EXPRESS LETTER

Anomalous geographical gap in carbon monoxide mixing ratios over Hokkaido (Japan) in summer 2004

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An anomalously low carbon monoxide (CO) episode was observed at Cape Ochi-ishi located in northern Japan in summer 2004. The low CO episode persisted for as long as twelve days from July 27 to August 7, 2004, and the CO levels at Cape Ochi-ishi during this episode were comparable to at Hateruma Island, a southernmost island of Japan. We explored regional distributions of CO and roles of synoptic-scale meteorology in this episode by using a regional chemistry-transport model. The model reproduced the observed levels and day-to-day variations of CO very well, and indicated that the low CO episode widely occurred around Japan. The model simulations revealed the presence of steep gradient in central Hokkaido, explaining the observed differences in CO mixing ratios between Cape Ochi-ishi and Rishiri Island. The eleven-year model results and backward trajectories suggested that the low CO event observed in 2004 was due to rapid transport of pristine air masses from the Pacific Ocean, driven by anomalously stronger easterly flows in the summer of 2004. This mechanism well explained the anomalous patterns observed for methane, carbon dioxide, and molecular hydrogen associated with low CO.

Keywords: carbon monoxide, Cape Ochi-ishi, anomaly, long-range transport, Japan

INTRODUCTION

Synoptic-scale meteorology plays an important role in controlling regional distributions and day-to-day variations of atmospheric trace gases of environmental importance. Of these atmospheric constituents, carbon monoxide (CO) is a key gaseous species that controls the abundance and lifetime of methane (CH₄), nonmethane hydrocarbons (NMHCs), and hydrofluorocarbons (HFCs) through the reactions with hydroxyl (OH) radicals. The major primary sources of CO include emissions from fossil fuel, biomass, and biofuel burning. Hence CO is often utilized as a relatively long-lived tracer of combustion. Chemistry-transport model analyses of spatial distributions and temporal variations of CO are useful for evaluating the emission strength of CO from various sources and regions, and subsequent long-range transport in the regional to hemispheric scales.

In East Asia, spatial and temporal variations of CO and other trace species including long-lived greenhouse gases (GHGs) such as CH₄ and carbon dioxide (CO₂) are

greatly controlled by continental and maritime air masses. For example, surface observations at Japanese stations showed that CO has a summertime minimum because of transport of maritime air masses from the Pacific Ocean driven by prevailing high-pressure systems, in contrast to an early-springtime maximum dominated by continental outflow from the Eurasian continent (Narita *et al.*, 1999). The maritime influence is generally larger in the south than in the north, yielding in substantial latitudinal gradient. Not only seasonal variations but also short-term (e.g., day-to-day) variations are greatly affected by long-range transport of continental and maritime air masses that occurs synoptically. Tohjima *et al.* (2002) reported that CH₄ levels at Cape Ochi-ishi were episodically low in summer (July and August). Wada *et al.* (2007) reported extremely low CO₂ events at Minamitorishima Island driven by rapid long-range transport of continental air masses associated with active biospheric uptake in the summer season. Better understanding of the roles of long-range transport controlled by synoptic-scale meteorology is needed to reconcile highly variable spatial and temporal variations of trace gases at the sites close to continents, since it helps better constrain and improve regional source/sink strength.

Here we report an anomalous episode of CO and several other trace gases observed at Cape Ochi-ishi located

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in Hokkaido (Japan) that have unusually persisted for as long as twelve days from July 27 to August 7, 2004. Using multi-year simulations of CO by a regional chemistry-transport model, we show regional patterns of CO and wind flows, and how anomalous they were during this episode in 2004. Finally we discuss the origin of air masses and the role of synoptic-scale meteorology in this anomalous “chemical signature”.

SITES AND MEASUREMENTS

We conduct continuous measurements of CH₄, CO₂, CO, and H₂ at Cape Ochi-ishi (COI, 43.15°N, 145.50°E, 45 m asl) and Hateruma Island (HAT, 24.05°N, 123.80°E, 10 m asl), as part of a long-term atmospheric composition monitoring program operated by Center for Global Environmental Research (CGER) at National Institute for Environmental Studies (NIES). The COI site is located on a cape in the east part of Hokkaido, a northernmost large Japanese island. The HAT site is on a small island situated south of Okinawa Island. On a research basis, continuous measurements of CO were made on Rishiri Island, a small island located in the west part of Hokkaido from 1998 to 2004 (Tanimoto *et al.*, 2000, 2002). The Rishiri Island site (RIS, 45.07°N, 141.12°E, 35 m asl) is located in the southwest of the island. The geographical locations of these stations are shown later (Fig. 3). All these surface stations are located generally in remote regions where influences of local pollution from the industrial activities are not dominant, and have been used to characterize trace gases in background air over the East Asian Pacific rim region.

For sampling at COI and HAT, the air intakes are placed on towers ~51 m and ~37 m above the ground level, respectively. A diaphragm pump is used to draw in outside air at a rate of a 5 L min⁻¹. Water vapor in the sample air is removed to a dew point of about -15°C by passing it through a Nafion tube dryer and then through a cold trap made of Pyrex glass immersed in a cold bath (-40°C). The measurement systems for CH₄, CO₂, CO, and H₂ at COI and HAT are essentially the same, and all of these systems are fully automated. Technical information of the measurements at COI and HAT was detailed previously (Tohjima *et al.*, 2002). Briefly, CH₄ was measured by a gas chromatograph (5890, Hewlett Packard Co. Ltd., USA) equipped with a flame ionization detector (FID) since 1995 and 1996 at COI and HAT, respectively. CO₂ was measured by a continuous instrument based on a non-dispersive infrared analyzer (NDIR, Shimadzu Co. Ltd., Japan) since 1995 and 1993 at COI and HAT, respectively (Mukai *et al.*, 2001). CO and H₂ were measured by a gas chromatograph/mercury oxide (GC/HgO) analyzer (RGA3, Trace Analytical Co. Ltd., USA) since 2002 and 2000 at COI and HAT, respectively. The mixing ratios of

Fig. 1. Time series of observed (upper panel) and modeled (lower panel) CO at three Japanese stations (Cape Ochi-ishi, COI; Hateruma Island, HAT; Rishiri Island, RIS). Time resolution is 1 hour and 3 hours for the observed and the modeled data, respectively. Time unit is Local Time (UTC + 9). The period of a persistently anomalous episode from July 27 to August 7, 2004 is yellow-shaded.

CH₄, CO₂, CO, and H₂ were determined with gravimetric standard gases that were referenced to the “primary” scale at NIES (Machida *et al.*, 2009).

At RIS, air samples were taken at the top of the inlet placed at 6 m above the ground level. No dehumidification for ambient air samples was made at RIS. CO was measured by an instrument based on non-dispersive absorption in the infrared wavelength regions (model 541, Kimoto Electric Co. Ltd., Japan). Calibration was made by a gravimetric gas standard at 1.8 ppmv (Tanimoto *et al.*, 2008). Correction for the different standard gases between COI/HAT and RIS was not made.

CHEMISTRY-TRANSPORT MODEL AND BACKWARD TRAJECTORY

A three-dimensional regional-scale chemistry transport model used in this study is based on the Models-3 Community Multi-scale Air Quality (CMAQ) modeling system (Byun and Schere, 2006). The detailed model setup was described previously (Tanimoto *et al.*, 2005; Uno *et al.*, 2007). Briefly, the model was driven by meteorological fields generated by the Regional Atmospheric

Fig. 2. Scatter plots of hourly CO at Rishiri Island (RIS) versus Cape Ochi-ishi (COI) observed during the persistently anomalous episode (gray circles) and whole July–August period except the anomalous period (pluses) in 2004. The regression line (solid line) is obtained by the reduced-major-axis (RMA) regression method. The dashed line depicts 1:1 correspondence. Error limits of the slope and intercept represent 95% confidence levels.

Modeling System (RAMS) (Pielke *et al.*, 1992). The horizontal and vertical resolutions were fixed to 80 km and 14 layers (up to 23 km), respectively. A global chemistry-transport model was used to generate monthly averaged lateral boundary conditions for RAMS/CMAQ. Since the CMAQ model used in this work was developed for the purpose to diagnose air quality issues, emissions and chemistry schemes for CO are included but those for CH₄ and CO₂ are not. In the model, CO is primarily emitted by combustion of coal, oil, biofuel, and biomass in various sources. The emissions inventory incorporated into the model is based on the Regional Emission inventory in Asia (REAS) (version 1.1) (Ohara *et al.*, 2007). Biomass burning sources were climatologically provided from Streets *et al.* (2003). Model calculation was conducted for the period from 1995 to 2005 (Ohara *et al.*, 2008). To examine the meteorological roles for CO, we used constant emissions inventory (the year 2000) for the whole period from 1995 to 2005 to exclude the impacts from changing emissions. The model outputs were obtained every three hours.

To complement the model analysis, five-day backward

Fig. 3. Modeled spatial distributions of CO and wind flows in the boundary layer for 11-year summertime (July and August) climatology from 1995 to 2005 (upper panel), during the persistently anomalous episode (July 27 to August 7) in 2004 (middle panel), and differences in the persistently anomalous episode relative to 11-year climatology (lower panel). The regions where the anomalous CO mixing ratios are in the range of ± 10 ppbv are shown in white. Locations of the ground-based stations (COI, Cape Ochi-ishi; HAT, Hateruma Island; RIS, Rishiri Island) are included.

Fig. 4. Five-day back-trajectories at Cape Ochi-ishi and Hateruma Island during the persistently anomalous episode (left panel) and in July–August except the episode in 2004 (right panel).

trajectories were calculated on the Meteorological Data Explorer (METEX) (Zeng *et al.*, 2003). The trajectory model uses a three-dimensional wind fields, driven by meteorological data sets provided by the National Centers for Environmental Prediction. For COI and HAT stations, starting heights for trajectory calculations were set at 500 m.

RESULTS AND DISCUSSION

Summertime (July and August) variations of CO measured at COI along with those at RIS and HAT are shown in Fig. 1. Temporal variations of CO at COI show baseline levels of about 100–110 ppbv with enhancements to 200 ppbv several times. We found a substantial drop in the CO levels by ~40 ppbv at COI that persisted for as long as twelve days from July 27 to August 7, 2004. The low CO episode is not observed at RIS, and the mean CO levels at RIS during this episode are even slightly enhanced. This is in great contrast to the fact that the levels and variations of CO at COI and RIS are generally in good agreement, as shown later. The CO levels observed at COI during this episode are nearly as low as those at HAT. Time series of CO from a regional chemistry-transport model are illustrated for comparison with the observation. The model reproduced well the observed CO levels and variations including this event at all of the COI, HAT, and RIS sites, whereas the modeled events at COI and RIS show broader peaks than the observed because of inherent nature of the Eulerian-type models and of relatively coarse horizontal resolution (i.e., $80 \times 80 \text{ km}^2$) in our model.

Figure 2 shows scatter plots of hourly CO mixing ra-

tios at RIS versus COI in summer 2004. In general these two data sets are in reasonably good agreement ($R^2 = 0.56$), reflecting that these two sites are located closely and at the same latitude region. This indicates that the air masses observed at COI and RIS were dominated by common synoptic-scale meteorology that controls transport of CO emitted from primary sources. By contrast, CO data at COI and RIS are not correlated during the anomalous episode. CO at RIS varies from 80 to 190 ppbv, while CO at COI is constant at ~60 ppbv. This feature clearly indicates that the air masses observed at COI and RIS during the episode were different from each other, contrary to other period in the summer 2004.

Figure 3 illustrates modeled spatial distributions of CO and wind flows in the boundary layer for the summertime (July and August, from 1995 to 2005) climatology and for the anomalous episode (July 27 to August 7 in 2004). Also shown are differences in CO and winds between the anomalous episode and the 11-year climatology. The modeled climatological distributions of CO show typical features observed in the East Asian Pacific rim region, showing quantitative consistency with previous observations (Narita *et al.*, 1999). The mean climatological CO levels modeled over Japan range from 100 to 120 ppbv, associated with lower levels (60–80 ppbv) over Okinawa during summer. The summertime CO in this region exhibits the annual minimum, driven by intrusion of maritime air masses, as indicated by weak easterly and southerly flows from the Pacific Ocean.

In contrast, the modeled CO distributions during the anomalous episode reveal that low CO region (<80 ppbv) covers most part of Japan including Okinawa, Kyushu, Shikoku, Honshu, and eastern Hokkaido; but western

Fig. 5. Five-day upwind positions of back-trajectories at Cape Ochi-ishi in summer (July and August) from 1995 to 2005. Color bars indicate altitude (m) of trajectories. Red boxes correspond to the approximate upwind positions during the persistently anomalous episode in 2004. The numbers of data counted in the red box are shown in parenthesis.

Hokkaido is not impacted. Steep gradient in CO is located along the coast of the Asian continent. This steep gradient runs between western and eastern Hokkaido, providing different “chemical signatures” between RIS and COI. Stronger easterly and southerly winds from the Pacific Ocean than the 11-year climatology are notable. The modeled mean CO levels at COI and HAT are 60–80 ppbv, with ~125 ppbv at RIS during the episode.

The simulated CO anomalies over Japan are –50 ppbv at the maximum (–30 to –40 ppbv for COI). The influence effectively spreads further west, over the Sea of Japan, and Korean peninsula. The main driver is stronger easterly and southerly flows from the Pacific Ocean (note that anomalies in winds are not apparent over continental regions). These flows split into two streams near Japan and deliver pristine maritime air masses to both COI and

Fig. 6. Time series of hourly CH_4 (upper panel), CO_2 (middle panel), and H_2 (lower panel) observed at Cape Ochi-ishi (COI) and Hateruma Island (HAT). Time unit is Local Time (UTC + 9). The period of a persistently anomalous episode from July 27 to August 7 is yellow-shaded.

HAT in the same period. Back-trajectories at COI and HAT also suggest long-range transport of pristine maritime air masses from the Pacific Ocean during the episode, unlike the other period during the summer in 2004 (Fig. 4). The model suggests that the gap obviously exists over central Hokkaido between RIS and COI. There is a positive anomaly belt over the north of the negative belt. The simulated positive anomaly is +30 ppbv (+10 ppbv for RIS), explaining the observed CO enhancement at RIS during the episode. The model indicates that the rapid and intense transport of maritime air masses prohibited anthropogenic pollution of East Asian continent from being transported toward the east, and promoted northward rerouting.

Five-day upwind positions of the back-trajectories at

COI in summer (July and August) from 1995 to 2005 are shown in Fig. 5. The positions of the trajectories responsible for the low CO episode at COI in 2004 are in a specific region ($15\text{--}35^\circ\text{N}$, $155\text{--}175^\circ\text{E}$). In 2004, the frequency with these trajectories is totally 12 days, which is anomalously higher than 11-year climatological value (i.e., 5 days). Although the frequency in 1999 is as high as in 2004 (i.e., 12 days in total), the CO measurements at COI were not started in 1999.

Figure 6 indicates temporal variations of CH_4 , CO_2 , and H_2 measured at COI and HAT in the summer of 2004. Sharp peaks of both CH_4 and CO_2 enhancements are often seen only at COI (e.g., August 10, 15, 19, 21, 22). These peaks are likely attributable to local influence such as accumulation of biogenic CO_2 and CH_4 emitted from the surface around the site in the nocturnal boundary layer, since they are not visible for CO. Hence these events are not representative for regional-scale phenomena. The CH_4 levels at COI are generally higher than at HAT by 50 to 100 ppbv. During the episode the CH_4 levels at COI are comparably low at HAT. The CO_2 levels at COI are generally lower than at HAT by 5 to 10 ppmv. During the anomalous episode, the CO_2 levels at COI show an enhancement by 7 ppmv, nearly comparable to at HAT. The temporal variations of CO_2 and CH_4 at COI are negatively correlated with each other, in particular for the low CH_4 and high CO_2 period. The CO_2 rise corresponds well to the CH_4 drop, and vice versa. These features reflect the fact that land surface like eastern Siberia acts as a source for CH_4 while it does as a net sink for CO_2 due to uptake by plants during the summer season. Hence high CH_4 associated with low CO_2 at COI are explainable by the continental influence. The variations of H_2 that has a sink by soil uptake are very similar to CO_2 . The variations of CH_4 , CO_2 , and H_2 at COI and HAT strongly support the meteorological mechanism for CO. This fact also indicates that rapid air mass transport from the Pacific Ocean has considerable impacts on variations and distributions of not only CO but also long-lived GHGs.

CONCLUDING REMARKS

An anomalous summertime episodes for CH_4 , CO_2 , and H_2 as well as CO observed in 2004 at Cape Ochi-ishi in northern Japan are reported and analyzed with a regional chemistry-transport model. The model simulations and backward trajectories indicate that the anomalous event occurred over broad region of Japan. The unusual chemical signatures are associated with rapid transport of pristine air masses from the Pacific Ocean, driven by stronger easterly flows in the summer of 2004. This anomalous transport features have potential impacts on spatial and temporal variations of other trace gases of atmospheric importance.

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