Cloud Deposition Monitoring
Clingmans Dome, Tennessee
Great Smoky Mountains National Park
2011

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

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Prepared for:

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List of Acronyms and Abbreviations

AMEC	AMEC Environment & Infrastructure, Inc.
°C	degrees Celsius
Ca^{2+}	calcium ion
CAAA	Clean Air Act Amendments
CAIR	Clean Air Interstate Rule
Campbell	Campbell Scientific, Inc.
CASTNET	Clean Air Status and Trends Network
CCV	continuing calibration verification spikes
CLOUD	cloud water deposition computer model
Cl^-	chloride ion
CLD303	Clingmans Dome, TN sampling site
cm	centimeter
cm/s	centimeters per second
CSAPR	Cross-State Air Pollution Rule
DAS	data acquisition system
EGU	electric generating unit
Element	Element DataSystem for laboratory information management
EPA	U.S. Environmental Protection Agency
$g/cm^2/min$	grams per square centimeter per minute
g/m^3	grams per cubic meter
GRS420	Great Smoky Mountains National Park, TN dry deposition sampling site
H^+	hydrogen ion
HNO_3	nitric acid
K^+	potassium ion
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^{2+}	magnesium ion
mL	milliliter
MLM	Multi-Layer Model dry deposition computer model

List of Acronyms and Abbreviations (continued)

N	nitrogen
Na^+	sodium ion
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NAPAP	National Acid Precipitation Assessment Program
NBP	NO_x Budget Trading Program
NH_4^+	ammonium ion
NIST	National Institute for Standards and Technology
NO_3^-	nitrate ion
NO_x	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
SO_4^{2-}	sulfate ion
SO_2	sulfur dioxide
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
$\mu g/m^3$	micrograms per cubic meter

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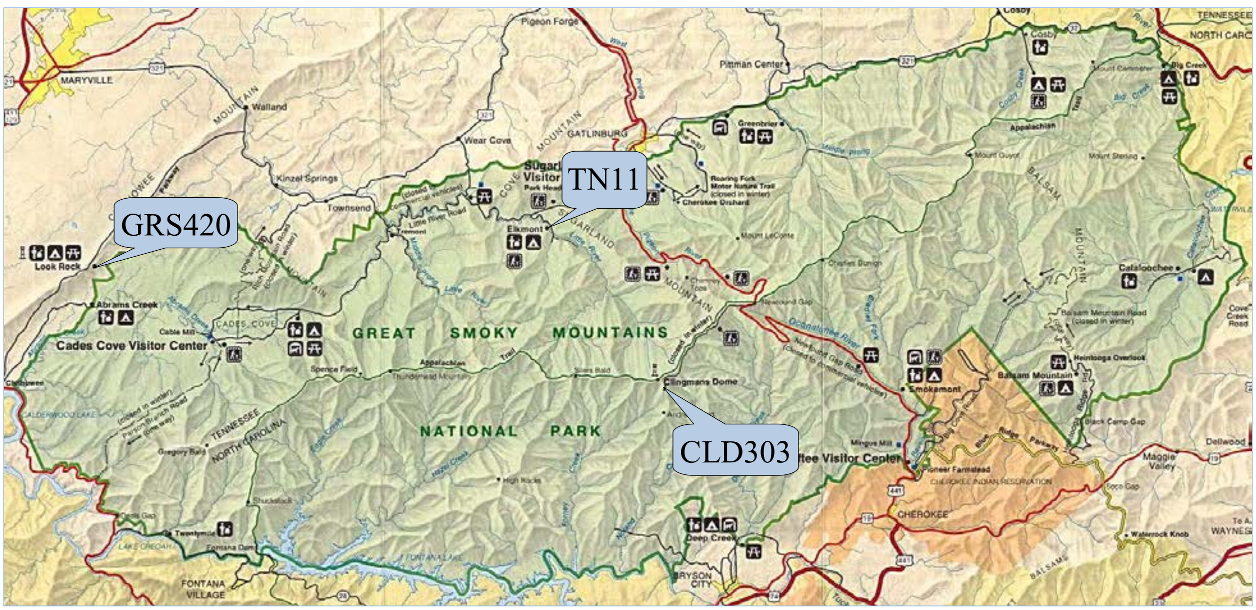
1.0 Introduction

The 1990 Clean Air Act Amendments (CAAA) established the Acid Rain Program, which mandated significant reductions in sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions from electric generating units (EGUs). The SO_2 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_x emission control programs also produced substantive declines in NO_x emissions in the eastern United States. These programs include the Ozone Transport Commission (OTC) NO_x Budget (1999–2002) and the NO_x State Implementation Plan Call/NO_x Budget Trading Program (NBP), which operated from 2003 through 2008. The NBP placed a cap on total NO_x 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_2 and NO_x emissions in the eastern United States. CAIR, as promulgated, established three compliance programs: an annual NO_x program, an ozone season NO_x program, and an annual SO_2 program. The first phase of the annual and ozone season NO_x requirements began in 2009. The SO_2 requirements began in 2010. On July 6, 2011, the U.S. Environmental Protection Agency (EPA) promulgated the Cross-State Air Pollution Rule (CSAPR) to replace CAIR. The CSAPR, which is also known as the Transport Rule, requires 28 states to achieve additional reductions in power plant SO_2 and NO_x emissions. On December 30, 2011, the United States Court of Appeals for the District of Columbia Circuit issued its ruling to stay the CSAPR pending judicial review. This decision is not a ruling on the merits of the CSAPR. EPA will continue to administer CAIR pending the Court's resolution of the petitions for review.

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 between emissions, air quality, deposition, and ecological effects. CASTNET measurements collected over the period 1990 through 2010 (AMEC, 2012a) have shown significant declines in atmospheric sulfur pollutants [SO_2 and particulate sulfate (SO_4^{2-})] and more recently, declines in nitrogen pollutants [nitric acid (HNO_3) and particulate nitrate (NO_3^-)]. The Mountain Acid Deposition Program (MADPro) was initiated in 1993 as part of the research necessary to support CASTNET's objectives. AMEC Environment & Infrastructure, Inc. (AMEC) operates both CASTNET and MADPro on behalf of EPA and other agencies.

MADPro's main objective is 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. From the 2002 sampling season forward, cloud water measurements have been collected solely from the site at Clingmans Dome, TN (CLD303). The project was not funded in 2008; therefore, the CLD303 site did not operate. Since the 2009 season CLD303 has been 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 2011 field sampling season.



For 2011, cloud water and meteorological parameters 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 2011, the site was installed in mid-May, and sample collection began in early June.

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 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. The scalar wind speed data required for calculation of cloud deposition estimates were obtained from the NPS instrument 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 diameter Teflon fibers strung between two circular disks (Falconer and Falconer, 1980; Mohnen and Kadlecek, 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 (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 g/m^3) and ambient air temperature [≥ 2 degrees Celsius (°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 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 Optical Cloud Detectors set at a threshold of approximately 0.04 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.

Particle Volume Monitor

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 another method for determining sample volume and complements the manual determination of 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

For the 2010 season, the upgraded valve/plumbing system was further modified/redesigned in order to eliminate the problem of air leakage through the valves, which was experienced during the 2009 season.

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 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 PVM is calibrated at start-up and again at the end of the season (weather permitting). Calibration checks of the PVM were performed biweekly (weather permitting) throughout the field season. The results were used to adjust the instrument immediately after the calibration check.

The site operator visits the site at least twice a week, whether or not collection has occurred, to perform his duties, which include gathering cloud water samples from the collector. 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 AMEC 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 2011, none of the 24-hour samples were combined into 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) Revision 7.0 (MACTEC, 2011). 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.

3-Stage Filter Pack

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 information management system, Element DataSystem (Element).

Cloud water samples for the 2011 sampling season were analyzed for sodium (Na^+), potassium (K^+), ammonium (NH_4^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), NO_3^-, and SO_4^{2-} ions in the AMEC CASTNET laboratory. All samples were analyzed for pH and conductivity in the AMEC CASTNET laboratory in Gainesville, FL for comparison with the field values.

Concentrations of the three anions (SO_4^{2-}, NO_3^-, and Cl^-) were determined by micromembrane-suppressed ion chromatography. Analysis of samples for Na^+, Mg^{2+}, Ca^{2+}, and K^+ was performed with a Perkin-Elmer Optima 7300 Dual View inductively coupled argon plasma-atomic emission spectrometer. The automated indophenol method using a Bran+Luebbe Autoanalyzer 3 was used to determine NH_4^+ concentrations. The 2011 hydrogen (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, 2011). Filter packs contain three filter types in sequence: a Teflon filter for collection of aerosols, a nylon filter for collection of HNO_3 and SO_2, and dual potassium carbonate-impregnated cellulose filters for collection of SO_2. Following receipt from the field, exposed filters and unexposed blanks were extracted and analyzed for SO_4^{2-}, NO_3^-, Cl^-, and the cations, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, and K^+, as described previously for cloud water samples. Refer to the CASTNET QAPP (MACTEC, 2011) 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 SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^- are calculated based on analysis of Teflon filter extracts; HNO_3 is calculated based on the NO_3^- found in the nylon filter extracts; some SO_2 is trapped by the nylon filter, so SO_2 is calculated based on the sum of 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-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 PVM data are validated based on the end-of-season calibration results, periodic calibration check results, 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 or his designee.

For cloud water samples, an additional check involves calculating the percent difference of cations versus anions (ion balance), which 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 (µg/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, 2011). 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 reported problems with sensors and equipment at the site and of the actions taken to solve such problems.
- 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 the National Institute for Standards and Technology (NIST). Continuing accuracy is verified by end-of-season calibrations by AMEC 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 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, 2012b) and the CASTNET annual reports for 1998 through 2010, the most recent of which can be found on EPA's Web site: http://java.epa.gov/castnet/documents.do.

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, 2011). 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

Cloud Collection Tower

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 1995 through 2007 and 2009 through 2011 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 2011 versus the historical monthly means (1994–2007, 2009–2010) 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 g/m^3, or:

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

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 2011 were lower than the historical means for June and July, but were slightly higher for August and September. The 2011 monthly mean cloud frequency value is also slightly lower than the monthly mean historical value. None of the 2011 monthly cloud frequency values were close to approaching project minimum or maximum values (Table 3-1, Figure 3-1).

Monthly mean, minimum, and maximum LWC values for the months of June through September for 1994 through 2007 and 2009 through 2011 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 g/m^3 during the month. Monthly mean LWC values for 2011 versus the historical monthly means (1994–2007, 2009–2010) are shown in Figure 3-4. Only valid values passing the 70 percent completeness criterion are plotted. The 2011 annual mean LWC value of 0.277 g/m^3 is slightly lower than the project mean of 0.287 g/m^3. Only three other years, 2000, 2007, and 2010, had lower annual mean LWC values.

3.2 Cloud Water Chemistry

During the 2011 sampling season, the CASTNET laboratory received 43 cloud water samples from CLD303. Samples sent to the CASTNET laboratory for analysis were packed in polystyrene foam 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 and stored at 4°C until analysis.

Annual summary statistics for cloud water chemistry and LWC for all analyzed samples 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 ≤ 100 microequivalents per liter (μeq/L), and the absolute value of the RPD was > 100 percent; or
- Either the anion sum or the cation sum was > 100 μeq/L, and the absolute value of the RPD was > 25 percent.

The RPD was calculated from the following formula:

$$RPD = 200 * |cations - anions| / (cations + anions)$$

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

Cloud water analytical and QC data for the 2011 sampling season are presented in Appendix B. One sample collected in June was invalidated resulting in a final count of 42 samples used for data analysis.

The June sample was invalidated because an accurate collection date could not be determined for this sample. There were no cloud events on the date assigned to this sample. Without an actual date and duration time, it is impossible to determine the sample LWC and wind speed. In addition, the sample volume was too low to allow for pH and conductivity analyses.

The field pH value for the sample collected on 7/1/2011 was also invalidated since either contamination or erroneous documentation is suspected to have occurred. The field pH value for this sample was 7.29, which is a value that is highly unlikely for a cloud water sample. The laboratory pH value for this sample was 5.04, which is much more reasonable.

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 2011 samples (approximately 7 percent for laboratory pH and 5 percent for field pH) had values of pH 3.9 or lower. The minimum pH values in 2011 for laboratory and field pH were 3.73 and 3.67, respectively, as listed in Table 3-2. The 2011 mean pH value of 4.29 for laboratory pH was lower than the 2010 mean laboratory pH value of 4.32. The 2010 mean pH value is the highest mean annual pH value in the history of the project. Historically (1994–2007, 2009–2010), 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 through 2011 are the only years in which the majority of the pH values were above 3.9.

3.2.3 Major Ions in Cloud Water

The major ions are identified as SO_4^{2-}, H^+, NH_4^+, and NO_3^-. Figure 3-7 presents the seasonal mean major ion concentrations in cloud water samples for 1995 through 2007 and 2009 through 2011. All 2011 mean major ion concentrations, except for H^+, show an increase with respect to 2010 mean concentrations. The 2011 mean NO_3^- concentration (148.48 μeq/L) shows a 31.9 percent increase from the 2010 mean, and the 2011 mean SO_4^{2-} concentration (278.45 μeq/L) is 21.8 percent higher than the 2010 mean. All 2011 seasonal concentrations, except H^+, peaked in August (Figure 3-8). H^+ concentrations peaked in July. All concentrations, except H^+, were lowest in September. H^+ concentrations were lowest in June. Summary statistics of all major ion concentrations, as well as Ca^{2+} concentrations, averaged across all years (1994–2007, 2009–2011) are presented in Table 3-4.

The increases in seasonal concentrations since 2009 may be partially explained by the lower LWC values during the 2010 and 2011 seasons. Lower LWC is often associated with higher concentrations as a result of the concentration of the ions in the lesser amount of water within the cloud.

3.2.4 Minor Ions in Cloud Water

Seasonal mean concentrations of the minor ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, and Cl^-) for 1995 through 2007 and 2009 through 2011 are presented in Figure 3-9. Concentrations of Ca^{2+}, Mg^{2+}, and K^+ increased with respect to 2010 concentrations; whereas, Na^+ and Cl^- concentrations decreased. Seasonal concentrations for the minor ions peaked in June except for Ca^{2+}, which peaked in August (Figure 3-10). All minor ions, except for Ca^{2+} and Mg^{2+}, again exhibited their lowest concentrations in September. Ca^{2+} and Mg^{2+} concentrations were lowest in July.

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) precipitation SO_4^{2-} and NO_3^- concentrations exhibited the same pattern as mean seasonal cloud water SO_4^{2-} and NO_3^- concentrations. Figures 3-11 and 3-12 show mean seasonal cloud water and precipitation concentrations for SO_4^{2-} and NO_3^-, respectively, from 2000 through 2011. The cloud water concentrations are plotted on the left y-axis and the precipitation concentrations are plotted on the right y-axis. Both figures show that the increases in the 2011 cloud water SO_4^{2-} and NO_3^- concentrations were mirrored by increases in precipitation SO_4^{2-} and NO_3^- concentrations, although the increases in the precipitation concentrations were not as great. The 21.8 percent increase in 2011 cloud water SO_4^{2-} concentrations from 2010 concentrations is tracked by a 10.3 percent increase in precipitation SO_4^{2-} concentrations. The 31.8 percent increase in 2011 cloud water NO_3^- concentrations from 2010 concentrations is echoed by a 9.2 percent increase in 2011 precipitation NO_3^- concentrations. On average, the seasonal precipitation SO_4^{2-} and NO_3^- concentrations are within 6 to 17 percent of the seasonal cloud water concentrations from 2000 through 2011.

View from Tower

4.0 Cloud Deposition

This section presents the modeled cloud water deposition estimates for Clingmans Dome from 1994 through 2007 and 2009 through 2011. 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 AMEC. The complete report discussing 2011 cloud deposition modeling results by Gary M. Lovett, (2011) 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:

- The surface area index of canopy tissues in each height layer in the canopy,
- The zero-plane displacement height and roughness length of the canopy,
- The wind speed at the canopy top,
- The LWC of the cloud above the canopy, and
- 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 ($g/cm^2/min$) and as a deposition velocity [flux rate/LWC, in units of centimeters per second (cm/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:

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

The 2011 data set contained 42 samples (or time periods), and the model was run for all 42 samples. Seasonal depositions for 2011, presented in Appendix A, 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, Appendix A (MACTEC, 2004; 2007) for details of the 2003 and 2006 procedures.

4.2 Results

4.2.1 Monthly Means

For the 2011 season, wind speed and cloud water deposition velocity values were relatively constant from month to month with the highest values for both parameters occurring in August (Appendix A, Figure 4). Duration-weighted mean monthly concentrations for SO_4^{2-}, NO_3^-, and NH_4^+ were highest in August, whereas H^+ peaked in July (Appendix A, Figure 1). All major ion concentrations were lowest in September. Ca^{2+} and Mg^{2+} exhibited lowest concentrations in July, and Na^+, K^+, and Cl^- concentrations were lowest in September (Appendix A, Table I-2). The volume-weighted mean LWC in 2011 (0.27 g/m^3) was slightly higher than in 2010 (0.23 g/m^3) and lower than the project mean of 0.31 g/m^3.

Monthly deposition estimates [kilograms per hectare (kg/ha)] for major ions, Ca^{2+}, and water for all months sampled during 1994, 1995, 1997 through 2007, and 2009 through 2011 are presented in Table 4-1. All concentrations, except H^+, increased in 2011 (Appendix A, Figure 2), as did total cloud deposition, including H^+, which showed a very slight increase from 0.07 kg/ha in 2010 to 0.08 kg/ha in 2011 (Appendix A, Tables I-1, I-2, I-3, and Figure 6).

The seasonal (June through September) monthly CLOUD model deposition estimates for the major ions and Ca^{2+} for years 1999 through 2007 and 2009 through 2011 are presented in Figures 4-1 through 4-5. There is no readily apparent trend for the seasonal monthly deposition estimates other than estimates of three of the major ions (SO_4^{2-}, NH_4^+, and NO_3^-) peaked in August and were lowest in September. H^+ depositions peaked in July and were lowest in June.

Table 4-2 presents the mean monthly deposition rates estimated for 1995 through 2007 and 2009 through 2011. 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 and Ca^{2+} are presented in Table 4-3. Data sets from 1997, 1999 through 2007 and 2009 through 2011 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 2011 data show that deposition estimates for all ions increased with respect to 2010 estimates. This increase in deposition estimates mirrors the increase in seasonal concentrations (except for H^+) and could reflect the lower water deposition in 2011. The water deposition was 9.1 cm/month in 2009, 2.9 cm/month in 2010, and 3.8 cm/month in 2011. The lowest water deposition before 2010 occurred during 2007 (3.5 cm/month), 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 2009 through 2011. When analyzed this way, the decreases in average SO_4^{2-}, NO_3^-, and NH_4^+ deposition estimates between 1999–2001 and 2009–2011 are 77 percent (84.2 kg/ha versus 19.6 kg/ha), 74 percent (48.8 kg/ha versus 12.6 kg/ha), and 56 percent (13.7 kg/ha versus 6.0 kg/ha), respectively. Figure 4-6 depicts in graphical form the same data as in Table 4-3 for SO_4^{2-}, NO_3^-, NH_4^+, and H^+. In this figure, the overall decrease in the seasonal deposition estimates is readily apparent. Because the H^+ deposition estimates are much lower with respect to the other three ions, only H^+ deposition estimates are plotted in Figure 4-7 to better illustrate the decrease in these values over the years.

4.3 Comparison of Cloud Water versus Wet Deposition Estimates

Wet deposition data from 2000 through 2011 were obtained from the NADP/NTN site TN11 for comparison to cloud water deposition estimates for 2000 through 2007 and 2009 through 2011. Figures 4-8 and 4-9 show the seasonal SO_4^{2-} and NO_3^- deposition estimates, respectively, for both cloud water and precipitation data. The cloud water deposition estimates are plotted against the left y-axis, and the wet deposition values are plotted against the right y-axis. Starting in 2003, both species follow a similar pattern for cloud water and wet deposition estimates with some exceptions. The main exceptions are: 1) the wet SO_4^{2-} deposition value for 2009 decreased with respect to the 2007 value, while the cloud SO_4^{2-} deposition value increased with respect to the 2007 value; 2) the wet NO_3^- deposition value shows a minor increase (0.63 percent) in 2010 with respect to the 2009 value, while the cloud NO_3^- deposition value shows a 48.9 percent decrease; and 3) both the wet deposition SO_4^{2-} and NO_3^- estimates show a greater variability from year to year, since 2003, than the cloud water deposition SO_4^{2-} and NO_3^- estimates. In 2011, both SO_4^{2-} and NO_3^- deposition estimates increased with respect to 2010 values, but the cloud SO_4^{2-} deposition showed a greater increase (29 percent) than the wet SO_4^{2-} deposition, which increased by 14 percent. The cloud NO_3^- deposition increased by 38 percent versus a 13 percent increase in wet NO_3^- with respect to 2010 values.

The June through September 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 SO_4^{2-} values are from 7 to 39 percent of cloud water SO_4^{2-} depositions, and wet deposition NO_3^- values are from 8 to 51 percent of cloud water NO_3^- depositions from 2000 through 2011. Both the SO_4^{2-} and NO_3^- seasonal precipitation concentrations were 6 to 17 percent of cloud water concentrations from 2000 through 2011.

View from Clingmans Dome Parking Area

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 impregnated cellulose filters. Weekly air pollutant concentrations measured during the 2011 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 NPS 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 2011 sampling season (June through September), the CASTNET laboratory analyzed 18 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 AMEC 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 SO_4^{2-} and/or NO_3^-. The Teflon filter received additional analyses for Cl^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+. Sample handling and analyses followed the procedures described in the CASTNET Laboratory Standard Operating Procedures (MACTEC, 2011). 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 (µg/m^3) resulting from analysis of each weekly filter pack exposed for sampling during the 2011 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. This procedural change was implemented to better match CASTNET protocols. CASTNET sites sample continuously, and due to their lower elevations, most of the CASTNET sites do not experience cloud events.

Filter pack sampling at CLD303 was discontinued altogether after 2004 due to funding limitations. From 2005 on, filter pack data have been obtained from the GRS420 CASTNET site. Besides continuous filter pack sampling, there is an elevation difference of 1,221 meters between the CLD303 site (elevation 2,014 m) and the GRS420 site (elevation 793 m). The differences in sampling protocols and elevation should be taken into consideration by the data user when comparing filter pack concentrations before and after 2005. Use of GRS420 data may result in an overestimate in dry deposition of sulfur and nitrogen species at CLD303. However, dry deposition is a small component of the total deposition at CLD303 (see Section 5.3), and the uncertainty due to use of GRS420 data should not be considered significant when evaluating total deposition at CLD303.

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 in the following equation:

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

The atmospheric concentrations for the filter pack samples were calculated by using the laboratory data (µg/filter) in the following equation.

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

The following constants were used for converting the chemistry data:

Teflon		Nylon		Cellulose	
Parameter	**Constant**	**Parameter**	**Constant**	**Parameter**	**Constant**
SO_4^{2-}	1.0	SO_4^{2-}	1.0	SO_2	0.667
NO_3^-	4.429	HNO_3	4.5	NA	NA
NH_4^+	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_2 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_2 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 2011 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 2011 field season is:

Total seasonal flux = 18/18 (sum of all valid weekly deposition estimates)

All 18 filter packs analyzed were used to calculate dry deposition estimates.

Since 1999, total dry sulfur deposition estimates have decreased 66.8 percent and total dry nitrogen deposition estimates have decreased 75.2 percent (Figure 5-1).

5.3 Total Deposition

Total sulfur and nitrogen deposition estimates for the 1999 through 2007 and 2009 through 2011 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_4^{2-} deposition estimated from the CLOUD model to sulfur (S). Total sulfur for the dry component was determined by using the SO_2 and SO_4^{2-} 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_3^- and NH_4^+ deposition estimated from the CLOUD model to nitrogen (N). Total dry nitrogen deposition was determined by converting the HNO_3, NO_3^-, and NH_4^+ 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 through 2011 sampling seasons. This figure shows that cloud water sulfur deposition for 2011 increased approximately 29 percent from 2010 measurements, and dry sulfur deposition remained virtually the same . Total nitrogen deposition increased 39.8 percent for cloud water and decreased 5.0 percent for dry deposition with respect to 2010. Despite the fact that the filter pack data for 2011 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.

CASTNET Dry Deposition Site at Great Smoky Mountains National Park, TN (GRS420)

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 interannual increases observed for both species in 2001, 2004, 2006, 2009, and 2011. Despite some annual variability, estimates of total deposition, i.e. deposition produced by cloud + dry components, show a general, overall decline since 1999 (Figure 6-1). Since 1999, total sulfur deposition decreased 80.1 percent and total nitrogen deposition decreased 64.5 percent. Total cloud water sulfur deposition has decreased 80.5 percent since 1999 with a 63.3 percent decrease in total cloud water nitrogen deposition. The 2011 seasonal estimates show that dry deposition is a small contributor to the deposition of pollutants at high elevations (Table 5-1). Cloud deposition is the significant pathway for deposition at these elevations.

The principal recommendation for the 2012 season is to continue cloud water sampling at CLD303, especially since all concentrations, except for H^+, and all depositions increased in 2011.

7.0 References

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* Now known as AMEC Environment & Infrastructure, Inc. (AMEC)

Tables

Table 3-1. Monthly Mean Cloud Frequency Summary

Clingmans Dome (CLD303)		1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2009	2010	2011	Mean[3]
May	Cloud Frequency[1]			81.78%			31.07%	47.17%	34.50%	91.67%					99.29%	44.52%		39.32%
	Cloud Hours[2]			67			174	350	256	330					279	329		
	Completeness			11%			75%	100%	100%	48%					38%	99%		
June	Cloud Frequency[1]			61.63%	48.58%	41.38%	49.72%	43.33%	43.47%	54.61%	67.89%	54.93%	23.62%	36.64%	48.80%	22.97%	24.03%	42.62%
	Cloud Hours[2]			106	205	276	270	312	313	361	387	390	163	255	326	164	173	
	Completeness			24%	59%	93%	75%	100%	100%	92%	79%	99%	96%	97%	93%	99%	100%	
July	Cloud Frequency[1]	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%	55.00%	28.67%	35.35%	43.35%
	Cloud Hours[2]	84	139	227	399	328	140	391	340	314	370	290	97	314	412	213	263	
	Completeness	38%	40%	89%	97%	99%	45%	92%	93%	99%	88%	96%	84%	87%	100%	100%	100%	
August	Cloud Frequency[1]	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%	27.36%	41.78%	40.12%
	Cloud Hours[2]	351		256	5	185	305	367	202	152	347	223	264	174	418	203	254	
	Completeness	95%		83%	1%	100%	94%	73%	97%	48%	100%	98%	65%	100%	100%	100%	82%	
September	Cloud Frequency[1]	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%	28.15%	43.14%	41.52%
	Cloud Hours[2]	106		212	170	172	349	136	322	242	334	89	363	394	359	201	283	
	Completeness	48%		93%	54%	86%	96%	50%	87%	85%	98%	96%	100%	88%	98%	99%	91%	
October	Cloud Frequency[1]		23.64%	35.52%	30.32%		5.98%	41.72%			48.56%	46.91%	32.65%		37.56%	44.49%		36.20%
	Cloud Hours[2]		78	200	211		34	141			287	296	159		246	331		
	Completeness		44%	76%	94%		76%	46%[3]			79%	85%	66%		88%	100%		
November	Cloud Frequency[1]			59.70%														
	Cloud Hours[2]			40														
	Completeness			9%														

Note: [1] Cloud frequency is not used in subsequent analyses if the completeness criterion of 70 percent is not met.

[2] Number of records where LWC ≥ 0.05 g/m^3

[3] The mean cloud frequency values are calculated only from those annual values that meet the completeness criterion and include data from 1994 (not shown in this table).

Table 3-2. Summary Statistics for Cloud Water Samples 2011

	2011 Total Records Accepted = 42				
	n	**mean**	**std dev**	**min**	**max**
LWC	42	0.309	0.168	0.138	1.11
pH - Field	39	4.31	0.40	3.67	5.57
pH - Lab	41	4.29	0.40	3.73	5.40
Cond - Field	40	86.4	44.80	9.2	199.90
Cond - Lab	38	83.2	43.70	5.7	181.60
H^+ - Field	39	49.51	39.83	2.69	213.80
H^+ - Lab	41	51.05	41.25	3.98	186.21
NH_4^+	42	253.03	163.03	3.80	619.13
SO_4^{2-}	42	278.45	167.32	12.62	679.55
NO_3^-	42	148.48	111.12	7.71	628.70
Ca^{2+}	42	94.94	109.24	3.25	656.22
Mg^{2+}	42	25.13	24.54	1.14	146.63
Na^+	42	30.18	25.0	0.88	114.18
K^+	42	7.80	6.78	0.29	30.36
Cl^-	42	21.58	15.05	0.90	64.40
Cations - Field	39	469.03	298.76	15.18	1351.62
Cations - Lab	41	463.80	290.64	25.10	1360.31
Anions	42	448.52	274.56	21.23	1301.60

Note: All units are µeq/L except for LWC (g/m^3), 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[a]	14	9	64
1995[a]	142	136	96
1996[a]	122	105	86
1997[a]	334	324	97
1998[a]	341	269	79
1999[a]	174	174	100
2000[b]	104	102	98
2001[c]	73	70	96
2002[c]	75	65	87
2003[c]	78	78	100
2004[c]	73	73	100
2005[c]	64	63	98
2006[c]	45	45	100
2007[c]	54	54	100
2009[c]	85	58	68
2010[c]	55	50	91
2011[c]	43	42	98
Total	**1876**	**1717**	**92%**

Note: [a] Hourly samples — sample collection bottle changed every hour.
[b] Hourly + daily samples (62 hourly and 42 24-hour samples in year 2000)
[c] Daily samples — sample collection bottle changed every 24 hours.

Table 3-4. Summary Statistics of Major Ion and Calcium Concentrations (µeq/L) of Cloud Water Samples (1994–2007, 2009–2011)

	H^{+} *	NH_4^+	SO_4^{2-}	NO_3^-	Ca^{2+}
Mean	304.44	221.51	400.15	166.21	50.26
Minimum	0.26	0.71	3.54	0.29	0.15
Maximum	2137.96	1650.01	3686.91	1342.88	1051.89
Median	213.80	174.69	306.20	130.80	27.64

Note: * Laboratory pH data instead of field pH data were used for calculating the 2001–2002, 2006–2007, and 2009–2011 hydrogen values.

Table 4-1. Cloud Water Monthly Deposition Estimates Produced by the CLOUD Model (kg/ha)[a]

Year	Month	H^+	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	H_2O (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 [b]	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 [c]	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 [d]	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
2010	June	0.02	2.95	2.13	0.99	0.31	3.19
	July	0.02	3.20	2.34	0.80	0.43	2.72
	August	0.02	4.09	2.21	1.28	0.32	3.05
	September	0.01	2.31	1.57	0.68	0.32	2.71
	October	0.00	1.63	2.33	0.57	0.62	2.89
2011	June	0.01	3.37	2.21	1.41	0.43	2.7
	July	0.04	5.08	3.19	1.49	0.47	3.6
	August	0.02	6.77	5.71	2.65	1.36	4.1
	September	0.01	2.53	2.17	0.82	0.49	4.8

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 Deposition Rates for Several Ions (kg/ha/month) and Water (cm/month)

Year	Water (cm/month)	H^+	NH_4^+	SO_4^{2-}	NO_3^-	Ca^{2+}
1995-98[a]	8.1	0.23	3.0	14.3	7.7	0.54
1999[b]	11.0	0.47	3.6	22.7	11.5	0.93
2000[a]	9.7	0.29	3.0	16.9	8.8	0.68
2001[a]	8.6	0.31	3.3	18.4	12.5	1.28
2002[a]	9.2	0.18	2.3	11.9	6.1	0.56
2003[a]	10.5	0.14	1.8	9.3	4.7	0.53
2004[c]	10.6	0.27	2.1	11.5	4.8	0.36
2005[c]	8.7	0.12	1.5	7.8	3.5	0.37
2006[d]	5.2	0.18	2.2	12.6	3.7	0.33
2007[b]	3.5	0.07	1.3	5.6	2.5	0.24
2009[b]	9.1	0.06	1.9	7.1	4.0	0.72
2010[c]	2.9	0.02	0.9	2.8	2.1	0.40
2011[b]	3.8	0.02	1.6	4.4	3.3	0.69

Note: [a] May through September
[b] June through September
[c] June through October
[d] June through August

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

Year	H^+	NH_4^+	SO_4^{2-}	NO_3^-	Ca^{2+}
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
2010	0.07	3.76	12.56	8.24	1.37
2011	0.08	6.37	17.76	13.28	2.75

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 ($\mu g/m^3$) – June through September 2011

			Teflon								Nylon		Cellulose					
Sample Number	On Date/Time	Off Date/Time	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HNO_3	SO_2	Total SO_2	Total NO_3^-	Comment Codes	Valid Hours	Actual Volume (m^3)
1122001-35	5/31/11 11:45	6/7/11 10:15	6.111	0.099	1.815	0.519	0.094	0.191	0.134	0.017U	0.597	2.775	1.406	1.804	2.830	W03	167	30.013
1123001-35	6/7/11 10:24	6/14/11 11:50	4.690	0.111	1.691	0.216	0.040	0.074	0.105	0.016U	0.318	1.696	0.684	0.897	1.780		169	30.405
1124001-35	6/14/11 11:55	6/21/11 10:55	2.878	0.059	0.791	0.159	0.038	0.118	0.080	0.017U	0.731	1.405	0.857	1.345	1.441	W03	167	30.043
1125001-35	6/21/11 11:00	6/28/11 10:38	2.119	0.053	0.535	0.119	0.031	0.121	0.082	0.017U	0.435	1.027	0.313	0.604	1.064	W03	162	30.225
1126001-35	6/28/11 10:44	7/5/11 13:08	3.423	0.139	1.056	0.304	0.049	0.029	0.107	0.016U	0.709	1.720	1.548	2.021	1.832	W03	171	30.764
1127001-35	7/5/11 13:14	7/12/11 11:00	3.904	0.065	1.199	0.140	0.029	0.062	0.109	0.017U	0.357	1.310	0.310	0.548	1.354	W03	162	29.844
1128001-35	7/12/11 11:45	7/19/11 11:00	3.717	0.235	0.949	0.131	0.068	0.420	0.085	0.017U	0.836	1.537	0.773	1.331	1.748	W03	168	30.214
1129001-35	7/19/11 11:07	7/26/11 11:30	6.434	0.029U	1.729	0.233	0.048	0.120	0.062	0.016U	0.645	1.606	0.444	0.874	1.609	W03	168	30.321
1130001-35	7/26/11 11:37	8/2/11 11:20	5.038	0.030	1.575	0.138	0.026	0.045	0.048	0.017U	0.650	1.261	0.583	1.017	1.271	W03	168	30.192
1131001-35	8/2/11 11:25	8/9/11 10:30	3.711	0.136	1.186	0.204	0.030	0.045	0.055	0.017U	0.495	1.227	0.936	1.266	1.344	W03	167	30.046
1132001-35	8/9/11 10:35	8/16/11 10:47	3.679	0.057	1.071	0.243	0.035	0.029	0.064	0.017U	0.830	1.547	1.034	1.588	1.579		168	30.224
1133001-35	8/16/11 10:52	8/23/11 10:28	3.962	0.077	1.392	0.135	0.023	0.030	0.050	0.017U	0.427	1.222	0.618	0.903	1.279		168	30.214
1134001-35	8/23/11 10:37	8/30/11 10:10	3.285	0.201	1.178	0.236	0.041	0.057	0.052	0.017U	0.482	1.273	1.233	1.555	1.453		168	30.228
1135001-35	8/30/11 10:55	9/6/11 13:04	3.334	0.172	1.176	0.146	0.027	0.083	0.049	0.016U	0.223	1.027	0.329	0.478	1.183	W03	164	30.620
1136001-35	9/6/11 13:10	9/13/11 11:10	1.950	0.289	0.717	0.197	0.025	0.013	0.048	0.017U	0.481	0.923	0.638	0.959	1.198	W03	166	29.910
1137001-35	9/13/11 11:20	9/20/11 10:57	2.125	0.085	0.674	0.140	0.023	0.028	0.078	0.018U	0.341	1.109	0.382	0.610	1.176	W03	167	27.065
1138001-35	9/20/11 11:05	9/27/11 10:55	1.906	0.055	0.621	0.051	0.011	0.036	0.040	0.017U	0.131	0.795	0.138	0.225	0.838	W03	167	30.038
1139001-35	9/27/11 11:03	10/4/11 11:38	1.323	0.456	0.516	0.299	0.041	0.022	0.047	0.017U	0.358	0.650	0.936	1.174	1.096		168	30.226
		Mean	3.533	0.130	1.104	0.201	0.038	0.085	0.072	0.017	0.503	1.339	0.731	1.067	1.449			
		Standard Deviation	1.407	0.109	0.416	0.103	0.019	0.096	0.027	0.000	0.202	0.468	0.397	0.486	0.436			

Data Status Flags: U = Value is less than detection limit.

Comment Codes: **03** = excessively wet filter
W = cellulose

Table 5-2. Great Smoky Mountains National Park, TN (GRS420) Dry Deposition Fluxes (kg/ha) Report for the 2011 Deposition Season (June through September)

Sample Number*	On Date	Off Date	Fluxes (kg/ha)					Deposition Velocities (cm/sec)		
			SO_2	HNO_3	SO_4^{2-}	NO_3^-	NH_4^+	SO_2	HNO_3	Particle
1122001-35	5/31/11 9:00	6/7/11 8:00	0.026	0.256	0.049	0.001	0.015	0.261	1.680	0.146
1123001-35	6/7/11 9:00	6/14/11 8:00	0.012	0.159	0.036	0.001	0.013	0.233	1.695	0.137
1124001-35	6/14/11 9:00	6/21/11 8:00	0.020	0.148	0.021	0.000	0.006	0.269	1.872	0.129
1125001-35	6/21/11 9:00	6/28/11 8:00	0.010	0.099	0.012	0.000	0.003	0.300	1.729	0.105
1126001-35	6/28/11 9:00	7/5/11 8:00	0.028	0.177	0.031	0.001	0.009	0.252	1.857	0.163
1127001-35	7/5/11 9:00	7/12/11 8:00	0.010	0.107	0.025	0.000	0.008	0.301	1.460	0.118
1128001-35	7/12/11 9:00	7/19/11 8:00	0.028	0.100	0.017	0.001	0.004	0.373	1.173	0.080
1129001-35	7/19/11 9:00	7/26/11 8:00	0.020	0.115	0.036	0.000	0.010	0.399	1.309	0.104
1130001-35	7/26/11 9:00	8/2/11 8:00	0.020	0.098	0.031	0.000	0.010	0.365	1.405	0.113
1131001-35	8/2/11 9:00	8/9/11 8:00	0.025	0.104	0.021	0.001	0.007	0.352	1.535	0.103
1132001-35	8/9/11 9:00	8/16/11 8:00	0.028	0.151	0.028	0.000	0.008	0.318	1.764	0.136
1133001-35	8/16/11 9:00	8/23/11 8:00	0.014	0.127	0.030	0.001	0.010	0.268	1.870	0.135
1134001-35	8/23/11 9:00	8/30/11 8:00	0.020	0.158	0.033	0.002	0.012	0.234	2.239	0.179
1135001-35	8/30/11 9:00	9/6/11 8:00	0.006	0.098	0.020	0.001	0.007	0.229	1.726	0.108
1136001-35	9/6/11 9:00	9/13/11 8:00	0.015	0.052	0.007	0.001	0.003	0.291	0.991	0.065
1137001-35	9/13/11 9:00	9/20/11 8:00	0.011	0.075	0.010	0.000	0.003	0.308	1.199	0.082
1138001-35	9/20/11 9:00	9/27/11 8:00	0.005	0.068	0.009	0.000	0.003	0.354	1.516	0.086
1139001-35	9/27/11 9:00	10/4/11 8:00	0.022	0.070	0.011	0.004	0.004	0.336	1.859	0.149
		Total Seasonal Flux	0.318	2.162	0.427	0.016	0.135			
		Mean Seasonal Deposition						0.302	1.604	0.119

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 AMEC laboratory information management system contain the suffix "-35" 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, 2009–2011)

	Year	Total Sulfur[a] (kg/ha)	Total NO_3^--N (kg/ha)	Total NH_4^+-N (kg/ha)	Total Nitrogen[b] (kg/ha)
Cloud Water	1999	30.362	10.36	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	6.010	9.655
	2010	4.194	1.862	2.920	4.782
	2011	5.930	3.001	4.946	7.947
Dry	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
	2010*	0.300	0.510	0.110	0.620
	2011*	0.301	0.485	0.105	0.589

Note: Season is defined as June through September.

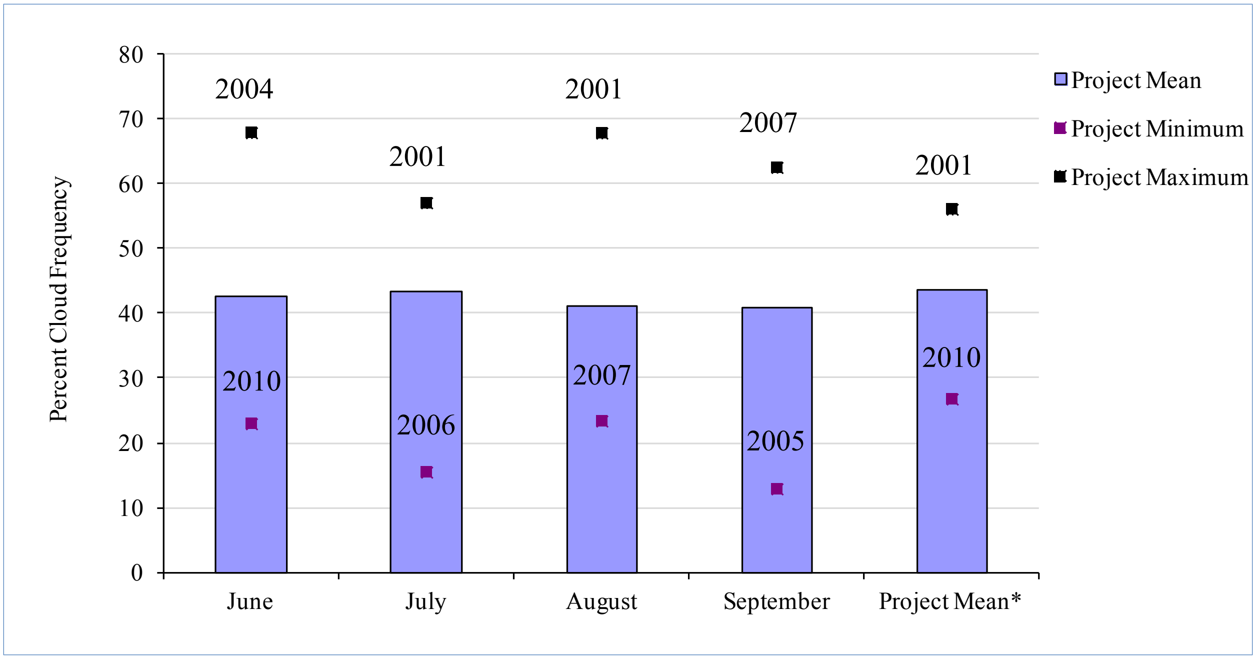
[a] Total sulfur deposition includes SO_4^{2-} in cloud water plus ambient SO_2 and SO_4^{2-}.

[b] Total nitrogen deposition includes NO_3^- and NH_4^+ in cloud water plus ambient NO_3^-, NH_4^+, and HNO_3.

*Dry deposition values for 2005 through 2007 and 2009 through 2011 were obtained from the Great Smoky Mountains National Park (GSR420) site at Look Rock, TN.

Figures

Figure 3-1. Monthly Cloud Frequency Statistics (1995–2007, 2009–2011)



Note: * Values associated with this column are based on seasonal averages.

Figure 3-2. Monthly Mean Cloud Frequency – 2011 versus Historical Mean Values (1995–2007, 2009–2010)

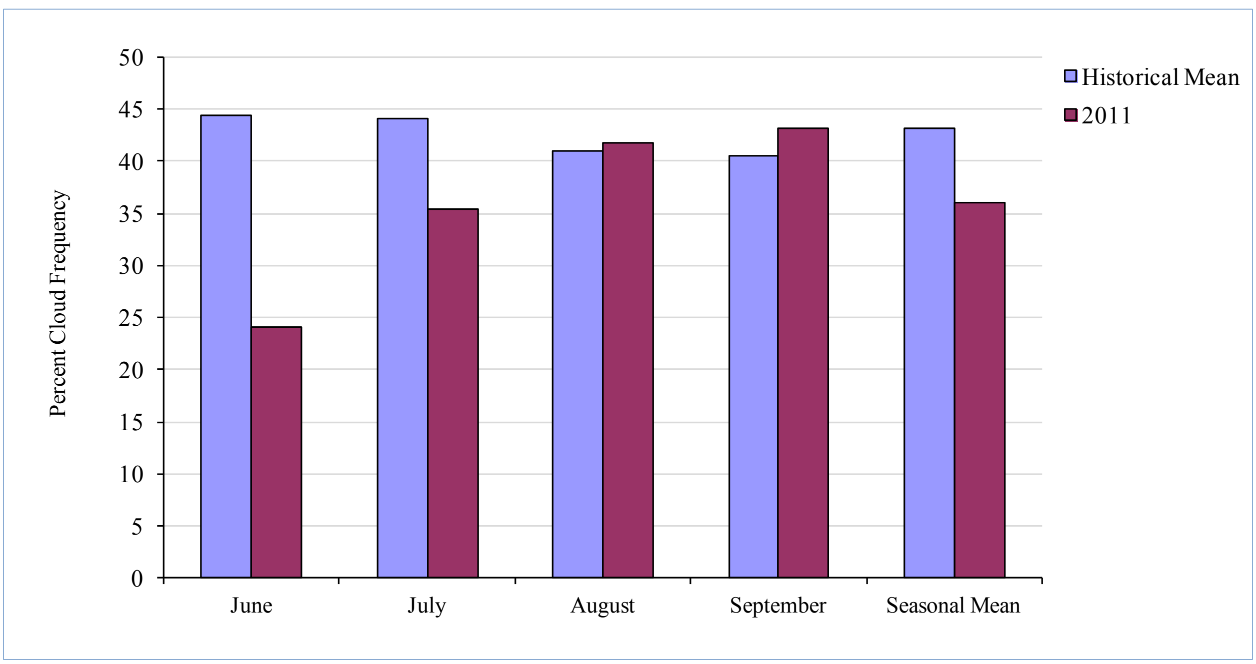
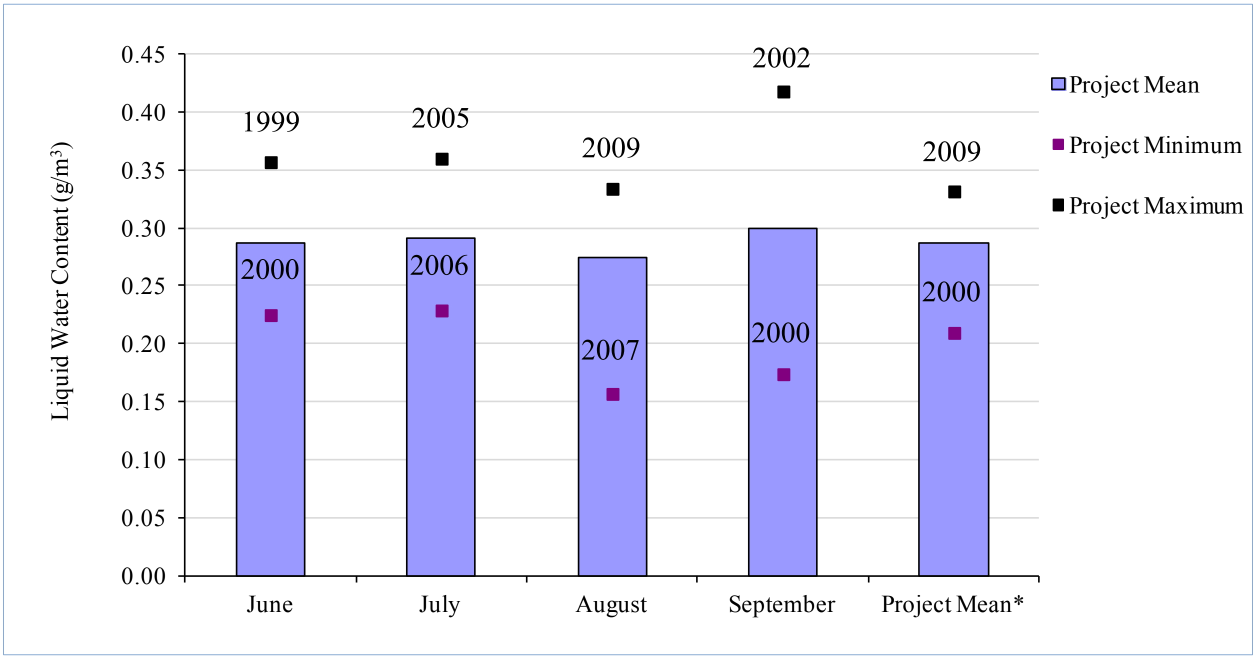


Figure 3-3. Monthly Mean Liquid Water Content Statistics (1995–2007, 2009–2011)



Note: * Values associated with this column are based on seasonal averages.

Figure 3-4. Monthly Mean Liquid Water Content – 2011 versus Historical Mean Values (1995–2007, 2009–2010)

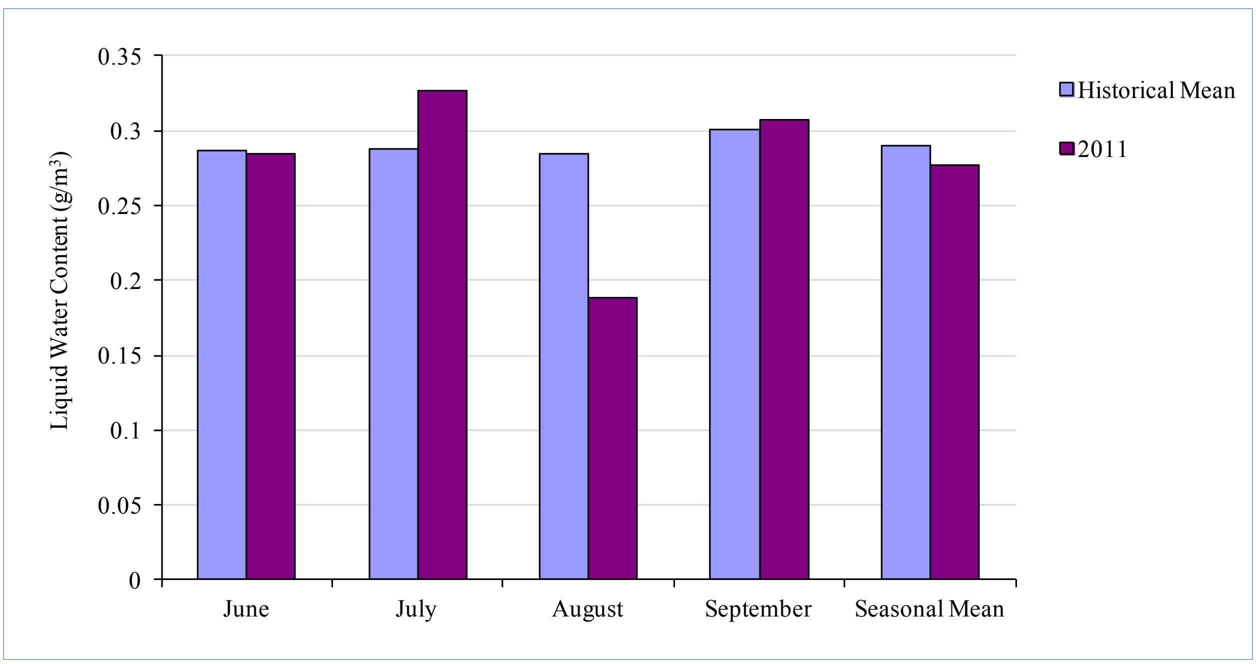


Figure 3-5. Frequency Distribution for Cloud Water pH (Laboratory) at Clingmans Dome, TN (2011)

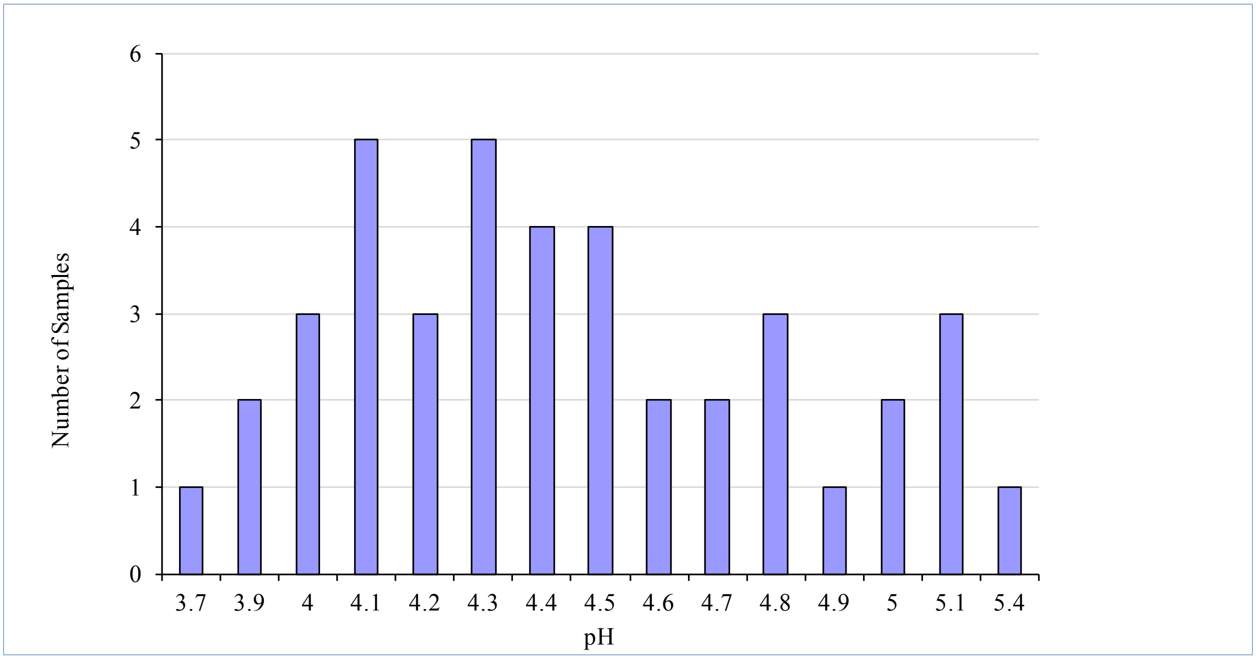


Figure 3-6. Frequency Distribution for Cloud Water pH (Field) at Clingmans Dome, TN (2011)

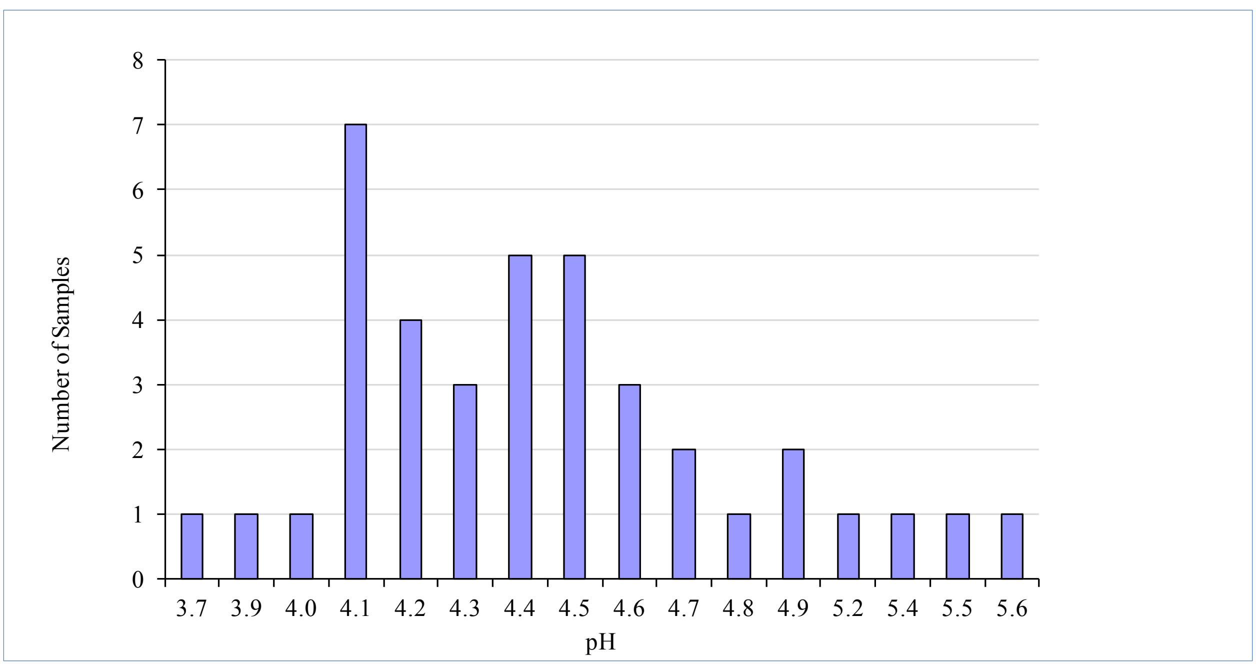
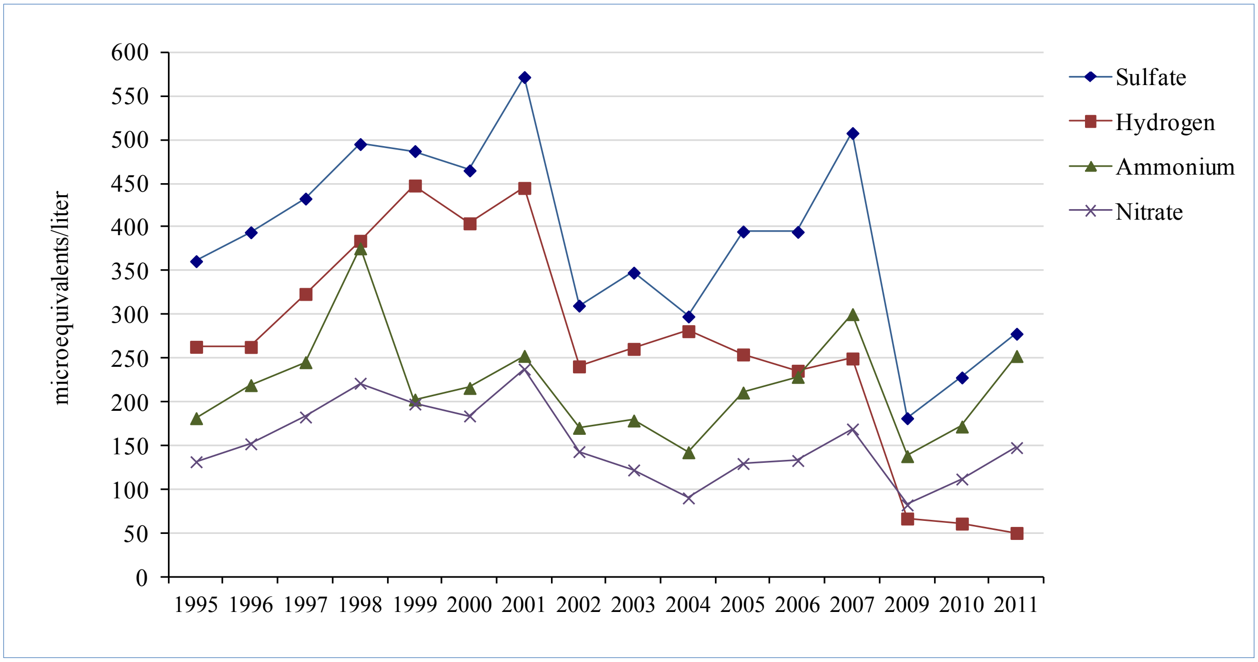


Figure 3-7. Mean Major Ion Concentrations of Cloud Water Samples (1995–2007, 2009–2011)



Note: * Laboratory pH data instead of field pH data were used for calculating the 2001, 2006, 2007, 2009, 2010 and 2011 hydrogen concentration values.

Figure 3-8. Mean Monthly Major Ion Concentrations for 2011

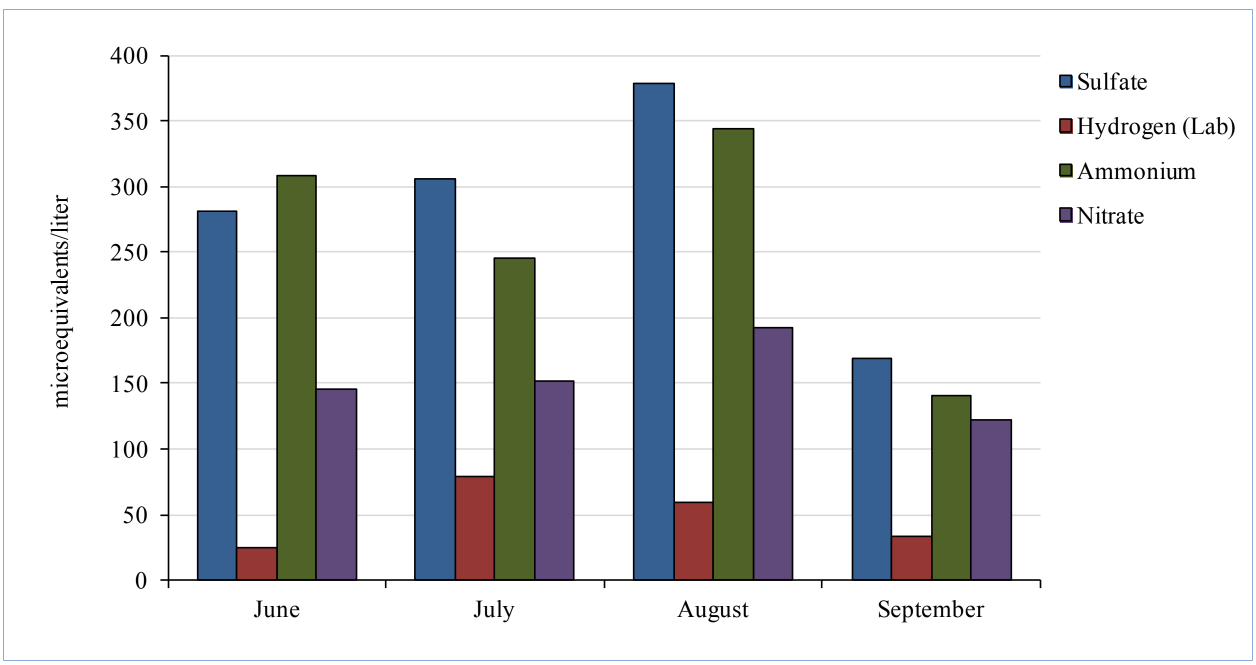


Figure 3-9. Mean Minor Ion Concentrations of Cloud Water Samples (Cations and Chloride) 1995–2007, 2009–2011

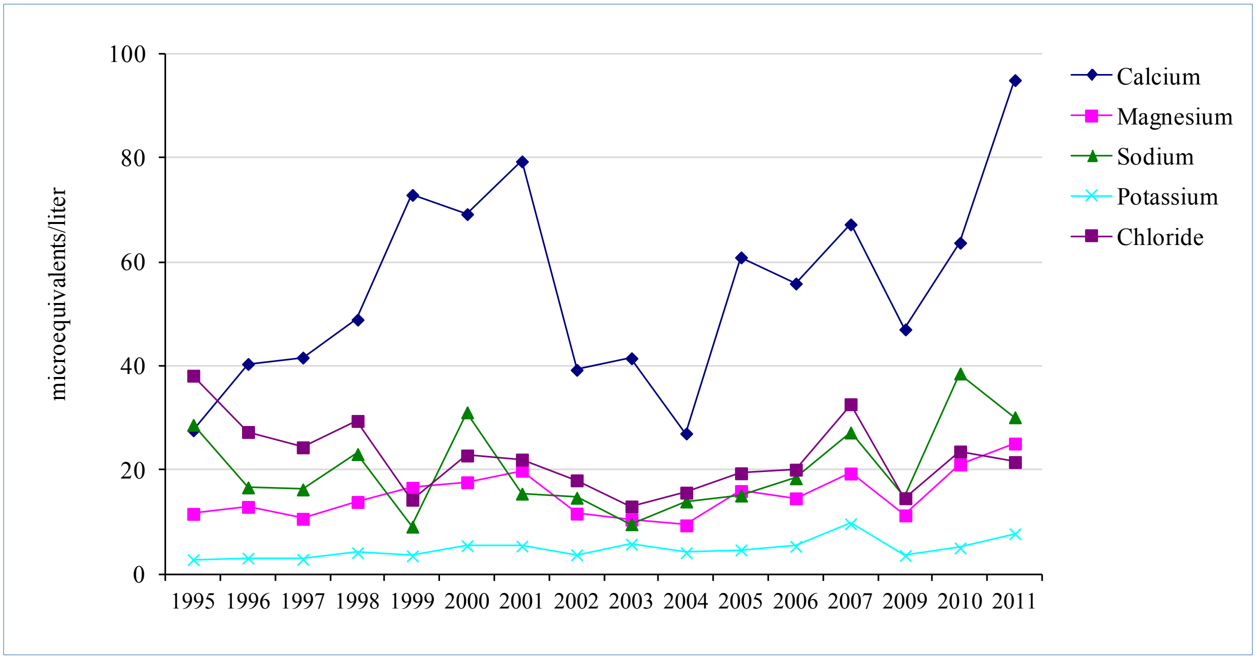


Figure 3-10. Mean Monthly Minor Ion Concentrations for 2011

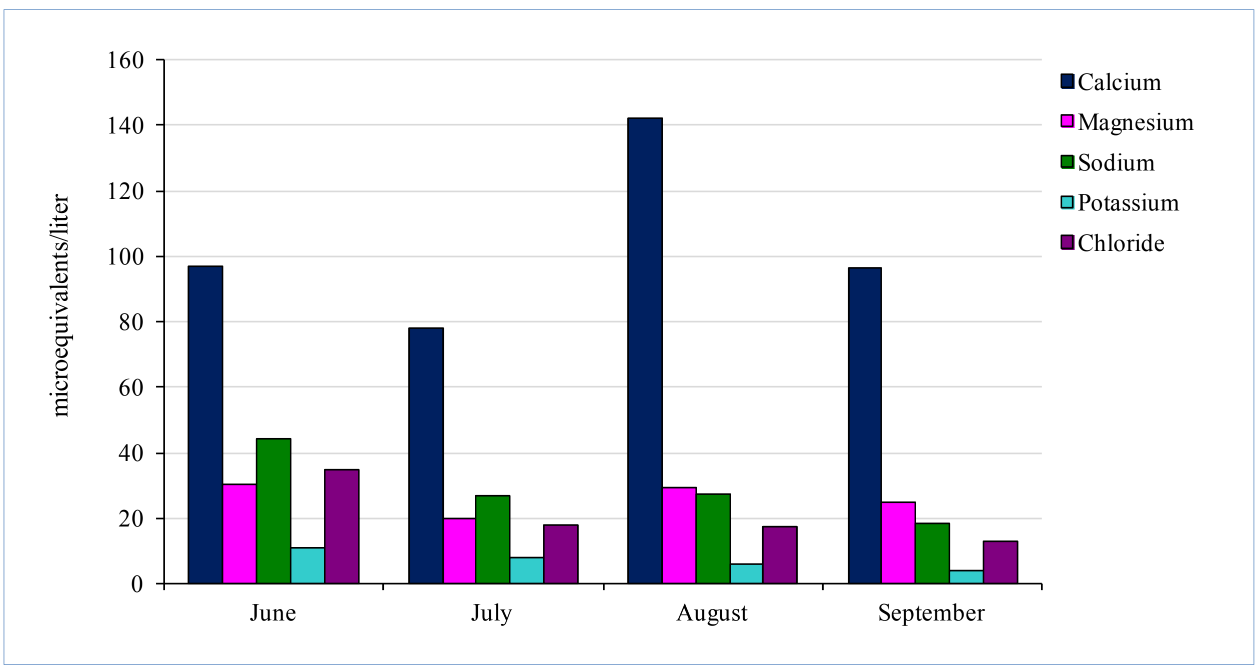


Figure 3-11. Mean Seasonal Cloud Water versus Mean Seasonal Precipitation Sulfate Concentrations, 2000–2011

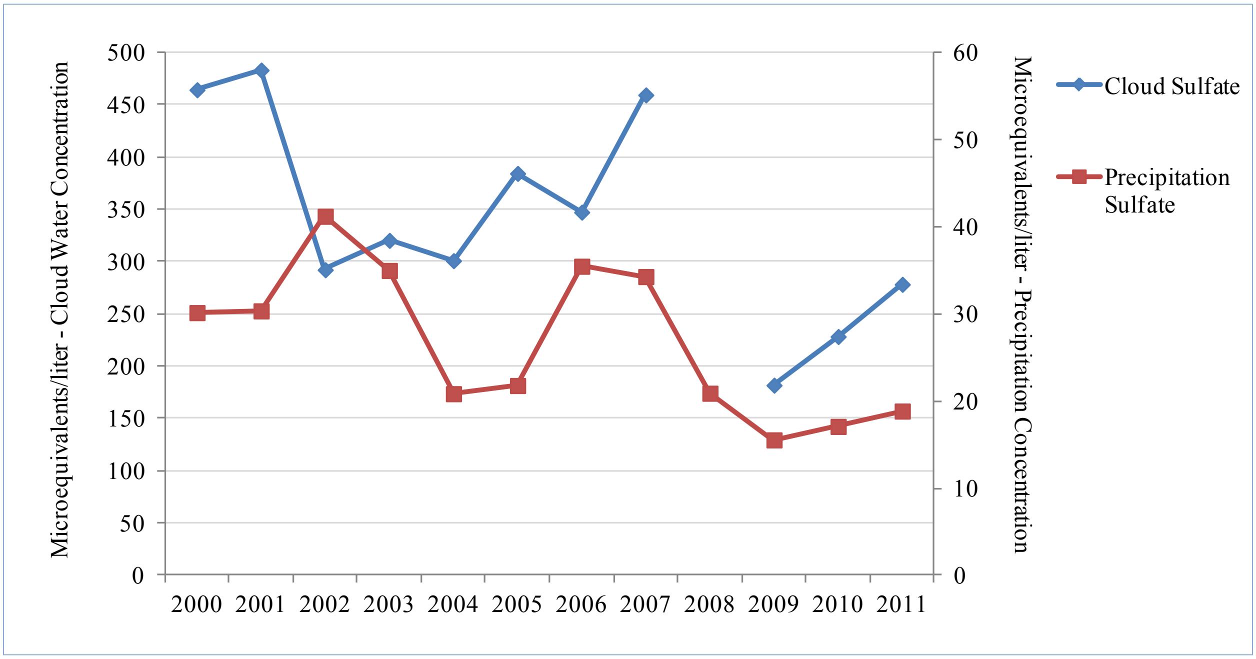


Figure 3-12. Mean Seasonal Cloud Water versus Mean Seasonal Precipitation Nitrate Concentrations, 2000–2011

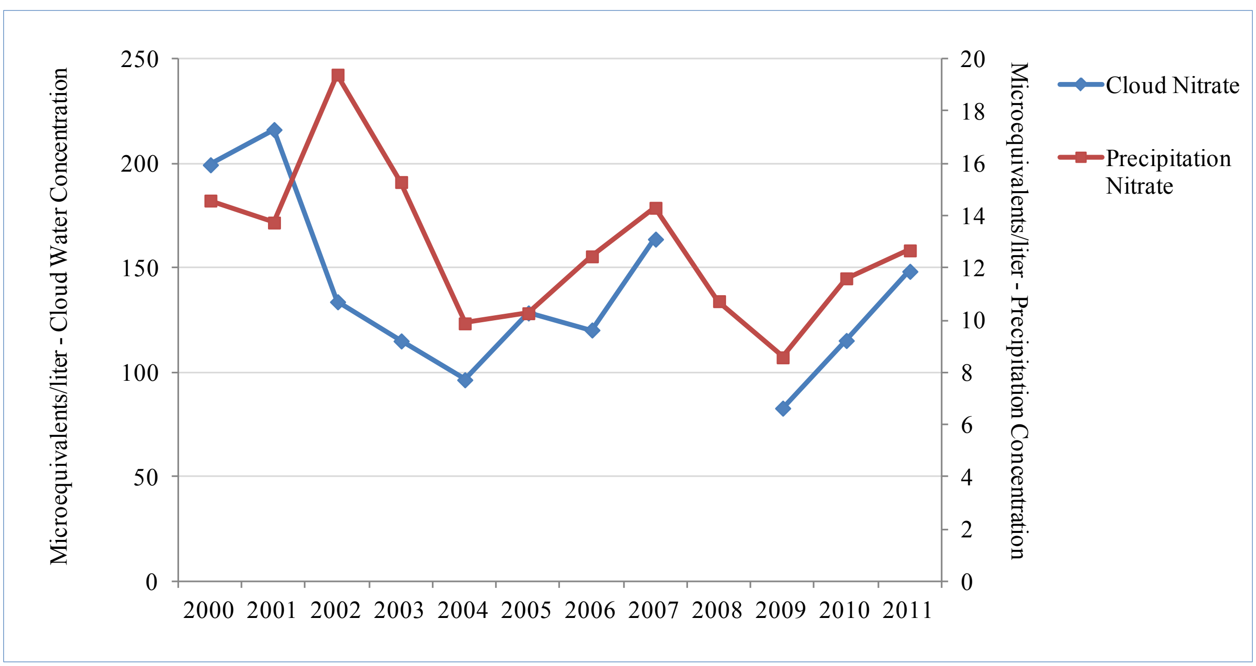


Figure 4-1. Monthly Deposition Estimates – CLOUD Model (SO_4^{2-})

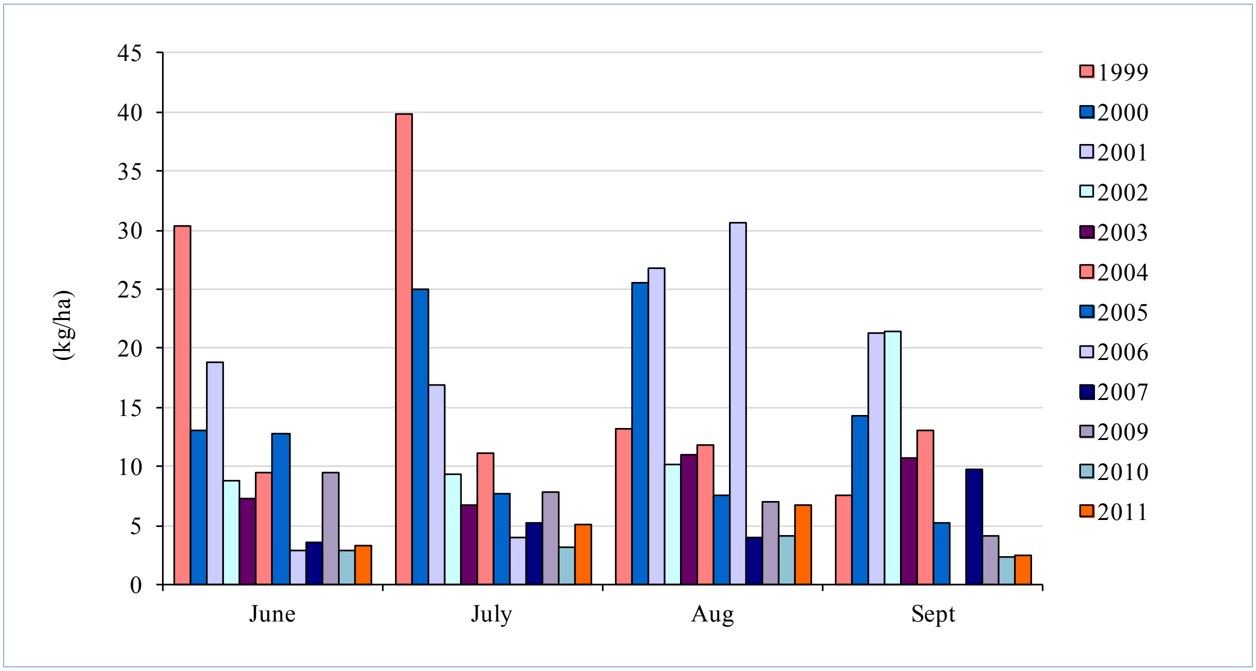


Figure 4-2. Monthly Deposition Estimates – CLOUD Model (NO_3^-)

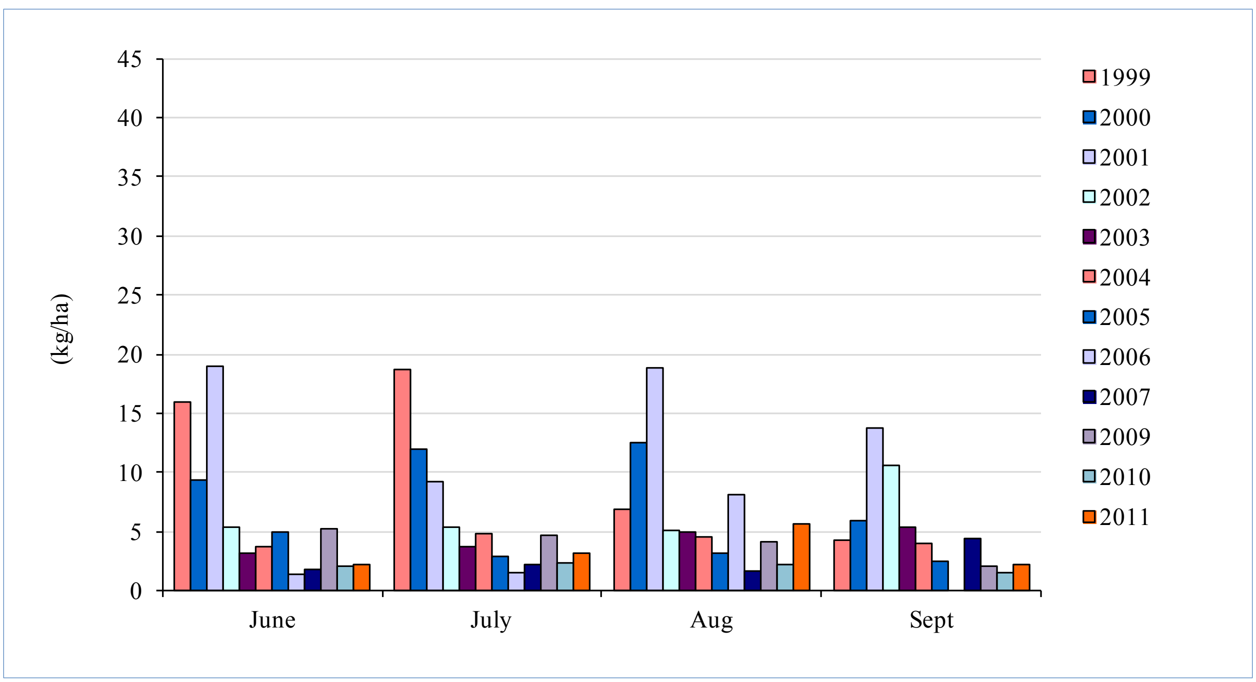


Figure 4-3. Monthly Deposition Estimates – CLOUD Model (NH_4^+)

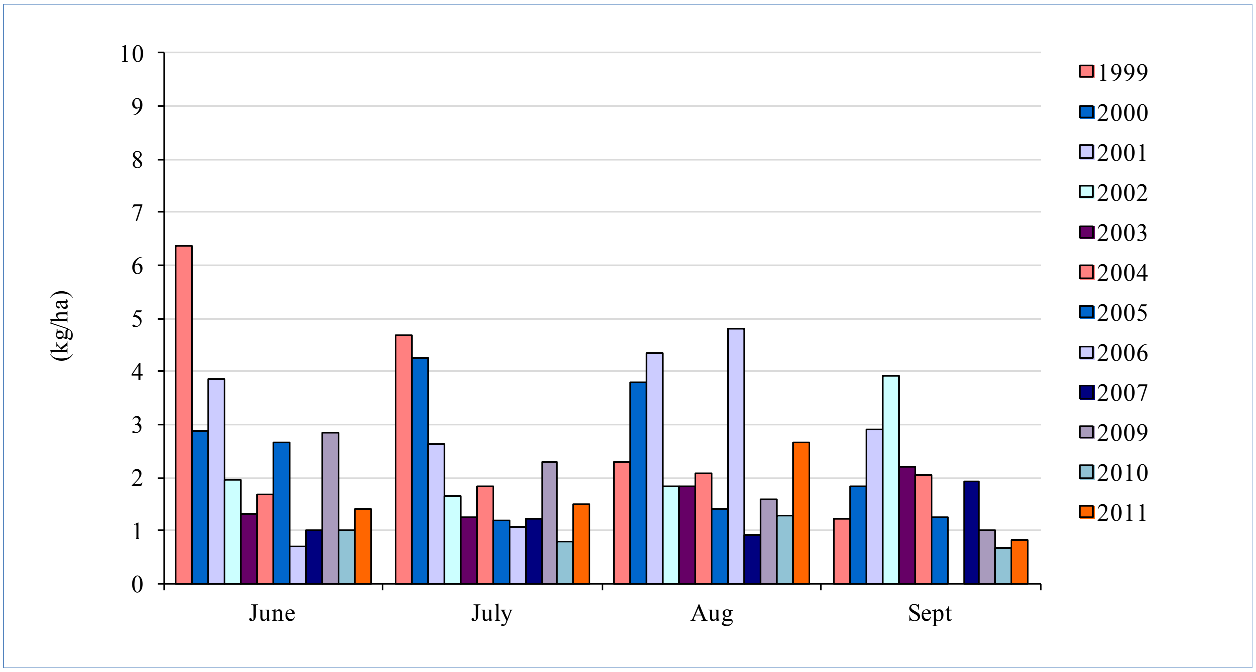


Figure 4-4. Monthly Deposition Estimates – CLOUD Model (H^+)

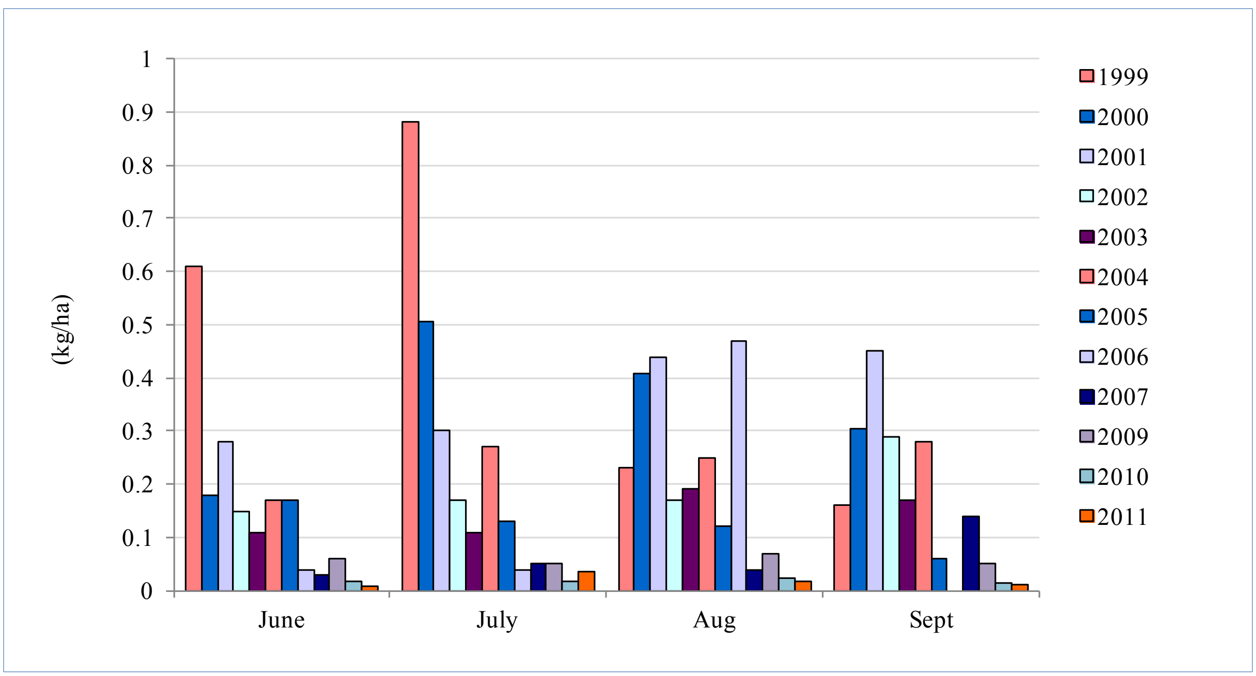


Figure 4-5. Monthly Deposition Estimates – CLOUD Model (Ca^{2+})

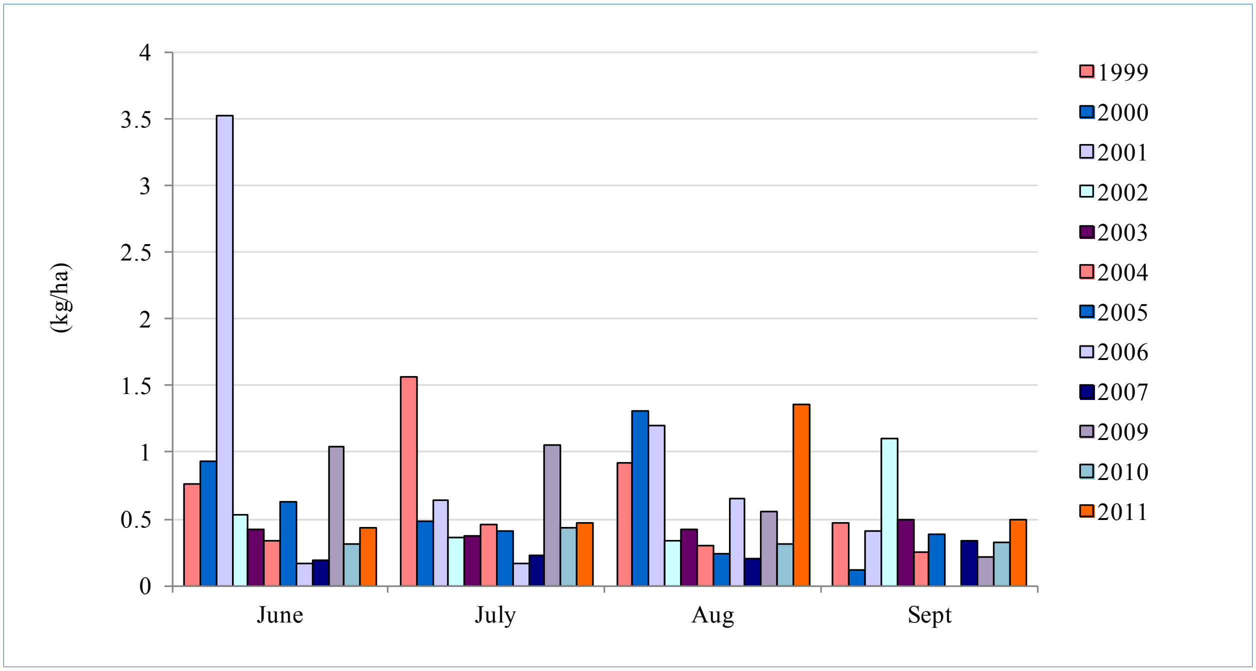


Figure 4-6. Seasonal Deposition Estimates for Major Ions (1999–2007, 2009–2011)

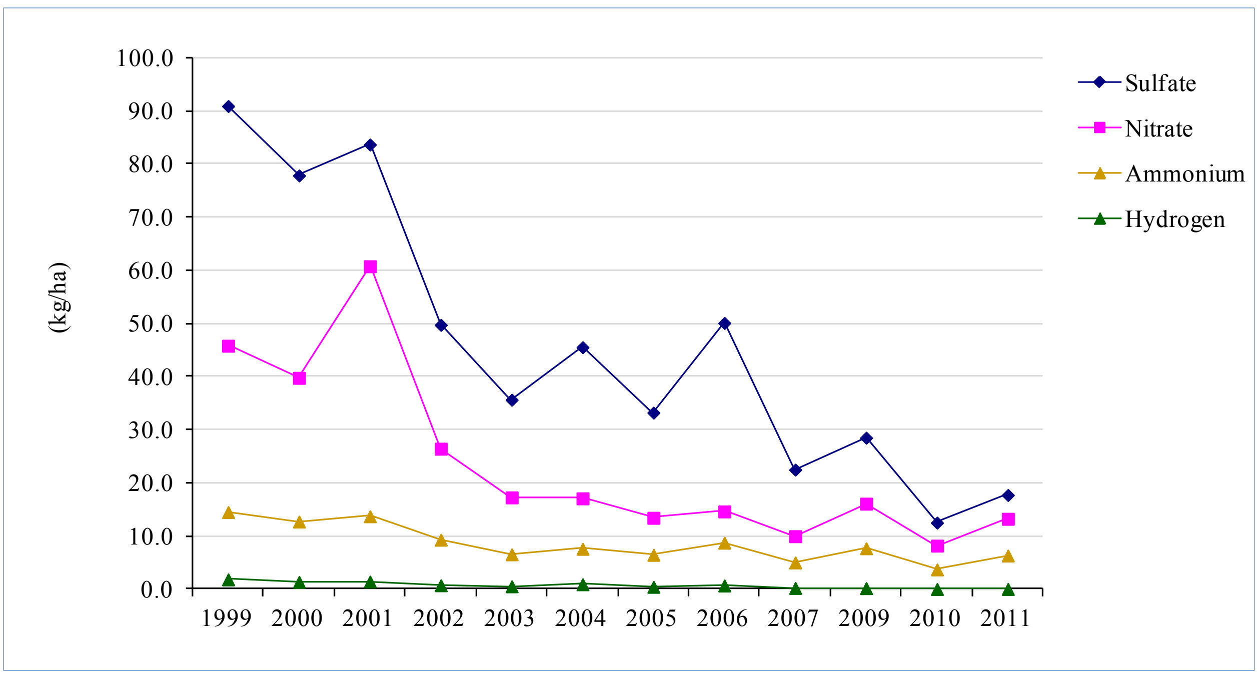


Figure 4-7. Seasonal Deposition Estimates for Hydrogen (1999–2007, 2009–2011)

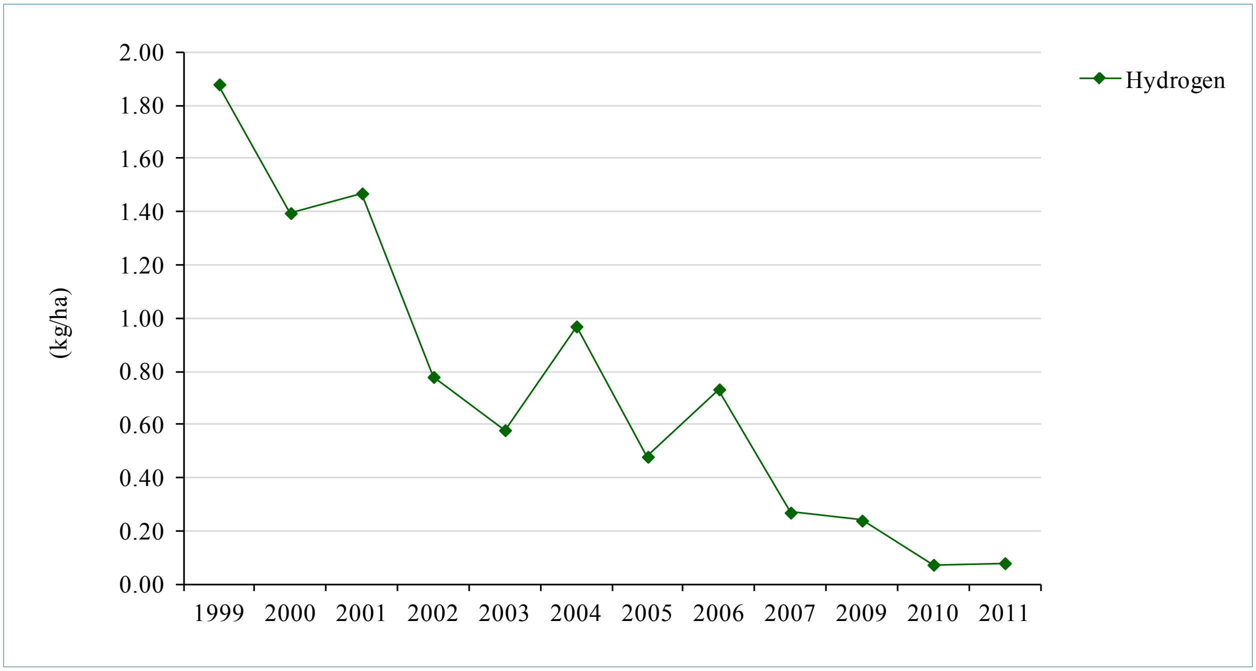


Figure 4-8. Cloud Water and Wet Sulfate Deposition Estimates (June through September, 2000–2011)

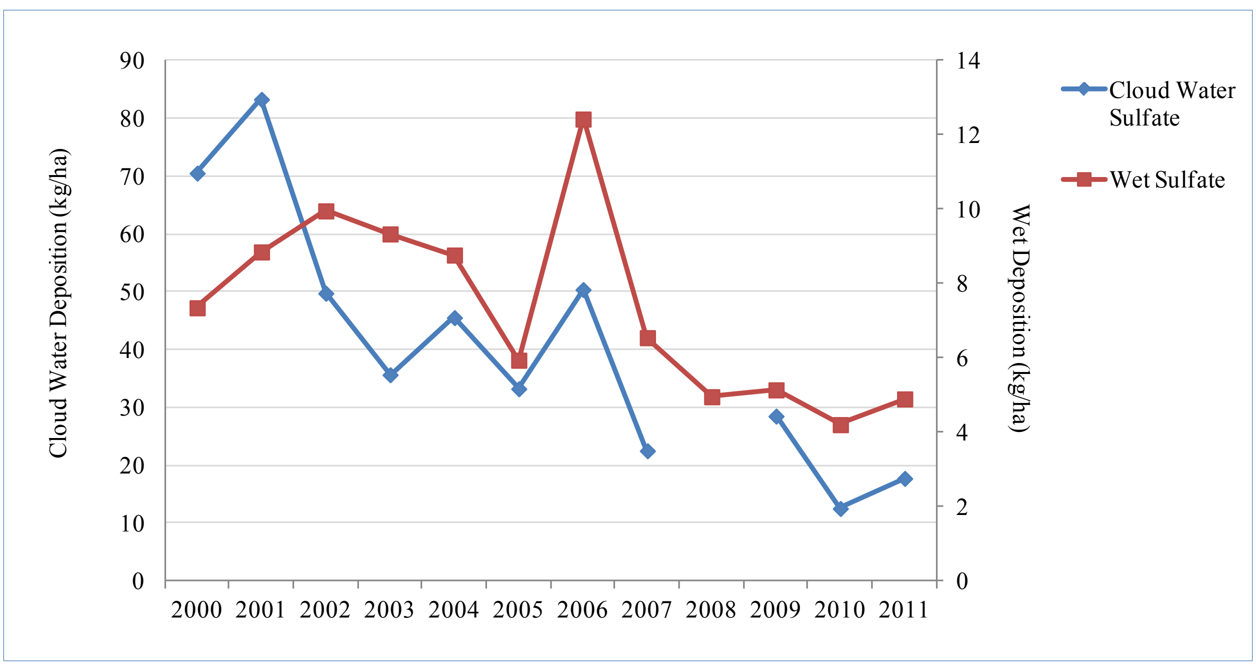


Figure 4-9. Cloud Water and Wet Nitrate Deposition Estimates (June through September, 2000–2011)

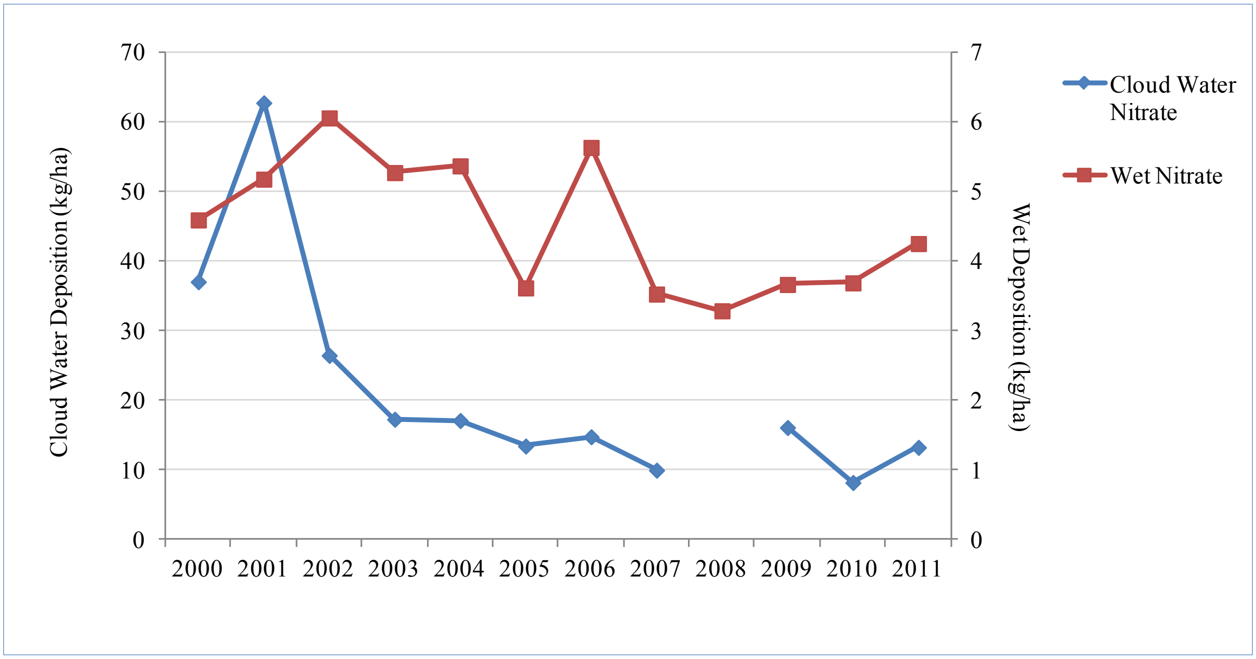


Figure 5-1. Total Sulfur and Nitrogen Cloud Water and Dry Deposition Estimates (June through September, 1999−2007, 2009–2011)

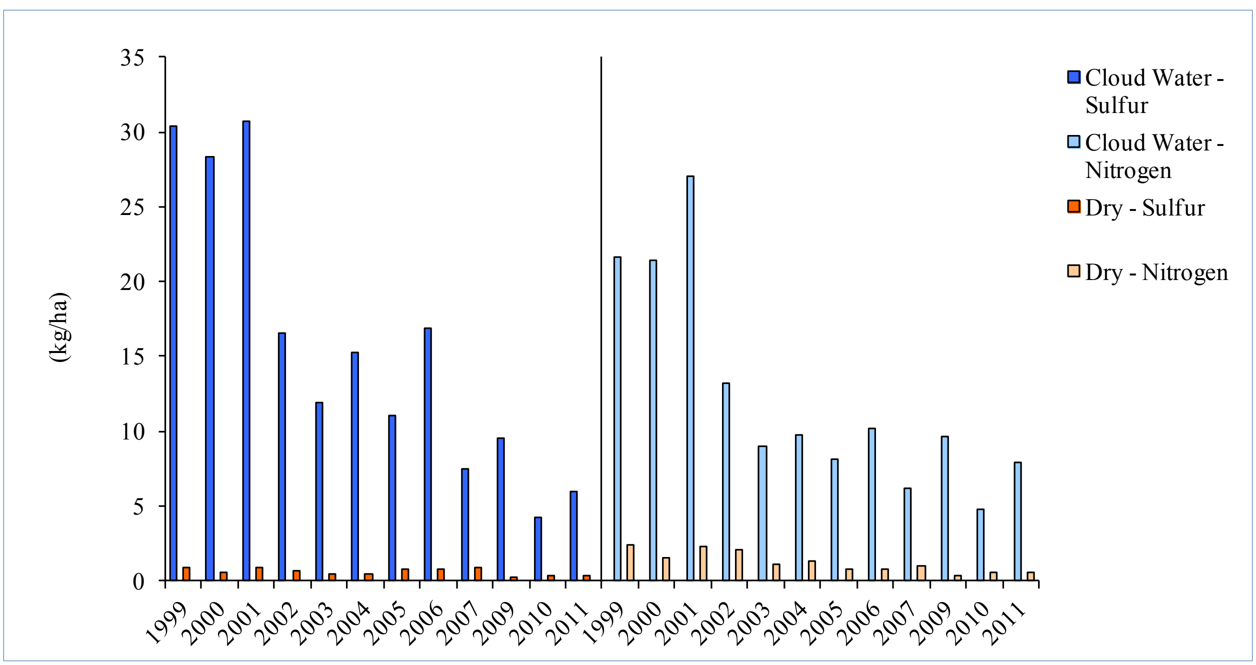
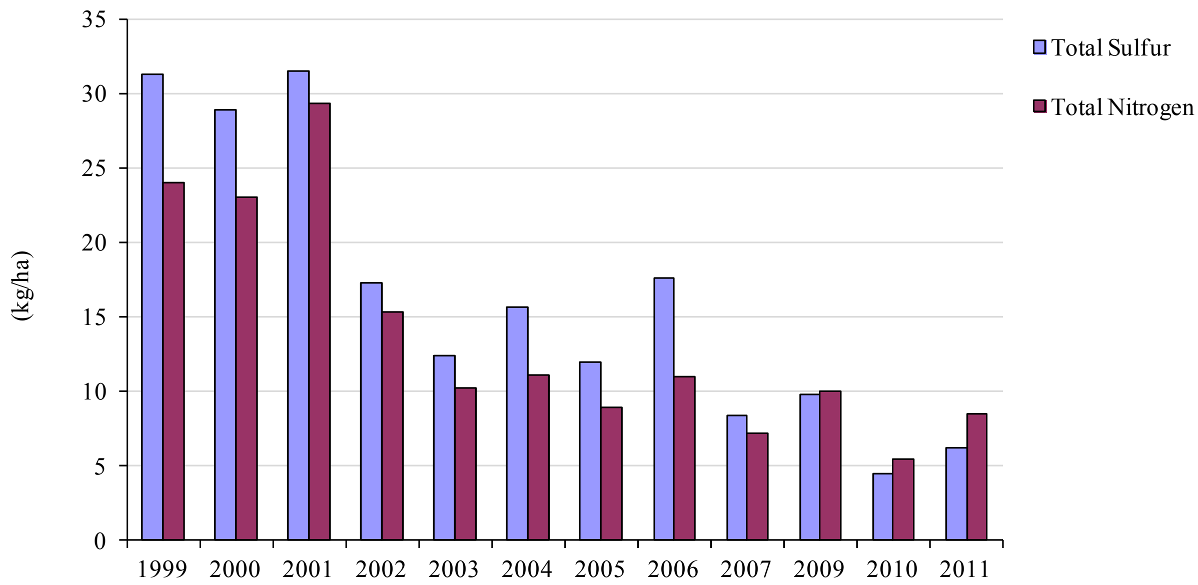


Figure 6-1. Total Sulfur and Nitrogen Deposition Estimates (Dry + Cloud Components) 1999–2007, 2009–2011



Appendix A

Cloud Water Deposition to Clingmans Dome in 2011

Cloud Water Deposition to Clingmans Dome in 2011

Report to AMEC Environment and Infrastructure
by

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AMEC Work Order C012300254
AMEC Project Number 6064110217 (MADPro)
Report Date: March 14, 2012

Introduction

This brief report accompanies the Excel spreadsheet CLD 2011.xls, which gives the results of the cloud water deposition modeling for the Clingmans Dome (CLD303) site for the field season of 2011. Raw chemical concentration, meteorological, and cloud frequency data were provided to me by AMEC Environment & Infrastructure, Inc. (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 (g cm^{-2} 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 2011 data set covered the period June-September 2011. Only cloud events in this 4-month period having valid wind speed, cloud LWC and event duration data were used for this modeling. Events meeting these criteria included 12 events in June, 16 in July, 5 in August, and 9 in September, for a total of 42 events for the season. Sampling completeness was 100% for June and July, 82% for August, and 91% for September.

The calculations done here for 2011 followed closely those done previously for the Clingmans Dome site (e.g., Lovett 2011). As in previous reports, 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. After the model was run for all sample periods, seasonal and monthly means and totals were calculated in a SAS program. Monthly deposition totals were calculated as the product of the duration-weighted mean concentration and the total measured cloud duration for the month. Total seasonal deposition was calculated by summing the five monthly totals.

Results

The model was run on 42 time periods as discussed above, and the results are presented as deposition velocities and deposition fluxes in the CLD 2011.xls spreadsheet and in Appendix I.

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 SO_4^{2-}, NO_3^- and NH_4^+ were highest in August, but H^+ concentrations were highest in July (Fig. 1).

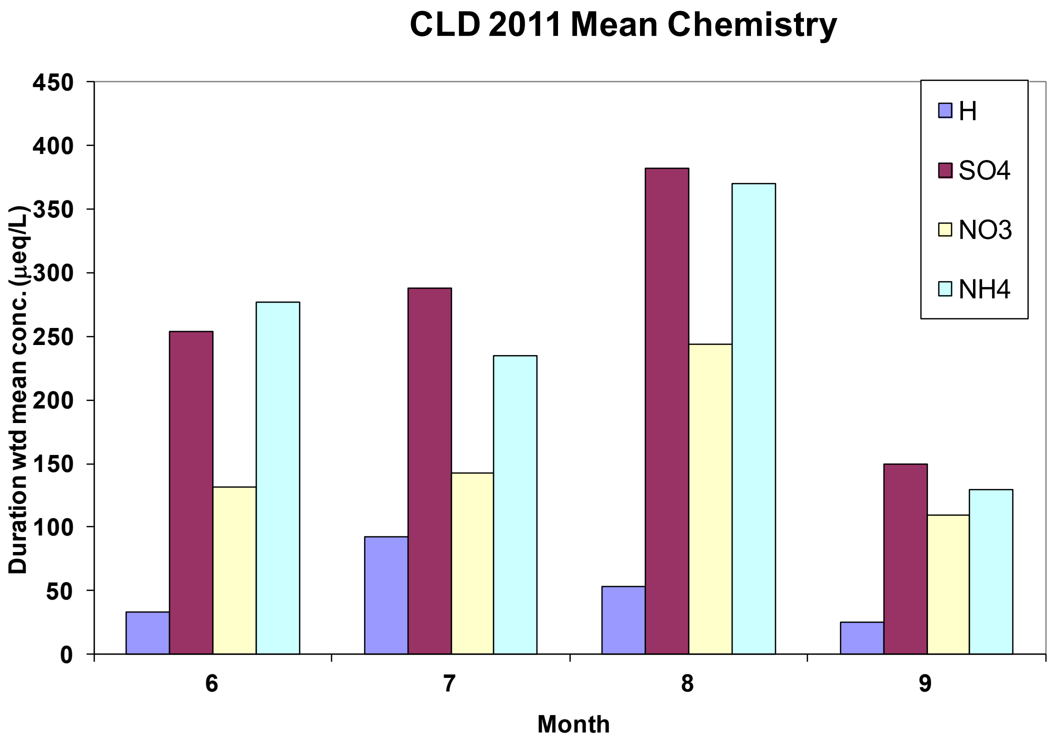

Figure 1. *Duration-weighted mean concentration of four ions in cloud water, calculated by month.*

Trends in seasonal mean concentrations (duration-weighted) of several key ions are shown in Figure 2. Since the late 1990s, the concentrations of hydrogen ion and sulfate have been in general declining. However, there has been an increasing trend in the anions sulfate and nitrate since 2009. This has not been accompanied by an increase in acidity (H^+), probably because neutralizing cations (calcium and ammonium) have also been increasing (Fig. 2). The reason for the increasing calcium and ammonium concentrations is unclear. In a continental location such as this one, ammonium emissions to the atmosphere are largely from agricultural activities, but can also include automobiles. Calcium emissions are usually associated with dust and fly ash.

Some of the variation from year to year in ion concentrations can be explained by dilution, as 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. We can 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), which removes some of the noise in the sulfate trend. There has been a general downward trend in dissolved sulfate since the 1990s (Fig. 3). However, the 2011 values show a slight increase over 2010 (Fig. 3), reflecting the fact that the cloud water sulfate concentration increased while the LWC remained nearly the same (Fig. 2).

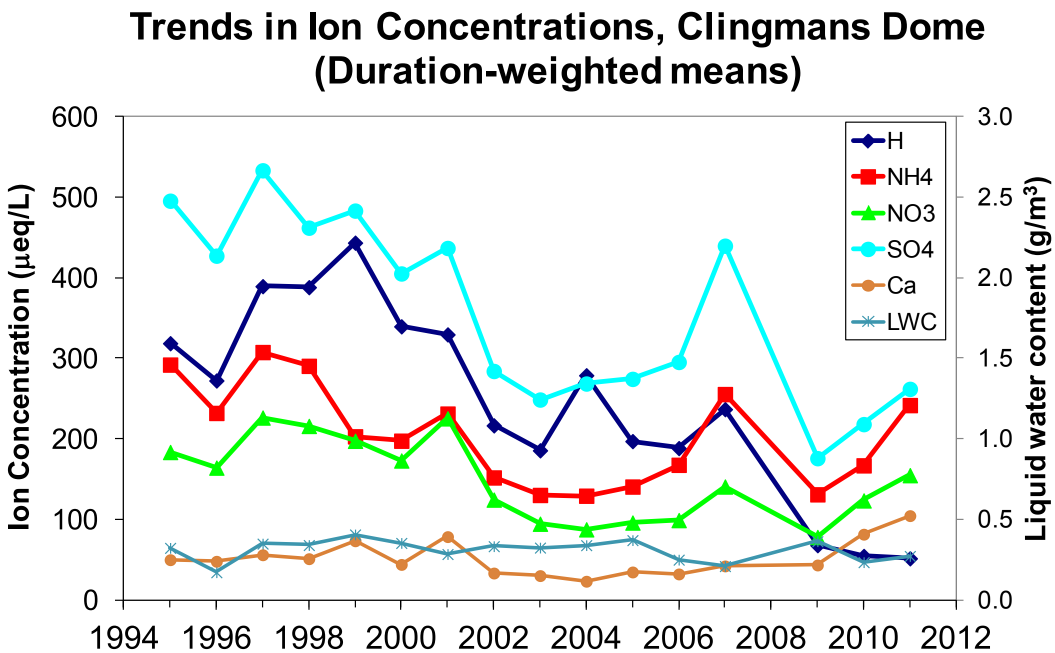

Figure 2. *Trends in ion concentrations and LWC at Clingmans Dome, 1995-2011. Data are duration-weighted means for the warm season and include only the samples for which deposition was modeled (i.e. LWC and meteorological data were also present).*

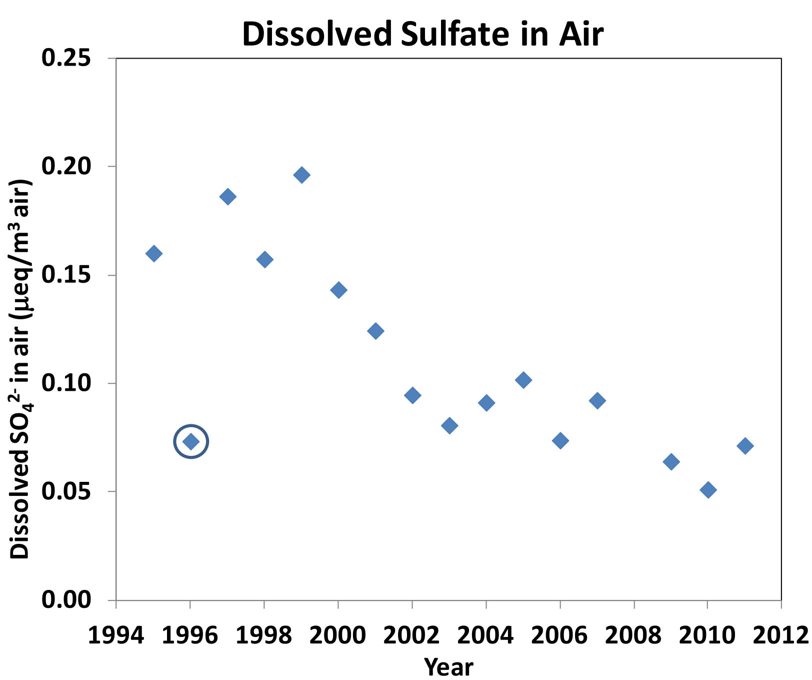

Figure 3. *Mean values of dissolved sulfate per cubic meter of air (= cloud water sulfate concentration x LWC/1000) for Clingmans Dome. Circled year (1996) has anomalously low LWC data, perhaps because of instrument error.*

The trends shown in Figures 2 and 3 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 Fig. 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^+ concentration, less acidic) than field pH values because H^+ is very reactive and is consumed during the sample holding period prior to laboratory analysis. Since 2006 we have used exclusively lab pH values in this analysis 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, with the highest values of both parameters in August (Fig. 4). Mean duration-weighted deposition velocity for the 2011 season was 14.7 cm/s, well below the 1995-2011 mean of 20.3 cm/s (see accompanying Excel workbook). The deposition velocity probably was lower than the long-term mean because the wind speed (3.2 m/s) was also lower than the long-term mean (4.5 m/s), and wind drives cloud water deposition.

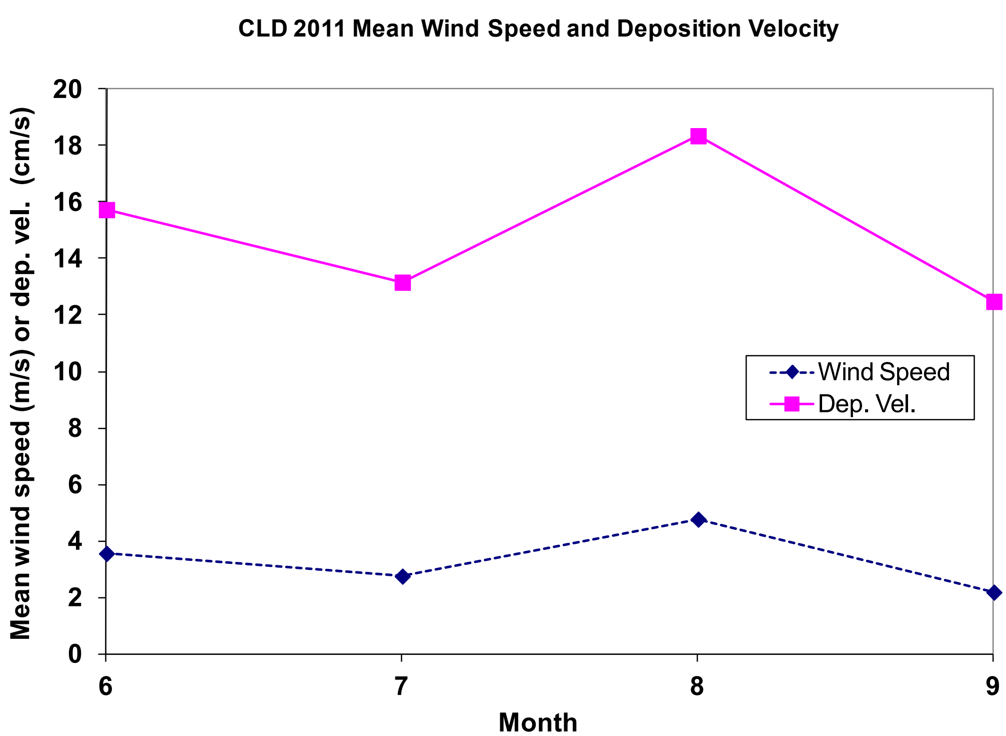

Figure 4. *Mean wind speed and deposition velocity for each month.*

Monthly mean cloud LWC was lowest in August and highest in September (Fig. 5), with a seasonal mean of 0.27 g/m^3, slightly below the long-term mean of 0.31.

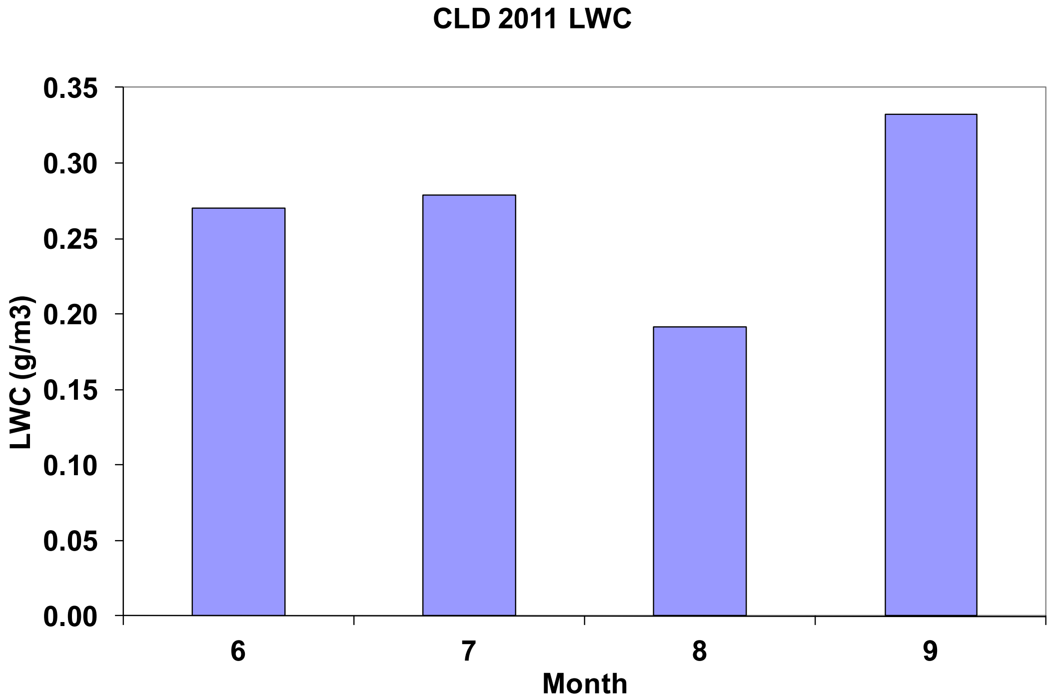

Figure 5. *Mean liquid water content for each month of the study.*

Seasonal deposition totals were calculated by summing across all 4 months. For comparison with the results of previous reports, these means are expressed in Figure 6 as the mean monthly deposition rate, calculated by dividing the seasonal total by 4. The rates for water and ion deposition for 2011 are low compared to early years in the record, but show a slight increase in sulfate, nitrate and ammonium ion deposition compared to 2010 because of the increased concentrations discussed above (Fig. 6).

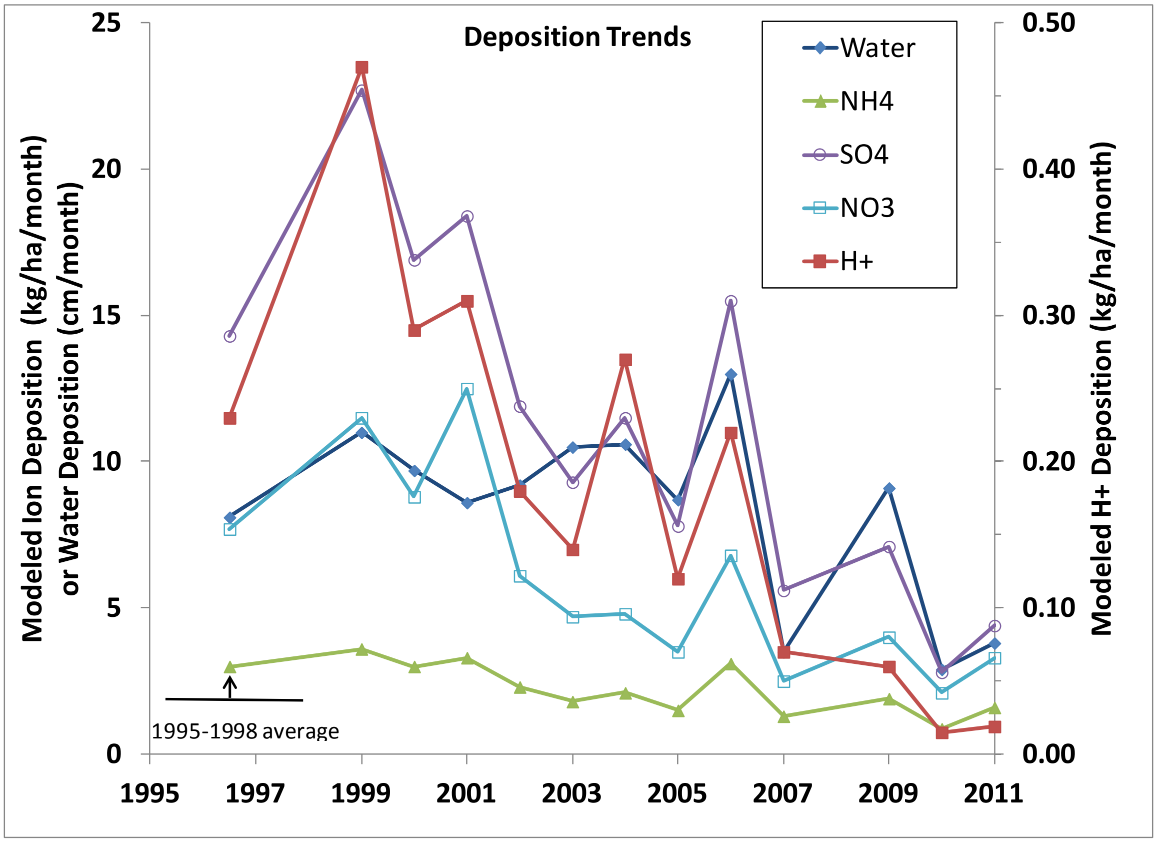

Figure 6. *Mean monthly deposition rates for several ions (in kg/ha/month) and water (cm/month) for the Clingmans Dome site for the 1995-2011 period. The seasonal averages include the months of June-September for 2007, 2009 and 2011; June-October for 2004-2006 and 2010; and May-September for years prior to 2004.*

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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. Monthly mean values of meteorological, chemical and deposition variables for 2011.

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 ($g/cm^2/min$) 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^3.

MONTH	OBS	DURATION	VOLUME	WS	LWC	TURBFLUX	SEDFLUX	TOTFLUX	TURBVD	SED VD	TOT VD
6	12	4.79	457.57	3.56	0.27	1.55E-04	1.03E-04	2.58E-04	9.53	6.20	15.73
7	16	7.31	507.36	2.75	0.28	1.13E-04	1.12E-04	2.25E-04	6.57	6.59	13.16
8	5	17.76	468.19	4.77	0.19	1.58E-04	5.93E-05	2.17E-04	13.37	4.98	18.35
9	9	13.53	1596.14	2.19	0.33	1.01E-04	1.57E-04	2.58E-04	4.90	7.59	12.48

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	33.10	76.31	26.45	9.42	51.23	276.79	253.77	131.08	36.38
7	91.92	64.31	16.28	6.03	20.20	234.65	287.54	142.03	14.69
8	53.72	190.37	36.11	8.20	27.99	369.79	382.03	243.29	16.94
9	25.50	87.99	22.29	3.55	16.24	129.27	149.91	109.58	10.95

Table I-3. Monthly deposition in μeq/m^2/month. Water deposition in cm/month.

Month	HDEP	KDEP	NADEP	CADEP	MGDEP	NH4DEP	SO4DEP	NO3DEP	CLDEP	H2ODEP
6	857.37	255.19	1280.38	2152.91	712.04	7806.72	7021.11	3564.17	927.76	2.68
7	3632.29	218.87	756.43	2329.01	590.41	8284.21	10580.08	5140.52	530.81	3.56
8	1837.51	306.99	1058.16	6779.43	1247.13	14703.08	14094.71	9200.23	639.52	4.06
9	1222.66	113.25	710.89	2449.29	663.29	4572.16	5270.27	3503.75	443.17	4.81

Appendix B

Cloud Water Data and QC Summary

Cloud Water Data and QC Summary

Analytical data for the 43 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, 2011). 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 ± 5 percent of the known value for anions, and within ± 10 percent of the known value for cations. 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 AMEC 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 ± 5 percent for anions and base cations, ± 10 percent for NH_4^+, and ± 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 criterion is ± 20 percent for anions and cations. For pH, the difference between the two values cannot be more than ± 0.05 pH units. The data from all required replicate samples are within the CASTNET QC criteria.

Table B-1. Cloud Water Analytical Data for 2011 Sampling Season (1 of 2)

Sample Date	Valid Hours	Volume mL	LWC g/m^3	Scalar Wind m/sec	pH Field	pH Lab	Cond. Field	Cond. Lab	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^+ mg/L	K^+ mg/L	NH_4^+ mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	Cl^- mg/L	Field Cation µeq/L	Lab Cation µeq/L	Anion µeq/L	Field Cation/ Anion	Lab Cation/ Anion
6/7/2011	5.89	568	0.295	3.12	3.99	4.63	100.7	109.1	101.477	23.452	19.990	10.093	492.583	364.340	182.805	20.844	722.691	694.150	567.990	23.97	19.99
6/8/2011	0.23	36	0.254	2.30	4.51	4.68	81.2	98.6	129.398	46.294	23.584	19.744	349.402	382.662	160.708	64.395	599.325	589.315	607.765	-1.40	-3.08
6/10/2011	NA	36	NA	0.80	NA	NA	NA	NA	I	I	I	I	I	I	I	I	NA	NA	NA	NA	NA
6/12/2011	4.78	246	0.341	2.69	4.32	4.44	74.2	86.9	93.268	27.912	26.979	9.230	350.687	324.159	109.661	17.347	555.939	544.384	451.167	20.81	18.73
6/13/2011	1.28	73	0.182	4.50	4.52	5.08	64.9	NA	156.395	42.972	52.110	20.320	449.496	337.067	227.033	37.514	751.493	729.611	601.615	22.15	19.23
6/14/2011	1.94	36	0.138	4.95	NA	5.09	NA	NA	17.311	5.928	9.508	1.299	15.178	28.335	17.277	6.516	NA	57.353	52.128	NA	9.54
6/15/2011	1.62	127	0.307	5.27	4.05	4.54	146.3	146.3	222.965	59.748	60.200	19.698	619.128	551.507	300.712	48.684	1070.865	1010.580	900.904	17.24	11.48
6/16/2011	0.34	55	0.307	4.70	4.44	4.67	63.2	76.9	130.296	31.334	14.836	6.253	293.286	321.869	128.795	13.201	512.313	497.385	463.864	9.93	6.97
6/19/2011	4.33	664	0.334	4.84	4.48	4.84	53.1	49.6	46.921	17.895	42.757	7.151	199.332	172.614	88.529	26.091	347.169	328.510	287.234	18.90	13.41
6/20/2011	3.32	246	0.205	4.18	4.58	4.57	97.6	100.5	71.012	35.752	109.830	12.617	413.371	373.709	181.698	48.459	668.885	669.497	603.866	10.22	10.31
6/21/2011	5.06	373	0.204	2.90	4.39	4.53	80.1	75.3	73.656	32.564	83.080	9.994	222.178	249.105	149.142	46.710	462.210	450.984	444.957	3.80	1.35
6/22/2011	7.37	846	0.286	2.78	4.40	4.29	55.6	46.8	30.960	19.250	61.679	6.373	39.502	94.333	68.181	60.192	197.574	209.050	222.707	-11.96	-6.33
6/24/2011	0.52	100	0.230	6.30	5.50	5.40	70.5	56.1	89.476	21.612	27.936	8.366	262.087	176.195	137.505	30.858	412.639	413.458	344.558	17.98	18.18
7/1/2011	0.75	127	0.233	5.00	I	5.04	199.9	93.5	144.468	34.876	32.283	30.358	411.515	376.416	178.200	24.681	NA	662.621	579.296	NA	13.42
7/4/2011	6.20	346	0.248	2.83	4.49	4.26	127.7	110.0	127.701	32.446	24.937	14.422	383.386	409.519	202.759	20.562	615.251	637.845	632.840	-2.82	0.79
7/7/2011	2.14	109	0.202	4.10	4.31	4.23	102.8	108.0	88.078	28.107	23.507	14.690	381.815	373.709	208.400	19.632	585.175	595.082	601.740	-2.79	-1.11
7/8/2011	8.58	1027	0.379	3.22	3.89	3.73	126.9	130.7	39.902	9.709	10.809	4.766	195.477	328.947	144.573	10.916	389.488	446.872	484.436	-21.73	-8.07
7/9/2011	4.67	191	0.235	2.42	4.17	4.05	101.9	99.2	72.059	12.058	13.247	1.821	255.019	308.149	166.206	14.724	421.814	443.330	489.078	-14.77	-9.81
7/10/2011	2.50	155	0.283	2.30	4.04	3.92	101.8	95.6	47.807	12.096	13.410	1.859	151.212	262.221	116.658	12.213	317.586	346.611	391.092	-20.74	-12.06
7/12/2011	2.38	200	0.377	3.63	4.44	4.32	97.8	96.1	147.961	25.312	41.287	5.985	322.844	306.671	212.255	20.986	579.697	591.252	539.911	7.11	9.08
7/13/2011	1.59	55	0.164	3.80	4.11	NA	107.9	NA	31.247	8.299	16.017	4.954	281.792	300.217	144.573	13.652	419.934	NA	458.442	-8.77	NA
7/14/2011	8.77	310	0.263	1.91	4.07	3.96	105.6	102.4	31.186	8.193	15.652	4.750	281.149	295.449	141.789	13.313	426.045	450.579	450.551	-5.59	0.01
7/15/2011	0.03	55	1.111	3.40	4.36	4.23	49.3	40.1	30.411	7.899	14.713	4.668	16.813	110.926	50.190	11.283	118.156	133.388	172.399	-37.34	-25.51
7/18/2011	4.30	200	0.234	3.62	4.45	4.39	32.5	24.7	9.142	3.168	5.252	1.342	5.754	36.434	19.776	4.908	60.141	65.397	61.118	-1.61	6.76
7/19/2011	0.63	100	0.429	3.50	3.67	4.08	199.9	155.7	142.223	55.309	114.180	15.253	461.705	679.547	284.149	44.199	1002.466	871.846	1007.895	-0.54	-14.48
7/22/2011	13.52	973	0.269	2.39	4.24	4.17	79.9	69.9	49.404	16.322	24.647	4.457	168.061	222.206	104.592	14.047	320.434	330.499	340.845	-6.17	-3.08
7/25/2011	0.01	36	0.399	3.80	NA	4.13	NA	NA	55.192	17.252	30.242	9.162	89.107	205.467	108.019	21.662	NA	275.085	335.149	NA	-19.69
7/29/2011	2.43	175	0.243	2.07	4.24	4.27	92.6	94.4	165.877	25.962	26.586	6.325	296.571	267.926	233.744	16.190	578.864	575.024	517.860	11.12	10.46
7/30/2011	1.88	150	0.336	2.57	4.06	3.85	117.5	115.3	63.376	25.270	25.695	5.979	227.247	414.932	108.162	20.506	434.665	488.822	543.600	-22.27	-10.61
7/31/2011	4.91	50	0.141	2.95	4.88	4.81	45.9	37.6	25.458	8.721	26.849	2.756	153.997	177.028	30.128	12.890	230.964	233.270	220.046	4.84	5.83
8/4/2011	5.49	428	0.303	3.07	4.12	3.97	132.4	137.5	148.211	28.737	20.604	5.999	440.644	525.483	202.902	12.834	720.052	751.347	741.219	-2.90	1.36

Table B-1. Cloud Water Analytical Data for 2011 Sampling Season (2 of 2)

Sample Date	Valid Hours	Volume mL	LWC g/m^3	Scalar Wind m/sec	pH Field	pH Lab	Cond. Field	Cond. Lab	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+} mg/L	K^{+} mg/L	NH_4^{+} mg/L	SO_4^{2-} mg/L	NO_3^{-} mg/L	Cl^{-} mg/L	Field Cation µeq/L	Lab Cation µeq/L	Anion µeq/L	Field Cation/ Anion	Lab Cation/ Anion
8/20/2011	22.23	227	0.138	4.60	4.13	4.08	144.2	153.3	303.009	58.962	34.107	11.641	443.142	521.944	349.97	21.521	924.993	934.038	893.439	3.47	4.44
8/21/2011	20.20	864	0.228	5.87	4.55	4.83	80.9	72.6	122.212	19.970	23.389	6.659	322.844	236.155	191.55	13.454	523.257	509.864	441.160	17.03	14.45
8/30/2011	1.09	138	0.254	4.70	4.33	4.11	89.5	108.5	111.632	29.636	30.896	2.376	358.969	433.045	189.90	26.937	580.283	611.134	649.890	-11.32	-6.15
9/1/2011	7.32	255	0.208	2.17	4.80	4.61	137.1	181.6	656.220	146.630	24.112	20.826	487.978	646.444	628.69	26.458	1351.615	1360.314	1301.598	3.77	4.41
9/4/2011	4.86	600	0.289	3.05	4.70	4.49	72.8	77.5	75.253	28.707	44.106	4.320	315.204	288.349	136.14	19.547	487.543	499.950	444.045	9.34	11.84
9/5/2011	1.71	184	0.244	5.00	4.16	3.97	83.9	93.3	50.002	18.089	41.274	3.880	207.756	267.030	136.93	28.545	390.184	428.153	432.509	-10.29	-1.01
9/6/2011	0.19	91	0.609	4.50	4.58	4.40	30.7	29.6	36.402	11.529	10.915	2.240	27.322	81.258	42.765	11.339	114.711	128.219	135.362	-16.52	-5.42
9/7/2011	15.85	3357	0.381	1.69	5.41	4.86	13.1	5.7	3.421	1.362	0.882	0.286	5.340	12.617	7.711	0.903	15.182	25.095	21.230	-33.22	16.69
9/8/2011	21.98	1775	0.319	1.75	4.68	4.43	39.3	41.9	28.087	10.441	26.463	1.826	114.752	132.016	65.111	15.626	202.462	218.723	212.754	-4.96	2.77
9/9/2011	7.20	609	0.245	3.19	5.57	5.02	27.6	14.3	3.246	1.433	2.106	1.128	77.327	38.599	38.910	4.005	87.931	94.790	81.514	7.57	15.06
9/15/2011	1.86	882	0.689	4.60	4.90	4.52	17.4	13.9	4.465	1.141	14.855	0.402	3.798	25.462	18.919	6.205	37.250	54.860	50.587	-30.37	8.10
9/16/2011	7.77	818	0.424	1.72	5.24	5.08	9.2	11.5	10.761	2.913	1.870	1.266	32.291	35.018	20.347	1.890	54.857	57.420	57.255	-4.28	0.29
					Volume Weighted Mean				94.942	25.125	30.176	7.799	253.025	278.454	148.47	21.582	469.028	463.798	448.515	-1.62	3.14

Note: NA = not available
I = invalid

Table B-2. Cloud Deposition 2011 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples (1 of 3)

Lab pH				
Batch Number	Lab Key	Target STD Units	Found STD Units	Percent Recovery
L107023	L107023-SRM1	4.28	4.31	100.7
L107023	L107023-SRM2	4.28	4.32	100.9
L108010	L108010-SRM1	7.65	7.64	99.9
L108010	L108010-SRM2	7.65	7.63	99.7
L108056	L108056-SRM1	4.28	4.30	100.5
L108056	L108056-SRM2	4.28	4.31	100.7
L109030	L109030-SRM1	7.65	7.60	99.3
L109030	L109030-SRM2	7.65	7.61	99.5
L110041	L110041-SRM1	9.01	9.00	99.9
L110041	L110041-SRM2	9.01	9.00	99.9
Mean				**100.1**
Standard Deviation				**0.56**
Count				**10**

NH_4^+-N				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L106046	L106046-SRM1	0.760	0.7759	102.1
L106046	L106046-SRM2	0.760	0.7993	105.2
L108008	L108008-SRM1	0.760	0.7773	102.3
L108008	L108008-SRM2	0.760	0.7849	103.3
L108023	L108023-SRM1	0.760	0.7622	100.3
L108023	L108023-SRM2	0.760	0.7525	99.0
L108050	L108050-SRM1	0.760	0.7827	103.0
L108050	L108050-SRM2	0.760	0.7999	105.3
L109037	L109037-SRM1	0.760	0.7756	102.1
L109037	L109037-SRM2	0.760	0.7932	104.4
L110021	L110021-SRM1	0.760	0.7582	99.8
L110021	L110021-SRM2	0.760	0.7590	99.9
Mean				**102.2**
Standard Deviation				**2.13**
Count				**12**

SO_4^{2-}				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L107001	L107001-SRM1	9.0	8.90	98.9
L107001	L107001-SRM2	9.0	8.84	98.3
L108012	L108012-SRM1	9.0	8.98	99.8
L108012	L108012-SRM2	9.0	8.91	99.0
L108054	L108054-SRM1	9.0	8.89	98.8
L108054	L108054-SRM2	9.0	8.96	99.6
L108054	L108054-SRM3	9.0	9.08	100.9
L108054	L108054-SRM4	9.0	9.17	101.9
L109040	L109040-SRM1	9.0	8.94	99.3
L109040	L109040-SRM2	9.0	9.08	100.9
L110023	L110023-SRM1	9.0	9.07	100.7
L110023	L110023-SRM2	9.0	8.89	98.8
Mean				**99.7**
Standard Deviation				**1.11**
Count				**12**

Table B-2. Cloud Deposition 2011 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples (2 of 3)

NO_3^--N					Cl^-					Ca^{2+}				
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**
L107001	L107001-SRM1	1.6	1.62	101.1	L107001	L107001-SRM1	0.93	0.969	104.2	L107003	L107003-SRM1	0.054	0.0526	97.4
L107001	L107001-SRM2	1.6	1.60	100.2	L107001	L107001-SRM2	0.93	0.968	104.1	L107003	L107003-SRM2	0.054	0.0531	98.4
L108012	L108012-SRM1	1.6	1.63	101.6	L108012	L108012-SRM1	0.94	0.985	104.8	L108013	L108013-SRM1	0.054	0.0536	99.3
L108012	L108012-SRM2	1.6	1.59	99.1	L108012	L108012-SRM2	0.94	0.953	101.4	L108013	L108013-SRM2	0.054	0.0537	99.5
L108054	L108054-SRM1	1.6	1.61	100.7	L108054	L108054-SRM1	0.94	0.980	104.3	L108051	L108051-SRM1	0.054	0.0536	99.3
L108054	L108054-SRM2	1.6	1.56	97.3	L108054	L108054-SRM2	0.94	0.939	99.9	L108051	L108051-SRM2	0.054	0.0531	98.3
L108054	L108054-SRM3	1.6	1.63	101.6	L108054	L108054-SRM3	0.94	0.973	103.5	L109041	L109041-SRM1	0.054	0.0530	98.1
L108054	L108054-SRM4	1.6	1.63	101.7	L108054	L108054-SRM4	0.94	0.970	103.2	L109041	L109041-SRM2	0.054	0.0541	100.2
L109040	L109040-SRM1	1.6	1.61	100.8	L109040	L109040-SRM1	0.94	0.978	104.0	L110024	L110024-SRM1	0.054	0.0538	99.6
L109040	L109040-SRM2	1.6	1.66	103.8	L109040	L109040-SRM2	0.94	0.980	104.3	L110024	L110024-SRM2	0.054	0.0538	99.6
L110023	L110023-SRM1	1.6	1.61	100.4	L110023	L110023-SRM1	0.94	0.975	103.7					
L110023	L110023-SRM2	1.6	1.61	100.3	L110023	L110023-SRM2	0.94	0.981	104.4					
Mean				**100.7**	**Mean**				**103.5**	**Mean**				**99.0**
Standard Deviation				**1.57**	**Standard Deviation**				**1.42**	**Standard Deviation**				**0.89**
Count				**12**	**Count**				**12**	**Count**				**10**

Table B-2. Cloud Deposition 2011 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples (3 of 3)

Mg^{2+}					Na^{+}					K^{+}				
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**
L107003	L107003-SRM1	0.052	0.0532	102.4	L107003	L107003-SRM1	0.40	0.399	99.9	L107003	L107003-SRM1	0.100	0.0996	99.6
L107003	L107003-SRM2	0.052	0.0533	102.4	L107003	L107003-SRM2	0.40	0.405	101.2	L107003	L107003-SRM2	0.100	0.1001	100.1
L108013	L108013-SRM1	0.052	0.0539	103.6	L108013	L108013-SRM1	0.40	0.402	100.6	L108013	L108013-SRM1	0.100	0.0994	99.4
L108013	L108013-SRM2	0.052	0.0540	103.8	L108013	L108013-SRM2	0.40	0.395	98.8	L108013	L108013-SRM2	0.100	0.0983	98.3
L108051	L108051-SRM1	0.052	0.0537	103.2	L108051	L108051-SRM1	0.40	0.402	100.5	L108051	L108051-SRM1	0.100	0.0995	99.5
L108051	L108051-SRM2	0.052	0.0537	103.3	L108051	L108051-SRM2	0.40	0.395	98.7	L108051	L108051-SRM2	0.100	0.0982	98.2
L109041	L109041-SRM1	0.052	0.0526	101.1	L109041	L109041-SRM1	0.40	0.394	98.4	L109041	L109041-SRM1	0.100	0.1011	101.1
L109041	L109041-SRM2	0.052	0.0535	102.9	L109041	L109041-SRM2	0.40	0.402	100.4	L109041	L109041-SRM2	0.100	0.1010	101.0
L110024	L110024-SRM1	0.052	0.0543	104.4	L110024	L110024-SRM1	0.40	0.404	100.9	L110024	L110024-SRM1	0.100	0.1027	102.7
L110024	L110024-SRM2	0.052	0.0545	104.8	L110024	L110024-SRM2	0.40	0.402	100.6	L110024	L110024-SRM2	0.100	0.1027	102.7
Mean				**103.2**	**Mean**				**100.0**	**Mean**				**100.3**
Standard Deviation				**1.07**	**Standard Deviation**				**0.99**	**Standard Deviation**				**1.59**
Count				**10**	**Count**				**10**	**Count**				**10**

Table B-3. Cloud Deposition 2011 Sampling Season – QC Batch Summary for Cloud Samples – CCV (1 of 3)

Lab pH					NH_4^+ -N					SO_4^{2-}				
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**
L107023	L107023-CCV1	5.00	5.01	100.2	L106046	L106046-CCV1	1.0	1.0120	101.2	L107001	L107001-CCV1	2.50	2.491	99.6
L107023	L107023-CCV2	5.00	5.00	100.0	L106046	L106046-CCV2	1.0	0.9862	98.6	L107001	L107001-CCV2	2.50	2.459	98.4
L107023	L107023-CCV3	5.00	5.03	100.6	L106046	L106046-CCV3	1.0	1.0311	103.1	L107001	L107001-CCV3	2.50	2.541	101.6
L107023	L107023-CCV4	5.00	5.00	100.0	L106046	L106046-CCV4	1.0	1.0356	103.6	L107001	L107001-CCV4	2.50	2.479	99.2
L107023	L107023-CCV5	5.00	5.03	100.6	L106046	L106046-CCV5	1.0	1.0398	104.0	L108012	L108012-CCV1	2.50	2.477	99.1
L108010	L108010-CCV1	5.00	5.01	100.2	L108008	L108008-CCV1	1.0	1.0080	100.8	L108012	L108012-CCV2	2.50	2.455	98.2
L108010	L108010-CCV2	5.00	5.03	100.6	L108008	L108008-CCV2	1.0	1.0232	102.3	L108012	L108012-CCV3	2.50	2.495	99.8
L108010	L108010-CCV3	5.00	5.03	100.6	L108008	L108008-CCV3	1.0	0.9928	99.3	L108012	L108012-CCV4	2.50	2.481	99.2
L108056	L108056-CCV1	5.00	5.02	100.4	L108008	L108008-CCV4	1.0	0.9952	99.5	L108012	L108012-CCV5	2.50	2.481	99.2
L108056	L108056-CCV2	5.00	5.01	100.2	L108008	L108008-CCV5	1.0	1.0112	101.1	L108054	L108054-CCV1	2.50	2.436	97.4
L108056	L108056-CCV3	5.00	5.03	100.6	L108008	L108008-CCV6	1.0	1.0284	102.8	L108054	L108054-CCV2	2.50	2.407	96.3
L109030	L109030-CCV1	5.00	5.03	100.6	L108023	L108023-CCV1	1.0	0.9911	99.1	L108054	L108054-CCV3	2.50	2.399	96.0
L109030	L109030-CCV2	5.00	4.98	99.6	L108023	L108023-CCV2	1.0	0.9990	99.9	L108054	L108054-CCV4	2.50	2.398	95.9
L109030	L109030-CCV3	5.00	5.04	100.8	L108050	L108050-CCV1	1.0	1.0259	102.6	L108054	L108054-CCV5	2.50	2.495	99.8
L109030	L109030-CCV4	5.00	4.98	99.6	L108050	L108050-CCV2	1.0	1.0290	102.9	L108054	L108054-CCV6	2.50	2.436	97.4
L110041	L110041-CCV1	5.00	5.03	100.6	L108050	L108050-CCV3	1.0	1.0340	103.4	L109040	L109040-CCV1	2.50	2.449	98.0
L110041	L110041-CCV2	5.00	5.02	100.4	L108050	L108050-CCV4	1.0	1.0338	103.4	L109040	L109040-CCV2	2.50	2.449	98.0
					L108050	L108050-CCV5	1.0	1.0313	103.1	L109040	L109040-CCV3	2.50	2.509	100.4
					L109037	L109037-CCV1	1.0	1.0169	101.7	L109040	L109040-CCV4	2.50	2.468	98.7
					L109037	L109037-CCV2	1.0	1.0111	101.1	L109040	L109040-CCV5	2.50	2.487	99.5
					L109037	L109037-CCV3	1.0	1.0016	100.2	L110023	L110023-CCV1	2.50	2.499	100.0
					L109037	L109037-CCV4	1.0	1.0281	102.8	L110023	L110023-CCV2	2.50	2.457	98.3
					L109037	L109037-CCV5	1.0	1.0269	102.7					
					L109037	L109037-CCV6	1.0	1.0377	103.8					
					L110021	L110021-CCV1	1.0	0.9876	98.8					
					L110021	L110021-CCV2	1.0	0.9887	98.9					
Mean				**100.3**	**Mean**				**101.6**	**Mean**				**98.6**
Standard Deviation				**0.36**	**Standard Deviation**				**1.78**	**Standard Deviation**				**1.44**
Count				**17**	**Count**				**26**	**Count**				**22**

Table B-3. Cloud Deposition 2011 Sampling Season – QC Batch Summary for Cloud Samples – CCV (2 of 3)

NO_3^--N				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L107001	L107001-CCV1	0.50	0.498	99.6
L107001	L107001-CCV2	0.50	0.500	100.0
L107001	L107001-CCV3	0.50	0.511	102.2
L107001	L107001-CCV4	0.50	0.503	100.6
L108012	L108012-CCV1	0.50	0.502	100.4
L108012	L108012-CCV2	0.50	0.504	100.8
L108012	L108012-CCV3	0.50	0.503	100.6
L108012	L108012-CCV4	0.50	0.496	99.2
L108012	L108012-CCV5	0.50	0.495	99.0
L108054	L108054-CCV1	0.50	0.496	99.2
L108054	L108054-CCV2	0.50	0.483	96.6
L108054	L108054-CCV3	0.50	0.484	96.8
L108054	L108054-CCV4	0.50	0.484	96.8
L108054	L108054-CCV5	0.50	0.509	101.8
L108054	L108054-CCV6	0.50	0.500	100.0
L109040	L109040-CCV1	0.50	0.501	100.2
L109040	L109040-CCV2	0.50	0.505	101.0
L109040	L109040-CCV3	0.50	0.508	101.6
L109040	L109040-CCV4	0.50	0.510	102.0
L109040	L109040-CCV5	0.50	0.516	103.2
L110023	L110023-CCV1	0.50	0.501	100.2
L110023	L110023-CCV2	0.50	0.501	100.2
Mean				**100.1**
Standard Deviation				**1.72**
Count				**22**

Cl^-				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L107001	L107001-CCV1	0.50	0.490	98.0
L107001	L107001-CCV2	0.50	0.497	99.4
L107001	L107001-CCV3	0.50	0.494	98.8
L107001	L107001-CCV4	0.50	0.509	101.8
L108012	L108012-CCV1	0.50	0.502	100.4
L108012	L108012-CCV2	0.50	0.510	102.0
L108012	L108012-CCV3	0.50	0.505	101.0
L108012	L108012-CCV4	0.50	0.493	98.6
L108012	L108012-CCV5	0.50	0.489	97.8
L108054	L108054-CCV1	0.50	0.495	99.0
L108054	L108054-CCV2	0.50	0.501	100.2
L108054	L108054-CCV3	0.50	0.490	98.0
L108054	L108054-CCV4	0.50	0.478	95.6
L108054	L108054-CCV5	0.50	0.484	96.8
L108054	L108054-CCV6	0.50	0.493	98.6
L109040	L109040-CCV1	0.50	0.506	101.2
L109040	L109040-CCV2	0.50	0.510	102.0
L109040	L109040-CCV3	0.50	0.500	100.0
L109040	L109040-CCV4	0.50	0.510	102.0
L109040	L109040-CCV5	0.50	0.505	101.0
L110023	L110023-CCV1	0.50	0.502	100.4
L110023	L110023-CCV2	0.50	0.501	100.2
Mean				**99.7**
Standard Deviation				**1.77**
Count				**22**

Ca^{2+}				
Batch Number	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L107003	L107003-CCV1	0.50	0.4974	99.5
L107003	L107003-CCV2	0.50	0.5017	100.3
L107003	L107003-CCV3	0.50	0.4963	99.3
L108013	L108013-CCV1	0.50	0.4949	99.0
L108013	L108013-CCV2	0.50	0.4977	99.5
L108013	L108013-CCV3	0.50	0.5071	101.4
L108013	L108013-CCV4	0.50	0.4961	99.2
L108051	L108051-CCV1	0.50	0.5074	101.5
L108051	L108051-CCV2	0.50	0.4987	99.7
L108051	L108051-CCV3	0.50	0.4949	99.0
L108051	L108051-CCV4	0.50	0.4974	99.5
L109041	L109041-CCV1	0.50	0.4939	98.8
L109041	L109041-CCV2	0.50	0.5094	101.9
L109041	L109041-CCV3	0.50	0.5044	100.9
L109041	L109041-CCV4	0.50	0.5021	100.4
L110024	L110024-CCV1	0.50	0.5022	100.4
L110024	L110024-CCV2	0.50	0.5023	100.5
Mean				**100.0**
Standard Deviation				**0.96**
Count				**17**

Table B-3. Cloud Deposition 2011 Sampling Season – QC Batch Summary for Cloud Samples – CCV (3 of 3)

Mg^{2+}					Na^{+}					K^{+}				
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**
L107003	L107003-CCV1	0.50	0.5007	100.1	L107003	L107003-CCV1	0.50	0.4979	99.6	L107003	L107003-CCV1	0.50	0.4970	99.4
L107003	L107003-CCV2	0.50	0.5017	100.3	L107003	L107003-CCV2	0.50	0.5006	100.1	L107003	L107003-CCV2	0.50	0.5011	100.2
L107003	L107003-CCV3	0.50	0.4953	99.1	L107003	L107003-CCV3	0.50	0.4957	99.1	L107003	L107003-CCV3	0.50	0.4936	98.7
L108013	L108013-CCV1	0.50	0.4956	99.1	L108013	L108013-CCV1	0.50	0.4941	98.8	L108013	L108013-CCV1	0.50	0.4960	99.2
L108013	L108013-CCV2	0.50	0.4989	99.8	L108013	L108013-CCV2	0.50	0.4967	99.3	L108013	L108013-CCV2	0.50	0.4992	99.8
L108013	L108013-CCV3	0.50	0.5050	101.0	L108013	L108013-CCV3	0.50	0.5067	101.3	L108013	L108013-CCV3	0.50	0.5071	101.4
L108013	L108013-CCV4	0.50	0.5003	100.1	L108013	L108013-CCV4	0.50	0.4965	99.3	L108013	L108013-CCV4	0.50	0.4955	99.1
L108051	L108051-CCV1	0.50	0.5015	100.3	L108051	L108051-CCV1	0.50	0.5065	101.3	L108051	L108051-CCV1	0.50	0.5082	101.6
L108051	L108051-CCV2	0.50	0.4967	99.3	L108051	L108051-CCV2	0.50	0.4978	99.6	L108051	L108051-CCV2	0.50	0.4993	99.9
L108051	L108051-CCV3	0.50	0.4951	99.0	L108051	L108051-CCV3	0.50	0.4942	98.8	L108051	L108051-CCV3	0.50	0.4956	99.1
L108051	L108051-CCV4	0.50	0.4979	99.6	L108051	L108051-CCV4	0.50	0.4974	99.5	L108051	L108051-CCV4	0.50	0.4959	99.2
L109041	L109041-CCV1	0.50	0.4885	97.7	L109041	L109041-CCV1	0.50	0.4938	98.8	L109041	L109041-CCV1	0.50	0.4961	99.2
L109041	L109041-CCV2	0.50	0.5091	101.8	L109041	L109041-CCV2	0.50	0.5092	101.8	L109041	L109041-CCV2	0.50	0.5061	101.2
L109041	L109041-CCV3	0.50	0.4995	99.9	L109041	L109041-CCV3	0.50	0.5043	100.9	L109041	L109041-CCV3	0.50	0.5040	100.8
L109041	L109041-CCV4	0.50	0.4999	100.0	L109041	L109041-CCV4	0.50	0.5012	100.2	L109041	L109041-CCV4	0.50	0.5012	100.2
L110024	L110024-CCV1	0.50	0.5034	100.7	L110024	L110024-CCV1	0.50	0.5026	100.5	L110024	L110024-CCV1	0.50	0.5009	100.2
L110024	L110024-CCV2	0.50	0.4987	99.7	L110024	L110024-CCV2	0.50	0.5001	100.0	L110024	L110024-CCV2	0.50	0.5014	100.3
Mean				**99.9**	**Mean**				**99.9**	**Mean**				**100.0**
Standard Deviation				**0.91**	**Standard Deviation**				**0.95**	**Standard Deviation**				**0.89**
Count				**17**	**Count**				**17**	**Count**				**17**

Table B-4. Cloud Deposition 2011 Sampling Season – Replicate Summary for Cloud Samples (1 of 3)

			SO_4^{2-}			
Sample No.	**Replicate No.**	**Station ID**	**Analysis Date**	**Sample Result**	**Replicate Result**	**Absolute RPD**
1124008-01	L107001-DUP1	CLD303	6/30/2011	16.190	16.130	0.37%
1125020-01	L108012-DUP1	CLD303	8/4/2011	4.531	4.574	0.95%
1134010-01	L108054-DUP1	CLD303	8/30/2011	25.070	25.090	0.08%
1136015-01	L109040-DUP3	CLD303	9/29/2011	12.830	12.980	1.17%
1136019-01	L109040-DUP4	CLD303	9/29/2011	1.854	1.854	0.00%
1137018-01	L110023-DUP1	CLD303	10/14/2011	1.682	1.711	1.72%
					Mean Percent Difference	0.72%
					Standard Deviation	0.007

			NO_3^- - N			
Sample No.	**Replicate No.**	**Station ID**	**Analysis Date**	**Sample Result**	**Replicate Result**	**Absolute RPD**
1124008-01	L107001-DUP1	CLD303	6/30/2011	3.180	3.191	0.35%
1125020-01	L108012-DUP1	CLD303	8/4/2011	0.955	0.959	0.42%
1134010-01	L108054-DUP1	CLD303	8/30/2011	4.902	4.921	0.39%
1136015-01	L109040-DUP3	CLD303	9/29/2011	1.918	1.914	0.21%
1136019-01	L109040-DUP4	CLD303	9/29/2011	0.545	0.548	0.55%
1137018-01	L110023-DUP1	CLD303	10/14/2011	0.285	0.289	1.40%
					Mean Percent Difference	0.55%
					Standard Deviation	0.004

			Cl^-			
Sample No.	**Replicate No.**	**Station ID**	**Analysis Date**	**Sample Result**	**Replicate Result**	**Absolute RPD**
1124008-01	L107001-DUP1	CLD303	6/30/2011	1.330	1.356	1.95%
1125020-01	L108012-DUP1	CLD303	8/4/2011	2.134	2.126	0.37%
1134010-01	L108054-DUP1	CLD303	8/30/2011	0.763	0.765	0.26%
1136015-01	L109040-DUP3	CLD303	9/29/2011	1.012	1.006	0.59%
1136019-01	L109040-DUP4	CLD303	9/29/2011	0.142	0.140	1.41%
1137018-01	L110023-DUP1	CLD303	10/14/2011	0.067	0.067	0.00%
					Mean Percent Difference	0.77%
					Standard Deviation	0.008

Table B-4. Cloud Deposition 2011 Sampling Season – Replicate Summary for Cloud Samples (2 of 3)

NH_4^+-N						
Sample No.	**Replicate No.**	**Station ID**	**Analysis Date**	**Sample Result**	**Replicate Result**	**Absolute RPD**
1123015-01	L106046-DUP1	CLD303	6/30/2011	4.8940	4.8960	0.04%
1125020-01	L108008-DUP1	CLD303	8/4/2011	0.5533	0.5490	0.78%
1127010-01	L108023-DUP1	CLD303	8/15/2011	5.3700	5.3420	0.52%
1129011-01	L108050-DUP1	CLD303	8/30/2011	2.3540	2.3520	0.08%
1135012-01	L109037-DUP3	CLD303	9/29/2011	4.4150	4.4380	0.52%
1136017-01	L109037-DUP4	CLD303	9/29/2011	0.0748	0.0733	2.01%
1137018-01	L110021-DUP1	CLD303	10/14/2011	0.4523	0.4509	0.31%
					Mean Percent Difference	0.61%
					Standard Deviation	0.007

Ca^{2+}						
Sample No.	**Replicate No.**	**Station ID**	**Analysis Date**	**Sample Result**	**Replicate Result**	**Absolute RPD**
1125015-01	L107003-DUP1	CLD303	7/1/2011	0.9402	0.9271	1.39%
1125020-01	L108013-DUP1	CLD303	8/5/2011	0.6204	0.6177	0.44%
1130010-01	L108051-DUP1	CLD303	8/30/2011	0.1832	0.1838	0.33%
1136015-01	L109041-DUP3	CLD303	9/30/2011	1.0020	0.9990	0.30%
1136019-01	L109041-DUP4	CLD303	9/30/2011	0.0651	0.0659	1.29%
1137018-01	L110024-DUP1	CLD303	10/17/2011	0.2156	0.2149	0.32%
					Mean Percent Difference	0.68%
					Standard Deviation	0.005

Mg^{2+}						
Sample No.	**Replicate No.**	**Station ID**	**Analysis Date**	**Sample Result**	**Replicate Result**	**Absolute RPD**
1125015-01	L107003-DUP1	CLD303	7/1/2011	0.2175	0.2176	0.05%
1125020-01	L108013-DUP1	CLD303	8/5/2011	0.2339	0.2331	0.34%
1130010-01	L108051-DUP1	CLD303	8/30/2011	0.0385	0.0387	0.62%
1136015-01	L109041-DUP3	CLD303	9/30/2011	0.2198	0.2201	0.14%
1136019-01	L109041-DUP4	CLD303	9/30/2011	0.0174	0.0174	0.00%
1137018-01	L110024-DUP1	CLD303	10/17/2011	0.0354	0.0350	1.13%
					Mean Percent Difference	0.38%
					Standard Deviation	0.004

Table B-4. Cloud Deposition 2011 Sampling Season – Replicate Summary for Cloud Samples (3 of 3)

Na^+

Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Absolute RPD
1125015-01	L107003-DUP1	CLD303	7/1/2011	0.9830	0.9770	0.61%
1125020-01	L108013-DUP1	CLD303	8/5/2011	1.4180	1.4010	1.20%
1130010-01	L108051-DUP1	CLD303	8/30/2011	0.1207	0.1221	1.16%
1136015-01	L109041-DUP3	CLD303	9/30/2011	0.9489	0.9534	0.47%
1136019-01	L109041-DUP4	CLD303	9/30/2011	0.0484	0.0489	1.03%
1137018-01	L110024-DUP1	CLD303	10/17/2011	0.0430	0.0430	0.07%
					Mean Percent Difference	0.76%
					Standard Deviation	0.004

K^+

Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Absolute RPD
1125015-01	L107003-DUP1	CLD303	7/1/2011	0.2796	0.2784	0.43%
1125020-01	L108013-DUP1	CLD303	8/5/2011	0.2492	0.2480	0.48%
1130010-01	L108051-DUP1	CLD303	8/30/2011	0.0525	0.0542	3.18%
1136015-01	L109041-DUP3	CLD303	9/30/2011	0.1517	0.1521	0.26%
1136019-01	L109041-DUP4	CLD303	9/30/2011	0.0441	0.0445	0.91%
1137018-01	L110024-DUP1	CLD303	10/17/2011	0.0495	0.0490	1.01%
					Mean Percent Difference	1.05%
					Standard Deviation	0.011

pH

Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Absolute RPD
1124007-01	L107023-DUP2	CLD303	7/14/2011	4.44	4.44	0.00%
1128014-01	L108010-DUP1	CLD303	8/5/2011	3.96	3.96	0.00%
1134012-01	L108056-DUP1	CLD303	8/31/2011	4.83	4.87	0.83%
1136019-01	L109030-DUP2	CLD303	9/23/2011	5.02	5.04	0.40%
1137018-01	L110041-DUP1	CLD303	10/27/2011	5.08	5.06	0.39%
					Mean Percent Difference	0.32%
					Standard Deviation	0.003

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 minor hits for calcium and sodium. 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, 2011). 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 ± 5 percent of the known value for anions and within ± 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 AMEC 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 ± 5 percent for anions and base cations, and ± 10 percent for 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 ± 20 percent for all analytes.

Table C-1. Dry Deposition Filter Concentrations for 2011 Sampling Season – GRS420, TN

			Teflon		Nylon		Cellulose	Teflon					
Sample No.	Station ID	Filter Date	SO_4^{2-} T.µg	NO_3^--N T.µg	SO_4^{2-} T.µg	NO_3^--N T.µg	SO_4^{2-} T.µg	NH_4^+-N T.µg	Ca^{2+} T.µg	Mg^{2+} T.µg	Na^+ T.µg	K^+ T.µg	Cl^- T.µg
1122001-35	GRS420	31-May-11	183.40	0.67	17.92	18.51	63.26	42.37	15.58	2.82	5.74	4.02	0.50U
1123001-35	GRS420	07-Jun-11	142.60	0.76	9.67	11.46	31.20	39.99	6.57	1.23	2.25	3.20	0.50U
1124001-35	GRS420	14-Jun-11	86.47	0.40	21.95	9.38	38.62	18.49	4.78	1.15	3.55	2.42	0.50U
1125001-35	GRS420	21-Jun-11	64.05	0.37	13.16	6.90	14.20	12.57	3.59	0.93	3.66	2.48	0.50U
1126001-35	GRS420	28-Jun-11	105.30	0.97	21.80	11.76	71.42	25.26	9.35	1.50	0.89	3.30	0.50U
1127001-35	GRS420	05-Jul-11	116.50	0.44	10.64	8.69	13.86	27.82	4.18	0.86	1.86	3.26	0.50U
1128001-35	GRS420	12-Jul-11	112.30	1.61	25.25	10.32	35.02	22.29	3.96	2.07	12.68	2.56	0.50U
1129001-35	GRS420	19-Jul-11	195.10	0.20U	19.56	10.82	20.18	40.77	7.05	1.46	3.64	1.88	0.50U
1130001-35	GRS420	26-Jul-11	152.10	0.21	19.62	8.46	26.41	36.97	4.16	0.78	1.35	1.46	0.50U
1131001-35	GRS420	02-Aug-11	111.50	0.93	14.86	8.19	42.18	27.70	6.12	0.90	1.36	1.66	0.50U
1132001-35	GRS420	09-Aug-11	111.20	0.39	25.08	10.39	46.86	25.17	7.35	1.07	0.89	1.92	0.50U
1133001-35	GRS420	16-Aug-11	119.70	0.52	12.91	8.20	27.99	32.70	4.09	0.69	0.91	1.50	0.50U
1134001-35	GRS420	23-Aug-11	99.30	1.37	14.58	8.55	55.88	27.68	7.13	1.23	1.73	1.56	0.50U
1135001-35	GRS420	30-Aug-11	102.10	1.19	6.83	6.99	15.10	28.00	4.47	0.84	2.54	1.50	0.50U
1136001-35	GRS420	06-Sep-11	58.33	1.95	14.38	6.14	28.62	16.68	5.89	0.74	0.38	1.44	0.50U
1137001-35	GRS420	13-Sep-11	57.51	0.52	9.24	6.67	15.52	14.18	3.78	0.63	0.75	2.11	0.50U
1138001-35	GRS420	20-Sep-11	57.26	0.38	3.94	5.31	6.20	14.51	1.54	0.34	1.07	1.19	0.50U
1139001-35	GRS420	27-Sep-11	39.98	3.11	10.82	4.36	42.40	12.13	9.02	1.25	0.68	1.41	0.50U

Note: U = value is less than detection limit
I = invalid
T.µg = total micrograms

Table C-2. Dry Deposition 2011 Sampling Season – Laboratory Filter Pack Blanks – GRS420, TN (1 of 2)

		Teflon		Nylon		Cellulose	Teflon					
Lab Key	Analysis Date	SO_4^{2-} T.µg	NO_3^--N T.µg	SO_4^{2-} T.µg	NO_3^--N T.µg	SO_4^{2-} T.µg	NH_4^+-N T.µg	Ca^{2+} T.µg	Mg^{2+} T.µg	Na^+ T.µg	K^+ T.µg	Cl^- T.µg
1123002-01	22-Jun-11	<1.000	<0.200			<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1123002-02	22-Jun-11	<1.000	<0.200			<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1124002-01	29-Jun-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1124002-02	29-Jun-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1125002-01	07-Jul-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1125002-02	07-Jul-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1126002-01	13-Jul-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1126002-02	13-Jul-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1127002-02	20-Jul-11			<1.000	<0.200							
1127002-02	20-Jul-11			<1.000	<0.200							
1128002-01	27-Jul-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1128002-02	27-Jul-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1129002-01	03-Aug-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1129002-02	03-Aug-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1130002-01	10-Aug-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1130002-02	10-Aug-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500

Table C-2. Dry Deposition 2011 Sampling Season – Laboratory Filter Pack Blanks – GRS420, TN (2 of 2)

		Teflon		Nylon		Cellulose	Teflon					
Lab Key	Analysis Date	SO_4^{2-} T.µg	NO_3^--N T.µg	SO_4^{2-} T.µg	NO_3^--N T.µg	SO_4^{2-} T.µg	NH_4^+-N T.µg	Ca^{2+} T.µg	Mg^{2+} T.µg	Na^+ T.µg	K^+ T.µg	Cl^- T.µg
1131002-01	17-Aug-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1131002-02	17-Aug-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1132002-01	24-Aug-11			<1.000	<0.200	<2.000						
1132002-02	25-Aug-11			<1.000	<0.200	<2.000						
1133002-01	31-Aug-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1133002-02	31-Aug-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1134002-01	07-Sep-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1134002-02	07-Sep-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1135002-01	15-Sep-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1135002-02	15-Sep-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1136002-01	21-Sep-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1136002-02	21-Sep-11	<1.000	<0.200	<1.000	<0.200		<0.500	0.3828	<0.075	0.1399	<0.15	<0.500
1137002-01	28-Sep-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1137002-02	28-Sep-11	<1.000	<0.200	<1.000	<0.200		<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1138002-01	06-Oct-11			<1.000	<0.200	<2.000						
1138002-02	06-Oct-11			<1.000	<0.200	<2.000						
1139002-01	12-Oct-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500
1139002-02	12-Oct-11	<1.000	<0.200	<1.000	<0.200	<2.000	<0.500	<0.15	<0.075	<0.125	<0.15	<0.500

Note: T.µg = total micrograms

Table C-3. Dry Deposition 2011 Sampling Season – QC Batch Summary for Teflon Filters – Reference Samples – GRS420, TN (1 of 3)

SO_4^{2-}					NO_3^- - N					NH_4^+ - N				
Batch	**QC Key**	**Target mg/L**	**Found mg/L**	**Percent Recovery**	**Batch**	**QC Key**	**Target mg/L**	**Found mg/L**	**Percent Recovery**	**Batch**	**QC Key**	**Target mg/L**	**Found mg/L**	**Percent Recovery**
L106036	L106036-SRM1	9	8.919	99.10	L106036	L106036-SRM1	1.6	1.601	100.06	L106033	L106033-SRM1	0.75999	0.7755	102.04
L106036	L106036-SRM2	9	8.984	99.82	L106036	L106036-SRM2	1.6	1.614	100.88	L106033	L106033-SRM2	0.75999	0.7979	104.99
L106045	L106045-SRM1	9	8.912	99.02	L106045	L106045-SRM1	1.6	1.605	100.31	L106043	L106043-SRM1	0.75999	0.7746	101.92
L106045	L106045-SRM2	9	8.952	99.47	L106045	L106045-SRM2	1.6	1.618	101.13	L106043	L106043-SRM2	0.75999	0.7942	104.50
L107007	L107007-SRM1	9	8.948	99.42	L107007	L107007-SRM1	1.6	1.599	99.94	L107005	L107005-SRM1	0.75999	0.7715	101.51
L107007	L107007-SRM2	9	9.013	100.14	L107007	L107007-SRM2	1.6	1.616	101.00	L107005	L107005-SRM2	0.75999	0.7870	103.55
L107016	L107016-SRM1	9	8.908	98.98	L107016	L107016-SRM1	1.6	1.594	99.63	L107013	L107013-SRM1	0.75999	0.7783	102.41
L107016	L107016-SRM2	9	9.002	100.02	L107016	L107016-SRM2	1.6	1.604	100.25	L107013	L107013-SRM2	0.75999	0.7856	103.37
L107033	L107033-SRM1	9	8.921	99.12	L107033	L107033-SRM1	1.6	1.599	99.94	L107031	L107031-SRM1	0.75999	0.7731	101.73
L107033	L107033-SRM2	9	9.079	100.88	L107033	L107033-SRM2	1.6	1.621	101.31	L107031	L107031-SRM2	0.75999	0.7893	103.86
L108003	L108003-SRM1	9	8.904	98.93	L108003	L108003-SRM1	1.6	1.594	99.63	L108001	L108001-SRM1	0.75999	0.7829	103.01
L108003	L108003-SRM2	9	8.953	99.48	L108003	L108003-SRM2	1.6	1.599	99.94	L108001	L108001-SRM2	0.75999	0.7959	104.73
L108006	L108006-SRM1	9	8.954	99.49	L108006	L108006-SRM1	1.6	1.603	100.19	L108004	L108004-SRM1	0.75999	0.7710	101.45
L108006	L108006-SRM2	9	8.977	99.74	L108006	L108006-SRM2	1.6	1.611	100.69	L108004	L108004-SRM2	0.75999	0.7593	99.91
L108018	L108018-SRM1	9	8.918	99.09	L108018	L108018-SRM1	1.6	1.599	99.94	L108015	L108015-SRM1	0.75999	0.7802	102.66
L108018	L108018-SRM2	9	8.981	99.79	L108018	L108018-SRM2	1.6	1.610	100.63	L108015	L108015-SRM2	0.75999	0.7874	103.61
L108030	L108030-SRM1	9	8.900	98.89	L108030	L108030-SRM1	1.6	1.605	100.31	L108027	L108027-SRM1	0.75999	0.7995	105.20
L108030	L108030-SRM2	9	8.915	99.06	L108030	L108030-SRM2	1.6	1.610	100.63	L108027	L108027-SRM2	0.75999	0.8279	108.94
L108052	L108052-SRM1	9	8.912	99.02	L108052	L108052-SRM1	1.6	1.599	99.94	L108048	L108048-SRM1	0.75999	0.7858	103.40
L108052	L108052-SRM2	9	8.998	99.98	L108052	L108052-SRM2	1.6	1.618	101.13	L108048	L108048-SRM2	0.75999	0.7980	105.00
L109001	L109001-SRM1	9	8.949	99.43	L109001	L109001-SRM1	1.6	1.609	100.56	L108053	L108053-SRM1	0.75999	0.7683	101.09
L109001	L109001-SRM2	9	8.992	99.91	L109001	L109001-SRM2	1.6	1.616	101.00	L108053	L108053-SRM2	0.75999	0.8080	106.32
L109009	L109009-SRM1	9	8.936	99.29	L109009	L109009-SRM1	1.6	1.605	100.31	L109005	L109005-SRM1	0.75999	0.7855	103.36
L109009	L109009-SRM2	9	8.961	99.57	L109009	L109009-SRM2	1.6	1.606	100.38	L109005	L109005-SRM2	0.75999	0.8117	106.80
L109017	L109017-SRM1	9	8.972	99.69	L109017	L109017-SRM1	1.6	1.606	100.38	L109013	L109013-SRM1	0.75999	0.7736	101.79
L109017	L109017-SRM2	9	9.209	102.32	L109017	L109017-SRM2	1.6	1.651	103.19	L109013	L109013-SRM2	0.75999	0.8150	107.24
L109025	L109025-SRM1	9	8.959	99.54	L109025	L109025-SRM1	1.6	1.599	99.94	L109023	L109023-SRM1	0.75999	0.7848	103.26
L109025	L109025-SRM2	9	9.066	100.73	L109025	L109025-SRM2	1.6	1.616	101.00	L109023	L109023-SRM2	0.75999	0.8122	106.87
L109038	L109038-SRM1	9	8.918	99.09	L109038	L109038-SRM1	1.6	1.602	100.13	L109032	L109032-SRM1	0.75999	0.7805	102.70
L109038	L109038-SRM2	9	8.988	99.87	L109038	L109038-SRM2	1.6	1.612	100.75	L109032	L109032-SRM2	0.75999	0.8186	107.71
L110016	L110016-SRM1	9	8.930	99.22	L110016	L110016-SRM1	1.6	1.603	100.19	L110014	L110014-SRM1	0.75999	0.7769	102.23
L110016	L110016-SRM2	9	8.988	99.87	L110016	L110016-SRM2	1.6	1.620	101.25	L110014	L110014-SRM2	0.75999	0.7946	104.55
L110022	L110022-SRM1	9	8.996	99.96	L110022	L110022-SRM1	1.6	1.616	101.00	L110018	L110018-SRM1	0.75999	0.7763	102.15
L110022	L110022-SRM2	9	9.193	102.14	L110022	L110022-SRM2	1.6	1.643	102.69	L110018	L110018-SRM2	0.75999	0.8027	105.62
Mean				99.71	**Mean**				100.59	**Mean**				103.81
Standard Deviation				0.80	**Standard Deviation**				0.76	**Standard Deviation**				2.12
Count				34	**Count**				34	**Count**				34

Table C-3. Dry Deposition 2011 Sampling Season – QC Batch Summary for Teflon Filters – Reference Samples – GRS420, TN (2 of 3)

Ca^{2+}					Mg^{2+}					Na^{+}				
Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery	Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery	Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery
L106034	L106034-SRM1	0.054	0.05321	98.54	L106034	L106034-SRM1	0.052	0.05350	102.88	L106034	L106034-SRM1	0.4	0.4054	101.35
L106034	L106034-SRM2	0.054	0.05346	99.00	L106034	L106034-SRM2	0.052	0.05362	103.12	L106034	L106034-SRM2	0.4	0.4050	101.25
L106044	L106044-SRM1	0.054	0.05379	99.61	L106044	L106044-SRM1	0.052	0.05416	104.15	L106044	L106044-SRM1	0.4	0.3975	99.38
L106044	L106044-SRM2	0.054	0.05430	100.56	L106044	L106044-SRM2	0.052	0.05485	105.48	L106044	L106044-SRM2	0.4	0.4124	103.10
L107006	L107006-SRM1	0.054	0.05241	97.06	L107006	L107006-SRM1	0.052	0.05359	103.06	L107006	L107006-SRM1	0.4	0.4028	100.70
L107006	L107006-SRM2	0.054	0.05284	97.85	L107006	L107006-SRM2	0.052	0.05397	103.79	L107006	L107006-SRM2	0.4	0.4051	101.28
L107014	L107014-SRM1	0.054	0.05300	98.15	L107014	L107014-SRM1	0.052	0.05281	101.56	L107014	L107014-SRM1	0.4	0.4079	101.98
L107014	L107014-SRM2	0.054	0.05327	98.65	L107014	L107014-SRM2	0.052	0.05358	103.04	L107014	L107014-SRM2	0.4	0.4050	101.25
L107035	L107035-SRM1	0.054	0.05420	100.37	L107035	L107035-SRM1	0.052	0.05301	101.94	L107035	L107035-SRM1	0.4	0.3995	99.88
L107035	L107035-SRM2	0.054	0.05412	100.22	L107035	L107035-SRM2	0.052	0.05309	102.10	L107035	L107035-SRM2	0.4	0.4000	100.00
L107035	L107035-SRM3	0.054	0.05469	101.28	L107035	L107035-SRM3	0.052	0.05381	103.48	L107035	L107035-SRM3	0.4	0.3986	99.65
L108002	L108002-SRM1	0.054	0.05421	100.39	L108002	L108002-SRM1	0.052	0.05408	104.00	L108002	L108002-SRM1	0.4	0.4050	101.25
L108002	L108002-SRM2	0.054	0.05477	101.43	L108002	L108002-SRM2	0.052	0.05399	103.83	L108002	L108002-SRM2	0.4	0.4000	100.00
L108005	L108005-SRM1	0.054	0.05299	98.13	L108005	L108005-SRM1	0.052	0.05325	102.40	L108005	L108005-SRM1	0.4	0.3924	98.10
L108005	L108005-SRM2	0.054	0.05353	99.13	L108005	L108005-SRM2	0.052	0.05385	103.56	L108005	L108005-SRM2	0.4	0.3999	99.98
L108017	L108017-SRM1	0.054	0.05308	98.30	L108017	L108017-SRM1	0.052	0.05349	102.87	L108017	L108017-SRM1	0.4	0.3982	99.55
L108017	L108017-SRM2	0.054	0.05331	98.72	L108017	L108017-SRM2	0.052	0.05391	103.67	L108017	L108017-SRM2	0.4	0.3986	99.65
L108028	L108028-SRM1	0.054	0.05345	98.98	L108028	L108028-SRM1	0.052	0.05362	103.12	L108028	L108028-SRM1	0.4	0.4042	101.05
L108028	L108028-SRM2	0.054	0.05392	99.85	L108028	L108028-SRM2	0.052	0.05379	103.44	L108028	L108028-SRM2	0.4	0.4020	100.50
L108049	L108049-SRM1	0.054	0.05340	98.89	L108049	L108049-SRM1	0.052	0.05255	101.06	L108049	L108049-SRM1	0.4	0.3961	99.03
L108049	L108049-SRM2	0.054	0.05369	99.43	L108049	L108049-SRM2	0.052	0.05335	102.60	L108049	L108049-SRM2	0.4	0.3989	99.73
L108057	L108057-SRM1	0.054	0.05374	99.52	L108057	L108057-SRM1	0.052	0.05308	102.08	L108057	L108057-SRM1	0.4	0.4035	100.88
L108057	L108057-SRM2	0.054	0.05370	99.44	L108057	L108057-SRM2	0.052	0.05347	102.83	L108057	L108057-SRM2	0.4	0.3976	99.40
L109007	L109007-SRM1	0.054	0.05295	98.06	L109007	L109007-SRM1	0.052	0.05340	102.69	L109007	L109007-SRM1	0.4	0.4016	100.40
L109007	L109007-SRM2	0.054	0.05322	98.56	L109007	L109007-SRM2	0.052	0.05395	103.75	L109007	L109007-SRM2	0.4	0.4043	101.08
L109015	L109015-SRM1	0.054	0.05358	99.22	L109015	L109015-SRM1	0.052	0.05409	104.02	L109015	L109015-SRM1	0.4	0.4099	102.48
L109015	L109015-SRM2	0.054	0.05331	98.72	L109015	L109015-SRM2	0.052	0.05387	103.60	L109015	L109015-SRM2	0.4	0.4028	100.70
L109024	L109024-SRM1	0.054	0.05326	98.63	L109024	L109024-SRM1	0.052	0.05406	103.96	L109024	L109024-SRM1	0.4	0.4063	101.58
L109024	L109024-SRM2	0.054	0.05280	97.78	L109024	L109024-SRM2	0.052	0.05437	104.56	L109024	L109024-SRM2	0.4	0.4020	100.50
L109035	L109035-SRM1	0.054	0.05388	99.78	L109035	L109035-SRM1	0.052	0.05396	103.77	L109035	L109035-SRM1	0.4	0.4028	100.70
L109035	L109035-SRM2	0.054	0.05434	100.63	L109035	L109035-SRM2	0.052	0.05435	104.52	L109035	L109035-SRM2	0.4	0.4051	101.28
L110015	L110015-SRM1	0.054	0.05506	101.96	L110015	L110015-SRM1	0.052	0.05470	105.19	L110015	L110015-SRM1	0.4	0.4046	101.15
L110015	L110015-SRM2	0.054	0.05502	101.89	L110015	L110015-SRM2	0.052	0.05467	105.13	L110015	L110015-SRM2	0.4	0.4050	101.25
L110020	L110020-SRM1	0.054	0.05303	98.20	L110020	L110020-SRM1	0.052	0.05371	103.29	L110020	L110020-SRM1	0.4	0.4015	100.38
L110020	L110020-SRM2	0.054	0.05487	101.61	L110020	L110020-SRM2	0.052	0.05405	103.94	L110020	L110020-SRM2	0.4	0.3963	99.08
Mean				99.39	**Mean**				103.38	**Mean**				100.56
Standard Deviation				1.25	**Standard Deviation**				1.00	**Standard Deviation**				1.03
Count				35	**Count**				35	**Count**				35

Table C-3. Dry Deposition 2011 Sampling Season – QC Batch Summary for Teflon Filters – Reference Samples – GRS420, TN (3 of 3)

K^+					Cl^-				
Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery	Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery
L107014	L107014-SRM2	0.1	0.1016	101.60	L107016	L107016-SRM2	0.9400	0.9669	102.86
L107035	L107035-SRM1	0.1	0.1033	103.30	L107033	L107033-SRM1	0.9400	0.9591	102.03
L107035	L107035-SRM2	0.1	0.1019	101.90	L107033	L107033-SRM2	0.9400	0.9656	102.72
L107035	L107035-SRM3	0.1	0.1008	100.80	L108003	L108003-SRM1	0.9400	0.9576	101.87
L108002	L108002-SRM1	0.1	0.1002	100.20	L108003	L108003-SRM2	0.9400	0.9721	103.42
L108002	L108002-SRM2	0.1	0.0995	99.53	L108006	L108006-SRM1	0.9400	0.9525	101.33
L108005	L108005-SRM1	0.1	0.1032	103.20	L108006	L108006-SRM2	0.9400	0.9606	102.19
L108005	L108005-SRM2	0.1	0.1026	102.60	L108018	L108018-SRM1	0.9400	0.9619	102.33
L108017	L108017-SRM1	0.1	0.0994	99.36	L108018	L108018-SRM2	0.9400	0.9624	102.38
L108017	L108017-SRM2	0.1	0.1008	100.80	L108030	L108030-SRM1	0.9400	0.9652	102.68
L108028	L108028-SRM1	0.1	0.1010	101.00	L108030	L108030-SRM2	0.9400	0.9687	103.05
L108028	L108028-SRM2	0.1	0.1009	100.90	L108052	L108052-SRM1	0.9400	0.9702	103.21
L108049	L108049-SRM1	0.1	0.1020	102.00	L108052	L108052-SRM2	0.9400	0.9686	103.04
L108049	L108049-SRM2	0.1	0.1011	101.10	L109001	L109001-SRM1	0.9400	0.9578	101.89
L108057	L108057-SRM1	0.1	0.1002	100.20	L109001	L109001-SRM2	0.9400	0.9765	103.88
L108057	L108057-SRM2	0.1	0.0999	99.90	L109009	L109009-SRM1	0.9400	0.9684	103.02
L109007	L109007-SRM1	0.1	0.1007	100.70	L109009	L109009-SRM2	0.9400	0.9778	104.02
L109007	L109007-SRM2	0.1	0.0996	99.59	L109017	L109017-SRM1	0.9400	0.9666	102.83
L109015	L109015-SRM1	0.1	0.1000	99.99	L109017	L109017-SRM2	0.9400	0.9707	103.27
L109015	L109015-SRM2	0.1	0.1008	100.80	L109025	L109025-SRM1	0.9400	0.9614	102.28
L109024	L109024-SRM1	0.1	0.1030	103.00	L109025	L109025-SRM2	0.9400	0.9801	104.27
L109024	L109024-SRM2	0.1	0.1025	102.50	L109038	L109038-SRM1	0.9400	0.9738	103.60
L109035	L109035-SRM1	0.1	0.1031	103.10	L109038	L109038-SRM2	0.9400	0.9719	103.39
L109035	L109035-SRM2	0.1	0.1009	100.90	L110016	L110016-SRM1	0.9400	0.9664	102.81
L110015	L110015-SRM1	0.1	0.1013	101.30	L110016	L110016-SRM2	0.9400	0.9789	104.14
L110015	L110015-SRM2	0.1	0.1014	101.40	L110022	L110022-SRM1	0.9400	0.9688	103.06
L110020	L110020-SRM1	0.1	0.1037	103.70	L110022	L110022-SRM2	0.9400	0.9760	103.83
L110020	L110020-SRM2	0.1	0.1029	102.90					
Mean				101.21	**Mean**				102.98
Standard Deviation				1.63	**Standard Deviation**				0.96
Count				35	**Count**				34

Table C-4. Dry Deposition 2011 Sampling Season – QC Batch Summary for Nylon Filters – Reference Samples – GRS420, TN

		SO_4^{2-}					NO_3^-		
Batch	**QC Key**	**Target mg/L**	**Found mg/L**	**Percent Recovery**	**Batch**	**QC Key**	**Target mg/L**	**Found mg/L**	**Percent Recovery**
L106037	L106037-SRM1	9	8.830	98.11	L106037	L106037-SRM1	1.6	1.609	100.56
L106037	L106037-SRM2	9	8.888	98.75	L106037	L106037-SRM2	1.6	1.613	100.83
L107004	L107004-SRM1	9	8.941	99.34	L107004	L107004-SRM1	1.6	1.584	99.01
L107004	L107004-SRM2	9	8.805	97.83	L107004	L107004-SRM2	1.6	1.567	97.92
L107004	L107004-SRM3	9	8.804	97.82	L107004	L107004-SRM3	1.6	1.570	98.14
L107008	L107008-SRM1	9	8.919	99.10	L107008	L107008-SRM1	1.6	1.601	100.04
L107008	L107008-SRM2	9	9.184	102.05	L107008	L107008-SRM2	1.6	1.612	100.74
L107019	L107019-SRM1	9	8.830	98.11	L107019	L107019-SRM1	1.6	1.574	98.38
L107019	L107019-SRM2	9	9.052	100.57	L107019	L107019-SRM2	1.6	1.612	100.74
L107028	L107028-SRM1	9	8.888	98.75	L107028	L107028-SRM1	1.6	1.610	100.61
L107028	L107028-SRM2	9	8.942	99.36	L107028	L107028-SRM2	1.6	1.615	100.94
L107032	L107032-SRM1	9	8.944	99.38	L107032	L107032-SRM1	1.6	1.613	100.83
L107032	L107032-SRM2	9	8.897	98.86	L107032	L107032-SRM2	1.6	1.607	100.44
L108007	L108007-SRM1	9	8.875	98.61	L108007	L108007-SRM1	1.6	1.589	99.30
L108007	L108007-SRM2	9	8.928	99.20	L108007	L108007-SRM2	1.6	1.594	99.63
L108019	L108019-SRM1	9	8.863	98.48	L108019	L108019-SRM1	1.6	1.602	100.11
L108019	L108019-SRM2	9	8.870	98.56	L108019	L108019-SRM2	1.6	1.598	99.89
L108029	L108029-SRM1	9	8.862	98.47	L108029	L108029-SRM1	1.6	1.600	100.03
L108029	L108029-SRM2	9	8.812	97.91	L108029	L108029-SRM2	1.6	1.607	100.44
L108046	L108046-SRM1	9	8.891	98.79	L108046	L108046-SRM1	1.6	1.611	100.68
L108046	L108046-SRM2	9	8.877	98.63	L108046	L108046-SRM2	1.6	1.599	99.93
L109002	L109002-SRM1	9	8.883	98.70	L109002	L109002-SRM1	1.6	1.593	99.56
L109002	L109002-SRM2	9	8.928	99.20	L109002	L109002-SRM2	1.6	1.596	99.76
L109006	L109006-SRM1	9	8.994	99.93	L109006	L109006-SRM1	1.6	1.622	101.38
L109006	L109006-SRM2	9	8.904	98.93	L109006	L109006-SRM2	1.6	1.600	100.03
L109018	L109018-SRM1	9	8.853	98.36	L109018	L109018-SRM1	1.6	1.587	99.16
L109018	L109018-SRM2	9	8.971	99.68	L109018	L109018-SRM2	1.6	1.602	100.09
L109027	L109027-SRM1	9	8.898	98.86	L109027	L109027-SRM1	1.6	1.596	99.77
L109027	L109027-SRM2	9	8.936	99.29	L109027	L109027-SRM2	1.6	1.611	100.69
L109039	L109039-SRM1	9	8.835	98.17	L109039	L109039-SRM1	1.6	1.595	99.71
L109039	L109039-SRM2	9	9.095	101.05	L109039	L109039-SRM2	1.6	1.630	101.90
L109039	L109039-SRM3	9	9.129	101.43	L109039	L109039-SRM3	1.6	1.630	101.85
L110009	L110009-SRM1	9	8.919	99.10	L110009	L110009-SRM1	1.6	1.595	99.67
L110009	L110009-SRM2	9	9.212	102.35	L110009	L110009-SRM2	1.6	1.646	102.89
L110019	L110019-SRM1	9	8.894	98.83	L110019	L110019-SRM1	1.6	1.601	100.04
L110019	L110019-SRM2	9	9.013	100.15	L110019	L110019-SRM2	1.6	1.613	100.83
Mean				99.19	**Mean**				100.18
Standard Deviation				1.11	**Standard Deviation**				1.01
Count				36	**Count**				36

Table C-5. Dry Deposition 2011 Sampling Season – QC Batch Summary for Cellulose Filters – Reference Samples – GRS420, TN

Batch	QC Key	SO_4^{2-} Target mg/L	Found mg/L	Percent Recovery
L106038	L106038-SRM1	9	8.916	99.06
L106038	L106038-SRM2	9	8.727	96.97
L107002	L107002-SRM1	9	9.082	100.91
L107002	L107002-SRM2	9	8.868	98.53
L107017	L107017-SRM1	9	8.942	99.36
L107017	L107017-SRM2	9	8.629	95.88
L107021	L107021-SRM1	9	8.797	97.74
L107021	L107021-SRM2	9	8.604	95.60
L107030	L107030-SRM1	9	8.833	98.14
L107030	L107030-SRM2	9	8.592	95.46
L107036	L107036-SRM1	9	8.824	98.04
L107036	L107036-SRM2	9	8.582	95.35
L108009	L108009-SRM1	9	8.836	98.18
L108009	L108009-SRM2	9	8.602	95.58
L108009	L108009-SRM3	9	8.794	97.71
L108020	L108020-SRM1	9	8.861	98.46
L108020	L108020-SRM2	9	8.828	98.09
L108032	L108032-SRM1	9	8.844	98.27
L108032	L108032-SRM2	9	8.662	96.24
L108032	L108032-SRM3	9	8.763	97.37
L108047	L108047-SRM1	9	8.863	98.47
L108047	L108047-SRM2	9	8.601	95.57
L109004	L109004-SRM1	9	8.857	98.41
L109004	L109004-SRM2	9	8.627	95.86
L109008	L109008-SRM1	9	8.869	98.54
L109008	L109008-SRM2	9	8.576	95.29
L109016	L109016-SRM1	9	8.889	98.77
L109016	L109016-SRM2	9	8.671	96.34
L109028	L109028-SRM1	9	8.856	98.40
L109028	L109028-SRM2	9	8.754	97.27
L110008	L110008-SRM1	9	8.908	98.98
L110008	L110008-SRM2	9	8.589	95.44
L110010	L110010-SRM1	9	8.915	99.06
L110010	L110010-SRM2	9	8.598	95.53
L110017	L110017-SRM1	9	8.917	99.07
L110017	L110017-SRM2	9	8.590	95.45
Mean				97.43
Standard Deviation				1.51
Count				36

Table C-6. Dry Deposition 2011 Sampling Season - CCV (%R) – GRS420, TN

Filter Type	Parameter	Mean	Standard Deviation	Count
Teflon	SO_4^{2-}	99.06	1.12	169
	NO_3^- - N	100.33	0.88	169
	Cl^-	101.23	0.92	169
	NH_4^+ - N	102.49	1.84	169
	Ca^{2+}	100.43	0.78	175
	Mg^{2+}	100.02	0.72	175
	Na^+	99.11	0.90	175
	K^+	100.04	0.81	175
Nylon	SO_4^{2-}	99.65	1.73	187
	NO_3^- - N	100.64	1.02	187
Cellulose	SO_4^{2-}	98.07	1.23	137

Note: %R = percent recovery

Table C-7. Dry Deposition 2011 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
1124001-35	L107002-DUP4	30-Jun-11	SO_4^{2-}	Cellulose	38.6200	38.3500	0.70	NA	NA	1
1137001-35	L109035-DUP5	28-Sep-11	Ca^{2+}	Teflon	3.7800	3.7390	1.08	NA	NA	1
1137001-35	L109035-DUP5	28-Sep-11	Mg^{2+}	Teflon	0.6324	0.6311	0.21	NA	NA	1
1137001-35	L109035-DUP5	28-Sep-11	K^{+}	Teflon	2.1060	2.1010	0.24	NA	NA	1
1137001-35	L109035-DUP5	28-Sep-11	Na^{+}	Teflon	0.7470	0.7373	1.30	NA	NA	1

Note: NA = not applicable