

## Evaluation Impact of NO<sub>2</sub> Values and Aerosol on Air Pollution

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**Abstract:** one of the useful technique for measuring aerosol and NO<sub>2</sub> is Differential optical absorption spectroscopy, the most important factor in environmental pollution. This paper reports on the results of dual path DOAS measurements recently conducted in a City using xenon flashlights equipped on tall constructions as aviation obstruction lights. Because of the proximity of the southern DOAS path to an industrial area, it is found that the level of air pollution generally increases with the dominance of westerly winds, from the plausible source area to the observation light path. Additionally it is confirmed that size information of aerosol particles can be derived from the DOAS data through the analysis of the wavelength dependence of the aerosol optical thickness, which shows fairly good correlation with the mass ratio suspended particulate matter obtained from the *in-situ* sampling station measurement. This situation is consistent with the result of wind lidar measurement covering a sector. In spite of the fact that the two DOAS paths are located in separated regions of City, the observed temporal behavior was similar for both nitrogen dioxide and aerosol, though the southern path tends to exhibit slightly higher pollution levels than the northern counterpart.

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### 1. Introduction

Air quality monitoring is one of the vital issues in large cities for the better understanding of conditions on both human health issues and radiative budget. Ground-based sampling stations can provide local data on concentrations of air pollutants. It often happens, however, that such point sampled data are affected by local sources, and consequently, they do not always represent air pollution conditions in a wider region. Owing to the recent progress in both light sources and detectors, the DOAS approach has so far been extended to wider wavelength regions (from UV to IR) to observe a number of pollution species, including volatile oxidized carbons (VCOs) as well as some greenhouse gases.

Along with the conventional DOAS setup that needs the deployment of an appropriate light source, the development of multi-axis DOAS (MAX-DOAS) has enabled the use of scattered solar radiation for monitoring air pollution. Also, the occultation method employed in airborne and satellite measurement can be considered as an extension of DOAS scheme for monitoring trace gas species on a global scale. The technique of differential optical absorption spectroscopy (DOAS) is capable of monitoring atmospheric environment along the optical path of several hundred meters to several kilometers. By utilizing appropriate wavelength range in the visible spectrum, the DOAS technique makes it

possible to measure the concentrations of nitric dioxide (NO<sub>2</sub>) and aerosol, two important species in urban environmental pollution. The present paper reports on the DOAS measurements conducted in Chiba City, Japan, during a campaign period in May-December, 2011. The measurements employed two independent DOAS paths having optical path lengths of 5.5 and 3.5 km that cover different areas in the central part of Chiba City, located along the eastern coast of the City Bay.

Also, through the analysis of wavelength dependence of aerosol extinction in the DOAS measurement, examination is made on the possibility of deriving information on fine particles, which are considered to be more hazardous to human health. The use of such dual light paths in DOAS has recently been reported for an urban air pollution study in City as well as for the monitoring of volcanic gas concentration. In addition, the novel aspect of the present paper is the simultaneous measurement using a Doppler wind lidar, which can provide more direct information on the wind field as compared with the weather station data.

### 2. Material and method

The wind lidar setup was located in a Chiba City facility (a community center), and the lidar measurement was conducted toward the direction of the industrial area including a steel mill. Both the

DOAS paths are in the central area of the Chiba City, characterized with heavy traffic and economic activities.

The volume concentration data of NO<sub>2</sub> and the mass concentration data of aerosol, or suspended particulate matter (SPM), are obtained from an *in-situ* sampling station [Soga nursery school (NS) sampling station] near the light source of the Samugawa DOAS path. The measurement was conducted in a city area about 30 km southeast of central city along the eastern coast of City Bay. The locations of the DOAS light paths, an *in-situ* sampling station, and the coverage area of wind lidar measurement. The optical path lengths in the northern and southern DOAS paths, hereafter called Chiba University DOAS and Samugawa DOAS, are 5.5 km and 3.5 km, respectively. The obvious advantage of this pulsed DOAS approach based on such flashlights is that a simple, home-made setup consisting of a commercially available astronomical telescope, a compact, charge-coupled device spectrometer, and a PC can achieve the continuous observation of the spectrum of transmitted light intensity.

The method of pulsed DOAS was employed for the present measurement. Xenon flash lamps (Sanken Electric, FX-7) mounted on an electric power tower or a smoke stack was exploited as DOAS light sources, providing flash events every 1.5 s during the daytime. The luminosity of these lights is more than  $2.0 \times 10^5$  cd, which ensures their role as good indicators of aviation obstruction lights recognizable even from locations several kilometers away. An optical fiber is used to connect the output from an astronomical telescope. Path was based on a xenon flashlight equipped on a 130 m tall smoke stack, the light emitted from which was observed near the rooftop of an eight story building at Chiba University, approximately at 30 m above ground level.

The pass length of this observation path was 5.5 km, covering the sea level height range approximately from smoke stack (155 m ASL.) to Chiba University observatory (50 m ASL.). The southern path, on the other hand, was from a 47-m tall electric power tower to an observation site situated on the third floor (approximately 10 m above ground level) of a building at Samugawa elementary school (hereafter Samugawa ES).

Because of the relatively robust construction of the detector setup, the maintenance of optical alignment was needed only once in a consecutive time period 2-3 weeks. The sea level height of this southern DOAS light path was from electric tower (55 m ASL.) to Samugawa ES (14 m ASL.). In consideration of the light intensity, the diameters of telescopes used for the northern (Chiba U.) and southern (Samugawa ES) paths were 200 and 100 mm, respectively. In the

present study, we compare our DOAS results with the ground sampling data taken at a nearby sampling station (Soga NS) operated by the environmental section of Chiba City, for both NO<sub>2</sub> and SPM. At this sampling station, the volume concentration of NO<sub>2</sub> is measured with an instrument based on chemiluminescence method (Horiba, APNA-3700, Japan), while another instrument based on the  $\beta$ -ray absorption method (DDK-Toa, DUV-222, Japan) is employed for the evaluation of SPM mass concentration. In addition to NO<sub>2</sub> that arises mainly from combustion processes, aerosol is an important component of air pollution in urban areas.

When referring to mass concentration observed at *in-situ*, ground sampling stations, the terminology of “suspended particulate matter” (SPM) is often employed instead of “aerosol”. Technically, SPM indicates particles whose diameters do not exceed 10  $\mu\text{m}$ . This is in contrast with the definition of PM<sub>2.5</sub>, which refers to particulate matters smaller than 2.5  $\mu\text{m}$  in the sense that their aerodynamic cutoff diameter is 2.5  $\mu\text{m}$  at 50% cutoff efficiency. In addition to SPM, the *in-situ* data includes also the mass concentration data of PM<sub>2.5</sub>, which is more influential to human health than SPM. DOAS data are considered to be more sensitive to SPM than to PM<sub>2.5</sub> because of the larger scattering cross-section (hence, larger optical thickness) of SPM particles. Nevertheless, the spectral data in the DOAS measurement enable one to study the wavelength dependence of the aerosol optical thickness (AOT) along the optical path. As explained in the following section, the aerosol size information obtained from DOAS AOT shows fairly good correlation with the ratio between PM<sub>2.5</sub> and SPM. The corresponding path length was 3.5 km, running along the seashore industrial district. The lidar instrument was operated on the fourth floor of a building of the Chiba City facility toward the direction of the industrial area along the City Bay.

Although wind data near the ground level can also be obtained from the meteorological observation data of Japan Meteorological Agency (JMA), such Doppler lidar measurement can give information on wind field at nearly the same height as the DOAS observation path. The lidar is an eye-safe system, operated at 1.5  $\mu\text{m}$  wavelength. The wind field within a sector of  $\pm 44^\circ$  was measured with the maximum observation distance of about 2.8 km. The pulse repetition rate was 4 kHz, and by integrating signals for  $201 \times 93$  pulses, the data along one direction were obtained in 5 s. In addition to the dual path DOAS measurements, wind field measurement was conducted using a fiber-based Doppler wind lidar during 2012.

#### 4. Results and Discussion

The data from the Samugawa DOAS and the sampling data from the Soga NS station are plotted together with the wind direction data observed at the JMA Chiba Observatory. The wind direction changed from southwest to northeast just before 18:00 JST. The temporal resolution of the DOAS measurement is 5 min, much shorter than that of the *in-situ* sampling measurement (60 min).

The average altitude of the DOAS measurement is approximately 30 m above ground level, which is much higher than the height of ambient air inlet (~3 m) for the sampling measurement. The highest value of NO<sub>2</sub> concentration was approximately 51 ppbv recorded in the sampling data just before 13:00. Although this pollution level is rather significant, it is still below the environmental standard of 59 ppbv evaluated on the daily average basis. It shows the temporal variation of NO<sub>2</sub> concentration observed on 16 April 2012. Therefore, the result of the *in-situ* measurement is usually more influenced by the local emission as compared with the DOAS result.

Thus, the comparison between these two different methods is not necessarily to seek for complete agreement, but to examine the temporal correlation between these two different data series. It is seen that the DOAS data tend to be smaller than the *in-situ* sampling data, though they exhibit similar temporal behavior. Thus, the effect of the wind direction change was more precisely recorded in the DOAS data than in the sampling data.

The sampling data exhibits temporal change similar to the Samugawa DOAS data, though the *in-situ* value tends to be larger than the Samugawa DOAS data. NO<sub>2</sub> concentrations observed along the two DOAS paths are plotted with the *in-situ* sampling data recorded at the Soga NS station. Note that for the sake of comparison, hourly average values are plotted for the DOAS data. Although the temporal behavior of the two DOAS data is similar, Samugawa data (southern DOAS path) are in general larger than Chiba U. data (northern DOAS path).

In, decrease in NO<sub>2</sub> concentration was seen for the Chiba U. DOAS data on the afternoon of 20-22 June 2011. It is likely that this decrease was caused by the photolysis of NO<sub>2</sub> due to strong solar radiation, as inferred from the data taken with a sunphotometer operated at the Chiba University site (data not shown). In contrast, such decrease in NO<sub>2</sub> was not clearly observed in the case of the Samugawa DOAS data. It shows the comparison of AOT derived from the two DOAS paths, in conjunction with the *in-situ* data from the Soga NS station. From this figure, it is found that the two DOAS paths have led to similar values of AOT (after conversion of Chiba U. AOT from 5.5 to 3.5

km), in spite of the fact that the two paths are covering separated regions of Chiba City. In comparison, the *in-situ* data indicate that the variation of SPM value is larger for the latter half (22-24 June) of the observation period than for the former half period.

The difference among the two DOAS data and sampling data can presumably be ascribed to the presence of more local sources in the southern path such as the emission from the steel mill complex or that from streets with heavy traffic along the City Bay. Also, the vertical distribution of NO<sub>2</sub> can be responsible for larger concentration values in the sampling data. In fact, it is likely that the variation of aerosol size distribution, as explained below in association with it, is closely related with the noticeable change of SPM data after June 2012. The DOAS data represent the temporal variation of an optical quantity (*i.e.*, AOT), whereas the SPM data show that of the mass concentration.

Therefore, in addition to the difference in the observation (sampling) altitude, care must be taken for the comparison between the optical (DOAS AOT) and SPM (sampling) data, since the change in aerosol property, especially the change in aerosol size distribution, can affect the conversion factor between the optical and mass concentration data.

Although the direct comparison is possible for NO<sub>2</sub> between the DOAS and sampling data, it must be noted that in the case of aerosol (SPM), DOAS result is plotted in terms of optical thickness (dimensionless), whereas the sampling result is indicated as volume concentration (mg/m<sup>3</sup>). They show the wind fields observed with the wind lidar in 2011 and 2012. In these panels, cold and warm colors indicate westerly and easterly winds, respectively; besides, the line along the coast indicates a portion of the Samugawa DOAS path. The diurnal variations of the NO<sub>2</sub> concentration and AOT from the DOAS data in 2012 are shown in panels (c) and (e), respectively. The wind direction indicated in panel (b) is westerly, from the steel mill complex to the lidar location. The DOAS results in panels (d) and (f) show that both the NO<sub>2</sub> concentration and AOT values were larger than the values observed on the previous day. From panels (a), (c) and (e), it is seen that when the wind direction was from southeast, both NO<sub>2</sub> and SPM concentrations were relatively low.

Thus, this figure shows the air pollution situation before and after the wind lidar data (2-3 November 2011). During the period of 30 October-6 November, the minimum and maximum temperatures were 12.0°C and 23.5°C, respectively. Clear sky conditions were observed on 1 and 2. Temporal variation of NO<sub>2</sub> concentration observed in a time period between 30 October 2011 and 6 November 2011. During 30 October-2 November 2011, on the

other hand, the nighttime increase in the NO<sub>2</sub> concentration was recorded, due presumably to the development of nocturnal inversion layer. It shows the Samugawa DOAS data and Soga NS sampling data, and shows the wind speed and wind direction data observed at the JMA Chiba Observatory. Comparison between and indicates that relatively high concentration of NO<sub>2</sub> was observed in association with westerly winds that occurred during the daytime 2012.

In, this ratio is plotted for the days between 19 and 27 June 2011 on the basis of the PM<sub>2.5</sub> and SPM data recorded at the Soga NS sampling station. The comparison of temporal variations between the Angstrom exponent,  $A$ , and the mass ratio, PM<sub>2.5</sub>/SPM, indicates that a reasonable correlation exists between these two independent parameters. The wavelength dependence of DOAS optical thickness can lead to the determination of the Angstrom exponent,  $A$ , as indicated in Equation. For this purpose, here we employ the DOAS AOT data at the two wavelengths of 532 and 756 nm. Generally, smaller values of the Angstrom exponent (such as  $A = 0.5$ ) indicates the dominance of relatively coarse particles from natural origins (e.g., sea salt and/or dust particles), while larger values (such as  $A = 2.0$ ) that of relatively fine particles mainly from anthropogenic origins.

The temporal variation of this parameter is depicted, which indicates that the value of  $A$  is mostly in the range of 0.7 -1.0 during 19-22 June, whereas the value decreased to 0.4 - 0.7 during 23-26 June. This change suggests that optically, the contribution of coarse particles became more important after 23 June. On 23 and 24 June 2011, strong winds (7 - 11 m/s) blew from the northwest direction. Thus, it is likely that the dominance of coarse particles was caused as a result of regional transport of relatively larger particles such as sea salt. Although aerosol size distribution data are not available from the *in-situ* sampling, it is possible to employ the ratio between PM<sub>2.5</sub> and SPM as proxy data. This result indicates that the DOAS AOT data can also be useful for estimating the contribution of PM<sub>2.5</sub> through the analysis of wavelength dependence of AOT.

## 5. Conclusions

This research has showed that this technique is capable of elucidating spatial and temporal variations of NO<sub>2</sub> and aerosol, important air pollutants in urban environment. Also, it has been shown that the technique can be useful for evaluating PM<sub>2.5</sub> contribution in the aerosol extinction in the lower troposphere. The comparison of DOAS data obtained from two different light paths has indicated that generally a good temporal correlation is found for

NO<sub>2</sub> between the DOAS and ground sampling data. For aerosol (SPM), the similarity was rather limited in temporal behavior between the DOAS and sampling data, though occasionally similar behavior was seen between the two quantities.

A fairly good correlation was found between the fractional contribution of fine particles to the mass concentration data (PM<sub>2.5</sub>/SPM) and the Angstrom exponent derived from DOAS data. This suggests that the optical measurement is useful not only for evaluating aerosol loading, but also for estimating the contribution of PM<sub>2.5</sub> to the DOAS-derived AOT value. This suggests the occurrence of concentration changes that took place on a relatively wide spatial scale (~10 km) during the observation period in 2013. The possible dominance of aerosols from the industrial area has been confirmed from the wind measurement using the wind lidar.

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