The Twentieth Senior Technical Manager's Meeting
of the Acid Deposition Monitoring Network in East Asia
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Consideration of follow-up action on Inter-laboratory Comparison (ILC) project

I. Introduction

1. The Inter-laboratory Comparison (ILC) project was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the quality assurance/quality control (QA/QC) programs of EANET. The ILC project has implemented since 1998 for wet deposition, 1999 for soil, 2000 for inland aquatic environment and 2005 for dry deposition. The objectives of ILC are shown below. It covers the evaluation of analytical results, analytical equipment and its operating condition and other practices, Regarding the third item, the follow-up action after the ILC results are received is important.

   (i) To recognize the analytical precision and accuracy of the measurement in each participating laboratory,
   (ii) To give further opportunities to improve the quality of the analysis on wet deposition, dry deposition (filter pack method), soil and inland aquatic monitoring of EANET,
   (iii) To improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

2. For past 10 year data (2009-2018) of ILC project, the ratios of flagged data for wet deposition are relatively stable for both high (5-10%) and low (9-21%) concentration samples. The ratios of flagged data for dry deposition are also in certain range for both large (6-29%) and small (15-43%) quantity samples. The ratios of flagged data are relatively stable (9-16%) also for inland aquatic environment. While all of analytical data of 2 laboratories satisfied Data Quality Objectives (DQOs) for wet deposition, the percentages of the data within DQOs of 7 laboratories were below 70%. These situations imply that there are large variations of analytical uncertainty among EANET participating laboratories, and thus the additional follow up after the implementation of ILC for some laboratories would be necessary.

II. Current status of follow-up action and use of the ILC sample as working standard

3. When site and laboratory audits for Japanese EANET sites are implemented, the ILC results for past 5 years are shown to local staffs and the reasons of outliers are discussed if necessary. Because the detection limit is one of importance factors for analytical performance, the past 5 year results of detection limits for ionic species are also discussed at laboratory audit. According to the discussions, key factors which cause large uncertainty and outlier for ion chromatography analysis were identified as follows; (i) Improper calibration curve, (ii) Contamination of the samples, apparatus, analyzer, auto sampler, (iii) Analytical Instability, (iv) unstable analytical condition. Improvement of these factor will lead to reduce analytical uncertainty. Moreover, preparation and understanding the

contents of Standard Operating Procedure (SOP) will avoid careless mistakes and keep constant analytical skills of laboratory and field operators.

4. The ILC sample in last year can be used for the working standard of ion species analysis to check analytical validity. It is recommended to prepare the table of prepared values and DQO ranges every year in order to check analytical validity of working standard. Example of the table of prepared values and DQO ranges is shown in Table 1 of Annex. If outlier data are found, it is necessary check each procedure and reanalyze the samples, if necessary. The results of working standard analysis which should be measured by each analytical run are reported to the national center of Japan. The reporting form is shown in Table 2 of Annex. These data can be checked long term stability and compatibility of ion analysis.

III. Draft time schedule in 2020 for follow-up action for EANET participating laboratories

5. The follow-up action after the ILC results a for EANET participating laboratories is planned according to the below draft schedule. The effectiveness of the follow-up could be evaluated by reducing the ratios of flagged data.

February 2020	Submission deadline ILC survey in 2019
April 2020	Announcement of setting values and analytical results from the NC to participating laboratories of ILC
May to June 2020	Request to the lab which flagged data were reported for reanalysis and submission of wet deposition data
July to August 2020	Technical guidance by the NC in order to identify factors which cause large uncertainty and outlier for ion chromatography analysis
September 2020	Report of ILC survey in 2019 at STM21

Annex

Table 1 Prepared values of each parameter in artificial rainwater (171w and 172w)

The prepared values of each parameter in artificial rainwater of inter-laboratory comparison projects of EANET
※ Those show the values of pH, EC and concentration of ions in sample No. 171w and No. 172w diluted by 100 times

each parameter / year		pH	EC [mS/m]	SO42- [μmol/l]	NO3- [μmol/l]	Cl- [μmol/l]	Na+ [μmol/l]	K+ [μmol/l]	Ca2+ [μmol/l]	Mg2+ [μmol/l]	NH4+ [μmol/l]
2018	the diluted sample No. 171w	4.85	2.98	60.0	30.9	33.2	26.2	4.8	33.9	9.5	52.1
	-15%	4.12	2.53	51.0	26.3	28.2	22.3	4.1	28.8	8.1	44.3
	-10%	4.37	2.68	54.0	27.8	29.9	23.6	4.3	30.5	8.6	46.9
	10%	5.34	3.28	66.0	34.0	36.5	28.8	5.3	37.3	10.5	57.3
	15%	5.58	3.43	69.0	35.5	38.2	30.1	5.5	39.0	10.9	59.9
	the diluted sample No. 172w	5.15	1.03	18.1	11.0	12.6	9.6	1.8	13.1	2.6	10.1
	-15%	4.38	0.88	15.4	9.4	10.7	8.2	1.5	11.1	2.2	8.6
	-10%	4.64	0.93	16.3	9.9	11.3	8.6	1.6	11.8	2.3	9.1
	10%	5.67	1.13	19.9	12.1	13.9	10.6	2.0	14.4	2.9	11.1
	15%	5.92	1.18	20.8	12.7	14.5	11.0	2.1	15.1	3.0	11.6

The prepared values of each parameter in artificial rainwater of inter-laboratory comparison projects of EANET
※ Those show the values of pH, EC and concentration of ions in sample No. 171w and No. 172w diluted by 100 times

each parameter / year		pH	EC [μS/cm]	SO42- [mg/l]	NO3- [mg/l]	Cl- [mg/l]	Na+ [mg/l]	K+ [mg/l]	Ca2+ [mg/l]	Mg2+ [mg/l]	NH4+ [mg/l]
2018	the diluted sample No. 171w	4.85	29.8	5.764	1.916	1.177	0.602	0.188	1.359	0.231	0.940
	-15%	4.12	25.3	4.899	1.629	1.000	0.512	0.160	1.155	0.196	0.799
	-10%	4.37	26.8	5.187	1.724	1.059	0.542	0.169	1.223	0.208	0.846
	10%	5.34	32.8	6.340	2.108	1.295	0.663	0.206	1.495	0.254	1.034
	15%	5.58	34.3	6.628	2.203	1.354	0.693	0.216	1.562	0.266	1.081
	the diluted sample No. 172w	5.15	10.3	1.739	0.682	0.447	0.221	0.070	0.525	0.063	0.182
	-15%	4.38	8.8	1.478	0.580	0.380	0.188	0.060	0.446	0.054	0.155
	-10%	4.64	9.3	1.565	0.614	0.402	0.199	0.063	0.473	0.057	0.164
	10%	5.67	11.3	1.913	0.750	0.491	0.243	0.077	0.578	0.070	0.200
	15%	5.92	11.8	2.000	0.784	0.514	0.254	0.081	0.604	0.073	0.210

Table 2 Reporting form of working standard measurement
(Working standard should be measured by each analytical run)

QC form of ion analysis

Site : Banryu

Analysis date : 2018/6/29-2018/8/17 Sample ID : 11 ～ 17

Analisis lab : ACAP Reporter: Responsible person

Item	Analitical method	Type of Instrument	Standard conc. (μmol/l)	Analysis results of working standard					
				Date	2018/6/29	Date	2018/7/17	Date	2018/8/17
				Setting (μmol/l)	Measured (μmol/l)	Setting (μmol/l)	Measured (μmol/l)	Setting (μmol/l)	Measured (μmol/l)
SO_4^{2-}	IC	IC	0.3, 0.6, 1.0, 3.1, 6.2	44.5	44.6	44.5	44.3	44.5	44.1
		Integrion	10.4, 31.2, 62.5, 104.1	10.2	9.8	10.2	10.2	10.2	10.0
NO_3^-	IC	IC	0.5, 1.0, 1.6, 4.8, 9.7	21.0	21.2	21.0	21.1	21.0	20.5
		Integrion	16.1, 48.4, 96.8, 161.3	8.4	8.3	8.4	8.4	8.4	8.2
Cl^-	IC	IC	0.8, 1.7, 2.8, 8.5, 16.9	32.3	32.6	32.3	33.1	32.3	31.1
		Integrion	28.2, 84.6, 169.2, 282.1	8.5	8.3	8.5	8.8	8.5	8.4
NH_4^+	IC	IC	1.3, 3.3, 5.5, 16.6, 33.3	31.5	31.5	31.5	32.1	31.5	31.2
		Integrion	55.4, 166.3, 332.6, 554.4	13.0	13.5	13.0	13.8	13.0	13.4
Na^+	IC	IC	1.3, 2.6, 4.3, 13.0, 26.1	18.3	18.7	18.3	18.5	18.3	18.6
		Integrion	43.5, 130.5, 261.0, 435.0	6.5	6.6	6.5	6.5	6.5	6.5
K^+	IC	IC	0.8, 1.5, 2.6, 7.7, 15.3,	6.9	7.0	6.9	6.8	6.9	6.8
		Integrion	25.6, 76.7, 153.5, 255.8	1.7	1.8	1.7	1.5	1.7	1.6
Ca^{2+}	IC	IC	0.7, 1.5, 2.5, 7.5, 15.0,	28.8	28.0	28.8	28.4	28.8	28.6
		Integrion	25.0, 74.9, 149.7, 249.5	3.7	3.7	3.7	3.7	3.7	3.8
Mg^{2+}	IC	IC	1.2, 2.5, 4.1, 12.3, 24.7,	7.0	7.3	7.0	6.8	7.0	7.0
		Integrion	41.1, 123.4, 246.9, 411.4	1.8	2.0	1.8	1.7	1.8	1.8
				Date	2018/7/3	Date	2018/7/12	Date	2018/8/13
EC	EC	Conductivity Meter	0.01mol/l	2.39	2.37	2.39	2.34	2.39	2.40
		HORIBA DS-15	KCl solution	0.67	0.72	0.67	0.71	0.67	0.73
pH	pH	pH/ION Meter	pH7,pH4	4.85	5.05	4.85	5.07	4.85	5.00
		HORIBA F-54		5.30	5.54	5.30	5.47	5.30	5.38

Unit of EC is mS/m