Intercomparison of NO_x, SO_2, O_3, and Aromatic Hydrocarbons Measured by a Commercial DOAS System and Traditional Point Monitoring Techniques

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ABSTRACT

A field-based intercomparison study of a commercial Differential Optical Absorption Spectroscopy (DOAS) instrument (OPSIS AB, Sweden) and different point-sample monitoring techniques (PM, based on an air monitoring station, an air monitoring vehicle, and various chemical methods) was conducted in Beijing from October 1999 to January 2000. The mixing ratios of six trace gases including NO, NO_2, SO_2, O_3, benzene, and toluene were monitored continuously during the four months. A good agreement between the DOAS and PM data was found for NO_2 and SO_2. However, the concentrations of benzene, toluene, and NO obtained by DOAS were significantly lower than those measured by the point monitors. The ozone levels monitored by the DOAS were generally higher than those measured by point monitors. These results may be attributed to a strong vertical gradient of the NO-O_3-NO_2 system and of the aromatics at the measurement site. Since the exact data evaluation algorithm is not revealed by the manufacturer of the DOAS system, the error in the DOAS analysis can also not be excluded.

Key words: Differential optical absorption spectroscopy, urban air pollution, intercomparison, remote-sensing technique

1. Introduction

The growing concern about air quality issues in China is currently compounded by a lack of detailed and long-term information on the concentrations of a number of important pollutant trace gases. (DOAS), based on the "fingerprint" absorption of the molecules in the atmosphere along a light path is becoming increasingly popular for fast and continuous measurements of key pollutants in the atmosphere (e.g., Edner et al., 1986, 1993; Evangelisti et al., 1995; Raveganani et al., 1997). Following the pioneering work of Platt and Perner (Perner and Platt, 1979; Platt et al., 1979), many improvements have been made in DOAS to monitor a wide range of trace gases in the troposphere (e.g., SO_2, NO_2, O_3, HCHO, HONO, NO_3, and BrO, etc.) (Platt, 1994; Geyer et al., 1999; Hebestreit et al., 1999; Stutz et al., 2002). The advantages of DOAS are its ability to detect many trace gases simultaneously at low detection limits of few ppt or ppb,

its contact-free method allowing the measurement of free radicals in the air, and the inherent calibration by well-known cross-section data. The DOAS technique has been extensively used in atmospheric research.

During the last two decades, the advances in the design of developers' grade DOAS systems for the detection of trace gases present at extremely low concentrations (e.g., OH, and NO_3) have facilitated the construction of commercial instruments for the routine monitoring of criteria compounds (O_3, NO_2, and SO_2) in air quality networks. Commercial systems designed for this purpose have the advantages over developers' grade systems in that they are easier to use and only require a minimum amount of expert knowledge. The detection limits of many species are, however, often considerably higher compared to developers' grade DOAS systems. Another difference can be found in the complexity of the DOAS data analysis and in the retrieval of absorption references (Platt, 1994). The analysis of many compounds, such as ben-

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zene and toluene, is very sensitive to cross interference with considerably stronger absorbers (Volkamer et al., 1998) and one has to be very careful to correctly separate the spectral structures of the various absorbing species. Since the data evaluation of many commercial DOAS systems cannot be revised by the user, it is important to compare the results obtained by commercial DOAS systems to the data measured by other techniques in order to test the reliability of the analysis procedure.

A number of intercomparison experiments have been performed for both developers' grade DOAS systems and commercial systems. Developers' grade DOAS systems generally show very good agreement with point monitors (Geyer et al., 1999; Alicke et al., 2003; Grossmann et al., 2003) and with other DOAS systems (Camy-Peyret et al, 1996). Comparison of commercial DOAS systems and point monitors often show agreement for NO_2, SO_2, and O_3 (Stevens et al., 1993; Casavant et al., 1992; Virkkula et al., 1997; Harder et al., 1997; Sturm et al., 1998; Kim and Kim, 2001), but have difficulties in benzene, toluene, and other aromatics (Barrefor, 1996; Kouritidis et al., 2000). Reliable DOAS measurements of aromatic hydrocarbons in urban air require skillful instrument operation, data evaluation, and instrument maintenance. It is presently unclear whether the problems for aromatics arise from cross-interferences with oxygen (Volkamer et al., 1998) or the sampling of different air masses.

Here we present the results of a comprehensive comparison experiment among a commercial DOAS system (OPSIS AB, Sweden), a point-sampling (PM) air monitoring station (made by KIMOTO Electric Co., LTD, JAPAN), an air monitoring vehicle (made by HORIBA LTD JAPAN), and chemical analyses of canister samples during four months in fall/winter 1999 in Beijing. Beijing is the biggest city in northern China and represents an area with a rapidly growing population and economy. The intercomparison focused on six key pollutants in urban areas: NO, NO_2, SO_2, O_3, benzene, and toluene. This experiment not only compared the DOAS data to the PM measurements, but also the PM data among each other. Since DOAS averages the measured concentrations over a distance of several hundreds of meters, it is less influenced by local emission than a point monitor. Special considerations are therefore needed regarding the possibility to monitor a different air mass than the point monitor.

2. Experiment

2.1 *System description*

The commercial DOAS system (OPSIS AB, Swe-

den) used in this study consists of an EM150 transmitter (diameter: 205 mm) and an ER130 receiver unit (diameter: 205 mm) in combination with an AR500 analyzer. The light beam is generated from a 150 W Xenon arc lamp powered by a PS 150 power supply in the EM150 unit and transmitted to the atmosphere. On the other side of the light path, the ER150 receiver unit collects and focuses the light onto the end of a fiber-optic cable, guiding the light into the AR500 analyzer unit. The spectrum is obtained by a UV spectrometer (0.5 m focal length, F/6 aperture) with a turnable grating in combination with a slotted scanning disk (rotating at 300 rpm) and a photomultiplier tube in the AR500 analyzer. Measurement routine control, concentration analysis, and data transfer to the central station are operated automatically. The manufacturer of the DOAS system specifies for most components a detection limit of the order of 1 μg m^{-3} over a measurement path of 500 meters. The detection limit is somewhat higher for aromatic hydrocarbons. The accuracy provided by the manufacturer is 2% for NO_2, SO_2, and O_3, and 3%–15% for NO and aromatic hydrocarbons. The uncertainty of literature DOAS cross-sections suggests, however, that the accuracy of all DOAS data is at least 10%.

The point monitoring measurements were done by different techniques and instruments (all approved by the Chinese EPA), including a KIMOTO air monitoring station (Model-367P SO_2, Model-267P NO/NO_2, Model-847P O_3), a HORIBA air monitoring vehicle (APSA-350E SO_2, APNA-350E NO/NO_2, APOA-350E O_3) and national standard chemical laboratory methods. These automatic point monitors applied UV-fluorescence, chemiluminescence, and UV absorption to measure SO_2, NO/NO_2 (NO_2 measured after conversion to NO with a molybdenum converter), and O_3, respectively. The detection limits for SO_2, NO/NO_2, and O_3 are all of the order of 1 ppb, and the precisions are 1%, 1%, and 2%, respectively. Besides automatic air monitoring stations, national standard chemical laboratory methods were used to investigate SO_2 and NO_2 by the Tetrachloromerecurate (TCM)-Pararosaniline method and the Saltzman method, respectively. Benzene and toluene were monitored by sampling air into canisters followed by gas chromatography (GC) analysis in the laboratory.

System calibration and QA/QC (quality assurance and quality control) were important for the comparison. To ensure that the data could be valid, both the DOAS and PM (Point Measurement) systems were multi-point calibrated prior to the measurement period to known calibration standards. The

concentration-linearity of the OPSIS DOAS was evaluated with an OPSIS CB100 calibration bench, CC001 calibration cells, and a CA150 calibration lamp. The calibration bench had a length of 1 meter. The CA150 calibration lamp and the ER130 receiver unit were attached at both ends of the bench. Reference gas cells of various lengths resulting in different optical column densities were used for calibration. The linearity of the DOAS system for all gases was found to be better than 0.994. It is worth noting that DOAS is a technique with inherent calibration by well-known cross-section data and does not require further calibration. This is another difference between OPSIS DOAS and other developer's DOAS systems. The other span checks of the PM monitors, including a single point (high value) and a zero gas measurement, were carried out every five days throughout the period.

2.2 *Site description*

The measurement site was located at the National Environmental Monitoring Center (NEMC) in the Chaoyang district in the northeast part of Beijing city, as shown in Fig. 1. Two existing air monitoring stations (KIMOTO and HORIBA) were on the campus of NEMC, and the ER 150 receiver of the DOAS was placed on the roof of the container of the KIMOTO station, about 4 meters above the ground (height of KIMOTO inlet: 5 m). The EM 150 transmitter was fixed on a cement tower on the roof of the Tibet Middle School to the west of NEMC (about 30 meters high). The light path was 224 meters and ran parallel to the Beisihuan Road, which is part of the fourth ring road of Beijing and often had heavy traffic during the experiment.

In order to measure the homogeneity of the air mass, which can be disturbed by local emissions, the HORIBA monitoring vehicle sampled air at two points 3.5 m above the ground under the light path indicated by NO. 1 (October 19–27) and NO. 2 (November 1– January 28) shown in Fig. 1. The air samplers for the

laboratory analyses were placed near to the HORIBA monitoring vehicle, but the sampling inlet was only 1.3 meters above the ground. The possible local sources in this area were traffic on Beisihuan Road and a gas station approximately 150 meters away the measurement path. During the course of the study from fall to winter 1999, the weather was usually dry. Heating in winter also resulted in the emission of pollutants into the atmosphere. Meteorological parameters, including temperature, wind speed, wind direction, and humidity, were monitored by the KIMOTO monitoring station. Note, however, that these meteorological data may only represent the conditions near the monitoring station, which is surrounded by high buildings.

During the study, the DOAS system, the KIMOTO station, and the HORIBA vehicle measured continuously at a time resolution of 5 min. Concerning the chemical methods, two samples were taken over a two-hour sampling period in the morning and afternoon, respectively, on several days (Table 1). In order to compare the data of the other systems with the sample results, all measurements were averaged over the 2-hour time period. The monitoring periods for all gases are given in Table 1. All systems were reset regularly to a common time.

3. Results and discussions

The comparison involves four datasets: one set recordes by the DOAS system and the other three datasets recorded by PM measurements, which were done by the Air Monitoring Station of KIMOTO, the Air Monitoring vehicle of HORIBA, and various National Standard Chemical Methods. All data obtained from 1 October 1999 to 20 January 2000 are discussed here, except for interruptions due to hardware failure, data backup, instrument maintenance, and calibration. Hourly averaged mixing ratio data were used for the correlation analysis, which uses a linear least-squares approach.

Table 1. Measurement intervals during the intercomparison experiment.

	OPSIS	KIMOTO	HORIBA (No.1 site)	HORIBA* (No.2 site)	Chemical methods
SO_2	Oct 1–Jan 25	Oct 1–Jan 25	Oct 19–Oct 27	Nov 1–Jan 28	Nov 12–Dec 11
NO	Oct 1–Dec 6	Oct 1–Dec 29	Oct 19–Oct 27	Nov 1–Jan 28	Nov 12–Dec 11
NO_2	Oct 1–Jan 25	Oct 1–Jan 25	Oct 19–Oct 27	Nov 1–Jan 28	Nov 12–Dec 11
O_3	Oct 1–Jan 25	Oct 1–Jan 25	Oct 19–Oct 27	Nov 1–Jan 28	—
Benzene	Oct 1–Jan 25	—	—	—	Nov 1–Dec 10
Toluene	Oct 1–Jan 25	—	—	—	Nov 1–Dec 10

*HORIBA was powered off during 29 December 1999 to 17 January 2000.

Table 2. Summary of correlation results for SO_2, NO_2, Benzene, and Toluene.

Type of comparison	Number of data pairs	Slope	Y intercept (μg m^{-3})	R
SO_2-KIMOTO PM vs. DOAS	2344	0.86	3.6	0.96
SO_2-HORIBA PM vs. DOAS	1751	0.77	5.3	0.97
SO_2-Chemical Method vs. DOAS	54	0.78	13.5	0.94
SO_2-KIMOTO vs. HORIBA	1751	0.88	11.0	0.94
NO_2-KIMOTO PM vs. DOAS	2491	0.95	4.5	0.94
NO_2-HORIBA PM vs. DOAS	1733	0.92	11.0	0.94
NO_2-Chemical Method vs. DOAS	55	0.80	10.3	0.97
NO_2-KIMOTO vs. HORIBA	1704	0.93	11.2	0.94
Ben-GC vs. DOAS	35	1.44	2.4	0.83
Tol-GC vs. DOAS	35	1.39	−3.6	0.91

Table 3. Average levels of SO_2, NO_2, Toluene, and Benzene during the comparison experiment.

	SO_2 (μg m^{-3})		NO_2 (μg m^{-3})		Toluene (μg m^{-3})	Benzene (μg m^{-3})
KIMOTO	122	122*	86	102*		
HORIBA	109	117*	90	100*		
Chemical method		116*		99*	53	36
DOAS	131	133*	87	110*	41	26

*Average values for the data taken during the sampling of chemical methods.

Table 4. Summary of correlation results for NO.

Type of comparison (Y: PM X: DOAS)	Number of data pairs	Slope	Y intercept	R
NO-KIMOTO PM vs. DOAS	1467	2.4	9.9	0.64
				0.88*, 0.76**
NO- HORIBA PM vs. DOAS	1467	2.6	10.9	0.70
NO- KIMOTO vs. HORIBA	1770	0.97	12.1	0.93

* Data of October were used only.

** Data of October and November 1999 were used.

3.1 *Intercomparison of* SO_2, NO_2, *benzene, and toluene*

Figure 2 shows the correlation between the DOAS and PM measurements for the species SO_2, NO_2, benzene, and toluene. The results of linear regression analyses among all the datasets are summarized in Table 2. Average values for SO_2, NO_2, toluene, and benzene are shown in Table 3.

All correlation coefficients for SO_2 and NO_2, either between the DOAS system and the PM measurements or among the PM measurements themselves, were better than R=0.94. While the average level of NO_2 over the whole experiment predicted by the DOAS system is in good agreement with the point monitor data, the DOAS results are about 10% higher than those of the other methods during the time when the air samples were taken (November 12–December 11). This result is also reflected in the slopes of the linear regression

analyses: the correlation of the DOAS data with the PM results yields slopes larger than 0.92. These slopes are comparable with the slope of the intercomparison of the two PM systems and are within the accuracies of both systems. During the time from mid-November to mid-December, the slope between DOAS and the chemical analysis is, however, only 0.8.

The data in Tables 2 and 3 show that the DOAS system generally measured higher SO_2 concentrations than the other techniques. The slopes of the comparisons between DOAS and the other techniques range from 0.77 to 0.86. It is interesting to note that the comparison of the KIMOTO data with the HORIBA results also shows a slope of 0.88 and a rather high intercept. The discrepancies are all higher than the combined uncertainties of the instruments: 4%–13% for the DOAS comparisons and 9% for the PM correlation. These deviations for SO_2 suggest that, in

contrast to NO_2, the concentration of SO_2, which was emitted in high amounts near the site, was highly variable in the observed air masses. Calibrations of different systems and air sampling of PMs (e.g., flow control) also could induce small errors.

Although the data of toluene and benzene obtained by the OPSIS DOAS and the GC method follow similar trends with correlation coefficients R=0.83 and 0.91, respectively, large discrepancies (26%–27%) were found for their values. The GC system generally measured a higher level of benzene and toluene. The slopes between the DOAS data and the canister samples of around 1.4 are significantly higher than the measurement error of 3%–15% of the DOAS data and 10%–15% for the chemical analyses. The discrepancy may be attributed to a vertical gradient of aromatics (the samples were taken at 1.5 m while the DOAS data was recorded at 4–30 m) or the inability of the DOAS analysis software to resolve the cross-interferences of aromatics with O_2 and O_3 absorptions. Both absorption structures were found to be extremely sensitive to ambient temperature (Volkamer et al., 1998). Since the exact evaluation algorithm of the OPSIS DOAS system is not revealed by the manufacturer, we cannot exclude a problem with the OPSIS DOAS analysis of benzene and toluene.

Barrefors (1996) suggested that the quality of the DOAS measurements might be checked by comparisons of determined and anticipated toluene and benzene ratios in vehicle-polluted urban air. Typical values of toluene/benzene for urban traffic exhaust range from 1.5–3.0 (Kirchstetter et al., 1996; Kurtenbach et al., 2002) and for evaporation losses from 2.7–4.0, respectively. The mean ratio between toluene and benzene measured by OPSIS DOAS for the whole time period is 1.4. During the sampling period of the GC (November/December) the ratio of toluene to benzene obtained by the DOAS system was around 1.6 while the GC system measured a ratio of 1.5. Both values are near the low limit of the expected toluene/benzene ratio. This ratio may, however, be different in China than in western countries.

3.2 *Intercomparison of* O_3 *and* NO

Figure 3 shows the time series of O_3, NO, NO_2, and the wind speed from November 11 to November 18 as an example. For ozone, considerably higher levels (approximately 50 μg m^{-3}) were measured by DOAS (4–30 m average) than by the PM systems. The lowest O_3 data was obtained by the HORIBA vehicle, which sampled the air at 3.5 m, somewhat lower than the KIMOTO station. These differences might be caused by differences in the zero calibration of one or more instruments, evaluation errors, or likely a vertical profile of the NO-O_3-NO_2 system.

In general, the zero gas used to calibrate the offset of a system might cause offset values that differ from zero by a few μg m^{-3}, but this cannot induce a difference of 50 μg m^{-3}. For investigating the additional sources, the fan, which kept the air ventilating to remove the O_3 generated from the Xenon lamp inside the telescope of the DOAS emitter unit, was checked. The fan was working but the air filter on the telescope was almost blocked by dust, probably resulting in additional O_3 in the light path. At 1800 LST 21 October we cleaned the air filter and at 1800 LST 25 October a new air filter was installed. Figure 4, which shows the ozone time series as measured by the three systems for this time period, on a first view suggests that the differences between DOAS and the two PM systems may be caused by blocked air filters. As discussed in the following sections, the good agreement with correlation coefficient 0.95 may, however, also be caused by high wind speeds and high atmospheric mixing rates, which reduce vertical gradients of the NO-O_3-NO_2 system.

Errors in the evaluation of the DOAS O_3 data are less probable because the strength of absorption of ozone is relatively high. However, we can, not exclude analysis errors since we have no information about the exact algorithm used by OPSIS for the O_3 evaluation.

Since all three systems took measurements measured at different altitudes (HORIBA: 3.5 m, KIMOTO: 5 m, DOAS: 4–30 m average), it is possible that the differences in O_3 arise from a vertical gradient of O_3. Although the height difference between the two PM measurements was only 1.5 m, the HORIBA system already measured significantly lower O_3 values most of the time. It is well known that the fast reaction of NO, which is emitted close to the ground, with O_3 can lead to strong vertical gradients of O_3 and also of NO and NO_2 (e.g., Zhang and Rao, 1999).

If the reaction of NO with O_3 is behind the differences in the O_3 measurements, we could expect to see differences also in the NO and NO_2 data. The comparison between KIMOTO and HORIBA shows that both NO data are similar in trends and levels (slope: 0.97, R: 0.93, Table 4). However, as apparent in Fig. 3, the DOAS NO data were generally lower than those of the KIMOTO station. Discrepancies of mixing ratios between DOAS and PM were varied from a factor around 0.36 in October to 0.13 towards the end of the measurement peried. The relative trends of the NO time series as measured by DOAS and the point monitors were, however, in good agreement. The correlation coefficient was higher in October than later during the campaign (Table 4).
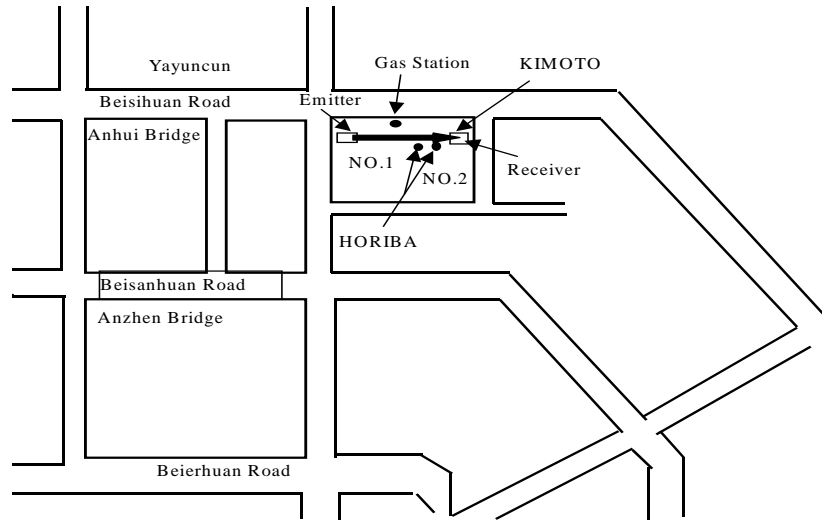
Fig. 1. Description of the measurement site. The arrow parallel to Beisihuan Road indicates the DOAS light path. The receiver of the DOAS system was on the top of the container of the KIMOTO station. The HORIBA vehicle sampled air at two positions, NO.1 and NO.2, during different time periods. The air samples were taken near the HORIBA vehicle.
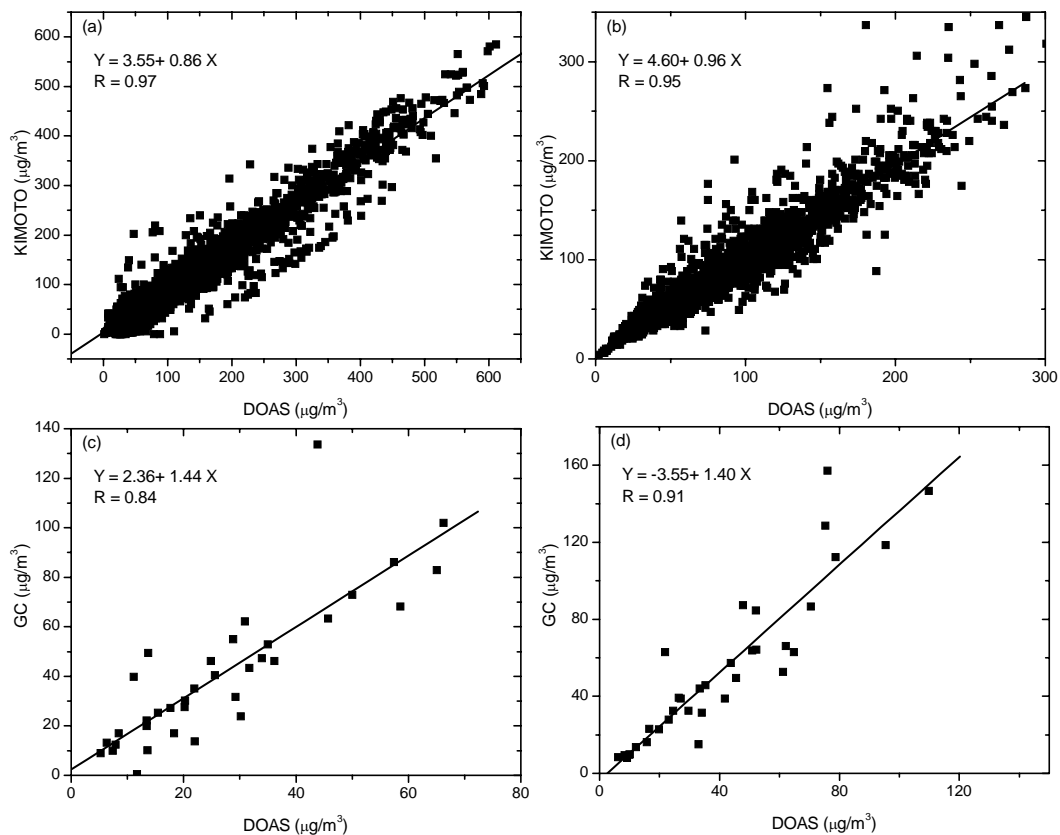
Fig. 2. Scatter plots and regression analyses of DOAS and PM methods for four species: (a) SO_2, (b) NO_2, (c) Benzene, and (d) Toluene. Good correlations are found for SO_2 and NO_2, both in their trends and values. (c) and (d) indicate that the data are correlated for toluene and benzene, but there are some discrepancies in the overall levels.
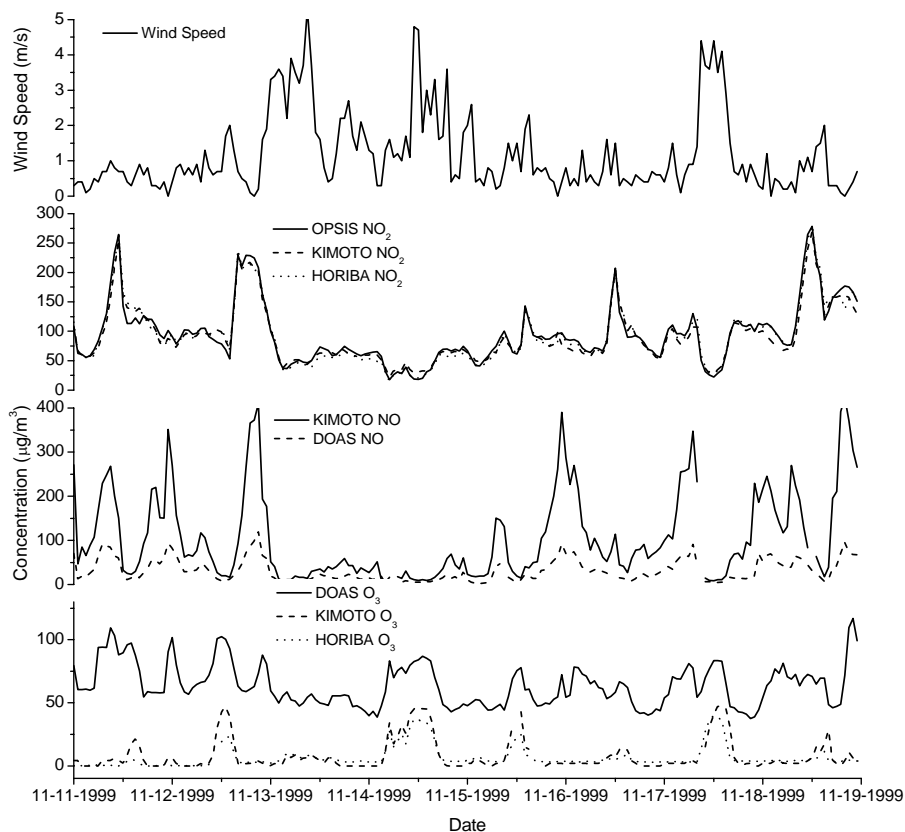
Fig. 3. Time series of O$_3$, NO, NO$_2$, and wind direction from 11 November to 19 November 1999. An offset of about 50 μg m^{-3} was observed in the O$_3$ data measured by the DOAS system compared to the PM measurements, which is probably caused by the vertical profile of the NO-O$_3$-NO$_2$ system.
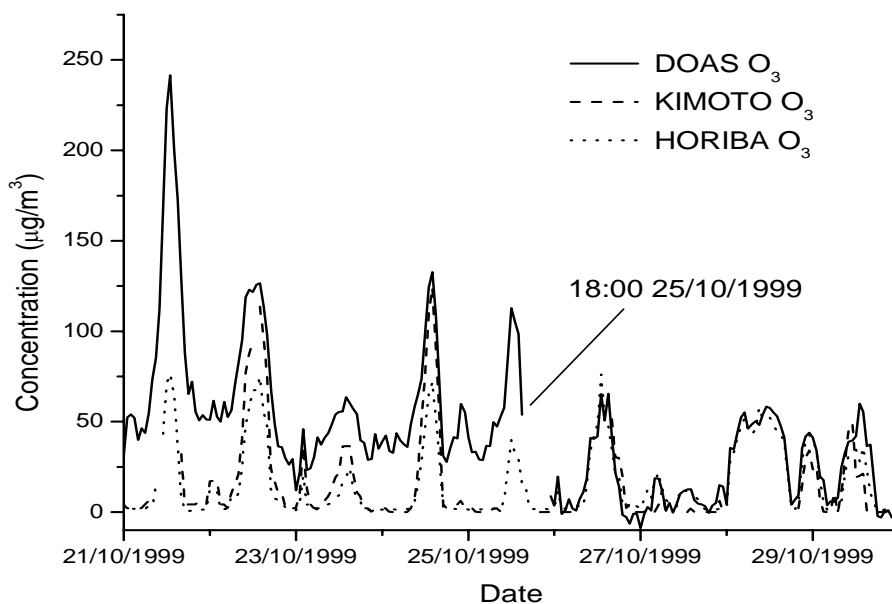
Fig. 4. Variation of the O$_3$ offset of the DOAS system after changing the air filter of the emitter unit at 1800 LST 25 October 1999.

As shown in Fig. 3, ozone was often anticorrelated with NO showing that the reaction $(NO+O_3 \rightarrow NO_2+O_2)$ is behind a large part of the O_3 and NO data differences. If we focus on time periods with low NO levels ($< 70 \, \mu g \, m^{-3}$), the difference between the two techniques is reduced and the ratio between the O_3 data from the KIMOTO station and DOAS is increased to 0.91.

The O_3 and NO differences in the earlier morning (rush hour: 0600–0800 LST) and at midnight (2300–0200 LST) were larger than at other times of the day. This result can be attributed to the higher atmospheric stability and high NO emissions at these periods of the day (heavy-duty trucks were only permitted to enter the city after midnight). During afternoon, when the air is generally better mixed, the differences were significantly lower. This result is also apparent in the correlation of the O_3 and NO concentration differences with the wind speed: between November 13 and November 15, when the wind speed was high, the differences were smaller for both NO and O_3.

It is interesting to find that NO_2 data from all the systems have no large differences, as we expected due to vertical gradients of the NO-O_3-NO_2 system. They are generally in agreement as discussed previously. This phenomenon may be explained by the fact that NO_2 production was limited by the low concentration of O_3 near the ground and the low level of NO at the height of the DOAS measurements. In other words, the presence of a negative NO vertical gradient and a positive O_3 vertical gradient at the measurement site led to a weak gradient of NO_2 production by the reaction of NO with O_3.

The reason for the increase in the NO concentration differences in winter may be attributed to the stronger stabilities during the day in winter compared to fall. It might also indicate an error of the DOAS evaluation for NO. The light intensity for the NO measurements was lower than that for SO_2, NO_2, and O_3 because it absorbs light about 100 nm deeper in the UV spectrum (210–230 nm), so the data quality was more sensitive to the light level. As a first step, the data of NO that did not satisfy a selected light level were all discarded. After finishing the experiment, the DOAS system was checked. A layer of pollutants, like sludge, adhering to the protection quartz windows and mirrors of both emitter and receiver, might have unknown absorption structures (anti-correlated absorption pattern with NO), which may have interfered with the NO evaluation, resulting in errors. Another possible reason could be lamp aging, which could result in a different lamp emission structure (Xenon lamp emission bands). Since it is not possible with the OPSIS system to record lamp emission references on a regular basis, we suggest performing a weekly on-line calibration for NO.

4. Conclusions

In this paper, we present an intercomparison experiment for six trace gases (SO_2, NO_2, NO, O_3, toluene, and benzene) between a commercial DOAS system (OPSIS AB) and various traditional point sampling techniques (KIMOTO air monitoring station, HORIBA air monitoring vehicle, and various chemical methods) performed in Beijing, China, from October 1999 to January 2000. The data obtained from the different systems are used to evaluate the applicability of the OPSIS DOAS system as a standard monitoring device. The differences among these systems were examined statistically using linear regression analyses. The results of the regression analyses showed good agreement between the OPSIS DOAS and the point monitors for SO_2 and NO_2. The deviations of the SO_2 and NO_2 levels measured by DOAS and a point monitor were comparable to those among the PMs themselves. The levels of toluene and benzene obtained by GC were on an average 28% and 38% higher. This difference is beyond the range of uncertainty given for the systems. It may be caused by a vertical gradient of the aromatics levels (dilution of the concentrations from the ground up to the light path of DOAS) or errors of the OPSIS aromatics evaluation with the cross-interferences of O_2 and O_3. Poor agreement was also found for O_3 and NO. Part of the differences in the O_3 and NO data between the OPSIS DOAS and the PMs can possibly be attributed to the vertical profile of the NO-O_3-NO_2 system near sources of NO.

A major disadvantage of the commercial DOAS system from OPSIS AB is that it is not possible to review the spectral evaluation and check for cross-interferences. It is therefore unclear whether recent advances in DOAS, for example, the evaluation of aromatics (Volkamer et al., 1998), are correctly considered by the OPSIS routines. The result of this experiment shows that (a) the significance of instrument comparison between point-monitors and line-integrating techniques near strong sources of NO is limited by the development of vertical gradients of many gases, and (b) monitoring instruments need to reveal their measurement and evaluation algorithms for quality control.

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