Reply to Referee #1

We would like to thank the reviewer for providing constructive comments on the manuscript. A detailed description of our revisions is provided below.

General:

• Results are obtained by making use of a MAX-DOAS type of instrument. Please discuss in more detail the reason to use for this study a MAX-DOAS instrument, whereas other methods are available. For example, the in-situ method used in reference 1 (see below) appears to have a much lower (better) detection limit. Reference 1 reports, although for a different geographical region, NO2 volume mixing ratios of approximately 10 pptv for long periods in a row (see e.g. Fig. 8 in this paper). These values are almost a factor of 10 lower than the mode of the PDF reported in this work.

> We agree with the reviewer that there are better instruments for NO₂ measurement. Our primary aim is to establish an automated measurement system (without any calibration system) for use on a vessel by employing a low-power/low-cost spectrometer with an active-type gimbal. As described in the text (p. 6071, lines 122–123), in this study we focus only on NO₂ because it is somewhat easier to retrieve than other components, although MAX-DOAS has the potential to perform simultaneous measurements on several components. After evaluating NO₂ retrieved by this system on a vessel, we develop a retrieval method for other components. Another point is that MAX-DOAS is useful for validating chemical transport models, because it can provide a mean/typical value for a layer (e.g., the mean value for the 0–1 km layer) and it is easy to compare the content with the model results, whereas *in situ* direct measurement can only obtain data at a point and it may be difficult to compare such measurement data with model results.

• It is mentioned that the detection limit of the method used in this study is approximately 0.1 ppbv (p.6078, 1.13-15). This would imply that the MAX-DOAS method cannot be used to determine a reliable PDF of the NO2 volume mixing ratio below this value. From this perspective, Fig. 11 may cause some confusion, since it suggests that values between 0.00 and 0.05 ppbv are very unlikely to be found and that the PDF has a mode around 0.1 ppbv (p. 6078, 1.21). This value for the mode seems to quite high when compared to the values reported in reference 1 (despite the fact that a different region is studied). The mode around 0.1 ppbv may therefore not reflect the mode of the real PDF over the remote ocean, but rather be due to the relatively high detection limit of the measurement technique. Perhaps Fig. 11 could be modified, such that a single bin is used below 0.1 (or 0.2) ppbv.

> Figure 8 shows good agreement (no systematic differences) between the two analyses (460–490 nm and 338–370 nm). At low NO₂ concentrations, both analyses show a maxima/mode around ~0.1 ppbv, with variability of ~0.05–0.1 ppbv. This blurry structure in the case of low concentrations over the remote ocean is also clear in Fig. 11. Consequently, we may say that the

background level over the remote ocean for the 0–1 km layer is ~0.1 \pm 0.1 ppbv. The variability of ~0.05–0.1 ppbv may correspond to the random error of NO₂ concentration over the remote ocean, although the calculated value in Table 2 is much smaller than this (i.e., smaller than ~0.05–0.1 ppbv). Because our original description of "detection limit" may have led to misunderstanding, we revised the relevant text.

• Compared to in-situ observations, a major strength of MAX-DOAS is the ability to measure tropospheric columns. In relation to transport of NO2 (p.6071, 1.3), this quantity is just as relevant as the volume mixing ratio. Please provide a figure with tropospheric NO2 columns (preferably similar to Fig. 11 and for the same subset of all observations), or otherwise mention why it is decided not to include this MAX-DOAS product despite its relevance in this context.

> We agree with the reviewer. We added the tropospheric column values in Table 2.

• A negative correlation is reported between NO2 (425-450 nm) and H2O (p.6076, 1.9-10). This finding is used to support the claim that H2O has a negative impact on the DOAS fit in this particular fitting window. Alternatively, one could hypothesize that the negative correlation is due to a chemical reaction (or a mechanism of reactions) involving both NO2 and H2O. Please provide correlations between H2O from this fitting window (425-450) and NO2 from the two other fitting windows (338-370nm and 460-490nm) to exclude this alternative hypothesis, or otherwise please comment on this point.

> The problem is that the NO₂ DSCD value for 425–450 nm was commonly negative and lower at lower elevation angles (Fig. 7), whereas it was positive for 460–490 nm (figure not shown). The negative values at lower ELs are unlikely to occur in the real atmosphere. The correlation between NO₂ for 460–490 nm (or NO₂ 338–370 nm) and H₂O was positive (figure not shown), as expected from the fact of a longer light path at lower EL. Therefore, the negative correlation in Fig. 7 is not due to a chemical reaction. Note that good agreements were observed between H₂O for 425–450 nm and H₂O for 460–490 nm, and between NO₂ for 460–490 nm and NO₂ for 338–370 nm (Fig. 8).

Note also that similarly negative and low DSCD values were found for the 425–490 nm fitting window (see the reply to the relevant comment by referee #2). These findings are explained in the revised manuscript.

Specific comments

- p.6074, 1.22-25 (Here, DSCD ... collision complex.): Please rephrase.
 - > Change made as suggested.
- p.6076, l.4: Please replace 'cause' by 'case'.
 - > Change made as suggested.

• p.6077, l.8-10: This sentence is a bit confusing, especially the part: 'the temperature dependence of trace gas in tropospheric'. Please rephrase.

> Change made as suggested.

• Fig. 9: The dashed line is not mentioned in the caption or in the text. Please explain it. Is it a linear fit? Which fitting method is used? It does not seem to describe well the higher values.

> We added the relevant information in the caption to Fig. 9.

Reply to Referee #2

We would like to thank the reviewer for carefully assessing our paper. In this study, we developed an instrument for use on ocean vessels by employing an active-type gimbal. We performed the first MAX-DOAS measurements using a compact, low-power/low-cost instrument on a vessel. Because NO₂ content is generally low over the remote ocean, and under such condition, H₂O contributed to the poor DOAS fitting. To our knowledge, this has not been fully recognized in the literature (in urban areas, the 425–450 nm or 425–490 nm fitting windows are likely to be appropriate because NO₂ DSCD is much higher than over the ocean; in fact, the 425–490 nm window was selected during the CINDI campaign). Following the reviewer's comment, we also conducted DOAS analysis using the 425–490 nm window, yielding similar results to those obtained with 425–450 nm.

Instrument and algorithms have been described in recent publications, e.g. Irie et al., 2011. All sensitivity studies do not contain any new information. The temperature dependency of the NO2 cross section is well-known and has been addressed by several authors before (e.g. J. P. Burrows, A. Dehn, B. Deters, S. Himmelmann, A. Richter, S. Voigt, and J. Orphal. Atmospheric remote-sensing reference data from GOME: Part 1. Temperature-dependent absorption cross-sections of NO2 in the 231–794 nm range. J. Quant. Spectrosc. Rad. Transfer, 60:1025–1031, 1998). That water vapour might be an issue in the DOAS fit in particular in regions with high humidity is also not very surprising. E.g. Van Daele et al., JGR, 2005 already discussed the possible impact of interfering species in that wavelength region. To minimize this effect participants of the most recent intercomparison campaign for UV/vis instruments in Cabauw, The Netherlands, agreed on a wavelength window of 425 to 490 nm for the analysis of NO2. Why the authors did not choose this fitting window?

> As noted by the reviewer, a previous study described our instrument and analysis method for measurements on land [i.e., Irie et al., AMT, 2011], but not for measurements from an ocean vessel; consequently, information relevant to measurements from a vessel is presented in this paper. We agree with the reviewer's statement that previous studies have focused on the temperature dependency of the NO_2 cross-section. However, these previous studies were based on satellite measurements rather than ground-based measurements.

One of the reasons for selecting the 460-490 nm window was that the difference between the representative wavelengths for NO₂ and O₄ can be very small, thereby minimizing the wavelength-dependence of air-mass factor information [Irie et al., AMT, 2011]. Following the reviewer's comment, we conducted the analysis by using the 425-490 nm fitting window, yielding similar results to those for 425-450 nm. That is, the correlation between NO₂ DSCD for 425-490 and H₂O DSCD was negative, and the NO₂ DSCD was negative on average; however, the value of NO₂ DSCD was slightly higher for the 425-490 nm window than for 425–450 nm. See Figure A below.



Figure A. As for Fig. 7, but for 425–490 nm.

Further comments: As referee #1 I'm quite sceptical about figure 11, where the authors show the probability function of NO2 concentrations in the boundary layer reporting a maximum at 0.1 ppb. How meaningful is that, when the detection limit of the system is in the same range? > Please see the reply to the relevant comment by referee #1. Fig. 8 shows good agreement between the two analyses of 460–490 nm and 338–370 nm. At low NO₂ concentrations, both analyses show maxima around ~0.1 ppbv, with variability of ~0.05–0.1 ppbv. We may say that the background level over the remote ocean for the 0–1 km layer is ~0.1±0.1 ppbv. The variability of ~0.05–0.1 ppbv may correspond to the random error of NO₂ concentration over the remote ocean. Because our original description of "detection limit" may have led to misunderstanding, we revised the relevant text.

How the authors explain the huge diurnal variation of NO2 e.g. on July 15, 2008? Dilution within the rising boundary layer? Emission peaks?

> Because Yokosuka is an urban site, we consider that such diurnal variation is reasonable; we compared the MAX-DOAS NO₂ for 0–1 km with *in situ* direct measurements performed near our station, and found a strong correlation between the two. The concentration at the surface was almost double that of MAX-DOAS for 0–1 km, but this finding is also reasonable because the source of NO₂ is located near the surface.

1 NO₂ observations over the western Pacific and Indian

2 Ocean by MAX-DOAS on *Kaiyo*, a Japanese research

3 vessel

4

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- 10

11 Abstract

12 Nitrogen dioxide (NO₂) profile retrievals were performed by ship-borne Multi-Axis 13 Differential Optical Absorption Spectroscopy (MAX-DOAS) using a compact/low-power spectrometer on the Japanese research vessel Kaiyo during two ocean cruises around Japan 14 15 and Japan-Bali (Indonesia)-Indian Ocean. DOAS analysis using a 425-450 nm fitting window revealed a clear land-ocean contrast in NO₂ differential slant column densities 16 17 (DSCDs) but poor fitting results and negative values, especially at low elevation angles at low 18 latitudes (<~20N°). The poor fitting resulted in sparse NO₂ volume mixing ratio (VMR) data 19 for the 0–1 km layer after applying our vertical profile retrieval method. In contrast, NO₂ 20 VMRs retrieved using fitting results from 460-490 nm are positive even at low latitudes, 21 while they are reasonably similar to those obtained from 425-450 nm at mid-latitudes. 22 Because NO₂ DSCD for 425–450 nm shows a negative correlation with water vapor (H_2O) 23 DSCD, the poor fitting appears to be due primarily to interference by H_2O . We analyzed a 24 338-370 nm fitting window, which is free from H₂O, and found good agreement between NO₂ VMRs retrieved from 460–490 nm and 338–370 nm, even at low latitudes, at NO₂ 25 VMRs higher than ~ 0.2 ppbv. The results indicate that the background value of NO₂ VMR 26 27 over the western Pacific and Indian Ocean during the cruises was less than ~0.2 ppbv, with occasional enhancement to levels of ~0.2–0.4 ppbv. 28

1 1 Introduction

Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) is a recently
developed remote sensing technique designed for atmospheric aerosol and gas profile
measurements using scattered solar radiation at several elevation angles [e.g., *Hönninger et al.*, 2004; *Wagner et al.*, 2004; *Sinreich et al.*, 2005; *Frieβ et al.*, 2006]. It is useful for
measuring *a priori* profiles for satellite retrievals and for validating chemical transport models.

Recently, multi-platform measurements by MAX-DOAS, such as from aircraft [e.g., *Volkamer et al.*, 2009] and ocean vessels [e.g., *Wagner et al.*, 2007; *Volkamer et al.*, 2009; *Sinreich et al.*, 2010], have been developed. Ship-borne measurements provide information on
background concentrations over the ocean and can be used to clarify transport processes from
polluted areas to the ocean, emissions from ocean to air, and emissions from ships. However,
even in the case of NO₂, spatial and temporal variations over the ocean are not fully
understood, due in part to the difficulties encountered in measuring low concentrations.

In general, MAX-DOAS measures the trace gas content over a long light path (up to ~10 km) with low elevation angles, thereby enabling the detection of low concentrations of the components of interest or weak absorbers near the ground. Thus, MAX-DOAS is useful for quantifying tropospheric trace gas over remote areas/ocean, where concentrations of the component of interest are generally low. As an example, NO₂ measurements by MAX-DOAS have been conducted at a remote Japanese island, Okinawa Island, yielding concentrations as low as ~0.2 ppbv [*Takashima et al.*, 2011].

21 Since 2007, the Japan Agency for Marine-Earth Science and Technology/Research Institute for Global Change (JAMSTEC/RIGC) has been conducting continuous MAX-DOAS 22 23 measurements at several sites in Asia and Russia using compact, low-power spectrometers [e.g., Irie et al., 2009, 2011; Takashima et al., 2009, 2011]. The instrument has been validated 24 25 with other instruments, yielding differences of less than $\sim 10\%$ for NO₂ and oxygen dimer (O₄) differential slant column densities (DSCDs) [Roscoe et al., 2010]. Here, we report on the 26 27 development of a MAX-DOAS instrument for use on ocean vessels, using an active-type gimbal to keep the telescope horizontal. 28

As a first step, we focus only on NO₂ because it is somewhat easier to retrieve than other components, although MAX-DOAS has the potential to perform simultaneous profile measurements on aerosol and several gas components, such as NO₂, water vapor (H₂O), SO₂, IO, BrO, HCHO, and CHOCHO [e.g., *Irie et al.*, 2011]. We also performed a sensitivity analysis with various fitting windows for NO₂ retrieval, because the sensitivity has yet to be
 fully investigated.

3

4 2 Measurements

5 2.1 Two ocean cruises on the Japanese R/V Kaiyo

6 Aerosol and gas measurements by MAX-DOAS were continuously conducted during two 7 ocean cruises on the Japanese R/V Kaiyo of JAMSTEC. The first cruise (KY08-05) was 8 undertaken during 10-17 July 2008 from Yura (Wakayama Prefecture; 135.11E°, 33.96N°) to 9 Yokosuka (Kanagawa Prefecture; 139.68E°, 35.28N°) in Japan (Figure 1). The second cruise (KY09-01) was conducted from 5 February to 10 May 2009 from Yokohama (Japan; 10 139.65E°, 35.45N°) to Bari (Indonesia; 115.21E°, 8.74S°), the Indian Ocean, Bari again, and 11 12 finally returning to Yokohama (Fig. 1). We did not perform measurements in the territorial 13 waters of Guam (United States) during cruise KY09-01 because we did not obtain permission from the relevant authorities. Note that this study is the first to report MAX-DOAS 14 15 measurements over the western Pacific and Indian Ocean.

16 **2.2** Compact, low-power instruments for MAX-DOAS

17 A compact, low-power and low-cost instrument for MAX-DOAS has been developed by 18 JAMSTEC/RIGC and PREDE Co., Ltd. (Tokyo, Japan), and the instrument has been used for 19 continuous measurements at several sites in Asia and Russia. In this study, we developed the 20 instrument for use on ocean vessels by employing an active-type gimbal to keep the telescope horizontal on the vessel. The gimbal-mounted telescope unit was installed on the top deck of 21 the vessel and the line of sight was toward the starboard side (Figure 2). The movable mirror 22 23 of the telescope unit rotates through six different elevation angles (ELs) of 3°, 5°, 10°, 20°, 30° , and 70° every 30 min, with a field of view of ~0.9°. 24

For the first cruise (KY08-05), a miniaturized UV/visible spectrometer (USB4000, Ocean Optics) was installed inside the telescope unit, and the spectra data were recorded by a laptop located indoors on the vessel. The telescope and spectrometer were connected to each other by a 1-m (KY08-05) or 10-m (the second cruise, KY09-01) fiber optic bundle cable that consists of seven cores with radii of 100 μ m. The typical exposure time was 0.08 seconds, and the spectra data were averaged and recorded every second by a laptop located indoors. Measurements were made over the spectral range of 230 to 560 nm with a spectral resolution of ~0.6–0.7 nm. To suppress background noise and wavelength shifts of the spectrum, the temperature of the spectrometer was kept at 45°C for KY08-05 and at 40°C for KY09-01, for the entire observation period. For KY09-01, the spectrometer (USB4000) was installed indoors, aiming at better temperature control.

For comparison with *in situ* measurements, we use MAX-DOAS data obtained at Yokosuka, Japan ($35.32^{\circ}N$, $139.65^{\circ}E$), which have been measured continuously since April 2007 using basically the same instrument as that used at Okinawa [*Takashima et al.*, 2009], employing a USB4000 spectrometer and 5-m fiber optics. The azimuth angle of the observations was set to +37.0 from north (the plus sign indicates a clockwise direction). A movable mirror turns through six different ELs (3° , 5° , 10° , 20° , 30° , and 90°) every 30 min, with a field of view of <1°. The spectrometer was kept 20°C.

13

14 **2.3 Active gimbal system**

To keep the telescope unit horizontal on the vessel, it was mounted on an active-gimbal developed by JAMSTEC/RIGC and PREDE. In this system, the gimbal is controlled horizontally by reducing the difference between the standard horizontal level and the present level for both the roll and pitch angles, using two inclinometers (SEIKA Mikrosystemtechnik GmbH, N2).

To monitor how well the gimbal maintains a horizontal orientation, we installed another sensor inside the telescope unit (Honeywell, HMR3500) and recorded the roll and pitch angels at a repetition rate of 5 Hz. For the spectral analysis, spectra data were selected with a criterion for the elevation angle to be within $\pm 0.2^{\circ}$ of the target (see below). In addition, we recorded the heading of the vessel, the roll and pitch angles of the vessel, longitude, latitude, and time.

Figure 3 shows an example of the pitch and roll angles of the vessel and the telescope unit. The telescope unit was installed on the starboard-side (roll) direction of the viewing azimuth angle. The figure shows that the orientation of the telescope unit was generally controlled well even when the roll and pitch angles of the vessel reached >2 degrees. During the KY08-05 and KY09-01 cruises, the telescope was kept within $\pm 0.2^{\circ}$ of the target elevation angle for ~60% of the time. In general, in the case of a regular cycle of ship motion (e.g., a sine function), the gimbal performs well in controlling the horizontal level, but it is commonly unable to control the horizontal level in the case of an irregular cycle. Fig. 3 shows an
example of variation of the maximum intensity of the spectrum, in which we can see change
in the intensity corresponding to change in the elevation angle (from 3° to 5°).

4

5 3 Data analysis

6 The measured 1-second spectra were selected with a criterion for the elevation angle to be 7 within $\pm 0.2^{\circ}$ of the target elevation angle and averaged every 1 minute. Here, we excluded 8 spectra data for periods when we changed the target elevation angle of the telescope-unit 9 mirror. The azimuth of the heading of the vessel, longitude, altitude were also averaged every 10 1 minute.

To retrieve a vertical profile of NO₂ concentration, we used the Japanese MAX-DOAS profile retrieval algorithm, version 1 (JM1) [*Irie et al.*, 2011]. The averaged spectrum was analyzed using the DOAS method [*Platt*, 1994], employing nonlinear least squares spectral fitting [*Rodgers*, 2000] to derive the DSCD of the oxygen collision complex (O₂-O₂ or O₄) and NO₂. Here, DSCD is defined as the difference between the column concentration integrated along the sunlight path measured at a low EL (EL<70°) and that at EL=70°.

The box air mass factor (A_{box}) , which is defined as the air mass factor for a given layer, was derived from the O₄ DSCD inversion with the Monte Carlo Atmospheric Radiative Transfer Simulator (MCARaTS) [*Iwabuchi*, 2006]. Using the A_{box}, we retrieved NO₂ profiles in the lower troposphere with a vertical step of 1 km from the NO₂ DSCD measurements. Details of the retrieval algorithm have been described elsewhere [e.g., *Irie et al.*, 2008, 2011; *Takashima et al.*, 2011].

23 We used NO₂ absorption cross-section data at 294 K of Vandaele et al. [1998], O₄ data 24 of Hermans et al. (http://spectrolab.aeronomie.be/o2.htm), H₂O data of the year 2004 edition of the High-Resolution Transmission (HITRAN) database (fitting windows and absorbers 25 26 fitted in DOAS analysis are shown in Table 1). In the retrieval, we applied the 460-490 nm 27 standard fitting window of JM1, but we also used the 425-450 nm window, which is one of the most widely used for NO2 retrieval [e.g., Boersma et al., 2004]. We also performed an 28 29 additional sensitivity analysis using a fitting window of 338–370 nm, and using different NO₂ 30 cross-section data at 220 K [Vandaele et al., 1998].

1 4 Results and discussion

2 4.1 NO₂ retrieval for three fitting windows

3 First, the NO₂ profile was retrieved using the JM1 algorithm with a standard fitting window of 4 460-490 nm. Figure 4 shows NO₂ concentrations for the 0-1 km layer, close to mainland 5 Japan (the area with highest concentrations during the cruises). A clear land-ocean contrast is 6 observed: during KY08-05, NO₂ concentrations were low over the ocean (<1 ppbv), with no clear diurnal variations; in contrast, concentrations were high (>1 ppbv) and with a clear 7 8 diurnal variation near the coast or when in port (19-21 July 2009, Fig. 4a). Although the 9 location of the port at the end of the KY08-05 cruise was located ~5 km from the Yokosuka 10 site, there is generally good agreement between the two datasets, with similar diurnal maxima (in the morning/evening) and minima (~1-2 ppbv around noon). For the KY09-01 cruise, the 11 port (the vessel) was located ~14 km from the Yokosuka site (e.g., 5-8 Feb), but similar 12 diurnal variations were also observed. These findings indicate successful NO₂ measurements 13 from onboard the vessel, at least for the high concentrations observed near Japan/mid-14 15 latitudes.

DOAS analysis using a 425–450 nm fitting window also revealed a clear land–ocean contrast in NO₂ DSCDs, with quite good agreement over the Japan region (Figure 5a, c), but poor fitting results (Figure 6c) and negative DSCD values, especially at low elevation angles at low latitudes (in the case of Fig. 6c, the NO₂ DSCD was positive). In general, lower NO₂ DSCD was obtained at lower ELs (see the following paragraph and Figure 7). This resulted in sparse NO₂ volume mixing ratio (VMR) data after applying our vertical profile retrieval methods (Fig. 5).

23 To consider the effect of H₂O in the fitting for the 425-450 nm window, the relationship between H₂O DSCD and NO₂ DSCD was investigated (Fig. 7); there is a clear 24 25 negative correlation between the two. At the same time the fitting residual is high for high 26 H₂O DSCD (not shown). These results suggest that the poor fitting at 425–450 nm is due in part to the H₂O interference in the fitting. At lower elevation angles, the amount of H₂O is 27 28 generally high; thus, the fitting is generally poor. It should be noted that the H₂O DSCD for 425-450 nm is consistent with that for 460-490 nm (figure not shown; a correlation 29 30 coefficient (r) for EL=3° was 0.98). We also investigated other relationships and found a negative correlation between H₂O DSCD and the Ring effect (not shown), suggesting that the 31 32 Ring effect also contributed to the poor fitting (Fig. 6c).

Note that we also retrieved NO₂ by using the 425–490 nm window, which was used
 for intercomparison during the Cabauw Intercomparison Campaign of Nitrogen Dioxide
 measuring Instruments (CINDI) campaign at Cabauw, the Netherlands [Roscoe et al., 2010].
 This retrieval yielded poor fitting results and negative DSCD values, as for the 425–450 nm
 window (figures not shown).

6 We next employed an ultraviolet (UV) fitting window (338-370 nm), which is 7 completely free from absorption by H₂O. Here, we considered O₄ for 338–370 nm to derive NO₂ VMR. Although the retrieval errors were higher than in the case of 460–490 nm (Table 8 9 2; see Section 4.2) due in part to the lower intensity (particularly in the morning/evening), 10 there is generally good agreement between NO₂ (460–490 nm) and NO₂ (338–370 nm) 11 concentrations for concentrations higher than ~ 0.2 ppbv (Figure 8). This result suggests that 12 our MAX-DOAS can at least detect NO₂ concentrations as low as ~0.2 ppbv for the 0–1 km 13 layer. The results also indicate that the background level over the western Pacific and Indian 14 Ocean during the cruise was less than ~0.2 ppbv for the 0-1 km layer. The 460-490 nm 15 standard fitting window of JM1 seems to be particularly useful for the retrieval of low NO₂ 16 concentrations over the ocean and in H₂O-rich areas.

17

18 **4.2 Sensitivity analysis and error estimates**

19 We next conducted a DOAS analysis using the NO₂ cross-section of 220 K as a sensitivity 20 test of cross-section temperature dependence, revealing a strong correlation between NO₂ 21 concentration using 220 and 294 K cross-sections (R = 0.99) but NO₂ concentration for 220 K 22 systematically underestimates NO₂ for 294 K of \sim 30% (Figure 9). Because the actual 23 temperature at 0–1 km is unlikely to have been as cold as 220 K, the sensitivity to the actual 24 temperature variation would have been much smaller than that obtained from the DOAS 25 analysis. Sanders [1996] and more recently Boersma et al. [2004] reported the temperature dependence of the NO₂ cross-section in tropospheric NO₂ retrieval from satellite observations. 26 27 Subsequently, Richter et al. (pers. comm.) indicated that the retrieved NO₂ concentration 28 using a 425–450 nm window shows a linear increase with applying a warmer cross-section, 29 because the NO₂ cross-section at high temperatures is smaller than that at low temperatures. 30 In their analysis, the temperature dependence is $\sim 0.36\%$ /K for the 425–450 nm fitting window, 31 which is similar to our result of $\sim 30\%/(294-220 \text{ K}) = 0.4\%/\text{K}$, despite the different fitting window used in the two studies. 32

1 Random and systematic errors for each MAX-DOAS measurement were estimated 2 following *Irie et al.* [2011] and *Takashima et al.* [2011]. The random error was estimated 3 from the residual in the fitting of the NO₂ DSCD, and the systematic error was estimated 4 assuming an additional 30% change in aerosol optical depth (AOD), for which A_{box} varies 5 accordingly.

6 The estimated random and systematic errors in the NO₂ concentration for the 460–490 7 nm standard window during the KY09-01 cruise over the ocean were 0.009 ppbv (7.6%) and 8 0.015 ppbv (12.6%), respectively (Table 2). The total error was as small as ~15% (~0.18 9 ppbv), even in the case of low background values over the remote ocean. These errors were of 10 a similar order to those for the retrieval with the 220 K NO₂ cross-section. Note that the 11 coldest and warmest temperatures below 1 km during KY09-01 were about -20 K (with 12 respect to 294 K) near Japan in February and +3 K in the tropics. These correspond to 13 systematic errors of -8% and +1%, respectively, based on the derived cross-section 14 temperature dependence of 0.4%/K. The range of this systematic error (~9% for 23 K) is of a 15 smaller order than the total error.

For UV, the errors were higher than those for 460–490 nm, due in part to lower intensity in our observation system, particularly in the morning/evening. The errors obtained near land (in the Japan region) for 460–490 nm are similar to those for 425–450 nm.

19 The errors over the ocean during KY09-01 are largely consistent with those reported 20 previously for a remote island (Okinawa Island, Japan; for which the systematic and random errors were 12.8% and 13.0%, respectively) by Takashima et al. [2011], although these error 21 22 values (i.e., of the present and previous studies) are much smaller than the background value 23 over the ocean (< ~ 0.2 ppbv). Note that over the remote ocean, variability in NO₂ 24 concentrations was less than ~0.1 ppbv at 0–1 km, as assessed from a time series (not shown) and from Figure 10. This variability could reflect the random error in NO₂ concentrations 25 26 over the remote ocean, although the calculated variability (Table 2) is much smaller than this 27 value (i.e., smaller than ~0.1 ppbv).

28

4.3 NO₂ variations over the remote ocean

We next discuss NO₂ variations over the remote ocean retrieved by JM1 with a standard 460– 490 nm fitting window for concentrations > 0.2 ppbv. Over the remote ocean during cruise KY09-01, NO₂ concentrations were generally very low (<0.5 ppbv at 0–1 km; Fig. 10). The

probability density function (PDF) for <1 ppbv during KY09-01 (Figure 11) yields a mode of 1 2 $\sim 0.1\pm 0.1$ ppbv, which appears to correspond to the background level over the remote ocean 3 (<0.2 ppbv). This value is similar to those obtained by direct measurements by airplane during 4 the TRACE-P observation campaign, which yielded NO₂ concentrations of less than ~ 0.05 5 ppbv over the western Pacific in the marine boundary layer during P3-B Flight 08 (data are 6 available from the NASA TRACE-P Web site at http://www-gte.larc.nasa.gov). Fig. 11 shows a skewed distribution of NO2 concentrations with some enhancements, including NO2 7 8 concentrations (~0.2–0.4 ppbv) higher than the background level, in which the fitting residual for NO₂ concentrations of 0.2–0.4 ppbv was as small as $\sim 8.1 \times 10^{-4}$ (the median value; an 9 example of the fitting is shown in Fig. 6b). 10

11 These enhancements over the remote ocean are also apparent in Fig. 10, with spatial variability. In some cases, the air mass was affected by polluted air (e.g., southwest of Guam, 12 13 where the air mass was advected from the direction of Guam), but this was infrequently observed. We also tested for the effect of emissions from the research vessel. To avoid such 14 15 contamination, we analyzed wind data recorded on the vessel and removed potentially contaminated NO₂ data before repeating the analysis; however, no significant difference was 16 17 observed in the PDF compared with the entire dataset. The enhancement may also reflect 18 emissions from ships over the ocean or long-range rapid transport from polluted areas, as 19 suggested by Takashima et al. [2011]. Additional measurements over the ocean are required 20 to quantify the background levels and the nature of spatial-temporal variations over the ocean.

21

22 5 Summary

NO₂ measurements by ship-borne MAX-DOAS with a compact/low-power spectrometer were conducted during two ocean cruises, around Japan and Japan–Bali (Indonesia)–Indian Ocean. The telescope was mounted on an active gimbal to ensure it was kept horizontal; it was successfully kept within $\pm 0.2^{\circ}$ of the target elevation angle for ~60% of the time.

To test the sensitivity of the fitting window for NO₂ retrieval, focusing on low NO₂ concentration over the ocean, we considered windows of 425–450, 425–490, 460–490, and 338–370 nm. DOAS analysis using a 425–450 nm fitting window, which is widely used for NO₂ retrieval, revealed a clear land–ocean contrast in NO₂ DSCDs but poor fitting results and negative values, especially at low elevation angles at low latitudes. Similar results were also obtained for the 425–490 nm window. The negative values resulted in sparse NO₂ VMR data,

1 whereas, NO₂ DSCDs retrieved using fitting results from the 460–490 nm standard fitting 2 window of JM1 are positive even at low latitudes, and NO₂ VMRs are very similar to those 3 obtained using a window of 425-450 nm at mid-latitudes. Because the NO₂ DSCD for 425-4 450 nm has a negative correlation with the H₂O DSCD (Fig. 7), the poor fitting appears to be 5 due to the H₂O interference in the fitting. We analyzed a 338–370 nm fitting window, which is completely free from absorption by H₂O, and found a good agreement between NO₂ VMRs 6 7 retrieved from 460–490 nm and 338–370 nm, even at low-latitudes, at NO₂ VMRs higher than 8 ~ 0.2 ppbv (Fig. 8). Consequently, the 460–490 nm fitting window seems to be useful for the 9 retrieval of low NO₂ concentrations over the ocean.

We also performed a sensitivity analysis using different NO₂ cross-sections (294 K and 220 K) for the 460–490 nm fitting window. The correlation between the two NO₂ concentrations was reasonably good, but NO₂ for 220 K systematically underestimates NO₂ for 294 K by \sim 30% (Fig. 9).

The results indicate that the background value of NO_2 over the western Pacific and Indian Ocean during the cruises was less than 0.2 ppbv, but occasional enhancement to values of ~0.2–0.4 ppbv was often observed, exceeding the background level. On rare occasions, the air mass was affected by polluted air.

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Fig. 1. Ship routes during the two ocean cruises by the Japanese R/V Kaiyo (KY0805 and KY0901).





Fig. 2. Photographs of the outdoor unit of the MAX-DOAS instrument installed on the top
deck of the R/V *Kaiyo*. The telescope unit was mounted on an active gimbal to ensure it was
kept horizontal. The yellow arrow indicates the travelling direction of the ship. The line of
sight of the instrument was toward starboard.



Fig. 3. Example of pitch (top) and roll (bottom) angles recorded for the vessel (red line) and
the active gimbal (blue line). The yellow line indicates the maximum count of the spectrum.
At approximately 180 seconds, the viewing elevation angle was changed from 3° to 5°.



4 Fig. 4. NO2 variations observed by MAX-DOAS on the R/V Kaiyo (blue) and at Yokosuka 5 (red) for 0-1 km during the three observation periods, focusing on the Japan region. Error bars indicate the total error of NO₂ measurements. Also shown is the latitude of the vessel 6 7 (green line).



Fig. 5. As for Fig. 3, but for NO₂ concentrations measured on the R/V *Kaiyo* at 0–1 km for
fitting windows of 460–490 nm (red) and 425–450 nm (black).



Fig. 6. Example of the result of nonlinear least squares spectral fitting for O₄ and NO₂
observed on 14 April 2009 on the R/V *Kaiyo* at 141.7°E, 11.1°N. For the NO₂ fittings, we
used three fitting windows (460–490, 425–450, and 336–370 nm, as shown in b, c, and d,
respectively). The red line shows the cross-section scaled to the spectrum (black) measured by
DOAS. The spectra are plotted in terms of differential optical depth from the reference
spectrum (elevation angle of 70°).



3 Fig. 7. Scatter plot of H₂O DSCD versus NO₂ DSCD for a fitting window of 425–450 nm at

- 4 elevation angles of 3° , 5° , 10° , 20° and 30° .



3 Fig. 8. Scatter plot of NO₂ concentrations for fitting windows of 460–490 and 338–370 nm

4 during cruise KY0901.

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Fig. 9. Scatter plot of NO₂ concentrations for cross-sections at 294 and 220 K during cruise
KY0901. Solid and dashed lines represent the 1:1 relationship and the linear least-squares fit,

- 5 respectively.





5 Fig. 10. NO₂ variations over the ocean for 0–1 km during the KY09-01 cruise. Pink lines

6 show the 48-hour backward trajectory for NO₂ concentrations higher than 0.3 ppbv. The

7 trajectory was calculated using meteorological analysis data from the Japan Meteorological

8 Agency's Climate Data Assimilation System (JCDAS) reanalysis with a kinematic trajectory

9 model.

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- 4 MAX-DOAS for concentrations of <1 ppbv. The distribution has been normalized so that the
- 5 integrated probability is equal to 1.

- 2 Table 1. Fitting windows and absorbers fitted in DOAS analysis. The representative
- 3 wavelength for each target component is the cross-section-weighted mean wavelength over
- 4 the fitting window.

Target component	Fitting window (nm)	Absorbers fitted	Representative wavelength (nm)
NO ₂ (474 nm)	460–490	O ₃ , NO ₂ , H ₂ O, O ₄ , Ring	474
NO ₂ (437 nm)	425–450	O ₃ , NO ₂ , H ₂ O, O ₄ , Ring	437
NO ₂ (452 nm)	425–490	O ₃ , NO ₂ , H ₂ O, O ₄ , Ring	452
NO ₂ (354 nm)	338-370	O ₃ , NO ₂ , HCHO, BrO, O ₄ , Ring	354

- 1 Table 2. (a) Median values of retrieved NO₂ (volume mixing ratios (VMR)) in the 0–1 km
- 2 layer; ppbv) and estimated errors (ppbv) during cruise KY09-01. The values for the
- 3 tropospheric column $[10^{15} \text{ molecules cm}^{-2}]$ are shown in (b). "Ocean" indicates NO₂
- 4 concentrations of less than 1 ppbv $/10^{15}$ molecules cm⁻²; "land" indicates latitudes higher than
- 5 33° north.
- 6 (a)

Component	VMR (ppbv)	Random error	Systematic error	Total error	# of data
NO_2 (476 nm) all	0.140	0.010	0.0176	0.020	735
NO_2 (476 nm) ocean	0.119	0.009	0.015	0.018	634
NO_2 (476 nm) land	8.858	0.179	0.951	1.050	88
NO_2 (437 nm) land	3.795	0.229	1.176	1.240	87
NO ₂ (220K)* all	0.118	0.009	0.015	0.017	698
NO_2 (220K)* ocean	0.102	0.008	0.013	0.015	602
NO_2 (354 nm) all	0.204	0.023	0.032	0.043	607
NO_2 (354 nm) ocean	0.145	0.017	0.023	0.030	497
NO_2 (354 nm) land	9.673	0.259	1.483	1.713	93

8 (b)

Component	Trop. Column	Random error	Systematic error	Total error	# of data
NO_2 (476 nm) all	0.536	0.016	0.063	0.067	735
NO_2 (476 nm) ocean	0.400	0.011	0.046	0.048	517
NO_2 (476 nm) land	27.38	0.26	0.781	0.877	88