Applications of Within-Event Precipitation Chemistry Measurements

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ABSTRACT: Chemical measurements from hourly sequential precipitation samples and simultaneous meteorological measurements and observations were analyzed to discover relationships between chemical species, to infer atmospheric mechanisms, to relate precipitation chemistry to meteorological events and conditions, and to identify probable pollutant source regions. Analytical methods that can be applied to short-period samples but usually not to event, weekly or monthly samples are described and illustrated.

Changes in concentrations of chemical species during precipitation events can be documented and used to infer atmospheric processes. These changes can also be related to meteorological conditions such as changes in rainfall rate and wind direction or to frontal passages. Source directions and probable source regions can be located by wind direction and trajectory analyses. Means of many samples taken under similar conditions can document relationships between meteorological conditions, concentrations in precipitation and amounts of wet deposition.

Key words

sequential precipitation sampling
precipitation chemistry
analytical methods
meteorological conditions and events
pollutant source regions
trajectory analysis

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Short-period, within-event sequential precipitation samples have been taken at only a few locations and usually for limited periods of time. Nearly all stations which sample precipitation collect event, weekly or monthly samples. Because of the changes in both precipitation chemistry and ambient conditions that almost always occur during precipitation events and over longer periods, such samples yield only mean measurements; significant relationships are obscured and many types of revealing analyses are impossible. The purpose of this paper is to describe and illustrate results of analytical methods that can usually be applied only to short-period samples and to demonstrate the usefulness of within-event sampling.

Methods

Hourly sequential precipitation samples have been taken at Brookhaven National Laboratory (BNL) since June 1976 and analyzed for pH, conductivity and concentrations of sulfate, nitrogen in nitrate plus nitrite, nitrogen in ammonium, sodium and chloride ions. The sampler used was designed and constructed at BNL [1]. Methods used for chemical analyses were described earlier [2,3]. Simultaneous meteorological measurements and observations were recorded including synoptic situation, precipitation type and amount, wind direction, wind speed, and temperature. Time and duration of each sample were also recorded to the nearest minute.

Data were analyzed to discover relationships between chemical species, to infer atmospheric mechanisms responsible for the chemical compositions found, to relate precipitation chemistry to meteorological events and conditions, and to identify probable pollutant source regions [2-7], all major objectives of the BNL precipitation chemistry studies. Conditions under which most wet deposition occurred were also studied [8,9]. Concentration ratios as well as actual concentrations were examined.

Results

Results presented were selected to illustrate the range of analytical methods that can be applied to short-period precipitation chemistry data. Results shown are not necessarily typical or representative of the majority of cases obtained and should not be interpreted as definitive findings or firm conclusions. More extensive analyses of various portions of the BNL measurements have been and are being published elsewhere [2-9] and should be consulted for actual results and conclusions based on larger bodies of data.

Concentration Changes Within Events

Concentrations of major ions sometimes change an order of magnitude or more during precipitation events. Several patterns can be found ranging from little change or apparently random variations to well-marked temporal trends. In one common pattern, concentrations of anthropogenic pollutants are high at the beginning of precipitation, gradually decrease, and then remain more or less constant. A pattern of this type for four constituents is shown in Figure 1. This event is somewhat atypical because of the large increase in sulfate concentration at the end which followed a marked decrease in rainfall rate. The high initial concentrations may result from both in-cloud and below-cloud scavenging and the lower values from in-cloud removal only.

All pollutants are not removed at the same rate during precipitation events. In the case shown in Figure 2, both sulfate and nitrogen in nitrate plus nitrite decreased with time but the nitrogen compounds decreased more rapidly as shown by the ratio curve at the top of the figure. This suggests that nitrate is removed more readily than sulfate or is not replenished as quickly. Findings such as this can give clues to atmospheric processes and

to the chemical forms existing before incorporation of the material into cloud or rain drops. The rapid removal suggests that the nitrate may have been present as the highly soluble nitric acid vapor.

Relationships Among Chemical Species

In many applications of precipitation chemistry, pH or the hydrogen ion (H^+) concentration is the parameter of primary interest. pH often changes greatly during events and sometimes changes systematically with other species. Ammonia appears to be the important neutralizing agent in the atmosphere although it is often not abundant enough to neutralize all of the acidic material present. Figure 3 shows a case with a good correlation between pH and the nitrogen in ammonium/sulfate ratio. Measurements have shown that ammonium concentrations in precipitation are more variable than sulfate concentrations [2,3,5,6]. If, therefore, sulfate concentrations are treated as constant, pH may be a function of ammonium concentrations to a first approximation.

Precipitation Chemistry and Meteorology

In many events direct relationships can be seen between changes in meteorological conditions and changes in concentrations of precipitation constituents. As an example, acidity (H^+ concentration) sometimes varies with rainfall rate as shown in Figure 4. Such cases are often due to convective showers occurring during a warm or stationary front rain. The convective clouds seem to tap sources of pollutants which are not being incorporated into the stratiform warm or stationary front clouds. On the other hand, the opposite trend is found in many storms without convective type precipitation. Here, the decrease in H^+ concentration or increase in pH with increased rainfall rate appears due to increased dilution of available

pollutants. Thus, detailed study of the sequence of both chemical and meteorological changes within events is necessary in order to infer atmospheric mechanisms responsible for the precipitation chemistry observed.

In some cases, however, direct cause and effect relationships are obvious. At BNL, sodium and chloride are largely derived from sea salt injected into the atmosphere from the ocean by wind-blown spray from breaking waves and the surf along the shore. Thus, concentrations of these ions are greater during periods of high winds and commonly increase with increasing wind speeds as shown in Figure 5.

Use of Averages

In many cases, clear-cut, hour-to-hour relationships are not obvious or are obscured by the large variability inherent in atmospheric processes and conditions. Averages taken over many cases occurring under similar conditions often show relationships that cannot be seen in individual events. Sulfate concentrations, for instance, can be averaged over all hours within a selected temperature or wind speed range or all hours with thunderstorm precipitation or all hours with cold front type precipitation. Such data are illustrated in Figure 6 which shows that sulfate concentrations average higher at both low and high precipitation rates than at moderate rates. They are also high with shower and thundershower precipitation, in the summer season and with cold front and squall line precipitation. Similar analyses have been made for other meteorological conditions, for other chemical species, and for concentration ratios [2,3,5,6].

The amount of each species deposited by precipitation can be analyzed in a similar manner to determine under which conditions most of each material is deposited. As an example, Figure 7 shows the frequency distribution

of precipitation rate and the amount of wet deposition of six species for each rainfall rate class. Although the bulk of the precipitation falls at moderate precipitation rates, most of the chemicals are deposited at the lower rates. Data for other species and other meteorological conditions have been presented elsewhere [8,9].

Identification of Sources

One of the goals of the BNL program is to identify sources or source regions of the anthropogenic species found in precipitation. Two methods have been used. In the first, concentrations of each species have been averaged for eight wind direction sectors. As shown in Figure 8, concentrations of sulfate average higher with west and northwest winds. This appears related to the presence of the New York Metropolitan area and more distant major source regions to the west of BNL. Hydrogen, nitrate, and ammonium ion concentrations show similar patterns but sodium and chloride are highest with southerly and easterly winds from the ocean.

Better identification of possible distant source regions can be gained from trajectory analyses. Studies are being made using the Heffter Interactive-Terminal Transport Model [10,11] to calculate back trajectories for three-day periods over selected height intervals [7]. The model calculates trajectories every six hours and gives a position of the air parcel at six-hour intervals along each trajectory. Results from a rain event of April 9-10, 1979 are shown in Figure 9. The hours and dates shown are the ending times of each trajectory which reached BNL during the rain event. The symbols along the trajectories indicate positions at six-hour intervals. In order to relate precipitation chemistry measurements to possible source regions, hourly measurements were averaged over six-hour periods centered on

the trajectory ending times. Sulfate concentrations for each of these time periods are shown beside the trajectories. The 00 Z (GMT) trajectory approached from the northwest and sulfate concentration averaged $63 \mu\text{eq l}^{-1}$. Six hours later, the air had come along the major source region of the Ohio River Valley and the average concentration had increased to $212 \mu\text{eq l}^{-1}$. The three later trajectories approached BNL along the same track from the southwest and sulfate concentrations were much lower and quite uniform. In this one case, therefore, the trajectory from the major eastern U.S. source region brought the higher concentrations of sulfate. Similar relationships were found for other anthropogenic pollutants [7].

Discussion and Conclusions

The foregoing results are presented as examples of those that can be obtained from short-period, sequential precipitation chemistry measurements by use of several analytical techniques. However, the list of techniques illustrated is by no means complete. Others have been used and additional ones will probably be applied by us and by other researchers. Useful tools, for instance, have been bivariate and multivariate correlation and regression analyses which have been applied to studies of relationships between two or more species in hourly precipitation samples [2,3,5,6].

Most of these analytical techniques, however, cannot normally be applied to event or longer period data because of the large changes in both precipitation chemistry and meteorological conditions that usually occur during events. Many storms include both warm front and cold front type rain and rainshowers, have a wide range of rainfall rates, and winds from many directions, perhaps from northeast through south to northwest in a typical frontal storm passage. Trajectories during the storm may come over widely

divergent tracks as shown in Figure 9. Thus, it is impossible to isolate and identify those conditions under which various percentages of the materials in the precipitation were deposited.

Sampling periods long enough to include more than one event are useful primarily for monitoring purposes, to detect long-term average trends or to measure inputs to soils and ground water. Event averages are more useful but still can only be related to ambient conditions as means over a possibly wide range of each parameter. All significant detail within the event is lost. Short-period sequential sampling is more costly and time consuming, and requires a more-elaborate apparatus but gives information obtainable in no other way. Furthermore, event and longer-period averages can easily be calculated from sequential samples. Understanding the complex processes that take place in the atmosphere between emission and wet deposition of pollutants, tracing pollutants from their sources to receptors, and developing or testing realistic mathematical models require a detailed precipitation chemistry data base and suitable analytical methods. More widespread establishment of sequential sampling stations and the most intensive analysis possible of the data collected seem necessary to provide the required degree of understanding.

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Illustrations

- Figure 1 Change of concentration with time of four chemical species in hourly sequential precipitation samples during one precipitation event.
- Figure 2 Change in sulfate and nitrogen in nitrate plus nitrite concentrations (below) and change in the nitrogen in nitrate plus nitrite/sulfate ratio (above) with time in hourly sequential precipitation samples during one precipitation event.
- Figure 3 Change with time of pH and the nitrogen in ammonium/sulfate ratio in hourly sequential precipitation samples during one precipitation event.
- Figure 4 Change with time of rainfall rate and hydrogen ion concentration in hourly sequential precipitation samples during one precipitation event.
- Figure 5 Change with time of wind speed and sodium and chloride ion concentrations in hourly sequential precipitation samples during one precipitation event.
- Figure 6 Weighted mean sulfate concentrations classified by season, synoptic type, precipitation rate and precipitation type.
- Figure 7 Wet deposition of six ionic species and precipitation amount classified by precipitation rate.
- Figure 8 Mean sulfate concentrations by wind direction sector.
- Figure 9 Trajectories ending at BNL at indicated dates and times with sulfate concentrations for the six-hour periods centered on the trajectory ending times beside each trajectory. Symbols on trajectories indicate air parcel locations at six-hour intervals.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8