Final Report
Coastal Bend Bays and Estuaries Program (CBBEP): Atmospheric Deposition Study

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Submitted to:
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2.0 Project Summary

There is a common thread that ties together diverse coastal problems including red tides, fish kills, some marine mammal deaths, outbreaks of shellfish poisoning, loss of sea grass habitats, coral reef destruction and “Dead Zones” like those described in the Gulf of Mexico (National Academy of Sciences, 2000). Nutrients are pollutants that are involved in these deleterious effects. Over the past 30 years researchers, coastal managers and public decision makers have recognized that coastal ecosystems suffer a number of environmental problems that can be attributed not only to local contaminant inputs but inputs from regional watersheds and air sheds. Atmospheric deposition of nutrients was recognized as a potentially important but inadequately studied input of nutrients. In order to provide better estimates of nutrient inputs as well as other contaminants to the Texas Coastal Bend Bay areas, studies were initiated first by the Corpus Christi Bay National Estuary Program (CCBNEP), Phase I, of this project, and continued by the Coastal Bend Bays and Estuaries Program (CBBEP), Phase II of this project.

Phase I of this project consisted of air, rain, and dry fallout sampling from two sampling sites on Corpus Christi Bay, one located on the campus of Texas A&M University, Corpus Christi (TAMUCC) and the second at Whites Point. Concentrations of organic contaminants including polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and organochlorine pesticides were determined in the atmosphere, from wet and dry deposition. Wet and dry deposition was determined using the methodology established by the NADP and were analyzed for conductance, calcium, magnesium, potassium, sodium, ammonium, nitrate, total phosphate, chloride, sulfate, copper, zinc, lead, cadmium, titanium, vanadium, chromium, nickel, arsenic, selenium and manganese. Phase II of this project followed the acceptance of the TAMUCC site as an official National Atmospheric Deposition Program (NADP) site selected to be representative of the Texas Coastal Bend Bays. The research results from this study (Phase II) and previous studies (Phase I) are critical to the understanding of the relative importance of atmospheric inputs to the Texas Coastal Bend Bays area. This study is an extension of the Phase I studies (Park et al., 2001A, 2001B, 2002; Wade et al., 2002). For Phase II wet only rain samples have been collected every week on Tuesday for five years (from January 2, 2002 through December 26, 2006). While information has been generated by other investigations regarding Coastal Bend Bays, such as EPA Environmental Monitoring and Assessment Program, National Oceanic Atmospheric Administration National Status and Trends Program, CBBEP projects and others, little reliable data is available to assess the impact of atmospheric deposition. The analytical results of Phase I and II of this project are comparable to those of other atmospheric deposition programs including EPA Great Waters, EPA National Estuaries Programs and National Atmospheric Deposition Program (NADP). The results of this study allow for an integrated assessment of the relationships between air and water pollution for Coastal Bend Bays to facilitate informed management decisions. These studies provide the data to estimate the direct deposition of nutrient nitrogen to the Coastal Bend Bays as well as to its drainage basin.

The detailed results of these studies are provided in this report and previous reports (Wade et al., 2002) and publications (Park et al., 2002). The results indicate that atmospheric deposition is an important source of nutrient nitrogen, trace element and organic contaminants to the Coastal Bend Bays. The yearly average pH of the rain from 2002 through 2006 ranged from 5.09 to 5.21

(average of 5.14) which is slightly acidic but comparable to pre-industrial revolution natural pH (5.0). Some of the major ions detected in the wet and dry deposition (Cl, Na, Mg) are from sea salts as anticipated for a site located on the coast. The majority of sulfate in rain and dry deposition is of anthropogenic origin. Potassium and calcium can have marine and anthropogenic sources. Forty-six percent (46%) of the nutrient nitrogen entering the Bays is from atmospheric deposition to the Bay and its watershed. While contaminant inputs have significant seasonal variability, the long term inputs are consistent over longer temporal intervals (e.g., years). Trace elements Zn, Pb, As, Cu and Cd have anthropogenic sources. Organic contaminants including polycyclic aromatic hydrocarbons (PAH), pesticides and PCB are deposited and removed from the Coastal Bend Bays by atmospheric deposition and gas exchange. These data provide a robust estimate of atmospheric deposition that can be applied to the Coastal Bend Bays ecosystem. Further research is required to determine how the timing of nutrient inputs to the Coastal Bend Bays system from atmospheric deposition affects phytoplankton species and abundance and their role in harmful alga blooms, hypoxia and sea grass abundance.

3.0 Purpose and Scope

The Coastal Bend Bays and Estuaries Program is a community-based effort to identify the problems facing the bays and estuaries of the Coastal Bend, and to develop a long-range, comprehensive conservation and management plan. The purpose of these studies is to determine the importance of atmospheric deposition of contaminants, especially nutrients to Coastal Bend Bays and Estuaries. Phase I of this project consisted of air, rain, and dry fallout sampling from two sampling sites on Corpus Christi Bay, one located on the campus of Texas A&M University, Corpus Christi (TAMUCC) and the second at Whites Point. Concentrations of organic contaminants including polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and organochlorine pesticides were determined in the atmosphere, from wet and dry deposition. Wet and dry deposition was determined using the methodology established by the NADP and were analyzed for conductance, calcium, magnesium, potassium, sodium, ammonium, nitrate, total phosphate, chloride, sulfate, copper, zinc, lead, cadmium, titanium, vanadium, chromium, nickel, arsenic, selenium and manganese. Phase II of this project followed the acceptance of the TAMUCC site as an official National Atmospheric Deposition Program (NADP) site selected to be representative of the Texas Coastal Bend Bays. The research results from this study (Phase II) and previous studies (Phase I) are critical to the understanding of the relative importance of atmospheric inputs to the Texas Coastal Bend Bays area. For Phase II wet only rain samples have been collected every week on Tuesday for five years (from January 2, 2002 through December 26, 2006). this data to provide estimates of the total loading of nutrients directly to Corpus Christi Bay as well as atmospheric deposition contribution to the drainage basin for the Bay.

The Coastal Bend bay system is one of 28 estuaries designated as an estuary of national significance under a program established by the United States Congress through the Water Quality Act of 1987. This bay system was so designated in 1992 because of its benefits to the state and the nation. Corpus Christi Bay is the gateway to the nation's sixth largest port, and home to the third largest refinery and petrochemical complex. The Port generates over $1 billion of revenue for related businesses, more than $60 million in state and local taxes, and more than 31,000 jobs for Coastal Bend residents. The bays and estuaries are famous for their recreational and commercial fisheries production. A study by Texas Agricultural Experiment Station in 1987 found that these industries, along with other recreational activities, contributed nearly $760 million to the local economy, with a statewide impact of $1.3 billion, that year. Of the approximately 100 estuaries around the nation, the Coastal Bend ranks fourth in agricultural acreage. Row crops (including cotton, sorghum, and corn) and livestock generated $480 million in 1994 with a statewide economic impact of $1.6 billion. There are over 2600 documented species of plants and animals in the Coastal Bend, including several species classified as endangered or threatened. Over 400 bird species live in or pass through the region every year, making the Coastal Bend one of the premier bird watching spots in the world. The CBBEP is gathering new and historical data to understand environmental status and trends in the bay ecosystem, determine sources of pollution, causes of habitat declines and risks to human health, and to identify specific management actions to be implemented over the course of several years. The 'priority problems' under investigation include:

1. Alteration of freshwater inflow into bays and estuaries.
2. Loss of wetlands and estuarine habitats.
3. Declines in living resources.
4. Degradation of water quality.
5. Alteration of estuarine circulation.
6. Bay debris.
7. Selected public health issues.

CBBEP characterization studies are or will be examining the contribution of point source discharges and agricultural and urban non-point sources to the nutrient and contaminant loading rates of these bays and estuaries. One potential contributor that has not been addressed is atmospheric deposition. This could become a problem for the CBBEP when discussion turns to the development and prioritization of management actions. It is critical to know the relative contribution of the different pollution inputs so that the appropriate level of attention is given to each source.

4.0 Study Area Description

The CBBEP study area includes three of the seven major estuary systems along the Texas Gulf Coast. These estuaries, the Aransas, Corpus Christi, and Upper Laguna Madre are shallow and biologically productive. Although connected, the estuaries are biogeographically distinct and increase in salinity from north to south. The Laguna Madre is unusual in being only one of three hyper-saline lagoon systems in the world. The study area is bounded on its eastern edge by a series of barrier islands, including the worlds longest, Padre Island. Recognizing that successful management of coastal waters requires an ecosystems approach and careful consideration of all sources of pollutants, the CBBEP study area includes the 12 counties of the Coastal Bend: Refugio, Aransas, Nueces, San Patricio, Kleberg, Kenedy, Bee, Live Oak, McMullen, Duval, Jim Wells, and Brooks. The city of Corpus Christi (population approx. 301,454) is located on the southern shore of Corpus Christi Bay within Nueces County.

This region is part of the Gulf Coast and South Texas Plain, which are characterized by gently sloping plains. Land use is largely devoted to range land (61%); with cropland and pastureland (27%) Urban (2%) and other mixed uses (10%). The region is semi-arid with a subtropical climate. Average annual rainfall varies from 63.5 to 96.5 cm (25 to 38 inches) and rainfall is highly variable from year to year. Winds in the region are predominantly from the southeast (March-September) and north (November-February). Summers are hot and humid, while winters are generally mild interspersed with “northers” that can cause occasional freezes. Hurricanes and tropical storms periodically affect the region. The Coastal Bend Bays includes 75 miles of coastline with a combine water surface area of 515 square miles.

4.1 Air Quality and Atmospheric Deposition in the CBBEP Study Area

In the Corpus Christi area, air quality problems have occurred in the past including ozone alerts and petrochemical plant emissions (the third largest petrochemical complex in the U.S. is located on the shores of the Nueces estuary) that have led to citizen complaints, legal action and inferences of environmental justice infringements. Although neither issue has directly affected the local bays, these incidents suggest that deposition of locally-generated air pollutants from motor vehicles and industry onto the local bays could be occurring. Ground level ozone has shown a marked improvement over the past decade based on the number of days with eight hour average ozone concentration greater than 85 ppb. The ozone level have not exceeded this benchmark for the past three years (2005 through 2007) and has shown a steady decrease from 5 days in 1999 to only 1 day in 2004. Considering that the study area population is projected to double in the next 40-50 years, internal combustion engine-related air pollutants and their effects on bay waters could become an area of concern. In addition to locally generated air pollutants, those from distant sources, Mexico or possibly from the heavily industrialized Houston/Beaumont area to the northeast could contain a variety of pollutants, which could be deposited in the local bays.

Atmospheric deposition might be directly related to one bay problem. In 1995, Nueces Bay was closed to oyster harvesting due to excessively high levels of zinc. Although there are several potential local sources of the zinc, it would be prudent to consider atmospheric deposition as a contributing source. The CBBEP is especially interested in characterizing loading rates of nutrient nitrogen into the bays from all sources, point and non-point. The Program funded projects that estimated nutrient (and other pollutants) loading rates from urban and non-urban lands. These characterization studies on non-point source pollution used data from the nearest National Atmospheric Deposition Program (NADP) monitoring site (Beeville, 50 miles from the coast) in a sub-watershed loadings model (Baird and Jennings, 1996). Based on this data, the model results indicate direct rainfall deposition contributes a significant portion of nutrient loadings to Oso Bay. The authors noted that the CBBEP study area needed atmospheric deposition data from a site nearer the coast that would include a more comprehensive list of parameters including the collection of dry deposition in addition to wet deposition data.

The Tampa Bay NEP and other such programs (most notably the Chesapeake Bay Program) have identified atmospheric deposition as a significant contributor of nitrogen and toxic substances to bays. A comparison of NADP data from the Tampa Bay area with the CBBEP study area (Beeville station) shows that nitrogen-loading values are similar. Nitrate-nitrogen loading rates (wet deposition only) in the Coastal Bend Bays area are nearly as high as Tampa (1.36 vs. 1.45 kg-N/ha-Yr). A comparison with data from the Florida Acid Deposition Study (Zephyrhills site) shows that levels of nitrate and ammonium between the two areas are comparable (nitrate 1.36

vs. 2.07 kg/ha-yr; ammonium 1.65 vs.1.67 kg/ha-yr). Compared to an area that has identified atmospheric deposition as a significant source of nitrogen, the CBBEP study area has comparable levels of atmospheric nitrogen loading.

4.2 Monitoring Efforts

The TCEQ Air Monitoring Program is a multi-faceted monitoring program currently focusing largely on ozone, NOx, SO_2, CO, particulates and volatile organic compounds (VOCs). This program is generally oriented towards monitoring air quality, not atmospheric deposition, so the parameters and how they are monitored differ significantly. Furthermore, most of the stations are located in the western half of Corpus Christi so with prevailing winds from the southeast and the north these stations are not situated to optimally sample air that passes over bay water. The agency did operate a continuous atmospheric monitoring station at Odem (northwest of Corpus Christi) from 1981-84 that monitored ozone; total suspended particulates (TSP) and selected pesticides. Also the agency collected TSP and heavy metal air quality data from 1978-1983 for three sites in the Coastal Bend area. The National Atmospheric Deposition Program has maintained a wet-fall only monitoring station at Beeville, Texas since 1984. Weekly samples are collected and analyzed for calcium, magnesium, potassium, sodium, ammonium, nitrate, chloride, sulfate, pH and conductance. Being located 50 miles from the coast, it was unknown if that station would provide data that would accurately characterize atmospheric deposition into the CBBEP bays. There are nine other NADP stations in Texas with none located along the coast. The closest coastal NADP monitoring station is at the Iberia Research Station in Louisiana. An air deposition monitoring station from Phase I of this study collected and analyzed wet and dry deposition of nutrients, trace elements, pesticides, polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH). This data has been reported (Wade et al., 2002) and is only summarized in this report. The present study (Phase II) concentrates on providing temporal data on nutrient from wet only deposition. Data from both Phase I and Phase II of atmospheric monitoring to Texas Coastal Bend Bays will be discussed in this report.

4.3 Study

Several long-term goals of the CBBEP are:

1. To determine the kinds of contaminants entering or present in the CBBEP estuaries.
2 To determine the respective contributions of point and non-point source pollution to the total loading rates of nutrients and contaminants to the CBBEP estuaries.
3. To characterize the temporal and spatial distributions of these sources.
4. To determine the fate of nutrients and contaminants in the CBBEP estuaries.
5. To identify the specific sources of nutrients and contaminants and their relative contributions to loading rates.

Current or planned projects focus on characterizing non-point source pollution based on historical data, agricultural land runoff, point source pollution and modeling of point and non-point sources. None of these projects deals, except peripherally, with non-point source pollution from atmospheric deposition.

The studies reported here are the first attempts to characterize atmospheric deposition in the vicinity of the local bays, with the focus on Nueces and Corpus Christi Bays. The objective of Phase I was to determine the weekly atmospheric loading rates of selected parameters in wet and dry deposition to the CBBEP estuary for at least one year at two monitoring stations. During the second year samples of wet deposition and air samples were collected and analyzed for additional parameters (PCBs, pesticides, PAH and selected trace elements) in order to characterize atmospheric deposition of these contaminants in the vicinity of the local bays, with the focus on Nueces and Corpus Christi Bays. Phase II was initiated to provide five years of additional wet deposition data for nutrient nitrogen and major ions present in rain.

4.4 Monitoring Station Description

Two monitoring stations were established for Phase I on the edges of the Nueces estuary (Figure 1). One station was located on the north shore of Nueces Bay at Whites Point (Figure 2). Figure 3 shows the other site, located on the campus of Texas A&M University-Corpus Christi (TAMU-CC). The Whites Point station is down-wind of Corpus Christi and “refinery row” during periods of southeast wind flow and receives deposition from land areas during periods of north winds. The TAMU-CC station is up-wind of most of the urbanized areas during periods of southeast wind flow and is down-wind of the petrochemical plants and Naval Station Ingleside located on the north shore of Corpus Christi Bay during periods of northerly winds. These station locations allowed for the assessment of the loading rates of monitored parameters due to atmospheric deposition on Corpus Christi and Nueces Bays. At times when a station is upwind of the major pollutant sources (north wind for Nueces Bay station and southeast wind for the university station), deposition at the up-wind site would reflect inputs from more distant sources and might be used as a correction for background deposition levels for the down-wind station. The location of these sites met as many of the criteria established by the EPA Great Waters Program for atmospheric deposition sampling sites as possible. For Phase II the TAMU-CC site was established as an official NADP sampling station TX 39 and operated from January 2, 2002 until December 26, 2006.

4.5 Instrumentation

Phase I each monitoring station consisted of two wet/dry deposition collectors as well as a rain gauge, wind speed and direction instrumentation, temperature sensor, relative humidity sensor, solar radiation sensor, rain gauge, and a data logger. Two AeroChemetric samplers were used, one for nutrients and one with a Teflon sampling train for trace metals. The dry deposition sample container consists of a pre-cleaned bucket filled with distilled water to mimic deposition directly to the bay surface. The Massachusetts Bay Program (Goulomb et al., 1996) has previously used this collecting technique. An AeroChemetric sampler was used during Phase II of the study but only wet deposition was collected. The samples from Phase I and II were sent to the Illinois State Water Survey (ISWS) for analyses. This is the laboratory where all the sample analyses for the U.S. national NADP are performed. This insures that all of the data produced from the CBBEP site are comparable to all NADP sites nationwide.

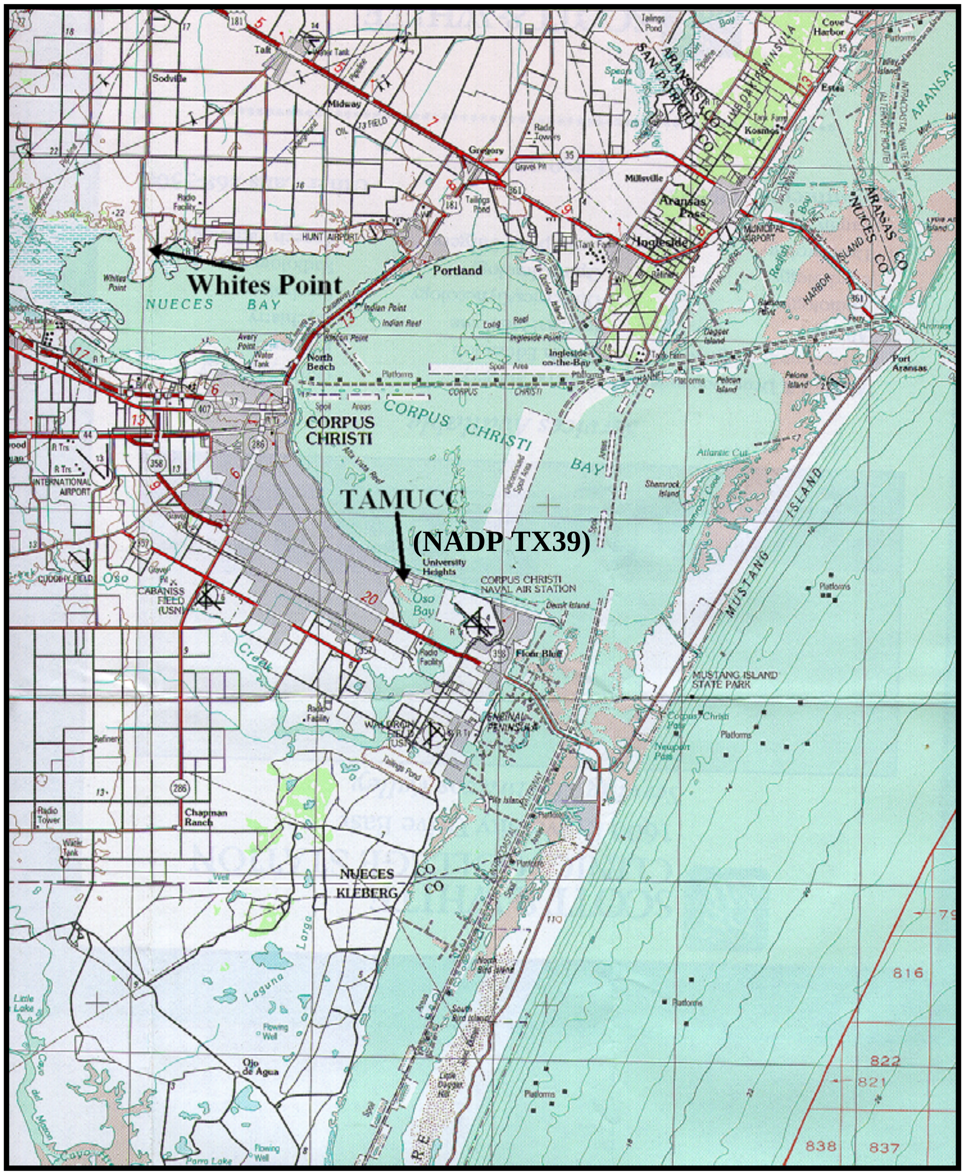

Figure 1. Location of Atmospheric Deposition Sampling Stations.

4.6 Sample Collection and Analysis

During Phase I each station was visited weekly; samples collected and station maintenance performed. In the field wet deposition samples, dry deposition samples, and meteorological data from weather instruments were retrieved. The samples were collected using the methodology established by the NADP and are analyzed for conductance, pH, calcium, magnesium, potassium, sodium, ammonium, nitrate, total phosphate, chloride, sulfate, aluminum, copper, zinc, lead, cadmium, titanium, vanadium, chromium, nickel, arsenic, selenium and manganese.

Figure 2. Whites Point Atmospheric Deposition Sampling Station, Note the Two AeroChemetric Samplers, the Belfort Rain Gauge, and the Meteorological Sensors Located in a Fenced Enclosure across from the Refineries in the Background.

For Phase II the station was visited weekly; samples collected and station maintenance performed. In the field wet deposition sample (if any) and meteorological data from weather instruments were retrieved. The samples were collected using the methodology established by the NADP and are analyzed for conductance, pH, calcium, magnesium, potassium, sodium, ammonium, nitrate, total phosphate, chloride and sulfate. This data provides information on year to year variability of nutrient wet-only deposition.

Figure 3. Texas A&M Corpus Christi Atmospheric Deposition Sampling Station, Note the Two AeroChemetric Samplers, the Belfort Rain Gauge, and the Meteorological Sensors Located in a Fenced Enclosure with Oso Bay in the Background.

4.7 Data Management, Quality Assurance and Analysis

To assure the collection of quality data, a Quality Assurance Project Plan based on EPA document QA/R-5 was prepared and followed during the course of these studies. Much of the methodology for collection and analysis of wet deposition samples was based on guidance from the NADP and EPA's Great Waters program. Data analyses included calculation of deposition rates (kilograms per hectare) for wet and dry deposition. Project data is compared with data from the Beeville NADP site. Data from Phase II is available on the NADP web site (http://nadp.sws.uiuc.edu).

5.0 Methods

5.1 Meteorological

Meteorological parameters measured include: temperature; relative humidity; wind speed; wind direction; solar radiation; total rainfall. Meteorological instruments were factory calibrated before receipt. Meteorological parameters are recorded directly from the corresponding meteorological instrument. Meteorological data were stored on storage modules that were downloaded on-site. The parameters measured included: date, time, year, temperature, relative humidity, light, battery voltage, grid voltage (indicating rain events), wind speed, and wind direction. The CBBEP site used a Campbell Scientific CR-10 data logger with SM-192 storage modules for data storage between site visits. Meteorological sensors included a Vaisala temperature and relatively humidity probe (HMP35C), a Met One wind speed (014A) and direction (024A) sensors, a LICOR (Li200X) pyranometer, and a Belfort (5915) rain gauge. The grid sensor normally outputted a voltage of zero unless the sensor was wetted in which case the voltage was approximately one volt. The data was logged every fifteen (15) minutes unless a rain event was occurring, then the data was logged every three (3) minutes until the rain ceased. A summary of the meteorological results have been reported.

5.2 Sampling

For Phase I sampling took place from April 22, 1997 to August 31, 1999 at TAMUCC and from June 3, 1997 to August 31, 1999 at Whites Point. Samples were collected once a week. Meteorological data, including temperature, relative humidity, wind speed, wind direction, and total rainfall, were obtained during each sampling event. For Phase II wet only rain samples were collected every week on Tuesday from January 2, 2002 until December 26, 2006. Each precipitation sample was comprised of the all individual rain events during the sampling period.

For the analysis of PAHs, PCBs, and selected pesticides, samples of ambient air were collected with an organic air sampler. The organic air sampler employed two filters followed by a large and small polyurethane foam (PUF) plugs. Particulate and vapor Phases were collected separately by glass fiber filter and PUF, respectively. Filters and PUFs were all cleaned before use. Rain samples for organic analyses were collected with a MIC sampler, a wet-only collector which is closed during dry periods or a large (1 m^2 surface area) stainless steel funnel for bulk samples (wet plus dry deposition). Rainwater was filtered through a glass fiber filter by gravity flow. The rainwater then passed through a XAD-2 resin cartridge. The filtered rainwater was collected in a reservoir. The total volume of collected rain was measured. Contaminants of interest are retained by the filter and/or resin. Blank filters, PUFs and XADs were collected from the field site periodically. Filters, PUFs and XADs were carried to the field, installed in the sampler, removed immediately, and returned to the laboratory for analysis. Laboratory blanks were clean, unused filters and PUFs. After sampling, the samples for organic analyses were sealed in pre-cleaned glass jars. Samples were returned with the field blanks to the laboratory for analyses.

Precipitation for major ions and trace metals analysis was collected using a commercial wet-dry sampler (Model 301, AeroChemetrics, Miami, FL). This sampler uses two large polyethylene buckets (29 cm ID) and features a moisture-activated lid with a Teflon sealing pad that covers the "wet" bucket during dry periods and covers the "dry" bucket when it is raining. A second sampler that is a modified version of the standard AeroChemetric sampler was used to collect precipitation samples for trace metals. This sampler has been described elsewhere (Vermette et al., 1995). In the modified sampler, the "wet" bucket is replaced by an all-Teflon sampling train consisting of a large Teflon-coated inlet funnel (28 cm ID) that is connected via a Teflon tube to a 2-liter, Teflon collection bottle. The area below the sampler is enclosed and ventilated with filtered air to protect the sample bottle from exposure to dust.

Each week the Illinois State Water Survey laboratory shipped 3 polyethylene buckets and one Teflon-coated funnel to the field sites. For analysis of major ions, the buckets were hand rinsed to remove adhering debris before being cleaned by power-rinsing with de-ionized water in an automatic washer. Teflon sample bottles were cleaned by soaking and rinsing with de-ionized water (Barnstead, E-Pure system). The cleaned buckets and bottles were placed in polyethylene bags for storage and shipment to the field. The procedure for cleaning the sample bottles, buckets, and funnels to be used to collect the trace metals samples included a nitric acid soak followed by a de-ionized water soak and exhaustive rinsing with de-ionized water. Details of this cleanup method are available elsewhere (USEPA, 1997a).

During the weekly visits to the field sites, the operator replaced the wet and dry buckets on the standard AeroChemetric sampler. Enough de-ionized water was then added to the dry-side bucket to maintain a layer of water in the bottom of the bucket throughout the one week sampling period. During the cool season (November – March), 2 liters were added. During the warmer months (April-October), 4 liters were required. The de-ionized water for these additions was sent from the laboratory in the weekly shipment of supplies. Any sample collected in the wet-side bucket and the remaining water in the dry side bucket were transferred to clean 2-liter Teflon bottles for return to the laboratory. If there were more than 2 liters of water in the bucket, the excess was measured using a graduated cylinder and recorded on the data sheet. The procedure for changing the dry-side bucket on the trace metals sampler is the same as for the standard AeroChemetric sampler. The sample on the wet side of this sampler is already in the 2-liter bottle and can simply be capped and returned to the laboratory. An overflow basin was provided so that if more than 2 liters of precipitation is collected (equivalent to about 3 cm); the excess was caught and measured.

Samples were shipped for 2nd day delivery. Upon receipt at the laboratory, sample volumes were determined by weight and aliquots were removed to determine pH and conductivity. The presence of any debris (insects, plant parts, dirt) was recorded on the data sheet. Samples to be analyzed for major ions were then filtered through a 0.45 μm filter and stored at 4°C until analysis. Samples for trace metals analysis were not filtered but were acidified with utlra-pure nitric acid (Fisher, Optima grade) to a final concentration of 0.2%. The acidified sample was left in the 2-liter sample bottle at least 24 hours to solubilize metals adhering to the bottle walls. The acidified dry-side sample was also equilibrated for 24 hours in the dry side sample bucket. This bucket was bagged in the field and returned to the laboratory with the samples. After equilibration, wet and dry side samples were transferred to small Teflon storage bottles and stored at room temperature prior to analysis.

Field blanks for major ions were prepared by adding 500 mL of de-ionized water to wet-side buckets that had been set out in the field during dry weeks. In these cases, the bucket was covered by the lid and sealing pad for the entire sampling period. Similarly, the trace metal sampling funnels from dry weeks were rinsed with de-ionized water to prepare a trace metal field blanks. Subsequent laboratory handling of the field blanks was the same as for samples. Finally, during part of the project the dry side bucket of the trace metals samplers were used for major ion sampling. Buckets cleaned for major ions (de-ionized water wash, no acid) were installed in the trace metals sampler, but no de-ionized water was added. These buckets were exposed to dry deposition side-by-side the normal major ion sampler buckets, which contained a layer of de-ionized water.

5.3 Organic Analyses

The XAD, sodium sulfate-dried filter samples, and PUF plugs were Soxhlet extracted. The XAD was extracted with 400 mL acetone:hexane (1:1) for 24 h. The filter samples were extracted with methylene chloride (CH_2Cl_2) for 24 h. The PUF air samples were extracted with pentane for 24 h (GERG, 1989a). Before extraction, internal standards were added. To facilitate the gas chromatographic analysis and remove interferences, extracts were cleaned-up by silica gel/ alumina column chromatography. The columns consisted of 5 g anhydrous sodium sulfate, 20 g silica gel, 10 g alumina, 5 g sand, and glass wool. The sample was added to the column containing pentane in 1 mL of hexane, and eluted with 200 mL of a mixture of pentane:dichloromethane (1:1). The eluted pentane:dichloromethane was concentrated and exchanged to 1 mL hexane (GERG, 1989a) which was separated into two 500 mL aliquots. For the analysis of the pesticides/PCBs, one 500 mL aliquot was evaporated to 100 mL using nitrogen before analyses. Analysis for PAHs and pesticides/PCBs were conducted using a gas chromatograph with capillary columns, equipped with either a mass selective detector (MSD) or an electron capture detector (ECD). Individual PAH, pesticides, and PCB congeners were identified by their retention times relative to standard solutions. The organic contaminants results have been published (Park et al., 2002).

5.4 Major Ions

The analytical methods used for major ions were the identical to those that are currently used by the National Atmospheric Deposition Program’s (NADP) Central Analytical Lab for samples from the Nation Trends Network (NTN). Full details are available from NADP in Standard Operating Procedures (Illinois State Water Survey, 1993).

5.4.1 Ion Chromatography (chloride, nitrate, sulfate)

Ion chromatography combines conductivity detection with the separation capabilities of ion exchange resins. A filtered 200 µl aliquot of sample is pumped through an ion exchange column where Cl^-, NO_3^-, and SO_4^{-2} are separated. Because different ions have different migration rates, the sample ions elute from the column as discrete bands. Each ion is identified by its retention time within the exchange column. The sample ions are selectively eluted off the separator column and into an anion self-regenerating suppressor. The eluent ions are neutralized and the sample ions are converted to their corresponding strong acid, which are detected in a conductance cell. The ion chromatographs are calibrated with standard solutions containing known concentrations of anions. The raw peak area data are collected by the computer from produced chromatograms and an anion method file is used to calculate the concentration of anions for each sample using the raw data.

Samples were run on a Dionex (Model DX-500) ion chromatograph. The ion exchange train consists of a guard column (Dionex AG4A), a Separator column (Dionex AS4A), and an anion suppressor (Dionex SRS). Detection was by conductivity detector (Dionex CD-20/Cell-DS-3). The eluent was sodium bicarbonate (1.75 mM) and sodium carbonate 1.80 mM. The flow rate was 2.0 mL/min. The detector sensitivity was 30 µS/cm.

5.4.2 Ammonium and Phosphate

These ions are determined using an automatic flow-injection colorimeter (Model 8000, Lachat Instruments, Milwaukee, Wisconsin). The method for ammonium ion is based on the Berthelot reaction. Sodium EDTA is added as a complexing reagent to reduce formation of hydroxide precipitates. Ammonia in the samples reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitro-ferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonium concentration. This method is appropriate for analysis of NH_4^+ in the range of 0.02-2.00 mg/L NH_4^+. A method detection limit has been determined to be 0.02 mg/L as NH_4^+. All samples to be analyzed for NH_4^+ are filtered as soon after receipt as possible to maintain sample integrity. High levels of both Ca and Mg ions will form a precipitate during analysis and interfere with proper detection of NH_4^+. Sample color and turbidity absorbing at 630 nm can also cause a false positive reading.

The orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate under acid conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex, which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample. This method is appropriate for analysis of PO_4^{3-} in the range of 0.003-0.50 mg/L PO_4^{3-}. A method detection limit has been determined to be 0.003 mg/L as PO_4^{3-}. All samples to be analyzed for PO_4^{3-} are filtered as soon after receipt as possible to maintain sample integrity. Silica forms a pale blue complex that also absorbs at 880 nm but has no significant affect until the concentration reaches 30 mg/L. Concentration levels >50 mg/L of ferric ion can also cause a negative error in the readings.

5.4.3 Atomic Absorption (sodium, potassium, magnesium, calcium)

Samples were run on an atomic absorption spectrophotometer (Model Spectra AA-800, Varian Associates, Sunnyvale, California) with hollow cathode lamps specific for each element (Varian Catalog numbers: NA-5610126200; K-5610127300; Mg-5610125100; Ca-5610122900). A solution containing the element(s) of interest is aspirated as a fine mist into a flame where it is converted to an atomic vapor consisting of ground state atoms. These ground state atoms are capable of absorbing electromagnetic radiation over a series of very narrow, sharply defined wavelengths. A distinct line source of light, usually a hollow cathode lamp specific to the metal of interest, is used to pass a beam through the flame. Light from the source beam, less whatever intensity was absorbed by the atoms of the metal of interest, is isolated by the monochromator and measured by the photo-detector. The amount of light absorbed by the analyte is quantified by comparing the light transmitted through the flame to light transmitted by a reference beam. The amount of light absorbed in the flame is proportional to the concentration of the metal in solution. This method is appropriate for the analysis of ions in precipitation in the range of 0.009-2.000 mg/L for Ca, 0.003-0.600 mg/L for Mg , 0.003-1.000 mg/L for Na, and 0.003-1.000 mg/L for K.

The method detection limit (MDL) has been determined to be 0.009 mg/L for Ca and 0.003 mg/L for each of Mg, Na, and K. All samples to be analyzed for these cations are filtered as soon after receipt as possible to maintain sample integrity. High levels of other chemicals (especially PO_4, SO_4, and Al) can enhance or suppress proper atomization of the metals being analyzed. Addition of matrix modifiers such as a suppressing reagent (La_2O_3) or an ionization reagent (CsCl) to the sample alleviates or greatly reduces interference problems. If a sample containing a low concentration of the metal being measured is analyzed immediately after a sample having a high concentration (above highest calibration standard), sample carry-over will possibly result in elevated readings. A de-ionized water wash is incorporated into the method so that the sample line and probe are rinsed between each sample and (or) standard. This step eliminates any sample carryover.

5.5 Trace Element Analysis

The analytical procedures for trace elements in precipitation are described in detail elsewhere (USEPA, 1997c). The analyses were carried out by the Hazardous Materials Laboratory of the Illinois Department of Natural Resources in Champaign, Illinois. Briefly, analysis is by inductively-coupled argon plasma mass spectrometry (ICP-MS) using a Perkin-Elmer Elan-Sciex 5000^{TM} instrument. The sample is completely atomized in the plasma providing measurements of total metal concentrations. Sample vials and transfer lines are cleaned by soaking in 20% ultrapure nitric acid and rinsing with de-ionized water and ASTM Type I water. Calibration is with certified elemental standard solutions. Lithium, yttrium, and thallium are used as internal standards. Detection limits for the elements reported are all at or below 0.1 μg/L except for Ni (0.2 μg/L) and Se (1.0 μg/L). Field blank values for Mn, Cu, Zn, and Pb are generally near these detection limits and well below average sample values. For V, Cr, Ni, As, Se, and Cd, most sample values are close to or below the detection limits.

6.0 Results and Discussion

The results of Phase I analyses provide an estimation of wet and dry deposition of atmospheric contaminants. The determination of dry deposition is not straightforward and no single adequate method exists to measure dry deposition directly or to calculate dry deposition based on theoretical assumptions. In spite of these limitations dry deposition, based on estimates from this study, represents an important process that should not be ignored. Results from Phase I are used to estimate dry deposition for Phase II. For the TX 39 site from 2002 thru 2006, the NADP used the data from 111 of 139 precipitation events. The data for the additional dates (28) were not used for various reasons based on the NADP program criteria. There was some type of visible contamination in 16 of these 28 samples which included insects, plastic, plant material, bird fecal material, etc. For eight of the samples there was a malfunction of the AeroChemetric sampler noted that caused the sample to be exposed for a period of time greater than 6 hours when it was not raining. Two of these eight also contained some type of visible contamination. The remaining four samples were considered bulk samples due to the AeroChemetric sampling lid remaining open during the entire sampling period. Two of the bulk samples also contained some visible contamination. Of the 20 samples where contamination was noted, nine contained detectable concentrations of phosphates which are known to be associated with bird fecal materials. There were five other samples that contained detectable concentrations of phosphates that were not considered contaminated based on the NADP program criteria. In summary, NADP did not include data from these 28 events from 2002 to 2006 sampling. AeroChemetric sampler malfunction was responsible for 12 of those data sets and 16 were associated with the notation of some form of visible contamination. The NADP has a rationale for the censoring of the data for their national program. However for our purpose it seems reasonable to determine if inclusion of these data in our evaluation would provide a more complete record. When the sampler malfunctions and bulk samples (wet plus dry deposition) are collected, the data will be biased high. While it is not our purpose to collect plastic, plant materials, insects and/or bird fecal materials, these materials are deposited to the Costal Bend Bays. We determined the inclusion of these sample results censored by the NADP did not seem to cause any significant changes to the estimated deposition.

6.1 Precipitation

During Phase I the amount of precipitation in cm was recorded at both sampling sites. The sampling was divided into three years 1997 (starting April 22 at TAMUCC and June 3 at Whites Point), 1998 (full year), and 1999 (through August 30). Thus only the yearly precipitation for 1998 was measured and that for 1997 and 1999 only estimated. The cumulative precipitation for 1998 was below the 30 year average until the late fall when substantial rainfall brought the cumulative rainfall at both sites (94 cm TAMU-CC and 102 cm Whites Point) above the average. Precipitation for 1999 was slightly less than the average until Hurricane Bret with 19.4 cm of rain at TAMUCC and 20.0 cm at Whites Point brought the yearly totals above the 30 year cumulative average. Total precipitation in 1998 was similar at TAMUCC, Whites Point, and the NADP Beeville site (Table 1). It is apparent from the rainfall records (Table 1), that there are

Table 1. Comparison of Precipitation Totals (in cm) at Beeville NADP Site (TX03), TAMUCC, NADP/CBBEP site (TX39), and Whites Point CBBEP Sites.

Year	NADP (Beeville)	TAMUCC	Whites Point
1998	92	86	102
2002	82.4	92.8	
2003	70.6	83.2	
2004	114.9	113.7	
2005	67.8	56.7	
2006	62.8	87.8	

large temporal and spatial variability in rainfall to Coastal Bend Bays. For example in 1998 the total precipitation at TAMUCC site was 16 cm less than the total at Whites Point, but only 6 cm less than the total at Beeville. A plot of the cumulative rainfall for Phase II sampling is provided in Figure 4. The variability is readily apparent with periods of low, high, and average rainfall accumulations. For example in 2006 there was very little rainfall for the first part of the year but then four rainfall events brought the cumulative rainfall to levels similar to other years. The cumulative amount of rainfall has a linear increase over the five year sampling period with a correlation coefficient (R^2 of 0.9829) indicating our ability to predict total rainfall over long periods of time at specific locations. It should be noted however that the seasonal distribution of the rain events varies considerably from year to year.

6.2 Nutrients

Nitrogen compounds can have both beneficial (e.g., soil fertility, plant nutrient) and harmful effects (ozone destruction, greenhouse effect, air pollution, acid rain, acidification and eutrophication of surface waters, and contamination of ground water). EPA took these deleterious effects into account and issued a mandate to evaluate and regulate nitrogen compounds under the Clean Air Act, the Clean Water Act, the Drinking Water Act, etc. Beside agricultural and sewage loadings of nitrogen via river and direct discharge, deposition of atmospheric nitrogen is a major fraction of anthropogenic nitrogen loadings to coastal ecosystems (Fisher et al., 1991; Hinga et al., 1991), which may cause harmful eutrophication (See collection of papers of eutrophication in the Baltic. In: Ambio, 1990). Since fossil fuel burning, automobile exhaust gas, etc., contribute significantly to atmospheric nitrogen (Duce et al., 1991), such human activities could potentially influence the productivity in the ocean (Owens et al., 1992). The concentrations of nitrate and ammonium depend on the amount of precipitation (Liken et al., 1987) and on the character of the air mass (Shon, 1994). Nitrate and ammonium appear to be derived primarily from gaseous constituents of the atmosphere (Gambell and Fisher, 1964). Different air masses reaching a sampling site appeared to cause temporal variations in inorganic and organic nitrogen concentrations in the precipitation

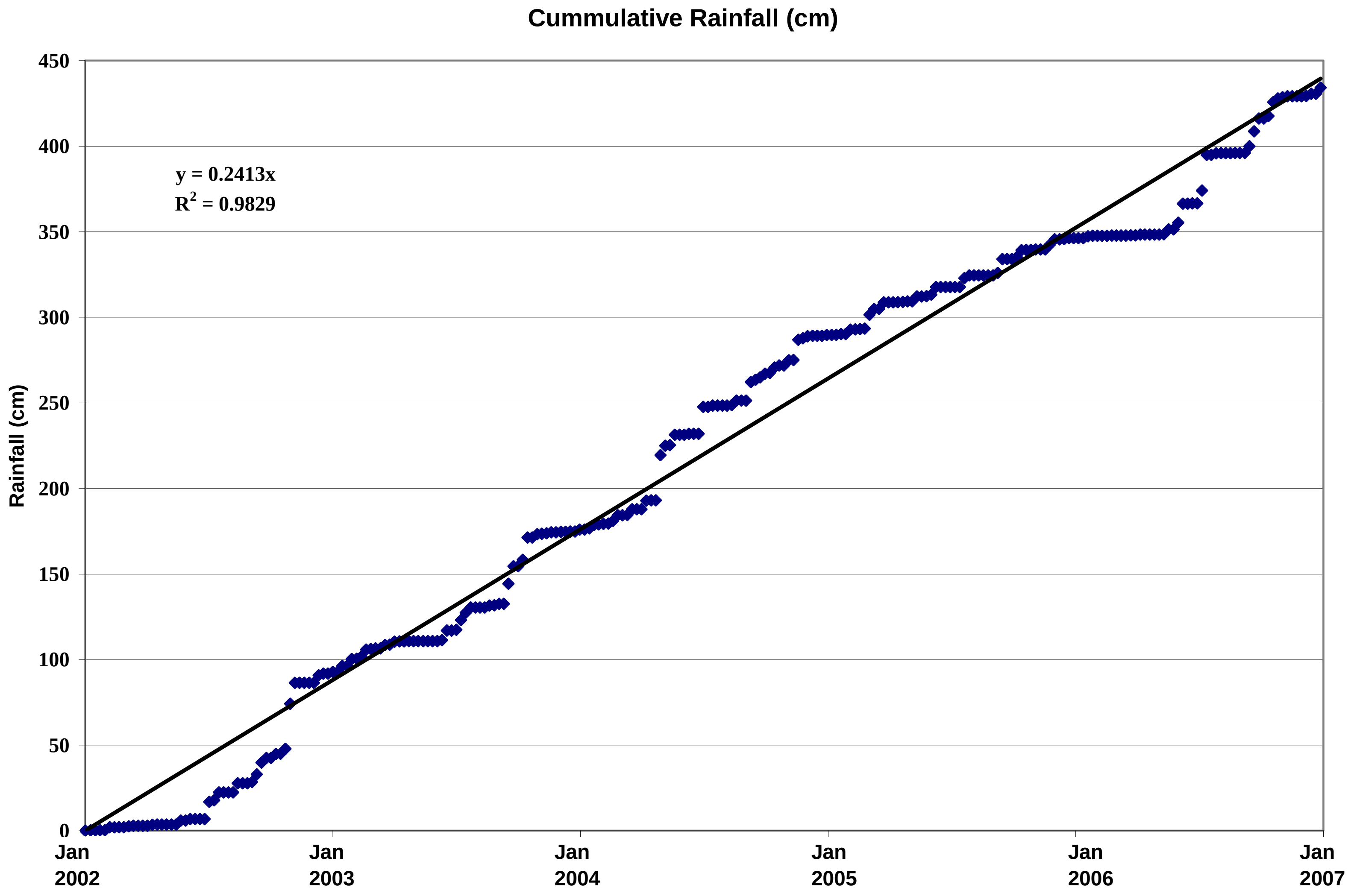

Figure 4. Cumulative Precipitation for Phase II at the Atmospheric Deposition Station, NADP TX39, Located in Corpus Christi TX.

(Loye-Pilot et al., 1990; Shon, 1994). The natural sources of nitrate in rain are lightning, causing the formation of nitric oxide, photochemical oxidation in the stratosphere of N_2O to NO and NO_2, chemical oxidation in the atmosphere of ammonia to NO_x, and soil production of NO by microbial processes. The anthropogenic sources of nitrate in rain are fossil fuel burning, mainly in automobile engines and power plants and biomass burning (Logan, 1981).

Another important nitrogen compound, ammonium, is found as gaseous NH_3 and NH_4+ in aerosol formed in the atmosphere, which can be used by plants as a nutrient. Ammonium results from the reaction of ammonia gas (NH_3) with water ($NH_3 + H_2O = NH_4$+ OH-). Thus the presence of gaseous ammonia in the atmosphere has been inferred by the measurement of the NH_4^+ ion in rainwater (Junge, 1963; McConnel, 1973). Shon (1994) summarizes that atmospheric ammonia is produced mainly by 1) decay of animal and human excrements, 2) bacterial decomposition of natural nitrogenous organic material in natural soils, 3) volatilization from nitrogen fertilizer, and 4) combustion of coal.

Urea is produced by plankton excretion and decomposition (Van Vleet and Williams, 1983; Carlson, 1983). Healy et al. (1974) suggested that the major source of ammonia appeared to be urea in animal urine in the U.K. Urea is likely to be directly volatilized from land and water surfaces into the atmosphere. High urea present in the total dissolved organic nitrogen (DON) concentrations has been reported in New Zealand, Japan (Timperley et al., 1985), and Texas (Shon, 1994).

However, it is often difficult to estimate the source of atmospheric nitrogen by evaluating the chemical composition of wet deposition, because of other removal mechanisms such as adsorption by plants (Hutchinson et al., 1972; Denmead et al., 1976) and oxidation by OH radical (McConnell, 1973). Thus, Lenhard and Gravenhorst (1980) conducted aircraft measurements over rural area in western Germany, in order to compare the result with theoretical estimations of ammonia emissions from the ground by natural and anthropogenic processes. They reported about half of the total ammonia emitted to the atmosphere is not rained out in the same area.

Dry deposition has been variously estimated to account for about one half to four times the wet deposition contribution for nitrogen (Sirois and Vet, 1985; Riggan et al., 1985; Vet et al., 1988, Anderson and Downing, 2006). Of the total dry deposition, 75% would be by adsorption of nitric acid to surfaces (Lovett and Lindberg, 1986). Although a common assumption is that dry deposition equals wet deposition (Fisher et al., 1991; Tyler, 1988; Schwarz, 1989), Galloway (1985) observed that wet deposition of DIN species (i.e., NO_3^- and NH_4^+) in continental areas was much greater than dry deposition of particulate and gas phase nitrogen (NO_3^-, HNO_3, NO_x, NH_3, and NH_4^+). The measurement of only inorganic forms of nitrogen (e.g., nitrate and ammonia) may sometimes underestimate the total nitrogen deposition. Dissolved organic nitrogen (DON) may be a large fraction of atmospheric nitrogen in wet deposition and contribute to the input of atmospheric nitrogen to the land and the oceans (Sidle, 1967; Timperley et al., 1985; Bottenheim and Gallant, 1987; Mopper and Zika, 1987; Pedulla, 1989; Gorzelska and Galloway, 1990). However, it is still difficult to assess the importance of atmospheric organic nitrogen, due to the lack of reliable data. Few studies have considered the nature, origin, or ecological significance of DON.

Atmospheric nutrient nitrogen may be important in some marine ecosystems (Paerl, 1985; Fanning, 1989; Loye-Piolt et al., 1990; Hinga et al., 1991; Owen et al., 1992) particularly where nitrogen is the limiting nutrient (Smith, 1984), even though there are some contrary reports (Knap et al., 1986; Michaels et al., 1993).

A study conducted on the Rhode River, sub-estuary of the Chesapeake Bay, found that deposition of all forms of atmospheric nitrogen (including ammonium) to the surface of the estuary contributed as much as 40 % of the total annual nitrogen loading (Corell and Ford, 1982). Patwardhan and Donigan (1995) estimated the contribution of atmospheric nitrogen deposition to Chesapeake Bay, Galveston Bay, and Tampa Bay, with respect to the nitrogen contribution from non-point and point sources. Their estimation was based on the method of Fisher et al. (1991) applied to Chesapeake Bay using estimates of 23% from point sources, 39% from atmospheric deposition (including both nitrate and ammonia), 34% from fertilizers, and 4% from animal wastes.

The nutrient nitrogen species measured were nitrate and ammonium in wet and dry deposition. The amount of nutrient nitrogen contributed by nitrate and ammonia in rain were nearly equal. For dry deposition (to clean water) ammonium deposition predominated. Dry deposition generally is responsible for more than half of the total deposition.

The cumulative wet deposition of ammonium, nitrate, and their sum (total) were estimated during Phase I. A summary of Phase I for wet deposition are provided in Table 2 along with a comparison to the closest NADP site (TX 03) in Beeville, Texas. Wet deposition (kg/ha-yr) was similar at all three sites except for Cl, Na, and Mg. For example in 1998 where there was a complete year of data for all sites, wet deposition of total nitrogen was 2.5, 3.2, and 3.1 kg N/ha-yr at the TAMUCC, Whites Point, and Beeville sites, respectively (Table 2). The reason that the Cl, Na and Mg are higher at the CCBNEP site is their proximity to the ocean. These ions are present in sea salts. This is documented by the ratio of Cl/Na of ~1.7 (Table 2) compared to seawater ration of 1.8. The Na and chloride have similar ratios at the Beeville site but are present at lower concentrations indicating a maritime source that has been diluted as the air moves inland.

A comparison of nutrient nitrogen data from the Corpus Christi area from Phase I, Phase II, a USGS study and NADP site TX 03 (Beeville, TX) are provided in Table 3. The USGS operated two atmospheric deposition sites from 1996 to 1998 (Ockerman and Livingston, 1999). Site 1 was located near Edroy, Texas in western San Patricio County. Site 2 was located east of Kingsville in northern Kleberg County. The annual total nitrogen deposition they reported (pounds/acre-yr) was converted to kg/ha-yr. They also report total nitrogen including organic nitrogen. They estimate that nitrate and ammonia account for 81% of the total nitrogen. Since NADP data only include nitrate and ammonium, the USGS data is reported on a similar bases (e.g. 2.06 pounds/acre-yr / 1.12 = 1.84 kg/ha x 0.81 = 1.49 kg/ha-yr of nitrate and ammonium).

Table 2. Wet Deposition (kg/ha-yr) Comparison of Beeville NADP Site and TAMUCC and Whites Point CBBEP Sites (1998*).

	NADP (Beeville)	TAMUCC	Whites Point
Ammonia	2.1	1.1	1.6
NO3-	1.1	1.4	1.5
Total Nitrogen	3.2	2.5	3.1
Total Precipitation (cm)	94	86	102
Sulfate	9	6.9	9.7
Chloride	6.3	33	20
Calcium	2.9	2.6	2.1
Magnesium	0.55	2.0	1.5
Sodium	3.8	19	12
Potassium	0.97	1.9	0.98
Phosphate		0.14	0.09
Ratio Cl/Na**	1.66	1.74	1.67

*Used 1998 data because full year of data available for all sites.

The range of reported annual average wet deposition fluxes ranges from 1.14 to 4.27 kg/ha-yr. The results for the CBBEP site at TAMU-CC (NADP TX 39) ranged from 1.90 to 3.28 with an average of 2.71 kg/ha-yr. The NADP TX 03 site wet only nitrogen deposition ranges from 1.88 to 4.27 with an average of 2.77 kg/ha-yr. It is apparent that while there are year to year variations and site to site variations, the average yearly wet nitrogen deposition is relatively consistent across this region. A reasonable average wet nutrient nitrogen flux for the Coastal Bend Bays is 2.7 kg/ha-yr.

The dry deposition to Coastal Bend Bays was operationally defined as nutrients collected in the AeroChemetric dry bucket containing water when it was not raining. This approach has also been used at several sites in Iowa (Anderson and Downing, 2006) where they found dry deposition to a water surface to be significant. Dry deposition ranged from 2.98 to 8.65 kg N/ha-yr (Table 3). The dry deposition for 1998 was from a whole year of sampling and is therefore, the best estimate of dry nutrient nitrogen deposition. For the TAMU-CC (TX 39) site the wet deposition from 1998 was 32.1% of the total deposition. This percentage was used to estimate the total deposition from wet deposition for TX 39 site for 2002 to 2006 (Table 3).

The estimation of total nitrogen deposition ranged from 8.06 to 10.56 kg N/ha-yr for inorganic nitrogen only (ammonia and nitrate). Ockerman and Livingston (1999) estimated organic nitrogen makes up 19% of the total nitrogen in rain. The estimated total deposition of nutrient nitrogen including organic nitrogen ranges from 9.27 to 13.04 kg N/ha-yr with an average of 10.98 kg N/ha-yr (Table 3) or 1,098 kg N /km^2-yr. Some areas in Europe have adopted a critical load that sets a goal of keeping atmospheric deposition of nitrogen to less than 1,000 kg N /km^2-yr (Bashkin, 1997 as cited in NAS, 2000). This level is exceeded in many northeastern US sites

Table 3. CBBEP Annual Nutrient N Deposition Rates.

Total as N Year	USGS 1 Wet Dep kg N/ha-yr	USGS 2 Wet Dep kg N/ha-yr	CCBNEP WP Wet Dep kg N/ha-yr	CCBNEP TAMU-CC Wet Dep kg N/ha-yr	NADP TX 03 Wet Dep kg N/ha-yr	CCBNEP WP Dry Dep kg N/ha	CCBNEP WP NH_4 & NO_3 kg N/ha-yr	CCBNEP WP Total kg N/ha-yr	CCBNEP TAMU-CC Dry Dep kg N/ha-yr	CCBNEP TAMU-CC NH_4 & NO_3 kg N/ha-yr	CCBNEP TAMU-CC Total kg N/ha-yr
1996	1.49	1.14			2.13						
1997	2.74	2.31	1.50	2.81	3.51	2.98	4.48	5.53	5.25	8.06	9.95
1998	2.24	2.07	3.10	2.51	3.24	3.91	7.01	8.65	5.32	7.83	9.67
1999			2.00	1.90	2.35	3.97	5.97	7.37	8.66	10.56	13.04
2000				**NADP**	2.64						
2001				**TX 39**	2.70						
2002				2.88	2.54					8.97	11.08
2003				2.41	2.40					7.51	9.27
2004				3.28	4.27					10.22	12.61
2005				2.79	2.80					8.69	10.73
2006				2.99	1.88					9.31	11.50
Average 3 years	2.12	1.72	2.20	2.41	3.03				**Average**	8.89	10.98
Standard Deviation (SD)	0.88	0.83	0.82	0.46	0.61						
Percent Relative SD	41.8%	48.3%	37.2%	19.3%	20.0%						
Average 2002 to 2006				2.87	2.78						
Standard Deviation (SD)				0.32	0.90						
Percent Relative SD				11.0%	32.4%						
Average All Years				2.70	2.77						
Standard Deviation (SD)				0.42	0.68						
Percent Relative SD				15.6%	24.5%						

and throughout much of Europe (NAS, 2000) as well as the Coastal Bend and Bays based on our study.

A nitrogen budget for the Coastal Bend Bays has been published (Brock, 2001). This budget used an estimate of atmospheric deposition from preliminary data from Phase I of this CBBEP study. That can now be revised and the direct atmospheric deposition of nitrogen to Coastal Bend Bays should be revised as 426 x 10^6 g/Yr. Based on the nitrogen loading budget, atmospheric deposition directly to Coastal Bend Bays is responsible for 11% of the total (4,210 + 85 = 4295 x 10^6 g) input. In addition, 2017 x 10^6 g nutrient nitrogen is added from direct or indirect rain inputs. Therefore, based on estimated inputs (Brock, 2001), 46% of the total nutrient nitrogen input comes from atmospheric deposition. This indicates almost half of the nutrient input to Coastal Bend Bays is due to atmospheric deposition. Estimates from other estuaries range from 1 to as high as 40% (NAS, 2000). The estimate for Galveston Bay was 39% of the total nitrogen input from atmospheric deposition (Patwardhan and Donigian, 1995). The estimate for Coastal Bend Bays is higher than these estimates as a result of a more reliable estimate of dry deposition (as a percentage of wet deposition) that was determined in Phase I and applied to the wet deposition collected during the entire project. It is obvious that atmospheric deposition of nutrient nitrogen to the Texas Coastal Bend Bays is an important anthropogenic input that must be considered when making management decisions regarding nutrient inputs.

The atmospheric deposition of nutrient nitrogen for Coastal Bend Bays (Table 4) is compared to that for Tampa Bay (Poor et al., 2001) and Galveston Bay (Sweet et al., 1999 and Wade and Sweet, 2008), the only estuaries on the Gulf coast where estimates are available. The comparisons are complicated due to the studies being done in different years and the fact that dry deposition was measured for Tampa Bay and Coastal Bend Bays by two different methods. For Galveston Bay no measurements of dry deposition were made so it was estimated by assuming that dry deposition was the same as wet deposition (e.g. ratio of dry/wet = 1). This is reasonable assumption since the estimates of the ratio of dry to wet deposition for nutrient nitrogen range from 0.78 to 2.0 (Table 4). Total nutrient nitrogen deposition for these three estuaries ranged from 7.3 to 12.3 kg N/ha-yr; good agreement considering the uncertainties. The wet and total nutrient nitrogen deposition estimated for Galveston Bay is the highest, followed by Texas Coastal Bend Bays and Tampa Bay. The wet deposition for Galveston Bay seems reasonable based on NADP regional site data from 1995-1996. Measurements of dry deposition for Galveston Bay would be required to improve the estimate of dry deposition. The direct

Table 4. Comparison of Nutrient Nitrogen Deposition.

	Total Nitrogen Deposition (kg-N/ha-yr)	Dry/Wet Ratio	Wet Deposition (kg-N/ha-yr)	Directly Deposition to Bay (kg-N/yr)
Coastal Bend Bays	7.5 to 10.6	1.3 to 2.0	1.9 to 3.3	1.46x 10^6
Tampa Bay	7.3	0.78	3.2	0.76 x 10^6
Galveston Bay	12.3 (2 x Wet)	1.0 (Est)	6.16	1.76 x 10^6

deposition to these bays is also provided. These calculations are dependent on the surface areas of each system. The direct deposition ranges from 0.76 to 1.76 kg N/yr. This is a significant input of nutrient nitrogen directly to these important estuaries.

In Phase I selected trace elements and dry deposition of major ions (including nitrate and ammonium) and trace elements were also measured. A summary of the annual average wet and dry deposition for 1998 is provided in Table 5. A comparison to NADP site major ion data for 1998 is also included. Complete data and a detailed interpretation have been previously reported (Wade et al., 2002). Of the major ions in the rain some of the ions are also major constituents of sea water. The ratio of chlorine to sodium and magnesium (Table 5) indicates that all three of these ions are derived predominantly from sea salt in the wet deposition and dry deposition at the CBBEP sites and also at the NADP TX 03 site. This is also apparent from the Phase II data. When the chloride concentration in the 111 rain samples collected from 2002 to 2006 is plotted versus the sodium concentration a linear correlation is observed with an R^2 of 0.9957 (Figure 5). The ratio of chloride to sodium in sea water is 1.7982. The average ratio of Cl/Na for the rain samples at TX 39 is 1.6938. This is very close to the ratio for seawater and indicates that the chloride and sodium in the rain samples is predominantly from sea salts. The ratio is slightly lower than sea water indicating a possible minor source of sodium to the rain. The average ratio of Cl/Na in dry deposition (Table 5) was slightly higher than of sea water. It is possible that there is a natural process that causes this slight shift of ratios. When chloride is plotted versus magnesium (Figure 6) for the rain samples from 2002 to 2006 a linear correlation is observed with an R^2 of 0.983. The average ratio of Cl/Mg for the rain samples is 14.116. This is very close to the ratio for seawater (14.98) and indicates that the chloride and magnesium in the rain samples is predominantly from sea salts. The ratio is slightly lower than sea water indicating a possible minor source of magnesium to the rain. The average ratio of Cl/Mg in dry deposition (Table 5) was slightly lower than that of sea water indicating a second source of magnesium to wet and dry deposition. For calcium and sulfate there are sources other than sea salt. When the chloride concentration is plotted versus the sulfate concentration a linear correlation is observed with an R^2 of 0.7015 and more scatter is seen in the data (Figure 7). The average ratio of Cl/SO4 for the rain samples is 1.73. This is significantly lower compared to the ratio that is found in seawater (7.14) and indicates that the major source of sulfate in the rain samples is not of a maritime origin. The average ratio of Cl/SO4 in dry deposition (Table 5) was also lower than that of sea water. Wet and dry deposition of sulfate is dominated by an anthropogenic source. Chloride is directly correlated to potassium with a correlation coefficient of 0.6894 although there is some scatter present in the data (Figure 8). The average ratio of Cl/K for the rain samples is 19.24 which is much lower than the ratio for seawater (48.50) suggesting that less than half of the potassium in the rain samples is from sea salt. Calcium is poorly correlated to the chloride concentration in the wet only deposition with correlation coefficient (r^2) of only 0.3598 (Figure 9). The average ratio of Cl/Ca for the rain samples is 2.85. This is much lower than the ratio for seawater (47.09) and indicates the primary source of calcium is not sea salt. The presence of calcium carbonate or gypsum has been reported from rain samples (Al-Momani, 2003).

Table 5. CBBEP Annual Wet, Dry, and Total Depositon Rates for 1998 (Phase I)

1998 Phase I Results	**NADP TX 03 Wet** kg N/ha-yr		**CCBNEP TAMU-CC Wet** kg N/ha-yr	**CCBNEP TAMU-CC Dry** kg N/ha-yr	**CCBNEP TAMU-CC Total** kg N/ha-yr	**CCBNEP TAMU-CC** % Wet	**CCBNEP WP Wet** kg N/ha-yr	**CCBNEP WP Dry** kg N/ha-yr	**CCBNEP WP Total** kg N/ha-yr	**CCBNEP WP** % Wet
Nitrate Nitrogen	1.23		1.15	0.91	2.06	55.8%	1.60	1.31	2.91	55.0%
Ammonium Nitrogen	2.02		1.36	4.41	5.77	23.6%	1.50	2.60	4.10	36.6%
Nutrient Nitrogen	3.25		2.51	5.32	7.83	32.1%	3.10	3.91	7.01	44.2%
	Wet kg/ha-yr	**Crustal Abundance** kg/ha-yr	**Wet** kg/ha-yr	**Dry** kg/ha-yr	**Total** kg/ha-yr		**Wet** kg/ha-yr	**Dry** kg/ha-yr	**Total** kg/ha-yr	
Chloride (Cl)	6.30	130	33.25	15.64	48.89	68.0%	20.08	14.48	34.56	58.1%
Sodium (Na)	3.80	28300	19.00	8.56	27.56	68.9%	12.04	7.82	19.86	60.6%
Sulfate (SO4)	9.00		6.88	5.30	12.11	56.8%	9.68	24.05	33.73	28.7%
Calcium (Ca)	2.90	36300	2.57	5.60	8.17	31.5%	1.93	32.28	34.21	5.6%
Magnesium (Mg)	0.55	20900	2.00	1.56	3.56	56.2%	1.52	1.27	2.79	54.5%
Potassium (K)	0.97	25900	1.85	1.75	3.60	51.4%	0.98	1.34	2.32	42.2%
Phosphate	NR		0.14	0.52	0.66	21.2%	0.09	0.79	0.88	10.2%
Ratios		**Sea Water**								
Cl/Na	1.66	1.80	1.75	1.83	1.77		1.67	1.85	1.74	
Cl/SO4	0.70	7.14	4.83	2.95	4.04		2.07	0.60	1.02	
Cl/Ca	2.17	47.09	12.94	2.79	5.98		10.40	0.45	1.01	
Cl/Mg	11.45	14.97	16.63	10.03	13.73		13.21	11.40	12.39	
Cl/K	6.49	48.50	17.97	8.94	13.58		20.49	10.81	14.90	

Table 5. CBBEP Annual Wet, Dry, and Total Deposition Rates for 1998 (Phase I) (continued)

1998 Phase I Results	**NADP TX 03 Wet** kg N/ha-yr	**Crustal Abundance** ppm	**CCBNEP TAMU-CC Wet** kg N/ha-yr	**CCBNEP TAMU-CC Dry** kg N/ha-yr	**CCBNEP TAMU-CC Total** kg N/ha-yr	**CCBNEP TAMU-CC** % Wet	**CCBNEP WP Wet** kg N/ha-yr	**CCBNEP WP Dry** kg N/ha-yr	**CCBNEP WP Total** kg N/ha-yr	**CCBNEP WP** % Wet
Aluminum	NR	81300	710	500	1210	58.7%	730	920	1650	44.2%
Zinc	NR	70	30	520	550	5.5%	1.00	910	911	0.1%
Lead	NR	13	2.33	4.15	6.84	34.1%	1.73	8.05	9.78	17.7%
Arsenic	NR	2	0.44	0.58	1.02	43.1%	0.46	1.85	2.31	19.9%
Nickel	NR	75	1.77	3.61	5.38	32.9%	1.24	6.06	7.30	17.0%
Chromium	NR	100	0.33	1.39	1.72	19.2%	0.38	3.48	3.86	9.8%
Copper	NR	55	0.01	17.09	18.52	0.1%	0.82	14.28	15.10	5.4%
Cadmium	NR	0	0.15	0.41	0.44	34.1%	0.02	0.40	0.42	4.8%
Titanium	NR	4400	1.98	5.57	7.55	26.2%	1.25	4.53	5.78	21.6%
Manganese	NR	950	10.65	37.54	48.19	22.1%	17.35	63.43	80.78	21.5%
Vanadium	NR	135	2.85	1.87	4.72	60.4%	2.28	7.16	9.44	24.2%
Average % Wet						**38.0%**				**25.8%**
		Ratio X/Al	**Ratio X/Al**	**Ratio X/Al**	**EF Wet**	**EF Dry**			**EF Wet**	**EF Dry**
Sodium (Na)		0.3481	26.761	17.114	76.88	49.16	16.493	8.4957	47.38	24.41
Calcium (Ca)		0.4465	3.6197	11.200	8.11	25.08	2.6438	35.087	5.92	78.58
Magnesium (Mg)		0.2571	2.8169	3.1200	10.96	12.14	2.0822	1.3804	8.10	5.37
Potassium (K)		0.3186	2.6056	3.5000	8.18	10.99	1.3425	1.4565	4.21	4.57
Zinc		0.0009	0.0423	1.0400	49.07	1207.89	0.0014	0.9891	1.59	1148.8
Lead		0.0002	0.0033	0.0083	20.52	51.91	0.0024	0.0088	14.82	54.72
Arsenic		0.0000	0.0006	0.0012	27.99	52.39	0.0006	0.0020	28.46	90.82
Nickel		0.0009	0.0025	0.0072	2.70	7.83	0.0017	0.0066	1.84	7.14
Chromium		0.0012	0.0005	0.0028	0.38	2.26	0.0005	0.0038	0.42	3.08
Copper		0.0007	0.0000	0.0342	0.03	50.52	0.0011	0.0155	1.66	22.94
Cadmium		0.0000	0.0002	0.0008	85.88	333.33	0.0000	0.0004	11.14	176.74
Titanium		0.0541	0.0028	0.0111	0.05	0.21	0.0017	0.0049	0.03	0.09
Manganese		0.0117	0.0150	0.0751	1.28	6.43	0.0238	0.0689	2.03	5.90
Vanadium		0.0017	0.0040	0.0037	2.42	2.25	0.0031	0.0078	1.88	4.69

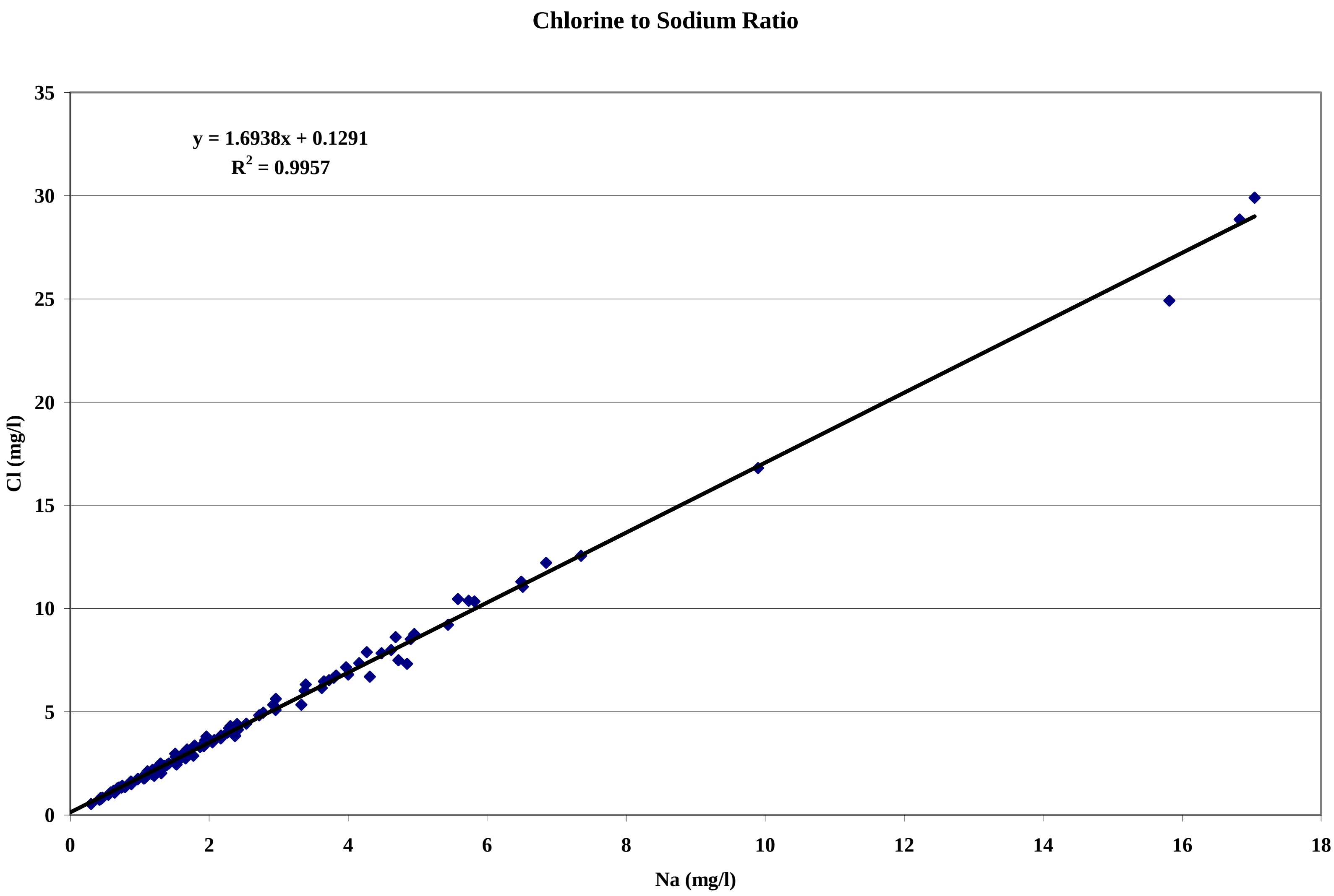

Figure 5. Chloride to Sodium Ratio from 2002 through 2006 in Wet-Only Deposition.

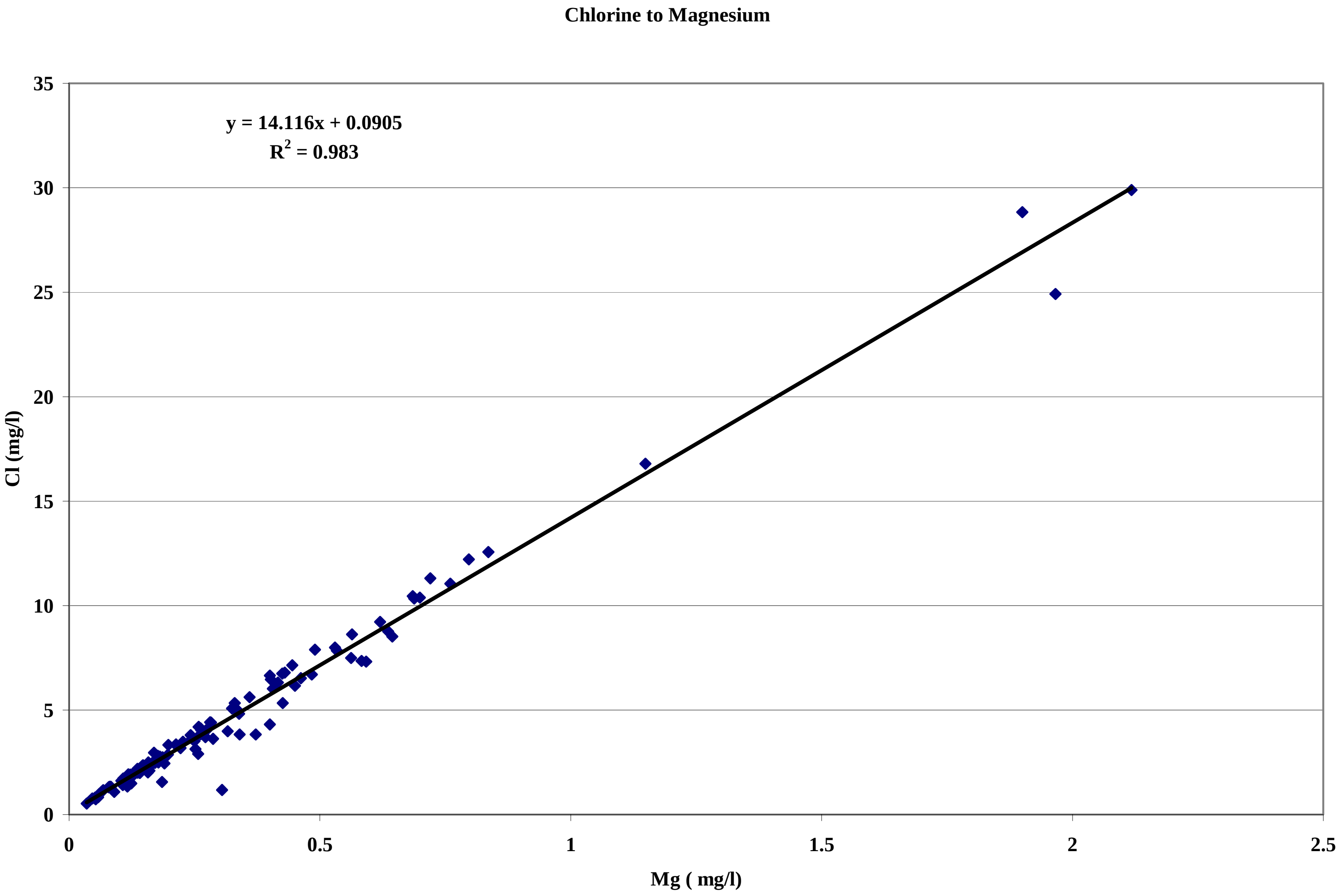

Figure 6. Chloride to Magnesium Ratio from 2002 through 2006 in Wet-Only Deposition.

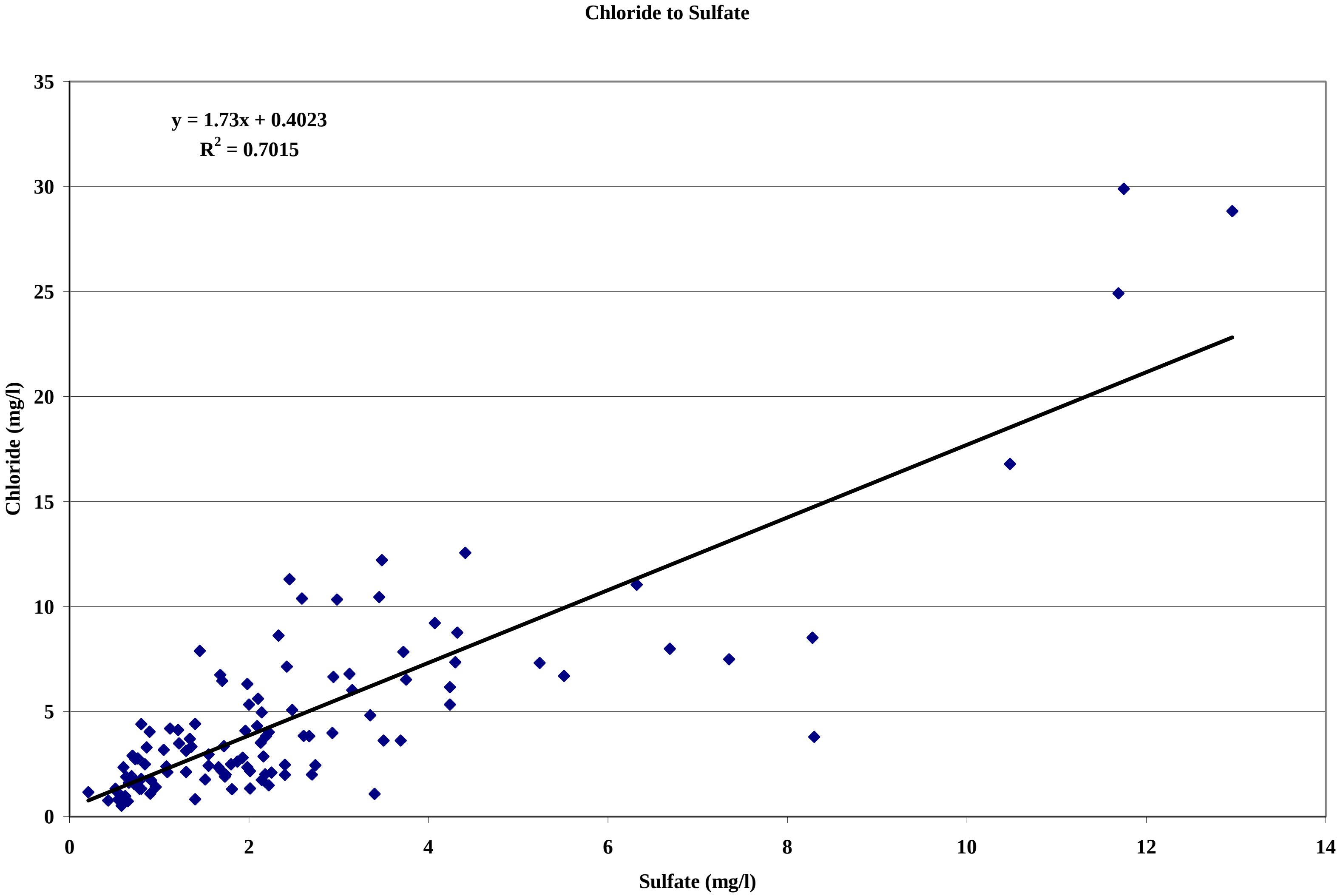

Figure 7. Chloride to Sulfate Ratio from 2002 through 2006 in Wet-Only Deposition.

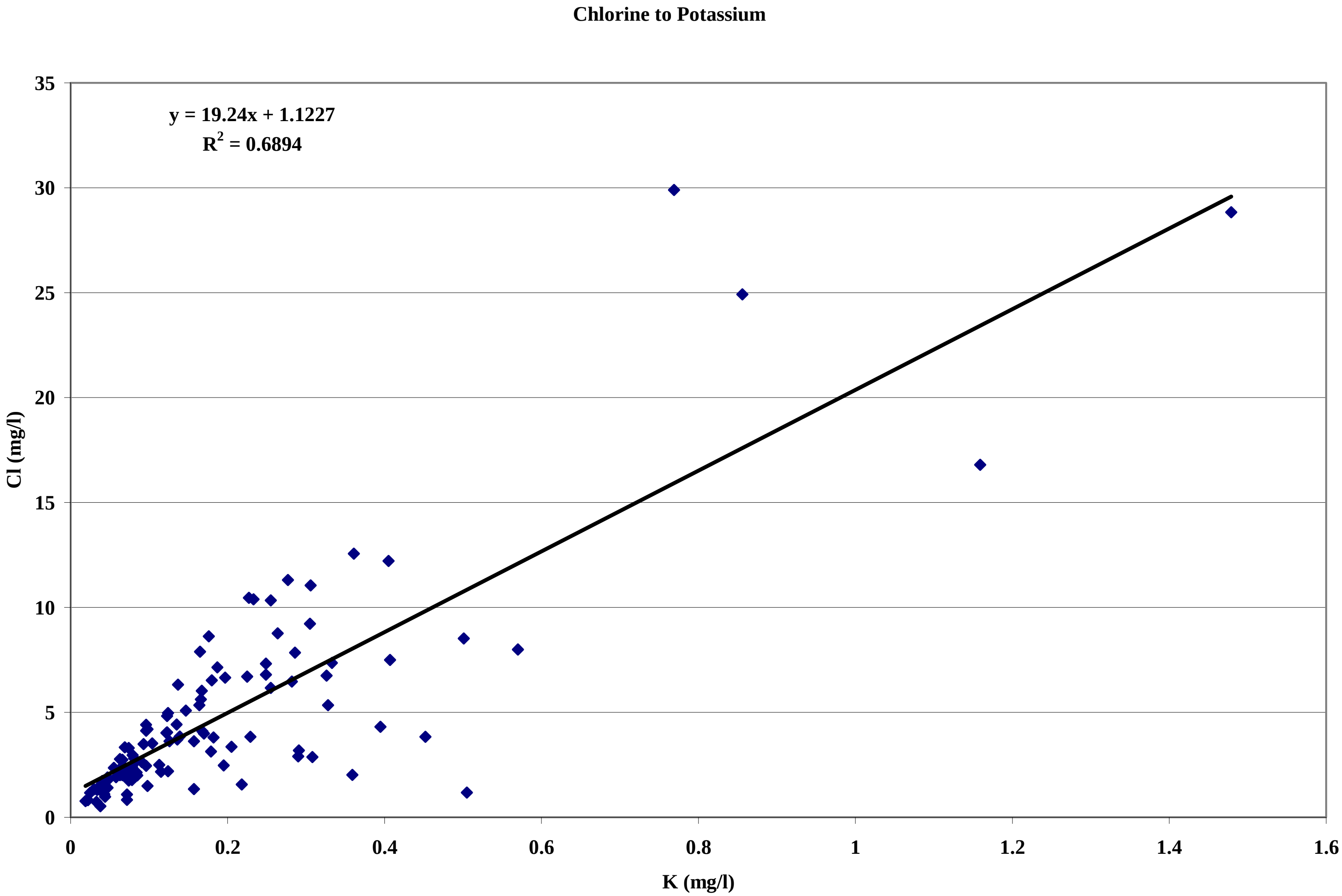

Figure 8. Chloride to Potassium Ratio from 2002 through 2006 in Wet-Only Deposition.

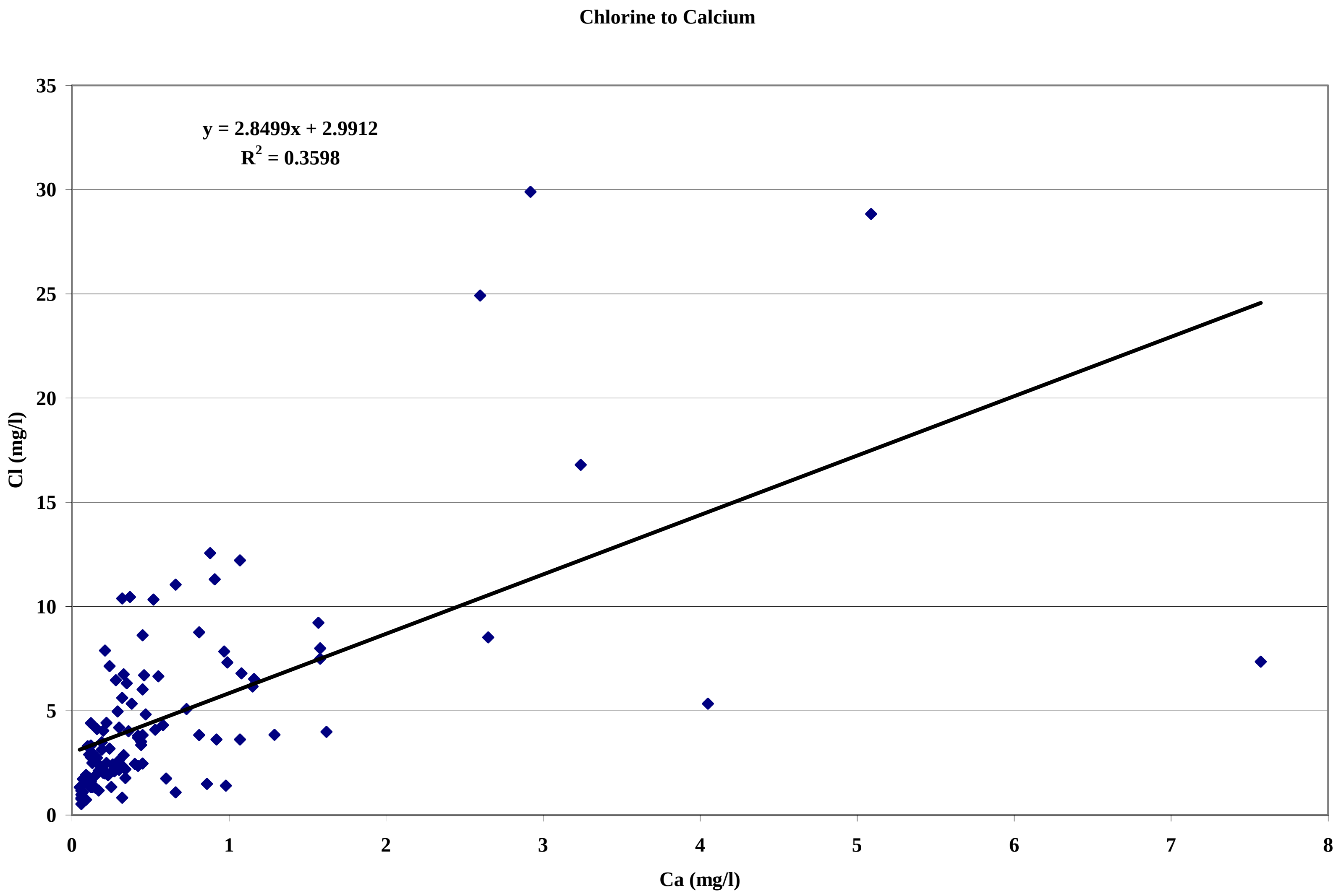

Figure 9. Chloride to Calcium Ratio from 2002 through 2006 in Wet-Only Deposition.

The amount of rainfall (cm) is plotted versus the amount of NO_3 in Figure 10. The curve is similar to results reported by others (Ockerman and Livingston, 2000). With small amounts of rain the NO_3 is quickly scavenged in the rain and is at a higher concentration. If the rain event continues there is less NO_3 in the atmosphere and the concentration tends to decrease with volume.

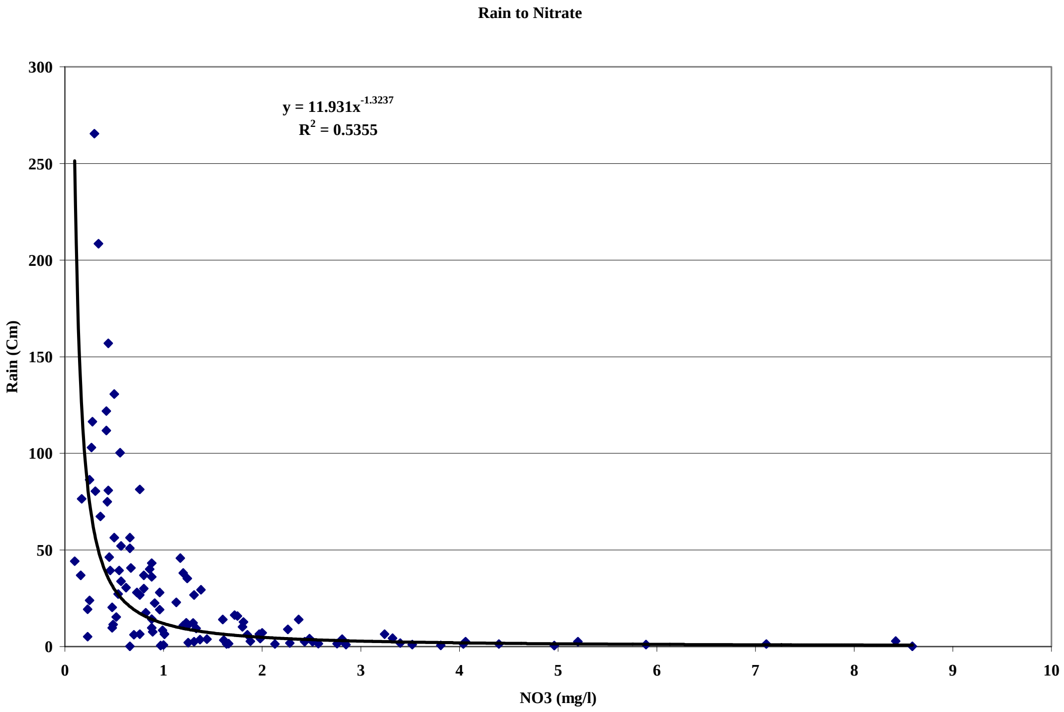

Figure 10. Nitrate Concentration as a Function of Precipitation.

Phosphate in the rain is typically near the detection limit and absent from most samples. Phosphate was found above the detection limit in 13 of the 139 rain events and all except one of these events were censored from the NADP data set. When it is detected, it frequently is found in samples noted as having bird fecal contamination which is the reason why the data is generally censored during data review by NADP.

Most of the trace metals are found at lower concentrations in the rain samples and are reported as g/ha-yr. The estimated depositions in g/ha-yr are summarized in Table 4. Trace element and some major ion enrichment factors (Galloway et al., 1982) were calculated (EF = (X/Al)rain / (X/Al)crust). Values over 1 would indicate sources other than crustal minerals. Due to natural variations in the relative abundance of crustal elements, enrichment is generally considered significant at ratios above 10. Based on this criteria Na, Ca, Mg, K, Zn, Pb, As, Cu (dry only) and Cd have significant sources other than crustal materials. As previously discussed, Na, Mg and some of the Ca and K are derived from sea salts. The Zn, Pb, As, Cu (dry only), Cd, SO_4, NO_3 and NH_4 are from anthropogenic inputs. Many of these inputs are related to high temperature sources (e.g. smelting and fossil-fuel combustion) and can be deposited in areas spatially separated from their input sources (Galloway et al., 1982). Most of these trace elements have low deposition fluxes compared to data from the northeastern U.S., with Pb and Zn being exceptions with enrichments in the range found for other urban areas.

6.3 Temporal Trends

The seasonal deposition of rain, nitrogen nutrients and major ions are plotted as a function of the season for the temporal period from 2002 through 2006 in Figures 11 through 13. Autumn generally experienced with the highest annual rainfall for 3 of the five years and was the second highest the other two years. Winter had the lowest rainfalls for three of the five years measured (2002, 2004 and 2006) and was the second lowest in 2003. There is considerable variability in the seasonal rainfall totals over the five year study period. The seasonal deposition of chloride and SO_4 mimics the seasonal rainfall with higher deposition in the fall and lower in the winter (Figure 11). The same general pattern is also observed for Na, Ca, Mg and K (Figure 12). The seasonal variability for Cl, Na, Mg, Ca, and K are the result of sea salt being removed from the atmosphere by rainfall. The nitrogen nutrient deposition shows a similar pattern with the highest deposition for NO_3, NH_4 and total nitrogen (sum of NO_3 and NH_4) in the fall in four of the years studied (2002, 2004, 2005 and 2006). However, the NO_3, NH_4 and total nitrogen deposition was lowest in the winter for only two of the five years (2002 and 2006). The deposition of rain, nutrient nitrogen and major ions is generally highest in the fall and lowest in the winter, but there are annual variations presumably due to regional and global climatic influences.

6.4 Organic Contaminants

Organic compounds in the atmosphere have been investigated in terms of total organic carbon (TOC), dissolved organic carbon (DOC), amino acids, pesticides, PCBs, hydrocarbons, vitamins, carboxylic acids, etc. Organic carbon is abundant and ubiquitous in rain. Precipitation contains very complex organic compounds in very low concentrations.

6.4.1 PAHs, PCBs, and Pesticides

The atmosphere plays an important role in the transport, deposition, and cycling of natural and anthropogenic (volatile and non-volatile) organic compounds (Eisenreich et al., 1981; Bidleman, 1988; Duce et al., 1991; Leister and Baker, 1994). For example, it has been estimated that when all inputs, including direct industrial discharge, are considered, more than 80% of PCBs entering the Great Lakes came from atmosphere deposition (Eisenreich et al., 1981). Thus atmospheric deposition may be a significant source of pollutants to surface waters, especially coastal waters of industrialized areas, including Texas.

Polycyclic aromatic hydrocarbons (PAHs) are emitted by volatilization of petroleum and incomplete fuel combustion (e.g., domestic heating, industrial plants and automobile traffic, etc.). Pesticides (e.g., DDT) and synthesized chemicals (e.g., PCBs) are mobilized into the atmosphere from agricultural and industrial activity (Bidleman, 1988). Thus, they are ubiquitous

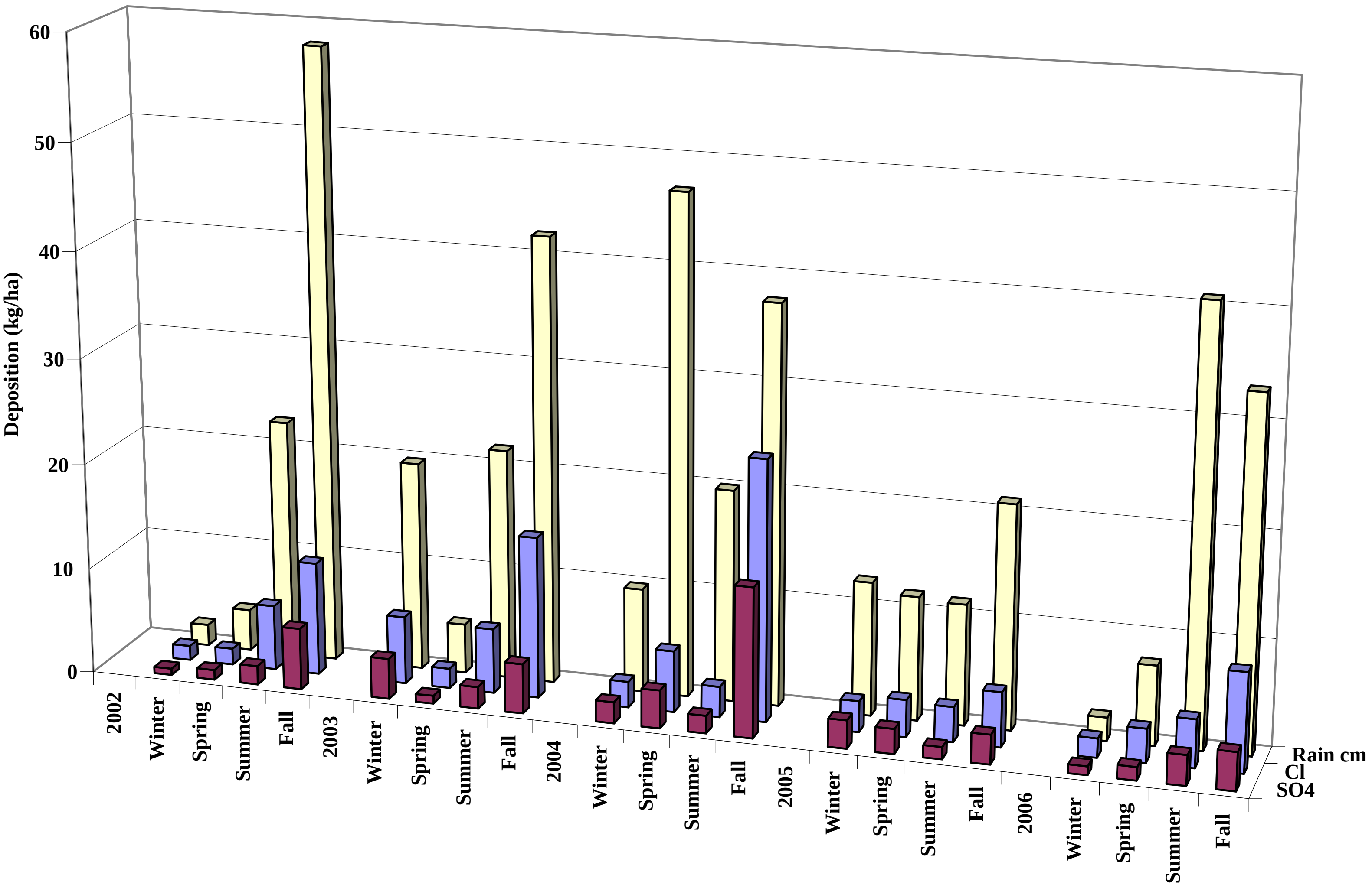

Figure 11. Seasonal Variability of Precipitation, Chloride Deposition and Sulfate Deposition during Phase II at the TAMUCC Atmospheric Deposition Station.

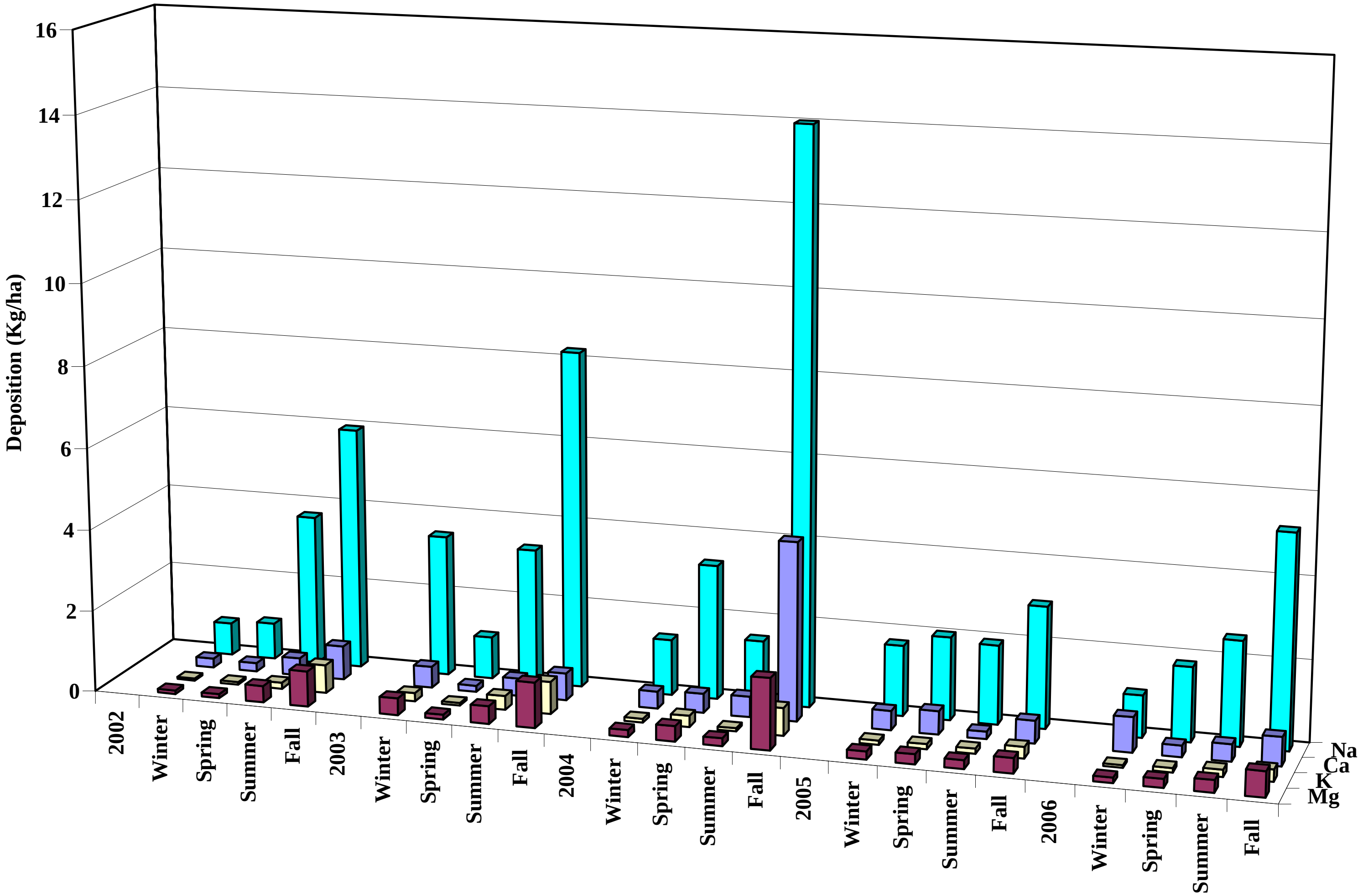

Figure 12. Seasonal Variability of Magnesium, Potassium, Calcium and Sodium Deposition during Phase II at the TAMUCC Atmospheric Deposition Station.

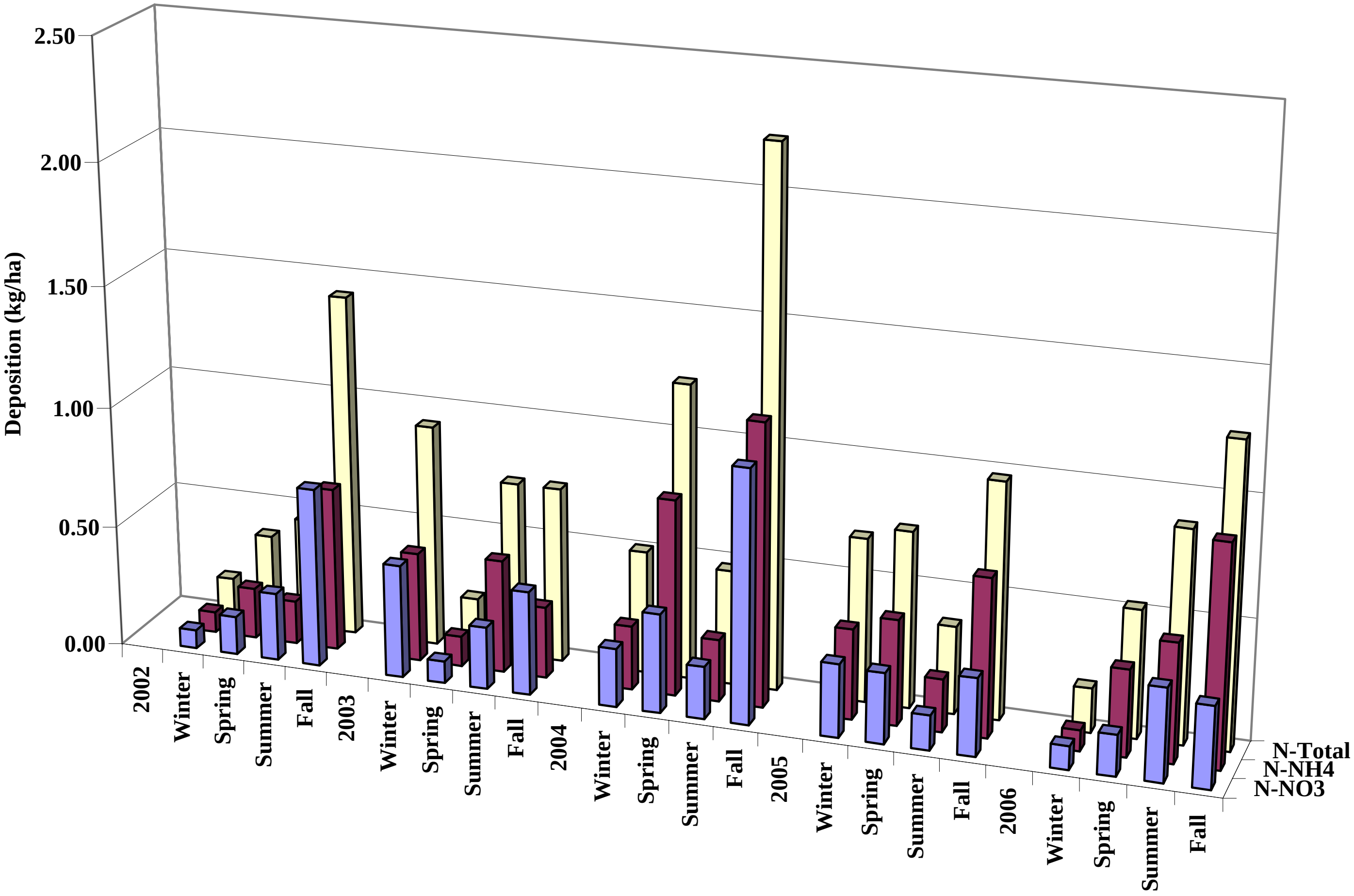

Figure 13. Seasonal Variability of Nitrogen Deposition during Phase II at the TAMUCC Atmospheric Deposition Station.

in the atmosphere, especially near urban and industrialized areas. These organic contaminants are characterized by their physicochemical properties of low water solubility, high octanol-water partition coefficients, the ability to bioconcentrate, and their chemical/microbiological stability (Eisenreich et al., 1981). Some PAHs (benzo(a)anthracene, chrysene, benzo(b and k)fluoranthene, benzo(a)pyrene, and others) and oxygenated and nitrated PAHs have been reported to be carcinogenic in fishes, mammals, and humans (Menzie et al., 1992).

Organic contaminants can be removed from atmosphere by dry deposition, wet removal, and air-water gas exchange (Bidleman, 1988; Duce et al., 1991). Dry deposition includes the sorption by the direct impact of particles and gaseous molecules on land, water, or vegetation. Wet scavenging includes the removal of aerosols and gases both within and below clouds during precipitation events, such as rain, snow, hail, fog and mist. Although there have been some reports that at least 50% of PAHs and organochlorines are removed from the atmosphere by precipitation scavenging (Murphy, 1981; Andren and Strand, 1981; Strachan and Eisenreich, 1986), insoluble compounds such as highly chlorinated PCBs and high molecular weight PAHs may not be readily washed out by precipitation, due to their hydrophobicity. Therefore, dry deposition of some PCBs and PAHs could be a significant mechanism of atmospheric deposition to land and water surfaces. Estimates of the total deposition of pollutants require assessment of both wet and dry deposition.

The distribution of atmospheric organics between vapor and particle phases strongly affects atmospheric removal processes (Eisenreich et al., 1981). The vapor to particle ratio is controlled by the compounds vapor pressure, ambient temperature and the total suspended particle concentration (Bidleman, 1988). Therefore, precipitation contains dissolved and particulate contaminants. With a high volume air sampler, the filter-retained organics are usually the high-molecular-weight and low-vapor pressure species (Murphy and Rzeszutko, 1977; Cautreels and Van Cauwenberghe, 1977). However, since a large fraction of high-molecular-weight species (e.g., PAH, phathalate esters) could occur in the vapor phase in urban atmospheres, trace organics distribution between the particle and vapor phases needs to be interpreted carefully (Eisenreich et al., 1981).

Higher molecular weight aromatics have been reported in smoke plumes from the TAMU Fireman's Training School and in ambient air in College Station, Texas (Atlas et al., 1985). Some higher molecular weight chlorinated hydrocarbons, such as chlordane, toxaphene, hexachlorocyclohexanes (HCH) and DDTs were found at concentrations of 1-100 ng/L in rain in College Station, Texas (Atlas and Wade, 1988). Similar concentrations to toxaphene and HCH were measured in the air along the Texas Coast (Change et al., 1985), though chlordane and DDTs were much lower. A local or regional source was suggested for higher chlordane and DDT concentrations in College Station (Atlas and Wade, 1988). PAHs concentration in rainwater from College Station was reported to be lower than those for urban areas, but higher than some west coast sites (Mazurek and Simoneit, 1983).

Molecular markers have been used in distinguishing biogenic and anthropogenic sources of atmospheric organic material (Lunde et al., 1977; Georgii and Schmitt, 1983; Pankow et al., 1984; Kawamura and Kaplan, 1984; Atlas and Wade, 1988). For example, distributions of alkanes and PAHs in rural and urban locations illustrate the different patterns characteristic of petrogenic and biogenic sources. The presence of primarily unsubstituted PAHs provides additional evidence of input from combustion sources.

6.4.2 Organic Air Samples

The organic air samplers were set to sample for 12 hours each Monday for the entire sampling period. The air sampler was calibrated so that the number of cubic meters of air the sampler pulled through the filters and plugs could be determined. The air sample concentrations are reported on a pg/m^3 basis for pesticides and a ng/m^3 basis for PAH. The results of this study have been published (Park et al., 2002) and only a summary of the findings are presented here.

From August 20, 1998 to September 16, 1999, air and rain samples were collected from two sampling sites on Corpus Christi Bay. One site is located at Texas A&M University at Corpus Christi (TAMUCC) where a high volume air sampler and a wet only rain sampler were installed. At the second site (Whites Point), bulk samples (dry deposition + wet deposition) were collected. Bay water samples were periodically collected at Corpus Christi Bay simultaneously with air samples so that the gas exchange between air and water could be calculated.

Concentrations of PAHs and PCBs in rain samples from the TAMUCC station were significantly higher than those in bulk samples from Whites Point station by a factor of 3. Eliminating the dry deposition from the bulk samples would only increase the difference. Monthly variations in the concentrations of PAHs and PCBs in air were not significant ($p>0.05$). Wet and dry depositions and gas exchange rates of polynuclear aromatic hydrocarbons (PAHs) to Corpus Christi Bay were estimated as 292, 68, and 1207 μg/m^2/year. And those of polychlorinated biphenys (PCBs) were estimated as 3.93, 0.98, and –120 μg/m^2/year (negative values indicate the loss from surface water to air). From these deposition rates, the total input of PAHs and PCBs directly to the surface of Corpus Christi Bay were estimated to be 2209 and –163 kg/year, respectively. These estimates indicate that Corpus Christi Bay is currently a net sink for PAHs, but a net source of PCBs to the atmosphere. Atmospheric input of PAHs to Corpus Christi Bay is not a large input compared to land runoff and periodic oil spills. Individual PAHs, for example, naphthalene and biphenyl were predominantly volatilized from water to air during the study period, while the gas transfer of other heavier PAH compounds such as phenanthrene, fluoranthene, and pyrene were transferred from air to surface water. As the population and industrial activity in the Corpus Christi Bay area increase, total atmospheric PAH input to the bay is also likely to increase, unless management strategies to lower atmospheric PAHs are developed.

Corpus Christi Bay receives inputs of PAHs and PCBs from atmospheric deposition. The concentrations of PAHs and PCBs in air and rain in Corpus Christi Bay area were in the range reported for the similar studies in Galveston Bay and Chesapeake Bay and the distribution of individual PAH compounds and PCB homologues were similar to Galveston Bay. Current techniques allow for fairly accurate measurement of wet deposition (with the exception of fog and hail). However, dry deposition and gas exchange are difficult to measure directly. The dry deposition and gas exchange are therefore estimated with effort to reduce the errors in the parameters, such as mass transfer coefficients. In spite of some limitations, gas transfer process for the vapor PAH and PCB fluxes between air and bay water are very important relative to the wet and dry depositions. It appears that Corpus Christi Bay waters receive a net influx of PAHs from atmospheric deposition. However, the bay is a net source of vapor PCBs to the atmosphere over the entire study period. Thus volatilization of PCBs from the surface water should be taken into account as an important loss of PCBs from the bay water, in addition to water exchange with the open sea. When comparing the atmospheric inputs indirectly to other input sources such as land run off, oil spills, and marine seeps, the contributions of atmospheric deposition of PAHs to the bay water were minor. PAHs and PCBs in the air samples do not follow the expected seasonal trends reported from other study. This may be due to the smaller differences in the average temperatures between seasons in this area compared to other colder regions. As the population and industrial activity in the Corpus Christi Bay area increase, total atmospheric PAH input to the bay is also likely to increase. Urban and industrialized areas still act as a source of PCBs to the atmosphere.

7.0 Conclusions

The detailed results of these studies are provided in this report and previous reports (Wade et al., 2002) and publications (Park et al., 2002). The results indicate that atmospheric deposition is an important source of nutrient nitrogen, trace elements and organic contaminants to the Coastal Bend Bays. The yearly average pH of the rain for 2002 to 2006 ranged from 5.09 to 5.21 (average of 5.14) which is slightly acidic compared to estimated natural pH (5.6). Some of the major ions detected in the wet and dry deposition (Cl, Na, Mg) are from sea salts as anticipated for a site located on the coast. The majority of sulfate in rain and dry deposition is of anthropogenic origin. Potassium and calcium can have both marine and anthropogenic sources. Over 40% of the nutrient nitrogen entering the bays is from atmospheric deposition to the bay and its watershed. While contaminant inputs have significant seasonal variability, the long term inputs are consistent over longer temporal scales (e.g., years). Trace elements Zn, Pb, As, Cu and Cd have anthropogenic sources. Organic contaminants including polycyclic aromatic hydrocarbons (PAH), pesticides and PCB are deposited and removed from the Coastal Bend Bays by atmospheric deposition and gas exchange. This data base provides a robust estimate of atmospheric deposition that can be applied to the Coastal Bend Bays ecosystem. Further research is required to determine how the timing of nutrient inputs to the Coastal Bend Bays system from atmospheric deposition affects phytoplankton species and abundance and their role in harmful alga blooms, hypoxia and sea grass abundance.

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