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Ship-based MAX-DOAS measurements of tropospheric NO_2 and SO_2 in the South China and Sulu Sea

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HIGHLIGHTS

- A profile retrieval approach to derive tropospheric NO_2 vertical columns is applied.
- The simple geometric approximation using 15° measurements can also be used.
- Time series of NO_2 and SO_2 are in good agreement in a busy shipping lane.

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ABSTRACT

In November 2011, ship-based Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements were performed within the SHIVA campaign on board RV Sonne in the South China and Sulu Sea. Spectral measurements for a total of eleven days could be used to retrieve tropospheric slant column densities (SCDs) of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) in the marine environment. The NO_2 fit was performed following recommendations developed during the CINDI campaign and adapted for the ship-based measurements. We found that the inclusion of a cross section for liquid water and an empirical correction spectrum accounting for the effects of liquid water and vibrational Raman scattering (VRS) slightly improved the NO_2 fit quality, especially at lower elevation angles and for lower NO_2 levels. The conversion of SCDs into tropospheric NO_2 vertical columns (TVC NO_2) has been achieved using both a simple geometric approach and the Bremian advanced MAX-DOAS Retrieval Algorithm (BREAM), which is based on the optimal estimation method and accounts for atmospheric radiative transfer. We found good agreement between the geometric approach using the 15° measurements and BREAM, revealing that measurements at 15° elevation angle can be used for retrieving TVC NO_2 in tropical marine environments when SZA is smaller than 75°. As expected, the values of TVC NO_2 were generally low ($<0.5 \times 10^{15}$ molec cm^{-2}) when no sources of NO_x were in proximity to the RV Sonne. However, we found increased values of TVC NO_2 ($>2 \times 10^{15}$ molec cm^{-2}) in the morning when the RV Sonne was heading along the coast of Borneo. This is in good agreement with satellite measurements. The results of the profile retrieval show that the boundary layer values of NO_2 are <30 pptv in the open and clean tropical marine environment. Interestingly, we also found elevated tropospheric SO_2 amounts for measurements taken in a busy shipping lane, consistent with the time series of tropospheric NO_2.

1. Introduction

Nitrogen oxides ($NO_x = NO + NO_2$) are well known and significant pollutants in the troposphere. Nitric oxide (NO) in the atmosphere is readily converted into the more harmful nitrogen dioxide (NO_2) by reaction with ozone (O_3). The reaction of NO_2 with the hydroxyl radical (OH) to form nitric acid (HNO_3) is the major loss process of NO_x during daytime. Loss processes at night are related to the formation of nitrate ion (NO_3) and dinitrogen pentoxide (N_2O_5) and the subsequent heterogeneous reactions of N_2O_5 at the surface and on aerosols. The main sources of NO_x are attributed to high-temperature combustion processes (e.g. fossil fuel burning, accidental and intentional biomass burning), soil microbial activity, and lightning (Lee et al., 1997).

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Sulfur dioxide (SO_2) is a main constituent in the tropospheric sulfur cycle. Besides the natural emissions of dimethylsulfide (DMS), the anthropogenic emissions of SO_2 are quantitatively the most important emissions in the sulfur cycle (Berglen et al., 2004).

The amounts and distributions of NO_2 and SO_2 can be retrieved from active and passive remote sensing techniques in the ultraviolet (UV) and visible regions of the electromagnetic spectrum (e.g. Brewer et al., 1973). The Differential Optical Absorption Spectroscopy (DOAS) method (Perner and Platt, 1979), which is selected for the detection of NO_2 and SO_2 in this study, is a widely used technique in the UV/visible and was initially applied to the detection of tropospheric trace gases by active remote sensing using artificial light sources. However, the DOAS method is also applicable for passive remote sensing using direct and scattered sunlight as light source (Platt and Stutz, 2008).

After successful application of the zenith scattered light DOAS method, which mainly yields stratospheric trace gas amounts (Noxon, 1975; Solomon et al., 1987; Richter et al., 1999; Wittrock et al., 2000), the development of Multi-Axis (MAX) DOAS allowed for the extension of the technique to tropospheric trace gases and aerosols by observing scattered sunlight at different viewing directions (Hönninger et al., 2004; Wagner et al., 2004; Wittrock et al., 2004).

Although MAX-DOAS is relatively simple to operate, the interpretation of the data requires detailed information about the radiation transport in the atmosphere, especially in terms of aerosol scattering (Mie scattering). For example, Wagner et al. (2004) developed a method for deriving atmospheric aerosol profiles by using MAX-DOAS measurements of the oxygen dimer (O_4) under clear sky conditions. They demonstrated that the O_4 measurements are sensitive to the aerosol extinction close to the ground and suggested the potential to retrieve aerosol profiles by the use of radiative transfer models such as SCIATRAN (Rozanov et al., 2005) and McArtim (Deutschmann et al., 2011).

Ship-based MAX-DOAS measurements of NO_2 amounts have so far been focused on both remote and coastal marine environments in the Indian and Pacific Ocean to obtain boundary layer background conditions. Peters et al. (2012) reported NO_2 background conditions <50 pptv in the remote Western Pacific boundary layer, with tropospheric NO_2 columns rarely exceeding the detection limit of the instrument. Higher values of up to 200 pptv were estimated from MAX-DOAS observations on board the Japanese research vessel Kaiyo in the western Pacific and Indian Ocean boundary layer (Takashima et al., 2012), presumably being influenced by anthropogenic sources. However, during the NASA Pacific Exploratory Mission (PEM) Tropics B field experiment, aircraft in-situ measurements of NO_2 over the clean Pacific yielded values <10 pptv in the boundary layer (Browell et al., 2001). Consequently, the detection limit of the MAX-DOAS instrument (30–50 pptv) may be too large for actual measurements of NO_2 background values in the boundary layer. Nevertheless, the MAX-DOAS technique has an important benefit in retrieving tropospheric profile information of trace gases (see Sect. 4.4). While the focus of these previous studies was on NO_2 amounts, SO_2 has received much less attention. However, SO_2 emissions in the open sea are high because of the high sulfur contents in heavy fuels often used by ships in international waters (Endresen et al., 2005).

The Southeast Asian region experiences rapid environmental changes with some of the highest rates of deforestation in humid tropical forests as observed within the last two decades (Achard et al., 2002; Miettinen et al., 2011). Large areas of natural forest have been replaced by agricultural land, especially oil palm plantations. Miettinen et al. (2011) estimated the loss of the total forest area in insular Southeast Asia to be in the order of 10% between 2000 and 2010 and emphasize the continuing deforestation in this region.

In recent years, there has been an increasing interest on studying the effect of land use changes on tropospheric chemistry in tropical regions. MacKenzie et al. (2011) observed tropospheric trace gases over a rainforest and an oil palm site on Borneo Island. The results show that NO_x mixing ratios over the oil palm plantation were higher by a factor of 1.5 resulting from nitrogen fertilizer application and on-site palm oil processing. Rising concentrations of NO_x and volatile organic compounds (VOCs) over these plantations have increased the concentrations of some photochemical pollutants and could eventually increase tropospheric O_3 levels due to further industrialization and economic development (Hewitt et al., 2009). In addition to land use changes, international shipping emissions in the South China Sea are strongly driven by the increasing Asian trade volume (De Ruyter De Wildt et al., 2012).

The purpose of this manuscript is to report on daytime tropospheric NO_2 vertical columns (TVC NO_2) and profiles as well as SO_2 slant columns measured by a ship-based MAX-DOAS instrument in the coastal and open waters of the South China and Sulu Sea in November 2011. TVC NO_2 is retrieved by the profile inversion method BREAM and compared to TVC NO_2 as obtained from a geometric approach and from satellite instruments.

The MAX-DOAS measurements have been performed as part of the SHIVA ship-based campaign, which is briefly introduced and described in Sect. 2. The MAX-DOAS instrument and the retrieval of tropospheric NO_2 columns and profiles are introduced in Sect. 3. The results of this study for NO_2 and SO_2 are presented in Sect. 4 and summarized in Sect. 5. The satellite-based instruments and data products as well as the HYbrid Single-Particle Lagrangian

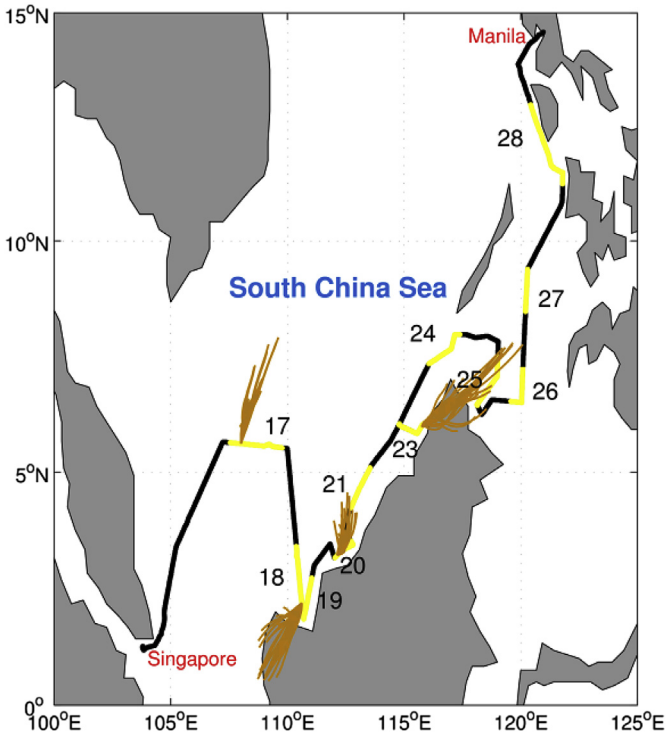

Fig. 1. Cruise track of the RV Sonne during SHIVA (black line), departing from Singapore on 15th November 2011 and arriving in Manila, Philippines on 29th November 2011. The sections of the cruise track highlighted in yellow indicate the distances traveled by the ship between the first and last daytime MAX-DOAS measurements presented in this study. The brown lines show ensembles of computed 12 h backward trajectories for selected case studies with TVC $NO_2 > 2 \times 10^{15}$ molec cm^{-2} (see Sect. 4.3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)