

# Inter-Comparison of Passive Samplers under Male declaration

Rajasekhar Bala

CAD Coordinator

# Outline

- **Introduction**
- **Objective**
- **Theory of Sampling**
- **Sampling & Analysis**
- **Results and Discussion**
- **Conclusion**
- **Acknowledgement**

# Introduction

- 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”.
- SACEP countries—Bangladesh, Bhutan, India, Iran, Maldives, Nepal, Pakistan, and Sri Lanka.
- Funded by the Swedish International Development Cooperation Agency, Sida, as part of the Regional Air Pollution in Developing Countries (RAPIDC) programme.



# Objectives

After completing some operations under Malé Declaration on Control and Prevention of Air Pollution and its Likely Transboundary Effects in South Asia, member countries have expressed interest to:

- Conduct an inter-comparison of passive samplers in order to identify passive samplers that could be produced and analysed within countries for routine measurements of trace gases.
- Assess the performance of different types of passive samplers for the analysis of  $\text{NO}_2$  and  $\text{SO}_2$

Reasons for top priority of these gaseous pollutants:

chemical transformations leading to acidic deposition, corrosion, and enhanced acidity of airborne particles, and ozone ( $\text{NO}_2$ ).

# Passive Sampling

## ❖ What is a passive sampler?



Passive vapor sampler



Inorganic Mercury sampler



Nitrogen dioxide-Drager sampler



Gastic Hydrogen cyanide dosimeter tube



Air passive sampler (NO<sub>2</sub>, SO<sub>2</sub>, Formaldehyde)

## Advantages of passive samplers:

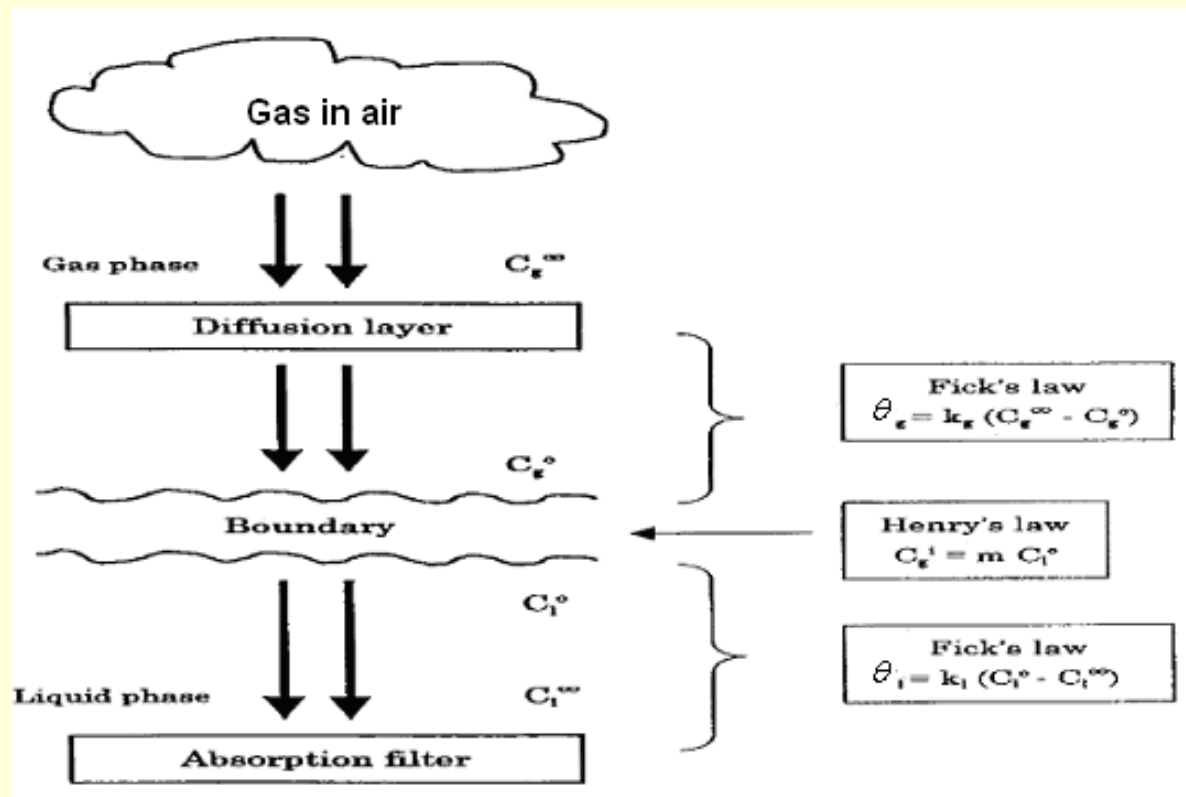
- Simplicity, natural diffusivity
- Cost-effectiveness, no pump required
- Capacity building opportunities

# Basic components of a diffusion-based passive sampler

- An inert barrier to convective air
- An air gap between the barrier and the trap
- A trap to collect the pollutant of interest, which diffuses in the air gap at a constant rate
- To avoid back-diffusion, the trap must be a perfect sink for the pollutant of interest

# Theory of Passive Sampling

Based on the diffusion of the gas molecules through a diffusive zone to the collection filter



The step of passive sampling theory

(adapted from Helaleh, Ngudiwaluyo, Korenaga & Tanaka, 2002)

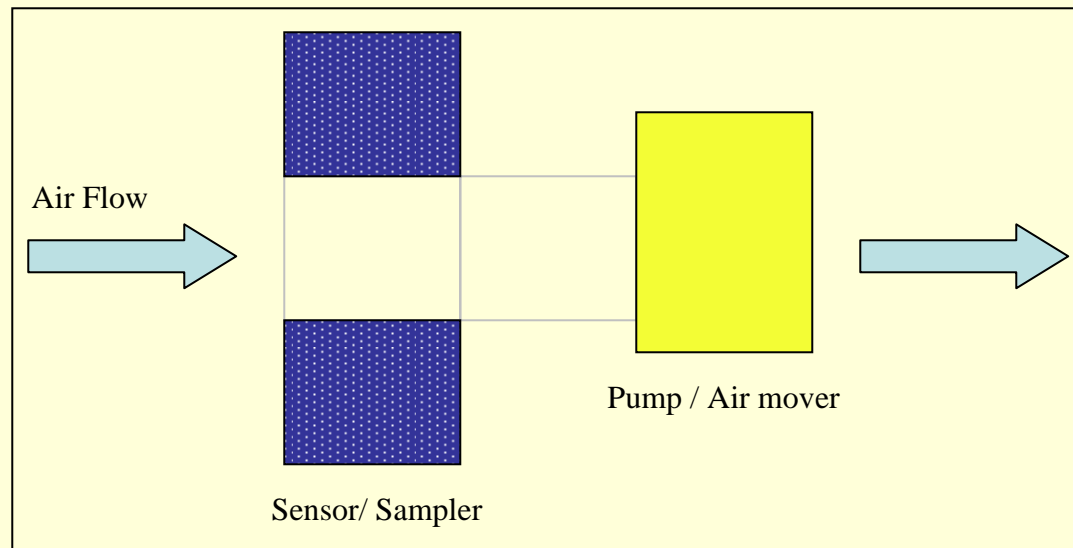
# Passive Sampling

Key questions:

- 1) How long the exposure should be?  
Sampling = absorption/adsorption;  
Sampling to be stopped before equilibrium reached;  
The amount of target molecules collected is dependent on length of sampling time.  
May be necessary to expose as long as 30 days for low concentrations of  $\text{NO}_2$  and  $\text{SO}_2$
- 2) Is there an accurate active sampler at the site for comparison?  
Denuder system.



# Theory of Active Sampling



Active Sampler (adapted from Lehtimaki & Willeke, 1993)

## Components of the proposed study

- Comparison of all chosen passive samplers at National University of Singapore as part of RAPIDC's Composition of Asian Deposition (CAD) Network activities
- Exposure of samplers at other chosen sites in South Asia and South Africa with contrasting conditions
- Parallel analysis of exposed samplers between National University of Singapore and Malé Countries

## List of Participating Labs

Lab Code	Participant Particulars	Sampler Type	Gases
KVL	Karin Sjoberg IVL Swedish Environmental Research Institute Ltd Sweden	IVL	NO <sub>2</sub> & SO <sub>2</sub>
NBRO	Thirandra Fernando National Building Research Org (NBRO), Sri Lanka	Ogawa	NO <sub>2</sub> & SO <sub>2</sub>
NWU-SA	Martin Kobus/Prof. J. J. Pienaar North West University, South Africa	IVL	NO <sub>2</sub> & SO <sub>2</sub>
CSIR-SA	Patrica Forbes CSIR, NRE, South Africa	CSIR	SO <sub>2</sub>
UP-SL	Prof. Namal Priyantha, University of Peradeniya, Sri Lanka	IVL	NO <sub>2</sub> & SO <sub>2</sub>
NUS	S. V. Perumal, Div of Environ Sci & Eng National University of Singapore, Singapore	Ogawa	NO <sub>2</sub> & SO <sub>2</sub>

# Sampling & Analysis

**Sampling-Phase I** (Comparison of all passive samplers in the study with active samplers at the National University of Singapore)

1) NUS atmospheric research station (67m above sea level)

24 Sept 2007-22 Oct 2007

Exposure of all passive samplers provided by the individual laboratories



**(a) Ogawa passive sampler**



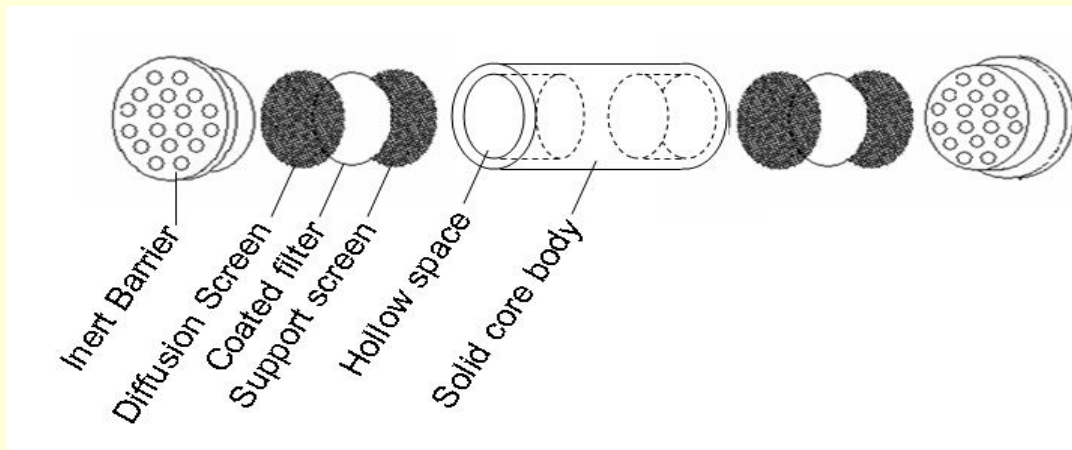
**(b) IVL diffusive sampler**



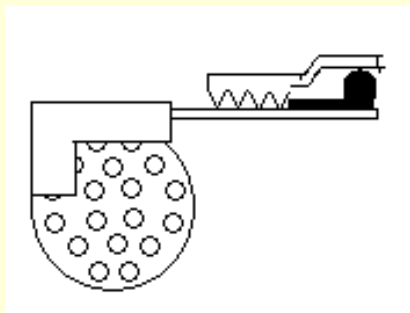
**(c) CSIR diffusive sampler**

# Sampling & Analysis (contd)

One of the samplers used -Ogawa



Exploded diagram of Ogawa passive sampler



Side view (pinclip & body)

# Passive samplers

## Transport and Storage

- Re-sealable plastic bag
- Airtight container

## Exposure in an outdoor environment

- Before exposure, all sampler components should be carefully washed and dried except for the commercially obtained filters
- Washing, drying, assembly of sampler and loading with the proper pre-coated filters in a clean area, free of  $\text{NO}_x$  contamination
- To protect the loaded sampler from moisture while exposed
- Use proper shelter to retain proper airflow to the device

# Sampling & Analysis (contd)

## Sampling-Phase I

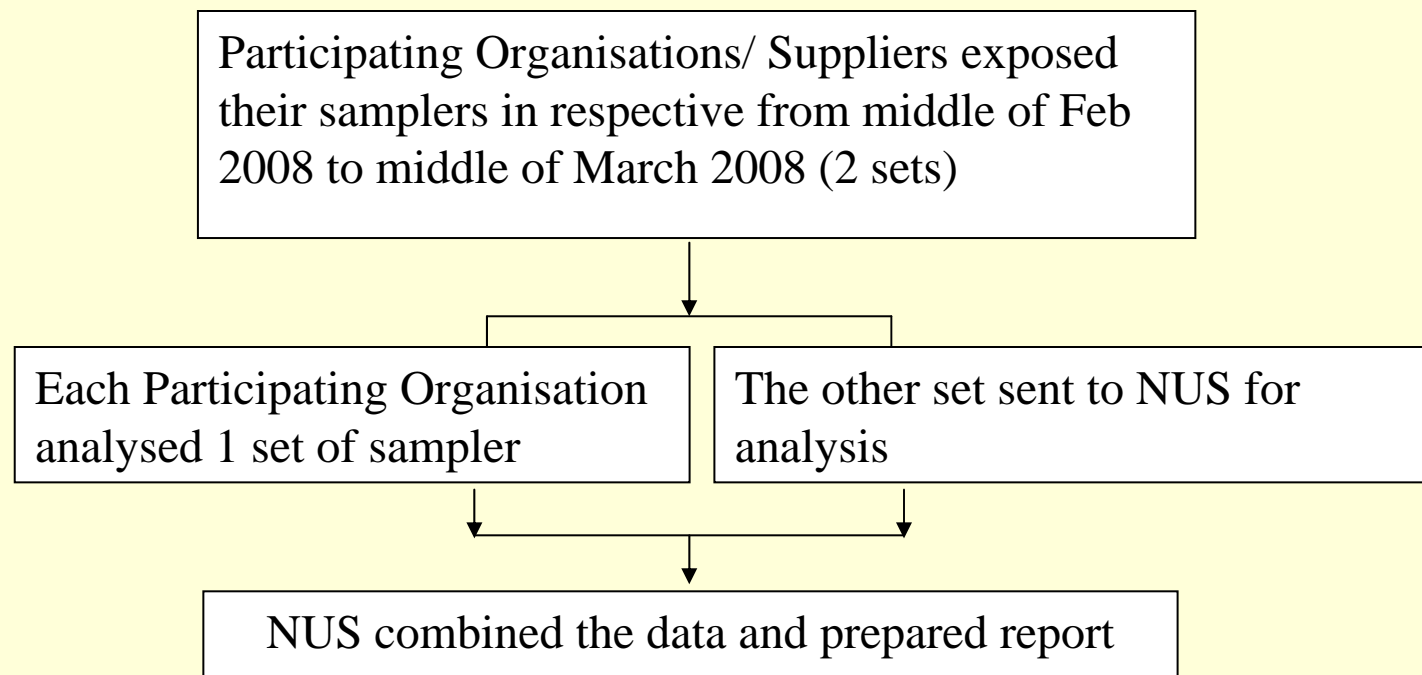
2) Sampling period:  
(24 Sept-22 Oct 2007),  
active samplers were  
deployed at the NUS site  
to collect data for  $\text{NO}_2$  and  
 $\text{SO}_2$  on a daily basis  
(exposure for 24 hrs)



← URG annular  
denuder  
system (ADS),  
coated with  
appropriate  
chemical  
reagents

# Sampling & Analysis (contd)

**Sampling Phase II** (Exposure of in-country passive samplers in respective countries and parallel analysis in those countries and at the National University of Singapore (NUS))

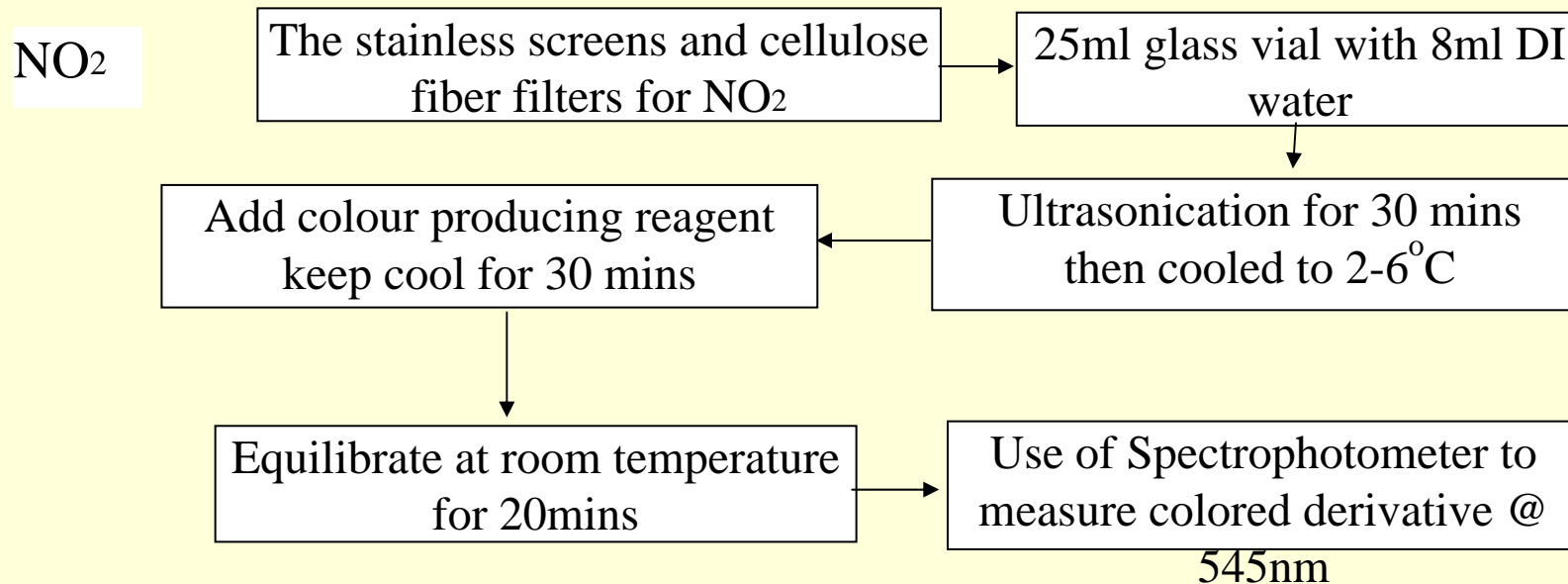




## Experimentation (cont'd)

### Analytical method

1) The procedures followed for chemical analysis in NUS lab is as follows:



# Sampling & Analysis (contd)

Spectrophotometric analysis of  $\text{NO}_2$  color derivatives



## Calculation of Concentration of NO<sub>2</sub> for Ogawa sampler

Concentration of NO<sub>2</sub> (ppbv)

$$= \alpha_{\text{NO}_2} \times \text{collected amount (ng)} / \text{Sampling time (min)}$$

Collected amount-obtained from UV measurement;

Sampling time-converted to minutes;

$\alpha_{\text{NO}_2}$ - Concentration conversion coefficients for NO<sub>2</sub>

## Calculation of Concentration of NO<sub>2</sub>

$\alpha_{\text{NO}_2}$ - Concentration conversion coefficients  
for NO<sub>2</sub>

$$\alpha_{\text{NO}_2} = 10000 / \{ (0.677 \times [P] \times [RH]) + (2.009 \times [T]) + 89.8 \}$$

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

$P_N = 17.535$  (water vapor pressure in mm Hg  
at 20<sup>o</sup> C)

## Calculation of Concentration of NO<sub>2</sub>

Example: [T] = 9 °C; [RH] = 60%;

weight collected of NO<sub>2</sub> on filter = 8000ng; sampling time = 40000 mins

Ans: P<sub>N</sub> = 17.535; P<sub>T</sub> = 8.609 (obtained by typical values)

$$[P] = \{2 \times 17.535 / (8.609 + 17.535)\}^{(2/3)} = 1.216;$$

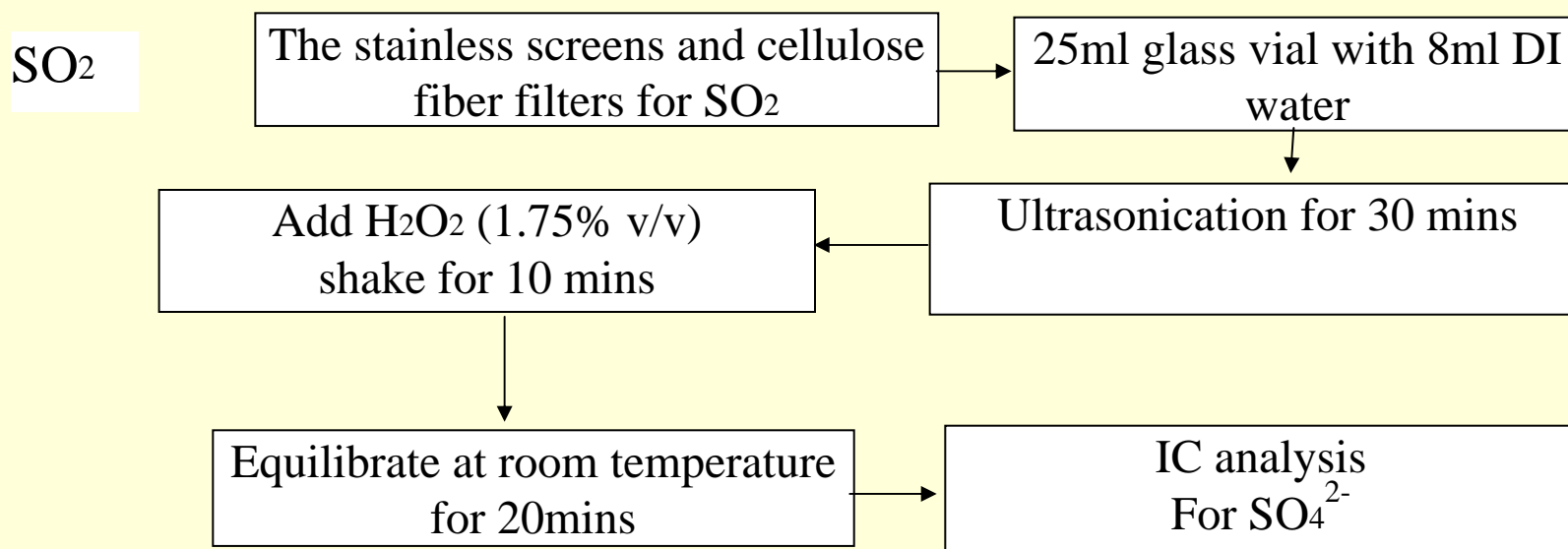
$$\alpha_{\text{NO}_2} = 10000 / [(0.677 \times 1.216 \times 60) + (2.009 \times 9) + 89.8] = 63.58$$

$$\text{NO}_2(\text{ppbv}) = 63.58 \times 8000 / 40000 = 12.72 \text{ ppbv}$$

# Sampling & Analysis (contd)

## Analytical method (cont'd)

The procedures followed for chemical analysis in NUS lab are:



2) The procedures followed for chemical analysis in member countries except for NUS are not known and not discussed

# Sampling & Analysis (contd)

## IC method for sulphate

```

Suppressor_Type = ASRS_4mm
; Pump_ECD.Carbonate = 0.0
; Pump_ECD.Bicarbonate = 0.0
; Pump_ECD.Hydroxide = 30.0
; Pump_ECD.Tetraborate = 0.0
; Pump_ECD.Other eluent = 0.0
; Pump_ECD.Recommended Current = 112
Suppressor_Current = 200 [mA]
Pressure.LowerLimit = 200 [psi]
Pressure.UpperLimit = 3000 [psi]
%A.Equate = "%A"
CR_TC = On
Concentration = 20.00 [mM] ← Eluent concentration
Curve = 5
Flow = 1.00 [ml/min] ← Flow rate

0.000 Message "Please Inject new sample"

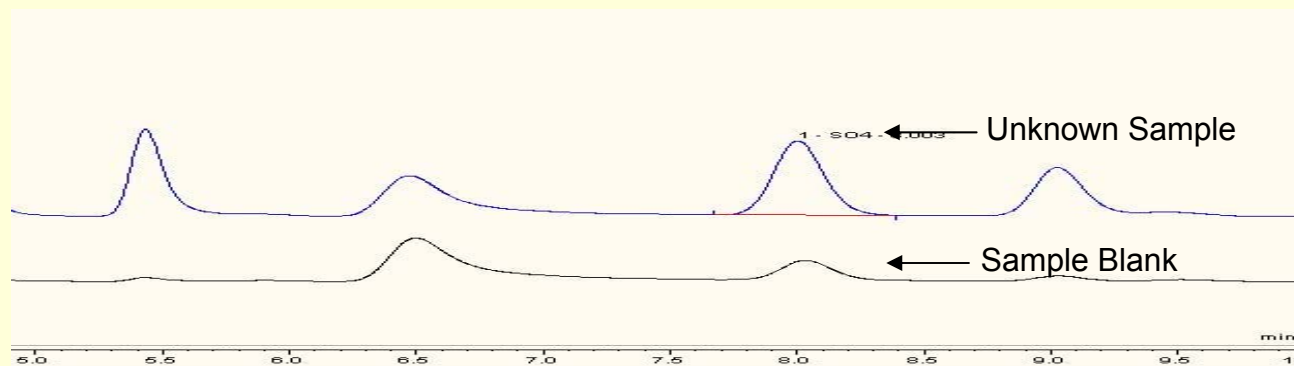
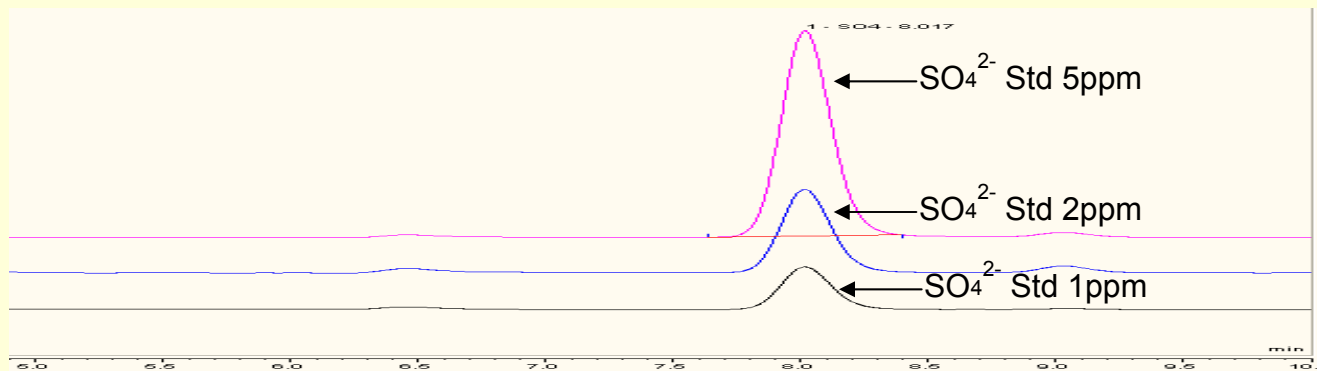
Autozero
ECD_1.AcqOn
Pump_InjectValve.InjectPosition Duration=60.00

10.000 ECD_1.AcqOff

End
    
```

# Sampling & Analysis (contd)

## IC chromatograph for $\text{SO}_4^{2-}$





## Calculation of Concentration of SO<sub>2</sub> for Ogawa sampler

Concentration of SO<sub>2</sub> (ppbv)

$$= \alpha_{\text{SO}_2} \times \text{collected amount (ng)} / \text{Sampling time (min)}$$

Collected amount-obtained from IC measurement;

Sampling time-converted to minutes;

$\alpha_{\text{SO}_2}$ - Concentration conversion coefficients for SO<sub>2</sub>

## Calculation of Concentration of $\text{NO}_2$

$\alpha_{\text{SO}_2}$ - Concentration conversion coefficients  
for  $\text{SO}_2$

$\alpha_{\text{SO}_2}$  only relevant to ambient temperature

At  $20^\circ\text{C}$  the value of  $\alpha_{\text{SO}_2} = 39$

If the sampling conditions are other than  
 $20^\circ\text{C}$ , we can refer to a table

which provides  $\alpha_{\text{SO}_2}$  at various commonly

## Conversion coefficient $\alpha_{SO_2}$ for SO<sub>2</sub> as a function of temperature

Temperature T °C	Diffusion Coefficient $D_T$ cm <sup>2</sup> /sec	Ratio of Diffusion Coefficients $D_{20}/D_T$	Conversion Coefficient $\alpha_{SO_2}$ Ppb-min/ng
-10	0.1068	1.22	47.5
-9	0.1076	1.21	47.2
-8	0.1083	1.20	46.9
...	...	...	...
15	0.1261	1.03	40.3
16	0.1269	1.03	40.0
17	0.1277	1.02	39.8
...	...	...	...
38	0.1452	0.90	35.0
39	0.1460	0.89	34.8
40	0.1469	0.89	34.6

## Calculation of Concentration of SO<sub>2</sub>

Example: [T] = 16.5 °C; weight collected of SO<sub>2</sub> on filter = 8000ng;  
sampling time=40000 mins

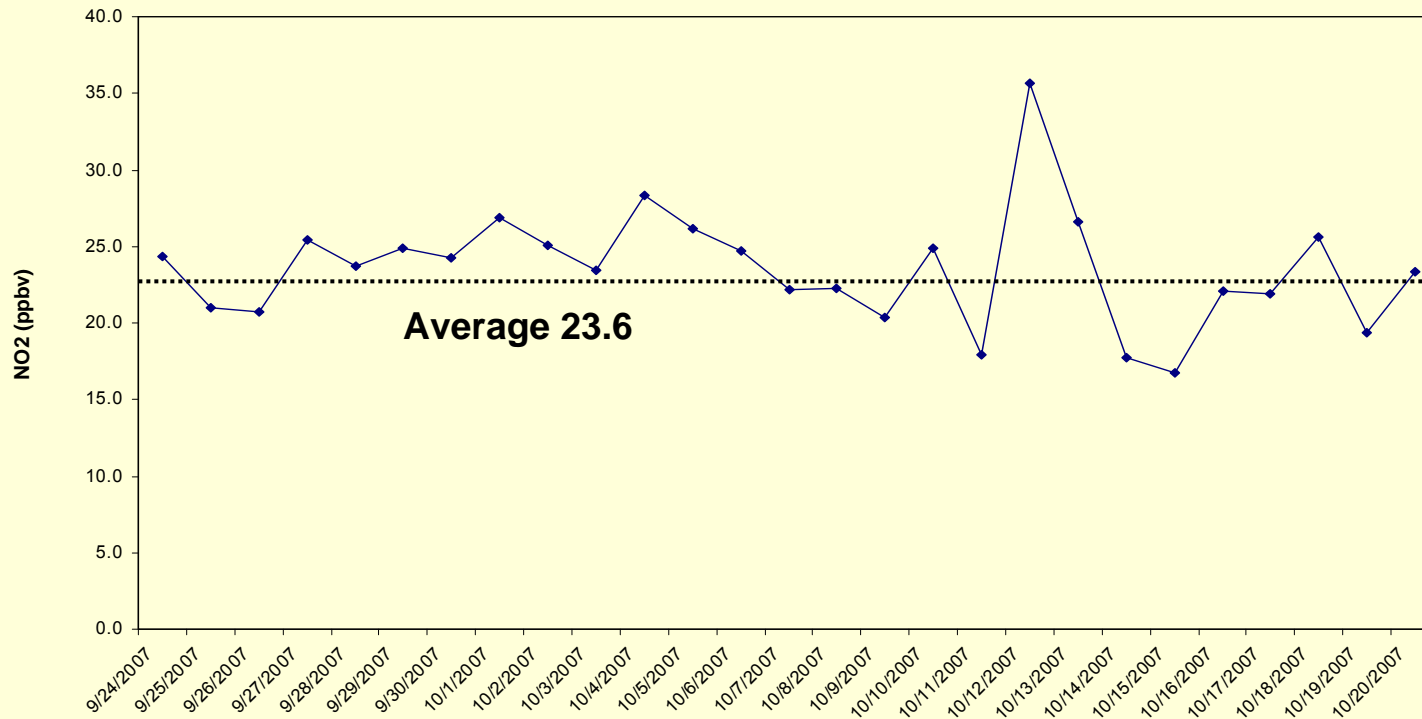
Ans: Refer to the table,

$$\alpha_{\text{SO}_2} = 39.9$$

$$\text{SO}_2(\text{ppbv}) = 39.9 \times 8000 / 40000 = 7.98 \text{ ppbv}$$

# Results and Discussion

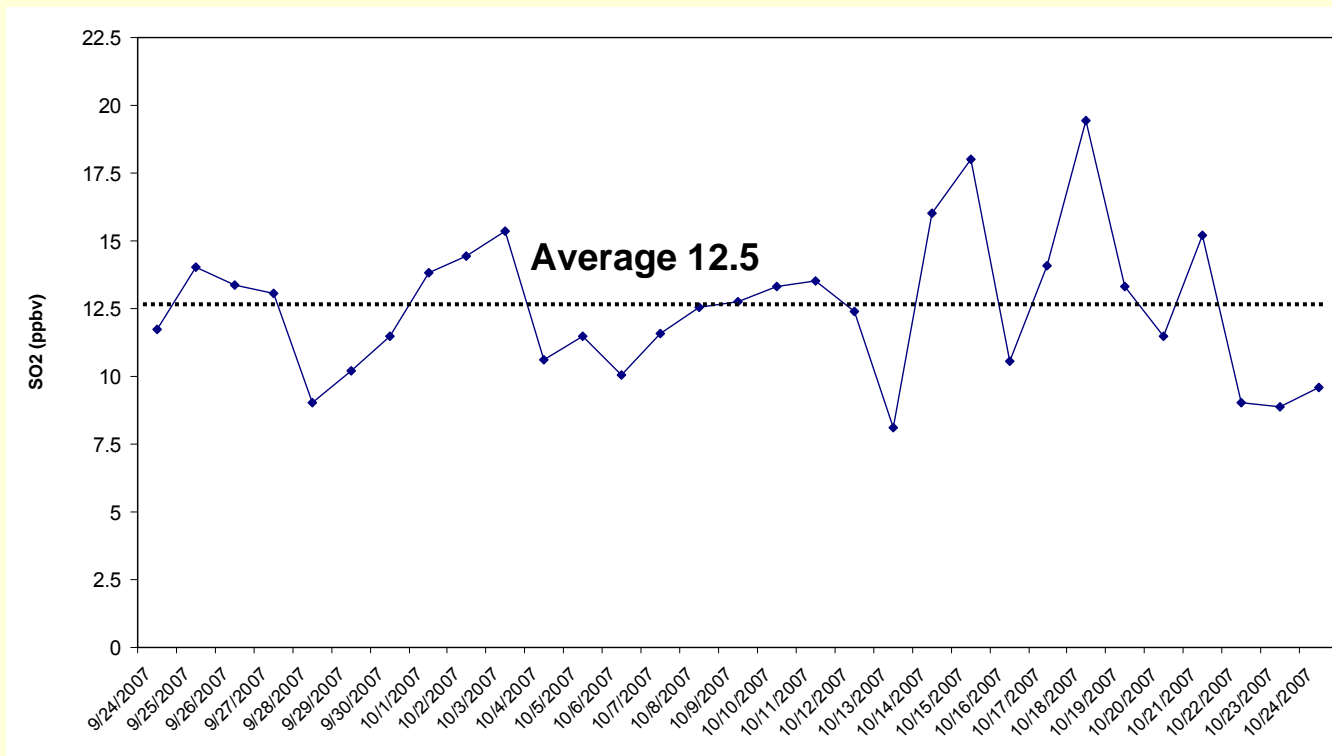
## Phase I-Active Sampler Data



Daily average concentration of NO<sub>2</sub>

# Results and Discussion

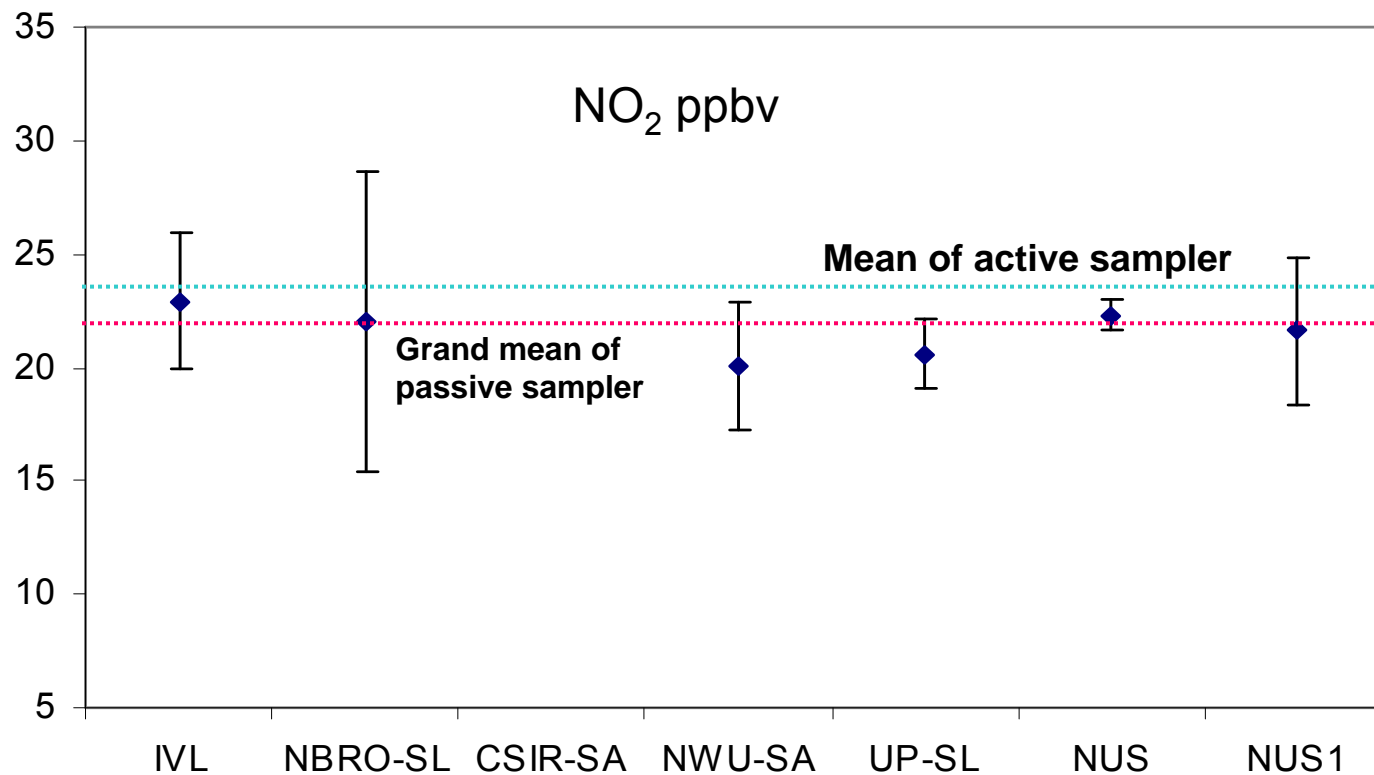
## Phase I-Active Sampler Data



Daily average Concentration of SO<sub>2</sub>

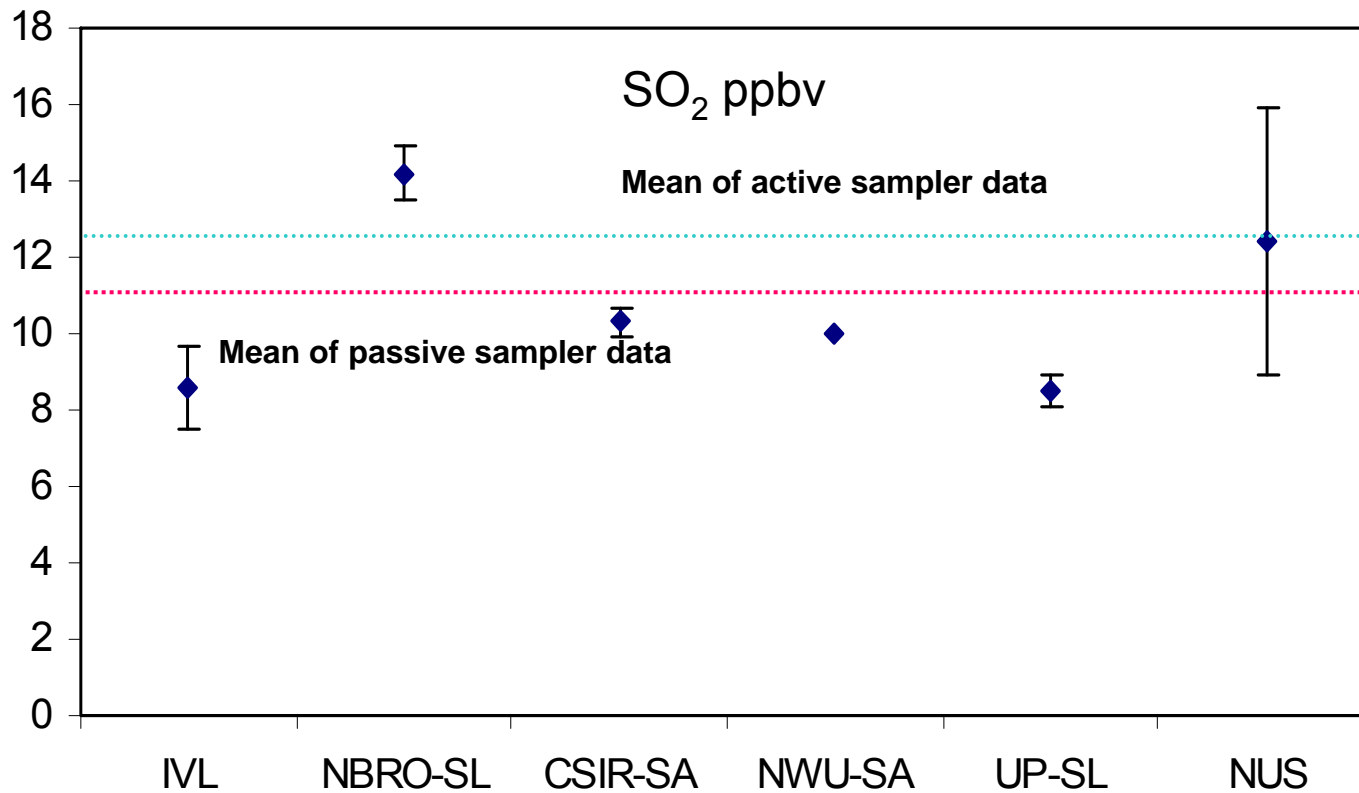
# Results and Discussion

## Inter comparison data-Phase I



# Results and Discussion

## Inter comparison data-Phase I





# Results and Discussion

## Phase I-Statistical Analysis of individual data by ANOVA

Analytes	F value	F Critical	P Value
NO <sub>2</sub>	1.46	3.1	0.27
SO <sub>2</sub>	2.95	3.1	0.06

ANOVA single factor analysis shows that results obtained from different passive samplers are not significantly different.

# Results and Discussion

## Phase II

Table 1 provides the details of the exposed samplers we have received from The participating laboratories as of now

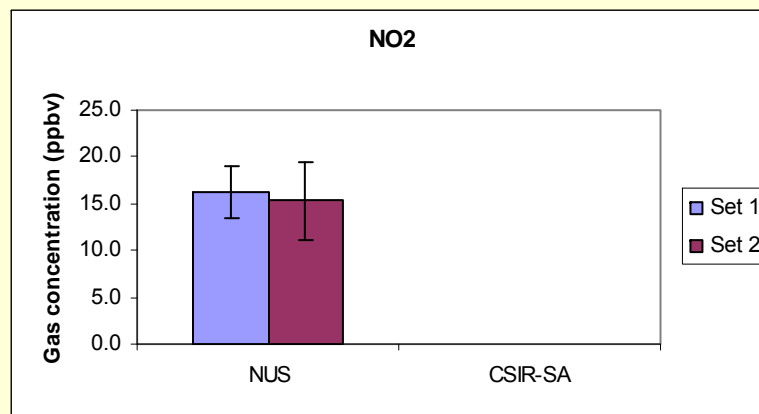
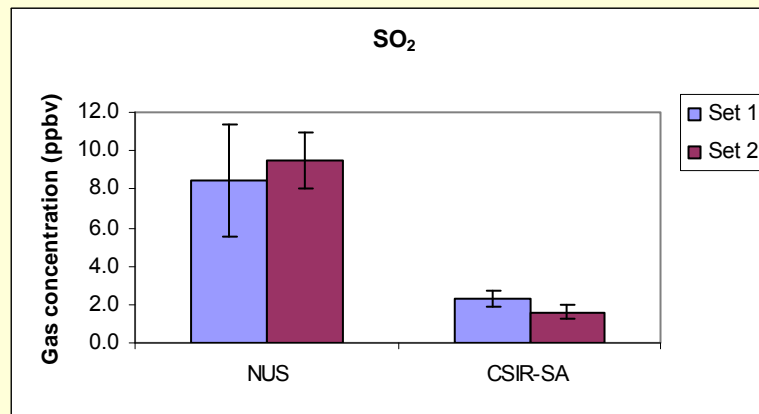
Sampling Sites Items	CSIR-SA	NUS
Sampler Type	CSIR	Ogawa
Sampling Time (min)	41760	47880
Average Temperature (°C)	23.6	26.6
Average Humidity (%)	63.0	84.6

- a. Set 1 was analyzed at NUS;
- b. Set 2 was analyzed in respective countries.
- Two sets of samples collected in NUS were analyzed by NUS lab.

# Results and Discussion

## Phase II

### In-country comparison of passive samplers for SO<sub>2</sub> and NO<sub>2</sub>



## Conclusion

- All three type passive samplers could be used for  $\text{NO}_2$  and  $\text{SO}_2$  in the outdoor environment under urban pollution conditions;
- Larger variation particularly for  $\text{SO}_2$  between the samplers of different types and also within the samplers of the same type is possibly due to: analytical uncertainties; the difference in the sampling efficiency based on different coating solutions

## Conclusions

- All three type passive samplers could be used for  $\text{NO}_2$  and  $\text{SO}_2$  in the outdoor environment under urban pollution conditions;
- Larger variation particularly for  $\text{SO}_2$  between the samplers of different types and also within the samplers of the same type is possibly due to: analytical uncertainties; the difference in the sampling efficiency based on different coating solutions

## Future work

- a) To continue to work with collaborative partners to complete the remaining phase of the study on “In-country comparison of passive samplers for SO<sub>2</sub> and NO<sub>2</sub>”;
- b) To start 2<sup>nd</sup> round robin tests in order to evaluate the performance of these passive samplers at different concentration levels under different weather and pollution conditions (dry season in Singapore);
- c) A comprehensive report will be prepared based on the proposed inter-comparison and inter-laboratory exercises.

# Acknowledgement

All the participating laboratories;

Dr. Kevin Hicks, Stockholm Environment Institute;

Professor Henning Rodhe, Stockholm University;

Iyngara & Jacob Kurian, UNEP;

Financial support provided by Sida(RAPIDC)/UNEP.