

# Sensitivity Analysis of the Multi-Layer Model Used in the Clean Air Status and Trends Network (CASTNET)

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EPA Contract No. EP-D-05-096

Prepared for

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#### **ABSTRACT**

The U.S. Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNET) and its predecessor, the National Dry Deposition Network (NDDN), as national air quality and meteorological monitoring networks. The purpose of CASTNET is to track the progress of the 1990 Clean Air Act Amendments (CAAA) emission reduction program for sulfur dioxide ( $SO_2$ ) and oxides of nitrogen ( $NO_x$ ) in terms of reductions in sulfur and nitrogen deposition, improved air quality, and changes to affected ecosystems. Both CASTNET and NDDN were designed to measure concentrations of sulfur and nitrogen gases and particles and to estimate dry deposition using an inferential model. The design was based on the concept that atmospheric dry deposition flux could be estimated as  $Flux = C*V_d$ , where C represents a measured air pollutant concentration and  $V_d$  represents a modeled deposition velocity. In other words, the flux is directly proportional to the deposition velocity. Consequently, an uncertainty in the deposition velocity produces an uncertainty in the flux estimate.

The Multi-Layer Model (MLM), the computer model used to simulate dry deposition, requires information on meteorological conditions and vegetative cover as model input. Specifically, the MLM requires hourly averages of wind speed, standard deviation of wind direction (sigma theta), temperature, relative humidity, and surface wetness. Also as input, the MLM uses plant speciation data specific to each monitoring site. Speciation data include minimum and maximum leaf area index (LAI) values and data on the temporal evolution of vegetation leaf-out characterizing the surroundings of the site within a radius of 1 kilometer (km). Previous studies have examined the sensitivity of the MLM estimates of deposition velocity and dry deposition flux to uncertainties in the meteorological and vegetation data and model formulation. For example, Cooter and Schwede<sup>1</sup> concluded that deposition velocity estimates for SO<sub>2</sub> and nitric acid (HNO<sub>3</sub>) were most sensitive to wind speed and sigma theta. Deposition velocity estimates for ozone were most sensitive to LAI values. Rogers and his colleagues<sup>2</sup> corroborated these results by showing that annual fluxes of SO<sub>2</sub>, HNO<sub>3</sub>, and aerosols were most sensitive to wind speed and sigma theta.

This research extends the previous sensitivity analyses by investigating the ability to substitute historical values of deposition velocity or nearby or historical meteorological measurements for missing on-site data in order to improve the completeness of the dry deposition flux estimates while not significantly increasing their uncertainty. Using the results from Lavery et al.<sup>3</sup>, this study also examines the effect of uncertainties in particulate NO<sub>3</sub> and HNO<sub>3</sub> concentrations on total nitrogen deposition. Finally, this research analyzes the sensitivity of deposition velocity estimates to the parameterization of non-vegetative surfaces such as rock and water.

# INTRODUCTION

The United States Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNET) to provide data for determining relationships between changes in emissions and any subsequent changes in air quality, atmospheric deposition, and ecological effects. The rural monitoring network was mandated by the 1990 Clean Air Act Amendments

(CAAA) to assess the effectiveness of requirements promulgated to reduce emissions of  $SO_2$  and  $NO_x$  as Congress recognized the need to track real-world environmental results as the Acid Rain Program was implemented.

Under the CAAA, the Acid Rain Program has produced significant reductions in SO<sub>2</sub> and NO<sub>x</sub> emissions from electric generating plants since 1995. More recent NO<sub>x</sub> emission control programs also produced substantive declines in NO<sub>x</sub> emissions in the eastern United States. These programs include the Ozone Transport Commission (OTC) NO<sub>x</sub> Budget, NO<sub>x</sub> State Implementation Plan (SIP) Call, and NO<sub>x</sub> Budget Trading Program. EPA relies on CASTNET and other long-term monitoring networks to generate the data and information used to assess the effectiveness of these emission control programs under several different mandates including the Government Performance and Results Act, The National Acid Precipitation Assessment Program (NAPAP), Title IX of the CAAA, and the United States – Canada Air Quality Agreement.

CASTNET has its origins with the National Dry Deposition Network (NDDN), which was established in 1986 and began operation in 1987. Many of the original NDDN sites are still operational after 20 years and provide useful information on trends in air quality.

CASTNET was designed primarily to measure seasonal and annual average concentrations and depositions over many years. Consequently, measurements of weekly average concentrations were selected as the basic sampling strategy. An open-face, three-stage filter pack was employed to measure gaseous and particulate sulfur and nitrogen pollutants as well as concentrations of other pollutant species. The filter pack technology and sampling protocol have been used consistently over the 20 years, providing a comparable data set each year and allowing for the analysis of long-term trends.

CASTNET is sponsored by EPA and the National Park Service (NPS). NPS began its participation in CASTNET in 1994 under an agreement with EPA. NPS is responsible for the protection and enhancement of air quality and related values in national parks and wilderness areas. The CASTNET sites sponsored by NPS as of September 2008 numbered 25. At that time, the network included 84 monitoring stations at 82 site locations throughout the continental United States, Alaska, and Canada, as shown in Figure 1. For more information on CASTNET, please visit <a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a>.



Figure 1. Locations of CASTNET Sites as of September 2008

Dry deposition processes are modeled as resistances to deposition. The original network design was based on the assumption that dry deposition or flux could be estimated as the linear product of measured pollutant concentration (C) and modeled deposition velocity  $(V_d)$ .

**Equation 1.** Estimation of flux.

$$Flux = C*V_d$$

Measured atmospheric concentrations are calculated based on the mass of each analyte in each filter extract and the volume of air sampled. The rate of deposition of a pollutant, also known as deposition velocity, is influenced by meteorological conditions, vegetation, and atmospheric and plant chemistry. The deposition velocity values are calculated for each hour of each year using the MLM. The MLM was described by Meyers et al.<sup>5</sup> and Finkelstein et al.<sup>6</sup>. The data used in the MLM to estimate dry deposition are derived from meteorological measurements and pollutant concentrations taken at the site together with an estimation of the vegetation leaf-out and leaf area index (LAI).

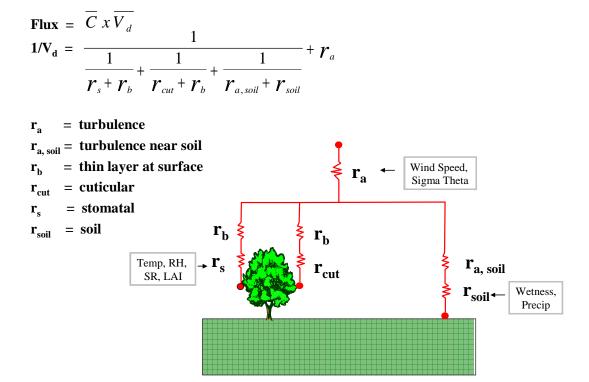
The influence of meteorological conditions and vegetation on the dry deposition process is simulated by  $V_d$ . Deposition velocity is calculated using an inferential model that uses resistances to deposition to model the naturally occurring dry deposition processes<sup>5,6,7,8</sup>.

**Equation 2.** Estimation of deposition velocity.

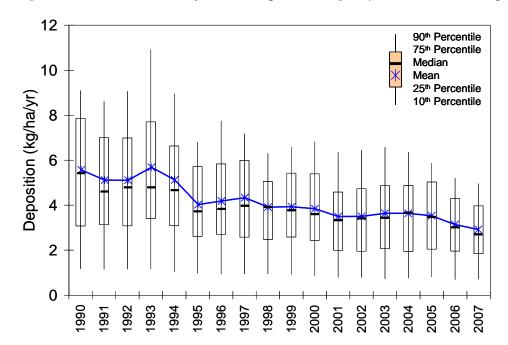
$$V_d = (R_a + R_b + R_c)^{-1}$$

The schematic of the MLM in Figure 2 shows the relationships among the various resistances and illustrates the meteorological and other data that are required as model input. An improved version of the MLM was produced by EPA's Office of Research and Development (ORD) during 2006<sup>9</sup>. This version includes changes to the soil moisture factor, which affects the stomatal and soil resistances, and to the radiation algorithm, which also affects the stomatal resistance. All deposition velocities and fluxes for the entire network were recalculated using the updated model.

Figure 2. Multi-Layer Model



As shown in Figure 3, CASTNET related measurements and estimates of the dry deposition component of total deposition are being used to demonstrate the successes and limitations of CAAA programs.



**Figure 3.** Time Series of Dry Sulfur Deposition (kg/ha/yr) from 1990 through 2007

# **DATA**

Data collected from CASTNET sites fall into two general categories: continuous and discrete. Continuous data include measurements obtained from the field program by instrumentation located at each site. They include meteorological parameters, ozone, and flow through the filter pack. Discrete data consist of laboratory results acquired through analyses of the 3-stage filter packs installed weekly at each site. These data products are combined by the MLM to create estimates of dry deposition, which is the end goal of the network. All data described are processed and validated, and instrumentation is calibrated, according to protocol described in the CASTNET Quality Assurance Project Plan (QAPP)<sup>10</sup>.

# **Continuous Field Measurements**

Continuous data are polled from each site via telephone or cellular modem. The on-site data acquisition system (DAS) calculates hourly averages for the meteorological parameters measured which are transferred to the Data Management Center.

- temperature (°C)
- difference in temperature between 2 and 9 meters (°C)
- solar radiation (W/m<sup>2</sup>)
- relative humidity (%)

- precipitation (mm)
- scalar wind speed (m/s)
- vector wind speed (m/s)
- wind direction (degrees)
- standard deviation of the wind direction within the hour
- wetness
- ozone (ppb)
- rate of flow through the filter pack (liters/min)

Of these, the MLM uses wind speed, standard deviation of the wind direction, solar radiation, temperature, relative humidity, precipitation, and wetness to parameterize soil moisture and to calculate estimates of hourly deposition velocity.

# **Dry Deposition Filter Pack Concentration Data**

The filter pack used at dry deposition configured CASTNET sites consists of three types of filters stacked in the following order: Teflon<sup>®</sup>, nylon, and cellulose. Filter packs are installed and run for a seven-day period. The Teflon<sup>®</sup> filter removes particulate  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $Ca^{2+}$ ,  $Mg^+$ ,  $Na^+$ , and  $K^+$ . The nylon filter removes  $HNO_3$  and some  $SO_2$ . Finally, two cellulose filters, which consist of a cellulose fiber base impregnated with potassium carbonate ( $K_2CO_3$ ), remove  $SO_2$ . The nylon filter  $SO_2$  and cellulose filters  $SO_2$  are summed to provide weekly total  $SO_2$  concentrations. The nylon filter  $HNO_3$  is converted to  $NO_3^-$  and added to the  $NO_3^-$  collected on the Teflon<sup>®</sup> filter to provide weekly total  $NO_3^-$  concentrations. Final atmospheric concentrations are calculated by multiplying the analyte concentrations (in micrograms) with the aggregated flow volume (in meters cubed) for the time period the filter pack was installed. These concentrations are maintained as micrograms per meter cubed.

# **Plant Speciation Information**

The MLM also requires data regarding the characteristics of the plant types that immediately surround the site. The CASTNET database includes this information for all of the vegetation in a 1 km radius around each site. The data include plant type and percent coverage within the 1 km radius. For each plant species, data include leaf area index minimum and maximum values, canopy profile, a static annual percent leaf out distribution, canopy height, and minimum stomatal resistance. Also, information regarding preferred temperature ranges for a plant type is included.

# **Dry Deposition Estimates from the MLM**

The MLM simulates hourly average deposition velocities in centimeters per second (cm/s) for SO<sub>2</sub>, HNO<sub>3</sub>, O<sub>3</sub>, and particles (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>). The estimates are dependent on the specific meteorological measurements and plant type information described previously. The hourly deposition velocities are combined with the filter pack and O<sub>3</sub> concentrations to estimate

hourly rates of dry deposition, in kilograms per hectare (kg/ha). The MLM post-processor aggregates the hourly deposition velocity and deposition rates into weekly, monthly, quarterly, seasonal, and annual values. Each aggregation step requires a percent completeness of 69 percent for the relevant underlying values. For example, 69 percent of the hourly values within a week must be valid in order for the weekly value to be valid. Weekly and monthly values are calculated from hourly values. Seasonal and quarterly values are calculated from weekly values. Annual values may be calculated from either seasonal or quarterly values, but standard CASTNET protocol is to calculate annual aggregates from the four quarterly values within a calendar year. Table 1 shows the aggregation criteria.

Table 1. Aggregation Percent Completeness Criteria

Aggregation Period	Requirement
Weekly	69% of hourly values must be valid.
Monthly	69% of hourly values must be valid.
Seasonal	69% of weekly values must be valid.
Quarterly	69% of weekly values must be valid.
Annual	At least 3 out of 4 quarters (or seasons) must be valid.

# **METHODS**

Because of the percent completeness requirements discussed in the DATA section, annual deposition estimates for many sites are unavailable in large part because of invalid meteorological inputs. In order to get a valid hourly deposition velocity estimate, wind speed, standard deviation of the wind direction, solar radiation, temperature, relative humidity, and precipitation values must all be valid. The failure of a single meteorological parameter during a semi-annual calibration visit to a site can lead to the loss of a valid flux estimate for the year. Because of the reliability of the flow system, concentration data are usually available and only occasionally cause the loss of an annual estimate. Table 2 shows the percentage of site-year estimates for 1987-2007 (all available) that are valid with a breakdown of how many are calculated from four valid quarters as opposed to three valid quarters. Approximately 1 in 4 site-years are not available because of incomplete data. Because of this, it is desirable to develop a protocol for replacing the missing deposition velocity data using a summary or historical value.

**Table 2.** Summary of Valid Site-Years

	Count of Site-Years	Percent Completeness
total	1404	
4 quarters valid	711	51%
3 quarters valid	291	21%
All valid site-years		
(3 or 4 quarters valid)	1002	71%

This study is divided into five tasks (A-E) that address the requirements of Task 2 from the Work Plan.

- A) Calculate 10-year mean deposition velocities (1998-2007) for all sites. Compare 10-year  $V_d$  values from all sites against one another to identify potential "near site" pairs. Compare sites against themselves to determine representativeness of 10-year mean. Analyze results with respect to current list of "near sites" used in MLM runs.
- B) Using estimates of the uncertainties of  $NO_3^-$  and  $HNO_3$  concentrations from Baumgardner et al. (2008), review the effects of these uncertainties on the weekly and annual dry deposition fluxes of  $NO_3^-$ ,  $HNO_3$ , and, most importantly, total measured nitrogen deposition  $(NO_3^- + HNO_3 + NH_4^+, as N)$ .
- C) Estimate annual fluxes by using the 10-year mean deposition velocities calculated during Task A along with annual mean concentrations. Compare the fluxes calculated using the 10-year mean deposition velocities with the actual (historical) annual flux estimates and with annual flux estimates calculated from annual mean deposition velocities and annual mean concentrations. Determine the differences that arise from using site-year with either three or four valid quarters (all valid site-years) compared with using only site-years with four valid quarters (complete year is represented).
- D) Examine the effect on deposition velocities from modifying the parameterization of non-vegetative plant types such as rock and water.
- E) Estimate deposition velocities and fluxes by replacing missing vector wind speed and sigma theta (standard deviation of the wind direction) data with near site values or historical weekly mean values. Compare these estimates with the actual annual flux estimates.

#### Task A:

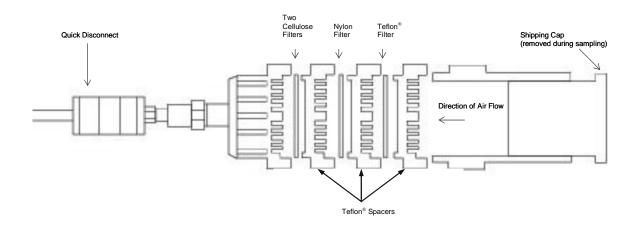
Ten-year mean deposition velocities for 1998-2007 were calculated for each site. Each site was compared against every other site regardless of geographic proximity. All site combinations where the percent difference between each of the estimated deposition velocities ( $SO_2$ ,  $HNO_3$ , and particles) was  $\pm 10$  percent were identified. This list was compared against the current list of "near sites" used for replacing missing meteorological data when conducting a MLM model run.

Each site was also compared against itself by comparing the 10-year mean deposition velocity with each of the ten annual mean depositing velocities from 1998-2007.

#### Task B:

The uncertainties of NO<sub>3</sub> and HNO<sub>3</sub> concentrations were estimated using results of the Maryland Aerosol Research and Characterization (MARCH) / CASTNET comparison from Lavery et al.<sup>3</sup>. MARCH was a state-of-the-science monitoring project conducted at Ft. Meade, MD. Results from the MARCH study were compared with results from the CASTNET site at Beltsville, MD (BEL116), which is approximately 10 km southwest of Ft. Meade. As previously described, CASTNET uses an open-face, 3-stage filter pack (Figure 4) to collect particles and gases. Particulate NO<sub>3</sub> is collected on the Teflon<sup>®</sup> filter (the first filter) and HNO<sub>3</sub> is collected on the nylon (second) filter. There are several issues with this collection protocol with respect to these two analytes. First, in warm conditions, particulate NO<sub>3</sub> may volatilize off the Teflon<sup>®</sup> filter and be captured by the nylon filter. When analyzed, the recaptured NO<sub>3</sub> will appear to be HNO<sub>3</sub>, thus artificially increasing the HNO<sub>3</sub> concentration for the week. Second, because the filter pack hangs on the tower for a week, HNO<sub>3</sub> may be released after capture on the nylon filter leading to lower HNO<sub>3</sub> concentrations. Finally, because the CASTNET filter pack is an openface measurement device, it captures both large and small NO<sub>3</sub> particles. There is evidence that a significant portion of the CASTNET measured NO<sub>3</sub> is actually sodium nitrate (NaNO<sub>3</sub>) and calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>] with a smaller portion attributable to ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>). This is a problem for deposition flux estimates because the particulate deposition velocity used to calculate fluxes of NO<sub>3</sub> is formulated using the assumption that the particle being deposited is small (less than 2.5 μm) such as NH<sub>4</sub>NO<sub>3</sub> or ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]. The deposition velocity for larger particles (greater than 5 µm) such as NaNO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> would be higher due in part to gravitational settling, which is not considered by the MLM.

Figure 4. Filter Pack Schematic



Despite the volatilization of  $NO_3^-$  off the Teflon<sup>®</sup> filter and subsequent collection on the nylon filter, which appears to be HNO<sub>3</sub>, the HNO<sub>3</sub> concentrations at BEL116 were still approximately 15 percent lower than the MARCH HNO<sub>3</sub> concentrations. The deposition velocity for HNO<sub>3</sub> is an order of magnitude higher than that for  $NO_3^-$  and  $NH_4^+$ , so any increase in HNO<sub>3</sub> concentrations would have a dramatic effect on total estimated nitrogen deposition. For  $NO_3^-$ , the comparison with MARCH led to a conclusion that, if considering only  $NH_4NO_3$  (or more generally,  $NO_3^-$  particles smaller than 2.5  $\mu$ m), CASTNET NO3 concentration may be as much as 200 to 400 percent higher than actual  $NH_4NO_3$  concentrations especially during warmer months.

The effects of these uncertainties on the weekly and annual dry deposition fluxes of NO<sub>3</sub>, HNO<sub>3</sub>, and, most importantly, total measured nitrogen deposition (NO<sub>3</sub>+HNO<sub>3</sub>+NH<sub>4</sub>+, as N) were reviewed by manipulating the annual flux values for BEL116 by modifying the percentages with the percentages listed above and recalculating the total measured nitrogen value.

# Task C:

Task C involves making comparisons between archived, historical MLM simulations of annual deposition rates with annual deposition estimates based on historical deposition velocity data. In particular, annual MLM results for each of ten years from the period 1998 through 2007 were compared with flux estimates calculated in two ways. The first involved multiplying 10-year mean deposition velocity (calculated during the performance of Task A) for each site for each pollutant by the measured annual mean concentration for each pollutant and comparing with the MLM results. The second involved multiplying annual mean deposition velocities for each year by the measured annual mean concentrations and then comparing with the respective MLM simulations.

# Task D:

There are five non-vegetative plant types used by the MLM:

- o WATER,
- o ROCK,
- o SAND.
- o URBAN, and
- o LAVA.

There is a sixth, MIXED RURAL, that is partly non-vegetative and partly vegetative. In July 2002 as part of an update of the plant related database that supports MLM operation, the parameterizations of WATER and ROCK were modified. To examine any changes this change introduced, model runs were conducted for two sites, Chiricahua National Monument, AZ (CHA467) and Indian River Lagoon, FL (IRL141), using the original parameterization and the updated parameterization. Differences in the model run results were evaluated.

Although the Work Plan called for manipulating the Leaf Area Index (LAI) values for the non-vegetative species, this does not make sense to do from a physical standpoint. All of the LAI values for all non-vegetative plant types have always been 0.0. Therefore, no model runs were conducted with manipulated LAI values.

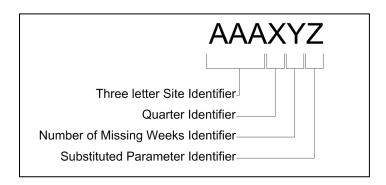
#### Task E:

Missing vector wind speed and sigma theta (standard deviation of the wind direction) data for the site at Lykens, OH (LYK123) were replaced with data from the Deer Creek, OH site (DCP114), which was determined from the analysis in Task A, and with historical weekly mean values from LYK123. These two parameter have been shown by previous sensitivity analyses to be the most influential in the estimation of deposition velocities<sup>1,2</sup>. The periods of missing data were artificially created using a scheme described below. Deposition velocity and flux estimates were calculated for 2007 by running the MLM using the replaced meteorological data. In total, 48 "sites" were run through the model. Each site represented a different combination of missing and replacement data. These estimates were compared with the actual annual flux estimates to determine if near site data or historical average values are better sources for substitution of missing data.

To create the dataset with missing data, values were removed from a specific number of randomly selected weeks for several parameters. Different substitution values could then be easily adapted to the same missing data scheme. Data were removed from six levels of completeness in two different quarters. First and third quarters were selected because they represent the weather extremes of winter and summer seasons. A site identification code was created to represent each combination of missing data. The result was a Cartesian product of each grouping: 12 identification codes per parameter, per site. Week numbers were randomly selected for each group of missing weeks and the same weeks were used for each site in the group. For example, weeks 1 and 2 were randomly selected for the Two Missing Weeks group and every site and parameter combination used these weeks for the Two Missing Weeks set. The value for the identified parameter was set to Null for each data point within the selected weeks.

Figure 5 shows the construction of the site id used to document the periods of missing data. Table 3 describes the meaning of the X, Y, and Z positions of the site id. Table 4 documents the weeks that were randomly removed for each scenario. Sites where missing data were replaced with data from DCP114 begin with a LYK site identifier. Sites where missing data were replaced with historical weekly averages begin with a HIS site identifier. The historical weekly averages were obtained by calculating the average of all valid sigma theta or vector wind speed for a particular week for the 10-year period of 1998-2007. This created a data set of 54 weekly averages for these two parameters. Missing hourly data were replaced by determining the week of the missing hour and then substituting the average value for that specific week.

Figure 5. Site Identification Codes



**Table 3.** Description of X, Y, and Z Coding

1	, ,	
X – Selected Quarter	Y – Number of Missing Weeks	Z – Missing Parameter
Identifier	Identifier	Identifier
O -> Quarter One	T -> Two Weeks	S -> Windspeed
T -> Quarter Three	F -> Four Weeks	G -> Sigma Theta
	S -> Six Weeks	
	E -> Eight Weeks	
	N -> Ten Weeks	
	A -> All Weeks	

Table 4. Randomly Selected Weeks Removed

Number of Weeks	Week Numbers
Two	1,2
Four	2,3,8,9
Six	5,6,9,10,11,12
Eight	1,2,4,5,7,8,9,10
Ten	1,2,3,4,5,6,7,8,9,12
All	All

# Examples:

- LYKOFS Four weeks of windspeed data were removed from quarter one at site LYK123 and replaced with data from DCP114.
- o **HISTAG** All weeks of sigma theta data were removed from quarter three at site LYK123 and replaced with historical weekly averages.

# Several important notes on these model runs:

- O No time was provided for spin up of the soil moisture parameterization. All runs were initialized with a soil moisture values of 20 mm. Because all runs started with the same value, the spin up is not important to the conclusions of the study.
- o Scalar wind speed was not used in the model runs. In normal model runs, it can be used as a backup when vector wind speed is either invalid or missing.

# **RESULTS**

### Task A:

The first analysis performed for Task A was a comparison of the 10-year mean deposition velocities for 1998-2007 for each site with the 10-year mean values for all other sites. All analyses for this tasks used site-years where all four quarters used in the annual mean were valid to ensure that all seasons were represented. The purpose is to identify and pairs of sites where the 10-year mean deposition velocities are similar thereby offering an indication that the sites could be used as "near sites" for the purposes of replacing missing meteorological data. For reference, the currently assigned "near sites" are presented in Table 5. These "near sites" have been in use throughout the history of the network. There are up to two "near sites" for each site.

The current "near sites" were assigned based on geographic proximity and similar terrain and land use. They were not assigned and had not been reviewed using any type of quantitative analysis to determine their value as a replacement data source. Also, it is possible that these assignments may have considered the comparability of the concentration values between the sites, which bears no relevance on the utility of the meteorological data as a source of data for replacing missing data at a nearby site.

Relative percent differences (RPD) were calculated for  $SO_2\ V_d$ ,  $HNO_3\ V_d$ , and particulate  $V_d$ . Comparisons were examined to determine which site pairs had a percent different for each of the three deposition velocities of  $\pm 10$  percent. The results are shown in Table 6. Rows that are color coded blue show sites that are currently designated as "near sites".

Rows that are color coded orange show the RPD values for the two pairs of collocated sites. The single row highlighted yellow designates the "near site" pair that was selected for use in the Task E section of this study (LYK123 and DCP114, which are currently designated as "near sites"). The N/S (North/South) Distance and E/W (East/West) Distance columns show the distance in kilometers that separate the sites.

Interestingly, only 5 current "near site" pairs are identified through this analysis as being a good match for replacing missing meteorological data. Most of the matches shown in this table are between sites that are not near one another. Therefore, they cannot be used as near sites and the good comparison is not related to the influence of similar synoptic scale meteorological conditions.

Also of interest is the comparison between the collocated sites. These pairs are located at the same monitoring location and should have the best comparisons. However, the RPD for  $SO_2 \ V_d$  is approximately 5 percent for MCK131/231 and -5 percent for ROM206/406. The RPD for HNO<sub>3</sub>  $V_d$  and particulate  $V_d$  are closer to zero.

 Table 5. Current Assigned Near Sites for All CASTNET Sites

CASTNET site_id	nearsite1	nearsite2	CASTNET site_id	nearsite1	nearsite2
ABT147			LCW121	SPD111	CDR119
ACA416			LRL117	PAR107	KEF112
ALC188			LYE145		
ALH157	VIN140	BVL130	LYK123	DCP114	OXF122
ALH257	VIN140	BVL130	MAC426		
ANA115	LYK123	SAL133	MCK131	ESP127	SPD111
ANL146	BVL130	SAL133	MCK231	ESP127	SPD111
ARE128	BEL116	PSU106	MEV405		
ARE228	BEL116	PSU106	MKG113	PSU106	KEF112
ASH135	WST109		MOR409		
ASH235	WST109		NCS415		
BBE401			OLY421		
BEL116	ARE128	WSP144	ONL102	ESP127	PBF129
BFT142			OXF122	DCP114	LYK123
BVL130	ALH157	SAL133	PAL190		
BWR139			PAR107	LRL117	CDR119
CAD150	CVL151		PAR207	LRL117	CDR119
CAN407			PBF129	ESP127	SPD111
CAT175			PED108	RTP101	
CDR119	PAR107	LRL117	PET427		
CDZ171			PIN414		
CHA267			PND165		
CHA467			PNF126	VPI120	ESP127
CHE185			POF425		
CKT136			PRK134	WEL149	
CND125	PED108		PSU106	ARE128	MKG113
CNT169			QAK172		
CON186			RCK163		
COW137	SPD111	LCW121	RCK263		
COW182			ROM206		
CTH110	KEF112	MKG113	ROM406		
CVL151	CAD150	SND152	RTP101	PED108	
DCP114	LYK123	OXF122	SAL133	BVL130	LYK123
DCP214	LYK123	OXF122	SAN189		
DEN417			SAV164		
DEV412			SCR180		
EGB181			SEK402		
EGB281			SEK430		
ESP127	MCK131	SPD111	SHN418	ARE128	VPI120
EVE419			SND152	GAS153	ESP127
GAS153	SND152		SPD111	ESP127	PBF129
GAS253	SND152		STK138		
GLR468			SUM156		
GRB411			SUM256		
GRC474			THR422		
GRS420			UIN162		
GTH161			UVL124	WEL149	ANA115
HBR183			VII423		
HOW132			VIN140	ALH157	BVL130
HOX148	PRK134	ANA115	VOY413		
HVT424			VPI120	SHN118	PNF126
HWF187	CAT175	LYE145	WEL149	PRK134	ANA115
IRL141			WFM105	WST109	
JOT403			WNC429		
KEF112	CTH110	MKG113	WPA103	WPB104	WSP144
KNZ184			WPB104	WPA103	WSP144
KVA428			WSP144	BEL116	ARE128
LAV410			WST109	WFM105	

**Table 6.** All Site Pairs with a Percent Difference of  $\pm 10$  Percent for each Deposition Velocity

			nt Difference of :			
site_id (1)	site_id (2)	N/S distance (km)	E/W distance (km)	so2_vd_RPD	hno3_vd_RPD	particulate_vd_RPD
ABT147	CHE185	676	1813	-7.7	-8.3	9.9
ABT147	SHN418	368	514	-8.8	-3.3	1.8
ALC188	ARE128	-1055	-1368	6.9	6.7	-3.5
ALC188	ASH235	-1796	-2079	0.6	-8.9	4.1
ALC188	DCP114	-1023	-892	-4.5	-2.4	0.8
ALC188	GAS153	-306	-800	5.7	-0.2	-7.8
ALC188	LYK123	-1165	-913	-0.2	3.5	-0.2
ALC188	SND152	-429	-675	-5.0	6.9	-2.0
ALH157*	BVL130*	-131	-100	2.1	-2.6	-5.3
ANA115	BWR139	441	-623	-3.9	1.1	1.0
ANA115	EGB181	-202	-330	8.8	6.9	-0.8
ANA115	HOW132	-311	-1215	3.2	-6.9	-2.2
ANA115	VPI120	565	-268	-0.3	-4.6	1.6
ARE128	CKT136	222	461	9.7	-7.4	-5.7
ARE128	GAS153	749	568	-1.2	-6.8	-4.3
ARE128	LYK123	-110	455	-7.0	-3.2	3.3
ARE128	OXF122	43	594	-0.5	5.1	4.8
ARE128	WSP144*	-43	-195	-4.3	4.4	5.2
ASH135	CHE185	1205	2101	9.3	2.5	-7.0
ASH235	DCP114	773	1188	-5.2	6.5	-3.3
BEL116	CVL151	558	1039	-3.2	-4.0	7.6
BEL116	EGB181	-578	237	-8.4	1.4	4.6
BEL116	PRK134	-686	1102	-5.8	2.2	7.2
BFT142	PNF126	-136	434	-0.1	-5.1	-7.1
BFT142	QAK172	-561	377	-9.3	-9.6	9.7
BFT142	SND152	66	748	5.3	9.7	8.9
BWR139	HOW132	-752	-592	7.1	-8.0	-3.2
BWR139	SAL133	-263	764	-8.5	9.8	6.9
BWR139	VPI120	124	356	3.7	-5.7	0.6
CAD150	KEF112	-823	-1147	-0.7	2.3	0.9
CAN407	JOT403	487	526	-4.6	-1.4	7.3
CDZ171	DCP114	-317	-367	6.7	-8.9	1.6
CDZ171	MCK231	-102	-224	-8.3	-4.1	6.7
CDZ171	PAR107	-256	-655	9.5	4.5	8.3
CDZ171	SND152	277	-150	6.2	0.5	-1.2
CDZ171	STK138	-611	172	-5.9	-5.9	7.3
CDZ171	VIN140	-217	-29	2.5	3.6	6.1
CHE185	CKT136	-241	-928	-5.2	3.7	-6.5
CHE185	LYE145	-810	-1729	6.1	5.8	2.0
CHE185	SHN418	-308	-1299	-1.2	5.0	-8.1
CKT136	SHN418	-67	-371	4.1	1.3	-1.6
CND125	HOW132	-1105	-890	-2.8	-6.6	8.7
CND125	PND165	-851	2396	7.8	-9.0	-2.7
CON186	MEV405	-333	-674	6.1	0.1	-2.8
CTH110	OXF122	318	646	-7.9	1.6	-8.9
CVL151	EGB181	-1135	-801	-5.2	5.4	-3.0
CVL151	PRK134	-1244	64	-2.7	6.2	-0.4
CVL151	SUM156	432	-385	-2.3	9.5	5.1
DCP114*	LYK123*	-142	-21	4.4	5.9	-1.0
DCP114	SND152	594	217	-0.5	9.4	-2.8
EGB181	PRK134	-108	865	2.6	0.8	2.6
EGB181	SUM156	1568	417	3.0	4.1	8.1
EVE419	PND165	-1947	2329	-5.1	-4.1	3.7
GAS153	LYK123	-859	-113	-5.8	3.6	7.6
GLR468	MOR409	194	650	0.2	-0.9	6.3
HOW132	VPI120	875	948	-3.5	2.3	3.8
HOX148	PED108	779	-595	6.0	9.1	9.3
HOX148*	PRK134	-114	389	-7.7	-3.9	-2.9
HOX148	SUM156	1562	-60	-7.3	-0.6	2.6
HVT424	SAN189	-2598	-4591	-4.6	-1.7	-4.6
LAV410	PIN414	450	-34	-5.8	-0.3	3.8
LYE145	VPI120	635	600	7.6	6.3	8.5
LYK123*	OXF122*	154	138	6.5	8.4	1.4

site_id (1)	site_id (2)	N/S distance (km)	E/W distance (km)	so2_vd_RPD	hno3_vd_RPD	particulate_vd_RPD
LYK123	PAR107	203	-267	-1.6	7.5	7.7
LYK123	PSU106	22	-405	-6.5	9.1	9.6
LYK123	SND152	736	238	-4.9	3.5	-1.8
LYK123	VIN140	242	359	-8.5	6.6	5.5
LYK123	WSP144	67	-650	2.7	7.6	1.9
MCK131	MCK231	0	0	5.5	2.5	1.3
MCK131	STK138	-509	396	7.9	0.8	2.0
MCK231	STK138	-509	396	2.4	-1.8	0.7
MKG113	UVL124	-243	257	-2.7	-2.8	-1.2
OXF122	PAR107	49	-405	-8.1	-0.9	6.2
OXF122	WSP144	-87	-788	-3.8	-0.7	0.4
PAR107	PSU106	-181	-138	-5.0	1.6	1.9
PAR107	SND152	533	505	-3.3	-4.0	-9.4
PAR107	VIN140	39	626	-7.0	-0.9	-2.1
PAR107	WSP144	-136	-383	4.3	0.1	-5.8
PIN414	SEK402	6	-191	-2.3	-1.1	7.5
PRK134	SUM156	1676	-449	0.4	3.3	5.5
PSU106	VIN140	220	764	-2.0	-2.5	-4.1
PSU106	WSP144	45	-245	9.2	-1.5	-7.7
ROM206	ROM406	0	0	-5.4	-0.8	-0.8
SEK430	VOY413	-1323	-2079	6.4	2.6	7.9
SND152	VIN140	-494	121	-3.7	3.1	7.3
SND152	WSP144	-669	-888	7.5	4.1	3.6
SPD111	UVL124	-793	-37	1.9	-7.4	9.5
STK138	VIN140	394	-201	8.4	9.4	-1.2
YEL408	YOS404	760	744	5.1	1.0	6.9

This study also compares the 10-year mean deposition velocities for each site with the annual mean deposition velocities used to create the 10-year value. Mean Absolute Percent Differences (MAPD) were calculated to show a summary of the differences, which in a few cases are between 10 and 15 percent. The results are shown in Table 7. MAPD greater than 10 percent are color coded with orange shading.

**Table 7.** Mean Absolute Percent Differences between 10-year Mean Deposition Velocities and Annual Mean Deposition Velocities

site_id	total_years	valid_years	SO2 MAPD	HNO3_MAPD	PART_MAPD
ABT147	10	5	4.8	2.4	3.1
ACA416	9	8	9.8	9.9	13.7
ALC188	4	3	6.6	4.4	5.2
ALH157	10	6	3.8	3.5	5.0
ANA115	10	5	4.3	3.1	3.7
ARE128	10	8	7.6	5.4	7.5
		8	9.2	2.3	2.3
ASH135	10 4	2	8.8	1.2	1.9
ASH235					
BBE401	10	8	2.1	2.8	4.3
BEL116	10	8	6.3	4.0	4.9
BFT142	10	9	6.3	2.2	2.2
BVL130	10	8	8.0	12.3	11.0
BWR139	10	7	7.6	2.2	2.6
CAD150	10	6	2.6	5.1	6.1
CAN407	10	8	1.8	2.5	3.3
CAT175	10	2	2.4	12.7	12.5
CDR119	10	7	4.5	4.9	6.5
CDZ171	10	1	0.0	0.0	0.0
CHA467	10	8	6.9	1.8	3.1
CHE185	6	1	0.0	0.0	0.0
CKT136	10	6	3.9	1.5	3.3
CND125	10	7	8.9	3.4	5.3
CNT169	10	5	3.6	3.3	3.4
CON186	5	4	4.1	0.8	3.0
COW137	10	10	7.1	2.4	3.1
CTH110	10	7	5.6	3.0	4.6
CVL151	10	5	5.0	4.7	4.4
DCP114	10	7	5.6	2.1	2.0
DEN417	9	7	13.6	3.8	3.9
DEV412	10	8	0.3	1.3	2.0
EGB181	10	8	6.7	2.8	2.8
ESP127	10	8	5.5	2.9	2.8
EVE419	9	6	8.2	8.4	6.8
GAS153	10	5	5.1	2.4	3.4
GLR468	10	6	5.6	8.1	8.6
GRB411	10	4	2.0	2.5	3.2
GRC474	10	9	8.7	10.3	11.9
GRS420	10	9	4.1	4.7	6.8
GTH161	10	5	4.8	2.7	2.6
HOW132	10	5	7.1	4.5	5.8
HOX148	7	6	11.3	2.3	2.4
HVT424	6	2	1.2	1.3	1.2
HWF187	6	4	5.6	2.5	1.4
IRL141	7	4	2.0	4.3	2.2
JOT403	10	8	8.5	4.6	5.7
KEF112	10	8	7.2	4.4	5.9
KNZ184	6	5	6.3	3.0	3.9
LAV410	10	8	4.7	2.3	3.7
LRL117	10	5	5.3	3.9	6.6
LYE145	10	2	2.6	1.2	0.6
LYK123	10	9	6.8	2.5	3.4
MAC426	6	5	8.2	0.5	3.2
MCK131	10	7	8.3	3.4	2.8
MCK231	10	7	4.9	2.4	3.7
MEV405	10	8	5.7	4.2	4.2
MKG113	10	10	5.9	2.6	6.8
MOR409	10	6	1.4	4.7	7.5
NCS415	10	5	5.3	4.0	4.0
OLY421	8	3	0.8	5.2	6.6
OXF122	10	10	7.9	2.5	3.7
PAL190	1	0			

site_id	total_years	valid_years	SO2_MAPD	HNO3_MAPD	PART_MAPD
PAR107	10	7	6.4	2.2	4.1
PED108	10	8	6.8	10.7	14.3
PET427	6	3	2.6	1.8	2.2
PIN414	10	8	6.5	2.9	2.9
PND165	10	8	2.7	4.5	5.6
PNF126	10	5	2.2	3.6	5.4
POF425	3	0			
PRK134	10	6	12.6	9.4	9.9
PSU106	10	6	9.3	2.4	3.0
QAK172	10	7	5.7	5.6	6.1
ROM206	7	3	4.7	1.8	3.3
ROM406	10	8	5.2	1.9	2.7
SAL133	10	6	5.1	1.6	2.0
SAN189	2	1	0.0	0.0	0.0
SEK402	7	2	1.5	3.1	4.2
SEK430	3	1	0.0	0.0	0.0
SHN418	10	7	6.4	2.2	3.8
SND152	10	7	7.1	2.0	4.2
SPD111	10	8	6.5	2.8	5.5
STK138	10	1	0.0	0.0	0.0
SUM156	10	6	5.5	4.6	6.0
THR422	9	7	5.4	2.9	3.2
UVL124	10	7	12.6	6.7	9.5
VII423	7	3	1.8	2.3	3.0
VIN140	10	9	3.8	2.5	3.3
VOY413	10	6	10.7	1.9	3.6
VPI120	10	7	7.6	5.6	7.2
WEL149	1	0			
WNC429	4	1	0.0	0.0	0.0
WSP144	10	6	5.9	2.7	5.0
WST109	10	3	5.4	5.8	7.6
YEL408	10	7	4.9	2.1	4.7
YOS404	10	4	5.3	1.7	3.6

# Task B:

Using the estimates of uncertainties in the  $NO_3^-$  and  $HNO_3$  concentrations detailed in the METHODS section, annual mean fluxes for the Beltsville, MD site (BEL116) were analyzed to provide a range of possible values. Total measured nitrogen deposition ( $NO_3^-+HNO_3+NH_4^+$ ) values were also modified. Because flux estimates are calculated by multiplying the modeled deposition velocity by the atmospheric concentration, any multiplication of the concentration essentially applies the same correction to the flux. Table 8 shows the results of the correction.

**Table 8.** Components of the Dry Deposition of Total Measured Nitrogen including Corrections for Estimates in Concentration Uncertainties

site_id	year	no3_flux	corrected no3_flux (/3.5)	hno3_flux	corrected hno3_flux (*1.15)	nh4_flux	
BEL116	1998	0.26	0.07	9.21	10.60	0.66	
BEL116	1999	0.39	0.11	10.53	12.11	0.74	
BEL116	2000	0.49	0.14	6.08	6.99	0.50	
BEL116	2001	0.30	0.09	8.26	9.49	0.65	
BEL116	2002	0.23	0.07	9.12	10.48	0.63	
BEL116	2003	0.28	0.08	7.80	8.97	0.55	
BEL116	2004	0.36	0.10	8.80	10.12	0.67	
BEL116	2005	0.42	0.12	7.86	9.03	0.52	
BEL116	2006	0.27	0.08	9.33	10.73	0.64	
BEL116	2007	0.17	0.05	8.56	9.84	0.59	

As Table 9 shows, differences from the corrections are relatively small (approximately 10 percent or less) reflecting the fact that the HNO<sub>3</sub> component dominates the total measured nitrogen dry deposition, and it was only modified by increasing the flux by 15 percent. Dry deposition of particulate NO<sub>3</sub><sup>-</sup> has a relatively small contribution to the total measured nitrogen flux and thus the large decrease in NO<sub>3</sub><sup>-</sup> concentrations does not have a significant effect on total deposition.

**Table 9.** Changes to Dry Deposition of Total Measured Nitrogen from Corrections to NO<sub>3</sub> and HNO<sub>3</sub> Fluxes

			NO3 correction	HNO3 correction	both
site_id	year	Total Measured N	only	only	corrections
BEL116	1998	2.62	2.58	2.93	2.89
BEL116	1999	3.00	2.94	3.35	3.29
BEL116	2000	1.85	1.77	2.05	1.97
BEL116	2001	2.41	2.36	2.68	2.64
BEL116	2002	2.57	2.53	2.87	2.84
BEL116	2003	2.23	2.18	2.49	2.44
BEL116	2004	2.56	2.50	2.85	2.79
BEL116	2005	2.25	2.18	2.51	2.44
BEL116	2006	2.63	2.59	2.94	2.90
BEL116	2007	2.40	2.38	2.69	2.66

## Task C:

The comparisons of fluxes calculated using 10-year mean deposition velocities and fluxes calculated with annual mean deposition velocities with historical annual flux values were evaluated by constructing histograms of percent differences. Comparisons were made using 10-year mean and annual mean values when either three or four quarters are valid (one quarter of the year may not be represented in the annual mean) and a second set of comparisons were made using 10-year mean and annual mean values where all four quarters are valid (the entire year is covered). Figures 6 through 15 present histograms of percent differences versus number of site-years. There are two histograms for each of five pollutants – SO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and

NH<sub>4</sub><sup>+</sup>. The first histogram shows results from the comparisons where either three or four quarters are valid. The second histogram for each pollutant shows results from the comparisons when all four quarters are valid. Each figure provides two sets of bars. One is based on fluxes estimated from a 10-year mean (maroon) deposition velocity and the second is based on annual mean (yellow) deposition velocities.

All ten figures suggest the distributions of differences are normal. The results for  $SO_2$ ,  $HNO_3$ ,  $NO_3$ , and  $NH_4^+$  show a positive bias in that the calculated fluxes are higher than the MLM results. The exception is for  $SO_4^{2^-}$  which shows a slight negative bias. Use of the 10-year mean allowed for the recovery of 131 site-years (37 percent). Many of the missing site-years are the start-up or shut-down years for a specific site. Use of the annual mean allowed for the recover y of only 8 site-years (2 percent) but was also useful in examining how comparable flux estimates calculated with annual average concentration and deposition velocities are with those aggregated using the accepted protocol.

The results for Task C show the comparison of  $SO_2$  fluxes as presented in Figure 6 (3 or 4 quarters valid). The simulations based on individual annual  $V_d$  values (yellow bars) better match the MLM results. About 96 percent of the calculated fluxes are within 20 percent of the MLM deposition rates; and about 53 percent of the calculated values are within 4 percent of the MLM results. The results based on the 10-year mean deposition velocities are shown by the maroon bars. Approximately 92 percent of the calculated fluxes are within 20 percent of the MLM values and about 31 percent are within 4 percent.

**Figure 6.** Histograms of Percent Difference versus Number of Site-Years for SO<sub>2</sub> (3 or 4 Quarters Valid)

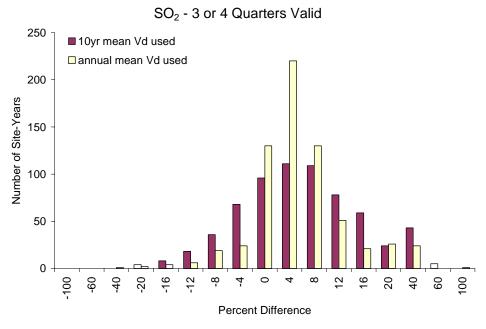
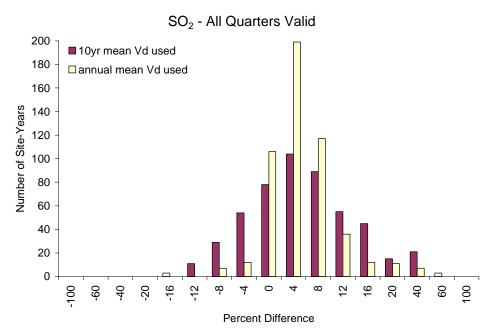


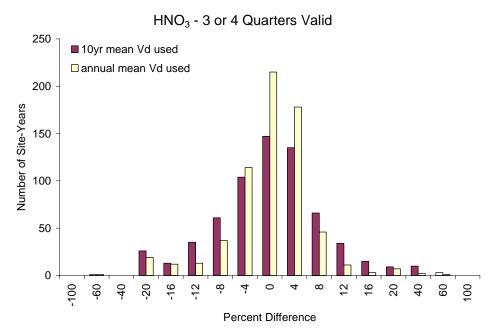
Figure 7 shows results for means calculated using years where all four quarters are valid. As would be expected, results are slightly better as compared with the results using years with either three or four valid quarters. Approximately 99 percent of the calculated fluxes are within 20 percent of the MLM deposition rates, and about 60 percent of the calculated values are within 4 percent of the MLM results. The results based on the 10-year mean deposition velocities are shown by the maroon bars. Approximately 95 percent of the calculated fluxes are within 20 percent of the MLM values and about 36 percent are within 4 percent

**Figure 7.** Histograms of Percent Difference versus Number of Site-Years for SO<sub>2</sub> (All Quarters Valid)

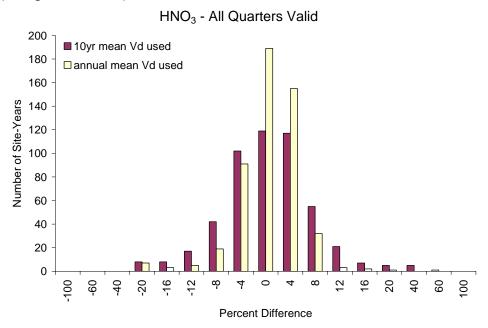


The results for fluxes of  $HNO_3$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  are provided in Figures 8 through 15. The data again show the flux estimates based on individual annual  $V_d$  values better match the MLM results. The fluxes based on 10-year mean  $V_d$  values for  $HNO_3$ ,  $SO_4^{2-}$ , and  $NH_4^+$  show an improvement over  $SO_2$ . In fact, more than 95 percent of the flux values based on 10-year mean  $V_d$  values are within 20 percent of the MLM annual values. The results for  $NO_3^-$  are generally poor. Particulate nitrate values are generally low and are more uncertain that the other parameters. For each parameter,

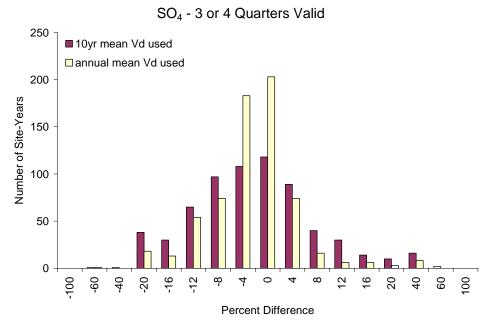
**Figure 8.** Histograms of Percent Difference versus Number of Site-Years for HNO<sub>3</sub> (3 or 4 Quarters Valid)



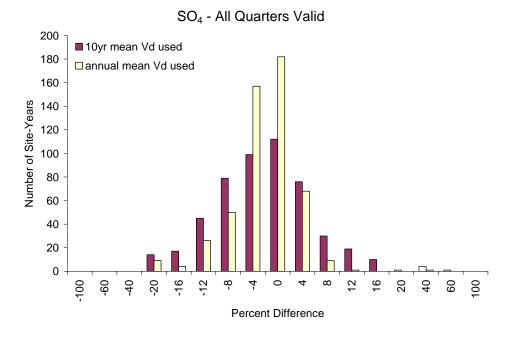
**Figure 9.** Histograms of Percent Difference versus Number of Site-Years for HNO<sub>3</sub> (All Quarters Valid)



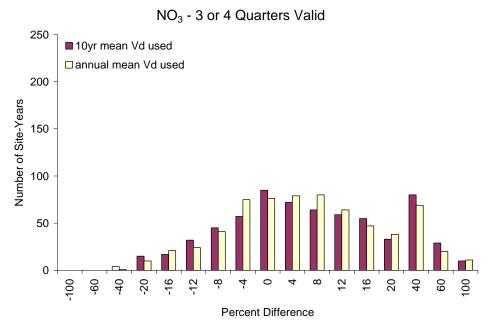
**Figure 10.** Histograms of Percent Difference versus Number of Site-Years for SO<sub>4</sub><sup>2-</sup> (3 or 4 Quarters Valid)



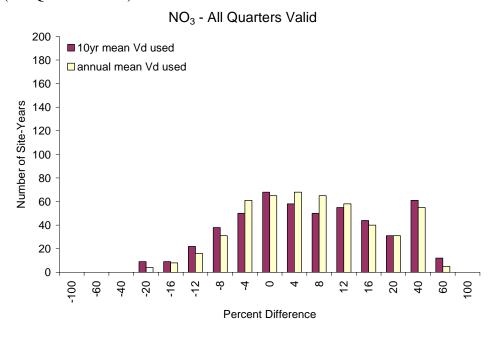
**Figure 11.** Histograms of Percent Difference versus Number of Site-Years for SO<sub>4</sub><sup>2-</sup> (All Quarters Valid)



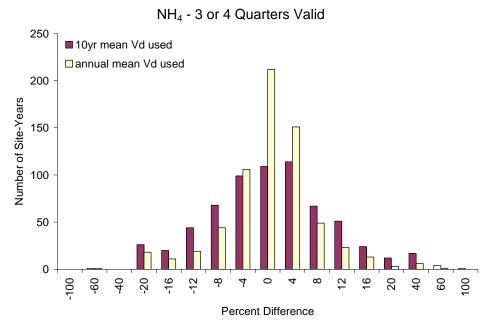
**Figure 12.** Histograms of Percent Difference versus Number of Site-Years for NO<sub>3</sub> (3 or 4 Quarters Valid)



**Figure 13.** Histograms of Percent Difference versus Number of Site-Years for NO<sub>3</sub><sup>-</sup> (All Quarters Valid)



**Figure 14.** Histograms of Percent Difference versus Number of Site-Years for NH<sub>4</sub><sup>+</sup> (3 or 4 Quarters Valid)



**Figure 15.** Histograms of Percent Difference versus Number of Site-Years for NH<sub>4</sub><sup>+</sup> (All Quarters Valid)

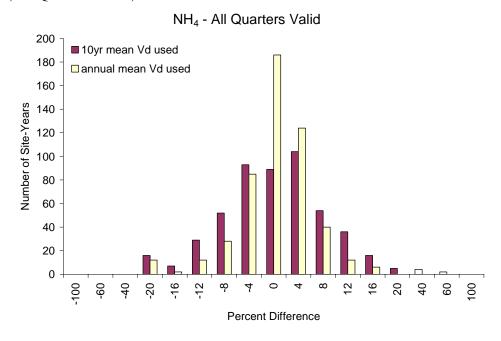


Table 10 summarizes the results from Task C. Focusing on the columns for percent of site-years within +- 20 percent of the historical flux estimate, results are encouraging. For the analysis done where all four quarters are valid, well over 90 percent of all site-years have a percent difference within the +- 20 percent window except for  $NO_3^-$ , which is slightly lower.

Table 10. Summary of 10-Year Mean and Annual Mean Calculated Flux Comparisons

	+-4 percent difference		+-20 percent difference	
parameter	3 or 4 quarters	All	3 or 4 quarters	All
so2_10yr_flux pct diff	31	36	92	95
so2_ann_flux pct diff	53	60	96	99
hno3_10yr_flux pct diff	43	47	94	97
hno3_ann_flux pct diff	60	68	97	99
so4_10yr_flux pct diff	31	37	91	96
so4_ann_flux pct diff	42	49	96	98
no3_10yr_flux pct diff	24	25	79	83
no3_ann_flux pct diff	24	26	83	87
nh4_10yr_flux pct diff	34	38	93	96
nh4_ann_flux pct diff	55	61	96	98

#### Task D:

Table 11 shows the difference between the current and original parameterizations for the WATER and ROCK plant types.

**Table 11.** ROCK/WATER Parameterizations

	Current Parameterization		Original Parameterization	
plant_type	WATER*	ROCK*	WATER*	ROCK*
min_stom	500	1000	1	1
light_res_coeff	20	20	1	1
opt_temp	40	30	-99	-99
max_no_stress_temp	50	50	-99	-99
min_no_stress_temp	20	10	-99	-99
profile_index	1	1	1	1
canopy_height	0.1	1	0.1	0.1

Comparisons of the weekly deposition velocity estimates are shown in Table 12. The percent difference is calculated between the actual weekly value and the value calculated using the older, original parameterization for water and rock. As shown by the table of Mean Absolute Percent Difference values, there is no difference between the two model runs. The change in parameterization of water and rock had no effect on the produced deposition velocities.

**Table 12.** Comparison between Current and Original Parameterizations of WATER and ROCK.

site_id	so2_vd_mapd	hno3_vd_mapd	particulate_vd_mapd
IRL141 (WATER)	0	0	0
CHA467 (ROCK)	0	0	0

### Task E:

Model runs were done replacing missing vector wind speed and sigma theta (standard deviation of the wind direction) data with either historical weekly mean values or "near site" values. For this part of the study, the "near site" pair of LYK123 and DCP114 was selected with LYK123 being the primary site. Model runs were done for 2007 and then compared with the actual deposition velocity estimates. For the actual deposition velocity estimates for 2007, LYK123 had a near perfect level of completeness with all 52 weeks having a percent completeness of greater than 90 percent. This makes this site the perfect candidate for this study.

Table 13 shows a summary of the differences in weekly deposition velocity estimates. Mean absolute percent differences (MAPD) were calculated for each site from the 52 weekly values. In general, results were excellent for the comparisons using the historical weekly means. MAPD values of greater than 5 percent are color coded orange. Only two of the "sites" have MAPD greater than 5; both involve particulate deposition velocity estimates and the substitution of sigma theta values for either 10 weeks or all weeks from the first quarter. Results from the runs that replaced missing data by using hourly values from DCP114 are not as good. Twelve "sites" have MAPD greater than 5 percent with three sites having MAPD greater than 10 percent.

Table 13. Mean Absolute Percent Differences between Weekly Estimates (Test Site vs. Actual)

				y Estimates (Test Dite vs. 7)
site_id	SO2_VD_MAPD			KEY
HISOTG	0.2	0.5	0.6	Q1, 2 Weeks, sigma_theta
HISOTS	0.8	0.8	0.3	Q1, 2 Weeks, windspeed
HISOFG	0.6	1.7	2.7	Q1, 4 Weeks, sigma_theta
HISOFS	0.8	1.2	1.1	Q1, 4 Weeks, windspeed
HISOSG	0.9	2.2	3.3	Q1, 6 Weeks, sigma_theta
HISOSS	1.5	2.6	2.6	Q1, 6 Weeks, windspeed
HISOEG	1.0	2.8	4.2	Q1, 8 Weeks, sigma_theta
HISOES	2.3	3.4	2.9	Q1, 8 Weeks, windspeed
HISONG	1.4	3.7	5.2	Q1, 10 Weeks, sigma_theta
HISONS	2.4	3.0	2.1	Q1, 10 Weeks, windspeed
HISOAG	1.8	4.4	6.4	Q1, All Weeks, sigma_theta
HISOAS	3.3	4.9	3.9	Q1, All Weeks, windspeed
HISTTG	0.3	1.0	1.0	Q3, 2 Weeks, sigma_theta
HISTTS	0.8	0.9	0.8	Q3, 2 Weeks, windspeed
HISTFG	0.5	1.2	1.1	Q3, 4 Weeks, sigma_theta
HISTFS	1.0	1.2	1.3	Q3, 4 Weeks, windspeed
HISTSG	0.5	1.1	1.0	Q3, 6 Weeks, sigma_theta
HISTSS	2.2	2.5	1.3	Q3, 6 Weeks, windspeed
HISTEG	0.8	2.3	2.6	Q3, 8 Weeks, sigma_theta
HISTES	2.7	2.8	1.7	Q3, 8 Weeks, windspeed
HISTNG	1.0	2.7	2.9	Q3, 10 Weeks, sigma_theta
HISTNS	3.1	3.3	2.5	Q3, 10 Weeks, windspeed
HISTAG	1.2	3.3	3.5	Q3, All Weeks, sigma_theta
HISTAS	4.3	4.7	2.6	Q3, All Weeks, windspeed
LYKOTG	0.2	0.6	0.9	Q1, 2 Weeks, sigma_theta
LYKOTS	0.3	0.3	0.3	Q1, 2 Weeks, windspeed
LYKOFG	0.6	2.3	4.5	Q1, 4 Weeks, sigma_theta
LYKOFS	1.2	1.7	2.0	Q1, 4 Weeks, windspeed
LYKOSG	1.2	3.7	6.8	Q1, 6 Weeks, sigma_theta
LYKOSS	1.5	2.1	2.5	Q1, 6 Weeks, windspeed
LYKOEG	1.3	4.2	7.7	Q1, 8 Weeks, sigma_theta
LYKOES	2.5	2.9	3.3	Q1, 8 Weeks, windspeed
LYKONG	1.7	5.5	10.0	Q1, 10 Weeks, sigma_theta
LYKONS	3.3	4.0	4.5	Q1, 10 Weeks, windspeed
LYKOAG	2.3	7.1	12.9	Q1, All Weeks, sigma_theta
LYKOAS	4.1	5.1	5.7	Q1, All Weeks, windspeed
LYKTTG	0.4	2.1	2.2	Q3, 2 Weeks, sigma_theta
LYKTTS	0.6	1.5	1.8	Q3, 2 Weeks, signia_trieta Q3, 2 Weeks, windspeed
LYKTFG	1.1	4.3	4.0	Q3, 4 Weeks, sigma_theta
LYKTFS	1.7	3.0	3.3	Q3, 4 Weeks, windspeed
LYKTSG	1.7	5.2	3.3 4.9	Q3, 6 Weeks, sigma_theta
LYKTSS	2.6	3.5	3.7	
				Q3, 6 Weeks, windspeed
LYKTES	2.0	7.5	7.6 5.5	Q3, 8 Weeks, sigma_theta
LYKTES	2.9	4.7		Q3, 8 Weeks, windspeed
LYKTNG	2.5	9.5	9.5	Q3, 10 Weeks, sigma_theta
LYKTNS	3.6	6.0	6.8	Q3, 10 Weeks, windspeed
LYKTAG	3.2	12.0	12.1	Q3, All Weeks, sigma_theta
LYKTAS	5.0	7.9	8.7	Q3, All Weeks, windspeed

Table 14 shows the percent difference between annual mean deposition velocities from the actual run for LYK123 and the 48 test runs. Percent differences less than -5 percent or greater than 5 percent are color coded orange As with the weekly comparison, results from the runs using historical weekly averages are excellent. Only one site has a percent difference of greater than 5 percent.

As with the weekly comparison, it involves the particulate deposition velocity estimate and the substitution of sigma theta values for all weeks from the first quarter. Twelve "sites" where the missing data are replaced with data from DCP114 have percent differences of less than - 5 percent or greater than 5 percent. For the annual comparisons, one "site", LYKTAS, has percent differences for  $SO_2\ V_d$ ,  $HNO_3\ V_d$ , and particulate  $V_d$  are all less than -5 percent.

**Table 14.** Percent Differences between Annual Estimates (Test Site vs. Actual)

Table 14			n Annuai Estimates (	,
site_id	SO2_VD_PCT	HNO3_VD_PCT	PARTICULATE_VD_PCT	KEY
HISOTG	0.1	0.3	0.3	Q1, 2 Weeks, sigma_theta
HISOTS	0.7	0.6	0.1	Q1, 2 Weeks, windspeed
HISOFG	0.4	1.5	2.0	Q1, 4 Weeks, sigma_theta
HISOFS	0.7	0.6	-0.2	Q1, 4 Weeks, windspeed
HISOSG	0.8	1.9	2.9	Q1, 6 Weeks, sigma_theta
HISOSS	1.1	1.3	0.4	Q1, 6 Weeks, windspeed
HISOEG	0.9	2.4	3.6	Q1, 8 Weeks, sigma_theta
HISOES	2.0	2.0	0.7	Q1, 8 Weeks, windspeed
HISONG	1.4	3.2	4.3	Q1, 10 Weeks, sigma_theta
HISONS	2.4	2.1	-0.1	Q1, 10 Weeks, windspeed
HISOAG	1.8	3.9	5.4	Q1, All Weeks, sigma_theta
HISOAS	3.1	3.2	0.9	Q1, All Weeks, windspeed
HISTTG	0.0	0.7	1.0	Q3, 2 Weeks, sigma_theta
HISTTS	0.5	0.7	-1.1	Q3, 2 Weeks, windspeed
HISTFG	0.3	1.2	1.3	Q3, 4 Weeks, sigma_theta
HISTFS	0.8	0.2	-1.7	Q3, 4 Weeks, signa_trieta Q3, 4 Weeks, windspeed
HISTSG	0.0	0.2	0.1	Q3, 6 Weeks, sigma_theta
HISTSS	2.3	2.2	0.0	Q3, 6 Weeks, windspeed
HISTEG	0.5	1.5	1.9	Q3, 8 Weeks, sigma_theta
HISTES	2.7	2.6	-1.2	Q3, 8 Weeks, windspeed
HISTNG	0.7	2.0	2.2	Q3, 10 Weeks, sigma_theta
HISTNS	3.1	3.1	-1.6	Q3, 10 Weeks, windspeed
HISTAG	0.9	2.2	2.4	Q3, All Weeks, sigma_theta
HISTAS	4.4	4.5	-1.5	Q3, All Weeks, windspeed
LYKOTG	0.1	0.4	0.5	Q1, 2 Weeks, sigma_theta
LYKOTS	0.0	-0.1	-0.2	Q1, 2 Weeks, windspeed
LYKOFG	0.5	2.0	3.5	Q1, 4 Weeks, sigma_theta
LYKOFS	-1.3	-1.6	-1.6	Q1, 4 Weeks, windspeed
LYKOSG	1.1	3.2	6.3	Q1, 6 Weeks, sigma_theta
LYKOSS	-1.2	-1.6	-2.1	Q1, 6 Weeks, windspeed
LYKOEG	1.2	3.7	6.8	Q1, 8 Weeks, sigma_theta
LYKOES	-2.0	-2.5	-3.1	Q1, 8 Weeks, windspeed
LYKONG	1.7	4.8	8.5	Q1, 10 Weeks, sigma_theta
LYKONS	-3.1	-3.5	-4.0	Q1, 10 Weeks, windspeed
LYKOAG	2.3	6.2	11.6	Q1, All Weeks, sigma_theta
LYKOAS	-3.8	-4.3	-5.3	Q1, All Weeks, windspeed
LYKTTG	0.1	2.4	3.0	Q3, 2 Weeks, sigma_theta
LYKTTS	-0.5	-1.7	-2.5	Q3, 2 Weeks, windspeed
LYKTFG	1.1	4.6	4.7	Q3, 4 Weeks, sigma_theta
LYKTFS	-1.8	-3.3	-3.9	Q3, 4 Weeks, windspeed
LYKTSG	1.8	5.1	4.9	Q3, 6 Weeks, sigma_theta
LYKTSS	-3.0	-3.6	-3.8	Q3, 6 Weeks, windspeed
LYKTEG	2.1	7.7	8.1	Q3, 8 Weeks, sigma_theta
LYKTES	-3.3	-5.0	-6.0	Q3, 8 Weeks, windspeed
LYKTNG	2.7	9.9	10.2	Q3, 10 Weeks, sigma_theta
LYKTNS	-4.0	-6.4	-7.6	Q3, 10 Weeks, windspeed
LYKTAG	3.5	12.6	12.8	Q3, All Weeks, sigma_theta
LYKTAS	-5.5	-8.4	-9.6	Q3, All Weeks, windspeed
	5.0	<u> </u>	3.0	

# **CONCLUSIONS**

# Task A:

The analysis of the comparison between 10-year mean deposition velocities shows that the practice of determining "near sites" based on geographic proximity and similar terrain and land use is not supported by a comparison of the data produced by the model. Of the 89 site pairs identified by looking for matches where the SO2  $V_d$ , HNO3  $V_d$ , and particulate  $V_d$  are all within  $\pm 10$  percent, only five are currently used as "near sites" and most of the site pairs identified were not near one another. From this analysis, it is recommended that the use of "near sites" for missing data replacement be terminated.

### Task B:

Previous studies have shown that CASTNET NO<sub>3</sub> and HNO<sub>3</sub> measurements have an associated uncertainty due to sampler design. Differences from the corrections enacted to examine the effects of these uncertainties are relatively small because the HNO<sub>3</sub> component dominates the total measured nitrogen dry deposition. Dry deposition of particulate NO<sub>3</sub> has a small contribution to the total measured nitrogen flux and thus the large decrease to NO<sub>3</sub> concentrations does not have a significant effect on the total measured nitrogen estimate. Similar to the conclusions of Lavery et al.<sup>3</sup> regarding total measured nitrogen concentrations, the dry deposition estimates of total measured nitrogen concentrations are reasonable despite the problems with NO<sub>3</sub> and HNO<sub>3</sub> collection.

# Task C:

Evaluation of the results in this Task shows that flux estimates calculated using 10-year mean deposition velocities and annual mean concentrations compare reasonably well. Most comparisons had a percent completeness between -20 and 20 percent. Results obtained using 10-year mean deposition velocities calculated using only years with four valid quarters were better than those calculated using all valid site-years (either three or four valid quarters). These results are encouraging and show that reasonable approximations of annual deposition estimates might be obtained using a summary deposition velocity such as a 10-year mean.

### Task D:

Changes to the parameterization for the WATER and ROCK plant types had no effect on the deposition velocity estimates.

# Task E.

The most promising results of this study come from the replacement of missing meteorological parameters (specifically vector wind speed and sigma theta) with historical weekly averages of these parameters using data from the same site. These model runs were much better than the results obtained by substituting for missing data using "near site" meteorological data.

The chief recommendation from this study is to proceed with the development of a missing or invalid data replacement scheme based on:

- 1) Use of a summary, 10-year mean deposition velocity, and
- 2) Use of historical weekly averages for all meteorological inputs used by the MLM.

Results from Tasks C and E show that both protocols have enough promise to warrant further study and investigation. The potential benefit is enormous in that all site-years missing due to a lack of available valid meteorological data could be recovered. Details of the replacement protocol will require further development including how many years are required, what is the backup to weekly averages, and what to do for missing data at new sites without a historical record. Similar issues were successfully dealt with when CASTNET converted to calculation atmospheric concentrations using local conditions (as opposed to standard conditions). The temperature replacement protocol could be viewed as a model of what has been done in the past to deal with missing or invalid meteorological data.

This study only examined a single site for one year. Further work in support of the development and testing of the final replacement protocol should perform a similar analysis on all sites for multiple years. Also, it would be beneficial to reconstruct Figures 3-3 thru 3-10 from the CASTNET 2007 Annual Report<sup>11</sup> using the results of Tasks C and E and review the differences. If results of the time series analyses are approximately the same, the finding would lend support and validation to the adoption of the replacement scheme.

# **DISCLAIMER**

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