Ozone–CO Correlations in Siberian Wildfire Plumes Observed at Rishiri Island

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Abstract

We used ozone (O₃) and carbon monoxide (CO) measurements conducted at Rishiri Island, a remote surface site located in northern Japan to characterize impacts of boreal forest fires in Siberia on photochemical O₃ formation. Hourly O₃ observations during severe fire seasons in 1998, 2002, and 2003 were examined based on large enhancement in the CO mixing ratios and backward trajectories. In total, we identified sixteen episodes impacted by Siberian biomass burning. Correlations of O₃ to CO in individual plumes were significant in eight wildfire plumes. The relative enhancement of O₃ to CO quantified in these fire plumes ranged from slightly negative to up to -0.4, depending on episodes. Two episodes in 2002 and 2003 suggested that O₃ formation in wildfire-polluted plumes was comparable to the magnitude typically observed in industrially-polluted air masses from the Asian continent. Possible physical, chemical, and biogeochemical factors leading to different O₃ to CO ratios were presented.

1. Introduction

The relative enhancement of O₃ to CO (the ΔO₃/ΔCO ratio) is often used as a diagnostic variable to evaluate photochemical O₃ formation in air masses of continental pollution. This could be from day-to-day episodes to the period that extends to a month. Although the O₃–CO correlation may become obscured by including different processes and air mass types, the monthly O₃–CO correlation often provides a valuable test for model predictions of anthropogenic influence on O₃ under prevailing synoptic-scale meteorological conditions.

Parrish et al. (1993) first introduced the use of the ΔO₃/ΔCO ratios to identify O₃ production from continental emissions. They focused on O₃ formation in continental outflow where the air masses were largely dominated by the North American sources, so that CO changes could be attributed to local emissions and O₃ changes to subsequent chemistry. Based on this method, O₃ formation from anthropogenic sources has been quantified in a number of field studies. Export of photochemical O₃ from continents has been studied using ground-based measurements during PEM-West-A (Jaffe et al. 1996) and NARE (Parrish et al. 1998). Zhang et al. (2006) recently showed strong positive O₃–CO correlations in the middle troposphere downwind of continental source regions by utilizing the Tropospheric Emission Spectrometer (TES) satellite observations.

Biomass burning is a major source of trace gases and aerosols to the atmosphere (Andreae and Merlet 2001). Boreal forest fires commonly occur in May through September across Siberia, Alaska, and Canada (Kasischke et al. 2005), although fire activities have large interannual variations (Soja et al. 2004). A number of studies reported huge enhancement of CO due to boreal forest fires in 1998, 2002, and 2003 (Tanimoto et al. 2000; Zhao et al. 2002; Novelli et al. 2003; Yurganov et al. 2004; Edwards et al. 2004; Yurganov et al. 2005). Wildfire plumes from boreal forest regions can be transported in a long-range. Trace gases and aerosols from the Canadian fires in 1998 were transported to Europe, leading to a large-scale haze layer (Forster et al. 2001). Pollutants from the Siberian forest fires in 2002 and 2003 were transported to the west coast of North America, resulting in elevated CO episodes (Bertschi et al. 2004; Bertschi and Jaffe 2005). Fire plumes originating in boreal regions can be lifted to the upper troposphere by pyro-convection (Fromm and Servranckx 2003) or a warm-conveyor belt (Nedelec et al. 2005).

In contrast to CO, only few reports are available for the impacts of boreal wildfires on tropospheric O₃. While an early report by Tanimoto et al. (2000) showed very low O₃ enhancement due to Siberian boreal fires in the summer of 1998, several recent reports suggested that boreal wildfires had significant impacts on tropospheric O₃ both in the boundary layer and in the free troposphere. In-plume O₃ production by Siberian fires affected surface air quality of the western United States (Jaffe et al. 2004), and North American fires resulted in high-O₃ episodes as observed at the summit of Pico in the Azores Islands (Honrath et al. 2004; Val Martin et al. 2006). These studies implied that substantial O₃ production took place in well-aged plumes originating from boreal fires. In addition, some plumes exhibited positive O₃–CO relationship, others did not. Thus, the number of studies on O₃ enhancement is still limited, and the impacts of boreal wildfires on tropospheric O₃ have been poorly characterized. Since the reported magnitude of O₃ enhancement due to boreal fires has large variability and uncertainties, identification of more fire plumes and quantification of the O₃–CO relationships in individual plumes are needed to understand factors leading to en-route O₃ production in boreal fire plumes.

We analyzed continuous measurements of O₃ and CO to characterize biomass burning plumes transported from an upwind Eurasian continent, with focus on the variations in the summer of 1998 and 2002, and in the spring of 2003 because of the active boreal fires. Biomass burning episodes in these seasons were scrutinized by a combination of observed CO enhancement and backward trajectories, with help of a global fire emissions database over Siberia. It should be noted that previously analyzed high-CO events in the summer of 1998 (Tanimoto et al. 2000) were partly revisited in this study. We identified wildfire-polluted plumes from Siberia, quantified the O₃ enhancement relative to CO, and discussed possible reasons for the ΔO₃/ΔCO observed.

2. Site and measurement

Rishiri Island is a remote site far from the Asian industrial source regions, and is closely located downwind of areas where Siberian wildfires frequently occur in eastern and far eastern Siberia (Supplement 1). It is one of the most intensely impacted locations by Siberian
fires, as comparative studies by Yurganov et al. (2004, 2005) clearly indicated. Continuous measurements at Rishiri Island are thus useful to diagnose immediate impacts by boreal fires. The Rishiri Island Observatory (RIS, 48.07 North, 141.12 East, 35 m asl) is located in the west of the island, which has a dormant volcano (1721 m asl) in the center. Air samples for O3 and CO are taken at about 5 m above the ground surface and directed to individual instruments by means of PFA-Teflon tubing.

The instruments for O3 and CO measurement have been described in detail elsewhere (Tanimoto et al. 2002). Briefly, the mixing ratios of O3 and CO were determined by using commercially available photometric instruments based on absorption in the ultraviolet and infrared wavelength regions, respectively. The O3 instrument utilizes absorption at 253.7 nm emitted by a low-pressure mercury lamp (model 1006-AHJ, Dasiib; or model 1150, Dylec) and is calibrated once a year by a working standard maintained by our laboratory (model 49PS, TEII). The ambient data presented here were scaled to ultraviolet absorption photometry using a standard reference photometer built by the National Institute of Standards and Technology (Tanimoto et al. 2007). The CO instrument (model 541, Kimoto) is based on non-dispersive absorption. The instrument was zeroed each hour and calibrated by an air-balanced gravimetric gas standard (1.8 ppmv CO) every 10 days. The gas standards were intercompared to the calibration scale maintained by the Meteorological Research Institute (Tanimoto et al. 2007).

3. Ozone in wildfire-polluted plumes

3.1. Short-term temporal variations

A satellite-based emissions inventory suggested that major fires took place in the summer (July–September) of 1998 and 2002, and in the spring (May–July) of 2003 (van der Wef et al. 2006). To characterize the air masses arriving at Rishiri Island in these periods, 5-day backward trajectories were calculated using a three-dimensional wind model, driven by the meteorological data sets provided by the National Centers for Environmental Prediction, on the Meteorological Data Explorer (METEX) (Zeng et al. 2003). The clean air masses include the continental air masses from Siberia coming from the north (N) and the maritime air masses from the Bering Sea (BM) and from the Pacific Ocean (PM). The industrially-polluted air masses include the continental air masses from industrial regions of East Asia (China and Korea: CH/KR), originally the maritime air masses that pass over Japan (JP), and the air masses that traverse between the CH/KR and N air masses (NW). The NW air masses are generally categorized as semi-polluted, but it is sometimes complicated to characterize the NW air masses, likely as a result of mixing of polluted and clean air masses. The back trajectories that have unexpectedly large divergence were treated as unclassified (UC).

Figure 1 depicts the time series of CO and O3 observed in 1998, 2002, and 2003, along with air mass categories. In 1998 a number of episodic CO plumes (>300 ppbv) were observed in the air masses that traversed Siberia (i.e., N and NW). In particular, the CO peaks around July 28–29 and August 21–24 were sharp, with hourly averages greater than 1000 ppbv, because of fire spots extremely close to Rishiri Island. The CO enhancement was less intense in 2002 and 2003 than in 1998. Fewer elevated CO peaks were observed in the air masses from Siberia (N) in 2002 and 2003, partly because the distance between the major fire locations and Rishiri Island was greater than in 1998 (see Supplement 1). Many of the high CO events due to biomass burning were rather sharp.

Table 1 summarizes the enhancement of O3 relative to CO in the wildfire-plumes identified in 1998, 2002 and 2003. Correlation coefficients and the ratios of O3 to CO were calculated for individual plumes. The correlations of \( \Delta O_3 / \Delta CO \) were statistically significant in half of the plumes, suggesting that the O3 enhancement was not typically well correlated with CO in the wildfire-polluted plumes from Siberia. Some fire plumes showed large positive O3 enhancement relative to CO, others did not. The upper limit of the relative enhancement of O3 to CO identified in wildfire-polluted plumes was ~0.4, as observed in 2002 and 2003. This value compares well to those typically observed in industrially-polluted plumes (CH/KR) (Supplement 2). Thus, the O3 enhancement in boreal fire plumes arriving at Rishiri Island was not always the case but substantial in some fire plumes. This feature is in great contrast to the O3 enhancement in the industrially-polluted air masses observed at Rishiri Island, which typically shows positive and tight O3/CO correlations.

The upper limit of the relative enhancement of O3 to CO (~0.4) observed at Rishiri Island in 2002 and 2003 is in well accordance with those (0.2–0.9) observed in Siberian fire plumes over the western United States and the North Atlantic in the same fire seasons of 2002 and 2003 (Bertschi et al. 2004; Honrath et al. 2004; Bertschi and Jaffe 2005).

The reason for large variability in the \( \Delta O_3 / \Delta CO \) ratios in the fire plumes at Rishiri Island is not clear, but possible reasons are explored below. The differences in the locations of fires, and hence the transport time (i.e.,
the degree of air mass aging) from the burning regions to the site may be important. The short transport time from burning regions in far-eastern Siberia to Rishiri Island might not allow substantial O₃ formation in such fresh air masses as in 1998. Burning types (i.e., flaming or smoldering) for O₃ precursor emissions are also key factors. The emission intensity of NOₓ and CO may vary between flaming and smoldering. Smoldering produces more CO and less NOₓ due to lower burning temperatures than flaming. In addition, interactions of O₃ with full of aerosols existing in fire plumes may inhibit the photochemistry. Loss of O₃ onto aerosol surfaces co-emitted by fires might play a part, assuming that huge amount of carbonaceous aerosols is initially present in smoke plumes. As the lifetime of aerosols is shorter than CO, the abundance of aerosols might have different impacts on the O₃–CO correlation as the air masses age. Model simulations of Leung et al. (2007) suggested the importance of injection height, and hence of burning type (smokes are often lifted up to the free troposphere by flaming, but not by smoldering). The injection of emissions in the free troposphere may result in higher O₃ production throughout the Northern Hemisphere due to longer sequestration of NOₓ by the formation of peroxyacetyl nitrate. In this case, large O₃ enhancement would not be expected at a surface site close to the fire location (like Rishiri Island), but downwind locations in the free troposphere (like Azores) would see O₃ enhancement more efficiently and frequently. For Rishiri, dry deposition of O₃ might be efficient during the transport, assuming that transport is mainly over land, and these air masses may be in close contact with boreal forest ecosystems.

4. Implications for air quality

By successful emissions control since the past photochemical smog decade of 1970s, the nationwide O₃ levels and frequency of high-O₃ days have decreased in Japan over the last two decades. Most of the decrease is attributed to reduced industrial and vehicle emissions of NOₓ. However, it is now well-known that trans-boundary transport of O₃ pollution significantly contributes to the O₃ levels at many rural and remote sites of Japan. Variability in the incoming O₃ has great importance in air quality control strategies at the ground level, because regulations of domestic precursor emissions must account for the increase in background levels intruding into a specific region (Fiore et al. 2003). This study revealed that, in two Siberian fire plumes, maximum O₃ levels exceeded 60 ppbv, which is the Air Quality Standard of Japan. It is suggested that the frequency and duration of boreal wildfires are likely linked to a global climate change, and those in Canada and Alaska have increased in the last two decades (Stocks 1998; Whitlock 2004). If boreal wildfires in Siberia also become more severe due to a climate change, Siberian fires may partly contribute to offset the downward trend in the O₃ levels in Japan, or even enhance the frequency of high-O₃ episodes in future, although uncertainty with this assumption lies in many factors including changes in regional meteorology, fire locations, and burning types.

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Comments and supplements


References

Bertschi, I. T., and D. A. Jaffe, 2005: Long-range transport of ozone, carbon monoxide, and aerosols to the NE Pacific


