Quality Assurance/Quality Control (QA/QC) Program for Soil and Vegetation Monitoring 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 levels 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 an 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 effects 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 program are to obtain reliable data that can be comparable among the countries of the East Asian region, and with other networks by ensuring data reliability 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 and work schedule in preparatory-phase monitoring

2.1. Roles of relevant entities

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

Intergovernmental Meeting/WG*

· Endorsement of the QA/QC Programs and review of their implementation

(Interim) Scientific Advisory Group*

· Review and adoption the QA/QC programs

(Interim) Network Center (INC)*

(Acid Deposition and Oxidant Research Center: ADORC)*

1 Preparation and implementation of QA/QC programs
- · Appointment of a QA/QC network manager
- · Development of data quality objectives
- · Preparation of information for preparing SOPs
- · Implementation of inter-laboratory comparison survey on soil
- · Assurance that adequate reference materials are used
- · Exchange of information with and technical support for National Centers
- · Comparative analysis of sampling and analytical methods in the participating countries

2 Preparation of the draft data report and the report on QA/QC implementation

3 Development and implementation of training programs for participating countries

4 Comparative analysis of QA/QC activities with other networks such as EMEP

National Government

National Center

1 Preparation of the national monitoring plan

2 Preparation and implementation of the national QA/QC programs

- Appointment of the national QA/QC manager
- Guidance for the preparation of SOPs at relevant organizations/Laboratories
- Distribution of samples for inter-laboratory comparison survey on soil, collection of the results and reporting them to INC
- Audits to sites and laboratories
- Comparison of sampling and analytical methods used in the country

3 Collection of monitoring data and reporting of data to INC

4 Development and implementation of national training programs

Fieldwork organization
Analysis laboratories

1 Appointment of personnel in charge and their supervisors
2 Preparation of SOPs in respective activities in the entity
3 Implementation of routine sampling and chemical analysis
4 Periodic reporting to the National Center
5 Participation in QA/QC activities conducted by the National Center, such as analysis of CRM

Figure -1 Roles of relevant entities

Note (*): The names and organizations 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 INC, 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 SOPs, according to the above mentioned roles (2.1). In these processes, the following fundamental matters should be taken into account.

The QA/QC program for soil and vegetation monitoring should be applied especially for basic survey. For intensive survey and ecosystem analysis survey, modified program will be established in the future, taking account of this program.

3.1. Development of national QA/QC programs

Each participating country should develop its own QA/QC programs, taking into consideration 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 QA/QC national 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. SOPs provide a method to ensure that all personnel perform the same procedures to avoid variance of data quality between personnel in charge, and that they conduct their work with good understanding of QA/QC. 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. In preparation, it is important that SOPs be sufficiently specific and easy to understand, and that they should be reviewed and updated on the basis of latest information and circumstances.

3.4. Fieldwork and physical and chemical analysis

3.4.1. Monitoring sites

Every step described in Section 4 should be recognized, then sites should be chosen. Each site must be kept in its original condition. All information about the sites must be recorded.

3.4.2. Fieldwork in monitoring sites

In soil and vegetation monitoring, fieldwork is especially important. Thus, fieldwork should be carried out and recorded according to the appropriate standard method by staffs who are trained sufficiently.

3.4.3. Sampling

Sampling of soils and plant leaves should be carried out with the standard method.

3.4.4. Analyses of samples

Samples of soils and plant leaves should be analyzed with the standard pretreatment, and then stored by the analysis laboratories.

3.5. Data quality objectives (DQOs) for basic survey

The objectives of basic survey of soil and forest are early detection of possible impact of acid deposition and establishment of good quality database. Decision of DQOs may be a basic step for quality control, and important for establishment of good quality database. The DQOs which are estimated in the following steps, may also be utilized for intensive survey and ecosystem analysis survey.

3.5.1. Estimation of data quality in the multi-stage sampling

In order to decide DQOs, the quality of each process in the monitoring procedure should be evaluated. As the first step, evaluation of each stage of the multi-stage sampling is important. The basic stages in the case of multi-stage soil sampling, as described in the technical manuals, can be described as follows:

(1) Area: in the country, areas for basic survey should be selected. Close to these areas, a deposition monitoring site, which is characterized either as Urban, Rural or Remote, may be established.
(2) Soil type: in each area, two soil types, sensitive and tolerant, will be selected.
(3) Plot: in each soil type that was selected as described above, a few plots should be selected randomly.
(4) Subplot: five subplots should be set in each plot.
(5) Horizon: soil samples should be collected from the uppermost and subsequent soil horizons in each subplot, after removing the litter layer.
(6) Period: soil sampling should be repeated regularly every 3 to 5 years.

Thus, for the evaluation of data quality, the following statistical model (multi-model) can be supposed and the quality of each stage can be estimated.

$$XA = \mu A + \alpha_i + \beta_{ij} + C_{ijk} + D_{ijkl} + \zeta_{ijklm} + \eta_{ijklmn}$$

XA, measured data; μA, total average; α_i, constant related to “Area” in multi-stage sampling ($\Sigma\alpha_i = 0$); β_{ij}, constant related to “Soil type” ($\Sigma\beta_{ij} = 0$); C_{ijk} and D_{ijkl}, variables for “Plot” and “Subplot”, respectively (average = 0; variance, σC^2 and σD^2, respectively). ζ_{ijklm}, constant related to “Horizon” ($\Sigma\zeta_{ijklm} = 0$); η_{ijklmn}, constant related to “Period” ($\Sigma\eta_{ijklmn} = 0$). i, j, k, l, m, and n, number of “Area”, “Soil type”, “Plot”, “Subplot” (= 5 in technical manual of the Network), “Horizon” (= 2 in the manual), and “Period”, respectively. Expected value and degree of freedom in variance of each sampling can be calculated by ANOVA in a branching experimental plan using a statistical variation model.

The above-described statistical analysis should not be applied for vegetation monitoring.

3.5.2. Estimation of analysis data quality

Not only for the evaluation of data quality in multi-stage sampling, but also for evaluation of quality in the whole system of soil and vegetation monitoring including every step of physical and chemical analysis, quality of analysis data should be estimated. For the estimation of the analysis data quality, "Repeatability", "Reproducibility-within-laboratory", and "Reproducibility" should be estimated by collaboration of as many analysis laboratories as possible.

"Repeatability" is defined as data quality in repeatability condition (analyst, time, and instruments are the same). "Reproducibility-within-laboratory" means data quality in within-laboratory-reproducibility condition (some or all persons, time, and instruments are different in for the same sample and laboratory), and "Reproducibility" means data quality in reproducibility condition (laboratory, analysts, time, and instrument are different for the same sample).

In this QA/QC program, the following model is used for measured data XB:

$$XB = \mu B + b + c + e$$

μB, true value; e, deviation in repeatability condition, $V(e)=\sigma r^2$; c, deviation without "e" in within-laboratory-reproducibility condition, $V(c)=\sigma c^2$; b, deviation without "c + e" in reproducibility condition, $V(b)=\sigma b^2$. In the model, variance in within-laboratory-reproducibility condition, σRW^2 can be supposed as follows.

$$\sigma RW^2 = \sigma r^2 + \sigma c^2$$

When averages of n data in within-laboratory-reproducibility condition are compared with each other among laboratories, variance in reproducibility condition,σR^2 can be calculated as follows

$$\sigma R^2 = \sigma b^2 + (\sigma r^2 + \sigma c^2)/n$$

3.5.3. Development of data quality objectives (DQOs)

DQOs depend on monitoring items. As described above, data quality in monitoring depends on statistical deviation in each step of each process from multi-stage sampling to physical and chemical analysis. In the soil and vegetation QA/QC program, using preliminary QA/QC activities, this statistical deviation would be evaluated. Suitable DQOs for soil and vegetation monitoring would be developed, taking account of the progress in monitoring experiences. The method for developing DQOs is described in this QA/QC program.

4. Selection of basic survey site

Soil and vegetation are characterized by area specific factors such as climate, geological and geographical features, etc.; these factors cannot be ignored. Thus, for the evaluation of data in soil and vegetation monitoring, these area specific factors should be reported accordingly. When a QA/QC program is carried out in a latitudinally wide area like East Asia, grasp and management of conditions in which data are taken are the most basic steps.

In order to select sites for permanent monitoring, preliminary surveys should be carried out, conditions of monitoring areas should be clarified, and reproducibility conditions of data should be recorded correctly.

4.1. Preliminary surveys: Preliminary research for selecting permanent monitoring sites

Preliminary surveys should be conducted over extensive areas in order to select sites for continuous monitoring to understand impacts of acid deposition on soil and vegetation.

Preliminary surveys should be carried out as follows, and every necessary item should be described. The geographical range of such surveys should preferably cover the area within a radius of approximately 50 km of acid deposition sampling sites.

4.1.1. Characteristics of basic survey site

The characterization of a basic survey site is described in the monitoring guidelines. Soil and forest monitoring should be carried out in a basic survey site. When some symptoms would be detected in the basic survey site, intensive survey for clarification of the implication with acid deposition should be undertaken.

4.1.2. Collection of soil and vegetation information: Collection and standardization of background information

In preliminary surveys, the following information on geography, soils and vegetation should be collected, fieldwork should be carried out if necessary, monitoring sites should be recorded correctly, and the character of the sites in the country should be clarified. Concerning climatic and meteorological information, the items, which can be obtained in accordance with the procedures of the meteorological monitoring system of each country, could be used. For soil maps and vegetation maps, it is desirable to collect comparable maps with standardized international taxonomy. If such maps are not available, soil profile descriptions and aerial photographs should be used. Soil and vegetation classification should be unified according to the FAO/UNESCO Soil Map of the World (FAO/UNESCO, 1977).

<Information required for preliminary surveys>
- Climatic/Meteorological information (Temperature, Precipitation, Evapotranspiration, Wind direction and speed, Insolation, etc.)
- Soil maps (or a columnar section of representative soil profile and analytical data)
- Vegetation maps (or aerial or satellite photographs that show vegetation)
- Surface geological maps
- Land use maps

4.1.3. Soil preliminary surveys: Description of distribution of soil types sensitive to acid deposition

According to the above information, soils should be classified into high, low, and moderately sensitive types with respect to acid deposition, and the distribution of each soil type should be described. If necessary, fieldwork should be done in order to obtain more detailed distributions of soils for selection of permanent monitoring sites. These results should be described on maps, then the area of distribution of each soils should be described. The standard of sensitivity of soil types is shown in Appendix 3 in the soil and vegetation monitoring manual.

4.1.4. Forest preliminary survey: Description of distribution of forest area

According to the above information concerning vegetation and land-use, distribution of forest area and each forest type should be clarified. This distribution map should be evaluated with respect to soil type, and some forest areas whose soil types are different may be identified.

4.2. Establishment of permanent monitoring sites

Permanent monitoring sites should be selected according to the following points; then “Plots” for soil and forest should be established in the sites.

4.2.1. Site selection criteria

The following criteria should be addressed at the selection of the monitoring site.

(a) Two forest sites, whose soils have different sensitivities to acid deposition, are recommended to be selected.
(b) Each site should be established in a continuous forest area of more than one hectare. If the area is surrounded with a suitable shelter belt, 0.2 hectare is sufficient.
(c) Sites must be accessible for surveying over a long period (decades). Therefore, sites on which land use patterns do not change over this period of observation should be selected.
(d) Preferably, a common tree species or the dominant vegetation type between the sites will be selected.

5. Fieldwork at basic survey sites and handling of samples

5.1. Monitoring items and manner

Monitoring items and manner of soil and forest monitoring for basic survey are as follows.

5.1.1. Soil monitoring

1) Soil profile description (for establishment of monitoring plots): Fieldwork
2) Chemical properties of soils: Soils collected at the site are air-dried in laboratory, and analyzed after sieving.
- pH (H_2O)
- pH (KCl)
- Exchangeable base cations (Ca, Mg, K, and Na)
- Exchangeable acidity
- Exchangeable Al and H*
- Effective cation exchange capacity (ECEC) (sum of exchangeable cations)
- Carbonate content
- Total carbon content (organic carbon content)*
- Total nitrogen content*
- Available phosphate**
- Sulfate**
3) Physical properties of soils:
- Fine earth bulk density*: Collection of soil by metal sampling cylinder
- Penetration resistance*: Fieldwork

“*” and “**”show optional and voluntary items, respectively. Carbonate content is a mandatory item for calcareous soil.

5.1.2. Forest monitoring

1) General description of monitoring forest: Fieldwork
- Description of trees (name of species, diameter at breast height, height of tree)
- Understory vegetation survey

2) Survey of tree decline: Fieldwork
- Observation and evaluation of decline
- Photographic record of tree crown*
- Estimation of decline cause*

"*" shows optional items.

5.1.3. Frequency of monitoring

Soil and forest monitoring should be carried out periodically in every 3 to 5 years.

5.2. Fieldwork and sampling

5.2.1. Registration of the person in charge of fieldwork and sampling and their supervisors

Each organization in charge of soil and vegetation monitoring will appoint supervisors in charge of fieldwork and sampling. Since experience and particular skills are necessary for some monitoring items, the persons in charge of fieldwork and sampling should be well trained. The supervisor and person who carry out fieldwork and sampling at each site 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.

For the fieldwork, a SOP which includes observation, record and sampling at the site should be described for quality control.

5.2.2. Fieldwork for soil monitoring

5.2.2.1. Soil profile description (for establishment of monitoring plots)

For the establishment of plots, the soil profile description should be prepared. The soil profile should be described near the center of the candidate plots before soil sampling. The methods, including practical procedures, survey parameters, and soil classification, should be unified according to FAO-guidelines for soil description (FAO, 1990). A description made according to domestic standard soil survey methods should also be reviewed to ensure the compatibility with the information obtained by other soil survey programs in each country. A large-scale geographical map (e.g. 1:1000) and /or sketch of the area around the plot and a photo of the soil profile with the scale should also be attached to the soil profile descriptions. When the results of soil profile description are similar to the expectation, five subplots should be selected in the plot as described below.

5.2.2.2. Selection of plots and subplots for soil monitoring

Several plots, at least two plots, occupying areas from 5 m x 5 m to 10 m x 10 m, should be selected randomly at each monitoring site. Five subplots for soil sampling, each occupying 1 m x 1 m, are selected in principle at the center and on the diagonal lines of the plot (5 m x 5 m to 10 m x 10 m). Soil samples are collected from these subplots and analyzed.

5.2.2.3. Sampling

In each subplot, after removing the litter layer (O horizon), 1-2 kg soil samples are collected by fixed depth. Two layers, uppermost (0-10cm) and underlying (10-20cm) layers should be collected with shovel or metal sampling cylinder. The sample is collected in equal proportions over the whole layer.

In the center subplot soil samples should be collected beside the hole for soil profile description. For the corner subplots, appropriate size of holes for sampling should be dug, then similar sampling procedures should be employed. From the next sampling, the same procedures should be adopted for the center subplot.

Note:

- Soil whose layers have limited depth may be sensitive to acid deposition. When the soil layers are significantly thin (e.g. less than 5 cm), each horizons should be collected for chemical analysis.
- Preferably, the uppermost layer (0-10cm) will be divided into two sub-layers (0-5cm and 5-10cm) in order to detect small change of chemical properties of the uppermost layer.

5.2.3. Fieldwork for forest monitoring

5.2.3.1. Selection of plots for forest monitoring

In each selected monitoring site, a measuring plot should be subdivided to three coaxial circles with radii of 7.98 m, 11.28 m and 17.85 m (0.02, 0.04, and 0.1 hectare, respectively), and the center and borders should be marked by stakes and color painting of the bark of trees.

5.2.3.2. General description of forest

Flora may change due to various environmental factors. For detection of the possible impact of acid deposition, these changes should be described in detail. For the description of the floral change in the forest area, description of trees and understory vegetation survey should be carried out.

5.2.3.3. Surveys of tree decline

The sample trees are selected systematically. Mark four points of north, south, east and west, 12 m apart from the center of the vegetation monitoring site. Select five dominant trees randomly around each such point. A total of twenty trees are thus selected as the monitoring trees. The serial number of each monitoring tree should be noted as numbering had been done at tree enumeration.

1) Observation

For recording leaf color, preferably the Munsell color chart will be used.
2) Record of tree crown by photographs
The photographs of tree crowns should be taken at the four points. Weather, time and date, kind of film, exposure scale, focal distance of lens, and camera height from the ground level should be recorded and attached to the photographs. Mark the point where the photograph was taken for the continuous monitoring.

For these monitoring items, standardization of evaluation and training of the staff are necessary.

5.2.4. Conservation of permanent monitoring sites

Permanent signs which are made of e.g. stainless steel to identify permanent sites for vegetation monitoring, occupying areas from 0.2 to 10 hectare, should be established. Similar signs for soil monitoring plots also should be maintained. In addition, the previous sampling points should also be marked with permanent signs.

5.2.5. Record of permanent monitoring sites

General description of the monitoring site should be described in Form (Soil & Vegetation B). When the site has particular characteristics that differ from the selection criteria, these characteristics should be recorded.

5.3. On-site inspection

Together with on-site audit, sampling plots and subplots, on-site sample handling and data documentation should be inspected by the National Center. The National Center should prepare a SOP for on-site inspection. The audit results should be recorded and stored.

6. Analysis of samples

6.1. Introduction

Contamination-free apparatus, materials and reagents for use in measurement and analysis should be confirmed beforehand; also the blank values should be as low as possible. The measurements and analyses should be executed by analysts who are well trained. In order to maintain high quality analyses, SOPs must be prepared for management of apparatus, materials and reagents.

6.1.1. Certified materials and certified samples

The measurements are evaluated by 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.
Certified Reference Materials (CRMs) certified in concentration are available for primary calibration of the analytical instruments; CRMs are necessary for progress in the quality of soil analysis.

6.1.2. Pretreatment and storage of samples

The samples should be dried immediately as soon as they arrive in the chemical analysis laboratory, and should be stored. The soil samples for chemical analysis are air-dried and passed through a 2-mm sieve to remove pebbles and plant residue.

6.1.3. Analytical methods

For chemical analysis of soil, many methods are proposed for each property. Results from different methods cannot be compared and evaluated directly. One of objectives of this QA/QC program is standardization of methods. Therefore the methods must be followed strictly. Analytical methods (extraction methods) for mandatory items are described as follows.

1) pH: glass electrodes. Air-dried soils are used and a 2.5- fold amount of deionized water is added.
2) Exchangeable Ca Mg, K, and Na: 1M CH_3COONH_4 (pH=7) extraction.
3) Exchangeable acidity: 1M KCl extraction.
4) Exchangeable Al and H: 1M KCl extraction
5) Effective cation exchangeable capacity (ECEC): Calculation as sum of exchangeable cations.
6) Carbonate content: Volumetric calcimeter

6.1.4. Adjustment of analytical instruments

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

a) pH meter
The pH is recommended to be measured at 25 ^{o}C in a water bath. 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. A vessel filled with certified standard solution should be soaked in a 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 (In form 0 of JIS, it is ±0.2 ^{o}C; in form I ±0.5 ^{o}C). It is necessary to measure the concentrations of a series of hydrochloric acid solutions made with pH values in the range of 4.0~5.0 approximately once a month, and confirm that the measurement results are within a stated range.
b) Ion chromatograph
After setting up the eluent and chromatograph 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.
c) Atomic absorption spectrometer
After setting up conditions of the current of the 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 corrections must be made to achieve sufficient reliability.

6.2. Evaluation of reliability

6.2.1. Sensitivity fluctuation of analytical instruments

While numerous samples are measured, measurement should be continued after confirming that the sensitivity fluctuation is below the prescribed range.

a) pH meter
More than once in every 20 samples, reference materials should be measured 3 times to confirm that their values are within ±0.05. If the sensitivity fluctuates over this range, the reasons should be found and removed; then the reference material should be measured again.
b) Ion chromatograph
More than once in every 20 samples, a reference material should be measured 3 times to confirm that its value is within ±15%. If the sensitivity fluctuates over this range, the reasons should be found and removed; then the reference material should be measured again.
If the retention time changes slowly while the separator column is deteriorating, then adequate actions could be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.
c) Atomic absorption spectrometer
More than once in every 20 samples, a reference material should be measured 3 times to confirm that its values are within ±15%. If the sensitivity fluctuates over this range, the reasons should be found and removed then the reference material should be measured again.

6.2.2. 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. 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 rainwater).

$$\text{Not detected} = 3\,s \quad (\mu\text{mol L}^{-1})$$
$$\text{Lowest determination limit} = 10\,s \; (\mu\text{mol L}^{-1})$$

Because the "lowest determination limit" is different among analytical instruments that we are using and analytical conditions vary, LDL should be determined whenever analytical conditions are established or changed.

6.3. Estimation of analytical quality

"Repeatability", "Reproducibility-within-laboratory" and "Reproducibility" should be estimated by collaboration of as many analysis laboratories as possible. In order to estimate these qualities at the same time, the collaboration should be done using a "Staggered type nested experiment" or "Completely repeated nested experiment", both of which are described in Appendix II of the technical manual.

The experimental design of the "Staggered type nested experiment" is shown in Figure 6.3 a). X_{i1}, X_{i2}, X_{i3} are data of laboratory "i". X_{i1} and X_{i2} are repeated in repeatability condition, X_{i3} is at within-laboratory-reproducibility condition to X_{i1} and X_{i2}. For example, "at the first day X_{i1} and X_{i2} are measured and the second day X_{i3} is measured". The design of

"Completely repeated nested experiment" is shown in Figure 6.3 b). Xijk is data "k" of laboratory "i" on day "j". Data repeated on a day is treated as repeatability condition. Data from different days ("j" is different) is treated as within-laboratory-reproducibility condition.

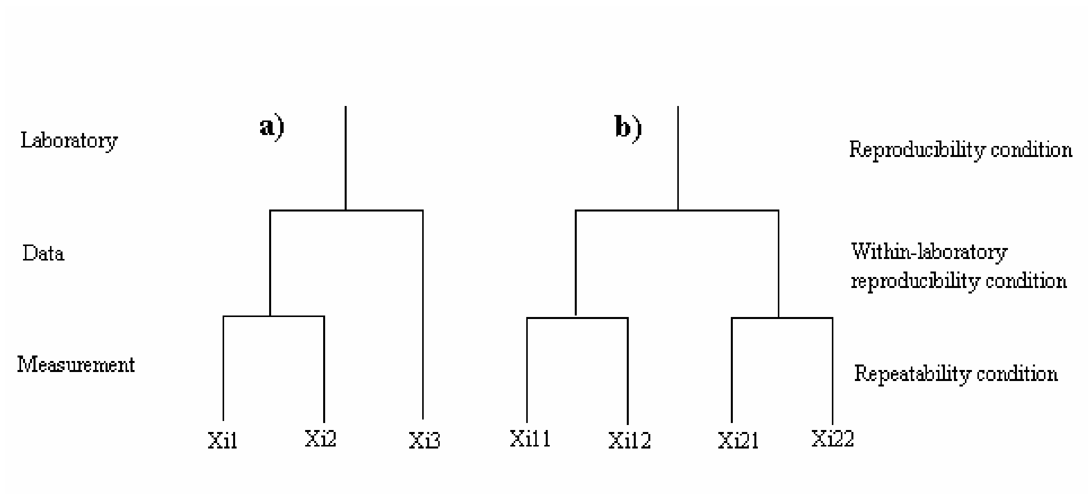

Figure 6.3. Schematic of a) Staggered type nested experiment and b) Completely repeated nested experiment.

6.3.1. Duplicate analysis

In order to evaluate variation in analysis data, analysis of an appropriate number of samples should be repeated under the same conditions (analyst, time, and instrument are the same).

The remaining samples should be stored.

6.3.2. Estimation of "Reproducibility-within-laboratory"

In order to evaluate within-laboratory-reproducibility condition, for all samples, analysis should be repeated with the condition that some or all of analyst, time, and instrument are different. Then, the data should be compared.

6.3.3. Evaluation of "Reproducibility"

In order to evaluate reproducibility condition, certain sample analysis should be repeated with the condition that all of laboratory, analyst, time, and instrument are different. Then, the data should be compared. Evaluation of "Reproducibility" should be done in the National Center.

6.4. Laboratory audit

Laboratory audits should be carried out together 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.

7. Data control

7.1. Introduction

There are three purposes of quality assurance of data control.

1) Assure that all sample data will be stored in databases in an adequate manner.
2) Mark with flags the data whose accuracy and representativeness 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 the Interim Network Center, individually.

7.2. Data check in analysis organizations

When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurement are significantly different, or when the ratio of a theoretical value to that for determined data in ion balances and electrical conductivity is far 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. When certified reference materials (CRMs) are analyzed more than twice in within-laboratory-reproducibility condition, average of each laboratory and homogeneity of reproducibility within-laboratory can be checked using Grubbs' method and Cochran's method, respectively. Critical limited values which are taken from these methods can be show information about abnormal data.

These problems will consume 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 problems in the future.

7.3. Evaluation of sampling sites

The process for selection of the monitoring sites should be evaluated according to 4.1 and 4.2.

7.4. Evaluation of data

When analytical data of soils and plant leaves are particularly different from the average (standard value) in a certain area or the previous data at the same site, data should be described with flag. Flag shows ratio of data to standard value with initial letter of the value. When the average are used, the origin of value should be described, e.g. three times of the previous data, P3; ten times of the average value, S10 (Chemical Dictionary) and so on.

8. Data reporting

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

8.1. Information about sites

Effort should be made to obtain the following information:

(1) Sampling sites (location, site classification, measurement items, etc.)
(2) Geographical, Soil, and Vegetation maps (name of maps, scale, sites on maps)
(3) Situations around the site at the on-site scale (within 150 m of the site; buildings, trees, parking lots, roads, circumstance and land use around the sampling site, etc.)
(4) Situations around the site on a local scale (from 150 m to 10 km from the site; major roads, traffic, aviation, navigation, farming, major stationary emission sources, surrounding cities, population, etc.)
(5) Situations around the site on a regional scale (from 10 to 50 km from the site; large stationary emission sources, main roads, cities, population, etc.)

Note: In the report of (3) or (4), two monitoring forests, which have soil type sensitive to acid deposition and insensitive soil type, should be clarified. Reporting formats for (3), (4) and (5) are the same as the formats for wet deposition.

8.2. Matters related to fieldwork

(1) Instruments used for fieldwork (pictures of instrument and design diagrams, model name, manufacturer, manufactured date, etc.)
(2) Conditions of fieldwork (detailed information about sampling site, sampling date, temperature, wind direction, wind speed, etc.)
(3) Method of Fieldwork (photographic record, etc.)

8.3. Matters related to sampling

(1) Sample collection instruments(pictures of instrument and design diagrams, model name, manufacturer and manufactured date, etc.)
(2) Conditions of each sample collection(detailed information about sampling site, sampling date, temperature, wind direction, wind speed etc.)
(3) Sample history(shipping frequency, packing procedures, etc.)

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 checking and maintenance, record of instrument adjustment (calibration of instruments)
(3) Names of producers and traceability of standard materials, measurement conditions of analytical instruments, etc.
(4) Results of analysis of lowest detectable limits and lowest determination limits
(5) Sensitivity variability of analytical instruments
(6) Duplicate analysis

(7) Evaluation of cation and anion balances and conductivity difference
(8) Results of site performance audit

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

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

INC should 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. INC 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

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

(1) INC should review QA/QC activities carried out by each National Center, to confirm 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) INC should, where appropriate, recommend changes that would improve the accuracy, precision, and completeness of the measurements.
(3) INC 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. Comparative analysis of sampling and chemical analysis methods

Quality of sampling and analytical methods in each country should be compared by collaboration of analysis laboratories. This exercise would reveal total data quality of the network.

9.3.1. Estimation of data quality in multi-stage sampling

Estimation of data quality in multi-stage sampling should be carried out according to the model in 3.5.1.

9.3.2. Estimation of analytical quality

“Repeatability”, “Reproducibility-within-laboratory” and “Reproducibility” should be estimated by collaboration of analysis laboratories as many as possible.

9.3.3. Assessment of analysis quality

In order to assess the reliability of certain analytical methods, standard materials, whose true properties are known or certified, should be analyzed in collaboration with as many laboratories as possible. INC provides standard soil samples and plant leaf samples to every laboratory through the National Centers, statistically analyzes the results, and then reports. These comparable results can be used for recognition of problems in the laboratories, finding the solution of them, and progress of quality.

9.4. Comparative analysis of the precision and accuracy between this Network and other networks

Based on item 9.3, INC should assess and compare the measurement methodology and quality assurance data of this network with other relevant international and domestic networks, and submit reports to the Interim Scientific Advisory Group.

9.5. Assurance that adequate reference materials are used

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

10. Training programs

In soil and vegetation monitoring, particular information and skills are necessary for most procedures. Therefore, INC and/or the other relevant organizations should carry out training for personnel responsible for the implementation of the monitoring activities in each country and technical training for leading technicians in national or local governments in East Asian countries. Especially for fieldwork items such as soil profile description and survey of tree decline, training of the staff is necessary, and the detailed program should be planned.

10.1. Technical training on monitoring methodologies

In Fiscal 1997, the Japan International Cooperation Agency (JICA) started a training course “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 FY1998, JICA has been carrying out this training course in close collaboration and coordination with training programs prepared by INC.

10.2. Training by the National Center in each participating country

The National Center should provide guidance for the preparation of SOPs to national sampling organizations and chemical analysis laboratories.

Appendix 1

Items to be covered in the national QA/QC program

1. Objectives

2. Application, roles of relevant entities and tentative work schedule
2.1. Roles of relevant entities
2.2. Tentative work schedule
2.2.1. National Centers
2.2.2. Fieldwork and Analysis Organizations

3. Fundamental matters regarding the QA/QC programs
3.1. Development of national QA/QC programs
3.2. Clear assignment of the responsibility
3.3. Standard operating procedures
3.4. Fieldwork and physical and chemical analysis
3.5. Data quality objectives

4. Site selection and record
4.1. Preliminary surveys
4.2. Establishment of permanent monitoring sites
4.3. Conservation of permanent monitoring sites
4.4. Record of permanent monitoring sites
4.5. Audit of permanent monitoring sites

5. Fieldwork at monitoring sites and handling of samples
5.1. Monitoring items and manner
5.2. Fieldwork and sampling
5.3. On-site inspection

6. Analysis of samples
6.1. Introduction
6.2. Reliability assessment of measurements
6.3. Estimation of analytical quality
6.4. Audit in laboratories

7. Data control
7.1. Introduction
7.2. Data check in analysis organizations
7.3. Evaluation of sampling sites
7.4. Evaluation of data

8. Data reporting
8.1. Information about sites
8.2. Matters related to fieldwork
8.3. Matters related to samplings
8.4. Reporting related to quality control

9. Training programs