Guidelines for Acid Deposition Monitoring in East Asia

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of

Acid Deposition Monitoring Network in East Asia

Table of contents

1. Introduction	1
2. Basic matters on acid deposition monitoring	2
2.1. Objectives	
2.2. Selection of monitoring sites	
2.2.1. Classification of monitoring sites	
2.2.1.1. Deposition monitoring sites	
2.2.1.2. Ecological survey sites	
2.2.2. Site selection criteria.	4
2.2.2.1. General	
2.2.2.2. Minimum distance of deposition monitoring sites from large	
emission sources	5
3. Wet deposition monitoring	5
3.1. Monitoring sites	
3.2. Monitoring frequency	
3.3. Measurement parameters	
3.4. Monitoring procedures	
3.4.1. Sampling and on-site measurements	
3.4.2. Storage and transportation of samples	
3.4.3. Analysis at analytical laboratories	
3.5. Analytical procedures	7
4. Dry deposition monitoring	9
4.1. Monitoring sites	
4.2. Monitoring frequency	
4.3. Monitoring parameters	
4.4. Monitoring methods	
····· ································	
5. Soil and vegetation monitoring	
5.1. Monitoring sites	
5.2. Monitoring parameters and frequency	
5.3. Monitoring procedures	
5.3.1. Selection of monitoring sites	
5.3.1.1. Preliminary surveys	
5.3.1.2. Establishment of permanent monitoring sites	
5.3.2. Basic survey	
5.3.2.1. Soil monitoring.	
5.3.2.2. Forest monitoring	
5.3.2.3. Intensive monitoring	
5.3.3. Terrestrial ecosystem analysis	
5.4. Analytical procedures	18

6. Monitoring on inland aquatic environment	19
6.1. Monitoring sites	19
6.2. Monitoring parameters and frequency	
6.2.1. Lakes	
6.2.2. Springs, headwaters and rivers	
6.3. Monitoring procedures	
6.3.1. Collection of information concerning monitoring sites	
6.3.2. Sample collection	
6.3.3. On-site measurement	
6.3.4. Handling and transportation of samples	
6.4. Analytical procedures	
7. Quality assurance/quality control	25
8. Data reporting	25

1. Introduction

Acid deposition is not just a domestic concern; it is also a regional environmental problem that transcends national boundaries. As emphasized in Chapter 9 of Agenda 21 (on transboundary atmospheric pollution), adopted at the 1992 United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro, acid deposition is a problem that requires international cooperative efforts for its solution.

East Asia is receiving considerable international attention. The East Asian region contains approximately 20 percent of the Earth's landmass and more than 30 percent of the world's population. It has shown rapid economic growth, except the last few years due to Asian economic crisis. The economic growth rates of many countries in East Asia are expected to recover soon. Despite the Asian economic crisis, energy consumption has been increasing in many countries. As a result, East Asia already accounts for one-third of total air pollutants released worldwide, and the region's overall rate of increase would be higher than that of other regions in the world. If current trends continue, there is great cause for concern that adverse effects from air pollution and acid deposition will develop over large areas of the region.

So far, there have been only a few reports of extensive damage due to acid deposition in the region. However, damage attributable to acid deposition, including deforestation and degradation of buildings, has been pointed out in some countries. The region is increasingly facing threats from acid deposition, and it is becoming essential to undertake measures to tackle these threats, both in the respective countries of the region and through regional cooperation.

Having the participation from ten countries in the region, (i.e. China, Indonesia, Japan, Republic of Korea, Malaysia, Mongolia, Philippines, Russia, Singapore and Thailand), the First Expert Meeting on Acid Precipitation Monitoring Network in East Asia was held in October 1993. The Meeting recognized that a regional acid precipitation monitoring network was needed.

Based on the results of the First Expert Meeting, the guidelines have been adopted at the Second Expert Meeting on Acid Precipitation Monitoring Network in East Asia, which was held in March 1995 in Tokyo.

From April 1998, the preparatory-phase activities of the Acid Deposition Monitoring Network in East Asia (EANET) started, based on the decision of the Intergovernmental Meeting on EANET, held in March 1998 in Yokohama, Japan. Ten countries in East Asia, namely, China, Indonesia, Japan, Malaysia, Mongolia, the Philippines, Republic of Korea, Russia, Thailand and Viet Nam, participated in the preparatory-phase activities. During the preparatory-phase, the participating countries made effort to comply with these guidelines to the extent possible. Based on the experience gained, and the latest scientific/technical information, the guidelines were revised and adopted at the Second Interim Scientific Advisory Group (ISAG) Meeting of EANET held in March 2000 in Jakarta, Indonesia.

Documents titled the Quality Assurance/Quality Control Programs for EANET Activities, and the Data Reporting Procedures and Formats should be regarded as the integral parts of these guidelines. Three technical manuals for wet deposition monitoring, soil and vegetation monitoring, and monitoring on inland aquatic environment have been prepared to supplement these guidelines.

It should be noted that these guidelines and technical manuals need to be flexibly applied, taking account of diversities in different sub-regions in East Asia.

These guidelines will be reviewed and updated in a timely and appropriate fashion, in keeping with advances in scientific/technical information. It is desirable that the countries in East Asia endeavor to improve monitoring systems for acid deposition by making effective use of these guidelines.

2. Basic matters on acid deposition monitoring

2.1. Objectives

The objectives of the Acid Deposition Monitoring Network are:

- (1) to create a common understanding of the state of the acid deposition problems in East Asia; and
- (2) to provide useful inputs for decision-making at local, national and regional levels aimed at preventing or reducing adverse impacts on human health and the environment due to acid deposition.
- 2.2. Selection of monitoring sites
- 2.2.1. Classification of monitoring sites

EANET monitoring sites are classified into two basic categories, namely deposition monitoring sites and ecological survey sites. Deposition monitoring sites are sampling sites to collect fundamental data on the temporal and spatial distribution of acid deposition, and are further classified into three sub-categories: remote sites, rural sites, and urban sites for the objectives of the monitoring. Ecological survey sites are those to provide basic data for assessing the effects of acidification on terrestrial ecosystems, and further classified into two sub-categories: basic survey sites, and ecosystem analysis sites. All sites in each country should be classified according to these categories. Regarding the deposition monitoring sites, at least one or more remote or rural sites should be established in a country participating in the EANET activities.

2.2.1.1. Deposition monitoring sites

Deposition monitoring sites in this network should be classified into three sub-categories:

remote sites, rural sites and urban sites according to the objectives of the monitoring. Wet deposition monitoring, and desirably dry deposition monitoring as well, should be carried out at these sites.

(a) Remote sites

Remote sites are to be established for the assessment of the state of acid deposition in background areas. The monitoring data can be used to evaluate long-range transport and transmission models of acidic substances in East Asia.

The location of these sites should be selected in areas with no or least influence from local emission and contamination sources. Therefore, remote sites should be located with sufficient distance from significant stationary sources such as urban areas, thermal power plants, large factories, and significant mobile sources such as major highways, ports, and railways, to minimize these influences. It is desirable for remote sites to be located at existing meteorological stations, in particular, upper wind monitoring stations, or in their vicinity.

(b) Rural sites

Rural sites are to be established for the assessment of the state of acid deposition in rural areas or hinterlands. The monitoring data can be used, for instance, to evaluate the effects of acid deposition on agricultural crops and forests.

The location of these sites should be selected in areas with minor influence from local emission and contamination sources. Therefore, rural sites should be sited away from significant stationary and mobile sources, and should be free from these influences to the extent possible.

Some rural sites which generally satisfy the criteria for remote sites may also be used to evaluate long-range transport and deposition models of acidic substances.

(c) Urban sites

Urban sites are to be established for the assessment of the state of acid deposition in urban areas. Urban and industrialized areas, and the areas immediately outside such areas, can be included. The monitoring data can be used, for instance, to evaluate the effects of acid deposition on buildings and historical monuments. Monitoring data at these sites may also be useful for the assessment of acidity of precipitation and the trends in urban areas.

2.2.1.2. Ecological survey sites

Ecological survey sites should be classified into two sub-categories: basic survey sites and ecosystem analysis sites, according to the objectives of the monitoring. Soil and vegetation monitoring, and monitoring in inland aquatic environment should be carried out at these sites.

(a) Basic survey sites

Basic survey sites are to be established at the deposition monitoring sites or in their vicinity in order to accumulate basic data on soil, forests and inland aquatic environment, and trends in properties. At these sites, chemical and physical analysis of soil, description of trees, surveys of understory vegetation and forest decline, and monitoring on inland aquatic environment should be carried out.

If forest decline or other changes in ecosystems are detected at basic survey sites, more intensive survey on soil and vegetation should be undertaken to assess the implication with deposition through application of intensive surveys such as stemflow and throughfall surveys.

(b) Ecosystem analysis sites

Ecosystem analysis sites are to be established for the assessment of acid deposition impacts on whole ecosystems through application of, for instance, terrestrial ecosystem analysis and/or catchment analysis. The location of these sites should be selected in areas where terrestrial ecosystems are sensitive to changes in atmospheric acidity. Some of these sites should also be located in ecologically conserved areas. At these sites, elemental dynamics in ecosystems should be surveyed, and environmental sensitivity to acid deposition should be estimated. Acidification models may also be developed for these sites.

2.2.2. Site selection criteria

2.2.2.1. General

Selection of sites is critical. Monitoring sites should be located in areas suitable to the objectives of the monitoring, should be free from the influence of nearby emission sources, and should properly represent the area in question. Sites should be selected in areas where monitoring can be continued over a long period, and where land use in the vicinity is likely to remain in almost the same condition for decades. The adequacy of sites should be reviewed periodically by assessing representativeness and completeness of monitoring.

It is desirable that sites be located at existing meteorological monitoring stations, or in their vicinity. The proper location of sampling equipment is also important in order to ensure that the samples represent the area in question

In selecting a deposition monitoring site, topographic features and land use types around the site, and meteorological conditions such as annual precipitation amounts and prevailing wind directions, should be adequately considered, on the basis of existing data. A deposition monitoring site should not be located in areas dominated by local meteorological conditions, such as mountaintops, cols, coastal sites which receive local wind effects, and valleys and basins which are subject to the formation of stagnant air. In selecting a deposition monitoring site, consideration must be given to the emission sources surrounding the proposed site. The guidelines of the Cooperative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP) recommend that when the major part of the emissions influencing the air quality in an area are located outside that area, selection of the site involves mainly considerations of the effects of the immediate surroundings and emissions within the nearest 20 km.

In general, a deposition monitoring site should not be located in areas dominated by local emission and contamination sources. Coastal areas may be influenced by sea spray. Volcanic areas and hot spring resorts may receive influence by geothermal emissions such as SO_2 , HCl and H₂S, gravel roads, farmyards and tilled agricultural fields by windblown soil dust, and grazing land and pasture by ammonia. In particular, ammonia is a special problem since the emissions are mainly linked with animal husbandry and agricultural activities. In selecting a deposition monitoring site, due consideration should be given to minimize such influences, and detailed information around the site and on possible influences by these sources should be recorded and reported as appropriate.

- 2.2.2.2 Minimum distance of deposition monitoring sites from large emission sources
- (a) Remote sites should not be located in areas within 50 km of large pollution sources such as cities, thermal power plants, and major highways.
- (b) Rural sites should not be located in areas within 20 km of large pollution sources.
- (c) Remote and rural sites should not be located in areas within 500 m from heavy traffic roads (more than 500 vehicles/day).

These were based on guidelines from European and North American monitoring programs with a mind to East Asian conditions. The distances given in this manual should be taken only as indicative. An appraisal of local emission influences on air and precipitation chemistry must be made on the basis of considerations of meteorological and topographic conditions at the site.

3. Wet deposition monitoring

Fundamental items of wet deposition monitoring are described below. In order to supplement these items, the technical manual for monitoring wet deposition has been developed for those who carry out wet deposition monitoring.

3.1. Monitoring sites

Monitoring sites should be selected in accordance with the criteria for deposition monitoring sites mentioned in Chapter 2.

3.2. Monitoring frequency

Samples should be collected every 24 hours in principle. Samples can be collected for each precipitation event, but this is operationally inconvenient and is not recommended.

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

3.3. Measurement parameters

(a) Precipitation chemistry parameters

pH, electric conductivity(EC) and concentrations of ionic species ($SO_4^{2^-}$, NO_3^- , CI^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) should be measured as required parameters.

In the case when ion balance is recognized not to be systematically attained by measuring the major ions described above, some additional ions relevant to the ion balance, such as fluoride, bicarbonate, nitrite and organic acids, are recommended to be identified and measured, as appropriate. Heavy metals, phosphate, aluminum and organic compounds may be measured for the characterization of precipitation.

(b) Meteorological measurement

Wind direction/speed, temperature, humidity, precipitation amount and solar radiation in relation to wet deposition should be measured on site or at the nearest meteorological station in accordance with the measurement frequencies and methods of the meteorological monitoring system in each country.

3.4. Monitoring procedures

Procedures for wet deposition monitoring are presented in Figure 3.1, and briefly described below.

3.4.1. Sampling and on-site measurements

An automatic wet deposition collector, a standard rain/snow gauge, and other meteorological instruments for measurement of temperature, wind direction and wind speed etc. are required as field measuring instruments.

Wet deposition samples should be "wet-only" samples. The most appropriate automatic collector is a wet-only collector. A wet/dry collector that is composed of two collection buckets, one for collection of precipitation during the wet period and the other for collection of dry fallout during the dry period, is also acceptable.

Precipitation amount should be measured and/or recorded at the sampling site with a standard precipitation gauge or its equivalent in each country. Standard precipitation gauges generally measure precipitation amount more efficiently and accurately than wet deposition collectors, and therefore, they should be operated in parallel with the collector.

Collection vessels (buckets, funnel, and bottles) should be cleaned at each field site before sampling. The collection vessel should be capped (and/or bagged) and removed from the collector. Operators should be wearing disposable plastic gloves whenever handling the collection vessel.

In addition to the on-site measurements by standard rain gauge depth (precipitation amount), it is recommended to measure sample volume gravimetrically before transport to the laboratory, particularly when the rain gauge is not available. Field blank should be evaluated monthly. After conductivity and pH measurement, all samples should be filtered with clean membrane filters (pore size:0.45m). All precipitation samples collected at a site should be identified with the information on the sample label and data form.

3.4.2. Storage and transportation of samples

Refrigeration should be done after measurement of sample volume, if a biocide is not in use. Samples should be refrigerated at 4°C before shipment to the analytical laboratory. In principle, the samples should be transported to the analytical laboratory weekly or biweekly.

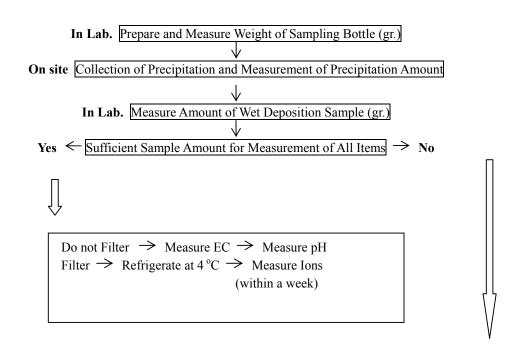
The samples must be kept chemically stable. The most common methods of achieving this are (a) minimizing the transportation time (e.g. by using overnight transportation services) and (b) cooling the samples during transportation (e.g. by using insulated containers with freezer packs).

3.4.3. Analysis at analytical laboratories

Analytical laboratories for precipitation chemistry should be equipped adequately to generate and to report analytical data of the highest quality. Samples arriving at laboratory should be kept in refrigerator and used for analysis as soon as possible.

3.5. Analytical procedures

Procedures suggested for rainwater analysis are specified in the table below. The analytical methods detailed in the table are typical for precipitation samples analyzed on

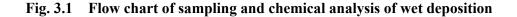


(a) After EC and pH measurement, Sample Volume is not Sufficient for Ion Measurement

Do not Filter \rightarrow Measure EC \rightarrow Measure pH Filter \rightarrow Refrigerate at 4 °C \rightarrow Dilute 2-10 Times \rightarrow Measure Ions

(b) Not Sufficient Volume for EC, pH and Ion Measurement

Filter \rightarrow Refrigerate at 4 °C \rightarrow Dilute 2-10 Times \rightarrow Measure Ions The Order of Measurement Priority (1) SO₄²⁻, NO₃ and Cl⁻ by IC (2) NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺ by IC, when a cation column is available (2) If not, NH₄⁺ by spectrophotometry (3) Na⁺, K⁺, Ca²⁺ and Mg²⁺ by AA (4) EC and pH



instrumentation commonly available in many laboratories at the time of writing, and not exhaustive. These methods will require modification and revision if new or different analytical systems are employed, or if sample composition is unusual.

Analysis	Instrumental Method
Electric Conductivity (EC)	Conductivity Cell
	Glass electrode (preferably with the
pН	Electrode of non-leak inner cell)
Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , NO ₂ ⁻ , F ⁻ , PO ₄ ³⁻	Ion Chromatography
NO_2^-, F^-, PO_4^{3-}	(preferably with suppressor)
	Spectrophotometry
NH4 ⁺	Ion Chromatography
	Spectrophotometry (Indophenol blue)*
$Na^+, K^+, Ca^{2+}, Mg^{2+}$	Ion Chromatography
	Atomic Absorption/ Emission Spectrometry
Heavy Metals, Al	Atomic Absorption Spectrometry with
	Graphite Furnace, ICP Emission
Hg	Spectrometry, ICP/MS, Mercury Analyzer
-	With a Gold Trap
Organic Acids	Ion Chromatography
-	

Table 3.1. Procedures suggested for rainwater major constituent analysis

* Not recommended if the biocide, thymol, is used in sample collection.

4. Dry deposition monitoring

To monitor dry deposition, one must either measure the dry deposition directly or measure air concentrations and calculate dry deposition by inferential methods. In some countries, it is feasible to apply direct measurement methodologies. However, most situations do not permit the routine application of such methods, because (i) the chemical sensors necessary are not yet suitable for routine unattended use, (ii) the cost involved is prohibitive, (iii) the requirement for skilled operators is unavoidable, and (iv) sites of suitable homogeneity are generally not available.

Consequently, most existing programs make use of an alternative approach, in which direct measurements are used to calibrate detailed relationships describing the factors that control dry deposition rates. These relationships are then used to infer dry deposition from measurements of key selected variables made at the sites in question. Such measurements are of air concentration of the chemicals of interest, and of variables known to be indicative of the processes controlling the exchange between the air and the underlying surface.

Measurements of air concentration are presently the easiest to make, in that the technology involved is well known. The options available are to use any of automatic real-time monitoring instruments, filter packs, denuders, or passive samplers. All available air sampling technologies appear to be somewhat imperfect.

Based on the "Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET", which was developed by the Task Force on Dry Deposition Monitoring, and endorsed by the First Interim Scientific Advisory Group (ISAG) in September 1999, air concentrations of gases, aerosols and their ion concentrations will be measured, for the time being, under the framework of EANET.

4.1. Monitoring sites

Monitoring sites should be selected in accordance with the criteria for deposition monitoring sites mentioned in Chapter 2. The same site used for a wet deposition monitoring is recommended. When air concentration monitoring is difficult at a wet deposition monitoring site, a new sampling site should be selected by sufficient consideration for uniformity of ground surface, in addition to the criteria for wet deposition monitoring.

4.2. Monitoring frequency

In the case of automatic instruments, hourly data are expected to be gathered. One-hour averaged values can be used for the purpose of the evaluation of air concentration after averaging for one-week. It is desirable that the air concentration monitoring by automatic instruments is carried out throughout a year. If it is difficult, adequate measurement duration in every month should be determined, taking account of the situation in respective countries.

In the case of concentrations of ions by denuder and/or filter pack methods, weekly data are expected. Daily data are also acceptable.

4.3. Measurement parameters

For the time being, the required parameters for air concentration monitoring of EANET should be SO₂, O₃, NO, NO₂ (urban), and particulate mass concentration (PM). The issue of PM10/2.5 should be further discussed and elaborated at future sessions of the Task Force and ISAG. Air concentrations of NO₂ (rural and remote), HNO₃, NH₃, and ion concentrations of particulate component are optional. Nevertheless, these components are recommended for measurement since concentrations of specific components (SO₄²⁻, NO₃⁻, NH₄⁺, and Ca²⁺) are relevant chemical species.

4.4. Monitoring methods

Procedures suggested for monitoring of air concentrations are specified in the table below. The methods detailed in the table are typical ones and not exhaustive. These methods will require modification and/or revision if new or different analytical methods are employed, or if the monitoring conditions are unusual.

For routine monitoring of the air concentration, automatic instruments are commercially available for SO₂ (ultraviolet fluorescent (UVF) method), NO (chemiluminescence detection (CLD) method), O₃ (ultraviolet photometric method and CLD method) and PM (Beta-ray absorption method and TEOM method) to obtain one-hour averaged values.

It should be noted that commercial "NOx chemiluminescence instruments" having a molybdenum converter should not be used for NO_2 measurement at rural and remote sites since its NOx mode responds not only to NO/NO_2 but also to HNO_3 and other organic nitrates without discrimination. The instruments could be used for NO/NOx^* (NO, NO_2 , PAN and partial HNO_3). Its use in urban sites near emission sources may be acceptable for NO_2 measurement since a major component of NOx would be NO_2 and NO in urban area.

Parameters	Methods for automatic instruments	Manual methods
SO ₂	Ultraviolet fluorescent (UVF) method	Filter packs
		Denuder
		(Passive sampler)
O ₃	Ultraviolet photometric method	(Passive sampler)
	CLD method	
NO	Chemiluminescence detection (CLD)	(Passive sampler)
NO_2 (urban)	Method	
HNO3	-	Filter packs
		Denuder
		(Passive sampler)
NH3	-	Filter packs
		Denuder
		(Passive sampler)
PM	Beta-ray absorption method	High-volume sampler
	TEOM method	Low- volume sampler
Concentrations	-	Filter packs
of Ions		Denuder
		High-volume sampler
		Low-volume sampler

Table 4.1. Methods suggested for concentration monitoring

(Note) The analytical methods for wet deposition (e.g. Ion Chromatography) can also be used for analysis of manual methods.

PM can be measured by using commercially-available impactors and cyclones. All other gaseous species, namely, NO₂, HNO₃, and NH₃, require the use of filter packs, denuders, scrubbers, or passive samplers (still further discussions be required at the Task Force on Dry Deposition Monitoring and ISAG). Since these methods need further elaboration, their priority has to be set as secondary, together with the components of aerosols ($SO_4^{2^-}$, NO_3^- , NH_4^+ , and Ca^{2^+}).

5. Soil and vegetation monitoring

The ultimate objective of the soil and vegetation monitoring will be to assess the impacts of acid deposition on terrestrial ecosystems in a comprehensive and systematic manner through establishment and maintenance of good quality databases. To achieve this ultimate objective, a step-wise approach should be adopted. The initial objectives of the soil and vegetation monitoring could be an establishment of baseline data, and also early detection of possible impacts of acid deposition, particularly on plants and forest ecosystems.

Two kinds of soil and vegetation monitoring will be undertaken under the framework of EANET. For the initial objectives, physical and chemical properties of soil should be analyzed as the soil monitoring items, and general description of forest and survey of tree decline should be carried out as the forest monitoring items. The baseline data concerning soil and vegetation may be established through these activities, then changes in soil and vegetation properties can be detected. The possible impacts of acid deposition on terrestrial ecosystem may be estimated based on the above data

For the approach to the ultimate objective, terrestrial ecosystem analysis is proposed. The terrestrial ecosystem analysis may be available for the description of elemental dynamics and the estimation of possible impact of acid deposition, although detailed methodologies of this approach have to be established.

5.1. Monitoring sites

Monitoring sites for soil and vegetation monitoring should be selected in accordance with the criteria for deposition monitoring sites mentioned in Chapter 2.

5.2. Monitoring parameters and frequency

Monitoring parameters, classification of parameters, and frequency of analysis for basic survey are presented below.

Monitoring parameters, classification of parameters, and frequency of measurement for ecological analysis remain to be developed.

Parameters	Unit	Criterion	Frequency of analysis
Chemical Properties of Soil			
a) Moisture Content	wt%	М	
b) pH (H_2O) and pH (KCl)		М	
c) Exchangeable Base Cations (Ca, Mg, K and	$cmol(+) kg^{-1}$	М	
Na)			
d) Exchangeable Acidity	$cmol(+) kg^{-1}$	М	-
e) Exchangeable A1, H	$cmol(+) kg^{-1}$ $cmol(+) kg^{-1}$	Ο	Every
f) Effective Cation Exchangeable Capacity		М	3 - 5 years
(ECEC)			
g) Carbonate Content (for calcareous soil)	%CaCO ₃	M*	
h) Total Carbon Content	g kg ⁻¹	0	
i) Total Nitrogen Content	g kg ⁻¹	Ο	
j) Available Phosphate	P mg kg ⁻¹	V	
k) Sulfate	S mg kg ⁻¹	V	
Physical Properties of Soil			
a) Fine Earth Bulk Density	Mg m ⁻³	0	
b) Penetration Resistance (in the fieldwork)	kg cm ⁻²	0	

Table 5.1. Monitoring parameters for soil

M: Mandatory items; O: Optional items; V: Voluntary items. Carbonate content is mandatory item only for calcareous soil.

Table 5.2. Monitoring items for general description of forest characteristics

Items	Classification	Frequency of monitoring
Description of trees		
Name of species	М	Every 3-5 years
Diameter at Breast Height	М	
Height of tree	М	
Understory vegetation	М	
survey		

M: Mandatory items

Table 5.3. Monitoring items for survey of tree decline

Items	Classification	Frequency of Monitoring
Observation of tree decline	М	Every 3-5 years
Photographic record of tree decline	0	
Estimation of decline causes	0	

M: Mandatory; O: Optional

5.3. Monitoring procedures

Overall procedures for soil and forest monitoring in a basic survey are described in Fig. 5.1. The monitoring described in this Figure should be carried out as a basic survey, separately from terrestrial ecosystem analysis at the ecosystem analysis sites.

Soils and vegetation are characterized by several types of variation. Quality of data from monitoring depends on such variability, plus experimental error at each step in the process from sampling through to chemical or physical analysis. A hierarchical system of sampling units is employed for soil monitoring in EANET as shown in Table 5.4. The statistical design of experiments used for evaluation of the variation and/or precision are: 1) staggered type nested experiment; and 2) completely repeated nested experiment, either of which can be used as appropriate.

Table 5.4. Hierarchical concepts of the sampling units in soil monitoring.

Unit	Number Size Examples in Japan.
• •	1-<50km in radius15 prefectures2-0.1-1 ha3-5 in an areaSeveral5m×5m/10m×10m2-4 in a site
Vertical -Horizon	2 layers - 2(uppermost & subsequent)
Temporal -Period	1 time Every 3-5 years* every 3 years

*Depending on the pollution regime

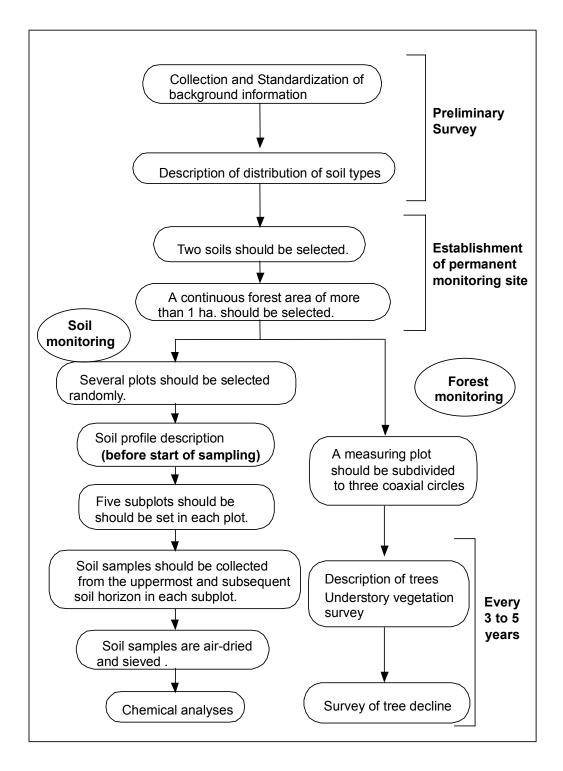


Figure 5.1. Overall process of basic survey of soil and forest

If some changes are detected through the above survey, more intensive survey should be undertaken to assess the implication with acid deposition. The terrestrial ecosystem analysis will be carried out independently of these surveys.

5.3.1. Selection of monitoring sites

5.3.1.1 Preliminary surveys

In order to select permanent monitoring sites for basic survey, preliminary surveys should be carried out, conditions of monitoring areas should be clarified, and reproducibility conditions of data should be recorded. 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. The geographical range of such surveys should preferably cover the area within a radius of approximately 50km of deposition monitoring sites. In preliminary surveys, the information on soils, vegetation, geography, and meteorology should be collected, fieldwork should be carried out if necessary, monitoring sites should be recorded correctly, and the characteristics of the sites in the country should be clarified.

5.3.1.2. Establishment of permanent monitoring sites

The following criteria should also be considered for the selection of forest 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.
- 5.3.2. Basic survey
- 5.3.2.1. Soil monitoring
- (a) Selection of plots for soil monitoring

When forest monitoring sites are selected, two forest sites, whose soils have different sensitivities to acid deposition, should be selected. 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 (each soil type). For establishment of plots, soil profile description should be carried out. In the plot, five subplots, each occupying 1m x 1m, are selected in principle at the center and on the diagonal lines of the plot.

(b) Soil sampling and pretreatment

In each subplot, after removing the litter layer (O horizon), soil samples should collected from the uppermost (0-10 cm) and the underlying (10-20 cm) soil layers. In the center subplot beside the hole for soil profile description, soil sample should be collected. For the corner subplots, holes of appropriate size for sampling should be dug, then similar sampling procedures should be carried out. The multi-stage sampling should be adopted for soil sampling.

The soil samples collected are broadened on laboratory trays, air-dried in room temperature for one to two weeks in laboratory, and passed through a 2-mm sieve to remove pebbles and plant residue, then subjected to chemical analysis. The Air-dried soil samples should be stored in the plastic bottles until chemical analysis.

5.3.2.2. Forest monitoring

To meet the initial objectives of soil and vegetation monitoring, the two surveys have been proposed: general description of forest, and survey of tree decline.

(a) General description of forest

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

For the purpose, the items in Table 5.2. should be described.

(b) Survey of tree decline

The tree decline can be caused by factors of air pollution and acid deposition as well as by external growth factors such as climatological (strong wind, cold wind, thunder, heavy rain, drought), biotic (animal, insect, disease, wood rot,) and human impacts (silvicultural practice, harvesting). For estimation of these causes, long term monitoring may be necessary. In the survey of tree decline, characteristics of tree decline should be observed and recorded regularly, then the cause of decline should be estimated considering environmental factors.

The items described in Table 5.3. should be carried out for survey of tree decline. These monitoring items should be carried out in the season when density of foliage reaches peak.

5.3.2.3 Intensive monitoring

Basic survey should be carried out at the deposition monitoring sites (urban, rural or remote) or in their vicinity. At these sites, baseline data will be accumulated, and changes

in properties of soil and forest may be detected. For evaluation of relationship among the changes and acid deposition, intensive monitoring should be carried out.

At these deposition monitoring sites, data of soil and forest should be evaluated using data of wet and dry deposition monitoring. However, the most sites for wet and dry deposition may be outside of forest area and apart from the sites for soil and forest monitoring. To estimate the dry and wet deposition accumulated to the forest area, rainwater including throughfall and stemflow will be collected in each permanent plot.

5.3.3. Terrestrial Ecosystem Analysis

The ultimate objectives of soil and vegetation monitoring on EANET will be to assess the impacts of acid deposition on terrestrial ecosystems in a comprehensive and systematic manner through establishment and maintenance of good quality databases. To achieve the ultimate objectives, catchment analysis can be one of the useful approaches, especially for description of nutrient dynamics and nutrient status.

The area where terrestrial ecosystem analysis such as catchment analysis will be carried out should be classified as an ecosystem analysis area.

5.4. Analytical procedures

Equipment/methods suggested for soil analysis are specified in Table 5.5. The analytical methods detailed in the table are typical for soil/vegetation samples analyzed in many laboratories at the time of writing, but are not exhaustive. These methods will require modification and revision if new or different analytical systems are employed, or if sample composition is unusual.

Parameters	Equipment/methods			
Chemical Properties of Soil				
a) Moisture Content	Drying oven, Balance			
b) pH (H_2O) and pH (KCl)	Glass electrode			
c) Exchangeable Base Cations (Ca, Mg, K and	AAS, ICP-AES or ICP-MS			
Na)	(CH ₃ COONH ₄ -Extraction)			
d) Exchangeable Acidity	Titration (KCl-Extraction)			
e) Exchangeable Al , H	ibid.			
f) Effective Cation Exchangeable Capacity	Calculation (as sum of exchangeable			
(ECEC)	cations)			
g) Carbonate Content (for calcareous soil)	Volumetric calcimeter			
h) Total Carbon Content	Titration (Walkley-Black method) or			
	CN-analyzer			
i) Total Nitrogen Content	Titration (Kjeldahl method) or			
	CN-analyzer			
j) Available Phosphate	Spectrophotometry (Bray-1 test)			
k) Sulfate	Turbidimetry, IC, ICP-AES or ICP-MS			
Physical Properties of Soil				
a) Fine Earth Bulk Density	Metal sampling cylinder, Drying oven,			
	Balance			
b) Penetration Resistance (in the fieldwork)	Pocket penetrometer			

Table 5.5. Analytical equipment/methods for soil monitoring

6. Monitoring on inland and aquatic environment

Fundamental items of monitoring for inland aquatic environment are described below. In order to supplement these items, the technical manual for monitoring inland aquatic environment has been developed for those who carry out monitoring for inland aquatic environment.

6.1. Monitoring sites

Monitoring sites should be selected in accordance with the criteria for ecological survey sites mentioned in Chapter 2.

It is recommended that harmonic lakes that are considered to be potentially susceptible to acidification should be selected. Natural lakes have higher priority for selection as 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. If there is no harmonic lake, dystrophic lakes could be selected for monitoring. However, in this case, appropriate monitoring methods should be developed and used. It is desirable to choose monitoring lakes that 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.

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).

If there are no appropriate lakes in the area, springs, headwaters or rivers that are potentially susceptible to acidification may be selected, where a minimum impacts of human activities such as deforestation, slash-and-burn farming, stock-farming or cultivation is being conducted or planned in the upper stream area of the water sampling site. Nature protection areas are desirable for monitoring. At upper reach of the stream area, monitoring should be done at one point, and measurement of flow is desirable. In case of river water, water flow and ion concentration change greatly with intense rainfall. Therefore, it is necessary to examine these items when there is no or small (below 10mm) rainfall within 2 days before monitoring.

6.2. Monitoring parameters and frequency

6.2.1. Lakes

(1) Items to be measured more than 4 times a year

(a) Mandatory parameters

- Water Temperature, pH, Electric Conductivity (EC), Alkalinity (at pH 4.8 baseline)
- NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+
- $NO_3^{-}, SO_4^{2^-}, Cl^{-1}$

(b) Optional parameters

- Phytoplankton (Diatom species)

(2) Items to be measured once a year

(a) Mandatory parameters

- Transparency, water color, DOC (if not possible, COD), NO₂⁻ and PO₄³⁻

(b) Optional Parameters

- Total Al (ion)

(3) Items to be measured once in 3-5 years

(a) Mandatory Parameters

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

(b) Optional Parameters

- Living organisms other than phytoplankton
- Sediment (Pb, Pb-210 and stable isotope of S)

6.2.2. Springs, Headwaters and Rivers

The water samples from springs, headwaters and rivers that are potentially susceptible to acidification should be measured more than 4 times a year for the same mandatory parameters as those for lake water. Epilithic algae should be collected instead of phytoplankton, as optional parameters.

	Mandatory Parameters	Optional Parameters
4 times/year	W.T., pH, EC, Alkalinity (at pH 4.8 baseline), NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ SO_4^{2-} , NO_3^- , Cl^-	Phytoplankton (diatom species)* Epilithic algae**
Once/year	Transparency, water color, DOC (if impossible, COD), NO_2^- and PO_4^{3-}	Total Al
Once in 3 ~ 5 years	Sediment (SO ₄ ²⁻ , NO ₃ ⁻ and NH ₄ ⁺ in pore water)*	Living organisms other than phytoplankton, Sediment (Pb, Pb-210 and stable isotope of S)*

Table 6.1 Mandatory and optional parameters

* parameter for lakes only

** parameter for springs, headwaters and rivers only

6.3. Monitoring procedures

6.3.1. Collection of information concerning monitoring sites

An inventory of lakes (including man-made reservoirs) based on their limnological significance and/or with water area of larger than 1 ha in each country should first be prepared. The monitoring lake should be selected from the inventory, based on the criteria for site selection. Then the information on both the monitoring lake and its watershed should be collected as much as possible from the past to the present.

6.3.2 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 two well-washed 1 L glass or polyethylene (polypropylene) bottles without air after washing by sample water.

6.3.3 On-site measurement

Water temperature should be measured on site and recorded on the field reporting form. Air temperature, transparency and outward appearance such as color are recommended to be measured on site and recorded on the field reporting form. Electric conductivity (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 EC and pH is useful as reference data. The measuring temperature of pH and EC should be 25° C in principle. The water sample for later chemical analysis should be put in a tightly stoppered glass or polyethylene bottle, and be stored in a cool and dark place. The water samples for determining alkalinity should be taken in a hard glass (such as pyrex) bottle without air.

6.3.4. 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. The water samples for analysis of chemical components other than alkalinity should be filtered at the sampling site with a glass fibre filter, and should be carried to the laboratory in a cool and dark box. pH, EC and alkalinity should be measured/analyzed immediately after arrival at the laboratory. All other items should be stored at 4 °C and analyzed within several days. If the filtered water samples must be stored for more than several days in the laboratory, they should be frozen in a refrigerator at -20 to -40 °C.

6.4. Analytical procedures

Procedures recommended for analysis of inland water quality are specified in Figure 6-1. Analytical methods suggested for water quality and lake sediment and its pore water is shown in Table 6-1 and 6-2 respectively. The analytical methods detailed in the tables are typical ones commonly available in many laboratories at the time of writing, but are not exhaustive. These methods will require modification and revision if new or different analytical systems are employed, or if sample composition is unusual.

Parameters	Analytical Methods
EC	Conductivity Cell
рН	Glass electrode (preferably with the electrode of non-leak iner cell)
Alkalinity	Titration by Burette or Digital Burette with pH Meter
NO ₃ ⁻ , NO ₂ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻	Ion Chromatography or Spectrophotometry
NH4 ⁺	Ion Chromatography or Spectrophotometry (Indophenol blue) *
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Ion Chromatography or Atomic Absorption/Emission Spectrometry
CI	Ion Chromatography or Titration
Total Al	Atomic Absorption Spectrometry with Graphite Furnace, ICP Emission Spectrometry or ICP/MS
DOC	Combustion-Infrared Method or Wet-Oxidation Method

Table 6.2.	Analy	tical	methods	suggested	for	water	quality

* Not recommended if the biocide, thymol, is used in sample collection.

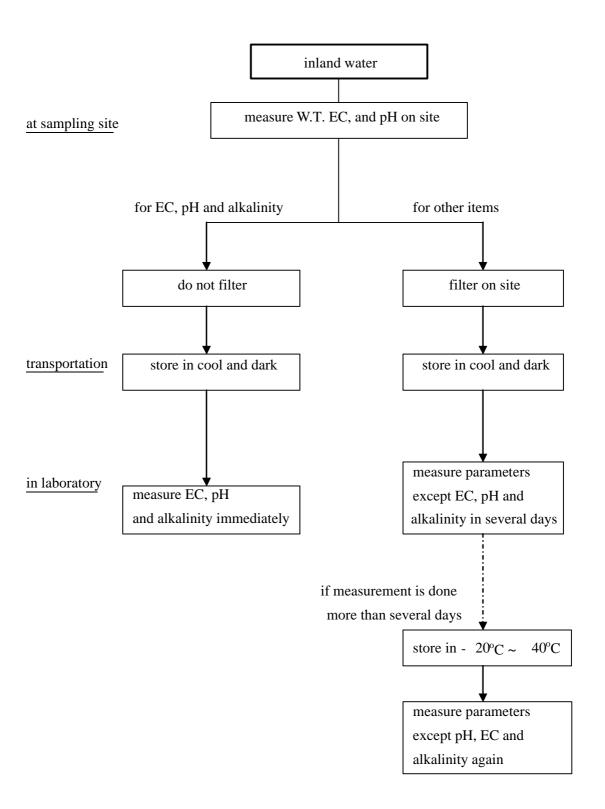


Fig. 6.1 Treatment procedure of inland water samples

Parameter	Analytical Methods
NO ₃ ⁻	Ion Chromatography or Spectrophotometry
NH4 ⁺	Ion Chromatography or Spectrophotometry (Indophenol) *
SO4 ²⁻	Ion Chromatography or Turbidimetry
РЬ	Atomic Absorption Spectrophotometry with Graphite Furnace after Acid Extraction, ICP Emission Spectrophotometry or ICP/MS
Sedimentation dating	Pb-210 Method (Pb-210 : Radiation Spectrometry)
S (stable isotopes ratio)	Isotope Mass Spectrometry by Ionization

Table 6.3. Analytical methods suggested for lake sediment and their pore water

* Not recommended if the biocide, thymol, is used in sample collection.

7. Quality assurance/quality control(QA/QC)

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 an adequate means for 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.

The participating countries in EANET should carry out QA/QC activities in accordance with the QA/QC programs adopted by the Interim Scientific Advisory Group (ISAG) and/or other appropriate EANET bodies, and the national QA/QC programs developed by respective countries, taking into account the specific national situations.

8. Data reporting

The participating countries in EANET should report the monitored data in accordance with the data reporting procedures and formats adopted by the Interim Scientific Advisory Group (ISAG) and/or other appropriate EANET bodies.