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Quantification of ozone reductions within the Saharan air layer through a 13-year climatologic analysis of ozone profiles

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HIGHLIGHTS

- We investigated ozone depletion occurred in Saharan dust plumes at the Canary Islands through a 13-year ozonesonde database.
- Meteorological conditions and air masses origin are studied.
- Data from satellite and ground based spectrometers and from two airborne campaigns are used to confirm these ozone depletion.
- Correlation with water vapor is explored.
- Water vapor must be considered as an additional factor influencing ozone depletion in Saharan dust plumes.

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ABSTRACT

Ozone (O_3) reduction caused by dust particles is a challenging topic that has not been sufficiently investigated. Previous studies have provided limited quantification of O_3, mainly based on case studies or short-term campaigns. In this paper, 157 O_3 vertical profiles from ozone soundings launched from the Canary Islands over 13 summers are analyzed. Using aerosol optical depth as a discrimination tool, the data are classified into two groups: clean atmospheric conditions and dusty conditions under the presence of the Saharan Air Layer (SAL). The results show that ozone mixing ratios on SAL days are systematically lower than those during clean conditions, with a difference of as much as 35%. An analysis of independent total ozone columns from ground-based and satellite spectrometers confirm the observed O_3 reductions. In addition, a vertical redistribution of the total water content takes place during these events. A comparison of the vertical shape of the O_3 reductions with the vertical distribution of dust loading and precipitable water vapor shows that although O_3 reductions occur in parts of the layer where the dust is present, a better correlation is found with the total amount of water present in the air. This finding suggests that the latter component plays a role in the observed O_3 reduction within the SAL.

1. Introduction

The Sahara is the largest aerosol source in the world. According to Zender et al. (2004), between 1000 and 2150 Tg yr^{-1} of dust is injected to the atmosphere every year. A significant portion of this mineral dust is further transported toward the Atlantic Ocean by mesoscale systems when meteorological conditions are favorable (Prospero, 1999). Su and Toon (2011) found 1088 Tg of dust crossing the 10W meridian in 2007. The thickness of the Saharan Air Layer (SAL) is very dependent on season, involving the marine boundary layer (MBL) and the free troposphere (FT). In summer, the SAL extends typically from near the surface to a height of 6–6.5 km, whereas in other seasons, the upper boundary of the SAL is at much lower altitudes Cuevas (1995).

There has long evidence of a negative correlation between O_3 and aerosols during desert dust outbreaks. In-situ measurements show a significant reduction in O_3 concentration under high dust concentrations (Prospero et al., 1995; de Reus et al., 2000; Bonasoni et al., 2004; Cuevas et al., 2013).

Three pathways were proposed by de Reus et al. (2000) to explain the observed O_3 reduction: a) a decrease in formation rates due to reductions in photolysis by extra scattering, b) the direct uptake of O_3 and c) HNO_3 heterogeneous removal. In addition to active processes that might occur during the transfer, the Saharan air that originates near the surface at lower latitudes can have

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lower O_3 concentrations than the surrounding air of the FT (Cuevas et al., 2013), adding complexity to the mechanism of ozone reduction in dusty conditions. Because direct measurements are rare, rates of reduction as a function of dust loading have primarily been calculated from laboratory measurements or estimated from models.

Dentener et al. (1996) investigated the role of mineral aerosol as reactive surfaces in the global troposphere. These authors noted that O_3 uptake coefficients could be of some significance, finding that 2–6% of observed O_3 destruction was caused by the direct uptake of O_3 on aerosol. However, the authors concluded that the destruction rates of O_3 by mineral dust were extremely uncertain.

Hanisch and Crowley (2003) performed laboratory experiments that investigated the heterogeneous reactions between O_3 and surfaces of Saharan dust particles sampled from Cape Verde islands. These authors found an uptake coefficient of $(7 \pm 3)10^{-3}$ for atmospheric conditions. As noted by Dentener et al. (1996), this value is too low to have a non-negligible effect on the atmospheric ozone budget because the mineral surface is rapidly passivated. Fairlie et al. (2010) did not observe a detectable depletion in Asian dust plumes during the INTEX-B flights. Moreover, the vertical distribution of the O_3 decrease has been largely unexplored due to the scarcity of ozonesonde programs downwind of large deserts. Recently, Jenkins et al. (2012), through 13 ozonesondes launched from Cape Verde during the summer of 2010, studied the influence of Saharan dust on O_3 at Cape Verde, finding a negative correlation between these parameters.

Johnson et al. (1999), using a chemical transport model (CTM) model, quantified the role of the various mechanisms that affect the budget of global tropospheric O_3 among other atmospheric oxidants. These authors found that 40% of O_3 destruction is caused by the following reactions:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (2)$$

Surprisingly, little work exploring the impact of changes in atmosphere water content on O_3 mixing ratios has been performed since that study. Reported observations refer to punctual in-situ ozonesonde or airborne campaigns. We extend the data here with vertical information on the entire dust layer by using a large database of ozone soundings to analyze 13 years of ozone vertical profiles.

The Canary archipelago is an excellent location to study the correlation between O_3 and Saharan dust because of the relatively high frequency of Saharan intrusions there. Alonso-Pérez et al. (2007) found 322 African dust intrusion days over Tenerife during the period 1998–2003. Moreover, the natural variability of O_3 in the subtropics is low, which minimizes interpretation problems related to large excursions often observed at higher latitudes due to strong horizontal gradients, stratospheric intrusions or pollution episodes.

In the present work, a correlation of a large database of ozone soundings and aerosol optical depth as an aerosol dust load marker is carried out with the aim of quantifying the observed O_3 reductions. Data from the nearby high-mountain Izaña Global Atmospheric Watch (GAW) observatory (IZO) are also used as well as the total ozone column (TOC) measured by ground-based, Brewer and differential optical absorption spectroscopy (DOAS) visible spectrometers and satellite spectrometers. The Brewer and DOAS spectrometers, as well as the ozonesondes, are part of the high-quality Network for the Detection of Atmospheric Composition Change (NDACC) program at IZO. The vertical distribution of relevant parameters observed from aircraft for particular events during the summers of 2005 and 2006 is also available. In particular, six profiles of aerosol vertical distribution were used in this analysis.

An additional characterization of the atmosphere from the point of view of atmospheric water content was performed based on humidity profiles from the ozone sounding dataset.

The paper is organized as follows: after this introduction, Section 2 describes the data used; the details about methodology are given in Section 3; the results are provided in Section 4; and Section 5 presents the summary and conclusions.

2. Data and measurements

A total of 157 O_3 vertical profiles were obtained for the period 1997–2011 from the AEMET ozonesonde program (Cuevas et al., 1994). Electrochemical concentration cells (ECCs) interfaced to a meteorological radiosonde (RS80 and RS92) were regularly launched on Wednesdays from a station at sea-level.

The present study focuses on extended summertime episodes (June–September), when Saharan dust extends up to the mid-troposphere. The preparation of sondes was perform using Komhyr (1986) recommendations and standard operating procedures (SOP) for ECC-sondes (Smit, 2011). The humidity in the atmosphere was calculated using the precipitable water vapor (PWV) index from the relative humidity of the sondes. Several intercomparison campaigns, performed to assess the quality and reliability of ECC ozonesondes, show that individual sondes operated according to SOP yielded a precision of 3–5% and an accuracy of 5–10% up to 30 km altitude during JOSIE (Smit et al., 2007) and BESOS (Deshler et al., 2008) campaigns.

The AOD at 440 nm was obtained at the Izaña AERONET site (Holben et al., 1998). Most of AERONET AOD data correspond to level 2.0, except for dates after January 2011 which are level 1.5. The root mean square of the differences at both levels is 0.01, which is in the range of the accuracy of the CIMEL AOD measurements (Dubovik et al., 2000). A total of 1657 days from a 1718-days dataset show the same daily mean AOD values for levels 1.5 and 2.0. To extend AOD dataset back to 1997, measurements from a zenith-operating DOAS spectrometer installed at IZO were used. A color index (CI), defined as the ratio of zenith radiance between 550 nm and 350 nm wavelengths, was found to be a good proxy of dust loading in the absence of direct-sun AOD measurements. Fig. 1 shows a cross-correlation of spectrometer-CI with CIMEL-AOD for

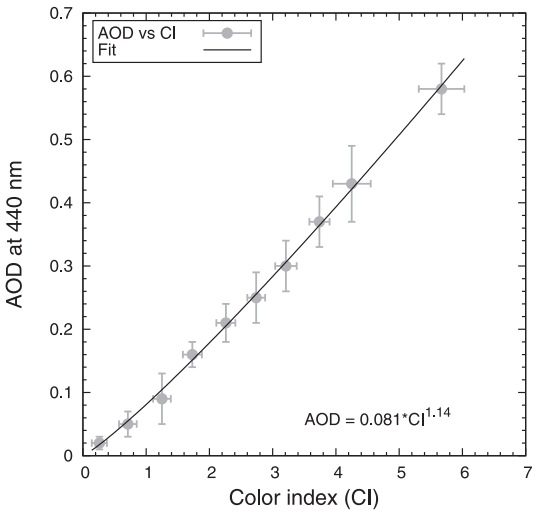

Fig. 1. Color index (CI) versus aerosol optical depth (AOD) after grouping in 0.05 CI bins. The mean and standard deviation of each mean point and the best-fit curve are also plotted.