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on Control and Prevention of Air Pollution
and its Likely Transboundary Effect for South Asia

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Report on Passive Sampler Inter-comparison

DRAFT: NOT TO BE QUOTED

This report has been composed by the inputs from the following institutes:

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- IVL Swedish Environmental Research Institute Ltd, Sweden
- National Building Research Organisation(NBRO), Sri Lanka
- National University of Singapore, Singapore
- North West University, South Africa

National Implementing Agencies and National Focal Points
- Pakistan Environmental Protection Agency, Pakistan
- Ministry of Environment, Pakistan
- Central Environmental Authority, Sri Lanka
- Ministry of Environment and Natural Resources, Sri Lanka

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1. Background

At the Seventh Governing Council of South Asia Cooperation Environment Programme (SACEP, 1998) meeting, 'Malé Declaration' was initiated for Control and Prevention of Air Pollution and Its Likely Transboundary Effects in South Asia" by eight participating countries—Bangladesh, Bhutan, India, Iran, Maldives, Nepal, Pakistan, and Sri Lanka. The initiative was funded by the Swedish International Development Cooperation Agency, Sida, as part of the Regional Air Pollution in Developing Countries (RAPIDC) programme.

Analysis of air pollution problems on the regional or global scale has indicated that data on spatial distributions of air pollutants are only sparsely available in the literature and also that those available data are not fully quality assured. There remains a strong need to develop a range of simple methods applicable for large-scale monitoring. One of the possibilities is the use of passive samplers at a network of locations for determining temporal and spatial distributions of key air pollutants. The member countries have expressed interest to conduct an inter-comparison study of passive samplers to identify passive samplers that could be produced and analysed within countries for routine measurements of trace gases.

It is known that the existence of both nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) is directly related to several environmental issues such as acidic deposition, photochemical smog formation, corrosion, etc. Consequently, passive sampler measurements of NO_2 and SO_2 were given a top priority. A correct quantitative assessment of their concentration and contribution to large scale air pollution is necessary to gain an understanding of their distribution and subsequent chemical reactions in the atmosphere*(1, 2)*. National University of Singapore (NUS) was given the responsibility to undertake this inter-comparison study involving passive samplers and to make suitable recommendations. In order to accomplish this goal, field experiments were proposed to be conducted in two phases. In phase 1, a set of passive samplers from each participating country have been exposed to ambient air in Singapore along with suitable active samplers for a sufficient period of time (at least 3 ~ 4 weeks) to assess their performance and measurement capabilities. Two round robin tests were conducted in this phase in order to evaluate these passive sampler performances at different concentration levels under different weather and pollution conditions. In phase 2, two sets of samplers have been exposed within members countries, out of which one set were sent to NUS for the chemical analysis and the other being processed in their respective countries according to their existing protocols.

Through the coordination of Associate Professor Rajasekhar Bala from National University of Singapore with kind support from Dr. Kevin Hicks from Stockholm Environment Institute and Mr. Mylvakanam Iyngararasan & Jacob Kurian from UNEP Regional Resource Center for Asia and the Pacific and close co-operation from all participants (Table 1), both field sampling and measurements have been successfully completed for this project. Results obtained from the inter-comparison study are presented and discussed in this report. The performance of passive samplers provided by all participating laboratories has been assessed on the basis of the intra- and inter-laboratory analysis.

2. Principles and Theories

2.1 Passive sampling

2.1.1 Absorption (e.g. diffusion tube-filter surface) *(3)*

The unidirectional flow of a gas_1 through a gas_2 is given by Fick's Law:

$$F_1 = -D_{12} dc_1 / dz \qquad (1)$$

where F_1 is the flux of gas (mol cm^{-2} s^{-1}), D_{12} is the diffusion coefficient of gas_1 in gas_2 (cm^2 s^{-1}), c_1 is the concentration of gas_1 in gas_2 (mol cm^{-3}) and z is the length of diffusion (cm). The quantity of gas transferred (Q_1 mol) in t seconds for a cylinder of radius r is given by Eqs. (2) and (3).

$$Q_1 = F_1(\pi r^2)t \qquad (2)$$

$$Q_1 = -D_{12}(c_1 - c_0)(\pi r^2)t / z \qquad (3)$$

Where c_0 is the concentration experienced at the absorber surface, $(c_1\text{-}c_0)/z$ is the concentration gradient along the cylinder length (z), and if an efficient absorber is used to remove gas_1 then c_0 effectively becomes zero.

2.1.2 Adsorption (e.g. diffusion tube-packed)

The pollutant concentrations in the air can be calculated by Cao and Hewitt *(4)*:

$$\text{Analyte concentration (ppm)} = \frac{\mathit{Mass\ uptake}\ (ng)}{\mathit{Uptake\ rate}\ (ng\ \ ppm^{-1}\ \mathrm{min}) \times \exp \mathit{osure\ time}(\mathrm{min})} \qquad (4)$$

The uptake rate in equation (4) is calculated as:

$$\text{Uptake rate (ng ppm}^{-1}\text{ min)} = \frac{DA}{L} \qquad (5)$$

Where D is the diffusion coefficient in air (cm^2s^{-1}), A is the cross-sectional area of the diffusion tube and L is the diffusion length of the tube.

2.2 Active sampling

It is well known that the sampling of gases and aerosols from the atmosphere can be affected by a variety of artifacts if conventional procedures based on air filtration are employed. The most successful approach to prevent positive and negative chemical artifacts is the use of diffusion denuders, which are finding increasing application in discriminating between gaseous and aerosol species *(5-8)*. When a laminar airstream passes through a suitably long tube whose wall acts as a perfect sorbent for a given gas, the gas diffuses to the wall because of the 3-6 orders of magnitude higher diffusion coefficient for the gas compared with submicron particles; the former is chemisorbed onto the wall whereas the latter just proceeds unaffected along the tube if without a back-up filter at the exit. The limitations of conventional hollow tubes have been overcome by the adoption of annular denuder system (ADS) where air flows between several coaxial glass cylinders *(9)*. In this configuration both surfaces defining the annulus act as sink and a single denuder can operate at large sampling flow rates with collection efficiency very close to unity *(10)*.

The mass transfer of a species from an airstream to the walls of a straight channel of constant cross-section is described by the infinite series solution to a three-dimensional steady-state diffusion plus convection equation *(10)*

$$\frac{C}{C_0} = \sum_{i=1}^{\infty} \alpha_i e^{-\lambda_i Z} \qquad (6)$$

Where C_o is the mean concentration of the species at the entrance of the channel and C is its concentration averaged over any cross-section located at a distance z from the axial coordinate origin. It is assumed that diffusion in the axial direction can be neglected and that velocity profile is fully developed at the channel inlet. The parameter Z is in turn defined as

$$Z = \frac{zD}{\upsilon_0 d_{eq}^2} \qquad (7)$$

where d_{eq} is the equivalent diameter of the channel, D is the diffusion coefficient of the species; υ_o is the mean velocity of the air in the channel and z is the coordinate along the axis. α_i and λ_i are coefficients of the series expansion whose values depend on the geometrical shape of the channel and wall reactivity.

The general solution (9) infers the existence of the following boundary condition

$$D(\frac{\delta C_i}{\delta n})\zeta = -K_i C_i \qquad (8)$$

which states that the mass flow of the i^{th} species through the interface is proportional to the concentration near the wall. In equation (9), ζ is the cross-section perimeter of the channel, n is the outward drawn normal from the wall and K_i a constant, whose value is an index of the surface reactivity for the i^{th} species. According to the presumptions and solutions of Allegrini et al.*(10)*, the following expressions have been obtained for both tubular denuder (TD) and annular denuder (AD):
Tubular denuder (TD)

$$\frac{C}{C_0} = 0.82\exp(-14.63\frac{\pi DL}{4F}) \qquad (10)$$

Annular denuder (AD)

$$\frac{C}{C_0} = 0.82\exp(-22.53\frac{\pi DL}{4F}\frac{d_1 + d_2}{d_2 - d_1}) \qquad (11)$$

In equation (11), d_1 and d_2 are the internal and external diameters of the annulus; L is the denuder length and F is the flow rate. From these two equations, it can be found that the sole parameter governing mass transfer to the wall of a hollow tube is the ratio of tube length/ air flow rate (C/C_0, being independent of the tube diameter) whereas the removal efficiency of an annular denuder depends also on the annulus diameter and the width of the annular section. Allegrini et al. found that the annular denuder can reach the same efficiency in $1/30^{th}$ of the length required for a tubular denuder or, that, for a given denuder length, the annular denuder can operate at flow rates 30 times larger. For example, such annular denuders could be used to remove reactive gases such as HNO_3, HNO_2, SO_2, NH_3 etc., from the airstream at flow rates up to 20 L min^{-1} while maintaining efficiencies greater than 96% *(10)*.

3. MATERIALS AND METHODS

3.1 Sampling of SO_2 and NO_2 using passive samplers

3.1.1 Passive sampler type and participating laboratories

Four types of passive samplers were specifically tested in this study: (a) Ogawa samplers for SO_2 and NO_2 measurements, (b) IVL samplers for SO_2 and NO_2 measurements, and (c) CSIR (South Africa) for SO_2 measurement only, (d) PaK samplers for SO_2 and NO_2 measurements. The configuration of these samplers is shown below (see Fig 1). Table 1 provides the details of the participating laboratories and their sampler types.

(a) Ogawa passive sampler (b) IVL diffusive sampler

(c) CSIR diffusive sampler (d) Pak diffusion sampler

Figure 1. Configurations of passive samplers tested in this study

Table 1 List of participating laboratories

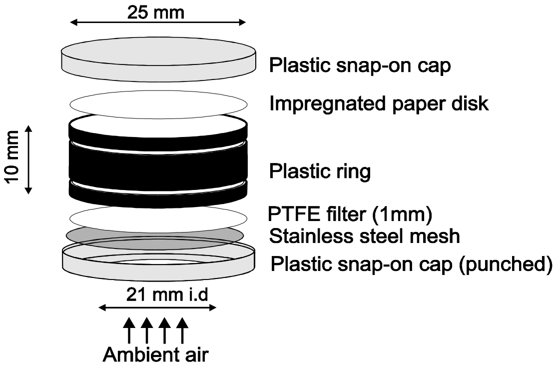
Lab Code	Participant Particulars	Sampler Type	Gases
KVL	Karin Sjoberg IVL Swedish Environmental Research Institute Ltd Sweden	IVL	NO_2 & SO_2
NBRO	Thirandra Fernando National Building Research Org (NBRO) Sri Lanka	Ogawa	NO_2 & SO_2
NWU-SA	Prof. J. J. Pienaar North West University South Africa	IVL	NO_2 & SO_2
CSIR-SA	Patrica Forbes CSIR, NRE, South Africa	CSIR	SO_2
UP-SL	Prof. Namal Priyantha, University of Peradeniya Sri Lanka	IVL	NO_2 & SO_2
PAK	Zia UL Islam Pakistan Environmental Protection Agency (Pak-EPA) Pakistan	Pak	NO_2 & SO_2
NUS	J. He; S. V. Perumal Div of Environ Sci & Eng National University of Singapore Singapore	Ogawa	NO_2 & SO_2

The functioning of the passive samplers is based on their chemical and a 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. Those passive samplers of Ogawa, IVL and CSIR with similar sampling principle by impregnated filter absorption have similar assembly structure as shown in Figure 2.

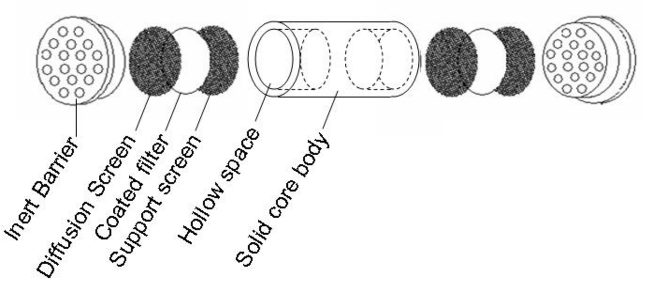
The method used by Pak-EPA has been developed by a Japanese scientist, Kazuyuki Aoki in 1978 *(11, 12)*, which also uses the gas phase diffusion. However, in this sampler, the absorbent solution is not coated on any filter but filled into small capillary tubes (Figure. 2 (d)), through which the gases could contact the absorbent solution surface directly and get captured efficiently as well.

3.1.2 Sampling in Phase I

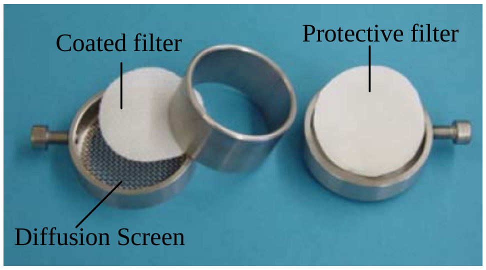
In accordance with the proposed plan, for the two round robin tests in phase I of this study, the countries that had expressed interest to participate in the inter-comparison study were requested to send 4 passive samplers (3 samplers for field measurements and 1 sampler to be treated as a blank) containing pre-coated filters for independent NO_2 and SO_2 measurements.



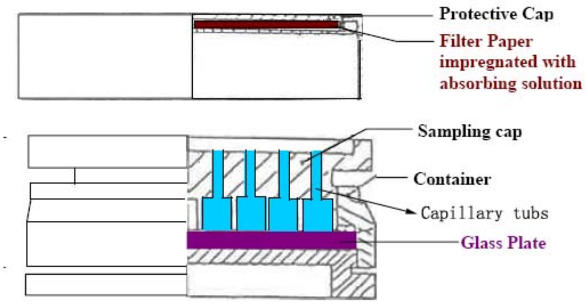
(a) IVL sampler



(b) Ogawa sampler



(c) CSIR sampler



(d) PAK sampler

Figure 2 Schematic representation of passive samplers assembly

In the first round robin test, all the passive samplers were mounted onto the sample holders provided by the individual laboratories and deployed at the rooftop of the NUS atmospheric research station (latitude 1.30, longitude 103.77; 67 m above sea level). Unfortunately, the passive samplers received from Pakistan were not used since the filters were not coated. The samplers were exposed to ambient air under the prevailing weather conditions in Singapore from 24 September to 22 October 2007, accounting for 670 hrs of total exposure. In the second round robin test, all the passive samplers were exposed the same way as above from 15 July to 6 August 2008 for 549.5 hrs of total exposure, except those samplers from UP-SL which were not applied because of the delay in shipping the samplers. During these two exposure periods, a few of the samplers got dislodged from the respective holders during the sampling period due to the rough weather (thunder storm events accompanied by heavy winds). However, these (unanticipated) weather conditions did not have a major negative impact on our study as at least one passive sampler from each participating laboratory was intact and thus exposed to ambient air.

After the exposure period, the passive samplers were carefully dismantled, stored in plastic containers, and transported to the organizing laboratory at NUS. The plastic containers were stored in a refrigerator until chemical analysis. In the case of IVL, the samplers were safely sent to their lab for analysis as per the agreement. Likewise, NBRO's passive samplers were sent back for the chemical analysis at their end as per the agreement. For the remaining passive samplers, exposed filters were removed from the filter holders and extracted with ultrapure water to be consistent with the recommended procedure.

3.1.3 Sampling in Phase II

In this phase, each participant was requested to expose two sets of passive samplers at Malé Declaration sites within members' countries from February to March 2008, out of which one set was sent to NUS for the analysis and the other being processed in their respective countries according to their own protocols. Each set includes 4 passive samplers (3 samplers for field measurements and 1 sampler to be treated as a blank), containing pre-coated filters for independent NO_2 and SO_2 measurements. Table 2 provides the sampling details at each Malé Declaration sites within members' countries.

Table 2 The sampling information at each Malé Declaration sites within members' countries

Sampling sites	Sampler type	Sampling time (min)	Average temperature (^oC)	Average relative humidity (%)
NUS	Ogawa	47880	26.6	84.6
NBRO-SL	Ogawa	31680	30.0	86.0
NWU-SA	IVL	43200	23.1	66.0
UP-SL	IVL	30480	17.0	80.0
PAK	PAK	20040	23.6	54.0
CSIR-SA	CSIR	41760	23.6	63.0

3.2 Sampling of SO_2 and NO_2 using active samplers

3.2.1 Selection of adsorbent and collection efficiency assurance

In this study, URG annular denuder system (ADS) was used without a filter-pack holder at the exit since only gaseous NO_2 and SO_2 were studied here. The adsorbent used in this study was activated carbon. Prior to use, carbon was extracted by using accelerated solvent extractor (ASE) with water, washed twice with 0.5M NaOH, twice with boiling water and then dried at 105 ^oC. The coating solution used in this study for acidic gases, NO_2 and SO_2, (2 % Na_2CO_3 + 1% glycerol in water-methanol) was prepared by adding 1.5 g of carbon to 10 ml of a 2% Na_2CO_3 and 1% glycerine in methanol/water 1/1 v/v solution. In fact, a series of experiments with the ADS mentioned above in the same environmental conditions have shown that the collection of NO_2 on a coating prepared from a mixture of 1.5% carbon + 2% Na_2CO_3 + 1% glycerine (w/v) or from a mixture of 1.5% carbon + 2% NaOH + 1% glycerine (w/v) was quite consistent and comparable *(13)*. In addition, it has been reported that the collection efficiency (E) of coating solution (Na_2CO_3 - glycerine in water/methanol) for acidic gases including NO_2 and SO_2 could be up to 98% *(10)*, for which the definition of E would be discussed later.

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

$$E = 1 - \frac{b}{a} \tag{12}$$

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 (Na_2CO_3 - 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^{-1} at NUS atmospheric research station and five samples were collected on daily basis right before the start of second 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

$$R_e = \frac{4F}{\gamma\pi(d_1 + d_2)} \tag{13}$$

where γ is the kinematic viscosity of air; based on the data obtained from the pre-experimental period, R_e was calculated as around 400.

3.2.2 Active sampling by ADS

During both sampling periods for round robin tests in NUS, active samplers were collocated in the field along with the passive samplers to collect data for NO_2 and SO_2 on a daily basis (exposure to ambient air for 24 hours). For this purpose, URG annular denuder systems (ADS), coated with appropriate chemical reagents (2% Na_2CO_3 + 1% glycerine, as mentioned above), were deployed in the field, operating with an air pump at a flow rate of 20 ~ 24 litres per minute. The absorbed gases from denuders were extracted by equilibrating with 20 ml ultra pure water and converted to nitrite and sulphate.

3.3 Methods of analysis and concentration calculation for different types of samplers

3.3.1 Ogawa

3.3.1.1 NO_2

Analysis

After exposure to the test environment, the stainless screens and cellulose fiber filter 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 ^{o} 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.

2) Calculation of ambient concentration

$$NO_2 \text{ concentration (ppbv)} = \alpha_{NO_2} \times \frac{W}{t} \qquad (14)$$

W : collected weight (ng)

t: sampling time (min)

$$\alpha_{NO_2} = \frac{10000}{(0.677 \times [P] \times [RH]) + (2.009 \times [T] + 89.8} \qquad (15)$$

[T]: ambient temperature in degree centigrade

[RH]: relative humidity in %

$$[P] = \{\frac{2P_N}{P_T + P_N}\}^{\frac{2}{3}} \qquad (16)$$

P_N: 17.535 water vapour pressure in mm Hg at 20 degC

P_T: vapour pressure of water at the ambient temperature [T]

3.3.1.2 SO_2

Analysis

After exposure to the test environment, the stainless screens and cellulose fiber filter were put into a 25 ml glass vial containing 8 ml water. The vial was then shaken immediately. Over the next 30 minutes, occasional shaking of the vials was applied. 0.2 ml H_2O_2 (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 resulting was analysed using IC. The same procedure was applied for blank samples.

Calculation of ambient concentration

SO_2 concentration (ppbv) = $\alpha_{SO_2} \times \frac{W}{t}$ (17)

W : collected weight (ng)

t: sampling time (min)

α_{SO_2} : conversion coefficient as a function of temperature could be obtained from the manual "NO, NO_2, NO_x and SO_2 Sampling Protocol Using The Ogawa Sampler" (V3.98, Ogawa & Co., USA, Inc)

3.3.2 IVL

Analysis

The analytical protocol applied in IVL lab is unknown and therefore not discussed in this report. Those IVL samples exposed at the NUS site were processed as per Ogawa protocol as above for NO_2 and SO_2, respectively, to get the amount of target compounds collected onto filters.

Calculation of ambient concentration

$$C_{avg} = \frac{1000XRT}{(Mr)Dt} \times \frac{L}{A} \qquad (18)$$

C_{avg} : average concentration of NO_2 or SO_2 during exposure period

X : the amount of NO_2 or SO_2 collected on filter

R : gas constant, 8.31 J K^{-1} mol^{-1}

Mr : the relative molecular mass of the gas in question

D : diffusion coefficient of gas, m^2s^{-1}

t : sampling time

L: diffusion path length, corrected for the Teflon filter, steel mesh and static air layer, m

A: cross sectional area of diffusion path, m^2

3.3.3 CSIR (only for SO_2)

Analysis

In NUS, the air samples collected by CSIR samplers were processed as per Ogawa protocol as above for SO_2 to get the amount of analyte of interest trapped on filters.

The analytical protocol applied in the CSIR lab is stated as below.

i. Remove the back cap from the sampler;

ii. Remove the filter pad from the sampler and place in a 100 ml beaker. At least one blank, with an unused filter pad, is similarly prepared;

iii. Add 20 ml of DI water and extract in an ultrasonic bath for 15 min;

iv. Analyse the extract by IC for sulphate (along with the standards and a certified standard), using a 100 µl loop and two injections per sample; KOH is used as the eluent (usually 32 mM).

Calculation of ambient concentration

$$C_{avg} = \frac{a \times M}{t} \tag{19}$$

C_{avg} : average ambient concentration of SO_2, ppbv

M : the amount collected on filters, ng

a : diffusive coefficient for SO_2

t : exposure time, minutes

$$a = \frac{172266}{T^{1.75}} \tag{20}$$

T : exposure ambient temperature, K

3.3.4 PAK

Due to the speciality of PAK samplers with capillary tubes containing liquid absorbent solution, the NUS lab exactly followed the analytical protocols for both NO_2 and SO_2 developed by Pakistan EPA lab.

3.3.4.1 SO_2

Analysis
i. Transfer 0.4ml of pRA solution (trichloroacetic acid plus pararosaniline chloride) to a small test tube with a stopper;
ii. Inject 5 ml of NaOH-NaN_3 solution to the PAK exposed sampler by loosening up the sampling cap by one turn;
iii. Loosen up the cap by another half turn, then tighten by a half turn. Repeat this several times to mix the extract solution inside the sampler;
iv. Take out 4 ml extract with a pipette, transfer it into another clean test tube and store it;

v. Add 0.04 ml of 1.4% HCHO and mix by shaking.

vi. Determine the absorbance by spectrophotometer at 580 nm.

Calculation

SO$_2$ (ppm) = $$\frac{A - A_0}{20(nmol/ppm.hr) \times T(hr) \times X(AU/nmol)} \qquad (21)$$

A : absorbance of sample

A_0 : absorbance of blank

T : exposure time (hr)

X : slope of the calibration line obtained by using SO$_2$ standard

3.3.4.2 NO$_2$

Analysis

i. Take off the protective cap and loosen the sampling cap by one turn;

ii. Add 5 ml of solution for extraction to the samplers through a capillary path with dispenser;

iii. Loosen the cap by another half turn. Repeat this several times to mix the extracts by shaking;

iv. Take out N ml of the extracts with a pipette and put it into the test tube. Add 5 ml of the colour reagent (sulphanilamide solution and NEDA solution in a 10:1 ratio). After 10 minutes, determine the absorbance at the wavelength of 540 nm. The amount of N ml is so chosen that the absorbance ranges from 0.1 to 0.8.

Calculation of ambient concentration

NO$_2$ (ppm)= $$\frac{(A - A_0)(5 + N)}{25.2(nmol/ppm.hr) \times T(hr) \times X(AU/nmol)} \qquad (22)$$

A : absorbance of sample

A_0 : absorbance of blank

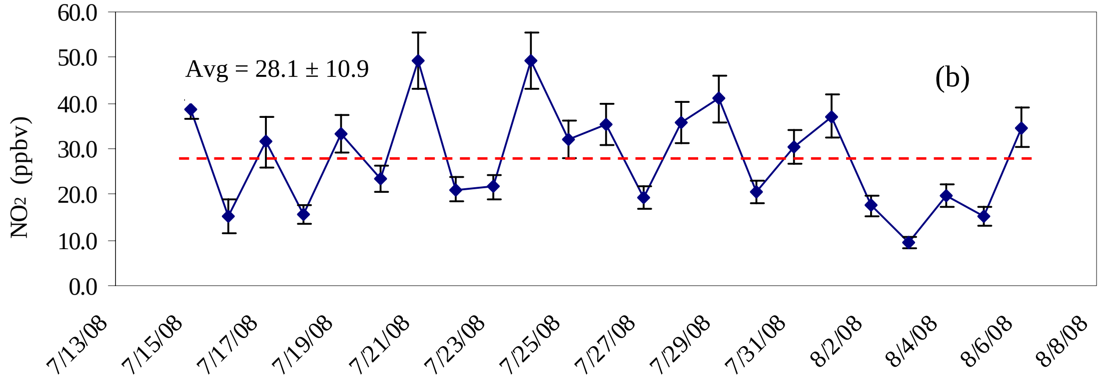
T : exposure time (hr)

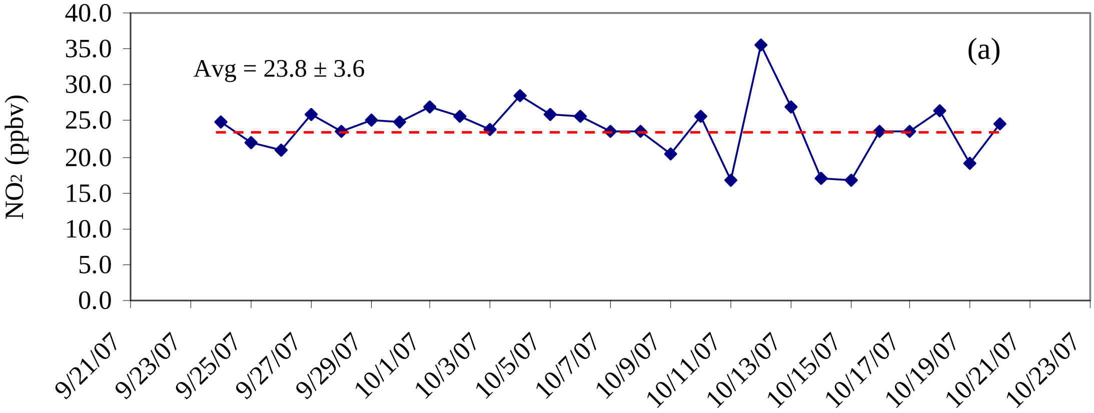
X : slope of the calibration line obtained by using NO$_2$ standard

4. Results and Discussion

4.1 Active Sampler Results for two round robin tests in Singapore

Figure 3 shows the daily average concentration of NO_2 during the study periods of two round robin tests in NUS. The daily average concentration varied from 16.7 to 35.6 ppbv (parts per billion by volume) with an average of 23.8 ± 3.6 ppb NO_2 during the first round robin test, and varied from 9.3 to 49.2 ppbv with an average of 28.1 ± 10.8 ppb NO_2 during the second round robin test, respectively. The average concentration of NO_2 measured in the first round robin test was relatively lower than that during the second round robin test, which might be due to the variability NO_2 profile affected by industrial and nearby biomass burning emissions(14). 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 NO_2 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 ($r^2 = 0.9$, slope = 0.8) which ensures the quality of the active sampler data.





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The daily average concentrations of SO_2 based on active sampler measurements are presented in Figure 4. The daily average concentration varied from 8 to 19.4 ppbv with an average of 12.5 ± 2.7 ppbv SO_2 during the first round robin test, and varied from 6.9 to 23.9 ppbv with an average of 14.9 ± 2.3 ppbv SO_2 during the round robin test, respectively. Both of the average concentrations measured during these study periods are close to our earlier data measured in 2005 (~9 ppbv)

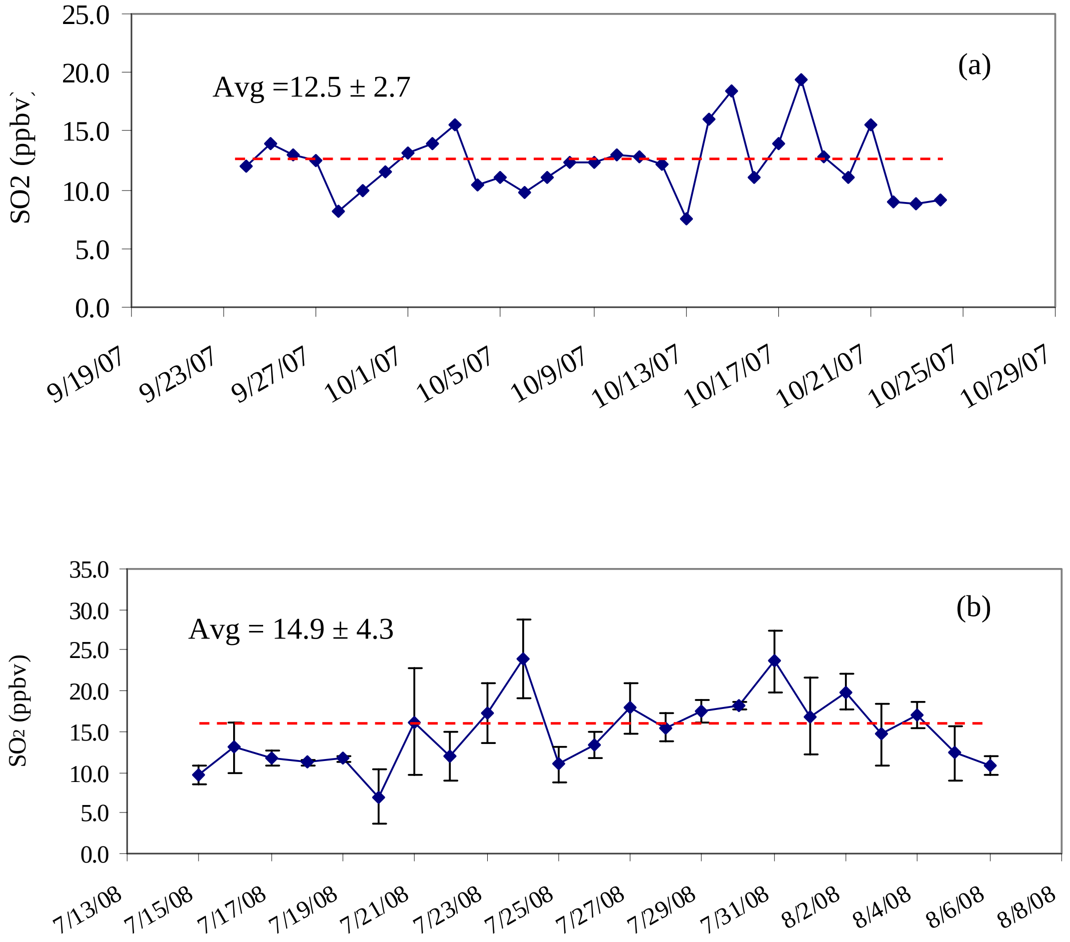


Figure 4
Daily average concentration of SO_2 (a. 1st round robin test from 24 September to 22 October 2007; b. 2nd round robin test from 15 July to 6 August 2008)

4.2 Passive Sampler Results for two round robin tests in Singapore

In the 1st round robin test, after completing the analysis, the aqueous solution concentration and the sampling duration were sent to the participants to calculate the final concentration in ppbv; in the case of IVL and NBRO, samplers were sent back to them for analysis; NO_2 analysis was done for NBRO at NUS due to labelling error. In the 2nd round robin test, after completing the analysis, the final ambient concentration in ppbv was converted by NUS side since all of the calculation procedures were obtained from each participant. The results obtained from various passive samplers are graphically presented in Figure 5 and Figure 6 for NO_2 and SO_2, respectively. The error bar indicates the standard deviation of the average values based on three independent measurements made for individual passive samplers. The blue dotted line is the average concentrations of NO_2 and SO_2 based on the active sampler data, and the red dotted line is the grand mean, calculated from various passive sampler data. From Figure 5 and Figure 6, it can be seen that grand means and active sampler average concentrations, for both NO_2 and SO_2, are in close agreement with each other as the deviation between the two values is less than 20 %, which should be acceptable considering two different sampling techniques. In the 1st round robin test, NUS have used two types of filters for NO_2 measurements; one is supplied by Ogawa (labelled as NUS), and the other is independently made by NUS (labelled as NUS1)). The large uncertainty for NO_2 observed in NBRO samplers and that for SO_2 in NUS samplers in the 1st round robin test could be due to unexpected cross contamination, which was reduced significantly in the 2nd round robin test. However, the large variations were also observed in PAK samplers for both NO_2 and SO_2 in the 2nd round robin test, which was not the case in the 1st round robin test, but the reason for this variation was unknown and further verification needs to be taken if and when possible.

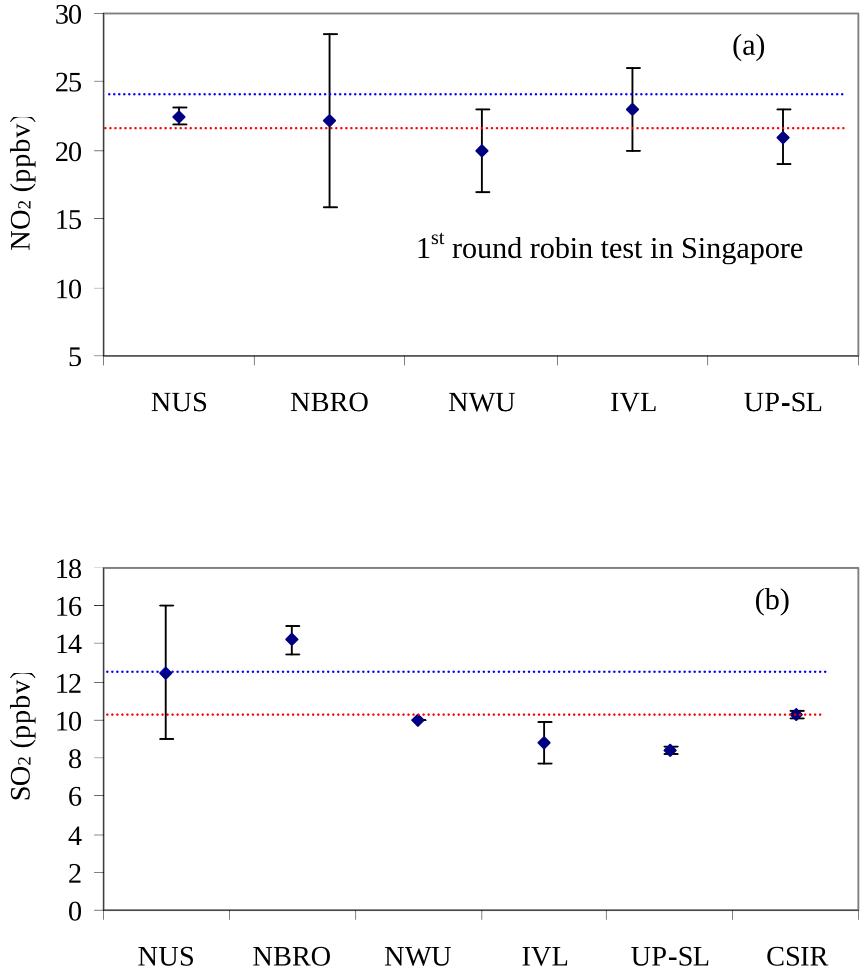


Figure 5

Inter comparison of Passive sampler for NO_2 and SO_2 analysis obtained in 1st round robin test in Singapore

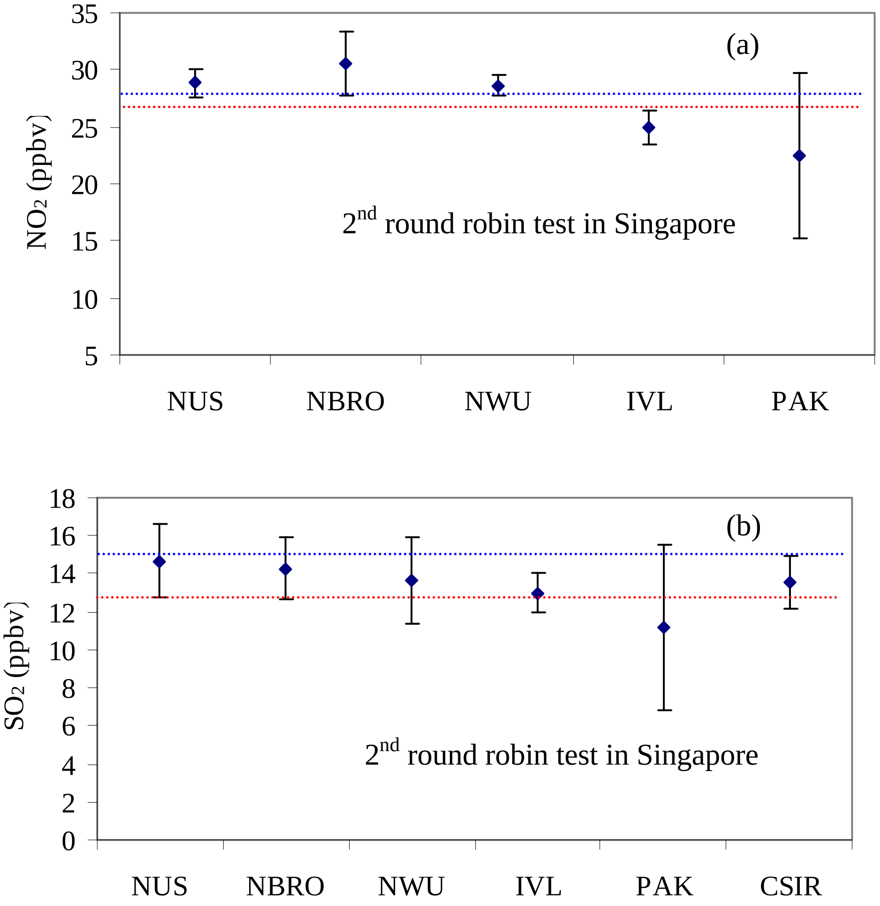
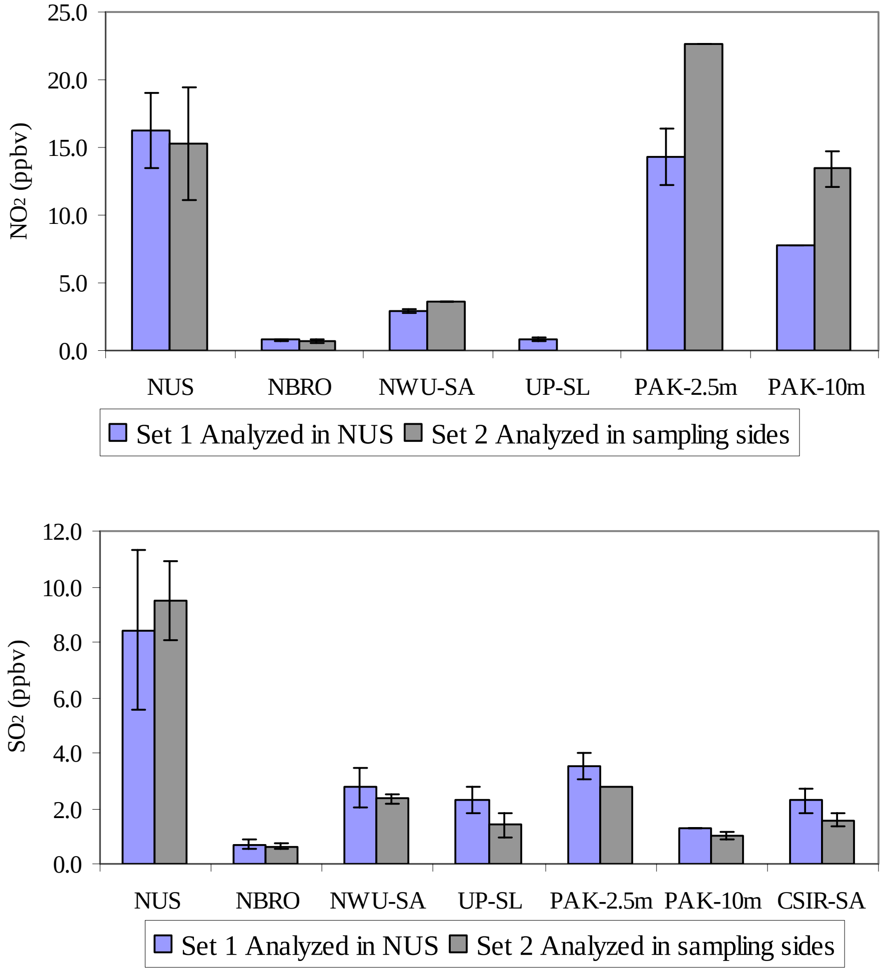


Figure 6

Inter comparison of Passive sampler for NO_2 and SO_2 analysis obtained in 2nd round robin test in Singapore

4.3 In-country comparison of passive samplers' performance for both NO_2 and SO_2

As stated above, for this in-country comparison, each participant exposed two sets of passive samplers at Malé Declaration sites within their own countries; after sampling, one set was sent to NUS for the analysis and the other being processed in their respective laboratories according to their own protocols. As of now, most of the analysis for those samples collected from Malé Declaration sites has been completed except for the analysis of NO_2 from UP-SL and all results are summarized in Figure 7. The error bar indicates the standard deviation (SD) of the average values based on two sets measurements. All laboratories reported results of NO_2 and SO_2 above the limit of detection (LOD) with the ranges from 0.71 to 22.6 ppbv and from 0.64 to 9.49 ppvb, respectively.



Note:

a. Two sets of samples collected in NUS were analyzed by NUS lab.
b. Analysis of NO_2 has not been completed in UP-SL
c. Different sampling heights were applied in Pakistan.

Figure 7 Concentration levels of NO_2 and SO_2 from different Malé Declaration sites

The intra- and inter-laboratory variations (relative standard deviation, RSD%) for analysis of both NO_2 and SO_2 are summarized in Table 3, which are used to assess analytical capabilities and consistencies of different laboratories involved in this study. Both sets of samples collected at the NUS atmospheric station were analyzed by the NUS lab; the intra-laboratory variations (relative SD) in NUS were estimated to be 21.9% and 18.8% for SO_2 and NO_2, respectively. For those samples collected from other sampling sites, the intra-lab and inter-laboratory RSD% for NO_2 varied from 0.3 to 23.9% and from 12.5 to 29.6%, respectively, while those for SO_2 ranged from 6.8% to 26.1% and 18.9% to 25.3%, respectively. The minimum intra-lab and inter-lab RSD% value was obtained for NO_2 in NWU samplers while the maximum intra-lab and inter-lab RSD% values were found to be in NBRO and PAK samplers, respectively. In addition, for the same type of passive samplers, the intra-lab RSD% value was generally lower than the inter-lab RSD% value as expected. Some of the intra- and inter-lab relative standard deviations (RSD%) were slightly greater than 20%, which should be still acceptable when considering the systematic differences in relation to the different analytical techniques used by the participants and various coating chemicals applied.

4.4 Statistical Analysis for two round robin tests in Singapore

The replicate measurements made ($n = 3$) from different passive samplers for NO_2 and SO_2 were statistically tested to verify whether there is any significant difference between the values for both round robin tests in Singapore. For this purpose, the data were treated with ANOVA-single factor using excel and the results are presented in Table 4. As could be seen from the table, for both round robin tests in Singapore, F values are less than the critical values for both NO_2 and SO_2 and P values were higher than 0.05 (α), indicating that there is no significant difference between different passive samplers employed in this inter-comparison study.

Table 3 Intra- or inter-lab RSD% for analysis of both NO_2 and SO_2

RSD% \ Sample		NUS	NBRO	NWU	UP-SL	PAK-2.5m	PAK-10m	CSIR
NO_2	Intra-lab (NUS)	18.8	12.5	6.6	16.1	14.9	N.A.[c]	N.A.[d]
	Intra-lab (Respective Lab)		23.9	0.3	N.A. [b]	N.A.[c]	14.3	
	Inter-lab (NUS + Respective lab)	N.A. [a]	18.4	12.5	N.A. [b]	29.5	29.6	
SO_2	Intra-lab (NUS)	21.9	26.1	6.8	19.9	N.A.[c]	N.A.[c]	19.6
	Intra-lab (Respective Lab)		18.8	26.1	22.8		15.0	22.6
	Inter-lab (NUS + Respective lab)		20.9	19.2	21.9		18.9	25.3

Note:

a. All samples collected from NUS were analyzed at the same lab of NUS
b. Analysis of NO_2 samples not completed yet in UP-SL
c. Only one sample analyzed so that the calculation of intra- or inter-lab RSD% is not applicable

Table 4 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

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

5. Conclusion

Both round robin field tests and the in-country comparison study of the inter-comparison of passive samplers for the analysis of NO_2 and SO_2 were successfully completed under urban-influenced conditions. The results presented here clearly indicate that all the four types of passive samplers studied can be used for monitoring of NO_2 and SO_2 in the outdoor atmosphere under urban pollution conditions. A comparison of NO_2 and SO_2 data obtained from this study showed larger variation particularly for SO_2 between the samplers of different types and also within the samplers of the same type especially in the 1st round robin test in Singapore; and in in-country comparison study, both the inter- and intra-lab variations for SO_2 analysis were generally greater than those for NO_2 analysis. This difference could be either due to analytical uncertainties, or the difference in the sampling efficiency based on different coating solutions. Most probably due to the systematic differences relating to the different analytical techniques used by all participants, the inter-lab variations were found to be greater than those intra-lab variations. However, it could still be seen that both inter- and intra-lab analyses have relatively systematic consistencies. In Pakistan’s case, the concentrations of both NO_2 and SO_2 were decreased with the increasing of the sampling vertical height as expected.

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