

Report of the Inter-laboratory Comparison Project 2002 on Wet Deposition *5th attempt*

Network Center for EANET
ADORC

1

Laboratories participated in this Inter-comparison project of the EANET

- Network Center (NC) shipped the artificial rainwater samples to all of these 24 laboratories.
- All Lab. submitted their analytical data.
- These laboratories' names were presented as short name in this report.



2

The purposes of this project

- (i) to recognize the analytical precision and accuracy of the data in each participating laboratory, and give an opportunity to improve the quality of the analysis on wet deposition monitoring.
- (ii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

3

Outline of the Artificial Rainwater

- ***Two kinds of sample: No.021(High Conc.)
No.022(Low Conc.)***
- ***Amount of sample: 100ml each***
- ***Container: Polypropylene bottle***
- ***Concentrated sample: each laboratory dilutes the samples exactly 100 times by de-ionized water before analysis***
- ***Parameter: pH, EC, Anions(3) and Cations(5)***

4

Concentration of the artificial rainwater

concentration of constituents were prepared below range

Parameter	Range	Parameter	Range
pH	4.0 – 5.5	Na ⁺	1 – 100 μmol/L
EC	0.3 – 10 mS/m	K ⁺	1 – 50 μmol/L
SO ₄ ²⁻	5 – 100 μmol/L	Ca ²⁺	1 – 50 μmol/L
NO ₃ ⁻	5 – 100 μmol/L	Mg ²⁺	1 – 50 μmol/L
Cl ⁻	5 – 150 μmol/L	NH ₄ ⁺	3 – 100 μmol/L

5

Summary of analytical results of the artificial rainwater samples (Reported data after outliers were removed)

Constituents	Prepared	Average	S.D.	N	Min.	Max.
[Sample No.021]						
pH	4.30	4.32	0.08	24	4.15	4.50
EC(mS/m)	3.75	3.54	0.22	24	2.93	4.03
SO ₄ ²⁻ (μmol/L)	40.3	40.2	2.57	23	34.4	49.4
NO ₃ ⁻ (μmol/L)	51.0	51.3	2.91	23	47.8	61.6
Cl ⁻ (μmol/L)	33.7	32.5	2.82	23	26.0	37.9
Na ⁺ (μmol/L)	13.7	13.6	1.15	24	11.4	16.5
K ⁺ (μmol/L)	6.92	7.2	1.12	24	5.3	10.5
Ca ²⁺ (μmol/L)	19.1	19.2	1.86	24	14.2	23.0
Mg ²⁺ (μmol/L)	7.02	7.0	0.89	24	5.2	8.9
NH ₄ ⁺ (μmol/L)	42.4	43.3	3.27	23	38.7	50.8
[Sample No.022]						
pH	5.15	5.19	0.14	24	4.94	5.61
EC(mS/m)	0.69	0.69	0.04	23	0.59	0.75
SO ₄ ²⁻ (μmol/L)	8.88	9.0	1.03	23	5.1	10.9
NO ₃ ⁻ (μmol/L)	8.49	8.5	0.87	23	6.4	11.6
Cl ⁻ (μmol/L)	9.13	10.0	1.85	23	8.5	15.8
Na ⁺ (μmol/L)	5.13	4.9	1.05	23	1.8	6.4
K ⁺ (μmol/L)	1.98	2.0	0.61	23	1.2	3.4
Ca ²⁺ (μmol/L)	6.61	7.1	1.96	24	2.1	10.0
Mg ²⁺ (μmol/L)	1.75	1.9	0.52	24	1.1	3.3
NH ₄ ⁺ (μmol/L)	4.54	4.2	1.04	22	1.3	7.0

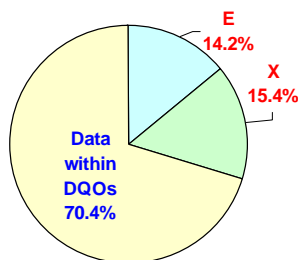
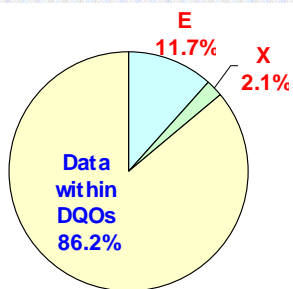
(Note) Prepared: Value or concentration, which was calculated from the amount of chemicals, used for the preparation of samples.

6

Percentage of flagged data for Sample No.021 and No.022

Sample No.021

Sample No.022

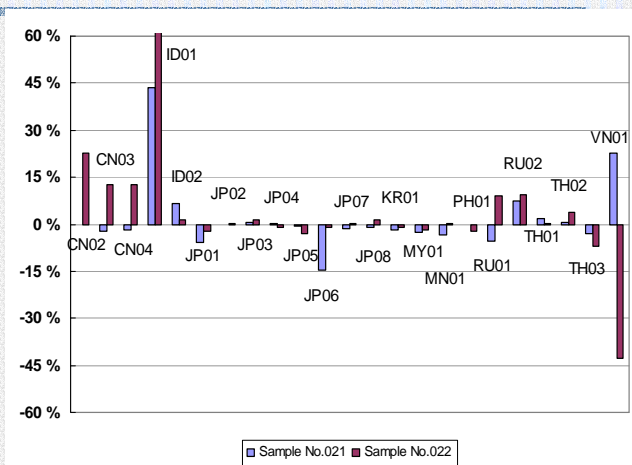


Flag E; exceeded the DQOs by a factor of 2

Flag X; exceeded the DQOs more than a factor of 2

7

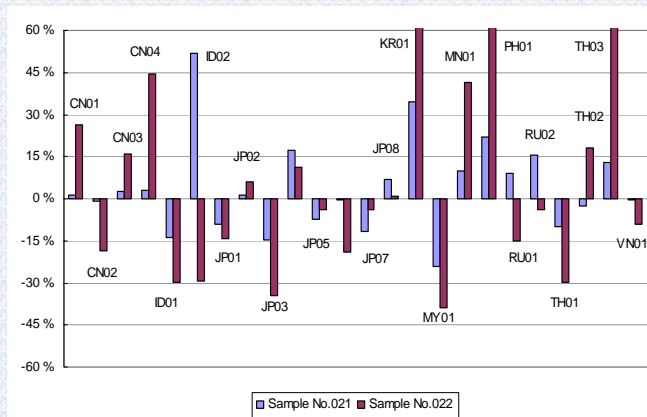
Analytical parameter Distribution of SO_4^{2-} data normalized by prepared concentration



8

Analytical parameter
Distribution of K⁺ data normalized by prepared concentration

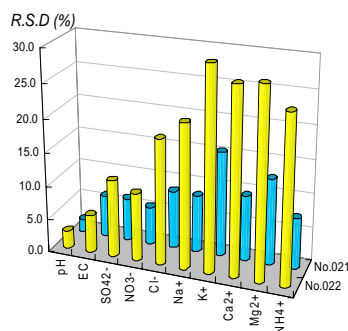
Relative standard deviation of K⁺ among laboratories was the largest (15.6% .29.9%)



9

Analytical parameter
Relative standard deviation of each constituents

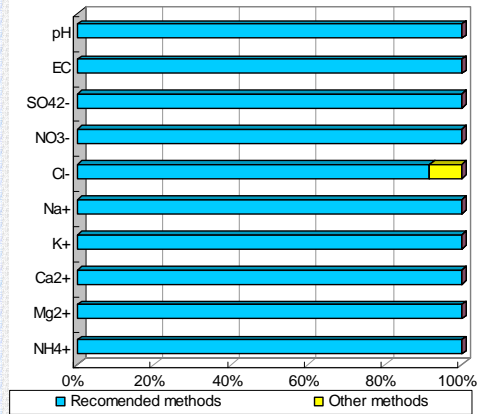
- Data on pH, EC were less varied compared with other ionic constituents.
- Analytical data of cations were varied particularly in the sample No.022
 Na⁺:21.4%, K⁺ :29.9%
 Ca²⁺: 27.5%,Mg²⁺:28%
 NH₄⁺ :24.7%
- It is expected to improve the quality of data that has large deviation through the QA/QC activities in each laboratory.



10

Circumstance of sample analysis Ratio of recommended method used in the project

- Most of participating laboratories employed recommended methods of EANET.
 - pH, EC, SO₄²⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺
- Not recommended methods of EANET were employed in some laboratories.
 - Titration: Cl⁻



11

Number of staff in charge of measurement

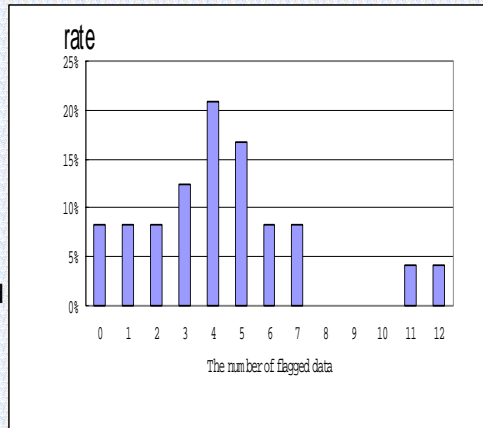
- In 14 laboratories (58%), only one person carried out measurement.
- In other laboratories, their responsibilities were usually separated by the methods used for analysis such as anions and cations.

Lab.ID	Total	pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
CN01	1	A	A	A	A	A	A	A	A	A	A
CN02	4	A	A	B	B	B	C	C	C	C	D
CN03	1	A	A	A	A	A	A	A	A	A	A
CN04	1	A	A	A	A	A	A	A	A	A	A
ID01	3	A	B	A	A	A	A	A	A	A	A
ID02	3	A	A	A	A	A	B	B	B	B	C
JP01	1	A	A	A	A	A	A	A	A	A	A
JP02	1	A	A	A	A	A	A	A	A	A	A
JP03	1	A	A	A	A	A	A	A	A	A	A
JP04	1	A	A	A	A	A	A	A	A	A	A
JP05	1	A	A	A	A	A	A	A	A	A	A
JP06	1	A	A	A	A	A	A	A	A	A	A
JP07	1	A	A	A	A	A	A	A	A	A	A
JP08	1	A	A	A	A	A	A	A	A	A	A
KR01	1	A	A	A	A	A	A	A	A	A	A
MY01	2	A	A	B	B	B	A	A	A	A	A
MN01	2	A	B	A	A	B	B	B	B	B	B
PH01	4	A	A	B	B	B	C	C	C	C	D
RU01	3	A	A	B	B	B	C	C	C	C	A
RU02	1	A	A	A	A	A	A	A	A	A	A
TH01	2	A	B	A	A	A	B	B	B	B	B
TH02	2	A	A	B	B	B	B	B	B	B	B
TH03	1	A	A	A	A	A	A	A	A	A	A
VN01	2	A	A	B	B	B	A	A	A	A	A

12

The distribution of laboratories with the number of flagged data

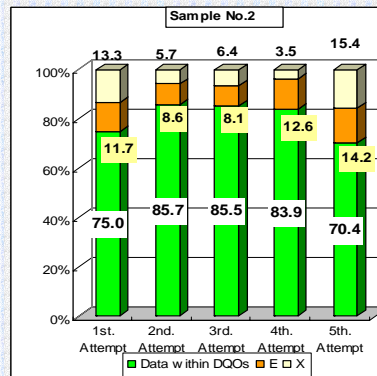
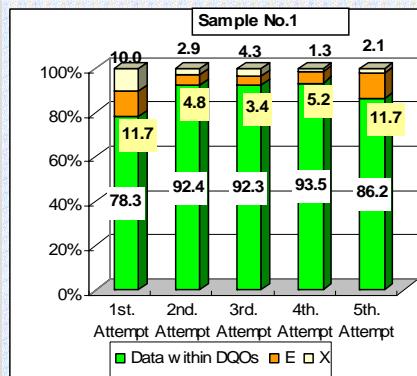
- Number of excellent laboratories without flagged data was 2 (8.3%)
- Due to the sample with low concentration, many labs had a large number of flagged data.
- 2 laboratories with more than 11 flagged data need some improvement.



13

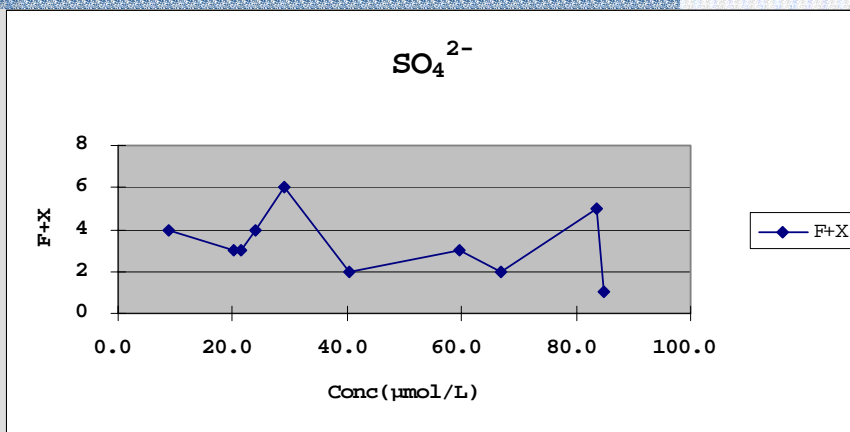
Comparison of 1st, 2nd, 3rd, 4th and 5th inter-laboratory project

- In this survey, the rates of within DQOs were 70 - 86%.
- Improvements are required in some laboratories.



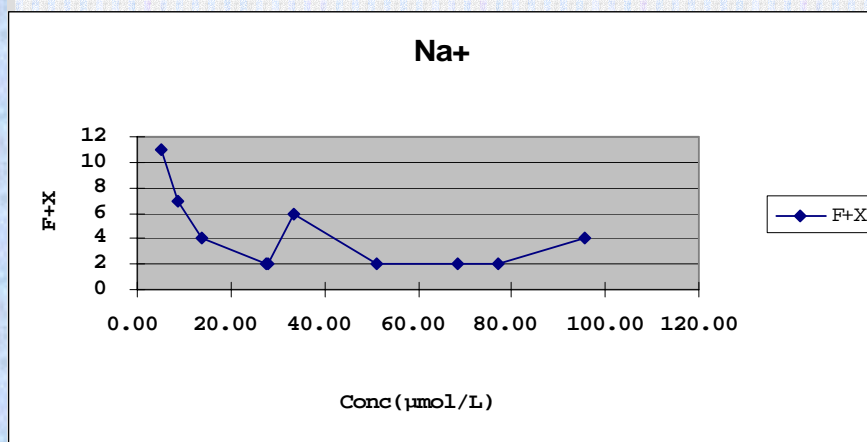
14

Concentration of Ions vs Number of Flagged Data



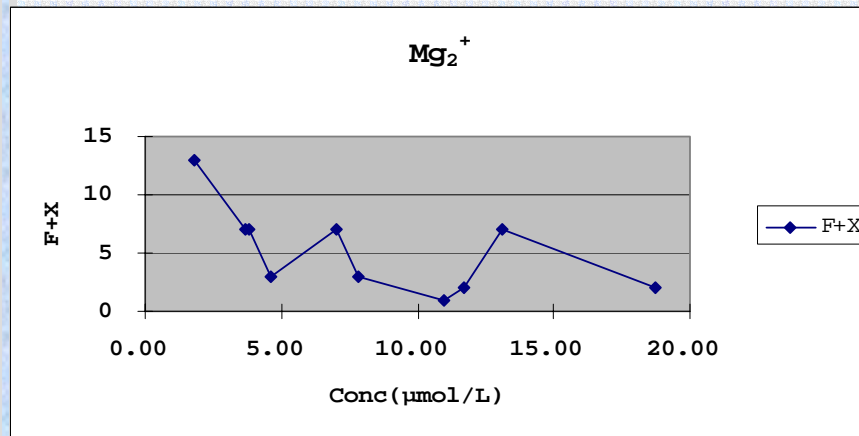
15

Concentration of Ions vs Number of Flagged Data



16

Concentration of Ions vs Number of Flagged Data



17

Concentration of Ions vs Number of Flagged Data

- This result means that it become more difficult when the concentration decreases.
- So analysis has to be carried out very carefully in the trace analysis.
- In this year's survey, NC will prepare samples that are close to the real rain's concentration level.

18

For improvement of measurement precisions(1)

■ **Fundamental measurement and analysis matters**

- ◇ **Freedom** from **contamination** of the apparatus, materials and reagents used for measurement.
- ◇ Measurement and analysis should be conducted by **persons** who are well trained.
- ◇ **SOPs** must be prepared for the management of apparatus, reagents, analytical procedure, and so on.
- ◇ **Others**
 - De-ionized pure water (<0.15mS/m)
 - Certified materials and certified samples(for standard,reference solutions)
 - Pretreatment of samples at analytical laboratory
 - Adjustment of analytical instruments

19

For improvement of measurement precisions(2)

■ **Evaluation of reliability**

- ◇ measurements should be continued after confirming that the sensitivity fluctuation is within the prescribed range.
- ◇ **calibration curve covers the range of concentration for constituents.**

■ **Data control**

- ◇ **Data check in analysis organizations**
 - Check by calculation of **ion balance (R1)** and **comparison between calculated and measured electrical conductivity (R2).**

20

Request from ADORC

- Please keep the deadline of the report submission.
- Please submit the measurement chart and calibration chart also.
- If participating laboratories have any request for the survey, please send it to NC by e-mail.