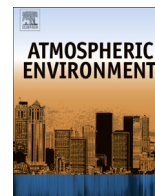




Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

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

Akie Yuba<sup>a,\*,1</sup>, Yasuhiro Sadanaga<sup>a,\*</sup>, Akinori Takami<sup>b</sup>, Shiro Hatakeyama<sup>c</sup>, Yoshihiko Masui<sup>a</sup>, Toshimasa Ohara<sup>b</sup>, Seiichiro Yonemura<sup>d</sup>, Shungo Kato<sup>e</sup>, Yoshizumi Kajii<sup>e,2</sup>, Hiroshi Bandow<sup>a</sup>

<sup>a</sup> Graduate School of Engineering, Osaka Prefecture University 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

<sup>b</sup> National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

<sup>c</sup> Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

<sup>d</sup> National Institute for Agro-Environmental Sciences, 3-1-3 Kannondai, Tsukuba, Ibaraki 350-8604, Japan

<sup>e</sup> Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minamiosawa, Hachioji, Tokyo 192-0397, Japan

### H I G H L I G H T S

- Total odd nitrogen species and total nitrate were measured at two remote sites.
- $\text{NO}_y$  and  $\text{T.NO}_3/\text{NO}_y$  were compared to show variation during transport.
- Decreasing  $\text{NO}_y$  during transport was dominated by dry and wet deposition.
- $\text{T.NO}_3/\text{NO}_y$  ratio variations depended on air mass age.
- $\text{NO}_y$  removal rate was calculated by comparing transport time and  $\text{NO}_y$  variation.

### A R T I C L E I N F O

#### Article history:

Received 29 August 2013

Received in revised form

7 April 2014

Accepted 8 April 2014

Available online xxx

#### Keywords:

Total reactive nitrogen

Long-range transport

Removal rate

Lifetime

East Asia

### A B S T R A C T

We conducted continuous measurements of  $\text{NO}_y$  and total nitrate ( $\text{T.NO}_3 = \text{HNO}_3 + \text{NO}_3^-(\text{p})$ ) at Fukue Island, Nagasaki, and Cape Hedo, Okinawa, Japan. We compared variations of  $\text{NO}_y$  or  $\text{T.NO}_3$  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  $\text{NO}_y$  at Hedo to that at Fukue ( $=R(\text{NO}_y)$ ) to find the predominant factor in  $\text{NO}_y$  removal.  $R(\text{NO}_y)$  were less than unity and decreased with the transport time difference. The ratios of  $\text{NO}_y/\text{CO}$  at Hedo to those at Fukue ( $R(\text{NO}_y/\text{CO})$ ) was assumed to be affected by the deposition process.  $R(\text{NO}_y/\text{CO})$  showed negative correlation with transport time difference as the same the case of  $R(\text{NO}_y)$ . This indicates that  $\text{NO}_y$  was mainly removed by deposition rather than dilution. Air mass ages were classified by the ratio of  $\text{T.NO}_3$  to  $\text{NO}_y$  at Fukue:  $\text{T.NO}_3/\text{NO}_y < 0.2$  was fresh air, 0.2–0.4 was middle-aged, and greater than 0.4 was aged. The ratios of  $\text{T.NO}_3/\text{NO}_y$  at Hedo to those at Fukue ( $R(\text{T.NO}_3/\text{NO}_y)$ ) in the fresh air mass were greater than unity. In contrast,  $R(\text{T.NO}_3/\text{NO}_y)$  values in the aged air mass were unity and were less correlated with transport time difference. This indicates that  $\text{T.NO}_3$  generation proceeded in fresh air mass. On the other hand,  $\text{T.NO}_3$  generation rate was comparable to removal rate in the aged air mass. According to the relationship between  $R(\text{NO}_y/\text{CO})$  and transport time difference, the removal rate constant and  $\text{NO}_y$  lifetime were  $(1.24 \pm 0.33) \times 10^{-5} \text{ s}^{-1}$  and 18–31 h, respectively.

© 2014 Elsevier Ltd. All rights reserved.

\* Corresponding authors.

E-mail addresses: [yuba-a@stelab.nagoya-u.ac.jp](mailto:yuba-a@stelab.nagoya-u.ac.jp) (A. Yuba), [sadanaga@chem.osakafu-u.ac.jp](mailto:sadanaga@chem.osakafu-u.ac.jp) (Y. Sadanaga), [takamia@nies.go.jp](mailto:takamia@nies.go.jp) (A. Takami), [hatashir@cc.tuat.ac.jp](mailto:hatashir@cc.tuat.ac.jp) (S. Hatakeyama), [tohara@nies.go.jp](mailto:tohara@nies.go.jp) (T. Ohara), [yone@affrc.go.jp](mailto:yone@affrc.go.jp) (S. Yonemura), [shungo@tmu.ac.jp](mailto:shungo@tmu.ac.jp) (S. Kato), [kajii.yoshizumi.7e@kyoto-u.ac.jp](mailto:kajii.yoshizumi.7e@kyoto-u.ac.jp) (Y. Kajii), [bandow@chem.osakafu-u.ac.jp](mailto:bandow@chem.osakafu-u.ac.jp) (H. Bandow).

<sup>1</sup> Now at Solar-Terrestrial Environment Laboratory, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan.

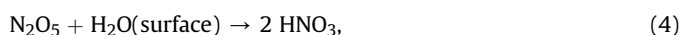
<sup>2</sup> Now at Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan.

<http://dx.doi.org/10.1016/j.atmosenv.2014.04.010>  
1352-2310/© 2014 Elsevier Ltd. All rights reserved.

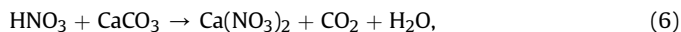
Please cite this article in press as: Yuba, A., et al., Concentration variations of total reactive nitrogen and total nitrate during transport to Fukue Island and to Cape Hedo, Japan in the marine boundary layer, Atmospheric Environment (2014), <http://dx.doi.org/10.1016/j.atmosenv.2014.04.010>

## 1. Introduction

Nitrogen oxides are important in atmospheric reactions and have effects on atmospheric, aquatic and biotic environments. Total reactive nitrogen species ( $\text{NO}_y$ ) consist of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ , peroxyacyl nitrates, alkyl nitrates, gaseous nitric acid ( $\text{HNO}_3$ ), particulate nitrate ( $\text{NO}_3^-$ (p)) and others.  $\text{NO}_y$  have different characteristics in atmospheric reactions;  $\text{NO}_2$  is a precursor of tropospheric ozone (Kanaya et al., 2002).  $\text{HNO}_3$  and  $\text{NO}_3^-$ (p) are acidic species and can be transported widely because of their long lifetimes (Takiguchi et al., 2008).  $\text{HNO}_3$  and  $\text{NO}_3^-$ (p) can affect the atmospheric environment in remote areas, owing to long-range transport.  $\text{HNO}_3$  is generated by the reaction of OH and  $\text{NO}_2$  during daytime (Eq. (1)) (Sadanaga et al., 2006).  $\text{HNO}_3$  is also produced by other reactions during nighttime (Eqs. (2)–(4)) (Bertram and Thornton, 2009; Brown et al., 2004):



where M represents a third body (mainly  $\text{N}_2$  and  $\text{O}_2$  in the troposphere).  $\text{NO}_3^-$ (p) is generated by uptake of  $\text{HNO}_3$  on the surfaces of dust and sea salt particles (Liu et al., 2007, 2008) or the reaction of  $\text{HNO}_3$  with  $\text{NH}_3$ :



The generation reaction of  $\text{NH}_4\text{NO}_3$  (Eq. (7)) is reversible, and  $\text{NH}_4\text{NO}_3$  can be decomposed to regenerate  $\text{NH}_3$  and  $\text{HNO}_3$  (Eq. (7')):



Kawakami et al. (2008) have reported that  $\text{HNO}_3$  and  $\text{NO}_3^-$ (p) are difficult to remove by photolysis and thermal decomposition, therefore dry or wet deposition is the major sink (Atkinson et al., 1997). Deposited  $\text{HNO}_3$  and  $\text{NO}_3^-$ (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  $\text{HNO}_3$  and  $\text{NO}_3^-$ (p) have a larger effect on the environment in remote areas where  $\text{NO}_x$  emission is low. The sum of  $\text{HNO}_3$  and  $\text{NO}_3^-$ (p) concentrations (total nitrate,  $\text{T.NO}_3$ ) is important to estimate the effects on the atmospheric environment in remote areas.  $\text{T.NO}_3$  is dominated mainly by coarse particulate nitrates ( $>1 \mu\text{m}$ ) 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  $\text{NO}_y$  and  $\text{T.NO}_3$  concentrations between the two observation sites (Okinawa and Nagasaki).

## 2. Measurement site and method

### 2.1. Measurement site

$\text{NO}_y$  and  $\text{T.NO}_3$  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  $26.68^\circ\text{N}$  and  $128.15^\circ\text{E}$ . 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 ( $32.8^\circ\text{N}$ ,  $128.7^\circ\text{E}$ ). 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  $\text{NO}_y$  at Hedo and Fukue in 2010 were  $0.98 \pm 0.78$  and  $2.91 \pm 2.16$  ppbv (parts per billion by volume =  $10^{-9}$ ), respectively. This indicates that both observation sites are in remote areas. We analyzed  $\text{NO}_y$  and  $\text{T.NO}_3$  data from January 2009 through December 2010.

### 2.2. Measurement method at Fukue and Hedo

The concentrations of  $\text{NO}_y$  and  $\text{T.NO}_3$  were measured by the scrubber-difference  $\text{NO}-\text{O}_3$  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 “ $\text{NO}_y$  line” (Ch. 1), and “ $\text{NO}_y-\text{T.NO}_3$  line” (Ch. 2), allowing simultaneous measurements of  $\text{NO}_y$  and  $\text{T.NO}_3$ . The  $\text{NO}_y$  line has a molybdenum reduction catalyst (Mo converter) (Thermo Electron Inc., part No. 9445) heated to 598 K, which reduces  $\text{NO}_y$  to  $\text{NO}$ , and then  $\text{NO}$  is measured by an  $\text{NO}-\text{O}_3$  chemiluminescent detector (Thermo Electron Inc., model 42C-TL). Williams et al. (1998) reported that an Mo converter can reduce gaseous  $\text{NO}_y$  to  $\text{NO}$ . Sadanaga et al. (2008b) reported that the reduction efficiency of particulate nitrates of diameter less than  $12 \mu\text{m}$  was  $92.6 \pm 2.8\%$  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  $\text{NO}_y-\text{T.NO}_3$  line has a polytetrafluoroethylene (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  $0.3 \mu\text{m}$ . The NaCl-coated denuder can remove 97.9% of  $\text{HNO}_3$  (Sadanaga et al., 2008a).  $\text{T.NO}_3$  concentrations were calculated by the difference of signal between Ch.1 and Ch.2. Flow rates of the two lines were regulated to  $0.5 \text{ L min}^{-1}$  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  $\text{NO}_x$  are mainly generated by fuel combustion, therefore CO concentrations are correlated with anthropogenic emissions of  $\text{NO}_x$  (Parrish et al., 1991). CO

Download English Version:

<https://daneshyari.com/en/article/6339850>

Download Persian Version:

<https://daneshyari.com/article/6339850>

[Daneshyari.com](https://daneshyari.com)