

**Quality Assurance/Quality Control (QA/QC)
Program
for
Monitoring on Inland Aquatic Environment
in East Asia**

March 2000

Adopted at:

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of
Acid Deposition Monitoring Network in East Asia**

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The QA/QC programs were developed and adopted at the First Interim Scientific Advisory Group (ISAG) Meeting in October 1998, mainly based on the Monitoring Guidelines and Technical Manuals for Acid Deposition Monitoring in East Asia, adopted at the Expert Meetings (1993-1997). It included some modifications, taking into account the progress after the Technical Manuals had been adopted.

Considering the latest scientific and technical information and experiences accumulated during the preparatory-phase activities of the Acid Deposition Monitoring Network in east Asia (EANET), the Monitoring Guidelines and Technical Manuals for Wet Deposition Monitoring, Soil and Vegetation Monitoring, and Monitoring for Inland Aquatic Environment were revised at the Second ISAG Meeting in Jakarta in March 2000. Accordingly, the QA/QC programs as well as the Data Reporting Procedures and Formats were also revised at the same time to maintain consistency with these technical documents.

The participating countries of EANET are expected to make efforts for implementing their QA/QC activities in accordance with these QA/QC programs, taking into account the situation in respective countries. Based on the experiences of the participating countries as well as the progress in scientific and technical information, these QA/QC programs will be reviewed and revised where necessary.

1. Objectives

1.1. Objectives of QA/QC programs

Considering the significance of possible future problems regarding acid deposition, it becomes increasingly important to obtain accurate and precise data on acid deposition. With this recognition, many countries of the world have already initiated their acid deposition monitoring programs. However, informed decisions cannot be made on the basis of unreliable data, and therefore certain level of data quality should be assured. A monitoring system without adequate QA/QC runs the risk of not being able to control the quality of data, and not being able to assure accuracy and precision. QA/QC has thus become essential part of all measurement systems in general, and acid deposition monitoring in particular, because it requires especially high international comparability of data.

For uses of acid deposition data in recent years, such as assessment of spatial distributions and temporal trends, research on acid deposition related processes and impacts on aquatic and terrestrial ecosystems, and the development and evaluation of long-range transport and transmission models, it is especially important that measured data satisfy specified levels of reliability with necessary information on measurement methods.

The objectives of this QA/QC programs are to obtain reliable data that can be comparable among the countries of the East Asian region, as well as with other networks by ensuring data accuracy, precision, representativeness and completeness in acid deposition monitoring.

1.2. Definitions

Quality control is defined as "the routine use of procedures designed to achieve and maintain a specified level of quality for a measurement system". Quality Assurance is

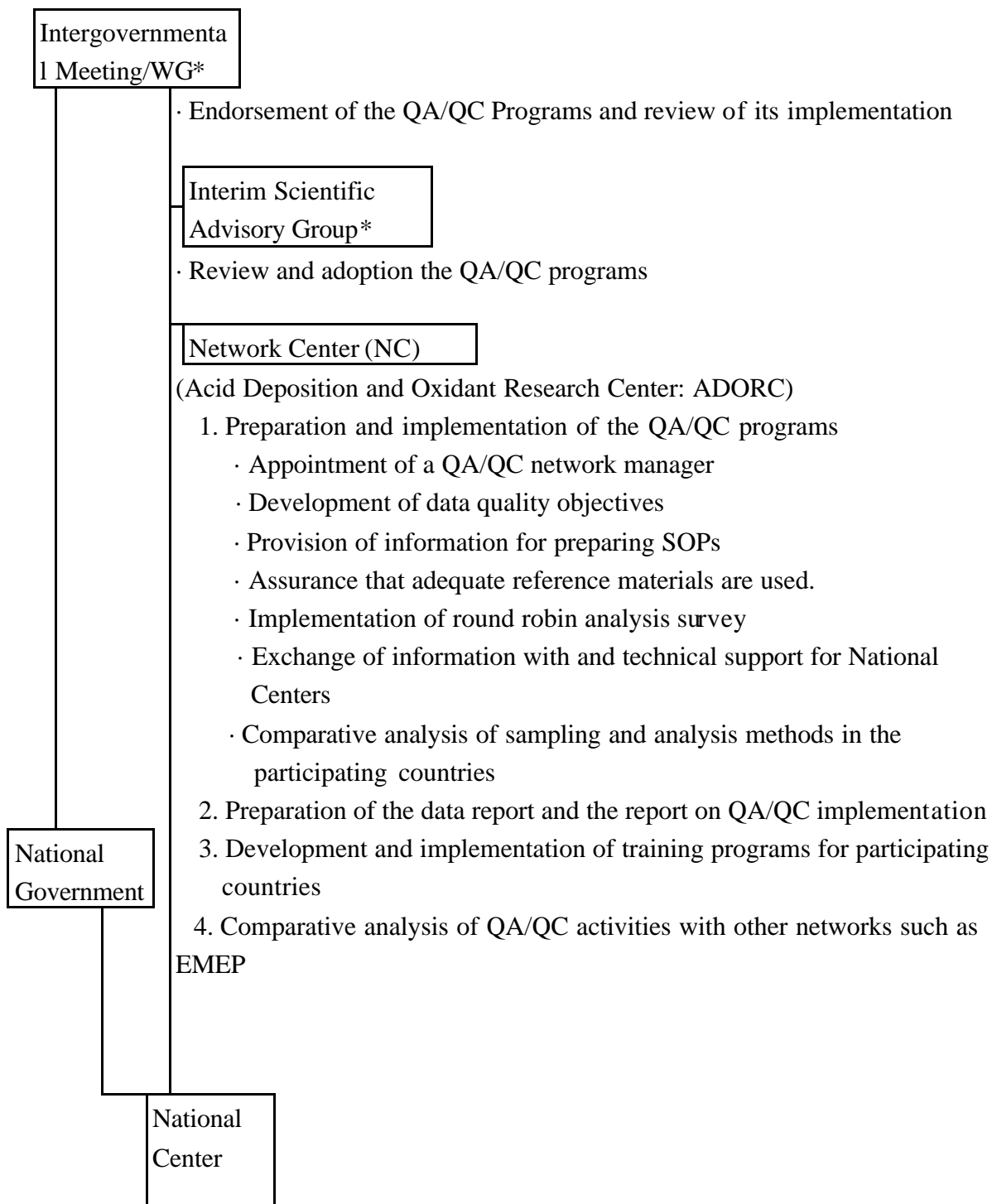
defined as "a set of coordinated actions such as plans, specifications, and policies used to assure that a measurement program can be quantifiable and produce data of known quality".

According to the United States Environmental Protection Agency, the difference between quality control and quality assurance is the following: quality control is a "system of activities to provide a quality product" and quality assurance is a "system of activities to provide assurance that the quality control system is performing adequately. In other words, quality assurance is quality control for quality control".

To assure specific data quality, QC activities should be implemented for all the steps of the measurement activities, from sample collection to data reporting. The QA/QC programs should include QA/QC activities for all the components of the measurement/analysis systems, i.e. the field (sampling sites), laboratory, data management and data reporting processes. All QA/QC activities should be documented.

2. Roles of relevant entities

The roles of relevant entities of QA/QC activities during the preparatory phase are shown in Figure 1.



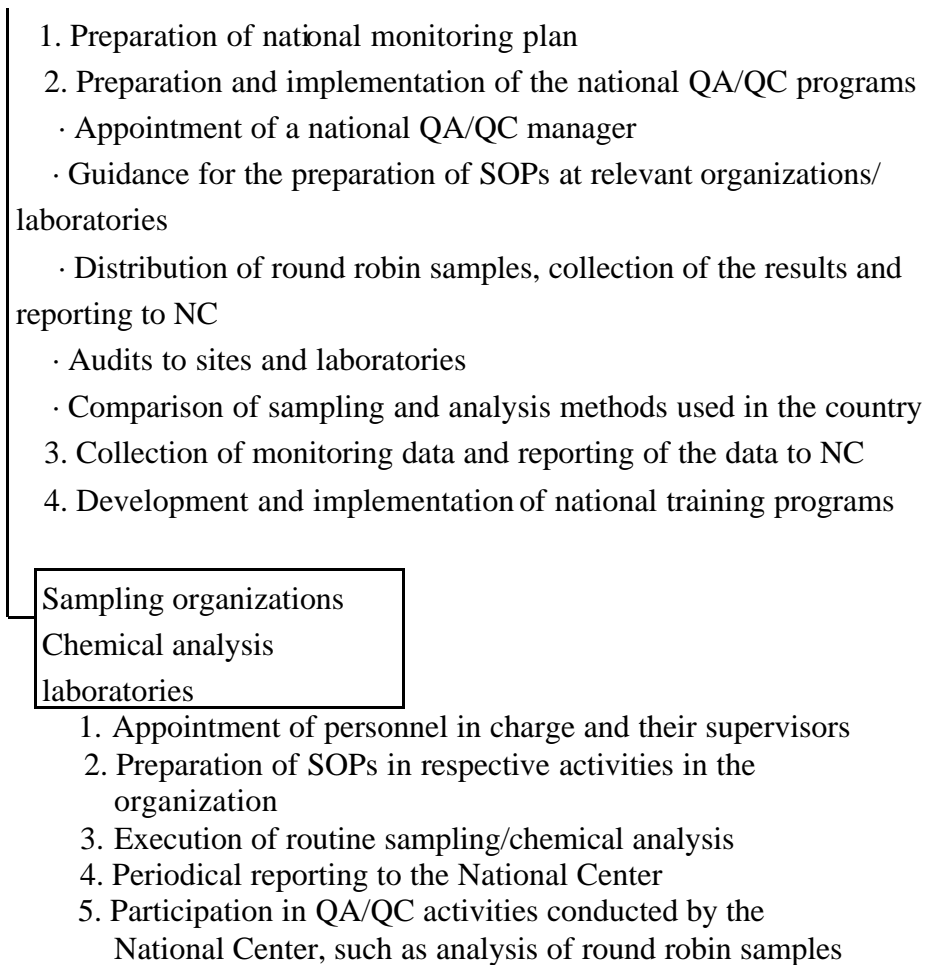


Fig. 1 Roles of relevant entities

Note(*): The name and organization will be changed as appropriate after the formal establishment of EANET.

3. Fundamental matters regarding the QA/QC programs

These QA/QC programs cover all QA/QC activities, including the activities of NC, the National Centers and the sampling/chemical analysis organizations. The National Centers and the sampling/chemical analysis organizations need to execute various QA/QC activities, including development of national QA/QC programs and of SOPs, according to the above mentioned roles (2.1). In these processes, the following fundamental matters should be taken into account.

3.1. Development of national QA/QC programs

Each participating country should develop its own QA/QC programs, taking into consideration the actual national conditions. The items to be covered in the national QA/QC program are listed in Appendix 1.

3.2. Clear assignment of responsibility

In the National Center, a national QA/QC manager should be appointed. In the sampling and/or chemical analysis organizations, personnel in charge of data management and reporting and their supervisors should be appointed; their names should be reported to the National Center.

3.3. Standard operating procedures (SOPs)

SOPs are the procedures used in all the processes of the monitoring system, i.e. in the field, laboratory, and data management areas. Each sampling and chemical analysis organization (laboratory) should make effort to prepare SOPs that meet the actual conditions of respective organizations, taking account of the technical manuals and the national QA/QC programs. SOPs provide a method to ensure that all personnel follow the same procedures to avoid variance of data quality between personnel in charge, and that they conduct their works with good understanding of QA/QC. In preparing SOPs, it is important that they are sufficiently specific and easy to understand, and that they should be reviewed and updated on the basis of latest information and circumstances. Appendix 2 presents major items that should be included in SOPs for the monitoring on inland aquatic environment.

3.4. Data quality objectives(DQOs)

The required data quality objective (DQO) values can be different, depending on the objectives of programs. The DQO values define the desirable levels of accuracy and precision required by the program.

The main objectives of inland aquatic environment monitoring are considered to be the understanding of trends in inland aquatic environment and/or verification of models on water quality. For these objectives, DQO values same as those for wet deposition monitoring may be applied (see Table 1). QA/QC activities mentioned in chapter 4 through 10 are needed to achieve such DQO values. The participating countries are expected to make efforts to meet these DQOs.

Table 1 Data quality objective values in monitoring on inland aquatic environment

a) Required accuracy and precision (unit: %)

Accuracy ¹⁾	Precision ²⁾
±15	15

1) Accuracy is calculated by the following formula:

$$A = [(\text{certified values}) - (\text{analytical values})] \times 100 / (\text{certified values})$$

2) Precision (S_i) is calculated by the following formula:

$$S_i = (Sd_i^2 / 2N_i)^{1/2} \times 100 / Av$$

where d_i and Av denote, the difference between the duplicate analyses and mean, respectively (see Appendix 3 2.3), and N_i is the number of sample pairs in the reporting period.

b) Detection limits and determination limits (both : determined as specified in Appendix 3)

Items	Detection limits		Determination limits	
	$\mu\text{mol L}^{-1}$	mg L^{-1}	$\mu\text{ mol L}^{-1}$	mg L^{-1}
SO_4^{2-}	0.3	0.03	1.0	0.10
NO_3^-	0.5	0.03	1.5	0.10
Cl	0.5	0.02	1.5	0.05
NH_4^+	0.8	0.01	3.0	0.05
Na^+	0.3	0.01	1.0	0.03
K^+	0.3	0.01	1.0	0.04
Ca^{2+}	0.2	0.01	0.6	0.03
Mg^{2+}	0.3	0.01	1.0	0.03
Alkalinity	5			
pH	Replicate measurement of RM should agree to within ± 0.05 pH value of RM.			
EC	Replicate measurement of deionized water (EC: less than 0.15mSm^{-1}) should be agree with $\pm 0.02 \text{mSm}^{-1}$.			

RM: Reference material can be diluted by a laboratory working standard for inland water analysis.

4. Sampling sites

4.1. Sampling sites

Sampling for inland aquatic environment should be done at the same sites with soil and vegetation, in particular in acid deposition vulnerable areas where acid deposition causes or is likely to cause significant adverse effects.

Sampling should be conducted in one of the sites that can be clearly defined in one of the two categories.

4.2. Criteria for site selection

It is recommended that harmonic lakes which are considered to be potentially susceptible to acidification should be selected. If there is no harmonic lake, dystrophic lakes could be selected for monitoring. However, in this case, appropriate monitoring methods should further be investigated. Natural lakes have higher priority for selection of sites than artificial lakes. If appropriate lakes are not available, then springs, headwaters or rivers that are potentially susceptible to acidification and have little artificial influence, should be considered.

It is desirable to choose monitoring lakes which are harmonic type, preferably having a depth of approximately 10m or less, a water retention time of 1 year or less, water area of 1 hector or more, low alkalinity (less than 0.05 meq/L) or electric conductivity, minimal anthropogenic water pollution and no coverage of the surface with aquatic plants.

4.3. Representativeness survey of sampling sites and time

Because the sampling point should be representative in the water bodies, it should be confirmed within half a year from the start of sampling, that the sampling site represents the water quality of the water body, by analyzing relevant items of surface water in several points (more than five sites including the center of the water body). In the case that there are islands at the center of lake, the detailed survey is needed to decide a representative point in the lake. It is desirable that the monthly and hourly variations be investigated to evaluate the representativeness of a sampling site (more than 4 times, in each season) in the preparatory phase. For the time being, on-site measurement of water temperature and electric conductivity can be deemed as a substitute method for these investigations.

4.4. Documentation of conditions of concerned water bodies

The information on characteristics of the water bodies concerned should be periodically reported to the Interim Network Center through the National Center.

4.5. Site performance audit

A site performance audit for inland aquatic environment monitoring network should be made at least once a year by the National Center. This audit provides field training and exchange of information. A site performance audit also should include following matters, such as the sample handling and data reporting and so on. The National Center should prepare the SOP relating the site audit. The results of the audit should be documented and

stored at the National Center.

5. Collection and handling of samples

5.1. Registration of the personnel in charge of collection of samples and their supervisors

Each organization in charge of collecting samples will appoint persons to collect samples and their supervisors. The persons to collect samples should be well trained. The persons who collect samples at each site and their supervisors should be registered to the National Center. The name of the person who collects each sample should be recorded in the on-site record table.

5.2. Sample collection

Surface water should be sampled directly by a clean polyethylene bucket or a dipper at the representative point of the lake. The duplicate samples should be collected at the same point. The water sample should be taken full up in well washed 2 L polyethylene or polypropylene bottle without air after washing by sample water.

5.3. Sampling frequency

According to the guidelines on EANET and the technical manual for monitoring on inland aquatic environment, the monitoring on inland aquatic environment as follows:

a. Items measured more than 4 times a year

1) Mandatory Parameters

- Water Temperature, pH, Electric Conductivity (EC), Alkalinity (at pH 4.8 baseline),
- NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+
- SO_4^{2-} , NO_3^- , Cl^-

2) Optional Parameters

Phytoplankton (Diatom species)

b. Items measured once a year

1) Mandatory Parameters

Transparency, water color, DOC (if impossible, COD), NO_2^- and PO_4^{3-}

2) Optional Parameters

Total Al

c. Items measured once 3-5 years

1) Mandatory Parameters

Sediment (SO_4^{2-} , NO_3^- and NH_4^+ in pore water)

2) Optional Parameters

Living organisms other than phytoplankton

Sediment (Pb, Pb-210 and stable isotope of S)

5.4. Handling and transportation of samples

Transportation of samples from sampling sites to chemical analysis laboratories must be done in cooler boxes filled in freezer packs.

5.5. On-site measurement

Water temperature should be measured on site and should be recorded on the field reporting form. Air temperature, transparency and outward appearance such as color are recommended to be measured on site and should be recorded on the field reporting form. EC and pH are recommended to be measured in the water bath at 25°C in the laboratory. If a temperature controlled water bath is not available, use of water bath without temperature control but containing at least 5 L of water may be considered. However, on-site measurement of pH and electric conductivity are useful as reference data.

6. Measurement and analysis

6.1. Measurement parameters

Measurement parameters are presented on Section 5.3 above.

6.2. Measurement procedures

Electric conductivity and pH of the samples are recommended to be measured in the water bath, which is thermostated at 25°C immediately after arriving to the laboratory. If a temperature controlled water bath is not available, use of water bath without temperature control but containing at least 5 L of water may be considered. And alkalinity should be measured by titration with a 0.01 mol/L or 0.001 mol/L sulfuric acid. The water samples for other chemical analysis should be filtered with a glass fiber filter (Whatman GF/C or Millipore GF filter which pore size is about 1µm with 47 mm diameter, dried at 100±5°C for 2 hours) if not done so on site, and stored in a refrigerator at 4°C. If the measurement and analysis are done more than several days after arrival at the laboratory, the samples should be stored between -20°C to -40°C. All chemical analysis should be finished within 1 week.

6.3. Fundamental measurement and analysis matters

Freedom from contamination of the apparatus, materials and reagents using in measurement and analysis must be confirmed beforehand: blank values of substances should be as low as possible. Measurement and analysis should be executed by persons who are well trained. To maintain high analytical quality, SOPs must be prepared for the management apparatus, materials and reagents.

6.4. Laboratory audit

Laboratory audits should be carried out with sampling site audits or separately by the National Center with similar frequencies. The laboratory audit consists of inspection and advice on sample handling, capacities of instruments, preparation and implementation of

SOPs, and other QA/QC activities and their records. The audit results should be recorded and stored.

Other details on measurement and analyses are mentioned in Appendix 3.

7. Data control

7.1. Introduction

There are three purposes concerning quality assurance of data control.

- 1) Assure that all sample data will be stored in database in an adequate manner.
- 2) Mark with flags the data, whose accuracy and representative are doubted.
- 3) Recognize and describe samples, that were measured without standard methods, i.e. with contamination, instrument trouble, bulk sampling, etc.

Quality assurance and quality control in data control should be carried out in analysis organizations, National Centers, and NC, individually.

7.2. Data check

7.2.1. Treatment of abnormal and unrecorded data

When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the ratio of a theoretical value to that for determined data in ion balances and electric conductivity is significantly different from 1, measurement should be repeated since reliability is low. In addition, when samples seem to be obviously contaminated, these data should be treated as unrecorded data.

These problems will waste much labor, time, and expense. In addition, abnormal or unrecorded data can corrupt research results. So careful checks are needed to avoid data of inadequate quality. When abnormal or unrecorded data appear, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

7.2.2. Judgment of valid data

All measured data should be checked for following R_1 and R_2 values. If necessary, re-measurement should be carried out and the adequacy of data should be checked. If the concentration or standard deviation of concentration of an ion differs greatly from the long term average concentration or standard deviation of concentration, respectively, during a given period, then this cause for concern and should be carefully considered.

a) Calculation of ion balance (R_1)

1) Total anion (A) of equivalent concentration ($\mu\text{eq L}^{-1}$) is calculated by summing the concentration of all anions (c : $\mu\text{eq L}^{-1}$) and alkalinity (ALK: $\mu\text{eq L}^{-1}$). Alkalinity considered to be corresponded to bicarbonate ions (HCO_3^-).

$$A (\mu\text{eq L}^{-1}) = c(\text{SO}_4^{2-}) + c(\text{NO}_3^-) + c(\text{Cl}^-) + (\text{ALK})$$

2) Total cation (C) equivalent concentration ($\mu\text{eq L}^{-1}$) are calculated each concentration of cations (C: $\mu\text{eq L}^{-1}$).

$$C (\mu\text{eq L}^{-1}) = 10^{(6-\text{pH})} + c(\text{NH}_4^+) + c(\text{Na}^+) + c(\text{K}^+) + c(\text{Ca}^{2+}) + c(\text{Mg}^{2+})$$

3) Calculation of ion balance (R_1)

$$R_1 = 100 \times (C-A) / (C+A)$$

4) R_1 , which is calculated using the above equation, should be compared with standard value in Table-2. When R_1 is not in the range, re-measurement, check with standard samples, or inspection of standard curve are necessary, or the flags which indicate unsatisfied data should be marked in the database.

When the concentration(C) of ion is shown as (mg L^{-1}), it should be changed in equivalent concentration($\mu\text{eq L}^{-1}$) as follow:

$$\mu\text{eq L}^{-1} = \text{mg L}^{-1} \times (1000/\text{equivalent weight})$$

thus the total of anions and cations are shown as follows:

$$A(\mu\text{eq L}^{-1}) = \{c(\text{SO}_4^{2-})/48.03 + c(\text{NO}_3^-)/62.01 + c(\text{Cl}^-)/35.45\} \times 1000 + (\text{ALK})$$

$$C(\mu\text{eq L}^{-1}) = 10^{(6-\text{pH})} + \{c(\text{NH}_4^+)/18.04 + c(\text{Na}^+)/22.99 + c(\text{K}^+)/39.10 + c(\text{Ca}^{2+})/20.04 + c(\text{Mg}^{2+})/12.16\} \times 1000$$

Table-2 Allowable ranges for R_1 in different concentration ranges

(C + A) $\mu\text{eq L}^{-1}$	R_1
<50	± 30
50-100	± 15
>100	± 8

The flags should be marked as follows.

999	Missing measurement, reason not specified.
899	Measurement not defined, reason not specified.
783	Low precipitation, concentration unknown.
782	Low precipitation, value is obtained from diluted sample (EANET original flags)
781	Below detection limit.
701	Less accurate than usual, reason not specified .
699	Mechanical problem, reason not specified.
599	Contamination not specified.

b) Comparison between calculations and measurement in electrical conductivity (R_2)

1) Total electric conductivity (Δ_{calc}) should be calculated as follows;

$$\Delta_{\text{calc}} (\mu\text{S cm}^{-1}) = 349.7 \cdot 10^{3-\text{pH}} + \{80.0 \cdot c(\text{SO}_4^{2-}) + 71.5 \cdot c(\text{NO}_3^-) + 76.3 \cdot c(\text{Cl}^-) + 73.5 \cdot c(\text{NH}_4^+) + 50.1 \cdot c(\text{Na}^+) + 73.5 \cdot c(\text{K}^+) + 59.8 \cdot c(\text{Ca}^{2+}) + 53.3 \cdot c(\text{Mg}^{2+}) + 44.5 \cdot (\text{ALK})\} / 1000$$

c: equivalent concentration ($\mu\text{eq L}^{-1}$) of ions in the parenthesis, each constant value is ionic equivalent conductivity at 25°C (see Table-3). Alkalinity considered to be corresponded to bicarbonate ions(HCO_3^-).

For SI unit system, convert $\Delta_{\text{calc}}(\mu\text{S cm}^{-1})$ into $\Delta_{\text{calc}}(\text{mS m}^{-1})$ following

$$\Delta_{\text{calc}}(\text{mS m}^{-1}) = \Delta_{\text{calc}}(\mu\text{S cm}^{-1}) \cdot (1/10)$$

2) Ratio (R_2) of calculations to measurements(Δ_{meas}) in electric conductivity should be calculated as follows;

$$R_2 = 100 \times (\Delta_{\text{calc}} - \Delta_{\text{meas}}) / (\Delta_{\text{calc}} + \Delta_{\text{meas}})$$

3) R_2 , which is calculated using the above equation, should be compared with standard

value in Table-4. When R_2 is not in the range, re-measurement, check with standard samples, or inspection of standard curve are necessary, or the flag which indicate unsatisfied data should be marked in the database.

Table-3 Equivalent weight of cations, anions and ionic equivalent conductivity

Ion	Equivalent Weight	Ionic Equivalent Conductivity λ (S cm ⁻² eq ⁻¹)	Ion	Equivalent Weight	Ionic Equivalent Conductivity λ (S cm ⁻² eq ⁻¹)
H ⁺	1.008	349.7	NO ₃ ⁻	62.01	71.5
NH ₄ ⁺	18.04	73.5	SO ₄ ²⁻	48.03	80.0
Ca ²⁺	20.04	59.8	Cl ⁻	35.45	76.3
K ⁺	39.10	73.5	HCO ₃ ⁻	61.02	44.5
Mg ²⁺	12.16	53.3	HCOO ⁻	45.0	54.6
Na ⁺	22.99	50.1	CH ₃ COO ⁻	59.1	40.9
			F ⁻	19.00	55.5
			Br ⁻	79.90	78.1
			NO ₂ ⁻	46.01	71.8
			PO ₄ ³⁻	26.32	69.0

Kagaku Binran, p.II-460. 3rd Ed., 1984, Maruzen, Tokyo.

Table-4 Allowable ranges for R_2 in different concentration ranges

Λ_{meas} (mS m ⁻¹)	R_2
<0.5	± 20
0.5-3	± 13
>3	± 9

$$(1 \text{ mS m}^{-1} = 10 \text{ } \mu\text{S cm}^{-1})$$

The flags should be marked as follows.

999	Missing measurement, reason not specified..
899	Measurement not defined, reason not specified..
783	Low precipitation, concentration unknown.
782	Low precipitation, value is obtained from diluted sample (EANET original flags)
781	Below detection limit.
701	Less accurate than usual, reason not specified .
699	Mechanical problem, reason not specified..
599	Contamination not specified.
477	Inconsistency between measured and estimated conductivity.

c) Double Measurement

Double measurement should be carried out in the laboratories. Double measurement (duplicate sampling and analysis) of inland water provides a measure of over all monitoring precision. Precision (S_i) is calculated by the following formula:

$$S_i = (\sum d_i^2 / 2N_i)^{1/2} \times 100 / \bar{A}_v$$

where d_i and \bar{A}_v denote, the difference between the duplicate analyses and mean, respectively. When the precision is larger than 15%, it may be recommended to be sampled and analyzed. For details, please see Section 2.2 of the Appendix 3 of this document.

8. Data reporting

Each organization responsible for field sampling and each analytical laboratory should record, control and store the following information.

8.1. Information about sampling sites

Efforts should be made to obtain the following information.

- (1) Information concerning watersheds of sampling lakes
- (2) Information concerning characteristics of lakes
- (3) Information concerning sediment in sampling lakes
- (4) Information concerning living organisms in sampling lakes

8.2. Matters related to collection of samples

The records of on-site information (lake name, sampling point, name in charge, sampling time, air and water temperature, out-looking of sample, transparency, climate, etc.), information about sample collection instruments (pictures of instrument and design diagrams, model name, manufacturer and manufactured date, etc.) if used and/or used tools should be reported to National Center.

8.3. Matters related to analytical procedures

- (1) Calibration and measurement procedures for analytical instruments
- (2) Miscellaneous other values required to obtain measurements

8.4. Local quality control activities

Each organization responsible for the field sampling and each analytical laboratory will record the following information and will store them with the data:

- (1) Performance of all procedures prescribed in SOPs
- (2) Routine instrument check and maintenance, record of instrument adjustment (calibration of instruments)
- (3) Names of producers and traceability of standard materials etc., institution of measurement conditions of analytical instruments and its results
- (4) Results of analysis of lowest detection limits and lowest determination limits

- (5) Results of duplicate analysis
- (6) Evaluation of cation and anion balance and conductivity difference
- (7) Results of site performance audit

9. QA/QC implemented by the (Interim) Network Center

9.1. Management of overall network QA/QC activities and preparation of reports on the network QA/QC activities

NC should prepare draft QA/QC program and will appoint a network manager, who is responsible for managing overall network QA/QC programs and will provide appropriate guidance and advice to the participating countries based on this QA/QC program. NC should prepare reports on the results of round robin analysis, duplicate analysis and parallel analysis, comparison of sampling, and analytical methods etc. and QA/QC levels with other relevant networks.

9.2. Technical support for National Centers

NC should provide technical support, as appropriate, to each National Center in order to attain such objectives as follows:

- (1) NC should review QA/QC activities carried out by each National Center, that the measurements are carried out and reported with the expected precision and accuracy and that all measurements activities are accurately documented and stored.
- (2) NC should, where appropriate, recommend changes that would improve the accuracy, precision, and completeness of the measurements.
- (3) NC should provide useful information in order that the organizations responsible for the field sampling and analytical laboratories in each country can prepare SOPs.

9.3. Round robin analysis

To review the accuracy of chemical analysis, NC should send to all chemical analysis laboratories artificial inland water for inter calibration samples at least once a year through each National Center, evaluate statistically the results of the analysis of the samples and prepare reports about the results.

The results of these inter calibrations should be used to study and find solutions on to existing laboratory problems and improve the quality of laboratory analyses.

9.4. Comparative analysis of sampling methods and chemical analysis methods

NC should compare the precision and accuracy of the field sampling and laboratory measurements, based on parallel precipitation measurement and duplicate sample analysis and grasp the overall precision and accuracy of inland aquatic environment monitoring of the network.

9.5. Assurance that adequate reference materials are used

NC should assure the adequacy of reference materials to be used by the laboratories of the network.

10. Training programs

It is necessary to improve knowledge and expertise related to inland aquatic environment monitoring. Therefore, NC and the others should carry out technical training for personnel responsible for the implementation of the monitoring activities in each National Center and for leading technicians in national or local governments in East Asian countries as follows:

10.1. Training on monitoring guidelines etc.

Based on the results of the 2nd Meeting of the Interim Scientific Advisory Group and the 4th Meeting of the Working Group held in March 2000, training for personnel responsible for implementation of the monitoring activities in each National Center should be carried out to disseminate the details of the Monitoring Guidelines and Technical Manuals, revised QA/QC programs, and Data Reporting Procedures and Formats adopted by these meetings.

10.2. Technical training on monitoring methodologies

In Fiscal 1997, the Japan International Cooperation Agency (JICA) started a training course on "Monitoring and Control Technology of Acid Deposition" in Hyogo Prefecture in Japan for 9 leading technicians from national or local governments in East Asia. From FY 1998, JICA has been carrying out this training course in close collaboration and coordination with the training programs prepared by the NC.

10.3. Training by the National Center in each participating country

The National Center in each participating country should take the lead to prepare a national training program in each year, and implement training on sampling and chemical analysis methodologies. The National Center should also provide guidance for the preparation and implementation of SOPs to national sampling organizations and chemical analysis laboratories.

Appendix 1

Items to be Covered in the National QA/QC Program for Monitoring on Inland Aquatic Environment

1. Objectives
2. Definition and importance of the QA/QC programs
3. Application and roles of relevant entities
 - 3.1. Application
 - 3.2. Roles of relevant entities
4. Fundamental matters in the QA/QC program
 - 4.1. Clear assignment of responsibility
 - 4.2. Preparation of standard operating procedures
 - 4.3. Outline of sampling and chemical analytical methods
 - 4.4. Data quality objectives
5. Sampling sites
 - 5.1. Criteria on selection of sampling sites
 - 5.2. Documentation of site conditions
 - 5.3. Assessment and documentation of representativeness
 - 5.4. Site audit
6. Collection and handling of samples
 - 6.1. Criteria for sampling apparatus
 - 6.2. Operation check of samplers
 - 6.3. Handling and transportation of samples
 - 6.4. On-site inspection
 - 6.5. Simultaneous sampling
7. Measurement and chemical analysis of samples
 - 7.1. Standard materials and standard solutions
 - 7.2. Custody and pre-treatment of samples
 - 7.3. Adjustment of instruments
 - 7.4. Fluctuation of instruments
 - 7.5. Calculation of detection limits and determination limits
 - 7.6. Duplicate and repeated analysis
 - 7.7. Ion balance check
 - 7.8. Comparison of calculated and measured conductivity
8. Data management
 - 8.1. Data check at laboratories
 - 8.2. Treatment of extraordinary data, and data validation
 - 8.3. Assessment of data quality by the National Center
 - 8.4. Assessment of adequacy of sampling sites, and completeness by the National Center
9. Data reporting
 - 9.1. Site information
 - 9.2. Sample collection
 - 9.3. Chemical analysis
 - 9.4. QA/QC activities
10. Training programs

Appendix 2

Major Items to be Included in SOPs in Monitoring on Inland Aquatic Environment

Standard operating procedures(SOPs) should be prepared in accordance with the inland aquatic environment monitoring manual to minimize of precision by person in charge for all elements of operation from sample collection through data reporting. It is important SOPs be complied with in actual operation. Even if the samplers or analytical instruments used are conformed to the monitoring manual, its makers and/or types may be different in each sampling organization or analytical laboratory. Therefore, SOPs should be prepared taking into account the actual condition of each organization laboratory. Individual SOPs should clearly describe scope of application, nomination of responsible supervisor and the person, in charge, and reporting form and so on. In the following table, the necessary items in individual SOPs on wet deposition monitoring are listed, but the additions and/or exclusion are needed according to the actual condition of each laboratory in preparing domestic SOPs.

1. Sampling
 - 1.1. Appointment of sampling staff and their supervisors
 - 1.2. Check of possible changes around the sampling sites
 - 1) Local situation (new construction of emission and contamination sources etc.)
 - 2) On-site situation
 - 1.3. Sampling methods
 - 1) Sampler (involving the documentation of check and maintenance)
 - 2) Sampling interval (sampling dates)
 - 3) Cleaning of vessels with sample water
 - 4) Duplicate sampling
2. Sample transportation and custody
 - 2.1. Transportation of samples
 - 2.2. Sample custody
3. Measurement and chemical analysis
 - 3.1. Appointment of analysis staff and their supervisors for each item
 - 3.2. Development of training plan
 - 3.3. Deionized water
 - 1) Daily maintenance
 - 2) Documentation of maintenance
 - 3.4. Measurement by instruments
 - 1) Measuring conditions of instruments
 - 2) Calibration
 - 3) Performance tests (sensitivity, stability, interference and its removal, documentation of repair)
 - 4) Calculation of lowest detection limits and lowest determination limits
 - 5) Documentation of maintenance
 - 3.5. Operating procedures for measurements
 - 1) Preparation of calibration curves
 - 2) Measurement/analysis of samples
 - 3) Repeated measurements/analyses
 - 4) Check of sensitivity fluctuation

- 3.6. Treatment of measurement results
 - 1) Calculation of concentrations
 - 2) Measurement of sensitivity fluctuation
 - 3) Repeat measurements/analyses
 - 4) Calculation of ion balances
 - 5) Comparison of measured and calculated conductivity
4. Quality assurance and quality control
 - 4.1. Evaluation of sample collection
 - 1) Comparison of precipitation amount with standard rain gauge
 - 2) Evaluation of ion balance
 - 3) Evaluation of conductivities
 - 4.2. Evaluation of reliability
 - 1) Evaluation of sensitivity fluctuations
 - 2) Evaluation of repeated measurements/analyses
 - 3) Evaluation of field blanks
 - 4) Comparison between measured data and lowest detection and lowest determination limits
 - 4.3. Evaluation of results
 - 1) Representativeness of sampling sites
 - 2) Evaluation of sample validity
 - 3) Evaluation of completeness for the sampling period
 - 4) Determination of total precision
4. Management of sampling instruments, laboratory, measurement/analysis instruments and reagent / glass ware
 - 5.1. Management of sampling instruments
 - 1) Appointment of management staff and their supervisors
 - 2) Documentation of names of manufactures, types, manufacture dates and operation methods
 - 3) Daily and regular maintenance and inspection methods (including trouble shooting, parts supply and recording)
 - 5.2. Laboratory management
 - 1) Appointment of management staff and their supervisors
 - 2) Daily and regular maintenance and inspection methods (including items and recording format)
 - 5.3. Management of measurement/analysis instruments
 - 1) Appointment of responsible staff for each instrument, and overall measurement
 - 2) Documentation of names of manufactures, types, manufacture dates and operation methods
 - 3) Daily and regular maintenance and inspection methods (including trouble shooting, parts supply and recording)
 - 5.4. Management of reagents, standard materials, etc.
 - 1) Appointment of management staff and their supervisors
 - 2) Receiving and disposal of reagents(recording format of dates, manufacture names, dealers, purity, degree of standard and valid period)
 - 5.5. Management of glassware and polyethylene vessels
 - 1) Appointment of management staff and their supervisors
 - 2) Cleaning methods
 - 3) Storage

- 4) Confirmation of cleanness

6. External audit
 - 1) Check of sampling sites
 - 2) Measurement of field blank values
 - 3) Operation check of samplers
 - 4) Evaluation of the results of quality control
 - 5) Evaluation of the measured results

Appendix 3

QA/QC on Measurements and Analyses of Samples

1. Measurements and analyses of samples

1.1. Deionized water

Water with a conductivity less than $1.5 \mu\text{S cm}^{-1}$ is acceptable for measurements, analyses and dilution of samples, and cleaning.

1.2. Certified materials and certified samples

The measurements are evaluated by the comparison of measured results of collected samples and certified materials. In order to assure the reliability of measurements, the certified solutions and certified materials that were certified for traceability should be used as much as possible.

For the analytical instruments, there are the US National Institute of Standards and Technology SRM etc. as the Certified Reference Materials (CRMs), certified in concentration. But since they are too expensive for daily use for instruments control, it is convenient to use simulated inland water as the Working Standard in the laboratories.

1.3. Adjustment of analytical instruments

Each of the analytical instruments must be calibrated when they are used, and they should be adjusted as appropriate.

a) pH meter

For the Quality Control, the pH should be measured at $25 \pm 1.0^\circ\text{C}$. The vessel which was filled with certified solution should be soaked in a temperature-controlled water bath; after calibration of the pH meter, tests of reproducibility and linearity are to be carried out to assure reliable measurement. It should be confirmed that the attached thermometer can also be reliable by comparison with a certified thermometer. It should be confirmed that the water bath can control the temperature fluctuation in the water bath to within the allowable range ($\pm 1.0^\circ\text{C}$).

The measurement of pH at the site should be carried out by using a portable electrometric pH meter with glass electrode. Before the determination at the site, the pH meter must be calibrated by using standard solutions for the instrument.

b) Electric conductivity meter (EC meter)

For the Quality Control, the conductivity should be measured at $25 \pm 1.0^\circ\text{C}$. It should be confirmed before the measurement that reliable data can be obtained with the calibration of the EC meter in a temperature-controlled water bath, with tests of reproducibility and linearity. It should also be confirmed that the attached thermometer can be reliable by comparison with a certified thermometer, and it should be confirmed that the constant-temperature water bath can control the temperature fluctuation in the water bath to within the standard ($25 \pm 1.0^\circ\text{C}$).

The measurement of electric conductivity at the site should be carried out by using a portable EC meter. Before the determination at the site, the pH meter must be calibrated by using standard solutions for the instrument. When the electric conductivity is measured at the water temperature of the site, it should be corrected to the value at 25°C . The equation for correcting is as follows.

$$(EC_t) = (EC_{25}) \cdot [1+0.019(t-25)]$$

where, t: water temperature at the site.

c) Ion chromatograph

After setting up the components of working eluent and condition of flux, and regulating the conditions under which target ions can be separated well, it should be then confirmed that the response is stable and the prescribed sensitivity is achieved.

d) Atomic absorption spectrometer

After setting up conditions of the current of midair cathode lamp, the height of the burner, the fluxes of fuel gas and combustion-supporting gas, measuring the wavelength and slit range, it should be confirmed that the response is stable and that the prescribed sensitivity is achieved. If there is a possibility of optical interference, then, must be made to achieve sufficient reliability.

e) Spectrophotometer

Regarding target ions, it should be confirmed that the absorption is stable and the prescribed sensitivity is achieved. If there is a possibility of optical interference, then, must be made to achieve sufficient reliability.

f) Digital burette with pH meter

For the measurement of alkalinity, digital burette with a pH meter should be used where possible. The end point of pH in the titration is 4.8. The pH meter attached to digital burette should be calibrated by same methods as a).

2. Evaluation of reliability

2.1. Analyses of Not Detected and Lowest Determination Limit

In determining the detection and determination limits for the respective methods (Ion chromatography, Spectrophotometry, Atomic absorption spectrometry) used in measuring the concentrations of several ions in wet deposition samples, a standard solution with concentration near the lower determination limit should be measured 5 times.

On methods (Ion chromatography, Spectrophotometry, Atomic absorption spectrometry) used in measuring the concentration of several kinds of ion in inland water samples, the certified solution in lowest concentration (near the Lowest Determination Limit) while making the calibration curve should be measured in 5 times with prescribed operation.

In this case, a standard deviation(s) is calculated as follows: 3 times this value is defined as Not Detected, and 10 times this value is defined as the Lowest Determination Limit (the unit of s is the same as that used for the concentration in water).

$$\text{Not Detected} = 3 s \ (\mu\text{mol L}^{-1})$$

$$\text{Lowest Determination Limit} = 10 s \ (\mu\text{mol L}^{-1})$$

Because the Lowest Determination Limit is different among analytical instruments used and analytical conditions vary, LDL should be determined whenever analytical conditions

are established or changed. It should be confirmed that LDL is below the DQO values described in Table 1 b) of main text 3.4.

2.2. Duplicate sample collection and replicate analysis

To estimate the contribution of sampling and analytical variability, duplicate sampling and replicate analyses of three times for each sample should be performed. It should be confirmed that the obtained relative standard deviation is below the Required Precision shown as Table-1. The standard deviation between the two samples should be calculated, and if the relative standard deviation is larger than 15%, it must be sampled once more and analyzed again.

2.3. Certification of cation and anion balance

The principle of electroneutrality in water requires that the total of anion equivalents is equal to the total of cation equivalents, and the proportion of them is 1.

The ion balance should be calculated following 7.2.2 a). If the required criteria (R1) have not been met, the analysis should be repeated or a flag should be marked in the database indicating that the results did not meet the required criteria.

2.4. Comparison of calculation and measurement conductivity

For dilute solutions (e. g. below 10^{-3} M), the total conductivity (or specific conductivity) can be calculated from the molar concentrations and molar or equivalent ionic conductivity (at infinite dilution) of the individual ions following 7.2.2 b). The obtained R2 should be compared with the criteria. If the required criteria have not been met, the analysis should be repeated or a flag should be marked in the database indicating that the results did not meet the required criteria.