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Observational evidence for direct uptake of ozone in China by Asian dust in springtime

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Abstract: While there is ample observational evidence for ozone uptake by Sahara dust, whether Asian dust exerts a similar effect on ozone has not been well-established in the literature due in part to limited observations. In this study we investigate the impacts of Asian dust on surface ozone (O_3) over northern China on a daily scale using observations from recently established air quality monitoring network during spring (March, April, May; MAM) 2015–2017, the peak season of Asian dust outbreaks. Dust days and non-dust days are selected based on the distribution of the coarse-mode particulate matter mass concentrations (PM_{coarse}) and then paired based on similar temperature (T) and relative humidity (RH) so as to minimize the effect of different local meteorological conditions on ozone. The majority of the dust days shows lower O_3 compared to non-dust days both temporally and spatially. The regional average of seasonal-mean O_3 differences between dust days and their reference non-day days are −10.1 ppbv (−24.6%), −2.4 ppbv (−4.8%) and −5.4 ppbv (−14.3%) over the Taklimakan Desert (TD), the Gobi Desert (GD) and North China (NC), respectively. The decrease of ozone tends to increase with increasing PM_{coarse}, although the use of PM_{coarse} to indicate dust is subject to uncertainty. Nitrogen dioxide (NO_2), sulfate dioxide (SO_2), and carbon monoxide (CO) appear to be higher during dust days outside dust source regions, possibly because of the compounding effects of large anthropogenic emissions over this region. In spite of higher or similar levels of primary pollutants, surface ozone concentrations are still lower during dust days over TD, GD and NC, supporting the mechanism of dust direct uptake of O_3.

1. Introduction

Mineral dust is the largest contributor of aerosols in the atmosphere. It is estimated that about 500–6000 Tg of dust aerosols are mobilized globally from arid or semiarid regions annually by strong winds and entrained into the atmosphere (Ginoux et al., 2001; Zender et al., 2003). The largest contributions to global dust loading are from the North African (50–70%) and Asian deserts (10–25%) (Tegen and Schepanski, 2009). Major dust sources in East Asia are the Taklimakan Desert in northwestern China, and the Gobi Desert over northern China and Mongolia. Dust storms over East Asia occur primarily in springtime, and suspended dust aerosols in the atmosphere can be transported long distances to the northern Pacific and even globally (Uno et al., 2009), affecting air quality (Yang et al., 2017), hydrological cycle (Rosenfeld et al., 2001; Shao et al., 2011), and regional climate (Huang et al., 2015). For example, a dust storm affected the Beijing metropolitan area on 15 April 2015 with surface hourly PM_{10} (particulate matter smaller than 10 μm in diameter) reaching more than 1000 μg/m^3 (http://www.chinadaily.com.cn/beijing/2015-04/16/content_20450286.htm). Under such high dust levels, the interactions of mineral dust with gases and other aerosol particulates in the atmosphere are expected to be complex and need to be understood.

One important aspect of mineral dust on atmospheric chemistry is uptake of gaseous species. For example, low ozone (O_3) mixing ratios have been measured concurrently with dust events. Bonasoni et al. (2004) reported that ozone mixing ratios were 4%–21% lower than the monthly mean background values during Saharan dust events in the Mediterranean region. Andrey et al. (2014) found systematically lower ozone mixing ratios during Saharan air layer days (SAL) than those during clean conditions, and the difference reached up to −35% based on 157 ozonesonde profiles launched from the Canary Islands over 13 summers. Jenkins et al. (2012) found a 20–30 ppbv decrease of ozone in some cases between SAL and non-SAL conditions in the Eastern Atlantic during the summer of 2010. Soler et al. (2016) recorded an average ozone reduction of 5.5% during Saharan events at a mountain station located near the eastern coast of the Iberian Peninsula from May to September 2012.

Three pathways have been proposed to explain the observed O_3

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reductions during dust events: (1) a decrease in net production rate of ozone due to the effect of dust on the transmissivity of solar radiation in the atmosphere; (2) the direct uptake of O_3 by dust; and (3) dust uptake of ozone precursors (e.g. nitrogen oxides). The latter two pathways involve heterogeneous reactions on dust. The uptake of O_3 on clean dust surface was found to be catalytic, and under dry conditions, the reactive sites were thought to be Lewis acid sites (Usher et al., 2003). Nitrogen oxides, as precursors of O_3, have a strong tendency to react with alkaline dust aerosols, forming water-soluble aerosols like calcium nitrate (Usher et al., 2003). Because of complex mechanisms and scarcity of direct field measurements, rates of ozone reduction as a function of dust loading have been primarily inferred from laboratory measurements (Crowley et al., 2010; Goodman et al., 2001; Hanisch and Crowley, 2003; Johnson et al., 2005; Michel et al., 2002; Underwood et al., 2001; Usher et al., 2002).

Based on laboratory information, modeling studies have assessed the impacts of dust on O_3, using laboratory-derived "best guess" of uptake coefficients of ozone and precursor gases on dust. The majority of published modeling studies, as listed below, suggest that light scattering by dust particles leads to a decrease of direct radiation but an increase of diffusive radiation in the lower atmosphere, and the combined radiative effect by dust is small for photolysis rate calculation. Therefore, heterogeneous reactions likely play the dominant role in the overall effects of dust on O_3. Reus et al. (2000) estimated a heterogeneous O_3 loss of 4 ppbv per day (half from nitrogen oxides uptake and the other half from O_3 uptake) near Tenerife, Canary Islands, in July 1997, compared to an estimated O_3 loss of 0.2 ppbv per day from low photolysis rate. Liao et al. (2003) included aerosols in their photolysis calculation and found the effect to be less than 0.2 ppbv reduction of monthly mean O_3. Bian and Zender (2003) showed that O_3 globally increased about 0.2% in the annual mean due to the impact of mineral dust on photolysis rates. Tang et al. (2004) simulated an O_3 decrease of about 20 ppbv as a result of heterogeneous reactions on dust in Asian dust outflow, compared to less than 1 ppbv decrease due to dust radiative influence. Bauer et al. (2004) suggested a decrease in global tropospheric ozone mass by about 5.4% due to heterogeneous reactions on dust, including 4.9% from nitrogen oxides uptakes and only 0.5% from O_3 uptake. Pozzoli et al. (2008) showed that heterogeneous reactions on dust would reduce ozone surface concentrations by 18–23% over the Asian outflow region and the global annual mean O_3 burden by 7%. Wang et al. (2012) estimated O_3 reductions of up to 3.8 ppb (~9%) by heterogeneous reactions on dust during the April 2001 dust storm episode over the trans-Pacific domain. These model simulations with heterogeneous reactions tend to have a better agreement with field observations.

Most of the field evidence in support of the modeling calculations was based on African dust events, although laboratory studies suggest both Asian and African dust uptake ozone and other gases. There were fewer direct field observations of Asian dust, and previous analysis of them had contradictory conclusions. Tang et al. (2004) showed lower O_3 mixing ratio during one Asian dust outflow episode during an aircraft campaign over the Yellow Sea in spring 2001. Fairlie et al. (2010) did not detect O_3 depletion in Asian dust plumes encountered during another aircraft campaign during spring 2006 over the northeast Pacific. The contradiction might be due to the fact that these aircraft campaigns were snap-shots of atmospheric composition a few hundred to thousand kilometers downwind of Asia, where suspended dust particle concentrations were much less than those near dust sources. Meteorological conditions can significantly affect ozone daily variability and may even dominate the dust effect. Furthermore, the properties of Asian dust particles may have been significantly influenced by anthropogenic air pollutants during their transport across polluted eastern China.

To assess the effects of Asian dust on ozone, we examine the dust-ozone relationship within or close to the source regions, using daily surface air quality observations in China along the dust transport route from the Taklimakan Desert (TD) in the west and the Gobi Desert (GD) in the central, to North China (NC) in the east. The rest of the paper is organized as follows. Section 2 describes the data source and study domain. Here daily observations of surface particulate matters (PM), ozone, and meteorological conditions during March, April, and May (MAM) are used to analyze the covariance between dust and ozone from 2015 to 2017, with a focus on 2015. Section 3 summarizes daily variations of springtime PM and O_3 in three representative regions over northern China. Due to the lack of dust observations, coarse particulate matter mass concentration (PM_{coarse}) is chosen as an indicator of dust and we verify this indicator with reported dust episodes. Section 4 demonstrates the significant meteorological effects on day-to-day O_3 variability. Section 5 investigates the differences of O_3 between dust and non-dust days, after the influences of meteorological factors are taken into consideration. In section 6, we discuss comparisons to previous field studies, mechanisms and limitations. Section 7 gives final conclusions.

2. Data and study domains

2.1. Surface air quality and meteorological observations

Hourly concentrations of $PM_{2.5}$ (particulate matter less than 2.5 μm in diameter), PM_{10}, O_3, nitrogen dioxide (NO_2), sulfate dioxide (SO_2) and carbon monoxide (CO) at 1497 surface sites in China were obtained from the China Ministry of Ecology and Environment (MEE). This dataset was made available to the public in 2013, and here we focus on the springtime (March, April, May; MAM) from 2015 to 2017. PM_{coarse} was calculated by subtracting $PM_{2.5}$ from PM_{10}. The original unit of these MEE observations is μg/m^3. For O_3, NO_2, SO_2, and CO, we converted them to mixing ratios (units: ppmv for CO and ppbv for the rest) using a constant temperature of 298 K and atmospheric pressure of 1013.25 hPa. The site-level data were averaged into horizontal grids of 0.25° × 0.25° resolution to reduce sampling differences between nearby sites and to match with the resolution of meteorological reanalysis data. Daily gridded observations were derived using the hourly gridded data. For simplicity, the observational analysis of the 2015 springtime data is presented below. Similar analyses of the 2016 and 2017 spring data are shown in the supplementary material.

To analyze the influence of meteorology on surface O_3 variability, we obtained 2 m temperature (T), 2 m dew point temperature, 10 m zonal (U) and meridional (V) wind component, mean sea-level pressure, surface net solar radiation, boundary layer height, and total precipitation from the European Centre for Medium-Range Weather Forecasts (ECMWF) Reanalysis Interim (ERA-Interim) at a horizontal resolution of 0.25° × 0.25°. The 2 m relative humidity (RH) is then derived from the 2 m dew point. The 10 m wind speed is calculated as the square root of total squares of U and V.

2.2. Study domains

Fig. 1 presents China's land use and land cover categories in 2010 (Zhang et al., 2014) and the distribution of MAM-mean surface $PM_{2.5}$ and PM_{10} in 2015. There are two major dust source regions in northwestern China (Fig. 1a): the Taklimakan Desert (TD; 75°–87.5° E, 36°–43° N) and the Gobi Desert (GD; 95°–110° E, 35°-41°N). As the prevailing transport routes of dust from TD and GD are eastwards in springtime, the populous, and economically important region of North China (NC, 110°–120° E, 35°–41° N) is chosen as the major downwind and receptor region of dust storms from TD and GD (Sun et al., 2001).

In spring, the high PM_{10} concentrations in northern China were found to be associated with the occurrence of dust events (Feng et al., 2011). Indeed, surface PM_{10} concentrations (Fig. 1b) show a clear west-to-east gradient, decreasing from the seasonal average of more than 300 μg/m^3 over TD to 100–125 μg/m^3 over GD and NC, consistent with the west-to-east transport pathway of dust. By comparison, PM_{10} in