Workshop Discussion and Conclusions

Purpose of the Conference

The conference brought together a group of recognized leaders in wet acid deposition studies, and other interested parties, for the following purposes:

1. To discuss and evaluate the need for standardization in precipitation collection, analysis, and reporting procedures.
2. To identify positive and negative consequences of such standardization.
3. To identify factors that would inhibit the development, approval, and adoption of standard methods and recommended practices.
4. To determine areas in which standardization is not appropriate.
5. To exchange information on existing measurement techniques and quality assurance practices used in the acid deposition measurement community.
6. To exchange information regarding the natural variability of meteorological variables and precipitation chemistry as an aid in determining the degree of precision and accuracy that would be appropriate for standard methods.

Conference Design

Papers presented at the conference addressed the variability of precipitation in time and space, mechanisms of precipitation scavenging, network design criteria, statistical analysis of data, and the NAVAIR Development Plan (NADP) quality control process. Additional papers focussed on the problems of chemical analysis, including the use of ion chromatography and pH measurements; the role of particulate material; and the development of simulated reference materials for rain. Short presentations were made on results of specific precipitation sampling programs.

At a workshop held in conjunction with the conference, the conferees were given the following set of thought-provoking questions:

1. How good is "good enough" when applied to data regarding rainwater constituents? By what criteria should "goodness" of data be measured? For

what purposes is the "goodness" of data least important? Most important? How does the method by which the rain is analyzed affect the "goodness" of the data?

2. Some people see the acid rain question as a special case of the larger question of deposition of acidic pollutants arising from man's activities. In this context, acid rain can be viewed as rain-aided deposition of acidic pollutants. Is this formulation satisfying to you? Why or why not? What implications does this view have for our understanding of the "acid rain" problem? Does it suggest different lines of research? In this context, which constituents of rain are likely to be most interesting? Which measure of acidity (pH or free hydrogen, available hydrogen, or ion balance) is likely to be most enlightening?

3. Bulk deposition measures the net acidity of wet and dry deposition from both local blowing soil and transported material. In your opinion, which effects are likely to dominate? What is the significance of measurements of bulk deposition to effects on soils? On lakes? On vegetation?

4. Measurements of rain under trees and shrubs indicate that the pH and ionic content of "through fall" is significantly different from that of rain falling in the open. The difference may be due to elution of atmospheric contaminants previously deposited on the leaves or of material produced or altered in the leaf. Do you consider the "through fall" to be acid rain or rain-aided deposition? How do you include this deposition when you estimate acid deposition to large land areas?

5. In your view, is the development, calibration, or standardization of existing or additional methods or both for the measurement of wet and dry deposition a high priority?

6. The "natural pH" of rain has been defined by its content of dissolved carbon dioxide at equilibrium. Is the deposition of carbon dioxide to soils, lakes, and so forth relevant? Is this definition of the natural pH satisfying? Various salts of strong acids and weak bases dissolve in rain to produce pH between 4 and 7, but the salts do not supply net hydrogen ions. What is the importance of the deposition of such salts in considering effects on lakes? Soils? Vegetation?

Over lunch, attendees and speakers discussed the conference and the questions that had been distributed. Each table selected two questions of particular interest to discuss, and one person from each table was asked to take responsibility for reporting the results of these deliberations during the afternoon discussion periods.

After the presentations were complete, all speakers and conferees were invited to discuss the desirability and difficulties of standardization. A report of that discussion was prepared from a tape recording of the session for use of ASTM and other interested parties.

Workshop Findings

The principal conclusions of the workshop were:

1. Since objectives of deposition measurement programs are varied, the same set of collection, analysis, and reporting methods will not be appropriate for all programs.
2. For programs that are intended only to determine long-term average rates of ion deposition in precipitation (such as NADP and Canadian Network for Sampling Precipitation [CANSAP]), broad areas of standardization may be possible. These include construction materials for collector buckets, sample handling procedures, and some detailed analytical procedures.
3. In general, collection frequency, siting criteria, and the parameters to be analyzed are program specific and should not be standardized.
4. Although standardization of individual analysis techniques is possible, it may be desirable to specify several analytical techniques for each parameter, with varying degrees of cost, sophistication, and, probably, precision and accuracy. Final selection of methods would then be left to the individual investigators.
5. Some standard analytical methods have already been approved within ASTM that can be applied to the analysis of rain. These include methods for determination of ions by ion chromatography and for analysis of metals by atomic absorption spectroscopy.
6. The principal inhibiting factor to adoption of standard techniques is the reluctance of the operators of existing programs to change their methodology. This demurral stems from valid concerns regarding the need to maintain program continuity and the cost of making changes.
7. The principal disadvantage of standardization is the chilling effect it may have on adoption of superior methods developed in the future.
8. There is a continuing need to develop precision and accuracy data for collection and analysis methods currently in use. Additionally, suitable standard reference materials must be developed for use in quality assurance programs.
9. Voluntary standards are preferable to imposed standards.

A more detailed description of the discussions follows.

Standardization Among Existing Networks

There was a general consensus that the major monitoring networks could adopt certain standard methods if the need were demonstrated. Conferees identified the following intrinsic differences caused by differing network objectives that were expected to prevent overall standardization:

1. Collection frequency—whether daily, weekly, or on an event basis.

2. Location and size of network—sample handling problems are very different for far flung networks in very hot or cold climates than for small networks in temperate climates.

3. Parameters to be studied—when metal concentrations are to be analyzed, samples must be stored in plastic and acidified. Samples to be analyzed for organic constituents may be stored in glass bottles.

4. Collector siting criteria—whether urban, rural, remote, or source specific.

5. Construction of rain sampling units—construction will vary depending on whether wet only or bulk collection is desired, how much snow is anticipated, accessibility of site, availability of electric power at site, and so forth.

Broad areas in which standardization could be attempted were identified as follows:

(1) site exposure,
(2) container composition and perhaps shape,
(3) sample storage procedures for specific analyses,
(4) precleaning protocols for sample handling equipment, and
(5) detailed protocols for specific analytical procedures.

Quality Assurance

All agreed that quality assurance must be conducted for every phase of sample handling and analysis. The best analytical techniques will be useless if sample degradation occurs, and the use of a poor pH electrode on an ideal sample will give poor results. When compromises must be made to reduce system costs, any effect on the precision and accuracy of the results must be determined, documented, and reported along with the results.

Standardization and Research Programs

The needs of the research community could work against standardization. Individuals often need to use novel or eccentric collection and analysis procedures to answer specific questions about the causes and effects of precipitation acidity. In such cases, the arbitrary imposition of specific standard methods may be counterproductive. However, investigators may voluntarily use available standard methods or practices for specific aspects of the program (such as sulfate analysis) where the details of the methodology are not important to the research design. Use of standard methods will become more widespread if the precision and accuracy are documented and they are known to be reliable.

Redundancy in Measurement Techniques

Conferees felt that under some conditions it would be useful to standardize several methods for measuring the same parameter. For laboratories analyzing many samples per day, automated methods are advantageous. For small laboratories and research programs, manual methods may be more cost effective. In addition, there may be a need for "quick and dirty" methods for some studies, and highly precise methods for other applications.

ASTM members pointed out that the "multiple path" approach to standardization has been followed in other types of ambient measurements: for fluoride, more than ten methods have been approved, including both automated and manual procedures. They encompass many analytical principles and vary in detection limit, precision, and reproducibility, as well as in cost and sophistication. Each method includes a "scope" that gives applicable concentration ranges, matrix materials, interferences, and the observed levels of precision and accuracy.

Advantages of Standardization

Conferees discussed some advantages of standardization, including improved data reliability and comparability. In addition, the existence of widely accepted and well-calibrated reference methods would facilitate evaluation of new techniques and serve as a benchmark in the review of old methods. Finally, these techniques will be attractive to individuals and groups establishing new monitoring and research efforts. Thus, the overall level of data comparability between small and large networks will be improved.

Disadvantages of Standardization

Some disadvantages of standardization were identified, principal among them the difficulty of replacing a recognized standard method with a new and better one. This problem is less acute with voluntary standardization than with imposed standardization since, in the former case, the parties can agree to change methods at any time. Within ASTM, the need to expedite adoption of new methods is met by provisions allowing for the rapid promulgation of new methods as proposals while the full standardization process proceeds.

One conferee was concerned that the widespread adoption of a standard method with an undetected bias would lead to subsequent loss of all data collected during a given time period. The use of parallel methods was offered as a guarantee against such an eventuality. Other conferees responded that even if a bias is uncovered, the data are still comparable and can be corrected. However, the comment illustrates the importance of conducting appropriate precision and accuracy studies during the standardization process and of maintaining ongoing quality assurance programs. These programs should include the regular use of laboratory standards, standard reference materials, spiked samples, field and laboratory blanks, and parallel measurement techniques.

Conclusion

The ASTM subcommittee on sampling and analysis of atmospheres has concluded that standardization of carefully selected techniques for sampling and analysis of rain is desirable and possible. However, a real tension exists between the needs of the regulatory and research communities, in that methods appropriate to one may be inappropriate to the other. The resolution of this tension requires a careful approach to standardization, perhaps a combination of recommended methods for storing and analysis of rain, recommended but discretionary practices in siting and collection frequency, and performance standards for quality assurance and reporting activities.

Postscript

In April, 1982, ASTM Committee D-22 authorized the establishment of a task group for standardization of atmospheric deposition measuring techniques. This task group, comprising members of both D-22 (atmospheres) and D-19 (water), is currently reviewing methods for analysis of water to determine their applicability to rain. Revisions to the D-19 pH measurement techniques are in the balloting process. Extension of this work to measurement of dry deposition is contemplated.

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