Continuous monitoring of urban air quality with a pulsed DOAS technique

Yasuaki Kambe*, Yotsumi Yoshii**, Kenshi Takahashi***, Kenichi Tonokura*
*the Univiesity of Tokyo, Tokyo, Japan; **Toyama National College of Maritime Technology, *** Kyoto University Pioneering Research Unit for Next Generation

Abstract
We have demonstrated the trace gas observation campaign at Tokyo metropolitan area in summer 2008. In this campaign, we have observed the temporal profiles of nitrogen dioxide (NO_2) by a pulsed differential optical absorption spectroscopy (PDOAS) technique. Two PDOAS apparatuses were used to characterize the regional profile of the average density of NO_2 through long path lengths of 7 and 6.3 km. The temporal profile of NO_2 was also measured by a normal NO_x meter, which was compared with data from the PDOAS. We obtained long distance slant column NO_2 concentrations for two directions from 1st to 23rd August, 2008.

Key words: Pulsed DOAS, Urban atmosphere, nitrogen dioxide

1. INTRODUCTION

NO_2 is emitted from anthropogenic sources and has a large influence on the production and extinction of tropospheric ozone. Therefore, in urban area, the continuous observation of NO_2 concentrations is important to control air quality. We present an NO_2 monitoring technique of pulsed differential optical absorption spectroscopy (PDOAS) (Fuqi et al., 2005, Yoshii et al., 2003) and its demonstration in the trace gas observation campaign at Tokyo metropolitan area in summer 2008.

2. EXPERIMENTAL

The measurement system consists of a light source, a telescope, a small CCD spectrometer, and a lap top PC (Figure 1). In the campaign, two PDOAS systems were utilized simultaneously to retrieve NO_2 column densities along different directions. As the light sources, high-intensity flashing white obstruction lights available on the top of exhaust flues of incinerator plants were employed, in which one Xe lamp light source was located 6.3-km east and another was 7-km north from the observation site at the Hongo campus of the University of Tokyo (Figure 2). The both flash lights are focused by the telescopes and detected by the CCD spectrometers through optical fibers.

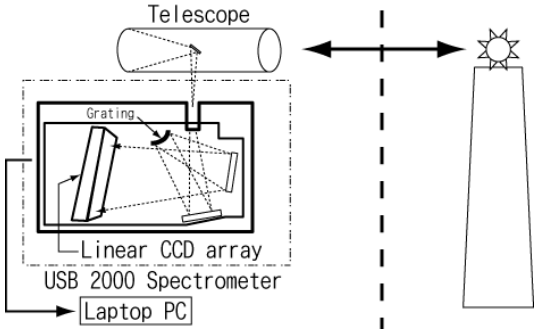

Figure 1. Experimental setup for measuring NO_2.

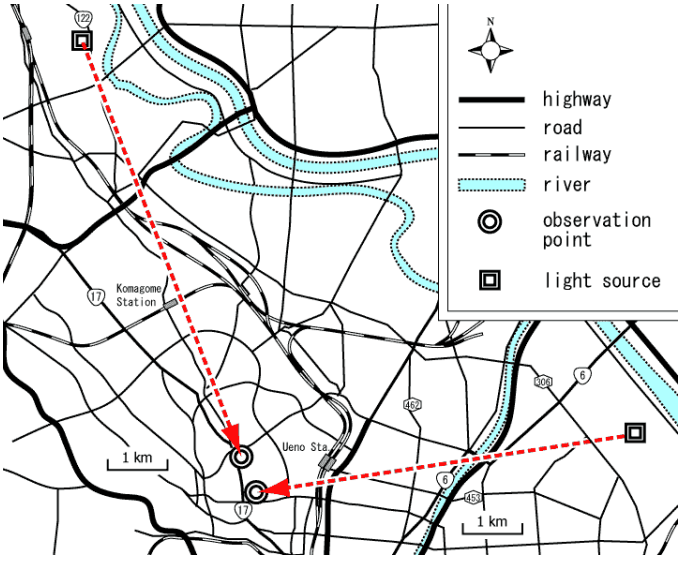

Figure 2. The PDOAS observation sites and the light sources. Two direction light paths for the PDOAS measurement are shown.

3. ANALYTICAL TECHNIQUE

The observed light spectra subtracted from the background lights is decayed by the absorption of NO_2 and the extinction of Rayliegh/Mie scattering in the range of 400-450 nm. In this range, there is no absorption of other trace gases except NO_2, so that the observed spectra is

$$I(\lambda) = kI_{ref}(\lambda)T_{NO2}(\lambda)T_m(\lambda)T_a(\lambda).$$

Here $I(\lambda)$ is the measured intensity, k is the system constant, $I_{ref}(\lambda)$ the unattenuated reference intensity, $T_{NO2}(\lambda)$ the NO_2 transmittance, $T_m(\lambda)$ the transmittance of air molecules (Rayleig scattering), $T_a(\lambda)$ the transmittance of aerosol particles. The transmittance is related to its optical density, by means of the Lambert-Beer law. The NO_2 transmittance is expressed as,

$$T_{NO2}(\lambda) = \exp(-\sigma(\lambda)Nl)$$

where $\sigma(\lambda)$,N, and l stand for the adsorption cross

* 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

section of NO_2, number density, and optical path length, respectively. The air molecules transmittance is shown as $T_m(\lambda) = \exp(-\tau_m(\lambda))$, where,

$$\tau_m(\lambda) = (p/p_0) \cdot 0.00864 \lambda^{-(3.916+0.074\lambda+0.05/\lambda)}$$

for an optical path of 7 km (Flohlich et al., 1980). Moreover, if it is assumed that the aerosol optical thickness exhibits wavelength dependence as given by the Angstrom exponent, we obtain

$$\tau_a(\lambda) = B\lambda^{-A}$$

where *A* is the Angstrom parameter and *B* is the turbidity constant (Smirnov et al., 2000). The observed spectra have two components, one varies rapidly with wavelength and another varies slowly. The differential absorption spectra are obtained by removing slowly changing part (smooth line) which is fitted to the observed spectra. The observation spectra is

$$\ln I'(\lambda) = \ln \frac{I(\lambda)}{I_{ref}(\lambda) T_m(\lambda)} = \ln k - B\lambda^{-A} - \sigma(\lambda) N l$$

Then, in the slowly varying component of the observed spectra, there is the effect of the extinction of Rayliegh/Mie scattering and the slowly varying absorption cross-section, so that the resulting structure of the observed spectra is only caused by the rapidly varying NO_2 cross-section. The slowly changing part is linearly fitted as,

$$\Delta\tau_g(\lambda) = -\left(\ln \frac{I(\lambda)}{I_{ref}(\lambda) T_m(\lambda)} - (a\lambda + b) \right)$$

where *a* and *b* are constant. The differential absorption cross-section is defined by considering the absolute cross-section as the sum of the spectrum, which varies rapidly with wavelength, and a slowly varying component. The rapidly changing part is

$$\sigma'(\lambda) = \sigma(\lambda) - \sigma^s(\lambda)$$

where $\sigma'(\lambda)$ is the fast varying absolute cross section. $\sigma(\lambda)$ is the absolute cross-section, $\sigma^s(\lambda)$ is the slowly varying absolute cross section. Finally we obtain the NO_2 concentration by peak-to-peak spectrum matching of the differential absorption spectra and the differential absorption cross-section (Figure 3).

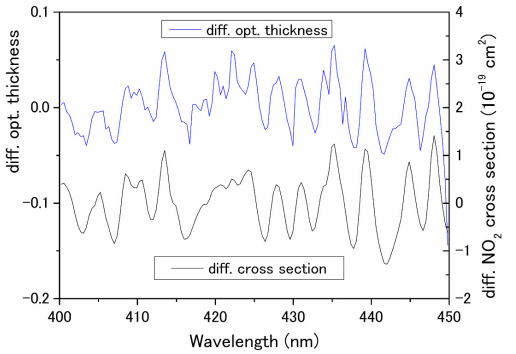

Figure 3. Spectrum matching between the differential absorption and the cross-sectional data (smoothed to the same resolution of the differential absorption).

4. RESULTS AND DISCUSSIONS

4.1. IMPROVEMENT OF THE CONNECTION BETWEEN THE TELESCOPE AND THE OPTICAL FIBER

The observed light was focused by the telescope, and its formatted image size was 45 μm on the well focused imaging plane. Before 5th August, the optical fiber core diameter we used was 50 μm to reduce the background light. But we found that this alignment between the focused image and the fiber core was very rigid so that the detected light intensity was weakened by small mechanical vibration of the telescope. Figure 4 shows a time series of NO_2 concentrations determined by the PDOAS and ground-based chemiluminescence analyzer set at the University of Tokyo from Aug.3 to Aug 9, 2008. It can be seen from Fig. 4 that the qualitative consistency between the temporal variations in the NO2 concentrations determined by both techniques has been improved significantly after modification of the fiber system.

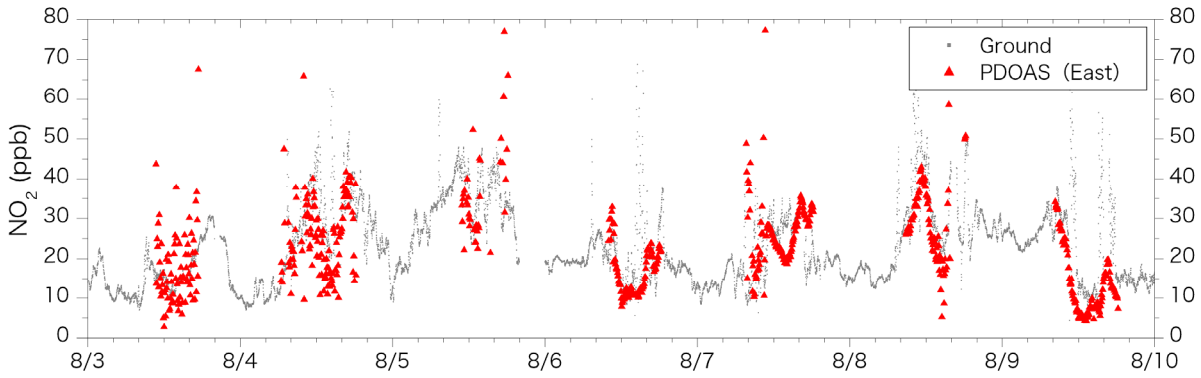

Figure 4. A time series of NO2 concentrations determined by the PDOAS and ground-based chemiluminescence analyzer.

4.2. CONCENTRATION OF NO_2 FROM TWO PDOAS AND GROUND MEASREMENTS

We performed two PDOAS systems in daytime from 1st to 23rd August, 2008, and for the reference, the NO_2 concentrations also measured by the single-point ground-based chemiluminescence analyzer. Figure 5 shows the NO_2 concentrations by the single-point ground-based observation and the PDOAS observation to the north and the east directions.

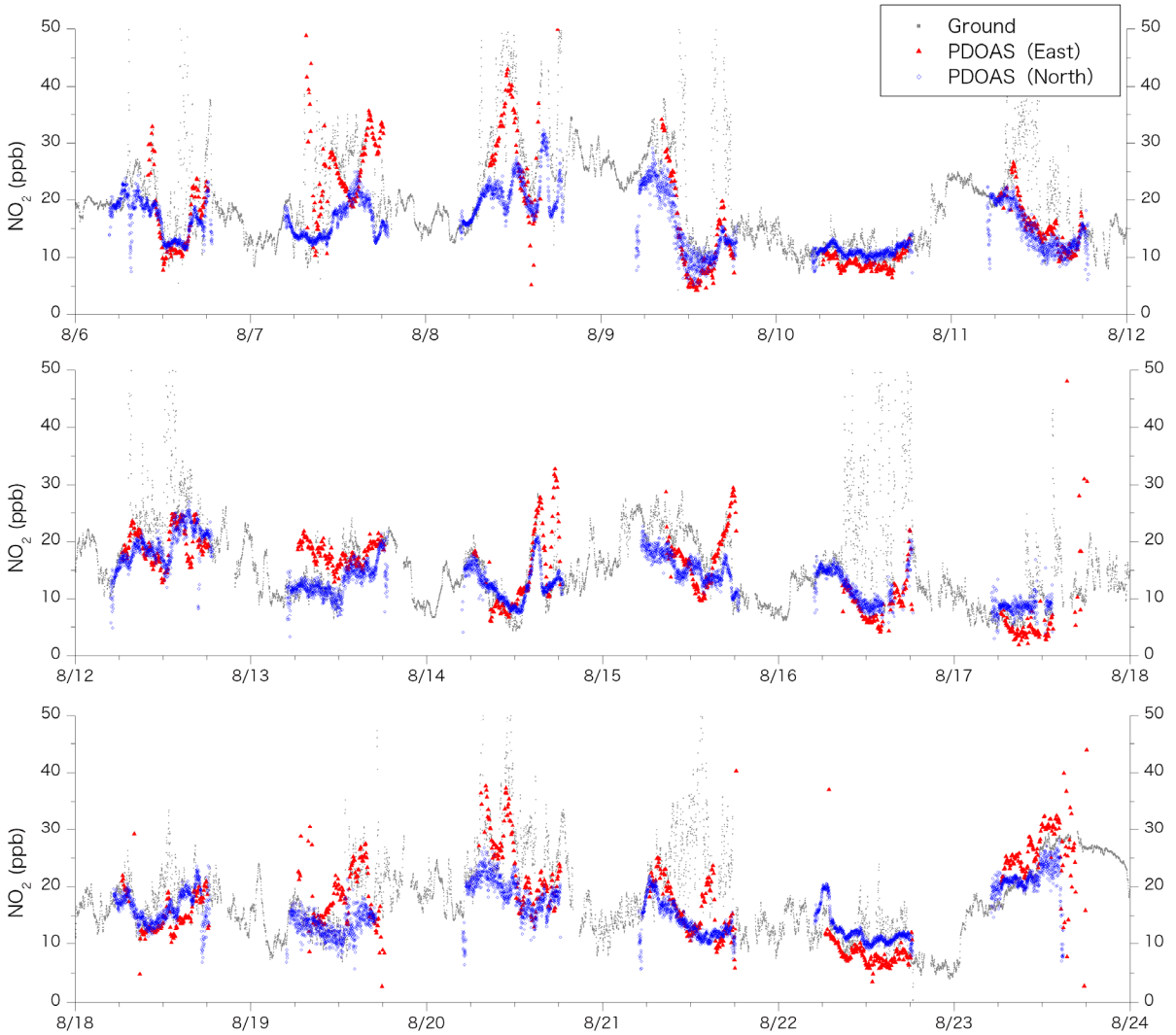

Figure 5. A time series of NO2 concentrations by the north and the east PDOAS system and the ground-based analyzer.

As is evident in Fig. 5, the NO_2 concentrations measured by the single-point ground-based chemiluminescence analyzer show a quantitative agreement with those from PDOAS (east) or, alternatively, from PDOAS (north). This result suggests that the spatial and temporal distributions of the NO_2 concentrations were highly inhomogeneous during the observation campaign. In the PDOAS systems we have demonstrated, they are free from frequent and complicated maintenance, and generally high-intensity flashing white obstruction lights are available on the top of buildings in urban area. The telescope we utilized in this study is commercially available and inexpensive. Thus, we can conclude that the PDOAS system is feasible for long-term automated operation for urban air quality monitoring in the daytime.

References

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