Derivation of the Ambient Nitrogen Dioxide Mixing Ratio over a Traffic Road Site Based on Simultaneous Measurements Using a Ground-based UV Scanning Spectrograph

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(Received November 1, 2010 : revised January 10, 2011 : accepted January 10, 2011)

Simultaneous measurements using a scanning spectrograph system and transmissometer were performed for the first time over an urban site in Gwangju, Korea, to derive the ambient NO₂ volume mixing ratio. The differential slant column densities retrieved from the scanning spectrograph system were converted to volume mixing ratios using the light traveling distance along the scanning line of sight derived from the transmissometer light extinction coefficients. To assess the performance of this system, we compared the derived NO₂ volume mixing ratios with those measured by an \textit{in situ} chemiluminescence monitor under various atmospheric conditions. For a cloudless atmosphere, the linear correlation coefficient (R) between the two data sets (i.e., data derived from the scanning spectrograph and from the \textit{in situ} monitor) was 0.81; the value for a cloudy atmosphere was 0.69. The two sets of NO₂ volume mixing ratios were also compared for various wind speeds. We also consider the measurement errors, as estimated from an error propagation analysis.

\textbf{Keywords} : Spectrograph, Passive remote sensing, Trace gas measurement, NO₂

\textbf{OCIS codes} : (280.0280) Remote sensing and sensors; (280.1120) Air pollution monitoring

\section{I. INTRODUCTION}

An understanding of the distribution of trace gases is required for constructing chemical transport models in urban areas. However, it is difficult to monitor the dispersion and distribution of ambient trace gas species. It is especially challenging to identify the spatial distribution of trace gases emitted from moving sources in an environment that contains complex structures, such as urban sites, for which high spatial and temporal resolution is required to identify the spatial distribution of pollutants. Many recent studies have demonstrated that both passive and active optical remote-sensing techniques can be applied to monitor trace gases with high temporal and spatial resolution [1-11].

Passive remote sensing techniques, which utilize scattered sunlight as a light source, have been widely used to...
monitor various trace gas species at sites for which access is limited. This approach has the advantage of recording light signals in any direction, because of the utilization of ubiquitous scattered sunlight. This is in contrast to other types of remote sensing techniques, including FTIR, for which the viewing direction is limited because direct natural light sources are used, such as direct sunlight. In addition, passive remote sensing techniques can only provide trace gas information in terms of column density because information on the light traveling distance between the detector and the last scattering location is unknown. Consequently, information on the light path length is important because it enables the conversion of the column density of trace gases to the volume mixing ratio. The merit of combining scanning spectrograph and transmissometer measurements is capability of retrieving surface trace gases in a distance of several kilometers in 360° horizontal directions. Additionally, mixing ratios of multi gases such as NO₂, SO₂, and HCHO can be simultaneously derived while in-situ monitors need the number of instruments to measure the corresponding number of trace gases.

In this study, we describe simultaneous measurements of traffic NO₂ mixing ratios using a scanning spectrograph system and transmissometer. The proposed measurement technique is applied to a traffic road site in Gwangju, Korea. The accuracy of the obtained data was assessed by comparison with data measured by an in situ monitor, for clear and cloudy atmospheric conditions and for various wind speeds over a period of approximately 1 month.

II. MEASUREMENTS AND NO₂ RETRIEVAL

The measurement system consists of a transmissometer and a scanning spectrograph equipped with a single array CCD detector. The scanning spectrograph device is composed of entrance optics, a small Czerny–Turner spectrograph, and a stepper motor unit (Fig. 1). The entrance optics consists of a quartz lens coupled to an optical fiber. The lens, which collects the scattered sunlight into an optical fiber, has a focal length of 40 mm and diameter of 20 mm. The optical fiber transfers the collected light onto the spectrograph entrance. The spectrograph (Ocean optics USB2000) covers the wavelengths between 289 and 431 nm with a spectral resolution of 0.7 nm on a charge coupled device (CCD) detector (Sony ILX511, 2,048 pixels). A Peltier cooler was attached to a spectrograph plate to reduce the dark current of the CCD detector and to maintain a constant spectrograph temperature (5±0.5°C).

Light extinction coefficients were obtained using a transmissometer (LPV-2, OPTEC) comprising a light transmitter and a receiver. The light receiver was installed near the site of the UV spectrograph, while the light transmitter was located at 0.7 km from the light receiver, across a local traffic road (Fig. 2). The transmissometer provided light extinction information centered at a wavelength of 550±50 nm [13]. The transmissometer measurements were performed concurrently with the scanning spectrograph measurements.

The scanning spectrograph system was operated for approximately 1 month, from 1 May to 4 June 2009 in Gwangju, Korea. The scanning spectrograph device was operated between 06:00 and 18:00 local time (LT) on the rooftop of the Advanced Photonics Research Institute building (35.13°N, 126.50°E). The viewing azimuth angle of the spectrograph scanner was 237°, pointing across a local traffic road. The scanning spectrograph was installed in an aluminum box connected to the stepper motor, which allowed the device to sequentially record scattered sunlight signals at elevation angles (EAs) of 3°, 10°, 20°, 30°, and 90° above the...
horizon during the measurement period. Scanning by the spectograph was performed hourly in an automated measurement loop, with each loop taking 10–20 minutes to scan the prescribed EAs. The measured spectra were analyzed to quantify the NO2 slant column density (SCD) based on the specific structured absorption features in the UV wavelength range [14].

Since the transmissometer measures light extinction coefficient at 0° EA, it would have been best for the spectograph to record spectra at 0° EA in order to reduce discrepancy in measurement geometries. However, spectra measured at 3° EA are best in terms of representing surface NO2 since lower EAs than 3° could possibly have led to shortened light path length along the lines of sight due to nearby surface obstacles with 0.43° filed of instrumental view. NO2 SCDs were derived by analyzing the recorded scattered sunlight signals collected at 3° EA, based on the DOAS technique [14–16]. The dark current and offset signals of the single array CCD detector, recorded before and after daily measurements, were removed from each of the collected scattered sunlight spectra. The pixel to wavelength calibration of the spectra was performed by fitting the collected spectra to a solar reference spectrum [17]. The wavelength interval between 390 and 417.5 nm was used to retrieve the NO2 SCDs. The spectrum recorded at around noon on May 28 was used as the reference spectrum. A 2nd-order polynomial was fitted to the data to account for broadband structured attenuations, including Rayleigh effects due to air molecules and Mie scattering due to atmospheric aerosol. Ring spectra [18] accounting for rotational Raman scattering effects were calculated from the reference spectra using the DOASIS software developed by Heidelberg University, Germany. NO2 reference absorption cross-section spectra [19] were convoluted with the instrumental function to adapt the spectral resolution of the scanning spectrograph system, as described previously [14].

Fig. 3 shows an absorption cross-section of NO2 [18], the reference spectrum, and the ring spectrum simultaneously fitted to the measured spectra using WinDOAS V2.10 [20] based on a nonlinear least-squares method [14, 21]. SCDs were then obtained from the following equation.

$$
\chi^2 = \sum_{\lambda} \left( \frac{I_{\text{measured}}(\lambda) - (\sigma_{\text{NO}_2}(\lambda) \cdot SCD_{\text{NO}_2} + \sigma_{\text{Ring}}(\lambda) \cdot SCD_{\text{Ring}})}{I_{\text{measured}}(\lambda)} \right)^2 
$$

where $I_{\text{reference}}$ and $I_{\text{measured}}$ denote a reference and measured spectrum, respectively. Examples of $I_{\text{reference}}$ and $I_{\text{measured}}$ are plotted in Fig. 3 (a). In Eq. (1), $\sigma_{\text{NO}_2}$ and $\sigma_{\text{Ring}}$ denote a respectively and SCDs of NO2 and Ring slant column densities, respectively. A NO2 absorption cross section ($\sigma_{\text{NO}_2}$) and calculated ring spectrum ($\sigma_{\text{Ring}}$) multiplied by unknown NO2 and Ring SCDs, respectively are plotted in Figure 3(b) and (d), respectively. Eq. (1) can be solved using the nonlinear least-squares (NLLS) method [13, 20]. In Eq. (1), $\tau_{\text{Residual}}$, an example of which is plotted in Fig. 3 (c), accounts for residual from NLLS optical density fitting using Eq. (1). The measured spectra at 3° EA were evaluated with the zenith spectrum ($\alpha = 90°$) in the same measurement loop, $n$. Differential slant column density (DSCD) is defined as follows:

$$
DSCD \left(n, \alpha \right) = SCD \left(n, \alpha \right) - SCD \left(n, 90° \right) 
$$

where $SCD(n, \alpha)$ denotes SCD at an EA of $\alpha$ in the same measurement loop, $n$. Eq. (2) shows how to remove contribution of stratospheric NO2 from the total measured NO2 SCD since this new technique is introduced to derive tropospheric NO2 mixing ratio. The quantity of DSCD in Eq. (2) is equal to the amount of tropospheric trace gas without the contribution of stratospheric NO2.

Fig. 4 shows the procedure for retrieving the NO2 volume mixing ratio based on the NO2 DSCD and the light extinction coefficient. The light path length was obtained using 1/\$\beta_{\text{ext}}$ at 405 nm (Fig. 5). The NO2 volume mixing ratios were then derived by dividing the NO2 DSCDs measured at an EA of 3° by the light path lengths, and multiplying the resulting concentrations by a constant for conversion of concentration into mixing ratio. Ångstrom exponent information,
FIG. 4. Procedure for the retrieval of the NO\textsubscript{2} volume mixing ratio using data obtained from simultaneous measurements by a scanning spectrograph system, a transmissometer, and a sunphotometer. Sunphotometer data are not needed for retrieval of the NO\textsubscript{2} mixing ratio if the transmissometer measures the light extinction coefficients at the same wavelength as those of the scanning spectrograph system.

FIG. 5. Temporal variations in light path length (km) derived from transmissometer measurements at Gwangju during the measurement period (1 May to 4 June 2009).

FIG. 6. Temporal variations in DSCD values obtained from scanning spectrograph measurements at Gwangju during the measurement period (1 May to 4 June 2009).

FIG. 7. Temporal variations in NO\textsubscript{2} volume mixing ratios derived by simultaneous measurements using a scanning spectrograph system and a transmissometer, compared with values measured by an \textit{in situ} chemiluminescence monitor at Gwangju during the measurement period (1 May to 4 June 2009).

III. RESULTS

Fig. 6 shows temporal variations in the NO\textsubscript{2} DSCDs retrieved at an EA of 3° during the measurement period. The maximum and minimum NO\textsubscript{2} DSCD values were $5.70 \times 10^{17}$ and $4.83 \times 10^{16}$ molec cm\textsuperscript{-2}, respectively. Fig. 7 shows temporal variations in the NO\textsubscript{2} volume mixing ratio as obtained from sunphotometer measurements, was also included to convert the light extinction coefficients at 550 nm to those at 405 nm. However, information on the Ångstrom exponent is not necessary if the transmissometer provides the light extinction coefficient at a wavelength that is also covered by the scanning spectrograph device. The errors associated with obtaining LPL can be reduced if a transmissometer provides the light extinction coefficient at a wavelength that is also covered by the scanning spectrograph.
measured by the scanning spectrograph and by the in situ chemiluminescence monitor (Ecotech, EC9841A). Linear regression of the two data sets revealed a linear correlation coefficient (R) of 0.73, and the scatter of the correlation was within ~35% throughout the entire measurement period (Fig. 8).

To assess the performance of the simultaneous measurement technique under cloudy conditions, we compared the NO2 volume mixing ratios obtained from the scanning spectrograph and the in situ monitor for both cloudless and cloudy atmospheric conditions (Fig. 9). Fig. 9(a) shows the results of a linear regression between the two sets of NO2 volume mixing ratios for cloudless conditions, which yielded a relatively high R value of 0.81 and reduced scatter (within the ~30% range) compared with the entire measurement period (R = 0.73, scatter within 35%). The discrepancies between the two datasets under cloudless conditions are ascribed to geometrical differences between the two sets of measurements.

Fig. 9(b) shows the NO2 volume mixing ratios obtained from the scanning spectrograph plotted against those measured in situ under cloudy conditions, yielding an R value of 0.69, which is lower than that obtained under clear conditions. The scatter of the correlation under cloudy conditions is similar to that for the entire measurement period, which indicates that cloudy conditions influence the retrieved NO2 volume mixing ratio derived from the scanning spectrograph. However, the discrepancy in the measured NO2 volume mixing ratio between the two measurement techniques must be understood in terms of the measured quantity and measurement geometry, including the physical extent of the target area. In addition, the in situ chemiluminescence measurements may overestimate the NO2 volume mixing ratio due to interference from NO3, especially from HNO3 and peroxyacetyl nitrate (PAN).

We also assessed the influence of wind speed on the discrepancy between the NO2 volume mixing ratios obtained from spectrograph measurements and in situ measurements, considering three ambient wind speeds (Fig. 10). The highest correlation coefficient of 0.65 was obtained under moderate wind speeds (> 2.5 and < 5.0 m s⁻¹). The results indicate that NO2 is not homogeneously distributed under stable atmospheric conditions (< 2.5 m s⁻¹; Fig. 10(a)) or during strong winds (5.0-7.5 m s⁻¹). NO2 may be diluted by strong winds, resulting in reduced ambient NO2 concentrations, as shown in Fig. 10(c), and resulting in heterogeneous NO2 distributions over the measurement site.

Error sources consist of the spectrum fit error and transmissometer measurement error. In order to estimate the total errors which consist of those two error sources, error propagation analysis was employed as follows:

\[
\sigma_{VMR}^2 = \sigma_{DSCD}^2 \left( \frac{\beta}{LPL} \right)^2 + \sigma_{LPL}^2 \left[ \frac{VMR}{LPL} \right]^2
\]

where \(\sigma_{VMR}\), \(\sigma_{DSCD}\), and \(\sigma_{LPL}\) indicate errors of the retrieved NO2 volume mixing ratio, spectrum fit error, and relative

![FIG. 8. Correlation between NO2 volume mixing ratios derived by simultaneous measurements using a scanning spectrograph system and a transmissometer, and those measured using an in situ chemiluminescence monitor at Gwangju during the measurement period (1 May to 4 June 2009).](image)

![FIG. 9. Correlation between NO2 volume mixing ratios derived by simultaneous measurements using a scanning spectrograph system and a transmissometer, and those measured using an in situ chemiluminescence monitor at Gwangju for (a) cloudless days and (b) cloudy days during the measurement period (1 May to 4 June 2009).](image)
Error of 13% associated with transmissometer measurements [22], respectively. \( \beta \), LPL, and VMR are the unit conversion constant, light path length, and volume mixing ratio, respectively. The NO\(_2\) DSCD error comes from residuals of spectrum fit procedures while the LPL error of 13% comes from the uncertainty in Angstrom exponent as well as systematic uncertainties. The errors during the entire measurement period were calculated to range from 12 to 17% of the derived NO\(_2\) volume mixing ratios which was estimated using Eq. (3). The average errors during the entire measurement, cloudless, and cloudy periods were estimated to be 15, 12 and 16%, respectively as shown in Table 1. The relative uncertainties during the entire measurement, cloudless, and cloudy periods were estimated to be 33, 33 and 50%, respectively as shown in Table 1.

### IV. CONCLUSION

Ambient NO\(_2\) volume mixing ratios were retrieved at an urban site in Gwangju, Korea, based on simultaneous measurements using a scanning spectrophotograph device and transmissometer. Although the retrieved NO\(_2\) volume mixing ratios may require additional validation, they are in good agreement with the ratios obtained from in-situ chemiluminescence measurements. The linear correlation coefficients (R) between the two datasets are 0.81 and 0.69 for measurements under clear and cloudy atmospheric conditions, respectively. We also obtained correlation coefficients of 0.59, 0.65, and 0.54 under conditions of calm wind (wind speed < 2.5 m s\(^{-1}\)), moderate wind (2.5 \( \leq \) 5.0 m s\(^{-1}\)), and strong wind (5.0 \( \leq \) 7.5 m s\(^{-1}\)), respectively. In future studies, this technique could be applied in obtaining the mixing ratio of various trace gas species (e.g., HCHO, SO\(_2\), and H\(_2\)O). To validate such measurements, the data should be compared with those obtained by long-path differential optical absorption spectroscopy (DOAS), to reduce differences in measurement geometries. The analysis of more than one horizontal line of scanning spectrophotograph sight could be of interest for monitoring plume dispersal and for locating the source of trace gases.

### ACKNOWLEDGMENT

This work was funded by the Korea Meteorological Administration Research and Development Program under the grant CATER 2009-3112.

### REFERENCES


