Final Project Report

Analysis of Atmospheric Deposition of Nitrogen and Sulfur in the Houston-Galveston Airshed Affecting Water Quality
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EXECUTIVE SUMMARY

Atmospheric deposition is a natural process by which pollutants are transferred from air to a ground (either water or land) surface. It occurs in both wet and dry deposition forms: Wet deposition is the process in which pollutants fall to the ground along with hydrometeors, and dry deposition involves the direct settling of pollutants through absorption and adsorption by the ground surface. For coastal estuaries, atmospheric deposition can affect water quality through both direct deposition (pollutants deposit on the water surface directly) and indirect deposition (some pollutants deposited on land are washed into the water).

There are a variety of atmospheric pollutants (e.g. nitrogen, mercury, sulfur dioxide) that may significantly impact the water quality of a coastal estuary through deposition. Atmospheric nitrogen deposition has been identified as a major nitrogen source for U.S. coastal estuaries. Over-abundance of nitrogen can result in harmful algal blooms, hypoxia, etc. in the water bodies. Sulfur dioxide, which is the main ingredient of acid rain, can cause bays, lakes and streams to become acidic and result in conditions that are unsuitable for reproduction and survival of fish in those waters. The primary sources of nitrogen and sulfur in the atmosphere come from anthropogenic emissions (e.g., burning of fossil fuels).

Galveston Bay is a coastal estuary located close to a heavily populated and industrialized metropolis, the Houston-Galveston-Brazoria (HGB) area. It is relatively rich in nutrients because of the nitrogen inflows from the San Jacinto and Trinity River. There are also many point sources around the bay that discharge waste water into the bay. Nitrogen from atmospheric sources can add to the problem since the HGB area is known to have elevated concentrations of several atmospheric pollutants. Atmospheric acid deposition (sulfuric and nitric acid) does not markedly impact the pH of Galveston Bay since the water pH is typically above 7.

University of Houston (UH) was contracted by the Galveston Bay Estuary Program (GBEP) to analyze the role of atmospheric deposition on the water quality of the Galveston Bay. Specifically, the Institute of Multi-Dimensional Air Quality Studies (IMAQS) of UH is tasked with understanding and quantifying the atmospheric nitrogen and sulfur deposition at Galveston Bay by analyzing the output from an air quality model (AQM). An AQM is the ultimate modeling tool for studying atmospheric deposition.

In this study, we (researchers at UH) analyzed the nitrogen and sulfur deposition at Galveston Bay and its watershed utilizing the one-year (2006) AQM simulations performed for the air quality forecasting of the HGB area. The focus of the present study is on dry deposition because: 1) there are few observations and past studies for the Bay and its watershed and 2) the model’s dry deposition results are more reliable compared to those of its wet deposition. To assess the impact of overall deposition, observation data of wet deposition were gathered and compounded with the dry deposition.

The key findings include:
• Atmospheric deposition (estimated dry and wet deposition) of inorganic nitrogen is a significant source of pollution to Galveston Bay. While it is impossible to calculate the exact percent contribution of atmospheric nitrogen due to outdated total nitrogen loading data at Galveston Bay, the percentage is estimated to be 11% or slightly higher assuming a small but steady decline in total nitrogen loading in recent years.

• Compared to other coastal estuaries in the U.S., the contribution percentage of atmospheric nitrogen at Galveston Bay is on the low end mainly because of the high total nitrogen loading. The percent contributions of atmospheric nitrogen to U.S. coastal estuaries are believed to be between 10% and 40% (Paerl et al 2002).

• The current total nitrogen deposition flux at Galveston Bay (direct deposition) is estimated to be 632 kg-N/(km²-yr). The current total nitrogen deposition flux at the Galveston Bay watershed is estimated to be 811 kg-N/(km²-yr). The deposition flux at Galveston Bay and its watershed is on the high end compared to other U.S. estuaries.

• Total direct deposition loading at Galveston Bay is estimated to be 982 ton-N/yr. Total indirect deposition loading at Galveston Bay is estimated to be 3347 ton-N/yr. Total nitrogen loading from atmospheric sources is about 4330 ton-N/yr. The percent contribution of direct and indirect nitrogen deposition are 2.6% and 8.7% respectively (to total N loading).

• Spatially, the dry nitrogen deposition is high on land and low on water. In the domain that covers southeast Texas and southwest Louisiana, there are two high deposition zones: Houston (LaPorte to the Woodlands) and Lake Charles. Other elevated deposition areas typically correspond to point sources of air emissions or busy highways. The spatial variation of dry nitrogen deposition is quite high, with a max/min ratio around 8.

• Overall, summer is the season with the highest dry nitrogen deposition while winter is the lowest. This is due to the heightened reactivity of nitrogen species in the summer as well as higher dry deposition velocities. At Galveston Bay, however, the highest deposition occurs during the fall season while the lowest deposition happens in summer due to the prevailing southerly wind.

• HNO₃ and NH₃ are the two dominant dry deposition species, followed by N₂O₅ and NTR (non-reactive organic nitrogen).

• Compared to observation, the model significantly overestimated dry nitrogen deposition at the observation site, which is located northwest of the Galveston Bay watershed. There are several possible causes behind the discrepancy. While the old 2000 emission inventory is an obvious source for the overestimation, more studies are needed to further identify/isolate other reasons such as biases in meteorological simulations.

• In spite of the overprediction at the observation site, we believe that the model results at the Galveston Bay and its watershed are reasonable. Our model results are very close to those
presented by Meyers et al (2001). Using a typical wet/total deposition ratio of 0.5 to 0.6, the model results matched well with an observation study in 1995-1996 (TRIADS).

- There is a significant emission reduction in NOx and SO$_2$ nationally since the 1990s. Our model’s emission inventory is based on the 2000 Texas Emission Inventory (TEI 2000). Therefore, the direct model results are valid for 2000. The current estimate is projected assuming a reduction of 10% in dry deposition (Sickles 2007).

- For sulfur dry deposition, the model showed that the distance from the emission centers rather than land or water surface is more important in determining the deposition rate. This is because the dry deposition velocities for sulfur species are generally higher than nitrogen species and sulfur tends to deposit closer to the sources and drop out of circulation earlier. The deposition flux decreased faster when moving away from emission centers. As a result, high sulfur depositions concentrate around major emission centers such as Houston, Beaumont and Lake Charles, and low deposition areas are found in the northern part of our domain.

The model overpredicted dry sulfur deposition by about 55% primarily due to the SO$_2$ overprediction. The relative sulfur dioxide fraction of the total sulfur mass in the model is much higher than in the observation, indicating possible partitioning problems in the model. More research is required to pinpoint the sources of the model bias.

**Recommendations for Future work:**

- Apply a newer emission inventory in the CMAQ when it becomes available. IMAQS is still testing Texas Point Source Inventory 2007 and other elements in the upcoming emission inventory. While the EPA and TCEQ are working on the new emission inventories, a projected 2007-2008 inventory from Texas Emission Inventory (TEI) 2000 may be used to estimate current atmospheric deposition.

- More efforts need to be directed toward analyzing the sources of model biases. Beyond the obvious higher 2000 inventory, the input meteorology from MM5, CMAQ internal inaccuracies, and observation/model comparison issues all can contribute to the overestimation. The observation/model comparison issues relate to the fact that model results are grid cell (4x4 km) averaged while observations are taken from a much smaller area.

- Although wet deposition is better understood than dry deposition at GBE, a parallel study of wet deposition will provide more details on the spatial and temporal patterns.

- Besides Galveston Bay, there are a number of other bays scattered along the Texas Gulf coast. The same methodology in this work can be applied to the other bays to study the impact of atmospheric deposition.
1. Introduction

Galveston Bay is an estuary located in Southeast Texas near the Houston-Galveston-Brazoria (HGB) area. It is the largest and most biologically productive estuary in Texas, and sits adjacent to one of the most heavily urban, industrialized areas in the nation. Prior to the mid-1970s, part of the Bay was seriously polluted primarily due to industrial and municipal point sources. In 1971, strict wastewater discharging rules were established and all the industries were required to upgrade their wastewater treatment facilities. Gradually, the water quality in the Bay improved, especially in the Houston Ship Channel section (Lester and Gonzales, 2002).

Nutrient enrichment, especially from nitrogen and phosphorus, has consistently ranked as one of the top causes of degradation in many U.S. waterbodies. Excess nitrogen and phosphorus lead to significant water quality problems including harmful algal blooms, hypoxia and declines in wildlife and wildlife habitat. For Galveston Bay, the primary nitrogen source is dissolved nitrogen from river discharge. The gauged riverflow accounts for about 59% of total new nitrogen sources (Stanley, 2001). Besides river discharge, nitrogen from atmospheric deposition (AD-N) is also an important new nitrogen source. Atmospheric deposition refers to the transport of trace gases and aerosols from the atmosphere to the ground surface. AD-N has been established as a major nitrogen source for U.S. coastal estuaries, contributing anywhere from 10% to over 40% of the total nitrogen loading (Paerl et al 2002). So far, the main reference for estimating the total contribution of AD-N at Galveston Bay Estuary (GBE) is “Nitrogen Loading in Coastal Waterbodies: An atmospheric perspective”, a book edited by Valigura et al (2001). A recent review article by Pinckney (2006) discussed the nitrogen balance and its seasonal pattern at GBE. It cited Valigura et al (2001) as the base for AD-N estimation.

The atmospheric deposition of sulfuric and nitric acids can decrease the pH of water, causing acidification in some situations. The average pH at Galveston Bay is about 7.7 (Lester and Gonzales, 2002), so acidification is not a serious concern for Galveston Bay. However, the atmospheric deposition of sulfuric and nitric acids still needs to be studied in order to understand the acidity and alkalinity balance in the Bay.

This study provides important information on atmospheric deposition of nitrogen and sulfur (AD-S) at GBE, which can assist in the planning and management of the Bay. The observed atmospheric deposition data are limited and are the not direct measurements of deposition at GBE. Because one of the criteria to select an observation site is to avoid anthropogenic air emission sources, the two observation sites measuring AD-N around GBE—the Clean Air Status and Trends Network (CASTNET) site ALC188 and the National Atmospheric Deposition Program (NADP) site TX10—are rural and located about 100 km away from the Bay. The GBE area is heavily populated and there are many air emission sources in the region, so spatial variation of AD-N is quite high and the actual AD-N at GBE is likely to be higher than is measured at the observation sites.

Besides relying on observations, another route to seek the AD-N estimation for GBE is sifting through past studies. The latest original research on AD-N at GBE by Valigura et al (2001) was published 7 years ago. That does not mean the studies in Valigura et al (2001) are 7 years
old. Some of the studies in Valigura et al (2001) were carried out in the 1990s, so the AD-N estimates for GBE in the book are valid mostly for those years. It is known that air emission has been falling nationwide since the 1990s due to tighter emission controls mandated in the 1990 Clean Air Act Amendments. As a result, the observed AD-N and AD-S is decreasing (Sickles et al 2007). The AD-N estimates at GBE by Valigura et al (2001) are likely to have a positive bias compared to current values.

The objectives in this original study are three-fold. First, it tries to update the AD-N estimate with more recent air emission and meteorological data using a more advanced atmospheric chemistry model, U.S. EPA’s Community Multidimensional Air Quality (CMAQ) model (Byun and Ching, 1999; Byun and Schere, 2006). Atmospheric chemistry models have long been employed to provide atmospheric deposition estimates for areas where observed data are sparse. At present, CMAQ is the model supported by EPA as the official air quality modeling tool and is used in this study. Second, it attempts to reconcile various AD-N estimates from different studies. Third, it will give an AD-S estimate at GBE which fills a void where no systematic research has been found.
2. Atmospheric Deposition in Galveston Bay Estuary

2.1 Galveston Bay and Its Watershed

Galveston Bay is a large, shallow estuary composed of four major sub-bays: Galveston, Trinity, East and West Bays (Figure 2.1). The two upper bays, Galveston and Trinity, comprise most of the area of the Bay. Galveston Bay encompasses an area of 384,000 acres (600 square miles, or 1554 square kilometers), making it the largest estuary along the Texas Gulf Coast (Lester and Gonzales, 2002).

Upper Galveston Bay receives the outflow of the San Jacinto River and much of the local drainage from the City of Houston via the Houston Ship Channel. Trinity Bay receives the outflow from the Trinity River, which is a major river in east Texas (I'm not sure if this is really necessary, but if you want to include it I would suggest putting it here rather than in the next paragraph). East Bay lies landward of Bolivar Peninsula and receives inflow from Oyster Bayou and other runoff from Chambers County. West Bay is situated landward of Galveston Island, and receives runoff from Chocolate Bayou, Mustang Bayou and other local bayous.

The Galveston Bay estuary system is greatly affected by natural processes and human activities occurring in its watershed, which spans north to the Dallas-Fort Worth area. The Galveston Bay watershed can be divided into two relatively independent parts, the upper and lower watersheds. The upper Galveston Bay watershed drains into the Trinity River and is basically the part of the Trinity River basin that lies above Lake Livingston (Figure 2.2). The lower Galveston Bay watershed (Figure 2.3) covers the area south of Lake Livingston. Approximately half the population of Texas lives within its boundaries and has a large potential impact on the estuary.
Figure 2.1 Galveston Bay and National Estuary Program (NEP) study area (Green shaded)

Figure 2.2 Upper Galveston Bay watershed (sand-yellow shaded)
The area of the Galveston Bay watershed is disputable according to different sources. The website of the Galveston Bay Estuary Program (GBEP) lists the watershed area as 33,000 square miles or 85,433 square kilometers. However, Alexander et al (2001) states that the watershed area is 63,158 square kilometers. Since this study is about atmospheric deposition, we adopt the number by Alexander et al for more consistent comparison. As a note, Alexander et al (2001) is a chapter in the book by Valigura et al (2001). The watershed to Bay area ratio is calculated as $63158/1554$, or about 41.

2.2 Atmospheric Nitrogen Deposition - An Introduction

Nitrogen is a naturally occurring element needed by all living things. While it is the most abundant element in the Earth’s atmosphere, nitrogen typically exists in a form that is unusable
by most organisms. Only after nitrogen is converted to a reactive form can it support the growth of plants and other organisms. Over the past century, human activity has greatly increased the amount of reactive nitrogen in the environment, increasing anthropogenic atmospheric “reactive” N emissions by almost 10 times (Howarth 1998).

Before the 1980s, understanding how nutrients (N and P) get into estuaries and coastal waters was centered on point sources (e.g., wastewater treatment plants, various industries) and diffuse sources (e.g., agricultural runoff, stormwater runoff, and groundwater). It was only after 1980 that scientists started to assess the importance of atmospheric sources as an extension to the acid rain studies. Much of the initial work came from NOAA's Air Resources Laboratory (ARL) under the auspices of the National Acid Precipitation Assessment Program (NAPAP), subsequently followed by the Atmospheric Nutrient Input to Coastal Areas (ANICA) program. In the 20+ years that have since passed, AD-N has become recognized as highly significant to the coastal water nitrogen budget (Paerl 1985, 1995, Paerl et al 2002) due to its large scale and magnitude.

Atmospheric N is deposited on land and water via dry and wet deposition processes. Dry deposition occurs when the trace gas parcels and aerosol particles in the atmosphere settle on the surface (transported via atmospheric turbulence). The rate of dry deposition is therefore governed by the level of atmospheric turbulence, the properties of the depositing species, and the nature of the surface. Wet deposition refers to the transfer of airborne compounds through falling hydrometeors (rain, snow, cloud and fog drops). Myers et al (2001) showed that wet N deposition generally comprises about 60% of the total AD-N after studying over 40 U.S waterbodies. Wet and dry depositions contribute N to a waterbody either directly (by falling onto the waterbody itself), or indirectly (when part of the deposition on the watershed is delivered to the waterbody). Indirect AD-N may enter the estuary along with stream flows, direct runoff (runoff returns to the waterbody directly, not through a stream) or groundwater. While the watersheds are typically much larger than the water surface of estuaries in size, the contribution from indirect N deposition is not as dominant as the sizes suggest since a majority of N deposited on the watershed is retained by the soil and plants. The role of indirect AD-N through groundwater is still largely uncertain and one of the areas with few studies.

The reactive atmospheric N can be divided into organic N and inorganic N, the latter of which is usually the dominant form and can be further classified into oxidized N and reduced N. Oxidized N in the atmosphere can be found mostly in gaseous NO (nitrogen oxide), NO₂ (nitrogen dioxide), N₂O₅ (nitrogen pentoxide), HNO₃ (nitric acid), and aerosol NO₃ (nitrate). NO and NO₂ is collectively known as NOx. N₂O₅ is frequently missing in literature as an oxidized N species in the AD-N process but our study shows that it is more important than either NO or NO₂. HNO₃ is the termination product of NOx and VOC (volatile organic compounds) in complex atmospheric photochemistry (Seinfeld and Pandis 2006). Aerosol NO₃ mostly exists in the form of NH₄NO₃ (ammonium nitrate). Gaseous NH₃ (ammonia) and HNO₃ can react in the atmosphere to form NH₄NO₃ which, along with (NH₄)₂SO₄ (ammonium sulfate) and NH₄HSO₄ (ammonium bisulfate), constitutes the bulk of fine particulates in heavily industrialized areas. The fine particulates can then be agglomerated into larger particles or they can be captured by larger-sized particles. The principle source of atmospheric oxidized N is the combustion of fossil fuels (e.g., by combustion engines, coal and oil burning power plants). The primary oxidized N
emission (directly emitted into the atmosphere) is NOx with NO being the primary species. Reduced N can be found in gaseous NH₃ and aerosol ammonium (NH₄⁺), which is part of NH₄NO₃. The bulk of anthropogenic NH₃ comes from agricultural sources such as fertilizer application and confined animal operations. In regions with many petro-chemical plants such as in HGB, NH₃ from industrial sources can be significant.

Widely present in the atmosphere, organic nitrogen (ON) is also an important part in the AD-N process. Compared to inorganic N, ON is poorly characterized (Cornell et al 2003). Furthermore, most existing research on ON deposition is about dissolved organic nitrogen (DON) in wet deposition. There are few studies on the dry deposition of ON. This study, with dry nitrogen deposition as the focus, will help bridge the gap in the study of dry ON deposition. Cornell et al (2003) summarized the atmospheric DON in 7 families of compounds, with nitrogen-containing aromatics, UREA, and PAN as the more important ones. Meyers et al (2001) compiled a list of studies on wet DON deposition. The reported percentage of DON is in the 7% to 28% range of total wet AD-N. Only one study reported total ON (wet + dry) as a fraction of total wet AD-N, which is about 31% in the case.

In summary, AD-N contributes a significant fraction of the total nitrogen entering coastal and estuarine ecosystems along the U.S. coast. AD-N to a coastal estuary is a complex process involving various aspects such as spatiotemporal distribution, gaseous / aerosol partitioning, wet / dry deposition, direct / indirect deposition, chemical constituents, and linkage to emission sources.

2.3 Atmospheric Nitrogen Deposition at Galveston Bay and Its Watershed – A Review

Several existing Galveston Bay AD-N studies originated from the book edited by Valigura et al (2001). The book itself is a compilation of eight chapters, each contributed by a different group of authors. The AD-N estimates for Galveston Bay and its watershed are scattered throughout several chapters. Due to the diverse data sources and modeling approaches used by the authors, the estimates are not exactly consistent. A few other studies outside of the book are also important, such as the on-site wet AD-N measurement by Sweet et al (1999) and the experimental study on cropland N yield by Eddleman (2000).

The most complete study to date on AD-N at Galveston Bay Estuary is likely to be the work by Meyers et al (2001), presented in the 3rd chapter of the Valigura book. Based on the data from three NADP sites during 1985 to 1996, Meyers et al. calculated the average wet deposition to be 188 kg-N/(km²-yr) for nitrate (NO₃⁻) and 182 kg-N/(km²-yr) for ammonium (NH₄⁺). Since the sites are closer to the watershed than the Bay water surface, the observed wet deposition is used on the watershed instead of on the water surface. The total inorganic N from wet deposition is about 397 kg-N/(km²-yr), which is on the high end of the 42 studied estuaries. The wet NH₄⁺ is multiplied by 1.15 to account for losses associated with weekly collection. Additionally, a study by Shon (1994) calculated a 17% DON contribution to the total wet AD-N, . From the two studies, the total wet AD-N is estimated to be around 478 kg-N/(km²-yr).

Since there was no dry deposition observation data at the time, Meyers et al. used a model, extended RADM (extRADM), to come up with an estimate for Galveston Bay Estuary.
The extended RADM model will be discussed in more depth in the next section. To calibrate the model, Meyers et al. compared the dry AD-N predicted by the model and observation at 22 coastal estuaries. 90% of the extRADM predictions are within ± 40% of the CASTNET estimates, and the differences do not suggest a serious bias in the model. The total dry AD-N at Galveston Bay watershed is estimated to be 394 kg-N/(km²-yr). Adding the wet deposition on the watershed, the total AD-N on the watershed is 891 kg-N/(km²-yr). For direct AD-N at the water surface, Meyers et al. used a reduction factor of 4 to calculate the direct dry AD-N. The wet AD-N is assumed to be the same for both watershed and water surface. The final estimate for total direct AD-N is 587 kg-N/(km²-yr), with dry direct AD-N close to 100 kg-N/(km²-yr). Using a watershed area of 61,830 square kilometers, the total AD-N loading on the Galveston Bay watershed is approximately 55,090 ton/yr.

Alexander et al (2001) applied an empirical watershed model, SPARROW (Spatially Referenced Regression on Watershed Attributes) to assess the indirect AD-N (Chapter 6 in Valigura’s book). A total of 40 coastal watersheds were studied and the results showed that from 4% to 35% of the total nitrogen in stream export originated from the atmosphere. The median is around 20%. For Galveston Bay Estuary, the total nitrogen exported from the watershed is 468 kg-N/(km²-yr). The contribution from the atmosphere is 62 kg-N/(km²-yr), or 13% of total exported N (Table 4). In Table 7, the AD-N delivered from land to the streams is 177 kg-N/(km²-yr). With an in-stream loss rate of 61%, the total AD-N entering the Bay is 177 * 0.39 or 69 kg-N/(km²-yr), which is slightly higher than what is shown in Table 4. The annual total AD-N delivered to the Bay by streams is 63518*62/1000 tons, or 3938 tons.

Stanley (2001) calculated the yearly average nitrogen input to Galveston Bay based on the data from 1977 to 1990 (Appendix 1 in Valigura’s book). The nitrogen sources are classified into 4 categories: gaged (from streams), ungaged (direct runoffs), returns (wastewater discharged by point sources) and precipitation (direct wet deposition). The fractional contributions to the total N for the 4 categories are 59.0%, 22.0%, 17.6%, and 1.4% respectively. The total annual N loading to the Galveston Bay is 38153 tons. For direct wet nitrogen deposition, Stanley used the average concentration from the 3 NADP sites and the precipitation volume reported by local National Weather Service stations to come up with an estimate of 528.5 ton-N/yr. If a bay surface area of 1554 square kilometers is assumed, the direct wet deposition rate is equal to 340 kg-N/(km²-yr), which is less than the estimate by Meyers et al (2001). Direct dry deposition is not considered in Stanley’s work. Stanley probably has underestimated the direct wet deposition rate; by accounting for the effects of NH₄⁺ loss and including DON, the calculation by Meyers et al appears to be more reasonable. However, even Meyers et al may have underestimated the wet deposition by using the measurements at NADP sites, all of which are rural. There are many industrial emission sources around the Houston Ship Channel (HSC) and the traffic in Houston is much heavier than the rural sites. Therefore, the atmospheric concentrations of the nitrogen compounds at Galveston Bay are likely higher than those at the NADP sites, resulting in a higher deposition rate. The on-site wet deposition measurements by Sweet et al showed that they are indeed higher.

Similar to Stanley (2001), Brock (2001) adopted the same classification for the nitrogen sources and likely the same datasets to calculate the range of total N loading to Galveston Bay. The mean total N loading is 38,350 ton-N/yr, which is slightly different from Stanley’s number.
The standard deviation is 11,488 ton-N/yr. The high interannual variability in N loading was due to the precipitation variation in the watershed, which led to the high variability in N loading of gaged and ungaged categories.

While all the above studies in the book by Valigura et al (2001) used data from NADP sites for direct wet deposition calculation, the study by Sweet et al (1999) is the only one that conducted on-site wet deposition measurements. The study is part of the Texas Regional Integrated Atmospheric Deposition Study (TRIADS). The sampling site is located at Friendship Park in Seabrook, a city on the west shore of Galveston Bay. The site was chosen partly because there is a CAMS (Continuous Ambient Monitoring Stations) station already established there. CAMS is a weather and air quality monitoring network operated by the Texas Commission on Environmental Quality (TCEQ). The wet deposition data collection lasted about one and half a years, from February 1995 to August 1996. Four species, NH$_4^+$, UREA, NO$_3^-$ and NO$_2$ were analyzed. NO$_3^-$ and NH$_4^+$ are the top two contributors. Based on the data, Sweet et al calculated the yearly nitrogen wet deposition rate to Galveston bay as 616 kg-N/(km$^2$-yr), which is higher than either Meyers’ or Stanley’s estimate. It should be noted that the interannual variability of wet deposition at NADP sites is relatively low. If all the measurements are accurate, the results by Sweet et al indicate that the higher deposition around the Bay is due to higher atmospheric concentrations instead of interannual variability. Sweet et al also applied a model by Patwardhan and Donigian (1997) to compute the total direct AD-N as a percentage of the total N input. The assumption is that the direct dry deposition is roughly equal to wet deposition and the total direct AD-N would be 1,760 ton-N/yr, or 8.6% of the total N input. With 2.8% indirect AD-N contribution from the watershed, the atmosphere deposition supplies about 11% of the total N inputs. The results by Patwardhan and Donigian (1997), however, put the contribution of AD-N to be 49% of the total N using so-called “spreadsheet analysis”. Obviously, the AD-N estimate by Patwardhan and Donigian is too high.

Despite the differences in the wet deposition rate by the NADP sites and the TRIAD study, all the measurements are of the same magnitude. Therefore, it is safe to say that the direct wet deposition rate is in the range of hundreds of kg-N/(km$^2$-yr). However, the indirect AD-N estimate by Alexander et al (2001) is difficult to verify. The study by Eddleman (2000), which measured the N yield rate at a cropland in south Texas, can provide some insight in evaluating the indirect AD-N. Eddleman’s field study was conducted on a large parcel of cropland near Corpus Christi, which is not far from Galveston Bay. The study lasted 3 years from 1996 to 1998. The measured average wet N deposition is 336 kg-N/(km$^2$-yr) and the export rate from the runoff is about 0.6%. In contrast, the overall land to water N yield in Alexander’s study is 23%. Since the Galveston Bay watershed is a mixture of urban, residential, forest, grassland, cropland and marshland areas, its N-yield should be higher than the cropland N yield; however, it is hard to argue that its yield could be over 30 times that of the cropland yield. Therefore, Alexander et al (2001) likely overestimates the contribution of indirect AD-N.

2.4 Observed Nitrogen Deposition at Galveston Bay Watershed

Currently, there are two active deposition measurement sites that are close to Galveston Bay. Figure 2.4 shows the two sites and the TRIAD site (C45), as well as the lower Galveston
Bay watershed (orange shaded). A few CAMS sites are also shown – they are used for indirect model verification (Section 2.10). Though neither of the two active sites is on the watershed, they are fairly close. CASTNET site Alabama-Coushatta (ALC188) is located east of the watershed and NADP site “Attwater Prairie Chicken National Wildlife Refuge” (TX10) is seated west of the watershed. NADP site TX21 (32.3786, -94.7117) is not considered here due to its distance from the watershed.

Figure 2.4 Observation sites: CASTNET – green dot; NADP – orange triangle; CAMS – blue squares

CASTNET is the nation’s primary monitoring network for dry deposition although it also records wet deposition data. The dry deposition rate is calculated using the concentration data and deposition velocity. CASTNET sites use filterpacks to collect air samples weekly and measure the concentration of nitric acid (HNO₃), particulate nitrate (NO₃⁻), and particulate ammonium (NH₄⁺) along with other pollutant species such as sulfur dioxide (SO₂), sulfate (SO₄), etc. Deposition velocities are calculated using the multi-layer resistance model (Seinfeld and Pandis 2006). As of May 2008 there are 50 CASTNET sites in operation. The measurement data for ALC188 are available online at CASTNET website (http://www.epa.gov/castnet/).
Table 2.1 Annual dry deposition flux (kg/ha) at ALC188 (1 kg/ha = 100 kg/ km²)

<table>
<thead>
<tr>
<th>YEAR</th>
<th>NH₄_FLUX</th>
<th>NO₃_FLUX</th>
<th>SO₂_FLUX</th>
<th>SO₄_FLUX</th>
<th>HNO₃_FLUX</th>
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<tr>
<td>2004</td>
<td>0.28</td>
<td>0.25</td>
<td>1.97</td>
<td>1.36</td>
<td>4.94</td>
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<td>2005</td>
<td>0.36</td>
<td>0.25</td>
<td>2.32</td>
<td>1.52</td>
<td>6.45</td>
</tr>
<tr>
<td>2006</td>
<td>0.29</td>
<td>0.31</td>
<td>2.16</td>
<td>1.41</td>
<td>5.43</td>
</tr>
<tr>
<td>Average</td>
<td>0.31</td>
<td>0.27</td>
<td>2.15</td>
<td>1.43</td>
<td>5.60</td>
</tr>
</tbody>
</table>

The observed dry deposition fluxes at ALC188 are displayed in Table 2.1. It is easy to see that the interannual variation is rather small. For dry N deposition, nitric acid (HNO₃) is the dominant species. The average yearly HNO₃ flux at ALC188 is 560 kg/ km², which is very close to the national average of 554 kg/km² (based on data 2000 to 2006). It should be noted that the flux data in table 2.1 are for individual species, not converted to N or S only.

Figure 2.5 shows the wet and dry N deposition (accumulated by species) at ALC188 based on the data from 2002 to 2004. The average wet N deposition is 420 kg-N/(km²-yr) and the average dry N deposition is 140 kg-N/(km²-yr). The wet N deposition contributes about 75% of the total deposition, compared to about 60% nationally (Meyers et al 2001).

![Wet and Dry N Deposition](image)

Figure 2.5 Wet and dry N deposition profile of ALC188 (Based on 2002-2004 data, graph is from CASTNet website)

Figure 2.6 shows the N deposition pie chart by wet and dry species. For wet deposition, the percentages of NO₃ and NH₄ are quite close. For dry deposition, HNO₃ contribution makes up 80% of the total dry AD-N. Ammonium and NO₃ provide the rest of dry AD-N.
The NADP-National Trends Network (NTN) was originally set up in 1978 to measure deposition of pollutants that cause acid rain, but is now considered the standard for wet deposition measurements of sulfate, nitrate, ammonium, and a few other species. The current number of active NADP sites (250) is much higher than that of CASTNET because the CASTNET sites are much more expensive to operate. NADP/NTN database contains monthly, seasonal and yearly ammonium and nitrate deposition data, and samples are collected weekly. Data for TX10 can be found at NADP website (http://nadp.sws.uiuc.edu).

Table 2.2 Annual wet deposition flux (kg/ha) at TX10 (1 kg/ha = 100 kg/ km²)

<table>
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<tr>
<th>YEAR</th>
<th>NH₄</th>
<th>NO₃</th>
<th>YEAR</th>
<th>NH₄</th>
<th>NO₃</th>
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<td>2.63</td>
<td>1996</td>
<td>1.48</td>
<td>5.09</td>
</tr>
<tr>
<td>1985</td>
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<td>7.05</td>
<td>1997</td>
<td>2.71</td>
<td>10.78</td>
</tr>
<tr>
<td>1986</td>
<td>2.07</td>
<td>9.27</td>
<td>1998</td>
<td>3</td>
<td>8.96</td>
</tr>
<tr>
<td>1987</td>
<td>2.79</td>
<td>7.45</td>
<td>1999</td>
<td>1.98</td>
<td>6.53</td>
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<td>5.88</td>
<td>2000</td>
<td>2.41</td>
<td>8.98</td>
</tr>
<tr>
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<td>4.76</td>
<td>2001</td>
<td>1.99</td>
<td>7.56</td>
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<td>2006</td>
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<tr>
<td>1995</td>
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<td>Average</td>
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<td>7.46</td>
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</table>
Table 2.2 shows the annual wet deposition flux at TX10 from 1984 to 2006. The average yearly (1985 to 2006) AD-N contribution from NH$_4$ and NO$_3$ are 165 and 171 kg-N/(km$^2$-yr), respectively. It should be noted that the table listed flux are for species, not the nitrogen portion. The 1984 data are abnormal and excluded from the calculation. The 1985 to 1995 average wet AD-N is very close to the average of 1996 to 2006, indicating no significant changes in the wet AD-N during the 22 years. To compare to the wet deposition at ALC188, we calculated the average N contribution from NH$_4$ and NO$_3$ during 2002 to 2004, which are 159.4 and 159.1 kg-N/(km$^2$-yr) respectively. Although the wet deposition fluxes of NH$_4$ and NO$_3$ are both less than those at ALC188, the NH$_4$/NO$_3$ ratio is almost identical. The AD-N difference in the two locations is likely the result of the difference in precipitation and air quality characteristics.

2.5 Atmospheric Deposition Modeling Using Atmospheric Chemistry Models

The study of atmospheric deposition using atmospheric chemistry models began in the 1980s. Besides providing deposition estimates for areas where observed data are sparse, the models can also be used to give a more detailed view of the spatial and seasonal variations in a region even when observed data are available. In addition, models are able to predict future deposition conditions caused by changes in emission, which in turn, are due to economic and regulatory changes.

Most atmospheric chemistry models are typically operated within an air quality modeling system (AQMS) since realistic atmospheric chemistry simulations need more than the chemistry alone. An AQMS simulates how pollutants are emitted into the atmosphere, how they react to each other, how they are transported, and how they are removed from the atmosphere. The ultimate removal is through atmospheric deposition. Therefore, emission, meteorology and atmospheric chemistry are the three interlinked components of AQMS.

There are a number of models that may be useful for atmospheric deposition studies, such as the Regulatory Modeling System for Aerosols and Deposition (REMSAD), Regional Acid Deposition Model (RADM), Community Multi-scale Air Quality Model (CMAQ), Comprehensive Air Quality Model with extensions (CAMx), California Puff Model (CALPUFF), Regional Lagrangian Model of Air Pollution (RELMAP), Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT), etc. The full 3D Eulerian chemistry models like RADM, CMAQ and CAMx are usually preferred for atmospheric deposition modeling since they are more comprehensive than other models in representing the physical and chemical processes in the life cycle of the atmospheric pollutants. In the real world, RADM, CMAQ and CAMx rarely work alone. Instead, each is usually integrated with an emission model, a meteorological model as well as several interfacing modules to form a modeling system. REMSAD (http://remsad.saintl.com/) can be considered a simplified 3D Eulerian model which focuses on aerosols and deposition. CALPUFF (http://www.src.com/calpuff/calpuf F1.htm/) is a Gaussian dispersion model which predicts the downwind concentration of air pollutants from discrete releases or “puffs”. RELMAP (Eder et al. 1986) is a relatively old Lagrangian dispersion model which is suited for non-reactive pollutants. The trajectory models such as HYSPLIT typically work with Eulerian models to replicate the path of pollutants, which helps to establish
the source-receptor relationship of pollutants. The “mainstream” 3D Eulerian chemistry models are briefly introduced below.

- **Regional Acid Deposition Model** (Chang et al. 1987) is an Eulerian trace-species transport, transformation, and removal model which was originally developed for acid deposition studies under the National Acid Precipitation Assessment Program (NAPAP). The structure of the original RADM is shown in Figure 2.7. RADM has been traditionally paired with Pennsylvania State University’s Mesoscale Model Version IV (MM4) (Anthes et al. 1987) to assess the relationship between emission and deposition of atmospheric pollutants such as nitric acid, nitrate and sulfate. Using a stand-alone meteorological model for meteorological input gives much credibility to the atmospheric chemistry model in representing the atmospheric processes.

![Figure 2.7 Structure of the original RADM (Chang et al. 1987)](image)

- **Extended RADM** (Mathur and Dennis 2000) is an extension of the original RADM, which added ammonia and aerosol physics relevant to N deposition through conversion of HNO₃ to NO₃⁻ and of NH₃ to aerosol NH₄⁺. Extended RADM contains many important physics and chemistry processes to account for the full budget of trace species related to N deposition. RADM / Extended RADM is also the predecessor of CMAQ, CAMx and various other AQMs.

- **Community Multi-scale Air Quality Model** (Byun and Ching 1999; Byun and Schere 2006) is the standard model used by EPA for air quality modeling. The CMAQ modeling system simulates various chemical and physical processes that are thought to be significant for understanding atmospheric trace gas transformations and distributions. The CMAQ system was designed to have a
flexible community modeling structure based on modular components. It greatly enhanced RADM by including the multi-scale capability similar to what is found in the meteorological models. It also improved the chemistry with the addition of more advanced reaction mechanism like CB4 and SAPRC99. The core of CMAQ, chemical transport model (CCTM), includes the following major processes: horizontal advection, vertical advection, mass conservation adjustments for advection processes, horizontal diffusion, vertical diffusion, emissions injection, deposition, gas-phase chemical reactions, aqueous-phase reactions and cloud mixing, aerosol dynamics, thermodynamics, chemistry, plume chemistry effects, photolytic rate computation, and process analysis. The UH CMAQ modeling system will be described in detail in Section 2.6.

- The Comprehensive Model with Extensions (CAMx) is a publicly available (www.camx.com) three-dimensional multi-scale photochemical grid model that is developed and maintained by ENVIRON International Corporation. CAMx was developed during the late 1990s using modern and modular coding practices. It has been widely used for a variety of air quality issues including ozone, particulate matter (PM), visibility, acid deposition, and air toxics. While sharing many structural and functional similarities, CAMx and CMAQ differ in some science areas such as the dynamics descriptions, vertical and horizontal grid structures, detailed physics and numerical algorithms used.

 Extended RADM and other enhanced RADM have been frequently adopted for nitrogen dry deposition research (Meyers et al. 2001, Paerl et al. 2002, Sullivan et al. 2003). The most common application is to estimate the dry deposition at locations where there is little to no observation available. All three studies used the Penn State Mesoscale Model to provide meteorological inputs. Since the Extended RADM generally was not run for a full year simulation due to limited computer resources, an aggregation method is used to calculate the annual AD-N estimates from a number of episodic runs. The aggregation method is based on the assumption that the atmospheric chemistry, transport, and deposition at a given location are governed by a number of different recurring weather patterns that can be combined to produce a realistic estimate of annual and seasonal synoptic and chemical climatology (Brook et al. 1995a, 1995b). In the study by Meyers et al, 19 weather patterns (clusters, or strata) were obtained by applying clustering analysis to the 850-hpa wind field. Then meteorological cases were randomly drawn from the weather patterns and deposition results were simulated with Extended RADM. The aggregation was based on the weighting (frequency) of the weather pattern and the number of actual cases drawn. The emission input was mostly based on the 1990 National Emission Inventory (NEI). Annual concentration and dry deposition results from the Extended RADM were compared to observations at 22 U.S watersheds. For ambient concentrations of total nitrate, the correlation between model and observation is 0.755. For total nitrate+nitrite dry deposition, the result is similar (correlation is 0.748). These results showed that the model is quite capable in simulating the nitrogen dry deposition.

2.6 Air Quality Modeling System at University of Houston
In order to address the impact of atmospheric deposition on water quality in Galveston Bay Estuary, we used a Community Multiscale Air Quality (CMAQ) modeling system to estimate nitrogen loading from dry deposition. The CMAQ modeling system, which comprises CMAQ, an emission model and a meteorological model, was developed and implemented at the University of Houston. Currently there are two setups of the UH-CMAQ modeling system, named F1 and F2, running every day to provide air quality forecasts for east Texas. The 2006 archived data from F1 were used in this study (TCEQ H45C Final Report 2007).

The UH-CMAQ F1 modeling system has three core components: CMAQ, an emission model named Sparse Matrix Operator Kernel Emissions system (SMOKE), and Penn State Mesoscale Model Version 5. The modular structure of the UH-CMAQ modeling system is shown in Figure 2.8.

![Figure 2.8 Schematic diagram of CMAQ modeling system](image)

Several interfacing processors provide linkage mechanisms among the meteorology, emissions, and chemistry transport modeling components. These processors include: the Emission-Chemistry Interface Processor (ECIP) that translates data from the SMOKE emission model for use in the CCTM; the Plume Dynamics Model that computes geometry of subgrid scale Lagrangian plumes for large elevated emitters; and the Meteorology-Chemistry Interface Processor (MCIP) that translates and processes outputs from the meteorology model for the CCTM. Initial condition and boundary condition processors (IC/BC Proc) provide concentration fields for individual chemical species for the beginning of a simulation and for the grids surrounding the modeling domain, respectively, and the photolysis processor (JPROC) calculates temporally varying photolysis rates.

The modeling protocols of the F1 system are summarized below. The detailed model setup is documented in Appendix A (Modeling protocols) of our project report HARC-45C (Byun et al., 2007 – HARC H45C final project report).
Modeling domain

The modeling domain of the UH-CMAQ F1 system consists of nested grids of varying resolution: a coarse grid domain (36-km cell size, 133 x 91 array) that covers the continental United States, a regional domain (12-km cell size, 89 x 89 array) over East Texas neighboring the Gulf of Mexico, and a fine domain (4-km cell size, 83 x 65) covering the Houston-Galveston-Brazoria area (Figure 2.8). The lower Galveston watershed and the Bay itself reside in the 4-km CMAQ domain. Both MM5 and CMAQ modeling domains are defined on a Lambert Conformal mapping projection, following the perfect sphere definition used in MM5 (projection origin: 100°W, 40°N). The horizontal grids employed for CMAQ (thin rectangles) modeling are smaller than the grids used in MM5 (thick rectangles).

![Image](image.png)

Figure 2.9 The F1 modeling system domain which comprises 3 Lambert nested grids. The thick rectangles are MM5 domains.

Model Vertical grid structure

There are 43 and 23 vertical sigma layers for MM5 and CMAQ, respectively, with higher resolution near the ground to better understand both the atmospheric structure and the deposition processes in the lower boundary layer. The altitudes above sea level are estimated according to the atmosphere assumptions used in MM5 (surface pressure of 1013 hpa, model top at 100 hpa, surface temperature of 304 K, and log-pressure lapse rate of 45 K/ln[p]). CMAQ uses 23 layers...
by collapsing two to three layers in the upper part of the MM5 43 layers. The MM5 and CMAQ vertical layer structures are the same for the various nested domains. CMAQ and corresponding MM5 vertical layer structures are presented in Table 2.3.

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<th>Layer top (AGL m)</th>
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<td>15</td>
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<td>0.825</td>
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</tr>
<tr>
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<td>13</td>
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<td>13</td>
<td></td>
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<td>1224</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>0.880</td>
<td>1081</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>0.895</td>
<td>940</td>
</tr>
<tr>
<td>10</td>
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<td>0.910</td>
<td>800</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>0.920</td>
<td>708</td>
</tr>
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<td>6</td>
<td>0.950</td>
<td>437</td>
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<td>5</td>
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<td>0.960</td>
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</tr>
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<td>4</td>
<td>4</td>
<td>0.970</td>
<td>260</td>
</tr>
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<td>2</td>
<td>0.990</td>
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</tr>
<tr>
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<td>1</td>
<td>0.996</td>
<td>34</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1.000</td>
<td>0</td>
</tr>
</tbody>
</table>

**Emissions Inventory**

Model-ready emissions estimates to generate a gridded emission inventory for CMAQ were processed using the SMOKE (Houyoux et al., 2000). For anthropogenic emissions, Texas Emissions Inventory (TEI) from TCEQ (Base5b imputed) was used to prepare CMAQ-ready inputs. The emission for F1 uses TEI base year of 2000 without projection. For biogenic emissions, the GloBEIS3-BEIS3 hybrid method and TCEQ’s 4km, 12km Land Use and Land
Cover (LULC) data was used to process the emissions (Byun et al., 2007 – HARC H45C final project report).

Meteorological model set up

Meteorological fields (three-dimensional gridded wind, temperature, humidity, cloud/precipitation, and boundary layer parameters) for the CMAQ simulations were prepared using the PSU/NCAR MM5 model (Grell et al., 1994) version 3.6.1. The MM5 model run was performed utilizing 24-category land use data from USGS and initial/lateral boundary conditions that are generated by interpolation of the National Centers for Environmental Prediction (NCEP) "ETA" model analysis fields. The explicit moisture scheme for simple ice, the radiation scheme of rapid radioactive transfer model (RRTM), and the surface scheme for the Noah land surface model (LSM) were adopted and the planetary boundary layer (PBL) was parameterized using the MRF-PBL. Forty-three full-sigma vertical levels were used, in the non-hydrostatic mode. Model simulations were conducted with one-way nested domains using the Nestdown process, which permitted high-resolution terrain and land-use to be incorporated for the nested domain but did not allow feedback from the nested grid back into the coarse grid domain. Specifically, grid nudging was performed at three-hour intervals both for the two-dimensional surface fields and for the three-dimensional fields aloft (Byun et al., 2007 – HARC H45C final project report).

Photochemical model set up

The CMAQ chemical transport model (CCTM) is designed for multiscale and multi-pollutant air quality modeling, and can simulate ozone, particulate matter, and air toxics from very small scales (such as urban areas) to very large scales (such as the US continent). CMAQ uses a generalized coordinate system, which makes it flexible enough to work with most known Eulerian weather modeling systems as long as the Jacobian of transformation is available. Mass consistency is one of the most important features for transport and transformation of air pollutants, so it is constantly monitored in the model during calculations. In cases of inconsistencies in the input, different algorithms for mass adjustment are available.

The MM5 fields were processed by the MCIP to produce CMAQ-ready meteorological inputs. The MCIP processor addresses: data format translation, conversion of units, diagnostic estimations of parameters not provided directly by MM5, extraction of data for appropriate window domains, reconstruction of meteorological data on different vertical grid resolutions through collapsing or interpolation as needed, and consistency among the meteorological variables (Byun, 1999a and 1999b). The MCIP options used in processing the MM5 out fields were: (1) the “pass-through” option where PBL values as estimated by MM5 were used directly; (2) radiation fields from MM5 files; and (3) the Model-3/CMAQ dry deposition (M3DDEP) routine to calculate dry deposition velocities.

The CMAQ chemical transport model (CCTM) ran with 23 vertical layers selected from 43 MM5 layers and then computed the concentrations and depositions of photochemical pollutants. The CCTM simulation used the CB-IV gas-phase chemistry mechanism, RADM-type aqueous chemistry and subgrid cloud processes, and the efficient Euler backward iterative (EBI) solver. The advection scheme chosen for the model was the piecewise parabolic method (PPM).
The multi-scale horizontal diffusion scheme was based on local wind deformation and vertical diffusion derived from eddy diffusivity theory. Initial and boundary conditions were provided by the seasonal averaged values from a global 3D chemistry/transport model with meteorology data from the Goddard Earth Observing System (GEOS-Chem) at a resolution of 2° latitude by 2.5° longitude.

**Model input/output**

The data associated with the project will be subject to rigorous quality checks using graphical and statistical software. The project requires preparation and maintenance of the LULC data, Eta Data Assimilation System (EDAS) meteorological assimilation data, emissions inventories, routine meteorological measurements, and air chemistry measurements from CAMS and air quality model outputs. For LULC data for the MM5 system, Texas Forest Service (TFS) LULC data (modified by UH) were used.

**Modeling codes**

The 365-day daily forecasts by the F1 system for year 2006 were completed in 2006. All the archived data, shell scripts and FORTRAN codes for running the CMAQ (as well SMOKE and MM5) simulation are maintained by Dr. Hyunchoel Kim of IMAQS.

2.7 Atmospheric Dry Deposition Process in CMAQ

As stated in Section 2.2, both atmospheric trace gases and aerosols are subjected to dry deposition. In CMAQ, the dry deposition of trace gases and aerosols are treated in different modules.

In atmospheric models, the dry deposition flux \( F \) is usually expressed as the product of local concentration \( C \) of the depositing species and the deposition velocity \( V_d \) (Equation 2.1). The advantage of using \( V_d \) is that all the complexities of the deposition process are overloaded to a single parameter. The deposition velocity depends on the type of pollutant, nature and type of surface, and the amount of turbulence or mixing in the atmosphere. Equation 2.1 applies to both gas-phase species and aerosols.

\[
F = -V_d \cdot C
\]  
(Equation 2.1)

In CMAQ, the gas-phase species concentrations are solved in the gas-phase chemistry module. The calculation of deposition velocities for important gaseous species using the surface and PBL parameters is performed by the M3DDEP routine in MCIP. There are two methods used for calculating the deposition velocities: the RADM dry deposition method (Wesley, 1989) and the surface exchange aerodynamic method (Pleim et al., 2001). The RADM (Wesley) method determines deposition velocities using friction velocities and aerodynamic resistances while the Models-3 (Pleim) method does the calculation using surface resistance, canopy resistance, and stomatal resistance. In MCIP run script, the environment variable “LDDEP” sets
the dry deposition method. The default is “1” which selects the RADM (Wesley) method. In our study, we used the “2” option which employs the Pleim method.

For gas-phase dry deposition, CMAQ computes the deposition flux of 18 reactive species and 2 inert species. Nine of the twenty species contain nitrogen, one of which is inert (NH₃), and two of which are organic nitrogen species (PAN and NTR) (Table 2.4).

Table 2.4 Gas-phase dry deposition Species containing nitrogen

<table>
<thead>
<tr>
<th>Specie</th>
<th>Name</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Nitric Oxide</td>
<td>30</td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrogen Dioxide</td>
<td>46</td>
</tr>
<tr>
<td>HONO</td>
<td>Nitrous Acid</td>
<td>47</td>
</tr>
<tr>
<td>NO₃</td>
<td>Nitrogen Trioxide</td>
<td>62</td>
</tr>
<tr>
<td>N₂O₅</td>
<td>Nitrogen Pentoxide</td>
<td>104</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Nitric Acid</td>
<td>63</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
<td>17</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacyl Nitrate</td>
<td>121</td>
</tr>
<tr>
<td>NTR</td>
<td>Organic Nitrate</td>
<td>130</td>
</tr>
</tbody>
</table>

The aerosol component “aero3” of CMAQ is derived from the Regional Particulate Model (RPM) (Binkowski and Shankar, 1995), which in turn, is based upon the paradigm of the RADM. In the aerosol component, the particles are divided into two groups, fine particles and coarse particles. These groups generally have separate source mechanisms and chemical characteristics. Aerosol deposition velocity is computed in routine “aero_depv”. Unlike gases, the deposition velocity for particles must be calculated from the aerosol size distribution, as well as meteorological and land-use information. The equations for calculating dry deposition velocity can be found in Binkowski and Shankar (1995).

In “aero3”, there are 26 aerosol species. Among them, dry deposition fluxes are computed for 22 species. 4 species (Table 2.5) contain nitrogen. Within the fine particulate group, the “accumulation” or “J” mode represents larger aged particles while “Aitken” or “I” mode is the smaller, freshly emitted particulates.

Table 2.5 Aerosol dry deposition species containing nitrogen

<table>
<thead>
<tr>
<th>Specie</th>
<th>Name</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANH₄J</td>
<td>Accumulation Mode Ammonium Mass</td>
<td>18</td>
</tr>
<tr>
<td>ANH₄I</td>
<td>Aitken Mode Ammonium Mass</td>
<td>18</td>
</tr>
<tr>
<td>ANO₃J</td>
<td>Accumulation Mode Nitrate Mass</td>
<td>62</td>
</tr>
<tr>
<td>ANO₃I</td>
<td>Aitken Mode Aerosol Nitrate Mass</td>
<td>62</td>
</tr>
</tbody>
</table>
2.8 Atmospheric Nitrogen Dry Deposition Results from CMAQ

The first step to obtain the CMAQ dry N deposition estimates is to gather model data. Since the F1 simulation data for each day in 2006 were archived in IDE hard disk drives, Dr. Hyunchoel Kim of IMAQS read the data from hard disk drives and uploaded them to one of IMAQS servers.

The uploaded archive data included the dry deposition data and surface level gas-phase concentration data in the 4-km CMAQ domain (D04). As D04 is large enough to cover the Galveston Bay watershed, there is no need to use the coarse 12-km or 36-km domain data. The concentration data was intended for indirect model verification with CAMS chemistry measurements. All the archived data have 1-hour temporal resolution which is considerably higher than the resolution in water quality research.

The model data were then downloaded to PC computer for further extraction, calculation, and analyses. The results are divided into two groups: the overall deposition in the 4-km domain and the direct dry deposition at the Bay waterbody. The detailed procedures for 4-km domain analyses are recorded in Table 2.6. The detailed procedures for the direct AD-N analyses are listed in Table 2.7. The 2 zoom-in images in procedure P1.8 and P1.9 include one zoomed to HGB, and one zoomed to Galveston Bay.

Table 2.6 Step-by-step procedures for dry AD-N analyses in the full 4-km domain

<table>
<thead>
<tr>
<th>Procedure No.</th>
<th>Description</th>
<th>Input File(s)</th>
<th>Output File(s)</th>
<th>Specie</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1.1</td>
<td>Extract Hourly Deposition for Each Day</td>
<td>CMAQ deposition files, UTC</td>
<td>365*13 Text Files, CST</td>
<td>Each of the 13 Species</td>
</tr>
<tr>
<td>P1.2</td>
<td>Sum up Daily Deposition Using Hourly Data; Compute the N Portion</td>
<td>Output from P1.1, CST</td>
<td>365*13 Text Files, CST</td>
<td>Each of the 13 Species</td>
</tr>
<tr>
<td>P1.3</td>
<td>Sum up Monthly N Deposition Using Daily Data</td>
<td>Output from P1.2, CST</td>
<td>12*13 Text Files, CST</td>
<td>Each of the 13 Species</td>
</tr>
<tr>
<td>P1.4</td>
<td>Sum up Seasonal Deposition Using Monthly Data</td>
<td>Output from P1.3, CST</td>
<td>4*13 Text Files, CST</td>
<td>Each of the 13 Species</td>
</tr>
<tr>
<td>P1.5</td>
<td>Sum up Annual Deposition Using Monthly Data</td>
<td>Output from P1.3, CST</td>
<td>1*13 Text Files, CST</td>
<td>Each of the 13 Species</td>
</tr>
<tr>
<td>P1.6</td>
<td>Sum up Total Seasonal Deposition of All Species</td>
<td>Output from P1.4, CST</td>
<td>4*1 Text Files, CST</td>
<td>All - Aggregated</td>
</tr>
<tr>
<td>P1.7</td>
<td>Sum up Total Annual Deposition of All Species</td>
<td>Output from P1.5, CST</td>
<td>1 Text File, CST</td>
<td>All - Aggregated</td>
</tr>
<tr>
<td>P1.8</td>
<td>Generate total Spatial AD-N Plot for 2006</td>
<td>Output from P1.6, CST</td>
<td>3 Image Files, 1 for Whole Domain, 2 Zoom-Ins</td>
<td>All - Aggregated</td>
</tr>
<tr>
<td>P1.9</td>
<td>Generate total Spatial AD-N Plot for Each Season</td>
<td>Output from P1.7, CST</td>
<td>3 Image Files, 1 for Whole Domain, 2 Zoom-Ins</td>
<td>All - Aggregated</td>
</tr>
</tbody>
</table>
Table 2.7 Step-by-step procedures for direct dry AD-N analyses at Galveston Bay

<table>
<thead>
<tr>
<th>Procedure No.</th>
<th>Description</th>
<th>Input File(s)</th>
<th>Output File(s)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2.1</td>
<td>Extract the Land-Water (LW) Mask File from MM5 input</td>
<td>MM5 Terrain File</td>
<td>1 Text File with LW Mask Data for Each Cell</td>
<td></td>
</tr>
<tr>
<td>P2.2</td>
<td>Generate Spatial Plot with LW Mask Data</td>
<td>Output from P2.1</td>
<td>1 Image File, Whole Domain</td>
<td></td>
</tr>
<tr>
<td>P2.3</td>
<td>Identify All GB Water Cells, Write Down Cell Coordinates</td>
<td>Output from P2.2 and A GB Map</td>
<td>1 Text File with the Coordinates of GB Cells</td>
<td></td>
</tr>
<tr>
<td>P2.4</td>
<td>Read Annual Total Deposition Data for Each GB Cell</td>
<td>Output from P2.3 and P1.6</td>
<td>1 Text File</td>
<td></td>
</tr>
<tr>
<td>P2.5</td>
<td>Read Monthly, Seasonal Deposition Data for Each GB Cell</td>
<td>Output from P2.3, and P1.7</td>
<td>4*1 Text Files</td>
<td></td>
</tr>
<tr>
<td>P2.6</td>
<td>Calculate Direct AD-N Flux (All Cell Average) for 2006</td>
<td>Output from P2.4</td>
<td>1 Text File</td>
<td></td>
</tr>
<tr>
<td>P2.7</td>
<td>Calculate Direct AD-N (All Cell Average) for Each Month, Season</td>
<td>Output from P2.5</td>
<td>4*1 Text Files</td>
<td></td>
</tr>
<tr>
<td>P2.8</td>
<td>Generate Pie Chart for Season AD-N</td>
<td>Output from P2.6</td>
<td>1 Image File</td>
<td></td>
</tr>
<tr>
<td>P2.9</td>
<td>Read Annual Total Deposition Data for Each GB Cell, 13 Species</td>
<td>Output from P2.3 and P1.5</td>
<td>13 Text File</td>
<td></td>
</tr>
<tr>
<td>P2.10</td>
<td>Calculate Direct AD-N (All Cell Average) for 2006, 13 Species</td>
<td>Output from P2.9</td>
<td>13 Text File</td>
<td></td>
</tr>
<tr>
<td>P2.11</td>
<td>Generate Pie Chart for Specie Composition</td>
<td>Output from P2.10</td>
<td>1 Image File</td>
<td></td>
</tr>
<tr>
<td>P2.12</td>
<td>Generate Line Chart for Monthly AD-N</td>
<td>Output from P2.7</td>
<td>1 Image File</td>
<td></td>
</tr>
</tbody>
</table>

2.8.1 Dry Deposition at the CMAQ 4-km Modeling Domain

By following the procedures in Table 2.6, we generated the annual and seasonal total dry AD-N spatial contour plots for our 4-km modeling domain. All the spatial plots in this study are created with Surfer V8, a popular software package which does spatial interpolation and draws various spatial plots. One attractive feature of Surfer is its powerful scripting capability which supports all functionalities in manual mode, similar to Microsoft Office, ArcGIS and AutoCad.

The annual total dry AD-N spatial distribution plot for 2006 is shown in Figure 2.10. Two zoom-in plots for Houston + Galveston Bay and Galveston Bay are shown in Figure 2.11 and 2.12, respectively. While the original model output is by 4x4 km cell, these plots have been interpolated by pixels within each grid cell. Therefore, there are no colored boxes (representing individual cells) shown in these plots. The maximum AD-N value is almost 1400 kg-N/(km²-yr) and the minimum is only 176 kg-N/(km²-yr), with a max/min ratio of 8. There are two high deposition spots: the Houston Ship Channel to the Woodlands, and Lake Charles where petrochemical refineries are concentrated. The Beaumont area shows elevated deposition but it is lower than those two spots. There are small areas along the major highway showing high
deposition, suggesting nitrogen from mobile sources is also significant. Clearly, the spatial variation is quite remarkable. Therefore, one site is inadequate to capture the deposition in the whole watershed.

Figure 2.10 Annual total dry AD-N spatial distribution for 4-km domain (D04) (sum of 13 species)
There are 5395 grid cells inside the 4-km domain, and the average dry AD-N is 528 kg-N/(km²-yr). Land cell count is 3631 and the average is 655 kg-N/(km²-yr). For water cells, the count is 1764 and the average is 267 kg-N/(km²-yr). The dry deposition flux ratio of land cells over water cells is about 2.5. Meyers et al (2001) discussed the difference of dry deposition on land and water. Since water surfaces are much more aerodynamically smooth than land surfaces, the dry deposition velocities on land are higher. The deposition velocities in forested watersheds are roughly 3 to 6 times higher than the velocities over water surfaces. Since the Galveston Bay watershed is a mixture of urban, residential area, forest, grassland, cropland and marshland, the land-water deposition velocity ratio should be smaller. This is because deposition velocity in forest typically is high. Considering that most water cells are located at Galveston Bay and the Gulf of Mexico where concentrations are lower, the model-estimated land-water flux ratio of 2.5 appears to be reasonable.

Overall, the model-simulated spatial variation in dry AD-N is plausible. The local high deposition spots can usually be traced to nearby point emission sources or busy highways.

Seasonal dry AD-N plots are shown in Figure 2.13 to Figure 2.24. The seasonality in dry AD-N is apparent: summer (JJA) has the highest deposition while winter (DJF) has the lowest. Since the dry depositions depend on the concentrations and deposition velocities, studying the
seasonality of concentrations and deposition velocities can shed light on the deposition seasonality.

Figure 2.13 Winter total dry AD-N spatial distribution for D04

Figure 2.14 Winter total dry AD-N spatial distribution for Houston and Galveston Bay
Figure 2.15 Winter total dry AD-N spatial distribution for Galveston Bay

Figure 2.16 Spring total dry AD-N spatial distribution for D04
Figure 2.17 Spring total dry AD-N spatial distribution for Houston and Galveston Bay

Figure 2.18 Spring total dry AD-N spatial distribution for Galveston Bay
Figure 2.19 Summer total dry AD-N spatial distribution for D04

Figure 2.20 Summer total dry AD-N spatial distribution for Houston and Galveston Bay
Figure 2.21 Summer total dry AD-N spatial distribution for Galveston Bay

Figure 2.22 Fall total dry AD-N spatial distribution for D04
Figure 2.23 Fall total dry AD-N spatial distribution for Houston and Galveston Bay

Figure 2.24 Fall total dry AD-N spatial distribution for Galveston Bay
In summer, the spatial variation is also higher, a result of more persistent southerly and southeasterly winds. Persistent winds tend to increase deposition in some places while decreasing it in other places, resulting in higher spatial variation. On the other hand, variable winds scatter the deposition doses around, lowering the spatial variation. As a reference on how wind pattern may affect the spatial distribution, the monthly windrose plots at a CAMS site in Galveston is attached in Appendix A.

2.8.2 Direct Dry Deposition at the Galveston Bay Waterbody

To find out the direct dry deposition at the bay surface, the water cells of Galveston Bay in D04 must be first identified. In MM5, each grid cell has a “land/water mask” (lwmask) attribute. The attribute takes two values – “0” means water and “1” means land. By plotting out the land/water mask values in D04, the GB water cells can be easily determined. Figure 2.25 is the land/water mask plot for D04.
A total of 80 water cells are determined to be part of Galveston Bay. A few water cells in West Bay may be left out since it is hard to differentiate them from the Gulf cells. This exclusion should not affect the results because we are interested in the average deposition flux and the spatial variation at the Bay is small. The yearly average deposition flux is calculated to be 289 kg-N/(km²-yr) for the 80 cells, which is slightly higher than the average of all water cells. This is expected since the majority of water cells are located at the Gulf where the air is cleaner.

![Total Direct Nitrogen Deposition By Species](image)

**Figure 2.26 Total direct nitrogen deposition by species – 2006**

The species composition pie chart of the direct dry deposition is shown in Figure 2.26. HNO₃ and NH₃ are the top two species, accounting for 70% of the total. The next two species are N₂O₅ and NTR, contributing 9% each. The aerosols appear to contribute minimally, with only coarse ammonium particles (ANH₄J) having a 2% share. Fine ammonium particles and all the nitrate particles are negligible. This is consistent with the observation that aerosol ammonium is dominant among PM species.

The pie chart of the seasonal direct dry deposition is shown in Figure 2.27. Monthly direct dry deposition is displayed in Figure 2.28. Unlike the dry deposition in the whole domain, the direct dry deposition is lowest in summer yet it peaks in fall. Again, it can be easily explained through the windrose plots in Appendix A. In summer, the prevailing winds bring in the clean marine air from south and southeast while the more variable winds in fall push in more dirty air from the HSC area. As a side note, the ozone level at Galveston shows a similar seasonal pattern.
Figure 2.27 Seasonal direct dry deposition at Galveston Bay

Figure 2.28 Monthly direct dry deposition at Galveston Bay
2.8.3 Dry Deposition GIS Database at the CMAQ 4-km Modeling Domain

The spatio-temporal patterns of dry AD-N are very valuable information in the management and planning of GBE. From a practical standpoint, creating a dry deposition GIS database for the bay and watershed is equally important. The default model output is on a grid that does not exactly match either the bay or the watershed. Also, the model has a grid size of 4x4 kilometers, which may still be too large although it is much finer than the CASTNET network. In practice, there is a need for databases with a finer spatial resolution like 1x1 kilometer.

To create a 1x1 km AD-N GIS database targeting the watershed, the 1x1 km data grid first needs to be generated from the 4x4 km data grid. The 1x1 gridded output are converted to data files recognizable by common GIS software such as the ArcGIS. Then a watershed shape file (.shp) can be used to adapt the gridded data to the irregularly-shaped watershed in a GIS software.

Spatial interpolation techniques may be used to interpolate the 4x4 km grid into a 1x1 km grid. There are many spatial interpolation and gridding methods such as inverse distance to a power, Kriging, minimum curvature, polynomial regression, radial basis function, triangulation with linear interpolation, etc. Among them, Kriging is the most frequently adopted method due to its accuracy, efficiency and robustness. Fundamentally, it is a two-dimensional linear interpolation or linear regression. Again, Surfer V8 was chosen to perform the Kriging. The AD-N GIS database contains a total of 30 variables: 12 monthly, 4 seasonal, 13 speciated, and one yearly total AD-N. After the Kriging, the gridded data files were converted to a text format akin to a database table with each row defining a data record. Finally, the text files were loaded to ArcGIS to create the database. Used in conjunction with the watershed shape files, one can find out the value of any AD-N variable (30 total) for any location inside the watershed.

2.9 Comparison of Model Simulated Dry Deposition to AD-N Measurements

Since ALC188 is the only site that has dry deposition measurements, we first evaluate model results with measurements at ALC188. There are two methods to obtain model data at the ALC188 location. The first one, “exact match”, picks the model value on the grid cell exactly matching the observation location. It is the most common approach to evaluate model results. The second method, “3x3 average”, uses the average of a 9-cell square with the observation site sitting in the center cell. The “3x3 average” can smooth out local discontinuities, which sometimes yields a more reasonable comparison. Here both methods were used for model assessment.

Because there are thirteen model species and only three measured species, we will not attempt to compare the total AD-N since it can be misleading. Instead we chose to compare the individual species. The lack of all the model species in measurements makes it difficult to have a full evaluation of model results. The comparison of the 3 species is listed in Table 2.8. The

---

1 The total dry observed AD-N at ALC188 (3 species) is 151 kg-N/(km²-yr) and the total model AD-N (13 species) is 594 kg-N/(km²-yr). The model result is almost 4 times of the observed.
“exact match” and “3x3 average” produced very close numbers so that there is virtually no
difference in choosing the method. From Figure 2.9, it is easy to see there is little spatial
variation in the ALC188 region.

Table 2.8 Model vs. observation: deposition of 3 nitrogen species – unit is kg-N/(km²-yr)

<table>
<thead>
<tr>
<th>Method</th>
<th>Model-HNO₃</th>
<th>Obs-HNO₃</th>
<th>Model-NO₃</th>
<th>Obs-NO₃</th>
<th>Model-NH₄</th>
<th>Obs-NH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Match</td>
<td>327.5</td>
<td>121</td>
<td>1.7</td>
<td>7</td>
<td>10.4</td>
<td>22.6</td>
</tr>
<tr>
<td>3x3 Average</td>
<td>327.3</td>
<td>121</td>
<td>1.4</td>
<td>7</td>
<td>10.4</td>
<td>22.6</td>
</tr>
</tbody>
</table>

While there are large differences between the model results and observations, they are of
the same magnitude. HNO₃ is the dominant species in both model results and observations.
There are several possible reasons behind the discrepancies.

- Model emission inventory is not projected which leads to inflated N emission.
- Model meteorology is inaccurate. There are significant biases in simulated
  meteorological fields such as turbulence, wind, etc. Though no data assimilation
  in the forecast runs may be considered a drawback, it is not a serious problem as
  long as it does not trigger long-term bias.
- The model has inaccurate LULC data which leads to problematic deposition
  velocities in the observation region.
- There are deficiencies in model dry deposition module.
- Model results are the average of a large area (16 sqkm), while measurements are
  taken from a small space.
- There are special site conditions that may lead to certain bias.
- Observed wet/total AD-N ratio is higher than the numbers in literature (0.75 vs.
  0.5-0.6).

The first two are likely the dominant factors causing the high model HNO₃ deposition.
Further studies are needed to explain the large differences.

Another potential issue is the role of NH₃. The lack of measurements suggests that NH₃ is
not a big player in the dry AD-N, yet in the model, NH₃ represents a quarter of the total AD-N.

Besides the measurements at ALC188, the wet deposition from the TRIADS study by
Sweet et al. (1999) can help assess the deposition near the Bay. The TRIADS study estimated
the total wet N deposition at Seabrook C45 to be 616 kg-N/(km²-yr). From our model, the total dry
deposition is 563 kg-N/(km²-yr) for “exact match” and 552 kg-N/(km²-yr) for “3x3 average”.
The wet/total AD-N ratio is 616/(560+616) or 0.52, which falls in the typical range of 0.5 to 0.6.
Based on the wet deposition data at 3 inland NADP sites, Meyers et al. estimated the average wet
deposition at the Galveston Bay watershed to be 497 kg-N/(km²-yr). The number is consistent
with the TRIADS study. Although the model overpredicted the AD-N at ALC188 by a large
margin, it is not the case at Seabrook C45. Using a wet/total AD-N ratio of 0.5 to 0.7 and a wet
deposition flux of 616 kg-N/(km²-yr), the dry AD-N at C45 will be in the range of 370 to 616 kg-
Both the model estimate [563 kg-N/(km²-yr)] and the Meyers’ estimate [394 kg-N/(km²-yr)] fall into the range. Using the range, the model dry AD-N at C45 is approximately 0.9 to 1.5 times of the actual number.

Overall, the model appears to overpredict dry AD-N in the piney woods region of ALC188. However, the model estimates become more reasonable approaching Galveston Bay. In general, we expect that model prediction to be 0.8 to 2.2 times that of the actual values at the watershed.

2.10 Verification of Model Nitrogen Species Using Observed Concentration Data

Since dry AD-N is calculated by multiplying the species concentration and deposition velocity, evaluating model’s concentration prediction can provide useful insight about its AD-N performance. The chemistry measurements from CAMS, mostly concentration data, have been routinely used by IMAQS to assess model performance. Compared to the sparse deposition monitoring network which has only two sites in the 4-km model domain, the TCEQ CAMS network has over 50 sites. Unlike the deposition sites, most of the CAMS sites inside the domain are located in and around metro Houston. Therefore the concentration data at CAMS sites are the direct measurements of air quality at the Galveston Bay Watershed.

Ideally, the concentration data of NO₃, HNO₃, NH₄+, NH₃ would be most relevant for evaluating nitrogen deposition. However, CAMS only provides measurements of nitrogen species such as NO, NO₂, and aerosol nitrate. It also has data for NOy, the sum of all reactive nitrogen species. In this section, we will concentrate on NO and NO₂, which are also critical species in atmospheric chemistry. The atmospheric chemistry models generally do not have high skills in predicting aerosols so we skip aerosol nitrate here.

2.10.1 Model Predicted NO and NO₂

Hourly NO, NO₂ observations for the year 2006 were extracted from the IMAQS CAMS data archive. IMAQS routinely accesses TCEQ’s online CAMS database and downloads all the recent measurements. All the valid measurements from the ~30 sites having NO and NO₂ measurements were extracted. Corresponding model NO, NO₂ concentration data were also obtained from the F1 forecast archives.

To evaluate model performance, we adopted a simple set of statistical protocols commonly used in the modeling community. The seven statistics are:

- Mean Bias (MB)
- Mean Absolute Error (MAE)
- Root Mean Square Error (RMSE)
- Correlation or R-Square
- Index of Agreement (IOA or d) – Willmott (1981)
- Mean of model and observed data

43
o Standard Deviation (Std Dev) of model and observed data

The statistics for NO and NO$_2$ are listed in Table 2.9 and 2.10. The first row is for all the sites while the 2$^{nd}$ and 3$^{rd}$ row are for sites Seabrook (C45) and Mauriceville (C311). C311 is the closest CAMS site to ALC188.

Table 2.9 Statistics for NO: All Sites, Seabrook (C45) and Mauriceville (C311)

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>Corr</th>
<th>IOA</th>
<th>RMSE</th>
<th>MAE</th>
<th>MB</th>
<th>O_M</th>
<th>M_M</th>
<th>O_SD</th>
<th>M_SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>230318</td>
<td>0.41</td>
<td>0.53</td>
<td>16.8</td>
<td>4.6</td>
<td>-1.3</td>
<td>4.5</td>
<td>3.3</td>
<td>18.3</td>
<td>9.7</td>
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<tr>
<td>C45</td>
<td>8221</td>
<td>0.58</td>
<td>0.56</td>
<td>5.6</td>
<td>1.8</td>
<td>0.1</td>
<td>1.6</td>
<td>1.7</td>
<td>4.6</td>
<td>5.3</td>
</tr>
<tr>
<td>C311</td>
<td>8133</td>
<td>0.08</td>
<td>0.23</td>
<td>6</td>
<td>2</td>
<td>-1.5</td>
<td>1.9</td>
<td>0.4</td>
<td>5.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 2.10 Statistics for NO$_2$: All Sites, Seabrook (C45) and Mauriceville (C311)

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>Corr</th>
<th>IOA</th>
<th>RMSE</th>
<th>MAE</th>
<th>MB</th>
<th>O_M</th>
<th>M_M</th>
<th>O_SD</th>
<th>M_SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>228442</td>
<td>0.49</td>
<td>0.63</td>
<td>13.6</td>
<td>8.4</td>
<td>5.8</td>
<td>8.8</td>
<td>14.5</td>
<td>10.4</td>
<td>13.4</td>
</tr>
<tr>
<td>C45</td>
<td>8000</td>
<td>0.54</td>
<td>0.56</td>
<td>11</td>
<td>7.2</td>
<td>5.9</td>
<td>5.9</td>
<td>11.8</td>
<td>5.5</td>
<td>11.1</td>
</tr>
<tr>
<td>C311</td>
<td>8133</td>
<td>0.29</td>
<td>0.49</td>
<td>7.3</td>
<td>4.9</td>
<td>2.8</td>
<td>3.9</td>
<td>6.6</td>
<td>4.4</td>
<td>6.6</td>
</tr>
</tbody>
</table>

- N – data points; Corr – Correlation; IOA – Index of Agreement; RMSE – Root Mean Square Error; MAE – Mean Absolute Error; MB – Mean Bias; O – Observation; M - Model; O_M – Observed Mean; M_M – Model Mean; SD – Standard Deviation
- Units for RMSE/MAE/MB/O_M/M_M/O_SD/M_SD: ppb

The statistics show that the model is slightly better in predicting the NO$_2$ than NO. One reason is that NO is mostly a primary pollutant (directly emitted into the atmosphere, not created during chemical reactions). Typically, then, NO daily time series in HGB have two peaks reflecting the two traffic peaks. However, the peaks can be affected by local meteorology and they are somewhat difficult to capture by the model. For the Seabrook site, the performance is on par with the average for both NO and NO$_2$. For the Mauriceville site, the NO and NO$_2$ performance is worse and the NO performance is particularly poor. It is likely due to the fact that the NO/ NO$_2$ at Mauriceville are mostly from transport and there are issues with the model meteorology.

The model slightly underpredicted the NO with a mean bias of -1.3 ppb. However, it has a larger positive bias of 5.8 ppb for NO$_2$. Since the model used an emission inventory of 2000, which is known to have higher NOx emission than in 2006, model predicted NOx is higher. The large positive bias in NO$_2$ and the higher average NO$_2$ concentration indicate that NO was converted to NO$_2$ quicker in the model than in the real world. At C311, both observed and model mean NO$_2$ are also slightly less than half of the all-site average, suggesting the overall transport in the model is fine.
2.10.2 The Relationship Between HNO₃ and NO/NO₂

As the contribution of NO and NO₂ to AD-N is very small, the statistics in Section 2.10.1 do not bear direct significance to the AD-N. However, we can look at the correlation between HNO₃ and NO/NO₂ to have a clue about the model’s HNO₃ performance.

![Figure 2.29 Correlation between HNO₃ and NO, simulated by CMAQ](image)

Figure 2.29 Correlation between HNO₃ and NO, simulated by CMAQ

![Figure 2.30 Correlation between HNO₃ and NO₂, simulated by CMAQ](image)

Figure 2.30 Correlation between HNO₃ and NO₂, simulated by CMAQ

Model simulated correlation between HNO₃ and NO is shown in Figure 2.29. A similar plot for NO₂ is in Figure 2.30. Although the noise levels are high in both figures, they both show that HNO₃ is positively correlated to NO and NO₃. It should be noted that the concentrations in both figures are daily averages of all sites. Due to the conversion between nitrogen species, the
hourly correlation can be different. From the two Figures, the higher NOx emission in the model is likely to lead to the higher predicted AD-N. At the end of Section 2.9, we suggested that model values are 0.8 to 2.2 times of the actual values at the watershed, but with the information in this section, we think predicted/actual ratio is more likely between 1.3 and 2.2.

2.11 Total Nitrogen Flux from Atmospheric Sources to Galveston Bay – A Current Estimate

Based on Stanley (2001), the nitrogen input to Galveston Bay may be classified into 4 categories: gaged, ungaged, returns and precipitation. The only source that does not include atmospheric contribution is the ‘returns’ which represents the waste water discharged into the bay. “Precipitation” means direct wet deposition falling onto the Bay surface. The streamflow (gaged) and the direct runoff (ungaged) carry the AD-N from the watershed. The direct dry deposition is not accounted by Stanley likely because of the relatively small amount of dry AD-N and the difficulties in estimating them. To calculate the total nitrogen flux from atmospheric sources we need to sum up the direct deposition (wet + dry) and the indirect deposition from the watershed. Since the data we have are mostly before 2000, a current estimate will be projected.

2.11.1 Direct Nitrogen Deposition

The direct dry nitrogen deposition estimate comes from this study – 289 kg-N/(km²-yr) in year 2000. A projected dry deposition in 2006 will be 260 kg-N/(km²-yr) assuming a 10% reduction in dry deposition (based on Sickles 2007 estimate). If the positive bias is 70% (assume predicted/actual ratio is 1.7), then the direct dry deposition will be 153 kg-N/(km²-yr).

The direct wet deposition may be estimated from the observed data at TX10 and the TRIAD study because there is no measurement of direct wet deposition. Since the precipitation generally dissolved all the soluble N species in the atmosphere, the wet deposition rates on the water surface and land should be similar as long as the concentration and precipitation amount are close. Therefore the wet deposition at TX10 should be a good proxy for the Bay. To estimate the current wet nitrogen deposition at TX10, we averaged the N flux during the 2001-2006 period. The wet N from NH₄⁺ and NO₃ are roughly the same, 157 kg-N/(km²-yr). Using the same method by Meyers et al (2001), which multiplies 1.15 to NH₄⁺ to compensate for losses and assumes DON is 25% of the sum of NO₃ and NH₄⁺, we arrive at 422 kg-N/(km²-yr) at TX10. Compared to 497 kg-N/(km²-yr) calculated by Meyers et al, it is a 16% reduction. Since TX10 is about 100 km from the Bay, the actual wet deposition at Bay is likely to be higher. A 10% markup will yield a direct deposition rate of 464 kg-N/(km²-yr).

The TRIAD study was conducted in 1995-1996. The yearly wet N deposition is 616 kg-N/(km²-yr). Considering the study site (Seabrook station) is located on the edge of the Bay, the actual wet deposition at the Bay should be slightly less than 616 kg-N/(km²-yr). This is because the concentrations of nitrogen species at the Bay are usually lower than those on land. Given the decline of NOx emissions in recent years, the wet N deposition should be even lower. A rough guess is a 10% reduction due to location and another 10% reduction due to reduced NOx emission. The current wet deposition would be 493 kg-N/(km²-yr).
Combining the two estimates from the two sources by averaging, we arrive at 479 kg-N/(km²-yr) for direct wet N deposition.

Total direct N deposition is the sum of wet and dry deposition, calculated to be 632 kg-N/(km²-yr). The estimate from Meyers et al (2001) is 587 kg-N/(km²-yr) for the 1990s. If projected to 2006, Meyers’ number would be 528 kg-N/(km²-yr) assuming a 10% reduction rate. The bulk of the difference between the two estimates is due to dry deposition. The dry deposition rate by Meyers et al is only 90 kg-N/(km²-yr), or 23% of the deposition on the watershed. In our study, the direct/watershed deposition ratio is 0.44. We think our direct/watershed deposition ratio is closer to the actual value since Meyers et al computed the direct dry deposition by assuming the concentration at the Bay and watershed are close.

2.11.2 Indirect Nitrogen Deposition from Watershed

The indirect nitrogen deposition can be computed from the total deposition on the watershed and the watershed-to-bay export ratio. The watershed-to-bay export ratio is different for the gaged and ungaged flows. For gaged flow, the ratio is lower due to the extra retention in the streams.

In section 2.8.1, we calculated the average dry deposition on land cells in the modeling domain as 655 kg-N/(km²-yr). Though we have not specifically calculated the dry deposition on the watershed, we assume the deposition rate is the same on the watershed. Assuming the same positive model bias of 70% and 10% reduction in trend, we concluded that the current dry deposition at the watershed is 347 kg-N/(km²-yr). Compared to the projected 2006 estimate from Meyers’ study, 354 kg-N/(km²-yr), our result is extraordinarily close. For wet deposition, we use the observation at TX10 as the base and slightly adjust upwards since TX10 has lower N concentration than the watershed. Assuming a 10% markup, the wet N deposition at the watershed is 422*1.1 or 464 kg-N/(km²-yr). The total N deposition at the watershed is 347+464 or 811 kg-N/(km²-yr).

The next step is to estimate the watershed-to-bay export ratio. As shown by Alexander et al (2001), the land to water N yields can vary greatly depending on the LULC type. Therefore, the uncertainty in watershed-to-bay export ratio is high. The overall N yield by Alexander et al is given to be 23% (section 2.3). However, based on Eddleman (2000), the cropland N yield is 0.6%. Therefore, the indirect AD-N estimate by Alexander (2001) appears to be too high. The true N yield may be close to half of 23%. With an in-stream N loss rate of 61%, the watershed-to-bay export ratio for gaged flow is 4.5%. For ungaged flow, the ratio is 11.5%. Since the majority of the land in the watershed drains into the streams, the overall watershed-to-bay export ratio should be around 6-7%.

Using the total N deposition at the watershed and the export ratio, the indirect AD-N from the watershed is 811*6.5%, or 53 kg-N/(km²-yr). The number is slightly lower than the estimate by Alexander et al, which is 62 kg-N/(km²-yr).

2.11.3 Total Nitrogen Input from Atmospheric Sources
Combining the direct and indirect AD-N, the current annual nitrogen input to Galveston Bay from atmospheric sources is:

\[ 632 \text{ kg-N/km}^2 \times 1554 \text{ km}^2 \text{ (direct)} + 53 \times \text{ kg-N/ km}^2 \times 63158 \text{ km}^2 \text{ (indirect)} \]

or 4330 ton.

Because the estimate of total nitrogen input to the Bay has not been updated in recent years, we will not attempt to calculate the current percentage of the AD-N contribution to the Bay. However, a rough estimate can be obtained by using the 1990s total N data. Assuming the total N input remains to be 38350 tons (Brock 2001), the percentage contribution from AD-N is 11.3%. The contribution from direct and indirect AD-N is 2.6% and 8.7% respectively.

2.12 Nitrogen Source Attribution

One important issue with nitrogen deposition is to determine the percentage contribution of emission sources in each category. The process is commonly known as source attribution. Source attribution studies are critical to emission strategies because they can determine how pollutant concentrations would respond to abatement measures which reduce emission rates for one or more source categories.

Since a strict AD-N source attribution can grow into a full-fledged study, here we chose to perform a basic source attribution on the atmospheric nitrogen concentration above Galveston Bay. We performed a source attribution study for an 8-day period in summer. Since the AD-N is also affected by the deposition velocities and they differ by species, the AD-N source attribution is not the same as the N-concentration source attribution but they should resemble each other.

High Order Decoupled Direct Method in 3D (HDDM-3D) analysis (Hakami et al. 2004) is typically used in source attribution studies. In this study, we applied HDDM-3D to the N concentration at an area slightly larger than the Galveston Bay (Figure 2.31). Therefore, the source attribution analysis is more relevant to the direct dry deposition at Galveston Bay than to the deposition at the watershed. The spatial variation of AD-N in Southeast Texas is quite large as seen in the spatial AD-N plots (Section 2.8).

The N-concentration is calculated by adding the N in all the gas phase nitrogen species (Table 2.4). Because there are a lot of uncertainties in aerosol emissions, the HDDM-3D is performed on the gas phase N only. For dry AD-N, the omission of aerosol contribution is not a big issue as seen in Section 2.4 and 2.8. HDDM-3D is a computation-intensive procedure during which the sensitivities of chemical species concentration to individual emission categories can be studied. A full-year HDDM-3D simulation may take over a month to be completed on the fastest IMAQS computer ISUN, which is beyond the scope of this study. For demonstration purposes, we chose an 8-day period in TexAQS-II for our source attribution analysis.
The gas phase N-concentration HDDM-3D results are shown in Figure 2.32. The detailed information about the emission categories can be found online at TCEQ’s website. Figure 2.32 shows that the N-concentration fluctuated during the 8-day period but the contribution of each category remains largely the same. Area and point emission sources are the top two categories, contributing over 80% N in the atmosphere most of the time, especially during the day. N transported from outside the domain boundary (“Boundary” in the plot) is the leading N source on one of the days (08/18) where overall N-concentration is low. Because the target area is mostly Galveston Bay, the source attribution results would be quite different if the target area were the HGB eight-county area where mobile sources would make a significant contribution. Due to the overall south/southeast winds in the period, the air above the bay is cleaner than in the eight-county area.

Figure 2.31 Area for nitrogen source attribution study: 08/17/2006 to 08/24/2006

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2 http://www.tceq.state.tx.us/implementation/air/areasource/Sources_of_Air_Pollution.html
Atmospheric sulfur in the form of sulfur dioxide (SO₂) and sulfate (SO₄) is the leading cause of acid rain. Since the Industrial Revolution, emissions of sulfur dioxide into the atmosphere have dramatically increased primarily due to fossil fuel burning, especially coal burning. Acid rain can cause serious long-term adverse ecological effects such as the decline of fish population, leaching of toxic metals from soil into surface water, slower growth/injury, or death of forests.

The atmospheric chemistry of sulfur is much less complicated than nitrogen chemistry. Sulfur is emitted into the atmosphere mostly in the form of sulfur dioxide, which can be oxidized into sulfur trioxide (SO₃). In the presence of water sulfur trioxide (SO₃) is converted rapidly to sulfuric acid (H₂SO₄). In aerosols, sulfur exists largely in the form of sulfate.

Galveston Bay is moderately alkaline due to the high buffering capacity of seawater, so acid rain or acid deposition is not much an issue; however, understanding the role of sulfur deposition is important to the study of the pH balance in the Bay.

There are 4 sulfur species in the CMAQ dry deposition modules. SO₂ and SO₄ are the gas phase species while ASO₄I and ASO₄J are the aerosol species.

The model data were processed using the same procedures described in Section 2.8. The total 2006 sulfur dry deposition in the 4-km domain is shown in Figure 3.1. Houston, Beaumont/Port Arthur, and Lake Charles are the three high sulfur deposition zones, which is not
surprising considering the many petro-chemical and power plants located there. Unlike AD-N where the values are low at water surfaces, AD-S at Galveston Bay and in the vicinity of the Gulf are quite high – higher than many land areas except for the three hot zones. This is probably because the deposition behavior of sulfur species is different from nitrogen species. Sulfur species such as SO₂ tend to have a higher deposition velocity than NH₄ and HNO₃. The higher deposition velocity will cause the sulfur species to deposit closer to the emission sources. The spatial variation is also higher than in the AD-N case.

The dry AD-S at observation site ALC188 and model results are displayed in Table 3.1. Similar to Section 2.9, the model results are obtained using “Exact Match” and “3x3 Average”. Obviously at ALC188, there is little difference in the two methods. It is obvious that SO₂ is the primary deposition species, contributing around 70% of total observed deposition. In the model, the contribution from SO₂ is higher – close to 95%.

Overall, the model overpredicted the AD-S by about 55% primarily due to the SO₂ overprediction. The relative weight of the SO₂ in the model is much higher than in the observation, indicating possible partitioning problems in the model. Model predicted SO₂ deposition is twice that of observations and the causes are likely similar to those in HNO₃ overprediction as listed in Section 2.9.

![Total S Dry Deposition (kg/sqkm) - 2006](image)

Figure 2.33 Annual total dry AD-S spatial distribution for the 4-km domain (D04) (sum of 4 species)
Table 2.11 Model vs. observation at ALC188 – unit is kg-S/(km²-yr)

<table>
<thead>
<tr>
<th>Method</th>
<th>Model-Total</th>
<th>Obs-Total</th>
<th>Model-SO₂</th>
<th>Obs-SO₂</th>
<th>Model-SO₄</th>
<th>Obs-SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Match</td>
<td>241</td>
<td>155</td>
<td>228.3</td>
<td>108</td>
<td>12.7</td>
<td>47</td>
</tr>
<tr>
<td>3x3 Average</td>
<td>239.9</td>
<td>155</td>
<td>229.2</td>
<td>108</td>
<td>12.7</td>
<td>47</td>
</tr>
</tbody>
</table>

* Model SO₄ is the sum of gas-phase and aerosol SO₄
3. Discussions and Conclusions

3.1 Atmospheric Nitrogen and Sulfur Deposition Trend

Atmospheric nitrogen and sulfur deposition rates are closely linked to the concentrations of nitrogen and sulfur species in the atmosphere, which in turn are heavily impacted by the anthropogenic emissions released into the atmosphere. In the past 30 years, the emissions of nitrogen oxides (NOx) and sulfur dioxide (SO2) in the United States have been declining despite strong economic and population growth. The SO2 emissions have decreased over 38% during the 1990-2006 period (Figure 3.2). The reduction of NOx emission is less dramatic, about 29% (Figure 3.1). The decrease of SO2 emissions has been steady over the years while the decrease in NOx emissions has mostly occurred since 1995.

Figure 3.1 Total US anthropogenic NOx emissions: 1990 to 2006 (EPA 2007)

Sickles and Shadwick (2007) gave a detailed study on the atmospheric nitrogen and sulfur deposition trend during 1990-2004 in the United States using the observations from CASTNET. They divided the 15-year period into 3 parts, 1990 – 1994 (P1), 1995 – 1999 (P2), and 2000 – 2004 (P3). In the South (containing Texas), the P1 to P3 reduction in total AD-N is about 6% while the total AD-S reduction is 25%. Therefore, we expect comparative nitrogen and sulfur deposition reduction rates between GBE and the South.

As stated in Section 2.5, the modeling study in Meyers et al (2001) used the NEI 1990 for emissions, so the AD-N estimates from the study are valid for the early 1990s. On the other hand, the emission inventory used in this study is the TEI base 2000 – making the AD-N estimates
effective for year 2000. Therefore, it is necessary to have a comparison of the emissions in 1990 and in 2000.

The detailed U.S. NOx and SO2 emission information during 1980-2000 can be found at EPA website: National Emissions Inventory (NEI) Air Pollutant Emissions Trends Data. The total U.S. NOx emissions are 25.5 million short tons in 1990 and 22.6 million short tons in 2000. Corresponding SO2 emissions are 23.3 and 16.3 million short tons respectively.

For Texas, the area and mobile NOx 1990-2010 emission trend is shown in Figure 3.3 (Environ 2001). The trend after 2000 is projected. During the 1990-2000 period, the area and mobile NOx emissions declined only slightly from 1.5 million ton to 1.37 million ton. For the HGB eight-county region we have not been able to locate the 1990-2000 total NOx emissions. However, the mobile NOx emissions for HGB between 2000 and 2007 are provided by Dr. Soon-Tae Kim of IMAQS. Figure 3.4 shows the mobile NOx emissions for different days in a week. 2000 and 2007 values are actual while 2005 values are interpolated. Figure 3.3 and 3.4 are surprisingly consistent though the region and emission types are not the same. Overall, they suggest that the area and mobile NOx emission is down by 40% during the 2000-2007 period. The sharp decline is the result of a combination of state regulations and programs geared toward vehicle emission reduction.

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3 http://www.epa.gov/ttn/chief/trends/
4 http://www.epa.gov/ttn/chief/trends/trends06/nationaltier1upto2006basedon2002finalv2.1.xls
Figure 3.3 Texas area and mobile NOx emissions (2001 and after are projected)

Figure 3.4 Mobile NOx emissions rates from HGB 8 counties for different days of the week. 2005 emissions rates were interpolated from 2000 and 2007 emissions inventories.
In summary, although the emission inventories used in Meyer’s study and this study are different, the actual NOx emissions in the two inventories (1990 and 2000) are close. Therefore, there should be no material change in AD-N between 1990 and 2000 from the emission side. The similar AD-N estimates from the two studies echo the point. However, there is a substantial decrease in mobile and area NOx emissions in HGB between 2000 and 2007. Since mobile and area sources make up about 65% of NOx emissions in the HGB region (per Dr. Soontae Kim of IMAQS), we should expect a decline in AD-N during the 2000-2007 period. More studies using the latest TCEQ emission inventory should give a better picture of current AD-N. For sulfur deposition, the situation is similar due to the decline of SO2 emission during the 2000-2007 period.

3.2 Conclusions and Discussions

In this study, we investigated the atmospheric nitrogen and sulfur dry deposition at Galveston Bay and its watershed using the daily forecast from our MM5-SMOKE-CMAQ modeling system. Spatial, seasonal and speciated nitrogen deposition results are presented for both the Bay and the watershed. The average dry nitrogen deposition rate for the land cells in our modeling domain is 655 kg-N/(km²-yr). The exact deposition rate at the watershed was not calculated but it should be slightly higher than the average land cells.

High deposition areas are identified from the spatial plots. Due to the prevailing south-southeasterly wind for the region, the high deposition areas are located slightly downwind of the major emission sources. The deposition on land is usually higher than that at the water surface due to the difference of dry deposition velocities. The deposition at the watershed is the highest in the summer and the lowest in the winter. However, the seasonal pattern of the direct deposition at the Bay is totally different, with the highest deposition in winter-spring and the lowest in the summer. The seasonal deposition pattern in the region is consistent with the seasonal wind pattern.

Although the modeled year is 2006, an emission inventory targeting 2000 was used since it was the latest at the time that model was run. Because the NOx emissions in the 2000 inventory are higher than the emissions in 2006, model results are likely to carry a positive bias. While the model substantially overpredicted at one observation site, the overall AD-N fluxes are consistent with past model studies. Current AD-N at the watershed is likely to be in the range of 40% to 80% of model prediction. It should be pointed out that there are substantial uncertainties in the model’s AD-N estimates. The uncertainties are due to the deficiencies of the model itself and the inaccurate input data, which reflect the highly complex nature of the process.

Despite the fact that wet nitrogen deposition is not derived from model output, the observation data are gathered as a way to evaluate model results. According to literature, the wet deposition typically constitutes 50% to 60% of total deposition. The direct dry deposition rate predicted by the model is found to agree well with the study by Sweet et al (1999) based on the wet/total deposition ratio.
Besides the direct comparison of model AD-N with observations, we also evaluated model predicted NO and NO\textsubscript{2} concentration using observed CAMS data. The correlation between modeled and observed concentration is 0.41 and 0.49 for NO and NO\textsubscript{2} respectively. We also studied the relationship between HNO\textsubscript{3}, the dominant deposition specie, and NO / NO\textsubscript{2}. The daily average HNO\textsubscript{3} concentration is positively correlated to the NO or NO\textsubscript{2} concentration.

Overall, the nitrogen dry deposition at GBE has not been well studied in the past. The only observation site in the region is neither at the Bay nor at the watershed. The study by Meyers et al (2001) provided only estimates for the Bay and the watershed. No seasonal or spatial patterns are presented. This study significantly expanded our knowledge on the nitrogen deposition at GBE with detailed spatio-temporal and speciated information. In addition, a 1-km resolution GIS database with 30 variables was created for the management and planning of the Bay.

For sulfur deposition, only the yearly results are calculated. Since the dominant sulfur species generally have a higher deposition rate than the dominant nitrogen species, high sulfur deposition zones are located closer to the major emission sources. Unlike nitrogen deposition, the sulfur deposition attenuated much faster downwind from the emission sources – resulting lower deposition rate for places away from the sources. Again the model overpredicted at the same observation site and part of the overshoot can be attributed to the higher SO\textsubscript{2} emission in the model.
3.3 Future Work

This work is by no means an exhaustive study on the atmospheric deposition issue at Galveston Bay Estuary. A number of limitations are present due to the scope of the study.

The most obvious one is the year 2000 emission inventory used in the model. To reflect current conditions of atmospheric deposition, a projected emission inventory based on the emission trend or an inventory incorporating the newer emission data (e.g., 2006 Texas Point Source Inventory or TPSI) may be used. The IMAQS’s F2 forecast system has been using a 2005 emission inventory projected from 2000. Therefore, it is possible to have an updated deposition estimate by using the output from the IMAQS F2 system.

The significant positive model AD-N bias at the observation site ALC188 has not been fully investigated in this study. We suspect the local model meteorology may not be well simulated. A comparison of seasonal model and observed meteorology at the region (Port Arthur – Beaumont – Kountze – Livingston) should shed more light on the seasonal deposition errors.

This work focuses primarily on the dry deposition side where the modeling efforts and observation data are relatively scarce. However, it is also quite informative to have the wet deposition estimate from the model. Since the modeled precipitation and moisture typically are not very reliable, it is not a good approach to derive the wet deposition solely from model output. Instead, the observed precipitation data from the ground network should be used along with modeled concentration data.

Besides Galveston Bay, there are a number of other bays scattering along the Texas Gulf coast. The same methodology in this work can be applied to the other bays to study the impact of atmospheric deposition. It should be noted that additional model simulations may be necessary since the modeling domains of F1 and F2 are not enough to cover the whole Texas Gulf coast.
4. References


U.S. Environmental Protection Agency, 2000: Deposition of Air Pollutants to the Great Waters, Third Report to Congress. EPA-453/R-00-005, June.


Appendix A1
Windrose Plots at C34 (Galveston Airport): Based on Hourly Data 1998-2006
Appendix A2
IMAQS F1 Model Dry Deposition Output Files

IMAQS F1 model has been performing daily air quality forecasts since 2005. Each day’s forecast run is completed in early morning and analysis plots/tables are generated and published around 7 AM.

Each day’s forecast output, plots, etc. are backed up in several sets of archives – one master archive and a few subsets containing frequently accessed variables. The dry deposition output files for 2006 were extracted from two sets of archives. The file contents are the same but the naming conventions are different. One set of archives uses UTC date-time while the other one uses Julian dates.

There are 3 dry deposition output files (ncdf format) in each day's forecast. Each day's forecast lasts 54 hours. The first file has output for hour 00 to 23. The second and the third file has output for hour 24-47 and 48-53.

Total file size is about 15 GB. All the project files have been uploaded to an IMAQS server machine “server-aqm”, under directory “sdg/TCEQ-Gbay”.

There are 14 days of data missing where IDE hard drives storing the archives are not readable. The missing dates are: 20060402, 20060403, 20060404, 20060405, 20060406, 20060407, 20060408, 20061026, 20061027, 20061028, 20061029, 20061030, 20061031, and 20061101. To patch up the missing dates, date 20060401 is used for 20060402 to 20060404; 20060409 is used for 20060405 to 20060408; 20061025 is used for 20061026 to 20061028; 20061102 is used for 20061029 to 20061101.

It should be noted that the “patching” above is unlikely to alter the findings in this report. This is because we are only interested in monthly, seasonal and yearly deposition. Also, the replacement dates should have fairly similar deposition to those of missing dates.

The "Julian" files are located at:

/F1_DryDep_2006_D04/Data/Julian

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11/30/2007  02:03 PM         5,071,904 F1.20060801.d04.CCTM.DRYDEP.cb4-ae3.2006080401-2006080406.L01

3 File(s)     45,525,264 bytes

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Appendix A3
Dry Deposition ncdf File Header

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dimensions:
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    DATE-TIME = 2 ;
    LAY = 1 ;
    VAR = 39 ;
    ROW = 65 ;
    COL = 83 ;

variables:
    int TFLAG(TSTEP, VAR, DATE-TIME) ;
        TFLAG:units = "<YYYYDDD,HHMMSS>" ;
        TFLAG:long_name = "TFLAG" ;
        TFLAG:var_desc = "Timestep-valid flags: (1) YYYYDDD or (2) HHMMSS" ;
    float NO2(TSTEP, LAY, ROW, COL) ;
        NO2:long_name = "NO2" ;
        NO2:units = "kg/hectare" ;
        NO2:var_desc = "hourly dry deposition values" ;
    float NO(TSTEP, LAY, ROW, COL) ;
        NO:long_name = "NO" ;
        NO:units = "kg/hectare" ;
        NO:var_desc = "hourly dry deposition values" ;
    float O3(TSTEP, LAY, ROW, COL) ;
        O3:long_name = "O3" ;
        O3:units = "kg/hectare" ;
        O3:var_desc = "hourly dry deposition values" ;
    float NO3(TSTEP, LAY, ROW, COL) ;
        NO3:long_name = "NO3" ;
        NO3:units = "kg/hectare" ;
        NO3:var_desc = "hourly dry deposition values" ;
    float N2O5(TSTEP, LAY, ROW, COL) ;
        N2O5:long_name = "N2O5" ;
        N2O5:units = "kg/hectare" ;
        N2O5:var_desc = "hourly dry deposition values" ;
    float HNO3(TSTEP, LAY, ROW, COL) ;
        HNO3:long_name = "HNO3" ;
        HNO3:units = "kg/hectare" ;
        HNO3:var_desc = "hourly dry deposition values" ;
    float HONO(TSTEP, LAY, ROW, COL) ;
        HONO:long_name = "HONO" ;
        HONO:units = "kg/hectare" ;
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    float H2O2(TSTEP, LAY, ROW, COL) ;
        H2O2:long_name = "H2O2" ;
        H2O2:units = "kg/hectare" ;
        H2O2:var_desc = "hourly dry deposition values" ;
    float CO(TSTEP, LAY, ROW, COL) ;
        CO:long_name = "CO" ;
        CO:units = "kg/hectare" ;
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    float FORM(TSTEP, LAY, ROW, COL) ;
        FORM:long_name = "FORM" ;

}
FORM:units = "kg/hectare";
FORM:var_desc = "hourly dry deposition values";

float ALD2(TSTEP, LAY, ROW, COL);
ALD2:long_name = "ALD2";
ALD2:units = "kg/hectare";
ALD2:var_desc = "hourly dry deposition values";

float PAN(TSTEP, LAY, ROW, COL);
PAN:long_name = "PAN";
PAN:units = "kg/hectare";
PAN:var_desc = "hourly dry deposition values";

float PACD(TSTEP, LAY, ROW, COL);
PACD:long_name = "PACD";
PACD:units = "kg/hectare";
PACD:var_desc = "hourly dry deposition values";

float NTR(TSTEP, LAY, ROW, COL);
NTR:long_name = "NTR";
NTR:units = "kg/hectare";
NTR:var_desc = "hourly dry deposition values";

float FACD(TSTEP, LAY, ROW, COL);
FACD:long_name = "FACD";
FACD:units = "kg/hectare";
FACD:var_desc = "hourly dry deposition values";

float AACD(TSTEP, LAY, ROW, COL);
AACD:long_name = "AACD";
AACD:units = "kg/hectare";
AACD:var_desc = "hourly dry deposition values";

float SO2(TSTEP, LAY, ROW, COL);
SO2:long_name = "SO2";
SO2:units = "kg/hectare";
SO2:var_desc = "hourly dry deposition values";

float SULF(TSTEP, LAY, ROW, COL);
SULF:long_name = "SULF";
SULF:units = "kg/hectare";
SULF:var_desc = "hourly dry deposition values";

float UMHP(TSTEP, LAY, ROW, COL);
UMHP:long_name = "UMHP";
UMHP:units = "kg/hectare";
UMHP:var_desc = "hourly dry deposition values";

float ASO4J(TSTEP, LAY, ROW, COL);
ASO4J:long_name = "ASO4J";
ASO4J:units = "kg/hectare";
ASO4J:var_desc = "hourly dry deposition values";

float ASO4I(TSTEP, LAY, ROW, COL);
ASO4I:long_name = "ASO4I";
ASO4I:units = "kg/hectare";
ASO4I:var_desc = "hourly dry deposition values";

float ANH4J(TSTEP, LAY, ROW, COL);
ANH4J:long_name = "ANH4J";
ANH4J:units = "kg/hectare";
ANH4J:var_desc = "hourly dry deposition values";

float ANH4I(TSTEP, LAY, ROW, COL);
ANH4I:long_name = "ANH4I";
ANH4I:units = "kg/hectare";
ANH4I:var_desc = "hourly dry deposition values";

float ANO3J(TSTEP, LAY, ROW, COL);
ANO3J:long_name = "ANO3J " ;
ANO3J:units = "kg/hectare  " ;
ANO3J:var_desc = "hourly dry deposition values ";

float ANO3I(TSTEP, LAY, ROW, COL) ;
ANO3I:long_name = "ANO3I " ;
ANO3I:units = "kg/hectare  " ;
ANO3I:var_desc = "hourly dry deposition values ";

float AORGAJ(TSTEP, LAY, ROW, COL) ;
AORGAJ:long_name = "AORGAJ " ;
AORGAJ:units = "kg/hectare  " ;
AORGAJ:var_desc = "hourly dry deposition values ";

float AORGAI(TSTEP, LAY, ROW, COL) ;
AORGAI:long_name = "AORGAI " ;
AORGAI:units = "kg/hectare  " ;
AORGAI:var_desc = "hourly dry deposition values ";

float AORGBJ(TSTEP, LAY, ROW, COL) ;
AORGBJ:long_name = "AORGBJ " ;
AORGBJ:units = "kg/hectare  " ;
AORGBJ:var_desc = "hourly dry deposition values ";

float AECJ(TSTEP, LAY, ROW, COL) ;
AECJ:long_name = "AECJ " ;
AECJ:units = "kg/hectare  " ;
AECJ:var_desc = "hourly dry deposition values ";

float ASEAS(TSTEP, LAY, ROW, COL) ;
ASEAS:long_name = "ASEAS " ;
ASEAS:units = "kg/hectare  " ;
ASEAS:var_desc = "hourly dry deposition values ";
float ASOIL(TSTEP, LAY, ROW, COL);
    ASOIL.long_name = "ASOIL"
    ASOIL:units = "kg/hectare"
    ASOIL:var_desc = "hourly dry deposition values"

float NH3(TSTEP, LAY, ROW, COL);
    NH3.long_name = "NH3"
    NH3:units = "kg/hectare"
    NH3:var_desc = "hourly dry deposition values"

// global attributes:
:IOAPI_VERSION = "2.2 2003141 (May 21, 2003)"
:EXEC_ID = ""
:FTYPE = 1
:CDATE = 2006246
:CTIME = 40155
:WDATE = 2006246
:WTIME = 40155
:SDATE = 2006246
:STIME = 10000
:TSTEP = 10000
:NTHIK = 1
:NCOLS = 83
:NROWS = 65
:NVARS = 39
:GDTYP = 2
:P_ALP = 30.
:P_BET = 60.
:P_GAM = -100.
:XCENT = -100.
:YCENT = 40.
:XORIG = 356000.
:YORIG = -1228000.
:XCELL = 4000.
:YCELL = 4000.
:VGTOP = 5000.f
:VGLVLS = 1.f, 0.996f
:GDNAM = "TCEQ_04_01"
:UPNAM = "OPDDEP"
:FILEDESC = "hourly 1-layer cross-point RADM dry deposition data"
:HISTORY = ""
Appendix A4

Compute Daily/Monthly/Seasonal/Yearly Dry Deposition - QA

To calculate the daily/monthly/seasonal/yearly dry deposition for each grid cell in the 4-km modeling domain D04, we first extract the hourly deposition from the dry deposition ncdf files. Then the hourly data are aggregated into daily, monthly, seasonal and yearly sums.

There are 13 nitrogen species in CMAQ contributing to the AD-N. As a demonstration, we use ammonia (NH3) to show the extraction and calculation process as well as the QA.

To extract data from the ncdf files, we coded IDL program "DryDep_Read_Vars_CST_Julian.pro" (for "Julian" type file extraction) and "DryDep_Read_Vars_CST_Date.pro" (for "UTC Date" type file extraction). Each IDL program is capable of extracting several variables at a time. The extracted outputs are text files containing hourly data blocks. Below is a sample screen shot of an extracted hourly data file (DRYD.NH3.CST.20060203.txt).

The first data value represents the dry deposition amount at the lower-left corner cell during the hour 20060203_00 CST, which is 0.3283 g/ha. The first row represents the south border of the D04 domain (shown partially).

- Hourly to Daily

The next step is to aggregate the hourly data into daily totals. The IDL program is “Calc_Daily_Sum.pro”. As an example, the output file for “DRYD.NH3.CST.20060203.txt” is “DRYD.NH3.CST.20060203.sum.txt”. To verify the process, we checked the grid cell (3,6), which is the 4th row, 7th column in “DRYD.NH3.CST.20060203.txt”. The first 24 hourly values are: 0.329341, 0.318744, 0.293517, 0.263497, 0.237690, 0.224105, 0.225050, 0.236673, 0.309621, 0.453264, 0.506697, 0.506289, 0.486167, 0.549578, 0.632022, 0.487377, 0.337049, 0.238542, 0.229609, 0.295565, 0.184976, 0.143428, 0.115282, 0.110644. Using a calculator, we have:

0.329341 + 0.318744 + 0.293517 + 0.263497 + 0.237690 + 0.224105 + 0.225050 + 0.236673 + 0.309621 + 0.453264 + 0.506697 + 0.506289 + 0.486167 + 0.549578 + 0.632022 + 0.487377 + 0.337049 + 0.238542 + 0.229609 + 0.295565 + 0.184976 + 0.143428 + 0.115282 + 0.110644 = 7.71473

Now let us check the 4th row, 7th column of output file “DRYD.NH3.CST.20060203.sum.txt”. It is 7.71473. This shows the calculation is correct in this step.

- Daily Species Deposition to N Deposition
The 3rd step is to compute the N portion in the species daily sum file. The IDL program is “calc_daily_sum_n_only_kg_sqkm.pro”. The total dry deposition of NH3 at grid cell (3,6) in 20060203 is 7.71473 g/ha as found in “DRYD.NH3.CST.20060203.sum.txt”. This step computes the nitrogen deposition from NH3, and changes the unit from g/ha to kg-N/sqkm. The output file is “DRYD.NH3.CST.20060203.N_Only.txt”.

To calculate the N portion of deposition, we need to find out the percentage of nitrogen in NH3. The molecular weight for NH3 is 17 and its percentage of N is 14/17. Additionally, the conversion from g/ha to kg-N/sqkm is: 1 g/hectare = 0.001 kg / 0.01 sqkm = 0.1 kg/sqkm

Therefore, the N deposition at grid cell (3,6) is:

\[ 7.71473 \times \frac{14}{17} \times 0.1 = 0.63533 \text{ (kg-N/sqkm)} \]

Now let us check the 4th row, 7th column of output file “DRYD.NH3.CST.20060203.N_Only.txt”. It is 0.63533. This shows the calculation is correct in this step.

• Daily to Monthly

The 4th step is to aggregate the daily data into monthly totals. The IDL program is “Calc_Monthly_Sum.pro”. As an example, we check the February file of NH3. The output file for February is “NH3.02.sum.txt”. To verify the process, we checked the grid cell (3,6) of all the days in February. The values are: 0.20713, 0.30603, 0.63533, 0.45776, 0.34311, 0.44312, 0.34613, 0.36509, 0.35314, 0.37304, 0.30439, 0.48494, 0.37179, 0.16065, 0.08608, 0.66428, 1.16000, 0.62470, 0.42637, 0.61530, 0.17961, 0.33812, 0.51461, 0.28215, 0.37132, 0.19459, 0.14611, 0.10980. Using a calculator, we have:

\[ 0.20713 + 0.30603 + 0.63533 + 0.45776 + 0.34311 + 0.44312 + 0.34613 + 0.36509 + 0.35314 + 0.37304 + 0.30439 + 0.48494 + 0.37179 + 0.16065 + 0.08608 + 0.66428 + 1.16000 + 0.62470 + 0.42637 + 0.61530 + 0.17961 + 0.33812 + 0.51461 + 0.28215 + 0.37132 + 0.19459 + 0.14611 + 0.10980 = 10.86469 \]

Now let us check the 4th row, 7th column of output file “NH3.02.sum.txt”. It is 10.86469. This shows the calculation is correct in this step.

• Monthly to Seasonal

The 4th step is to aggregate the monthly data into seasonal total. The IDL program is “Calc_Season_Sum.pro”. As an example, we check the winter file of NH3. The input files are “NH3.12.sum.txt”, “NH3.01.sum.txt”, and “NH3.02.sum.txt”. The output file for winter is “NH3. DJF.sum.txt”. To verify the process, we checked the grid cell (3,6) for December, January and February. The values are: 13.29221, 12.73909, 10.86469. Using a calculator, we have:

\[ 13.29221 + 12.73909 + 10.86469 = 36.89599 \]

Now let us check the 4th row, 7th column of output file “NH3. DJF.sum.txt”. It is 36.89599. This shows the calculation is correct in this step.

• Monthly to Yearly

The 5th step is to aggregate the monthly data into yearly total. The IDL program is “Calc_Year_Sum.pro”. As an example, we check the whole year deposition of NH3. The input files are “NH3.01.sum.txt”, “NH3.02.sum.txt” etc. The 12 monthly deposition values at grid cell (3,6) are: 12.73909, 10.86469, 6.40152, 11.97986, 17.26128, 12.48790, 13.24189, 15.29456, 18.89746, 12.44759, 11.92086, 13.29221. Using a calculator, we have:

Now let us check the 4th row, 7th column of output file “NH3. year.sum.txt”. It is 156.8289. This shows the calculation is correct in this step.