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Concentration variations of total reactive nitrogen and total nitrate during transport to Fukue Island and to Cape Hedo, Japan in the marine boundary layer

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HIGHLIGHTS

- Total odd nitrogen species and total nitrate were measured at two remote sites.
- NO_y and $T.NO_3/NO_y$ were compared to show variation during transport.
- Decreasing NO_y during transport was dominated by dry and wet deposition.
- $T.NO_3/NO_y$ ratio variations depended on air mass age.
- NO_y removal rate was calculated by comparing transport time and NO_y variation.

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ABSTRACT

We conducted continuous measurements of NO_y and total nitrate ($T.NO_3 = HNO_3 + NO_3^-(p)$) at Fukue Island, Nagasaki, and Cape Hedo, Okinawa, Japan. We compared variations of NO_y or $T.NO_3$ concentrations measured at two remote sites when the air masses were originated from the same regions of the Asian Continent. Long-range transport events from the Asian Continent were extracted by CO concentration peaks at Fukue and Hedo and backward trajectory analyses. We compared the transport time difference at two sites from the Asian continent with the ratios of NO_y at Hedo to that at Fukue ($=R(NO_y)$) to find the predominant factor in NO_y removal. $R(NO_y)$ were less than unity and decreased with the transport time difference. The ratios of NO_y/CO at Hedo to those at Fukue ($R(NO_y/CO)$) was assumed to be affected by the deposition process. $R(NO_y/CO)$ showed negative correlation with transport time difference as the same the case of $R(NO_y)$. This indicates that NO_y was mainly removed by deposition rather than dilution. Air mass ages were classified by the ratio of $T.NO_3$ to NO_y at Fukue: $T.NO_3/NO_y < 0.2$ was fresh air, 0.2–0.4 was middle-aged, and greater than 0.4 was aged. The ratios of $T.NO_3/NO_y$ at Hedo to those at Fukue ($R(T.NO_3/NO_y)$) in the fresh air mass were greater than unity. In contrast, $R(T.NO_3/NO_y)$ values in the aged air mass were unity and were less correlated with transport time difference. This indicates that $T.NO_3$ generation proceeded in fresh air mass. On the other hand, $T.NO_3$ generation rate was comparable to removal rate in the aged air mass. According to the relationship between $R(NO_y/CO)$ and transport time difference, the removal rate constant and NO_y lifetime were $(1.24 \pm 0.33) \times 10^{-5}$ s^{-1} and 18–31 h, respectively.

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1. Introduction

Nitrogen oxides are important in atmospheric reactions and have effects on atmospheric, aquatic and biotic environments. Total reactive nitrogen species (NO_y) consist of NO, NO_2, NO_3, N_2O_5, peroxyacyl nitrates, alkyl nitrates, gaseous nitric acid (HNO_3), particulate nitrate (NO_3^-(p)) and others. NO_y have different characteristics in atmospheric reactions; NO_2 is a precursor of tropospheric ozone (Kanaya et al., 2002). HNO_3 and NO_3^-(p) are acidic species and can be transported widely because of their long lifetimes (Takiguchi et al., 2008). HNO_3 and NO_3^-(p) can affect the atmospheric environment in remote areas, owing to long-range transport. HNO_3 is generated by the reaction of OH and NO_2 during daytime (Eq. (1)) (Sadanaga et al., 2006). HNO_3 is also produced by other reactions during nighttime (Eqs. (2)–(4)) (Bertram and Thornton, 2009; Brown et al., 2004):

$$NO_2 + OH + M \rightarrow HNO_3 + M, \quad (1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2, \quad (2)$$

$$NO_2 + NO_3 + M \rightleftarrows N_2O_5 + M, \quad (3)$$

$$N_2O_5 + H_2O(\text{surface}) \rightarrow 2\,HNO_3, \quad (4)$$

where M represents a third body (mainly N_2 and O_2 in the troposphere). NO_3^-(p) is generated by uptake of HNO_3 on the surfaces of dust and sea salt particles (Liu et al., 2007, 2008) or the reaction of HNO_3 with NH_3:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl, \quad (5)$$

$$HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O, \quad (6)$$

$$HNO_3 + NH_3 + M \rightarrow NH_4NO_3 + M. \quad (7)$$

The generation reaction of NH_4NO_3 (Eq. (7)) is reversible, and NH_4NO_3 can be decomposed to regenerate NH_3 and HNO_3 (Eq. (7′)):

$$NH_4NO_3 + M \rightarrow HNO_3 + NH_3 + M \quad (7')$$

Kawakami et al. (2008) have reported that HNO_3 and NO_3^-(p) are difficult to remove by photolysis and thermal decomposition, therefore dry or wet deposition is the major sink (Atkinson et al., 1997). Deposited HNO_3 and NO_3^-(p) may lead to eutrophication of land and surface water and change of biological productivity in the remote area (Barile and Lapointe, 2005). Long-range transported HNO_3 and NO_3^-(p) have a larger effect on the environment in remote areas where NO_x emission is low. The sum of HNO_3 and NO_3^-(p) concentrations (total nitrate, T.NO_3) is important to estimate the effects on the atmospheric environment in remote areas. T.NO_3 is dominated mainly by coarse particulate nitrates (>1 μm) according to the previous measurements at Cape Hedo, Okinawa and Fukue Island, Nagasaki (Takiguchi et al., 2008; Hayami, 2005). The size distribution measured in other remote marine boundary layers showed coarse particulate nitrates are dominated (Xia and Gao, 2010; Matsumoto et al., 1998). Concentration variations of N-containing species have been observed by ground-, aircraft- and ship-based *in-situ* measurements (Zhang et al., 2007; Kawakami et al., 2008). The spatial and temporal variations of these species during transport are mainly estimated by numerical simulation, because concentration variations of nitrogen oxide over the ocean are difficult to be obtained by ground-based measurement (Shepon et al., 2007; Deutsch et al., 2007; Doney et al., 2007). In this paper, the removal rate and chemical transformation of nitrogen oxides during the long-range transport are also estimated by comparison of NO_y and T.NO_3 concentrations between the two observation sites (Okinawa and Nagasaki).

2. Measurement site and method

2.1. Measurement site

NO_y and T.NO_3 have been observed continuously since March 2008 at Cape Hedo, Okinawa (Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS)), and since November 2008 at Fukue Island, Nagasaki. Hedo is located at 26.68°N and 128.15°E. The measurement site is in the village of Kunigami, which has a population of 6000 and is 100 km north of Naha, the largest city in Okinawa. The Fukue measurement site is in northwestern Fukue Island (32.8°N, 128.7°E). The site is 16 km from the central part of the island. There are no large industrial areas on either Fukue Island or Kunigami. Details of both measurement sites were described elsewhere (Takiguchi et al., 2008; Kanaya et al., 2002; Hayami, 2005; Takami et al., 2005). Annual average concentrations of NO_y at Hedo and Fukue in 2010 were 0.98 ± 0.78 and 2.91 ± 2.16 ppbv (parts per billion by volume = 10^{-9}), respectively. This indicates that both observation sites are in remote areas. We analyzed NO_y and T.NO_3 data from January 2009 through December 2010.

2.2. Measurement method at Fukue and Hedo

The concentrations of NO_y and T.NO_3 were measured by the scrubber-difference NO—O_3 chemiluminescence (SD-CL) method (Yamamoto et al., 2001; Sadanaga et al., 2008a; Yuba et al., 2010). The methods at both Fukue and Hedo used two inlet-lines for the air sample, the "NO_y line" (Ch. 1), and "NO_y—T.NO_3 line" (Ch. 2), allowing simultaneous measurements of NO_y and T.NO_3. The NO_y line has a molybdenum reduction catalyst (Mo converter) (Thermo Electron Inc., part No. 9445) heated to 598 K, which reduces NO_y to NO, and then NO is measured by an NO—O_3 chemiluminescent detector (Thermo Electron Inc., model 42C-TL). Williams et al. (1998) reported that an Mo converter can reduce gaseous NO_y to NO. Sadanaga et al. (2008b) reported that the reduction efficiency of particulate nitrates of diameter less than 12 μm was 92.6 ± 2.8% according to the comparison of particulate nitrates measured by the SD-CL method and filter pack. This result indicates that the loss of particulate nitrates in the inlet can be ignored and particulate nitrates can also be reduced by the Mo converter. The NO_y—T.NO_3 line has a polytetrafluorethylene (PTFE) filter (Advantec, PF020) and an annular denuder coated with NaCl, in advance of another Mo converter. The PTFE filter can remove almost all particulate nitrates of diameter greater than 0.3 μm. The NaCl-coated denuder can remove 97.9% of HNO_3 (Sadanaga et al., 2008a). T.NO_3 concentrations were calculated by the difference of signal between Ch.1 and Ch.2. Flow rates of the two lines were regulated to 0.5 L min^{-1} by two mass-flow controllers (KOFLOC, 3660). CO concentrations were measured using a non-dispersive infrared CO analyzer (Thermo Electron Instruments, 48C).

3. Analyses of concentration variations and chemical compositions

3.1. Concurrent transport events to Fukue and to Hedo

The air masses transported from the Asian continent concurrently to Fukue and to Hedo were examined using concentration variations of CO at those two sites. CO and NO_x are mainly generated by fuel combustion, therefore CO concentrations are correlated with anthropogenic emissions of NO_x (Parrish et al., 1991). CO

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