major source of stratospheric sulfate layer (Andreae and Crutzen, 1997; Notholt et al., 2003), which has significant impact on the radiation budget of the stratosphere, its dynamical structure, and its chemistry (Brasseur et al., 1999). Close to the surface, the COS lifetime varies between 1.5 and 3 years (Montzka et al., 2007).

Although previous measurements of COS were aimed to understand its sources and sinks due to its implications to the sulfur cycle and stratospheric aerosols, recent field studies suggest its usefulness as a robust carbon cycle tracer for gross primary production (GPP; Campbell et al., 2015; Campbell et al., 2008). Terrestrial plants consume COS by a mechanism closely linked to CO₂ uptake by leaves, catalyzed by carbonic anhydrase. The tracer approach is based on the relative COS to CO₂ uptake and spatial separation of COS sinks and sources (Campbell et al., 2015). Thus, measurements of atmospheric COS concentrations would be useful to constrain carbon assimilation in the biosphere without the need for measurements of plant and soil respiration (Commane et al., 2013; Blonquist et al., 2011).

Despite the immense potential of COS measurements to the understanding of several biospheric and atmospheric processes, its measurements are limited over the globe. Consequently, the global atmospheric COS budget is poorly understood and seems to have either an overestimation of sources or underestimation of sinks (Watts, 2000). Modeling investigations have highlighted the weaknesses in current understanding of the temporal and spatial fluxes of COS (Kettle et al., 2002). The global emission of COS is estimated at 1.31 ± 0.35 Tg a⁻¹, out of which CS₂ oxidation contributes 0.42 ± 0.12 Tg a⁻¹, outgassing from oceans contributes 0.30 ± 0.15 Tg a⁻¹, DMS oxidation produces 0.17 ± 0.04 Tg a⁻¹, and anthropogenic emissions account for 0.12 ± 0.06 Tg a⁻¹ (Watts, 2000). Further, recent studies show that multifarious human activities could account up to 25% of atmospheric COS (Aydin et al., 2002). These activities include biomass burning, coal combustion, chemical processing, sulfur recovery, vehicular emissions and aluminum production. There has been some debate as to whether the oceans are a source or a sink for COS, but in the analysis of Watts (2000) the oceans are taken as a source. Uptake by vegetation (0.56 ± 0.10 Tg a⁻¹) and deposition to soils are important loss processes for COS apart from its oxidation (0.13 ± 0.10 Tg a⁻¹), although the large uptake by oxic soils (0.92 ± 0.78 Tg a⁻¹) is particularly uncertain.

In the Northern Hemisphere, COS flux seems to be driven primarily by high COS vegetation uptake in summer, while the Southern

Hemisphere flux appears to be driven mostly by high oceanic fluxes of RSCs in summer. While global estimates of COS fluxes and lifetimes are based on only surface and aircraft measurements, mostly from periodic campaigns, it must be mentioned that measurements are very scarce in the southern hemisphere compared to the northern hemisphere. This has not allowed a coherent picture of the atmospheric distribution, seasonality, and interannual variability of COS across the Northern and Southern hemispheres (Montzka et al., 2007), and reconciliation of measurements with known sources and sinks. Thus, long-term measurements at various sites covering equatorial, mid-latitudes and polar regions in both the hemispheres are desired for a clear picture of how background surface mixing ratios of COS vary across broad scales in response to ocean emissions and vegetation uptake (Kettle et al., 2002). Further, there has been speculation regarding whether atmospheric concentration of COS is increasing due to human activities (Bingemer et al., 1990). It is pertinent to mention here that till now, there are no reports of COS levels over the Indian subcontinent, which could be an important player in the global sulfur cycle due to strong sources (oceans, wetlands, strong oxidative power of the atmosphere due to geographical location, ever growing anthropogenic activities specifically fast growing traffic sector) and sinks (large areas of forests and croplands) (Mallik et al., 2014). The present study is an attempt to reduce this gap by understanding the COS mixing ratios in light of its sources and sinks over a semi-arid urban region in India.

2. Methodology

2.1. The study location

Despite being a pre-dominantly agricultural country, about 32% of Indian population lives in urban areas (<http://data.worldbank.org/indicator/SP.URB.TOTL.IN.ZS>). Although the largest population densities in India are found along the Indo-Gangetic Plain (IGP) and eastern coastal regions, the western part of India (Gujarat and Maharashtra) is more industrialized (Table 2.1 of ASI 2008–09). A part of this region, the Golden corridor, contains the maximum number of large point sources (LPS) in India. Atmospheric concentrations of COS reported in this study were measured in a laboratory in Ahmedabad (23.0°N, 72.6°E, 49 m amsl), a major urban region in the golden corridor (Fig. 1). It is the largest city in Gujarat (the fifth largest in India) with a population of about 6.3 million and has a hot, semi-arid climate. The city receives about 750 mm rainfall during June–August (monsoon) with maximum in July (average: 247 mm) and August (average: 288 mm). Among the pre-monsoon months (March–May), the climatologically hottest daytime temperature occurs during May (mean: 41.5 °C). It is influenced by oceanic air masses during monsoon, agricultural and marshlands during pre-monsoon and air masses from continental north-western India during winter. The experimental setup was developed in Physical Research Laboratory (Section 2.2), and direct in-situ measurements were done during 2013, by sampling air from 20 m above ground level from the terrace of the institute (23°02′11″N, 72°32′37″E). The site is surrounded by trees on all sides. To the east and north is a university campus with lots of greenery, to the south a private road separates the PRL campus from other institutes which also have lots of green cover. Another big road, located 0.5 km to the west separates the site from the university ground used for various festive celebrations. No large buildings or industries are located in the immediate vicinity, only transport sector is a potential source of COS, but it must be noted that the surrounding roads are built for private use for institute and university staff. More details about the site are available in Mallik et al. (2015). The experiments were conducted once every month for 2 continuous days (including days and nights). During each of these periods spanning 48 h, on the average 25 measurements were obtained, once in every 2 h. Measurements could not be conducted during January, June, July and December 2013.

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