

DESCRIPTION OF PARAMETERS INCLUDED IN NADP/NTN REPORT OF PRECIPITATION-WEIGHTED MEANS (Precipitation-Weighted Mean Concentrations Reported in Milligrams/Liter)

Site ID

Alpha-numeric site identification code, first two characters of which are the abbreviation of the state in which the site is located. (For intercomparison sites this order is reversed.)

Summary Period

Summary period types are: annual, water, winter, spring, summer, fall, jan, feb ... dec. Annual represents calendar years and Water represents water years (Oct-Sep). Months represent calendar months. Seasons are defined as follows:

winter=Dec-Feb,
spring=Mar-May,
summer=Jun-Aug,
fall=Sep-Nov.

Note that winter begins with December of the previous year. Also note that because the seasons are offset relative to the calendar year, the annual (calendar-year) totals and means cannot be computed using the totals or means for the four seasons.

Standard NADP operating procedures specify that weekly samples be collected on Tuesday mornings. Beginning and ending dates of all summary periods are adjusted to accommodate this sampling schedule.

Year

Year of the summary period being reported. Note that the winter summary period includes December of the previous year.

*Data Completeness Criteria

Criteria established by the NADP Technical Committee to provide a measure of whether the data available are adequate to characterize the summary period as a whole. DATA USERS ARE URGED TO USE THIS INFORMATION TO ASSESS WHETHER THE DATA ARE ADEQUATE FOR AN INTENDED APPLICATION. The NADP requires Completeness Criteria values ≥ 75 for criteria 1, 3 and 4, and ≥ 90 for criterion 2, in its standard applications of weighted-mean concentration data (e.g., published maps and data summary tables); however, data users may wish to select different cut-off values, depending upon the intended application of the data. Note that precipitation-weighted mean concentrations and precipitation totals are reported regardless of whether the NADP Completeness Criteria were met. Following are brief definitions of the four criteria. For a more complete explanation, see the attached excerpt from the NADP/NTN Annual Data Summary for 1991.

- Criterion 1 - Percentage of the summary period for which there are valid samples.
- Criterion 2 - Percentage of the summary period for which precipitation amounts are available either from the rain gage or from the sample volume.
- Criterion 3 - Percentage of the total measured precipitation associated with valid samples.
- Criterion 4 - Collection efficiency. This is the sum of the sample bucket depths (in centimeters) in the summary period divided by the sum of the rain gage amounts (in centimeters) for all valid samples where both values are available. Criterion 4 is reported as a percentage.

*Laboratory Means

Precipitation-weighted means computed using measurements made on VALID weekly samples at the Network's Central Analytical Laboratory (CAL). See Valid Samp. below for a description of the valid samples included in the means.

Precipitation-weighted mean concentrations are reported in milligrams per liter for calcium, magnesium, potassium, sodium, ammonium, nitrate, chloride and sulfate. In cases where the weekly ion concentration was below the analytical detection limit, one-half the detection limit value (or, in the case of a diluted sample, one-half of the product of the detection limit value and the dilution factor) was used in computing the mean.

Precipitation-weighted mean hydrogen concentration is reported as pH; precipitation-weighted mean conductance is reported in microsiemens per centimeter.

*Field Means

Precipitation-weighted means computed using measurements made on VALID weekly samples by the site operator in the field laboratory. Precipitation-weighted mean hydrogen concentration is reported as pH; precipitation-weighted mean conductance is reported in microsiemens per centimeter. See Valid Samp. below for a description of the valid samples included in the means.

Field means are not reported for periods prior to 1987. A set of screening criteria have been approved by the NADP Technical Committee for use in assessing the validity of individual field chemistry measurements. Only those field chemistry measurements which meet all of the screening criteria are selected for use in calculating the field means. Individual field measurements made before 1987 cannot be adequately screened because sufficient measurements of a quality control check sample were not required by the Network. For more information about the field chemistry data and the screening criteria applied to them, see the attached excerpt from the NADP/NTN Annual Data Summary for 1991.

*Ratio

Equivalence ratio of cations to anions. This value is calculated as the sum of the weighted-mean cation concentrations, in microequivalents per liter, divided by the sum of the weighted-mean anion concentrations, in microequivalents per liter. Orthophosphate and bicarbonate are not included in these ratios. Hydrogen concentrations used are those computed from the laboratory (CAL) measurements of pH.

*Svol

Total volume, in milliliters, of precipitation collected by the sampler for VALID samples during the summary period.

*Ppt

Total amount of precipitation, in centimeters, measured by the rain gage during the summary period. This value includes precipitation amounts calculated from the sample volumes in cases where the weekly rain gage measurements were unavailable.

*% Ppt Rep. by F Chem.

The percentage of the total measured precipitation (Ppt) represented by the field means. DATA USERS ARE URGED TO USE THIS VALUE TO ASSESS WHETHER THE FIELD MEANS ARE ADEQUATE FOR AN INTENDED APPLICATION. The NADP requires this percentage to be ≥ 50 in its standard applications of weighted-mean field concentrations (e.g., published maps and data summary tables); however, data users may wish to select a different cut-off value, depending upon the intended application of the data. Note that weighted-mean field values are reported regardless of whether this criterion is met.

In most cases, Data Completeness Criterion 3 is equal to the percentage of precipitation represented by the laboratory means. Precipitation amounts from sampling intervals during which < 0.01 inch of precipitation occurred are included in the Criterion 3 percentage, if less than 10 mL of sample was collected. Complete laboratory analyses are not performed on such samples. Therefore, the percentage of precipitation represented by the laboratory means is sometimes over-estimated by Criterion 3. This occurs more frequently and to a greater degree for monthly summary periods than for seasonal or annual periods. Data users may contact the Coordination Office for more information.

Valid Samp.

Numbers of samples used in calculating the precipitation-weighted mean concentrations for the summary period.

L - Number of samples used in calculating the laboratory means. Only VALID samples with complete, valid LABORATORY (CAL) analyses and a valid measurement of precipitation amount (from the rain gage or sample

volume) are used.

- F - Number of samples used in calculating the field means. Only VALID samples with complete, valid LABORATORY AND FIELD analyses, and a valid measurement of precipitation amount (from the rain gage or sample volume) are used. The samples used in calculating the field means are the same samples or a subset of the samples used in calculating the laboratory means.

Days

Number of days included in the summary period.

Dates

The beginning date of the first sample included in the summary period and the ending date of the last sample included in the summary period, reported in Greenwich Mean Time (GMT), mmddyy.

*Missing values are indicated by --.

DATA SELECTION CRITERIA

A. Criteria for Determining a Valid Sample

Individual weekly samples are screened to determine their validity using criteria based on the following parameters:

- Rain gage depth
- Sample volume
- Sampling interval
- Lab type
- Sample validation codes

- Rain gage depth is the precipitation depth measured by the rain gage collocated with the wet/dry precipitation collector (see Bigelow 1984 for details).
- Sample volume is the amount of precipitation contained in the wet-side sample bucket as determined by weight in the field laboratory.
- Sampling interval is the time period over which the precipitation sample was collected. The standard interval is one week, from 9:00 a.m. Tuesday to 9:00 a.m. Tuesday of the following week. Samples are collected on this schedule whether or not precipitation occurs.
- Lab type is a code assigned to samples received at the CAL, based on the volume of the sample available for analysis. Each lab type keys a different set of sample processing and measurement steps. A complete set of laboratory measurements (pH, specific conductance, concentrations of major cations and anions) is made only on samples with a lab type of wa or w, which are samples of 10 mL volume or more. (Samples of lab type wa are diluted in the laboratory to produce sufficient volume for analysis;

samples of lab type w are large enough to be analyzed without dilution.) Lab type t samples are samples of less than 10 mL. Laboratory measurements of pH and conductance are made on these samples if there is sufficient undiluted sample volume. No other chemical constituents are measured for lab type t samples. A lab type of da indicates that the sample bucket was dry when it arrived in the laboratory. Chemical analyses for lab type da samples are not included in this report.

- Sample validation codes (Bowersox 1985, Aubertin et al. 1990) are assigned during routine NADP/NTN quality assurance evaluations to identify samples that were not collected and/or processed according to NADP/NTN protocols, or were contaminated. Samples are considered valid and are included in calculations of ion concentration and deposition summary statistics if all of the following sample validity criteria are met:

1. NADP/NTN criteria for site location, sample collection and handling, and measurement protocols are satisfied (Bigelow 1984, Bigelow and Dossett 1988).
2. The sample consists of "wet-only deposition," i.e., it was not exposed to excess dry deposition (see Bowersox 1985).
3. The sample is not contaminated (see Bowersox 1985).
4. A complete set of chemical measurements (made at the CAL) is reported for the sample.
5. The sampling interval is 6-8 days.
6. There is a rain gage depth or sample volume reported for the sample.

In the evaluation of data completeness, two additional sample types are considered valid:

1. All samples from sampling periods during which it was confirmed that no precipitation occurred are considered valid. These samples are generally of lab type da.
2. All samples from sampling periods during which a trace of precipitation (<0.01 in.) occurred are considered valid if the sample volume was less than 10 mL (lab type da or t).

When calculating data Completeness Criterion 1 values (see Section III.C) for periods of one year or longer, all sampling intervals with <0.02 in. of precipitation are treated as valid. (Note that this relaxation of the above criteria applies only to the calculation of data Completeness Criterion 1 and to summary periods of one year or longer.)

B. Criteria for Determining the Validity of Field Chemistry Measurements

Measurements of precipitation pH and conductance made by site operators ("field pH" and "field conductance" measurements) are screened to determine their validity based on the following information:

- Sample validation codes
- CAL measurements of pH and conductance
- Field measurements of the quality control check sample

- Field pH and conductance measurements of the precipitation sample

Sample validation codes are applied to exclude samples that fail to meet sample validity criteria 1-3, described in Section III.A. Criterion 4, the requirement for complete chemical analyses, is relaxed for field chemistry measurements; it is required only that there be valid laboratory pH and conductance measurements for the sample (see below). Criteria 5 and 6 are not applied to individual field chemistry measurements; however, to be included in calculations of weighted-mean field pH and hydrogen ion deposition for seasonal and annual summary periods, and in the statistical summaries of field pH and hydrogen ion concentrations in Section VII.C, samples must meet all six of the criteria.

CAL measurements of pH and conductance are used by the CAL to screen samples for possible contamination. Valid laboratory measurements of these parameters are required to ensure that the samples have been subjected to this screening.

Field measurements of the quality control check sample are used to evaluate the accuracy of the equipment and the site operator's measurement technique. Prior to making field pH and conductance measurements, the site operator measures and records the pH and conductance of a quality control check sample (Bigelow and Dossett 1988). The CAL-certified values of the quality control check sample are 22 microsiemens per centimeter (S/cm) for conductance and 4.3 pH units for pH, and are known to the site operator. For field precipitation chemistry measurements to be considered valid, both of the quality control check sample measurements must have been made, and the reported values must be 22.0 4.0 S/cm for conductance and 4.30 0.10 pH unit for pH.

Field pH and conductance measurements of the precipitation sample are used to check for inconsistencies between the reported field pH and conductance values. For the field chemistry measurements to be considered valid, the reported conductance must be equal to or greater than the calculated conductance based entirely on the hydrogen ion concentration. The calculated conductance is the product of the hydrogen ion concentration (determined in the field laboratory) and the equivalent conductance of hydrogen ion at 25 degrees Celsius (Franson 1985, Weast 1989). This check ignores the potential contribution of other ions to the conductance, thus only identifies certain cases where the hydrogen ion concentration is likely to have been overestimated by the field pH measurement. While it is also possible that the conductance measurement was inaccurate, this risk is reduced by excluding field conductance measurements where the quality control check sample conductance is reported as being outside the acceptable range of 22.0 4.0 S/cm. Furthermore, field measurements of conductance meet NADP/NTN accuracy goals more frequently than field measurements of pH (Nilles et al. 1993).

C. Criteria for Including a Site in the Annual Isopleth Maps and Seasonal Data Summary Tables

Four Completeness Criteria form the basis for the decision to include

the laboratory chemistry data from a site in the Annual Isopleth Maps and Seasonal Data Summary Tables in Section VI. All four criteria must be met. The criteria are listed below.

- Criterion 1. There must be valid samples (as defined in Section III.A) for at least 75 percent of the summary period.
- Criterion 2. For at least 90 percent of the summary period there must be precipitation amounts (including zero amounts) either from the rain gage or from the sample volume.
- Criterion 3. There must be valid samples (as defined in Section III.A) for at least 75 percent of the total precipitation amount reported for the summary period.
- Criterion 4. For the entire summary period the total precipitation as measured from the sample volume must be at least 75 percent of the total precipitation measured by the rain gage for all valid samples where both values are available.

Criteria 1 and 2 ensure that measurements on valid wet deposition samples and of precipitation amounts were reported for a minimum acceptable fraction of the summary period. This requires a properly operating wet/dry collector and rain gage. Criterion 3 ensures that there are valid precipitation chemistry data to represent 75 percent of the precipitation that was estimated to have occurred during the summary period. Criterion 4 sets the minimum acceptable level for the collection efficiency of the wet/dry collector relative to the rain gage. This ensures some consistency in the operation of the rain gage and wet/dry collector.

It is important to recognize that if all the criteria were satisfied at the lower limit of acceptability, the summary could still account for less than 75 percent of the actual precipitation at the site. This could occur because the 90 percent precipitation coverage criterion (Criterion 2) is based on time and there may be no record of the amount of precipitation missed during the unsampled 10 percent of the period. Where the precipitation coverage is 100 percent, however, these criteria ensure that at least 75 percent of the precipitation is represented by valid samples.

The following example illustrates the interpretation of the Completeness Criteria values for a hypothetical site. For the annual summary period, the hypothetical values for this site are:

Criterion 1	(Percent valid samples)	91%
Criterion 2	(Percent precipitation coverage)	95%
Criterion 3	(Percent precipitation with valid samples)	65%
Criterion 4	(Percent collection efficiency)	98%

The values for Criteria 1 and 2 indicate that valid samples were obtained for 91 percent of the summary period while valid precipitation

measurements were obtained for 95 percent of the summary period. (The amount of precipitation that occurred during the remaining 5 percent of the period is unknown.) Criterion 3 relates the amount of precipitation represented by valid samples to the total measured precipitation. The value for this criterion is calculated by summing the rain gage measurements associated with valid samples (substituting the sample volume where necessary), then dividing by the total measured precipitation. In this case, although 91 percent of the summary period was represented by valid samples, only 65 percent of the measured precipitation was associated with valid samples. (This can occur when a few very large precipitation events are not represented by valid samples.) Finally, the value reported for Criterion 4 indicates that for valid samples, the amount of precipitation captured by the wet-side bucket on the wet/dry collector was 98 percent of that measured by the rain gage. It should be noted that since Criterion 3 was not met for this hypothetical site, annual NADP/NTN Completeness Criteria are not satisfied; therefore, this site would not be included in annual isopleth maps in this report.

For each site, two sets of hydrogen ion values are included in this report. One set is from pH measurements made at the CAL ("laboratory pH"); the other is from measurements made in the field laboratory at the site ("field pH"). While the CAL laboratory measurements are subject to more rigorous quality assurance and offer greater standardization among sites than the field measurements, the field measurements have the advantage of providing information about the chemistry of the sample shortly after the sample was collected. Comparisons of field and laboratory pH measurements, as well as analyses of natural and simulated precipitation samples processed according to the same protocols as NADP/NTN samples, have shown that hydrogen ion concentrations tend to decrease between the time the pH is measured in the field and when it is measured again in the laboratory. This loss of hydrogen ion has been variously attributed to microbial activity, degradation of organic acids, dissolution of particulate matter, and ion exchange processes involving the walls and/or lid of the shipping container (Bigelow et al. 1989). In NADP/NTN samples, the annual median losses have ranged from 4 microequivalents per liter (eq/L) to 6 eq/L (Bigelow et al. 1989). Because the pH scale is logarithmic, these losses have little effect on sample pH values if the hydrogen ion concentrations are initially high. However, where hydrogen ion concentrations are relatively low, as in the western United States, these losses can result in changes of several tenths of a pH unit. Given the magnitude of these changes, the NADP/NTN has elected to display both the field-measured and laboratory-measured hydrogen ion values in this report.

Precipitation-weighted means of field pH measurements are included in the annual isopleth maps and seasonal data summary tables if: (a) all four of the Completeness Criteria were met for the summary period, and (b) at least 50 percent of the precipitation which occurred during the summary period is represented by samples with complete, valid laboratory chemistry data and valid field pH measurements. (Only these samples are included in calculations of weighted-mean field pH and hydrogen ion deposition). The required percentage of precipitation represented by valid field pH

measurements is lower than that for the laboratory-determined ion concentrations because NADP/NTN protocols call for field chemistry measurements to be omitted on samples of less than 70 mL.