Comparative Measurements of Criteria Pollutants Using DOAS and Conventional In-situ Monitoring Technique at Sung Nam city of Korea

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Abstract

To test the compatibility of differential optical absorption spectroscopy (DOAS) and conventional in-situ monitoring technique, we conducted a comparative analysis of the two systems using hourly measurement data sets of three criteria pollutants including NO_2, O_3, and SO_2 collected in months between April and June of 2001 at Sung Nam city, Kyung Gi Province, Korea. The results of our comparative analysis were useful to evaluate the various aspects of DOAS performance, of particular the level of agreement with the counterpart method through computation of percent differences and correlation analysis. Interpretation of the mixing ratio data for those chemical species was however confined in terms of explaining the differences affected by the changes in environmental conditions because measurements of important meteorological parameters were limited during most of the study period. Nevertheless, the overall results of this study strongly demonstrated that the mixing ratios of major pollutants measured by the two different systems maintain strong compatibility from various respects.

1. INTRODUCTION

The introduction of differential optical absorption spectroscopy (DOAS) system has offered diverse perspectives on the studies of pollution phenomena and/or processes occurring in the atmosphere (Platt and Perner, 1979; Platt et al., 1979). It is known that the system is potent enough to allow instantaneous measurements of airborne pollutants along an open light path. In the recognition of its wide applicability in the field of air quality monitoring (AQM), its use has been phenomenal from many regions of the globe in recent years. In some countries, the analytical reliability of DOAS has been acknowledged after comprehensive testing procedures taken under the regulation of their official research institutions or organizations (such as US EPA or TÜV in Germany: TÜV, 1999; Stevens et al., 1993). As such, evidence is strong enough to support the suitability of DOAS system for the employment with the AQM purpose (Casavant and Kamme, 1992). However in many countries and regions around the globe, chances were yet scarce enough to restrict the proper evaluation of its performance for such applications.

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As part of project to examine the compatibility be-
tween DOAS and conventional in-situ measurement
technique, we conducted a field measurement study
from a Korean Environmental Management Corpora-
tion (hereafter as EMC) building located at Sung Nam
city of Kyung Gi Province in Korea during the period
of Apr. through Jun. 2001. The study was undertaken
by simultaneously measuring the mixing ratios of NO_2,
O_3, and SO_2 using the two independent measurement
techniques under the guidance of the Environmental
Instrument Inspection (EII) team of the EMC in Korea.
These experiments were initially designed and con-
ducted with an aim of checking the reliability of DOAS
in the field application as the performance approval test
of the Korean EMC. However, we expect that the re-
sults of the study can also be used to help aid the esta-
blishment of the data base for DOAS application in the
Korean peninsula. Here we present the results of a field
measurement study through which the compatibility of
the two measurement techniques were checked for the
total duration of about 50 days.

2. MATERIALS AND METHODS

This study was carried out from the Korean EMC
office building located at Sung Nam city of Kyung Gi
province in Korea during April~June 2001 (Fig. 1).
The site is located several kilometers (kms) south of
Seoul metropolitan city. While being located in a vast
agricultural area surrounded by hilly terrains, the site is
also exposed by a major traffic road connecting to An
Yang city on the western bound. Hence, we expect that
the site is to be influenced by the mixed effects of both
natural and anthropogenic processes ongoing in the
area. Intercomparison between two different measure-
ment techniques was made using hourly-averaged
mixing ratio data for three pollutants (NO_2, O_3, and
SO_2) that were measured concurrently by both DOAS
(Opsis AB, Sweden) and the conventional point mea-
surement system (Thermo Environment Instrument
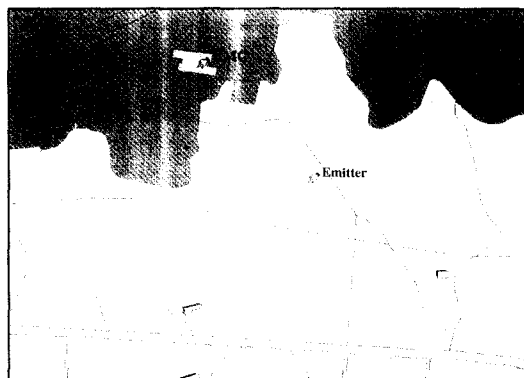Inc., USA: hereafter as TE).

**Fig. 1. A map of location for the comparative analysis
between DOAS and point monitoring technique.
This study was conducted from an EMC building
located at Sung Nam city in Korea.**

The DOAS system used in this study consists of an
emitter (ER 150) and receiver (RE 150) in combination
with the AR 500 analyzer (TÜV, 1999). The ER sys-
tem was installed on the top of the 5th floor Korean
EMC building, while the RE system was placed on the
roadside at distance of 260 m apart from ER for the
analysis of pollutants over that pathlength. The RE sys-
tem was interfaced with the AR system designed to
conduct PC-based spectral analysis; the light for spec-
tral analysis is generated from a 150 W xenon lamp in
the ER system and corrected in the RE system. Analy-
sis of the pollutants was made by a UV-spectrometer
with a moveable grating in combination of a slotted
disk for scanning (at user-defined integration time of
less than 5 minutes) and a single photomultiplier tube
(PMT) as a detector. The quantitative analysis of trace
compounds is based on Lambert Beer's law (e.g., Platt,
1994):

$$I_1 = I_0 e^{-\alpha LC}$$

Here I_1 and I_0 denote the light intensity at a specific
wavelength with and without absorption, respectively.
In addition, α, L, and C denote the absorption coeffi-
cient, the length of open path, and the mixing ratio of
trace gas, respectively. Since the broadband absorption
has little spectral structure, the DOAS technique only

considers the narrow band structure. Hence for the derivation of concentrations, the differential cross sections ($\Delta\alpha$) over several wavelength channels are taken into account. The cross sections for the wavelengths (gases) of interest have been pre-recorded by the manufacturer and stored in the analyzer's memory. The strength of absorption for each trace gas however varies as a function of wavelength. Thus, to optimize the detectibility of each gas for the DOAS system, wavelength region of the strongest absorption was selected and used for each gas such as: $406.2 \sim 444.2$ nm (NO_2), $265.7 \sim 304.4$ (O_3), and $280.7 \sim 319.3$ (SO_2). The AR system was adjusted to analyze each of the 40 nm band windows resolved into 1,000 channels; the system can perform 100 scan per second basis.

The data with the light intensity below 10% were all discarded prior to data analysis because of high photon noise (e.g., the data obtained during the incidental May period). The sensitivity of DOAS technique is also suspected to be affected by temperature. According to UMEG's report (1993), temperature change of 10 K can influence $\pm2\%$ of the DOAS sensitivity at 20°C. The precision of our DOAS system for the three gases was quantified using replicate analysis of cell references and was generally found in the range of 1 to 2%. Although detection limits (DLs) for three trace gases investigated were not quantified directly during this study, they may be estimated roughly from the results of previous study such as those reported by Martini et al. (1994). These authors made measurements using a similar system with a similar path length (500 m), reporting the DL values of 0.07 (SO_2), 0.1 (NO_2), and 1 ppb (O_3). During this measurement period, the calibration of the DOAS system was made once using the cell reference system of the Opsis AB, right after the initial installation (Apr. 2001). Because of minor problems encountered in the calibration of O_3, DOAS data sets were recalibrated and readjusted at the end of experiment.

For the purpose of our intercomparative study, the data sets collected by DOAS were referenced against those of the TE system that has been conducting the

measurements on a routine basis for the national monitoring system. The analysis of NO_2, O_3, and SO_2 by the latter system was made by the combination of three models 42CTL, 49C, and 43CTL, respectively. The principles for these systems involve photometric detection of chemiluminiscence, UV absorption, and UV fluorescence, respectively. The basic analytical parameters for these systems are well known. The DLs for NO_2, O_3, and SO_2 are estimated to be 0.4, 1, and 1 ppb, respectively. Their precisions are normally found at 1% range. The TE system was calibrated both at the beginning and ending period of experiment following the maintenance protocols of the Korean Ministry of Environment. Except for the three species of our interest, measurements of basic parameters (such as meteorological data sets) were also attempted. However, insertion of those data was limited, as they were made from the month of June which was toward the end of the whole experiment period.

3. RESULTS AND DISCUSSION

3. 1 A scheme for the data assortment

The main criteria to accommodate the requirement for the approval test were initially set up by the Korean National Institute of Environmental Research (KNIER) on behalf of Korean Ministry of Environment (KMOE) as follows: (1) to obtain continuous measurement data sets for at least 50 consecutive days, (2) to make the valid data sets for direct comparison by more than 80% of the whole hourly measurement data (implying the total quantity of invalid data sets less than 20%), and (3) to maintain agreement of two measurement techniques within 40% in terms of percent difference (PD) values defined below. The details of conditions how these three criteria are applied to our field data sets can be explained as follows.

3. 1. 1 Requirements for the minimum number of days for consecutive runs

As we started our experiment at 9 : 00 AM on 20 Apr. 2001, it should have ended up at the same time on

9 June to meet the minimum requirement of 50 days in a row. However, an accident took place which caused the production of meaningless data sets; the position of the emitter was altered during an electric maintenance operation by the local electricity service near its installation area (12 May). As a consequence, the data with significantly low light level (e.g., below 20%) had been accumulated for about 9-day period until we fixed the problem on 21 May. Hence the data acquired during that incidental period were excluded from further analysis, and the experiment was extended to the 18th of June 2001 to meet the basic criteria for the experimental duration. In processing of those concurrently determined data sets, it may be desirable to treat them in a logistical manner to explain their distribution and behavior. Hence, we defined the initial data sets, collected either prior to or after the May incident, to be the category of stage I.

3.1.2 Requirements for the minimum number of data at hourly duration

All the measurement data were initially programmed to be retrieved at every 5 min interval, regardless of instrumental system. Hence in light of the excessive amount of data for statistical analysis, they were first converted into the hourly data sets; a time span of hour is typically considered to be the minimum duration for the evaluation of environmental data sets in Korea. As a means to assure the representativeness of hourly data sets, we set the criteria for the validity of hourly data as follows; we accepted the cases, only if a total of more than six 5-min data points were collected at hourly intervals. In accordance with this data discrimination scheme we employed, we defined all the data sets that meet 50% requirement for hourly duration to be the category of the stage II.

3.1.3 Requirements for the agreement level between two techniques

As an attempt to evaluate the level of agreement in the observed data sets between the two different systems, we computed the perecent difference (PD) values for each of hourly matching data pairs obtained by the

two as follows:

$$\text{Percent difference (PD)} = \frac{[C_D - C_P] * 100}{C_D}$$

where subscripts D and P denote DOAS and point monitoring technique. According to this formula, PD values can be assigned with both positive and negative values. For example, if the mixing ratio of DOAS is larger or smaller by 10 times than that of counterpart, the resulting PD values can be either 90 or -900%, respectively. Considering the non-existence of criteria to judge the absolute accuracy of line-integrating measurement data relative to point monitoring technique, the computed PD values can be used as simple criteria to distinguish the observed differences between comparable data pairs. Hence, the last stage of data assortment was made by deleting the data pairs that exhibit the concentration differences of either larger or smaller by four times than each other (i.e., PD values of above 75 or below -300%). The difference of four times was selected to arbitrarily control the quantity of data sets sufficiently large enough for comparative purpose; this is to comply with the KNIER-suggested requirement of the third type aforementioned. Hence, those data remaining after this screening stage were termed as the category of the stage III.

3.2 The overall features of comparable measurements

For the simple comparison of the distribution patterns for each chemical specie, their daily mean values are depicted as a function of time (Fig. 2). A statistical summary of all the hourly measurement data is presented across different stages defined above (Table 1). The concentrations of each chemical specie determined by both methods can hence be compared directly between stages. Although the concentrations of all species measured by the DOAS system tend to be higher rather than those measured by the counterpart system, they all seem to exhibit strong consistencies in data distribution through time. As the whole study was conducted during the late spring to early summer, it may

be reasonable to see the generally enhanced O_3 (e.g., around 30 ppb) and reduced SO_2 concentration levels (e.g., around 3~4 ppb). In addition, detailed comparison of their temporal variabilities indicates several interesting aspects in their distribution patterns. Fig. 1 indicates a large compatibility in the temporal distribution patterns of mixing ratio values between NO_2 and SO_2 over the study period. However, NO_2 tends to

exhibit much smaller variability over daily scale (smaller standard error (SE) values as seen by smaller error bars shown in Fig. 2). In addition, while a fairly strong agreement between two measurement systems is apparent for NO_2, the level of agreement appears to be much weak for the rest of two species. This trend even became intensified, after the resumption of experiment on 21 June.
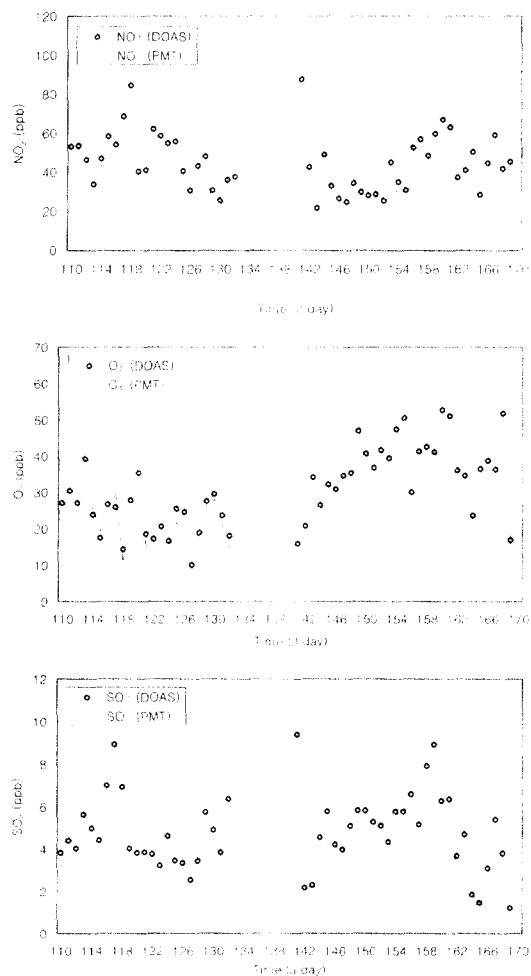

Fig. 2. Temporal distribution patterns of three trace gases (NO_2, O_3, and SO_2) over the entire study period of Apr. 20 (Julian day = 110) through 18 Jun. 2001. PMT in the figure legend denotes point monitoring technique employed for this comparative analysis.

Table 1. A statistical summary of pollutant species measured using two different measurement techniques of DOAS and conventional point monitoring technique (PMT). Data are compared at three different stages of I, II, and III. All concentrations in ppb unit.

	NO_2 (DOAS)	O_3 (DOAS)	SO_2 (DOAS)	NO_2 (PMT)	O_3 (PMT)	SO_2 (PMT)
(1) Stage I: all hourly measurement data collected for the whole study period were used.						
Mean	44.49	28.77	4.75	35.08	20.96	3.12
SE	0.68	0.55	0.08	0.48	0.50	0.05
Median	40.45	25.28	4.31	31.89	16.88	2.89
SD	23.46	18.99	2.68	16.67	17.54	1.65
Min	1.79	2.55	0.19	6.63	0.08	0.44
Max	115.55	107.17	19.77	85.99	84.36	11.92
N	1208	1208	1208	1207	1207	1207
CI(90%)	1.11	0.90	0.13	0.79	0.83	0.08
(2) Stage II: hourly data were deleted, if 5 minute data points were collected less than 6 times per hour.						
Mean	44.52	28.74	4.75	35.06	20.97	3.12
SE	0.68	0.55	0.08	0.48	0.51	0.05
Median	40.48	25.17	4.31	31.89	16.90	2.89
SD	23.49	19.00	2.68	16.66	17.54	1.65
Min	1.79	2.55	0.19	6.63	0.08	0.44
Max	115.55	107.17	19.77	85.99	84.36	11.92
N	1205	1205	1205	1204	1204	1204
CI(90%)	1.11	0.90	0.13	0.79	0.83	0.08
(3) Stage III: hourly data data were deleted, if there were 4 times difference between the two systems.[*]						
Mean	44.45	30.99	4.67	35.15	23.49	3.18
SE	0.68	0.60	0.08	0.48	0.53	0.05
Median	40.43	28.14	4.26	31.93	19.83	2.92
SD	23.41	19.24	2.58	16.62	17.15	1.63
Min	7.27	2.55	0.92	6.63	0.97	0.44
Max	115.55	107.17	19.77	85.99	84.36	11.92
N	1197	1032	1162	1196	1031	1161
CI(90%)	1.11	0.99	0.12	0.79	0.88	0.08

[*] If compared in terms of PD values, the cases with less than −300% or more than 75% belong to this category

To learn more about the temporal distribution pat-terns of pollutants determined side-by-side through an employment of two different measurement techni-ques, we checked for the short-term variabilities of each pollutant over 24 hour scale. As our measure-ments made during this study period lack the quantifi-cation of most environmental parameters, comparison of data over short time scale can be useful enough to derive some patterns associated with the changing meteorological conditions (It is easy to expect that diurnal scale will be more periodical than that observ-ed over long-term scale such as over the whole mea-surement period of about 50 days). It is well acknowl-edged that compound like ozone is a very sensitive indicator of photochemical processes which tends to be influenced by the changes in the light level or tempera-ture (Virkkula, 1997). In fact, the results shown in Fig. 3 indicate very contrasting patterns among different species. Since the production of ozone tends to be maximized by the strongest photochemical reaction during the daytime, its mixing ratio reaches the maxi-mum value at that time. By contrast, the mixing ratios of NO_2 which tends to act as ozone precursor exhibits the minimum value at that specific time period.

Comparison of these temporal patterns in general indicates the existence of strong compatibility between the two different techniques. Detailed comparison shows that O_3 exhibits the strongest disagreement between the two technique during the daytime around 2 pm, while that for NO_2 is completely contrasting with the best agreement at that specific time. The level of agreement (or disagreement) seems to vary in a highly systematic manner through time. Although the causes of such phenomenon may not be accountable to a full extent, the variations in the mixing conditions for che-mical species involved in such chemical reactions ap-pear to be reflected in a highly selective manner by both measurement techniques. This may lead to the ob-served levels of compatibility between the two mea-surement techniques. It is interesting to note that the pattern of SO_2, while not so sensitive resembles the case of NO_2 to a large degree.
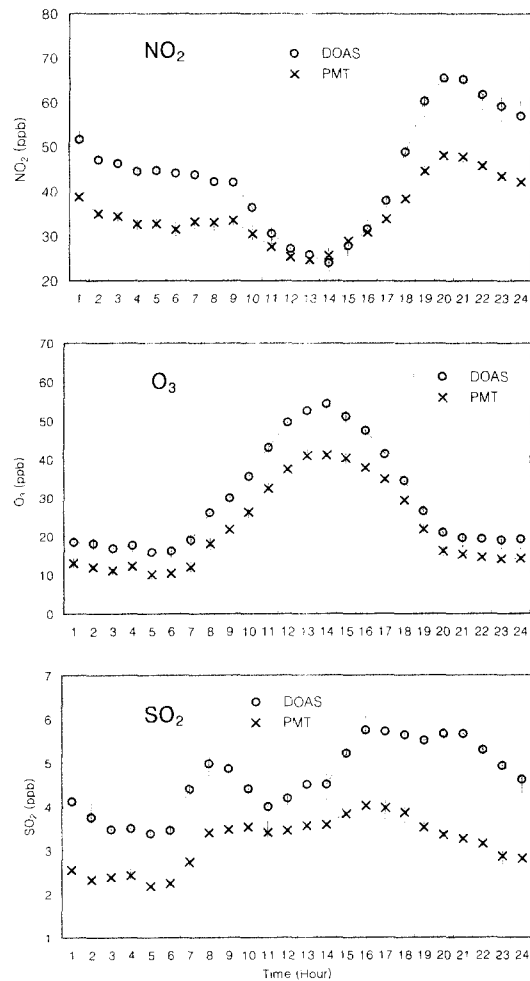
Fig. 3. Short-term variabilities of three trace gases over 24-h period were compared using the data sets collected during this time period. Their patterns are compared using data sets obtained by both measurement techniques. PMT in the figure legend denotes point monitoring technique employed for this comparative analysis.

3. 3 Evaluation of bias structure between two measurement techniques

The principles of DOAS and commercial in-situ measurement technique are based on different metho-dologies, namely line-integrating and point-oriented analysis, respectively. Hence, direct evaluation of DOAS-derived data relative to its counterpart (for this

study) can be subject to various limitations from the start. As the spatial scope of DOAS application is highly extensive horizontaly, interpretation of its data is to be more liable to changes in meteorological conditions. While acknowledging many inherent differences between two techniques, relative differences of comparable data sets collected concurrently can be assessed basically in terms of percent difference (PD) values described above. Table 2 presents a statistical summary of PD computation results at varying stage
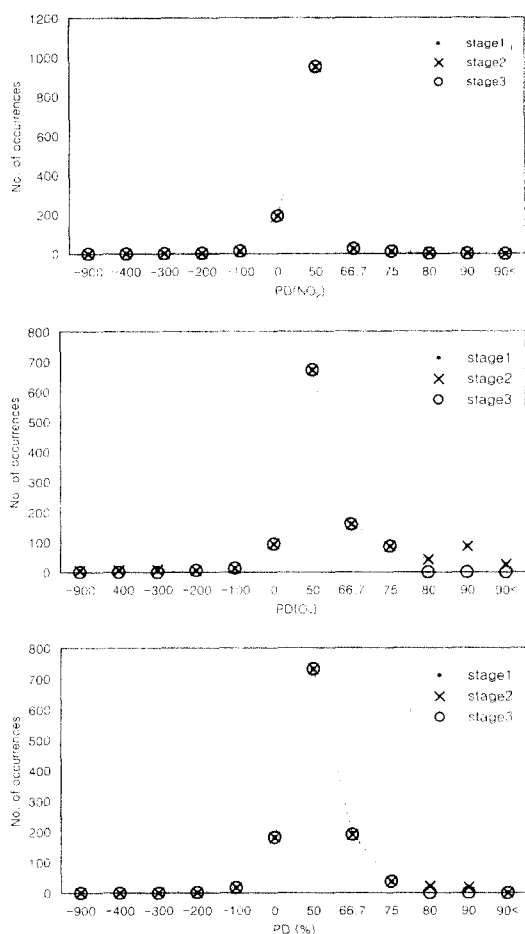

Fig. 4. Frequency distribution patterns of percent difference (PD) values computed for each chemical specie. The patterns for each specie are plotted for each stage of data screening employed in this study.

we defined earlier. The strength of compatibility for two techniques can be checked simply by the proximity of PD values to zero. The experimental data sets of the optimal condition at the stage III show that the magnitude of the agreement level, if assessed in terms of PD values, decreases on the order of NO_2 (14.0%), SO_2 (22.8%), and O_3 (26.9%). This pattern is in fact in a strong compliance with those seen from other respects of the methodological compatibility. For example, if the similarity of the mean values (for a given specie) between the two methods is concerned, the best agreement is found from NO_2. Moreover, if we make a comparison of the total number of valid data points at different screening steps (e.g., with increasing stage number); NO_2 exhibits the smallest data loss rate.

Table 2. Comparison of percent difference (PD) values derived using the two different measurement techniques.

|	PD(NO_2)	PD(O_3)	PD(SO_2)
1. Stage I			
Mean	13.34	24.08	22.98
SE	1.17	2.90	1.89
Median	22.31	34.08	31.34
SD	40.82	100.74	65.76
Min	−886.51	−1372.78	−1782.61
Max	100.00	100.00	100.00
N	1208	1208	1208
CI (90%)	1.93	4.77	3.11
2. Stage II			
Mean	13.32	24.00	22.90
SE	1.18	2.91	1.90
Median	22.33	34.08	31.26
SD	40.79	100.93	65.78
Min	−886.51	−1372.78	−1782.61
Max	81.47	99.60	88.92
N	1202	1202	1202
CI (90%)	1.94	4.79	3.12
3. Stage III			
Mean	14.02	26.88	22.78
SE	0.86	1.25	1.10
Median	22.31	30.08	30.38
SD	29.80	39.98	37.46
Min	−235.91	−299.80	−268.66
Max	74.95	74.96	74.65
N	1194	1029	1159
CI (90%)	1.42	2.05	1.81
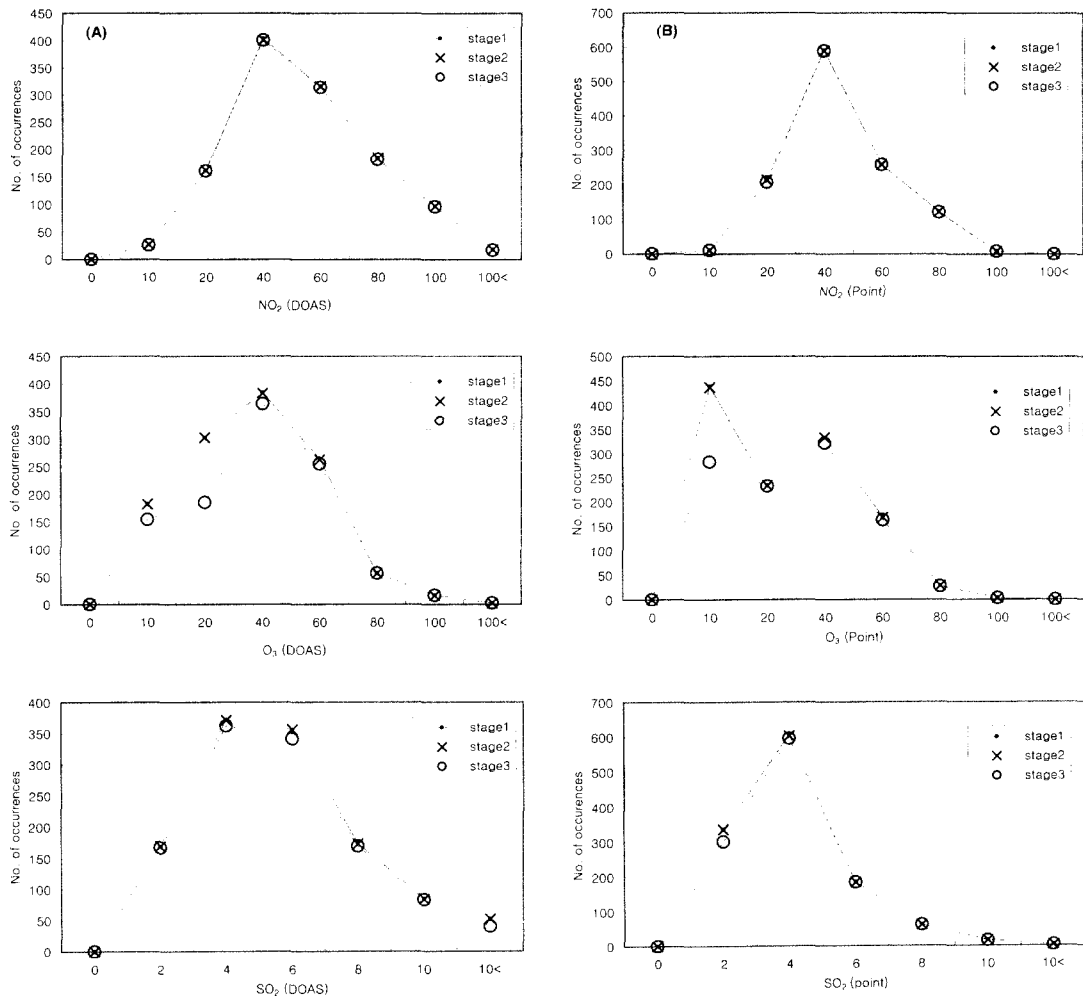
Fig. 5. Frequency distribution patterns of the mixing ratios for three different trace gases determined during this study. The patterns can be compared for each stage of data screening employed in this study: (a) DOAS, and (b) conventional in-situ method. For both (a) and (b), all concentrations in ppb unit.

Table 3. Comparison of light level (%) measured for each of three pollutants measured by the DOAS system during the whole study period.

	NO_2	O_3	SO_2
Mean	65.70	57.30	60.19
SE	0.15	0.17	0.16
Median	66.58	58.58	61.00
SD	5.11	5.82	5.49
Min	22.17	10.00	14.92
Max	73.08	66.92	68.75
N	1198	1198	1198
CI(90%)	0.24	0.28	0.26

To be able to provide more accurate descriptions of bias structure, the frequency distribution patterns were compared for each individual chemical specie investigated in this study in Fig. 4. The PD values listed on the x-axis of graph are selected to correspond to the absolute differences of 2, 3, 4, 5, and 10 times between two systems. (For example, if the concentration of DOAS is larger or smaller by 4 times than the counterpart, the corresponding PD values can be computed to be 75% or -300%, respectively.) The results shown in Fig. 4

clearly demonstrate that the most dominant portion is at PD values of 0 to 50%, regardless of chemical species. It hence indicates that the mixing ratios determined by the DOAS system were measured to be systematically larger than those of conventional ones by within the differences of two times. It is however interesting to note that the general features of the frequency distribution patterns differ greatly among chemical species. In the case of NO_2, its distribution patterns exhibit the least variabilities (or the strongest consistencies) across the stage. On the contrary, those of ozone tend to vary most dramatically across the stage; this is in fact compatible with the results seen from the comparison from other respects (e.g., Table 2). It is noteworthy that the deletion of the ozone data (at stage 3) occurred most intensively at PD values above 75%, implying that enhancement of DOAS values was more prominent to create odd PD values in the case of O_3 (Fig. 4). The frequency distribution of each specie were also compared using their mixing ratio value of both systems in Fig. 5. The largest variation across different stage again appears to be the most significant for O_3 data set, regardless of measurement method.

If PD values can be used to distinguish the extent of observed differences between the two methods, it is important to explain the factors affecting their variations such as their relationships with meteorological conditions. However because of significant delay in our measurement schedule of meteorological parameters, the factors affecting the bias structure cannot be inferred more descriptively. Because of such limitations, we looked for other aspects to explain the differences of the two measurement techniques, such as examining the mixing ratios in relation with the concurrently determined light level data. As explained above, the least agreement is expected at significantly reduced light levels (e.g., data sets of less than 20% measured during the May incident period described above). Table 3 shows the results of the light level measurement that were acquired in conjunction with the DOAS measurements of three criteria pollutants of our interests. Fig. 6 presents the temporal patterns of PD values and light
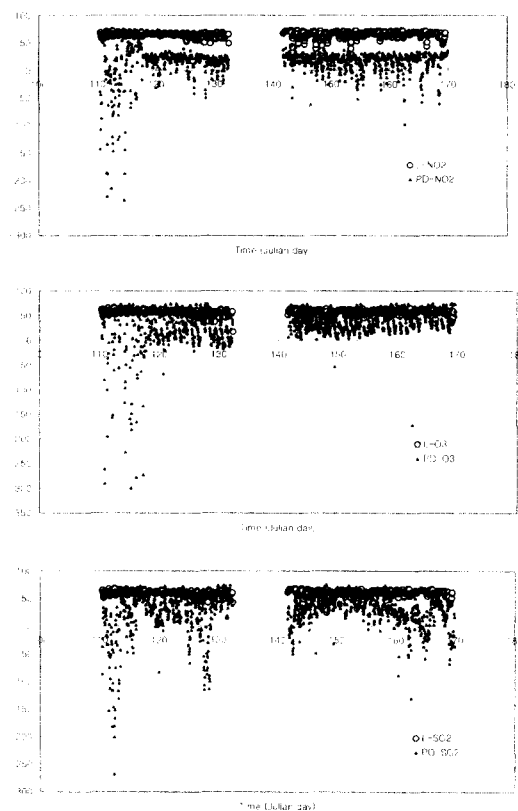

Fig. 6. Temporal pattern of PD values and light level data for the whole study period. Those two parameters measured for each specie are simply plotted as a function of time. The capital letters L and PD in figure legend denote light level and percent differences between the two measurement methods.

level data simultaneously. It is seen consistently that the largest PD values for each specie tend to occur most intensively at the very beginning period of experiments. In the case of NO_2, there exists a very contrasting pattern between the very beginning and ending period. Whereas highly negative values were seen at the very earlier phase, they became highly stable with the values approaching zero with the progress of time. Contrary to the observed pattern of NO_2, the results of O_3 exhibited positive values throughout the experiment. It may hence be reasonable to conclude that the occurrences of enhanced DOAS concentration data relative to the conventional method must have been
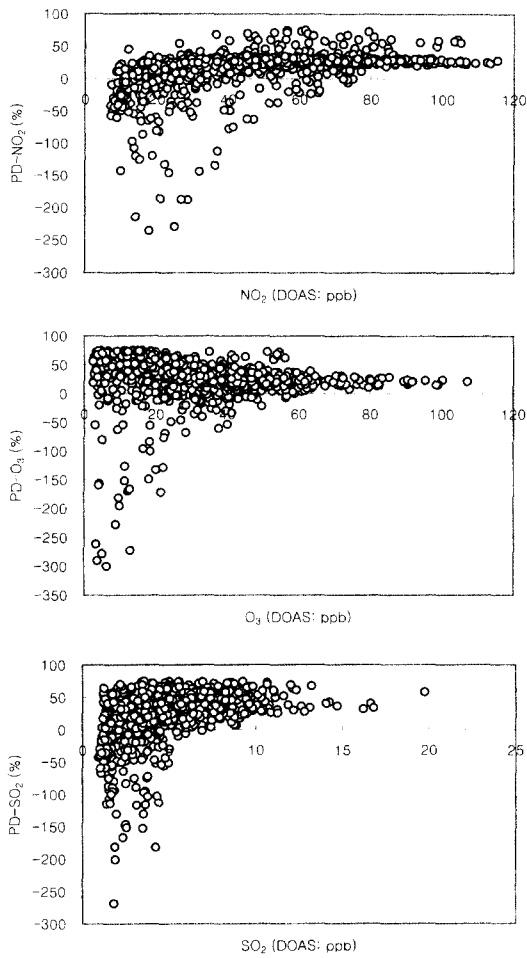
Fig. 7. Comparison of the mixing ratios determined by DOAS and the coresponding PD values derived by the formula.

Fig. 8. Comparison of light level (L-) in percent and PD values in percent for each chemical specie.

highly consistent through time. Examination of PD values as a function of time hence seems to be valuable to assess the relative relationship of two methods through time.

To further study the general characteristics of bias, we checked for the relationships between PD values and the DOAS concentrations that were used for the derivation of PD values in Fig. 7. The results of this analysis indicate that the development of large negative PD values is apparent at smaller concentration range (of all species investigated), while positive PD
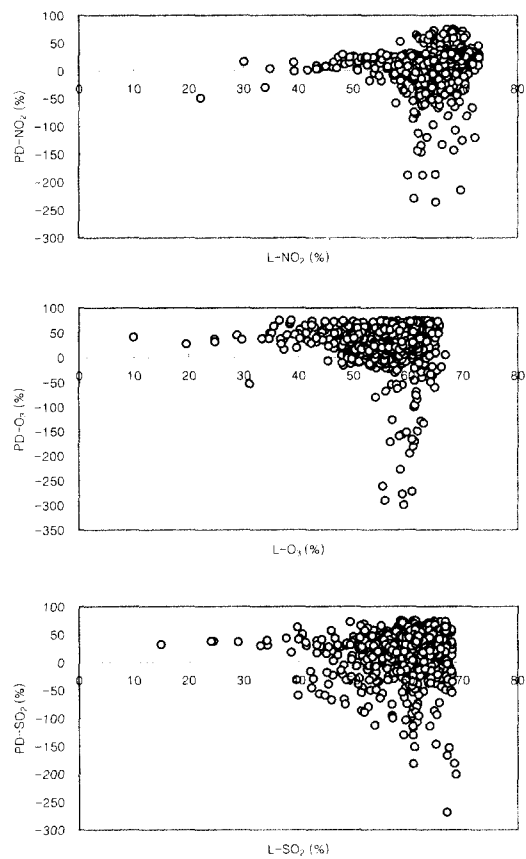
values are predominant at higher concentration range. This observation thus clearly demonstrates that the concentrations determined by the DOAS technique tend to be smaller at low concentration range but larger at high concentration range. This contrasting pattern appears to reflect the systematic differences inherent in the instrumental sensitivity to a certain extent (For example, DOAS is expected to show more delicate changes in the lower concentration range for its lower DL values than the counterparts). In addition, we examined the PD values directly as a function of light level in Fig. 8. It is seen that the PD values exhibit rather constant values at lower light level , once most of outlying values were filtered out by deleting those of

the May incident. With the increase of light level, the PD values appear to show values at more diverse range of both positive and negative values. However, the frequency of the PD values approaching zero appears to be much more abundant. Overall, the inspection of the PD characteristics suggests that the bias between the two systems observed during this study period may have been affected more strongly by other factors than the simple impact of the light level on DOAS performance. Hence, concurrent examination of other parameters including meteorological data may be prerequisite to derive more meaningful conclusions for comparing the results with such aspects.

3. 4 Evaluation of the extent of correlations

In order to assess the level of agreement (or disagreement) between the two measurement techniques, PD values were used as basic parameter. However, to properly evaluate the performance of DOAS, evaluation of the strength of correlations between the two methods may also have to be checked thoroughly as one of essential steps. The results of correlation analysis, presented in Fig. 9, show some differences from those seen as the results of the PD computations. If we simply compare the correlation coefficients (r) of each chemical specie, both methods seem to maintain very strong correlations with r values typically approaching 0.7 (SO_2) to 0.9 (NO_2 and O_3). Considering that the number of matching data pairs for this analysis is above 1,000, they seem to exhibit the existence of highly significant correlations between the methods.

If 'r' values are useful to evaluate the degree to which each matching data pair agree, the slope and offset values (derived from such regression analysis) can be used to explain their relationships in more quantitative aspects. If the measurement data of two different systems are perfectly comparable, the slope and offset value should come up with 1.0 and 0, respectively. However, most of previous studies showed that such values can be moderately apart from the theoretical ones (Martini et al., 1994). Hence, the slope values of about 0.6 and 0.8 for NO_2 and O_3 appear to be
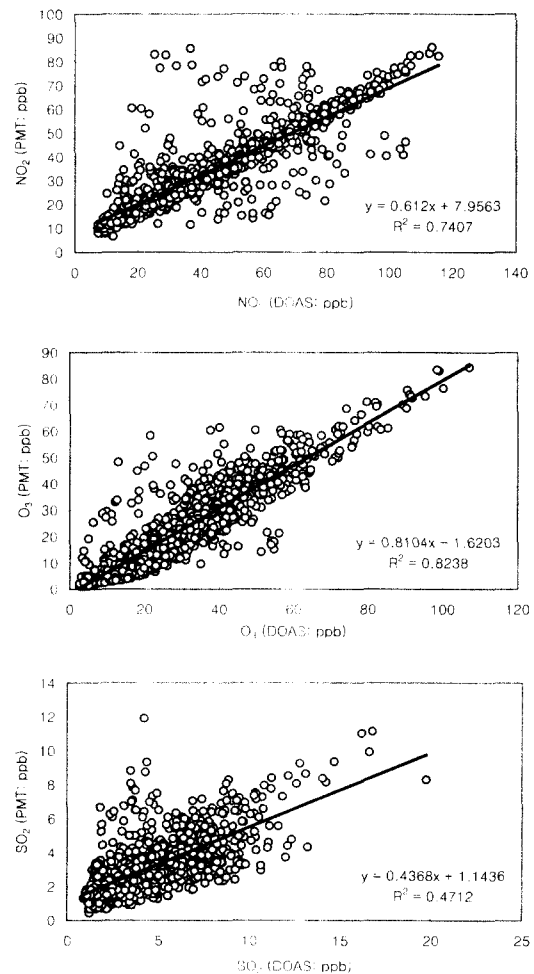

Fig. 9. Results of linear regression analysis using the mixing ratio data sets for three trace gases measured during Apr. through Jun. 2001. PMT in the figure legend denotes point monitoring technique employed for this comparative analysis.

moderate. The offset value near zero, found in the case of ozone analysis by the two method, is very ideal. However, the results of SO_2 which showed more comparable pattern from the comparison of PD values are now much complicated to interpret in terms of this approach. While its slope value was computed to be 0.44, offset value yielded a rather large value of 1.14 which corresponds to about one fourth of its mean concentration. Comparison of regression results in general

indicates that DOAS data can be systematically higher under most circumstances than the conventional method. Although the extent of deviations is apparent from ideal slope or offset values, these results are still compatible with those seen from previous studies. In studies of the same criteria pollutants using DOAS at Banpo district of Seoul during the year of 2000, Kim and Kim (2001) reported slope and offset values of 0.64 to 1.04 and −7.3 to 7.45, respectively.

4. CONCLUSIONS

To test the compatibility of DOAS performance in relation with the conventional in-situ monitoring technique, we conducted measurements of three criteria pollutants including NO_2, O_3, and SO_2 at EMC office building of Sung Nam city, Korea during April through June 2001. Through a series of analysis for data sets collected by both systems, we were able to make useful comparison of two different monitoring techniques for criteria pollutants. To maintain reasonable amounts of valid data points for comparison, we applied procedures to discriminate data sets at varying stages. If the data are sorted out by the number of 5 min data points within hourly duration and by the PD values, large differences were apparent among different chemicals. In terms of simple comparison of PD values, NO_2 exhibited the best agreement between the two measurement techniques followed by SO_2; however, O_3 yielded the weakest agreement mainly because of systematically higher concentrations derived by DOAS. Consequently, the data loss rate of O_3 was most significant throughout the screening procedure employed between stages. However, the results of correlation analysis indicated more complexities involved in comparative analysis. Unlike the PD results, O_3 exhibited fairly good compatibility between the two systems, while SO_2 suffered from the lack of correlation relative to two other species investigated concurrently. Although the scope of data interpretation was limited to a certain extent by the absence of environmental parameters

(e.g., meteorological data) at present stage, the results of statistical analysis on our data sets still suggest that one can obtain high quality data sets to meaningfully compare the mixing ratio data sets produced by the two independent monitoring techniques. If our measurement data are checked against the initial standards established to test compatibility of different measurement techniques by KMOE, our test results appear to be moderately compatible with those.

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