



Comparison of NO₂ and SO₂ Measurements Using Different Passive Samplers in Tropical Environment

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ABSTRACT

This report describes the results of an inter-comparison study conducted for the sampling and analysis of NO₂ and SO₂ by using different type of passive samplers in tropical urban environment. For this purpose, field experiments were proposed to be conducted by two round robin tests from Sept. 2007 to Aug. 2008 in Singapore. A set of different types of passive samplers have been exposed to ambient air at atmospheric research station in National University of Singapore along with suitable active samplers (as reference method) for a sufficient period of time (3–4 weeks). Annular denuder system (ADS) active sampling data showed that NO₂ concentration level (23.8–28.1 ppb) in Singapore was slightly higher than the WHO guideline but SO₂ concentration (12.5–14.9 ppb) was approximately twice the value of WHO guideline. For the two round robin tests, accuracy analysis by using active sampling data as reference demonstrated that grand mean values from passive air sampling (PAS) and active sampler average concentrations, for both NO₂ and SO₂, are in close agreement with each other. Precision evaluation based on the triplicate samplers co-located at the same sampling site - Singapore showed that most of the passive samplers applied here had repeatability. ANOVA statistical analysis also showed no significant difference between the measurement data obtained by different type of passive samplers for both round robin tests in Singapore.

Keywords: Inter-comparison study; Passive sampling; Nitrogen dioxide; Sulfur dioxide.

INTRODUCTION

Air pollution, with its short- and long-term impacts on environment and human health, has been a globally recognized problem due to rapid population growth, industrialization and urbanization in recent decades. Ambient air quality standards were established by many countries around the world together with air quality guidelines by World Health Organization (WHO) for the protection of the local, regional and global atmosphere (Lim *et al.*, 2005). Routine air quality monitoring studies are of particular importance in order to identify long-term air quality trends, assess the effectiveness of air quality control regulations and improve air quality management efforts (Özden *et al.*, 2008). Nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) are the most monitored criteria air pollutants in ambient air

because of their effects on the human respiratory system, their contributions to the acidification of the ecosystems, the acidity of airborne particulate matter and its health impacts and the role of NO₂ in the formation of photochemical oxidants (Plaisance *et al.*, 2002; Cox, 2003). In addition, both NO₂ and SO₂ can also impact visibility as their corresponding oxidation products are incorporated into ambient aerosols. Therefore, routine monitoring of NO₂ and SO₂ at a global network of sampling locations with reliable measurement methods is needed to investigate both temporal and spatial changes in air quality on local to global scales (Lefohn and Shadwick, 1991; Hewitt, 2001).

Spatial distributions of NO₂ and SO₂ on the regional and/or global scales are only sparsely available in the literature as their automated measurement systems are expensive and require considerable maintenance. Consequently, there remains a strong need to develop simple and cost-effective methods applicable for large-scale monitoring of both NO₂ and SO₂. The use of passive samplers at a network of sampling locations has received increasing attention in the last decade for determining temporal and spatial distributions of key air pollutants. Passive samplers are simple devices that are capable of capturing gas pollutants from the

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atmosphere, without an air pump or a flow meter for sample collection (Cruz *et al.*, 2004). The sampling rate is controlled by a physical process, which can be molecular diffusion through a static air layer or permeation through a membrane filter (Brown *et al.*, 1984). The average atmospheric concentration can be calculated based on Fick's law of diffusion during the intended sampling period under specific meteorological conditions (Palmes and Lindenboom, 1979). Based on the pioneering work by Palmes and Gunnison (1973) on passive sampling design, several passive samplers have been developed for application under the field conditions (Ayers *et al.*, 1998; De Santis *et al.*, 2002; Sather *et al.*, 2007; Swaans *et al.*, 2007). The low cost of passive samplers in conjunction with their flexibility of deployment in the field makes them attractive for assessing spatial distributions of gases of interest such as NO_2 , SO_2 , O_3 , and NH_3 over large areas, validating atmospheric transport and deposition models, base-line studies and establishing atmospheric monitoring networks, etc. (Carmichael *et al.*, 2003; Cox, 2003; Cruz *et al.*, 2004).

The appropriateness of the use of passive samplers has been questioned in the past due to concerns related to reliability and accuracy. To address this issue, a systematic inter-comparison study involving different kinds of passive samplers was initiated during 2007–2008 for measurements of NO_2 and SO_2 in ambient air under different meteorological conditions together with established active sampling methods in Singapore. From Sept. 2007 to Aug. 2008, a few sets of different types of passive samplers were exposed to ambient air in National University of Singapore (NUS) along with suitable active samplers for a sufficient period of time (3–4

weeks) to assess their performance and measurement capabilities. Two round robin tests were conducted during this period in order to evaluate the performance of passive samplers at the same sampling site. Results obtained from the inter-comparison study are presented and discussed in this article.

METHODS

Sampling of NO_2 and SO_2 Using Passive Samplers

Four types of passive samplers were specifically tested in this study: (a) Ogawa samplers (Ogawa & Co. USA Inc), (b) NUS samplers, prepared by NUS, and (c) samplers from The Council for Scientific and Industrial Research in South Africa (CSIR), (d) Capillary samplers, prepared by Kazuyuki Aoki's method (Komeiji *et al.*, 1997). The functioning of the passive samplers is based on their chemical and physical processes i.e., chemical reaction and laminar diffusion, respectively. The rates at which gases in ambient air diffuse into the sampler are controlled by the diffusion coefficients of the respective gases. At the rear end of the sampler, the gases meet a filter (paper disk) which has been impregnated with a chemical capable of reacting very specifically with and quantitatively trapping the pollutant of interest. As the solid support is impregnated with a small quantity of absorbent material dissolved in a volatile solvent, the gases that come into contact with it impact against a high surface area and are trapped efficiently. The above sampling principle was applied by those passive samplers of Ogawa, NUS and CSIR with similar assembly structures using the impregnated filter absorption (Fig. 1).

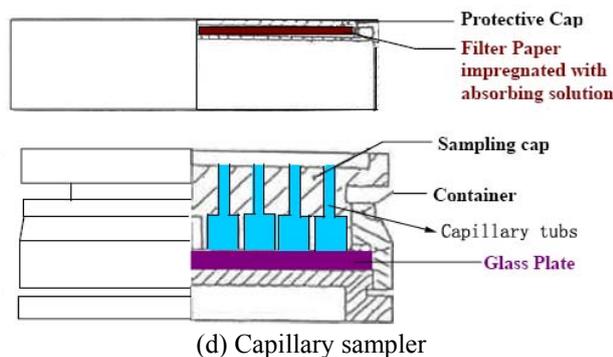
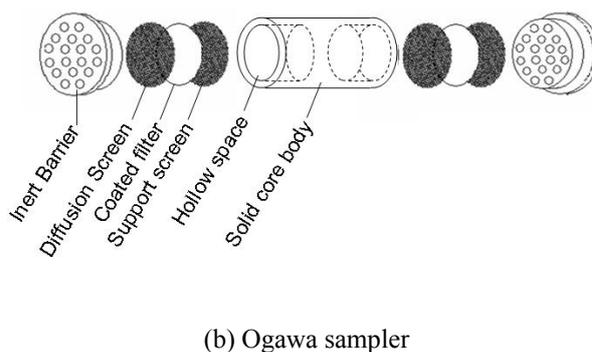
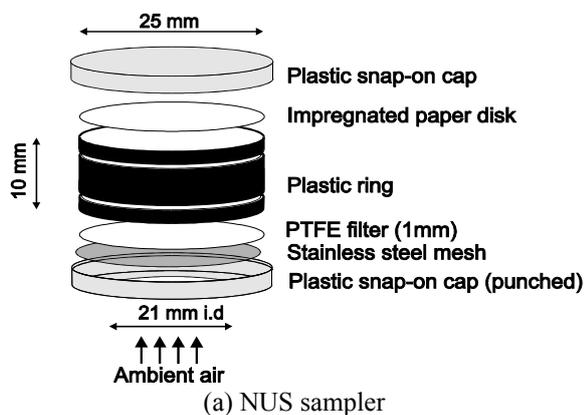


Fig. 1. Schematic representation of passive sampler assembly.

The Capillary sampler was developed by a Japanese scientist, Kazuyuki Aoki in 1978 (Komeiji *et al.*, 1997), which also uses the gas phase diffusion. However, in this sampler, the absorbent solution is not coated on any filter but filled into small capillary tubes (Fig. 1), through which the gases could contact the absorbent solution surface directly and get captured efficiently as well.

For this inter-comparison study, 4 passive samplers of each type (3 samplers for field measurements and 1 sampler to be treated as a blank) were applied for independent NO₂ and SO₂ measurement. For the two round robin tests, all the passive samplers were deployed at the Atmospheric Research Station in NUS (1°18'N and 103°46'E). The sampling site is 67 m above the sea level, and is approximately 1 km away from the open sea. The air quality at the sampling site is influenced by local emissions from chemical industries, major power plants, and petroleum refineries located in the southwest direction and also by urban vehicular traffic. There are two main seasons, the Northeast Monsoon from December to March and the Southwest Monsoon from June to early September. These two seasons are separated by two relatively short inter-monsoon periods, with winds blowing in no fixed direction. The months of February and March are relatively drier.

In this intercomparison study, all samplers were exposed to ambient air under the prevailing weather conditions in Singapore from September to October 2007 (670 hrs of total exposure, pre-monsoon season) and July to August 2008 (549.5 hours of total exposure, Southwest monsoon season), respectively. After the sampling, the passive samplers were carefully dismantled, stored in plastic containers, and transported to the analytical laboratory at NUS for chemical analysis.

Sampling of NO₂ and SO₂ Using Active Samplers

In this study, URG-2000 annular denuder system (ADS) was used without a filter-pack holder at the exit since only gaseous NO₂ and SO₂ were studied here. The adsorbent used in this study was activated carbon. Prior to use, carbon was extracted by using ultrasonicator with water, washed twice with 0.5 M NaOH, twice with boiling water and then dried at 105°C. The coating solution used in this study for acidic gases, NO₂ and SO₂, (2 % Na₂CO₃ + 1% glycerol in water-methanol) was prepared by adding 1.5 g of carbon to 10 mL of a 2% Na₂CO₃ and 1% glycerine in methanol/water 1/1 (v/v) solution. In fact, a series of experiments with the ADS in the same environmental conditions have shown that the collection of NO₂ on a coating prepared from a mixture of components as mentioned above was quite consistent and comparable (De Santis *et al.*, 1996). In addition, it has been reported that the collection efficiency (E) of coating solution (Na₂CO₃ - glycerine in water/methanol) for acidic gases including NO₂ and SO₂ could be up to 98% (Allegrini *et al.*, 1987), for which the definition of E would be discussed later.

Active Sampling by ADS

During both sampling periods for round robin tests in NUS, active samplers were co-located in the field along with the passive samplers to collect data for NO₂ and SO₂

on a daily basis (exposure to ambient air for 24 hours). For this purpose, URG annular denuder systems (ADS), coated with appropriate chemical reagents as mentioned above, were deployed in the field, operating with an air pump at a flow rate of 20 L/min.

Analytical Methods

For Ogawa, NUS and CSIR filters, the protocols used in NUS for NO₂ and SO₂ were detailed as follows. For NO₂ samples, after exposure to the test environment, the stainless screens and cellulose fiber filters were put into a 25 mL glass vial, containing 8 mL water, and then shake immediately. Over the next 30 minutes, occasional shaking of the vials was applied. At the end of first 30 minutes period, vials were cooled to 2–6°C, and 2 mL of colour producing reagent (sulphanilamide solution and the NEDA solution in a 10:1 ratio) was added. After adding the colour-producing reagent and shaking the vials for thorough mixing, they were kept cold for an additional 30 minutes. Vials were then allowed to equilibrate at room temperature, for about 20 minutes. The amount of coloured derivative was determined with a spectrophotometer at a wavelength of 545 nm. The same procedure was applied for blank samples and standard solutions.

For SO₂ samples, the stainless screens and cellulose fiber filters were put into a 25 mL glass vial containing 8 mL water after exposure. The vial was then shaken immediately. Over the next 30 minutes, occasional shaking of the vials was applied. 0.2 mL H₂O₂ (1.75%) was added, and vials were shaken slowly for 10 minutes. Vials were then equilibrated at room temperature for about 20 minutes, and the extracts were analysed using ion chromatography (IC). The same procedure was applied for blank samples.

Due to the speciality of Capillary samplers with capillary tubes containing liquid absorbent solution, the NUS lab exactly followed the analytical protocols for both NO₂ and SO₂ described by Komeiji *et al.* (1997).

For NO₂ samples, after exposure the protective cap was taken off and the sampling cap was loosen by one turn; then 5 mL of ultra pure water was added through a capillary path with dispenser and thoroughly mixed inside. N mL of the extracts were taken out and put into a test tube where another 5 mL colour reagent (sulphanilamide solution and NEDA solution (10:1)) was added and mixed. After 10 mins, the absorbance at the wavelength of 540 nm was determined. The amount of N mL is so chosen that the absorbance ranges from 0.1 to 0.8. The same procedure was applied for blank samples and standard solutions.

For SO₂ samples, 0.4 mL of pRA solution (trichloroacetic acid plus pararosaniline chloride) was added to a small test tube with a stopper. Five mL of NaOH-NaN₃ solution was spiked into the Capillary exposed sampler by loosening up the sampling cap by one turn and thoroughly mixed inside. Then 4 mL extract was taken out with a pipette and transferred to the same test tube for pRA and another 0.04 mL of 1.4% HCHO was added and mixed immediately. After 10–15 mins, the absorbance was determined at 580 nm.

After extraction and analysis by spectrophotometry and IC, all the results were converted to ambient concentrations

of NO₂ and SO₂ by taking the specific meteorological conditions (ambient temperature and relative humidity during the sampling period) into account.

For ADS samples, the absorbed gases from denuders were extracted by equilibrating with 20 mL ultra-pure water. NO₂ was measured spectrophotometrically using sulphanilamide and NEDA while SO₂ was analysed using Dionex ion chromatography following the calibration of the instruments with suitable standards. The same protocol was used as for passive samplers (Ogawa, NUS and CSIR) for the sake of consistency.

Quality Control

The analytical quality of the data was determined using limit of detection (LOD), calibration linearity, and by checking instrument status during analysis. During each phase of this sampling campaign, at least one set of unexposed different samplers as blank samples loaded with blank filters (e.g., Ogawa, NUS and CSIR) and with adsorbent solution (Capillary sampler) were deployed along with those being exposed samplers at each sampling site. After sampling, all these blank samples were immediately taken back to laboratories and analyzed accordingly. Limits of detection were derived from the blanks and quantified as the mean plus three times the standard deviation of the amounts in the blanks. For this inter-comparison study, LODs for both NO₂ and SO₂ ranged from 6.4–40.8 ng/sample and 18.8–52.3 ng/sample, respectively. Since the blank values were very minor, all the concentrations from passive sampling were reported here without blank value deduction. The linearity of calibration standards was calculated by regression analysis with values ranging from 0.99–1.00 (r^2) for both NO₂ and SO₂ by spectrophotometry and IC. Samples spiked with standards were analyzed regularly to check instrument performance during analysis.

Some drawbacks by using passive samplers for acidic gases have to be admitted here. Previous studies have reported that the chemical reaction between O₃ and NO within diffusion tubes may result in an overestimation of NO₂ in urban environment (Heal and Cape, 1997; Heal *et al.*, 1999); in addition, the lack of specificity of some absorbents used for NO₂ may cause the absorption of SO₂ which can reduce the collection efficiency of the sampler by acidifying those adsorbents (Cox, 2003). However, it has been impossible to establish generally applicable empirical correction factors as the concentrations of these gases vary both spatially and temporally (Vardoulakis *et al.*, 2009).

The most substantial approach for sampling a gas in the presence of corresponding aerosol particles is the denuder technique (Trebs *et al.*, 2004). Dry-coated diffusion denuders are reliable but provide only long time-average concentration measurements (Dasgupta, 1993). The flow rate of sampling during the exposure period can affect whether or not the sampling is carried out stably and precisely. The flow rate was used for assessment because a low flow rate results in a small sampling volume, which leads to a small amount of target pollutants captured; the variation of flow rate can also cause the bias of total volume of air collected by denuder system. In this study, the flow rate was constantly

adjusted to 20 L/min over the sampling period (~24 h) to minimize the bias of ambient air concentrations of pollutants when calculation was processed.

To validate our data quality obtained from the IC measurements, in the 1st round robin test, 10 filter extracts were chosen randomly out of 30 samples and analyzed separately for NO₂ using a spectrophotometer as was done for the passive sampler measurements. The results obtained from these two independent analytical techniques were comparable to each other ($r^2 = 0.93$, slope = 0.96) which ensures the quality of the active sampler data.

RESULTS AND DISCUSSION

Active Sampling of NO₂ and SO₂ in Singapore

Collection efficiency (E) of the denuder in actual operation can be determined by using sequential pairs of the denuders, which is defined as (Ferm, 1979)

$$E = 1 - \frac{b}{a} \quad (1)$$

where a and b are the amounts of the same ionic species extracted from the first and the second denuder, respectively. In order to assess the collection efficiency of ADS with coating solution (Na₂CO₃ - glycerine in water/methanol) under tropical conditions with high ambient temperature and relative humidity, two sequential pairs of ADS was deployed with flow rate 20 L/min at NUS atmospheric research station and five samples were collected on daily basis right before each round robin test. It was found that the efficiency of ADS used here is still above 98%. The Reynolds number, R_e , which in a laminar stream must be less than 2000, was calculated as

$$R_e = \frac{4F}{\gamma\pi(d_1 + d_2)} \quad (2)$$

where γ is the kinematic viscosity of air, d_1 and d_2 are the internal and external diameters of the annulus, F is the flow rate; based on the data obtained from the pre-experimental period, R_e was calculated as around 400.

Occurrence Level of NO₂ and SO₂

Figs. 2 and 3 show the daily average concentrations of NO₂ and SO₂ based on active sampling measurements during the study period of two round robin tests at NUS. In the 1st round robin test, only one set of denuder system was deployed co-located with all the passive samplers; while in the 2nd round robin test, duplicate ADS systems were placed and error bars in Figs. 2(b) and 3(b) are the standard deviations of duplicate daily concentrations of NO₂ and SO₂, respectively.

The daily average concentration varied from 16.7 to 35.6 ppb (parts per billion by volume) with an average of 23.8 ± 3.6 ppb NO₂ (dotted line in Fig. 2(a)) during the first round robin test, and varied from 20.1 to 37.2 ppb with an average of 28.1 ± 4.1 ppb NO₂ (dotted line in Fig. 2(b))

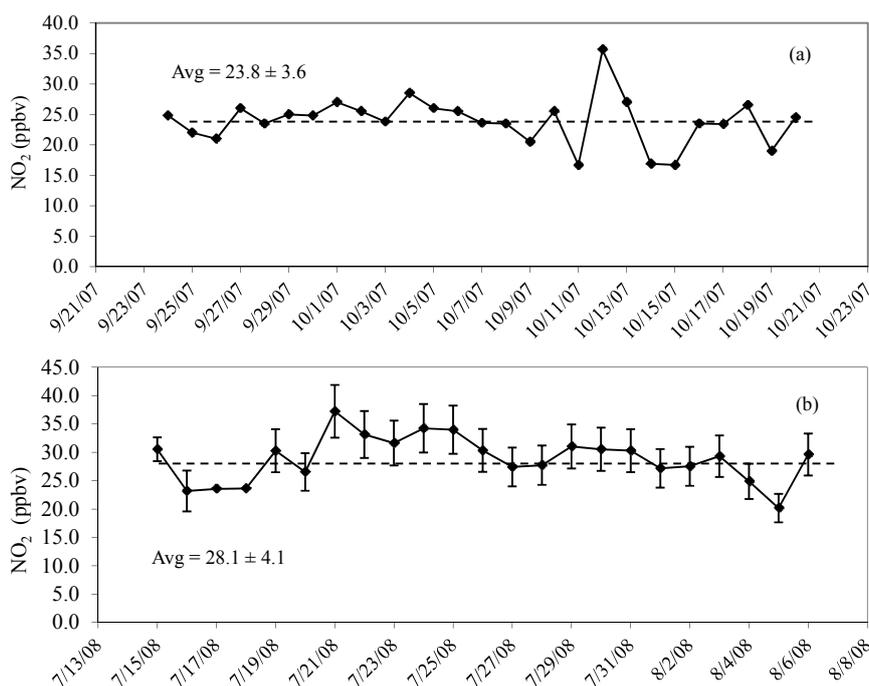


Fig. 2. Daily average concentration of NO₂ ((a) 1st round robin test from September to October 2007; (b) 2nd round robin test from July to August 2008).

during the second round robin test, respectively. The average concentration of NO₂ measured in the first round robin test was not significantly different from that obtained during the second round robin test. These values were relatively higher than those recently measured in El Paso (6–18 ppb), Texas (Sather *et al.*, 2007), Eskişehir of Turkey (11.4 ± 8.6 ppb) (Özden *et al.*, 2008), Mulhouse (11.2 ± 3.2 ppb) of France (de Fouquet *et al.*, 2007) and Az-Zour area (7.89 ppb) of Kuwait (Ramadan, 2010), while they were lower than the occurrence level in Beijing (48.9 ppb) (Meng *et al.*, 2008). NO₂ level in Singapore was very close to the annual mean value (21.4 ppb, converted from 40 µg/m³) of WHO guideline (WHO, 2005).

The daily average concentrations of SO₂ based on active sampling are shown in Fig. 3. The daily average concentration varied from 8 to 19.4 ppb with an average of 12.5 ± 2.7 ppb SO₂ (dotted line in Fig. 3(a)) during the first round robin test, and varied from 6.9 to 23.9 ppb with an average of 14.9 ± 2.3 ppb SO₂ (dotted line in Fig. 3(b)) during the second round robin test, respectively. Both of these two average concentrations were close to each other. The occurrence level of SO₂ here was higher than the winter season average in Lahore (7.2 ppb), Pakistan (Biswas *et al.*, 2008), Taichung (0.99 ± 0.34 ppb), Central Taiwan (Cheng and Horng, 2007), urban side of Mt. Gokurakuji (2.48 ppb) and Higashi-Hiroshima (2–12 ppb) in Japan (Chiwa *et al.*, 2008; Tham *et al.*, 2008), and were also much higher than those measured in surrounding places such as Tanah Rata (0.1 ppb) and Lawa Mandau (0.2 ppb) in Malaysia, and Bukit Kototabang (0.07 ppb) and Kalimantan (0.15 ppb) in Indonesia (Carmichael *et al.*, 2003). Taichung, Mt. Gokurakuji and surrounding areas are with less population/population density, traffic and industrial emissions as compared to Singapore, so SO₂ levels

are expected to be significantly lower in these places. In comparison, average concentration of SO₂ in Singapore was comparable to the annual average concentration of SO₂ in New York (10.2 ppb) of USA (Bari *et al.*, 2003), and approximately twice the value (7.7 ppb, converted from 24 hr mean 20 µg/m³) of WHO guideline (WHO, 2005).

Air Concentration Variation between Subsequent Active Air Samples

From both Figs. 2 and 3, the temporal profile of NO₂ and SO₂ concentrations during both robin tests show some variability from one sampling event to the next. In addition to the standard deviations of daily concentrations mentioned in the above section, the variability in an AAS data series can be quantified by the Active Sampling Variation (ASV) (Hayward *et al.*, 2010):

$$ASV = \frac{\sum_{i=0}^n |C_i - C_{i+1}|}{nC_{avg}} \quad (3)$$

where C_i is the air concentration during a given sampling event, C_{i+1} is the air concentration during the following sampling period, and n is the number of sampling events in the calculation. C_{avg} is the average air concentration during the n sampling events. In this study, ASV has been used to compare the variability of air concentrations within and between different round robin tests.

For NO₂, ASV values are 0.16 and 0.14 for 1st round and 2nd round robin test; while for SO₂, these values are 0.20 and 0.23 for 1st round and 2nd round robin test, respectively. ASVs for both NO₂ and SO₂ show very low values. The

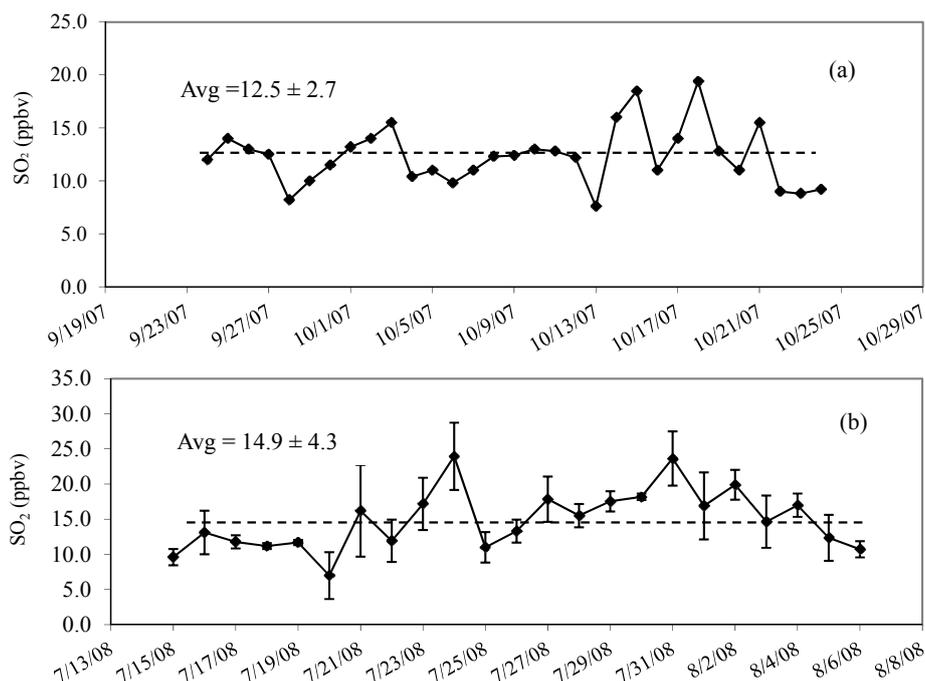


Fig. 3. Daily average concentration of SO₂ ((a) 1st round robin test from September to October 2007; (b) 2nd round robin test from July to August 2008).

ratio of ASV of each species obtained during different round robin test helps to identify during which sampling period the respective species has higher variability. In present study, both NO₂ and SO₂ have ASV_{round 1}/ASV_{round 2} ratios (1.1 and 0.87, respectively) close to unity, indicating that the variability of concentrations of NO₂ and SO₂ measured in the first round robin test was not significantly different from that obtained during the second round robin test.

Passive Sampling for Two Round Robin Tests in Singapore

The results obtained from various passive samplers are graphically presented in Fig. 4 for NO₂ and SO₂, and all three measured values for each sampler type are shown during 1st and 2nd round robin tests, respectively.

The accuracy of the passive sampling was evaluated by using the relative bias (%), calculated from the relationship (Vardoulakis *et al.*, 2009):

$$\text{Bias} = \frac{(C_P - C_A)100}{C_A} \quad (4)$$

where C_P is the pollutant concentration measured with a passive sampler, and C_A is the concentration measured with the active sampler, which was used as the reference method in this study. From Fig. 4, it can be seen that grand means and active sampler average concentrations, for both NO₂ and SO₂, are in close agreement with each other, even though most passive sampling events underestimated the levels of these two acidic gases with negative biases (Fig. 5). Ogawa samplers for both NO₂ and SO₂ had the minimum bias in both round robin tests. Except the NUS-SO₂, CSIR-SO₂ in the 1st round robin test (bias: -29.6% and -32.8%,

respectively) and Capillary-SO₂ in the 2nd round robin test (bias: -24.9%), most of the biases calculated for the samplers used in these two round robin tests are within 20%, which should be acceptable considering different sampling techniques. Minor variations of the measurement results between different types of passive samplers also occurred. There are several factors that may affect the accuracy of NO₂ and SO₂ passive sampling measurements. In this study, all the samplers were co-located at the same atmospheric research stations in Singapore, the effects from meteorology were minimized by specially designed protective screens and shelters. The factors such as different materials of the tubes, non-consistent diffusion paths and areas for different samplers and various absorbent solutions applied may result in the variations of the measurement accuracy (Glasius *et al.*, 1999; Kirby *et al.*, 2000; Vardoulakis *et al.*, 2009). In addition, it should be noted that the biases derived are associated with both sampling and analytical methods.

The precision of the passive sampling measurements for NO₂ and SO₂ was assessed by using triplicate samplers co-located in Singapore for two round robin tests. The relative standard deviation, a statistical measure of repeatability, was calculated for each pollutant and presented in Fig. 6. For NO₂, the RSD ranged from 2.7% (Ogawa) to 16.7% (Capillary) and from 2.4% (CSIR) to 19.0% (Capillary) during the 1st and 2nd round robin test, respectively; for SO₂, the RSD varied in the range of 4.2%–18.8% and 7.9%–20.7% for 1st and 2nd round robin test, respectively. It clearly shows that the chemical impregnated filter based samplers (Ogawa, CSIR and NUS) had smaller variations than the capillary tubes based samplers. The large variations were observed in Capillary samplers for both NO₂ and SO₂ in this study, but the reason for this variation was unknown

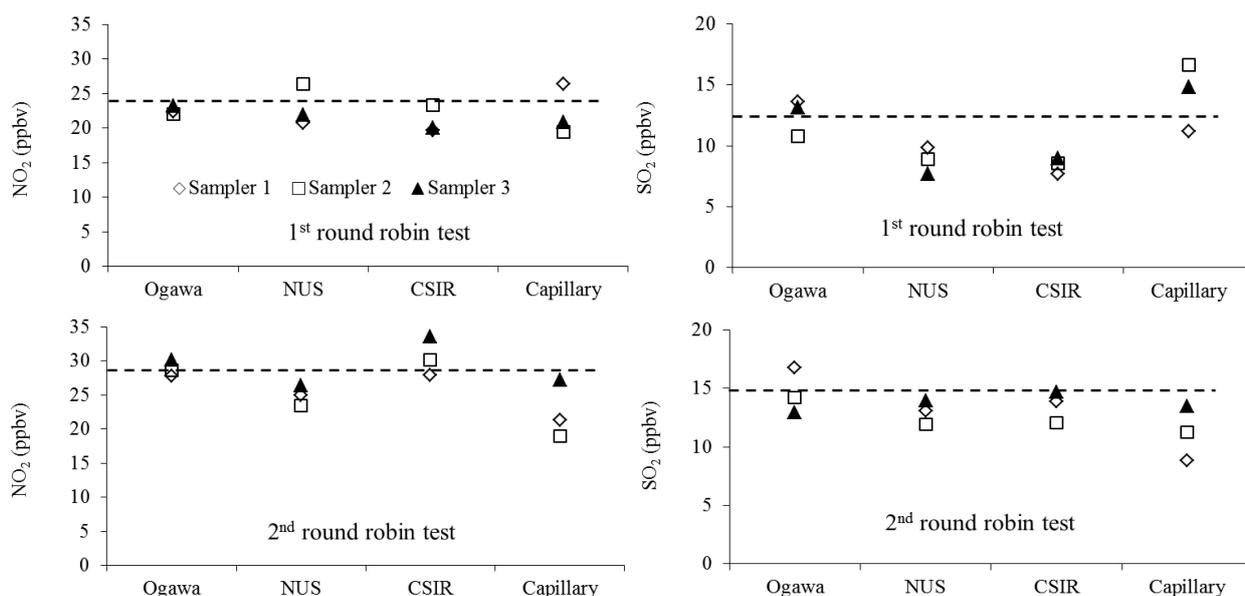


Fig. 4. Inter-comparison of passive sampling for NO₂ and SO₂ obtained by two round robin tests in Singapore (dashed lines represent the average ADS concentrations for both NO₂ and SO₂ during each round robin test).

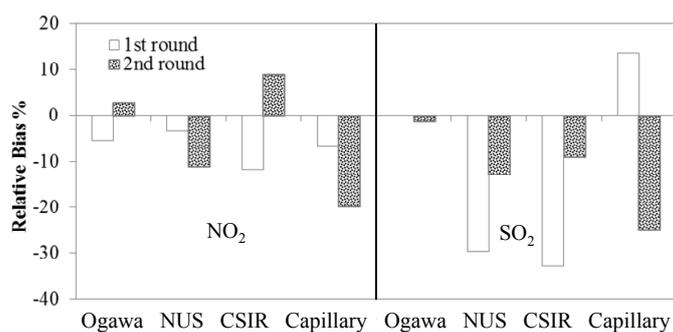


Fig. 5. Relative biases (%) for different passive samplers.

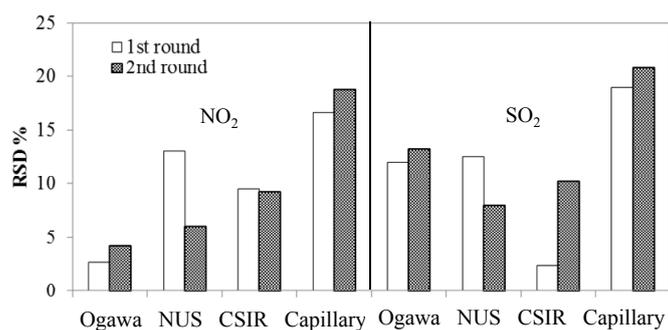


Fig. 6. Relative standard deviations (RSD%) for different passive samplers.

and further verification needs to be taken if and when possible. One of the possible reasons might be because of the inconsistent amount of absorbent solution manually injected into the capillary tubes for different set samplers.

The replicate measurements made ($n = 3$) from different passive samplers for NO₂ and SO₂ were statistically tested by ANOVA analysis to assess whether there is any significant difference between the values obtained by different type of passive sampler for these two round robin

tests in Singapore. For this purpose, the data were treated statistically with ANOVA-single factor analysis and the results are presented in Table 1. As could be seen from the table, for NO₂, F values are 1.46 and 1.03 with P values 0.27 and 0.44 for both 1st and 2nd round robin test, respectively; for SO₂, F values are 2.95 and 1.14 with P values 0.06 and 0.39 for both 1st and 2nd round robin test, respectively. As F values are less than the critical values for both NO₂ and SO₂ and P values were higher than 0.05

Table 1. Statistical comparison of the measurement data.

Analytes		F value	F Critical	P Value
NO ₂	a	1.46	3.1	0.27
	b	1.03	3.5	0.44
SO ₂	a	2.95	3.1	0.06
	b	1.14	3.1	0.39

a. 1st round robin test; b. 2nd round robin test.

(significance level- α), it can be said that the measurement results from the different passive samplers showed no significant difference during these two round robin tests in Singapore.

CONCLUSIONS

Both round robin field tests for the inter-comparison of passive samplers for the analysis of NO₂ and SO₂ were successfully completed under urban-influenced conditions. The results presented here showed that the chemical impregnated filter based samplers (Ogawa, CSIR and NUS) had smaller RSD for both NO₂ and SO₂ than the capillary tubes based samplers. In addition, this study indicated larger variations particularly for SO₂ between the samplers of different types and also within the samplers of the same type especially in the 1st round robin test in Singapore. This difference could be either due to analytical uncertainties, or the difference in the sampling efficiency based on different coating solutions. However, it could still be seen that this inter-comparison study has relatively systematic consistencies. A more comprehensive study might be needed by using more replicate samplers to further assess the performance of individual type of samplers as well as the organizer's laboratory analytical capability.

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REFERENCES

- Allegrini, I., De Santis, F., Di Palo, V., Febo, A., Perrino, C. and Possanzini, M. (1987). Annular Denuder Method for Sampling Reactive Gases and Aerosols in the Atmosphere. *Sci. Total Environ.* 67: 1–16.
- Ayers, G.P., Keywood, M.D., Gillett, R., Manins, P.C., Malfroy, H. and Bardsley, T. (1998). Validation of Passive Diffusion Samplers for SO₂ and NO₂. *Atmos. Environ.* 32: 3587–3592.
- Bari, A., Ferraro, V., Wilson, L.R., Luttinger, D. and Husain, L. (2003). Measurements of Gaseous HONO, HNO₃, SO₂, HCl, NH₃, Particulate Sulfate and PM_{2.5} in New York, NY. *Atmos. Environ.* 37: 2825–2835.
- Biswas, K.F., Ghauri, B.M. and Husain, L. (2008). Gaseous and Aerosol Pollutants during Fog and Clear Episodes in South Asian Urban Atmosphere. *Atmos. Environ.* 42: 7775–7785.
- Brown, R.H., Harvey, R.P., Purnell, C.J. and Saunders, K.J. (1984). A Diffusive Sampler Evaluation Protocol. *Am. Ind. Hyg. Assoc. J.* 45: 67–75.
- Carmichael, G.R., Ferm, M., Thongboonchoo, N., Woo, J.H., Chan, L.Y., Murano, K., Viet, P.H., Mossberg, C., Balasubramanian, R., Boonjawat, J., Upatum, P., Mohan, M., Adhikary, S.P., Shrestha, A.B., Pienaar, J.J., Brunke, E.B., Chen, T., Tang, J., Ding, G.A., Leong, C.P., Dhiharto, S., Harjanto, H., Jose, A.M., Kimani, W., Kirouane, A., Lacaux, J.P., Richard, S., Barturen, O., Cerda, J.C., Athayde, A., Tavares, T., Cotrina, J.S. and Bilici, E. (2003). Measurements of Sulfur Dioxide, Ozone and Ammonia Concentrations in Asia, Africa, and South America Using Passive Samplers. *Atmos. Environ.* 37: 1293–1308.
- Cheng, M.T. and Horng, C.L. (2007). Characteristics of Atmospheric Aerosol and Acidic Gases from Urban and Forest Sites in Central Taiwan. *Bull. Environ. Contam. Toxicol.* 79: 674–677.
- Chiwa, M., Kondo, H., Ebihara, N. and Sakugawa, H. (2008). Atmospheric Concentrations of Nitric Acid, Sulfur Dioxide, Particulate Nitrate and Particulate Sulfate, and Estimation of Their Dry Deposition on the Urban- and Mountain-facing Sides of Mt. Gokurakuji, Western Japan. *Environ. Monit. Assess.* 140: 349–360.
- Cox, R.M. (2003). The Use of Passive Sampling to Monitor Forest Exposure to O₃, NO₂ and SO₂: A Review and Some Case Studies. *Environ. Pollut.* 126: 301–311.
- Cruz, L.P.S., Campos, V.P., Silva, A.M.C. and Tavares, T.M. (2004). A Field Evaluation of a SO₂ Passive Sampler in Tropical Industrial and Urban Air. *Atmos. Environ.* 38: 6425–6429.
- Dasgupta, P.K. (1993). Automated Measurement of Atmospheric Trace Gases-diffusion-based Collection and Analysis. *Adv. Chem. Ser.* 232: 41–90.
- de Fouquet, C., Gallois, D. and Perron, G. (2007). Geostatistical Characterization of Nitrogen Dioxide Concentration in an Urban Area Part I: Spatial Variability and Cartography of the Annual Concentration. *Atmos. Environ.* 41: 6701–6714.
- De Santis, F., Allegrini, I., Di Filippo, P. and Pasella, D. (1996). Simultaneous Determination of Nitrogen Dioxide and Peroxyacetyl Nitrate in Ambient Atmosphere by Carbon-coated Annular Diffusion Denuder. *Atmos. Environ.* 30: 2637–2645.
- De Santis, F., Dogeroglu, T., Fino, A., Menichelli, S., Vazzana, C. and Allegrini, I. (2002). Laboratory Development and Field Evaluation of a New Diffusive Sampler to Collect Nitrogen Oxides in the Ambient Air. *Anal. Bioanal. Chem.* 373: 901–907.
- Ferm, M. (1979). Method for Determination of Atmospheric Ammonia. *Atmos. Environ.* 13: 1385–1393.
- Glasius, M., Calsen, M.F., Hansen, T.S. and Lohse, C. (1999). Measurements of Nitrogen Dioxide on Funen

- Using Diffusion Tubes. *Atmos. Environ.* 33: 1177–1185.
- Heal, M.R. and Cape, J.N. (1997). A Numerical Evaluation of Chemical Interferences in the Measurement of Ambient Nitrogen Dioxide by Passive Diffusion Samplers. *Atmos. Environ.* 31: 1911–1923.
- Heal, M.R., O'donoghue, M.A. and Cape, J.N. (1999). Overestimation of Urban Nitrogen Dioxide by Passive Diffusion Tubes: A Comparative Exposure and Model Study. *Atmos. Environ.* 33: 513–524.
- Hewitt, C.N. (2001). The Atmosphere Chemistry of Sulphur and Nitrogen in Power Station Plumes. *Atmos. Environ.* 35: 1155–1170.
- Kirby, C., Fox, M. and Waterhouse, J. (2000). Reliability of Nitrogen Dioxide Passive Diffusion Tubes for Ambient Measurement: In Situ Properties of the Triethanolamin Absorbent. *J. Environ. Monit.* 2: 307–312.
- Komeiji, T., Oohashi, T., Suga, K. and Aoki, K. (1997). Relationship between Dry Deposition Amount of NO₂ and Growth Rate of Forest, Annual Report of the Institute of Environmental Sciences (In Japanese), p. 292–296.
- Lefohn, A.S. and Shadwick, D.S. (1991). Ozone, Sulfur Dioxide, and Nitrogen Dioxide Trends at Rural Sites Located in the United States. *Atmos. Environ.* 25A: 491–501.
- Lim, L.L., Hughes, S.J. and Hellowell, E.E. (2005). Integrated Decision Support System for Urban Air Quality Assessment. *Environ. Modell. Softw.* 20: 947–954.
- Meng, Z.Y., Ding, G.A., Xu, X.B., Xu, X.D., Yu, H.Q. and Wang, S.F. (2008). Vertical Distributions of SO₂ and NO₂ in the Lower Atmosphere in Beijing Urban Areas, China. *Sci. Total Environ.* 390: 456–465.
- Özden, Ö., Döğeroğlu, T. and Kara, S. (2008). Assessment of Ambient Air Quality in Eskişehir, Turkey. *Environ. Int.* 34: 678–687.
- Palmes, E.D. and Gunnison, A.F. (1973). personal Monitoring Device for Gaseous Contaminants. *Am. Ind. Hyg. Assoc. J.* 34: 78–81.
- Palmes, E.D. and Lindenboom, R.H. (1979). Ohm's Law, Fick's Law and Diffusion Samplers for Gases. *Anal. Chem.* 51: 2400–2401.
- Plaisance, H., Sagnier, I., Saison, J.Y., Galloo, J.C. and Guillermo, R. (2002). Performances and Application of a Passive Sampling Method for the Simultaneous Determination of Nitrogen Dioxide and Sulfur Dioxide in Ambient air. *Environ. Monit. Assess.* 79: 301–315.
- Ramadan, A.A. (2010). Air Quality Assessment in Southern Kuwait Using Diffusive Passive Samplers. *Environ. Monit. Assess.* 160: 413–423.
- Sather, M.E., Slonecker, E.T., Mathew, J., Daughtrey, H. and Williamms, D.D. (2007). Evaluation of Ogawa Passive Sampling Devices as an Alternative Measurement Method for the Nitrogen Dioxide Annual Standard in El Paso, Texas. *Environ. Monit. Assess.* 124: 211–221.
- Swaans, W., Goelen, E., De Fre, R., Damen, E., Van Avermaet, P., Roekens, E. and Keppens, V. (2007). Laboratory and Field Validation of a Combined NO₂-SO₂ Radiello Passive Sampler. *J. Environ. Monit.* 9: 1231–1240.
- Tham, Y.W.F., Takeda, K. and Sakugawa, H. (2008). Exploring the Correlation of Particulate PAHs, Sulfur Dioxide, Nitrogen Dioxide and Ozone, a Preliminary Study. *Water Air Soil Pollut.* 194: 5–12.
- Trebs, I., Meixner, F.X., Slanina, J., Otjes, R., Jongejan, P. and Andreae, M.O. (2004). Real-time Measurements of Ammonia, Acidic Trace Gases and Water-soluble Inorganic Aerosol Species at a Rural Site in the Amazon Basin. *Atmos. Chem. Phys.* 4: 967–987.
- Vardoulakis, S., Lumberras, J. and Solazzo, E. (2009). Comparative Evaluation of Nitrogen Oxides and Ozone Passive Diffusion Tubes for Exposure Studies. *Atmos. Environ.* 43: 2509–2517.
- WHO (2005). WHO (World Health Organization) Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide-global Update 2005, p. 15.

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