



**Precipitation Chemistry Data  
Handling and Preparation**

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## 1.0 Introduction

The Precipitation Chemistry Data Handling and Preparation guidance outlines the best practices for compiling, verifying and analyzing precipitation chemistry laboratory results. The practices outlined in this handbook have been adopted from the Global Atmosphere Watch (GAW) manual for the GAW Precipitation Chemistry Programme. This guidance document should be used to prepare data for submission into Alberta's Ambient Air Quality Data Warehouse and the national NatChem database.

## 2.0 Merging of Field Data and Laboratory Results

The requirements for precipitation chemistry sample collection are outlined in Alberta's Air Monitoring Directive, Chapter 4 Monitoring. Field sheets will be filled out at the time of sample collection. Field information recorded for each sample include:

- (1) Station name;
- (2) Operator (name/organization and contact information);
- (3) Equipment type;
- (4) Precipitation occurrence (yes, no, uncertain);
- (5) Precipitation type (rain, snow, freezing rain, mixed and dew or frost);
- (6) Sample year;
- (7) Sample week number;
- (8) Sample start date/time;
- (9) Sample end date/time;
- (10) Equipment condition (function/malfunction);
- (11) Sample condition;
- (12) Precipitation gauge depth; and
- (13) Field comments.

Copies of the field sheet and laboratory analysis results are submitted to a designated person within the Alberta Environmental Monitoring, Evaluation and Reporting Agency (AEMERA) by the laboratory. When preparing to submit the data to either Alberta's Ambient Air Quality Data Warehouse or the national NatChem database, the information on the field sheet must be merged with the chemical data from the laboratory. This combined dataset will be used for assessing data quality. A copy of the digitized field sheet and laboratory submitted results should be archived as per the Air Monitoring Directive.

### 3.0 Data Quality Flags

When preparing precipitation chemistry data for submission, each data point must have a quality flag. Flags are used to identify the quality and validity of data. There are three classes of flags:

- V indicates valid data with quality indication where needed (see Table 1);
- M indicates missing or invalid data; and
- H indicates historical data which has not been validated.

If a data point has been found to be invalid, it must be set to -9999.9 and the flag code M2 applied when reporting the data. The laboratory reported data must be retained in its original form. A data point may be invalidated as a result of quality control checks performed in the field, the laboratory analysis or the data handling process. Table 1 provides specific descriptions of the data quality flags.

**Table 1**      **Data quality flags<sup>1</sup>**

<b>Flag Code</b>	<b>Flag Definitions</b>
V0	Valid
V2	Extreme and unusual value assessed and deemed valid
V4	Valid but does not meet quality control or statistical criteria (see Section 4.0)
V5	Valid but qualified due to possible contamination
V6	Valid but qualified due to non-standard sampling conditions
V7	Valid but value below detection limit and set equal to the reporting limit
M1	Missing because no value available
M2	Missing because the data was invalidated
H1	Historical data that has not been validated

### 4.0 Data Quality Control Checks

As part of the data handling process there are three quality control checks that must be performed on precipitation chemistry data:

- ion balance, which compares the balance between total cation concentration and anion concentration;
- comparing the measured and calculated conductivity; and
- statistical evaluation.

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<sup>1</sup> Selected from Manual for the GAW Precipitation Chemistry Programme (2004)

#### 4.1 Cation and Anion Balance

The cation and anion balance will be used to check analysis results for a sample and flag the data. The laboratory reports ion concentration in  $\mu\text{Eq L}^{-1}$ . The anions and cations reported by the laboratory are listed in Table 2. Using ion concentrations, sum of all ions (IS) is calculated as:

$$IS = \sum Ca_i + \sum An_i \quad \text{Eq 1}$$

where  $Ca_i$  and  $An_i$  are the  $i^{\text{th}}$  cation and  $i^{\text{th}}$  anion equivalent concentration ( $\mu\text{Eq L}^{-1}$ ), respectively.

The difference between cations and anions (ID) is calculated as:

$$ID = \sum Ca_i - \sum An_i \quad \text{Eq 2}$$

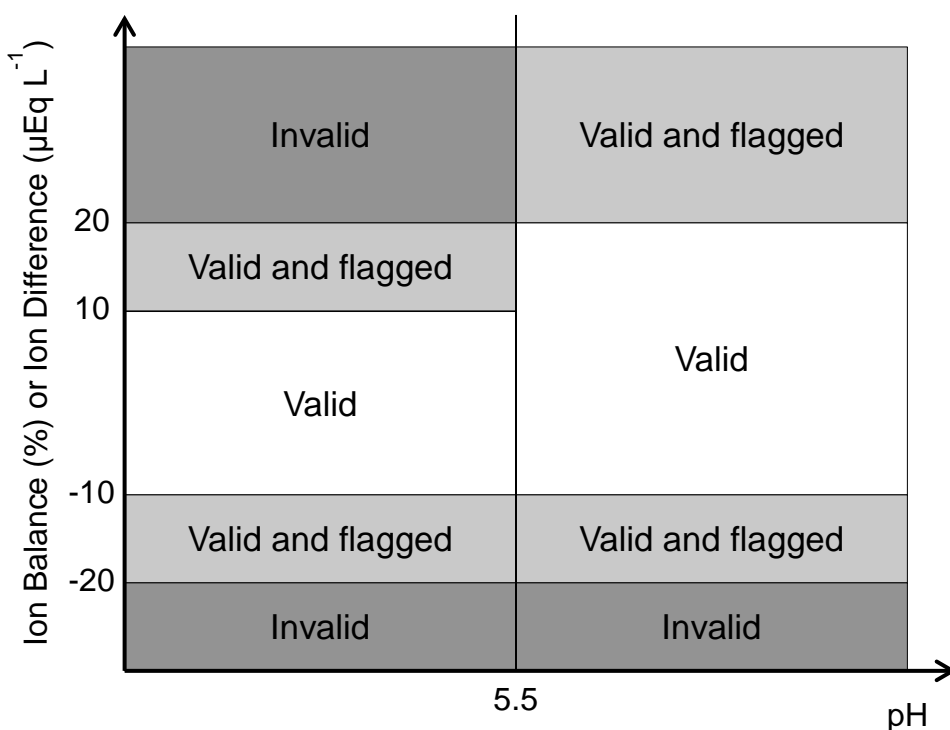
**Table 2 Laboratory reported anions and cations**

	<b>Name</b>	<b>Symbol</b>
<b>Anions</b>	chloride	$\text{Cl}^-$
	nitrate	$\text{NO}_3^-$
	orthophosphate	$\text{PO}_4^{3-}$
	sulphate	$\text{SO}_4^{2-}$
<b>Cations</b>	sodium	$\text{Na}^+$
	ammonium	$\text{NH}_4^+$
	potassium	$\text{K}^+$
	magnesium	$\text{Mg}^{2+}$
	calcium	$\text{Ca}^{2+}$

The ion balance (IB) is then calculated as a percentage using ID and IS:

$$IB = \frac{ID}{IS} \times 100 \quad \text{Eq 3}$$

For samples with ion concentration (IS)  $\geq 100 \mu\text{Eq L}^{-1}$ , IB is used to set the criteria for flagging sample data. When IS is  $< 100 \mu\text{Eq L}^{-1}$ , criteria for data flagging is based on ion difference (ID) in  $\mu\text{Eq L}^{-1}$  rather than IB. In addition, samples with pH values higher than 5.5 have an apparent deficit of anions. For this reason, a separate criteria is developed for these samples. Figure 1 summarizes criteria for using ion concentration to flag sample data. Data that fall within the invalid range will be invalidated (data point replaced by -9999.9 and the M2 data flag applied). Data that fall within the valid range will have the V4 data flag applied.



Adopted from (World Meteorological Organization Global Atmosphere Watch, 2004).

**Figure 1** Data quality criteria for ion balance (for samples with IS  $\geq 100 \mu\text{Eq L}^{-1}$ ) or ion difference (for samples with IS  $< 100 \mu\text{Eq L}^{-1}$ )

#### 4.2 Comparison of Measured and Calculated Conductivity

Measured conductivity values ( $\kappa_{\text{measured}}$ ) are reported by the laboratory in  $\mu\text{S cm}^{-1}$ . Ionic conductivity ( $\kappa$ ) is calculated as follows:

$$\kappa = \sum(C_i \times \Lambda_i^\circ) \quad \text{Eq 4}$$

where  $C_i$  is ionic concentration of the  $i^{\text{th}}$  ion in  $\text{mmol L}^{-1}$ , and  $\Lambda_i^\circ$  is the molar ionic conductance of the  $i^{\text{th}}$  ion in  $\text{S cm}^2 \text{mol}^{-1}$ . Table 3 lists molar ionic conductance for ions of interest. Ion concentrations are reported by the laboratory in  $\text{mg L}^{-1}$ . These would need to be converted to  $\text{mmol L}^{-1}$  by dividing by the molecular weight of the ion ( $\text{g/mol}$ ). pH can be used to determine hydrogen ion concentration ( $[\text{H}^+]$ ).

Calculated conductivity values are compared to measured values as follows:

$$\Delta\kappa(\%) = 100 \times \left( \frac{\kappa - \kappa_{\text{measured}}}{\kappa_{\text{measured}}} \right) \quad \text{Eq 5}$$

Table 4 lists acceptable conductivity difference; samples with  $\Delta\kappa$  values outside of the acceptable range should be flagged using the V4 flag code.

**Table 3 Molar Ionic Conductance at infinite dilution and 25°C**

Ion	Molar Ionic Conductance $\Lambda_I^\circ$ (S cm <sup>2</sup> mol <sup>-1</sup> )
H <sup>+</sup>	349.65
Cl <sup>-</sup>	76.31
NO <sub>3</sub> <sup>-</sup>	71.42
SO <sub>4</sub> <sup>2-</sup>	160.0
NH <sub>4</sub> <sup>+</sup>	73.5
Na <sup>+</sup>	50.08
K <sup>+</sup>	73.48
Mg <sup>2+</sup>	106.0
Ca <sup>2+</sup>	119.0
PO <sub>4</sub> <sup>3-</sup>	207.0

**Table 4 Acceptable conductivity difference to be used in flagging sample results**

Laboratory Measured conductivity ( $\mu\text{S cm}^{-1}$ )	Conductivity Difference $\Delta\kappa$ (%)
$\leq 5$	$\leq \pm 50$
$> 5 \leq 30$	$\leq \pm 30$
$> 30$	$\leq \pm 20$

### 4.3 Percent Total Precipitation

At collection sites where standard precipitation gauges have been installed, precipitation depth from standard gauge readings will be provided in the field sheet. As a quality assurance step, precipitation depth from a standard gauge reading at the monitoring site should be compared to depth calculated from the sample volume:

$$S_D = \frac{S_V}{\pi r^2} \times \frac{1000 \text{ mm}}{\text{ml}} \quad \text{Eq 6}$$

$S_D$  is calculated sample depth (mm) and  $S_V$  is sample volume (ml), also known as catch of collection.  $S_V$  is provided in ml by the laboratory. The radius of the sample (r) collector is known and may change over time. Percent total precipitation (TP) is calculated using the standard gauge precipitation depth ( $P$ ) and calculated sample depth is determined by:



$$TP(\%) = \frac{S_D}{P} \times 100 \quad \text{Eq 7}$$

Acceptable *TP* is  $\geq 70\%$ . Samples outside the acceptable *TP* should be flagged using the V6 flag code.

#### 4.4 Statistical Evaluation

Statistical evaluation allows for the identification of potential extreme values or erroneous data. In conducting statistical evaluation of a new data point, the reviewer needs to compare the new data to historical data collected at the site. Each ion concentration should be compared with all the data collected within the previous five years at the site. An ion concentration from a new sample that is greater than the 90<sup>th</sup> percentile of the historical value at the site should be closely examined. Notes and comments should be used to develop historical knowledge of conditions that result in typical and atypical concentrations. If an extreme data point (greater than 99<sup>th</sup> percentile) is noted but is deemed to be valid, the data point should be flagged using the V2 flag code.

### 5.0 Reporting Below Detection Values

At times, the laboratory reports contain ion concentrations that are preceded by “<”. For example, the concentration of phosphate ion may be reported as <0.015 mg L<sup>-1</sup>. This value is the reporting detection limit for that ion. The reporting detection limit is an adjusted method detection limit, based on whether the sample needs dilution for analyzing that ion. In such cases, the ion concentration in mg L<sup>-1</sup> should be set to the reporting detection limit and the data will be flagged using the V7 flag code.

#### 5.1 Precipitation Chemistry Summary

Ion concentration is reported in mg L<sup>-1</sup> for each sample and the field sheet contains information on precipitation depth. This information along with associated meta data, flags, and data quality control check values are submitted and archived in Alberta’s Ambient Air Quality Data Warehouse. In addition, a seasonal and/or annual summary of precipitation chemistry should be prepared using the ion concentrations and precipitation depth. This summary should include, but may not be limited to:

- station identification;
- station classification indicating which background stations were met or failed;
- number of valid concentration for each site;
- number of samples below detection limit for each site;
- mean ion concentration at each site;
- 10<sup>th</sup>, 50<sup>th</sup>, 90<sup>th</sup> percentile of the ion concentration at each site;

- total precipitation depth at each site;
- wet deposition of ion ( $\text{kg ha}^{-1}$ ) at each site; and
- data completeness measure, including percent precipitation coverage length and percent total precipitation.

The requirements for evaluating sampling sites against criteria for a background monitoring site are outlined in the AMD.

## 5.2 Significant Figures

The submitted ion deposition data must reflect the accuracy of the measured results. This being said, rounding off to the correct significant figures should be done after all calculations are complete.

For addition or subtraction, the number of decimal places in the resulting number should be the same as the least number of decimal places in the numbers being added (or subtracted).

E.g.,  $63 + 8.047 + 2 = 73.047$  would be reported as 73

For multiplication and division, the number of significant figures in the resulting number should be the same as the least number of significant figures in any of the operands.

E.g.,  $\frac{4.25}{0.032} = 132.8125$  would be reported as 130

## 5.3 Ion Deposition Rate

The ion deposition rate ( $D$ ) for a period is calculated using precipitation-weighted mean concentration ( $C_{pw}$ ) and total precipitation depth ( $P_{tot}$ ) (World Meteorological Organization Global Atmosphere Watch, 2004). A period could be a month, season or year.  $D$  is determined in  $\text{kg ha}^{-1}$ , therefore when using Eq 8 the appropriate unit conversion must apply:

$$D = C_{pw} \times P_{tot} \quad \text{Eq 8}$$

$C_{pw}$  is determined using valid ion concentration ( $C_i$ ) and associated precipitation depth ( $P_i$ ). Where ion concentrations are reported by the laboratory in  $\text{mgL}^{-1}$  and precipitation depth is in mm, the unit conversion would be:

$$= \frac{1\text{kg}}{10^6\text{mg}} \times \frac{1\text{L}}{10^6\text{mm}^3} \times \frac{10^{10}\text{mm}^2}{\text{ha}} = \frac{1}{100}$$

$$C_{pw} = \sum_{i=1}^m (C_i \times P_i) / P_{tot} \quad \text{Eq 9}$$

where  $m$  is the total number of valid samples.

Total precipitation for the period is calculated as:

$$P_{tot} = \sum_{i=1}^n P_i \quad \text{Eq 10}$$

where  $n$  is the total number of samples including missing and invalid concentrations, thus  $n > m$ . When there are no missing or invalid concentrations  $n$  is equal to  $m$ , and as a result the following applies:

$$D = \begin{cases} C_{pw} \times P_{tot}, & \text{if } n > m \\ \sum_{i=1}^n C_i \times P_{tot}, & \text{if } n = m \end{cases} \quad \text{Eq 11}$$

#### 5.4 Data Completeness Measure

For each summary period Percent Total Precipitation (%TP) and Percent Precipitation Coverage Length (%PCL) should be indicated.

%TP is the percent of the total precipitation depth associated with valid precipitation chemistry for the summary period. This should be calculated for each ion. If the total precipitation depth is 1000 mm, but valid ionic concentration was only available for 800 mm then %TP is calculated as  $(800/1000) \times 100 = 80\%$ .

%PCL is calculated as the number of sample weeks for which the precipitation gauge was operational over the total number of sample weeks for the summary period. If the gauge was not operational for 2 of the 52 sample weeks then  $\%PCL = (50/52) \times 100 = 96\%$ .

## 6.0 References

World Meteorological Organization Global Atmosphere Watch. (2004). *Manual for GAW Precipitation Chemistry Program*.