

DESCRIPTION OF PARAMETERS INCLUDED IN NADP/NTN REPORT OF WEEKLY CONCENTRATION DATA

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.)

Date/Time

- On - Date on which the sample bucket was installed on the collector, reported in Greenwich Mean Time (GMT), mm/dd/yyyy hh:mm:ss.
- Off - Date on which the sample bucket was removed from the collector, reported in Greenwich Mean Time (GMT), mm/dd/yyyy hh:mm:ss.

*Ion concentrations

Concentrations of Ca, Mg, K, Na, NH₄, NO₃, Cl and SO₄ reported in mg/L. Concentrations which are below the detection limit of the analysis are indicated with a "<" preceding the value. The value reported is the actual limit of detection or, in the case of a diluted sample, the product of the detection limit value and the dilution factor. (In calculating weighted-mean concentrations and depositions NADP/NTN substitutes one-half the reported detection limit for concentrations below the limit of detection.)

*pH and Cond.

pH reported as the negative log of hydrogen ion concentration and conductance reported in microsiemens per centimeter.

lab - pH or conductance of the precipitation sample as measured in the laboratory at the CAL.
 field - pH or conductance of the precipitation sample as measured by the site operator in the field laboratory.
 FV - field validity code. The NADP Technical Committee has approved a set of screening criteria to be used in assessing the validity of field chemistry measurements. DATA USERS ARE URGED TO USE THE CODES IN THE COLUMNS WITH THE HEADING "FV" TO DETERMINE WHETHER THE FIELD MEASUREMENTS TO THE LEFT OF THE CODES ARE ADEQUATE FOR AN INTENDED APPLICATION. Note that pH and conductance measurements are screened independently; the code assigned to the pH measurement for a particular sample may not match the code assigned to the conductance measurement. Field validity codes currently in use are:

- p - the field measurement passes all of the screening criteria
- f - the field measurement fails to pass all of the screening criteria
- i - incomplete information. Some of the information required to complete the screening is unavailable.
 (In the case of incomplete information, none of the information that IS available would warrant the assignment of a field validity code of "f".)
 Complete information is available only for field chemistry measurements made since the beginning of 1987, because sufficient measurements of a quality control check sample were not required by the Network prior to that time.

For more information about the field chemistry data and the screening criteria applied to them, see Section III.B and pages 4-5 of the attached excerpt from the NADP/NTN Annual Data Summary for 1991.

*Svol

Volume of sample, in milliliters, captured in the wet-side bucket of the wet/dry sampler.

*RG ppt

Precipitation amount as measured by the rain gage in millimeters. Trace amounts are indicated by -7.00.

***Sub ppt**

Precipitation amount used by NADP/NTN in calculating weighted-mean concentrations, depositions and precipitation totals. In most cases sub ppt equals the rain gage reading. Where the rain gage reading is a trace amount, sub ppt is assigned a value of 0.127mm; in cases where the rain gage reading is missing or invalid, sub ppt is calculated by converting the sample volume to its equivalent depth. (The area of the sampler bucket used for this conversion is 678.9 square centimeters.)

Lab type

A code indicating the condition of the sample upon arrival at the CAL.

- w - sample volume of approximately 35mL or more
- wa or wd - sample volume less than 35mL; dilution was required
- t - trace sample of less than approx. 10mL; analyses are incomplete
- da - dry sample
- ga - quality assurance sample submitted in lieu of a wet-side sample bucket for a week during which no precipitation occurred

Valcode

A code which indicates whether a sample is considered valid according to NADP/NTN data validation rules. In the case of a valid sample, the code indicates how the sample is used in calculations of weighted-mean concentrations, depositions and data completeness estimates.

- 0 - invalid sample
- t - valid trace sample
- d - valid dry collection period
- w - valid sample of lab type w
- wa - valid sample of lab type wa

Only samples with valcodes of w and wa are used by NADP/NTN in calculating weighted-mean concentrations and depositions.

Invalidcode

A series of codes assigned to samples which are considered invalid by NADP/NTN for the purposes of computing weighted-mean concentrations, depositions and data completeness estimates. The codes indicate the reasons for invalidation.

- b - bulk sample (Collector was open continuously.)
- u - undefined sample (Collector was open for > 6 hours and less than the entire sampling interval when no precipitation was occurring.)
- f - field protocol departure
- c - contaminated sample
- v - inadequate volume for analysis
- e - extended sampling interval (> 8 days)
- l - lab error
- i - incomplete chemical analyses
- n - no sample collected
- p - precipitation amount unknown
- x - reasons other than described above

Notes

Coded summary of the CAL screening codes and remarks written on the Field Observer Report form by field personnel, CAL staff and Coordination Office staff.

- bu - bulk sample. Sample was continuously exposed to both wetfall and dryfall. (Collector was open continuously.)
- na - Results are not yet available (predominantly dry samples).
- nn - Information was never reported and will never be available.
- ns - No chemistry data will be reported because of extreme contamination, undefined sampling protocol, leakage, loss in the mail, etc.
- sp - Sample was collected at a nonapproved sampling site or with nonapproved equipment.

*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 \pm 4.0 S/cm for conductance and 4.30 \pm 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 \pm 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.