Measurement of trace gases in the lower troposphere using visible and near-infrared light sources

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Abstract

We have developed spectroscopic methods for continuous monitoring trace species in the lower atmosphere. Such kind of approach based on in-situ, long path length measurement is complementary to the conventional methods based on air sampling. First, differential optical absorption spectroscopy (DOAS) has been applied to simultaneously monitor aerosol and nitrogen dioxide, both being the most important air pollutants in the urban atmosphere. A pulsed xenon lamp equipped on a tall smokestack has been exploited as a light source of the DOAS measurement with an optical path length of 5.5 km. By analyzing the DOAS data with ancillary data from ground sampling, sunphotometer as well as weather data, aerosol behavior characteristic of the Chiba area has been revealed in relation to the regional wind system. Second, the long-path measurement using infrared light sources has demonstrated the capability of measuring atmospheric concentration of carbon dioxide, one of the most important greenhouse gases.

Keywords **:** Differential Optical Absorption Spectroscopy (DOAS), Air pollution, Aerosol, Molecular absorption, Trace gas species

1. Introduction

The air pollution in Chiba city, which is located along the coast of the Tokyo Bay, exhibits complicated behavior influenced by both local sources such as heavy traffic and industrial complexes and advection from the larger Tokyo metropolitan area. The dominance of southwesterly winds in summer generally causes high humidity from the bay area, whereas that of north to northwesterly winds in winter results in high level air pollution in conjunction with the formation of nocturnal inversion layer [1] . Here we employ the long-term differential optical absorption spectroscopy (DOAS) data taken with an optical path of 5.5 km that connects the observation setup at CEReS and a 130 m tall smokestack of a garbage incinerator operated by the city government. Also the data provided from a collateral sunphotometer and nearby ground sampling stations are employed to elucidate the behavior of major pollution species, aerosol (suspended particulate matter, SPM) and NO_2. Since the DOAS data can be obtained every 5 min, it provides much higher temporal resolution than the ground sampling data, which are produced on hourly basis.

The analysis has indicated that both coarse particles (such as sea salt) and fine particles (such as sulfates) are transported by sea breeze from the southwestern part of the city, where industrial complexes are located along the Tokyo Bay. Since our observation path is severely affected by traffic exhaust from major highways, a significant level of air pollution sometimes takes place depending on the sea/land wind conditions and the development of inversion layer. It has been observed that especially in winter, radiative cooling and weak wind conditions often result in considerable accumulation of pollutants.

Similar long-path optical absorption can also be applied to the monitoring of carbon dioxide (CO_2), the most important greenhouse gases of anthropogenic origins. As a counter-measure for increasing CO_2 concentrations, reliable and less costly approach that enables the in-situ measurement of CO_2 and other greenhouse gases are becoming more and more important. The Greenhouse gases Observing SATellite (GOSAT) was launched on January 23, 2009 by JAXA and NIES (http://www.jaxa.jp/projects/sat/gosat/index). The data for CO_2 column amount retrieved by a ground-based Fourier transform spectrometer (FTS) are useful for the validation of satellite data (Bosch et al., 2006). A network of FTS's has been established by NIES on a global scale (Total Carbon Observing Network : TCCON, https://TCCON- wiki.caltech.edu/) [3] The column amounts of both CO_2 and CH_4 (XCO_2 and XCH_4) from TCCON are calibrated to the concentration scale of WHO with the help of airborne sampling data of these trace gas species [4]. In our approach, on the other

hand, the absorption spectra of both CO_2 and water vapor have been measured along an optical path length of 6.2 km by means of DOAS approach using a halogen lamp and a super luminescent diode (SLD). Conventionally the CO_2 concentration measurement has been undertaken using sampling methods, giving precise but very local concentration of this greenhouse gas species. In contrast, the present method is able to provide data averaged over a long path length, thus better representing the regional concentration. Although the present effective resolution of approximately 8 nm is still insufficient for resolving each rovibrational transition in the 1.6 μm band, further improvement of the detection system will enable the concentration measurement with the accuracy of a few ppm.

2. Instruments

Pulsed flashlights equipped at tall constructions, called aviation obstruction lights, have successfully employed as light sources for the DOAS measurements of NO_2, the most important air pollution species in urban areas [5]. Also, this approach makes it possible to monitor the quantity of aerosol, or suspended particulate matter (SPM). Conventionally aerosol measurements have been carried out by means or ground sampling or sunphotometer, giving data that represent local atmosphere or column amount, or aerosol optical thickness (AOT), toward the solar direction. Thus, the DOAS measurement based on nearly horizontal light path near the ground level provides complementary information as compared with these existing approaches. Both the DOAS and sunphotometer measurements can yield the information on the wavelength dependence of aerosol scattering or extinction, in the form of Angstrom exponent. Here we make interpretation of the DOAS data in comparison with the data from ground sampling and sunphotometer measurements, as well as meteorological data such as wind speed and wind direction. The DOAS instrument, located at CEReS with a height of about 25 m above ground (45 m ASL), is composed of an astronomical telescope and a compact CCD spectrometer connected to a PC. The light source at the top of a 130-m tall incinerator stack (160 m ASL) is a xenon flashlight, giving short (0.5 ms), intense (2×10^5 cd) pulses every 1.5 s. Both NO_2 and aerosol quantities are obtained along the 5.5 km light path.

For CO_2 measurement, we employ both a halogen lamp (Ushio, JCS1000WBGX) and a super luminescent diode (DenseLight, CS5403A) as light sources. A 10-cm diameter telescope is used to collimate the light beam from either of these sources. The detection is attained with an InGaAs photodiode array (Hamamatsu, C9914GB) with a nominal resolution of 8 nm. In order to increase the resolution, and hence the sensitivity of the CO_2 detection, we have also constructed a home-made high-resolution spectrometer for the detection of CO_2 absorption band at 1.6 μm wavelength. Briefly, the spectrometer is equipped with a reflective, blazed grating for the use in the near-infrared region, and two cylindrical lenses are employed for coupling the diffracted light onto the array detector (Hamamatsu, G10768-1024D), resulting in a better resolution of 0.1-0.3 nm/pixel.

3. Results and discussion

3.1 *Continuous monitoring of air pollution using DOAS*

Here we describe the DOAS data in winter, since higher level of air pollution often takes place during the cold season because of the stable and dry weather conditions. Figure 1 shows the DOAS NO_2 data between 9-10 December 2009 observed at CEReS in comparison with the nearly collateral ground sampling data observed at the Miyanogi station. Since the xenon flashlight is operated only during the daytime, only the sampling data are shown during the nighttime. On 9 December, northwestern wind (land breeze) around 1 m/s speed was observed, while during the subsequent night, wind was nearly nonexistent. Consequently, relatively high concentration of NO_2 (30- 40 ppb) was observed until the morning of 10 December, presumably ascribable to the traffic exhaust. After 6 JST, the increase of both the atmospheric boundary height and wind speed (up to 3 m/s) resulted in the reduced concentration of NO_2 (ca. 15 ppb), representing the diffusion of the pollutants.

Figure 2 shows the aerosol parameters (extinction coefficient, AOT, and Angstrom exponent) in relation to the wind data on 22 February 2009. Relatively smaller values of the Angstrom exponent (α_{ang}) indicate the dominance of coarse particles, mostly due to sea salt particles from the Tokyo Bay. Relatively larger values, on the other hand, suggest that aerosol is from land sources composed of fine particles originating from NO_2 and H_2SO_4. After around 15 JST on 22 February 2001, strong wind from the WSW direction was observed, and as a result, the advection of sea salt particles resulted in the decreased value of α_{ang}.

3.2 *Near-infrared, long-path monitoring of CO_2 concentration*

Figure 3 shows the absorption spectra of CO_2 and water vapor observed over the atmospheric path length of 6 .2 km (30 July 2009). Broad water band are seen in the wavelength regions of 1250-1550 nm and 1750-1975 nm, whereas two CO_2 bands are observed around 1600 nm and 2000 nm. Figure 4

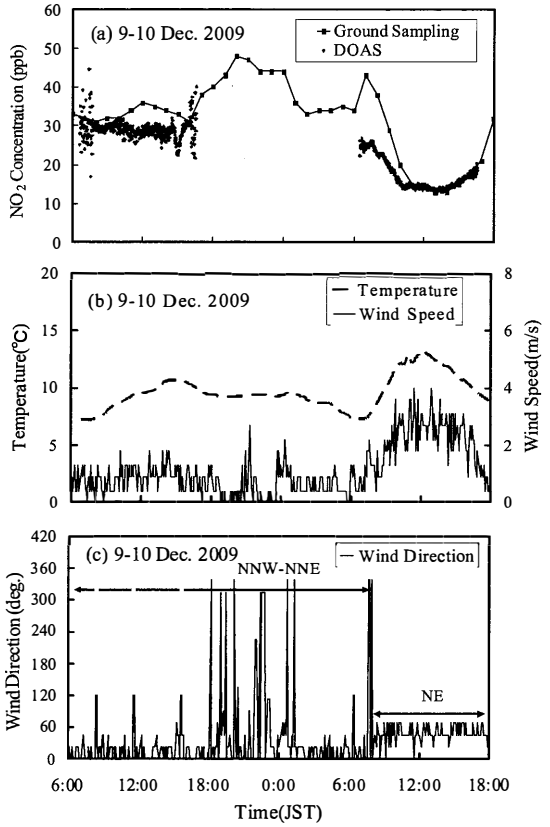

Fig.1 Temporal change of NO_2 concentration comparison between the DOAS and ground observation results , and temperature and wind speed changes during 9-10 December 2009.

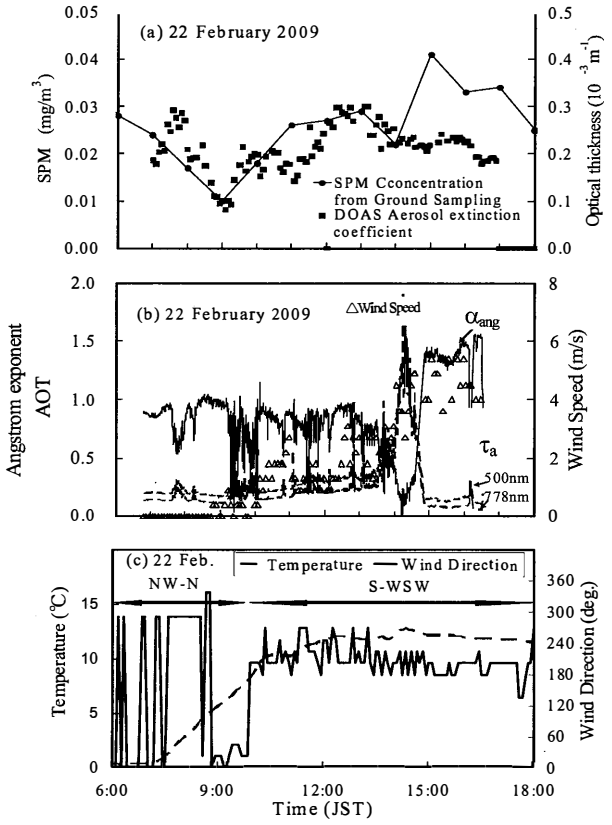

Fig.2 Change of aerosol type on 22 February 2009. Panels show the temporal changes of (a) SPM concentration and aerosol extinction coefficient, (b) Angstrom exponent, AOT, and wind speed, and (c) temperature and wind direction.

shows the band in 1950-2050 nm in an expanded scale. Since it is known that the spectrum of the halogen lamp is relatively smooth, the laboratory observed spectrum can be used as a reference (I_0) with appropriate scaling. The transmittance after the absorption ($T = I / I_0$) can be calculated in this way. As illustrated in Fig. 5, the fitting between the observed (blue) and simulation (red) curves yields the CO_2 concentration of 350 ppm. Here, the simulation has been performed with the MODTRAN radiative transfer code, with an optical resolution of 7.0 nm.

The atmospheric measurement has indicated that a better resolution of the detection system is needed in order to attain better accuracy in CO_2 concentration values from the optical long-path measurement. For this purpose, we have conducted a laboratory experiment in which a super-luminescent diode (SLD) and an InGaAs photodiode array. With a homemade grating spectrometer, the absorption has been obtained in the wavelength region of 1570-1590 nm (Fig. 6). Here the CO_2 absorption is observed with a 1.5-m long cell filled with 1 atm CO_2 gas. For comparison, laser lines emitted from a narrow-band external cavity diode laser (ECDL) are also shown with a simulated curve based on the HITRAN molecular absorption database. Although very similar absorption features are observed in Fig. 6, the observed absorbance indicates that the effective resolution attained with the experiment has been less than 0.5 nm. Further improvement of the spectrometer is undertaken for realizing better resolution, and hence better detection sensitivity of CO_2 in the real atmospheric experiment.

4. Summary

Since the DOAS data can be obtained in every 5 min, the resultant temporal resolution is much higher than that obtained from the ground sampling that provides air pollution data based on accumulation period of 1 h. We have considered the mechanism of the severe air pollution that often takes place in association with the development of the nocturnal boundary layer by combining the DOAS,

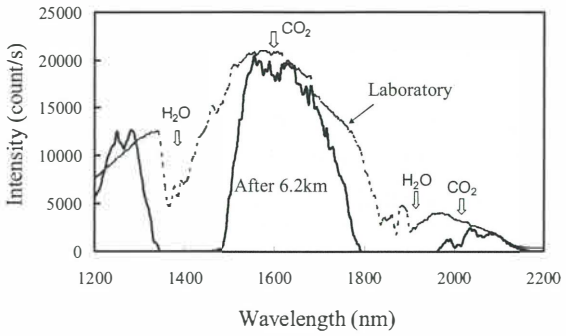

Fig. 3 Molecular absorption spectra observed in the atmospheric measurement over a path length of 6 .2 km

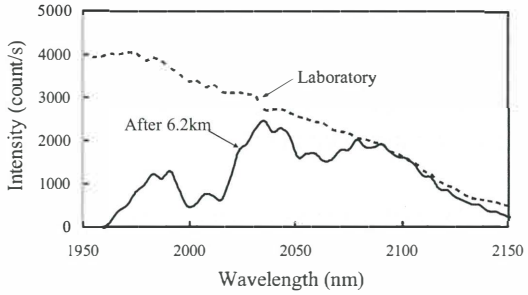

Fig.4 Determination of CO_2 concentration: comparison of the laboratory and atmospheric spectra

sunphotometer, and meteorological data.

Conventionally the CO_2 concentration in the atmosphere has been measured as a column amount from in-situ sampling based on ground and/or airborne measurements. In the present paper, we have demonstrated that the capability of the atmospheric long-path measurement for monitoring the concentration of CO_2 and water vapor by utilizing infrared light propagation over a distance of 6.2 km. Such an approach will be useful for carbon fixation studies related to agriculture and forestry, as well as monitoring CO_2 emissions from factories, power plants, and other types emission sources.

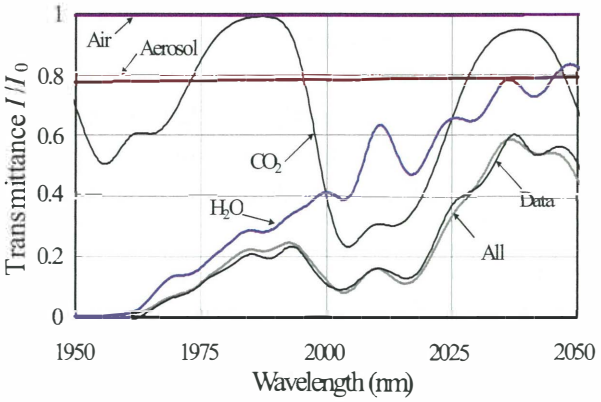

Fig. 5 Determination of CO_2 concentration: MODTRAN4 simulation was conducted with Atmosphere=Mid-Latitude Winter, Aerosol=Urban, P_0=1014.7 hPa, T_0=26.1 degC, RH =74.6%, RAT=1.30, VIS=20.0 km, L = 6.216 km, CO_2 =350.4 ppmv, and FWHM = 7.0 nm.

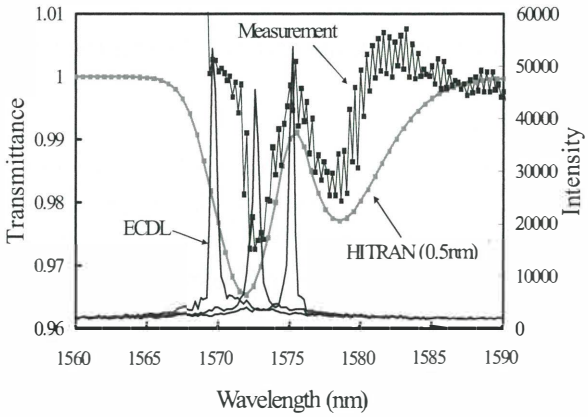

Fig. 6 Laboratory absorption spectrum of CO_2 observed with the homemade spectrometer, with an absorption path length of 1.5 m and CO_2 pressure of 1 atm. For comparison, the atmospheric absorption over a path length is simulated with the HITRAN database .

References

[1] S. Fukagawa, H. Kuze, G. Bagtasa, S. Naito, M. Yabuki, T. Takamura, N. Takeuchi, Characterization of seasonal variation of tropospheric aerosols in Chiba, Japan, Atmos. Environ, 40, 2160-2168, 2006.

[2] H. Bosch et al, Space-based near-infrared CO_2 measurements: Testing the Orbiting Carbon Observatory retrieval algorithm and validation concept using SCIAMACHY observations over Park Falls, Wisconsin, J. Geophys. Res. 11, D233302, 2006.

[3] O. Uchino, N. Kikuchi, T. Sakai, I. Morino, Y. Yoshida, T. Nagai, A. Shimizu, T. Shibata A.Yamazaki, A. Uchiyama, S. Oshchepkov, A. Bril, T. Yokota, Influence of aerosols and thin cirrus clouds on the GOSAT-observed CO_2: a case study over Tsukuba, Atmos. Chem. Phys. Discus. 11, 29883-29914, 2011.

[4] D. Wunch et al., Calibration of the Total Carbon Column Observing Network using aircraft profile data, Atmos. Meas. Tech., 3, 1351-1362, 2010.

[5] Y. Yoshii, H. Kuze, N. Takeuchi, Long-path measurement of atmospheric NO_2 with an aviation obstruction flashlight and a charge coupled device spectrometer, Appl. Opt., 42 (21), 4362-4368, 2003.