

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

2006

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List of Acronyms and Abbreviations

°C degrees Celsius Ca²⁺ calcium ion

CAAA Clean Air Act Amendments

CASTNET Clean Air Status and Trends Network
CLOUD cloud water deposition computer model

Cl chloride ion

CLASS[™] Chemical Laboratory Analysis and Scheduling System

CLD303 Clingmans Dome, TN sampling site

cm centimeter

cm/s centimeters per second

CVS continuing verification sample

DAS data acquisition system

EPA U.S. Environmental Protection Agency g/cm²/min grams per square centimeter per minute

g/m³ grams per cubic meter

GRS420 Great Smoky Mountains National Park, TN dry deposition sampling site

H⁺ hydrogen ion

Harding ESE Harding ESE, Inc., now known as MACTEC Engineering and Consulting, Inc.

HNO₃ nitric acid

IC ion chromatography

ICP-AES inductively coupled argon plasma - atomic emission spectrometer

K⁺ potassium ion

K₂CO₃ potassium carbonate kg/ha kilograms per hectare

Lpm liters per minute
LWC liquid water content

m meter

m/sec meters per second

List of Acronyms and Abbreviations (continued)

MACTEC Engineering and Consulting, Inc.

MADPro Mountain Acid Deposition Program MCCP Mountain Cloud Chemistry Program

Mg²⁺ magnesium ion

mL milliliter

MLM Multi-Layer Model

mm millimeter
N nitrogen
Na⁺ sodium ion

NADP/NTN National Atmospheric Deposition Program/ National Trends Network

NAPAP National Acid Precipitation Assessment Program

NH₄ ammonium ion

NIST National Institute for Standards and Technology

NO₃ nitrate ion

NO_x oxides of nitrogen NPS National Park Service pH p(otential of) H(ydrogen)

PVC polyvinylchloride

PVM particle volume monitor

QA quality assurance

QAPP Quality Assurance Project Plan

QC quality control

RPD relative percent difference

 $\begin{array}{ll} S & sulfur \\ SO_4^2 & sulfate ion \\ SO_2 & sulfur dioxide \end{array}$

SOP standard operating procedure SSRF Site Status Report Form

TN11 Elkmont, TN wet deposition sampling site

TVA Tennessee Valley Authority

µeq/L microequivalents per liter

µg/filter micrograms per filter

μg/m³ micrograms per cubic meter

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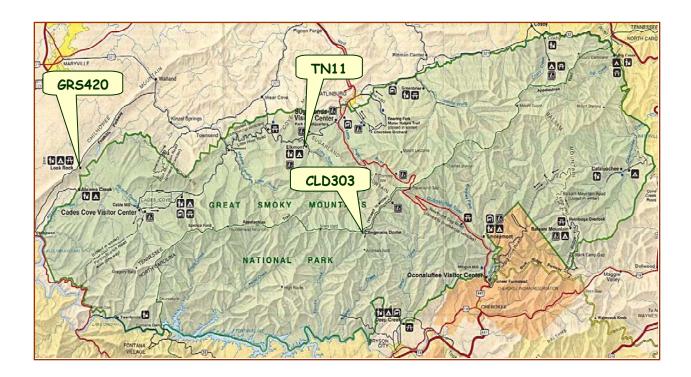
1.0 Introduction

The 1990 Clean Air Act Amendments (CAAA) established the Acid Deposition Control Program, which mandated significant reductions in sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions from electric generating plants. The SO₂ 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. Emission reductions of NO_x began in 1999. The Acid Deposition Control Program has resulted in substantive emission reductions since 1995.

Titles IV and IX of the CAAA require that the environmental effectiveness of the Acid Deposition Control 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 the U.S. Environmental Protection Agency (EPA) in 1991 to provide an effective monitoring and assessment network for determining the status and trends in air quality and pollutant deposition as well as relationships among emissions, air quality, deposition, and ecological effects. CASTNET measurements collected over the period 1990 through 2005 (MACTEC, 2006a) have shown significant declines in atmospheric sulfur pollutants [SO₂ and particulate sulfate (SO₄²)] and more recently suggest declines in nitrogen pollutants [nitric acid (HNO₃) and particulate nitrate (NO₃)]. The Mountain Acid Deposition Program (MADPro) was initiated in 1993 as part of the research necessary to support CASTNET's objectives. MACTEC Engineering and Consulting, Inc. (MACTEC) operates both CASTNET and MADPro on behalf of EPA and other agencies.

MADPro's two main objectives were to develop cloud water measurement systems to be used in a network-monitoring environment and to update the cloud water concentration and deposition data collected in the Appalachian Mountains during the National Acid Precipitation Assessment Program (NAPAP) in the 1980s. MADPro measurements were conducted from 1994 through 1999 during the warm season (May through October) at three mountaintop sampling stations. These sampling stations were located at Whiteface Mountain, NY; Clingmans Dome, TN; and Whitetop Mountain, VA. A mobile manual sampling station also was operated at two locations in the Catskill Mountains in New York during 1995, 1997, and 1998. Measurements during the 2000 and 2001 sampling seasons were collected from two sites: Whiteface Mountain, NY and Clingmans Dome, TN. During the 2002 through 2006 sampling seasons, measurements were only collected from the one site at Clingmans Dome, TN (CLD303). Currently, CLD303 is being 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 2006 field sampling season.

This report consists of five additional sections and three appendices. Section 2.0, Site Description and Methods, presents an overview of field, laboratory, and data operations and the quality assurance (QA) program. Section 3.0, Liquid Water Content and Cloud Water Chemistry, presents analyses of cloud frequency, liquid water content (LWC), cloud chemistry, and summary statistics for the 2006 data with comparisons to the 1994 through 2005 data sets. Cloud deposition estimates are presented in Section 4.0. The deposition estimates were calculated by applying the cloud water deposition computer model (CLOUD) (Lovett, 1984), parameterized with site-specific cloud water chemistry and meteorological data. Section 5.0 presents filter pack concentrations, modeled dry deposition fluxes, and estimates of total (cloud and dry) deposition. Finally, Section 6.0 discusses the conclusions and recommendations for MADPro.



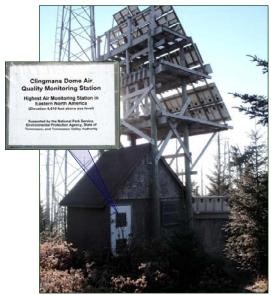
For 2006, cloud water and meteorological data were measured at the CLD303 site. Dry deposition data for estimating dry deposition were obtained from the nearest CASTNET site (GRS420, TN). Wet deposition data for estimating wet deposition were obtained from Elkmont, TN (TN11), which is operated by NPS 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 2006, the site was installed during the first week of May, but because of equipment problems and power limitations, the site was not fully operational until May 31. Sampling then continued through October 31, 2006.



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 LWC, and a data acquisition system (DAS) for collection and storage of electronic information from the various monitors and sensors. In 2004, a microprocessor was added to the suite of instrumentation, specifically for monitoring cloud collector status and to control all sampler functions. A set of meteorological instruments for continuous measurements of wind speed, wind direction, temperature, solar radiation, relative humidity, wetness, and precipitation were deployed through 2004. Beginning in 2005, only those sensors essential for the operation of the cloud collector (namely, temperature and precipitation sensors and a rain gauge) were deployed. Other meteorological data required for calculation of cloud deposition estimates (scalar wind speed) were obtained from the NPS instruments situated on a tower located next to the cloud collection tower. Up until 2005, the site deployed the same three-stage filter pack system for dry deposition estimation that is used at all CASTNET sites. Starting in 2005, these data were obtained from CASTNET site Great Smoky Mountains

National Park, TN (GRS420). The 2006 wet deposition data used in estimating wet deposition were collected at Elkmont, TN (TN11), which is operated by NPS for NADP/NTN.

The core of the automated cloud collection system is a passive string collector previously used in the Mountain Cloud Chemistry Program (MCCP) study. Collection occurs when ambient winds transport cloud water droplets onto 0.4-millimeter (mm) Teflon[®] fibers strung between two circular disks (Falconer and Falconer, 1980; Mohnen and Kadlecek, 1989). Once impacted, the droplets slide down the strings, are collected in a funnel, and flow through Teflon[®] tubing into sample bottles in a refrigerated carousel. The development and design of this 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/m³) of air. The microprocessor is programmed so that the collector will be activated and projected out of the protective housing when threshold levels for LWC (0.05 g/m³) and ambient air temperature



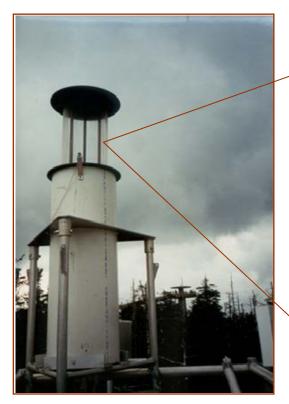
Particle Volume Monitor

 \geq 2 degrees Celsius (°C) are reached. In addition, the system is activated only when no precipitation is measured. Within the context of this work assignment, a cloud is defined by a LWC of 0.05 g/m³ 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/m³ (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, however, the collection of at least 30 mL of sample has not been an issue. Therefore, the wind speed threshold criterion was eliminated starting in 2004. The temperature limit serves to protect against

damage from rime ice formation. The absence of rainfall is required because within the objectives of this study, as well as MCCP, only samples from non-precipitating clouds are collected. If a rain detector is activated, the string collector will retract into the protective case

and collection will be suspended. Beginning with the 1999 field season, a modified automated cloud collector has been used. The collector was modified by switching from a battery-powered to a pneumatically-powered system to send the collector up and down. This system 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. The tipping bucket is calibrated so that the weight of 5.44 mL of collected liquid causes the apparatus to tip into the funnel. In 2004, the tipping bucket was removed from the cloud collection system as it was no longer necessary to track hourly collection volumes.

If the threshold criteria described above are not met for a 5-minute period, the collector comes down. A new 10-liter collection bottle is rotated into position after every 24-hour period allowing for the collection of daily bulked samples.





Cloud Collector in Up Position

The PVM is operated continuously. Consequently, collection of cloud samples only when the threshold criteria are met does not result in loss of cloud frequency and cloud duration information. All LWC values of 0.05 g/m³ 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 be biased by not sampling for cloud deposition that occurs during precipitating clouds. However, the bias due to this lack of sampling during a precipitation event is offset by the fact that cloud deposition totals are estimated by multiplying the duration-weighted mean chemical fluxes by the cloud-hours for the month. The cloud-hours are calculated as the cloud frequency times the total hours in the month.

The site operator gathers cloud water samples from the collector on Tuesday and Friday, whether or not collection has occurred. The time, date, and volume of each bulk sample are recorded on the Cloud Water Sample Report Form. Each sample is then carefully decanted into one pre-cleaned 250-mL sample bottle. Excess sample volume is discarded. The sample date and time are recorded on the 250-mL sample bottle label. The site operator analyzes each sample for pH and conductivity and records the results on the Cloud Water Sample Report Form. The samples are then packed into coolers with the corresponding form and shipped to the CASTNET laboratory in Gainesville, FL. Periodically, selected rinse samples are included in shipments. Starting in 2005, some of the 24-hour samples shipped from the field were bulked together in the MACTEC laboratory in order to keep the number of samples analyzed by the laboratory within the number of samples allotted for analysis in the budget. It was not necessary to utilize this procedure in 2006.

Filter packs for collection of dry deposition samples are prepared and shipped to the field on a weekly basis and exchanged at the site every Tuesday. For a description of the filter pack set-up, types of filters used, and the fraction collected on each filter, refer to the CASTNET Quality Assurance Project Plan (QAPP) (MACTEC, 2005a) and/or the CASTNET Deposition Summary Report (EPA, 1998). A discussion of filter pack sampling artifacts can be found in Anlaulf *et al.* (1986). Filter pack flow is maintained at 3.0 liters per minute (Lpm) with a mass flow controller.



3-Stage Filter Pack

All field equipment received start-up and end-of-season calibrations. Calibration checks were scheduled to be performed bi-weekly (weather permitting) on the PVM throughout the field

season and the results used to adjust the instrument immediately after the calibration check. However, in 2006, because of the inexperience of the site operator, these checks were performed only sporadically, and none at all in September and October due to breakage of the calibration disk. Calibrations on the remaining instruments were conducted using standards traceable to the National Institute for Standards and Technology (NIST). The calibrations at the beginning and end of the 2006 field season were within the control limits stated in the CASTNET QAPP (MACTEC, 2005a)

2.3 Laboratory Operations

Cloud water samples for the 2006 sampling season were analyzed for sodium (Na⁺), potassium (K⁺), ammonium (NH₄⁺), calcium (Ca²⁺), magnesium (Mg²⁺), chloride (Cl⁻), NO₃, and SO₄²⁻ ions in the CASTNET laboratory. pH and conductivity were analyzed in the field, and most samples were also analyzed for pH and conductivity in the laboratory for comparison with the field values.

Samples 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.

Concentrations of the three anions (SO₄², NO₃, Cl²) were determined by micromembrane-suppressed ion chromatography (IC). Analysis of Na⁺, Mg²⁺, Ca²⁺, and K⁺ was performed with a Perkin-Elmer Optima 3000 DV inductively coupled argon plasma-atomic emission spectrometer (ICP-AES). The automated indophenol method using a Bran+Luebbe Autoanalyzer[™] 3 was used to determine NH₄⁺ concentrations. Hydrogen (H⁺) ion concentrations for 2006 were determined for each sample 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, 2005a). Filter packs contain three filter types in sequence: a Teflon[®] filter for collection of aerosols, a nylon filter for collection of HNO₃, and dual potassium carbonate (K₂ CO₃)-impregnated cellulose Whatman filters for collection of SO₂. Following receipt from the field, exposed filters and unexposed blanks were extracted and analyzed for Cl⁻ and the cations, NH₄, Na⁺, Mg²⁺, Ca²⁺, and K⁺ as described previously for cloud water samples. Refer to the CASTNET QAPP (MACTEC, 2005a) for detailed descriptions of laboratory receipt, breakdown, storage, extraction, and analytical procedures.

Results of all valid cloud water analyses are stored in the laboratory data management system, Chemical Laboratory Analysis and Scheduling System (CLASS TM). Results of all valid filter pack analyses are stored in the laboratory data management system, Element DataSystem TM .

Atmospheric concentrations 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; and 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 by daily polling via telephone modem. The polling software also recovers status files and power failure logs from the previous seven days. The 5-minute data are downloaded from the DAS cartridge at least once weekly and e-mailed to MACTEC. The hourly data and associated status flags are ingested into Microsoft[®] Excel[™] spreadsheets. The continuous data are validated based on the end-of-season calibration results, periodic calibration check results (PVM, only), and information provided by status flags and logbook entries.

Discrete data for cloud water sample results are managed by $CLASS^{TM}$. Discrete data for filter pack sample results are managed by Element DataSystem In $CLASS^{TM}$ and Element DataSystem, 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 verification samples (CVS) 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.

Atmospheric concentrations for filter pack samples are calculated by merging validated continuous flow data with the laboratory data [micrograms per filter (μ g/filter)]. For cloud water samples, a second check involves three interparameter consistency checks:

Percent difference of cations versus anions (ion balance),
 Percent difference of predicted versus measured conductivity, and
 pH versus conductivity relationship of the sample compared to the expected relationship when rainfall is assumed to be controlled by strong inorganic acid.

Evaluation of these interparameter consistency checks provides a method for determining whether the analysis should be repeated or verified.

2.5 Quality Assurance

The QA program consists of the same routine audits performed for CASTNET, if applicable, and testing/comparison of instruments unique to cloud water sampling.

2.5.1. Field Data Audits

The following audits are conducted for field data:

- 1. Review of all reported problems with sensors and equipment at the site and of the actions taken to solve such problems.
- 2. Review of calibration files for completeness and adherence to standard operating procedures (SOP). Certification results for transfer standards are also reviewed, and transfer sensor serial numbers are cross-referenced with the transfer sensor serial numbers on the calibration forms.
- 3. 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:

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

2.5.3. Precision and Accuracy

With the exception of the automated cloud sampler and PVM, accuracy of field measurements (i. e., meteorological instruments used in conjunction with the cloud collection system and PVM) is determined by challenging instruments with standards that are traceable to NIST. Continuing accuracy is verified by end-of-season calibrations by MACTEC personnel. No certified standards are currently available for determination of cloud sampler 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 Deposition Summary Report (EPA, 1998) and the CASTNET annual reports for 1998 through 2005 (www.epa.gov/CASTNET/library.html).

Accuracy of laboratory measurements is determined by analyzing an independently prepared reference sample in each batch and calculating the percent recovery relative to the target value. The percent recovery is expected to meet or exceed the acceptance criteria listed in the

CASTNET QAPP (MACTEC, 2005a). 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 CVS run within that batch. CVS 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.



The Automated Cloud Collector (in the down position) on top of the CASTNET tower at Clingmans Dome, TN

3.0 Liquid Water Content and Cloud Water Chemistry

3.1 Cloud Frequency and Mean Liquid Water Content

Monthly mean cloud frequencies by year from 1994 through 2006 are summarized in Table 3-1. Cloud frequencies by month and year are also depicted as a bar chart in Figure 3-1. 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:

$$CF = \frac{100*(\# of \ valid \ hourly \ LWC \ values \ge 0.05 \ g \ / \ m^3)}{n}$$
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 (Harding ESE, 2001-2003 and MACTEC, 2004; 2005b; and 2006b). As can be seen from Table 3-1, the monthly cloud frequencies for June and July 2006 were the lowest monthly means for these months thus far in the project. The August 29, 2006 mean (although below the completeness criterion) was higher with respect to the historical mean.

In 2006, the LWC data from August 29th through the end of the season were invalidated due to the suspiciously high values obtained during this time period. Although the instrument optical offset values were out of acceptance range during these months, it was observed that the PVM was accurately detecting the presence of clouds at the threshold level of 0.05 g/m³. Since all that is required for determination of cloud frequency and cloud hours is the count of values equal to and greater than 0.05 g/m³, and not the accuracy of values above this threshold, the September and October LWC data could still be utilized for calculating these statistics. LWC data after August 30th, however, could not be used for calculation of monthly mean LWC values.

Monthly mean LWC values for 1994 through 2006 are shown in Figure 3-2. Mean LWC was calculated by taking the average of all hourly LWC values equal to or greater than 0.05 g/m³ during the month. Monthly mean LWC values for 2006 versus the historical monthly means are shown in Figure 3-3. Normally, only valid values passing the 70 percent completeness criterion are plotted. However, because of the invalidation of the September and October LWC data, it was decided to include the August 2006 data in Figures 3-2 and 3-3 despite the completeness rate for this month of 65 percent. Since these 65 percent of August data are valid, these values are presented for informational purposes only in these figures.

3.2 Cloud Water Chemistry

During the 2006 sampling season, the CASTNET laboratory received 45 samples from CLD303. All of the samples received had sufficient volume for complete analysis. Samples sent to the CASTNET laboratory for analysis were packed in Styrofoam® coolers with frozen ice packs to keep the samples cool during shipping. Upon receipt of the samples, the sample receiving technician verified the condition of the samples and the contents of the shipment against the enclosed Cloud Water Sample Report Form. All samples were received in good condition. Cloud water analytical and QC data for the 2006 sampling season are presented as Appendix B.

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

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

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. Cloud Water pH

The pH values for CLD303 are shown in Figures 3-4 and 3-5. The frequency distribution in both figures shows that a majority of the 2006 samples (approximately 69 percent for laboratory pH and 84 percent for field pH) had values of pH 3.9 or lower. Historically, the majority of the pH values measured at CLD303 fall within the range of pH 3.2 to 3.8. This range is identified in the 1992 NAPAP report to Congress (1993) as "acidic cloud water." Therefore, these measured pH values, when in combination with other stresses, might affect the high elevation spruce forests of Clingmans Dome.

As can be seen from these figures and the summary statistics for pH and hydrogen ion concentrations in Table 3-2, the 2006 field pH values are lower than the laboratory pH values. The mean field hydrogen ion concentration (Table 3-2) is approximately 48 percent higher than

the mean laboratory hydrogen ion concentration. Field pH values are known to be generally lower than pH values measured in the laboratory due to microbial activity, degradation of organic acids, dissolution of particulate matter, and ion exchange processes involving the walls and/or lid of the shipping container (Bigelow *et al.*, 1984). The difference between the field and laboratory pH values in 2006, however, was greater even than in previous years. The cation/anion ratios also yielded greater percent differences than usual when using field pH. Because of these results and the lack of any QC data associated with the field pH meter, the laboratory data were used this year (rather than field data) for calculation of the cloud hydrogen deposition values.

3.2.2. Major lons in Cloud Water

The major ions are identified as SO_4^{2-} , H^+ , NH_4^+ , and NO_3^- . Figure 3-6 presents the mean seasonal major ion concentrations in cloud water samples for 1995 through 2006. All 2006 mean major ion concentrations show a decrease with respect to 2005 mean concentrations. The 2006 mean nitrate concentration (120.42 μ eq/L) shows a 6.3 percent decrease from the 2005 mean, and the 2006 mean sulfate concentration (347.45 μ eq/L) is 9.6 percent lower with respect to the 2005 mean. The month of August exhibited the highest monthly major ion concentrations in 2006 for sulfate, nitrate, and laboratory hydrogen (Figure 3-7), and September had the highest mean for field hydrogen ion concentrations. Summary statistics of all major ion concentrations, as well as calcium concentrations, averaged across all years (1994-2006) are presented in Table 3-4.

3.2.3. Minor lons in Cloud Water

Mean seasonal concentrations of the minor ions (Ca²+, Mg²+, Na+, K+, and Cl⁻) for 1995 through 2006 are presented in Figure 3-8. Concentrations of sodium and potassium increased with respect to 2005 mean concentrations, whereas concentrations of calcium, magnesium, and chloride showed decreases. Concentrations for the minor ions peaked in various months with no discernible pattern.



The road to Clingmans Dome, TN

4.0 Cloud Deposition

This section presents the modeled cloud water deposition estimates for Clingmans Dome from 1994 through 2006. Deposition was estimated by applying the CLOUD model (Lovett, 1984), parameterized with site-specific cloud water chemistry and meteorological data from CLD303 as screened and provided by MACTEC. The complete report discussing 2006 cloud deposition modeling results by Gary M. Lovett, Ph.D. is presented in Appendix A. The following subsections present a summary of Dr. Lovett's results.

4.1 Cloud Water Deposition Model

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

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

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

From these input parameters, the model calculates the deposition of cloud water, expressed both as a water flux rate in grams per square centimeter per minute (g/cm²/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. Starting with the

2002 sampling season, the calculation of the evaporation rate from the canopy was not invoked, resulting in estimation of only the gross deposition rate.

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

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

The 2006 data set contained 45 samples (or time periods), and the model was run for 43 samples/time periods. Although the site was set up in early May, equipment problems and power issues delayed the official start until May 31, 2006. Collection continued through October, however, to offset the late start. Therefore, the season was identified as May 31 through October 31, 2006. Deposition rates and duration-weighted means could not be calculated for two samples in early August due to lack of sample LWC, wind speed, and duration data. Both the September and October LWC data were invalidated. However, these data were included in the calculations of the 2006 monthly depositions as the September and October LWC data were invalidated after the deposition calculations were completed. In addition, the LWC value for one sample from the end of August was also invalidated after calculation of the deposition estimates. Consequently, this invalid LWC value was used in calculation of the August monthly deposition estimate. The results for these months are presented for informational purposes only in Appendix A. Except for seasonal depositions, all calculations presented in this section for 2006 followed the same procedures as calculations for 2000-2002 and 2004-2005. Seasonal depositions for 2006, presented in Tables 4-3 and 5-3 and Figures 5-1 and 6-1, were calculated by averaging the monthly depositions for June through August and then multiplying this average by four. Similar procedures were employed for the 2003 season because of a shorter sampling season and lack of data completeness for some of the months due to equipment malfunction. Please refer to the 2003 MADPro Report (MACTEC, 2004) for details of the 2003 procedures. The seasonal depositions presented in Appendix A were calculated using the same procedures used for calculation of the 2000-2002 and 2004-2005 seasonal depositions.

4.2 Results

4.2.1 Monthly Means

The June mean monthly wind speed was higher with respect to the July and August means and this in turn contributed to the higher deposition velocity for this month. The monthly cloud frequency was highest in August (50.87 percent). Duration-weighted mean monthly concentrations for all ions, except hydrogen and sulfate, were the highest in July. Hydrogen and sulfate concentrations were highest in August.

Monthly deposition estimates [kilograms per hectare (kg/ha)] for major ions, Ca²⁺, and water for 1994, 1995, and 1997 through 2006 are presented in Table 4-1. Despite the fact that most concentrations peaked in July 2006 (Table I-2, Appendix A), total cloud deposition of all ions was highest in August (Table I-3, Appendix A). Deposition estimates for most ions were lowest in the month of June.

The monthly deposition estimates for the major ions and calcium as determined from the CLOUD model for years 1999 through 2006 are also presented in Figures 4-1 and 4-2. The monthly mean deposition estimates for June and July 2006 are the lowest since 1999 for sulfate, nitrate, ammonium, hydrogen, and calcium. The monthly mean deposition estimates for August 2006 are the highest since 1999 for sulfate and ammonium. However, it should be taken into account that this estimate may be biased high due to the inclusion of one sample with an invalid (biased high) LWC value.

Table 4-2 presents the monthly mean deposition rates estimated for 1995 through 2006. These estimates are based on available data shown in Table 4-1. It is difficult to compare the 2006 estimates to previous years since these rates were for June through August, whereas the estimates for all other years are for either May through September or June through October.

4.2.2 Seasonal Deposition Estimates

The seasonal deposition values for major ions are presented in Table 4-3. Only the data sets from 1997 and 1999 through 2006 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 2006 data show that the deposition estimate for ammonium was the highest since 2002 and the deposition estimate for sulfate was the highest since 2001. The nitrate deposition estimate was slightly higher compared to the 2005 estimate after a steady drop in this deposition estimate since 2001.

5.0 Filter Pack Concentrations, Dry Deposition, and Total Deposition

Atmospheric sampling for sulfur and nitrogen species was integrated over weekly collection periods (Tuesday) using a three-stage filter pack. In this approach, particles and selected gases were collected by passing air at a controlled flow rate through a sequence of Teflon®, nylon, and dual cellulose filters. Weekly air pollutant concentrations measured during the 2006 field season, together with the weekly dry deposition values estimated from the concentrations and modeled deposition velocities, are presented in this section. The data presented here are from the CASTNET site at Great Smoky Mountains National Park, TN (GRS420) since filter pack sampling at CLD303 was discontinued for 2005 and 2006.

5.1 Filter Pack Concentrations

Over the course of the 2006 sampling season, the CASTNET laboratory analyzed 22 filter pack samples. The filter packs were installed on the sampling tower each Tuesday and then removed the following Tuesday. The site operator sealed each exposed filter pack with end caps and placed it in a resealable plastic bag for return shipment to MACTEC. Each filter pack was securely packed into a polyvinyl chloride (PVC) shipping tube with its corresponding Site Status Report Form (SSRF) and returned to MACTEC weekly. Any discrepancies or problems with the shipment were recorded on the SSRF by the receiving laboratory technician. All of the filter pack samples were received in good condition.

Upon receipt, all of the samples were logged in and unpacked. Each filter type was extracted and analyzed by the CASTNET laboratory for SO_4^2 and/or NO_3^2 . The Teflon® filter received additional analysis for Cl 2 , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . Sample handling and analyses followed the procedures described in the CASTNET Laboratory SOP (MACTEC, 2005a). 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/m³) resulting from analysis of each weekly filter pack exposed for sampling during the 2006 sampling season. Upon receipt of each weekly filter pack, the receiving technician assigned a sample number composed of various identifiers for sample type, year, week, and site. The on/off dates and times presented in Table 5-1 correspond with the entries recorded on the SSRF. Starting in 1996 and continuing through the 2003 sampling season, the flow to the filter pack at the CLD303 site was programmed to shut off during a cloud or rain event to allow for determination of dry deposition only. In 2004, the filter pack sampled during rain events as well, and the flow was shut off only during a cloud event. The filter pack at GRS420, as well as at all other CASTNET sites, samples continuously throughout the week. This difference in sampling protocol should be taken into consideration when comparing filter pack concentrations after 2004

and previous years. In addition, there is a substantial difference in elevation of 1,221 meters between the CLD303 site (elevation 2,014 m) and the GRS420 site (elevation 793 m).

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

Volume in meters³ =
$$\frac{hours\ sampled\ (hr)\ x\ average\ flow\ x\ 60}{1,000}$$

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

Atmospheric

Concentrations =
$$\mu g$$
 of analyte/filter x analyte dependent constant

 $(\mu g/m^3)$ Volume

The following constants were used for converting the chemistry data:

Tefl	on [®]	Nyl	lon	Cellulose		
Parameter	Parameter Constant		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	NO_3	4.429	
NH_4^+	1.286	NA	NA	NA	NA	
Ca^{2+}	1.0	NA	NA	NA	NA	
Mg^{2+}	1.0	NA	NA	NA	NA	
Na ⁺	1.0	NA	NA	NA	NA	
$\mathbf{K}^{^{+}}$	1.0	NA	NA	NA	NA	
Cl ⁻	1.0	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 SO₂ was determined by this equation:

Total
$$SO_2 = cellulose SO_2 + (Nylon SO_4^2 * 0.667)$$

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. More recent data (Finkelstein *et al.*, 2000) suggest that the MLM underestimates deposition velocities for SO₂ 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 fluxes, and the seasonal mean deposition velocities for 2006 are presented in Table 5-2. The seasonal (June through September) 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 2006 field season is:

total seasonal flux = 18/17 (Sum of all valid weekly deposition estimates)

Only 18 of the 22 filter packs analyzed were used to calculate deposition estimates as the last four filter packs were run completely during the month of October. The deposition season is defined as June through September.

5.3 Total Deposition

Total sulfur and nitrogen deposition estimates for the 1999 through 2006 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 NO₃ and NH₄ deposition estimated from the CLOUD model to nitrogen (N). Total dry nitrogen deposition was determined

by converting the HNO₃, NO₃, and NH₄ 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 2006 sampling seasons. This figure shows that cloud water sulfur deposition for 2006 increased approximately 52 percent from 2005 measurements and dry sulfur deposition decreased by about 11 percent (0.829 kg/ha for 2005 versus 0.738 kg/ha for 2006). Total nitrogen deposition increased 10 percent for cloud water and decreased four percent for dry deposition. The increases in cloud sulfur and nitrogen deposition are influenced by the high monthly deposition rate for August which includes one sample with a LWC value that was biased high. Despite the fact that the filter pack data for 2006 are from a different site with a substantially lower elevation, it is still evident that dry deposition was and continues to be a minor 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.



At an elevation of 2,014 meters, ice, rime ice, and frost crystals regularly form on exposed equipment during the cold season (November through April). Cloud sampling occurs only during the warm season (May through October).

6.0 Conclusions and Recommendations

The Clingmans Dome cloud water measurements show an overall decline in sulfur and nitrogen deposition over the last several years with the exceptions of 2004 and 2006 when increases were observed for both species. The estimate of 2006 cloud sulfate deposition is the highest since 2002. Estimates of total deposition, i.e., deposition produced by clouds and dry deposition, also show a general overall decline over the last several years with the exceptions of 2004 and 2006 results (Figure 6-1). It should be noted that the 2006 cloud deposition results were extrapolated to account for the absence of a valid deposition estimate for the month of September. The LWC values after August 29, 2006 were biased high due to operational problems with the LWC instrument. Regardless of these concerns, the 2006 seasonal estimates show that dry deposition is still a minor contributor to the deposition of pollutants at high elevations. Cloud deposition is the significant pathway for deposition at these elevations.

The principal recommendation is to continue cloud sampling at Clingmans Dome and to reinstitute collocated filter pack sampling during the 2007 season. The GRS420 measurements cannot be considered representative of CLD303 due to the differences in elevation, distance, and other site-specific factors. The Clingmans Dome data constitute a major source of information on deposition to high elevation, sensitive ecosystems and will continue to help gauge the effectiveness of the Acid Deposition Control Program in reducing atmospheric pollutant deposition.

In addition to continuing laboratory pH and conductivity measurements in order to verify proper operation of the field pH meter and probe and to provide back up measurements for this important parameter, an audit of the field laboratory is recommended. This recommendation results from problems encountered with the field pH and conductivity measurement and documentation protocols during the 2006 field season. The audit should also include the LWC calibration procedures and documentation as well as cloud water sample collection, handling, and documentation procedures.

Additionally, the microcontroller program needs evaluation and will possibly require updates in order to improve operation of the cloud collection system. The operational problems experienced with the PVM during the last portion of 2006 season have already been addressed. It is recommended that more frequent and careful monitoring of the PVM should be implemented in upcoming seasons in order to circumvent similar problems. New site operators should also be provided with continuous on-the-job training during the first year of performance.

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Tables

Table 3-1. Clingmans Dome Monthly Mean Cloud Frequency Summary

Clingmans D	Clingmans Dome (CLD303)														
		1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	Mean ¹
May	Cloud Frequency*				81.78%			31.07%	47.17%	34.50%	91.67%				37.58%
	Cloud-Hours**				82			560	742	742	360				
	Completeness				11%			75%	100%	100%	48%				
June	Cloud Frequency*				61.63%	48.58%	41.38%	49.72%	43.33%	43.47%	54.61%	67.89%	54.93%	23.62%	47.37%
	Cloud-Hours**				172	422	667	543	720	720	661	387	390	163	
	Completeness				24%	59%	93%	75%	100%	100%	92%	79%	99%	96%	
July	Cloud Frequency*		29.47%	46.64%	34.34%	55.42%	44.75%	41.67%	57.08%	49.06%	42.78%	56.66%	40.50%	15.50%	44.01%
	Cloud-Hours**		285	298	661	720	733	336	685	693	734	370	290	97	
	Completeness		38%	40%	89%	97%	99%	45%	92%	93%	99%	88%	96%	84%	
August	Cloud Frequency*		49.44%		41.49%	71.43%	24.93%	43.45%	67.84%	28.02%	42.58%	46.64%	30.63%	50.87%	41.56%
	Cloud-Hours**		710		617	7	742	702	541	721	357	347	223	264	
	Completeness*		95%		83%	1%	100%	94%	73%	97%	48%	100%	98%	65%	
September	Cloud Frequency*	32.41%	30.37%		33.18%	43.93%	27.65%	50.65%	37.78%	51.60%	39.74%	47.18%	12.92%	50.42%	39.17%
	Cloud-Hours**	395	349		639	387	622	689	360	624	609	334	89	363	
	Completeness	55%	48%		93%	54%	86%	96%	50%	87%	85%	98%	96%	100%	
October	Cloud Frequency*	40.27%		23.64%	35.52%	30.32%		5.98%	41.72%			48.56%	46.91%	32.65%	34.59%
	Cloud-Hours**	663		330	563	696		562	338			287	296	159	
	Completeness	89%		44%	76%	94%		76%	46% [¥]			79%	85%	66%	
November	Cloud Frequency*				59.7%										
	Cloud-Hours**				67										
	Completeness				9%										

^{*} Cloud frequency is not used in subsequent analyses if the completeness criterion of 70 percent is not met. Monthly deposition estimates for 2003 and August 2006 were exceptions.

** Number of records where LWC > 0.05 g/m³

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

The average cloud frequency values are calculated only from those annual values that meet the completeness criterion.

Table 3-2. Summary Statistics for Cloud Water Samples (Clingmans Dome, TN) 2006

2006											
	Total Records Accepted = 45										
	n	mean	std dev	min	max						
LWC	19	0.25	0.09	0.11	0.43						
pH - Field	45	3.40	3.54	2.92	4.89						
pH - Lab	45	3.68	3.82	3.26	4.78						
Cond - Field	44	104.06	68.98	5.90	262.00						
Cond - Lab	45	126.96	82.97	9.30	319.00						
H⁺- Field	45	395.84	287.49	12.88	1202.26						
H⁺- Lab	45	211.37	150.82	16.60	549.54						
NH ₄	45	200.92	172.60	2.66	786.60						
SO_4^2	45	347.45	246.32	20.80	1022.24						
\mathbf{NO}_{3}^{\cdot}	45	120.42	82.36	8.14	331.27						
Ca ²⁺	45	47.93	56.62	0.78	253.81						
$\mathbf{Mg}^{^{2+}}$	45	12.44	14.23	0.27	57.57						
$\mathbf{Na}^{\scriptscriptstyle +}$	45	15.86	26.51	0.22	127.07						
\mathbf{K}^{+}	45	5.14	4.14	0.60	26.05						
Cl ⁻	45	17.83	22.11	0.68	132.01						
Cations - Field	45	678.12	339.43	30.36	1590.18						
Cations - Lab	45	493.66	342.53	31.70	1477.17						
Anions	45	485.70	330.03	31.43	1378.27						

All units are μ eq/L except for LWC (g/m³), 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
- If either or both of the cation or anion sums were greater than 100 μ eq/L, then the RPD criterion was \leq 25 percent for a record to be accepted.
- (3) max maximum
 - min minimum
 - 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 for CLD303, TN

Year	Total Number of Samples	Number of Samples Accepted	Percent Accepted
1994*	14	9	64
1995*	142	136	96
1996*	122	105	86
1997*	334	324	97
1998*	341	269	79
1999*	174	174	100
2000**	104	102	98
2001***	73	70	96
2002***	75	65	87
2003***	78	78	100
2004***	73	73	100
2005***	64	63	98
2006***	45	45	100
Total	1639	1513	92%

Note:

Table 3-4. Summary Statistics of Major Ion and Calcium Concentrations ($\mu eq/L$) of Cloud Water Samples for Clingmans Dome 1994-2006

	$\mathbf{H}^{^{+}}^{*}$	$\mathbf{NH}_{4}^{^{+}}$	SO_4^{2-}	NO ₃	Ca ²⁺
Mean	332.15	223.64	416.35	171.84	47.92
Minimum	0.54	0.71	3.54	0.29	0.15
Maximum	2137.96	1650.01	3686.91	1342.88	1051.89
Median	251.19	175.71	318.70	135.09	24.90

Note:

^{*} Hourly samples — sample collection bottle changed every hour.

^{**} Hourly + bulk samples (62 hourly and 42 bulk samples in year 2000)

^{***} Bulk samples — sample collection bottle changed every 24 hours.

^{*} Laboratory pH data instead of field pH data were used for calculating the 2001, 2002, and 2006 hydrogen values.

Table 4-1. Cloud Water Monthly Deposition Estimates Produced by the CLOUD Model (kg/ha)^a at Clingmans Dome

Year	Month	$\mathbf{H}^{^{+}}$	SO ₄ ²	NO ₃	NH ₄	Ca ²⁺	H ₂ O (cm)
1994	October	0.04	3.90	2.30	1.05	0.24	6.42
1995	August	0.13	9.33	4.96	1.67	0.35	9.83
	July	0.23	14.13	6.87	3.03	0.54	5.54
1997	August	0.24	14.16	8.37	3.04	0.69	8.74
1997	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
1990	October	0.22	11.79	9.83	3.02	0.78	9.10
	June	0.61	30.31	15.90	6.36	0.76	20.27
1999	July	0.88	39.79	18.75	4.67	1.57	7.80
1999	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
	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
2000	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
	May	0.09	8.19	6.72	2.83	0.64	5.01
2001	June	0.28	18.84	18.92	3.87	3.53	9.34
2001	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
	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
2002	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
	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
2003	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
	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
2004	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
	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
2005	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
	June	0.04	2.92	1.37	0.71	0.17	3.72
2006	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

Note:

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

Table 4-2. Cloud Water Mean Monthly (May – September) Deposition Rates for Several Ions (kg/ha/month) and Water at Clingmans Dome, TN

	Water				NO:	C 2+
Year	(cm/month)	$\mathbf{H}^{\scriptscriptstyle +}$	NH ₄ ⁺	SO ₄ ²	NO ₃	Ca ²⁺
1995-98	8.1	0.23	3.0	14.3	7.7	0.54
1999*	11.0	0.47	3.6	22.7	11.5	0.93
2000	9.7	0.29	3.0	16.9	8.8	0.68
2001	8.6	0.31	3.3	18.4	12.5	1.28
2002	9.2	0.18	2.3	11.9	6.1	0.56
2003	10.5	0.14	1.8	9.3	4.7	0.53
2004**	10.6	0.27	2.1	11.5	4.8	0.36
2005**	8.7	0.12	1.5	7.8	3.5	0.37
2006***	5.2	0.18	2.2	12.6	3.7	0.33

Note:

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

Year	$\mathbf{H}^{\scriptscriptstyle{+}}$	$\mathbf{NH}_{4}^{^{+}}$	\mathbf{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	1.40	12.76	77.87	39.80	2.84
2001	1.47	13.76	83.69	55.79	5.78
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

Note

^{*} June through September

^{**} June through October

^{***} June through August

^{*} 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 (GRS420) Ambient Concentrations (μg/m³) – June through October 2006

	-					Teflo	n®				Nyl	on	Cellulose					
Sample Number	On Date/Time	Off Date/Time	SO ₄ ²	NO ₃	NH ⁺ ₄	Ca ²⁺	$\mathbf{Mg}^{^{2+}}$	Na⁺	$\mathbf{K}^{\scriptscriptstyle{+}}$	Cl ⁻	SO ₄ ²	HNO ₃	SO ₂	Total SO ₂	Total NO ₃	Comment Codes*	Valid Hours	Actual Volume
0622001**	05/30/06 11:10	0 06/6/06 11:46	6.860	0.029U	1.933	0.149	0.030	0.041	0.069	0.017U	0.795	1.762	1.906	2.436	1.763		168	30.190
0623001	06/6/06 12:00	06/13/06 12:05	6.972	0.474	2.096	0.522	0.080	0.028	0.106	0.016U	0.932	2.569	3.656	4.277	3.002		169	30.395
0624001	06/13/06 12:1	5 06/20/06 10:53	8.743	0.122	2.723	0.265	0.060	0.125	0.069	0.017U	0.603	1.764	2.919	3.321	1.859		166	29.842
0625001	06/20/06 12:4	5 06/27/06 11:53	5.545	0.037	1.629	0.183	0.035	0.050	0.068	0.017U	0.962	1.630	2.068	2.710	1.642		167	30.029
0626001	06/27/06 11:58	8 07/4/06 9:06	8.565	0.115	2.770	0.479	0.057	0.026	0.104	0.017U	0.803	2.277	4.744	5.279	2.356		166	29.876
0627001	07/4/06 9:09	07/11/06 13:00	7.704	0.029U	2.044	0.136	0.030	0.041	0.110	0.016U	0.920	1.645	2.860	3.474	1.647		172	30.921
0628001	07/11/06 13:0	5 07/18/06 11:52	6.636	0.030U	1.860	0.138	0.040	0.123	0.084	0.017U	0.845	1.534	2.260	2.824	1.539		166	29.867
0629001	07/18/06 12:00	0 07/25/06 11:40	7.668	0.029U	1.998	0.150	0.028	0.031	0.071	0.017U	0.768	1.664	1.424	1.937	1.667		168	30.229
0630001	07/25/06 12:00	0 08/1/06 12:00	5.694	0.029U	1.200	0.345	0.084	0.208	0.085	0.016U	0.595	1.750	1.356	1.753	1.751		169	30.398
0631001	08/1/06 12:00	08/8/06 11:53	8.944	0.152	2.066	0.447	0.112	0.269	0.101	0.017U	0.812	2.122	3.191	3.733	2.241		168	30.221
0632001	08/8/06 11:53	08/15/06 11:55	6.465	0.029U	1.505	0.145	0.041	0.126	0.059	0.017U	0.831	1.601	2.716	3.270	1.605		166	30.211
0633001	08/15/06 12:00	0 08/22/06 11:50	11.180	0.029U	2.578	0.165	0.035	0.062	0.079	0.017U	1.026	2.142	2.795	3.479	2.137		168	30.214
0634001	08/22/06 12:1	5 08/29/06 11:12	10.168	0.030U	2.342	0.171	0.038	0.074	0.076	0.017U	0.672	1.742	2.134	2.583	1.744		167	30.014
0635001	08/29/06 11:2	7 09/5/06 11:52	4.847	0.048	1.074	0.077	0.019	0.040	0.061	0.017U	0.503	1.367	1.052	1.388	1.394		168	30.203
0636001	09/5/06 12:06	09/12/06 11:55	9.579	0.107	2.513	0.142	0.026	0.054	0.088	0.017U	0.580	1.743	1.758	2.145	1.822		167	30.003
0637001	09/12/06 12:18	8 09/19/06 12:00	6.611	0.029U	1.572	0.103	0.019	0.037	0.058	0.017U	0.549	1.523	1.735	2.101	1.528		168	30.194
0638001	09/19/06 12:13	3 09/26/06 12:01	3.979	0.029U	1.045	0.201	0.033	0.063	0.068	0.017U	0.444	1.434	2.413	2.709	1.440		168	30.208
0639001	09/26/06 12:09	9 10/3/06 11:57	3.826	0.121	1.162	0.269	0.030	0.022	0.066	0.017U	0.619	1.708	4.122	4.535	1.802		167	30.032
0640001	10/3/06 12:05	10/10/06 9:51	4.498	0.060	1.250	0.146	0.028	0.083	0.054	0.017U	0.528	1.797	2.535	2.887	1.828		165	29.680
0641001	10/10/06 9:55	10/17/06 17:23	1.611	0.155	0.428	0.231	0.029	0.036	0.047	0.016U	0.326	1.436	2.423	2.641	1.568		172	31.656
0642001	10/17/06 17:3	1 10/24/06 13:08	2.624	0.092	0.834	0.082	0.015	0.014	0.036	0.017U	0.417	1.347	3.177	3.456	1.418		160	29.473
0643001	10/24/06 13:30	0 10/31/06 13:40	1.852	0.098	0.530	0.209	0.035	0.026	0.044	0.017U	0.330	2.205	4.275	4.495	2.268		168	30.240
		Mean	6.390	0.085	1.689	0.216	0.041	0.072	0.073	0.017	0.676	1.762	2.615	3.065	1.819			
		Standard Deviation	2.631	0.098	0.689	0.126	0.024	0.064	0.020	0.000	0.206	0.317	0.968	0.985	0.379			

Data Status Flags:

U = Value is less than detection limit

^{*} No comments are associated with the comment code column

^{**} Original sample numbers within the MACTEC laboratory information management system contain the suffix "-39" to indicate that the sample was collected from the GRS420, TN site.

Table 5-2. Great Smoky Mountains National Park (GRS420) Dry Deposition Fluxes (kg/ha) Report for the 2006 Deposition Season

(June through September)

	(UUIII UIII U	agn septem		F	luxes (kg/ha)		Deposit	tion Velocities	(cm/sec)
Sample Number	On Date	Off Date	SO ₂	HNO ₃	SO ₄ ²	NO ₃	$\mathbf{NH}_{4}^{^{+}}$	SO ₂	HNO ₃	Particle
0622001*	5/30/06	6/6/06	0.053	0.196	0.056	0.000	0.016	0.388	1.974	0.146
0623001	6/6/06	6/13/06	0.089	0.270	0.060	0.004	0.018	0.377	1.909	0.156
0624001	6/13/06	6/20/06	0.054	0.187	0.066	0.001	0.020	0.291	1.890	0.135
0625001	6/20/06	6/27/06	0.033	0.118	0.030	0.000	0.009	0.222	1.311	0.098
0626001	6/27/06	7/4/06	0.084	0.167	0.050	0.001	0.016	0.288	1.332	0.106
0627001	7/4/06	7/11/06	0.065	0.168	0.058	0.000	0.015	0.337	1.826	0.135
0628001	7/11/06	7/18/06	0.054	0.154	0.048	0.000	0.014	0.346	1.816	0.131
0629001	7/18/06	7/25/06	0.032	0.140	0.046	0.000	0.012	0.303	1.533	0.110
0630001	7/25/06	8/1/06	0.028	0.118	0.028	0.000	0.006	0.295	1.223	0.090
0631001	8/1/06	8/8/06	0.050	0.136	0.043	0.001	0.010	0.245	1.166	0.088
0632001	8/8/06	8/15/06	0.046	0.105	0.031	0.000	0.007	0.255	1.177	0.087
0633001	8/15/06	8/22/06	I	ı	ı	I	I	I	ı	I
0634001	8/22/06	8/29/06	0.041	0.147	0.059	0.000	0.013	0.288	1.528	0.104
0635001	8/29/06	9/5/06	0.028	0.106	0.024	0.000	0.005	0.362	1.391	0.088
0636001	9/5/06	9/12/06	0.043	0.128	0.048	0.001	0.013	0.360	1.310	0.090
0637001	9/12/06	9/19/06	0.047	0.165	0.045	0.000	0.011	0.397	1.917	0.119
0638001	9/19/06	9/26/06	0.059	0.181	0.029	0.000	0.008	0.384	2.209	0.127
0639001	9/26/06	10/3/06	0.088	0.151	0.022	0.001	0.007	0.345	1.553	0.103
	Total S	easonal Flux	0.949	2.792	0.788	0.011	0.212			
	Mean Seasona	al Deposition						0.322	1.592	0.113

Data Status Flags: I = Invalid filter pack data

Note: MLM simulations were performed for each 24-hour period from 0800 on the On Date to 0800 on the Off Date.

^{*} Original sample numbers within the MACTEC laboratory information management system contain the suffix "-39" 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 2000 – 2006)

		Total Sulfur ¹	Total NO ₃ -N	Total NH ₄ -N	Total Nitrogen ²
	Year	(kg/ha)	(kg/ha)	(kg/ha)	(kg/ha)
	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
Cloud Water	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
	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
Dry	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

Note:

Season is defined from June through September

¹ Total sulfur deposition includes SO₄² in cloud water plus ambient SO₂ and SO₄²

² Total nitrogen deposition includes NO₃ and NH₄ in cloud water plus ambient NO₃, NH₄, and HNO₃

^{*} Values for 2005 and 2006 were obtained from the Great Smoky Mountains National Park (GSR420) site at Look Rock, TN

Figures

Figure 3-1. Monthly Cloud Frequency (1994 – 2006) Clingmans Dome, TN

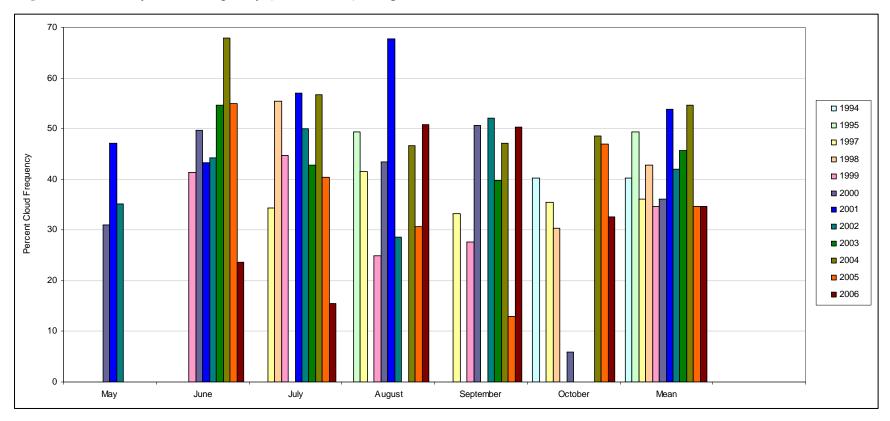


Figure 3-2. Monthly Mean Liquid Water Content (g/m³) of Clouds (1994 – 2006) Clingmans Dome, TN

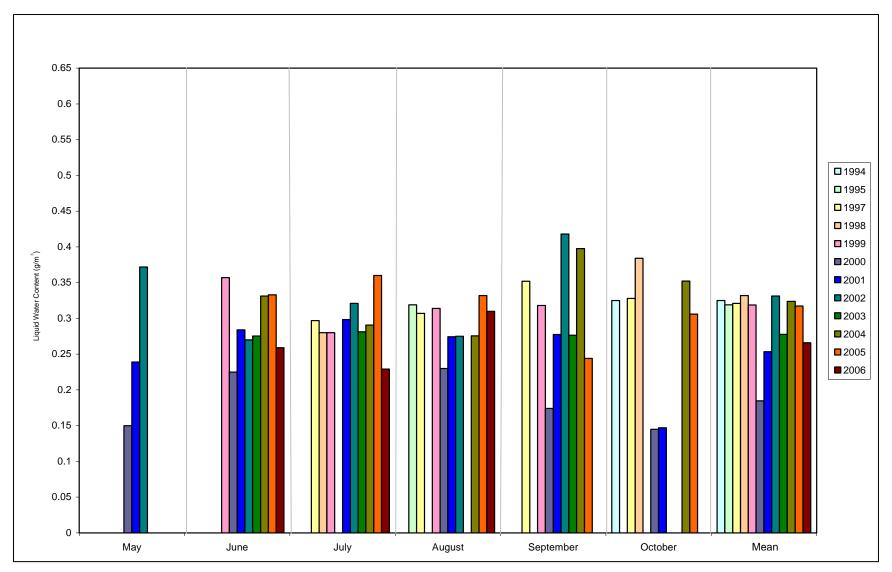


Figure 3-3. Monthly Mean Liquid Water Content (g/m³) 2006 versus Historical Mean Values (1994-2005)

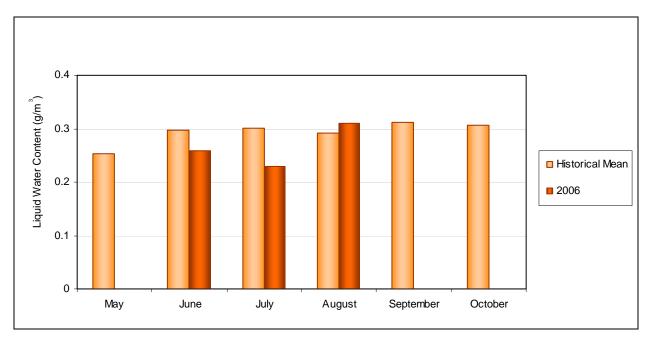


Figure 3-4. Frequency Distribution for Cloud Water pH (Laboratory) at Clingmans Dome, TN (2006)

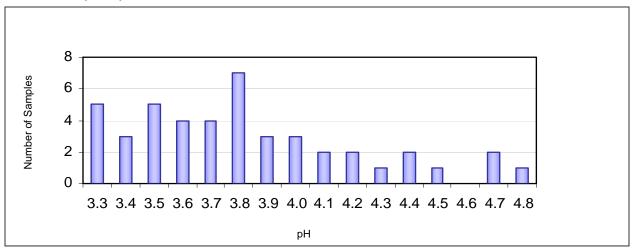


Figure 3-5. Frequency Distribution for Cloud Water pH (Field) at Clingmans Dome, TN (2006)

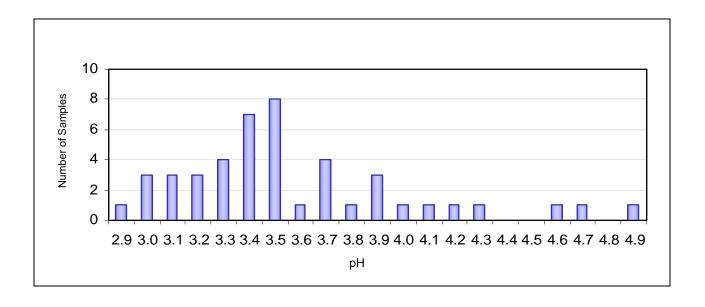
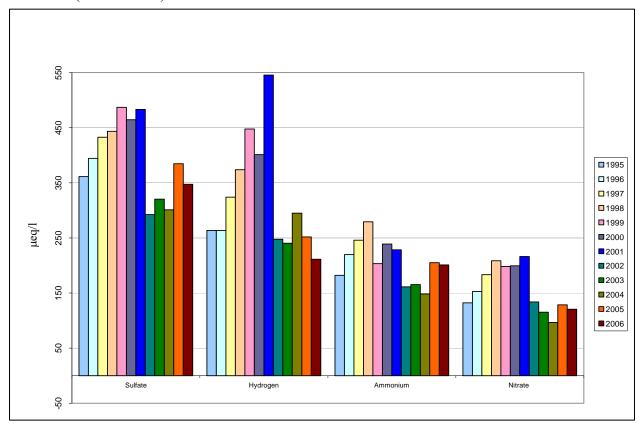
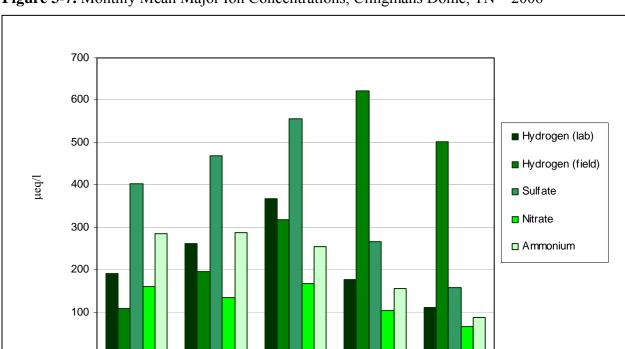


Figure 3-6. Mean Major Ion Concentrations of Cloud Water Samples, Clingmans Dome, TN (1995-2006)



June

July



August

September

October

Figure 3-7. Monthly Mean Major Ion Concentrations, Clingmans Dome, TN – 2006

Figure 3-8. Mean Minor Ion Concentrations of Cloud Water Samples (Cations and Chloride) Clingmans Dome, TN (1995 – 2006)

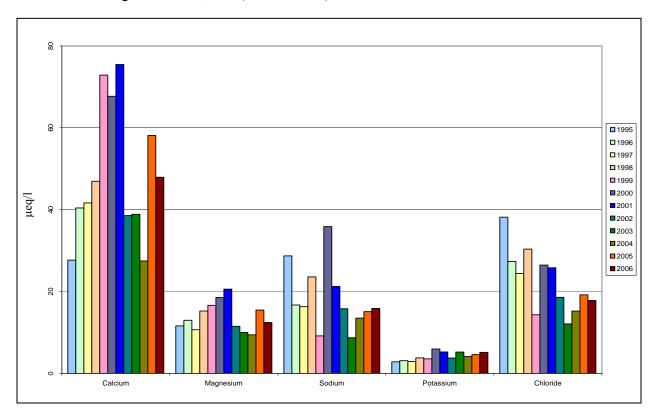
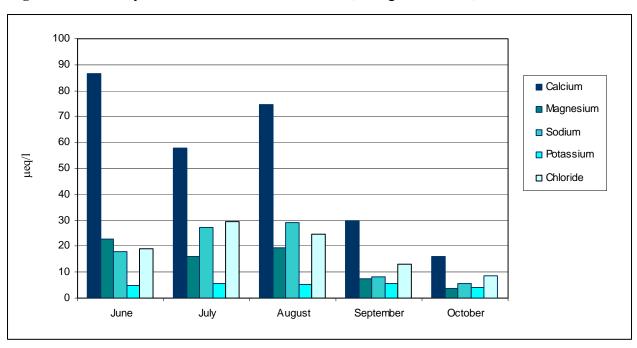


Figure 3-9. Monthly Mean Minor Ion Concentrations, Clingmans Dome, TN – 2006



45 4 ■ 1999 ■ 2000 35 **2001** 30 ■ 2002 ■ 2003 25 ■ 2004 ■ 2005 20 ■ 2006 15 10

July

Aug

 NO_3

Figure 4-1. Monthly Deposition Estimates – CLOUD Model (SO₄, NO₃, NH₄)

Note:

May 2003 data represent May 17-31, 2003 only. August 2003 had only 48 percent completeness. August 2006 had only 65 percent completeness.

Aug

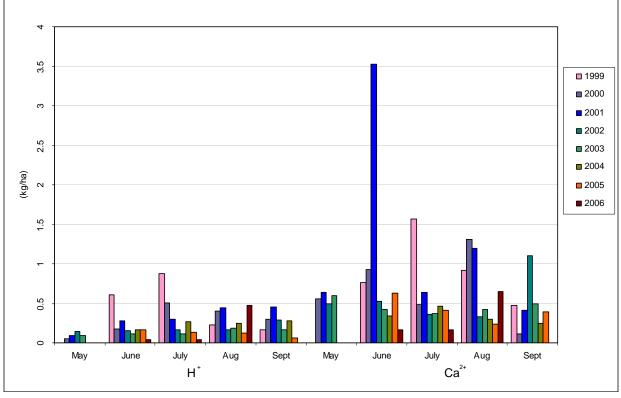
Sept

July

 SO_4^{2-}

 NH_4^{\dagger}

Figure 4-2. Monthly Deposition Estimates – CLOUD Model (H⁺, Ca²⁺)



Note:

May 2003 data represent May 17-31, 2003 only. August 2003 had only 48 percent completeness. August 2006 had only 65 percent completeness.

Figure 5-1. Total Sulfur and Nitrogen Cloud Water and Dry Deposition Estimates for Clingmans Dome (June – September) 2000 through 2006

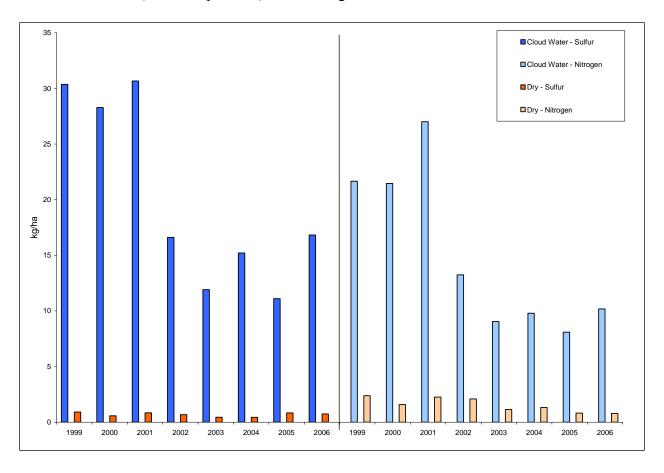
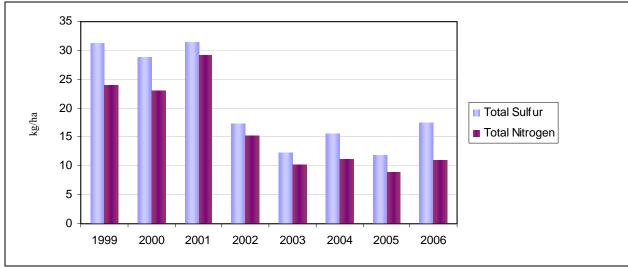


Figure 6-1. Total Sulfur and Nitrogen Deposition Estimates (Dry and Cloud Components) for 2000 through 2006



Appendix A

Cloud Water Deposition to Clingmans Dome in 2006

Cloud Water Deposition to Clingmans Dome in 2006

Report to MACTEC by

MACTEC Purchase/Work # 60060076G

Gary M. Lovett
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Report Date: February 18, 2007

Introduction

This brief report accompanies the Excel spreadsheet CLD 2006.xls, which gives the results of the cloud water deposition modeling for the Clingmans Dome (CLD303) site for the field season of 2006. Raw chemical concentration, meteorological, and cloud frequency data were provided to me by MACTEC (Selma Isil). I ran the CLOUD model (Lovett 1984) on these data to estimate cloud water deposition to this site.

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 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, only gross deposition rate was required so the evaporation routine was not invoked.

The 2006 data set covered the period June-October 2006. Two sampling dates (August 3 and August 7) were excluded from this analysis because there were no wind speed, cloud liquid water content or event duration data, thus deposition rates and duration-weighted mean concentrations could not be calculated. Excluding those two samples, there were 43 sample periods. All months had sampling completeness values greater than 75%, except August (69.8%) and October (65.5%).

The calculations done here for 2006 followed closely those done previously for the Clingmans Dome (e.g., Lovett 2006). After the model was run for all sample periods, seasonal and monthly means and totals were calculated in a SAS program. I calculated total seasonal deposition by summing the five monthly totals.

As in previous results, these model runs were made assuming a 10-m tall, intact, homogeneous conifer canopy. The actual canopy structure at Clingmans Dome has not been quantified, but I have observed that there are many dead trees at that site, and those still alive are generally taller than 10m. Consequently, this deposition estimate is best viewed 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 the same "standard" canopy were present at each site and time.

Because the measurement periods vary in length, I weighted all the means presented here by the duration of the sampling event. In this way, when calculating seasonal and monthly means, I avoid giving the same weight to a 10-minute event as I do to a 10-hour event.

Results

The model was run on 43 time periods as discussed above, and the results are presented as deposition velocities and deposition fluxes in the CLD 2006.xls spreadsheet and in Appendix I.

The period of measurement was June - October 2006. 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 all ions were highest in July and August (Fig. 1).

Seasonal mean concentrations (duration weighted) of these ions in 2006 continued trends seen from the last few years. Beginning in 1997 there was a general decline in hydrogen ion, sulfate, nitrate and ammonium ion concentrations, but since 2003 hydrogen ion and nitrate appear to have leveled off while sulfate and ammonium are showing consistent increases (Fig. 2). The pH trends (or lack thereof) 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. For these 2006 data we used exclusively lab pH values because of concerns about the quality of the field pH measurements. In previous years, primarily field pH values have been used.

Note that the trends shown in Figure 2 are based on duration-weighted mean concentrations and represent only those data used for modeling cloud water deposition (i.e. those events for which liquid water content and wind speed were also measured). These trends may not match other calculations of trends if more complete chemistry datasets or non-duration-weighted means are used.

Subtle variation in mean wind speed from month to month can cause substantial differences in cloud water deposition velocity. In September and October 2006, relatively high mean wind speeds are associated with high calculated deposition velocities (Figure 3). The high deposition velocities in September and October also reflect higher estimated cloud droplet diameters for those months. In the model, the mean of the droplet diameter distribution is estimated from the cloud liquid water content (LWC) using an empirical relationship from the cloud physics literature. Cloud LWC measurements for September and October are quite high (see next paragraph), which would lead to high estimated droplet diameters as well. The high deposition velocities lead in turn to high calculated deposition rates for cloud water and for some ions (e.g., chloride and potassium) for those months. For other ions (e.g., sulfate) lower

concentrations in September in October partially offset the higher water deposition rates, so that the highest deposition rates were in August (Appendix I, Table I-3).

Mean duration-weighted deposition velocity for the 2006 season was 23.4 cm/s. The overall mean LWC for the season was 0.61 g/m³, well above the 1995-2006 mean of 0.35 g/m³. The high mean LWC is a result of consistently high LWC measurements from August 31 through September and November, which are reflected in the September and October mean LWC values (Figure 4). It is unclear whether this late-season increase is a real phenomenon or was a result of instrument or operator error, consequently I advise interpreting the LWC results (and consequently the calculated deposition rates) with caution.

Seasonal deposition totals were calculated by summing the values across all five months. For comparison with the results of the previous reports, I express these in Table 1 as the mean monthly deposition rate in kg/ha/month. Cloud water deposition rate in 2006 was the highest yet recorded for this site, leading to the highest ion deposition rates (hydrogen ion, sulfate, nitrate and ammonium) since 2002 (Table 1).

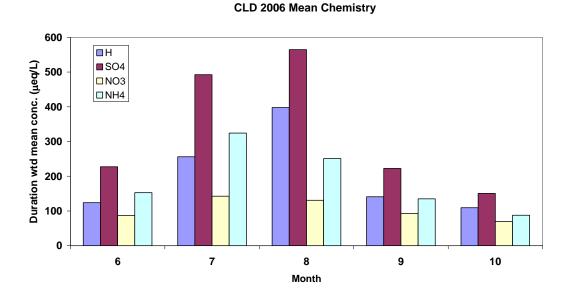


Figure 1. Duration-weighted mean concentration of four ions in cloud water, calculated by month.

Trends in Ion Concentrations, Clingmans Dome

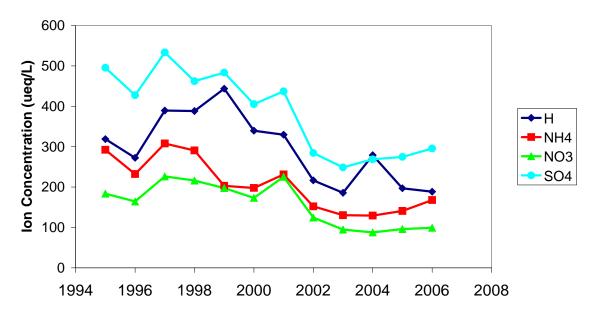


Figure 2. Trends in ion concentrations at Clingmans Dome, 1995-2006. Data are duration-weighted means for the warm season and include only the samples for which deposition was modeled (i.e. LWC and meteorological data were also present).



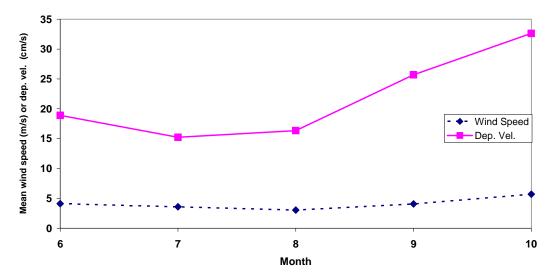


Figure 3. Mean wind speed and deposition velocity for each month.

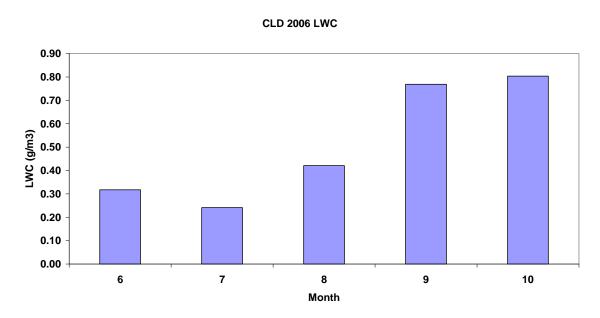


Figure 4. Mean liquid water content for each month of the study.

Table 1. Mean monthly deposition rates for several ions (in kg/ha/month) and water (cm/month) for the Clingmans Dome site for the 1995-2006 period. The seasonal averages include the months of June-October for 2004-2006 and May-September for previous years.

	Water	H^{+}	NH ₄	SO_4	NO ₃
CLD 2006	13.0	0.22	3.1	15.5	6.8
CLD 2005	8.7	0.12	1.5	7.8	3.5
CLD 2004	10.6	0.27	2.1	11.5	4.8
CLD 2003	10.5	0.14	1.8	9.3	4.7
CLD 2002	9.2	0.18	2.3	11.9	6.1
CLD 2001	8.6	0.31	3.3	18.4	12.5
CLD 2000	9.7	0.29	3.0	16.9	8.8
CLD 1999	11.0	0.47	3.6	22.7	11.5
CLD 1995-98	8.1	0.23	3.0	14.3	7.7

Literature Cited

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Appendix I.

Table I-1. Monthly mean meteorological and deposition variables. All means are duration-weighted. TUBFLUX, SEDFLUX and TOTFLUX are turbulent, sedimentation and total water fluxes ($g/cm^2/min$) 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	OBC	DURATION	VOLUME	We	LWC	TURBFLUX	SEDFLUX	TOTELLIV	TURB	SED	TOT
MONTH	OBS	DURATION	VOLUME	WS	LVVC	TURBFLUX	SEDFLUX	TOTFLUX	VD	VD	VD
6	7	10.69	1059.04	4.11	0.317	0.000230	0.000134	0.000365	12.27	6.62	18.89
7	8	8.60	864.78	3.57	0.241	0.000141	0.000086	0.000226	9.38	5.85	15.23
8	5	17.01	4623.05	3.04	0.421	0.000224	0.000231	0.000455	8.37	7.98	16.35
9	14	15.33	7363.71	4.06	0.769	0.000683	0.000547	0.001231	14.12	11.58	25.70
10	9	14.09	7342.66	5.70	0.803	0.000974	0.000578	0.001551	21.26	11.37	32.63

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

Month	H (field)	Ca	Mg	K	Na	NH4	SO4	NO3	Cl
6	123.94	39.30	11.37	3.05	10.74	152.69	227.40	86.68	10.55
7	256.11	54.03	15.97	5.61	28.32	324.41	492.60	142.57	29.56
8	397.74	41.29	9.68	4.43	9.42	251.11	564.58	130.98	14.17
9	141.12	30.12	7.11	5.43	7.56	134.99	222.44	92.67	10.91
10	109.20	15.26	3.73	3.67	6.24	87.66	150.55	69.38	9.23

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

Month	HDEP	KDEP	NADEP	CADEP	MGDEP	NH4DEP	SO4DEP	NO3DEP	CLDEP	H2ODEP
6	0.04	0.03	0.08	0.17	0.03	0.71	2.92	1.37	0.11	3.72
7	0.04	0.04	0.10	0.16	0.03	1.07	4.05	1.47	0.16	1.57
8	0.47	0.17	0.17	0.65	0.10	4.81	30.62	8.16	0.50	10.32
9	0.33	0.52	0.39	1.78	0.23	6.13	25.96	14.96	0.92	26.81
10	0.22	0.32	0.26	0.55	0.09	2.94	13.88	8.19	0.64	22.61

Appendix B Cloud Water Data and QC Summary

Cloud Water Data and QC Summary

Analytical data for the 45 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, 2005a). 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 outside laboratory supplies these reference samples with a certificate of analysis stating the target values. A reference sample is analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the calibration curve. The QC limits require the measured value to be within \pm 5 percent of the known value for anions, within \pm 10 percent of the known value for cations, and within \pm 15 percent of the known value for conductivity. For pH, the QC limits require the measured value to be within \pm 0.05 pH units of the known value. The data from all required reference samples analyzed with the Clingmans Dome samples are within the CASTNET QC criteria.

The results of the analyses of the CVS for each parameter in each analytical batch are provided in Table B-3. A CVS is a NIST traceable solution supplied in a matrix similar to that of the sample being analyzed with a target value at approximately the midpoint of the calibration curve. This QC solution is supplied to MACTEC by an outside laboratory independent of the laboratory supplying the reference sample solution. A CVS is analyzed after every 10 environmental samples to verify that the instrument calibration has not drifted more than \pm 5 percent for anions and base cations, \pm 10 percent for NH $_4^+$, \pm 0.05 pH units for pH, and \pm 15 percent for conductivity. The results of all CVS analyses were within acceptance criteria.

Table B-4 summarizes the percent difference between samples reanalyzed within the same analytical batch. Five percent of the samples in each analytical batch were randomly selected for replicate analysis. This table presents only the samples that were replicated. The replicate percent difference criteria are \pm 5 percent for anions and base cations, \pm 10 percent for NH $_4^+$, and \pm 15 percent for conductivity for samples with concentrations greater than five times the analytical detection limit. For samples with lower concentrations, the difference between the two values cannot be more than the analytical detection limit. For pH, the difference between the two values cannot be more than \pm 0.05 pH units. The data from all required replicate samples are within the CASTNET QC criteria.

Table B-1. Cloud Deposition 2006 Sampling Season – Clingmans Dome, TN (1 of 2)

Number	Sample Date	alid Hours	olume mL	WC g/m³	Scalar Wind m/sec	H Field	I Lab	Cond. Field	Ca²⁺ mg∕L	Mg²+ mg/L	a⁺ mg/L	mg/L	NH¹,mg/L	SO⁴² mg/L	NO; mg/L	l'mg/L	Field Cation μeq/L	Lab Cation μeq/L	Anion µeq/L	Field Cation/ Anion	Lab Cation/ Anion
Ź	Sa	Š	>	<u> </u>	Sc n	Hd	Hd	చ		Σ	Za	×	Z	S	ž	<u></u> 5	E an	L H	Ā	Ę 4	P. L.
1	6/2/2006	12.8	1824	0.425	2.44	3.91	3.89	92.1	0.3765	0.0718	0.2316	0.1044	2.2346	11.50	0.986	0.314	320.004	325.802	318.675	0.42	2.21
2	6/3/2006	15.1	1121	0.337	5.48	4.89	4.48	18.7	0.0291	0.0091	0.0060	0.0264	0.2008	1.52	0.209	0.024	30.356	50.586	47.244	-43.53	6.83
3	6/1/2006	1.2	73	0.136	1.20	3.91	3.90	103.1	1.3886	0.1905	0.0822	0.1815	3.2162	14.50	1.910	0.337	445.832	448.697	447.750	-0.43	0.21
4	6/5/2006	2.1	274	0.265	3.15	4.59	4.09	119.5	5.0860	0.5654	0.1001	0.2667	4.6641	22.50	3.780	0.600	670.196	725.775	755.231	-11.93	-3.98
5	6/13/2006	4.1	165	0.113	3.43	3.62	3.57	155.4	1.9122	0.3876	0.0936	0.3161	4.4157	21.70	2.710	0.484	694.611	723.881	658.912	5.27	9.40
6	6/18/2006	3.4	179	0.233	5.90	4.19	3.65	124.7	0.8051	0.2646	1.4454	0.1606	2.3026	14.50	1.680	1.480	357.884	517.191	463.570	-25.73	10.93
7	6/17/2006	1.3	107	0.150	6.25	3.75	3.32	NA	2.5509	0.4363	0.9359	0.3139	11.0178	49.10	4.410	1.460	1176.367	1477.169	1378.265	-15.81	6.93
8	7/6/2006	3.9	420	0.223	2.37	3.44	3.40	213.2	0.7086	0.1550	0.3787	0.2861	3.7647	28.40	1.520	0.693	703.760	738.789	719.339	-2.19	2.67
9	7/5/2006	11.1	645	0.229	2.31	3.72	3.76	89.1	0.3651	0.0908	0.1141	0.0922	0.6486	10.50	0.569	0.186	269.864	253.098	264.474	2.02	-4.40
10	7/11/2006	6.1	1150	0.339	5.16	3.45	3.42	219.0	0.4319	0.0970	0.3503	0.2577	7.2186	31.90	1.990	0.745	921.540	946.916	827.229	10.79	13.49
11	7/12/2006	11.5	1363	0.234	4.05	3.41	3.54	262.3	0.8638	0.1815	0.8207	0.3091	10.2966	36.70	3.500	0.943	1225.804	1125.162	1040.552	16.35	7.81
12	7/20/2006	4.1	660	0.260	3.13	4.34	3.82	74.3	0.6750	0.0863	0.0985	0.0935	1.7715	9.55	1.310	0.206	219.644	325.292	298.163	-30.33	8.70
13	7/22/2006	9.8	820	0.245	3.70	3.95	3.45	198.0	0.8960	0.1348	0.0996	0.1331	3.7070	27.40	2.180	0.438	440.400	683.012	738.447	-50.57	-7.80
14	7/24/2006	6.6	668	0.197	4.05	4.68	4.29	98.5	3.9864	0.6617	2.9214	0.4211	2.3434	16.50	2.250	4.680	579.420	609.813	636.164	-9.34	-4.23
15	7/26/2006	1.0	147	0.110	4.53	4.05	3.52	150.7	1.3314	0.1661	0.2449	0.1328	2.4434	19.50	1.820	0.516	357.726	570.596	550.471	-42.45	3.59
16	8/3/2006	NA	411	NA	NA	3.52	3.51	180.0	4.0470	0.6996	2.2746	0.3406	3.1400	29.70	3.850	2.320	893.344	900.378	958.644	-7.05	-6.27
17	8/7/2006	NA	776	NA	NA	3.69	3.68	140.7	0.4237	0.0531	0.1602	0.0593	2.1016	14.00	1.140	0.213	388.213	392.969	378.870	2.44	3.65
18	8/29/2006	3.7	992	0.380	3.49	3.39	3.29	215.0	3.1470	0.4873	1.6566	0.3805	6.4792	38.70	4.640	1.830	1148.886	1254.367	1188.599	-3.40	5.38
19	8/20/2006	20.0	3863	0.282	2.66	3.46	3.46	129.1	0.6996	0.0909	0.1619	0.0852	3.0224	22.90	1.580	0.388	614.131	614.131	600.512	2.24	2.24
20	8/18/2006	16.0	2294	0.248	3.10	3.37	3.33	231.0	1.5050	0.1987	0.2778	0.2628	5.1297	36.20	2.440	0.631	903.067	944.223	945.664	-4.61	-0.15
21	8/22/2006	15.3	3929	0.355	3.49	3.67	3.75	69.1	0.2723	0.0517	0.0654	0.1698	1.1653	10.70	0.984	0.289	322.022	286.053	301.172	6.69	-5.15
22	9/5/2006 8/31/2006	8.0	5551 8715	 	3.58 2.92	3.54 3.48	3.76	58.5 52.3	0.2003	0.0394	0.0433 0.0612	0.1722 0.1521	0.7070	8.29	0.893 1.730	0.280 0.426	358.404	243.781	244.246	37.89	-0.19
23 24	9/1/2006	18.7 20.4	10000		2.30	3.40	3.26 3.79	179.0	0.3794 0.1418	0.0578 0.0307	0.0012	0.1054	4.0053 0.3798	35.00 6.34	0.816	0.420	647.327 716.749	865.736 202.847	864.209 196.148	-28.70 114.05	0.18 3.36
25	9/2/2006	19.4	8390		2.70	3.38	3.73	95.2	1.1904	0.1001	0.0288	0.1034	4.2702	18.10	2.380	0.416	798.198	567.537	558.484	35.34	1.61
26	9/3/2006	13.3	7920		3.11	3.69	3.73 4.17	35.2	0.5515	0.1521	0.0536	1.0186	1.6578	7.48	0.960	0.717	408.258	271.692	244.492	50.18	10.54
27	9/7/2006	8.9	6850	i	2.88	3.31	4.65	100.3	0.1993	0.0185	0.4313	0.0331	0.3447	1.86	0.300	0.089	527.647	60.255	60.582	158.80	-0.54
28	9/11/2006	13.6	6175	' 	4.03	3.50	4.03	69.3	1.1198	0.3091	0.0217	0.3682	3.0236	13.70	2.150	0.009	665.332	444.603	466.141	35.21	-4.73
29	9/14/2006	6.7	3278	i	3.97	3.24	3.64	99.2	0.2371	0.0435	0.3772	0.1254	2.8212	16.50	1.380	0.478	802.321	455.968	455.528	55.14	0.10
30	9/15/2006	4.5	4025	i	1.98	3.11	3.36	157.2	0.5027	0.0763	0.0773	0.2359	4.6122	29.00	2.240	0.474	1146.290	806.559	777.057	38.39	3.73
31	9/17/2006	6.4	2192	ı	4.43	3.28	3.74	88.8	0.4073	0.0822	0.3804	0.1359	2.9660	16.20	1.220	0.657	783.673	440.836	442.908	55.56	-0.47
32	9/18/2006	20.5	8452	i	3.82	3.04	4.68	10.9	0.0157	0.0033	0.0050	0.0234	0.1251	1.05	0.119	0.038	922.813	31.695	31.428	186.83	0.85
33	9/19/2006	15.2	6712	I	3.43	3.05	3.62	11.7	0.5356	0.0859	0.1522	0.1585	2.3170	17.30	1.510	0.346	1101.141	449.773	477.741	78.97	-6.03

Table B-1. Cloud Deposition 2006 Sampling Season – Clingmans Dome, TN (2 of 2)

Number	Sample Date	Valid Hours	Volume mL	LWC g/m³	Scalar Wind m/sec	pH Field	pH Lab	Cond. Field	Ca²⁺ mg∕L	$\mathbf{Mg}^{2^+}\mathbf{mg/L}$	Na⁺ mg/L	K⁺ mg/L	NH⁴mg/L	$\mathrm{SO}_4^2\mathrm{mg/L}$	NO; mg/L	Cl · mg/L	Field Cation μeq/L	Lab Cation μeq/L	Anion µeq/L	Field Cation/ Anion	Lab Cation/ Anion
34	9/22/2006	22.3	10000	I	9.42	3.03	4.39	27.8	0.9000	0.0679	0.0178	0.0775	1.3987	5.510	1.000	0.115	1086.369	193.853	189.353	140.630	2.35
35	9/23/2006	6.3	4558	1	5.60	2.92	3.28	209.0	1.3740	0.1670	0.2461	0.2301	4.0482	29.600	3.910	1.410	1590.179	912.722	935.178	51.870	-2.43
36	9/26/2006	9.7	4903	1	2.20	3.29	3.96	64.8	1.0476	0.0793	0.0816	0.1132	1.6143	8.680	1.400	0.272	693.360	290.147	288.337	82.510	0.63
37	10/1/2006	9.5	4833	1	6.31	3.03	3.83	57.8	0.1632	0.0321	0.1647	0.0766	1.1062	8.570	0.828	0.438	1032.139	246.795	249.891	122.030	-1.25
38	10/6/2006	5.7	3265	1	6.97	3.07	3.59	115.1	0.8170	0.1060	0.2000	0.3747	3.4764	21.500	2.080	0.526	1167.107	573.009	610.955	62.560	-6.41
39	10/8/2006	16.2	3271	1	8.38	3.20	3.76	94.3	0.8734	0.0966	0.3000	0.1277	2.2732	13.300	1.930	0.524	861.099	403.922	429.470	66.890	-6.13
40	10/11/2006	22.0	9147	1	3.60	3.29	3.92	55.4	0.2405	0.0607	0.2451	0.0995	1.9417	8.450	1.420	0.449	681.689	289.054	289.969	80.630	-0.32
41	10/17/2006	15.6	10000	1	4.11	3.47	4.43	12.2	0.0260	0.0041	0.0255	0.2010	0.0372	1.340	0.135	0.212	349.385	47.694	43.516	155.700	9.16
42	10/19/2006	6.1	8916	1	3.02	3.36	3.95	52.2	0.5640	0.0663	0.0711	0.1690	1.5503	8.960	1.230	0.170	588.213	263.899	279.152	71.260	-5.62
43	10/20/2006	6.7	5468	1	5.87	3.94	4.78	5.9	0.0955	0.0175	0.0481	0.1764	0.1734	0.999	0.114	0.176	140.004	41.785	33.902	122.020	20.83
44	10/22/2006	7.0	6780	1	4.27	3.47	4.19	19.5	0.0689	0.0104	0.0480	0.1293	0.2030	2.250	0.364	0.167	363.026	88.747	77.542	129.600	13.48
45	10/27/2006	14.6	10000	1	8.41	3.43	4.11	23.5	0.0693	0.0153	0.0266	0.0999	0.3058	3.040	0.365	0.111	401.797	107.886	92.481	125.160	15.38
					Volum	e Weigh	ted Mea	n	0.9600	0.1510	0.3650	0.2010	2.8140	16.689	1.687	0.632	678.124	493.660	485.703	40.609	2.225

Note:

NA = not available

I = invalid liquid water content

Table B-2. Cloud Deposition 2006 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples – Clingmans Dome, TN (1 of 3)

_		Lab pH		_	_	N	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
G100640	P126977*1	6.03	6.02	99.8	G100634	ERAP108505*1	1.038	1.0306	99.3	G100632	HP603026*1	10.1	10.20	101.0
G100640	P126977*2	6.03	6.03	100.0	G100634	ERAP108505*2	1.038	1.0345	99.7	G100632	HP603026*2	10.1	10.20	101.0
G100676	P126977*1	6.03	6.00	99.5	G100677	ERAP108505*1	1.038	1.0427	100.5	G100657	HP603026*1	10.1	10.00	99.0
G100676	P126977*2	6.03	6.01	99.7	G100677	ERAP108505*2	1.038	1.0373	99.9	G100657	HP603026*2	10.1	9.97	98.7
G100790	P126977*1	6.03	6.02	99.8	G100715	ERAP108505*1	1.038	1.0218	98.4	G100700	HP603026*1	10.1	10.20	101.0
G100790	P126977*2	6.03	5.99	99.3	G100715	ERAP108505*2	1.038	1.0256	98.8	G100700	HP603026*2	10.1	10.20	101.0
G100801	P126977*1	6.03	6.02	99.8	G100770	ERAP108505*1	1.038	1.0340	99.6	G100713	HP603026*1	10.1	10.20	101.0
G100801	P126977*2	6.03	6.01	99.7	G100770	ERAP108505*2	1.038	1.0354	99.7	G100713	HP603026*3	10.1	10.20	101.0
G100845	P126977*1	6.03	6.00	99.5	G100791	ERAP108505*1	1.038	1.0350	99.7	G100767	HP603026*1	10.1	10.20	101.0
G100845	P126977*2	6.03	6.05	100.3	G100791	ERAP108505*2	1.038	1.0374	99.9	G100767	HP603026*2	10.1	10.30	102.0
					G100811	ERAP108505*1	1.038	1.0239	98.6	G100789	HP603026*1	10.1	9.96	98.6
					G100811	ERAP108505*2	1.038	1.0178	98.1	G100789	HP603026*2	10.1	9.90	98.0
										G100813	HP603026*1	10.1	10.20	101.0
										G100813	HP603026*2	10.1	10.30	102.0
Mean				99.80					99.40	Mean				100.40
Standard De	Standard Deviation				Standard I	Deviation			0.72	Standard [Deviation			1.28
Count				10	Count				12	Count				14

Table B-2. Cloud Deposition 2006 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples – Clingmans Dome, TN (2 of 3)

Batch Number	Lab Key	NO ₃ -N Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Cl ⁻ Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Ca ²⁺ Target mg/L	Found mg/L	Percent Recovery
G100632	HP603026*1	1.6	1.61	100.6	G100632	HP603026*1	0.98	0.955	97.4	G100627	HP603026*1	0.052	0.0536	103.1
G100632	HP603026*2	1.6	1.61	100.6	G100632	HP603026*2	0.98	0.953	97.2	G100627	HP603026*2	0.052	0.0539	103.7
G100657	HP603026*1	1.6	1.60	100.0	G100657	HP603026*1	0.98	0.979	99.9	G100652	HP603026*1	0.052	0.0529	101.7
G100657	HP603026*2	1.6	1.59	99.4	G100657	HP603026*2	0.98	0.982	100.2	G100652	HP603026*2	0.052	0.0527	101.3
G100700	HP603026*1	1.6	1.62	101.3	G100700	HP603026*1	0.98	0.972	99.2	G100652	HP603026*3	0.052	0.0526	101.2
G100700	HP603026*2	1.6	1.63	101.9	G100700	HP603026*2	0.98	0.974	99.4	G100703	HP603026*1	0.052	0.0532	102.3
G100713	HP603026*1	1.6	1.62	101.3	G100713	HP603026*1	0.98	0.975	99.5	G100703	HP603026*2	0.052	0.0528	101.5
G100713	HP603026*3	1.6	1.61	100.6	G100713	HP603026*3	0.98	0.976	99.6	G100711	HP603026*1	0.052	0.0554	106.5
G100767	HP603026*1	1.6	1.62	101.3	G100767	HP603026*1	0.98	0.963	98.3	G100711	HP603026*2	0.052	0.0550	105.8
G100767	HP603026*2	1.6	1.62	101.3	G100767	HP603026*2	0.98	0.967	98.7	G100711	HP603026*3	0.052	0.0547	105.2
G100789	HP603026*1	1.6	1.59	99.4	G100789	HP603026*1	0.98	0.951	97.0	G100763	HP603026*1	0.052	0.0536	103.1
G100789	HP603026*2	1.6	1.58	98.8	G100789	HP603026*2	0.98	0.964	98.4	G100763	HP603026*2	0.052	0.0539	103.7
G100813	HP603026*1	1.6	1.63	101.9	G100813	HP603026*1	0.98	0.966	98.6	G100785	HP603026*1	0.052	0.0540	103.8
G100813	HP603026*2	1.6	1.64	102.5	G100813	HP603026*2	0.98	0.965	98.5	G100785	HP603026*2	0.052	0.0548	105.4
										G100808	HP603026*1	0.052	0.0526	101.2
										G100808	HP603026*2	0.052	0.0529	101.7
Mean				100.80	Mean				98.70	Mean				103.20
Standard [Deviation			1.07	Standard D	eviation			0.99	Standard	Deviation			1.77
Count				14	Count				14	Count				16

Table B-2. Cloud Deposition 2006 Sampling Season – QC Batch Summary for Cloud Samples – Reference Samples – Clingmans Dome, TN (3 of 3)

Batch Number	Lab Key	Mg ²⁺ Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Na [†] Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	K ⁺ Target mg/L	Found mg/L	Percent Recovery
G100627	HP603026*1	0.05	0.0506	101.2	G100627	HP603026*1	0.4	0.3726	93.2	G100627	HP603026*1	0.097	0.0983	101.3
G100627	HP603026*2	0.05	0.0513	102.6	G100627	HP603026*2	0.4	0.3791	94.8	G100627	HP603026*2	0.097	0.0984	101.4
G100652	HP603026*1	0.05	0.0516	103.2	G100652	HP603026*1	0.4	0.3799	95.0	G100652	HP603026*1	0.097	0.0971	100.1
G100652	HP603026*2	0.05	0.0504	100.8	G100652	HP603026*2	0.4	0.3774	94.4	G100652	HP603026*2	0.097	0.0969	99.9
G100652	HP603026*3	0.05	0.0506	101.2	G100652	HP603026*3	0.4	0.3776	94.4	G100652	HP603026*3	0.097	0.0964	99.4
G100703	HP603026*1	0.05	0.0508	101.6	G100703	HP603026*1	0.4	0.3716	92.9	G100703	HP603026*1	0.097	0.0990	102.1
G100703	HP603026*2	0.05	0.0501	100.2	G100703	HP603026*2	0.4	0.3705	92.6	G100703	HP603026*2	0.097	0.0963	99.3
G100711	HP603026*1	0.05	0.0513	102.6	G100711	HP603026*1	0.4	0.3852	96.3	G100711	HP603026*1	0.097	0.1012	104.3
G100711	HP603026*2	0.05	0.0513	102.6	G100711	HP603026*2	0.4	0.3835	95.9	G100711	HP603026*2	0.097	0.1001	103.2
G100711	HP603026*3	0.05	0.0508	101.6	G100711	HP603026*3	0.4	0.3821	95.5	G100711	HP603026*3	0.097	0.1014	104.5
G100763	HP603026*1	0.05	0.0513	102.6	G100763	HP603026*1	0.4	0.3809	95.2	G100763	HP603026*1	0.097	0.1007	103.8
G100763	HP603026*2	0.05	0.0506	101.2	G100763	HP603026*2	0.4	0.3817	95.4	G100763	HP603026*2	0.097	0.0992	102.3
G100785	HP603026*1	0.05	0.0517	103.4	G100785	HP603026*1	0.4	0.3834	95.9	G100785	HP603026*1	0.097	0.0992	102.3
G100785	HP603026*2	0.05	0.0513	102.6	G100785	HP603026*2	0.4	0.3867	96.7	G100785	HP603026*2	0.097	0.0976	100.6
G100808	HP603026*1	0.05	0.0507	101.4	G100808	HP603026*1	0.4	0.3750	93.8	G100808	HP603026*1	0.097	0.0979	100.9
G100808	HP603026*2	0.05	0.0509	101.8	G100808	HP603026*2	0.4	0.3768	94.2	G100808	HP603026*2	0.097	0.0966	99.6
Mean				101.90	Mean				94.80	Mean				101.60
Standard De	viation			0.91	Standard De	viation			1.21	Standard D	eviation			1.74
Count				16	Count				16	Count				16

Table B-3. Cloud Deposition 2006 Sampling Season – QC Batch Summary for Cloud Samples – CVS – Clingmans Dome, TN (1 of 3)

	o. cloud Dep	Lab pH					NH ₄ -N		<u> </u>		<u> </u>	SO ₄ ²⁻		
Batch	Lab Key	Target	Found STD Units	Percent	Batch	Lob Voy	Target	Found	Percent	Batch	Lob Voy	Target	Found	Percent
Number	•			•		Lab Key	mg/L	mg/L	Recovery		Lab Key	mg/L	mg/L	Recovery
G100640	SP1*180714IIB	4.81	4.83	104.7		SP1*QC*1	1	0.9921	99.2		SP1*QC*1	2.5	2.47	98.8
G100640	SP2*180714IIB	4.81	4.83	104.7		SP2*QC*1	1	1.0044	100.4		SP2*QC*1	2.5	2.50	100.0
G100640	SP3*180714IIB	4.81	4.82	102.3	G100634	SP3*QC*1	1	1.0050	100.5	G100632	SP3*QC*1	2.5	2.49	99.6
G100676	SP1*180716IA	4.81	4.81	100.0	G100677	SP1*QC*1	1	1.0006	100.1	G100657	SP1*QC*1	2.5	2.45	98.0
G100676	SP2*180716IA	4.81	4.81	100.0	G100677	SP2*QC*1	1	0.9945	99.5	G100657	SP2*QC*1	2.5	2.47	98.8
G100676	SP3*180716IA	4.81	4.84	107.2	G100677	SP3*QC*1	1	0.9995	100.0	G100657	SP3*QC*1	2.5	2.47	98.8
G100676	SP4*180716IA	4.81	4.83	104.7	G100715	SP1*QC*1	1	0.9769	97.7	G100657	SP4*QC*1	2.5	2.47	98.8
G100790	SP1*180716IA	4.81	4.78	93.3	G100715	SP2*QC*1	1	0.9864	98.6	G100700	SP1*QC*1	2.5	2.48	99.2
G100790	SP2*180716IA	4.81	4.76	89.1	G100770	SP1*QC*1	1	0.9856	98.6	G100700	SP2*QC*1	2.5	2.48	99.2
G100790	SP3*180716IA	4.81	4.77	91.2	G100770	SP2*QC*1	1	0.9962	99.6	G100713	SP1*QC*1	2.5	2.47	98.8
G100801	SP1*180716IA	4.81	4.80	97.7	G100770	SP3*QC*1	1	0.9910	99.1	G100713	SP2*QC*1	2.5	2.48	99.2
G100801	SP1*180719IA	4.81	4.83	104.7	G100791	SP1*QC*1	1	0.9881	98.8	G100713	SP3*QC*1	2.5	2.49	99.6
G100801	SP2*180716IA	4.81	4.78	93.3	G100791	SP2*QC*1	1	0.9986	99.9	G100767	SP1*QC*1	2.5	2.48	99.2
G100801	SP3*180716IA	4.81	4.77	91.2	G100791	SP3*QC*1	1	0.9977	99.8	G100767	SP2*QC*1	2.5	2.49	99.6
G100845	SP1*180719IA	4.81	4.82	102.3	G100811	SP1*QC*1	1	0.9800	98.0	G100767	SP3*QC*1	2.5	2.47	98.8
G100845	SP2*180719IA	4.81	4.79	95.5	G100811	SP2*QC*1	1	0.9805	98.1	G100789	SP1*QC*1	2.5	2.44	97.6
G100845	SP3*180719IA	4.81	4.82	102.3	G100811	SP3*QC*1	1	0.9764	97.6	G100789	SP2*QC*1	2.5	2.41	96.4
										G100789	SP3*QC*1	2.5	2.42	96.8
										G100789	SP4*QC*1	2.5	2.48	99.2
										G100813	SP1*QC*1	2.5	2.52	100.8
										G100813	SP2*QC*1	2.5	2.51	100.4
										G100813	SP3*QC*1	2.5	2.50	100.0
										G100813	SP4*QC*1	2.5	2.51	100.4
Mean				99.10	Mean				99.10	Mean				99.00
Standard D	eviation			5.75	Standard D	eviation			0.93	Standard D	eviation			1.07
Count				17	Count				17	Count				23

Table B-3. Cloud Deposition 2006 Sampling Season – QC Batch Summary for Cloud Samples – CVS – Clingmans Dome, TN (2 of 3)

		NON		T 8			Cl		impies evo		iuns Donie	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
G100632	SP1*QC*1	0.5	0.491	98.2	G100632	SP1*QC*1	0.5	0.485	97.0	G100627	SP1*QC*1	0.5	0.5029	100.6
G100632	SP2*QC*1	0.5	0.491	98.2	G100632	SP2*QC*1	0.5	0.487	97.4	G100627	SP2*QC*1	0.5	0.5034	100.7
G100632	SP3*QC*1	0.5	0.493	98.6	G100632	SP3*QC*1	0.5	0.481	96.2	G100627	SP3*QC*1	0.5	0.5005	100.1
G100657	SP1*QC*1	0.5	0.492	98.4	G100657	SP1*QC*1	0.5	0.493	98.6	G100652	SP1*QC*1	0.5	0.5050	101.0
G100657	SP2*QC*1	0.5	0.497	99.4	G100657	SP2*QC*1	0.5	0.497	99.4	G100652	SP2*QC*1	0.5	0.5002	100.0
G100657	SP3*QC*1	0.5	0.492	98.4	G100657	SP3*QC*1	0.5	0.492	98.4	G100652	SP3*QC*1	0.5	0.5021	100.4
G100657	SP4*QC*1	0.5	0.497	99.4	G100657	SP4*QC*1	0.5	0.495	99.0	G100652	SP4*QC*1	0.5	0.5036	100.7
G100700	SP1*QC*1	0.5	0.498	99.6	G100700	SP1*QC*1	0.5	0.499	99.8	G100703	SP1*QC*1	0.5	0.5026	100.5
G100700	SP2*QC*1	0.5	0.500	100.0	G100700	SP2*QC*1	0.5	0.497	99.4	G100703	SP2*QC*1	0.5	0.5023	100.5
G100713	SP1*QC*1	0.5	0.496	99.2	G100713	SP1*QC*1	0.5	0.495	99.0	G100711	SP1*QC*1	0.5	0.5061	101.2
G100713	SP2*QC*1	0.5	0.498	99.6	G100713	SP2*QC*1	0.5	0.500	100.0	G100711	SP2*QC*1	0.5	0.4980	99.6
G100713	SP3*QC*1	0.5	0.497	99.4	G100713	SP3*QC*1	0.5	0.494	98.8	G100711	SP3*QC*1	0.5	0.4997	99.9
G100767	SP1*QC*1	0.5	0.493	98.6	G100767	SP1*QC*1	0.5	0.489	97.8	G100763	SP1*QC*1	0.5	0.5123	102.5
G100767	SP2*QC*1	0.5	0.495	99.0	G100767	SP2*QC*1	0.5	0.491	98.2	G100763	SP2*QC*1	0.5	0.5024	100.5
G100767	SP3*QC*1	0.5	0.490	98.0	G100767	SP3*QC*1	0.5	0.486	97.2	G100785	SP1*QC*1	0.5	0.5046	100.9
G100789	SP1*QC*1	0.5	0.492	98.4	G100789	SP1*QC*1	0.5	0.491	98.2	G100785	SP2*QC*1	0.5	0.5056	101.1
G100789	SP2*QC*1	0.5	0.485	97.0	G100789	SP2*QC*1	0.5	0.484	96.8	G100785	SP3*QC*1	0.5	0.5122	102.4
G100789	SP3*QC*1	0.5	0.492	98.4	G100789	SP3*QC*1	0.5	0.481	96.2	G100808	SP1*QC*1	0.5	0.4960	99.2
G100789	SP4*QC*1	0.5	0.507	101.4	G100789	SP4*QC*1	0.5	0.508	101.6	G100808	SP2*QC*1	0.5	0.5009	100.2
G100813	SP1*QC*1	0.5	0.499	99.8	G100813	SP1*QC*1	0.5	0.487	97.4					
G100813	SP2*QC*1	0.5	0.500	100.0	G100813	SP2*QC*1	0.5	0.491	98.2					
G100813	SP3*QC*1	0.5	0.498	99.6	G100813	SP3*QC*1	0.5	0.504	100.8					
G100813	SP4*QC*1	0.5	0.506	101.2	G100813	SP4*QC*1	0.5	0.501	100.2					
Mean				99.10	Mean				98.50	Mean				100.60
Standard D	eviation			1.01	Standard De	eviation			1.42	Standard D	eviation			0.82
Count				23	Count				23	Count				19

Table B-3. Cloud Deposition 2006 Sampling Season – QC Batch Summary for Cloud Samples – CVS – Clingmans Dome, TN (3 of 3)

Batch Number	Lab Key	Mg ²⁺ Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	Na ⁺ Target mg/L	Found mg/L	Percent Recovery	Batch Number	Lab Key	K ⁺ Target mg/L	Found mg/L	Percent Recovery
G100627	SP1*QC*1	0.5	0.5001	100.0	G100627	SP1*QC*1	0.5	0.4960	99.20	G100627	SP1*QC*1	0.5	0.5022	100.4
G100627	SP2*QC*1	0.5	0.4988	99.8	G100627	SP2*QC*1	0.5	0.4980	99.60	G100627	SP2*QC*1	0.5	0.5040	100.8
G100627	SP3*QC*1	0.5	0.5034	100.7	G100627	SP3*QC*1	0.5	0.5004	100.08	G100627	SP3*QC*1	0.5	0.5008	100.2
G100652	SP1*QC*1	0.5	0.5103	102.1	G100652	SP1*QC*1	0.5	0.4998	99.96	G100652	SP1*QC*1	0.5	0.5086	101.7
G100652	SP2*QC*1	0.5	0.4940	98.8	G100652	SP2*QC*1	0.5	0.4993	99.86	G100652	SP2*QC*1	0.5	0.5018	100.4
G100652	SP3*QC*1	0.5	0.4973	99.5	G100652	SP3*QC*1	0.5	0.5002	100.04	G100652	SP3*QC*1	0.5	0.4993	99.9
G100652	SP4*QC*1	0.5	0.4999	100.0	G100652	SP4*QC*1	0.5	0.5026	100.52	G100652	SP4*QC*1	0.5	0.5026	100.5
G100703	SP1*QC*1	0.5	0.5006	100.1	G100703	SP1*QC*1	0.5	0.4995	99.90	G100703	SP1*QC*1	0.5	0.5048	101.0
G100703	SP2*QC*1	0.5	0.4983	99.7	G100703	SP2*QC*1	0.5	0.4997	99.94	G100703	SP2*QC*1	0.5	0.5034	100.7
G100711	SP1*QC*1	0.5	0.5026	100.5	G100711	SP1*QC*1	0.5	0.5028	100.56	G100711	SP1*QC*1	0.5	0.5083	101.7
G100711	SP2*QC*1	0.5	0.4994	99.9	G100711	SP2*QC*1	0.5	0.4964	99.28	G100711	SP2*QC*1	0.5	0.5028	100.6
G100711	SP3*QC*1	0.5	0.4995	99.9	G100711	SP3*QC*1	0.5	0.4995	99.90	G100711	SP3*QC*1	0.5	0.5005	100.1
G100763	SP1*QC*1	0.5	0.5073	101.5	G100763	SP1*QC*1	0.5	0.5120	102.40	G100763	SP1*QC*1	0.5	0.5122	102.4
G100763	SP2*QC*1	0.5	0.5013	100.3	G100763	SP2*QC*1	0.5	0.5001	100.02	G100763	SP2*QC*1	0.5	0.5055	101.1
G100785	SP1*QC*1	0.5	0.5049	101.0	G100785	SP1*QC*1	0.5	0.5045	100.90	G100785	SP1*QC*1	0.5	0.5078	101.6
G100785	SP2*QC*1	0.5	0.4991	99.8	G100785	SP2*QC*1	0.5	0.5058	101.16	G100785	SP2*QC*1	0.5	0.5068	101.4
G100785	SP3*QC*1	0.5	0.5035	100.7	G100785	SP3*QC*1	0.5	0.5101	102.02	G100785	SP3*QC*1	0.5	0.5091	101.8
G100808	SP1*QC*1	0.5	0.4964	99.3	G100808	SP1*QC*1	0.5	0.4952	99.04	G100808	SP1*QC*1	0.5	0.5005	100.1
G100808	SP2*QC*1	0.5	0.5034	100.7	G100808	SP2*QC*1	0.5	0.5005	100.10	G100808	SP2*QC*1	0.5	0.5040	100.8
Mean				100.20	Mean				100.20	Mean				100.90
Standard De	eviation				Standard De	eviation			0.88	Standard Do	eviation			0.70
Count				19	Count				19	Count				19

Table B-4. Cloud Deposition 2006 Sampling Season – Replicate Summary for Cloud Samples – Clingmans Dome, TN (1 of 3)

			SO ₄ ²⁻			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	1.52	1.51	0.66
C06303*9	RP*C06303*9	CLD303	7/10/2006	10.50	10.40	0.95
C06303*12	RP*C06303*12	CLD303	7/20/2006	9.55	9.55	0.00
C06303*17	RP*C06303*17	CLD303	8/7/2006	14.00	14.00	0.00
C06303*21	RP*C06303*21	CLD303	8/29/2006	10.70	10.60	0.93
C06303*33	RP*C06303*33	CLD303	9/19/2006	17.30	17.20	0.58
C06303*37	RP*C06303*37	CLD303	10/1/2006	8.57	8.67	1.17
					Mean	0.61
					Standard Deviation	0.00

			NO ₃ - N			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	0.209	0.209	0.00
C06303*9	RP*C06303*9	CLD303	7/10/2006	0.569	0.567	0.35
C06303*12	RP*C06303*12	CLD303	7/20/2006	1.310	1.310	0.00
C06303*17	RP*C06303*17	CLD303	8/7/2006	1.140	1.140	0.00
C06303*21	RP*C06303*21	CLD303	8/29/2006	0.984	0.986	0.20
C06303*33	RP*C06303*33	CLD303	9/19/2006	1.510	1.510	0.00
C06303*37	RP*C06303*37	CLD303	10/1/2006	0.828	0.825	0.36
					Mean	0.11
					Standard Deviation	0.00

			Cl			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	0.024	0.024	0.00
C06303*9	RP*C06303*9	CLD303	7/10/2006	0.186	0.183	1.61
C06303*12	RP*C06303*12	CLD303	7/20/2006	0.206	0.210	1.94
C06303*17	RP*C06303*17	CLD303	8/7/2006	0.213	0.217	1.88
C06303*21	RP*C06303*21	CLD303	8/29/2006	0.289	0.292	1.04
C06303*33	RP*C06303*33	CLD303	9/19/2006	0.346	0.346	0.00
C06303*37	RP*C06303*37	CLD303	10/1/2006	0.438	0.434	0.91
					Mean	1.05
					Standard Deviation	0.01

Table B-4. Cloud Deposition 2006 Sampling Season – Replicate Summary for Cloud Samples – Clingmans Dome, TN (2 of 3)

	. 1		NH ₄ -N		· · · · · · · · · · · · · · · · · · ·	,
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*7	RP*C06303*7	CLD303	6/19/2006	11.0178	11.0352	0.16
C06303*20	RP*C06303*20	CLD303	8/23/2006	5.1297	5.1330	0.06
C06303*22	RP*C06303*22	CLD303	8/30/2006	0.7070	0.7054	0.23
C06303*26	RP*C06303*26	CLD303	9/3/2006	1.6578	1.6590	0.07
C06303*29	RP*C06303*29	CLD303	9/14/2006	2.8212	2.8212	0.00
C06303*36	RP*C06303*36	CLD303	9/28/2006	1.6143	1.6238	0.59
C06303*44	RP*C06303*44	CLD303	10/22/2006	0.2030	0.1915	5.67
					Mean	0.97
					Standard Deviation	0.02

			Ca^{2+}			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	0.0291	0.0289	0.69
C06303*9	RP*C06303*9	CLD303	7/10/2006	0.3651	0.3591	1.64
C06303*12	RP*C06303*12	CLD303	7/20/2006	0.6750	0.6787	0.55
C06303*16	RP*C06303*16	CLD303	8/4/2006	4.0470	4.0296	0.43
C06303*21	RP*C06303*21	CLD303	8/29/2006	0.2723	0.2759	1.32
C06303*27	RP*C06303*27	CLD303	9/7/2006	0.1993	0.2014	1.05
C06303*37	RP*C06303*37	CLD303	10/1/2006	0.1632	0.1631	0.06
					Mean	0.82
					Standard Deviation	0.01

			Mg^{2+}			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	0.0091	0.0091	0.00
C06303*9	RP*C06303*9	CLD303	7/10/2006	0.0908	0.0905	0.33
C06303*12	RP*C06303*12	CLD303	7/20/2006	0.0863	0.0857	0.70
C06303*16	RP*C06303*16	CLD303	8/4/2006	0.6996	0.6971	0.36
C06303*21	RP*C06303*21	CLD303	8/29/2006	0.0517	0.0510	1.35
C06303*27	RP*C06303*27	CLD303	9/7/2006	0.0185	0.0177	4.32
C06303*37	RP*C06303*37	CLD303	10/1/2006	0.0321	0.0313	2.49
					Mean	1.36
					Standard Deviation	0.02

Table B-4. Cloud Deposition 2006 Sampling Season – Replicate Summary for Cloud Samples – Clingmans Dome, TN (3 of 3)

			Na ⁺			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	0.0060	0.0061	1.67
C06303*9	RP*C06303*9	CLD303	7/10/2006	0.1141	0.1121	1.75
C06303*12	RP*C06303*12	CLD303	7/20/2006	0.0985	0.0991	0.61
C06303*16	RP*C06303*16	CLD303	8/4/2006	2.2746	2.2914	0.74
C06303*21	RP*C06303*21	CLD303	8/29/2006	0.0654	0.0661	1.07
C06303*27	RP*C06303*27	CLD303	9/7/2006	0.0217	0.0213	1.84
C06303*37	RP*C06303*37	CLD303	10/1/2006	0.1647	0.1637	0.61
					Mean	1.18
					Standard Deviation	0.01

			K ⁺			
Sample No.	Replicate No.	Station ID	Analysis Date	Sample Result	Replicate Result	Percent Diff
C06303*2	RP*C06303*2	CLD303	6/2/2006	0.0264	0.0269	1.89
C06303*9	RP*C06303*9	CLD303	7/10/2006	0.0922	0.0908	1.52
C06303*12	RP*C06303*12	CLD303	7/20/2006	0.0935	0.0946	1.18
C06303*16	RP*C06303*16	CLD303	8/4/2006	0.3406	0.3404	0.06
C06303*21	RP*C06303*21	CLD303	8/29/2006	0.1698	0.1717	1.12
C06303*27	RP*C06303*27	CLD303	9/7/2006	0.0331	0.0328	0.91
C06303*37	RP*C06303*37	CLD303	10/1/2006	0.0766	0.0768	0.26
					Mean	0.99
					Standard Deviation	0.01

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 are four laboratory blanks for the cellulose filters with "hits" for sulfate. Such "hits" are not uncommon with the cellulose filters. 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. 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 outside laboratory supplies these reference samples with a certificate of analysis stating the known or target value. A reference sample is analyzed at the beginning and end of each analytical batch to verify the accuracy and stability of the instrument response. The QC limits require the measured value be within \pm 5 percent of the known value for anions and within \pm 10 percent of the known value for cations. The data from all reference samples analyzed with the Great Smoky Mountains National Park, TN (GSR420) samples are within the CASTNET QC criteria.

Summary statistics from the analysis of CVS for each parameter and filter type are presented in Table C-6. A CVS is a NIST-traceable solution supplied in a matrix similar to that of the sample being analyzed with a target value at approximately the midpoint of the calibration curve. This QC solution is supplied to MACTEC by a second outside laboratory. A CVS is analyzed after every 10 environmental samples to verify that the instrument calibration has not drifted more than \pm 5 percent for anions and base cations, and \pm 10 percent for NH $_4^+$. All CVS 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 samples that were replicated. The replicate percent difference criteria are \pm 5 percent for anions and base cations and \pm 10 percent for NH $_4^+$ for samples with concentrations greater than five times the analytical detection limit. For samples with lower concentrations, the difference between the two values cannot be more than the analytical detection limit. All of the GSR420 replicated samples are within the QC criteria.

Table C-1. Dry Deposition 2006 Sampling Season – Great Smoky Mountains National Park, TN

			Teflon® SO ₄ ²⁻	Teflon® NO ₃ -N	Nylon SO ₄ ²⁻	Nylon NO ₃ -N	Cellulose SO ₄ ²⁻	Teflon® NH ₄ -N	Teflon® Ca ²⁺	Teflon® Mg ²⁺	Teflon® Na⁺	Teflon® K⁺	Teflon® Cl
Sample No.	Station ID	Filter Date	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg
0622001-39	GRS420	5/30/06	207.100	<0.200	24.000	11.820	86.250	45.380	4.485	0.914	1.246	2.095	<0.500
0623001-39	GRS420	6/6/06	211.900	3.252	28.320	17.350	166.600	49.540	15.860	2.421	0.846	3.207	<0.500
0624001-39	GRS420	6/13/06	260.900	0.825	18.000	11.700	130.600	63.200	7.895	1.786	3.743	2.070	<0.500
0625001-39	GRS420	6/20/06	166.500	0.253	28.900	10.880	93.100	38.030	5.498	1.064	1.493	2.031	<0.500
0626001-39	GRS420	6/27/06	255.900	0.775	23.980	15.120	212.500	64.360	14.300	1.709	0.778	3.095	<0.500
0627001-39	GRS420	7/4/06	238.200	<0.200	28.450	11.300	132.600	49.140	4.193	0.932	1.267	3.400	<0.500
0628001-39	GRS420	7/11/06	198.200	<0.200	25.250	10.180	101.200	43.190	4.120	1.194	3.667	2.523	<0.500
0629001-39	GRS420	7/18/06	231.800	<0.200	23.220	11.180	64.550	46.960	4.547	0.852	0.949	2.161	<0.500
0630001-39	GRS420	7/25/06	173.100	<0.200	18.100	11.820	61.800	28.370	10.500	2.567	6.335	2.588	<0.500
0631001-39	GRS420	8/1/06	270.300	1.040	24.550	14.250	144.600	48.540	13.520	3.399	8.118	3.052	<0.500
0632001-39	GRS420	8/8/06	195.300	<0.200	25.100	10.750	123.000	35.360	4.366	1.248	3.801	1.792	<0.500
0633001-39	GRS420	8/15/06	337.800	<0.200	31.000	14.380	126.600	60.560	4.975	1.053	1.872	2.380	<0.500
0634001-39	GRS420	8/22/06	305.200	<0.200	20.180	11.620	96.050	54.660	5.139	1.143	2.229	2.288	<0.500
0635001-39	GRS420	8/29/06	146.400	0.330	15.200	9.175	47.650	25.230	2.311	0.564	1.196	1.842	<0.500
0636001-39	GRS420	9/5/06	287.400	0.723	17.400	11.620	79.100	58.620	4.275	0.790	1.607	2.637	<0.500
0637001-39	GRS420	9/12/06	199.600	<0.200	16.580	10.220	78.550	36.910	3.096	0.580	1.132	1.742	<0.500
0638001-39	GRS420	9/19/06	120.200	<0.200	13.400	9.625	109.300	24.540	6.069	1.010	1.913	2.069	<0.500
0639001-39	GRS420	9/26/06	114.900	0.822	18.580	11.400	185.600	27.140	8.074	0.911	0.671	1.976	<0.500

Table C-2. Dry Deposition 2006 Sampling Season - Laboratory Filter Pack Blanks - Great Smoky Mountains National Park, TN

	Tefl	on®	Nyl		Cellulose			Teflon®		
	SO ₄ ²	NO ₃ -N	SO ₄ ²	NO ₃ -N	SO ₄	NH⁴-N	Ca^{2+}	$\mathbf{Mg}^{^{2+}}$	$\mathbf{Na}^{\scriptscriptstyle +}$	$\mathbf{K}^{\scriptscriptstyle{+}}$
Lab Key	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg	T.µg
0624002-01					2.100					
0624002-02					<2.000					
0625002-01	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	< 0.075	<0.125	<0.125
0625002-02	<1.000	< 0.200	<1.000	< 0.200		<0.500	0.2673	< 0.075	<0.125	<0.125
0626002-01			<1.000	< 0.200	<2.000	<0.500				
0626002-02			<1.000	< 0.200	<2.000	<0.500				
0627002-01	<1.000	< 0.200			<2.000	<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0627002-02	<1.000	< 0.200			<2.000	<0.500	< 0.0750	< 0.075	< 0.125	<0.125
0628002-01	<1.000	< 0.200	<1.000	< 0.200	<2.000	<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0628002-02	<1.000	< 0.200	<1.000	< 0.200	<2.000	<0.500	< 0.0750	< 0.075	< 0.125	<0.125
0629002-01	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0629002-02	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	< 0.075	< 0.125	<0.125
0630002-01			<1.000	< 0.200	2.250					
0630002-02			<1.000	< 0.200	<2.000					
0631002-01	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0631002-02	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	<0.075 <0.075	< 0.125	< 0.125
0632002-01	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0632002-02	<1.000	< 0.200	<1.000	< 0.200		<0.500	< 0.0750	<0.075 <0.075	< 0.125	< 0.125
0633002-01	<1.000	< 0.200				<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0633002-02	<1.000	< 0.200				<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0634002-01			<1.000	< 0.200						
0634002-02			<1.000	< 0.200						
0635002-01	<1.000	< 0.200			<2.000	<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0635002-02	<1.000	< 0.200			<2.000	< 0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0636002-01	<1.000	< 0.200	<1.000	< 0.200	<2.000		< 0.0750	< 0.075	< 0.125	< 0.125
0636002-02	<1.000	< 0.200	<1.000	< 0.200	<2.000		< 0.0750	< 0.075	< 0.125	< 0.125
0637002-01	<1.000	< 0.200	<1.000	< 0.200	2.350	<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0637002-02	<1.000	< 0.200	<1.000	< 0.200	<2.000	< 0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0638002-01			<1.000	< 0.200	<2.000	< 0.500				
0638002-02			<1.000	< 0.200	<2.000	< 0.500				
0639002-01	<1.000	< 0.200			<2.000		< 0.0750	< 0.075	< 0.125	< 0.125
0639002-02	<1.000	<0.200			<2.000		< 0.0750	< 0.075	<0.125	<0.125
0640002-01			<1.000	< 0.200	<2.000	< 0.500				
0640002-02			<1.000	<0.200	<2.000	<0.500				
0641002-01	<1.000	< 0.200			<2.000	<0.500	< 0.0750	< 0.075	< 0.125	< 0.125
0641002-02	<1.000	<0.200			2.250	< 0.500	< 0.0750	< 0.075	<0.125	<0.125
0642002-01	11.000	10.200	<1.000	< 0.200	<2.000	10.000	10.07.00	10.0.0	101120	101.120
0642002-02			<1.000	<0.200	<2.000					
0643002-01	<1.000	< 0.200	11.000	10.200	<2.000	<0.500	< 0.0750	< 0.075	<0.125	<0.125
0643002-02	<1.000	<0.200			<2.000	< 0.500	< 0.0750	<0.075 <0.075	<0.125	<0.125
0644002-01	<1.000	<0.200	<1.000	< 0.200	,	< 0.500	< 0.0750	< 0.075	<0.125	<0.125
0644002-01	<1.000	<0.200	<1.000	<0.200	1	<0.500	< 0.0750	<0.075 <0.075	<0.125	<0.125
0645002-01	<1.000	<0.200	11.000	10.200	<2.000	< 0.500	< 0.0750	<0.075	<0.125	<0.125
0645002-01	<1.000	<0.200			<2.000	< 0.500	< 0.0750	<0.075	<0.125	<0.125
0646002-01	11.000	10.200	<1.000	< 0.200	12.000	10.000	10.0100	30.070	30.120	30.120
0646002-01			<1.000	<0.200	1					

Table C-3. Dry Deposition 2006 Sampling Season – QC Batch Summary for Teflon[®] Filters – Reference Samples – Great Smoky Mountains National Park, TN (1 of 5)

	Mount		ionai i a	rk, 1 N (1	01 5)									
		SO_4^{2-}					NO N					$NH_4^+ - N$		
		Target	Found	Percent			Target	Found	Percent			Target		Percent
Batch	QC Key	mg/L	mg/L	Recovery	Batch	QC Key	mg/L	mg/L	Recovery	Batch	QC Key	mg/L	Found mg/L	Recovery
L606021	SRM1	10.1	9.904	98.06	L606021	SRM1	1.6	1.622	101.38	L606019	SRM1	1.038	1.055	101.64
L606021	SRM2	10.1	10.050	99.50	L606021	SRM2	1.6	1.649	103.06	L606019	SRM2	1.038	1.102	106.17
L606027	SRM1	10.1	9.898	98.00	L606027	SRM1	1.6	1.630	101.88	L606032	SRM1	1.038	1.041	100.29
L606027	SRM2	10.1	10.000	99.01	L606027	SRM2	1.6	1.653	103.31	L606032	SRM2	1.038	1.025	98.75
L607006	SRM1	10.1	9.882	97.84	L607006	SRM1	1.6	1.627	101.69	L607002	SRM1	1.038	1.056	101.73
L607006	SRM2	10.1	9.932	98.34	L607006	SRM2	1.6	1.639	102.44	L607002	SRM2	1.038	1.088	104.82
L607016	SRM1	10.1	10.080	99.80	L607016	SRM1	1.6	1.600	100.00	L607009	SRM1	1.038	1.027	98.94
L607016	SRM2	10.1	10.140	100.40	L607016	SRM2	1.6	1.608	100.50	L607009	SRM2	1.038	1.055	101.64
L607017	SRM1	10.1	9.766	96.69	L607017	SRM1	1.6	1.609	100.56	L607012	SRM1	1.038	1.033	99.52
L607017	SRM2	10.1	9.934	98.36	L607017	SRM2	1.6	1.637	102.31	L607012	SRM2	1.038	1.046	100.77
L607017	SRM3	10.1	9.877	97.79	L607017	SRM3	1.6	1.623	101.44	L607028	SRM1	1.038	1.052	101.35
L607017	SRM4	10.1	10.040	99.41	L607017	SRM4	1.6	1.650	103.13	L607028	SRM2	1.038	1.069	102.99
L607029	SRM1	10.1	9.749	96.52	L607029	SRM1	1.6	1.610	100.63	L608001	SRM1	1.038	1.043	100.48
L607029	SRM2	10.1	9.861	97.63	L607029	SRM2	1.6	1.627	101.69	L608001	SRM2	1.038	1.032	99.42
L607033	SRM1	10.1	9.721	96.25	L607033	SRM1	1.6	1.606	100.38	L608005	SRM1	1.038	1.036	99.81
L607033	SRM2	10.1	9.786	96.89	L607033	SRM2	1.6	1.618	101.13	L608005	SRM2	1.038	1.042	100.39
L608003	SRM1	10.1	9.729	96.33	L608003	SRM1	1.6	1.613	100.81	L608016	SRM1	1.038	1.033	99.52
L608003	SRM2	10.1	9.910	98.12	L608003	SRM2	1.6	1.641	102.56	L608016	SRM2	1.038	1.042	100.39
L608018	SRM1	10.1	9.655	95.59	L608018	SRM1	1.6	1.607	100.44	L608029	SRM1	1.038	1.033	99.52
L608018	SRM2	10.1	9.823	97.26	L608018	SRM2	1.6	1.631	101.94	L608029	SRM2	1.038	1.034	99.61
L608027	SRM1	10.1	9.722	96.26	L608027	SRM1	1.6	1.626	101.63	L608033	SRM1	1.038	1.038	100.00
L608027	SRM2	10.1	9.906	98.08	L608027	SRM2	1.6	1.654	103.38	L608033	SRM2	1.038	1.036	99.81
L608027	SRM3	10.1	9.878	97.80	L608027	SRM3	1.6	1.654	103.38	L609012	SRM1	1.038	1.038	100.00
L608032 L608032	SRM1	10.1	9.717	96.21	L608032 L608032	SRM1	1.6 1.6	1.625 1.653	101.56	L609012 L609015	SRM2	1.038 1.038	1.058	101.93 98.36
L609001	SRM2 SRM1	10.1 10.1	9.921 9.689	98.23 95.93	L609001	SRM2 SRM1	1.6	1.627	103.31 101.69	L609015 L609015	SRM1 SRM2	1.038	1.021 1.030	98.36
L609001	SRM2	10.1	9.009	93.93 98.45	L609001	SRM2	1.6	1.657	103.56	L609013	SRM1	1.038	1.046	100.77
L609001	SRM1	10.1	10.220	101.19	L609001	SRM1	1.6	1.626	103.56	L609018	SRM2	1.038	1.050	100.77
L609006	SRM2	10.1	10.220	101.39	L609006	SRM2	1.6	1.623	101.44	L609032	SRM1	1.038	1.037	99.90
L609017	SRM1	10.1	9.699	96.03	L609017	SRM1	1.6	1.622	101.38	L609032	SRM2	1.038	1.054	101.54
L609017	SRM2	10.1	9.821	97.24	L609017	SRM2	1.6	1.641	102.56	L609034	SRM1	1.038	1.037	99.90
L609028	SRM1	10.1	9.713	96.17	L609028	SRM1	1.6	1.627	101.69	L609034	SRM2	1.038	1.053	101.45
L609028	SRM2	10.1	9.812	97.15	L609028	SRM2	1.6	1.629	101.81	L610010	SRM1	1.038	1.042	100.39
L610002	SRM1	10.1	9.720	96.24	L610002	SRM1	1.6	1.628	101.75	L610010	SRM2	1.038	1.056	101.73
L610002	SRM2	10.1	9.764	96.67	L610002	SRM2	1.6	1.628	101.75	L610015	SRM1	1.038	1.046	100.77
L610009	SRM1	10.1	9.698	96.02	L610009	SRM1	1.6	1.628	101.75	L610015	SRM2	1.038	1.043	100.48
L610009	SRM2	10.1	9.809	97.12	L610009	SRM2	1.6	1.648	103.00	L610023	SRM1	1.038	1.076	103.66
L610016	SRM1	10.1	9.692	95.96	L610016	SRM1	1.6	1.601	100.06	L610023	SRM2	1.038	1.030	99.23
L610016	SRM2	10.1	9.858	97.60	L610016	SRM2	1.6	1.623	101.44	L611004	SRM1	1.038	1.029	99.13
L610021	SRM1	10.1	10.050	99.50	L610021	SRM1	1.6	1.597	99.81	L611004	SRM2	1.038	1.023	98.55
L610021	SRM2	10.1	9.813	97.16	L610021	SRM2	1.6	1.560	97.50	L611010	SRM1	1.038	1.022	98.46
L610028	SRM1	10.1	9.778	96.81	L610028	SRM1	1.6	1.614	100.88	L611010	SRM2	1.038	1.020	98.27
L610028	SRM2	10.1	9.908	98.10	L610028	SRM2	1.6	1.630	101.88	L611018	SRM1	1.038	1.029	99.13
L611009	SRM1	10.1	9.768	96.71	L611009	SRM1	1.6	1.609	100.56	L611018	SRM2	1.038	1.033	99.52
L611009	SRM2	10.1	9.913	98.15	L611009	SRM2	1.6	1.635	102.19					
L611019	SRM1	10.1	9.813	97.16	L611019	SRM1	1.6	1.616	101.00	1				
L611019	SRM2	10.1	9.944	98.46	L611019	SRM2	1.6	1.634	102.13					
Mean				97.65	Mean				101.62	Mean				100.48
Standard Devia	ation			1.38 47	Standard Devi	ation			1.15	Standard Devia	ation			1.64
Count				4/	Count				47	Count				44

Table C-3. Dry Deposition 2006 Sampling Season – QC Batch Summary for Teflon[®] Filters – Reference Samples – Great Smoky Mountains National Park, TN (2 of 5)

L606017 SRM1 0.052 0.05470 105.19 L606017 SRM1 0.05 0.05241 104.82 L606017 SRM2 L606017 SRM2 0.052 0.05459 104.98 L606017 SRM2 0.05 0.05162 103.24 L606017 SRM2 L606017 SRM3 0.052 0.05451 104.83 L606017 SRM3 0.05 0.05150 103.00 L606017 SRM3 L606023 SRM1 0.052 0.05530 106.35 L606023 SRM1 0.05 0.05278 105.56 L606023 SRM2 L606023 SRM2 0.052 0.05431 104.44 L606023 SRM2 0.05 0.05146 102.92 L606023 S L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 S L607003 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 <t< th=""><th>Na QC Key Target mg/L SRM1 0.4 SRM2 0.4 SRM3 0.4 SRM1 0.4 SRM2 0.4 SRM3 0.4</th><th>Found mg/L 0.3792 0.3754 0.3750 0.3872 0.3810</th><th>Percent Recovery 94.80 93.85 93.75 96.80</th></t<>	Na QC Key Target mg/L SRM1 0.4 SRM2 0.4 SRM3 0.4 SRM1 0.4 SRM2 0.4 SRM3 0.4	Found mg/L 0.3792 0.3754 0.3750 0.3872 0.3810	Percent Recovery 94.80 93.85 93.75 96.80
L606017 SRM1 0.052 0.05470 105.19 L606017 SRM1 0.05 0.05241 104.82 L606017 SRM2 L606017 SRM2 0.052 0.05459 104.98 L606017 SRM2 0.05 0.05162 103.24 L606017 SRM2 L606017 SRM3 0.052 0.05451 104.83 L606017 SRM3 0.05 0.05150 103.00 L606017 SRM3 L606023 SRM1 0.052 0.05530 106.35 L606023 SRM1 0.05 0.05278 105.56 L606023 SRM2 L606023 SRM2 0.052 0.05431 104.44 L606023 SRM2 0.05 0.05146 102.92 L606023 S L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 S L607003 SRM4 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05141 <t< th=""><th>SRM1 0.4 SRM2 0.4 SRM3 0.4 SRM1 0.4 SRM2 0.4</th><th>0.3792 0.3754 0.3750 0.3872</th><th>94.80 93.85 93.75</th></t<>	SRM1 0.4 SRM2 0.4 SRM3 0.4 SRM1 0.4 SRM2 0.4	0.3792 0.3754 0.3750 0.3872	94.80 93.85 93.75
L606017 SRM2 0.052 0.05459 104.98 L606017 SRM2 0.05 0.05162 103.24 L606017 SRM2 L606017 SRM3 0.052 0.05451 104.83 L606017 SRM3 0.05 0.05150 103.00 L606017 SRM2 L606023 SRM1 0.052 0.05530 106.35 L606023 SRM1 0.05 0.05278 105.56 L606023 SRM2 L606023 SRM2 0.052 0.05431 104.44 L606023 SRM2 0.05 0.05146 102.92 L606023 S L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 S L606023 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 102.82 L606023 S L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 1	SRM2 0.4 SRM3 0.4 SRM1 0.4 SRM2 0.4	0.3754 0.3750 0.3872	93.85 93.75
L606017 SRM3 0.052 0.05451 104.83 L606017 SRM3 0.05 0.05150 103.00 L606017 SRM2 L606023 SRM1 0.052 0.05530 106.35 L606023 SRM1 0.05 0.05278 105.56 L606023 SRM2 L606023 SRM2 0.052 0.05431 104.44 L606023 SRM2 0.05 0.05146 102.92 L606023 SRM2 L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 SRM3 L606023 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 102.82 L606023 SRM4 L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 106.28 L607003 SRM2 L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249	SRM3 0.4 SRM1 0.4 SRM2 0.4	0.3750 0.3872	93.75
L606023 SRM1 0.052 0.05530 106.35 L606023 SRM1 0.05 0.05278 105.56 L606023 S L606023 SRM2 0.052 0.05431 104.44 L606023 SRM2 0.05 0.05146 102.92 L606023 S L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 S L606023 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 102.82 L606023 S L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 106.28 L607003 S L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249 104.98 L607003 S	SRM1 0.4 SRM2 0.4	0.3872	
L606023 SRM2 0.052 0.05431 104.44 L606023 SRM2 0.05 0.05146 102.92 L606023 S L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 S L606023 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 102.82 L606023 S L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 106.28 L607003 S L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249 104.98 L607003 S	SRM2 0.4		96.80
L606023 SRM3 0.052 0.05422 104.27 L606023 SRM3 0.05 0.05179 103.58 L606023 SRM2 L606023 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 102.82 L606023 SRM2 L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 106.28 L607003 SRM2 L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249 104.98 L607003 SRM2			05.05
L606023 SRM4 0.052 0.05424 104.31 L606023 SRM4 0.05 0.05141 102.82 L606023 SRM2 L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 106.28 L607003 SRM2 L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249 104.98 L607003 SRM2			95.25
L607003 SRM1 0.052 0.05480 105.38 L607003 SRM1 0.05 0.05314 106.28 L607003 SRM2 L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249 104.98 L607003 SRM2		0.3790	94.75
L607003 SRM2 0.052 0.05609 107.87 L607003 SRM2 0.05 0.05249 104.98 L607003 S	SRM4 0.4 SRM1 0.4	0.3790 0.3812	94.75 95.30
	SRM2 0.4	0.3875	96.88
2007003 SKWS 0.032 0.03400 103.30 E007003 SKWS 0.03 0.03177 103.34 E007003 K	SRM3 0.4	0.3797	94.93
L607008 SRM1 0.052 0.05507 105.90 L607008 SRM1 0.05 0.05206 104.12 L607008 S	SRM1 0.4	0.3842	96.05
	SRM2 0.4	0.3840	96.00
	SRM3 0.4	0.3878	96.95
	SRM1 0.4	0.3840	96.00
	SRM2 0.4	0.3755	93.88
	SRM3 0.4	0.3794	94.85
	SRM1 0.4	0.3820	95.50
	SRM2 0.4	0.3805	95.13
	SRM3 0.4	0.3760	94.00
	SRM1 0.4	0.3824	95.60
L607030 SRM2 0.052 0.05467 105.13 L607030 SRM2 0.05 0.05081 101.62 L607030 S	SRM2 0.4	0.3799	94.98
L607030 SRM3 0.052 0.05567 107.06 L607030 SRM3 0.05 0.05127 102.54 L607030 S	SRM3 0.4	0.3824	95.60
L608006 SRM1 0.052 0.05323 102.37 L608006 SRM1 0.05 0.05122 102.44 L608006 S	SRM1 0.4	0.3770	94.25
L608006 SRM2 0.052 0.05480 105.38 L608006 SRM2 0.05 0.05151 103.02 L608006 \$	SRM2 0.4	0.3814	95.35
L608011 SRM1 0.052 0.05503 105.83 L608011 SRM1 0.05 0.05085 101.70 L608011 S	SRM1 0.4	0.3867	96.68
L608011 SRM2 0.052 0.05381 103.48 L608011 SRM2 0.05 0.05094 101.88 L608011 S	SRM2 0.4	0.3793	94.83
L608011 SRM3 0.052 0.05517 106.10 L608011 SRM3 0.05 0.05051 101.02 L608011 S	SRM3 0.4	0.3812	95.30
	SRM1 0.4	0.3820	95.50
L608023 SRM2 0.052 0.05513 106.02 L608023 SRM2 0.05 0.05121 102.42 L608023 S	SRM2 0.4	0.3797	94.93
	SRM3 0.4	0.3820	95.50
	SRM4 0.4	0.3794	94.85
	SRM1 0.4	0.3802	95.05
	SRM2 0.4	0.3831	95.78
	SRM3 0.4	0.3832	95.80
	SRM1 0.4	0.3846	96.15
	SRM2 0.4	0.3791	94.78
	SRM3 0.4	0.3773	94.33
	SRM1 0.4	0.3760	94.00
	SRM2 0.4	0.3775	94.38
	SRM3 0.4	0.3792	94.80
	SRM1 0.4	0.3744	93.60
	SRM2 0.4 SRM3 0.4	0.3794 0.3763	94.85 94.08
	SRM3 0.4 SRM1 0.4	0.3763	94.08

Table C-3. Dry Deposition 2006 Sampling Season – QC Batch Summary for Teflon[®] Filters – Reference Samples – Great Smoky Mountains National Park, TN (3 of 5)

	1.1001			IK, 111 (5)	010)		2+					+		
		Ca ²⁺					Mg^{2+}					Na ⁺		
Batch	QC Key	Target mg/L	Found mg/L	Percent Recovery	Batch	OC Kev	Target	Found mg/L	Percent Recovery	Batch	QC Key	Target mg/L	Found mg/I	Percent Recovery
							mg/L						Found mg/L	
L609021	SRM2	0.052	0.05483	105.44	L609021	SRM2	0.05	0.05135	102.70	L609021	SRM2	0.4	0.3790	94.75
L609021	SRM3	0.052	0.05565	107.02	L609021	SRM3	0.05	0.05163	103.26	L609021	SRM3	0.4	0.3855	96.38
L609030	SRM1	0.052	0.05496	105.69	L609030	SRM1	0.05	0.05137	102.74	L609030	SRM1	0.4	0.3829	95.73
L609030	SRM2	0.052	0.05473	105.25	L609030	SRM2	0.05	0.05138	103.08	L609030	SRM2	0.4	0.3763	94.08
L609030	SRM3	0.052	0.05418	104.19	L609030	SRM3	0.05	0.05116	1.18	L609030	SRM3	0.4	0.3715	92.88
L610005	SRM1	0.052	0.05290	101.73	L610005	SRM1	0.05	0.05077	45.00	L610005	SRM1	0.4	0.3757	93.93
L610005	SRM2	0.052	0.05291	101.75	L610005	SRM2	0.05	0.05092	101.84	L610005	SRM2	0.4	0.3765	94.13
L610005	SRM3	0.052	0.05353	102.94	L610005	SRM3	0.05	0.05080	101.60	L610005	SRM3	0.4	0.3800	95.00
L610013	SRM1	0.052	0.05308	102.08	L610013	SRM1	0.05	0.05159	103.18	L610013	SRM1	0.4	0.3774	94.35
L610013	SRM2	0.052	0.05398	103.81	L610013	SRM2	0.05	0.05083	101.66	L610013	SRM2	0.4	0.3789	94.73
L610018	SRM1	0.052	0.05213	100.25	L610018	SRM1	0.05	0.05023	100.46	L610018	SRM1	0.4	0.3729	93.23
L610018	SRM2	0.052	0.05347	102.83	L610018	SRM2	0.05	0.05030	100.60	L610018	SRM2	0.4	0.3751	93.78
L610025	SRM1	0.052	0.05450	104.81	L610025	SRM1	0.05	0.05172	103.44	L610025	SRM1	0.4	0.3871	96.78
L610025	SRM2	0.052	0.05538	106.50	L610025	SRM2	0.05	0.05125	102.50	L610025	SRM2	0.4	0.3819	95.48
L611003	SRM1	0.052	0.05409	104.02	L611003	SRM1	0.05	0.05122	102.44	L611003	SRM1	0.4	0.3853	96.33
L611003	SRM2	0.052	0.05545	106.63	L611003	SRM2	0.05	0.05087	101.74	L611003	SRM2	0.05	0.3830	95.75
L611013	SRM1	0.052	0.05470	105.19	L611013	SRM1	0.05	0.05112	102.24	L611013	SRM1	0.05	0.3852	96.30
L611013	SRM2	0.052	0.05618	108.04	L611013	SRM2	0.05	0.05106	102.12	L611013	SRM2	0.05	0.3848	96.20
Mean				104.74	Mean				100.29	Mean				95.05
Standard Devi	iation			1.64	Standard Devia	ntion			14.80	Standard Devi	ation			0.99
Count				62	Count				62	Count				62

Table C-3. Dry Deposition 2006 Sampling Season – QC Batch Summary for Teflon[®] Filters – Reference Samples – Great Smoky Mountains National Park, TN (4 of 5)

	17100		National F	uik, iiv	(1013)				
		$\mathbf{K}^{^{+}}$					Cl.		
	0.077	Target		Percent		0.077	Target		Percent
Batch	QC Key	mg/L	Found mg/L	Recovery	Batch	QC Key	mg/L	Found mg/L	Recovery
L606017	SRM1	0.097 0.097	0.09881	101.87	L606021	SRM1	0.98 0.98	0.9910	101.12
L606017 L606017	SRM2 SRM3	0.097	0.09701 0.09976	100.01 102.85	L606021 L606027	SRM2 SRM1	0.98	1.0050 0.9964	102.55 101.67
L606017	SRM1	0.097	0.10160	102.85	L606027	SRM2	0.98	0.9964	102.01
L606023	SRM2			104.74	L607006	SRM1	0.98		102.01
L606023	SRM3	0.097 0.097	0.09747	100.48	L607006	SRM2	0.98	0.9900	101.02
L606023	SRM4	0.097	0.09750 0.09821	100.52	L607016	SRM1	0.98	0.9951 0.9550	97.45
L607003	SRM1	0.097	0.10080	103.92	L607016	SRM2	0.98	0.9520	97.43 97.14
L607003	SRM2	0.097	0.10270	105.88	L607017	SRM1	0.98	0.9808	100.08
L607003	SRM3	0.097	0.10380	107.01	L607017	SRM2	0.98	0.9977	101.81
L607008	SRM1	0.097	0.09983	102.92	L607017	SRM3	0.98	0.9938	101.41
L607008	SRM2	0.097	0.09892	101.98	L607017	SRM4	0.98	1.0060	102.65
L607008	SRM3	0.097	0.10060	103.71	L607029	SRM1	0.98	0.9796	99.96
L607013	SRM1	0.097	0.09902	102.08	L607029	SRM2	0.98	0.9929	101.32
L607013	SRM2	0.097	0.09738	100.39	L607033	SRM1	0.98	0.9789	99.89
L607013	SRM3	0.097	0.09927	102.34	L607033	SRM2	0.98	0.9812	100.12
L607023	SRM1	0.097	0.09915	102.22	L608003	SRM1	0.98	0.9809	100.09
L607023	SRM2	0.097	0.09664	99.63	L608003	SRM2	0.98	0.9945	101.48
L607023	SRM3	0.097	0.09685	99.85	L608018	SRM1	0.98	0.9788	99.88
L607030	SRM1	0.097	0.09895	102.01	L608018	SRM2	0.98	0.9960	101.63
L607030	SRM2	0.097	0.09652	99.51	L608027	SRM1	0.98	0.9892	100.94
L607030	SRM3	0.097	0.09587	98.84	L608027	SRM2	0.98	0.9984	101.88
L608006	SRM1	0.097	0.09533	98.28	L608027	SRM3	0.98	0.9987	101.91
L608006	SRM2	0.097	0.09822	101.26	L608032	SRM1	0.98	0.9911	101.13
L608011	SRM1	0.097	0.09937	102.44	L608032	SRM2	0.98	1.0060	102.65
L608011	SRM2	0.097	0.09695	99.95	L609001	SRM1	0.98	0.9843	100.44
L608011	SRM3	0.097	0.09826	101.30	L609001	SRM2	0.98	1.0080	102.86
L608023	SRM1	0.097	0.10130	104.43	L609006	SRM1	0.98	1.0000	102.04
L608023	SRM2	0.097	0.09852	101.57	L609006	SRM2	0.98	0.9860	100.61
L608023	SRM3	0.097	0.10000	103.09	L609017	SRM1	0.98	0.9877	100.79
L608023	SRM4	0.097	0.09998	103.07	L609017	SRM2	0.98	0.9958	101.61
L608028	SRM1	0.097	0.09847	101.52	L609028	SRM1	0.98	0.9853	100.54
L608028	SRM2	0.097	0.09908	102.14	L609028	SRM2	0.98	0.9893	100.95
L608028	SRM3	0.097	0.09918	102.25	L610002	SRM1	0.98	0.9819	100.19
L608036	SRM1	0.097	0.10020	103.30	L610002	SRM2	0.98	1.0000	102.04
L608036	SRM2	0.097	0.09702	100.02	L610009	SRM1	0.98	0.9903	101.05
L608036	SRM3	0.097	0.09585	98.81	L610009	SRM2	0.98	1.0030	102.35
L609005	SRM1	0.097	0.09846	101.51	L610016	SRM1 SRM2	0.98 0.98	0.9795	99.95
L609005	SRM2	0.097	0.09892	101.98	L610016			0.9971	101.74
L609005 L609011	SRM3 SRM1	0.097 0.097	0.09888 0.09990	101.94 102.99	L610021 L610021	SRM1 SRM2	0.98 0.98	0.9520 0.9310	97.14 95.00
L609011	SRM2	0.097	0.09990	102.99	L610021 L610028	SRM2 SRM1	0.98	0.9310	95.00 99.59
L609011	SRM3	0.097	0.09805	101.08	L6110026	SRM2	0.98	0.9960	101.63
L609021	SRM1	0.097	0.09706	100.06	L611019	SRM1	0.98	0.9790	99.90
L609021	SRM2	0.097	0.09789	100.00	L611019	SRM2	0.98	0.9889	100.91
L609021	SRM3	0.097	0.09877	101.82	2011013	OINIVIZ	0.50	0.3003	100.31
L609030	SRM1	0.097	0.10130	104.43					
L609030	SRM2	0.097	0.09953	102.61					
L609030	SRM3	0.097	0.09948	102.56					
L610005	SRM1	0.097	0.09764	100.66					
L610005	SRM2	0.097	0.09804	101.07					
L610005	SRM3	0.097	0.09929	102.36					
L610013	SRM1	0.097	0.10120	104.33					
L610013	SRM2	0.097	0.09969	102.77					
L610018	SRM1	0.097	0.09591	98.88					
L610018	SRM2	0.097	0.09551	98.46					

Table C-3. Dry Deposition 2006 Sampling Season – QC Batch Summary for Teflon[®] Filters – Reference Samples – Great Smoky Mountains National Park, TN (5 of 5)

Batch	QC Key	K ⁺ Target mg/L	Found mg/L	Percent Recovery	Batch	QC Key	Cl ⁻ Target mg/L	Found mg/L	Percent Recovery
L610025	SRM1	0.097	0.10070	103.81					
L610025	SRM2	0.097	0.09768	100.70					
L611003	SRM1	0.097	0.10010	103.20					
L611003	SRM2	0.097	0.09723	100.24					
L611013	SRM1	0.097	0.10090	104.02					
L611013	SRM2	0.097	0.09966	102.74					
Mean				101.83	Mean				100.76
Standard De	viation			1.79	Standard Dev	riation			1.52
Count				62	Count				47

Table C-4. Dry Deposition 2006 Sampling Season – QC Batch Summary for Nylon Filters – Reference Samples – Great Smoky Mountains National Park, TN

	TVIOUITU	1115 1 1441	onar rark,	111					
		SO ₄					NO,		
		Target		Percent			Target	Found	Percent
Batch	Lab Key	mg/L	Found mg/L	Recovery	Batch	Lab Key	mg/L	mg/L	Recovery
L606018	SRM1	10.1	10.300	101.98	L606018	SRM1	1.6	1.616	101.00
L606018	SRM2	10.1	10.330	102.28	L606018	SRM2	1.6	1.625	101.56
L606025	SRM1	10.1	10.090	99.90	L606025	SRM1	1.6	1.578	98.63
L606025	SRM2	10.1	10.190	100.89	L606025	SRM2	1.6	1.603	100.19
L607005	SRM1	10.1	10.190	100.89	L607005	SRM1	1.6	1.594	99.63
L607005	SRM2	10.1	10.270	101.68	L607005	SRM2	1.6	1.611	100.69
L607011	SRM1	10.1	10.180	100.79	L607011	SRM1	1.6	1.590	99.38
L607011	SRM2	10.1	10.210	101.09	L607011	SRM2	1.6	1.601	100.06
L607015	SRM1	10.1	10.190	100.89	L607015	SRM1	1.6	1.592	99.50
L607015	SRM2	10.1	10.210	101.09	L607015	SRM2	1.6	1.601	100.06
L607027	SRM1	10.1	10.340	102.38	L607027	SRM1	1.6	1.627	101.69
L607027	SRM2	10.1	10.400	102.97	L607027	SRM2	1.6	1.635	102.19
L607031	SRM1	10.1	10.350	102.48	L607031	SRM1	1.6	1.621	101.31
L607031	SRM2	10.1	10.350	102.48	L607031	SRM2	1.6	1.631	101.94
L608010	SRM1	10.1	10.060	99.60	L608010	RM1	1.6	1.565	97.81
L608010	SRM2	10.1	10.100	100.00	L608010	SRM2	1.6	1.572	98.25
L608015	SRM1	10.1	10.040	99.41	L608015	SRM1	1.6	1.592	99.50
L608015	SRM2	10.1	10.180	100.79	L608015	SRM2	1.6	1.617	101.06
L608025	SRM1	10.1	9.999	99.00	L608025	SRM1	1.6	1.561	97.56
L608025	SRM2	10.1	9.983	98.84	L608025	SRM2	1.6	1.567	97.94
L608034	SRM1	10.1	10.180	100.79	L608034	SRM1	1.6	1.594	99.63
L608034	SRM2	10.1	10.250	101.49	L608034	SRM2	1.6	1.614	100.88
L609004	SRM1	10.1	10.260	101.58	L609004	SRM1	1.6	1.608	100.50
L609004	SRM2	10.1	10.280	101.78	L609004	SRM2	1.6	1.612	100.75
L609007	SRM1	10.1	10.240	101.39	L609007	SRM1	1.6	1.604	100.25
L609007	SRM2	10.1	10.270	101.68	L609007	SRM2	1.6	1.612	100.75
L609013	SRM1	10.1	10.220	101.19	L609013	SRM1	1.6	1.613	100.81
L609013	SRM2	10.1	10.240	101.39	L609013	SRM2	1.6	1.615	100.94
L609024			10.130	100.30	L609024	SRM1	1.6	1.580	98.75
L609024	SRM2	10.1	10.080	99.80	L609024	SRM2	1.6	1.568	98.00
L610001	SRM1	10.1	10.090	99.90	L610001	SRM1	1.6	1.577	98.56
L610001	SRM2	10.1	10.200	100.99	L610001	SRM2	1.6	1.596	99.75
L610003	SRM1	10.1	10.050	99.50	L610003	SRM1	1.6	1.603	100.19
L610003	SRM2	10.1	10.160	100.59	L610003	SRM2	1.6	1.599	99.94
L610014	SRM1	10.1	10.130	100.30	L610014	SRM1	1.6	1.573	98.31
L610014	SRM2	10.1	10.220	101.19	L610014	SRM2	1.6	1.596	99.75
L610024	SRM1	10.1	10.090	99.90	L610024	SRM1	1.6	1.601	100.06
L610024	SRM2	10.1	9.861	97.63	L610024	SRM2	1.6	1.592	99.50
L610027	SRM1	10.1	10.280	101.78	L610027	SRM1	1.6	1.609	100.56
L610027	SRM2	10.1	10.320	102.18	L610027	SRM2	1.6	1.622	101.38
L611008	SRM1	10.1	10.090	99.90	L611008	SRM1	1.6	1.595	99.69
L611008	SRM2	10.1	10.350	102.48	L611008	SRM2	1.6	1.623	101.44
L611015	SRM1	10.1	10.060	99.60	L611015	SRM1	1.6	1.571	98.19
L611015	SRM2	10.1	10.120	100.20	L611015	SRM2	1.6	1.587	99.19
L610014	SRM1	10.1	10.130	100.30	L610014	SRM1	1.6	1.573	98.31
L610014	SRM2	10.1	10.220	101.19	L610014	SRM2	1.6	1.596	99.75
Mean				100.84	Mean				99.95
Standard Devia	ation			1.14	Standard Devi	ation			1.20
Count				44	Count				44

Table C-5. Dry Deposition 2006 Sampling Season – QC Batch Summary for Cellulose Filters– Reference Samples – Great Smoky Mountains National Park, TN

	TVIOUITUIII	S Ivational	ı uın,	111
		SO ₄		
Batch	Lab Key	Target mg/L	Found mg/L	Percent Recovery
L606020	SRM1	10.1	10.240	101.39
L606020	SRM2	10.1	10.240	101.39
L606020	SRM1	10.1	10.240	101.19
L606029	SRM2	10.1	10.240	101.19
L607001	SRM1	10.1	10.240	101.39
L607001	SRM2	10.1	10.240	101.98
L607007	SRM1	10.1	10.300	101.49
L607007	SRM2	10.1	10.250	101.49
L607018	SRM1	10.1	10.160	100.59
L607018	SRM2	10.1	10.170	100.69
L607025	SRM1	10.1	10.180	100.79
L607025	SRM2	10.1	10.210	101.09
L607032	SRM1	10.1	10.190	100.89
L607032	SRM2	10.1	10.190	100.89
L608004	SRM1	10.1	10.180	100.79
L608004	SRM2	10.1	10.140	100.40
L608017	SRM1	10.1	10.230	101.29
L608017	SRM2	10.1	10.160	100.59
L608026	SRM1	10.1	10.310	102.08
L608026	SRM2	10.1	10.280	101.78
L608037	SRM1	10.1	10.250	101.49
L608037	SRM2	10.1	10.240	101.39
L609003	SRM1	10.1	10.270	101.68
L609003	SRM2	10.1	10.260	101.58
L609009	SRM1	10.1	10.270	101.68
L609009	SRM2	10.1	10.250	101.49
L609022	SRM1	10.1	10.280	101.78
L609022	SRM2	10.1	10.260	101.58
L609029	SRM1	10.1	10.270	101.68
L609029	SRM2	10.1	10.260	101.58
L610004	SRM1	10.1	10.290	101.88
L610004	SRM2	10.1	10.280	101.78
L610006	SRM1	10.1	10.290	101.88
L610006	SRM2	10.1	10.280	101.78
L610019	SRM1	10.1	10.240	101.39
L610019	SRM2	10.1	10.275	101.73
L610026	SRM1	10.1	10.232	101.31
L610026	SRM2	10.1	10.297	101.95
L611005	SRM1	10.1	10.175	100.74
L611005	SRM2	10.1	10.119	100.19
L611012	SRM1	10.1	10.196	100.95
L611012	SRM2	10.1	10.195	100.94
L611017	SRM1	10.1	10.192	100.91
L611017	SRM2	10.1	10.194	100.93
Mean				101.32
Standard Deviation	,			0.47
Count	•			44
Jount				

Table C-6. Dry Deposition 2006 Sampling Season – CVS (%R) – Great Smoky Mountains National Park, TN

	1 &		, ,	
Filter Type	Parameter	Mean	Standard Deviation	Count
Teflon®	SO_4^{2-}	99.62	1.13	243
	NO_3 - N	99.38	1.07	243
	Cl	99.41	1.38	243
	NH_4^+ - N	99.41	1.63	227
	Ca^{2+}	100.77	1.00	257
	$\mathrm{Mg}^{^{2+}}$	100.14	0.71	257
	Na^{+}	100.19	0.95	257
	K^{+}	100.43	0.93	257
Nylon	SO ₄ ²⁻	99.91	1.84	227
	NO_3 - N	100.11	1.86	227
Cellulose	SO_4^{2-}	99.53	0.60	169

Note:

%R = percent recovery

Table C-7. Dry Deposition 2006 Sampling Season – Replicate Summary – Great Smoky Mountains National Park, TN

Sample No.	Replicate No.	Date	Parameter	Filter Type	Sample Result	Replicate Result	Percent Difference	Mean Percent Difference	Standard Deviation	Count
L607013	RP*L607013	6/27/2006	Calcium	Teflon	14.300	13.9900	2.17	NA	NA	1
L607013	RP*L607013	6/27/2006	Magnesium	Teflon	1.709	1.7000	0.53	NA	NA	1
L607013	RP*L607013	6/27/2006	Potassium	Teflon	3.095	3.1470	-1.68	NA	NA	1
L607013	RP*L607013	6/27/2006	Sodium	Teflon	0.778	0.7611	2.17	NA	NA	1
L609024	RP*L609024	9/5/2006	NO ₃ -N	Nylon	11.620	11.5000	1.03	NA	NA	1
L609024	RP*L609024	9/5/2006	SO ₄ ²⁻	Nylon	17.400	17.0800	1.84	NA	NA	1
L606029	RP*L606029	6/13/2006	SO ₄ ²⁻	Cellulose	166.600	166.9000	-0.18	NA	NA	1