Car MAX-DOAS observation of NO_2 and comparison with OMI satellite data in the west coastal areas of Korean peninsula

Jihyo Chong[1], Young J. Kim[1,*], Myojeong Gu[2], Thomas Wagner[2], and Chul Han Song[1]
[1]*Advanced Environmental Monitoring Research Center, Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology, 1 Oryong dong, Buk-gu, Gwangju 500-712,Republic of Korea*
[2]*Max-Planck-Institute for Chemistry, Mainz 55128 Germany*
*corresponding author: yjkim@gist.ac.kr

ABSTRACT

For the mobile observations measurements in the west coastal areas of Korean peninsula, the Mini-MAX-DOAS instruments was mounted on the roof top of a mobile lab vehicle with the telescope mounted parallel to the driving direction, pointing forward. The measurements were conducted from 21 to 24 December 2010, following the west coastal areas from Gomso harbor (35.59E, 126.61N) to Gunsan harbor (35.98E, 126.67N). The total round-trip distance was 164 km. Aerosol particles were also measured at every 10 km for 5~10 mins. The DOAS measurements were carried out on the move as well as during the stop. The Mini-MAX-DOAS is a fully automated, light weighted spectrometer (13 cm×19 cm×14 cm) designed for the spectral analysis of scattered sunlight. It consists of a sealed aluminum box containing the entrance optics, a fiber coupled spectrograph and the controlling electronics. A stepper motor mounted outside the box rotates the whole instrument to control the elevation of the viewing angle. The sequence of elevation angles was chosen 4×20 degree, 1×45 degree, and 1×90 degree and the duration of an individual measurement was about 30 s. A handy GPS was used to track the coordinates of the route along which the observations were made. During car MAX-DOAS observations, high elevation angles have been used to avoid shades from nearby obstacles such as trees. The measured spectra are analyzed by using WinDOAS software. A wavelength range 400–419 nm was selected for the analysis. The wavelength calibration was performed based on a high resolution solar spectrum. The output of the spectral analysis is the slant column density (SCD), the integrated trace gas concentration along the light path through the atmosphere. Since a measured spectrum is used as Fraunhofer reference, the retrieval result represents the difference of the SCDs of the measurement at low elevation angle and the Fraunhofer reference spectrum taken at 90 degree elevation, which is so called differential SCD or DSCD.

For the determination of the tropospheric vertical column density (VCD), the air mass factor (AMF) is retrieved approximated by the so called geometric approximation. The tropospheric AMF was found to be 1.9 and 0.41 for elevation angles of 20 degree and 45 degree, respectively. The tropospheric NO_2 VCDs derived from car MAX-DOAS were compared directly to the satellite observations. The DOMINO product, v1.02, http://www.temis.nl/airpollution/no2.html, was used. Car MAX-DOAS VCD was in good agreement with OMI tropospheric VCD on most days. However, OMI tropospheric VCD was much higher than that of car MAX-DOAS on 23 December 2010. One probable reason for this discrepancy is that on that day air with enhanced NO_2 concentrations was transported over the measurement site from China. At least part of the polluted air masses are probably located in the free troposphere, for which the MAX-DOAS observations are less sensitive while the sensitivity of the OMI observations increase. Also, the car MAX-DOAS observations cover only relatively small fractions of the individual ground pixels. The car MAX-DOAS observations reveal much finer spatial patterns with stronger spatial gradients, which are not resolved from the OMI data.

INTRODUCTION

The measurements of atmospheric trace gases are important for monitoring the air quality and for understanding the radiative forcing and its impact on climate. Currently, large uncertainties still exist with respect to the total emissions of pollutants and their impact on local, regional, and possibly also global scale. Nitrogen oxides (NO_x = NO + NO_2) is involved in chemical reactions that lead to catalytic ozone formation in the troposphere. NOx is also harmful to vegetation and human health. Short-term exposure causes airway responsiveness while long-term exposure leads to malfunction of the human immune system and respiratory infections (US Environmental Protection Agency, 2003). Measurements of NO_2 emitted from the stack of industrial facility and exit of traffic vehicles can be performed using direct sampling methods, in situ monitoring methods, or remote sensing techniques. The Differential Optical Absorption Spectroscopy (DOAS) technique has been used to measure the absorption features of many trace species in a light path between an UV source and a detector (Platt, 1994). Besides active DOAS, also passive DOAS measurements are performed, e.g. using scatted sunlight. Such measurements yield slant column densities (SCDs) of the respective absorbers. Through the incorporation of multi-axis viewing geometries, information on the profile and spatial distribution of trace gases can also be retrieved by the MAX-DOAS technique. This research describes the application of car MAX-DOAS in the west coastal areas of Korean peninsula, which measures the scattered sunlight at three viewing angles.

MAX-DOAS OBSERVATIONS AND DATA ANALYSIS

MAX-DOAS instrument

The MAX-DOAS technique detects the scattered sunlight under different elevation angles to study the vertical distribution of atmospheric trace gases. The technique yields slant column densities (SCDs) by analysing the signal integrated along the light path at each elevation angle and a reference spectrum measured at 90˚. A mini MAX-DOAS instrument (Hönninger and Platt, 2002; Lee et al., 2009) was built, which is a weatherproof and light-weighted instrument. The MAX-DOAS system mainly consists of a small aluminium box containing a miniature spectrograph and a telescope. The miniature spectrograph (OceanOptics USB2000, cross Czerny-Turner type, 1/f = 2.2) consists of a grating (2,400 grooves/mm) yielding a spectral range of 289 to 431 nm (with 0.7 nm FWHM spectral resolution) and a CCD detector (2,048 pixels at 14 μm center-to-center spacing), which was coupled to a 12-bit ADC connected to a laptop computer via USB interface. The spectrometer was kept at 10°C by thermoelectric cooling to reduce the thermal noise. The MAX-DOAS box was attached directly to a stepper motor, allowing sequential measurements of scattered sunlight at various elevation angles. The system was operated using the DOASIS software (Kraus, 2006) developed at the Institute of Environmental Physics, University of Heidelberg, Germany.

Overview on car MAX-DOAS measurements

For the mobile observations measurements in the west coastal areas of Korean peninsula, the mini MAX-DOAS instrument was mounted on the roof top of a car with the telescope mounted parallel to the driving direction, pointing forward. The car MAX-DOAS measurement was conducted from 21 to 24 December 2010, following the west coastal areas from Gomso harbor (35.59E, 126.61N) to Gunsan harbor (35.98E, 126.67N). The routes are shown in Fig. 1 for all the four days (21, 22, 23, and 24 December 2010). The sequence of elevation angles was chosen as 4×20 degree, 1×45 degree, and 1×90 degree and the duration of an individual measurement was about 30 s. A handy GPS was used to track the coordinates of the route along which the observations were made. In contrast to MAX-DOAS observations at fixed places, higher elevation angels were used to avoid shades from nearby obstacles such as trees for car MAX-DOAS observations. From such high elevation angles usually no profile information can be retrieved, but the total tropospheric trace gas column density can be obtained. Measurements at high elevation angles are less affected by aerosol than observations at more low elevation angles (Shaiganfar et al., 2011).

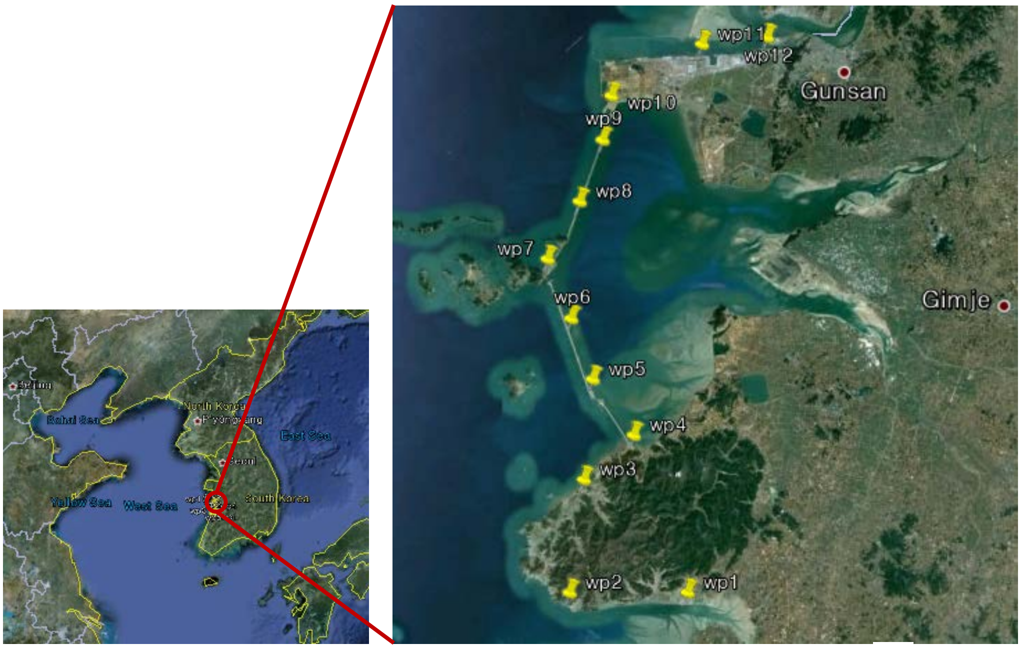

Fig. 1. Driving routes in the west coastal areas from Gomso harbor (wp1) to Gunsan harbor (wp12).

Spectral analysis

The DOAS spectra were calibrated by fitting them to a high resolution solar reference spectrum (Kurucz et al., 1984). Slant Colum Densities (SCDs) of NO_2 are derived from the calibrated DOAS spectra using the WinDOAS V2.10 software (van Roozendael and Fayt, 2001). Several trace gas absorption cross sections (NO_2 at 294K (Vandaele et al., 1998), O_4 at 296K (Greenblatt et al., 1990), as well as a Fraunhofer reference spectrum, a Ring spectrum (calculated from the Fraunhofer spectrum) and a polynomial of fourth order) were included in the spectral fitting process.

Since a measured spectrum is used as Fraunhofer reference, the retrieval result represents the difference of the SCDs of the measurement at low elevation angle and the Fraunhofer reference spectrum taken at 90 degree elevation, the so called differential SCD or DSCD. We have considered elevation angles (α) of 21 and 22 for measurements during December 2010. DSCDs with RMS of residuals smaller than 2.5×10^{-3} were considered.

Estimation of the tropospheric VCD

To determine the SCD of a measurement, the $SCD_{Fraunhofer}$ (together with the change of the stratospheric SCD) has to be added to the DSCD (Wagner et al., 2010). The VCD_{trop} is obtained from the SCD by dividing by the air mass factor (AMF).

For the determination of tropospheric the vertical column density (VCD), usually the AMF is retrieved from radiative transfer simulations (Solomon et al., 1987), but here the so called geometric approximation (Brinksma et al., 2008) is used. The tropospheric AMF was found to be 1.92 and 0.41 for elevation angles of 20 degree and 45 degree, respectively. Depending on the aerosol load, cloud condition and vertical trace gas profile, the true AMF can show substantial deviations from the geometric approximation. However, NO_2 is generally located near the surface (Shaiganfar et al., 2011).

RESULTS AND DISCUSSIONS

During the measurement period, NO_2 differential slant column densities (DSCDs) were determined for two different elevation angles on December 2010 (Figure 2). NO_2 differential slant column densities (DSCDs) were observed with car MAX-DOAS from 21 to 24 December 2010. The average NO_2 DSCD of 20 degree elevation angles on 21 to 24 December 2010 were $3.15\pm1.07\times10^{16}$, $2.78\pm1.55\times10^{16}$, $2.33\pm0.78\times10^{16}$, and $5.56\pm5.94\times10^{15}$ molecules/cm^2, respectively. The average NO_2 DSCD of 45 degree elevation angles on 21 to 24 December 2010 were $1.09\pm0.33\times10^{16}$, $6.90\pm4.36\times10^{15}$, $6.60\pm4.62\times10^{15}$, and $6.60\pm4.62\times10^{15}$ molecules/cm^2, respectively.

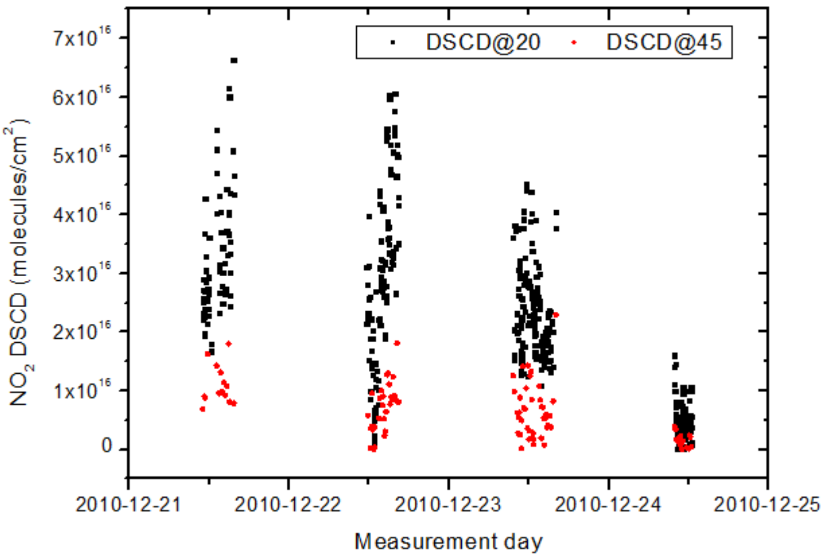

Fig. 2. Temporal variations in the NO_2 DSCD from 21 to 24 December 2010

Figure 3 shows the retrieved variations of car MAX-DOAS NO_2 VCD on 21 December 2010 as a function of locations. As can be seen in Figure 3, the NO_2 VCD increased at polluted areas at that day. On the other hand, it was higher nearby way point 4. The vertical column densities of NO_2 were derived using 20 degree elevation angle.

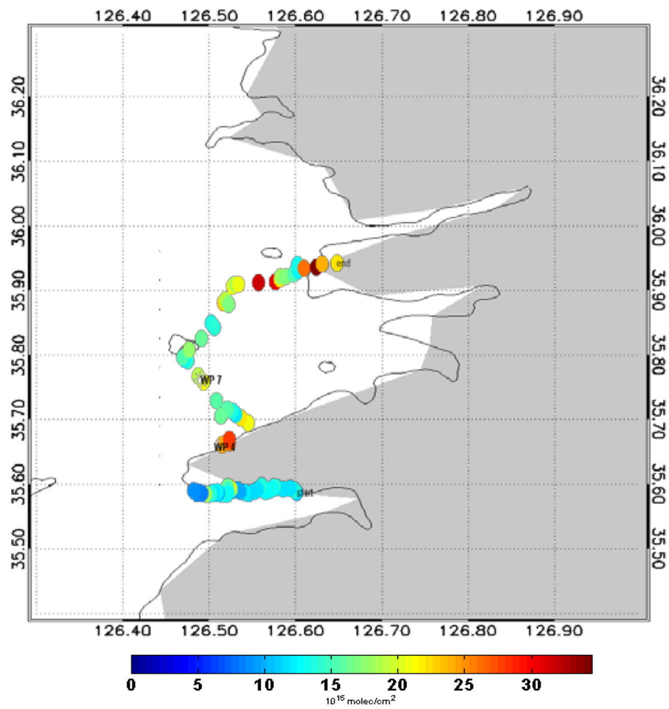

Fig. 3. Temporal NO_2 VCD variations of car MAX-DOAS on 21 Dec. 2010

Comparison with OMI satellite data

We compare the results from the car MAX-DOAS measurements to OMI satellite observations. The NO_2 VCDs derived from car MAX-DOAS were compared directly to the satellite observations. The DOMINO product, v1.02, http://www.temis.nl/airpollution/no2.html (Boersma et al., 2007) of satellite observations was used. Comparison between car MAX-DOAS NO_2 VCD and Ozone Monitoring Instrument (OMI) tropospheric NO_2 VCD is presented in Figure 4. The OMI tropospheric vertical column was in good agreement with car MAX-DOAS VCD except 23 December 2010. Based on the air mass backward trajectory, the air mass came from the Northwest on 23 December, which indicates long range transport from China. At least part of the polluted air masses is probably located in the free troposphere, for which the MAX-DOAS observations are less sensitive while the sensitivity of the OMI observations increases.

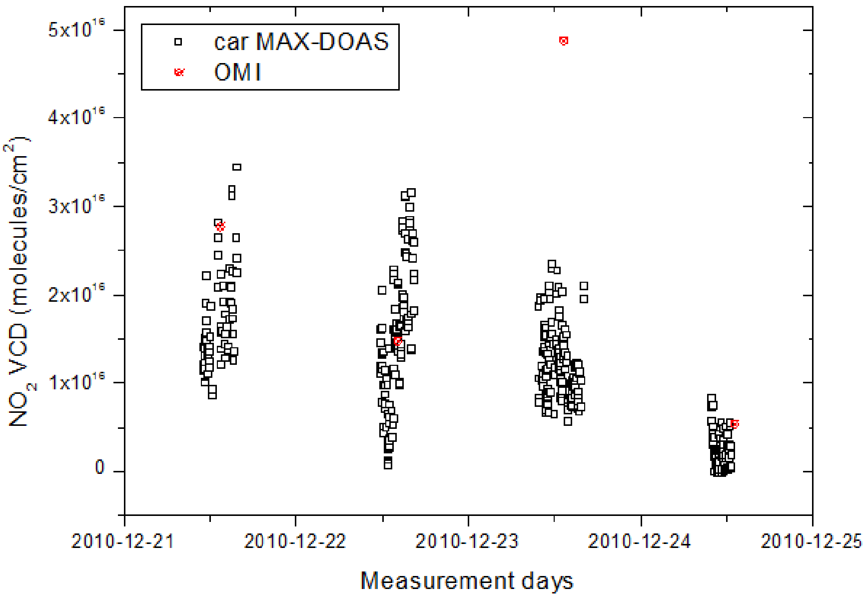

Fig. 4. NO_2 Vertical Column Densities (VCDs) from car MAX-DOAS and OMI on Aura satellite on 21-24 December 2010

CONCLUSION

Remote sensing of the reactive trace species, NO_2 was made using the car MAX-DOAS technique at the western coastal areas in Korean peninsula from 21 to 24 December 2010. The car MAX-DOAS measurements were used for the validation of tropospheric OMI NO_2 VCDs. OMI observations were chosen because of its relatively small pixel sizes. Comparison between car MAX-DOAS and Ozone Monitoring Instrument (OMI) tropospheric NO_2 vertical column densities during the measurement period was made. Daily OMI tropospheric slant column density varied from 0.54 to 4.87×10^{16} molecules/cm^2 while car MAX-DOAS NO_2 VCDs varied from 1.64, 1.44, 1.21, and 0.24×10^{16} molecules/cm^2, respectively. The comparison of absolute values shows overall a fair agreement. However, the discrepancies were especially large during episodes of long range transport from China.

ACKNOWLEDGEMENTS

This research was supported by the Eco-Innovation Project 2012000160004 from Korean Ministry of Environment through the Advanced Environmental Monitoring Research Center. We acknowledge the free use of tropospheric NO_2 column data from the OMI sensor from www.temis.nl. Many thanks to Reza Shaiganfar for giving many comments on analysis.

REFERENCES

Brinksma, E. J., Pinardi, G., Volten, H., Braak, R., Richter, A., Sch¨onhardt, A.,Van Roozendael, M., Fayt, C., Hermans, C., Dirksen, RJ., Vlemmix, T., Berkhout, A. J. C., Swart, D. P. J., O¨ tjen, H., Wittrock, F., Wagner, T., Ibrahim, O. W., de Leeuw, G., Moerman, M., Curier, R. L., Celarier, E. A., Knap, W. H., Veefkind, J. P., Eskes, H. J., Allaart, M., Rothe, R., Piters, A. J. M., and Levelt, P. F.: The 2005 and 2006 DANDELIONS NO2 and Aerosol Validation Campaigns, J. Geophys. Res., 113, D16S46, doi:10.1029/2007JD008808, 2008.

Boersma, K. F., Eskes, H. J., Veefkind, J. P., Brinksma, E. J., van der A, R. J., Sneep, M., van den Oord, G. H. J., Levelt, P. F., Stammes, P., Gleason, J. F., and Bucsela, E. J.: Near-real time retrieval of tropospheric NO2 from OMI, Atmos. Chem. Phys., 7, 2103–2118, doi:10.5194/acp-7-2103-2007, 2007.

Greenblatt, G. D., J. J. Orlando, J. B. Burkholder, and A. R. Ravishankara: Absorption measurements of oxygen between 330 and 1140 nm, J. Geophysical. Res., 95(D11), 18,577-518,582, 1990.

Hermans, C., Vandaele, A. C., Carleer, M., Fally, S., Colin, R., Jenouvrier, A., Coquart, B., and M´erienne, M.-F.: Absorption Cross-Sections of Atmospheric Constituents, NO2, O2, and H2O, Environ. Sci. Pollut. Res., 6, 151–158, 1999.

Hönninger, G. and Platt, U.: Observations of BrO and its vertical distribution during surface ozone depletion at Alert, *Atm. Env.*, 36, 2481–2489, 2002.

Kraus, S., DOASIS - A Framework Design for DOAS. Shaker Verlag Aachen, ISBN-10:3832254528, 2006.

Kurucz, R. L., Furenlid, I., Brault, J., and Testerman, L.: Solar flux atlas from 296nm to 1300 nm, National Solar Observatory Atlas No. 1, Office of University publisher, Harvard University, Cambridge, 1984.

Lee Hanlim, Kim Y.J., Irie H., Noh Youngmin, Lee Chulkyu, Kim Yeosook, and Chun Kee. J., Retrieval of aerosol extinction in the lower troposphere based on UV MAX-DOAS measurements. *Aerosol Science and Technology*, 43:502-509, 2009

Platt U., Differential optical absorption spectroscopy (DOAS), in *Monitoring by Spectroscopic Techniques* (ed. Sigrist, M.) 27-84 (Wiley & Sons, New York, 1994.

Shaiganfar, R., S. Beirle, M. Sharma, A. Chauhan, R. P. Singh, and T. Wagner, Estimation of NOx emissions from Delhi using Car MAX-DOAS observations and comparison with OMI satellite data, Atmos. Chem. Phys., 11, 10871–10887, 2011.

Solomon, S., Schmeltekopf, A. L., and Sanders, R. W.: On the interpretation of zenith sky absorption measurements, J. Geophys. Res., 92, 8311–8319, doi:10.1029/JD092iD07p08311, 1987.

US Environmental Protection Agency. National Air Quality and Emissions Trends Report 2003. Research Triangle Park, NC, 2003.

Vandaele, A. C., C. Hermans, P. C. Simon, M. Carleer, R. Colin, S. Fally, M. F. Merienne, A. J.enouvrier, and B. Coquart: Measurements of the NO2 absorption cross-section from 42 000 cm^{-1} to 10 000 cm^{-1} (238-1000 nm) at 220K and 294K, J. Quant. Spectros. Ra., 59(3-5), 171-184, 1998.

Van Roozendael M. and Fayt C. *WinDOAS 2.1 Software User Manual*; Uccle, IASB/BIRA, 2001.

Wagner, T., Ibrahim, O., Shaiganfar, R., and Platt, U.: Mobile MAX-DOAS observations of tropospheric trace gases, Atmos. Meas. Tech., 3, 129–140, doi:10.5194/amt-3-129-2010, 2010.

Chong, J., Gu, M., Jeoung, H., and Kim, Y.J., “Retrieval of NO2 Vertical Profile in the Troposphere by MAX-DOAS Technique over Cabauw, Netherlands During the 2009 CINDI Campaign,” Proc. of the 8th International Symposium on Advanced Environmental Monitoring, June 2010, pp. 72-78, 2010.