1. INTRODUCTION

This document provides guidance for Global Atmosphere Watch (GAW) precipitation chemistry and deposition measurements. It describes standard operating procedures and provides guidelines on methods and procedures. Chapter 1 describes the background and goals of GAW precipitation chemistry and deposition measurements and describes data quality objectives for these measurements. The chapter ends with an outline of the document.

1.1 Background

Atmospheric deposition occurs as manmade and naturally occurring gases and particles are removed from the atmosphere and deposited on the surface of the earth. When associated with precipitation, it is defined as wet deposition. Precipitation (AMS, 2000) includes any product of the condensation of atmospheric water vapor that falls under gravity. Among the forms of precipitation are rain, snow, sleet, hail, and graupel. Other forms of wet deposition occur when fog impacts the surface or when dew settles on the surface, though gravity alone does not govern these forms of deposition. All other forms of deposition are defined as dry deposition. Total atmospheric deposition encompasses the combination of wet and dry deposition. This manual focuses on wet deposition and exclusively on how to make representative measurements of the amount and chemistry of precipitation. Fog and dew are not addressed.

The Global Atmosphere Watch (GAW) identifies atmospheric deposition as “a major environmental issue due to concerns over acidification and eutrophication of natural ecosystems, bioaccumulation of toxics and metals, impacts on biogeochemical cycling and biodiversity, human health, and global climate change”. These issues continue to grow in importance as an increasing world population accompanied by the demand for goods and services compete with requirements for food and energy security. Many of the effects of atmospheric deposition are related to combustion products, especially sulfur and nitrogen compounds emitted during energy production, land and sea vehicular transportation, industrial production, crop production, and animal husbandry. Sea salt, too, is an important source of sulfur and other major ions in coastal areas. It also is important to measure base cations to evaluate fully the potential for acidic deposition to exceed the amount that an ecosystem sensitive to acidification can withstand without leading to long-term harmful effects. Concerns over climate change, health effects, and biogeochemical cycling have broadened the set of pollutants of concern to include, among others, black carbon, carbon compounds, phosphorus, mercury, and other toxics and metals.

Background information on documented environmental effects of atmospheric deposition is summarized in the introduction to a global assessment of precipitation chemistry and deposition (Vet, etal. 2014), which was produced by an international team of 21 scientists under the auspices of the GAW Science Advisory Group for Precipitation Chemistry (SAG-PC), now the SAG for Total Atmospheric Deposition. The goal of the assessment was to provide the international science and policy communities with the best available data and information on regionally-representative precipitation chemistry and atmospheric deposition. The assessment features figures, tables, and maps that address the spatial distribution and temporal trends of atmospheric deposition on a global scale. Where the geographic coverage of measurements was too sparse, maps were generated from a combination of measurements and model estimates. A major product of the assessment was the preparation of data sets of quality-assured ion concentrations and wet deposition, dry deposition estimates, and model results. The assessment data sets can be accessed via the World Data Centre for Precipitation Chemistry website. Figure 1 is a map of station locations used in this assessment.

The assessment identified some important needs for wet deposition measurements and monitoring:

(1) commitment to long-term, regionally representative measurements of all major ions to enable a comprehensive assessment of spatial and temporal trends around the globe;

(2) increased geographic coverage of deposition measurements in data sparse areas such as South America, much of Africa, Asia, and Oceania, and parts of North America;

(3) expansion of measurement programs to include total nitrogen (inorganic and organic nitrogen), total phosphorus (orthophosphate, hydrolysable and organic phosphorus), and organic acids (formate, acetate, oxalate); and
(4) adoption of standardized methods of sample collection and chemical analysis with an emphasis on acceptable data quality objectives.

This manual focuses on standard methods for collecting representative precipitation samples, for handling, storage, and chemical analysis of samples, for quality assurance // quality control, and for managing the data.

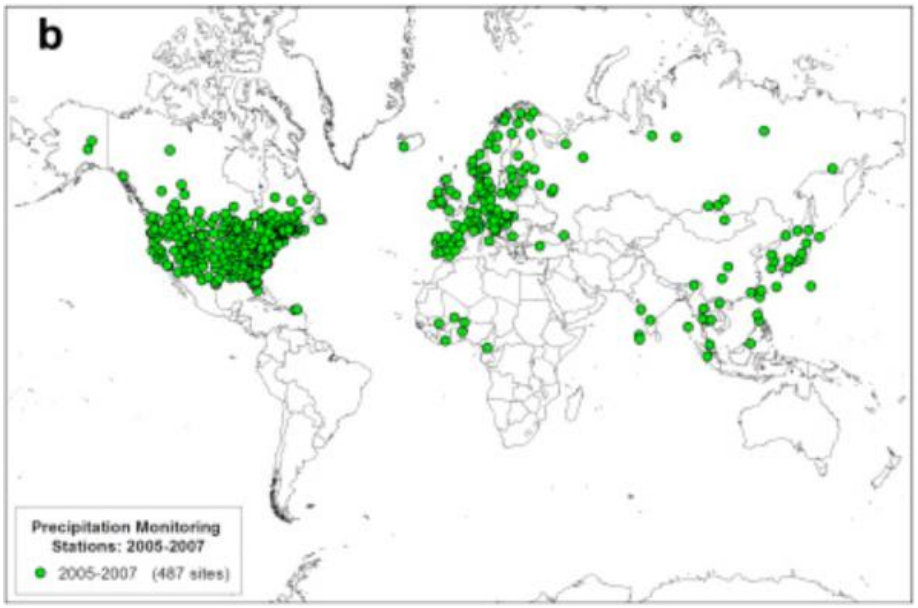

Figure 1. Precipitation monitoring stations with 2005-2007 data used in the global assessment.

Links to general information:

(1) ***World Meteorological Organization*** ***(https://public.wmo.int/en)***
(2) ***Global Atmosphere Watch*** ***(https://public.wmo.int/en/programmes/global-atmosphere-watch-programme)***
(3) ***GAW Station Information System*** ***(https://gawsis.meteoswiss.ch/GAWSIS/index.html#/)***
(4) ***GAW Total Atmospheric Deposition Programme*** **(https://community.wmo.int/activity-areas/gaw/science/total-atmospheric-deposition)**
(5) **Quality Assurance Science Activity Centre – Americas** **(http://www.qasac-americas.org/)**
(6) ***World Data Centre for Precipitation Chemistry*** **(http://wdcpc.org/)**
(7) ***Global Assessment of Precipitation Chemistry and Deposition*** ***(http://wdcpc.org/global-assessment-data)***
(a) ***Journal article*** ***https://www.sciencedirect.com/science/article/pii/S1352231013008133?via%3Dihub***
(b) ***Assessment Data Sets*** ***(http://wdcpc.org/global-assessment-data).***

1.2 Goals of GAW Precipitation Chemistry and Deposition Measurements

Operations

- Harmonize precipitation chemistry and deposition measurements conducted by GAW global, regional, local, and contributing networks by promoting
  (1) implementation of data quality objectives,
  (2) utilization of standard operating procedures and guidelines for collecting, handling, and chemically analyzing precipitation samples, and
  (3) application of quality control/quality assurance and data management practices
  presented in this document.
- Encourage participation in the semiannual Inter-laboratory Comparison Studies conducted by the Quality Assurance Science Activity Centre.
- Encourage the archival and dissemination of precipitation chemistry and deposition data via the World Data Centre for Precipitation Chemistry.
- Continue to encourage the commitment to long-term, regionally representative measurements of all major ions.
- Assist with the implementation of new sites, especially in data sparse and poorly represented areas and provide training and capacity building opportunities.
- Explore new data products and ways to facilitate data usage.

Organization

- Seek linkages with other GAW measurement programmes.
- Seek to facilitate joint efforts to measure gas and aerosol species in support of making dry deposition estimates.
- Promote the use of precipitation chemistry and deposition data among users in the scientific, educational, regulatory, and planning communities.

Research Support

- Facilitate scientific assessments of atmospheric deposition, especially the quantification of deposition patterns and trends on global and regional scales.
- Provide data for evaluating the effects of atmospheric deposition in major ecosystems, such as coastal and sensitive areas, and for developing control measures.
- Provide data for evaluating models and measurement-model fusion methodologies.
- Encourage the measurement of chemicals that currently do not have a measurement requirement but are of scientific interest, examples include total nitrogen, total phosphorus, organic acids, mercury, black carbon, carbon compounds, toxics, and other persistent organic pollutants.

Table 1. Chemical measurements addressed by these guidelines (See Laboratory Operations).

Analyte	Status	Preferred Methods	Alternate
sulfate, nitrate, chloride	Required	ion chromatography (IC)	
ammonium	Required	flow injection analysis (FIA)	IC
calcium, magnesium, sodium, potassium	Required	inductively coupled plasma – atomic emission spectroscopy	IC, flame atomic Absorption
pH	Required	electrode	
conductivity	Required	conductivity cell	
hydrogen carbonate	Required	IC (recommended for pH > 6)	calculate from pH
total nitrogen	Optional	FIA - digestion	
total phosphorus	Optional	FIA - digestion	
organic acids	Optional	IC	ion exclusion chromatography.

1.2.1 Data Quality Objectives

Data Quality Objectives (DQOs) are the cornerstone for establishing and maintaining the quality of a measurement system. DQOs are statements of the overall uncertainty that is acceptable if the data are to meet the objectives of the measurement system.

The DQOs for GAW precipitation chemistry measurements are listed in Table A.1. Decades of experience in measuring and statistically analyzing precipitation chemistry have helped to develop the form and value of these DQOs. **It is the responsibility of every participating organization to review Table A.1 and adjust their GAW precipitation chemistry measurement programme to meet or exceed the DQOs listed there.** Further discussion of DQOs is found in Chapter 6. A detailed description of how the DQOs were established and how participating organizations can calculate their own data quality indicators for comparison to the DQOs is given in Appendix A.

1.3 This Document

This document describes operational objectives, station siting requirements, field and laboratory operating procedures, data management, and quality assurance for GAW precipitation chemistry and deposition measurements. The sections are designed with the intent of promoting the use of up-to-date measurement methods, high level quality assurance and quality control procedures, proven instrumentation, and consistent laboratory techniques. A **Glossary** defines abbreviations, units of measure, and common terms. **References** are included in each section. **Appendices** provide detailed materials and are an integral part of the document.

This document is organized as follows:

1. **Introduction**
- Background
- Goals of GAW Precipitation Chemistry and Deposition Measurements
- Data Quality Objectives

2. **Siting**
- Siting considerations and requirements
- Global and regional sites
- Site documentation

3. **Field Protocols**
- Sample collection and site facilities
- Field instrumentation and routine checks and maintenance
- Accepted sampling periods
- Sample preservation, handling, and shipping
- Field blanks
- Sample documentation

4. **Laboratory Operations**
- Overview, including list of analytes and preferred methods
- Data Quality Objectives
- Quality Assurance / Quality Control (QA/QC) Activities: instrument calibration, QC solutions, control charting, replicate analyses, deionized water, blind samples, dilution checks, standard & certified reference materials, inter-laboratory comparisons, QA reporting, data verification & reporting, inventory management & control, personnel & training, safety, audits
- Sample Handling
- Analytical Measurement Procedures: pH, conductivity, chloride, nitrate, sulfate, hydrogen carbonate, carboxylic acids, calcium, magnesium, sodium, potassium, ammonium, total phosphorus, total nitrogen

5. Data Management

- Data collection, reporting, merging, and formatting
- Submission to the QA/SAC Americas, QA/SAC Americas data quality assurance procedures
- Data quality assurance
- Data analysis
- Data archiving and distribution

6. Quality Assurance and Quality Control

- The objectives of QA/QC
- Data Quality Objectives
- Overarching aspects of QA/QC for siting, field, laboratory, and data

APPENDIX A. Data Quality Objectives and Assessment

APPENDIX B. Site Description Forms

APPENDIX C. Preparation of Quality Control Solutions

APPENDIX D. Resources for Consensus Standards and Certified Reference Materials

APPENDIX G. Station Registration Forms

APPENDIX H. Non-Sea-Salt Sulphate Correction Algorithm

References

American Meteorological Society. (2000). Glossary of Meteorology (second edition). Retrieved from http://amsglossary.allenpress.com/glossary/search?id=precipitation1.

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