

Strategy Paper
for
Future Direction of Dry Deposition Monitoring of EANET

Second Edition

September 2005

Table of Contents

| | |
|--|----|
| 1. <u>Introduction</u> | 1 |
| 2. <u>Status quo of dry deposition monitoring</u> | 2 |
| 3. <u>Priority chemical species for dry deposition monitoring in EANET</u> | 4 |
| 3.1. Major chemical species for acid deposition monitoring | |
| 3.2. Major chemical species for air quality monitoring | |
| 3.3. Priority chemical species in EANET | |
| 4. <u>Future strategy</u> | 6 |
| 4.1. Scope of future activities of the task force on dry deposition monitoring | |
| 4.2. Step-wise approaches for dry deposition monitoring | |
| 4.3. Future direction on dry deposition flux estimation | |
| | |
| <u>Annex 1</u> | 11 |
| FUTURE DIRECTION OF DRY DEPOSITION MONITORING OF EANET (Paper approved at the First ISAG Meeting) | |
| | |
| <u>Annex 2</u> | 13 |
| Selected reference materials | |

1. Introduction

The First Interim Scientific Advisory Group (ISAG) Meeting on EANET, held on 12-14 October 1998 in Yokohama, Japan intensively discussed the future strategy on dry deposition monitoring, and agreed on the identification of the priority chemical species. For further elaboration of the strategy on dry deposition monitoring, it developed and approved a document titled "Future Direction of Dry Deposition Monitoring of EANET" (attached as Annex 1), and established a Task Force on Dry Deposition Monitoring (hereinafter referred to as the "Task Force"). The Terms of Reference of the Task Force are i) to prepare a draft QA/QC program for the first priority chemicals and particles during the preparatory phase, for consideration and adoption by ISAG, and ii) to develop a strategy paper for future direction of dry deposition monitoring of EANET, for consideration by ISAG.

After ISAG1, the Task Force prepared those two documents. "Strategy paper for future direction of dry deposition monitoring of EANET (Strategy Paper)" was finally endorsed with some modifications by ISAG through the diplomatic channel in September 1999. On the other hand, "QA/QC program for the air concentration monitoring in East Asia" was finally endorsed with some modifications by the Science Advisory Committee (SAC) at its First Session held on 14-16 November 2001 in Chiang Mai, Thailand.

The QA/QC program indicated that "Since more discussions are needed at the Task Force concerning QA/QC activities for other air concentration monitoring, such as filter packs, denuders, and passive samplers for the second priority chemicals, the QA/QC activities for these methods will be integrated in this program in the future, taking account of the progress of the discussions at the Task Force." In line with this suggestion of the QA/QC program and in response to request by the EANET participant countries using filter packs, "Technical Document for Filter Pack Method in East Asia" was developed by the Task Force. This technical document was finally endorsed by SAC3, held on 24-26 November 2003 in Pattaya, Thailand.

After the publications of those documents, SAC4 held on 3-5 November 2004 in Siem Reap, Cambodia discussed some pending issues on dry deposition monitoring of EANET pointed out in those documents and/or in previous SAC meetings. It is important to clarify the pending issues like the expansion of

measurement parameters considered by wide use of Filter Pack method in regular phase or their importance for evaluating atmospheric environment. In this context, Second Edition of the Strategy Paper was prepared mainly based on the outcomes at SAC4.

2. Status quo of 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. For example, in the Netherlands and in the United Kingdom, eddy correlation methods have been employed at some selected locations and for some chemical species. 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. It appears unlikely that some specific standardized sampling methodology could suit all conditions.

The factors involved in calculating deposition velocity (V_d) are conveniently characterized in terms of resistances in a conceptual model analogous to an electrical resistance network, with individual resistances R_a , R_b and R_c corresponding to aerodynamic, boundary layer, and residual resistance. V_d is then computed as

$$V_d = 1/(R_a + R_b + R_c)$$

It should be noted that each of R_a , R_b and R_c is site-specific. In essence, dry deposition is a site-specific variable. For any location where dry deposition data are desired, it must first be decided precisely what surface is of major interest, and then instrumentation must be deployed so as to provide data relevant to that surface. It must also be noted that the surface-specific nature of dry deposition means that collection vessels and surrogate surfaces do not yield answers that are indicative of deposition to the biological surface that is generally of major interest.

The collection of on-site data indicative of the processes controlling local dry deposition is necessary. The focus of these measurements must be on quantifying each of R_a , R_b and R_c . The disciplinary skills required to assemble a coherent dry deposition sampling network program may include micrometeorology, plant physiology, and chemistry. Reference could be made for the Dry Deposition Inferential Method (DDIM) for details about R_a , R_b , and R_c .

Each of the resistances will display a strong diurnal cycle. Field experiments now available indicate that the quantification of R_a is fairly precise, at least for sites that are spatially homogeneous. R_b is less well understood, but the basic dependence on the leaf area index and the friction velocity (u^*) impose a diurnal cycle that is expected in theory but difficult to detect in practice. R_c displays a strong diurnal cycle due to stomatal function and so on. In addition, each of resistances will also display a strong seasonal variation at some case such as snow covered field and rainy season. Some parameters such as Leaf Area Index could be useful to assess the seasonal variation.

The desired dry deposition estimate will require careful and thorough analysis of the meteorological, biological and surface data obtained at sampling sites. Once this process has yielded values of the dry deposition velocities that are needed, then they must be combined with the appropriate chemistry data to produce dry deposition rates. It must be anticipated that there will be need, as part of this process, to account for the effects of such factors as the diurnal cycles affecting V_d .

Several methods have been examined for determining dry deposition of gases such as SO_2 , NO_2 , HNO_3 and O_3 and of aerosol components such as SO_4^{2-} and

NO_3^- to soil and vegetation (e.g. a red pine forest in Ohsiba Highland, Nagano, Japan; an agricultural area in Kyunggi, Republic of Korea). Details of the methods mentioned above are aerodynamics, gradient, and modified Bowen ratio to vegetation, and direct deposition to soil. A method was developed for determining total deposition of sulfur oxides to forest from the analysis of throughfall and stemflow. The method was applied to the deposition of SO_x to a masson pine forest in Zhenwu Mountain, Chongqing, China and to a cedar forest in Gumma, Japan. Moreover gradient and modified Bowen ratio methods for SO_2 and O_3 have been examining in a teak forest, Lampang, Thailand under the Joint Research on Dry Deposition Flux between Network Center for EANET and National Center of Thailand (Pollution Control Department). The Dry Deposition Inferential Method was examined in some of those experiments. In this connection, this inferential method was applied to estimate dry deposition at Japanese EANET sites in the Comprehensive Summary Report on Acid Deposition Monitoring Survey, which is the assessment report of acid deposition during 20 years in Japan. In addition to these methods, the novel technology employing surrogate surface has been now gaining more attention because of its ease for implementation and maintenance.

3. Priority chemical species for dry deposition monitoring in EANET

3.1. Major chemical species for acid deposition monitoring

The purposes of dry deposition monitoring are (i) to provide data for the evaluation of total acid deposition on soil, vegetation etc. for the assessment of the adverse effects on specified ecosystems, (ii) to provide data for the evaluation of the regional budget of sulfur and nitrogen with the aid of numerical model. Although O_3 is not an acidic but rather an oxidizing species, it is known to be very harmful to plants. Its deposition rate on vegetation is large and is generally believed to affect ecosystems synergistically with acid deposition. Thus, it is highly recommended to evaluate O_3 deposition together with acid deposition. Moreover Na^+ in particles also concerns the regional budget of sulfur to estimate sea-salt or non-sea-salt sulfate. For these purposes, the concerned chemicals are primarily gaseous SO_2 , NO , NO_2 , O_3 , HNO_3 , HCl , NH_3 , and the particulate SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ and Ca^{2+} .

Hourly data are expected where diurnal cycles in deposition velocity are to be monitored explicitly. However for evaluation of dry deposition, the sampling

period of air concentrations could be longer than one day, e.g., a week for certain circumstances at monitoring site.

3.2. Major chemical species for air quality monitoring

From the viewpoint of air quality monitoring, major substances of concern are gaseous SO₂, NO/NO₂, O₃, and the particulate mass. Among these substances, SO₂, NO₂, O₃ and particulate matter (PM) are all well-known air pollutants from the viewpoint of health impacts etc. Although NO is not very harmful per se, it is a primary pollutant and it easily converts to NO₂ in the atmosphere. It is also a precursor of O₃. Thus, it is highly recommended to measure NO whenever feasible. For the measurement of PM, PM10 is important to detect total amounts of acid and base components in particles; PM2.5 is effective to define national, regional and hemispheric transport characteristics.

3.3. Priority chemical species in EANET

The priority chemical species for EANET dry deposition monitoring are recommended to be as follows:

First priority: SO₂, O₃, NO, NO₂ (urban), HNO₃, HCl, NH₃,

Particulate component (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, Mg²⁺, K⁺, and Ca²⁺), PM10

Second priority: NO₂ (rural and remote), PM2.5

SO₂, HNO₃, HCl, NH₃ and particulate components require the use of filter pack. Automatic instruments for SO₂ (UV fluorescence method), O₃ (UV photometric method) and NO (chemiluminescence detection method) are suitable to obtain one-hour averaged values of these species for air quality monitoring. Units of ppb for gas and µg m⁻³ for particle can be used for data reporting. For calibration of the ozone monitoring equipment, traceability to the international standard of National Institute for Standard and Technology (NIST), USA should be considered. These one-hour averaged values can of course be used for the purpose of the evaluation of dry deposition after averaging over longer periods -- e.g. for one week.

It should be emphasized that commercial "NO_x chemiluminescence instruments" with molybdenum converter should not be used for NO₂ measurement at rural and remote sites since its NO_x mode responds not only to NO/NO₂ but also to HNO₃ and other organic nitrates unspecifically. The instruments could be used for NO/NO_x* (NO, NO₂, PAN and partial HNO₃). Its use in urban sites near emission sources may be acceptable for NO₂ measurement since a major component of NO_x would be NO₂ and NO in urban area. In remote and rural areas, passive sampler could be used to measure NO₂, unless advanced research-grade methods can be used. Passive sampler also could be used to measure O₃.

To obtain one-hour averaged values of PM₁₀ and PM_{2.5}, Tapered Element Oscillating Microbalance (TEOM) method or β-ray method coupling with commercially-available impactors and cyclones are suitable.

4. Future strategy

4.1. Scope of future activities of the task force on dry deposition monitoring

The combination of research activities and routine monitoring, and step-wise expansion of dry deposition monitoring activities are required continued attention in East Asia. The continued activities of the Task Force on Dry Deposition Monitoring, with the scope of medium, long-term activities in this area, are requested. Terms of Reference (TOR) of the Task Force reorganized at ISAG2 held on 13-15 March 2000 in Jakarta, Indonesia includes (i) to further develop and elaborate a strategy for dry deposition monitoring in the region, as well as specific action plans, for consideration by SAC, (ii) to review and guide the relevant activities, based on the strategy and specific action plans finalized by SAC, and (iii) to communicate and coordinate with the activities of Global Atmosphere Watch (GAW) of the World Meteorological Organization (WMO) and in other regions. The new Task Force will consist of experts of the participating countries and other international organizations, and will review the steps outlined below.

4.2. Step-wise approaches for dry deposition monitoring

A step-wise approach has been proposed for developing dry deposition monitoring in the East Asian region, in combination with research and routine monitoring activities.

Step 1. Implement of concentration monitoring for Priority chemical species

As described in the section 3, the actual measurement items can be decided by taking account of the presently available air quality monitoring and feasibility of additional monitoring activities as well. This monitoring might employ either of real-time monitors or integrating samplers (filter packs, denuders, or passive samplers, as may be determined appropriate).

It should be noted that air sampling technologies such as filter pack appear to be somewhat (if not greatly) susceptible to sampling problems when humidity is high. This could be a significant problem for operation in equatorial Asia. Thus, sampling technologies need to be carefully examined and tailored to conditions prevailing in the various countries of EANET. It appears unlikely that some specific standardized air sampling methodology will suit all conditions in the region. Further researches on the air sampling technologies such as filter packs are expected by NC and participating countries.

QA/QC activities such as inter-laboratory comparison of filter pack samples and inter-calibration of O₃ monitors should be encouraged.

Step 2. Intensive research on the methodology for dry deposition monitoring

(1) Setting up of special sites, where more direct measurements of dry deposition are initiated

In order to do direct measurement, these sites should be flat, and the surroundings should be uniform as far as a distance of 500 m in all upwind directions. Needless to say, the depositing species in question must have measurable concentrations around the sites. It is desirable to set up the sites on several different surfaces such as coniferous and deciduous forests, cropland, rice field, etc. The special sites are expected to be set up firstly in some selected countries such as Japan and Republic of Korea, then gradually increased to include different surfaces typical in East Asia, for instance, arid regions and tropical forests. Since the operation of the special sites is expensive, an itinerant method may be considered. An appropriate policy is to include locations and organizations where there is an ongoing flux measurement capability ready for extension to dry deposition.

The first priority method to be employed at these sites is the modified Bowen ratio method, since this method is suited to a long-term automatic measurement and is relatively inexpensive. In addition, some experiences have been obtained in its application in South East Asia. As the measurement proceeds, other methods such as eddy correlation, eddy accumulation, relaxed eddy accumulation, etc. should be introduced for the comparative study on their applicability to each specific circumstance.

Along with the dry deposition fluxes (F), the air concentrations (C) of depositing species will be measured, permitting direct computation of the deposition velocity as $V_d = F/C$.

(2) Selection of schemes for calculating deposition resistances

The review should be done bearing in mind the various different surfaces typifying East Asia. As a result of this review, suitable schemes for use as starting points for inferring resistances will be selected, and the variables to be measured at all dry deposition field sites will be identified.

On the basis of the results of this review, several candidate schemes or formulations are to be selected by which the deposition resistances can be inferred from variables suitable for routine measurement. Measurement of the variables (meteorological, biological and surface) relates to the process controlling the exchange between the air and the underlying surface. The required variables should be decided later, but at least the following variables are expected to be measured:

- wind speed [m s^{-1}];
- wind direction;
- temperature [degree];
- humidity [%];
- solar radiation with one hour resolution [W m^{-2}];
- leaf area index [$\text{m}^2 \text{m}^{-2}$];
- soil moisture [$\text{m}^3 \text{m}^{-3}$];
- surface wetness (hourly data);
- plant water stress; and
- biological species distribution.

(3) Study on the methods for direct flux measurement

On the experience obtained at the special sites, the applicability and credibility of different methods should be examined to develop techniques more readily usable in many places in the region.

(4) Study on schemes for inferring Vd or resistances Ra, Rb and Rc

Ra : Field experiments now available indicate that the Ra can be quantified with adequate accuracy from local wind speed data and atmospheric stability which is derived from an indication of solar radiation and cloudiness.

Rb : This resistance depends on the friction velocity (u)*, which can be derived from the leaf area index and the wind velocity profile.

Rc : This is the most difficult of the three resistances to evaluate theoretically, since it depends on physical, chemical and biological interactions of the depositing substance with the surface. A reasonable approach is to evaluate it as a residual:

$$R_c = 1/V_d (\text{field observed}) - (R_a + R_b)$$

then compare the value with that calculated by some existing model, and improve the model so that it is applicable to Asian conditions. For example, information is to be sought to obtain stomatal resistance expressions relevant to biological species of East Asia. It is helpful to this approach to measure and calculate the resistance for water vapor, since more information on the exchange between the air and the surface has been obtained for water vapor than for other substances.

(5) Others

A possibility should be explored to undertake a sub-program for developing chemical sensors of air concentrations suited for dry deposition monitoring. If any solid state sensor can be developed to a usable level, it would greatly improve the monitoring performance.

A possibility should be explored to establish a specialized central laboratory for dry deposition in the East Asian region, possibly within an existing organization in the region, in order to carry out and coordinate the above mentioned studies.

Step 3. Selection of specific monitoring sites suitable for dry deposition computation from among the concentration monitoring sites

These sites should satisfy the same geographical and surface conditions as those for the special site mentioned above. It should be noted that there must be some leniency permitted here. The state of science is not yet such that we can defend a strict application of guidelines. These sites should be instrumented with the sensors for site-specific properties necessary to quantify V_d (as mentioned in Step 2). Detailed records of these properties that control V_d must be maintained and sent to a central laboratory, where the information from the dry deposition monitoring sites is aggregated and used to assess V_d on a site-specific and time-changing basis. There will be need, as a part of this process, to account for the effects of such factors as the diurnal cycles affecting V_d .

A sub-program should be carried out for developing schemes for estimating dry deposition rates to a selected area of some special importance from the data obtained at several sites scattered in the area. These estimation methods are expected to cover the whole region in the future.

4.3. Future direction on dry deposition flux estimation

There are several methods in estimating dry deposition flux including monitoring method and numerical model based methods. Therefore, further studies on the constraints and uncertainty of the methods are required before these two approaches can be considered to be used in EANET. Also monitoring parameters and monitoring sites should be selected to be used for the model validation.

FUTURE DIRECTION OF DRY DEPOSITION MONITORING OF EANET

(Paper approved at the First ISAG Meeting)

The quality assurance/quality control (QA/QC) program for dry deposition monitoring will be prepared, taking into account the progress in the consideration on the technical manual for dry deposition monitoring. In this document, however, the future direction of dry deposition monitoring of EANET is discussed. During the preparatory phase, the QA/QC activities for dry deposition will be implemented, paralleling the QA/QC programs for wet deposition, where applicable.

1. Monitoring sites

Selection of sampling sites is a critical factor in the monitoring. The same sites used for wet deposition monitoring are recommended for dry deposition and/or air concentration monitoring. When dry deposition monitoring is difficult at the wet deposition monitoring site, a new but nearby sampling site should be selected by considering the site-selection constraints for measuring dry deposition, such as the uniformity of the ground surface, in addition to the criteria for wet deposition monitoring.

It should be noted that dry deposition is a surface-specific variable. For any location where dry deposition data are desired, it must first be decided precisely what kind of surface is of major interest, and then instrumentation must be deployed so as to provide data relevant to that surface.

2. Future direction

EANET requires dry deposition data, yet such data are very hard to obtain. In this respect, the Intergovernmental Meeting on EANET, held in March 1998, agreed that air concentrations monitoring is a step along the path leading to dry deposition evaluations. There are other good reasons to measure air concentrations - for basic air quality reasons, on the top of dry deposition evaluations. It should be noted that most items required for air concentrations monitoring also contribute to dry deposition monitoring.

Priority chemical species

First priority: NO₂ (urban), SO₂, O₃, and NO, and particle mass concentration;

Second priority: NO₂ (rural and remote), HNO₃, NH₃ and Particles (SO₄²⁻, NO₃⁻, NH₄⁺, and Ca²⁺)

(Note) Measurement methods for NO₂ concentrations, particularly for remote and rural areas, NH₃ and HNO₃, need further elaboration

For particles, it is recommended to start with a 10 μm cut-off and add 2.5 μm as it becomes feasible. On the basis of discussions at the First ISAG Meeting, ISAG reaffirms that the start should be with air concentrations monitoring. In this connection, a QA/QC program for air concentrations monitoring should be developed.

The next step should be a move towards implementing the inferential approach, in which deposition velocity (Vd) is derived from on-site data.

A strategy should then be developed for future direction of dry deposition monitoring of EANET

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