



Project Summary

Comparison of Weekly and Daily Wet Deposition Sampling Results

L. E. Topol, M. Lev-On, A. K. Pollack, and T. J. Permutt

The objectives of this project were to evaluate the changes in chemical composition that may occur when precipitation is stored up to seven days in collectors, and to assess the significance of the variability of those changes from site-to-site and from season-to-season. In a one-year field program, two pairs of identical wet deposition samplers were deployed at three sites; for each pre-designated pair, either daily samples or weekly samples were collected. Two sites also had a pair of collocated weighing bucket rain gauges. Common procedures were used at all three field sites and all samples were analyzed at the same laboratory.

The data obtained were used to determine differences between daily and weekly sampling for (a) collection efficiency (by reference to the same rain gauge) for each site and by precipitation type, (b) precision of daily and weekly monitoring, (c) concentration bias (expressed as the relative difference between derived weekly and measured weekly concentrations) overall and by season, and (d) deposition bias (defined as the difference between the deposition calculated from the daily measurements and that from the weekly measurements).

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Precipitation sampling networks in the United States generally collect either daily (UAPSP, MAP3S) or weekly (NADP/NTN) samples. Under a weekly schedule, samples can remain in the collector under ambient conditions for up to seven days, possibly resulting in more chemical changes than might occur if the samples remain in collectors for at most 24 hours. When comparing chemical composition and trends calculated from weekly and daily deposition networks, it is important to know the occurrence and magnitude of such changes.

To determine the importance of such chemical changes, a collocated sampling study was performed at three sites of the Utility Acid Precipitation Study Program (UAPSP) network from October 1983 to October 1984. The sites—Uvalda, Georgia; Lancaster, Kansas; Underhill, Vermont—were selected to represent the southeastern, central (west of the Mississippi River), and northeastern regions of the United States.

The three UAPSP monitoring sites were equipped with four identical precipitation samplers, two collecting daily samples, and two, weekly samples. This was done to allow precision data to be calculated for both sampling schedules and also to allow a comparison to be made of the chemical composition for the daily and weekly samples. All analyses were performed in the same laboratory and except for the sampling schedule, all procedures were identical. In

addition, two sites had collocated rain gauges so that the precision of precipitation depth and deposition could also be determined.

Procedures

Field Procedures

All operators were trained in site operations based on the U.S. EPA "Operation and Maintenance Manual for Precipitation Measurement Systems" and the UAPSP "Field Operator Instruction Manual." Daily site visits were made at about 0900 to check the equipment and remove any precipitation collected by the daily samplers.

Daily samples were weighed and a portion removed from each for pH and conductivity measurements. These measurements were made about an hour after sample removal from the collector to allow for temperature equilibration with the standard solutions required for meter calibration and the pH quality control check. When the sample was frozen or contained snow, it was allowed to thaw before an aliquot was removed for field analysis. If the sample remaining after pH and conductivity measurement was greater than 20 g, a 500 ml sample (or whole sample if less than 500 ml) was transferred to a clean, labeled, plastic bottle and sealed; the rest of the sample was discarded. If pH and conductivity measurement were less than 20 g, the sample was discarded.

Weekly samples were removed on Monday from the Georgia and Vermont sites and on Tuesday at the Kansas site. The same procedures were followed with the weekly samples as with the daily samples, except that the weekly samples were shipped on the day of pickup and were not refrigerated prior to shipment. However, both daily and weekly samples stored at 4°C, were shipped together to the analytical laboratory. If no event occurred within a week, the buckets were rinsed with deionized water to remove any dust that may have deposited, and then reused. The rinse water was shipped to the central laboratory for analysis as a dynamic blank.

Each sample was identified by site, sampler, date, and weight. To prevent confusion of the sample identity, since there were four samplers at a site, the sampler buckets were inscribed with an identification number. The information was recorded both on the sample bottle and on a data sheet. Also listed on the

data sheet were the site values of the pH and conductivity, the rain gauge precipitation reading(s) in inches per event, the number of lid openings, and any pertinent observations by the site operator.

Analytical Procedures

When a sample arrived at the laboratory, the temperature of the box interior was measured. Each sample was logged in, and the temperature and any pertinent codes were recorded on the data sheets. Approximately every twentieth sample was marked for analysis in duplicate as a quality control measure. All the samples were assigned consecutive numbers. The chemist performing the analysis in the laboratory was not aware of either the collection schedule or the identity of the collocated samples.

All samples were analyzed without filtration. Filtration has the advantage of removing both bacteria, which can degrade nitrogen and phosphorus compounds as well as organic acids, and soil particles, which are generally basic and react with hydrogen ion. However, filtration has the disadvantage of being a source of contamination. To minimize degradation, the samples were kept cold after removal from the collector, during shipment, and before and after analysis at the laboratory. In addition, portions of the sample removed for analysis were decanted to eliminate sedimented particles.

Conductivity and pH were determined within one week of sample receipt, using standard laboratory pH and conductivity meters. SO_4 , NO_3 and Cl were determined by ion chromatography and NH_4 was determined by a colorimetric method. Na, K, Ca, and Mg were determined by an atomic absorption technique. Generally, all samples were analyzed for their ion concentration within six weeks of receipt.

Results

A statistical analysis of the data using nonparametric techniques determined the following:

- The collection efficiencies were highest for rain and about equal for snow and mixed precipitation; i.e., a value of about 1.1 for rain and 0.75 for mixed precipitation and snow. Generally, small differences were observed between weekly and daily sampling and among sites for the same precipitation type.

- The precision of ionic concentration determinations was comparable or better for daily than for weekly samples. Overall measurement precision for both sampling protocols (with the exception of potassium) was less than 20 percent of the ionic concentration.
- The measured weekly concentrations were, in most cases, approximately 10 percent higher than the weekly concentrations derived from daily samples.
- The differences between weekly and composited daily concentrations varied by constituents, but generally were less than 10 percent of the mean concentration. Also, the individual ion concentration biases were of similar magnitudes and direction among the sites except for acidity and sodium.
- There were seasonal variations in the concentration bias between daily composited and weekly samples.
- Differences in paired rain gauge depths at the two sites equipped with collocated rain gauges were greatest for snow samples. Overall, the paired rain gauges at the Vermont site measured significantly different precipitation amounts; the differences were greatest in the winter quarter.
- Precision of daily depositions (calculated from the two daily collectors and the two rain gauges) was better at the Kansas site (for most ions the precision was 5 to 15 percent). At the Vermont site, where the rain gauge differences were larger, the precision of the ion depositions was 10 to 30 percent.
- Calculated deposition amounts varied by season at each site. Peak sulfate deposition occurred in the spring at the Kansas and Georgia sites, and in the summer at the Vermont site. Peak acidity deposition values occurred in the summer at the Vermont and Georgia sites, and in the spring at the Kansas site.

Conclusions

This study determined that for most ions, concentrations measured by daily sampling were more precise than those from weekly sampling. In other words, daily sampling provided narrower confidence intervals for concentration means, and could allow earlier detection of significant trends in precipitation

composition. Although weekly measured concentrations were generally higher than weekly concentrations derived from daily samples, the seasonal variability in the results obtained from daily versus weekly sampling was not consistent either in magnitude or direction. This indicated that daily and weekly sample collection can provide consistent spatial distribution results (at least for the three sites studied), but that temporal distributions obtained from weekly samples might be incompatible with those obtained from daily samples. Therefore, for a network that changes from daily to weekly sampling, the bias in the results could interfere with trend analysis.

L. Topol and M. Lev-On are with Combustion Engineering, Newbury, CA 91320; and A. Pollack and T. Permutt are with Systems Applications Inc., San Rafael, CA 94903.

W. J. Mitchell is the EPA Project Officer (see below).

The complete report, entitled "Comparison of Weekly and Daily Wet Deposition Sampling Results," (Order No. PB 87-168 837/AS; Cost: \$18.95, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268



U.S. OFFICIAL MAIL
U.S. POSTAGE
0 3 3

Official Business
Penalty for Private Use \$300

EPA/600/S9-87/006

0000329 PS

U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604