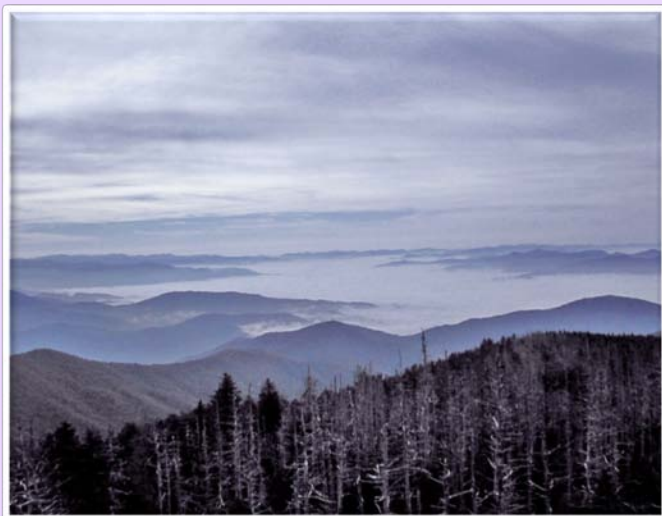


# Cloud Deposition Monitoring, Clingmans Dome, TN

## Great Smoky Mountains National Park - 2009



**U.S. Environmental Protection Agency  
Clean Air Markets Division  
Office of Air and Radiation  
Washington, DC**



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**Cloud Deposition Monitoring  
Clingmans Dome, TN  
Great Smoky Mountains National Park  
2009**

**Prepared for:**

U.S. Environmental Protection Agency  
Clean Air Markets Division  
Office of Air and Radiation  
Washington, DC

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## List of Acronyms and Abbreviations

°C	degrees Celsius
Ca <sup>2+</sup>	calcium ion
CAAA	Clean Air Act Amendments
CAIR	Clean Air Interstate Rule
Campbell	Campbell Scientific, Inc.
CASTNET	Clean Air Status and Trends Network
CLOUD	cloud water deposition computer model
Cl <sup>-</sup>	chloride ion
CLD303	Clingmans Dome, TN sampling site
cm	centimeter
cm/s	centimeters per second
CCV	continuing calibration verification spikes
DAS	data acquisition system
EGU	electric generating unit
Element	Element DataSystem
EPA	U.S. Environmental Protection Agency
g/cm <sup>2</sup> /min	grams per square centimeter per minute
g/m <sup>3</sup>	grams per cubic meter
GRS420	Great Smoky Mountains National Park, TN dry deposition sampling site
H <sup>+</sup>	hydrogen ion
HNO <sub>3</sub>	nitric acid
IC	ion chromatography
ICP-AES	inductively coupled argon plasma - atomic emission spectrometer
IP	Internet protocol
K <sup>+</sup>	potassium ion
K <sub>2</sub> CO <sub>3</sub>	potassium carbonate
kg/ha	kilograms per hectare
Lpm	liters per minute
LWC	liquid water content
m	meters
m/sec	meters per second
MACTEC	MACTEC Engineering and Consulting, Inc.
MADPro	Mountain Acid Deposition Program
MCCP	Mountain Cloud Chemistry Program
Mg <sup>2+</sup>	magnesium ion
mL	milliliter
MLM	Multi-Layer Model dry deposition computer model
mm	millimeter

## List of Acronyms and Abbreviations (continued)

N	nitrogen
Na <sup>+</sup>	sodium ion
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NAPAP	National Acid Precipitation Assessment Program
NBP	NO <sub>x</sub> Budget Trading Program
NH <sub>4</sub> <sup>+</sup>	ammonium ion
NIST	National Institute for Standards and Technology
NO <sub>3</sub> <sup>-</sup>	nitrate ion
NO <sub>x</sub>	oxides of nitrogen
NPS	National Park Service
OTC	Ozone Transport Commission
pH	p(otential of) H(ydrogen)
PVM	particle volume monitor
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RPD	relative percent difference
S	sulfur
SIP	State Implementation Plan
SO <sub>4</sub> <sup>2-</sup>	sulfate ion
SO <sub>2</sub>	sulfur dioxide
SOP	standard operating procedure
SSRF	Site Status Report Form
TN11	Elkmont, TN NADP/NTN wet deposition sampling site
TVA	Tennessee Valley Authority
µeq/L	microequivalents per liter
µg/filter	micrograms per filter
µg/m <sup>3</sup>	micrograms per cubic meter

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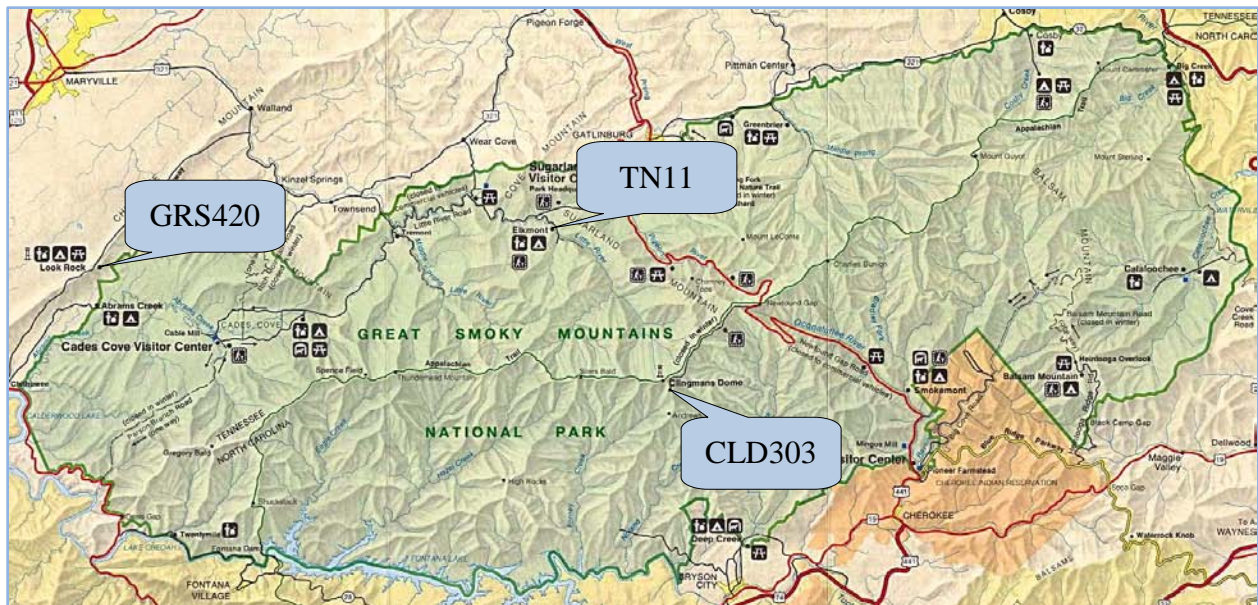
## 1.0 Introduction

The 1990 Clean Air Act Amendments (CAAA) established the Acid Rain Program, which mandated significant reductions in sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) emissions from electric generating units (EGUs). The SO<sub>2</sub> emission reductions were implemented in two phases. The first phase began in 1995 when large electric generating facilities reduced emissions. The second phase began in 2000 and targeted other power plants. More recent NO<sub>x</sub> emission control programs also produced substantive declines in NO<sub>x</sub> emissions in the eastern United States. These programs include the Ozone Transport Commission (OTC) NO<sub>x</sub> Budget (1999–2002) and the NO<sub>x</sub> State Implementation Plan (SIP) Call/NO<sub>x</sub> Budget Trading Program (NBP), which operated from 2003 through 2008. The NBP placed a cap on total NO<sub>x</sub> emissions from EGUs in the eastern United States during the ozone season (May 1 through September 30) when the potential for ozone formation is high. The Clean Air Interstate Rule (CAIR), which was issued in March 2005, aimed to permanently lower SO<sub>2</sub> and NO<sub>x</sub> emissions in the eastern United States. CAIR, as promulgated, established three compliance programs: an annual NO<sub>x</sub> program, an ozone season NO<sub>x</sub> program, and an annual SO<sub>2</sub> program. Although CAIR was remanded back to the U.S. Environmental Protection Agency (EPA) in 2008, these programs remain in effect while EPA works to develop a replacement rule. The first phase of the annual and ozone season NO<sub>x</sub> requirements began in 2009. The SO<sub>2</sub> requirements will begin in 2010.

Titles IV and IX of the CAAA require that the environmental effectiveness of the Acid Rain Program be assessed through environmental monitoring. This monitoring is required to gauge the impact of emission reductions on air pollution, atmospheric deposition, and the health of affected human populations and ecosystems. The Clean Air Status and Trends Network (CASTNET) was established by EPA in 1991 to provide an effective monitoring and assessment network for determining the status and trends in air quality and pollutant deposition, as well as relationships among emissions, air quality, deposition, and ecological effects. CASTNET measurements collected over the period 1990 through 2008 (MACTEC, 2010a) have shown significant declines in atmospheric sulfur pollutants [SO<sub>2</sub> and particulate sulfate (SO<sub>4</sub><sup>2-</sup>)] and more recently, declines in nitrogen pollutants [nitric acid (HNO<sub>3</sub>) and particulate nitrate (NO<sub>3</sub><sup>-</sup>)]. The Mountain Acid Deposition Program (MADPro) was initiated in 1993 as part of the research necessary to support CASTNET's objectives. MACTEC Engineering and Consulting, Inc. (MACTEC) operates both CASTNET and MADPro on behalf of EPA and other agencies.

MADPro's two main objectives are to develop cloud water measurement systems to be used in a network-monitoring environment and to update the cloud water concentration and deposition data collected in the Appalachian Mountains during the National Acid Precipitation Assessment Program (NAPAP) in the 1980s. MADPro measurements were conducted from 1994 through 1999 during the warm season (May through October) at three mountaintop sampling stations. These sampling stations were located at Whiteface Mountain, NY; Clingmans Dome, TN; and Whitetop Mountain, VA. A mobile manual sampling station also was operated at two locations

in the Catskill Mountains in New York during 1995, 1997, and 1998. Measurements during the 2000 and 2001 sampling seasons were collected from two sites: Whiteface Mountain, NY and Clingmans Dome, TN. During the 2002 through 2007 sampling seasons, measurements were collected from only the one site at Clingmans Dome, TN (CLD303). The project was not funded in 2008; therefore, the CLD303 site did not operate. For the 2009 sampling season, CLD303 was operated under the direction and funding of EPA and the Tennessee Valley Authority (TVA) with infrastructure support provided by the National Park Service (NPS). This report is specifically for the activities and results from the CLD303 site during the 2009 field sampling season.



For 2009, cloud water and meteorological data were measured at the CLD303 site. Atmospheric pollutant concentrations for estimating dry deposition were obtained from the nearest CASTNET site (GRS420, TN). Wet deposition data were obtained from Elkmont, TN (TN11), which is operated by NPS for the National Atmospheric Deposition Program / National Trends Network (NADP/NTN).

## 2.0 Site Description and Methods

### 2.1 Site Description

Clingmans Dome (35°33'47"N, 83°29'55"W) is the highest mountain [summit 2,025 meters (m)] in the Great Smoky Mountains National Park. The solar-powered MADPro site is situated at an elevation of 2,014 m approximately 100 m southeast of the summit tourist observation tower. Electronic instrumentation is housed in a small NPS building, and the cloud water collector, particle volume monitor (PVM), and meteorological sensors are positioned on top of a 50-foot scaffold tower.

Collection at the site is initiated each spring as soon as local weather conditions allow. In 2009, the site was installed during the third week of May, but because of equipment problems, the site was not fully operational until June 3. Sampling then continued through October 28, 2009.

### 2.2 Field Operations

The site collects cloud water samples and measures those meteorological parameters necessary for operation of the automated cloud collection system and PVM. The cloud collection system consists of an automated cloud water collector for bulk cloud water sampling, a PVM for continuous determination of cloud liquid water content (LWC), and a data acquisition system (DAS) for collection and storage of electronic information from the various monitors and sensors. The DAS was upgraded in 2009 with a Campbell Scientific, Inc. (Campbell) data logger fitted with a relay bank to control the various mechanical functions and monitor the status of all components of the cloud water collector. Continuous measurements of wind speed, wind direction, temperature, solar radiation, relative humidity, wetness, and precipitation were collected through 2004. Beginning in 2005, only those sensors essential for the operation of the cloud collector (namely, temperature and precipitation sensors, and a rain gauge) were deployed. Other meteorological data required for calculation of cloud deposition estimates (scalar wind speed) were obtained from the NPS instruments situated on a tower located next to the cloud collection tower. Prior to 2005, the site deployed the same 3-stage filter pack system for dry deposition estimation that is used at all CASTNET sites. Starting in 2005, these data were obtained from the Great Smoky Mountains National Park, TN, CASTNET site (GRS420), which is located 26 miles west, northwest of the Clingmans Dome cloud water sampling site.

The core of the automated cloud collection system is a passive string collector previously used in the Mountain Cloud Chemistry Program (MCCP) study. Collection occurs when ambient winds transport cloud water droplets onto 0.4-millimeter (mm) Teflon fibers strung between two circular disks (Falconer and Falconer, 1980; Mohnen and Kadlec, 1989). Once impacted, the droplets slide down the strings, are collected into a funnel, and flow through Teflon tubing into a tipping bucket for sample volume determination and then into sample collection bottles housed in an enclosure. The development and design of the original system is described in detail in Baumgardner *et al.* (1997).

The PVM-100 by Gerber Scientific (Gerber, 1984) measures LWC and effective droplet radius of ambient clouds by directing a diode-emitted 780-nanometer wavelength laser beam along a 40-centimeter (cm) path. The forward scatter of the cloud droplets in the open air along the path is measured, translated, and expressed as water in grams per cubic meter ( $\text{g/m}^3$ ) of air. The data logger is programmed so that the collector will be activated and projected out of the protective housing when threshold levels for LWC ( $0.05 \text{ g/m}^3$ ) and ambient air temperature [ $\geq 2$  degrees Celsius ( $^{\circ}\text{C}$ )] are reached. In addition, the system is activated only when no precipitation is measured. Within the context of MADPro, a cloud is defined by a LWC of  $0.05 \text{ g/m}^3$  or higher, as measured by the PVM. This threshold was established to maintain comparability with the MCCP measurements, which were made for the most part with Mallant



Particle Volume Monitor

Optical Cloud Detectors set at a threshold of approximately  $0.04 \text{ g/m}^3$  (Mohnen *et al.*, 1990). In previous years, a wind speed threshold of 2.5 meters per second (m/sec) was also used because hourly cloud water collection is erratic and inefficient at lower wind speeds. Higher wind speeds were necessary to yield the minimum 30 milliliters (mL) of cloud water required for sample analysis. Since the commencement of 24-hour bulk sampling in 2000, however, the collection of at least 30 mL of sample has not been an issue. Therefore, the wind speed threshold criterion was eliminated starting in 2004. The temperature limit serves to protect against damage from rime ice formation. The absence of rainfall is required because within the objectives of this study, as well as MCCP, only samples from non-precipitating clouds are collected. If a rain detector is activated, the string collector will retract into the protective case and collection will be suspended.

Beginning with the 1999 field season, a modified automated cloud collector has been used. The collector was modified by switching from an electrical to a pneumatic system to send the collector up and down. This collector measures and accumulates the cloud sample using a funnel positioned under a tipping bucket that is hooked up to the cloud collector with Teflon tubing. In 2004, the tipping bucket was removed from the cloud collection system, as it was no longer necessary to track hourly collection volumes. In 2009, the tipping bucket was reintegrated into the system for determination of total sample volume. The tipping bucket provides an accurate means of determining sample volume and eliminates the need to manually determine

this important parameter. Modifications made to the cloud collection system during 2009 included:

- upgrading the communication system to conform with the Federal Communications Commission's mandated transition from analog to digital communication
- installing a Campbell data logger
- incorporating a tipping bucket into the sampling stream for determination of sample volume
- installing a pressure transducer for monitoring the air tank pressure
- installing a new optical rain detector
- reconfiguring and installing new control boxes to house the DAS and communications system, as well as the valve system for directing the flow of cloud water
- installing additional collection bottles
- upgrading the electrical and plumbing systems
- automating the cloud water rinse mechanism

The PVM is operated continuously. Consequently, collection of cloud samples only when the threshold criteria are met does not result in the loss of cloud frequency and cloud duration information. All LWC values of  $0.05 \text{ g/m}^3$  or greater, independent of the type of cloud (i.e., precipitating or non-precipitating), are used to calculate cloud frequency and cloud duration information. It is possible that the cloud deposition estimates presented later in Section 4.0 may underestimate actual cloud deposition because clouds are not sampled when precipitating. However, the bias due to this lack of sampling during a precipitation event is offset by the fact that cloud deposition totals are estimated by multiplying the duration-weighted mean chemical fluxes by the cloud hours for the month. The cloud hours are calculated as the cloud frequency times the total hours in the month.

The site operator gathers cloud water samples from the collector at least twice a week, whether or not collection has occurred. The time, date, and volume of each 24-hour bulk sample are recorded on the Cloud Water Sample Report Form. Each sample is then carefully decanted into one pre-cleaned 250-mL sample bottle. Excess sample volume is discarded. The sample date and time are recorded on the 250-mL sample bottle label. The site operator analyzes each sample for pH and conductivity and records the results on the Cloud Water Sample Report Form. The samples are then packed into coolers with the corresponding form and shipped to the CASTNET laboratory in Gainesville, FL. Periodically, selected rinse samples are included in shipments. Starting in 2005, some of the 24-hour samples shipped from the field were bulked together in the MACTEC laboratory in order to keep the number of samples analyzed by the laboratory within the number of samples allotted for analysis in the budget. In 2009, 57 of the 24-hour samples collected between June 20 and September 30 were combined into 20 bulk samples.

Filter packs for collection of dry deposition samples at the nearby GRS420 site are prepared and shipped to the field on a weekly basis and exchanged at the site every Tuesday. For a description of the filter pack set-up, types of filters used, and the fraction collected on each filter, refer to the CASTNET Quality Assurance Project Plan (QAPP) (MACTEC, 2008). A discussion of filter pack sampling artifacts can be found in Anlauf *et al.* (1986) and Lavery *et al.* (2007). Filter pack flow is maintained at 3.0 liters per minute (Lpm) with a mass flow controller. All field equipment received start-up and end-of-season calibrations. Calibration checks of the PVM were scheduled to be performed biweekly (weather permitting) throughout the field season. The results were used to adjust the instrument immediately after the calibration check. Calibrations on the remaining instruments were conducted using standards traceable to the National Institute for Standards and Technology (NIST). The calibrations at the beginning and end of the 2009 field season were within the control limits stated in the CASTNET QAPP (MACTEC, 2008).

### 2.3 Laboratory Operations

Cloud water samples and filter extracts were stored at 4 °C until analysis. All analyses were performed within 30 days of sample receipt at the laboratory. The effects of storage on wet deposition samples have been addressed in NAPAP Report #6 (Sisterson *et al.*, 1991). This discussion applies, for the most part, to cloud water samples as well. Results of all valid filter pack and cloud water analyses are stored in the laboratory data management system, Element DataSystem (Element).

Cloud water samples for the 2009 sampling season were analyzed for sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), ammonium ( $\text{NH}_4^+$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), chloride ( $\text{Cl}^-$ ),  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  ions in the CASTNET laboratory. pH and conductivity were analyzed in the field through July 23, 2009. No additional pH analyses were conducted in the field after this date due to problems with the pH probe. All samples were analyzed for pH and conductivity in the MACTEC Gainesville laboratory for comparison with the field values.

Concentrations of the three anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) were determined by micromembrane-suppressed ion chromatography (IC). Analysis of samples for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  was performed with a Perkin-Elmer Optima 3000 DV inductively coupled argon plasma-atomic emission spectrometer (ICP-AES). The automated indophenol method using a Bran+Luebbe Autoanalyzer 3 was used to determine  $\text{NH}_4^+$  concentrations. The 2009 hydrogen ( $\text{H}^+$ ) ion concentrations for each sample were determined based on laboratory pH measurements.

Filter pack samples were loaded, shipped, received, extracted, and analyzed at the CASTNET laboratory. For specific extraction procedures refer to Anlauf *et al.* (1986) and the CASTNET QAPP (MACTEC, 2008). Filter packs contain three filter types in sequence: a Teflon filter for collection of aerosols, a nylon filter for collection of  $\text{HNO}_3$  and  $\text{SO}_2$ , and dual potassium carbonate ( $\text{K}_2\text{CO}_3$ )-impregnated cellulose filters for collection of  $\text{SO}_2$ . Following receipt from the

field, exposed filters and unexposed blanks were extracted and analyzed for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and the cations,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ , as described previously for cloud water samples. Refer to the CASTNET QAPP (MACTEC, 2008) for detailed descriptions of laboratory receipt, breakdown, storage, extraction, and analytical procedures.

Atmospheric concentrations derived from filter extracts are calculated based on the volume of air sampled following validation of the hourly flow data. Atmospheric concentrations of particulate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  are calculated based on analysis of Teflon filter extracts;  $\text{HNO}_3$  is calculated based on the  $\text{NO}_3^-$  found in the nylon filter extracts; some  $\text{SO}_2$  is trapped by the nylon filter, so  $\text{SO}_2$  is calculated based on the sum of  $\text{SO}_4^{2-}$  found in nylon and cellulose filter extracts.

## 2.4 Data Management

Continuous data (temperature, precipitation, LWC, and cloud collector status information) are collected in hourly and 5-minute averages. Hourly data are collected daily via Internet protocol (IP)-based polling. The polling software also recovers status files and power failure logs from the previous seven days. The hourly data and associated status flags are ingested into Microsoft Excel spreadsheets. The continuous data are validated based on the end-of-season calibration results, periodic calibration check results (PVM only), and information provided by status flags and logbook entries.

Discrete data for cloud water sample results and filter pack sample results are managed by Element. In Element, the analytical batches are processed through an automated quality control (QC) check routine. For each analytical batch, an alarm flag is generated if any of the following occur:

- Insufficient QC data were run for the batch;
- Sample response exceeded the maximum standard response in the standard curve (i.e., sample required dilution);
- Continuing calibration verification (CCV) spikes exceeded recovery limits; or
- Reference samples exceeded accuracy acceptance limits.

A batch with one or more flags is accepted only if written justification is provided by the Laboratory Operations Manager.

For cloud water samples an additional check involves calculating the percent difference of cations versus anions (ion balance), and provides another diagnostic for determining whether the analysis should be repeated or verified.

Atmospheric concentrations for filter pack samples are calculated by merging validated continuous flow data with the laboratory data [micrograms per filter ( $\mu\text{g}/\text{filter}$ )].

## **2.5 Quality Assurance**

The quality assurance (QA) program consists of the same routine audits performed for CASTNET, if applicable, and testing/comparison of instruments unique to cloud water sampling. QA procedures are documented in greater detail in the MADPro Quality Assurance Plan, which is an appendix to the CASTNET QAPP (MACTEC, 2008). The sections below provide a brief description of those procedures.

### **2.5.1 Field Data Audits**

The following audits are conducted for field data:

- Review of all reported problems with sensors and equipment at the site and of the actions taken to solve such problems.
- Review of calibration files for completeness and adherence to standard operating procedures (SOP). Certification results for transfer standards are also reviewed, and transfer sensor serial numbers are cross-referenced with the transfer sensor serial numbers on the calibration forms.
- Comparison of final validated data tables to the raw data tables for identification and verification of all changes made to the data. Summary statistics and results of diagnostic tests for assessment of data accuracy are also reviewed.

### **2.5.2 Laboratory Data Audits**

Laboratory data audits consist of:

- Review of all media acceptance test results,
- Review of chain-of-custody documentation, and
- Review of all QC sample results associated with analytical batches.

### **2.5.3 Precision and Accuracy**

With the exception of the automated cloud collector and PVM, accuracy of field measurements (i.e., meteorological instruments used in conjunction with the cloud collection system and PVM) is determined by challenging instruments with standards that are traceable to NIST. Continuing accuracy is verified by end-of-season calibrations by MACTEC personnel. No certified standards are currently available for determination of cloud collector and the PVM accuracy on a routine basis. Overall precision of field measurements is best determined by collocating instruments and assessing the difference between simultaneous measurements. Even though collocated dry deposition and meteorological sampling is not conducted at the CLD303 site, it is conducted at two other nearby CASTNET sites. Since the meteorological instrumentation on the CLD303 tower is identical to that used at CASTNET sites, precision of these instruments can be inferred from the precision and accuracy results presented in the CASTNET Quarterly QA Reports (e.g., MACTEC, 2010b) and the CASTNET annual reports for 1998 through 2008, the four most recent of which can be found on EPA's Web site: <http://www.epa.gov/castnet/docs.html>.

Accuracy of laboratory measurements is determined by analyzing an independently prepared reference sample in each batch and calculating the percent recovery relative to the target value.



The percent recovery is expected to meet or exceed the acceptance criteria listed in the CASTNET QAPP (MACTEC, 2008). When possible, the references are traceable to NIST or obtained directly from NIST. On occasion, references are ordered from other laboratories.

Analytical precision within sample batches is assessed by calculating the relative percent difference (RPD) and percent recovery of CCV run within that batch. CCV are independently produced standards that approximate the midpoint of the analytical range for an analyte and are run after every tenth environmental sample. Precision within a batch is also assessed by replicating 5 percent of the samples within a run. Replicated samples are selected randomly.



Cloud Water Collector



Collector in Up Position



3-Stage Filter Pack

### 3.0 Liquid Water Content and Cloud Water Chemistry

#### 3.1 Cloud Frequency and Mean Liquid Water Content

Monthly mean cloud frequencies by year from 1994 through 2007 and 2009 are summarized in Table 3-1. Monthly mean, minimum, and maximum cloud frequency statistics are also depicted as a bar chart in Figure 3-1. Monthly mean cloud frequency values for 2009 versus the historical monthly means (1994–2007) are shown in Figure 3-2. Monthly cloud frequencies were determined by calculating the relative percent of all hourly LWC values equal to or greater than  $0.05 \text{ g/m}^3$ , or:

$$CF = \frac{100 * (\# \text{ of valid hourly LWC values } \geq 0.05 \text{ g / m}^3)}{n}$$

where:  $n$  is the number of valid hourly LWC values per month and

$CF$  is cloud frequency

Any month with less than 70 percent valid LWC data is usually not considered representative of the monthly weather conditions for that month. Cloud frequencies vary from month to month, year to year, and from location to location. As can be seen from Figure 3-2, the monthly cloud frequencies for 2009 were higher than the historical means. The July 2009 cloud frequency value came close to the historical maximum for the month but did not exceed it (Table 3-1).

Monthly mean, minimum, and maximum LWC values for 1994 through 2007 and 2009 are shown in Figure 3-3. Mean LWC was calculated by taking the average of all hourly LWC values equal to or greater than  $0.05 \text{ g/m}^3$  during the month. Monthly mean LWC values for 2009 versus the historical monthly means (1994–2007) are shown in Figure 3-4. Only valid values passing the 70 percent completeness criterion are plotted. The highest monthly LWC value in the history of the project for August was observed in 2009. This correlates with the August 2009 cloud frequency value, which was the second highest in the history of the project. The highest annual mean LWC observed in the history of the project also occurred in 2009 with an annual mean LWC value of  $0.324 \text{ g/m}^3$  versus  $0.292 \text{ g/m}^3$  for the historical mean.

#### 3.2 Cloud Water Chemistry

During the 2009 sampling season, the CASTNET laboratory received 122 cloud water samples from CLD303. Samples sent to the CASTNET laboratory for analysis were packed in Styrofoam coolers with frozen ice packs to keep the samples cool during shipping. Upon receipt of the samples, the sample receiving technician verified the condition of the samples and the contents of the shipment against the enclosed Cloud Water Sample Report Form. All samples were received in good condition.

Annual summary statistics for cloud water chemistry and LWC are presented in Table 3-2. Table 3-3 lists the total number of samples or “records” that were collected each season of operation at CLD303. Samples were accepted and used for estimation of cloud water deposition if they met acceptance criteria based on the cation-to-anion ratio. Samples were usually eliminated if:

- Both the anion sum and cation sum were  $\leq 100$  microequivalents per liter ( $\mu\text{eq/L}$ ) and the absolute value of the RPD was  $> 100$  percent; or
- Either the anion sum or the cation sum was  $> 100 \mu\text{eq/L}$  and the absolute value of the RPD was  $> 25$  percent.

The RPD was calculated from the following formula:

$$\text{RPD} = 200 * |\text{cations} - \text{anions}| / (\text{cations} + \text{anions})$$

On occasion, samples exceeding these criteria will be accepted and used for analyses if there is valid justification to do so. In most of these cases, a low field pH value (high hydrogen concentration) causes the cation sum to be larger, which in turn causes exceedance of the acceptance criteria.

### **3.2.1 Samples Accepted for Analysis**

Fifty-seven of the 122 cloud water samples were bulked into 20 analytical samples, which resulted in a total of 85 cloud water samples analyzed for the 2009 season. Cloud water analytical and QC data for the 2009 sampling season are presented in Appendix B. All samples collected in May and October were invalidated along with five other samples collected from June through September resulting in a final count of 58 samples used for data analysis.

The May samples, collected from May 20–31, were invalidated because, after initial site set-up on May 18–19, the remainder of May was used for testing the new cloud collection system and working out the minor equipment and programming problems associated with it. The collection and handling of the cloud water samples during this time also served as a training period for the new site operator.

The 10 October samples collected between October 5–24, were invalidated due to QC failures (5 samples did not pass the anion/cation ratio criteria) or the suspect nature of the ancillary data. Due to leaks in the pinch/solenoid valves that persisted throughout the season, a series of tests on the cloud collection portion of the system were conducted during the month of October. Portions of the cloud collection system were shut down for several hours and/or days at a time to verify that the leaks were only occurring in the pinch/solenoid valves. Because of the on/off nature of operations, testing procedures, and suspect dates/volumes associated with the October samples, as well as half of the samples failing acceptance criteria, all 10 samples for this month were invalidated.

Five additional samples were invalidated (sample numbers 13, 15, 29, 63, and 73). Two of these samples (15 and 73) were invalidated due to a substantial amount of rain in the samples. The remaining three samples (13, 29, and 63) were invalidated due to the samples failing the anion/cation ratio criteria with percent differences of 50 percent, 63 percent, and 48 percent, respectively.

### **3.2.2 Cloud Water pH**

The pH values for CLD303 are shown in Figures 3-5 and 3-6. The frequency distribution in both figures shows that a minority of the 2009 samples (approximately 12 percent for laboratory pH and 5 percent for field pH) had values of pH 3.9 or lower. The minimum pH values in 2009 for laboratory and field pH were 3.5 and 3.9, respectively. The 2009 mean pH value of 4.17 for laboratory pH was higher than the 2007 mean laboratory pH value of 3.63. The 2009 mean pH value is the highest mean annual pH value in the history of the project. Historically (1994–2007), the majority of the pH values measured at CLD303 fell within the range of pH 3.2 to 3.8 which is the range identified in the 1992 NAPAP report to Congress (1993) as “acidic cloud water.” Annual pH values for 2009 represent the first time ever that the majority of the pH values were above 3.9.

As can be seen from these figures and the summary statistics for pH and hydrogen ion concentrations in Table 3-2, the 2009 field pH values are higher than the laboratory pH values. The mean field hydrogen ion concentration (Table 3-2) is approximately 5 percent higher than the mean laboratory hydrogen ion concentration. Field pH values are known to be generally lower than pH values measured in the laboratory due 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.*, 1984). The fact that the 2009 field pH values are higher than the laboratory pH values was unexpected and maybe explained in part by the inexperience of the site operators in operating the pH equipment and/or contamination of the aliquots that were analyzed for pH. Because of the lack of field pH data for the last two and a half months of the 2009 sampling season, the laboratory pH data were used this year (rather than field data) for calculation of the cloud hydrogen deposition values for purposes of maintaining consistency in results throughout the season.



View of the Cloud Collection Tower and NPS Radio Tower

### 3.2.3 Major Ions in Cloud Water

The major ions are identified as  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ . Figure 3-7 presents the seasonal mean major ion concentrations in cloud water samples for 1995 through 2007 and 2009. All 2009 mean major ion concentrations show a decrease with respect to 2007 mean concentrations. The 2009 mean nitrate concentration ( $83.30 \mu\text{eq/L}$ ) shows a 49.3 percent decrease from the 2007 mean, and the 2009 mean sulfate concentration ( $182.01 \mu\text{eq/L}$ ) is 60.4 percent lower than the 2007 mean. Sulfate and ammonium concentrations peaked in June (Figure 3-8). The mean monthly nitrate concentrations were very similar in June and July with the July value ( $94.48 \mu\text{eq/L}$ ) slightly edging out the June value ( $93.99 \mu\text{eq/L}$ ). Except for hydrogen, the major ions had the lowest concentrations in September (Figure 3-8). Summary statistics of all major ion concentrations, as well as calcium concentrations, averaged across all years (1994–2007 and 2009) are presented in Table 3-4.

The large decreases in seasonal concentrations between 2007 and 2009 can partially be explained by the higher LWC values during the 2009 season. Higher LWC is often associated with lower concentrations as a result of the dilution of the ions in the greater amount of water within the cloud (Lovett, 2010; see Appendix A).

### 3.2.4 Minor Ions in Cloud Water

Seasonal mean concentrations of the minor ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ ) for 1995 through 2007 and 2009 are presented in Figure 3-9. Concentrations of all minor ions decreased with respect to 2007 concentrations. Concentrations for the minor ions peaked in various months with no discernible pattern (Figure 3-10) other than exhibiting the lowest concentrations in September. Since potassium and sodium are considered non-pollutant ions, the decrease in the seasonal concentrations of these ions lends support to higher LWC values diluting the concentrations of all ions in cloud water (Lovett, 2010; Appendix A).

## 3.3 Comparison of Cloud Water versus Precipitation Concentrations

Precipitation concentration data were obtained from the NADP/NTN site at Elkmont, TN (TN11) to assess whether mean seasonal (June through September) sulfate and nitrate concentrations exhibited the same pattern as mean seasonal cloud water sulfate and nitrate concentrations. Of particular interest was whether the substantial drop in 2009 cloud water sulfate and nitrate concentrations with respect to 2007 concentrations was also evident in precipitation concentrations. Figures 3-11 and 3-12 show mean seasonal cloud water and precipitation concentrations for sulfate and nitrate, respectively, from 1995 through 2007 and 2009. The cloud water concentrations are plotted on the left y-axis and the precipitation concentrations are plotted on the right y-axis. The mean seasonal precipitation concentrations were determined by taking the average of precipitation weighted monthly concentrations from June through September. Both figures clearly show that the large drop in the 2009 cloud water sulfate and nitrate concentrations is also mirrored by precipitation sulfate and nitrate concentrations. The 60.4 percent decrease in 2009 cloud water sulfate concentrations from 2007 concentrations

is paralleled by a 64.3 percent decrease in precipitation sulfate concentrations. The 49.3 percent decrease in 2009 cloud water nitrate concentrations is matched by a 52.2 percent decrease in 2009 precipitation nitrate concentrations with respect to 2007 concentrations. On average, both the seasonal precipitation sulfate and nitrate concentrations are from 6 to 17 percent of the seasonal cloud water concentrations from 1995 through 2009.

## 4.0 Cloud Deposition

This section presents the modeled cloud water deposition estimates for Clingmans Dome from 1994 through 2007 and 2009. Deposition was estimated by applying the CLOUD model (Lovett, 1984), parameterized with site-specific cloud water chemistry and meteorological data from CLD303 as screened and provided by MACTEC. The complete report discussing 2009 cloud deposition modeling results by Gary M. Lovett, PhD is presented in Appendix A. The following subsections present a summary of Dr. Lovett's results.

### 4.1 Cloud Water Deposition Model

Briefly, the CLOUD model uses an electrical resistance network analogy to model the deposition of cloud water to forest canopies. The model is one-dimensional, assuming vertical mixing of droplet-laden air into the canopy from the top. Turbulence mixes the droplets into the canopy space where they cross the boundary layers of canopy tissues by impaction and sedimentation. Sedimentation rates are strictly a function of droplet size. Impaction efficiencies are a function of the Stokes number, which integrates droplet size, obstacle size, and wind speed (Lovett, 1984). The impaction efficiency as a function of the Stokes number is based on wind tunnel measurements by Thorne *et al.* (1982).

The forest canopy is modeled as stacked 1-m layers containing specified amounts of various canopy tissues such as leaves, twigs, and trunks. Wind speed at any height within the canopy space is determined based on the above-canopy wind speed and an exponential decline of wind speed as a function of downward-cumulated canopy surface area. The wind speed determines the efficiency of mixing of air and droplets into the canopy and also the efficiency with which droplets impact onto canopy surfaces. The model is deterministic and assumes a steady state, so that for one set of above-canopy conditions it calculates one deposition rate. The model requires as input data:

1. The surface area index of canopy tissues in each height layer in the canopy,
2. The zero-plane displacement height and roughness length of the canopy,
3. The wind speed at the canopy top,
4. The LWC of the cloud above the canopy, and
5. The mode of the droplet diameter distribution in the cloud.

From these input parameters, the model calculates the deposition of cloud water expressed both as a water flux rate in grams per square centimeter per minute ( $\text{g}/\text{cm}^2/\text{min}$ ) and as a deposition velocity [flux rate/LWC, in units of centimeters per second ( $\text{cm}/\text{s}$ )]. Deposition rates of ions are calculated by multiplying the water deposition velocity by the ion concentration in cloud water above the canopy. In the original version of the model, a calculation of the evaporation rate from the canopy was also included in order to estimate net deposition of cloud water. For this project, the calculation of the evaporation rate from the canopy was not invoked, resulting in estimation of only the gross deposition rate.



The structure of the CLOUD model and its application to these data followed exactly the procedures used to calculate fluxes for the MADPro cloud sites reported by Lovett (2000). After the model was run for all time periods, seasonal and monthly means and totals were calculated in a SAS program. Approaches in data analysis that were different between this effort and the analysis reported by Lovett (2000) are:

1. The data provided to Lovett for this report were pre-screened by MACTEC.
2. Because there were no missing months, summed deposition fluxes were calculated for the season by simply summing all the monthly deposition amounts.

The 2009 data set contained 58 samples (or time periods), and the model was run for all 58 samples/time periods. Although the site was set up in late May, equipment problems delayed the official start until June 3, 2009. Collection continued through October, however, to offset the late start. Therefore, while the sampling season was identified as June 3 through October 28, 2009, the model was run only on samples collected from June through the end of September. See Section 3.2.1 for a discussion of invalidated samples for the 2009 season. All calculations presented in this section for 2009 followed the same procedures as calculations for 2000–2002, 2004–2005, and 2007. Seasonal depositions for 2009 were calculated by summing the monthly depositions for June through September. Slightly different procedures were employed for the 2003 and 2006 seasons because of either a shorter sampling season or lack of data completeness for some of the months due to equipment malfunction. Please refer to the 2003 and 2006 MADPro Reports (MACTEC, 2004 and 2007) for details of the 2003 and 2006 procedures. The seasonal depositions presented in Section 4.2.2 and related tables and figures were calculated using the same procedures used for calculation of the 2000–2002, 2004–2005, and 2007 seasonal depositions.

## **4.2 Results**

### **4.2.1 Monthly Means**

For the 2009 season, wind speed and cloud water deposition velocity values were relatively constant from month to month with the exception of a minor decline in both values in September (Appendix A). Duration-weighted mean monthly concentrations of all analytes, except for  $K^+$ , were lowest in September; whereas the mean monthly LWC value was highest in September ( $0.394 \text{ g/m}^3$ ). These results support Lovett's observation (see Appendix A and Section 3.2.3) that dilution partially explains the substantial decrease in 2009 major ion concentrations with respect to 2007. The mean LWC in 2009 was significantly higher than in 2007. Higher LWC is usually associated with lower concentrations since there is more water in the same cloud to dissolve the ions. The dilution effect is demonstrated by Lovett by normalizing the 2009 sulfate concentrations for LWC. In Figure 3 of Appendix A the 2009 sulfate concentrations are slightly lower than the relatively flat trend seen from 2002 to 2007.

Monthly deposition estimates [kilograms per hectare ( $\text{kg/ha}$ )] for major ions,  $\text{Ca}^{2+}$ , and water for 1994, 1995, 1997 through 2007, and 2009 are presented in Table 4-1. Despite the fact that all

concentrations declined in 2009 (Figures 3-7 and 3-9), total cloud deposition increased in 2009 for all ions except hydrogen (Appendix A Table I-1). The duration-weighted mean concentrations of all ions, except  $H^+$ ,  $Mg^{2+}$ ,  $Na^+$ , and  $Cl^-$ , peaked in June, and all ions, except  $K^+$ , exhibited the lowest concentrations for the season in September.

The monthly deposition estimates for the major ions and calcium, as determined from the CLOUD model for years 1999 through 2007 and 2009, are also presented in Figures 4-1 through 4-4. There is no readily apparent trend for the monthly deposition estimates other than estimates of three of the major ions ( $SO_4^{2-}$ ,  $NH_4^+$ , and  $NO_3^-$ ) also peaked in June and were lowest in September. In this regard, the concentrations and depositions estimates tracked each other relatively well. Most concentrations and depositions were lowest in September and highest in June. The June 2009  $NO_3^-$  deposition was the highest since 2002, and the June 2009  $NH_4^+$  deposition was the highest since 2001.

Table 4-2 presents the mean monthly deposition rates estimated for 1995 through 2007 and 2009. These estimates are based on available data shown in Table 4-1. It is difficult to compare the estimates from year to year since the mean monthly deposition rates were calculated for different combinations of months for different years depending on data completeness.

#### **4.2.2 Seasonal Deposition Estimates**

The seasonal deposition values for major ions are presented in Table 4-3. Data sets from 1997, 1999 through 2007, and 2009 were sufficiently complete to estimate a seasonal value. A season is defined as June through September, and three of the four months were required to calculate the seasonal deposition. The 2009 data show that deposition estimates for all ions, except for hydrogen, increased with respect to 2007 estimates. This increase in deposition estimates is opposite to the decrease in seasonal concentrations and is a reflection of the higher water deposition in 2009 (Lovett, 2010; see Appendix A). The water deposition in 2009 was 9.1 cm/month versus 3.5 cm/month in 2007, which was a drought year.

The information in Table 4-3 can also be compared by averaging the data in 3-year increments from 1999 through 2001 and from 2006 through 2009. When analyzed this way, the decreases in average sulfate, nitrate, and ammonium deposition estimates between 1999–2001 and 2006–2009 are 59 percent (81.6 kg/ha versus 33.7 kg/ha), 72 percent (48.5 kg/ha versus 13.6 kg/ha), and 47 percent (13.5 kg/ha versus 7.2 kg/ha), respectively. Figure 4-5 depicts in graphical form the same data as in Table 4-3 for  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $H^+$ . In this figure, the increase in the seasonal deposition estimates is readily apparent. Because the hydrogen deposition estimates are much lower with respect to the other three ions, only hydrogen deposition estimates are plotted in Figure 4-6 to better illustrate the decrease in these values over the years.

### ***4.3 Comparison of Cloud Water versus Wet Deposition Estimates***

Wet deposition data for the summer seasons (June through August) from 1999 through 2007 and 2009 were obtained from NADP/NTN site TN11 for comparison to cloud water deposition estimates for the same years. The cloud water deposition estimates were recalculated for the months of June through August to allow for this comparison. Figures 4-7 and 4-8 show the summer sulfate and nitrate deposition estimates, respectively, for both cloud water and wet deposition data. It should be noted that the cloud water deposition estimates presented in Figures 4-5 and 4-6 are seasonal deposition estimates (June through September) instead of summer deposition estimates (June through August) as in Figures 4-7 and 4-8. The cloud water deposition estimates are plotted against the left y-axis and the wet deposition values are plotted against the right y-axis. Both species basically follow the same pattern for cloud water and wet deposition estimates starting in 2003. The main exception is that the wet sulfate deposition value for 2009 decreased with respect to the 2007 value, and the cloud sulfate deposition value increased with respect to the 2007 value. The nitrate depositions for both cloud and wet deposition show increases in 2009 with respect to the 2007 values.

The June through August deposition values for cloud water and precipitation show a larger range of percentages with respect to each other from year to year than the concentration values. Wet deposition sulfate values are from 7 to 33 percent of cloud water sulfate depositions, and wet deposition nitrate values are from 8 to 51 percent of cloud water nitrate depositions from 1999 through 2009. Both the sulfate and nitrate seasonal precipitation concentrations were 6 to 17 percent of cloud water concentrations from 1995 through 2009.

## 5.0 Filter Pack Concentrations, Dry Deposition, and Total Deposition

Atmospheric sampling for sulfur and nitrogen species was integrated over weekly collection periods (Tuesday to Tuesday) using a 3-stage filter pack. In this approach, particles and selected gases were collected by passing air at a controlled flow rate through a sequence of Teflon, nylon, and dual cellulose filters. Weekly air pollutant concentrations measured during the 2009 field season, together with the weekly dry deposition values estimated from the concentrations and modeled deposition velocities, are presented in this section. The data presented here are from the CASTNET site at Great Smoky Mountains National Park, TN (GRS420) since filter pack sampling at CLD303 was discontinued after the 2004 sampling season.

### 5.1 Filter Pack Concentrations

Over the course of the 2009 sampling season (June-September), the CASTNET laboratory analyzed 17 filter pack samples. The filter packs were installed on the sampling tower each Tuesday and then removed the following Tuesday. At the site, the site operator sealed each exposed filter pack with end caps and placed it in a resealable plastic bag. Subsequently, each filter pack was securely packed into a polyvinyl chloride shipping tube with its corresponding Site Status Report Form (SSRF) and returned to MACTEC weekly. Any discrepancies or problems with the shipment were recorded on the SSRF by the receiving laboratory technician. All of the filter pack samples were received in good condition.

Upon receipt, all of the samples were logged in and unpacked. Each filter type was extracted and analyzed by the CASTNET laboratory for  $\text{SO}_4^{2-}$  and/or  $\text{NO}_3^-$ . The Teflon filter received additional analysis for  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ . Sample handling and analyses followed the procedures described in the CASTNET Laboratory SOP (MACTEC, 2008). The filter pack analytical and QC data for the sampling season are presented in Appendix C.

Table 5-1 presents the atmospheric concentrations in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) resulting from analysis of each weekly filter pack exposed for sampling during the 2009 sampling season. Upon receipt of each weekly filter pack, the receiving technician assigned a sample number composed of various identifiers for sample type, year, week, and site. The on/off dates and times presented in Table 5-1 correspond with the entries recorded on the SSRF.

Starting in 1996 and continuing through the 2003 sampling season, the flow to the filter pack at the CLD303 site was programmed to shut off during a cloud or rain event to allow for determination of dry deposition only. In 2004, the filter pack sampled during rain events as well, and the flow was shut off only during a cloud event. The filter pack at GRS420, as well as at all other CASTNET sites, samples continuously throughout the week. This difference in sampling protocol should be taken into consideration when comparing filter pack concentrations after 2004 with previous years. In addition, there is a substantial difference in elevation of 1,221 meters between the CLD303 site (elevation 2,014 m) and the GRS420 site (elevation 793 m).

The average flow is presented in units of Lpm and represents the average filter pack flow during dry deposition sampling events. The volume for each sample was determined by using the hours sampled and average flow as shown in the following equation:

$$\text{Volume in cubic meters} = \frac{\text{hours sampled (hr)} \times \text{average flow} \times 60}{1,000}$$

The atmospheric concentrations for the filter pack samples were calculated by using the laboratory data ( $\mu\text{g}/\text{filter}$ ) in the following equation.

$$\text{Atmospheric concentrations } (\mu\text{g}/\text{m}^3) = \frac{\mu\text{g of analyte}/\text{filter} \times \text{analyte dependent constant}}{\text{volume}}$$

The following constants were used for converting the chemistry data:

Teflon		Nylon		Cellulose	
Parameter	Constant	Parameter	Constant	Parameter	Constant
SO <sub>4</sub> <sup>2-</sup>	1.0	SO <sub>4</sub> <sup>2-</sup>	1.0	SO <sub>2</sub>	0.667
NO <sub>3</sub> <sup>-</sup>	4.429	HNO <sub>3</sub>	4.5	NA	NA
NH <sub>4</sub> <sup>+</sup>	1.286	NA	NA	NA	NA

**Note:** NA = not applicable

Table 5-1 presents the ambient concentrations for each sample and filter type for the captured particles and gases. Total ambient SO<sub>2</sub> was determined by this equation:

$$\text{Total SO}_2 = \text{cellulose SO}_2 + (\text{nylon SO}_4^{2-} * 0.667)$$

## 5.2 Dry Deposition

The Multi-Layer Model (MLM) was used to calculate dry deposition velocities (Meyers *et al.*, 1998; Finkelstein *et al.*, 2000), which were combined with the measured concentrations to estimate dry deposition for Clingmans Dome. The MLM calculations were considered reasonable and representative for Clingmans Dome, at least through 2004, because on-site meteorological measurements were used directly in the model as well as filter pack measurements obtained from a filter pack system collocated with the automated cloud sampler. Starting in 2005, both the filter pack and meteorological measurements used for estimating dry deposition were obtained from the GRS420 site. The representativeness of these measurements to Clingmans Dome is questionable due to the difference in elevation, distance, and sampling protocol with respect to the CLD303 site. However, the data are presented here since the results may still be useful in a very general way.

Even though the MLM was developed and evaluated using measurements from flat terrain settings, the model evaluation results are considered roughly applicable to this site. The data from Meyers *et al.* (1998) show little overall bias and up to 100 percent differences for individual 1/2-hour simulations. Other data (Finkelstein *et al.*, 2000) suggest that the MLM underestimates deposition velocities for SO<sub>2</sub> for complex, forested sites. The differences are expected to be lower for longer averaging times (i.e., monthly and seasonal periods). Consequently, the uncertainty in the dry deposition estimates is approximately 100 percent or lower, and the MLM calculations probably underestimate the dry fluxes.

The weekly dry deposition estimates, the seasonal (June through September) fluxes, and the seasonal mean deposition velocities for 2009 are presented in Table 5-2. The seasonal fluxes were calculated by summing the weekly fluxes and then multiplying this sum by the number of weeks in the season and dividing by the number of weeks with valid flux estimates. The formula used for the 2009 field season is:

$$\text{Total seasonal flux} = 17/17 \text{ (sum of all valid weekly deposition estimates)}$$

All 17 filter packs analyzed were used to calculate deposition estimates.

### 5.3 Total Deposition

Total sulfur and nitrogen deposition estimates for the 1999 through 2007 and 2009 sampling seasons are presented in Table 5-3. The deposition season is defined as the period from June through September. For cloud water, the total sulfur deposition was determined by converting the SO<sub>4</sub><sup>2-</sup> deposition estimated from the CLOUD model to sulfur (S). Total sulfur for the dry component was determined by using the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> total seasonal fluxes presented in Table 5-2. These values were converted to S and then summed to determine the total dry sulfur deposition.

Total cloud water nitrogen deposition was determined by converting the NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> deposition estimated from the CLOUD model to nitrogen (N). Total dry nitrogen deposition was determined by converting the HNO<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> total seasonal fluxes presented in Table 5-2 to N. All of the nitrogen species were summed to provide the total nitrogen deposition.

Figure 5-1 presents total sulfur and nitrogen deposition estimates for both the cloud water and dry components during the 1999 through 2007 and 2009 sampling seasons. This figure shows that cloud water sulfur deposition for 2009 increased approximately 21.0 percent from 2007 measurements, and dry sulfur deposition decreased by about 72.2 percent. Total nitrogen deposition increased 36.0 percent for cloud water and decreased 60.1 percent for dry deposition. The increases in cloud sulfur and nitrogen deposition are influenced by higher seasonal mean LWC value for 2009 (0.324 g/m<sup>3</sup> for 2009 versus 0.234 g/m<sup>3</sup> for 2007) as well as the slightly higher seasonal mean wind speed values (3.59 m/s for 2009 versus 3.48 m/s for 2007). Despite

the fact that the filter pack data for 2009 are from a different site with a substantially lower elevation, it is still evident that dry deposition was and continues to be a small contributor to the deposition of pollutants to high elevations, while cloud deposition was and still is a significant source. This figure does not present the contribution from deposition produced by precipitation.



View from the Clingmans Dome Parking Area

## 6.0 Conclusions and Recommendations

The Clingmans Dome cloud water deposition estimates show an overall decline in sulfur and nitrogen deposition estimates over the history of the project despite increases observed for both species in 2004, 2006, and 2009. The small increase in the 2009 cloud water deposition estimates (Figure 4-5) is attributed to the higher amount of water deposition in 2009 and offsets the substantial decreases in ion concentrations (Figure 3-7). Despite some annual variability from year to year, estimates of total deposition, i.e. deposition produced by cloud + dry components, show a general overall decline since 2001 (Figure 6-1). The 2009 seasonal estimates show that dry deposition is still a small contributor to the deposition of pollutants at high elevations. Cloud deposition is the significant pathway for deposition at these elevations.

The principal recommendation for the 2010 season is to replace the solenoid/pinch valves of the cloud collection system with motorized ball valves. Air leaks occurred throughout the 2009 season in either the pinch or solenoid valves. The motorized ball valves will replace both the pinch and solenoid valves, will not leak, and will significantly reduce power consumption, which has always been a cause for concern during long stretches of cloudy weather.

An additional recommendation is to reinstitute collocated filter pack sampling during the 2010 season. The GRS420 measurements cannot be considered representative of CLD303 due to the differences in elevation, distance, and other site-specific factors. The Clingmans Dome data constitute a major source of information on deposition to high elevation, sensitive ecosystems and will continue to help gauge the effectiveness of the Acid Rain Program and other more recent control programs in reducing atmospheric pollutant deposition.

In addition to continuing laboratory pH and conductivity measurements in order to verify proper operation of the field pH meter and probe and to provide backup measurements for this important parameter, an audit of the field laboratory is recommended. This recommendation results from problems encountered with the field pH and conductivity measurement protocols during the 2006, 2007, and 2009 field seasons. The audit should also include the PVM calibration procedures and documentation, as well as cloud water sample collection, handling, and documentation procedures. New site operators should be provided with continual on-the-job training during the first year of performance. Returning site operators should continue to be trained and monitored carefully since the cloud water collection system is complex with many different components (some of which were redesigned in 2009) and requires several years of operational experience before proficiency can be achieved. There will be additional minor modifications to the cloud collection system for the 2010 season.





The automated cloud collector (in the down position) on top of the CASTNET tower at Clingmans Dome, TN

## 7.0 References

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## **Tables**

**Table 3-1. Monthly Mean Cloud Frequency Summary**

Clingmans Dome (CLD303)		1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2009	Mean <sup>4</sup>
May	Cloud Frequency <sup>1</sup>				81.78%			31.07%	47.17%	34.50%	91.67%					99.29%	37.58%
	Cloud Hours <sup>2</sup>				67			174	350	256	330					279	
	Completeness				11%			75%	100%	100%	48%					38%	
June	Cloud Frequency <sup>1</sup>				61.63%	48.58%	41.38%	49.72%	43.33%	43.47%	54.61%	67.89%	54.93%	23.62%	36.64%	48.80%	46.44%
	Cloud Hours <sup>2</sup>				106	205	276	270	312	313	361	387	390	163	255	326	
	Completeness				24%	59%	93%	75%	100%	100%	92%	79%	99%	96%	97%	92.8%	
July	Cloud Frequency <sup>1</sup>		29.47%	46.64%	34.34%	55.42%	44.75%	41.67%	57.08%	49.06%	42.78%	56.66%	40.50%	15.50%	48.38%	55.38%	45.44%
	Cloud Hours <sup>2</sup>		84	139	227	399	328	140	391	340	314	370	290	97	314	412	
	Completeness		38%	40%	89%	97%	99%	45%	92%	93%	99%	88%	96%	84%	87%	100%	
August	Cloud Frequency <sup>1</sup>		49.44%		41.49%	71.43%	24.93%	43.45%	67.84%	28.02%	42.58%	46.64%	30.63%	50.87%	23.39%	56.41%	41.22%
	Cloud Hours <sup>2</sup>		351		256	5	185	305	367	202	152	347	223	264	174	418	
	Completeness		95%		83%	1%	100%	94%	73%	97%	48%	100%	98%	65%	100%	99.6%	
September	Cloud Frequency <sup>1</sup>	32.41%	30.37%		33.18%	43.93%	27.65%	50.65%	37.78%	51.60%	39.74%	47.18%	12.92%	50.42%	62.54%	51.07%	42.70%
	Cloud Hours <sup>2</sup>	128	106		212	170	172	349	136	322	242	334	89	363	394	359	
	Completeness	55%	48%		93%	54%	86%	96%	50%	87%	85%	98%	96%	100%	88%	97.6%	
October	Cloud Frequency <sup>1</sup>	40.27%		23.64%	35.52%	30.32%		5.98%	41.72%			48.56%	46.91%	32.65%		37.56%	65.02%
	Cloud Hours <sup>2</sup>	267		78	200	211		34	141			287	296	159		246	
	Completeness	89%		44%	76%	94%		76%	46% <sup>3</sup>			79%	85%	66%		88%	
November	Cloud Frequency <sup>1</sup>				59.7%												
	Cloud Hours <sup>2</sup>				40												
	Completeness				9%												

**Note:** <sup>1</sup> Cloud frequency is not used in subsequent analyses if the completeness criterion of 70 percent is not met. Monthly deposition estimates for 2003 and August 2006 were exceptions.

<sup>2</sup> Number of records where LWC ≥ 0.05 g/m<sup>3</sup>

<sup>3</sup> Site was shutdown on 10/16. Completeness based at time of shutdown is 91.85 percent.

<sup>4</sup> The average cloud frequency values are calculated only from those annual values that meet the completeness criterion.

**Table 3-2. Summary Statistics for Cloud Water Samples 2009**

<b>2009</b>					
<b>Total Records Accepted = 58</b>					
	<b>n</b>	<b>mean</b>	<b>std dev</b>	<b>min</b>	<b>max</b>
<b>LWC</b>	58	0.324	0.130	0.05	0.619
<b>pH - Field</b>	21	4.32	4.62	3.92	5.7
<b>pH - Lab</b>	58	4.17	4.26	3.45	6.1
<b>Cond - Field</b>	56	57.7	34.26	12.20	197.8
<b>Cond - Lab</b>	58	61.72	36.27	12.90	217.0
<b>H<sup>+</sup> - Field</b>	21	48.25	24.26	2.00	120.23
<b>H<sup>+</sup> - Lab</b>	58	67.50	54.90	0.80	354.81
<b>NH<sub>4</sub><sup>+</sup></b>	58	138.72	110.75	9.20	604.35
<b>SO<sub>4</sub><sup>2-</sup></b>	58	182.01	114.50	37.29	534.64
<b>NO<sub>3</sub><sup>-</sup></b>	58	83.03	48.59	16.42	193.19
<b>Ca<sup>2+</sup></b>	58	47.06	43.48	1.35	198.91
<b>Mg<sup>2+</sup></b>	58	11.34	8.62	0.58	36.59
<b>Na<sup>+</sup></b>	58	14.76	11.74	1.02	47.67
<b>K<sup>+</sup></b>	58	3.62	2.70	0.31	12.30
<b>Cl<sup>-</sup></b>	58	14.64	11.30	1.52	53.54
<b>Cations - Field</b>	21	319.76	138.90	148.79	677.60
<b>Cations - Lab</b>	58	282.99	175.21	51.49	835.90
<b>Anions</b>	58	279.68	164.36	63.17	748.58

**Note:** All units are µeq/L except for LWC (g/m<sup>3</sup>), pH (standard units), and conductivity (micro ohms/cm)

The following acceptance criteria were used based on the cation and anion concentrations:

- 1) If both cation and anion sums were less than or equal to 100 µeq/L, then the RPD criterion (defined below) was ≤ 100 percent for a record to be accepted.
- 2) If either or both of the cation or anion sums were greater than 100 µeq/L, then the RPD criterion was ≤ 25 percent for a record to be accepted.

max = maximum

min = minimum

n = sample size used in calculations

RPD = The absolute value of difference in cation and anion concentrations divided by the average of the cation and anion concentrations multiplied by 200

std dev = sample standard deviation

**Table 3-3.** Number of Cloud Water Samples Accepted for Analyses

Year	Total Number of Samples	Number of Samples Accepted	Percent Accepted
1994*	14	9	64
1995*	142	136	96
1996*	122	105	86
1997*	334	324	97
1998*	341	269	79
1999*	174	174	100
2000**	104	102	98
2001***	73	70	96
2002***	75	65	87
2003***	78	78	100
2004***	73	73	100
2005***	64	63	98
2006***	45	45	100
2007***	54	54	100
2009***	85	58	68
<b>Total</b>	<b>1778</b>	<b>1625</b>	<b>91.3%</b>

**Note:** \* Hourly samples — sample collection bottle changed every hour.  
 \*\* Hourly + daily samples (62 hourly and 42 24-hour samples in year 2000)  
 \*\*\* Daily samples — sample collection bottle changed every 24 hours.

**Table 3-4.** Summary Statistics of Major Ion and Calcium Concentrations ( $\mu\text{eq/L}$ ) of Cloud Water Samples (1994–2007 and 2009)

	$\text{H}^+$ *	$\text{NH}_4^+$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Ca}^{2+}$
Mean	319.22	222.24	409.20	168.30	48.41
Minimum	0.54	0.71	3.54	0.29	0.15
Maximum	2137.96	1650.01	3686.91	1342.88	1051.89
Median	234.42	173.42	310.37	131.52	26.18

**Note:** \* Laboratory pH data instead of field pH data were used for calculating the 2001, 2002, 2006, 2007, and 2009 hydrogen values.

**Table 4-1.** Cloud Water Monthly Deposition Estimates Produced by the CLOUD Model (kg/ha)<sup>a</sup>

Year	Month	H <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	H <sub>2</sub> O (cm)
1994	October	0.04	3.90	2.30	1.05	0.24	6.42
1995	August	0.13	9.33	4.96	1.67	0.35	9.83
1997	July	0.23	14.13	6.87	3.03	0.54	5.54
	August	0.24	14.16	8.37	3.04	0.69	8.74
	September	0.18	11.10	4.52	2.03	0.28	10.43
	October	0.31	19.71	12.22	4.71	0.67	7.02
1998	July	0.45	23.58	13.33	7.61	0.75	10.76
	October	0.22	11.79	9.83	3.02	0.78	9.10
1999	June	0.61	30.31	15.90	6.36	0.76	20.27
	July	0.88	39.79	18.75	4.67	1.57	7.80
	August	0.23	13.25	6.94	2.29	0.92	7.37
	September	0.16	7.58	4.25	1.23	0.47	8.56
2000	May	0.05	6.88	4.46	2.00	0.56	4.74
	June	0.18	13.00	9.40	2.89	0.93	9.68
	August	0.41	25.54	12.52	3.78	1.31	10.22
	September	0.30	14.36	5.85	1.84	0.11	12.82
	October	0.09	4.63	2.86	1.14	0.15	1.11
2001	May	0.09	8.19	6.72	2.83	0.64	5.01
	June	0.28	18.84	18.92	3.87	3.53	9.34
	July	0.30	16.85	9.22	2.63	0.64	9.16
	August	0.44	26.77	18.88	4.35	1.20	10.50
2002	May	0.14	9.51	4.08	1.97	0.50	9.50
	June	0.15	8.84	5.34	1.95	0.53	5.98
	July	0.17	9.33	5.40	1.64	0.36	10.80
	August	0.17	10.18	5.12	1.84	0.33	4.90
	September	0.29	21.41	10.61	3.92	1.10	14.86
2003	May <sup>b</sup>	0.09	7.32	4.23	1.60	0.60	14.52
	June	0.11	7.35	3.18	1.32	0.42	8.53
	July	0.11	6.72	3.69	1.25	0.37	7.63
	August <sup>c</sup>	0.19	10.93	5.01	1.83	0.42	5.89
	September	0.17	10.68	5.43	2.20	0.50	7.20
2004	June	0.17	9.43	3.77	1.67	0.34	9.69
	July	0.27	11.12	4.82	1.83	0.46	11.81
	August	0.25	11.88	4.57	2.08	0.30	6.44
	September	0.28	13.12	3.97	2.05	0.25	16.96
	October	0.35	12.10	6.71	2.69	0.46	8.06
2005	June	0.17	12.77	4.89	2.66	0.63	14.85
	July	0.13	7.65	2.93	1.18	0.41	9.85
	August	0.12	7.59	3.16	1.42	0.24	6.83
	September	0.06	5.25	2.49	1.24	0.39	1.75
	October	0.15	5.68	3.97	0.92	0.20	10.35
2006	June	0.04	2.92	1.37	0.71	0.17	3.72
	July	0.04	4.05	1.47	1.07	0.16	1.57
	August <sup>d</sup>	0.47	30.62	8.16	4.81	0.65	10.32
2007	June	0.03	3.54	1.75	1.00	0.19	2.66
	July	0.05	5.17	2.23	1.22	0.23	4.88
	August	0.04	4.06	1.65	0.91	0.20	1.02
	September	0.14	9.76	4.38	1.94	0.34	5.53
2009	June	0.06	9.52	5.22	2.83	1.04	9.02
	July	0.05	7.83	4.69	2.29	1.05	8.90
	August	0.07	7.05	4.14	1.60	0.56	11.54
	September	0.05	4.13	2.08	1.02	0.22	6.95

**Note:** a Deposition estimates for 1996 were not calculated.  
 b May 2003 data represent May 17-31, 2003 only.  
 c August 2003 had only 48 percent completeness.  
 d August 2006 deposition estimate includes one invalid sample LWC value.



**Table 4-2.** Cloud Water Monthly Mean (May through September) Deposition Rates for Several Ions (kg/ha/month) and Water (cm/month)

Year	Water (cm/month)	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>
1995-98	8.1	0.23	3.0	14.3	7.7	0.54
1999*	11.0	0.47	3.6	22.7	11.5	0.93
2000	9.7	0.29	3.0	16.9	8.8	0.68
2001	8.6	0.31	3.3	18.4	12.5	1.28
2002	9.2	0.18	2.3	11.9	6.1	0.56
2003	10.5	0.14	1.8	9.3	4.7	0.53
2004**	10.6	0.27	2.1	11.5	4.8	0.36
2005**	8.7	0.12	1.5	7.8	3.5	0.37
2006***	5.2	0.18	2.2	12.6	3.7	0.33
2007*	3.5	0.07	1.3	5.6	2.5	0.24
2009*	9.1	0.06	1.9	7.1	4.0	0.72

**Note:** \* June through September  
 \*\* June through October  
 \*\*\* June through August

**Table 4-3.** Cloud Water Seasonal\* Deposition Estimates Produced by the CLOUD Model (kg/ha)

Year	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>
1997	0.86	10.20	52.53	26.35	2.01
1999	1.88	14.55	90.93	45.84	3.72
2000	1.19	11.35	70.53	37.03	3.13
2001	1.36	14.47	83.28	62.69	7.16
2002	0.78	9.35	49.76	26.47	2.32
2003	0.58	6.60	35.68	17.31	1.71
2004	0.97	7.63	45.55	17.13	1.35
2005	0.48	6.50	33.26	13.47	1.67
2006	0.73	8.80	50.40	14.80	1.32
2007	0.27	5.07	22.54	10.01	0.95
2009	0.24	7.74	28.53	16.13	2.87

**Note:** \* Season is defined from June through September  
 Three of the four months were required to calculate seasonal deposition. The 3-month deposition was multiplied by 4/3.

**Table 5-1. Great Smoky Mountains National Park, TN (GRS420) Ambient Concentrations ( $\mu\text{g}/\text{m}^3$ ) – June through September 2009**

Sample Number	On Date/Time	Off Date/Time	Teflon								Nylon		Cellulose	Total SO <sub>2</sub>	Total NO <sub>3</sub>	Comment Codes	Valid Hours	Actual Volume (m <sup>3</sup> )
			SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HNO <sub>3</sub>	SO <sub>2</sub>					
0923001-36	6/2/09 12:23	6/9/09 11:35	4.180	0.048	1.329	0.112	0.022	0.026	0.065	0.017U	0.312	1.198	0.721	0.930	1.227		167	30.046
0924001-36	6/9/09 11:40	6/16/09 10:45	3.325	0.077	1.036	0.122	0.025	0.082	0.068	0.017U	0.399	1.341	0.564	0.830	1.397	T01	166	30.042
0925001-36	6/16/09 10:52	6/23/09 11:45	3.631	0.044	0.919	0.185	0.043	0.175	0.085	0.017U	0.534	1.409	0.691	1.047	1.431		165	30.183
0926001-36	6/23/09 12:04	6/30/09 11:30	2.679	0.102	0.857	0.147	0.022	0.019	0.027	0.017U	0.542	0.833	0.994	1.355	0.922		165	29.700
0927001-36	6/30/09 12:15	7/7/09 12:00	2.981	0.092	0.651	0.447	0.059	0.013	0.080	0.017U	0.365	1.367	0.707	0.950	1.437		168	30.205
0928001-36	7/7/09 12:05	7/14/09 11:28	4.181	0.029U	1.304	0.109	0.032	0.105	0.076	0.017U	0.368	1.146	0.546	0.792	1.157		167	30.039
0929001-36	7/14/09 11:35	7/21/09 12:52	3.091	0.304	0.969	0.327	0.045	0.023	0.087	0.016U	0.332	0.947	0.528	0.749	1.236		169	30.401
0930001-36	7/21/09 13:00	7/28/09 12:30	3.160	0.140	1.032	0.158	0.024	0.022	0.126	0.017U	0.291	0.767	0.415	0.609	0.895		166	30.060
0931001-36	7/28/09 12:50	8/4/09 12:32	2.318	0.046	0.632	0.097	0.029	0.055	0.088	0.017U	0.202	0.673	0.180	0.314	0.708		168	30.240
0932001-36	8/4/09 12:40	8/11/09 11:00	4.545	0.120	1.296	0.191	0.046	0.107	0.124	0.017U	0.323	1.322	0.753	0.969	1.421		166	29.880
0933001-36	8/11/09 11:00	8/18/09 11:28	3.579	0.142	1.056	0.138	0.042	0.146	0.105	0.032	0.211	1.132	0.244	0.385	1.257		169	30.398
0934001-36	8/18/09 11:35	8/25/09 11:40	3.441	0.034	0.957	0.079	0.020	0.074	0.136	0.017U	0.389	0.800	0.370	0.629	0.822		168	30.223
0935001-36	8/25/09 11:50	9/1/09 11:55	3.702	0.110	1.095	0.166	0.036	0.052	0.085	0.017U	0.304	1.039	0.479	0.681	1.132		168	30.224
0936001-36	9/1/09 12:00	9/8/09 11:32	3.663	0.146	1.221	0.121	0.030	0.087	0.078	0.017U	0.288	1.336	0.524	0.716	1.461		168	30.224
0937001-36	9/8/09 11:40	9/15/09 12:08	5.310	0.068	1.731	0.088	0.020	0.042	0.086	0.016U	0.320	1.258	0.648	0.861	1.306		169	30.416
0938001-36	9/15/09 12:19	9/22/09 11:35	1.925	0.030	0.571	0.021	0.008	0.030	0.167	0.017U	0.107	0.377	0.051	0.123	0.401		166	29.857
0939001-36	9/22/09 11:42	9/29/09 11:45	2.102	0.131	0.693	0.157	0.030	0.076	0.062	0.017U	0.270	0.767	0.463	0.643	0.886		168	30.224
		<b>Mean</b>	3.401	0.098	1.021	0.157	0.031	0.067	0.091	0.017	0.327	1.042	0.522	0.740	1.123			
		<b>Standard Deviation</b>	0.877	0.068	0.301	0.099	0.013	0.047	0.033	0.004	0.108	0.298	0.231	0.292	0.304			

**Data Status Flags:** U = Value is less than detection limit T = Teflon 01 = unidentified debris/particles on filter

**Table 5-2.** Great Smoky Mountains National Park, TN (GRS420) Dry Deposition Fluxes (kg/ha) Report for the 2009 Deposition Season (June through September)

Sample Number	On Date	Off Date	Fluxes (kg/ha)					Deposition Velocities (cm/sec)		
			SO <sub>2</sub>	HNO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>	SO <sub>2</sub>	HNO <sub>3</sub>	Particle
23001-36	6/2/09 9:00	6/9/09 8:00	0.019	0.088	0.020	0.000	0.006	0.374	1.318	0.087
24001-36	6/9/09 9:00	6/16/09 8:00	0.016	0.078	0.013	0.000	0.004	0.343	1.041	0.072
25001-36	6/16/09 9:00	6/23/09 8:00	0.023	0.116	0.020	0.000	0.005	0.406	1.482	0.099
26001-36	6/23/09 9:00	6/30/09 8:00	0.030	0.068	0.018	0.001	0.006	0.400	1.468	0.121
27001-36	6/30/09 9:00	7/7/09 8:00	0.022	0.143	0.024	0.001	0.005	0.410	1.893	0.145
28001-36	7/7/09 9:00	7/14/09 8:00	0.019	0.107	0.027	0.000	0.008	0.420	1.667	0.116
29001-36	7/14/09 9:00	7/21/09 8:00	0.018	0.092	0.021	0.002	0.007	0.432	1.723	0.122
30001-36	7/21/09 9:00	7/28/09 8:00	0.014	0.067	0.020	0.001	0.007	0.401	1.558	0.116
31001-36	7/28/09 9:00	8/4/09 8:00	0.007	0.059	0.013	0.000	0.004	0.392	1.564	0.100
32001-36	8/4/09 9:00	8/11/09 8:00	0.022	0.118	0.029	0.001	0.008	0.424	1.629	0.119
33001-36	8/11/09 9:00	8/18/09 8:00	0.009	0.100	0.022	0.001	0.006	0.413	1.591	0.109
34001-36	8/18/09 9:00	8/25/09 8:00	0.015	0.082	0.023	0.000	0.006	0.428	1.824	0.120
35001-36	8/25/09 9:00	9/1/09 8:00	0.014	0.082	0.020	0.001	0.006	0.378	1.410	0.094
36001-36	9/1/09 9:00	9/8/09 8:00	0.014	0.082	0.016	0.001	0.005	0.340	1.102	0.078
37001-36	9/8/09 9:00	9/15/09 8:00	0.016	0.080	0.026	0.000	0.008	0.328	1.132	0.088
38001-36	9/15/09 9:00	9/22/09 8:00	0.002	0.025	0.005	0.000	0.001	0.293	1.083	0.044
39001-36	9/22/09 9:00	9/29/09 8:00	0.012	0.062	0.012	0.001	0.004	0.350	1.450	0.103
<b>Total Seasonal Flux</b>			0.273	1.450	0.330	0.010	0.098			
<b>Mean Seasonal Deposition</b>								0.384	1.467	0.102

**Note:** MLM simulations were performed for each 168-hour period from 0800 on the On Date to 0800 on the Off Date.

\* Original sample numbers within the MACTEC laboratory information management system contain the suffix "-36" to indicate that the sample was collected from the GRS420, TN site

**Table 5-3.** Cloud Water and Dry Sulfur and Nitrogen Deposition for Clingmans Dome  
(June through September 1999–2007 and 2009)

	<b>Year</b>	<b>Total Sulfur<sup>1</sup> (kg/ha)</b>	<b>Total NO<sub>3</sub>-N (kg/ha)</b>	<b>Total NH<sub>4</sub><sup>+</sup>-N (kg/ha)</b>	<b>Total Nitrogen<sup>2</sup> (kg/ha)</b>
<b>Cloud Water</b>	1999	30.362	10.360	11.298	21.658
	2000	28.288	10.003	11.460	21.463
	2001	30.670	14.127	12.882	27.009
	2002	16.610	5.982	7.260	13.242
	2003	11.917	3.912	5.129	9.041
	2004	15.210	3.871	5.925	9.796
	2005	11.100	3.043	5.047	8.090
	2006	16.828	3.345	6.833	10.178
	2007	7.526	2.262	3.937	6.199
	2009	9.526	3.645	6.01	9.655
<b>Dry</b>	1999	0.907	2.184	0.194	2.378
	2000	0.572	1.453	0.124	1.577
	2001	0.843	2.043	0.214	2.257
	2002	0.675	1.904	0.183	2.087
	2003	0.439	1.027	0.107	1.134
	2004	0.434	1.212	0.107	1.319
	2005*	0.829	0.657	0.165	0.822
	2006*	0.738	0.624	0.165	0.789
	2007*	0.888	0.783	0.222	1.005
	2009*	0.247	0.325	0.076	0.401

**Note:** Season is defined as June through September

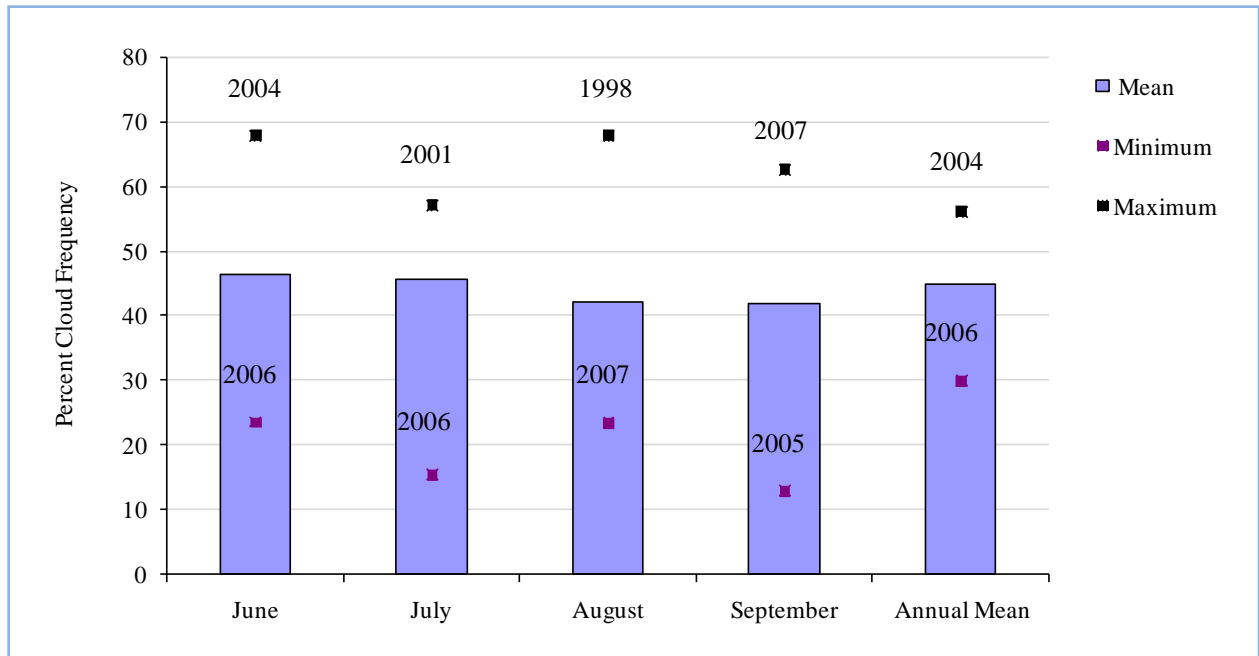
<sup>1</sup> Total sulfur deposition includes SO<sub>4</sub><sup>2-</sup> in cloud water plus ambient SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>

<sup>2</sup> Total nitrogen deposition includes NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in cloud water plus ambient NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and HNO<sub>3</sub>

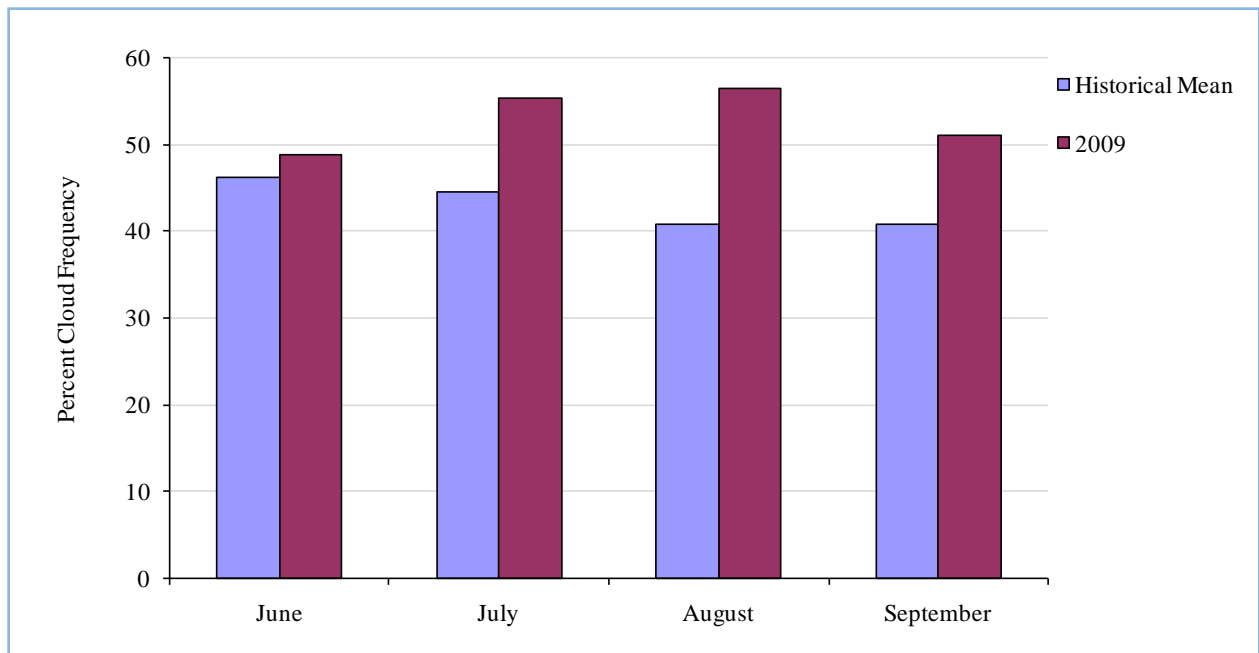
\*Dry deposition values for 2005 through 2007 and 2009 were obtained from the Great Smoky Mountains National Park (GSR420) site at Look Rock, TN

## **Figures**

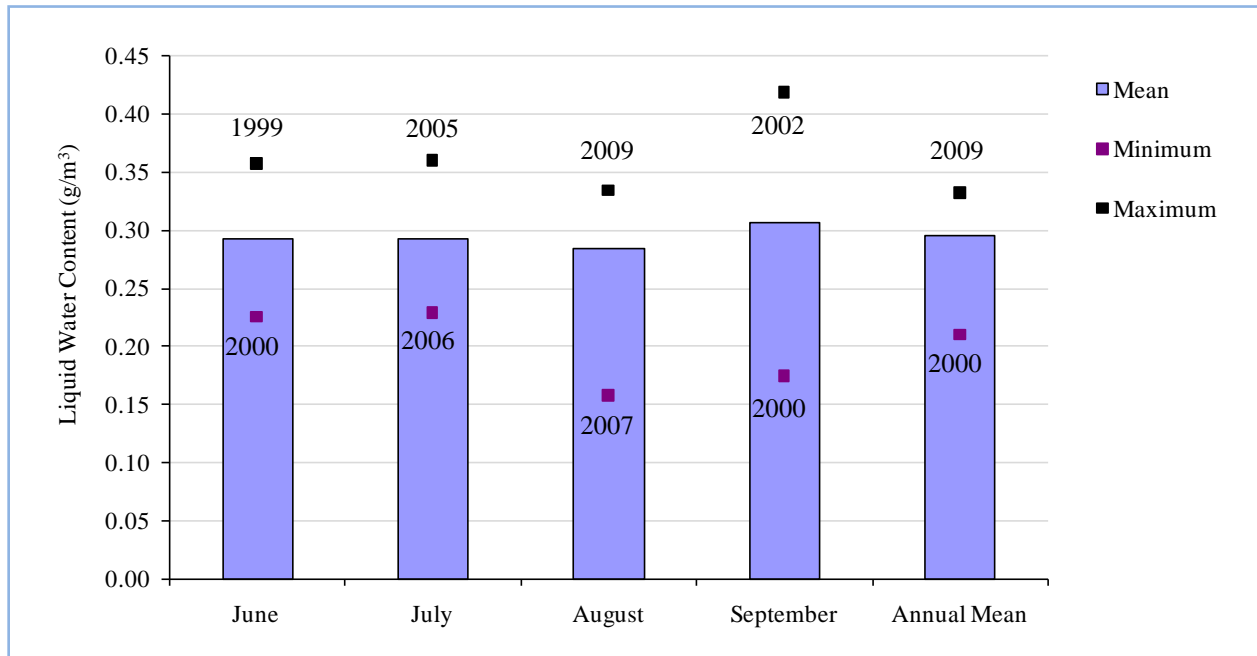
**Figure 3-1.** Monthly Cloud Frequency Statistics (1994–2007 and 2009)



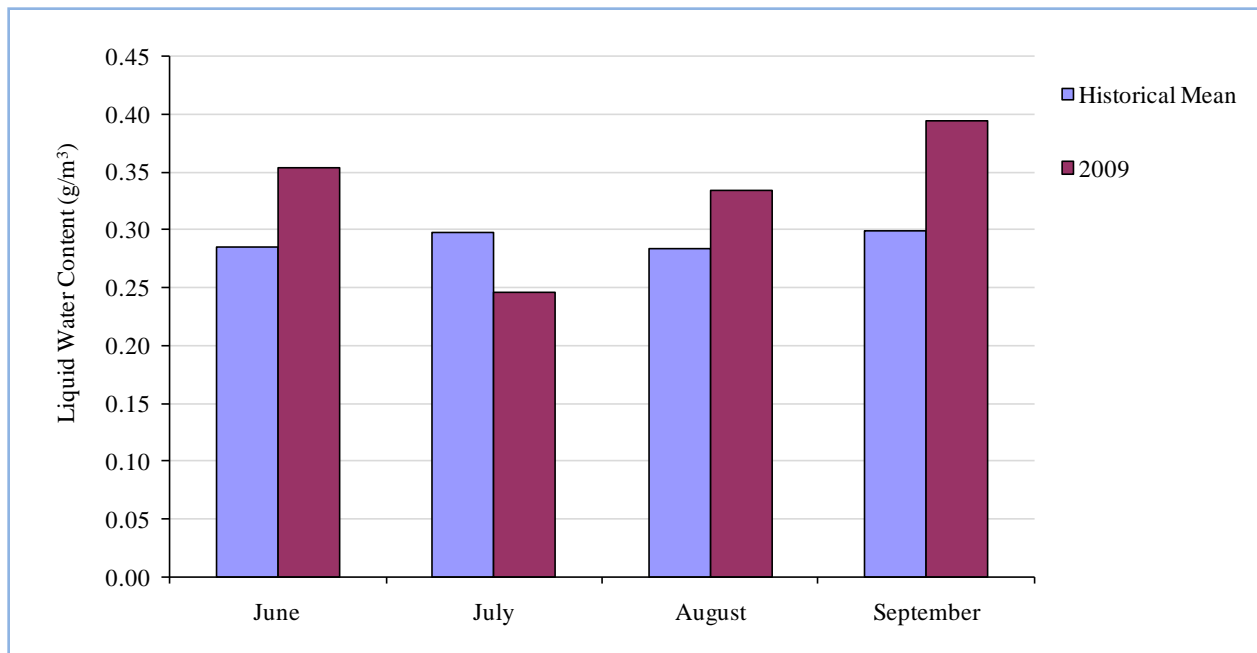
**Figure 3-2.** Monthly Mean Cloud Frequency – 2009 versus Historical Mean Values (1994–2007)



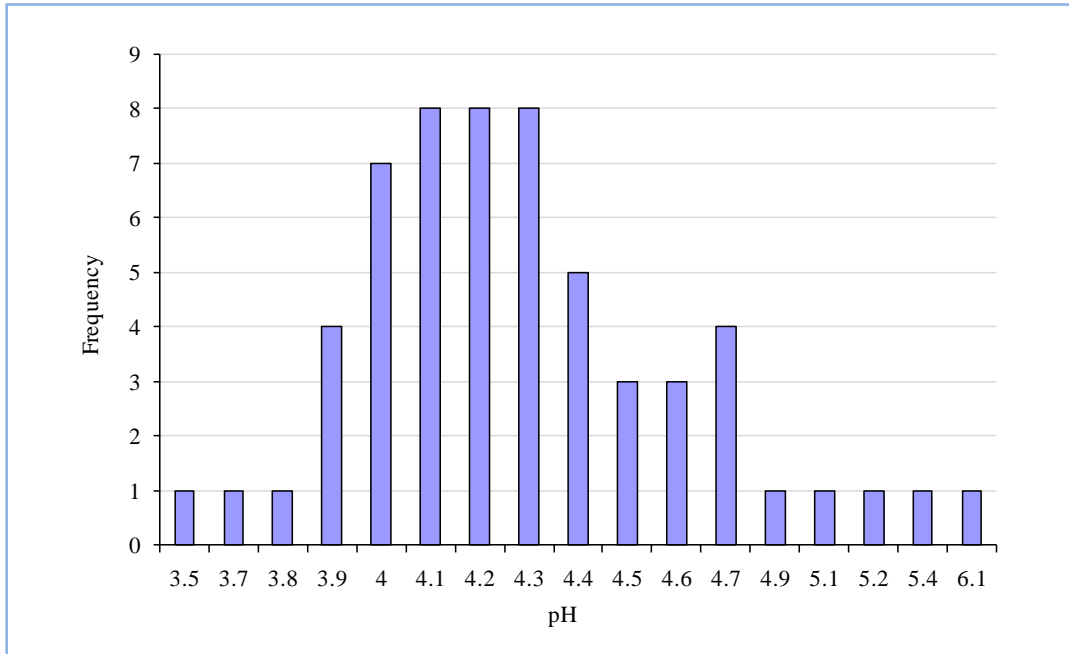
**Figure 3-3.** Monthly Mean Liquid Water Content Statistics (1994–2007 and 2009)



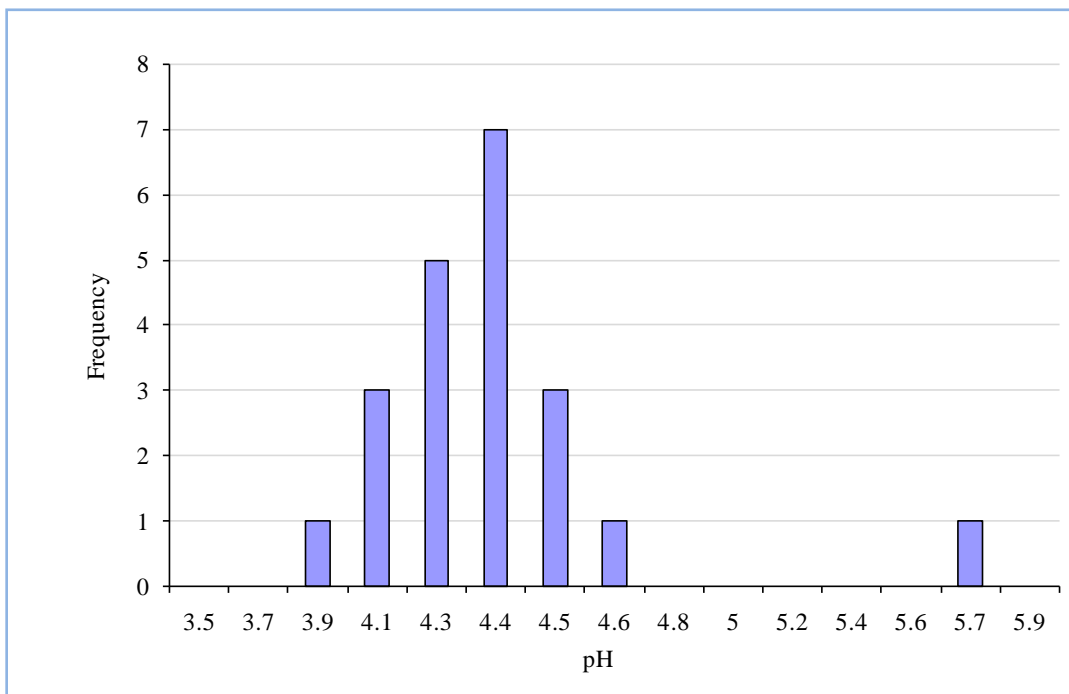
**Figure 3-4.** Monthly Mean Liquid Water Content (g/m³) – 2009 versus Historical Mean Values (1994–2007)



**Figure 3-5.** Frequency Distribution for 2009 Cloud Water pH (Laboratory)

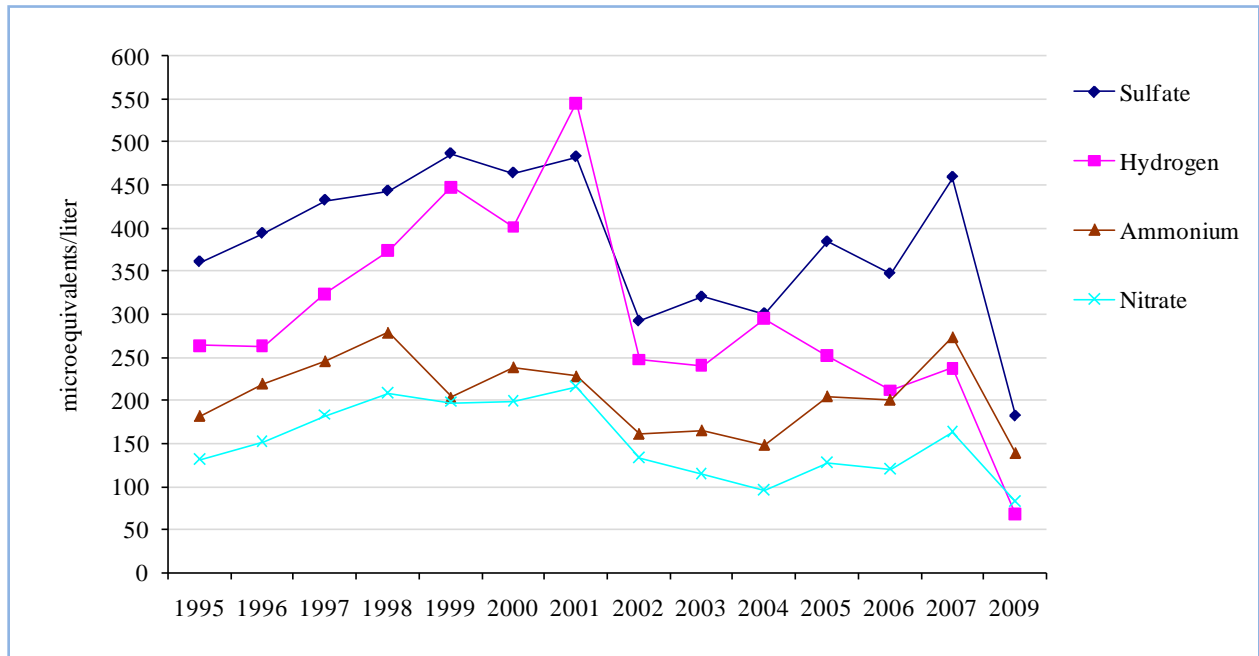


**Figure 3-6.** Frequency Distribution for 2009 Cloud Water pH (Field)



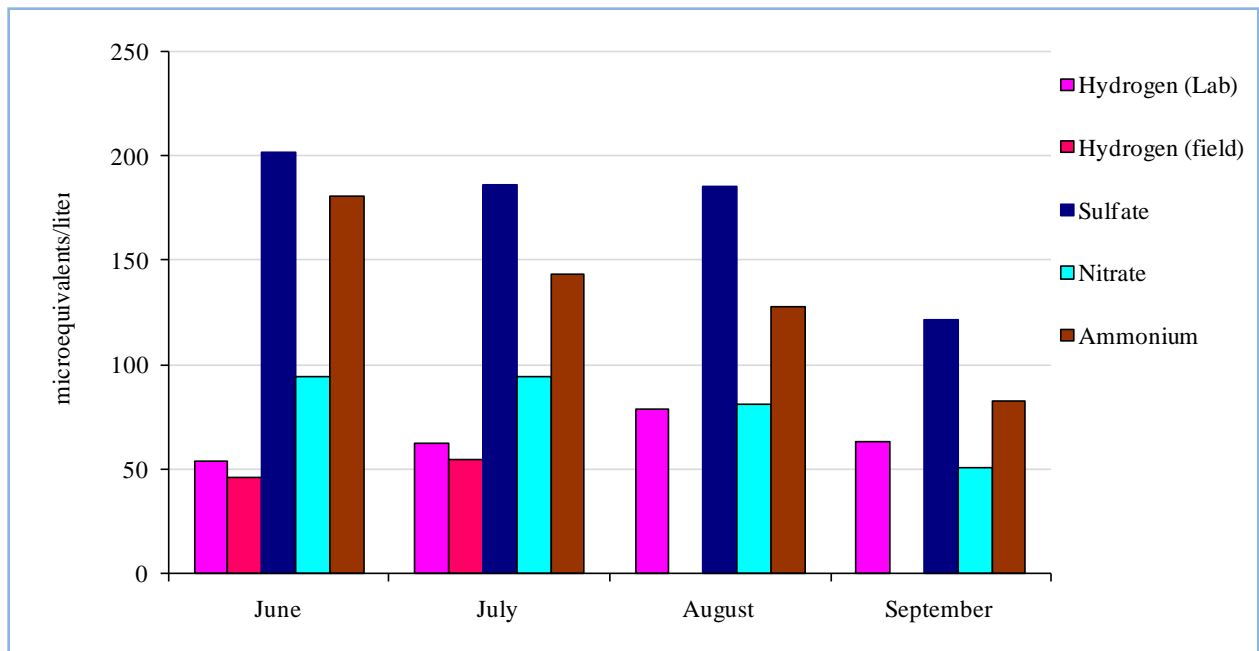


**Figure 3-7.** Mean Major Ion Concentrations of Cloud Water Samples (1995–2007 and 2009)

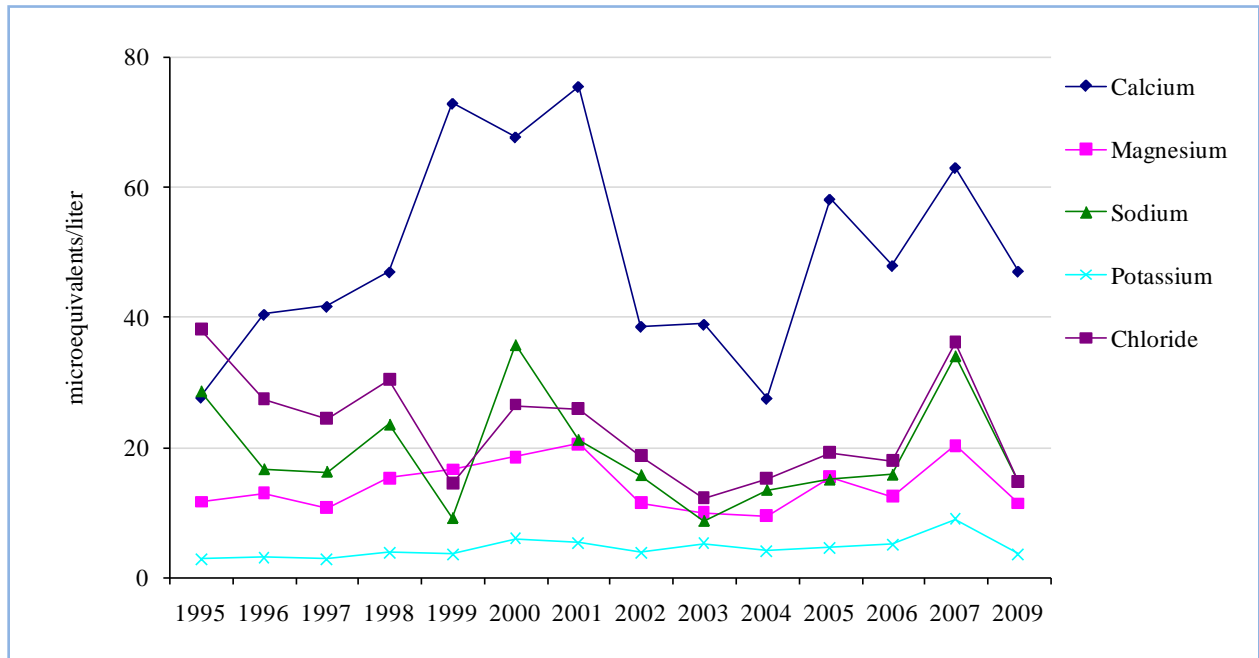


**Note:** \* Laboratory pH data instead of field pH data were used for calculating the 2001, 2006, 2007, and 2009 hydrogen concentration values.

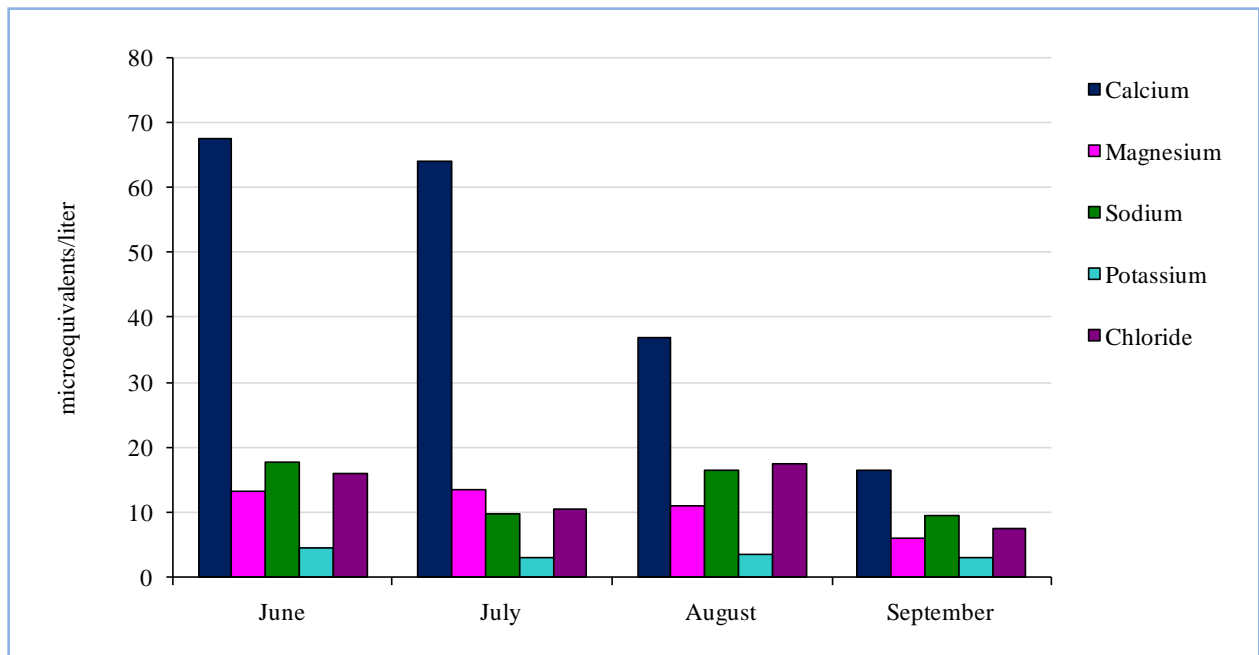
**Figure 3-8.** Monthly Mean Major Ion Concentrations for 2009



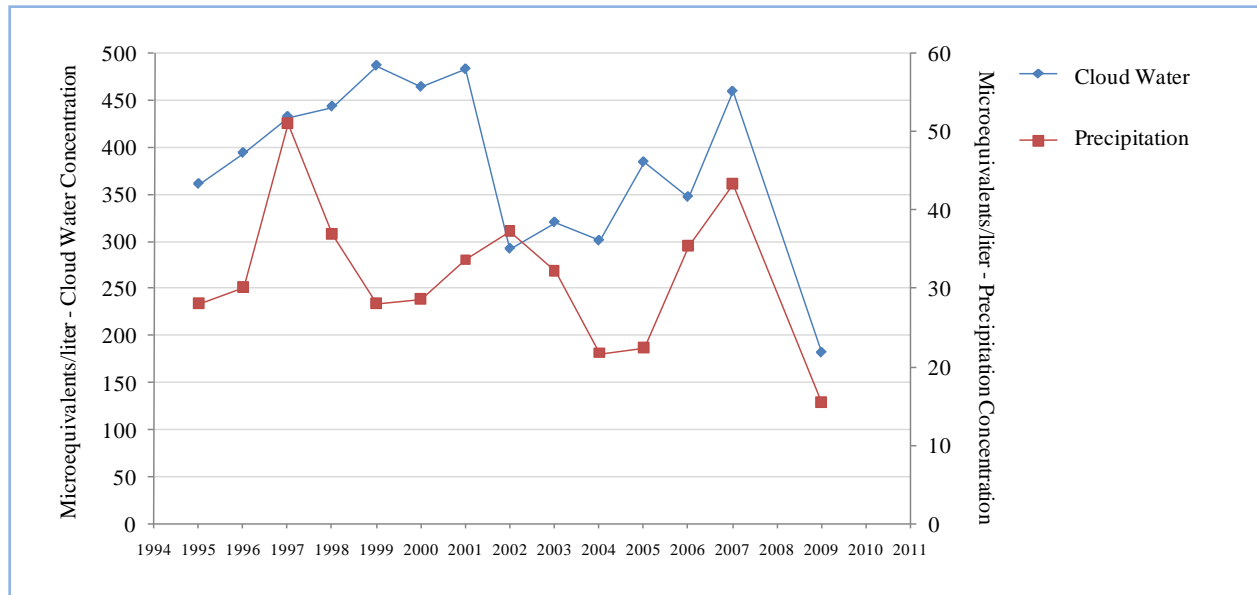
**Figure 3-9.** Mean Minor Ion Concentrations of Cloud Water Samples (Cations and Chloride) 1995–2007 and 2009



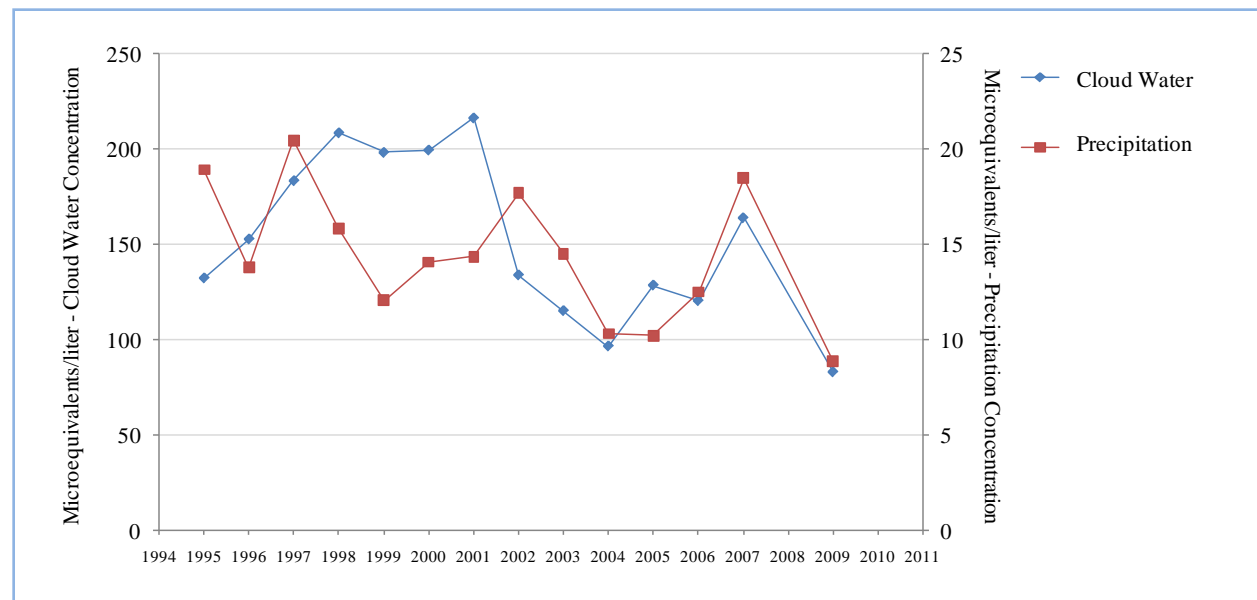
**Figure 3-10.** Monthly Mean Minor Ion Concentrations for 2009



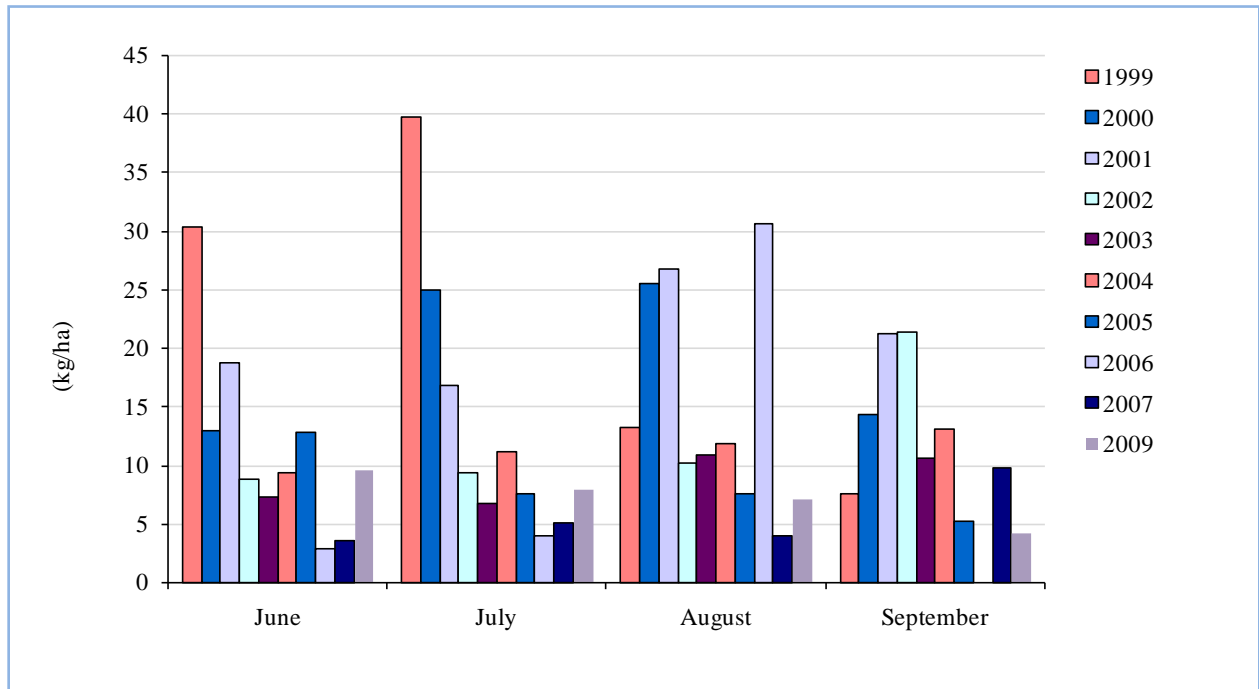
**Figure 3-11.** Mean Seasonal Cloud Water versus Mean Seasonal Precipitation Sulfate Concentrations, 1995–2007 and 2009



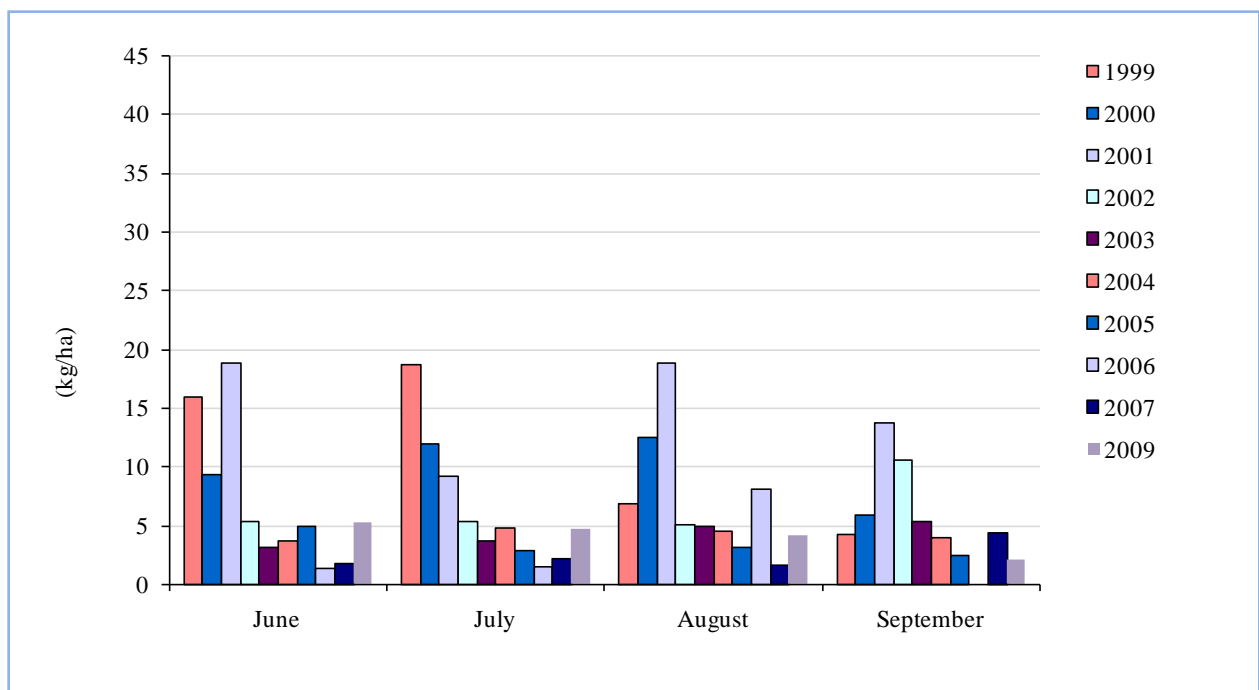
**Figure 3-12.** Mean Seasonal Cloud Water versus Mean Seasonal Precipitation Nitrate Concentrations, 1995–2007 and 2009



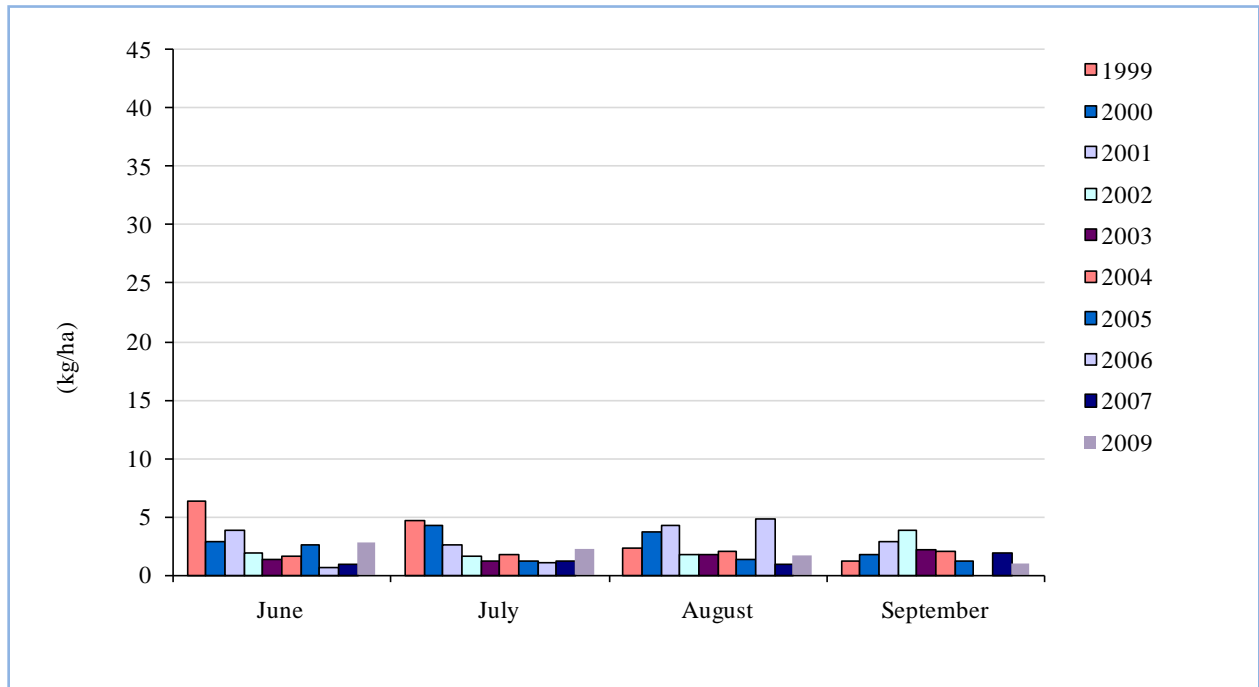
**Figure 4-1.** Monthly Deposition Estimates – CLOUD Model ( $\text{SO}_4^{2-}$ )



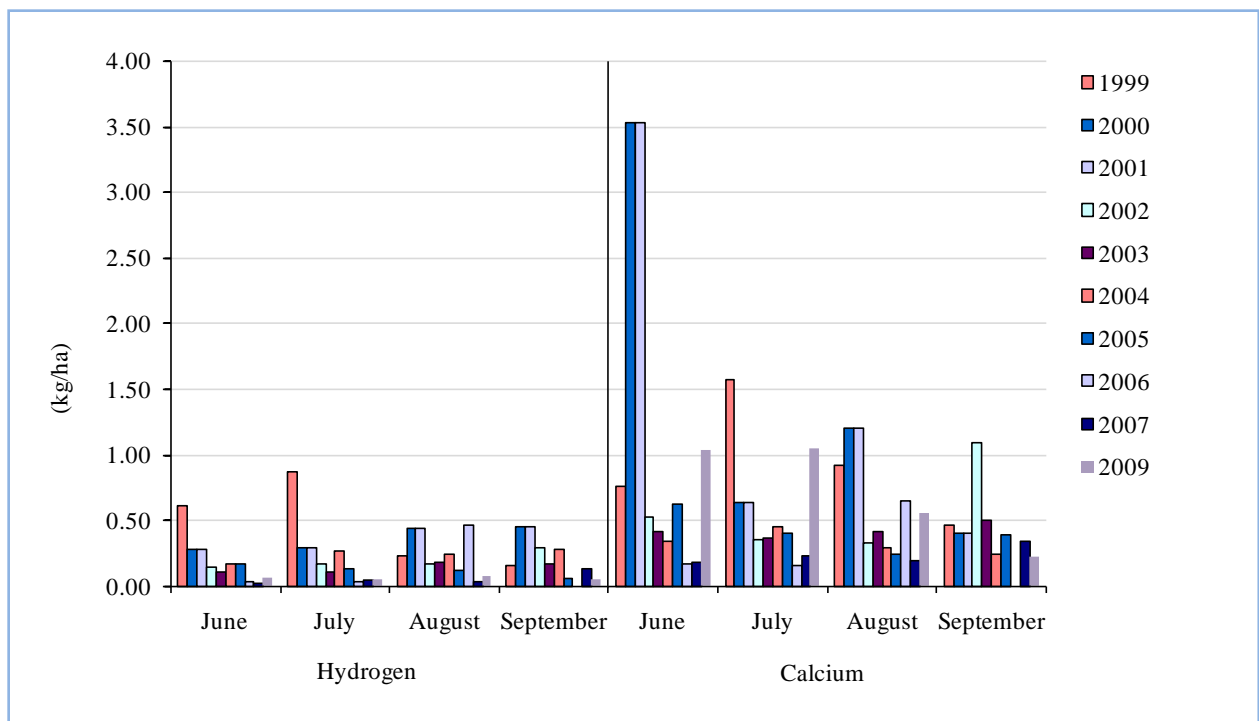
**Figure 4-2.** Monthly Deposition Estimates – CLOUD Model ( $\text{NO}_3$ )



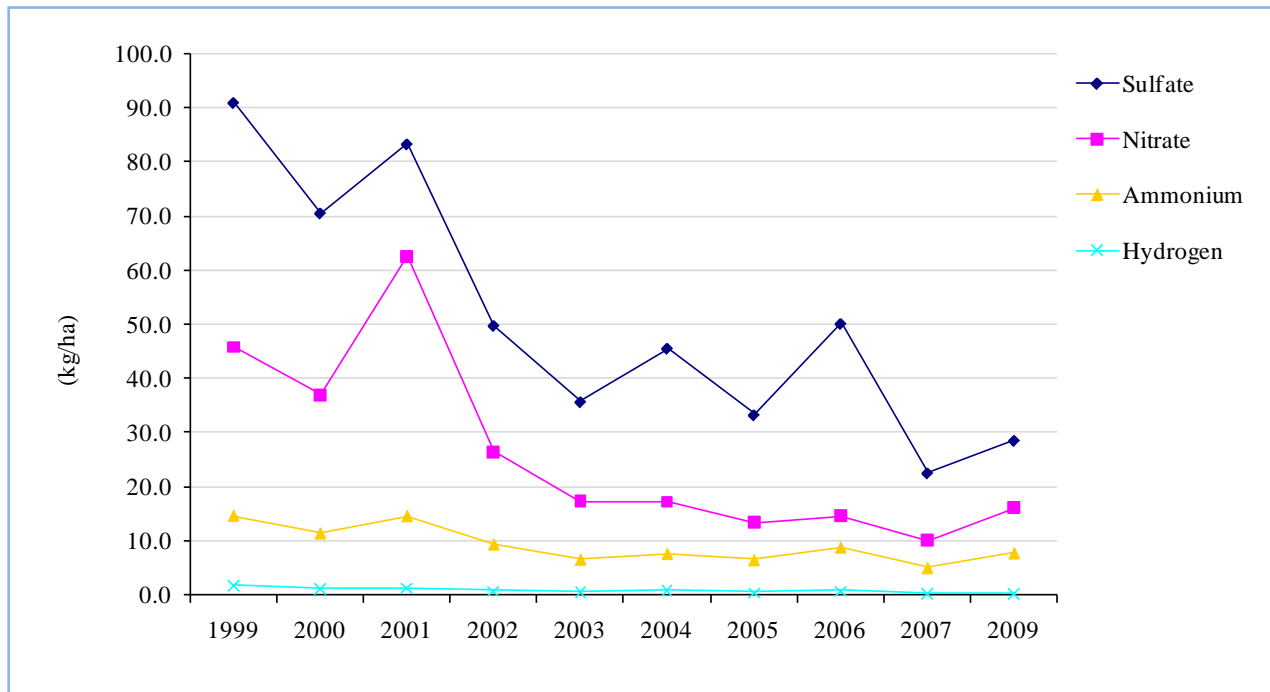
**Figure 4-3.** Monthly Deposition Estimates – CLOUD Model ( $\text{NH}_4^+$ )



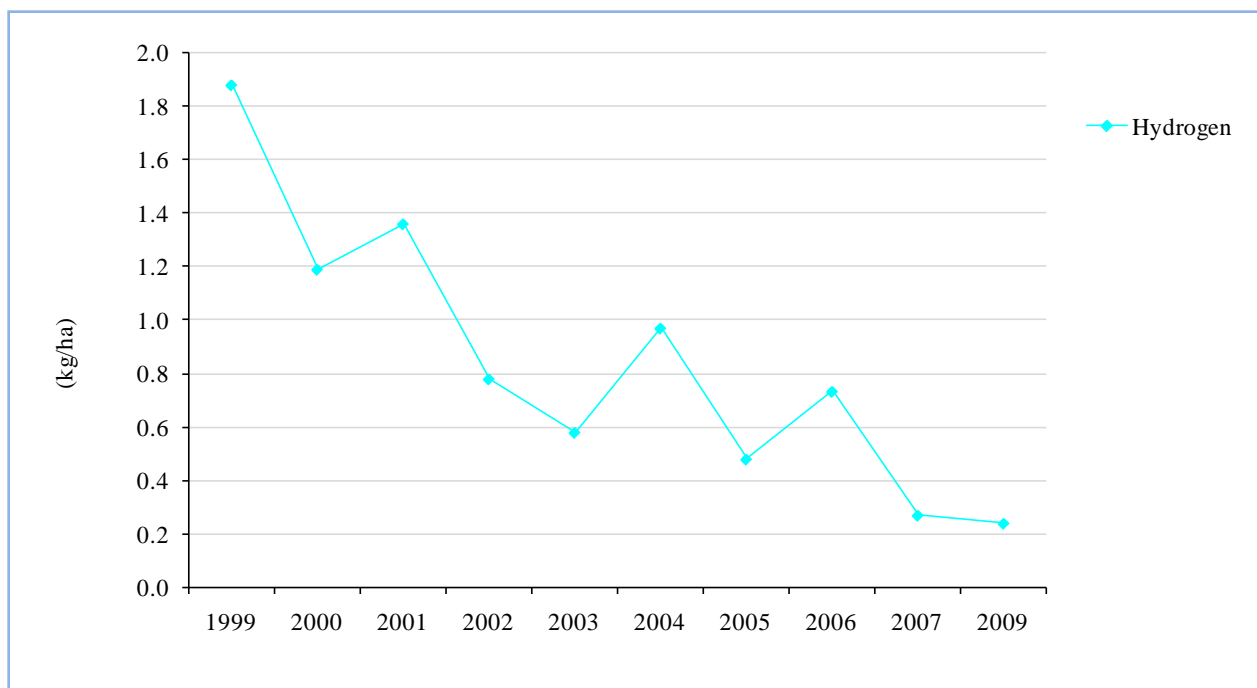
**Figure 4-4.** Monthly Deposition Estimates – CLOUD Model ( $\text{H}^+$  and  $\text{Ca}^{2+}$ )



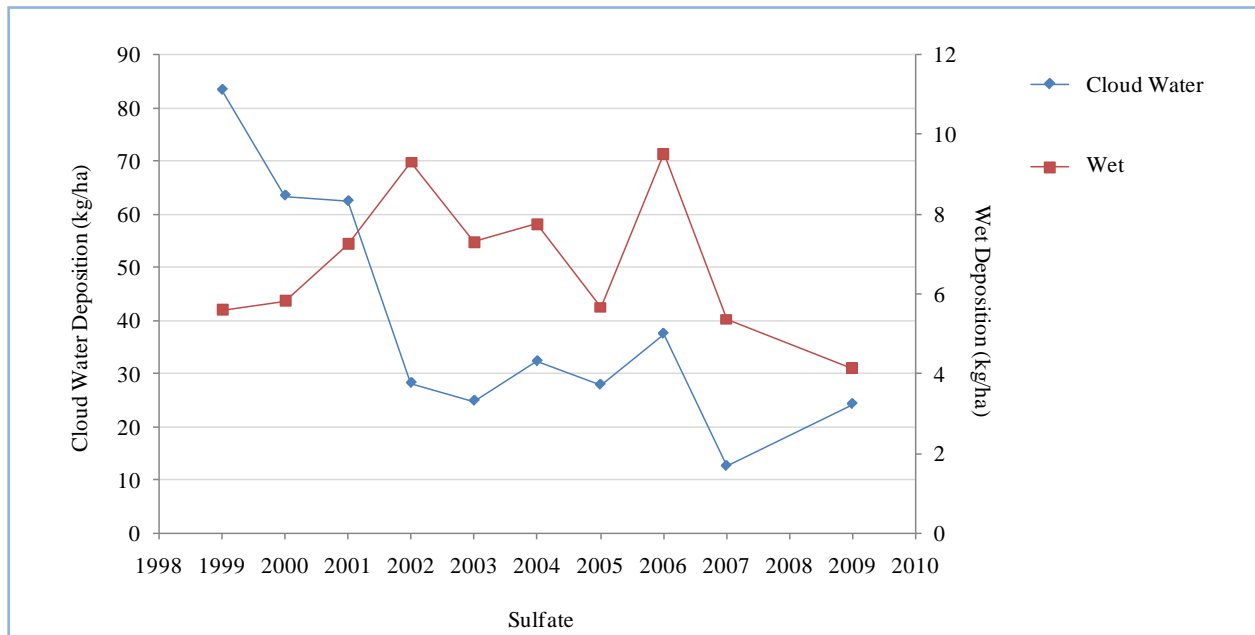
**Figure 4-5.** Seasonal Deposition Estimates for Major Ions (1999–2007 and 2009)



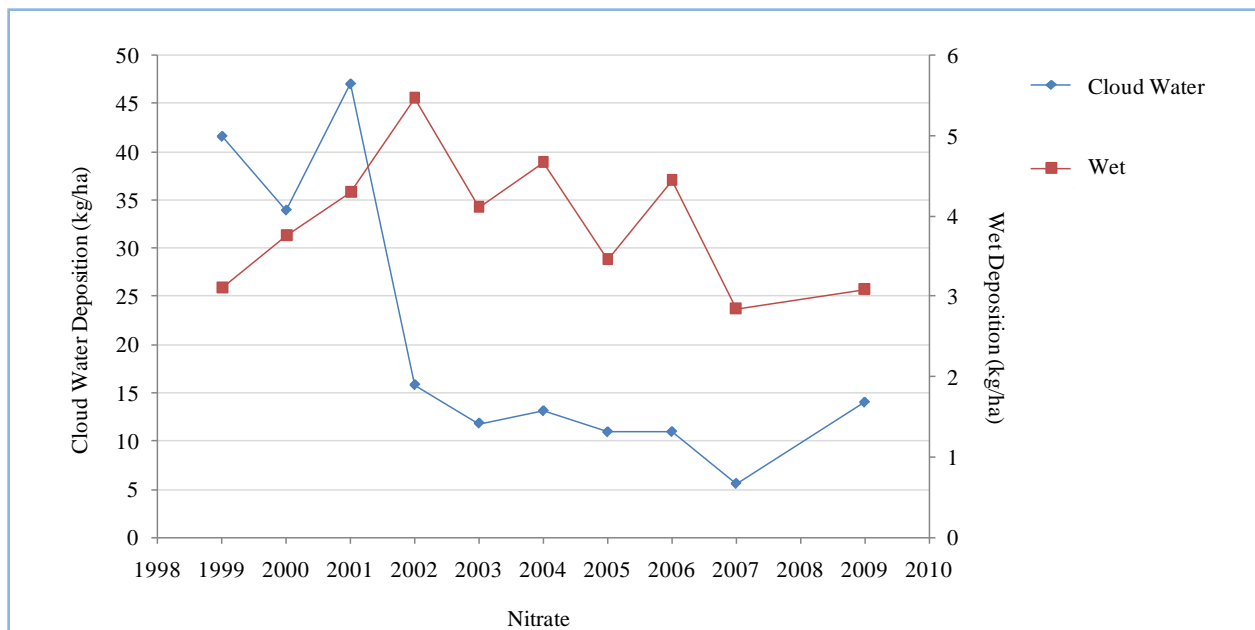
**Figure 4-6.** Seasonal Deposition Estimates for Hydrogen (1999–2007 and 2009)



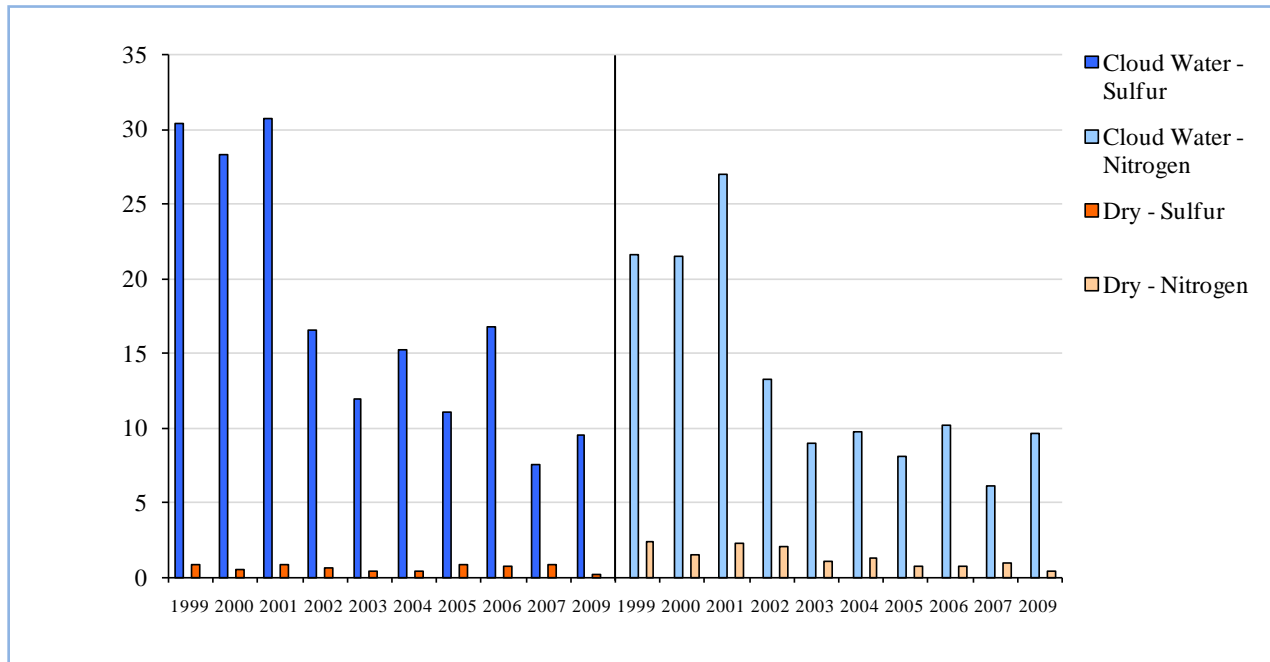
**Figure 4-7.** Cloud Water and Wet Sulfate Deposition Estimates (June through August), 1999–2007 and 2009



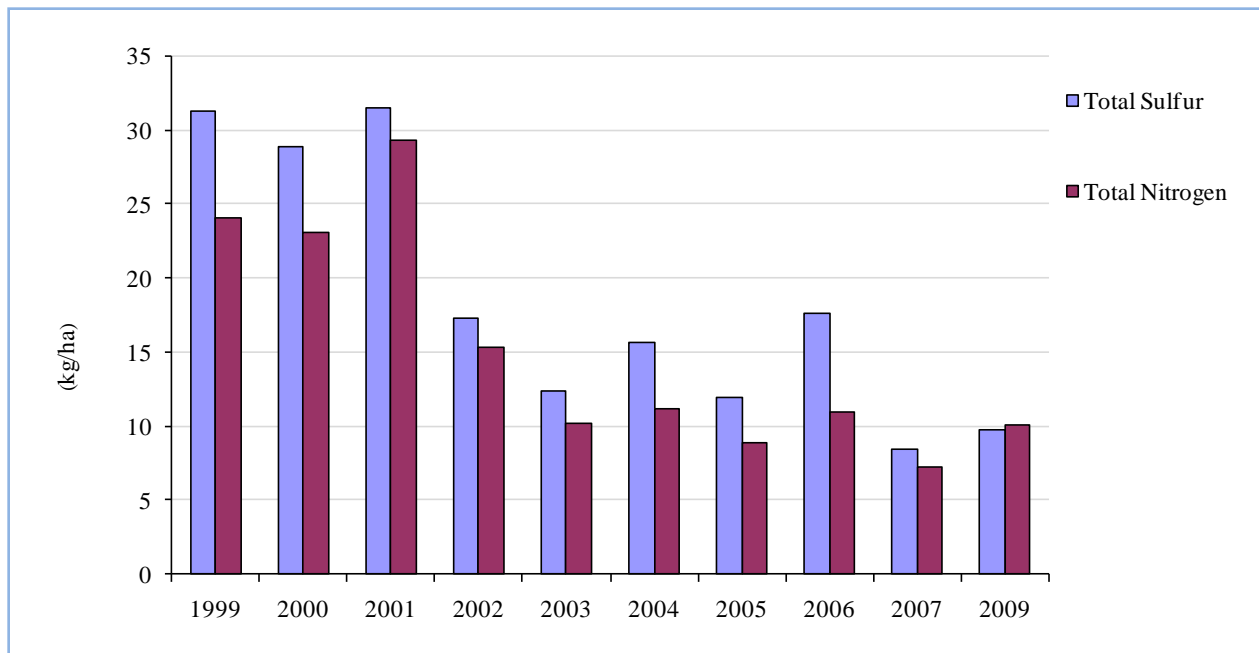
**Figure 4-8.** Cloud Water and Wet Nitrate Deposition Estimates (June through August), 1999–2007 and 2009



**Figure 5-1.** Total Sulfur and Nitrogen Cloud Water and Dry Deposition Estimates (June through September) 1999–2007 and 2009



**Figure 6-1.** Total Sulfur and Nitrogen Deposition Estimates (Dry + Cloud Components) for 1999–2007 and 2009





## **Appendix A**

### **Cloud Water Deposition to Clingmans Dome in 2009**

## Cloud Water Deposition to Clingmans Dome in 2009

Report to MACTEC by

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CNET IV Mountain Cloud  
Task Order #0002  
EP-W-09-028

Report Date: March 4, 2010

### Introduction

This brief report accompanies the Excel spreadsheet CLD 2009.xls, which gives the results of the cloud water deposition modeling for the Clingmans Dome (CLD303) site for the field season of 2009. Raw chemical concentration, meteorological, and cloud frequency data were provided to me by MACTEC (Selma Isil). I ran the CLOUD model (Lovett 1984) on these data to estimate cloud water deposition to this site, and calculated seasonal and monthly mean values of key parameters.

Briefly, the CLOUD model uses an electrical resistance network analogy to model the deposition of cloud water to forest canopies. The model is one-dimensional, assuming vertical mixing of droplet-laden air in to the canopy from the top. Turbulence mixes the droplets into the canopy space, where they cross the boundary layers of canopy tissues by impaction and sedimentation. Sedimentation rates are strictly a function of droplet size. Impaction efficiencies are a function of the Stokes number, which integrates droplet size, obstacle size, and wind speed (Lovett 1984). The impaction efficiency is calculated as a function of the Stokes number based on wind tunnel measurements by Thorne et al (1982).

The forest canopy is modeled as stacked 1-m layers containing specified amounts of various canopy tissues such as leaves, twigs, and trunks. Wind speed at any height within the canopy space is determined based on the above-canopy wind speed and an exponential decline of wind speed as function of downward-cumulated canopy surface area. The wind speed determines the efficiency of mixing of air and droplets into the canopy and also the efficiency with which droplets impact onto canopy surfaces. The model is deterministic and assumes a steady-state, so that for one set of above-canopy conditions it calculates one deposition rate. The model requires as input data:

- 1) the surface area index of canopy tissues in each height layer in the canopy,
- 2) the zero-plane displacement height and roughness length of the canopy

- 3) the wind speed at the canopy top
- 4) the liquid water content (LWC) of the cloud above the canopy
- 5) the mode of the droplet diameter distribution in the cloud

From these input parameters, the model calculates the deposition of cloud water, expressed both as a water flux rate ( $\text{g cm}^{-2} \text{min}^{-1}$ ), and as a deposition velocity (flux rate/LWC, in units of cm/s). Deposition rates of ions are calculated by multiplying the water deposition rate by the ion concentration in cloud water above the canopy. In the original version of the model, a calculation of the evaporation rate from the canopy was also included in order to estimate net deposition of cloud water. For this project, only gross deposition rate was required so the evaporation routine was not invoked.

The 2009 data set covered the period June-September 2009. There were 58 sample periods with valid data that were used for this analysis. All months had sampling completeness values greater than 75%.

The calculations done here for 2009 followed closely those done previously for the Clingmans Dome site (e.g., Lovett 2008). After the model was run for all sample periods, seasonal and monthly means and totals were calculated in a SAS program. Total seasonal deposition was calculated by summing the four monthly totals.

As in previous results, these model runs were made assuming a 10-m tall, intact, homogeneous conifer canopy. The actual canopy structure at Clingmans Dome has not been quantified, and may differ substantially from the modeled canopy structure. Consequently, this deposition estimate is best viewed as an index of cloud deposition that can be used to compare the effects of changing meteorological and cloud chemical conditions across different sites and different times, assuming that the same “standard” canopy was present at each site and time.

Because the measurement periods vary in length, all the means presented here are weighted by the duration of the sampling event. Duration-weighting the seasonal and monthly means in this way avoids giving a 10-minute event the same weight as a 10-hour event. This is analogous to the standard practice of volume-weighting the means of precipitation chemistry.

## Results

The model was run on 58 time periods as discussed above, and the results are presented as deposition velocities and deposition fluxes in the CLD 2009.xls spreadsheet and in Appendix I.

The period of measurement was June - September 2009. Monthly mean concentrations of ions in cloud water and in meteorological and deposition variables are given in Appendix I. During the measurement period, duration-weighted mean concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were highest in June and decreased through the subsequent months (Fig. 1). Seasonal mean concentrations (duration-weighted) of these ions in 2009 were in general substantially lower than in 2007 (Fig. 2). Since 2003, the concentrations of hydrogen ion,

nitrate, sulfate and ammonium have been level or slightly rising, but all ions showed a substantial increase in 2007, and declined again to pre-2007 levels or below in 2009. This decrease in concentration in between 2007 and 2009 is partially explained by dilution, as the mean cloud liquid water content (LWC) was significantly higher in 2009 than in 2007 (Figure 2) and higher LWC is often associated with lower concentrations. In essence, if the same amount of sulfate (or any soluble pollutant) is dissolved in a larger amount of water, the result will be a lower concentration. Several lines of evidence suggest that this explains part, but not all, of the decline in concentrations in 2009. First, most ions decreased in concentration this year, including the non-pollutant ions K and Na (see accompanying Excel workbook), suggesting a dilution/concentration effect rather than a change in the pollutant emissions. Second, if we correct the sulfate trend for changes in LWC by calculating the amount of dissolved sulfate per cubic meter of air (by multiplying the sulfate concentration in cloud water by the LWC), the trends look very different (Figure 3). In these data, the 2009 values appear to be slightly lower than the relatively flat trend seen between 2002-2007. This indicates that the dilution effect explains most of the difference in sulfate between 2007 and 2009, but that there may be a reduction in total dissolved sulfate beyond the dilution effect. Finally, if we compare concentrations in 2009 with a year that had a similar mean LWC (for instance, 2005) the ion concentrations for most ions are similar to those we measured in 2009, but H<sup>+</sup> and sulfate are substantially lower in 2009, while Ca is somewhat higher. This suggests that there was both a reduction in sulfate pollution and perhaps an increase in dust pollution (as a source of Ca) in 2009, that goes beyond a simple LWC dilution effect.

The trends shown in Figure 2 are based on duration-weighted mean concentrations and represent only those data used for modeling cloud water deposition (i.e. those events for which liquid water content and wind speed were also measured). These trends may not match other calculations of trends if more complete chemistry datasets or non-duration-weighted means are used. Also, the trends in hydrogen ion shown in Figure 2 must be interpreted with caution because of the variation from year to year in whether lab pH or field pH was used. In general, lab pH values are higher (i.e. lower H<sup>+</sup> concentration, less acidic) than field pH values because H<sup>+</sup> is very reactive and is consumed during the sample holding period prior to laboratory analysis. For these 2009 data we used exclusively lab pH values because of an incomplete record of field pH.

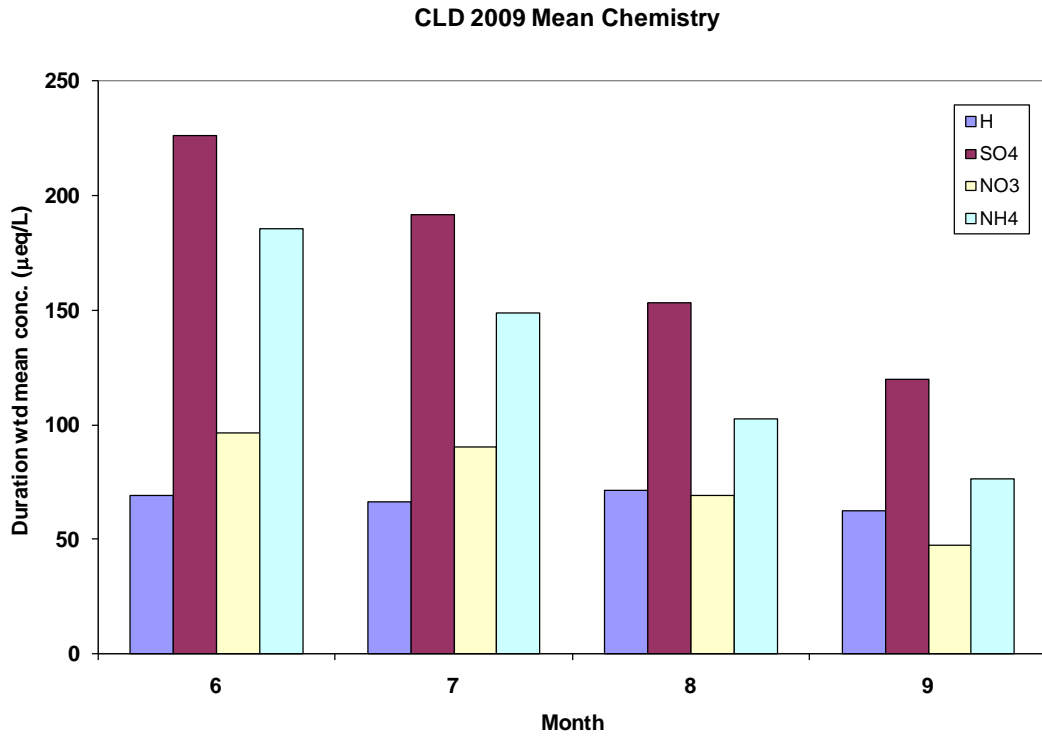
Wind speed and cloud water deposition velocity were relatively constant from month to month during the sampling period, except for a slight decline in both properties in September (Figure 4). Mean duration-weighted deposition velocity for the 2009 season was 17.7 cm/s, well below the 1995-2009 mean of 21.1 cm/s (see accompanying Excel workbook). The deposition velocity probably was lower than the average because the mean wind speed (3.6 m/s) was also lower than the average (4.6 m/s). Monthly mean cloud LWC was relatively constant through the season between 0.3 and 0.4 g/m<sup>3</sup> (Figure 5), with a seasonal mean of 0.36 g/m<sup>3</sup>, slightly above the long-term mean of 0.32.

Seasonal deposition totals were calculated by summing the values across all four months. For comparison with the results of the previous reports, these means are expressed in Table 1 as the mean monthly deposition rate in kg/ha/month. Compared to

2007, the lower ion concentrations in 2009 were offset by the higher amount of water deposition. Thus, deposition of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were all higher in 2009 than in 2007 despite the lower concentrations. Hydrogen ion deposition was similar to 2007.

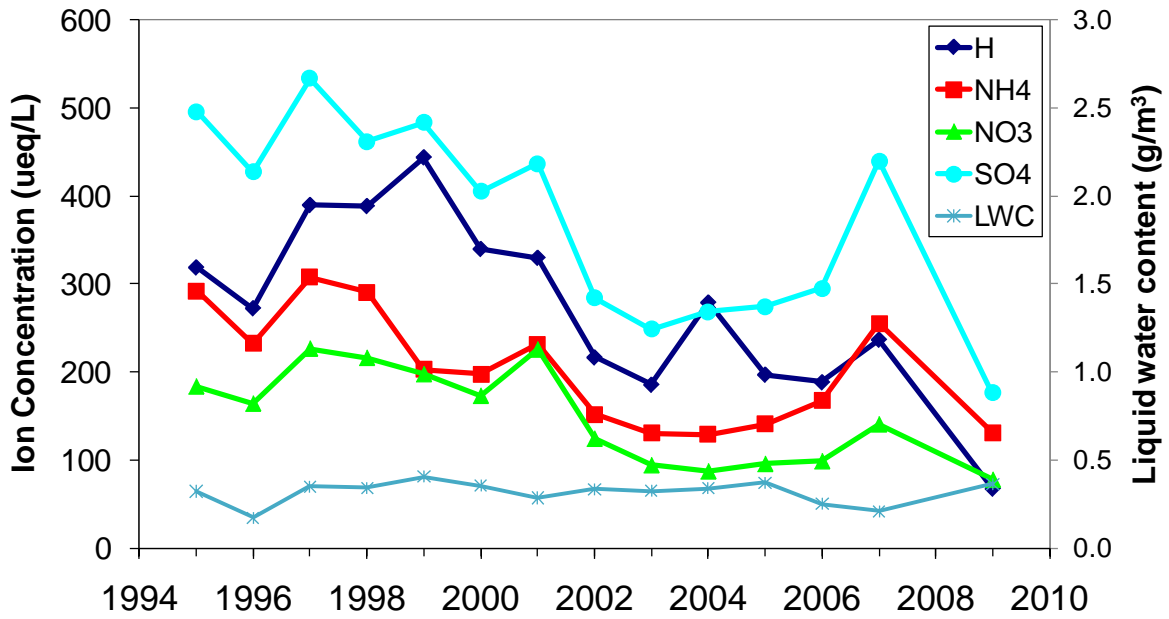
**Table 1. Mean monthly deposition rates for several ions (in kg/ha/month) and water (cm/month) for the Clingmans Dome site for the 1995-2009 period. The seasonal averages include the months of June-September for 2007 and 2009, June-October for 2004-2006 and May-September for previous years. The data in this table for 2006 include the months of September and October, because the calculations were made prior to the invalidation of the LWC data from those months.**

	Water	H <sup>+</sup>	NH <sub>4</sub>	SO <sub>4</sub>	NO <sub>3</sub>
<b>CLD 2009</b>	<b>9.1</b>	<b>0.06</b>	<b>1.9</b>	<b>7.1</b>	<b>4.0</b>
CLD 2007	3.5	0.07	1.3	5.6	2.5
CLD 2006	13.0	0.22	3.1	15.5	6.8
CLD 2005	8.7	0.12	1.5	7.8	3.5
CLD 2004	10.6	0.27	2.1	11.5	4.8
CLD 2003	10.5	0.14	1.8	9.3	4.7
CLD 2002	9.2	0.18	2.3	11.9	6.1
CLD 2001	8.6	0.31	3.3	18.4	12.5
CLD 2000	9.7	0.29	3.0	16.9	8.8
CLD 1999	11.0	0.47	3.6	22.7	11.5
CLD 1995-98	8.1	0.23	3.0	14.3	7.7

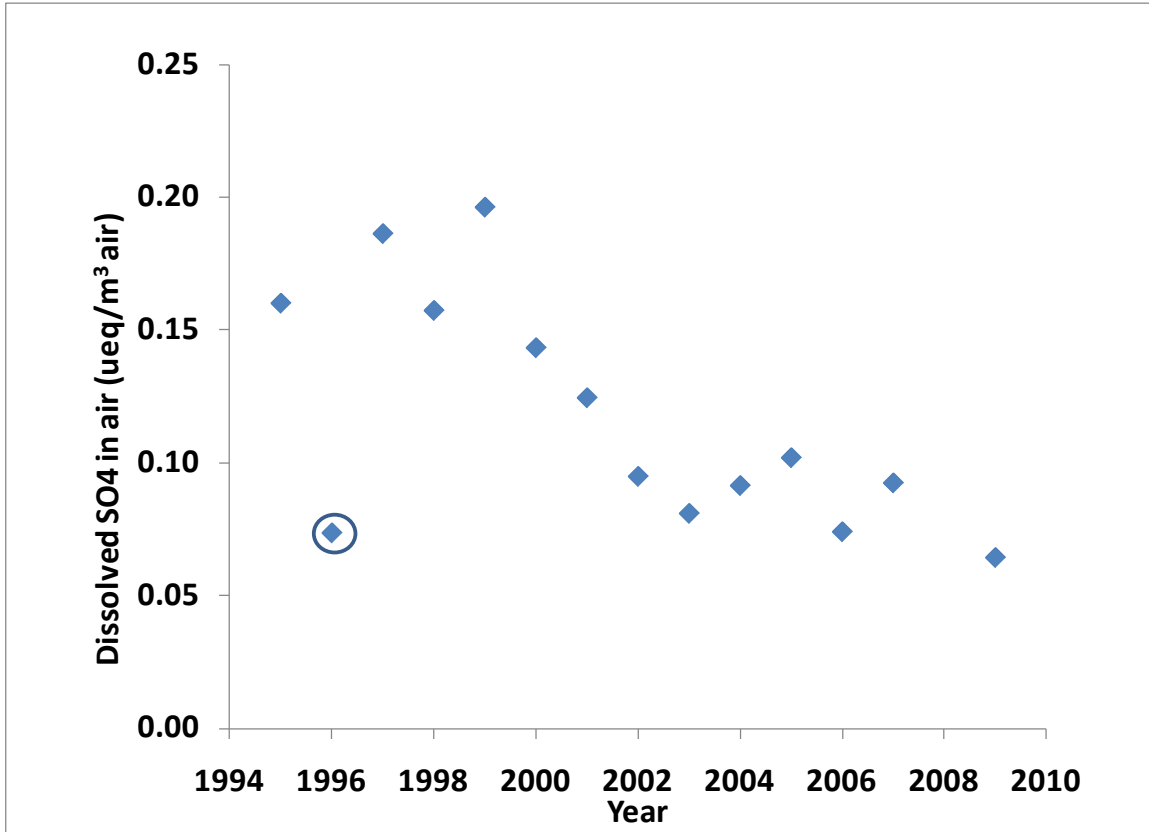


**Figure 1. Duration-weighted mean concentration of four ions in cloud water, calculated by month.**

## Trends in Ion Concentrations, Clingmans Dome



**Figure 2. Trends in ion concentrations and LWC at Clingmans Dome, 1995-2009.** Data are duration-weighted means for the warm season and include only the samples for which deposition was modeled (i.e. LWC and meteorological data were also present). LWC data for 2006 do not include September and October, for which LWC data were invalidated due to instrument error.



**Figure 3. Mean values of dissolved sulfate per cubic meter of air (= cloud water sulfate concentration x LWC/1000) for Clingmans Dome. Circled year (1996) has anomalously low LWC data, perhaps because of instrument error. LWC data for 2006 do not include September and October, for which LWC data were invalidated due to instrument error.**



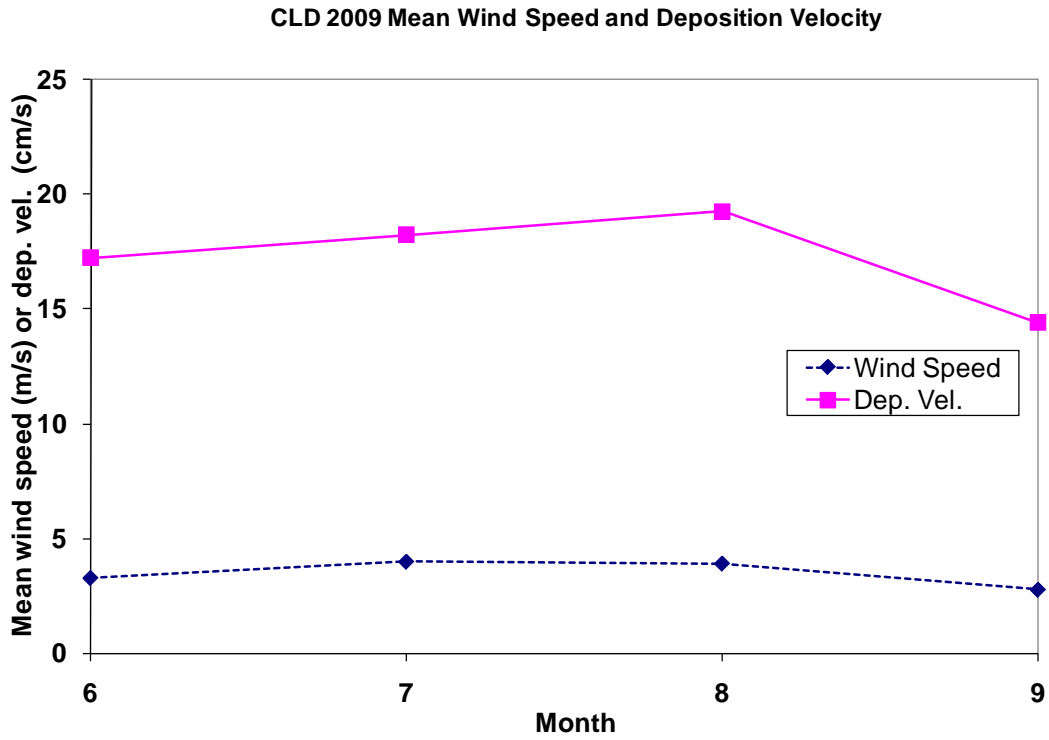


Figure 4. Mean wind speed and deposition velocity for each month.

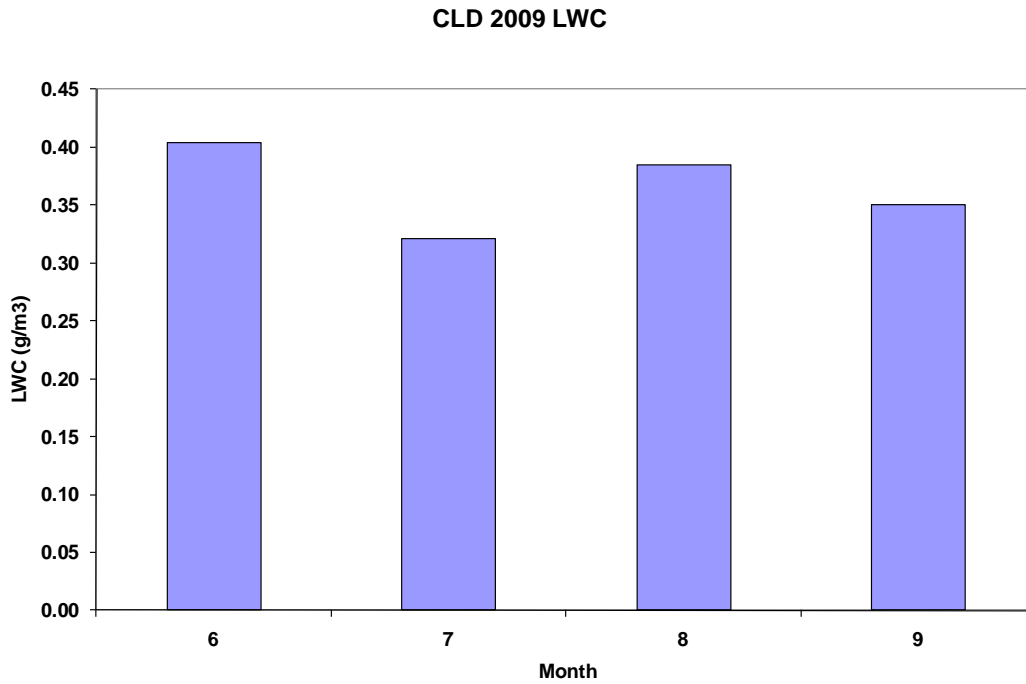


Figure 5. Mean liquid water content for each month of the study.

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- Lovett, G. M. 1984. Rates and mechanisms of cloud water deposition to a subalpine balsam fir forest. *Atmospheric Environment* **18**:361-371.
- Lovett, G.M. 2008. Cloud water deposition to Clingmans Dome in 2007. Report to MACTEC, March 2008. 8 pp.
- MACTEC. 2007. Cloud Deposition Monitoring, Clingmans Dome, TN, Great Smoky Mountains National Park, 2006. Report for EPA Contract 68-D-03-052. MACTEC Engineering and Consulting, Inc. Gainesville, FL.
- Thorne, P. G., G. M. Lovett, and W. A. Reiners. 1982. Experimental determination of droplet deposition on canopy components of balsam fir. *J. Appl. Meteorol.* **21**:1413-1416.

Appendix I.

Table I-1. Monthly mean meteorological and deposition variables. All means are duration-weighted. TUBFLUX , SEDFLUX and TOTFLUX are turbulent, sedimentation and total water fluxes (g/cm<sup>2</sup>/min) for the time period, and TURBVD, SEDVD and TOTVD are the corresponding deposition velocities (cm/s). WS is wind speed (m/s) and LWC is cloud liquid water content in g/m<sup>3</sup>.

MONTH	OBS	DURATION	VOLUME	WS	LWC	TUBFLUX	SEDFLUX	TOTFLUX	TURB VD	SED VD	TOT VD
6	15	30.23	6576.28	3.28	0.40	2.35E-04	1.93E-04	4.28E-04	9.49	7.73	17.22
7	10	33.29	5894.86	3.99	0.32	2.24E-04	1.36E-04	3.60E-04	11.64	6.60	18.24
8	26	14.99	3784.13	3.91	0.38	2.82E-04	1.76E-04	4.58E-04	11.95	7.31	19.26
9	7	26.71	5588.24	2.77	0.35	1.51E-04	1.64E-04	3.15E-04	7.02	7.39	14.41

Table I- 2. Monthly mean ion concentrations (µeq/L). All means are duration-weighted.

Month	H (lab)	Ca	Mg	K	Na	NH4	SO4	NO3	Cl
6	69.29	61.89	11.99	3.26	16.80	185.52	226.14	96.21	14.17
7	66.46	57.31	12.51	2.89	8.93	148.48	191.54	90.44	9.95
8	71.48	29.16	9.17	2.51	17.19	102.46	153.25	69.09	17.87
9	62.36	18.46	5.75	2.66	7.19	76.45	119.82	47.20	6.27

Table I-3. Monthly deposition in kg/ha/month. Water deposition in cm/month.

Month	HDEP	KDEP	NADEP	CADEP	MGDEP	NH4DEP	SO4DEP	NO3DEP	CLDEP	H2ODEP
6	0.06	0.10	0.37	1.04	0.12	2.83	9.52	5.22	0.45	9.02
7	0.05	0.10	0.16	1.05	0.14	2.29	7.83	4.69	0.28	8.90
8	0.07	0.09	0.44	0.56	0.11	1.60	7.05	4.14	0.72	11.54
9	0.05	0.07	0.12	0.22	0.05	1.02	4.13	2.08	0.16	6.95

## **Appendix B**

### **Cloud Water Data and QC Summary**

## Cloud Water Data and QC Summary

Analytical data for the 58 cloud deposition samples are presented in Table B-1 including measured field pH, field conductivity, sample volume, average LWC, valid hours, average scalar wind speed, and calculated cations and anions. A cumulative volume-weighted mean is shown for the various indicated analytes and ions.

Tables B-2, B-3, and B-4 provide summaries of the QC results associated with the samples. The QC results for all parameters are within the measured criteria of the CASTNET QC program (MACTEC, 2008). Table B-2 summarizes the QC data for the reference samples for each parameter in each analytical batch. The reference sample is traceable to NIST and is supplied in a matrix similar to the cloud samples. An independent laboratory supplies these reference samples with a certificate of analysis stating the target values. A reference sample is analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. The QC limits require the measured value to be within  $\pm 5$  percent of the known value for anions, and within  $\pm 10$  percent of the known value for cations. For pH, the QC limits require the measured value to be within  $\pm 0.05$  pH units of the known value. The data from all required reference samples analyzed with the Clingmans Dome samples are within the CASTNET QC criteria.

The results of the analyses of the CCV for each parameter in each analytical batch are provided in Table B-3. A CCV is a NIST-traceable solution supplied in a matrix similar to that of the sample being analyzed with a target value at approximately the midpoint of the calibration curve. This QC solution is supplied to MACTEC by a laboratory independent of the laboratory supplying the reference sample solution. A CCV is analyzed after every 10 environmental samples to verify that the instrument calibration has not drifted more than  $\pm 5$  percent for anions and base cations,  $\pm 10$  percent for  $\text{NH}_4^+$ , and  $\pm 0.05$  pH units for pH. The results of all CCV analyses were within acceptance criteria.

Table B-4 summarizes the percent difference between samples reanalyzed within the same analytical batch. Five percent of the samples in each analytical batch were randomly selected for replicate analysis. This table presents only the samples that were replicated. The replicate percent difference criteria are  $\pm 5$  percent for anions and base cations, and  $\pm 10$  percent for  $\text{NH}_4^+$ , for samples with concentrations greater than five times the analytical detection limit. For samples with lower concentrations, the difference between the two values cannot be more than the analytical detection limit. For pH, the difference between the two values cannot be more than  $\pm 0.05$  pH units. The data from all required replicate samples are within the CASTNET QC criteria.





**Table B-2.** Cloud Deposition 2009 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples (1 of 3)

Lab pH					NH <sub>4</sub> <sup>+</sup> -N					SO <sub>4</sub> <sup>2-</sup>				
Batch Number	Lab Key	Target STD Units	Found STD Units	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L907013	L907013-SRM1	5.40	5.37	99.4	L906022	L906022-SRM1	0.832	0.8571	103.0	L907007	L907007-SRM1	10.0	9.87	98.7
L907013	L907013-SRM2	5.40	5.41	100.2	L906022	L906022-SRM2	0.832	0.8610	103.5	L907007	L907007-SRM2	10.0	9.97	99.7
L908031	L908031-SRM1	5.40	5.44	100.7	L907001	L907001-SRM1	0.832	0.8493	102.1	L907007	L907007-SRM3	10.0	10.01	100.1
L908031	L908031-SRM2	5.40	5.44	100.7	L907001	L907001-SRM2	0.832	0.8480	101.9	L907007	L907007-SRM4	10.0	10.03	100.3
L909014	L909014-SRM1	5.40	5.38	99.6	L908023	L908023-SRM1	0.760	0.7438	97.9	L909001	L909001-SRM1	10.0	9.89	98.9
L909014	L909014-SRM2	5.40	5.37	99.4	L908023	L908023-SRM2	0.760	0.7492	98.6	L909001	L909001-SRM2	10.0	9.97	99.7
L909027	L909027-SRM1	5.40	5.41	100.2	L908029	L908029-SRM1	0.760	0.7394	97.3	L909001	L909001-SRM3	10.0	9.99	99.9
L909027	L909027-SRM2	5.40	5.43	100.6	L908029	L908029-SRM2	0.760	0.7456	98.1	L909001	L909001-SRM4	10.0	10.01	100.1
L910035	L910035-SRM1	5.40	5.40	100.0	L909008	L909008-SRM1	0.760	0.7405	97.4	L909012	L909012-SRM1	10.0	9.95	99.5
L910035	L910035-SRM2	5.40	5.39	99.8	L909008	L909008-SRM2	0.760	0.7460	98.2	L909012	L909012-SRM2	10.0	9.71	97.1
L912010	L912010-SRM1	5.40	5.40	100.0	L909020	L909020-SRM1	0.760	0.7408	97.5	L909021	L909021-SRM1	10.0	9.79	97.9
L912010	L912010-SRM2	5.40	5.45	100.9	L909020	L909020-SRM2	0.760	0.7443	97.9	L909021	L909021-SRM2	10.0	9.85	98.5
					L910023	L910023-SRM1	0.760	0.7384	97.2	L910028	L910028-SRM1	10.0	9.99	99.9
					L910023	L910023-SRM2	0.760	0.7410	97.5	L910028	L910028-SRM2	10.0	9.95	99.5
					L911016	L911016-SRM1	0.760	0.7390	97.2	L911017	L911017-SRM1	10.0	9.73	97.3
					L911016	L911016-SRM2	0.760	0.7366	96.9	L911017	L911017-SRM2	10.0	9.81	98.1
<b>Mean</b>				<b>100.1</b>	<b>Mean</b>				<b>98.9</b>	<b>Mean</b>				<b>99.1</b>
<b>Standard Deviation</b>				<b>0.51</b>	<b>Standard Deviation</b>				<b>2.29</b>	<b>Standard Deviation</b>				<b>1.04</b>
<b>Count</b>				<b>12</b>	<b>Count</b>				<b>16</b>	<b>Count</b>				<b>16</b>



**Table B-2.** Cloud Deposition 2009 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples (2 of 3)

NO <sub>3</sub> <sup>-</sup> -N					Cl <sup>-</sup>					Ca <sup>2+</sup>				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L907007	L907007-SRM1	1.6	1.59	99.1	L907007	L907007-SRM1	0.96	0.959	99.9	L906029	L906029-SRM1	0.050	0.0547	109.5
L907007	L907007-SRM2	1.6	1.59	99.4	L907007	L907007-SRM2	0.96	0.976	101.7	L906029	L906029-SRM2	0.050	0.0536	107.2
L907007	L907007-SRM3	1.6	1.61	100.6	L907007	L907007-SRM3	0.96	0.978	101.9	L908026	L908026-SRM1	0.053	0.0551	104.0
L907007	L907007-SRM4	1.6	1.61	100.9	L907007	L907007-SRM4	0.96	0.984	102.5	L908026	L908026-SRM2	0.053	0.0562	106.1
L909001	L909001-SRM1	1.6	1.60	99.7	L909001	L909001-SRM1	0.96	0.981	102.2	L909010	L909010-SRM1	0.053	0.0542	102.3
L909001	L909001-SRM2	1.6	1.58	98.6	L909001	L909001-SRM2	0.96	0.981	102.2	L909010	L909010-SRM2	0.053	0.0537	101.3
L909001	L909001-SRM3	1.6	1.61	100.8	L909001	L909001-SRM3	0.96	1.005	104.7	L909022	L909022-SRM1	0.053	0.0540	101.8
L909001	L909001-SRM4	1.6	1.63	101.8	L909001	L909001-SRM4	0.96	0.964	100.4	L909022	L909022-SRM2	0.053	0.0548	103.4
L909012	L909012-SRM1	1.6	1.63	101.7	L909012	L909012-SRM1	0.96	0.972	101.3	L910036	L910036-SRM1	0.053	0.0525	99.0
L909012	L909012-SRM2	1.6	1.61	100.6	L909012	L909012-SRM2	0.96	0.986	102.7	L910036	L910036-SRM2	0.053	0.0526	99.2
L909021	L909021-SRM1	1.6	1.60	100.1	L909021	L909021-SRM1	0.96	0.968	100.8	L912007	L912007-SRM1	0.053	0.0525	99.0
L909021	L909021-SRM2	1.6	1.59	99.3	L909021	L909021-SRM2	0.96	0.967	100.7	L912007	L912007-SRM2	0.053	0.0533	100.6
L910028	L910028-SRM1	1.6	1.60	99.7	L910028	L910028-SRM1	0.96	0.977	101.8					
L910028	L910028-SRM2	1.6	1.56	97.5	L910028	L910028-SRM2	0.96	0.972	101.3					
L911017	L911017-SRM1	1.6	1.56	97.7	L911017	L911017-SRM1	0.96	0.961	100.1					
L911017	L911017-SRM2	1.6	1.58	98.8	L911017	L911017-SRM2	0.96	0.969	100.9					
<b>Mean</b>				<b>99.8</b>	<b>Mean</b>				<b>101.6</b>	<b>Mean</b>				<b>102.8</b>
<b>Standard Deviation</b>				<b>1.26</b>	<b>Standard Deviation</b>				<b>1.18</b>	<b>Standard Deviation</b>				<b>3.38</b>
<b>Count</b>				<b>16</b>	<b>Count</b>				<b>16</b>	<b>Count</b>				<b>12</b>

**Table B-2.** Cloud Deposition 2009 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples (3 of 3)

<b>Mg<sup>2+</sup></b>					<b>Na<sup>+</sup></b>					<b>K<sup>+</sup></b>				
<b>Batch Number</b>	<b>Lab Key</b>	<b>Target mg/L</b>	<b>Found mg/L</b>	<b>Percent Recovery</b>	<b>Batch Number</b>	<b>Lab Key</b>	<b>Target mg/L</b>	<b>Found mg/L</b>	<b>Percent Recovery</b>	<b>Batch Number</b>	<b>Lab Key</b>	<b>Target mg/L</b>	<b>Found mg/L</b>	<b>Percent Recovery</b>
L906029	L906029-SRM1	0.052	0.0539	103.6	L906029	L906029-SRM1	0.39	0.402	103.0	L906029	L906029-SRM1	0.099	0.1013	102.3
L906029	L906029-SRM2	0.052	0.0535	103.0	L906029	L906029-SRM2	0.39	0.391	100.4	L906029	L906029-SRM2	0.099	0.0928	93.7
L908026	L908026-SRM1	0.052	0.0526	101.2	L908026	L908026-SRM1	0.39	0.398	102.0	L908026	L908026-SRM1	0.099	0.1013	102.3
L908026	L908026-SRM2	0.052	0.0535	102.9	L908026	L908026-SRM2	0.39	0.396	101.5	L908026	L908026-SRM2	0.099	0.0993	100.3
L909010	L909010-SRM1	0.052	0.0541	104.1	L909010	L909010-SRM1	0.39	0.390	99.9	L909010	L909010-SRM1	0.099	0.0982	99.2
L909010	L909010-SRM2	0.052	0.0533	102.5	L909010	L909010-SRM2	0.39	0.385	98.8	L909010	L909010-SRM2	0.099	0.0959	96.9
L909022	L909022-SRM1	0.052	0.0540	103.8	L909022	L909022-SRM1	0.39	0.396	101.5	L909022	L909022-SRM1	0.099	0.1000	101.0
L909022	L909022-SRM2	0.052	0.0527	101.4	L909022	L909022-SRM2	0.39	0.392	100.6	L909022	L909022-SRM2	0.099	0.1009	101.9
L910036	L910036-SRM1	0.052	0.0530	101.9	L910036	L910036-SRM1	0.39	0.393	100.7	L910036	L910036-SRM1	0.099	0.0970	97.9
L910036	L910036-SRM2	0.052	0.0531	102.1	L910036	L910036-SRM2	0.39	0.391	100.2	L910036	L910036-SRM2	0.099	0.0948	95.7
L912007	L912007-SRM1	0.052	0.0530	101.9	L912007	L912007-SRM1	0.39	0.393	100.7	L912007	L912007-SRM1	0.098	0.0939	95.8
L912007	L912007-SRM2	0.052	0.0531	102.2	L912007	L912007-SRM2	0.39	0.396	101.4	L912007	L912007-SRM2	0.098	0.0936	95.5
<b>Mean</b>				<b>102.5</b>	<b>Mean</b>				<b>100.9</b>	<b>Mean</b>				<b>98.6</b>
<b>Standard Deviation</b>				<b>0.94</b>	<b>Standard Deviation</b>				<b>1.09</b>	<b>Standard Deviation</b>				<b>3.02</b>
<b>Count</b>				<b>12</b>	<b>Count</b>				<b>12</b>	<b>Count</b>				<b>12</b>

**Table B-3.** Cloud Deposition 2009 Sampling Season – QC Batch Summary for Cloud Samples – CCV (1 of 3)

Lab pH					NH <sub>4</sub> <sup>+</sup> -N					SO <sub>4</sub> <sup>2-</sup>				
Batch Number	Lab Key	Target STD Units	Found STD Units	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L907013	L907013-CCV1	5.00	5.01	100.2	L906022	L906022-CCV1	1	0.9903	99.0	L907007	L907007-CCV1	2.5	2.45	97.9
L907013	L907013-CCV2	5.00	4.97	99.4	L906022	L906022-CCV2	1	0.9957	99.6	L907007	L907007-CCV2	2.5	2.43	97.3
L907013	L907013-CCV3	5.00	5.00	100.0	L906022	L906022-CCV3	1	0.9926	99.3	L907007	L907007-CCV3	2.5	2.50	100.1
L907013	L907013-CCV4	5.00	4.98	99.6	L906022	L906022-CCV4	1	0.9928	99.3	L907007	L907007-CCV4	2.5	2.46	98.3
L907013	L907013-CCV5	5.00	5.02	100.4	L906022	L906022-CCV5	1	1.0052	100.5	L907007	L907007-CCV5	2.5	2.50	100.0
L908031	L908031-CCV1	5.00	5.05	101.0	L907001	L907001-CCV1	1	0.9918	99.2	L907007	L907007-CCV6	2.5	2.48	99.2
L908031	L908031-CCV2	5.00	5.02	100.4	L907001	L907001-CCV2	1	0.9972	99.7	L907007	L907007-CCV7	2.5	2.48	99.2
L908031	L908031-CCV3	5.00	5.05	101.0	L908023	L908023-CCV1	1	0.9955	99.6	L909001	L909001-CCV1	2.5	2.45	97.8
L908031	L908031-CCV4	5.00	5.05	101.0	L908023	L908023-CCV2	1	0.9975	99.8	L909012	L909012-CCV1	2.5	2.47	98.8
L908031	L908031-CCV5	5.00	5.00	100.0	L908023	L908023-CCV3	1	0.9995	100.0	L909001	L909001-CCV2	2.5	2.48	99.2
L909014	L909014-CCV1	5.00	4.99	99.8	L908023	L908023-CCV4	1	0.9851	98.5	L909012	L909012-CCV2	2.5	2.51	100.2
L909014	L909014-CCV2	5.00	5.03	100.6	L908023	L908023-CCV5	1	0.9897	99.0	L909001	L909001-CCV3	2.5	2.43	97.2
L909014	L909014-CCV3	5.00	5.00	100.0	L908023	L908023-CCV6	1	1.0053	100.5	L909012	L909012-CCV3	2.5	2.48	99.0
L909027	L909027-CCV1	5.00	5.05	101.0	L908023	L908023-CCV7	1	1.0043	100.4	L909001	L909001-CCV4	2.5	2.51	100.2
L909027	L909027-CCV2	5.00	4.98	99.6	L908029	L908029-CCV1	1	0.9886	98.9	L909001	L909001-CCV5	2.5	2.51	100.6
L909027	L909027-CCV3	5.00	5.05	101.0	L908029	L908029-CCVA	1	0.9868	98.7	L909001	L909001-CCV6	2.5	2.48	99.3
L910035	L910035-CCV1	5.00	5.02	100.4	L908029	L908029-CCVB	1	0.9881	98.8	L909001	L909001-CCV7	2.5	2.47	98.6
L910035	L910035-CCV2	5.00	4.97	99.4	L908029	L908029-CCV2	1	0.9877	98.8	L909001	L909001-CCV8	2.5	2.50	100.0
L910035	L910035-CCV3	5.00	5.02	100.4	L908029	L908029-CCV3	1	0.9939	99.4	L909021	L909021-CCV1	2.5	2.48	99.4
L912010	L912010-CCV1	5.00	4.99	99.8	L908029	L908029-CCV4	1	0.9797	98.0	L909021	L909021-CCV2	2.5	2.41	96.4
L912010	L912010-CCV2	5.00	5.04	100.8	L908029	L908029-CCV5	1	0.9840	98.4	L909021	L909021-CCV3	2.5	2.45	97.8
L912010	L912010-CCV3	5.00	5.03	100.6	L908029	L908029-CCV6	1	0.9930	99.3	L910028	L910028-CCV1	2.5	2.47	98.8
					L908029	L908029-CCV7	1	1.0011	100.1	L910028	L910028-CCV2	2.5	2.48	99.3
					L908029	L908029-CCV8	1	0.9940	99.4	L910028	L910028-CCV3	2.5	2.43	97.2
					L908029	L908029-CCV9	1	0.9957	99.6	L911017	L911017-CCV1	2.5	2.44	97.5
					L909008	L909008-CCV1	1	0.9856	98.6	L911017	L911017-CCV2	2.5	2.44	97.5
					L909008	L909008-CCV2	1	0.9886	98.9	L911017	L911017-CCV3	2.5	2.40	96.1
					L909008	L909008-CCV3	1	0.9979	99.8					
					L909008	L909008-CCV4	1	0.9899	99.0					
					L909020	L909020-CCV1	1	0.9911	99.1					
					L909020	L909020-CCV2	1	0.9965	99.7					
					L909020	L909020-CCV3	1	0.9870	98.7					
					L909020	L909020-CCV4	1	0.9869	98.7					
					L910023	L910023-CCV1	1	0.9822	98.2					
					L910023	L910023-CCV2	1	0.9903	99.0					
					L911016	L911016-CCV1	1	0.9879	98.8					
					L911016	L911016-CCV2	1	0.9957	99.6					
					L911016	L911016-CCV3	1	0.9932	99.3					
<b>Mean</b>				<b>100.3</b>	<b>Mean</b>				<b>99.2</b>	<b>Mean</b>				<b>98.6</b>
<b>Standard Deviation</b>				<b>0.55</b>	<b>Standard Deviation</b>				<b>0.61</b>	<b>Standard Deviation</b>				<b>1.23</b>
<b>Count</b>				<b>22</b>	<b>Count</b>				<b>38</b>	<b>Count</b>				<b>27</b>

**Table B-3.** Cloud Deposition 2009 Sampling Season – QC Batch Summary for Cloud Samples – CCV (2 of 3)

NO <sub>3</sub> <sup>-</sup> -N					Cl <sup>-</sup>					Ca <sup>2+</sup>				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L907007	L907007-CCV1	0.5	0.490	98.0	L907007	L907007-CCV1	0.5	0.508	101.6	L906029	L906029-CCV1	0.5	0.5080	101.6
L907007	L907007-CCV2	0.5	0.500	100.0	L907007	L907007-CCV2	0.5	0.509	101.8	L906029	L906029-CCV2	0.5	0.4997	99.9
L907007	L907007-CCV3	0.5	0.505	101.0	L907007	L907007-CCV3	0.5	0.508	101.6	L906029	L906029-CCV3	0.5	0.4942	98.8
L907007	L907007-CCV4	0.5	0.501	100.2	L907007	L907007-CCV4	0.5	0.511	102.2	L906029	L906029-CCV4	0.5	0.4925	98.5
L907007	L907007-CCV5	0.5	0.501	100.2	L907007	L907007-CCV5	0.5	0.500	100.0	L906029	L906029-CCV5	0.5	0.4977	99.5
L907007	L907007-CCV6	0.5	0.502	100.4	L907007	L907007-CCV6	0.5	0.502	100.4	L906029	L906029-CCV6	0.5	0.4981	99.6
L907007	L907007-CCV7	0.5	0.500	100.0	L907007	L907007-CCV7	0.5	0.505	101.0	L906029	L906029-CCV7	0.5	0.4968	99.4
L909001	L909001-CCV1	0.5	0.492	98.4	L909001	L909001-CCV1	0.5	0.491	98.2	L906029	L906029-CCV8	0.5	0.4982	99.6
L909001	L909001-CCV2	0.5	0.489	97.8	L909001	L909001-CCV2	0.5	0.490	98.0	L906029	L906029-CCV9	0.5	0.5030	100.6
L909001	L909001-CCV3	0.5	0.498	99.6	L909001	L909001-CCV3	0.5	0.495	99.0	L908026	L908026-CCV1	0.5	0.4979	99.6
L909001	L909001-CCV4	0.5	0.499	99.8	L909001	L909001-CCV4	0.5	0.488	97.6	L908026	L908026-CCV2	0.5	0.4984	99.7
L909001	L909001-CCV5	0.5	0.496	99.2	L909001	L909001-CCV5	0.5	0.481	96.2	L908026	L908026-CCV3	0.5	0.4980	99.6
L909001	L909001-CCV6	0.5	0.486	97.2	L909001	L909001-CCV6	0.5	0.499	99.8	L908026	L908026-CCV4	0.5	0.5000	100.0
L909001	L909001-CCV7	0.5	0.494	98.8	L909001	L909001-CCV7	0.5	0.501	100.2	L908026	L908026-CCV5	0.5	0.5032	100.6
L909001	L909001-CCV8	0.5	0.498	99.6	L909001	L909001-CCV8	0.5	0.486	97.2	L908026	L908026-CCV6	0.5	0.5014	100.3
L909012	L909012-CCV1	0.5	0.504	100.8	L909012	L909012-CCV1	0.5	0.498	99.6	L908026	L908026-CCV7	0.5	0.5029	100.6
L909012	L909012-CCV2	0.5	0.510	102.0	L909012	L909012-CCV2	0.5	0.495	99.0	L909010	L909010-CCV1	0.5	0.5016	100.3
L909012	L909012-CCV3	0.5	0.508	101.6	L909012	L909012-CCV3	0.5	0.501	100.2	L909010	L909010-CCV2	0.5	0.5015	100.3
L909021	L909021-CCV1	0.5	0.498	99.6	L909021	L909021-CCV1	0.5	0.497	99.4	L909010	L909010-CCV3	0.5	0.4967	99.3
L909021	L909021-CCV2	0.5	0.490	98.0	L909021	L909021-CCV2	0.5	0.490	98.0	L909022	L909022-CCV1	0.5	0.5030	100.6
L909021	L909021-CCV3	0.5	0.485	97.0	L909021	L909021-CCV3	0.5	0.489	97.8	L909022	L909022-CCV2	0.5	0.5105	102.1
L910028	L910028-CCV1	0.5	0.499	99.8	L910028	L910028-CCV1	0.5	0.488	97.6	L909022	L909022-CCV3	0.5	0.4974	99.5
L910028	L910028-CCV2	0.5	0.488	97.6	L910028	L910028-CCV2	0.5	0.486	97.2	L910036	L910036-CCV1	0.5	0.4972	99.4
L910028	L910028-CCV3	0.5	0.493	98.6	L910028	L910028-CCV3	0.5	0.484	96.8	L910036	L910036-CCV2	0.5	0.4996	99.9
L911017	L911017-CCV1	0.5	0.493	98.6	L911017	L911017-CCV1	0.5	0.481	96.2	L912007	L912007-CCV1	0.5	0.4947	98.9
L911017	L911017-CCV2	0.5	0.494	98.8	L911017	L911017-CCV2	0.5	0.480	96.0	L912007	L912007-CCV2	0.5	0.5024	100.5
L911017	L911017-CCV3	0.5	0.487	97.4	L911017	L911017-CCV3	0.5	0.483	96.6	L912007	L912007-CCV3	0.5	0.4985	99.7
<b>Mean</b>				<b>99.3</b>	<b>Mean</b>				<b>98.9</b>	<b>Mean</b>				<b>99.9</b>
<b>Standard Deviation</b>				<b>1.34</b>	<b>Standard Deviation</b>				<b>1.88</b>	<b>Standard Deviation</b>				<b>0.78</b>
<b>Count</b>				<b>27</b>	<b>Count</b>				<b>27</b>	<b>Count</b>				<b>27</b>

**Table B-3.** Cloud Deposition 2009 Sampling Season – QC Batch Summary for Cloud Samples – CCV (3 of 3)

Mg <sup>2+</sup>					Na <sup>+</sup>					K <sup>+</sup>				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L906029	L906029-CCV1	0.5	0.5045	100.9	L906029	L906029-CCV1	0.5	0.5097	101.9	L906029	L906029-CCV1	0.5	0.5065	101.3
L906029	L906029-CCV2	0.5	0.4946	98.9	L906029	L906029-CCV2	0.5	0.4999	100.0	L906029	L906029-CCV2	0.5	0.5008	100.2
L906029	L906029-CCV3	0.5	0.4969	99.4	L906029	L906029-CCV3	0.5	0.4935	98.7	L906029	L906029-CCV3	0.5	0.4945	98.9
L906029	L906029-CCV4	0.5	0.5009	100.2	L906029	L906029-CCV4	0.5	0.4923	98.5	L906029	L906029-CCV4	0.5	0.4912	98.2
L906029	L906029-CCV5	0.5	0.5007	100.1	L906029	L906029-CCV5	0.5	0.4971	99.4	L906029	L906029-CCV5	0.5	0.4989	99.8
L906029	L906029-CCV6	0.5	0.4984	99.7	L906029	L906029-CCV6	0.5	0.4978	99.6	L906029	L906029-CCV6	0.5	0.4988	99.8
L906029	L906029-CCV7	0.5	0.4999	100.0	L906029	L906029-CCV7	0.5	0.4971	99.4	L906029	L906029-CCV7	0.5	0.4950	99.0
L906029	L906029-CCV8	0.5	0.5003	100.1	L906029	L906029-CCV8	0.5	0.4962	99.2	L906029	L906029-CCV8	0.5	0.4973	99.5
L906029	L906029-CCV9	0.5	0.4996	99.9	L906029	L906029-CCV9	0.5	0.5027	100.5	L906029	L906029-CCV9	0.5	0.5027	100.5
L908026	L908026-CCV1	0.5	0.4889	97.8	L908026	L908026-CCV1	0.5	0.5008	100.2	L908026	L908026-CCV1	0.5	0.4968	99.4
L908026	L908026-CCV2	0.5	0.4993	99.9	L908026	L908026-CCV2	0.5	0.4991	99.8	L908026	L908026-CCV2	0.5	0.4971	99.4
L908026	L908026-CCV3	0.5	0.5038	100.8	L908026	L908026-CCV3	0.5	0.4981	99.6	L908026	L908026-CCV3	0.5	0.4976	99.5
L908026	L908026-CCV4	0.5	0.4983	99.7	L908026	L908026-CCV4	0.5	0.4992	99.8	L908026	L908026-CCV4	0.5	0.4985	99.7
L908026	L908026-CCV5	0.5	0.4991	99.8	L908026	L908026-CCV5	0.5	0.5007	100.1	L908026	L908026-CCV5	0.5	0.5008	100.2
L908026	L908026-CCV6	0.5	0.4995	99.9	L908026	L908026-CCV6	0.5	0.5006	100.1	L908026	L908026-CCV6	0.5	0.5012	100.2
L908026	L908026-CCV7	0.5	0.4998	100.0	L908026	L908026-CCV7	0.5	0.5037	100.7	L908026	L908026-CCV7	0.5	0.4987	99.7
L909010	L909010-CCV1	0.5	0.5030	100.6	L909010	L909010-CCV1	0.5	0.5031	100.6	L909010	L909010-CCV1	0.5	0.5002	100.0
L909010	L909010-CCV2	0.5	0.4995	99.9	L909010	L909010-CCV2	0.5	0.5035	100.7	L909010	L909010-CCV2	0.5	0.4993	99.9
L909010	L909010-CCV3	0.5	0.4974	99.5	L909010	L909010-CCV3	0.5	0.4971	99.4	L909010	L909010-CCV3	0.5	0.4979	99.6
L909022	L909022-CCV1	0.5	0.5006	100.1	L909022	L909022-CCV1	0.5	0.5077	101.5	L909022	L909022-CCV1	0.5	0.4987	99.7
L909022	L909022-CCV2	0.5	0.5184	103.7	L909022	L909022-CCV2	0.5	0.5104	102.1	L909022	L909022-CCV2	0.5	0.5081	101.6
L909022	L909022-CCV3	0.5	0.5023	100.5	L909022	L909022-CCV3	0.5	0.4979	99.6	L909022	L909022-CCV3	0.5	0.4976	99.5
L910036	L910036-CCV1	0.5	0.4980	99.6	L910036	L910036-CCV1	0.5	0.4973	99.5	L910036	L910036-CCV1	0.5	0.4957	99.1
L910036	L910036-CCV2	0.5	0.5011	100.2	L910036	L910036-CCV2	0.5	0.4994	99.9	L910036	L910036-CCV2	0.5	0.4983	99.7
L912007	L912007-CCV1	0.5	0.4976	99.5	L912007	L912007-CCV1	0.5	0.4950	99.0	L912007	L912007-CCV1	0.5	0.4935	98.7
L912007	L912007-CCV2	0.5	0.5007	100.1	L912007	L912007-CCV2	0.5	0.5033	100.7	L912007	L912007-CCV2	0.5	0.5038	100.8
L912007	L912007-CCV3	0.5	0.5005	100.1	L912007	L912007-CCV3	0.5	0.4972	99.4	L912007	L912007-CCV3	0.5	0.4979	99.6
<b>Mean</b>				<b>100.0</b>	<b>Mean</b>				<b>100.0</b>	<b>Mean</b>				<b>99.8</b>
<b>Standard Deviation</b>				<b>0.94</b>	<b>Standard Deviation</b>				<b>0.89</b>	<b>Standard Deviation</b>				<b>0.73</b>
<b>Count</b>				<b>27</b>	<b>Count</b>				<b>27</b>	<b>Count</b>				<b>27</b>

**Table B-4.** Cloud Deposition 2009 Sampling Season – Replicate Summary for Cloud Samples (1 of 3)

<b>SO<sub>4</sub><sup>2-</sup></b>						
<b>Sample No.</b>	<b>Replicate No.</b>	<b>Station ID</b>	<b>Analysis Date</b>	<b>Sample Result</b>	<b>Replicate Result</b>	<b>Absolute RPD</b>
0922012-01	L907007-DUP1	CLD303	7/1/2009	1.647	1.632	0.91%
0925015-01	L907007-DUP2	CLD303	7/2/2009	8.886	8.836	0.56%
0932013-01	L909001-DUP2	CLD303	8/31/2009	4.487	4.521	0.76%
0934012-01	L909012-DUP1	CLD303	9/8/2009	7.165	7.144	0.29%
0935015-01	L909021-DUP1	CLD303	9/14/2009	15.380	15.370	0.07%
0940010-01	L910028-DUP1	CLD303	10/20/2009	3.939	3.903	0.91%
0943009-01	L911017-DUP1	CLD303	11/17/2009	2.976	2.960	0.54%
<b>Mean Percent Difference</b>						<b>0.58%</b>
<b>Standard Deviation</b>						<b>0.00</b>

<b>NO<sub>3</sub><sup>-</sup> - N</b>						
<b>Sample No.</b>	<b>Replicate No.</b>	<b>Station ID</b>	<b>Analysis Date</b>	<b>Sample Result</b>	<b>Replicate Result</b>	<b>Absolute RPD</b>
0922012-01	L907007-DUP1	CLD303	7/1/2009	0.259	0.261	0.77%
0925015-01	L907007-DUP2	CLD303	7/2/2009	1.271	1.273	0.16%
0932013-01	L909001-DUP2	CLD303	8/31/2009	0.961	0.970	0.94%
0934012-01	L909012-DUP1	CLD303	9/8/2009	0.938	0.955	1.81%
0935015-01	L909021-DUP1	CLD303	9/14/2009	2.343	2.302	1.75%
0940010-01	L910028-DUP1	CLD303	10/20/2009	0.736	0.728	1.09%
0943009-01	L911017-DUP1	CLD303	11/17/2009	0.460	0.458	0.43%
<b>Mean Percent Difference</b>						<b>0.99%</b>
<b>Standard Deviation</b>						<b>0.01</b>

<b>Cl<sup>-</sup></b>						
<b>Sample No.</b>	<b>Replicate No.</b>	<b>Station ID</b>	<b>Analysis Date</b>	<b>Sample Result</b>	<b>Replicate Result</b>	<b>Absolute RPD</b>
0922012-01	L907007-DUP1	CLD303	7/1/2009	0.114	0.113	0.88%
0925015-01	L907007-DUP2	CLD303	7/2/2009	0.717	0.721	0.56%
0932013-01	L909001-DUP2	CLD303	8/31/2009	0.592	0.592	0.00%
0934012-01	L909012-DUP1	CLD303	9/8/2009	1.898	1.913	0.79%
0935015-01	L909021-DUP1	CLD303	9/14/2009	1.286	1.309	1.79%
0940010-01	L910028-DUP1	CLD303	10/20/2009	0.414	0.422	1.93%
0943009-01	L911017-DUP1	CLD303	11/17/2009	1.348	1.349	0.07%
<b>Mean Percent Difference</b>						<b>0.86%</b>
<b>Standard Deviation</b>						<b>0.01</b>

**Table B-4.** Cloud Deposition 2009 Sampling Season – Replicate Summary for Cloud Samples (2 of 3)

<b>NH<sub>4</sub><sup>+</sup>-N</b>						
<b>Sample No.</b>	<b>Replicate No.</b>	<b>Station ID</b>	<b>Analysis Date</b>	<b>Sample Result</b>	<b>Replicate Result</b>	<b>Absolute RPD</b>
0922012-01	L906022-DUP1	CLD303	6/22/2009	0.3862	0.3840	0.57%
0924016-01	L906022-DUP2	CLD303	6/22/2009	1.8850	1.8750	0.53%
0925014-01	L907001-DUP1	CLD303	7/1/2009	1.1790	1.1830	0.34%
0932015-01	L908023-DUP2	CLD303	8/18/2009	1.7300	1.6500	4.62%
0932011-01	L908029-DUP1	CLD303	8/20/2009	1.9110	1.9030	0.42%
0934014-01	L909008-DUP1	CLD303	9/4/2009	0.3388	0.3366	0.65%
0935016-01	L909020-DUP1	CLD303	9/14/2009	0.3995	0.3969	0.65%
0940010-01	L910023-DUP1	CLD303	10/16/2009	1.3450	1.3280	1.26%
0943009-01	L911016-DUP1	CLD303	11/16/2009	0.8566	0.8530	0.41%
<b>Mean Percent Difference</b>						<b>1.05%</b>
<b>Standard Deviation</b>						<b>0.01</b>

<b>Ca<sup>2+</sup></b>						
<b>Sample No.</b>	<b>Replicate No.</b>	<b>Station ID</b>	<b>Analysis Date</b>	<b>Sample Result</b>	<b>Replicate Result</b>	<b>Absolute RPD</b>
0922009-01	L906029-DUP1	CLD303	6/25/2009	0.0430	0.0440	1.66%
0923018-01	L906029-DUP2	CLD303	6/25/2009	0.1010	0.1000	0.79%
0925013-01	L906029-DUP3	CLD303	6/25/2009	1.3240	1.3250	0.08%
0925016-01	L906029-DUP4	CLD303	6/25/2009	1.1080	1.1040	0.36%
0932015-01	L908026-DUP2	CLD303	8/19/2009	2.7240	2.7240	0.00%
0934014-01	L909010-DUP1	CLD303	9/8/2009	0.3994	0.3964	0.75%
0935016-01	L909022-DUP1	CLD303	9/15/2009	0.9642	0.9506	1.41%
0940010-01	L910036-DUP1	CLD303	10/22/2009	0.4340	0.4330	0.25%
0943009-01	L912007-DUP1	CLD303	12/3/2009	0.1120	0.1110	0.45%
<b>Mean Percent Difference</b>						<b>0.64%</b>
<b>Standard Deviation</b>						<b>0.01</b>

<b>Mg<sup>2+</sup></b>						
<b>Sample No.</b>	<b>Replicate No.</b>	<b>Station ID</b>	<b>Analysis Date</b>	<b>Sample Result</b>	<b>Replicate Result</b>	<b>Absolute RPD</b>
0922009-01	L906029-DUP1	CLD303	6/25/2009	0.0490	0.0490	0.55%
0923018-01	L906029-DUP2	CLD303	6/25/2009	0.0100	0.0100	0.10%
0925013-01	L906029-DUP3	CLD303	6/25/2009	0.1390	0.1380	0.58%
0925016-01	L906029-DUP4	CLD303	6/25/2009	0.1550	0.1550	0.06%
0932015-01	L908026-DUP2	CLD303	8/19/2009	0.4447	0.4436	0.25%
0934014-01	L909010-DUP1	CLD303	9/8/2009	0.1268	0.1258	0.79%
0935016-01	L909022-DUP1	CLD303	9/15/2009	0.1709	0.1699	0.59%
0940010-01	L910036-DUP1	CLD303	10/22/2009	0.1010	0.1010	0.00%
0943009-01	L912007-DUP1	CLD303	12/3/2009	0.1010	0.1010	0.20%
<b>Mean Percent Difference</b>						<b>0.34%</b>
<b>Standard Deviation</b>						<b>0.00</b>

**Table B-4.** Cloud Deposition 2009 Sampling Season – Replicate Summary for Cloud Samples (3 of 3)

<b>Na<sup>+</sup></b>						
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Absolute RPD
0922009-01	L906029-DUP1	CLD303	6/25/2009	0.3490	0.3530	1.23%
0923018-01	L906029-DUP2	CLD303	6/25/2009	0.0180	0.0170	1.08%
0925013-01	L906029-DUP3	CLD303	6/25/2009	0.3500	0.3480	0.80%
0925016-01	L906029-DUP4	CLD303	6/25/2009	0.7530	0.7540	0.08%
0932015-01	L908026-DUP2	CLD303	8/19/2009	0.3394	0.3396	0.06%
0934014-01	L909010-DUP1	CLD303	9/8/2009	0.6088	0.6085	0.05%
0935016-01	L909022-DUP1	CLD303	9/15/2009	0.5404	0.5326	1.44%
0940010-01	L910036-DUP1	CLD303	10/22/2009	0.4380	0.4350	0.59%
0943009-01	L912007-DUP1	CLD303	12/3/2009	0.8810	0.8770	0.50%
<b>Mean Percent Difference</b>						<b>0.65%</b>
<b>Standard Deviation</b>						<b>0.01</b>

<b>K<sup>+</sup></b>						
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Absolute RPD
0922009-01	L906029-DUP1	CLD303	6/25/2009	0.0440	0.0450	1.24%
0923018-01	L906029-DUP2	CLD303	6/25/2009	0.0120	0.0120	0.49%
0925013-01	L906029-DUP3	CLD303	6/25/2009	0.1410	0.1400	1.06%
0925016-01	L906029-DUP4	CLD303	6/25/2009	0.1610	0.1610	0.06%
0932015-01	L908026-DUP2	CLD303	8/19/2009	0.3522	0.3528	0.17%
0934014-01	L909010-DUP1	CLD303	9/8/2009	0.0540	0.0553	2.41%
0935016-01	L909022-DUP1	CLD303	9/15/2009	0.1253	0.1247	0.48%
0940010-01	L910036-DUP1	CLD303	10/22/2009	0.1820	0.1820	0.27%
0943009-01	L912007-DUP1	CLD303	12/3/2009	0.0780	0.0770	0.99%
<b>Mean Percent Difference</b>						<b>0.80%</b>
<b>Standard Deviation</b>						<b>0.01</b>

<b>pH</b>						
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Absolute RPD
0921014-01	L907013-DUP1	CLD303	7/8/2009	5.110	5.110	0.00%
0925014-01	L907013-DUP2	CLD303	7/8/2009	4.170	4.180	2.28%
0928011-01	L908031-DUP2	CLD303	8/21/2009	4.290	4.320	6.67%
0933015-01	L909014-DUP1	CLD303	9/9/2009	3.920	3.880	9.65%
0935013-01	L909027-DUP1	CLD303	9/17/2009	5.050	5.080	6.67%
0938016-01	L910035-DUP1	CLD303	10/21/2009	4.390	4.410	4.50%
0940010-01	L910035-DUP2	CLD303	10/21/2009	4.850	4.840	2.33%
0942013-01	L912010-DUP1	CLD303	12/4/2009	5.640	5.630	2.33%
<b>Mean Percent Difference</b>						<b>4.30%</b>
<b>Standard Deviation</b>						<b>3.17%</b>



## **Appendix C**

### **Filter Pack Data and QC Summary**

## Filter Pack Data and QC Summary

Table C-1 presents the total microgram data for each filter type from each sample.

Table C-2 presents the results of the analyses of the laboratory filter blank samples. Laboratory filter blanks are prepared weekly while the filter packs are being prepared for the field. Each laboratory blank is prepared using filters from the same lot of filters used to prepare the field filter packs. The analytical results of the laboratory blanks demonstrate no significant contamination. There is one laboratory blank for the Teflon filters with a minor “hit” for potassium. The field and laboratory blank results indicate that logistical and analytical processes did not contribute to the measured analytes.

The QC results for all parameters are within the measurement criteria of the CASTNET program (MACTEC, 2008). Tables C-3 through C-5 summarize the reference sample QC data for each filter type and parameter in each analytical batch. Each reference sample is a NIST-traceable solution in a matrix similar to the filter sample extracts. An independent laboratory supplies these reference samples with a certificate of analysis stating the known or target value. A reference sample is analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the instrument response. The QC limits require the measured value be within  $\pm 5$  percent of the known value for anions and within  $\pm 10$  percent of the known value for cations. The data from all reference samples analyzed with the Great Smoky Mountains National Park, TN (GSR420) samples are within the CASTNET QC criteria.

Summary statistics from the analysis of CCV for each parameter and filter type are presented in Table C-6. A CCV is a NIST-traceable solution supplied in a matrix similar to that of the sample being analyzed with a target value at approximately the midpoint of the calibration curve. This QC solution is supplied to MACTEC by a second independent laboratory. A CCV is analyzed after every 10 environmental samples to verify that the instrument calibration has not drifted more than  $\pm 5$  percent for anions and base cations, and  $\pm 10$  percent for  $\text{NH}_4^+$ . All CCV analyzed with the GSR420 samples are within the CASTNET QC criteria.

Table C-7 summarizes the percent difference of replicate samples reanalyzed within the same analytical batch. Samples are randomly selected from each analytical batch for replicate analysis. This table presents only the GRS420 samples that were replicated. The replicate percent difference criterion is  $\pm 20$  percent for all analytes.

**Table C-1.** Dry Deposition Filter Concentrations for 2009 Sampling Season – GRS420, TN

Sample No.	Station ID	Filter Date	Teflon		Nylon		Cellulose	Teflon					
			SO <sub>4</sub> <sup>2-</sup> T.µg	NO <sub>3</sub> <sup>-</sup> -N T.µg	SO <sub>4</sub> <sup>2-</sup> T.µg	NO <sub>3</sub> <sup>-</sup> -N T.µg	SO <sub>4</sub> <sup>2-</sup> T.µg	NH <sub>4</sub> <sup>+</sup> -N T.µg	Ca <sup>2+</sup> T.µg	Mg <sup>2+</sup> T.µg	Na <sup>+</sup> T.µg	K <sup>+</sup> T.µg	Cl <sup>-</sup> T.µg
0922001-36	GRS420	5/26/09	85.75	1.42	12.38	8.30	24.05	24.88	7.44	1.19	0.95	1.82	0.50U
0923001-36	GRS420	6/2/09	125.60	0.32	9.38	8.00	32.50	31.05	3.36	0.67	0.77	1.96	0.50U
0924001-36	GRS420	6/9/09	99.90	0.52	12.00	8.95	25.40	24.20	3.65	0.76	2.47	2.03	0.50U
0925001-36	GRS420	6/16/09	109.60	0.30	16.12	9.45	31.25	21.58	5.57	1.29	5.29	2.57	0.50U
0926001-36	GRS420	6/23/09	79.56	0.68	16.10	5.50	44.25	19.80	4.38	0.67	0.57	0.81	0.50U
0927001-36	GRS420	6/30/09	90.03	0.63	11.02	9.18	32.00	15.29	13.49	1.79	0.39	2.41	0.50U
0928001-36	GRS420	7/7/09	125.60	0.20U	11.05	7.65	24.60	30.47	3.27	0.97	3.16	2.28	0.50U
0929001-36	GRS420	7/14/09	93.98	2.09	10.08	6.40	24.05	22.91	9.95	1.37	0.71	2.65	0.50U
0930001-36	GRS420	7/21/09	94.98	0.95	8.75	5.13	18.70	24.13	4.76	0.72	0.66	3.77	0.50U
0931001-36	GRS420	7/28/09	70.11	0.31	6.10	4.53	8.15	14.86	2.92	0.87	1.66	2.66	0.50U
0932001-36	GRS420	8/4/09	135.80	0.81	9.65	8.77	33.75	30.12	5.70	1.39	3.21	3.70	0.50U
0933001-36	GRS420	8/11/09	108.80	0.98	6.43	7.65	11.10	24.95	4.20	1.27	4.44	3.19	0.96
0934001-36	GRS420	8/18/09	104.00	0.23	11.75	5.38	16.75	22.48	2.39	0.61	2.23	4.11	0.50U
0935001-36	GRS420	8/25/09	111.90	0.75	9.18	6.97	21.70	25.74	5.01	1.10	1.59	2.57	0.50U
0936001-36	GRS420	9/1/09	110.70	1.00	8.70	8.98	23.75	28.70	3.67	0.91	2.62	2.36	0.50U
0937001-36	GRS420	9/8/09	161.50	0.47	9.73	8.50	29.55	40.95	2.66	0.60	1.29	2.61	0.50U
0938001-36	GRS420	9/15/09	57.48	0.20	3.20	2.50	2.30	13.26	0.62	0.23	0.90	4.98	0.50U
0939001-36	GRS420	9/22/09	63.53	0.89	8.15	5.15	21.00	16.28	4.75	0.89	2.31	1.86	0.50U
0940001-36	GRS420	9/29/09	54.56	2.21	8.40	4.32	16.40	11.27	7.95	1.00	0.44	1.69	0.50U

**Note:** U = Value is less than detection limit

**Table C-2. Dry Deposition 2009 Sampling Season - Laboratory Filter Pack Blanks – GRS420, TN**

Lab Key	Analysis Date	Teflon		Nylon		Cellulose	Teflon					
		SO <sub>4</sub> <sup>2-</sup> T.µg	NO <sub>3</sub> <sup>-</sup> -N T.µg	SO <sub>4</sub> <sup>2-</sup> T.µg	NO <sub>3</sub> <sup>-</sup> -N T.µg	SO <sub>4</sub> <sup>2-</sup> T.µg	NH <sub>4</sub> <sup>+</sup> -N T.µg	Ca <sup>2+</sup> T.µg	Mg <sup>2+</sup> T.µg	Na <sup>+</sup> T.µg	K <sup>+</sup> T.µg	Cl <sup>-</sup> T.µg
0925002-01	07-Jul-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0925002-02	07-Jul-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0926002-01	09-Jul-09	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0926002-02	09-Jul-09	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	0.2073	<0.500
0927002-01	15-Jul-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0927002-02	15-Jul-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0928002-01	23-Jul-09			<1.000	<0.200	<2.000						
0928002-02	23-Jul-09			<1.000	<0.200	<2.000						
0929002-01	30-Jul-09	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0929002-02	30-Jul-09	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0930002-01	05-Aug-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0930002-02	05-Aug-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0931002-01	12-Aug-09	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0931002-02	12-Aug-09	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0933002-01	26-Aug-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0933002-01	26-Aug-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0933002-02	26-Aug-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0933002-02	26-Aug-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0934002-01	09-Sep-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0934002-02	09-Sep-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0935002-01	16-Sep-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0935002-02	16-Sep-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0936002-01	17-Sep-09			<1.000	<0.200	<2.000						
0936002-02	17-Sep-09			<1.000	<0.200	<2.000						
0937002-01	24-Sep-09	<1.000	<0.200			<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0937002-02	24-Sep-09	<1.000	<0.200			<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0938002-01	01-Oct-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0938002-02	01-Oct-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0939002-01	08-Oct-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
0939002-02	08-Oct-09	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500





**Table C-3. Dry Deposition 2009 Sampling Season – QC Batch Summary for Teflon Filters – Reference Samples – GRS420, TN (3 of 3)**

K <sup>+</sup>					Cl <sup>-</sup>				
Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery	Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery
L906020	L906020-SRM1	0.09899	0.09544	96.41	L906028	L906028-SRM2	0.95999	0.96499	100.52
L906020	L906020-SRM2	0.09899	0.09247	93.41	L907015	L907015-SRM1	0.95999	0.97610	101.68
L906026	L906026-SRM1	0.09899	0.09516	96.12	L907015	L907015-SRM2	0.95999	0.99720	103.88
L906026	L906026-SRM2	0.09899	0.09286	93.80	L907020	L907020-SRM1	0.95999	0.97509	101.57
L907012	L907012-SRM1	0.09899	0.09725	98.24	L907020	L907020-SRM2	0.95999	0.99370	103.51
L907012	L907012-SRM2	0.09899	0.09672	97.70	L907025	L907025-SRM1	0.95999	0.97970	102.05
L907017	L907017-SRM1	0.09899	0.10279	103.84	L907025	L907025-SRM2	0.95999	0.99739	103.90
L907017	L907017-SRM2	0.09899	0.09998	100.99	L907039	L907039-SRM1	0.95999	0.98629	102.74
L907026	L907026-SRM1	0.09899	0.10076	101.78	L907039	L907039-SRM2	0.95999	0.99510	103.66
L907026	L907026-SRM2	0.09899	0.10074	101.76	L908002	L908002-SRM1	0.95999	0.98150	102.24
L907038	L907038-SRM1	0.09899	0.09843	99.42	L908002	L908002-SRM2	0.95999	0.99940	104.10
L907038	L907038-SRM2	0.09899	0.09740	98.38	L908011	L908011-SRM1	0.95999	0.98320	102.42
L907041	L907041-SRM1	0.09899	0.09959	100.60	L908011	L908011-SRM2	0.95999	0.99099	103.23
L907041	L907041-SRM2	0.09899	0.09909	100.10	L908020	L908020-SRM1	0.95999	0.98269	102.36
L908009	L908009-SRM1	0.09899	0.10147	102.50	L908020	L908020-SRM2	0.95999	0.98110	102.20
L908009	L908009-SRM2	0.09899	0.09914	100.15	L908020	L908020-SRM3	0.95999	0.98320	102.42
L908018	L908018-SRM1	0.09899	0.10039	101.41	L908040	L908040-SRM1	0.95999	0.98820	102.94
L908018	L908018-SRM2	0.09899	0.09802	99.02	L908040	L908040-SRM1	0.95999	0.98820	102.94
L908018	L908018-SRM3	0.09899	0.09862	99.62	L908040	L908040-SRM2	0.95999	0.99930	104.09
L908037	L908037-SRM1	0.09899	0.10003	101.05	L908040	L908040-SRM2	0.95999	0.99930	104.09
L908037	L908037-SRM1	0.09899	0.10003	101.05	L909011	L909011-SRM1	0.95999	0.98869	102.99
L908037	L908037-SRM2	0.09899	0.09643	97.41	L909011	L909011-SRM2	0.95999	0.98760	102.88
L908037	L908037-SRM2	0.09899	0.09643	97.41	L909017	L909017-SRM1	0.95999	0.98919	103.04
L909006	L909006-SRM1	0.09899	0.09971	100.73	L909017	L909017-SRM2	0.95999	1.00600	104.79
L909006	L909006-SRM2	0.09899	0.09830	99.30	L909031	L909031-SRM1	0.95999	0.98919	103.04
L909015	L909015-SRM1	0.09899	0.10084	101.87	L909031	L909031-SRM2	0.95999	0.98979	103.10
L909015	L909015-SRM2	0.09899	0.09883	99.83	L909045	L909045-SRM1	0.95999	0.98610	102.72
L909026	L909026-SRM1	0.09899	0.10460	105.66	L909045	L909045-SRM2	0.95999	0.99570	103.72
L909026	L909026-SRM2	0.09899	0.09784	98.83	L910005	L910005-SRM1	0.95999	0.98710	102.82
L909041	L909041-SRM1	0.09899	0.09939	100.40	L910005	L910005-SRM2	0.95999	0.98830	102.95
L909041	L909041-SRM2	0.09899	0.09850	99.50	L910016	L910016-SRM1	0.95999	0.98600	102.71
L909041	L909041-SRM3	0.09899	0.09881	99.81	L910016	L910016-SRM2	0.95999	1.00390	104.57
L910003	L910003-SRM1	0.09899	0.09726	98.24					
L910003	L910003-SRM2	0.09899	0.09525	96.22					
L910014	L910014-SRM1	0.09899	0.09943	100.44					
L910014	L910014-SRM2	0.09899	0.09796	98.96					
<b>Mean</b>				<b>99.50</b>	<b>Mean</b>				<b>103.00</b>
<b>Standard Deviation</b>				<b>2.49</b>	<b>Standard Deviation</b>				<b>0.91</b>
<b>Count</b>				<b>36</b>	<b>Count</b>				<b>32</b>

**Table C-4. Dry Deposition 2009 Sampling Season – QC Batch Summary for Nylon Filters – Reference Samples – GRS420, TN**

SO <sub>4</sub> <sup>2-</sup>					NO <sub>3</sub>				
Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery	Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery
L906021	L906021-SRM1	10	9.851	98.51	L906021	L906021-SRM1	1.6	1.600	100.00
L906021	L906021-SRM2	10	9.893	98.93	L906021	L906021-SRM2	1.6	1.609	100.56
L906030	L906030-SRM1	10	9.733	97.33	L906030	L906030-SRM1	1.6	1.592	99.50
L906030	L906030-SRM2	10	9.680	96.80	L906030	L906030-SRM2	1.6	1.586	99.13
L907009	L907009-SRM1	10	9.870	98.70	L907009	L907009-SRM1	1.6	1.600	100.00
L907009	L907009-SRM2	10	9.948	99.48	L907009	L907009-SRM2	1.6	1.616	101.00
L907019	L907019-SRM1	10	9.916	99.16	L907019	L907019-SRM1	1.6	1.607	100.44
L907019	L907019-SRM2	10	10.184	101.84	L907019	L907019-SRM2	1.6	1.648	103.00
L907028	L907028-SRM1	10	9.907	99.07	L907028	L907028-SRM1	1.6	1.612	100.75
L907028	L907028-SRM2	10	9.909	99.09	L907028	L907028-SRM2	1.6	1.611	100.69
L907035	L907035-SRM1	10	9.804	98.04	L907035	L907035-SRM1	1.6	1.584	99.00
L907035	L907035-SRM2	10	9.979	99.79	L907035	L907035-SRM2	1.6	1.629	101.81
L907043	L907043-SRM1	10	9.894	98.94	L907043	L907043-SRM1	1.6	1.596	99.75
L907043	L907043-SRM2	10	10.097	100.97	L907043	L907043-SRM2	1.6	1.632	102.00
L908014	L908014-SRM1	10	9.805	98.05	L908014	L908014-SRM1	1.6	1.608	100.50
L908014	L908014-SRM2	10	9.936	99.36	L908014	L908014-SRM2	1.6	1.638	102.38
L908021	L908021-SRM1	10	9.875	98.75	L908021	L908021-SRM1	1.6	1.605	100.31
L908021	L908021-SRM2	10	9.914	99.14	L908021	L908021-SRM2	1.6	1.610	100.63
L908038	L908038-SRM1	10	9.831	98.31	L908038	L908038-SRM1	1.6	1.606	100.38
L908038	L908038-SRM1	10	9.831	98.31	L908038	L908038-SRM1	1.6	1.606	100.38
L908038	L908038-SRM2	10	9.953	99.53	L908038	L908038-SRM2	1.6	1.630	101.88
L908038	L908038-SRM2	10	9.953	99.53	L908038	L908038-SRM2	1.6	1.630	101.88
L909016	L909016-SRM1	10	9.886	98.86	L909016	L909016-SRM1	1.6	1.594	99.63
L909016	L909016-SRM2	10	9.993	99.93	L909016	L909016-SRM2	1.6	1.612	100.75
L909028	L909028-SRM1	10	9.705	97.05	L909028	L909028-SRM1	1.6	1.570	98.13
L909028	L909028-SRM2	10	9.957	99.57	L909028	L909028-SRM2	1.6	1.622	101.38
L909033	L909033-SRM1	10	9.725	97.25	L909033	L909033-SRM1	1.6	1.564	97.75
L909033	L909033-SRM2	10	9.969	99.69	L909033	L909033-SRM2	1.6	1.607	100.44
L910002	L910002-SRM1	10	9.750	97.50	L910002	L910002-SRM1	1.6	1.566	97.88
L910002	L910002-SRM2	10	9.823	98.23	L910002	L910002-SRM2	1.6	1.577	98.56
L910006	L910006-SRM1	10	9.903	99.03	L910006	L910006-SRM1	1.6	1.612	100.75
L910006	L910006-SRM2	10	9.977	99.77	L910006	L910006-SRM2	1.6	1.618	101.13
L910015	L910015-SRM1	10	9.763	97.63	L910015	L910015-SRM1	1.6	1.567	97.94
L910015	L910015-SRM2	10	9.966	99.66	L910015	L910015-SRM2	1.6	1.595	99.69
<b>Mean</b>				<b>98.88</b>	<b>Mean</b>				<b>100.29</b>
<b>Standard Deviation</b>				<b>1.08</b>	<b>Standard Deviation</b>				<b>1.30</b>
<b>Count</b>				<b>34</b>	<b>Count</b>				<b>34</b>



**Table C-5. Dry Deposition 2009 Sampling Season – QC Batch Summary for Cellulose Filters – Reference Samples – GRS420, TN**

		$\text{SO}_4^{2-}$		
Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery
L906018	L906018-SRM1	10	9.849	98.49
L906018	L906018-SRM2	10	9.991	99.91
L906031	L906031-SRM1	10	9.871	98.71
L906031	L906031-SRM2	10	9.959	99.59
L907008	L907008-SRM1	10	9.791	97.91
L907008	L907008-SRM2	10	9.841	98.41
L907021	L907021-SRM1	10	9.894	98.94
L907021	L907021-SRM2	10	9.845	98.45
L907024	L907024-SRM1	10	9.860	98.60
L907024	L907024-SRM2	10	10.003	100.03
L907032	L907032-SRM1	10	10.001	100.01
L907032	L907032-SRM2	10	9.973	99.73
L908001	L908001-SRM1	10	9.867	98.67
L908001	L908001-SRM2	10	9.861	98.61
L908010	L908010-SRM1	10	9.794	97.94
L908010	L908010-SRM2	10	9.880	98.80
L908027	L908027-SRM1	10	9.788	97.88
L908027	L908027-SRM2	10	10.157	101.57
L908039	L908039-SRM1	10	9.829	98.29
L908039	L908039-SRM1	10	9.829	98.29
L908039	L908039-SRM2	10	9.956	99.56
L908039	L908039-SRM2	10	9.956	99.56
L909007	L909007-SRM1	10	9.786	97.86
L909007	L909007-SRM2	10	9.933	99.33
L909023	L909023-SRM1	10	9.840	98.40
L909023	L909023-SRM2	10	10.044	100.44
L909030	L909030-SRM1	10	9.781	97.81
L909030	L909030-SRM2	10	9.943	99.43
L909038	L909038-SRM1	10	9.739	97.39
L909038	L909038-SRM2	10	9.864	98.64
L910001	L910001-SRM1	10	9.856	98.56
L910001	L910001-SRM2	10	9.897	98.97
L910010	L910010-SRM1	10	9.788	97.88
L910010	L910010-SRM2	10	9.960	99.60
<b>Mean</b>				<b>98.89</b>
<b>Standard Deviation</b>				<b>0.90</b>
<b>Count</b>				<b>34</b>

**Table C-6. Dry Deposition 2009 Sampling Season – CCV (%R) – GRS420, TN**

Filter Type	Parameter	Mean	Standard Deviation	Count
<b>Teflon</b>	SO <sub>4</sub> <sup>2-</sup>	98.55	0.79	183
	NO <sub>3</sub> <sup>-</sup> - N	98.61	0.92	183
	Cl <sup>-</sup>	99.34	1.02	178
	NH <sub>4</sub> <sup>+</sup> - N	99.02	1.12	182
	Ca <sup>2+</sup>	100.25	0.92	187
	Mg <sup>2+</sup>	100.09	0.87	187
	Na <sup>+</sup>	100.14	0.98	187
	K <sup>+</sup>	100.00	0.85	187
<b>Nylon</b>	SO <sub>4</sub> <sup>2-</sup>	99.19	1.58	184
	NO <sub>3</sub> <sup>-</sup> - N	99.74	1.49	184
<b>Cellulose</b>	SO <sub>4</sub> <sup>2-</sup>	99.76	1.11	139

**Note:** %R = percent recovery

**Table C-7. Dry Deposition 2009 Sampling Season – Replicate Summary – GRS420, TN**

Sample No.	Replicate No.	Date	Parameter	Filter Type	Sample Result	Replicate Result	Percent Difference	Mean Percent Difference	Standard Deviation	Count
0931001-36	L908018-DUP5	12-Aug-09	Ca <sup>2+</sup>	Teflon	0.11390	0.11388	0.01	NA	NA	
0937004-36	L909041-DUP2	24-Sep-09	Ca <sup>2+</sup>	Teflon	< 0.15	< 0.15	NA	NA	NA	2
0932001-36	L908040-DUP1	26-Aug-09	Cl <sup>-</sup>	Teflon	< 0.50	< 0.50	NA	NA	NA	1
0931001-36	L908018-DUP5	12-Aug-09	Mg <sup>2+</sup>	Teflon	< 0.075	< 0.075	NA	NA	NA	
0937004-36	L909041-DUP2	24-Sep-09	Mg <sup>2+</sup>	Teflon	< 0.075	< 0.075	NA	NA	NA	2
0931001-36	L908019-DUP5	12-Aug-09	NH <sub>4</sub> <sup>+</sup>	Teflon	0.59030	0.59040	-0.02	NA	NA	1
0932001-36	L908040-DUP1	26-Aug-09	NO <sub>3</sub> <sup>-</sup> as N	Teflon	< 0.20	< 0.20	NA	NA	NA	1
0931001-36	L908018-DUP5	12-Aug-09	K <sup>+</sup>	Teflon	<0.15	<0.15	NA	NA	NA	
0937004-36	L909041-DUP2	24-Sep-09	K <sup>+</sup>	Teflon	<0.15	<0.15	NA	NA	NA	2
0932001-36	L908040-DUP1	26-Aug-09	SO <sub>4</sub> <sup>2-</sup>	Teflon	5.43880	5.44000	-0.02	NA	NA	1
0931001-36	L908018-DUP5	12-Aug-09	Na <sup>+</sup>	Teflon	<0.125	<0.125	NA	NA	NA	
0937004-36	L909041-DUP2	24-Sep-09	Na <sup>+</sup>	Teflon	<0.125	<0.125	NA	NA	NA	2

