Journal of Quantitative Spectroscopy & Radiative Transfer 186 (2017) 81–95

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt


Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

Optimized approach to retrieve information on atmospheric carbonyl sulfide (OCS) above the Jungfraujoch station and change in its abundance since 1995

Bernard Lejeune [a,*], Emmanuel Mahieu [a], Martin K. Vollmer [b], Stefan Reimann [b], Peter F. Bernath [c,d], Christopher D. Boone [d], Kaley A. Walker [e], Christian Servais [a]

[a] Institute of Astrophysics and Geophysics of the University of Liège, Liège, Belgium
[b] EMPA, Laboratory for Air Pollution/Environmental Technology, Duebendorf, Switzerland
[c] Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia
[d] Department of Chemistry, University of Waterloo, Ontario, Canada
[e] Department of Physics, University of Toronto, Ontario, Canada

ARTICLE INFO

Article history:
Received 14 February 2016
Received in revised form
1 June 2016
Accepted 1 June 2016
Available online 7 June 2016

Keywords:
OCS
FTIR spectroscopy
Jungfraujoch
ACE-FTS
GCMS

ABSTRACT

In this paper, we present an optimized retrieval strategy for carbonyl sulfide (OCS), using Fourier transform infrared (FTIR) solar observations made at the high-altitude Jungfraujoch station in the Swiss Alps. More than 200 lines of the ν_3 fundamental band of OCS have been systematically evaluated and we selected 4 microwindows on the basis of objective criteria minimizing the effect of interferences, mainly by solar features, carbon dioxide and water vapor absorption lines, while maximizing the information content. Implementation of this new retrieval strategy provided an extended time series of the OCS abundance spanning the 1995–2015 time period, for the study of the long-term trend and seasonal variation of OCS in the free troposphere and stratosphere.

Three distinct periods characterize the evolution of the tropospheric partial columns: a first decreasing period (1995–2002), an intermediate increasing period (2002–2008), and the more recent period (2008–2015) which shows no significant trend. Our FTIR tropospheric and stratospheric time series are compared with new in situ gas chromatography mass spectrometry (GCMS) measurements performed by Empa (Laboratory for Air Pollution/Environmental Technology) at the Jungfraujoch since 2008, and with space-borne solar occultation observations by the ACE-FTS instrument on-board the SCISAT satellite, respectively, and they show good agreement. The OCS signal recorded above Jungfraujoch appears to be closely related to anthropogenic sulfur emissions.

1. Introduction

With a global average tropospheric mixing ratio of about 500 pptv (parts per trillion by volume) [1] and an atmospheric lifetime of about 2.5 years [2], OCS is the most abundant sulfur-containing compound in the free troposphere. The main sources of atmospheric OCS are [3]: the atmospheric oxidation of dimethyl sulfide (DMS) from marine plankton, oxidation of carbon disulfide (CS_2) from industrial and marine natural origin, and the gas exchange of OCS between the oceans and the atmosphere. The main sinks are uptake by land plants, uptake by oxic soils, and atmospheric oxidation by hydroxyl radicals.

OCS is an atmospheric trace gas which is gaining increasing attention from the scientific community. First considered for its role in the Earth's radiation balance as a contributor to

---

[*] Corresponding author.
E-mail address: bernard.lejeune@ulg.ac.be (B. Lejeune).

http://dx.doi.org/10.1016/j.jqsrt.2016.06.001
0022-4073/© 2016 Elsevier Ltd. All rights reserved.

the non-volcanic background sulfate layer in the stratosphere [4], it has been suggested more recently that atmospheric OCS measurements have the potential to become an atmospheric tracer of Gross Primary Production (GPP) and thus it holds great promise for studies of carbon cycle processes [2]. As a result, numerous studies have been undertaken to improve our knowledge of OCS vegetation uptake (e.g., [5-12]).

Despite its high tropospheric abundance and this increased interest, large uncertainty remains in both the OCS source and sink budgets. Watts [13] and Kettle et al. [3] proposed a mass budget described as balanced within the range of estimated uncertainty, but in fact it is imbalanced with sinks higher than sources. More recent modeling studies [5,8,14] suggested an additional oceanic source concentrated in the tropics to balance the increased global vegetation sink required to reproduce the seasonal variation observed in atmospheric concentration measurements.

Stratospheric sulfate aerosol (SSA) is important for a number of processes that affect the chemical and radiation balance of the atmosphere: heterogeneous chemistry reducing ozone, stratospheric warming and tropospheric cooling [15]. Crutzen [4] was the first to suggest that photodissociation of OCS may contribute significantly to the non-volcanic background sulfate layer in the stratosphere discovered by Junge et al. [16]. Because OCS is relatively inert in the troposphere it can be transported into the stratosphere where it is broken down by photodissociation through the absorption of ultraviolet sunlight. Other sulfur-containing gases such as sulfur dioxide (SO_2) contribute also to SSA, but the contribution of each one is uncertain. Some model and isotopic fractionation studies (e.g., [17-20]) suggested that production of SSA from OCS oxidation is too small to maintain the SSA background level and proposed that SO_2 transported from the troposphere is the most important precursor for the SSA layer, allowing for the possible influence on SSA by human emissions. However, several recent papers are in disagreement with this view [21-23]. The most recent one [24] estimated that OCS supplies about 56% of the background SSA burden, suggesting that upward transport of OCS from the troposphere largely controls the sulfur budget and the aerosol loading of the background stratosphere.

The lack of any substantial trend in OCS atmospheric loading over the last decades of the 20th century (e.g., [25]) was consistent with a balanced mass budget within the range of estimated uncertainty. This ‘no-trend’ argument was also used in the discussion about the contribution of OCS to SSA, when compared with the increasing trend observed in stratospheric aerosol loading since 2002 (e.g., [26]). However, a small (less than 1% per year) but statistically significant long-term decrease was reported from ground-based infrared measurements recorded above Jungfraujoch (Swiss Alps) from 1990 to 2002 ([27], also noticed by Rinsland et al. [25], above Kitt Peak in Arizona between 1978 and 2002). The updated Jungfraujoch data set revealed an increase of OCS over 2002–2008. More recently, Kremser et al. [28] have observed positive trends in their ground-based infrared measurements recorded at three Southern Hemisphere sites from 2001 to 2014. At a more global scale, a relatively small positive trend in global OCS derived from surface observations (1.8 pptv per year) was also reported in the WMO Scientific Assessment of Ozone Depletion (2010) for the period 2000–2008 [29] and recent observations from the NOAA (National Oceanic and Atmospheric Administration) surface network updated through 2012 suggest that any systematic changes in global OCS since 2000 have been small (less than 3%), with an increase of 0.4% from 2011–2012 [1].

The impact of OCS anthropogenic emissions on the abundance of atmospheric OCS is another matter of debate in the scientific community. Turco et al. [30] estimated that increasing anthropogenic emissions of OCS could cause measurable climate alterations within the next century. The anthropogenic part of global OCS sources has increased with time in the global mass budgets, from less than 25% in 1984 [31] to about 40% in 2002 [3], with oxidation of industrial CS_2 emissions as the main contributor. Using campaign-type atmospheric measurements above the western Pacific region, Blake et al. [32] observed that air masses of Chinese and Japanese origin were characterized by high OCS mixing ratios coming from land-based sources, suggesting underestimated Chinese emissions (most likely because emission ratio from Chinese coal burning is poorly characterized). A new global anthropogenic inventory for the years 1850–2013 based on new emission measurements and material-specific data results in a smaller growth in the OCS anthropogenic source than previously estimated [33]. Derived from ice and firn air analyses, the history of OCS atmospheric mixing ratios since 1850 seems to be closely related to historical anthropogenic sulfur emissions [34].

Moreover, the slow and long-term increase in atmospheric OCS deduced from ice and firn data analysis on a large temporal scale could indicate a decline in terrestrial productivity [35], increasing the scientific interest for OCS as a proxy of the first global history of GPP [33].

In view of these studies, precise and long-term sets of tropospheric and stratospheric OCS measurements are needed for trend evaluation and to obtain insights into source and sink strengths and their geographic locations [25]. In this paper, we report on the evolution of the vertical carbonyl sulfide loading integrated over the free troposphere and stratosphere above the high-altitude Jungfraujoch station, derived from the spectrometric analysis of Fourier transform infrared (FTIR) solar observations made at that site between 1995 and 2015. Related findings are compared with new in situ gas chromatography mass spectrometry (GCMS) measurements performed by Empa (Laboratory for Air Pollution/Environmental Technology) at the Jungfraujoch since 2008, as well as with spaceborne solar occultation observations performed by the ACE-FTS instrument on-board the SCISAT satellite.

With respect to the previous ground-based FTIR work, the present analysis has been performed with a new optimized retrieval strategy, mainly an updated set of microwindows and line parameters, with the goal of providing a more accurate and extended time series of tropospheric and stratospheric abundances, long-term trends and seasonal variations.