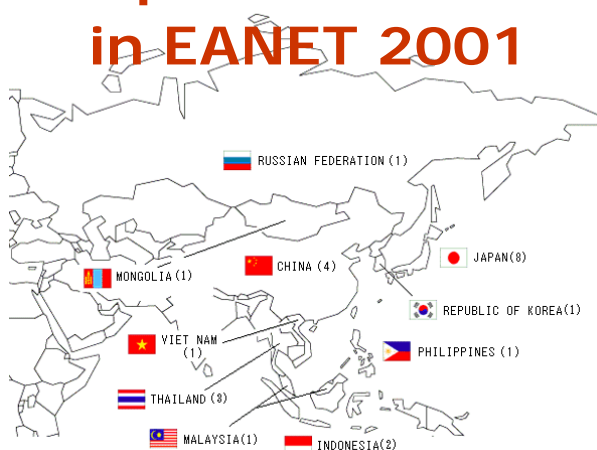


## Methodology and Technical Issues on Wet/Dry Deposition Monitoring in EANET

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## Wet Deposition Monitoring in EANET 2001



Data report on the Acid Deposition  
in the East Asian Region 2001:

## **The Technical Manual for Wet Deposition Monitoring**

1. Introduction
2. Fundamental Items Concerning  
Monitoring on Wet Deposition
3. Wet Deposition Sampling Methods
4. Analytical Methods
5. Data Control and Data Reporting
6. Quality Assurance/Quality Control  
Appendix

## **QA/QC Program for Wet Deposition Monitoring**

- Sampling sites
- Collection and handling of samples
- Measurements and analyses of samples
- Data control
- Data reporting
- QA/QC implemented by the NC
- Training program

## Deposition monitoring sites

### -Remote sites

*To be established for the assessment of acid deposition in background areas.*

### -Rural sites

*To be established for the assessment of the state of acid deposition in rural areas or hinterlands.*

### -Urban sites

*Data can be used to evaluate the effects of acid deposition on buildings and historical monuments.*

### -Minimum Distance to Emission and Contamination Sources

- Regions *within 50 km* of large pollution sources should be excluded as *remote sites*.
- Regions *within 20 km* of large pollution sources should be excluded as *rural sites*.
- Regions *within 500 m* of main roads should be excluded as *remote and rural sites*.



## -Monitoring Frequency

- -every 24 hours,
- -precipitation event: *operationally inconvenient*
- -Where analysis of daily samples is not practical, combining daily samples for a weekly (7 days ) composite or sampling for an week can be acceptable *only when* the integrity of sample composition can be maintained, for instance, *by refrigerating and/or adding biocide to samples.*

## Monitoring Frequency and Characteristics of Monitoring Site 2001

- Sampling Frequency in 2000
  - Daily: 28 sites (21) +7
  - Event: 2 sites (9) - 7
  - Weekly: 11 sites (11) -
- Characteristics
  - Urban: 15 sites (15) -
  - Rural: 12 sites (9) +3
  - Remote: 16 sites (16) -

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## On-site inspection

- Together with on-site audit, operation of sampling instruments, the cleanliness of sampling instruments and vessels, on-site sample handling and data documentation should be inspected by National Center.

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## -Measurement Parameters

- -Required parameters  
*pH, EC and major ions ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ )*
- -When ion balance is not obtained,  
 *$F^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $HCO_3^-$ , Organic Acids*
- -For characterization of precipitation,  
*Heavy metals,  $PO_4^{3-}$ , Al, Organic compounds*

## -Laboratory treatment of samples

- Sample arrival.
- Check agreement of samples and the sample list.
- Measure sample amount, EC, pH ASAP.
- Filtrate by clean membrane filters (0.45 $\mu$ m)
- Refrigerate at 4 ..
- Measure other parameters with in a week.

## Analytical Methods 1

- **The Order of Measurement Priority**

1)  $SO_4^{2-}$ ,  $NO_3^-$  and  $Cl^-$  by IC

2)  $NH_4^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  by IC,  
when a cation column is available

3) If not,  $NH_4^+$  by spectrophotometry

4)  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  by AA

- **Duplicate Analysis**

-For QA/QC of analytical procedure,  
duplicate analysis is recommended every  
10 to 20 sample measurements.

## Analytical Methods 2

- **-Measurement of EC and pH**

The samples and the standard solutions are **recommended to be measured at 25 °C** in a water bath **if available.**

- **-Analysis by Ion Chromatography**

Both isochratic and gradient methods are available for IC analysis.

## -Data Check

- **Statistical Tests**

*Comparison of new data with already stored in the database*

- **Ion balance and conductivity balance check**

(R<sub>1</sub> and R<sub>2</sub>)

- **Analytical Precision *should be tested by duplicate analysis***

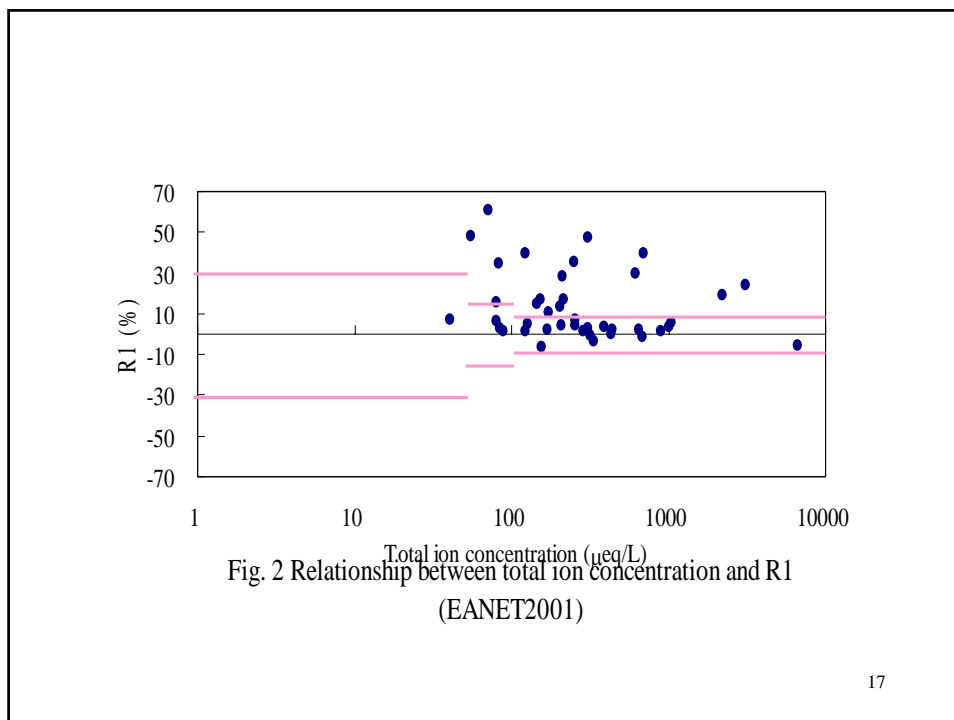
## Ion Balance Check

- $R_1 = ((C - A)/(C + A)) \times 100 \%$
- Where C and A represents cation and anion equivalents, respectively

- **Table Required criteria for R<sub>1</sub>**

<u>(C + A), <math>\mu\text{eq/L}</math></u>	<u>R<sub>1</sub>, %</u>
<50	±30
50-100	±15
>100	±8





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### Check by Comparison between calculated and measurement EC

- $R_2 = \left( \frac{\Lambda_{\text{calc}} - \Lambda_{\text{meas}}}{\Lambda_{\text{calc}} + \Lambda_{\text{meas}}} \right) \times 100 \%$

$$\Lambda_{\text{calc}} = \sum c_i \Lambda_i^0 \times 10^{-4}$$

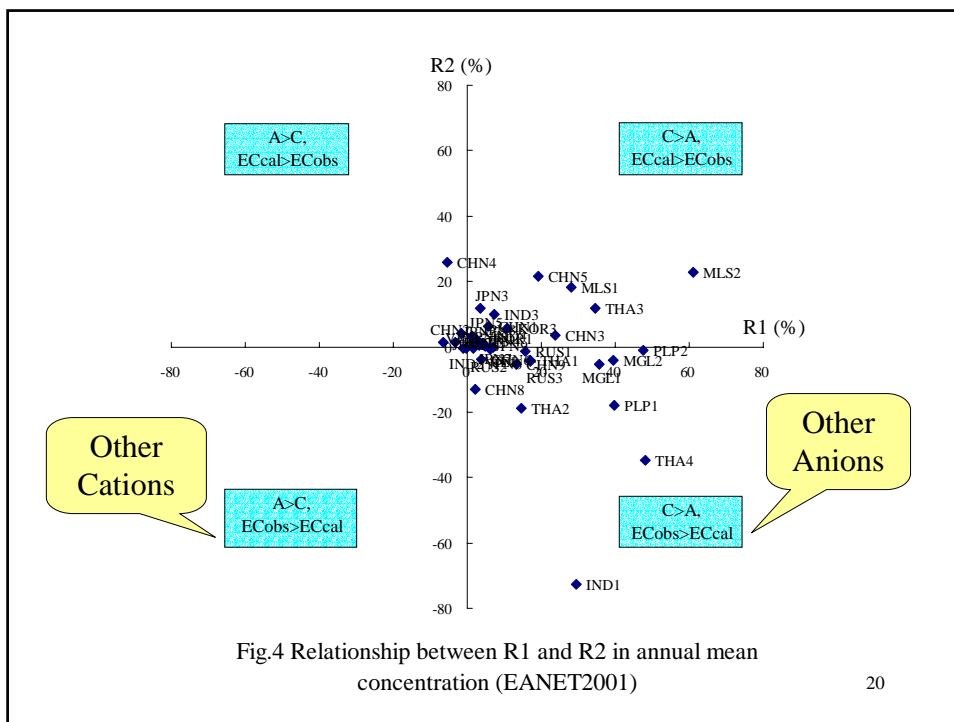
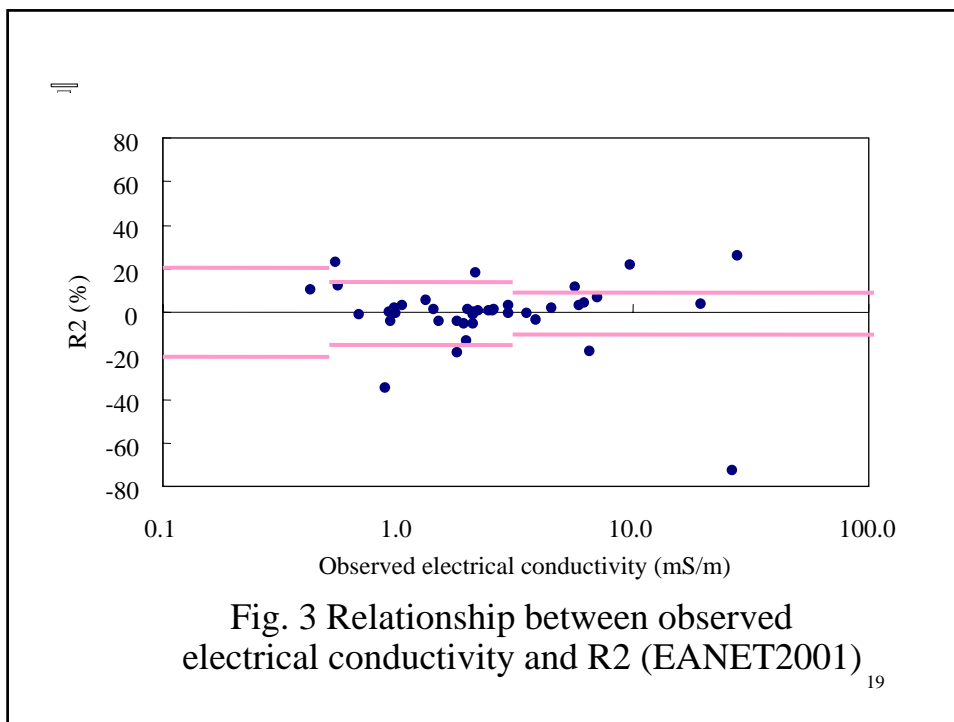
$\Lambda_{\text{calc}}$ : calculated conductivity (mS/m),

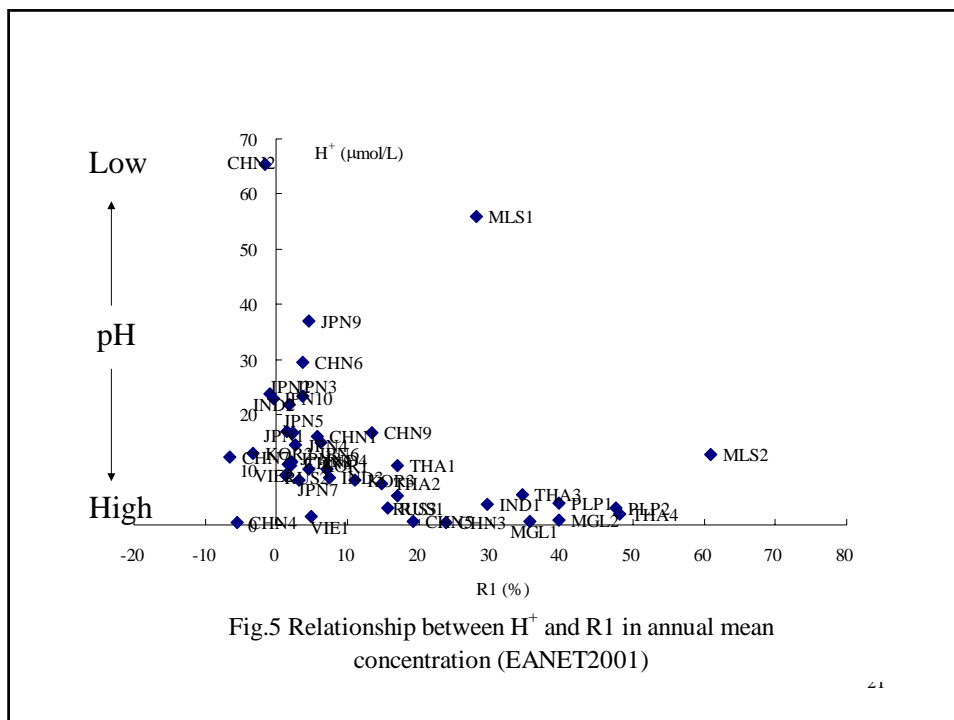
$c_i$ : ionic concentration ( $\mu\text{mol/L}$ ),

$\Lambda_i^0$ : molar conductivity ( $\text{S cm}^2/\text{mol}$ )

Table Required criteria for  $R_2$

$\Delta_{\text{meas}}$ , mS/m	$R_2$ , %
< 0.5	± 20
0.5 – 3	± 13
> 3	± 9





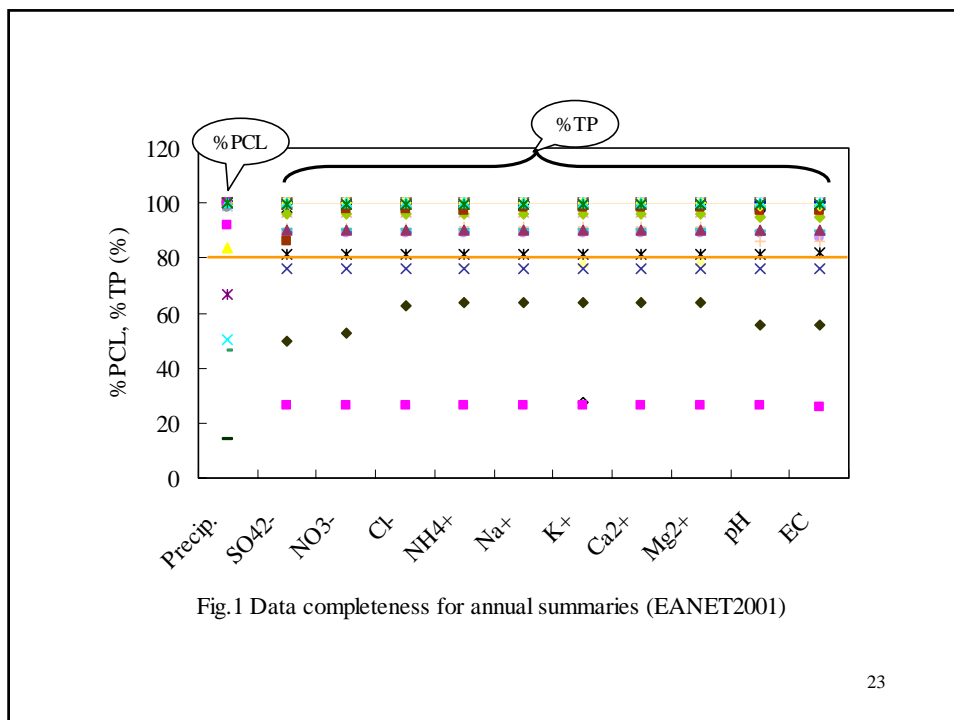
## Data Completeness

- (1) the portion of the data summary period (season or year) with complete records of the amount of precipitation that fell (**%PCL: Percent precipitation coverage length**),

$$\%PCL = \left( \frac{\text{(Number of days in the summary period)} - \text{(Number of days with missing or unknown precipitation)}}{\text{(Number of days in the summary period)}} \right) * 100$$

- (2) the portion of the precipitation associated with valid chemical analysis and valid sample collection (**%TP: Percent total precipitation**),

$$\%TP = \left( \frac{\text{Sum of precipitation amounts for samples with valid sample component measurements}}{\text{Sum of precipitation amounts for all samples}} \right) * 100$$



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### Sea salt contribution for wet deposition

In EANET, there are some sites located in island or peninsula.

Therefore, sea salt contribution for wet deposition has to be estimated accurately, because wet deposition is acidified mainly by air pollutant emitted from non-sea salt sources.

In Japan, it is considered that sodium, magnesium, and chloride in wet deposition are derived from sea salt, because concentration ratios among these ions in wet deposition are confirmed to agree with that in seawater.

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Based on this relation, sulfate and calcium in wet deposition are divided into two parts, sea salt and non-sea salt origin, by estimation using sodium concentration and ratios,  $\text{SO}_4^{2-}/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$  of seawater.

$$[\text{nss-SO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.06028 \times [\text{Na}^+]$$

$$[\text{nss-Ca}^{2+}] = [\text{Ca}^{2+}] - 0.02161 \times [\text{Na}^+]$$

( $\text{Na}^+$ : 468.3 mmol/L,  $\text{SO}_4^{2-}$ : 28.23 mmol/L,  $\text{Ca}^{2+}$ : 10.12 mmol/L; "Guide to maritime observation" Oceanographic Society of Japan)

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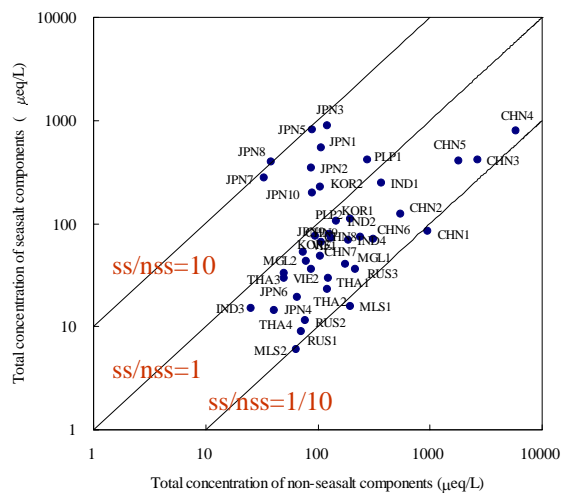


Fig. 6 Relationship between nss- and ss-components in annual mean concentration (EANET2001)

**Non-sea salt components:**  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{nss-Ca}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{nss-SO}_4^{2-}$

**Sea salt components:**  $\text{ss-Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{ss-SO}_4^{2-}$ , and  $\text{Cl}_6^-$

Data report on the Acid Deposition  
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**Dry deposition  
monitoring  
(Air concentration)**

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**Priority chemical species for dry  
deposition monitoring in EANET**

- The priority of the chemical species is defined in the "Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET" (1999) as follows:
  - First:  $\text{NO}_2$  (urban),  $\text{SO}_2$ ,  $\text{O}_3$ ,  $\text{PM}_{\text{mass}}$
  - Second:  $\text{NO}_2$  (Urban and Remote),  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{PM}_{\text{component}}$  ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ )

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## Applied monitoring methods in 2001

- Automatic monitoring method
  - UVF (SO<sub>2</sub>) , CLD (NO, NO<sub>2</sub>) UV photometric (O<sub>3</sub>), TEOM, β-ray (PM) etc.
  - *China, Japan, Thailand*
- Filter pack method
  - *Indonesia, Malaysia, Mongolia, Philippines, (Republic of Korea), Russia, Thailand, Vietnam*
- Other methods
  - Passive sampler & Aerosol sampler
  - *Malaysia*

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## Automatic monitoring methods

- China
  - SO<sub>2</sub>: UVF or Open pass, NO<sub>2</sub>: CLD or Open pass
  - PM<sub>10</sub>: β-ray, TEOM
- Japan
  - SO<sub>2</sub>: UVF, NO<sub>x</sub>: CLD, O<sub>3</sub>: UVP
  - PM<sub>10</sub>, PM<sub>2.5</sub>: TEOM or β-ray
- Thailand
  - SO<sub>2</sub>: UVF, NO<sub>x</sub>: CLD, O<sub>3</sub>: UVP
  - PM<sub>10</sub>: β-ray

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## Filter pack method for EANET

- Sampling period
  - Weekly sampling with low flow rate seems to be feasible taking into account capacities of most participating countries.
- Filters
  - Four-stage method (Teflon, Nylon, Alkali Cell., Acid Cell.) is suggested from the experiences in Japan.

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## Four-stage filter pack method



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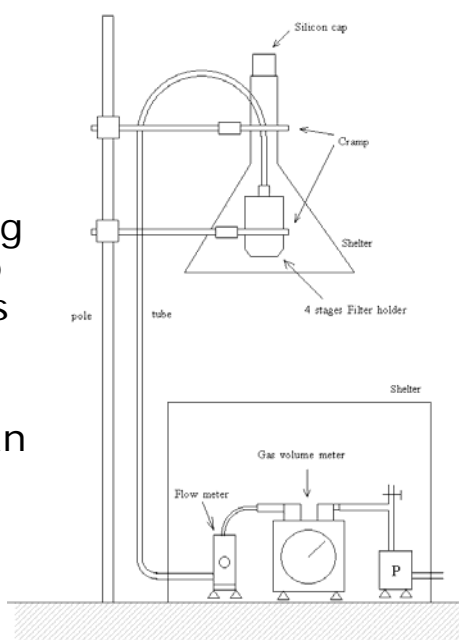
## Reactions on filters

Stage	Reaction	Collected specie
1 <sup>st</sup> (F0)	Filtration	aerosols
2 <sup>nd</sup> (F1)	Adsorption	HNO <sub>3</sub> , partial SO <sub>2</sub> , Partial HCl
	Neutralization by collected acid gases	partial NH <sub>3</sub>
3 <sup>rd</sup> (F2)	Neutralization by alkali impregnated cellulose filter	SO <sub>2</sub> , HCl
4 <sup>th</sup> (F3)	Neutralization by acid impregnated cellulose filter	NH <sub>3</sub>

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## Sampling system

- The inlet of sampling air should be set up from 5 to 10 meters above the ground.
- It should be around 3 meters higher than the height of the buildings if the inlet is on the buildings. (QA/QC program)



## Flow rate

- A flow rate at 1 liter/min is recommended for weekly or biweekly sampling.
- If it is difficult to detect concentrations in remote sites, flow rates could be increased to 2 liter/min.

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## Extraction

Stage	Species analyzed by IC	Solvent
F0	SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	20mL Water
F1	SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	20mL Water
F2	SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup>	20mL 0.05% H <sub>2</sub> O <sub>2</sub>
F3	NH <sub>4</sub> <sup>+</sup>	20mL Water

*20 minute shake with a shaker or an ultrasonic bath*

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