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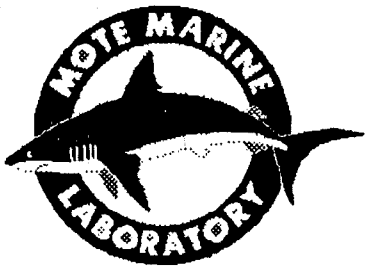

ASSESSMENT OF BULK ATMOSPHERIC DEPOSITION TO THE TAMPA BAY WATERSHED

Final Report
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EXECUTIVE SUMMARY

The objectives of the study were to evaluate the spatial variability in deposition of trace metals and nutrients across the watershed of Tampa Bay. Seven sites were established in representative areas of the watershed for the collection of bulk deposition over a one year period. The project was carried out under an EPA-approved Project Quality Assurance Plan. Integrated weekly samples were collected and analyzed for copper, lead, zinc, aluminum, nitrogen species (nitrate-nitrite-nitrogen, ammonium-nitrogen, total Kjeldahl nitrogen) and total phosphorus. Synthetic organic sampling (biweekly composites analyzed for pesticides, PAHs, and PCBs) was conducted at five of the seven stations for a 12 week period.

The measurement of bulk deposition in this project represented a compromise in that it was likely to be an underestimation of the total atmospheric deposition to an area, most notably for gaseous species. As a result, **the bulk deposition collected during this study is indicative of the wet deposition (rainfall) and the dry deposition which occurred to a standardized surface.** Values produced permited the assessment of spatial variation of **potential** total deposition. Species under-represented by the bulk deposition measurement include nitric acid and nitrogen dioxide. Literature values for these species were used to augment the measured bulk deposition and to calculate loadings of nitrogen to Tampa Bay for the 1985-1991 time period.

Data were censored for non-representative contamination and the mean annualized depositions used to perform loadings calculations. Outliers cannot be discarded as atmospheric deposition is, by nature, an episodic process. Examination of the various weekly nutrient and metals loads as a function of rainfall amounts indicate significant ($p < 0.001$) regressions for all. Links of loadings to rainfall amounts and inter-annual variations in rainfall add uncertainty to assessments drawn from the measurement of deposition during a single year.

Metals

For all metals, there were significant differences between stations for weekly loadings. The most northern and least urbanized station consistently recorded among the lowest annual loadings of all stations. Of copper, lead, and zinc, the urbanized stations received many of the highest loadings. At the urban stations, the occurrence of several metals were not linked to resuspended soils. The variation in metal loadings among stations clearly show that the development and use of a single loading value for a particular metal is an approximation for the Tampa Bay watershed, and probably for water surfaces of Tampa Bay as well. depositions in urban settings may be more representative of loads to the northern portion of the Bay.

With revised loadings from the current bulk deposition project, atmospherically derived (direct deposition plus 10% of watershed deposition) copper, lead, and zinc were estimated to consist of 11%, 3%, and 8%, respectively, of total Bay loads. Nonpoint source loadings from the urbanized areas dominated loads to Tampa Bay with loads in urban runoff exceeding atmospheric deposition to the same areas by factors of 5 or greater. It is clear that anthropogenic activities within the watershed are the dominant factors in metals loadings to Tampa Bay.

Nutrients

Weekly loadings of total phosphorus and ammonium nitrogen were significantly different among stations. Phosphorus loads were higher at the stations in the eastern portion of the watershed, consistent with the geology and watershed activities of the region.

For nitrate-nitrite-nitrogen and inorganic nitrogen, weekly loadings in the northern and northwestern portion of the watershed were significantly different from and **lower** than the watershed mean for the week. The implication is that the watershed variations in nitrate or inorganic nitrogen deposition are not due to sources to the north of the watershed. For both parameters, background levels (at the lowest station) exceed the range of within-watershed variations. For ammonia, total Kjeldahl nitrogen, organic nitrogen, and total nitrogen, however, localized activities or sources in the central or southern portions of the watershed are the dominant factor in depositional loads as the highest station exceeds the lowest by factors of 2-3.

As determined by this project, the revised estimate for **direct** atmospheric loadings of nitrogen to Tampa Bay is 32%, and, as in previous estimates, is second to nonpoint source loadings (46%). For phosphorus, estimates of direct atmospheric loads are 5% of Bay totals. (Direct loadings include only the wet and dry deposition which occurs to the waters of Tampa Bay proper.) Nonpoint sources (39%) and point sources (36%) dominate the loadings of phosphorus to Tampa Bay.

Atmospheric loadings of nitrogen to the various basins of the watershed were also compared to nonpoint source loadings to determine approximate watershed transfer coefficients. Over the watershed as a whole, estimated nonpoint source runoff is mathematically equal to 25% of the total atmospheric deposition of nitrogen, or a net watershed retention rate of 75%. The transfer coefficient in this instance represent the net sum of all watershed activities, including all biological uptake and release, as well as all ground-based anthropogenic "imports", such as fertilization, into the system. More heavily urbanized basins have higher nonpoint source nitrogen loading rates in proportion to the atmospheric loads, which may result from a combination of differing ambient air quality, increased impervious area, increased runoff, and human activities.

If the bulk of nonpoint source loadings are assumed to represent atmospheric loadings, then the total atmospherically derived nitrogen loading to Tampa Bay could be as high as 70-80% of total Bay loadings. This represents an upper boundary of the extent of atmospheric influence, ignoring anthropogenic "imports". For phosphorus, however, comparison of nonpoint source loads with atmospheric deposition loads indicate that watershed geology and activities contribute far more phosphorus than does atmospheric deposition.

Pesticides, PAHs and PCBs

The occurrence of pesticides was linked to localized activities rather than to long range transport. One station received over half of all pesticides collected during the 12 week project and appeared heavily influenced by agriculture. Chlordane and dieldrin, the most abundant pesticides in the 1970s, were not detected in the present study. Total DDT (DDT plus DDD and DDE) loadings were about 20% of those reported in the 1970s. Endosulfans were the most

abundant pesticides in the present study. Overall, annualized chlorinated pesticide atmospheric loading to Tampa Bay was about one third of previous estimates. The winter and spring growing season was not sampled.

Similar to the pesticide data, one station received 75% of all the PAHs collected. In general, the sites in proximity to urban/industrial areas exhibited the greatest amount of total PAH, with rural sites having the least. As with the above pesticide samples, depositions appeared linked to localized activities. Biweekly depositions of PCBs were erratic to the extent that no one station received significantly different weekly loads, and the most rural station received the highest annualized depositions. The total PCB loadings for the present study were about 50% of that observed from a 1970s study.

NADP/NTN Data

Data from the nearby Verna Wellfield were examined for further information. From chloride and calcium data, the bulk of sulfates had sources other than seawater aerosols or soils. The linear relationships between weekly loadings of nitrate and sulfate implied a common source, most probably combustion products.

Annual loadings (1984-1994) at the NADP/NTN site displayed a significant increase in inorganic nitrogen loads with time. While a slight increase in annual rainfall has occurred over the same period, the trend is not significant and loadings do not clearly reflect the extremely low rainfall totals observed in 1989 and 1990. The trend was primarily noted in the summer quarter. Population figures for the surrounding counties mirror the increase in nitrogen loads and imply that, in the absence of stricter emissions controls on mobile and stationary sources, atmospheric loadings of inorganic nitrogen will continue to increase with population growth.

The long term record provided by the NADP/NTN data illustrates not only the increasing loads with time, but also illustrates the high variability of atmospheric deposition. The inherent variability in depositional loads, as demonstrated for inorganic nitrogen, are strong arguments for continuing any atmospheric deposition program over a minimum number of years.

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GLOSSARY

airshed	Geographic extent of an air mass which contributes to deposition in a given region
Al	Aluminum
As	Arsenic
bulk deposition	All materials collected by an open vessel (a combination of wet deposition and dryfall, not equivalent to total [wet plus dry] deposition)
Ca^{+2}	Calcium ion
CASTNET	Clean Air Status and Tends Network
CBAD	Chesapeake Bay Atmospheric Deposition
Cd	Cadmium
CFR	Code of Federal Regulations
Cl^-	Chloride ion
CO	Carbon monoxide
Cu	Copper
dry deposition	Theoretical quantity of materials desposited during dry periods (includes gravitational settling of particulates, settling and capture of aerosols, chemical absorption of gaseous species, and transport of materials into vegetation) (not directly measurable)
dryfall	Particulate and gaseous materials collected by an open vessel during periods of no rainfall (not equivalent to dry deposition)
EPRI	Electric Power Research Institute
ETFE	Specific formulation of inert plastic ("teflon")
FADMP	Florida Acid Deposition Monitoring Program
FADS	Florida Acid Deposition Study
FAMS	Florida Atmospheric Mercury Study
FCG	Florida Electric Power Coordinating Group
FDEP	Florida Department of Environmental Protection (formerly FDER)
FDER	Florida Department of Environmental Regulation
FEP	Specific formulation of inert plastic ("teflon")
FPC	Florida Power Corporation
FPL	Florida Power and Light
GC/MS	gas chromatograph with mass spectrometer detector
GC/ECD	gas chromatograph with electron capture detector
GFAA	Graphite furnace atomic absorption
HB	Hillsborough Bay
HCEPC	Hillsborough County Environmental Protection Commission
HCMPO	Hillsborough County Metropolitan Planning Organization
HDPE	high density polyethylene
HEPA	high efficiency particulate air (filter)
Hg	Mercury
HNO_3	nitric acid
HWM	High molecular weight
K^+	Potassium ion

LTB	Lower Tampa Bay
mg	milligram, 10^{-3} grams
Mg^{+2}	Magnesium ion
MML	Mote Marine Laboratory
MTB	Middle Tampa Bay
mton	metric ton (1000 kilograms, 2203.6 pounds)
N_2	nitrogen
Na^+	Sodium ion
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NDDN	National Dry Deposition Network
ng	nanogram, 10^{-9} grams
NH_3	ammonia
$NH4^+$, NH_4-N	ammonium ion, ammonium nitrogen
NOAA	National Oceanic and Atmospheric Administration
NO_2	nitrogen dioxide
$NO3^-$, NO_3-N	nitrate ion, nitrate nitrogen
NO_x	nitrogen oxides, comprised of nitrogen dioxide (NO_2) and nitrogen oxide (NO)
NPSLAM	NonPoint Source Load Analysis Model
NTN	National Trends Network
NURP	Nationwide Urban Runoff Program
OTB	Old Tampa Bay
PAH	Polycyclic aromatic hydrocarbons
Pb	Lead
PCB	Polychlorinated biphenyls
PCDEM	Pinellas County Department of Environmental Management
PO_4^{-3}, PO_4-P	Ortho- or reactive phosphate ion, orthophosphate phosphorus
ppb	Parts per billion, equivalent to $\mu g\ L^{-1}$
QA	Quality assurance
RDF/MSW	Refuse derived fuel / municipal solid waste
RSD	relative standard deviation
SFWMD	South Florida Water Management District
SO_4^{-2}	Sulfate ion
SOC	Semi-volatile organic compounds
SWFWMD	Southwest Florida Water Management District
TBNEP	Tampa Bay National Estuary Program
TECO, TEC	Tampa Electric Company
TKN	Total Kjeldahl nitrogen, the sum of ammonia and organically bound nitrogen
total deposition	All materials deposited (equivalent to wet plus dry deposition, not directly measurable)
μg	microgram, 10^{-6} grams
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	volatile organic compounds
wet deposition	Dissolved or scavenged materials deposited during rain events (synonymous with wetfall, or wet-only deposition)

1.0 INTRODUCTION

1.1 Background

Much of the management effort by the Tampa Bay National Estuary Program (TBNEP) has focussed on the restoration of seagrasses, whose declines from historical coverages have been linked to decreased water clarity. Changes in water clarity in the Bay have resulted primarily from changes in phytoplankton or chlorophyll content. Chlorophyll content, in turn, is linked to nitrogen loads to the Bay, as the Tampa Bay estuary (**Figure 1.1.**), like many in Florida, is nitrogen limited with respect to primary productivity. In order to promote the recovery of seagrasses, therefore, an accurate assessment of nitrogen loadings from all sources was necessary before the allocation of load reductions could be objectively evaluated. In estimating nitrogen loads to the Bay from point, nonpoint, groundwater, fugitive emissions, and atmospheric sources (Zarbock, *et al.*, 1994), it quickly became apparent that nitrogen deposited from the atmosphere formed a substantial portion of the total.

For Tampa Bay, initial estimates for nitrogen indicated that the direct atmospheric inputs to Tampa Bay are on the order of 26-27% of the total loads to the Bay (Zarbock, *et al.*, 1994), with deposition to the watershed and eventual transport to the Bay increasing the atmospherically derived nitrogen loading by some unknown fraction. Direct atmospheric loadings of phosphorus and toxics were less dramatic in total tonnage (Zarbock, *et al.*, 1994; Frithsen, *et al.*, 1995), but still substantial, and for phosphorus, direct atmospheric loading was estimated to represent as much as 31% of Bay totals.

Localized contaminated sediments were also present in many portions of the Bay (Schropp, 1990; Alexander, *et al.*, 1993; Brooks and Doyle, 1991; Long, *et al.*, 1991, 1994; Zarbock, *et al.*, 1996) with both toxic metals and synthetic or fuel-derived organics detected in levels sufficient that biological effects could be expected. The TBNEP has identified a number of contaminants of concern as those with most potential for local impacts (Frithsen, *et al.*, 1995). The source of the contaminants was not immediately known but indicated a persistent presence and there was at least a potential for atmospheric contributions. Atmospheric deposition of copper, lead, and zinc to Tampa Bay was estimated at 18%, 20%, and 4% of the total loads, respectively (*ibid*). Estimates of atmospheric loadings of synthetic organics vary by compound and many compounds have few data available from which to prepare estimates. In the case of chlordane, however, atmospheric loadings may constitute as much as 21% of total Bay loadings (*ibid*).

Atmospheric deposition of materials has been increasingly recognized as a significant, but highly complex, pathway for the addition of both nutrients and toxic materials to aquatic systems. The pathway can be both direct, consisting of the direct deposition on open water surfaces; and indirect, occurring as deposition within the watershed with the eventual transport of some fraction to the receiving waterbody. In watersheds with small watershed to waterbody area ratios, the total of direct atmospheric loadings can form a substantial portion of total loads to a waterbody. Literature-based values of atmospheric deposition, however, may not always be appropriate for other sites as they reflect ambient air conditions and, until recently, were available primarily for rural areas. The mechanisms of direct deposition to waterbodies is also relatively poorly quantified due to the logistical difficulties of maintaining mid-Bay sampling sites.

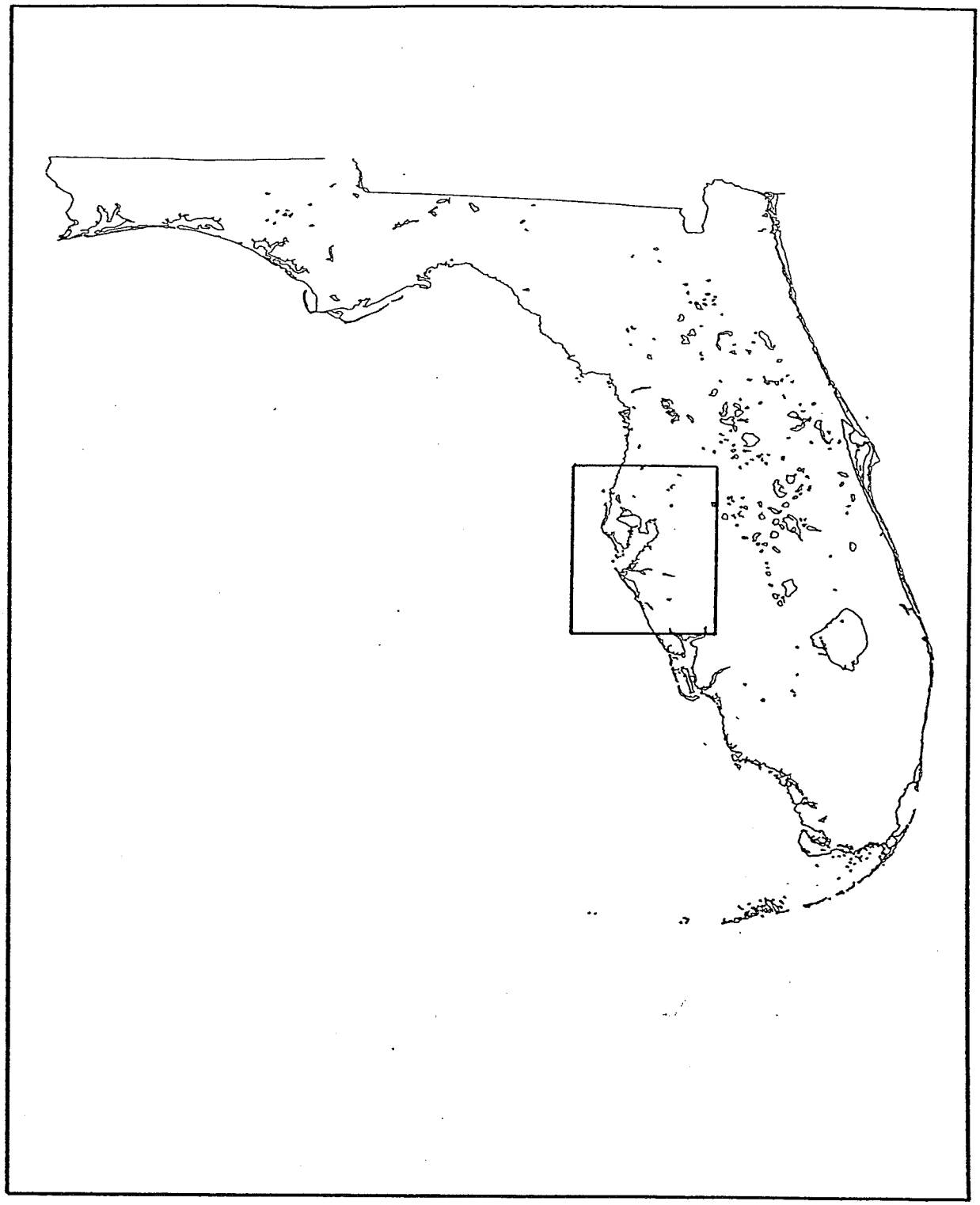

Figure 1.1. General region of study area surrounding Tampa Bay, Florida

The mechanisms of atmospheric loading are also complex in that deposition can occur through both wet and dry modes, each selectively incorporating varying particle sizes, aerosols, and gaseous materials. Rainfall characteristics and solubilities of various species influence the efficiency of precipitation scavenging of materials, while vegetation characteristics and diurnal micrometeorological parameters control dry deposition rates. Loading rates can generally be said to reflect ambient air quality, but dominant modes of deposition vary not only with parameter, but also over both large and small temporal and spatial scales.

Nitrogen oxides are primarily produced during combustion processes such as transportation, fossil fuel energy production, and waste incineration. Trace metals are co-emitted with sulfur and nitrogen, and deposition in urban areas can be many times that observed in remote or rural areas. Major sources of trace metals include fossil fuel energy production, metal mining and refining, waste incineration, and transportation, with perhaps all but metal smelting important aspects to the present investigation in Tampa Bay.

A variety of pesticides, synthetic and petroleum- or fuel-based organics are in ubiquitous use in residential, industrial, and agricultural settings, and of course many recalcitrant toxic compounds (such as DDT) are still in evidence in the environment, despite many years with controls or bans on usage. Many of the compounds are classified as semi-volatile, with significant vapor pressures and therefore a gaseous component. As a result, atmospheric transport and deposition is a major contributor of organic contaminants to water bodies (Cotham and Bidleman, 1995). Aerial and ground high pressure spray applications readily distribute pesticides into the atmosphere. In addition, tilling soil releases pesticide-containing soil particles into the air for distribution by prevailing winds. Polycyclic aromatic hydrocarbons (PAHs) enter the environment from petroleum products as well as from combustion processes. Industrial chemicals, such as polychlorinated biphenyls (PCBs) are volatilized from industrial processes and waste disposal or incineration sites (Bidleman, 1988; Holsen and Noll, 1992).

1.2. Objectives

The objectives of the present study were to synthesize existing deposition information for nutrients and trace metals, both specific for and pertinent to the Tampa Bay region, in a literature survey (Dixon, 1996; **Appendix A**), and to evaluate the spatial variability in deposition of these parameters across the watershed of Tampa Bay. Within the constraints of the study, total deposition figures were to be refined or verified. Toxic metals were originally the emphasis of the study, with nitrogen and phosphorus data of interest as well. Scope revisions and additional funding also permitted a smaller scale investigation of chlorinated pesticides, PAHs, and PCBs. Refined estimates of atmospheric deposition obtained during the study would ideally reflect the large urban influences and substantial mobile and stationary sources within the watershed.

1.3. Project Summary

Seven sites were established in representative areas of the Tampa Bay watershed for the collection of bulk deposition. Integrated weekly samples were collected and analyzed for copper, lead, zinc, aluminum, nitrogen species (nitrate-nitrite-nitrogen, total Kjeldahl nitrogen) and total phosphorus. During a 12 week period in late summer and early fall, deposition of selected chlorinated pesticides, PCBs, and PAHs was also monitored. In addition, Mote Marine Laboratory (MML) also provided analyses of ammonium-nitrogen for comparisons with existing

monitoring programs and assessment of inorganic and organic nitrogen loadings. Toxic parameters chosen for analysis for this project were based upon the recommendations of the Atmospheric Deposition Technical Review Committee assembled by the TBNEP, and were included in the "contaminants of concern" identified previously (Frithsen, *et al.*, 1995).

The bulk deposition monitoring plan was designed as the first phase of a long term effort to detect spatial and temporal patterns of deposition of analytes. Due to the inherent erratic nature of rainfall and the resultant episodic nature of wet deposition, a long term record is crucial for "averaging out" the effects of year to year climatological variations.

Consistent with the long term goals, weekly integrated samples were collected to minimize the economic impact of sample collection and maximize the number of sample sites maintained. Site installations in general followed National Atmospheric deposition Program/National Trends Network (NADP/NTN) site protocols (orientation with respect site obstructions, near ground level, etc.). Exceptions to the siting protocol were in the nearness of urbanized areas (which NADP/NTN requires be up to 40 km distant).

1.4. Bulk deposition

The measurement of bulk deposition in this project represents a technical and financial compromise in that it is likely to be an underestimation of the total atmospheric deposition to an area. The currently accepted method to determine total deposition is to collect wet-only samples with automated equipment, determine dry deposition, and then sum the products. Unfortunately, there is no universally accepted single method for measuring all aspects of dry deposition, as each of the three common methods (micrometeorological, inferential, and surface analysis) are most appropriate for only a portion of the entire dry deposition process.

Dry deposition of various particle sizes is well summarized by Lovett (1994) and is restated below. Dry deposition of large particles (greater than 2-5 microns) typically occurs through gravitational sedimentation and inertial impaction and includes soils, dust, sea salt, calcium, magnesium, aluminum, sodium, chloride, most metals, as well as some sulfate and nitrate (NO_3^-) ions. Fine aerosols (between 2 and 0.2 microns) are not readily dry deposited and often travel long distances. deposition occurs primarily through scavenging by precipitation and species include most sulfate and nitrate ions, lead, ammonium (NH_4^+) and hydrogen ions. Gaseous materials are wet deposited depending on solubility and rainfall characteristics, and are dry deposited by molecular diffusion and absorption onto substrates, leaf stomata uptake and retention, or solution into a waterbody. Gases include sulfur and nitrogen dioxides (NO_2), nitric acid (HNO_3), ammonia (NH_3), and ozone, with nitrogen dioxide an important component near urban areas. Nitric acid vapor is reported to account for a large fraction of dry nitrate deposition in the eastern US (Lovett and Lindberg, 1986, 1993). Nitric oxide (NO) and ammonia depositions can often be exceeded by releases from vegetation, soils, and animal manure.

Micrometeorological methods to measure dry deposition employ vertical arrays of sensitive and rapid response sensors and species measured are limited to those for which sensors are suitable. Inferential methods measure ambient air concentrations, and with deposition velocities, calculate deposition. deposition velocities, however, are controlled by meteorological and vegetation characteristics, and are not readily transferrable without quantifying the additional parameters.

Surface analyses typically employ washing of vegetation, or the collection of throughfall and stemflow, and while simple technologically, again are not readily transferrable and ignore uptake or leaching of materials by vegetation. Each method individually is likely to represent an underestimate of total dry deposition, while the summation of values determined by the various methods undoubtedly includes overlaps and is a resultant overestimation.

As a result, **the bulk deposition collected during this study is indicative of the wet deposition (rainfall) and the dry deposition which occurred to a standardized surface** (a polycarbonate funnel of a specified shape and size). Values produced permit the assessment of spatial variation of potential total deposition across the watershed, recognizing that actual depositions to "natural" substrates or vegetation may have been greater. Materials associated with the large size fractions (>5 microns) which settle primarily through gravitation are likely to be collected efficiently. Gaseous and aerosol species, however, have more difficulty overcoming boundary layer resistance, are affected more by atmosphere:surface interactions, leaf surface area, canopy structure, and micrometeorological conditions (humidity, temperature, sunlight, dew, cloud conditions), and can include a significant uptake of gases through leaf stomata. The parameters associated with the submicron sized particles (such as NO_3^-, NH_4^+, NH_3, HNO_3, NO_2, and NO) are most likely to be under-represented in dry deposition collected by the bulk samplers, although the soluble species will be scavenged by rainfall and collected adequately.

While the bulk deposition collection effort may underestimate the true deposition which would occur from aerosol or gaseous particles, it should again be emphasized that the purpose of the study is to evaluate spatial differences in deposition across an urbanized watershed. The technique will adequately collect wet and large particle deposition. Species under-collected can be estimated from literature values specific to those compounds, although with unknown accuracy at sites with differing meteorology, vegetation, soils, and structures.

1.5. Watershed

The watershed to Tampa Bay includes approximately 5879 km^2 (Frithsen, *et al.*, 1995) located predominantly in three counties; Pinellas, Hillsborough, and Manatee, with additional portions in Pasco, Polk and Sarasota Counties. The water surface of the Bay itself is approximately 1031 km^2 (Frithsen, *et al.*, 1995), for a watershed to estuarine area ratio of 5.7:1. The airshed, however, the region from which emissions can influence deposition within either the Bay or the watershed, is undoubtedly a much larger region and varies on both large and small temporal scales with changing climatological and meteorological patterns. The transport of some pollutants can occur over thousands of kilometers, and, coupled with plume dispersion from stationary or area sources, makes absolute source attribution a difficult task.

Land use within the watershed is defined by Florida Land Use, Cover and Form Classification System and consists of relatively equal portions of agriculture, urban, and forest/rangelands classifications (26%, 24%, and 23%, respectively). Less than 20% of the watershed is classified as wetlands or open water, and less than 10% is defined as mining. Distribution among the major drainage basins is uneven, however, with the watersheds of Boca Ciega Bay and Hillsborough Bay having 84% and 49% urbanized land uses, respectively, while the Manatee River watershed is only 11% urbanized. **Figure 1.2.** illustrates transportation corridors as an approximation of urbanized areas within the watershed.

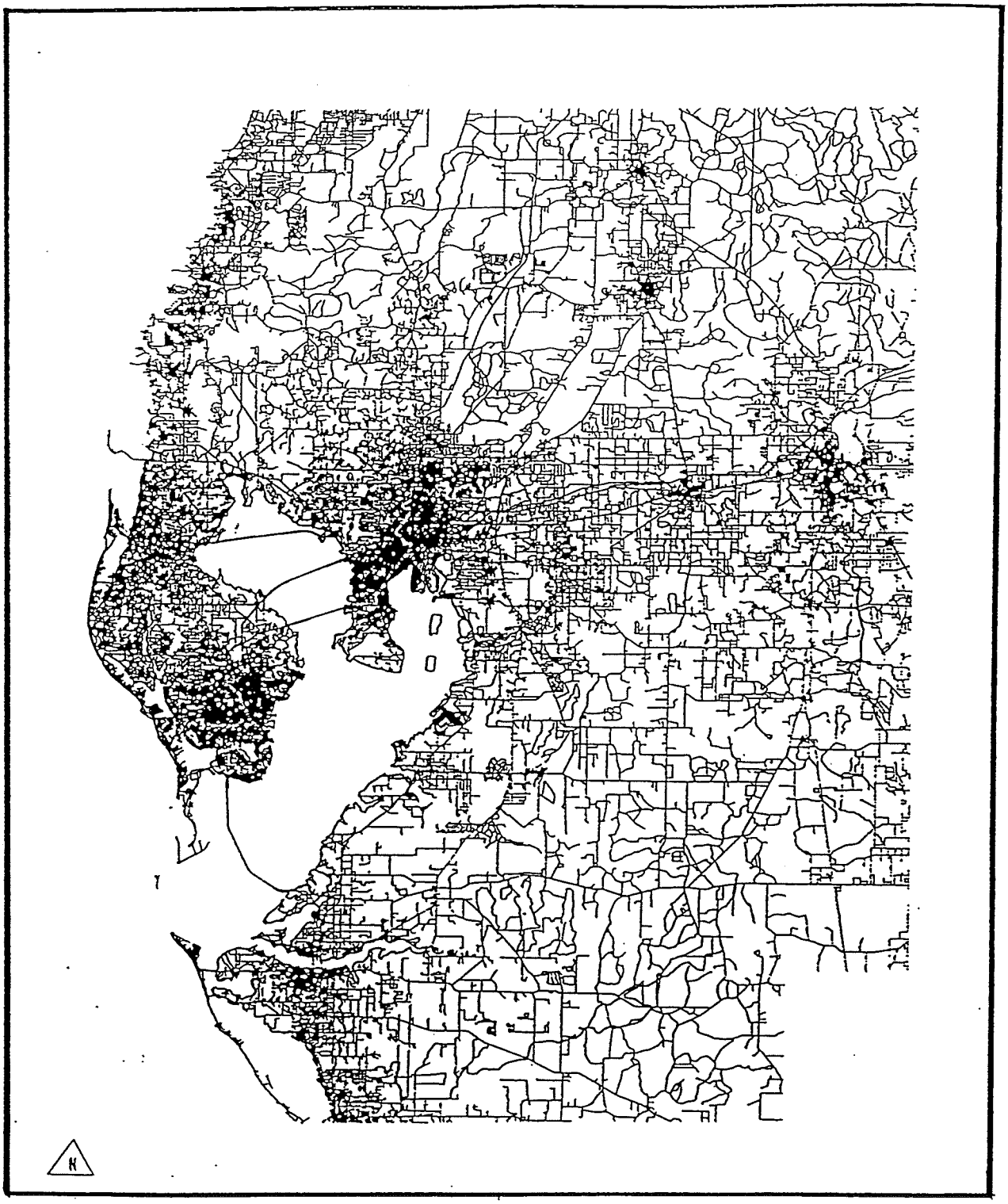

Figure 1.2 Roadway density within the Tampa Bay watershed, as a surrogate for areas of mobile emissions (from Dames and Moore, 1990).

Sources of both toxic contaminants (Frithsen, *et al.*, 1995) and nutrients (Zarbock, *et al.*, 1994) have been the subject of previous work by the TBNEP and each has included an atmospheric deposition component with discussions of sources. Dixon (1996; **Appendix A**) also summarized 1992 NO_x emissions for counties in the Tampa Bay watershed, and estimated that total NO_x emissions in the Tampa Bay area are roughly one fourth of state totals. Statewide allocations by source type for 1982 were 43% mobile sources, 32% utilities, and 21% non-utility stationary sources (Pollman, 1993). More recent compilations by Mr. Tom Rogers (unpublished data) for the Tampa Bay area during 1993 indicate slight increases in relative mobile emissions and estimate NO_x emissions of mobile and stationary sources at 44% and 56% of area totals, respectively.

2.0. METHODS

2.1. Site Selection - Regional

Following guidance from the National Estuary Program and the Atmospheric Deposition Technical Review Committee, seven sites (**Figure 2.1**, **Table 2.1**) were distributed over the Tampa Bay watershed. While recognizing constraints such as access to private property and attempts to avoid the direct influence of point sources, the spatial arrangement could be considered to be randomly distributed within a regular grid placed across the watershed, although the spatial density of stations is low for estimating areal extent of annual depositional loads. If a number of weekly loads from a particular season are examined for spatial estimates, in order to increase the total number of observations per grid, one must assume that weekly samplings of bulk deposition are equivalent to random sampling within the grid section by virtue of highly variable air mass transport during the weekly sampling period. The extremely variable nature of atmospheric deposition, and the presence of point sources and gradients in air quality or deposition within a single grid will also reduce the precision of generated estimates.

Table 2.1. Location of bulk deposition sites.

Station	Latitude	Longitude
Station 1	27° 53.5'	82° 47.3'
Station 2	28° 05.4'	82° 42.3'
Station 3	28° 20.2'	82° 15.1'
Station 4	28° 00.5'	82° 21.1'
Station 5	28° 01.5'	82° 06.3'
Station 6	27° 42.3'	82° 08.1'
Station 7	27° 29.7'	82° 21.5'

In general, sites within urbanized grid sections were selected to generate urban-specific loading values, reflecting a regionalized concentration of stationary and mobile sources, without being unduly weighted by an immediately adjacent point source. The NADP/NTN siting criteria for avoiding known point sources by a minimum of 10-20 km was relaxed since the region adjoining point sources included much of the urbanized area for which loadings were desired. As a result, only areas immediately adjacent to major transportation corridors, or to known point sources were avoided. In general, urbanized areas have very differing micrometeorlogical influences, including, but not limited to, more complex circulation patterns, increased turbulence near buildings, differing thermal convection regimes, and more extreme temperatures ranges.

Sites in Pinellas County were located in heavily urbanized Largo, at the Pinellas County Sheriff's Administration Offices (Station 1), coincident with one of Pinellas County's air quality monitoring locations. The vehicle fueling stations and open turfed fields were adjacent and the site was approximately 150 meters from Ulmerton Road, a major Largo thoroughfare. No

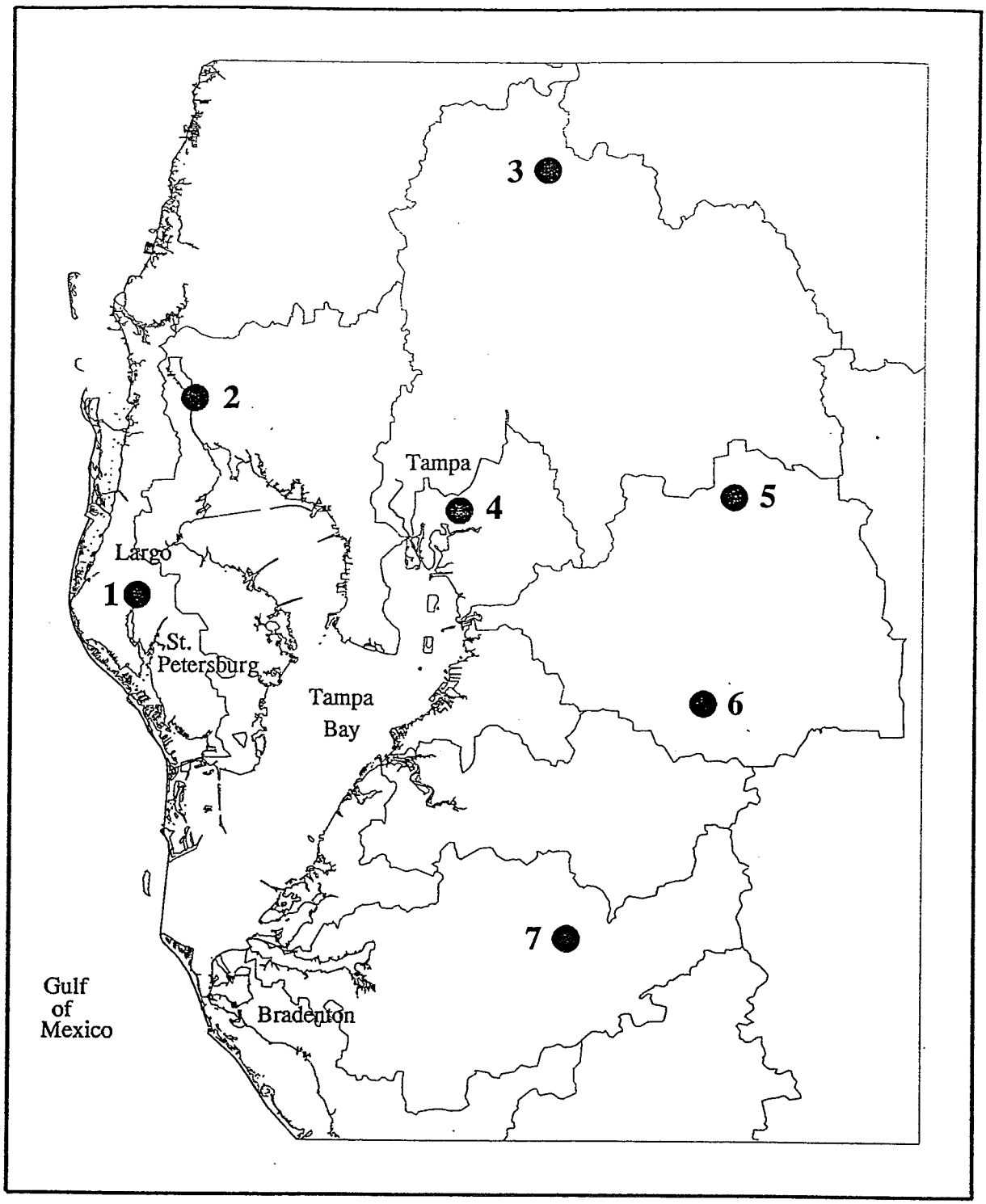

Figure 2.1. Bulk atmospheric deposition station locations within the Tampa Bay watershed.

irrigation of turfed area was observed. Station 2 was also located in Pinellas County, at John Chestnut, Sr. County Park on the eastern shore of Lake Tarpon, again coincident with a Pinellas air quality station (Eastlake). The area surrounding Station 2 is not as urbanized as Station 1, having heavier development between the western shore of the lake and U.S. 19 than the residential and agricultural uses to the east. The park as a whole was irrigated as needed with well water, but the site was located beyond the reach of direct spray and drift. Pesticides, PAHs, and PCBs were not sampled at Station 2.

In the northern portion of the watershed, in Pasco County, Station 3 was located on the grounds of St. Leo College in a vacant field behind the college buildings. The field was not irrigated, but occasionally mowed during the study. The surrounding area is little developed and nearby agricultural activities appear to consist primarily of cattle grazing and citrus rather than row cropping.

In Hillsborough County, Station 4 was located on the grounds of the Tampa Office of the Southwest Florida Water Management District (SWFWMD), approximately 1 kilometer north of Interstate 4 and roughly 150 meters east of U.S. 301. Sited on the banks of the Tampa Bypass Canal, the station is immediately opposite Vandenberg Airport. Other atmospheric influences which may be present include dairy feed lots nearer to I-4. No irrigation occurred at the site. During a portion of the MML study, SWFWMD was conducting a loading and treatment efficiency study of stormwater retention ponds on the property which entailed collection and analyses of precipitation samples.

In Plant City, Station 5 was located on the grounds of the Hillsborough County Community College - Plant City Campus, roughly 1 km south of I-4. No irrigation occurred in this site, which was in an open field adjacent to the Administration Building. To the south, Station 6 was located approximately 1 km to the east of S.R. 39 on the Ft. Lonesome mine property of IMC-Agrico Company. The site was in open fields with little tree cover in the immediate vicinity, and the mine was not operating at any time during the study. In addition to mining, land uses in the region included citrus, cattle grazing, and lesser amounts of row cropping. Pesticides, PAHs and PCBs were not sampled at Station 6.

In Manatee County, Station 7 was located on the northeastern side of the Lake Manatee dam. Although the immediate area around the site is undeveloped, including both the spillway and Lake Manatee Recreation Area, row cropping and citrus are prevalent in the region. The site was not irrigated.

2.2. Collector Siting Criteria - Local

Within each site, placement of the sampler itself followed NADP/NTN siting guidelines, summarized below. Collectors were installed over undisturbed land, with annual vegetation maintained at less than two feet in height. Areas were either level or on mild slopes with no sudden changes in slope within 30 meters of the collectors. Ground cover surrounded the collectors for at least approximately 30 meters, with the exception of Station 4 where the canal adjoined the property,and at Station 1 where an asphalted area was within approximately 10 m. (In urban areas, installations may be on rooftops or in small parks with smaller or no vegetated areas).

No object or structure (including trees, buildings, anemometer towers, and overhead wires) projected onto the collectors with an angle greater than 45° from the horizontal. The distance from the collectors to adjacent objects, therefore was at least equal to the height of the object, and generally greater than 1.5 times the height of the object.

2.3. Sampling Duration

Sampler deployment for nutrients and metals at seven stations began on October 11, 1994, and was originally scheduled for a six month period. Additional funding permitted the extension of the project to an entire year, as well as allowing the collection of samples for selected pesticides, PCBs, and PAHs for six - two week periods at five sites (total of 30 samples). **Synthetic organic sampling** began July 5, 1995, and was completed on September 26, 1995, and strictly, **represents only the collection period, providing only approximate estimates of annual loads.** In particular, winter and spring growing seasons are not represented, although summer rains and associated depositions should be well represented. The 52 weeks of the metals and nutrients sampling was completed on October 18, 1995, resulting in 364 samples. Paired samplers for nutrients and metals were then deployed for two additional one week periods for assessment of within-site variability.

2.4. Parameter Selection

Of trace metals, lead, copper, and zinc are certainly those with some of the highest anthropogenic contributions, with global atmospheric emissions totalling 2,000,000, 286,000, and 924,000 tons per year, respectively (Nriagu, 1992). Emissions of these metals are also estimated to have increased some 6 to 8-fold since 1900 (Nriagu, 1979). (Reduction in the use of leaded gasoline, however, has reduced emissions of this element in the United States twenty-fold between 1979 and 1992, with resulting improvements in ambient air concentrations [US EPA, 1988;1993].)

Sediments within Tampa Bay are enriched in lead and zinc in many regions, particularly in Hillsborough Bay. Sediments are less enriched for copper (Brooks and Doyle, 1991; Zarbock, *et al.*, 1996). Mercury was not included in the present study due to financial constraints, and the relative insolubility and the resultant long range transport of dominant mercury species.

Nutrients, in view of the natural resource emphasis and goals of the TBNEP, were of obvious interest. Inorganic species of nitrogen, and to a lesser extent phosphorus, have direct and relatively immediate impacts on the trophic structure of Tampa Bay. As organic nitrogen may be a substantial portion of atmospheric nitrogen (Pedulla, 1988), the examination of total nutrient concentrations was appropriate. Phosphorus inputs, although considered a sampling artifact or contaminant for many programs, may be regionally significant in light of the concentrations of phosphate mining, processing, and shipping industries in the area. Organic contaminants were selected from those of interest (Frithsen, *et al.*, 1995) and included at a minimum the chlorinated pesticides dieldrin, endrin, DDT, and chlordane, PCBs, and PAHs.

The analytical suite consisted of nitrate-nitrite-nitrogen, total kjeldahl nitrogen, total phosphorus, copper, lead, zinc, and aluminum. Aluminum permitted the assessment of soil-associated metals. In addition, ammonium-nitrogen was added by MML to permit comparisons with other programs and assessment of organic nitrogen loadings. Chlorinated pesticides selected for analysis included 19 compounds, both under current use (chlorpyriphos, endosulfan), as well as

some persistent compounds no longer approved (total DDT, chlordane). Samples were also examined for a total of 16 PAHs, and 20 PCB congeners.

2.5. Collector design

The bulk collector design used was modeled after the deposition collectors employed in the Florida Atmospheric Mercury Study (FAMS) supported by the Florida department of Environmental Protection (Dr. Bill Landing, personal communication). Samples were collected by polycarbonate funnel, (12.0 cm in diameter), with a uniform overall height of about 20 cm. Funnels were connected to FEP teflon tubing (0.64 cm O.D.) with polyethylene connector blocks and teflon compression fittings, and similar blocks and fittings connecting the tubing to the sample collection bottle. Tubing loops reduced evaporation and a teflon filter screen (1.00 and 0.21 mm) prevented insect and coarse particle entry into the collection bottle. The air vent in the lower connector block and the collection bottle was covered with a white polyethylene bag during deployment. To discourage birds, a variety of deterrents were used, with the most effective arrangement consisting of monofilament line tied to supports (wooden dowels) projecting at 45° from the sampler.

The sample collection bottles for metals samples were one liter FEP Teflon bottles, with one liter high density polyethylene (HDPE) bottles used for nutrient samples. A stainless steel frame and laboratory clamps held all assemblies, or collection units, deployed at a station for the week. The funnels were always placed so clamps were below the level of the funnel and so that bird deterrents were outside a cone at 45° from the mouth of the funnels. The funnel mouths were approximately 3.4 m above grade. As sample collection bottles were 1 L in volume, approximately 9.2 cm of rain could be collected in a week before sample overflow.

Each week, final cleaning and assembly of apparatus for nutrients and metals collections was carried out in a clean area supplied with HEPA filtered air and maintained at positive pressure. Collection units were preassembled, the funnels covered with cleaned zipper-type plastic bags, and the entire unit sealed in large plastic bags, plastic boxes and an additional plastic bag for transport to the field. Cleaning procedures at MML for this project are listed in **Appendix B.**

Samples for organic analytes were collected using apparatus similar to that used for inorganics. Major differences included the use of all Teflon or stainless steel construction. The funnel portion consisted of a Teflon 2-liter bottle with the bottom removed. The connector caps were constructed from Teflon rod stock fabricated and threaded for a stainless steel fitting (Swagelock). Teflon tubing connected sampling funnel and teflon sample collection bottle (1 L). After cleaning and assembly, in preparation for transport to the deployment site, the funnel was covered with cleaned aluminum foil and secured with a large zip tie. The completed assembly was then double bagged in plastic bags.

2.6. Sample Collection

Collectors for metals, nutrients, and synthetic organics were deployed for 7 days at a time, with the metals and nutrients samples analyzed individually. The organics samples were individually extracted to meet holding time requirements and then composited into two week periods for analysis. Weekly visits were made to each site to replace entire collection units (funnel, tubing, collection bottle) with precleaned equipment and to transport the previous week's samples to the laboratory for processing and analysis.

In the field, sample funnels for nutrients and metals were covered with cleaned zipper-type plastic bags before removing from the frame, and the entire collection assembly bagged in the field. On return to the laboratory, samples were transferred to the clean area, evaluated as to the degree of non-representative contamination, and then funnels were rinsed with 100 mL of laboratory water acidified with the acid preservative to be used on the fraction. Sample container, saple, and rinse weights were recorded and used to compute sample volumes. Metals samples were acidified with ultrapure nitric acid sufficient for a 0.2% v/v solution and to a pH less than 2.00 SU. Samples for nutrients were acidified with reagent grade sulfuric acid, also to a pH of less than 2.00. After acidification, collection bottles were allowed to equilibrate overnight before samples were quantitatively transferred to parameter-specific, precleaned HDPE sample containers for analysis. All analyses were performed on unfiltered samples (except for the coarse mesh as noted in the collection funnels).

For organics sample collection, funnels were covered with aluminum foil in the field and secured with a zip tie before removal from the frame. The entire assembly was then bagged for transport to the laboratory. Upon return to the lab, any residues on funnels and tubing were rinsed into the collection bottle with methylene chloride. Solvent and aqueous sample was then transferred to a 2-liter separatory funnel for liquid-liquid extraction.

Compromised samples (*i.e.* obvious bird droppings, insect, particulates) were evaluated, assigned a subjective rating, and processed by performing as much of the funnel rinsing procedure as possible without introducing additional non-representative contaminants into the sample. Samples in which bird debris was obviously in the sample collection bottle were censored.

2.7. Analytical Methods - Data Reduction

For the bulk deposition investigation, **Table 2.2** lists parameters for analysis, method references, maximum holding times, and required preservatives. Nutrient samples were analyzed via Technicon Autoanalyzer II and acid extractable metals by single channel graphite furnace using Smith-Hieftje background correction. Organic samples were analyzed for PAHs using GC/MS and for pesticides/PCBs using GC/ECD. GC/MS analysis was also used in an attempt to verify the identity of chlorinated organic compounds in select samples.

Analytical values obtained in concentration units (mg L^{-1}, μg L^{-1}, ng L^{-1}) were subsequently multiplied by the total volume in each sample bottle (rainfall plus rinse) to obtain loads per week in mg or μg of material. For values less than the method detection limit, loads were computed in two ways; one as if the concentration were zero and another (following NADP/NTN protocol) using a concentration value of one half of the method detection limit (½ MDL) for calculation purposes. The results of these two methods are compared, but further discussion and watershed loading estimates are prepared using the statistically robust NADP/NTN protocol (Lynch, *et al.*, 1995; Helsel and Hirsch, 1992).

Weekly loads at a site were corrected for the loading indicated by the equipment blank (cleaned equipment processed with a standard rinse from the same lot number) for each week if the blank was greater than the analytical method detection limit. The resulting microgram or milligram quantities attributable to bulk deposition were then transformed to units of grams $hectare^{-1}$ $week^{-1}$ or kilograms $hectare^{-1}$ $week^{-1}$ using funnel areas (113.1 cm^2) and annualized by multiplying by

Table 2.2. Parameters, method references, holding times, and preservatives for the assessment of atmospheric deposition to Tampa Bay.

Analysis	Units	Description	Method Ref. Number	Holding Time	Preservations
Metals Digest	Acid Extractable	SM 3030C	6 months	-	
Al	$\mu g\ L^{-1}$	GFAA	SM 3111B	6 months	HNO_3 to pH<2
Cu	$\mu g\ L^{-1}$	GFAA	SM 3113B	6 months	HNO_3 to pH<2
Pb	$\mu g\ L^{-1}$	GFAA	SM 3113B	6 months	HNO_3 to pH<2
Zn	$\mu g\ L^{-1}$	GFAA	EPA[1] 289.2	6 months	HNO_3 to pH<2
NO_{2+3}-N	$mg\ L^{-1}$	Auto, Cd Reduct	EPA[1] 353.2	28 days	4°C, H_2SO_4 to pH<2
NH_4-N	$mg\ L^{-1}$	Auto, Phenol	EPA[1] 350.1	28 days	4°C, H_2SO_4 to pH<2
TKN	$mg\ L^{-1}$	Semi Auto, Block	EPA[1] 351.2	28 days	4°C, H_2SO_4 to pH<2
TP	$mg\ L^{-1}$	Semi Auto, Block	EPA[1] 365.4	28 days	4°C, H_2SO_4 to pH<2
Cl Pest	$ng\ L^{-1}$	GC/ECD, GC/MS*	EPA[2] 608	7 days,40 days	4°C
PCBs	$ng\ L^{-1}$	GC/ECD, GC/MS*	EPA[2] 608	7 days,40 days	4°C
PAHs	$\mu g\ L^{-1}$	GC/MS	EPA[2] 625	7 days,40 days	4°C

SM - Standard Methods for the Examination of Water and Wastewater, 17TH Edition, APHA
EPA[1] - Methods for Chemical Analysis of Water and Wastes, 1979, EPA-600/4-79-020
EPA[2] - 40 CFR part 136, July 1, 1990.
* - EPA 625, for verification in select samples

52 to obtain g ha^{-1} yr^{-1} and kg ha^{-1} yr^{-1}. All nutrient values are in elemental concentrations or loads. Inorganic nitrogen loading was determined as the sum of ammonium- (NH_4^+) and nitrate-nitrite-nitrogen ($NO_2^-+NO_3^-$-N), organic nitrogen as total kjeldahl nitrogen (TKN) less ammonium, and total nitrogen as total kjeldahl nitrogen plus nitrate-nitrite-nitrogen.

2.8. Statistical Methods

For the presentation of loading results, both median and mean values are reported for both individual and pooled stations. The data set was previously censored by removing values with obvious contamination by bird debris. A total of 37 out of 364 nutrient samples (10%) and 33 out of 364 metals samples (9%) were censored. As data are annualized, use of the mean is equivalent to replacing missing or censored data with the mean weekly deposition prior to performing a sum for annual loads. While the **median** is less sensitive to the inclusion of outlier data, the **mean** is a more accurate representation of total annual loads, unless the outlier data is the result of non-representative sample contamination.

The apparent outliers remaining in the data set, however, do not have any evidence that would lead one to conclude that a non-representative contamination had occurred. As a result, loading evaluations are performed for the levels established by the means, with the revised atmospheric loading values inserted into prior estimates of loadings to Tampa Bay (Frithsen, *et al.*, 1995; Zarbock, *et al.*, 1994).

Distributions of annualized loadings at a site were typically non-normal (heavily skewed) for all parameters and log transforms inadequate for meeting the assumptions of parametric methods. Station to station comparisons primarily employed analyses of variance on pooled ranks (Kruskal-Wallis). **Station differences noted describe the relative distribution of the weekly events (multiplied by 52) rather than differences between annual loads**, although if weekly events are typically larger at one station then annual loads will be, as well. The converse is not necessarily true, however, as substantial and meaningful differences in total annual loading between stations did exist even with no statistically significant difference in the distribution of weekly events.

2.9 Quality Assurance

The project was carried out under an EPA-approved Project Quality Assurance Plan (Dixon and Allen, 1994). Field-related quality assurance measures included weekly analysis of equipment blanks, batch verification (biweekly) of rinse water blanks, and lot verification of sample container blanks. For organic analyses, equipment blanks were collected weekly and composited biweekly for analysis, as were samples. Additionally, following the 52 weeks of the study, two further deployments were conducted with paired nutrient and paired metals collection units to evaluate sampling variability for these parameters. Laboratory quality assurance measures included set rates of assessment of precision and accuracy through sample reanalysis (minimum 10% duplicates) and confirmation of digestion and method suitability (minimum 5% spiked samples). Reagent and digestion blanks were processed with each sample digestion group. Data quality objectives appear in **Table 2.3** for metals and nutrients. A total of 364 samples were scheduled for analysis under this project (7 sites times 52 weeks). Total number of samples analyzed was 491.

Table 2.3. QA objectives for assessment of atmospheric deposition to Tampa Bay.

Parameter	Ref.	%RSD	%Rec	Completeness
Al	SM3113B, 3111D	30	82-116	98%
Cu	SM 3113B	12	82-117	98%
Pb	SM 3113B	13	82-119	98%
Zn	EPA 289.2	23	80-122	98%
TP	EPA 365.4	13	80-111	98%
NO_{2+3}-N	EPA 353.2	15	81-116	98%
TKN	EPA 351.2	18	86-119	98%
NH_4-N	EPA 350.1	20	86-113	98%

EPA = Methods for Chemical Analysis of Water and Wastes, 1979, EPA-600/4-79-020
SM = Standard Methods for the Examination of Water and Wastewater, 17TH Edition, APHA

3.0. QUALITY ASSURANCE AND RAINFALL - RESULTS AND DISCUSSION

3.1. Quality Assurance

Results of blank analyses (rinse water, container, and equipment) appear in **Tables C1** through **C3** of **Appendix C**. **Table 3.1** lists project mean results for the metals and nutrient equipment blanks. Equipment blanks incorporate a total assessment of any contamination added to samples via contact with equipment surfaces, rinse water, sample containers, and typical sample handling, including analysis. This is evident in that rinse and container blanks are almost all less than the method detection limit, while equipment blanks demonstrate frequent detectable levels, most notably for aluminum and zinc, two ubiquitous laboratory contaminants.

Equipment blanks for nutrients and metals were prepared on all but one of the 52 weeks of the study. On this occasion, vandalism forced crew to use the equipment scheduled for blank measurement to replace a sample collection apparatus. For samples collected on this date (November 8, 1994), the project mean equipment blank was used to correct weekly loadings data from each site. Analysis of blank samples for organic contaminants showed no contamination for any of the analytes above the method detection limit. All precision and accuracy data for metals and nutrients were within the project data quality objectives (**Table 2.3**, above). Quality assurance results for organics analyses appear in **Appendix C** and **Table C4.**

Table 3.1. Mean equipment blanks (n=51) for bulk deposition apparatus.

Parameter	mg	µg	ng
Nitrate-nitrite-nitrogen	<0.0005		
Ammonium-nitrogen	<0.0005		
Total Kjeldahl nitrogen	<0.005		
Total phosphorus	<0.005		
Copper		<0.01	
Lead		<0.02	
Zinc		0.11	
Aluminum		1.45	
PAHs*			<10.0
PCBs*			< 0.6
Cl Pesticides*			< 0.6

* - For organics analyses, n = 6

3.2. Excessive Rainfall and Collection Efficiency

Sample collection containers were nominally one liter in volume, capable of collecting slightly over 9.2 cm of rainfall before overflow. An active hurricane year and multiple tropical systems provided several weeks with high rainfall totals. Reference to NADP/NTN records (October

18, 1994 through September 12, 1995) indicate four weeks in which rainfall amounts at Verna Wellfield, Sarasota, exceeded 9.2 cm. Rainfall records (October 11, 1994 through September 30, 1995) obtained from SWFWMD from the stations **nearest** each of the MML sites also recorded three to four weeks with rainfall amounts greater than 9.2 cm. Reference to project sampling records indicated 24 occasions (with a maximum of five per station) when sample collection bottles were completely full. At these times, weekly loads may have been underestimates, although for the soluble chemical species for which precipitation scavenging or "wash-out" is a dominant mode of deposition (HNO_3, NO_3^-), the degree of underestimation by truncating the end of a large rain event is likely to be slight.

Weekly rainfall totals at the SWFWMD stations nearest the MML sites indicate that 92% to 93% of the rainfall that fell during this period (between 118.8 and 150.7 cm) could be retained by the samplers without overflow. SWFWMD weekly data were truncated to reflect the amount that **could** be retained by the MML samplers, and compared with the rainfall totals actually captured by the MML project. The MML samplers (12.0 cm diameter) appear to have been approximately 84% efficient in comparison to an 20.3 cm (8 inch) diameter, National Weather Services Standard, rainfall gage, provided no true spatial biases existed between the SWFWMD and MML sites. The SWFWMD rainfall sites averaged 2.5 km distance from the MML stations. The bias appeared very uniform at all sites (ranging from 81% to 87%) and, if real, likely reflects a combination of increased wind speeds at 3.4 m above grade and the aerodynamic qualities of the smaller open funnel (12 cm diameter) as opposed to the larger funnel or the screened opening typical of most rainfall station installations.

The apparent relative differences in rainfall collection efficiency between SWFWMD and MML installations could be used to increase the loadings measured during the project by a factor of approximately 1.2. The implied assumption with this augmentation, however, is that dry deposition collection was similarly under-represented. As any bias in dry deposition is unknown, and as the distance between SWFWMD and MML sites was as great as 4.3 km, loads presented below were calculated using the rainfall volumes and sample concentrations as collected by the MML samplers with no adjustment.

3.3. Rainfall

Over the course of the project year, rainfall amounts were not significantly different between the metals and nutrient samplers. Median weekly rainfall totals at the seven stations ranged between 0.9 cm and 1.7 cm with no significant differences in weekly rainfall amounts among stations. Weekly totals, however, were higher in southeastern portion of the watershed.
Project (annual) rainfall totals, as collected by the 12.0 cm funnels, appear in **Table 3.2**, and are below long term annual averages (Flannery, 1989). Annual rainfall totals were also slightly higher in the southern portion of the watershed, the result of a few weeks of extremely high and concentrated rainfall in the region, with the range in annual precipitation between stations higher than would be expected. Flooding problems were noted to the south of the watershed, particularly in the Myakka basin, but the extreme rainfall events did not extend into the northern portion of the project area. Annual rainfall totals were between 10 and 28 cm (4 and 11 inches) below long term averages, which, for the study area, are typically between 127 and 140 cm year^{-1} (50 and 55 inches year^{-1}), with Tampa and the interbay peninsula receiving the lowest amounts (*ibid*, 1989).

Table 3.2. Annual rainfall totals collected at the bulk deposition stations in the Tampa Bay watershed. Collections truncated during weeks with greater than 9.2 cm.

Station	------Annual Rainfall----- (cm)	(inches)
1	110.9	43.7
2	108.7	42.8
3	108.4	42.7
4	117.7	46.3
5	99.4	39.1
6	129.8	51.1
7	125.6	49.4

4.0. METALS AND NUTRIENTS - RESULTS AND DISCUSSION

4.1. Summary Data

The results of bulk depositions by station, following NADP/NTN protocols (½ MDL) for dealing with concentrations less than the method detection limit, appear in **Table 4.1**. Also included are pooled measures of mean and median, as well as arithmetic averages of station means. While the **median** is less sensitive to the inclusion of outlier data, the **mean** is a more accurate representation of total annual loads unless the outlier data is the result of non-representative sample contamination. One should recall that the episodic nature of atmospheric deposition is expected to generate skewed distributions and that not all outliers can be assumed to be erroneous measurements.

It should be restated that depositions occurred to a standardized polycarbonate funnel, 12 cm in diameter, and at approximately 3.4 m above grade. To the extent that interactions between active "natural" substrates (water surface, vegetation, soils, manmade structures) and airborne species are not duplicated by the polycarbonate, the loadings calculated may under-estimate actual fluxes to a watershed. Species such as metals in which the primary transport modes are associated with the larger particulates (>2 microns) are expected to be well represented.

Other cautions in data interpretation include the fact that since collections were made weekly, inorganic nitrogen species could have undergone bacterial and/or chemical transformations. The analyses of inorganic species data, therefore, is focussed on station to station differences, and comparisons with NADP/NTN results, which uses a comparable weekly collection protocol.

Station to station comparisons were carried out through the analysis of variance on pooled ranks of annualized weekly loads, and several significant differences were observed. **Differences noted describe the relative distribution of the weekly events (multiplied by 52) rather than differences between annual loads**, although if weekly events are typically larger at one station then annual loads will be, as well. The converse is not necessarily true, however, as substantial and meaningful differences in total annual loading between stations did exist even with no statistically significant difference in the distribution of weekly events.

4.2. Metals

Distributions of metal data (**Appendix D, Figures D1** through **D4**) are quite skewed. Pooled study medians and means were 5.43 and 8.01 g ha^{-1} yr^{-1} for copper, 3.86 and 6.52 g ha^{-1} yr^{-1} for lead, 46.16 and 79.20 g ha^{-1} yr^{-1} for zinc, and 236 and 451 g ha^{-1} yr^{-1} for aluminum. Data, even though censored for bird debris, still include at least one unusually high value for each of copper, lead, and zinc. While all three occurred at Station 7, each occurred on a different day, with no obvious contamination present in the funnel. Aluminum was unusual in that the highest values at almost all stations were recorded during a single week (**Figure 4.1.**). (Equipment blanks were typical on this occasion, however.) The noteworthy event occurred during a week with heavy rainfall (approximately three weeks following Hurricane Allison), and the aluminum presumably represented entrained soils, most likely Saharan dust (Landing, *et al.*, 1995). Storms such as these are excellent illustration of an true episodic event producing an apparent outlier and a substantially larger annual load.

Table 4.1. Summary results of bulk deposition for the Tampa Bay watershed. Trace metals are in units of g ha^{-1} yr^{-1}; nutrients are in units of kg ha^{-1} yr^{-1}. Data censored for bird debris and other obvious contamination.

Param-Sta	Median	Mean	n	Stddev	Max	75%	25%
Copper							
1	5.61	7.97	50	6.62	36.40	9.89	4.09
2	4.37	5.95	52	5.98	34.00	6.81	2.53
3	3.72	4.82	49	3.98	15.50	7.14	1.87
4	6.92	9.18	44	8.06	38.30	10.10	3.91
5	4.64	6.78	42	7.06	30.50	8.64	2.07
6	5.36	7.48	44	6.98	29.40	9.17	2.39
7	7.04	13.87	49	27.00	186.60	15.30	3.07
Pooled Data	5.43	8.01	330	12.10	186.60	9.21	2.67
Sta. Arith Avg.	5.38	8.01					
Lead							
1	4.78	7.00	50	5.64	21.20	11.20	2.90
2	3.84	5.82	52	6.76	36.20	6.35	2.00
3	2.85	5.14	49	6.56	35.10	6.67	1.18
4	8.07	10.56	44	10.50	46.20	13.20	3.75
5	3.45	5.17	42	4.74	22.10	6.81	1.98
6	3.52	5.87	44	6.49	28.20	6.97	1.38
7	2.62	6.25	49	13.20	87.90	6.44	1.06
Pooled Data	3.86	6.52	330	8.23	87.90	7.64	1.93
Sta. Arith Avg.	4.16	6.54					
Zinc							
1	70.53	101.90	50	122.73	858.80	113.66	57.84
2	42.58	56.67	52	45.74	228.70	71.52	27.08
3	24.37	34.26	49	27.54	137.70	49.21	14.21
4	49.59	113.80	44	137.70	671.60	191.34	30.39
5	37.77	67.65	42	94.24	494.90	61.80	25.06
6	52.65	91.40	43	116.33	676.80	127.52	20.62
7	33.89	92.99	49	318.40	2252.20	74.45	11.10
Pooled Data	46.16	79.20	330	152.01	2252.20	83.47	23.01
Sta. Arith Avg.	44.48	79.81					
Aluminum							
1	159.89	539.16	50	1709.09	12097.50	456.84	36.19
2	203.89	421.70	52	797.81	5126.40	424.70	60.88
3	186.72	300.90	49	464.03	2948.90	345.09	69.55
4	222.19	472.74	44	1094.38	7210.80	362.86	129.06
5	296.93	540.62	42	912.18	5787.90	659.19	73.01
6	359.07	493.36	44	480.61	2150.40	628.59	205.45
7	200.69	412.35	49	591.65	3516.90	461.31	84.63
Pooled Data	236.83	451.67	330	946.62	12097.50	473.59	83.53
Sta. Arith Avg.	232.78	454.40					

Table 4.1. (continued). Summary results of bulk deposition for the Tampa Bay watershed. Trace metals are in units of g ha^{-1} yr^{-1}; nutrients are in units of kg ha^{-1} yr^{-1}. Data censored for bird debris and other obvious contamination.

Param-Sta	Median	Mean	n	Stddev	Max	75%	25%
Nitrate-Nitrite Nitrogen							
1	2.48	3.28	51	3.30	19.86	4.33	1.31
2	1.70	2.74	52	3.31	22.30	3.82	0.87
3	1.59	2.50	48	2.48	12.87	2.92	0.97
4	1.77	3.77	44	5.36	26.94	3.98	1.22
5	1.54	2.83	42	3.59	17.66	2.85	0.69
6	1.93	3.02	43	3.19	14.44	3.84	0.98
7	1.75	3.52	47	4.95	30.21	4.58	0.81
Pooled Data	1.84	3.09	327	3.80	30.20	3.84	0.97
Sta. Arith Avg.	1.82	3.08					
Ammonium-Nitrogen							
1	0.83	1.49	51	1.89	9.56	1.98	0.23
2	0.71	1.28	52	1.84	9.43	1.36	0.23
3	1.13	1.78	48	1.86	9.84	2.53	0.60
4	1.56	2.58	44	2.55	9.70	3.91	0.69
5	1.93	3.30	42	4.05	16.97	2.71	0.60
6	1.98	2.55	43	2.10	9.38	3.45	0.88
7	0.90	2.24	47	3.92	24.00	2.44	0.30
Pooled Data	1.15	2.12	327	2.76	24.00	2.67	0.41
Sta. Arith Avg.	1.29	2.17					
Inorganic Nitrogen							
1	3.49	4.77	51	4.56	23.40	6.01	1.85
2	2.60	4.02	52	4.91	31.70	5.13	1.29
3	2.78	4.28	48	4.00	17.50	5.26	1.72
4	3.47	6.36	44	7.36	34.00	7.45	1.91
5	4.16	6.13	42	6.41	24.20	7.86	1.66
6	4.26	5.57	43	4.75	19.70	8.08	2.05
7	2.60	5.75	47	7.28	33.10	7.10	1.06
Pooled Data	3.27	5.21	327	5.69	34.00	6.17	1.66
Sta. Arith Avg.	3.34	5.27					
Total Kjeldahl Nitrogen							
1	2.39	7.33	51	15.85	71.36	5.37	0.79
2	1.84	3.28	52	3.82	19.45	4.48	0.81
3	2.23	3.86	48	6.57	44.97	4.39	1.17
4	3.43	5.17	44	6.51	41.01	6.41	2.07
5	3.06	10.02	42	22.15	118.12	6.44	1.66
6	3.13	4.31	43	5.20	31.86	5.56	0.92
7	2.10	4.48	47	7.99	49.66	4.97	0.49
Pooled Data	2.58	5.42	327	11.39	118.10	5.36	0.96
Sta. Arith Avg.	2.60	5.49					

Table 4.1. (continued). Summary results of bulk deposition for the Tampa Bay watershed. Trace metals are in units of g ha^{-1} yr^{-1}; nutrients are in units of kg ha^{-1} yr^{-1}. Data censored for bird debris and other obvious contamination.

Param-Sta	Median	Mean	n	Stddev	Max	75%	25%
Organic Nitrogen							
1	1.01	5.89	51	15.03	64.60	2.34	0.25
2	1.13	2.03	52	3.06	18.57	2.23	0.53
3	0.92	2.11	48	5.19	35.13	2.01	0.28
4	1.73	2.64	44	5.21	34.99	2.81	0.74
5	0.94	6.73	42	18.71	101.15	2.94	0.46
6	1.29	1.92	43	3.93	25.75	1.99	0.32
7	0.74	2.28	47	4.20	25.66	3.06	0.21
Pooled Data	1.15	3.35	373	9.71	101.20	2.44	0.37
Sta. Arith Avg.	1.11	3.37					
Total Nitrogen							
1	5.20	10.61	51	16.50	76.46	8.83	2.64
2	4.12	6.02	52	5.97	35.31	8.27	2.28
3	3.66	6.36	48	7.79	49.33	8.29	2.23
4	5.22	8.94	44	9.84	45.43	9.54	3.63
5	5.27	12.85	42	23.01	123.82	12.64	2.39
6	5.01	7.34	43	7.00	35.77	9.47	3.08
7	3.98	7.99	47	10.71	55.27	8.76	1.43
Pooled Data	4.60	8.51	327	12.68	123.80	8.72	2.48
Sta. Arith Avg.	4.63	8.59					
Total Phosphorous							
1	0.32	0.89	51	1.50	8.55	0.98	0.23
2	0.41	0.58	52	0.55	2.48	0.78	0.16
3	0.32	0.52	48	0.76	5.24	0.58	0.16
4	0.53	0.64	44	0.49	2.39	0.87	0.30
5	0.99	1.76	42	2.31	10.02	1.93	0.46
6	0.78	1.31	43	1.75	10.39	1.45	0.43
7	0.51	0.83	47	1.32	8.05	0.87	0.23
Pooled Data	0.51	0.91	327	1.40	10.40	1.01	0.23
Sta. Arith Avg.	0.55	0.93					

The annualized weekly loadings by station for four metals are further illustrated in **Figure 4.2** and significant differences (Kruskal-Wallis analysis of variance on ranks) by station were noted for lead and zinc ($p<0.001$), copper ($p<0.01$), and aluminum ($p<0.05$). The results of pairwise multiple comparisons (Dunn's method) appear in **Table 4.2**, although the comparisons did not detect station differences in weekly loadings for aluminum. As aluminum concentrations are used to indicate the soils component of deposition, it is clear that aluminum deposition (and therefore suspended and redeposited soils) are more uniform over the watershed than are deposition of other metals. Variations in metals across the watershed can therefore be linked to site- or area-specific anthropogenic activities other than soil disturbance.

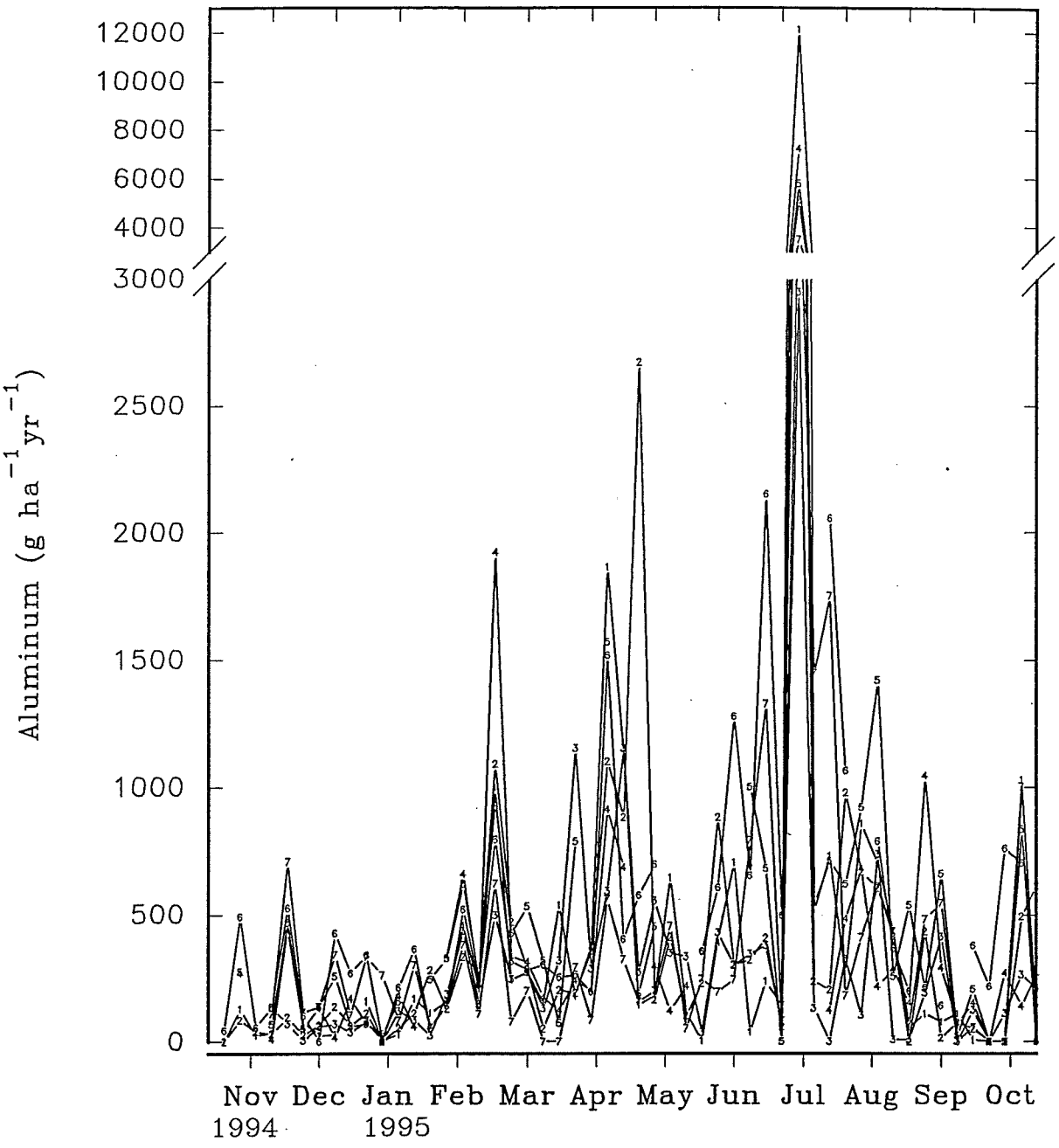

Figure 4.1. Annualized weekly loadings of aluminum (bulk deposition) over time.

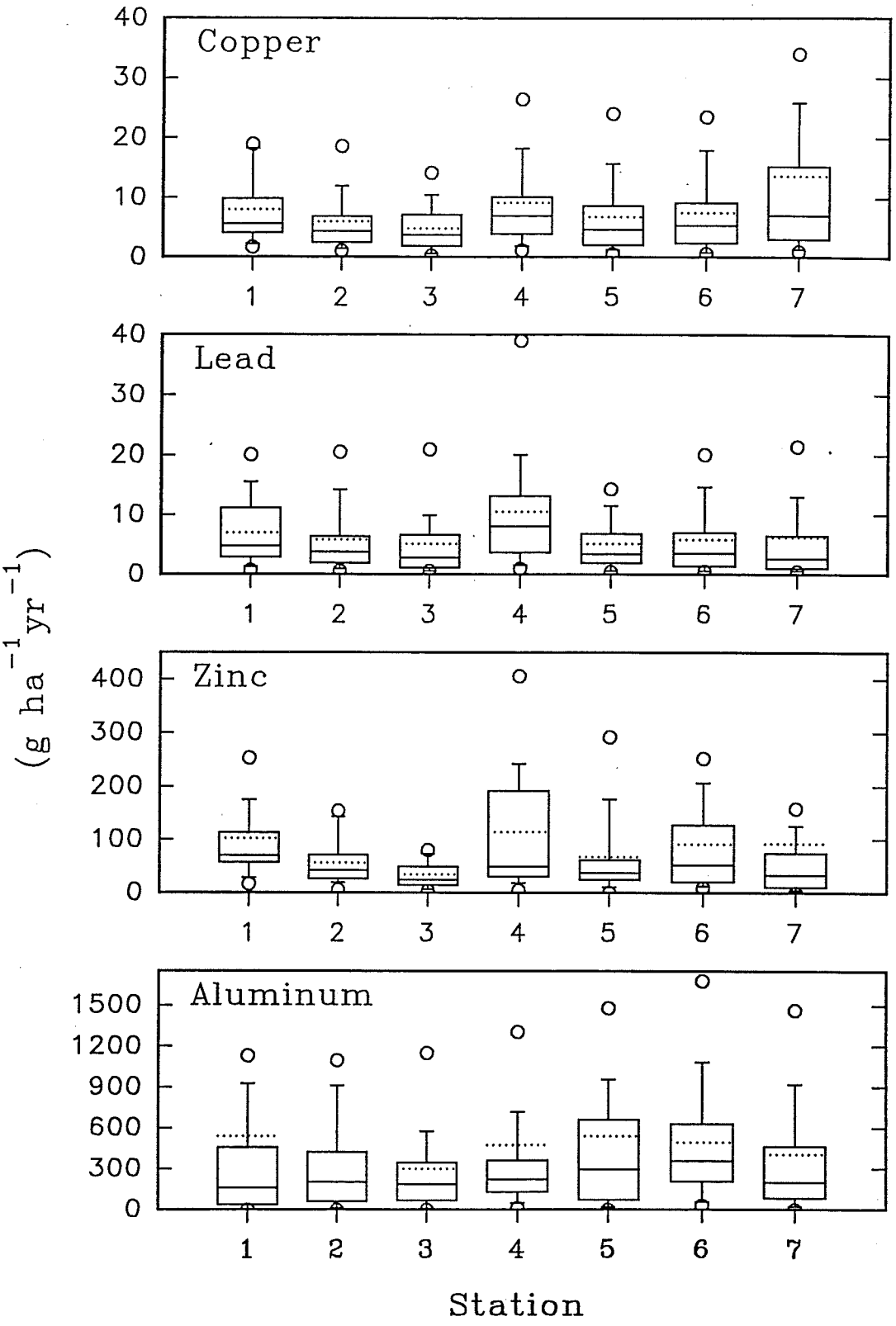

Figure 4.2. Distribution of annualized weekly loadings of metals by station. Solid lines represent 25th, 50th, and 75th percentiles. Dotted lines are mean loadings. Capped bars represent 10th and 90th percentiles, and open circles represent 5th and 95th percentiles.

Table 4.2. Results of pairwise multiple comparisons (Dunn's method) of ranks by station. (* - $P < 0.05$).

COPPER							
Stations	1	2	3	4	5	6	7
1	-						
2		-					
3			-	*			*
4				-			
5					-		
6						-	
7							-
LEAD							
Stations	1	2	3	4	5	6	7
1	-						
2		-					
3			-	*			
4				-			*
5					-		
6						-	
7							-
ZINC							
Stations	1	2	3	4	5	6	7
1	-	*	*		*		*
2		-					
3			-	*		*	
4				-			
5					-		
6						-	
7							-

Station 3, in the northern and least urbanized portion of the watershed, consistently recorded among the lowest metals loadings of all stations. Aluminum values were low, as well, indicating a relative absence of cultivation, construction, or other soil disturbances which could permit wind induced entrainment of local terrestrial materials into the atmosphere. Station 6 and 5, on the other hand, had higher aluminum values, consistent with observed land uses in those regions. Surprisingly, Station 7, although soils deposition was presumed based on pesticide transport during at least a portion of the year (See Pesticides, below), was not consistently high in aluminum deposition.

Another anomaly at Station 7 was the comparatively high copper loads at that station. Operations of Lake Manatee as a potable water supply include application of copper for control of taste- and odor-producing algae. Application periods of copper during the study were from April 18, 1995 through August 22, 1995 (personal communication, Mr. Mark Simpson, Water Quality Supervisor, Manatee County Public Services Division), and did **not** include the week

in which the anomalously high value of over 180 g ha^{-1} yr^{-1} was recorded. Average annualized depositions were 12.15 g ha^{-1} yr^{-1} during the application periods and 8.66 g ha^{-1} yr^{-1} during the reminder of the year. The difference, however, cannot be attributed to copper application in Lake Manatee alone. Comparable seasonal variations in copper loadings were observed at all other stations, presumably in areas where copper was not being applied.

Each week, the three highest loadings of copper, lead, and zinc always included Stations 1 and 4. These stations were located in the most urbanized regions of the watershed and the higher depositions are consistent with the urban:rural variations reported in other references and summarized in Dixon (1996; **Appendix A**). In addition, Spearman Rank Correlation of the various metals at a given station with aluminum (as an indicator of terrestrial origin) revealed that significant relationships did exist for all, with the exception of lead at Stations 1 and 4, and zinc at Station 1. In these three instances, metals deposition is clearly **not** linked to the deposition of previously suspended soils but originates with some other, presumably anthropogenic, source.

The variation in metal loadings among stations clearly show that the development and use of a single loading value for a particular metal is an approximation for the Tampa Bay watershed, and probably for water surfaces of Tampa Bay as well. While annual aluminum loads range by a factor of 1.8 between highest and lowest stations during the MML study, lead, copper, and zinc range by factors of 2.0, 2.8, and 3.3. In particular, depositions in urban settings may be more representative of loads to the northern portion of the Bay.

4.3. Nutrients

Nutrient data were also skewed (**Appendix D, Figures D5** through **D8**), including several weekly loads that were notably high. Again it is difficult to separate potentially contaminated samples from true depositions, except to state that the presence of the higher values was not correlated with the relative assessment of bird debris or other observable contaminants. There are no objective criteria for removal of the higher points from the data set, and so they were included in the following analyses.

Summarized weekly distribution of nutrient loads appear in **Figures 4.3** and **4.4**, and include both analytical and computed parameters. Of all the nutrients, the typical weekly loads of total phosphorus and ammonium nitrogen were the only parameters which varied ($p < 0.001$) among stations. Phosphorus loads were higher at the stations in the eastern portion of the watershed (Station 5 and 6), consistent the terrestrial influences and mining operations centered in that region. Weekly loads of ammonium-nitrogen were highest at Stations 5, 4, and 6, and, as ammonium deposition is reported to reflect local influences (Lovett, 1994), may indicate contributions from the dairy near Station 4, and agricultural activities near Stations 5 and 6.

No station to station differences in **weekly** deposition were noted for nitrate-nitrite-nitrogen, total Kjeldahl nitrogen, inorganic nitrogen, or organic nitrogen, despite wide ranges in either mean or median annual loadings. Annualized weekly loadings (means) for the parameters with no statistically significant differences between stations ranged between 2.50 to 3.77 kg ha^{-1} yr^{-1} for nitrate-nitrite-nitrogen, 4.02 to 6.36 kg ha^{-1} yr^{-1} for inorganic nitrogen, 3.28 to 10.02 kg ha^{-1} yr^{-1} for total Kjeldahl nitrogen, 1.92 to 6.73 kg ha^{-1} yr^{-1} for organic nitrogen and 6.02 to 12.85 kg ha^{-1} yr^{-1} for total nitrogen.

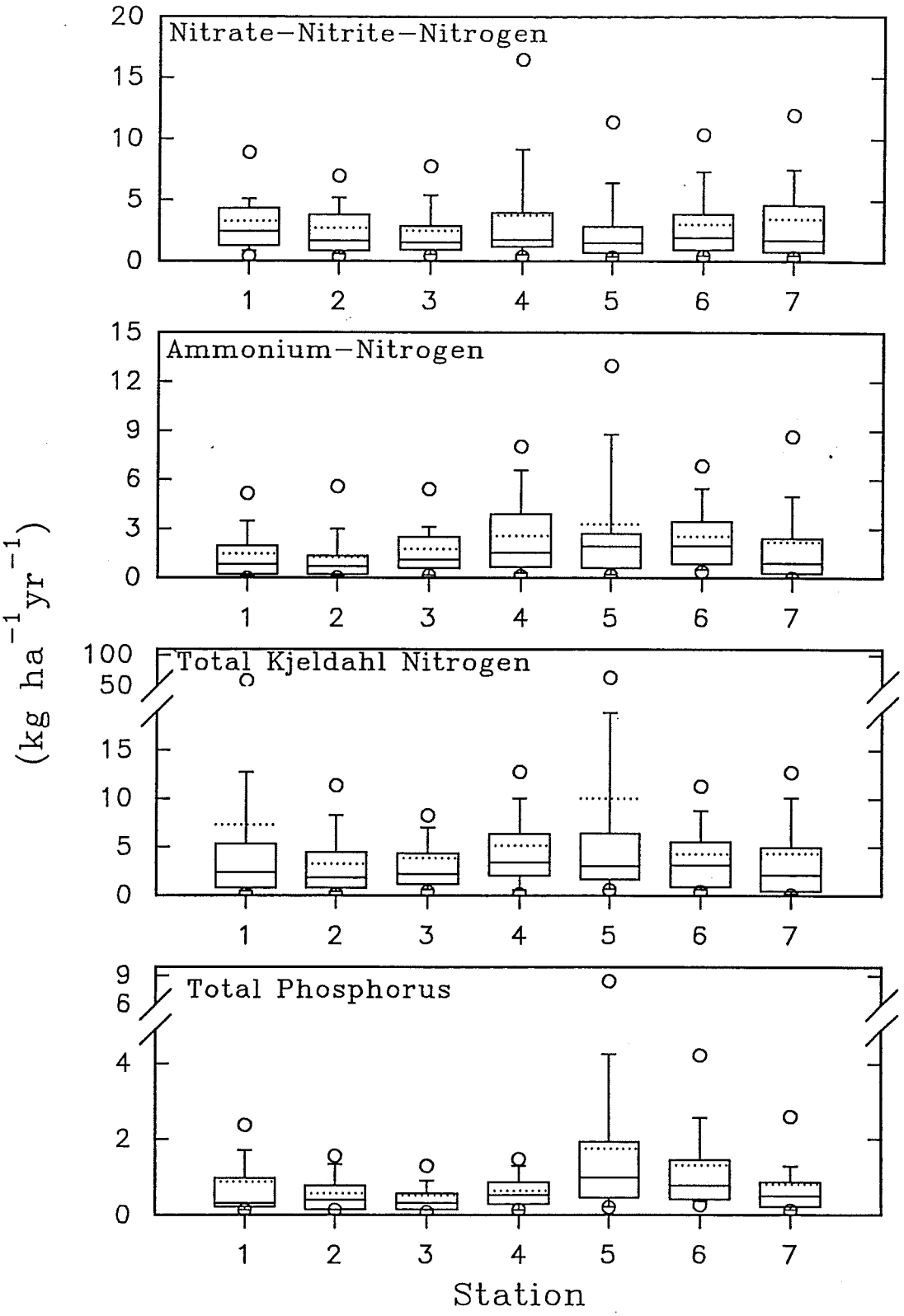

Figure 4.3. Distribution of annualized weekly loadings of nutrients by station. Solid lines represent 25th, 50th, and 75th percentiles. Dotted lines are mean loadings. Capped bars represent 10th and 90th percentiles, and open circles represent 5th and 95th percentiles.

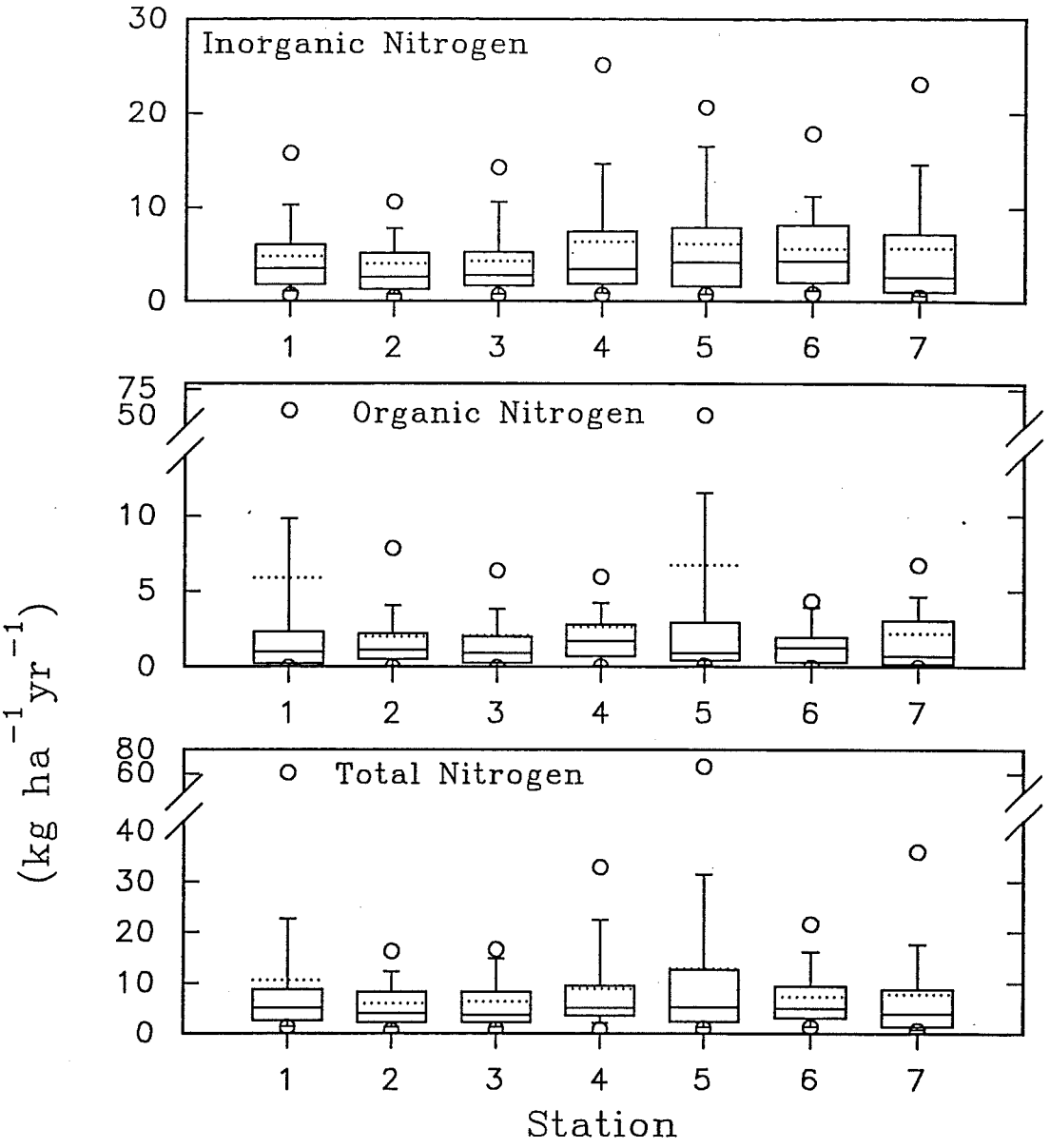

Figure 4.4. Distribution of annualized weekly loadings of calculated nutrient parameters by station. Solid lines represent 25th, 50th, and 75th percentiles. Dotted lines are mean loadings. Capped bars represent 10th and 90th percentiles, and open circles represent 5th and 95th percentiles.

As weekly loadings at all stations were very episodic, and as annual loads among stations with no significant differences in weekly loads varied by a factor of three at times, it was apparent that the weekly variation may well obscure any consistent spatial patterns. Weekly data of selected nutrient parameters were transformed to the difference between the station value and the weekly mean of all available stations. Station data were then tested (Student's t) for significant difference from 0.00, (*i.e.* was weekly loading at a station consistently different from the mean loading at all stations?).

For nitrate-nitrite-nitrogen, results indicated that weekly loadings at Station 3, in the northern portion of the watershed, were significantly different from and **lower** than the mean of all stations, with the remaining stations in more urbanized regions weighting the weekly mean toward higher loadings of nitrate-nitrite-nitrogen. The stations at which weekly loadings averaged higher than the mean, although not at significant levels, were in the central and southern portions of the study area (Stations 1, 4, 6, and 7). The implication is that the localized variation in nitrate in bulk deposition is not due to sources to the north of the watershed. As nitrate-nitrite-nitrogen deposition at Station 3 was 2.50 kg ha^{-1} yr^{-1}, and the highest value observed (at Station 4) was 3.77 kg ha^{-1} yr^{-1}, it is also apparent that "background" levels of nitrate-nitrite-nitrogen may exceed within-watershed variations.

For total nitrogen, total Kjeldahl nitrogen, and organic nitrogen, weekly loads at Station 2 were significantly lower than the watershed means. For inorganic nitrogen, both Stations 2 and 3 had weekly loads significantly lower than the weekly means over the entire watershed. Again, Stations 2 and 3 are to the north and northwest within the watershed. Sources in the central and southern portions of the watershed apparently influence localized variation in inorganic nitrogen loadings, but the substantial levels at all sites exceed the range of values between stations.

For ammonia, total Kjeldahl nitrogen, organic nitrogen, and total nitrogen, general spatial patterns were similar, but the stations with the highest values of these parameters were two to three times greater than the lowest values at Station 2. For these nitrogen species, localized activities or sources to the south and west can be said to be the dominant factor in depositional loads.

4.4. Seasonal Distributions

Seasonal patterns of increasing loads with increasing rainfall were present in all nutrient and metal parameters, generally illustrated in **Figure 4.5** for nitrate-nitrite-nitrogen and rainfall (as the mean of all stations for the week). Examination of the various weekly parameter loads as a function of rainfall amounts indicate significant ($p < 0.001$) regressions for all, illustrated for nutrient parameters at all seven stations in **Figure 4.6** (Much of the relationship of phosphorus loads with rainfall, however, appears due to be an artifact of using one half of the detection limit for computation of loads.) The relationship of parameter loadings with rainfall is further indicated by a two way analysis of variance on ranks in which calendar quarter as a treatment was significant ($p < 0.05$) for all parameters with the exception of ammonium-nitrogen. Quarter and rainfall obviously covary in Florida, with the dominant wet season contained within the summer and early fall months.

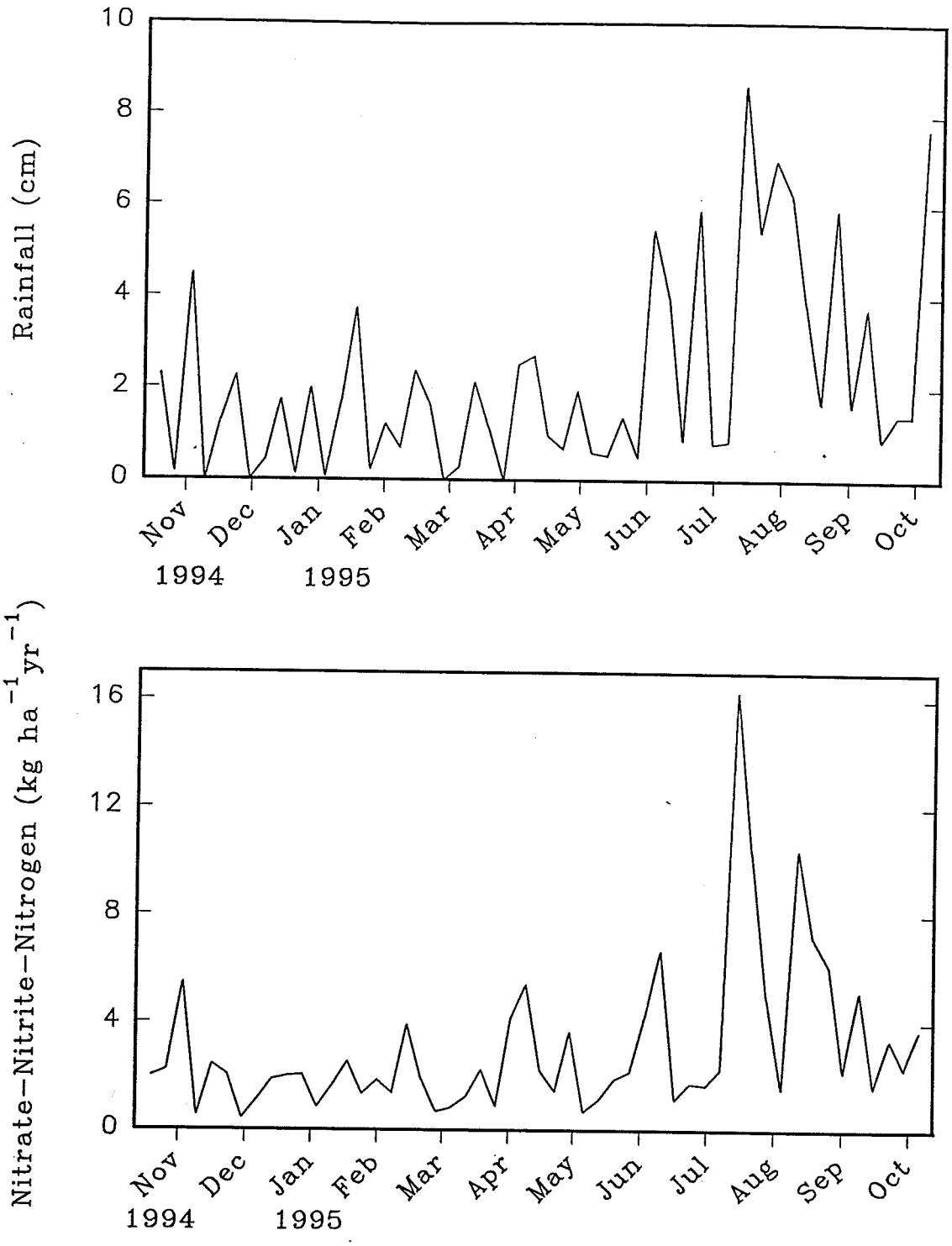

Figure 4.5. Generalized seasonal patterns of rainfall and nitrate-nitrite-nitrogen loading (as watershed averages) over the course of the bulk deposition study.

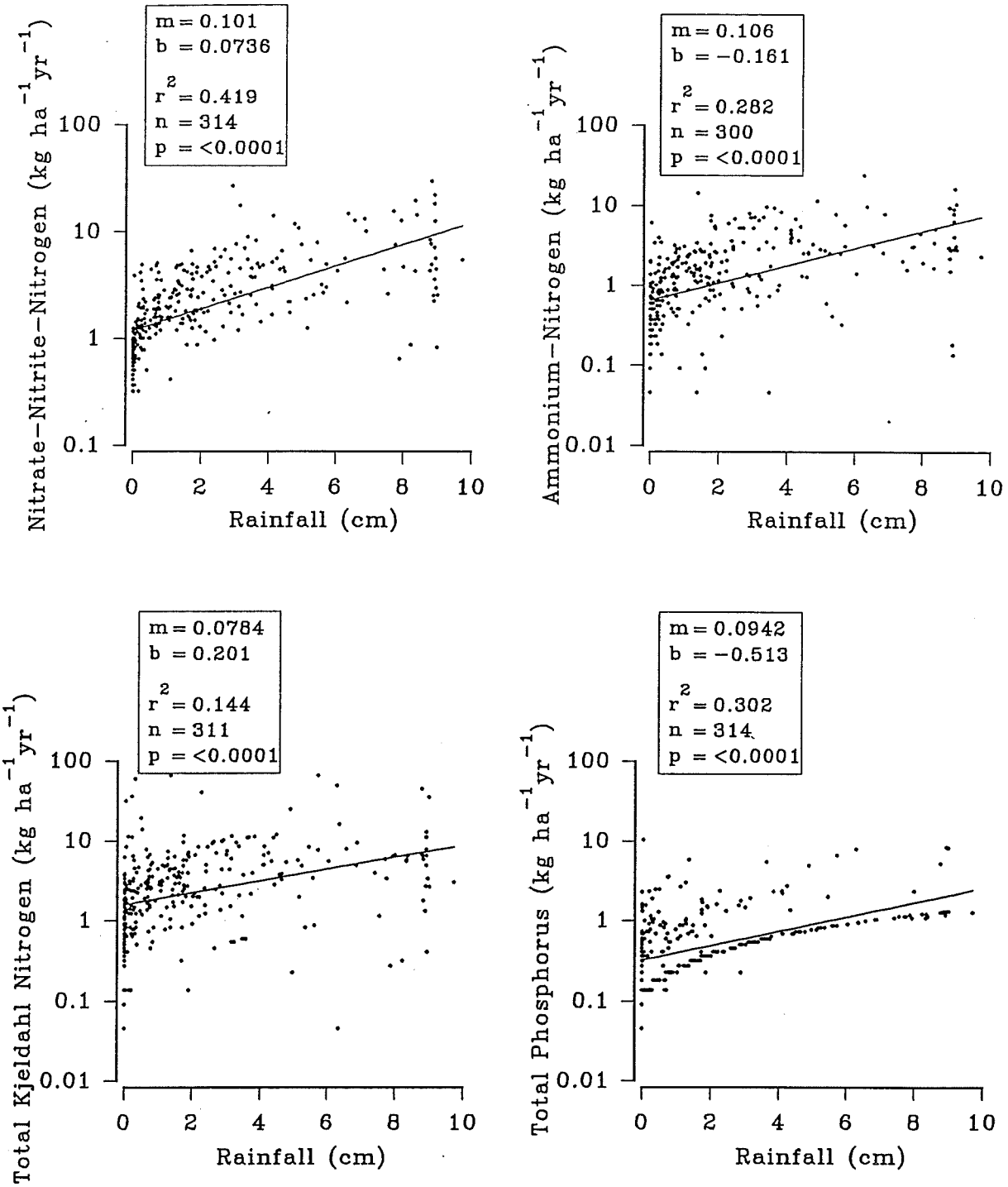

Figure 4.6. Regression of annualized weekly nutrient loading as a function of rainfall, all stations pooled.

Individual station data is comparable in appearance, although intercepts (background loads in absence of rainfall) and slopes (increase in loads with rainfall) vary among stations. Illustrated in **Figure 4.7** for nitrate-nitrite-nitrogen, Station 1 has by far the highest background levels of NO_{2+3}-N, followed by Station 4 and 6. Those stations in the south and southwestern portions of the watershed (Stations 4, 5, 6, and 7) produce higher loadings of nitrate-nitrite-nitrogen for a given amount of rainfall (higher slope) than do the remaining stations.

Table 4.3 summarizes quarterly deposition totals (according to quarters as defined by NADP/NTN) and underlines the importance of conducting deposition studies over a minimum period of at least a year. Metals depositions during the MML project varied by factors of approximately two or greater between quarters, while nutrient quarterly loads varied by factors of 1.2 up to 3.3. Links of loadings to rainfall amounts (**Figures 4.6** and **4.7**, above) and interannual variations in rainfall add further uncertainty to assessments drawn from the measurement of deposition during a single year.

Table 4.3. Mean annualized loadings by quarter. Quarter 1 = Months 12, 1, 2; Quarter 2 = 3, 4, 5; Quarter 3 = 6, 7, 8; Quarter 4 = 9, 10, 11. Metals loadings in g ha^{-1} yr^{-1}. Nutrient loadings in kg ha^{-1} yr^{-1}.

Quarter	Copper	Lead	Zinc	Aluminum	Rainfall (cm)
1	4.33	4.17	55.1	267.5	16.7
2	8.17	7.50	70.8	459.9	15.8
3	10.44	7.93	121.3	890.0	57.2
4	9.34	6.63	68.7	173.5	23.7

Quarter	Total Kjeldahl Nitrogen	Nitrate-Nitrite-Nitrogen	Ammonium Ammonium Nitrogen	Total Phosphorus	Total Nitrogen	Organic Nitrogen
1	4.94	1.78	1.42	0.67	6.72	3.62
2	5.39	2.23	2.32	0.80	7.62	3.10
3	6.18	5.86	2.64	1.15	12.04	3.55
4	5.21	2.53	2.17	1.05	7.74	3.08

4.5. Dryfall deposition

The **lower bounds** of dry deposition, **the dryfall collected by MML samplers**, was estimated by totaling the loads received during weeks with no rainfall and extrapolating this rate to the entire year (**Table 4.4**). These values undoubtedly underestimate total dry deposition that occurs within the watershed, as important gaseous species (nitric acid and nitrogen dioxide) are not thought to be well collected by the apparatus. Estimates for the gaseous species are included when watershed loadings are considered (Section 4.12).

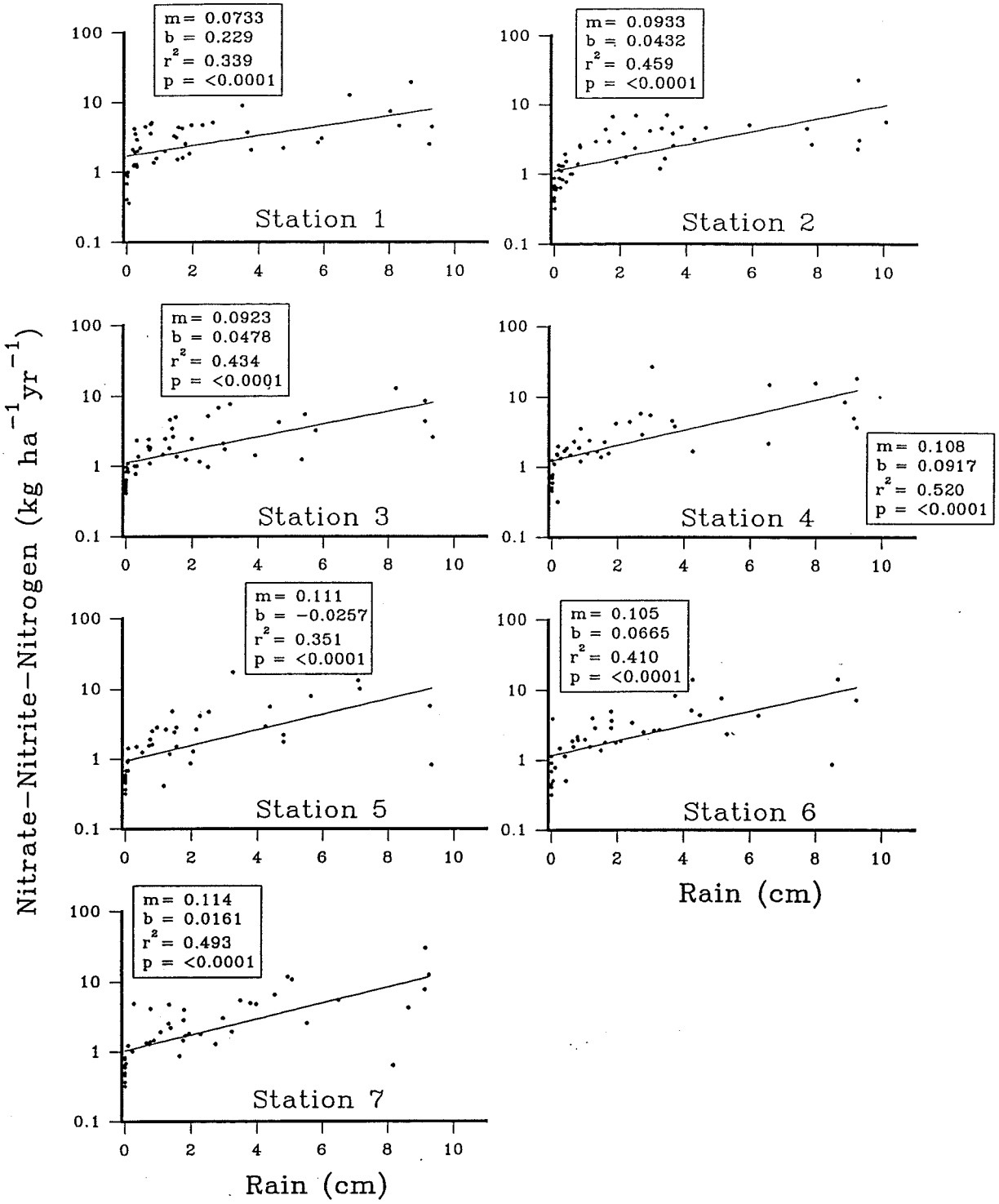

Figure 4.7. Regressions of annualized weekly nitrate-nitrite-nitrogen loading as a function of rainfall, by individual station.

Table 4.4. Comparison of deposition rates during six to eight weeks when no rainfall was received, and over the entire project. Metals units are in g ha^{-1} yr^{-1}, while nutrients are in kg ha^{-1} yr^{-1}.

	Annualized Deposition Rates		Dry as
	Dry	Bulk	Percentage of Bulk (%)
Copper	4.11	7.98	52
Lead	3.74	6.54	57
Zinc	20.40	79.70	26
Aluminum	178.10	453.10	39
Nitrate-nitrite-nitrogen	0.61	3.08	20
Ammonium-nitrogen	0.40	2.17	18
Inorganic Nitrogen	1.01	5.25	19
Total Kjeldahl nitrogen	1.77	5.48	32
Organic nitrogen	0.79	3.36	24
Total nitrogen	1.79	8.59	21
Total Phosphorus	0.44	0.93	47

A total of five to eight weekly values were available for each of the seven MML stations. This calculation presumes that particulate capture efficiencies are equivalent to rainfall capture characteristics, and that dryfall loading rates are comparable over the entire year. Values were then compared with the project means. For the metals copper, lead, zinc, and aluminum, estimated dryfall was 52%, 57%, 26%, and 39% of total depositional rates, respectively. For nutrients, dryfall formed a slightly lower portion of the total, with inorganic species approximately 20% of the total (20% for nitrate-nitrite-nitrogen, 18% for ammonium-nitrogen), total Kjeldahl nitrogen near 32%, and organic nitrogen near 24%. Total nitrogen averaged about 21%, with total phosphorus dry deposition near 47% of total loading rates. These estimates fall within the values of dry deposition determined through a variety of methods throughout the U.S. (Lovett, 1994), in which NO_3^- dry deposition accounted for between 25-70% of totals, and NH_4^+ dry deposition consisted of 2-33% of totals.

4.6. Censored Data Protocol

Table 4.5 compares the measures of central tendency (mean and median) between loads determined by either using one-half the method detection limit or zero for calculations. The differences are minimal except for those parameters, such as lead or phosphorus, in which much of the data consisted of values less than the method detection limit. Particularly for nitrogen, therefore, protocols for processing data below the detection limit do not materially effect the resulting annual loads.

Table 4.5. Comparison of mean and median loads using ½ the method detection limit or zero for calculation with concentration data less than the method detection limit.

Param-Sta	Median <MDL=½ MDL	Median <MDL = 0	Mean <MDL=½ MDL	Mean <MDL= 0
Copper				
1	5.61	5.61	7.97	7.79
2	4.37	4.28	5.95	5.82
3	3.72	3.72	4.82	4.63
4	6.92	6.92	9.18	9.16
5	4.64	4.64	6.78	6.64
6	5.36	5.36	7.48	7.33
7	7.04	7.04	13.87	13.78
Lead				
1	4.78	4.28	7.00	6.31
2	3.84	3.22	5.82	5.23
3	2.85	0.00	5.14	4.03
4	8.07	7.52	10.56	9.93
5	3.45	3.08	5.17	4.29
6	3.52	2.44	5.87	4.99
7	2.62	0.00	6.25	4.75
Zinc				
1	70.53	70.53	101.90	101.90
2	42.58	42.58	56.67	56.67
3	24.37	24.37	34.26	34.26
4	49.59	49.59	113.80	113.79
5	37.77	37.77	67.65	67.65
6	52.65	52.65	91.40	91.40
7	33.89	33.89	92.99	92.98
Aluminum				
1	159.89	159.89	539.16	538.68
2	203.89	203.89	421.70	421.70
3	186.72	186.72	300.90	300.39
4	222.19	222.19	472.74	472.74
5	296.93	296.93	540.62	540.62
6	359.07	359.07	493.36	493.36
7	200.69	200.69	412.35	412.35
Nitrate-Nitrite Nitrogen				
1	2.48	2.48	3.28	3.28
2	1.70	1.70	2.74	2.74
3	1.59	1.59	2.50	2.50
4	1.77	1.77	3.77	3.77
5	1.54	1.54	2.83	2.83
6	1.93	1.93	3.02	3.02
7	1.75	1.75	3.52	3.52

Table 4.5. (continued). Comparison of mean and median loads using ½ the method detection limit or zero for calculation with concentration data less than the method detection limit.

Param-Sta	Median		Mean	
	<MDL=½ MDL	<MDL = 0	<MDL=½ MDL	<MDL= 0
Ammonium Nitrogen				
1	0.83	0.83	1.49	1.48
2	0.71	0.71	1.28	1.27
3	1.13	1.13	1.78	1.78
4	1.56	1.56	2.58	2.58
5	1.93	1.93	3.30	3.30
6	1.98	1.98	2.55	2.55
7	0.90	0.90	2.24	2.24
Inorganic Nitrogen				
1	3.49	3.49	4.77	4.76
2	2.60	2.58	4.02	4.01
3	2.78	2.79	4.28	4.28
4	3.47	3.47	6.36	6.36
5	4.16	4.16	6.13	6.13
6	4.26	4.28	5.57	5.57
7	2.60	2.60	5.75	5.75
Total Kjeldahl Nitrogen				
1	2.39	2.39	7.33	7.27
2	1.84	1.82	3.28	3.20
3	2.23	2.10	3.86	3.85
4	3.43	3.43	5.17	5.12
5	3.04	3.04	10.02	10.02
6	3.13	3.13	4.31	4.29
7	2.10	2.10	4.48	4.43
Organic Nitrogen				
1	1.01	0.92	5.89	5.84
2	1.13	1.13	2.03	1.99
3	0.92	0.92	2.11	2.11
4	1.73	1.73	2.64	2.63
5	0.94	0.94	6.72	6.72
6	1.29	1.29	1.92	1.91
7	0.74	0.74	2.28	2.27
Total Nitrogen				
1	5.20	5.20	10.61	10.55
2	4.12	3.94	6.02	5.94
3	3.66	3.66	6.36	6.34
4	5.22	5.22	8.94	8.90
5	5.27	5.26	12.85	12.85
6	5.01	5.01	7.34	7.21
7	3.98	3.98	7.99	7.94

Table 4.5. (continued). Comparison of mean and median loads using ½ the method detection limit or zero for calculation with concentration data less than the method detection limit.

Param-Sta	Median		Mean	
	<MDL=½ MDL	<MDL = 0	<MDL=½ MDL	<MDL= 0
Total Phosphorus				
1	0.32	0.00	0.89	0.59
2	0.41	0.00	0.58	0.23
3	0.32	0.00	0.52	0.20
4	0.53	0.00	0.64	0.30
5	0.99	0.87	1.76	1.61
6	0.78	0.51	1.31	1.09
7	0.51	0.00	0.83	0.52

4.7. Correlation with Other Meteorological Parameters

Wind data (speed and direction) were available for several sites from various County air monitoring programs. Where county sites were representative of the MML deposition stations, regression analyses were performed which incorporated weekly average wind speed, direction, rainfall, temperature, and loadings of various parameters. Average wind directions were transformed in a variety of ways, but little of significance besides correlation with rainfall amounts was observed. Since hourly ambient air concentrations at selected county sites did demonstrate dependence on hourly wind direction (Dixon, 1996; **Appendix A**), a lack of significance between deposition and average wind direction was attributed to the variable wind directions over a weekly period, and lack of information on rainfall characteristics and wind direction during rainfall events.

4.8. Replicate Collections

Following the 52 weeks of the regularly scheduled project, samplers were deployed in pairs (*i.e.* either two nutrient or two metals collections at the same site) for two one week periods. A total of seven pairs each of nutrients and metals were collected to evaluate replicate sample precision. Differences between replicate analytical values averaged 0.4 $\mu g\ L^{-1}$ for copper, 0.4 $\mu g\ L^{-1}$ for lead, 5.4 $\mu g\ L^{-1}$ for zinc, and 22.5 $\mu g\ L^{-1}$ for aluminum, in contrast to respective detection limits of 0.2, 0.5, 0.2, and 2 $\mu g\ L^{-1}$. For nutrients, differences between replicate samples averaged 0.11, 0.108, 0.043, and 0.23 mg L^{-1} for total phosphorus, nitrate-nitrite-nitrogen, ammonium-nitrogen, and total Kjeldahl nitrogen, respectively. MML sampling precisions for bulk deposition of nitrate-nitrite-nitrogen and ammonium nitrogen were equivalent to NADP/NTN precisions obtained from a one year intercomparison site maintained at the Verna Wellfield.

4.9. Comparison with Other Programs

4.9.1. National Atmospheric deposition Program

The National Atmospheric deposition Network/National Trend Network (NADP/NTN) operates 200 sites nationwide. Sites are required to be located in rural areas (up to 40 km from urban

centers), presently emphasize the analysis of wet deposition of major ions alone (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, specific conductance, and pH), and do not typically measure trace metals or organically bound nutrients. The NADP/NTN site nearest Tampa Bay is at the Verna Wellfields in Sarasota County to the south of the study area and has data available from mid-1983 to present (September, 1995).

Collection of weekly integrated nitrate-nitrite-nitrogen and ammonium-nitrogen deposition by the NADP/NTN program is analogous to the MML methods with the exception that NADP/NTN collects wet deposition only, rather than bulk. The phosphorus species analyzed by NADP/NTN is ortho-phosphorus, rather than total phosphorus. Phosphorus results are not typically reported as NADP/NTN considers the presence of phosphorus to indicate non-representative contamination, but are available by special request.

Precipitation quality results obtained from NADP/NTN were converted to elemental concentrations, the data set was censored according to NADP/NTN protocols for valid samples, and weekly deposition rates calculated from rainfall and concentrations and summed (**Table 4.6**). The period available from NADP/NTN included from October 18, 1994 through September 12, 1995, and the MML data set was truncated to match, as well as eliminating MML loads received during weeks with no rainfall. Comparisons with all stations of the MML set employed Kruskal-Wallis analyses of variance, with Dunn's method for pairwise comparisons. More detailed comparisons were conducted with MML Station 7, as it was the closest geographically to the NADP/NTN Verna Wellfield site.

Table 4.6. Comparison of MML bulk deposition rates (only during weeks with rainfall) with the NADP/NTN site wet deposition at Verna Wellfield, Sarasota, FL. Period compared is from October 18, 1994 through September 12, 1995. Units are in kg ha^{-1} $period^{-1}$.

	NADP/NTN Wet Deposition	------MML Bulk Deposition------ All Stations	Station 7
Nitrate-nitrite-nitrogen	2.07	2.04 - 2.96	2.96
Ammonium-nitrogen	1.18	1.17 - 2.39	1.93
Inorganic nitrogen	3.26	3.46 - 4.89	4.89
Total Phosphorus	NA	0.34 - 1.26	0.68
Ortho-phosphate	0.01	NA	NA

NA - Not analyzed

All of the MML stations received higher phosphorus depositions than were measured at the NADP/NTN site. This is not surprising due to the differences in species measured (total phosphorus - MML; reactive or ortho-phosphate - NADP/NTN), and to the dry deposition collected by the MML project. Clearly, the combination of these two factors results in the measurement of substantial loads of phosphorus, in comparison to the wet deposition of reactive phosphorus alone.

deposition of inorganic nitrogen at the NADP/NTN site was the lowest of any of the MML stations, and ranged between 60% and 70% of the bulk deposition collected at Station 7 during the same period, implying that on the order of 30% to 40% of bulk deposition occurred as dryfall. If the relative collection efficiency of the MML collectors is considered, as well however, then dry deposition of inorganic nitrogen may represent 40% to 50% of the total inorganic nitrogen deposition.

Interestingly, variation in weekly loading rates of nitrate-nitrogen at the NADP/NTN sites was greater than the variation observed at four of the MML sites. The variation in weekly loading rates for ammonium-nitrogen at the NADP/NTN site were also within the range of variations noted at MML sites. As the NADP/NTN data are collected under rigorous and nationally accepted quality assurance guidelines and sample validation procedures, this result is indirect confirmation of the validity of MML sample screening and censoring processes.

4.9.2. Southwest Florida Water Management District

During a portion of the MML project year, SWFWMD operated a stormwater loading and removal project at the Tampa offices within approximately 100 m of Station 4, but closer to U.S. 301. Data were collected by SWFWMD on an event basis rather than as weekly composites as in the MML work, and included a total of eight rainfall events between November 1, 1994 and January 24, 1995. Parameters collected under the SWFWMD program that were common to the MML project included rainfall and rainfall concentrations of copper, lead, zinc, ammonia, nitrate-nitrite-nitrogen, organic nitrogen, and total phosphorous. Data from the SWFWMD program were obtained (unpublished data, Dr. Betty Rushton) and compared for reasonableness with the bulk deposition collected by MML during the same time periods. It should be recalled that bulk samples were processed weekly and nitrogen speciation changes could have occurred. Comparisons of individual nitrogen species between the two studies should be used as general guidelines only.

Table 4.7 summarizes the comparisons between the wet and bulk deposition studies at Station 4. Total rainfall amounts were comparable (13.0 cm vs 14.0 cm, or 93%) and do not reflect as much bias from the smaller MML funnels as were estimated using nearby SWFWMD rainfall stations. Nutrient loadings indicated that only 19% of bulk total phosphorus deposition occurred as wetfall. Bulk nitrate-nitrite-nitrogen loads were slightly higher than the wet deposition values, with lesser amounts of ammonium-nitrogen (83%) and organic nitrogen (77%). As mentioned above, the differences in nitrogen could easily reflect species transformations over time as total nitrogen in wet deposition was 95% of the total nitrogen measured in bulk loads. If no correction is made for bias in rainfall collection, little dry deposition of total nitrogen was collected at Station 4 during this short portion of the MML project.

For metals data, lead deposition values agreed well between the two studies, with wet deposition during the period accounting for 97% of the loading determined through bulk deposition measurements. Values of copper and zinc, however, were both approximately an order of magnitude greater in wet deposition than in bulk loads. Precipitation weighted average rainfall concentrations in the SWFWMD project were 2 $\mu g\ L^{-1}$ higher for copper and 15 $\mu g\ L^{-1}$ higher for zinc than were recorded for the MML project. Blanks analyzed for the SWFWMD study ranged from <1 to 6 $\mu g\ L^{-1}$ for copper and <30 $\mu g\ L^{-1}$ for zinc and, if consistent, could

Table 4.7. Comparison of wetfall and bulk deposition results at Station 4. Data represent summed loads over eight individual rainfall events (SWFWMD) and six individual weekly bulk depositions (MML).

Parameter	Units	MML	SWFWMD
Rainfall	cm	13.000	14.000
Nitrate-nitrite-nitrogen	kg ha^{-1} $period^{-1}$	0.333	0.381
Ammonium-nitrogen	kg ha^{-1} $period^{-1}$	0.298	0.249
Organic nitrogen	kg ha^{-1} $period^{-1}$	0.170	0.132
Copper	g ha^{-1} $period^{-1}$	0.309	2.989
Lead	g ha^{-1} $period^{-1}$	0.478	0.464
Zinc	g ha^{-1} $period^{-1}$	2.920	23.84

account for some of the differences observed. The difference for zinc, at least, was within the SWFWMD reported detection limits, and serves to emphasize the variability of trace level analyses.

Additionally, the SWFWMD site was closer to U.S. 301, and dust suspended by vehicle traffic may influence this site more than the MML Station 4. Evidence of this has been reported by SWFWMD (Dr. Rushton, unpublished data), in that levels of copper, lead, and zinc in rainfall (in at least 20 events) increased when the collector was relocated on the property to its present location somewhat nearer U.S. 301. High spatial variability on a fine scale is indicated when near discrete sources. It is uncertain why lead values should agree so closely between the MML and SWFWMD work, while an order of magnitude difference existed for copper and lead.

4.9.3. Florida Atmospheric Mercury Study

The Florida Atmospheric Mercury Study (FAMS), funded by the Florida department of Environmental Regulation (FdeR), Electric Power Research Institute (EPRI), and Florida Power & Light Company (FPL), is designed to address sources of mercury contamination within Florida. This extensive program (analyzing for various forms of mercury, trace metals, and major ions) currently includes a site at Lake Barco (near Gainesville in central Florida), Caryville in the panhandle region, as well as four in southern Florida, south of Lake Okeechobee, and on both east and west coasts. The FAMS project differs from most deposition collection efforts in that sample platforms are approximately 15 meters above grade to avoid site-specific disturbances, and to more accurately reflect background levels of measured parameters. Recently published data from the FAMS project (**Table 4.8**) include bulk deposition rates for five locations throughout Florida (Landing, *et al.*, 1995). Stations are located in regions with a variety of urban and municipal influences, and also include some relatively rural areas.

Collection devices used by the MML project were modelled after and essentially identical to the bulk deposition collectors used by the FAMS project. Major differences were that some portions of the collectors were polyethylene rather than teflon (as mercury was not a analyte in the MML work) and collector height above grade was 3.4 m in Tampa Bay and slightly over 15 m for the

Table 4.8. Comparison of MML bulk deposition rates (pooled means and station maximums) with FAMS bulk deposition rates. LM - Lake Barco; FM - Fort Myers; FS - Fakahatchee Strand; TT - Everglades National Park, Tamiami Trail; EG - Everglades National Park, (Homestead). Units are g ha^{-1} yr^{-1}.

	FAMS (1993-1994)					MML(1994-1995)	
	LB	FM	FS	TT	EG	Mean	Maximum
Aluminum	620	760	640	1060	1480	453	540
Copper	4.30	14.00	10.80	9.50	18.40	7.98	13.7
Lead	4.96	9.74	4.03	6.77	5.30	6.54	10.6
Zinc	53.20	64.80	58.00	58.20	119.20	79.7	113.8

FAMS project. The collector height for the MML project was above NADP siting criteria for wet-only deposition to minimize collection of resuspended materials, but was substantially lower than FAMS project for reduced impact on property owners (and therefore increased access to a variety of sites) and cost control. The rural sites of FAMS, together with a potentially lower component of terrestrial materials at 15 m elevation, should provide a lower bounds for the MML loading values.

Loading rates between the two projects were quite comparable, with the project means for the MML work within the range observed in the FAMS project for copper, lead, and zinc. Individual station means from the Tampa Bay region were also generally within the range of values reported by FAMS, although the maximum loading rate for lead in Tampa Bay did slightly exceed the FAMS maximum lead loading rate seen near Fort Myers. Maximums for copper, zinc, and aluminum were observed near Homestead, with aluminum primarily the result of Saharan dust in a few rain events (Landing, *et al.*, 1995). In addition, the site is located in a region of intensive agriculture (row crops) and potentially in the urban plume of Miami. Influences in Fort Myers, where copper and lead fluxes were noteworthy, include municipal incineration.

Compilation of FAMS and MML bulk loading rates illustrate few consistent spatial patterns for metals deposition, with the exception of aluminum. Variations in the depositional rates of copper, lead and zinc appear primarily linked to site-specific anthropogenic activities. Further, as the Lake Barco site values were lowest for all but lead, that is further evidence that the sources of metal deposition to the Tampa Bay watershed does not originate to the north. This is consistent with the results under the MML work in which the northernmost station also recorded some of the lowest depositional rates.

4.10. Analysis of NADP/NTN Data

The available NADP/NTN data set, from August 1993 to September 1995 was examined for general relationships and temporal trends. Analyses employed both annual and quarterly

depositions calculated by NADP/NTN, as well as weekly loads calculated from valid precipitation quality data and rainfall amounts. Significant correlations between parameters are indicative of a common source, (or sources with equivalent elemental ratios) while poor relationships demonstrate a variety of contributing sources.

In weekly loadings data, all parameters exhibited precipitation scavenging, with loads displaying a tendency to increase with increasing amounts of precipitation. Accordingly, summer loadings of inorganic nitrogen species in particular were 1.5 to 3.0 times greater than depositions during the remaining quarters (**Figure 4.8**), with summer loadings occurring in repeatable annual patterns.

Predictably, sodium and chloride provided an almost linear relationship (r^2 = 0.987, n=232) with weight proportions (0.57:1 for sodium:chloride) clearly indicative of seawater ratios of 0.56:1 (Riley and Chester, 1971) (**Figure 4.9**). Further, the intercept of the relationship is near zero, indicating minimal alternative sources of sodium or of chloride.

The regressions of magnesium, calcium, and sulfate were also significant against chloride (**Figure 4.9**), although with lower r^2 values (r^2 = 0.925, 0.204, and 0.110, n=232, respectively). Calcium and sulfates in precipitation, and to a much lesser extent magnesium, were all enriched over an exclusively seawater source and have additional sources other than seawater aerosols. Calcium and magnesium loadings in excess of that expected from seawater contributions appear in ratios consistent with carbonate composition (Hem, 1970) and undoubtedly reflect some portion of resuspended terrestrial material. In particular, calcium loadings were approximately four times greater than could be provided by seawater aerosols.

Sulfate of seawater origin, based on chloride present in precipitation samples and general oceanic ratios (Riley and Chester, 1971) accounts for only 8% of the total sulfate present in precipitation. Contributions of carbonate soils (based on excess calcium loadings) can account for less than 1% of total sulfate loadings. The relationship of sulfate with chloride (**Figure 4.9**) or sulfate with calcium also displayed a distinct, positive intercept, indicative of background sources in addition to seawater aerosols or terrestrial materials. Reportedly, the vast majority of ambient SO_x results from stationary source fuel combustion, with 70% of national emissions produced by electric utilities (US EPA, 1993).

Regression of nitrate with the other parameters revealed the best agreement between weekly loadings of nitrate and sulfate in wetfall (r^2 = 0.836, n = 232, **Figure 4.10**) and observed linearity implies some measure of a common source. All parameters, however, displayed at least some degree of significant relationship with nitrate, a probable result of many parameters dependence on rainfall and resulting covariance.

Annual loadings were also examined from the period 1984 through 1994, the years with a complete available record. A clear indication of increasing nitrate-nitrogen, ammonium-nitrogen, and inorganic nitrogen with time is apparent (**Figure 4.11** through **4.13**). While a slight increase in annual rainfalls has occurred over the same period, the trend is not significant, loadings do not clearly reflect the extremely low rainfall totals observed in 1989 and 1990, and multiple linear regressions of nitrogen as a function of year and annual rainfalls indicate that inclusion of year as a parameter has the higher significance. Superimposing the population figures (Shermyen, *et al.*, 1990; Pierce, 1995) for Pinellas, Hillsborough, Manatee, and Pasco,

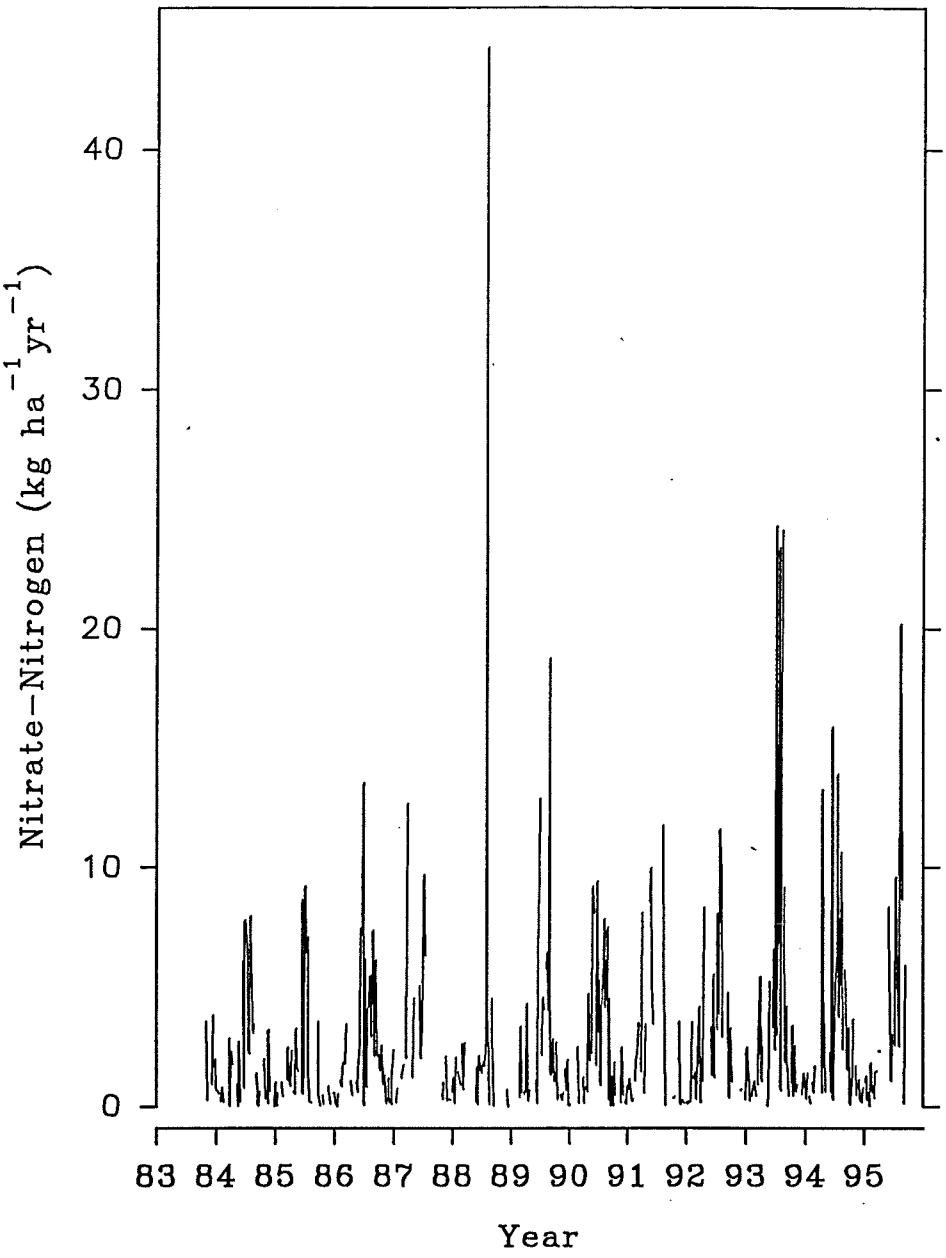

Figure 4.8. Seasonal patterns of nitrate-nitrogen loading in wet-only deposition. Data from the NADP/NTN Verna Wellfield site.

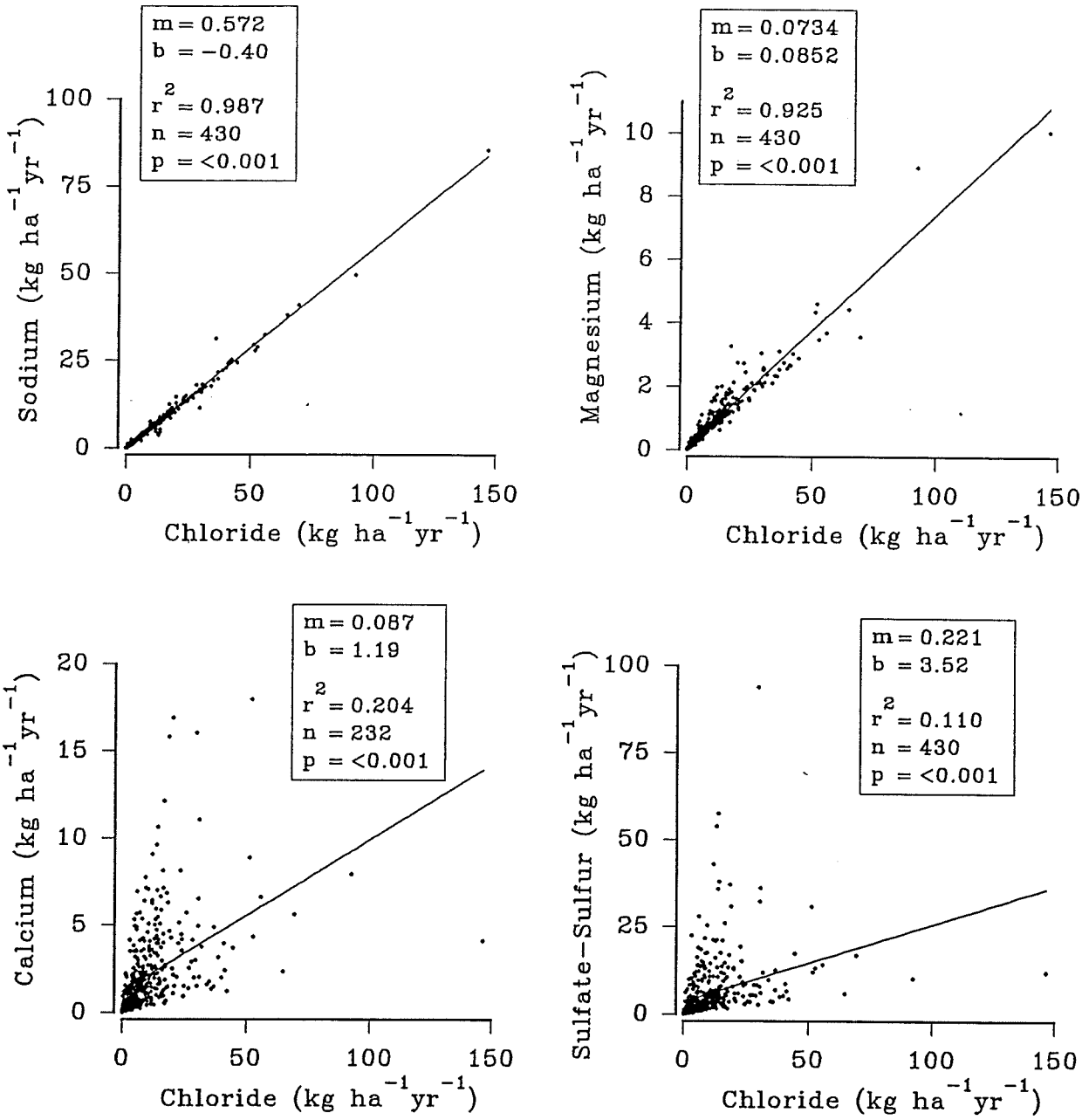

Figure 4.9. Parameter relationships with chloride in NADP/NTN Verna Wellfield data.

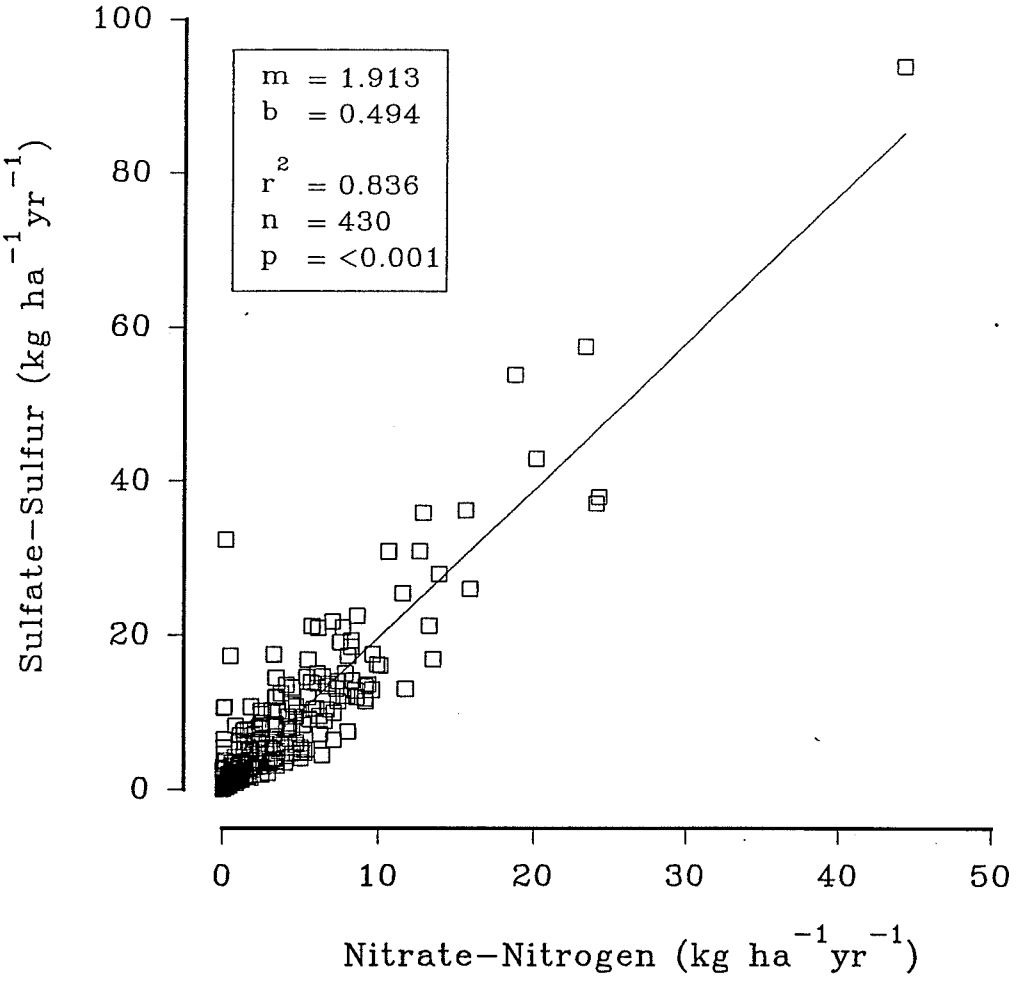

Figure 4.10. Regression of nitrate-nitrogen and sulfate in NADP/NTN Verna Wellfield data.

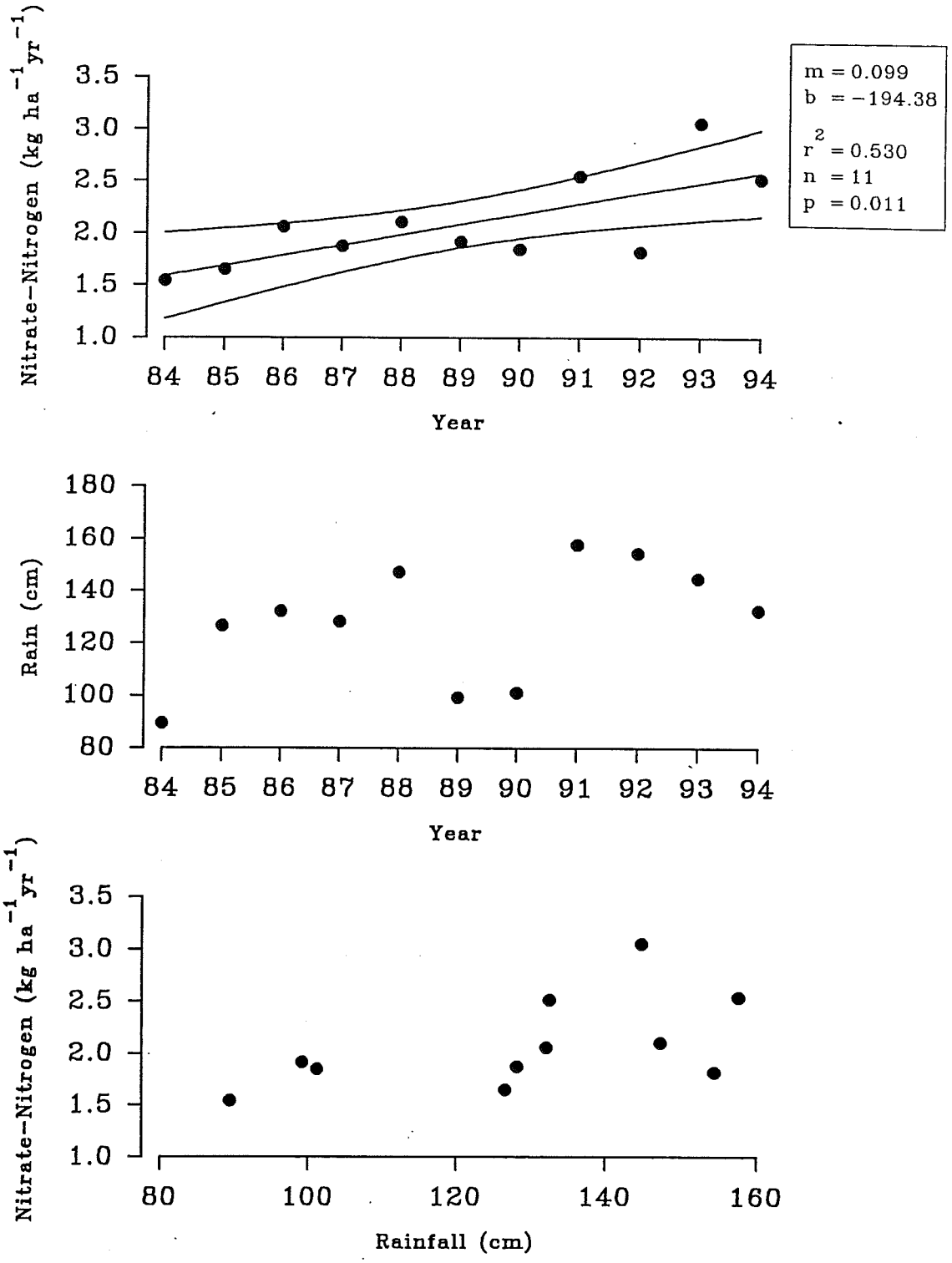

Figure 4.11. Regression of nitrate-nitrogen, rainfall, and year in NADP/NTN Verna Wellfield data. Significant regressions described.

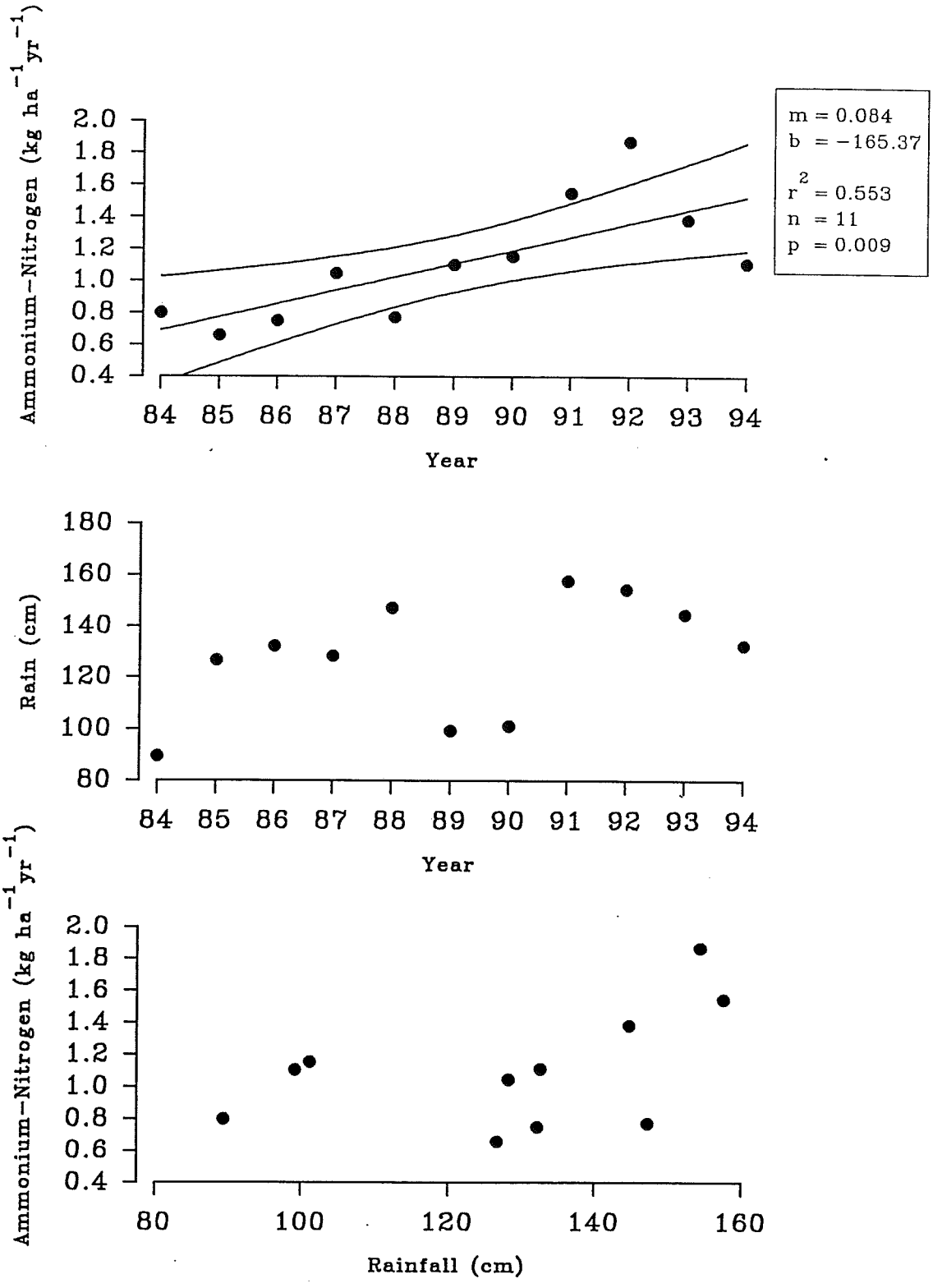

Figure 4.12. Regression of ammonium-nitrogen, rainfall, and year in NADP/NTN Verna Wellfield data. Significant regressions described.

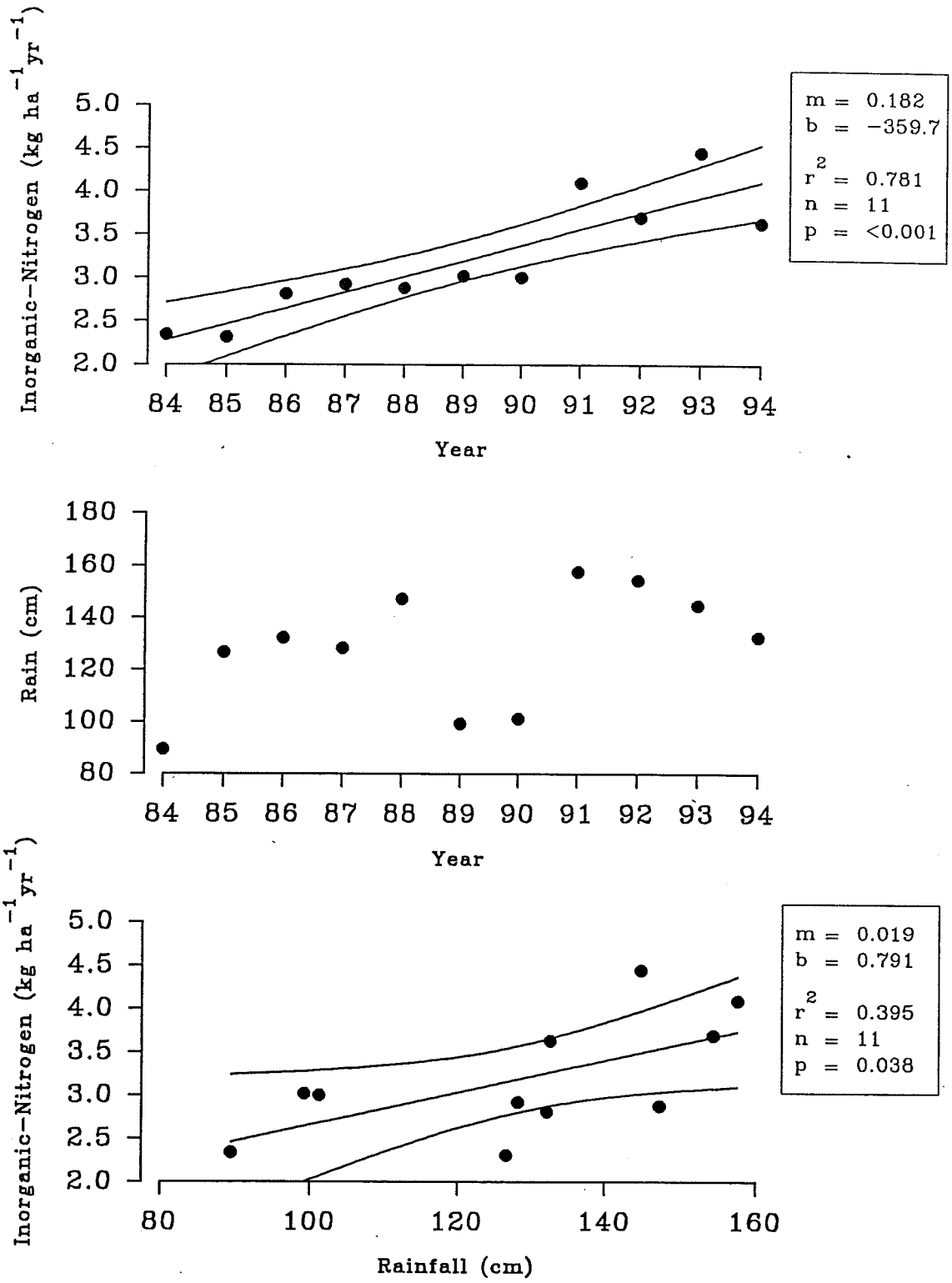

Figure 4.13. Regression of inorganic nitrogen, rainfall, and year in NADP/NTN Verna Wellfield data. Significant regressions described.

the nitrate-nitrogen loads, and the rainfall data on a single time line is quite instructive (**Figure 4.14**), and implies that, in the absence of stricter emissions controls on mobile and stationary sources, loadings of inorganic nitrogen will continue to increase with population growth.

As the summer quarter is responsible for the highest loadings of nitrogen during the year, deposition during the various quarters was examined. For both ammonium and nitrate-nitrogen, the increase with time was most apparent for the summer quarter, with no significant increases in the winter, spring, and fall (**Figure 4.15**). While seasonal patterns of deposition may result both from increased ambient air concentrations and from increased efficiency of scavenging mechanisms during the summer compared to the remaining quarters, the implications remain clear that atmospheric loads of nitrogen are steadily increasing with time.

Additional examination of NADP/NTN weekly loadings of nitrate-nitrogen and ammonium-nitrogen was performed using a 52 week moving average of both nitrogen and of rainfall over the period of record available (**Figure 4.16**). Each point plotted is analogous to the project mean developed for the same parameter under the MML project. While the increasing trend in deposition is still clearly evident, what is instructive is that for nitrate-nitrogen, a variation of 12 weeks in project start date can result in a difference of over 1.0 kg ha^{-1} yr^{-1} in measured annual loads in precipitation. Presumably, variation in bulk deposition can be as great. Variability in ammonium-nitrogen deposition is generally not as great, with potential variations usually near 0.5 kg ha^{-1} yr^{-1}. A regression of the moving average against time indicates that the standard error of the estimate is on the order of 0.35 kg ha^{-1} yr^{-1} for nitrate and 0.24 kg ha^{-1} yr^{-1} for ammonium-nitrogen. The inherent variability in depositional loads as demonstrated for inorganic nitrogen, are strong arguments for continuing any atmospheric deposition program over a minimum number of years.

4.11. Local Trends in NO_x Emissions

A more detailed analysis of NO_x emissions was provided by the Air Resources Management Section of the Florida department of Environmental Protection (Mr. Tom Rogers) for the period 1985 through 1993 (**Figure 4.17**). Data were compiled from a five county area (Hillsborough, Pinellas, Pasco, Polk, and Manatee). Figures for stationary sources were based on Annual Operating Reports, the accuracy of which has improved for the more recent years, as conservatively high estimates from earlier years are replaced with continuous monitoring data of actual emissions. Metropolitan Planning Organization figures, department of Transportation mileage estimates, average composite emission factors at specified speeds, and a variety of adjustments were employed for mobile source estimates. In sum, the estimates of total, point source, and mobile emissions do not demonstrate the same increase with time as either population, or nitrate loadings (**Figure 4.14**), but may not be inconsistent if emissions estimates for earlier years were conservatively high.

4.12. Tampa Bay Loadings - Nutrients

Sources of both toxic contaminants (Frithsen, *et al.*, 1995) and nutrients (Zarbock, *et al.*, 1994) have been the subject of previous work by the TBNEP and each has included estimates of atmospheric contributions to total Bay loadings. Nutrient loading estimates prepared by Zarbock, *et al.*, (1994) considered as atmospheric deposition only direct deposition, *i.e.* that portion falling directly on the estuary surface. Loads were calculated from precipitation volumes and average rainfall concentrations rather than precipitation weighted means which may

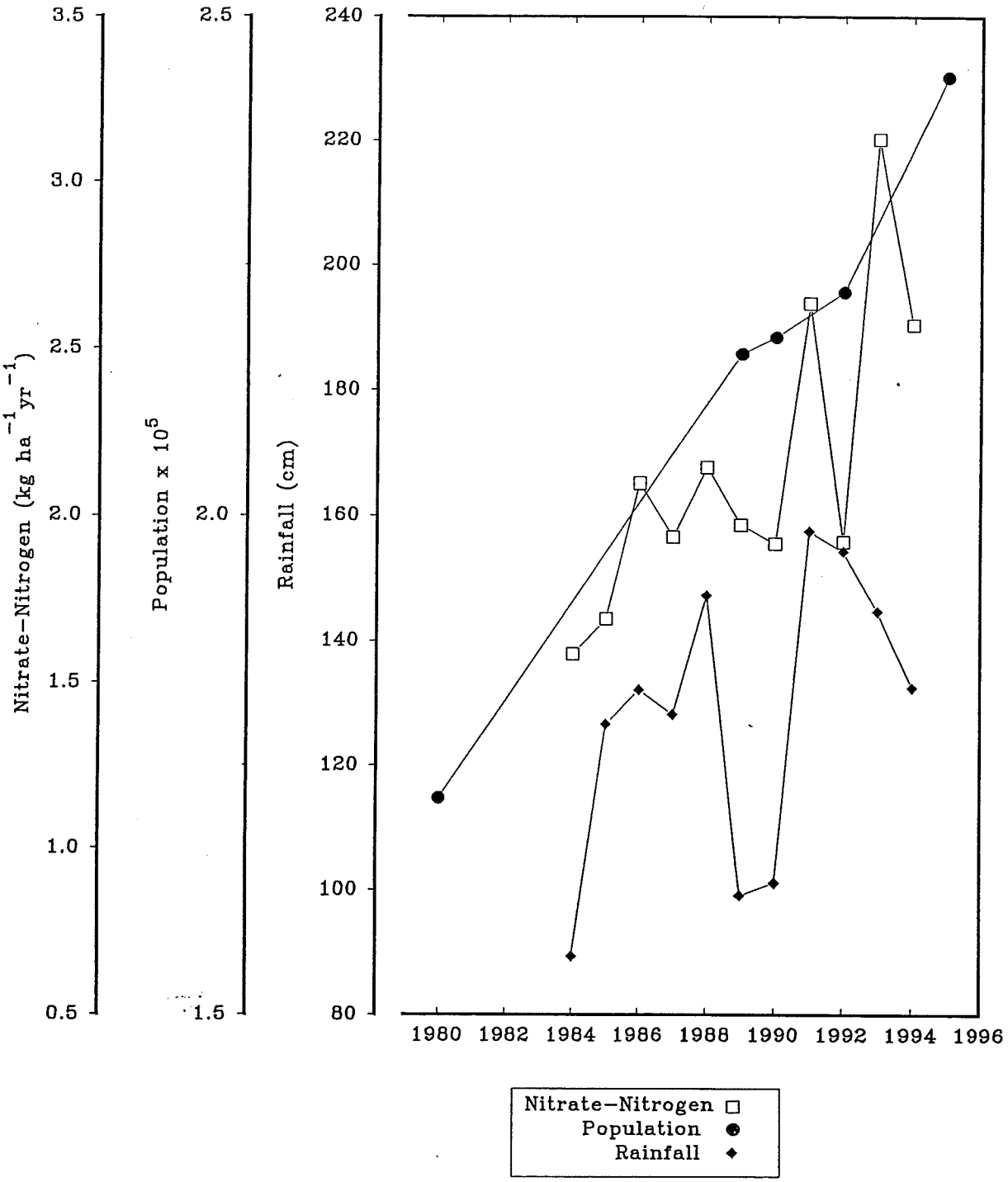

Figure 4.14. Nitrate-nitrogen and annual rainfall totals over time at the NADP/NTN Verna Wellfield site. Population of the Hillsborough, Pinellas, and Manatee Counties.

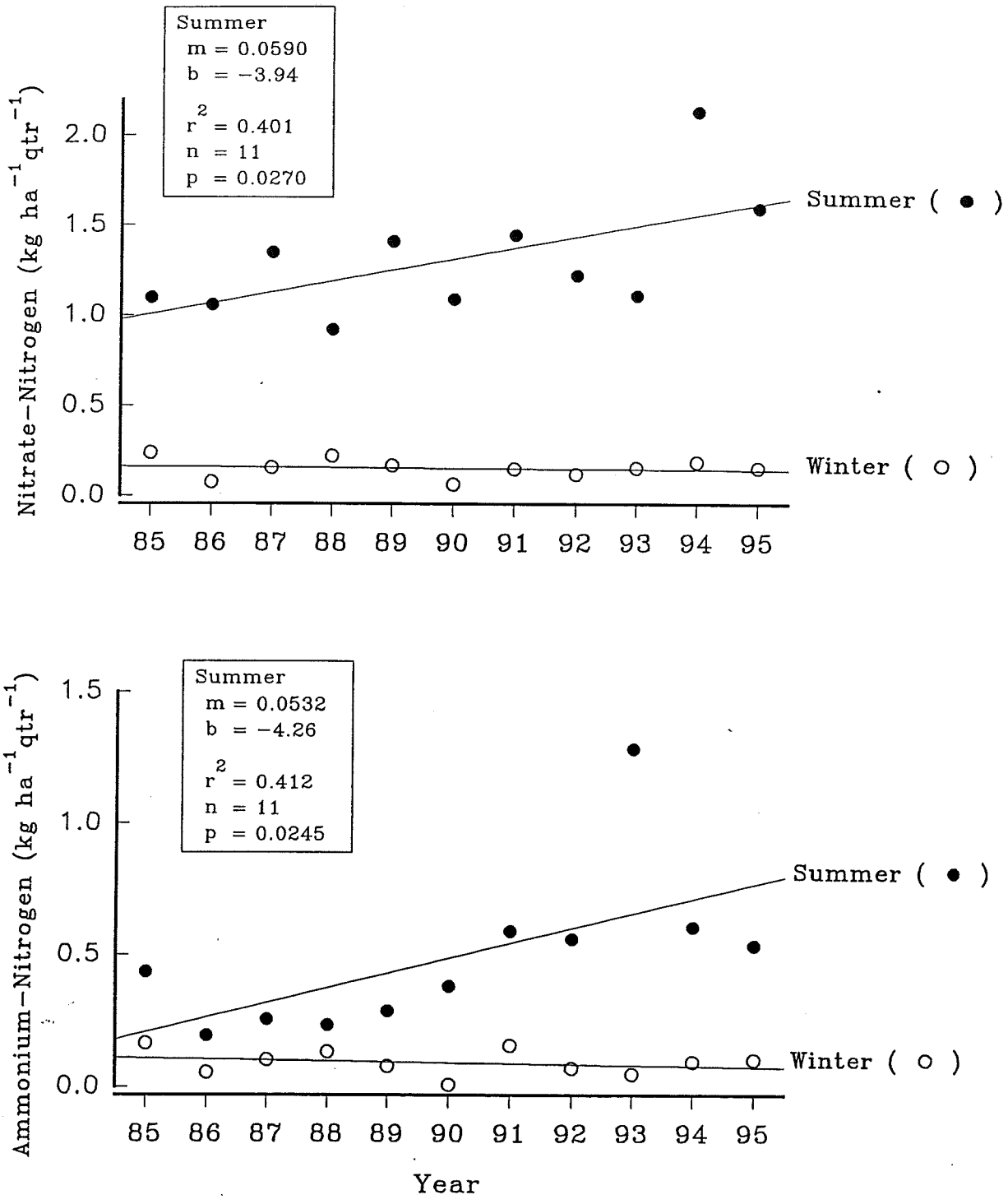

Figure 4.15. Temporal trends of inorganic nitrogen during summer and winter quarters at the NADP/NTN Verna Wellfield site.

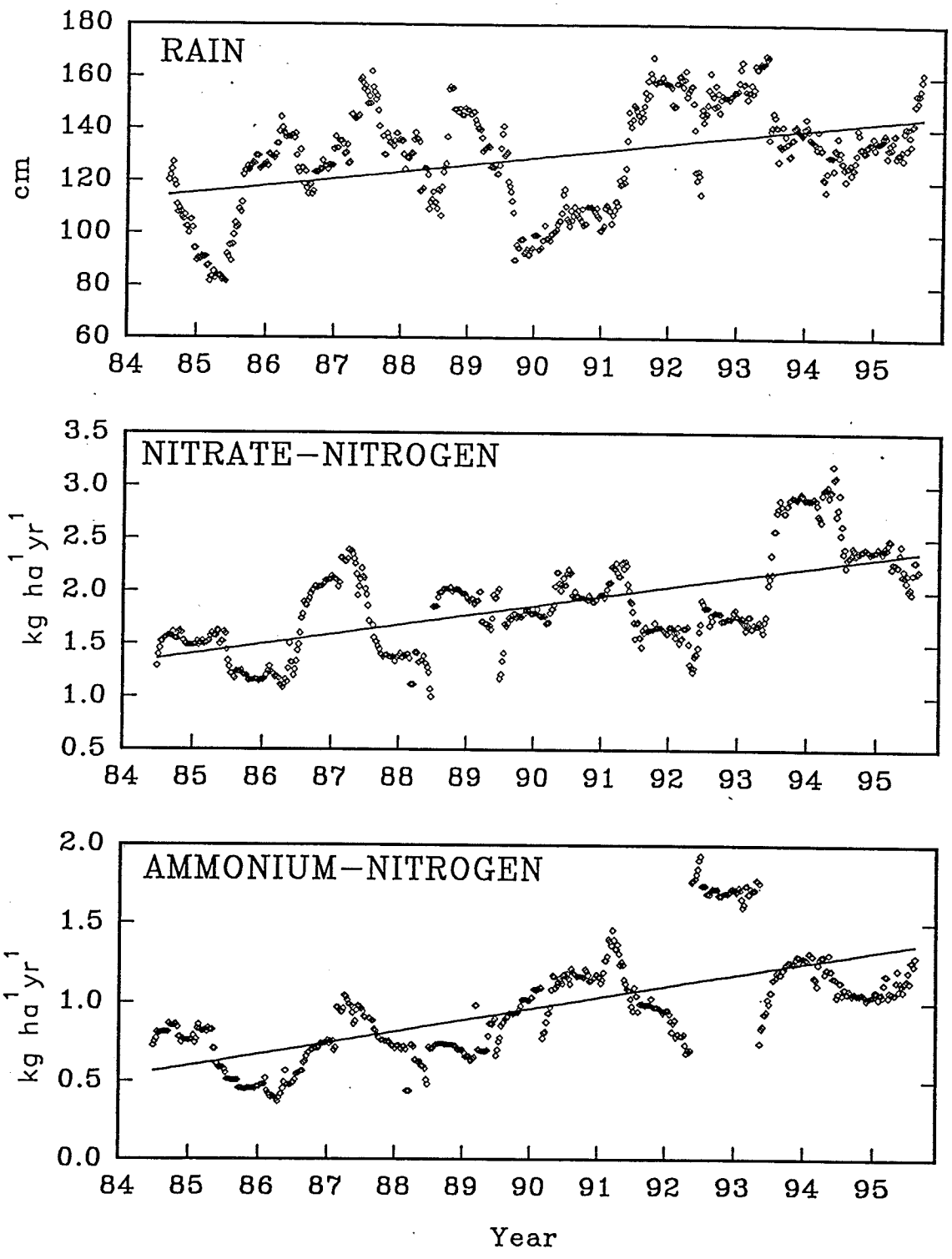

Figure 4.16. A 52 week moving summation of weekly rainfall and inorganic nitrogen loadings at the NADP/NTN Verna Wellfield site.

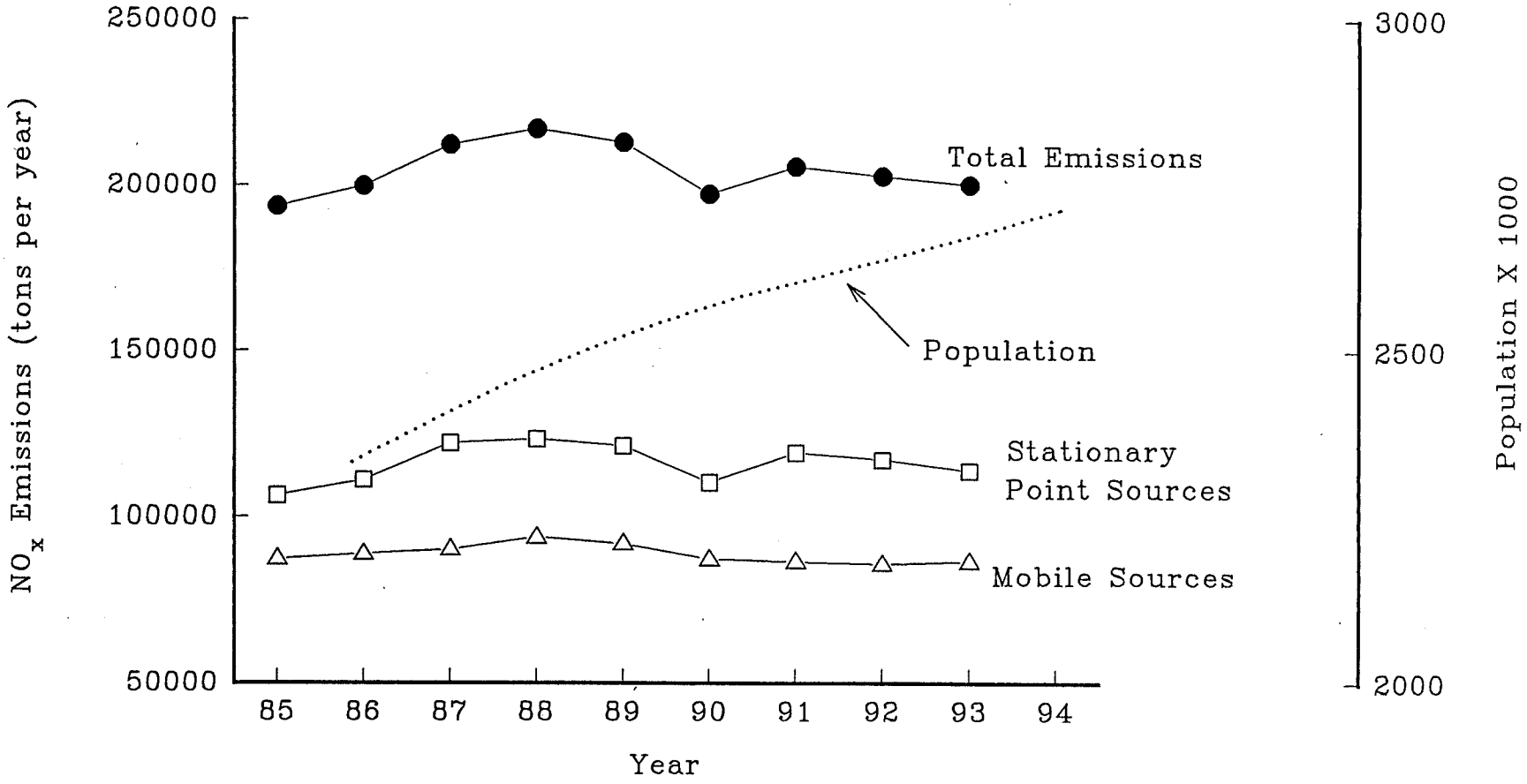

Figure 4.17. FDEP estimates of total NO_x emissions from stationary and mobile sources within a five county area (Hillsborough, Pinellas, Pasco, Polk, and Manatee).

overestimate loadings slightly. The mean of ammonium- and nitrate-nitrogen at the NADP/NTN Verna Wellfield site between 1985 and 1991 was used as a surrogate for total nitrogen (0.86 mg L^{-1}) and does not include organic nitrogen. For total phosphorus, the average concentration collected under the National Urban Runoff Program (NURP) in the early 1980s was used (0.195 mg L^{-1}). Wetfall nitrogen loadings were further multiplied by a Florida-specific factor of 3.04 (determined during the Florida Atmospheric deposition Study) to include dryfall components. The indirect atmospheric component of urban and nonpoint source runoff was not separated from estimates of surface runoff due to the many uncertainties regarding watershed transfer coefficients.

In computing the revised loadings to Tampa Bay with the results of the MML project, some adjustments to measured loads were necessary to account for that portion of the dry deposition (aerosol and gaseous species) which was assumed to be under-collected by the bulk samplers (Baker, 1993; Lovett, 1994). A variety of literature values were employed, including species- and regionally-specific loads, which were primarily determined through ambient air measurements and selection of appropriate deposition velocities. The uncertainties associated with deposition velocities are quite high, as previously discussed, and the applicability of deposition velocities form one site to another adds further uncertainty. In general, assumptions were made such that loading estimates prepared were conservatively low. In keeping with this premise, no adjustment was performed for the potential bias in rainfall collection by the bulk deposition samplers.

For nutrients, no adjustments were made for phosphorus. This element was assumed to be present entirely in the larger particulate phase, to be associated with soils, and to have been representatively collected by the bulk samplers used.

For nitrogen, some nitrates are contained in the larger particulate sizes. The 2.0 to 0.2 micron size class, while not readily dry deposited, are easily scavenged by precipitation, particularly as the nitrate and ammonium ions species are very soluble. The gaseous phases are contained in wet precipitation according to solubility, but the dry deposition of nitric acid and nitrogen dioxide may be substantially under collected by artificial substrates. Nitrogen dioxide is particularly prevalent in urban settings (Hanson, *et al.*, 1989), as is nitric acid, and nitric acid, in addition, is reported to form a large portion of the total dry deposition in the Eastern U.S. (Johnson and Lindberg, 1992). Nitric oxide and ammonia fluxes are reported to be small, and releases from soil can at times balance deposition (Lovett, 1994).

Of the nitrogen species, therefore, nitrogen dioxide and nitric acid appear to be the nitrogen forms which would not be well collected by an artificial substrate, but which form a substantial portion of total nitrogen deposition. In order to provide estimates of total nitrogen deposition, the bulk deposition data collected by the MML project was augmented by literature values of nitric acid and nitrogen dioxide dry deposition. The technique is similar to the analyses performed by Baker (1993) in which dry bucket data was summed with deposition rates determined with deposition velocities for nitric acid and nitrogen dioxide.

The Florida Atmospheric deposition Study (FADS)(Hunter/ESE, 1989; Edgerton and Lavery, 1992) and the National Dry deposition Network (Dr. Ralph Baumgardner, Clean Air Status and Trends Network project officer, National Dry deposition Network, personal communication) obtained nitric acid deposition rates of between 1.04 and 1.40 kg ha^{-1} yr^{-1} with an average of

1.21 kg ha^{-1} yr^{-1}. The stations at which determinations were made were comparatively rural; ambient air concentrations were likely lower than the urban areas of the Tampa Bay watershed, and yet the leaf area and canopy structure was undoubtedly higher. Other work during FADS (Hunter/ESE, 1989) determined rates of 2.96 kg ha^{-1} yr^{-1} for deposition of nitrogen dioxide at a site in Zephyrhills (within the Tampa Bay watershed) between 1982 and 1983. Again ambient air concentrations in rural areas should be lower, and yet substrate areas may be higher. The increasing nitrogen deposition measured at the NADP/NTN site implies worsening air quality, and indicates that a dry deposition determined during the early 1980s may underestimate present day loadings.

The calculated 1994-1995 total nitrogen load consists of the total bulk nitrogen as measured at the MML sites (8.59 kg ha^{-1} yr^{-1}), plus 2.96 and 1.21 kg ha^{-1} yr^{-1} for the dry deposition of nitrogen dioxide and nitric acid respectively. Total nitrogen deposition rates, as measured at the seven sites and adjusted for gaseous dry deposition, ranged from 10.19 to 17.02 kg ha^{-1} yr^{-1}, with an average of 12.76 kg ha^{-1} yr^{-1}. Phosphorus (with no adjustment) ranged from 0.52 to 1.76 kg ha^{-1} yr^{-1} at the seven sites, with a watershed average of 0.93 kg ha^{-1} yr^{-1}. In the absence of more information regarding gradients between stations with significant differences, the arithmetic averages of station means were used to compute loads for both the Bay segments and the watershed.

Inorganic nitrogen loads (measured by the NADP/NTN program) have been increasing steadily, however. The bulk deposition measured in 1994-1995 was presumed to have experienced comparable increases and to be greater than if the bulk deposition had been determined between 1985-1991, the baseline year for determination of the remaining loads to Tampa Bay (Zarbock, *et al.*, 1994). The 8.59 kg ha^{-1} yr^{-1} of total nitrogen bulk deposition was therefore reduced by the ratio of 1985-1991 inorganic nitrogen wetfall to 1994-1995 inorganic nitrogen wetfall, and dry deposition estimates for nitric acid and nitrogen dioxide subsequently added to account for under-represented dry deposition. **The resulting total nitrogen deposition estimated for 1985-1991 is 12.05 kg ha^{-1} yr^{-1}. Phosphorus loadings (0.93 kg ha^{-1} yr^{-1}) measured in the MML project were assumed to be unchanged from 1985-1991 levels.**

Table 4.9 summarizes estimates of direct nitrogen and phosphorus loadings by segment for the 1985-1991 time period, and the atmospheric percentage of total Bay loadings during that period. For percentages, segment loadings calculated by Zarbock, *et al.*, (1994) for point and nonpoint sources, fugitive emissions, groundwater, and springs were augmented by the atmospheric data derived under the MML project. Estimates for nitrogen are quite close to previous calculations (Zarbock, *et al.*, 1994), 32% as opposed to 27% determined previously, with atmospheric deposition still second to nonpoint source loadings (**Figure 4.18.**). For phosphorus, new estimates of direct atmospheric loads are substantially lower (5%) baywide as compared to previous estimates of 31 % (*ibid*). Nonpoint sources (39%), followed by point sources (domestic and industrial, 36%) dominate the loadings of phosphorus to Tampa Bay.

Atmospheric loadings of nitrogen to the various basins of the watershed (at 12.05 kg ha^{-1} yr^{-1}) were also compared to the nonpoint source loadings determined in Zarbock, *et al.*, (1994) to determine approximate watershed transfer coefficients. Nonpoint source loadings were computed from either gaged flow or from an empirical model of flow as a function of rainfall, land use, and soil types, together with land use-specific water quality loading coefficients. In-stream processes were not considered. As water quality coefficients and therefore loads from specific

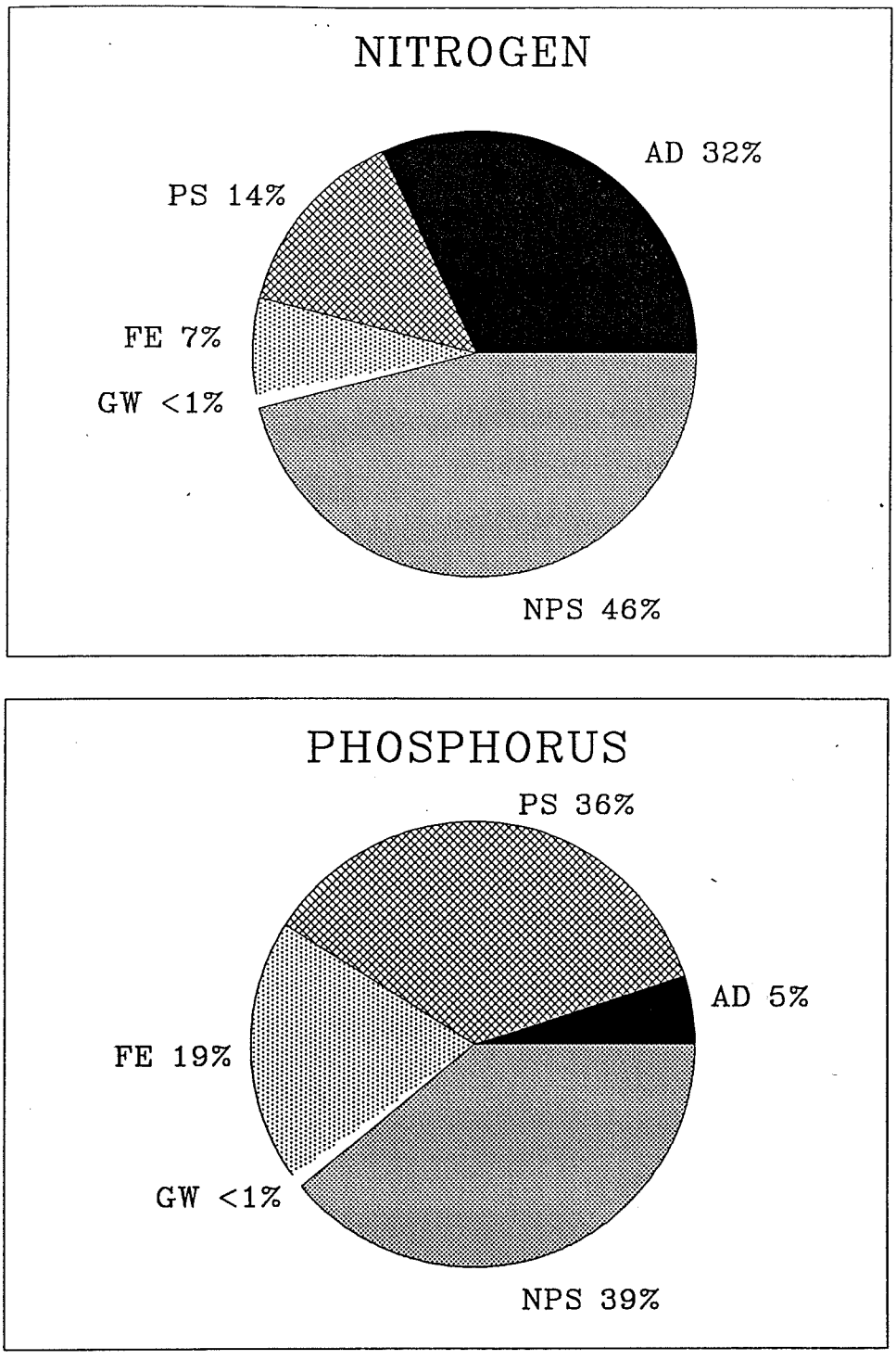

Figure 4.18. Relative loading of nitrogen and phosphorus to Tampa Bay for the 1985-1991 time period. Atmospheric deposition (AD), direct to the Bay, as determined under the current study. Remaining data from Zarbock, et al., (1994); PS - point source, FE - fugitive emissions, GW - groundwater, NPS - non-point source.

Table 4.9. Estimates of atmospheric loading of total nitrogen directly to the segments of Tampa Bay, for the 1985-1991 time period, as metric tons per year, and as a percentage of total segment and Bay loading.

Bay Segment	km^2	Nitrogen mton yr^{-1}	%	Phosphorus mton yr^{-1}	%
Old Tampa Bay	201	242	48	18.7	16
Hillsborough Bay	105	127	9	9.8	1
Middle Tampa Bay	310	373	49	28.8	21
Lower Tampa Bay	247	297	82	22.9	33
Boca Ciega Bay	93	112	45	8.7	26
Terra Ceia Bay	21	25	60	1.9	30
Manatee River	55	66	14	5.1	5
Total Tampa Bay	**1031**	**1242**	**32**	**95.9**	**5**

land uses have been developed from a large empirical data set, the loads from nonpoint source runoff reflect a "typical" sum of both precipitation quality (atmospheric deposition), sources (anthropogenic "imports", biogenic recycling) and sinks (biological removal) within a basin.

Over the watershed as a whole, estimated nonpoint source runoff represents 25% of the total atmospheric deposition of nitrogen, or a watershed retention rate of 75% (**Table 4.10**). More heavily urbanized basins such as Boca Ciega Bay transfer larger amounts of material, retaining only 40%. Higher transfers undoubtedly result both from a more impervious basin (higher urbanization and runoff quantity) as well as from activities within the basin (residential fertilization, etc.). The retention rates do not reflect instream removal processes or wetland sources or sinks of nutrients. Additionally, spatial differences in Tampa Bay precipitation quality are not incorporated except to the extent that literature values of urban or agricultural runoff water quality may reflect localized differences in ambient air quality.

Watershed retention rates of nitrogen for Tampa Bay as a whole (75%) are comparable to literature estimates for other systems although the reported range is quite large (25% to 98%, Scudlark and Church, 1993). Values used for inorganic nitrogen retention range between 80% (Scudlark and Church, 1993) for Delaware Bay and 76% to 100% for Chesapeake Bay (Tyler, 1988). Instream removals and denitrification further increase estimates of retention and other authors have used further delivery ratios (applied to in-stream nonpoint source loads of inorganic nitrogen) of 50% to 80% (Tyler, 1988).

If the bulk of nonpoint source loadings is assumed to be derived from atmospheric loadings (ignoring anthropogenic "imports" to the watershed), then the total atmospherically derived nitrogen contributed to Tampa Bay **could** be as much 70-80% (32% direct plus 46% nonpoint source) of total Bay loadings. This represents an upper boundary for the influence of

Table 4.10. Nonpoint source loadings of nitrogen as a fraction of watershed atmospheric deposition used to estimate net transfer of nitrogen from the watershed to Tampa Bay. For the 1985-1991 time period. Land use area percentages from Zarbock, *et al.* (1994).

	Basin Area km^2	NPS Loads	Atmospheric Loads	% Retention	% Urban	%* Agric. Area
		------- mtons yr^{-1} -------				
Coastal OTB	646	199	778	74	37	15
Alafia River	1090	390	1313	70	33	38
Coastal Hillsborough	381	121	459	74	36	29
Hillsborough River	1744	215	2102	90	23	41
Coastal MTB	206	106	248	57	22	11
Little Manatee River	574	260	692	62	7	65
Coastal LTB	95	37	114	67	5	12
Terra Ceia Bay	28	11	34	68	26	24
Manatee River	921	319	1110	71	12	54
Boca Ciega Bay	193	136	233	41	58	6
Watershed	**5879**	**1794**	**7082**	**75**	**25**	**35**

* Total agricultural area, including rangeland.

atmospheric loading on the Bay, as residential and agricultural fertilization undoubtedly contributes some unknown fraction of nonpoint source loads.

While it is certainly a simplification to attribute all nonpoint source loading to an atmospheric origin, event mean concentrations between urban (residential and commercial) and heavily fertilized agricultural land uses are not dissimilar (Zarbock, *et al.*, 1994; Zarbock, 1991), with the exception of feed lots. When these water quality concentrations are coupled with the higher impervious areas and runoff coefficients in urbanized land uses, total urban loadings can exceed agricultural loadings on a per acre basis. As a result, basins with higher proportions of agricultural land uses, generally have higher calculated nitrogen retention values, with urbanized basins retaining comparatively less nitrogen. It may be that hydrologic alterations contribute more overall to nonpoint source loadings than do actual land use practices.

For phosphorus, however, comparison of nonpoint source loads with atmospheric deposition loads indicate that watershed geology and activities contribute far more phosphorus than does atmospheric deposition. Many basin retention percentages are less than zero, with total nonpoint source loadings near 150% of the total atmospheric deposition to the watershed (**Table 4.11**). Mining land use and/or regional geology can be linked with much of this result, particularly in the Alafia, Little Manatee River and Coastal Lower Tampa Bay basins, but urbanized regions such as Boca Ciega Bay also have substantial sources of phosphorus within the basin.

Table 4.11. Nonpoint source loadings of phosphorus as a fraction of watershed atmospheric deposition used to estimate net transfer of phosphorus from the watershed to Tampa Bay. Percent mining represents the amount of nonpoint source loading for the basin attributed to mining land use. For the 1985-1991 time period.

	Basin Area km^2	NPS Loads -- mtons yr^{-1} --	Atmos Loads	% Transfer	% Mining	% Urban
Coastal OTB	646	47	60	79	3	49
Alafia River	1090	316	101	312	29	12
Coastal Hillsborough	381	33	35	92	13	42
Hillsborough River	1744	172	162	106	7	22
Coastal MTB	206	21	19	109	10	48
Little Manatee River	574	87	53	163	12	6
Coastal LTB	95	14	9	154	22	21
Terra Ceia Bay	28	3	3	105	0	38
Manatee River	921	101	86	118	9	11
Boca Ciega Bay	193	23	18	126	<1	84
Watershed	**5879**	**815**	**547**	**149**	**16**	**24**

4.13. Tampa Bay Loadings - Metals

For metals, no adjustments to measured deposition rates were necessary as crustal material and associated metals are contained in larger particulates, and are assumed to be well collected by bulk samplers. Gravitational settling or scavenging by precipitation is the dominant form of deposition for this particle size and typically results in deposition quite close to emissions sources (Scudlark, *et al.*, 1992). Although some non-crustal, anthropogenic metals from high temperature combustion, particularly lead (Lovett, 1994), are contained in sub-micron sized aerosols, no regional data on the proportions and size fractionation of this element were available.

Earlier atmospheric loadings presented in Frithsen, *et al.*, (1995) employed Florida rainfall concentration data summarized in 1980 (Irwin and Kirkland, 1980) in which loadings of some metals appeared much greater than more recent data for the Tampa Bay area (Rushton, 1991; 1993). The earlier data could not include the effects of either documented improvements in ambient air quality for lead or presumed improvements in sample handling procedures and analytical detection limits. A comparison of the loading rates used by Frithsen, *et al.*, (1995) and the bulk deposition measured during this project appear below in **Table 4.12**.

Additionally, Frithsen, *et al.*, (1995), based on work by Scudlark and Church, (1993), assumed a 0.1 transfer coefficient (90% retention) for transport of contaminants deposited on the watershed. As a result of the size of the watershed to Tampa Bay, indirect atmospheric

Table 4.12. Comparison of selected metal loading rates used for estimating atmospheric deposition of metals to Tampa Bay and the watershed.

	Frithsen, *et al.* (1995) g ha^{-1} yr^{-1}	MML 1994-1995 g ha^{-1} yr^{-1}
Copper	13.79	8.01
Lead	61.66	6.54
Zinc	39.80	79.81

deposition was calculated to comprise 57% of direct deposition to the estuary. Runoff from non-urbanized areas (agricultural and undeveloped lands) was not calculated explicitly but was included in the 0.1 coefficient of the entire watershed. Other sources of metals to the Bay included point sources, groundwater, and nonpoint source runoff from urbanized areas only. In calculating nonpoint source runoff, the loads originating from atmospheric deposition in urban areas and subsequently transported to the estuary were removed from urban runoff totals.

Atmospherically derived metals (direct deposition plus 10% of watershed deposition) were initially estimated to consist of 18%, 20%, and 4% of total loads to the Bay (Frithsen, *et al.*, 1995). With revised loadings from the bulk deposition project, and using the same computation method of direct plus 10% of indirect, atmospherically derived loads for copper, lead, and zinc were 11%, 3%, and 8%, respectively, of total Bay loads. Of these amounts, direct deposition to the Bay for the same metals consisted of 7%, 2%, and 5%. Nonpoint source loadings from the urbanized areas dominated loads to Tampa Bay with loads in urban runoff exceeding atmospheric deposition to the same areas by average factors of 5.2, 32.7, and 10.0 for copper, lead, and zinc respectively. It is clear that anthropogenic activities in the watershed are the dominant factors in metals loadings to Tampa Bay. Total loads by source appear in **Table 4.13.**

Table 4.13. Relative sources of metals to Tampa Bay. Revised from Frithsen, *et al.*, (1995), using project atmospheric deposition rates and assumed 90% watershed retention for indirect deposition. Units are kg yr^{-1}.

	Point Sources	Ground Water	Urban Non-Point Sources	Direct	Atmos 10%	Atmos Indirect % Atmos
Copper	4,438	481	5,369	824	470	7-11
Lead	5,505	4,444	29,745	675	384	2-3
Zinc	16,078	130,417	107,898	8221	4682	5-8

5.0. PESTICIDES, PAHs AND PCBs - RESULTS AND DISCUSSION

The organic contaminants monitored under this project are semi-volatile organic compounds (SOCs), substances with sufficient vapor pressure to volatilize and exist in equilibrium between gaseous and particulate phases. Atmospheric deposition of SOCs occurs by rain (and snow) scavenging gaseous and particulate SOCs from the air, and by direct deposition of SOC-containing dry particles (Bidleman, 1988; Bidleman *et al.*, 1986; Koester and Hites, 1992). The vapor-to-particle ratio (V/P) in the atmosphere is a determinant of Henry's Law constant, a function of the volatility and solubility of each compound. Lower molecular weight SOCs (including 2 to 4 ring PAHs and hexachlorohexane) are preferentially dissolved in rain drops and removed from the atmosphere in wet deposition (Pankow, 1984). Less soluble SOCs (including PCBs, DDT and larger PAHs) are preferentially adsorbed to dry particulates and removed either by dry deposition (Ligocki *et al.*, 1985) or scavenging of particulates by rainfall.

Studies of wet and dry deposition of SOCs in industrial/urban and rural areas showed marked differences in the type and amount of organic contaminants collected. Meteorological conditions and source proximity were major factors controlling the type and amounts of contaminants deposited (Bidleman, 1988; Koester and Hites, 1992; Cotham and Bidleman, 1995).

5.1. Pesticide deposition

Results of the pesticide analyses and the method detection limits (MDLs) are given in **Appendix E** showing the total concentration of each pesticide collected at each of the five stations through out the three-month sampling period. The mean annual pesticide loadings for each collection station and for each segment of Tampa Bay, are given in **Table 5.1**. The area representing each segment of Tampa Bay was calculated as the water area of the Bay + 10% of the area of the watershed draining into that portion of the Bay (Firthsen *et al.*, 1994), representing both the deposition occurring directly to the Bay surface, and the assumption that 10% of the material falling in the watershed is transported to the Bay. The annualized loadings were extrapolated from the mean value of the six 2-week concentrations (mean biweekly load x 26) by two methods: a) using 0 for none detected (<MDL) and b) using one-half of the MDL for none detected (<MDL). Only those pesticides found at one or more sites were included. Due to the large range of variability among the samples, these results showed no significant difference between mean value calculated using 0 or ½ MDL.

Although the GC/ECD method (EPA-608) is very sensitive for detecting low levels of chlorinated compounds, it is prudent to provide compound verification by performing GC/MS analyses on representative samples. Because of the low concentrations of chlorinated pesticides in the 2-week deposition samples, GC/MS verification proved to be inconclusive. Therefore, it is important to note that the chlorinated compound concentrations reported were derived by GC/ECD only.

More than half of the overall mass of pesticides collected were recovered at Station 7 (**Figure 5.1**), reflecting the importance of agricultural activities in that area. The total values among stations were tested by the Student-Newman-Keuls pair wise multiple comparison methods and Station 7 data were shown to be significantly different than all other sites. Although the total amount of pesticides was similar to the other four sites, the types of pesticides varied, indicating different pesticide fluxes to each of the collection stations.

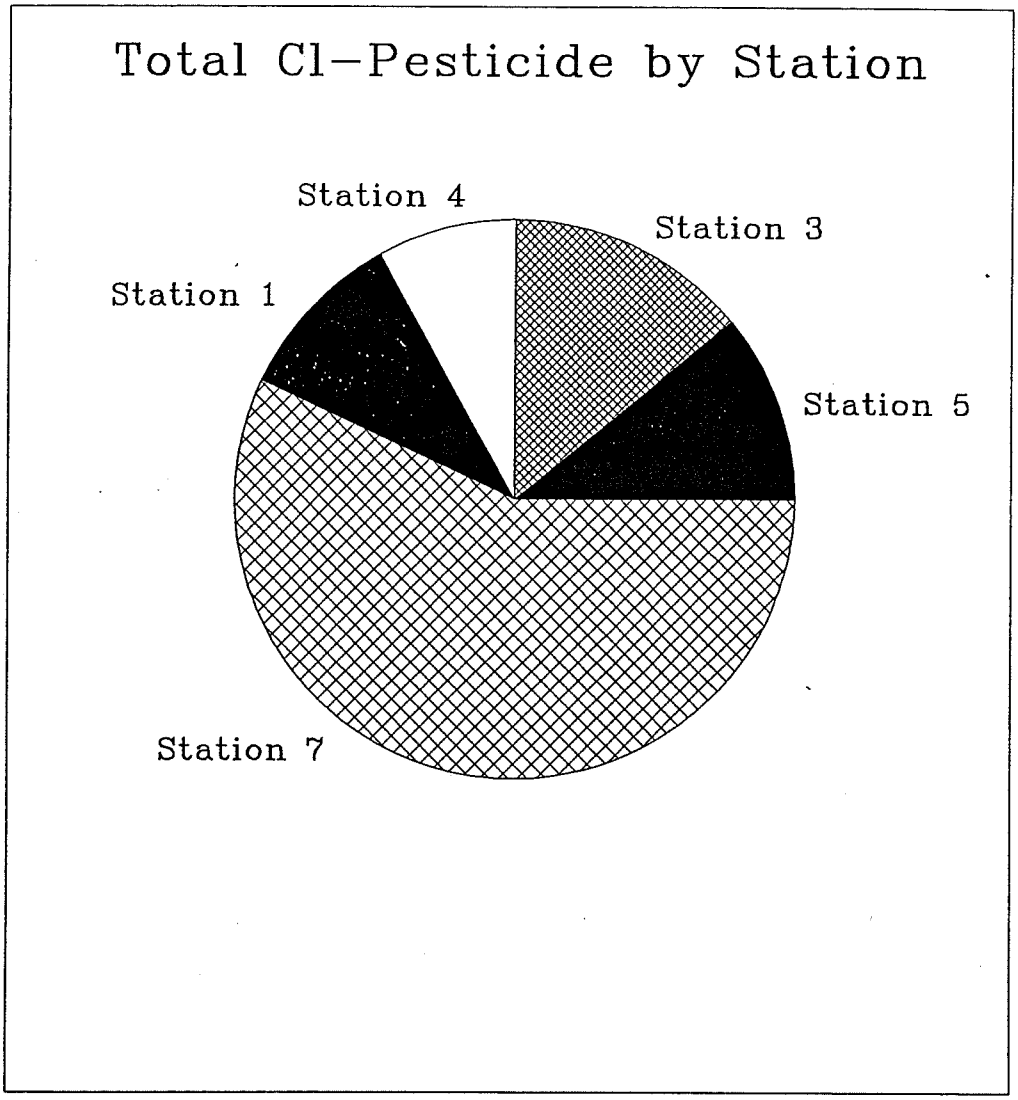

Figure 5.1. Relative deposition of total chlorinated pesticides during the 12 week collection period by station.

Table 5.1. Summary of annualized total chlorinated pesticide deposition to individual stations and Bay segments. Extrapolated from a 12 week period.

At Each Collection Station - $\mu g\ m^{-2}\ yr^{-1}$

	STA-1	STA-3	STA-4	STA-5	STA-7	Mean±S.D.
Loading						
<MDL=½ MDL	5.7	6.6	4.1	4.9	22.0	8.7±7.5
<MDL=0	3.5	5.0	2.8	3.8	21	7.2±7.7

For Each Segment of Tampa Bay - $kg\ yr^{-1}$

Segment	OTB	HB	MTB	LTB	Terra Ceia	Boca Ciega	Total
Area* (km^2)	265.3	426.7	387.9	256.1	23.4	112.4	1,471.8
Loading $kg\ yr^{-1}$							
<MDL=½ MDL	2.3	3.7	3.4	2.2	0.20	0.98	12.8
<MDL=0	1.9	3.1	2.8	1.8	0.17	0.81	10.6

* Area = Water area + (0.1 x watershed area)

The most abundant pesticides of Station 7 were β BHC, endosulfan-I and -II, and pp'DDT. Knowledge of agricultural practice is important for understanding these results. During July and early August, the fields are tilled in preparation for the mid-summer planting of tomato fields. The presence of the parent compound, pp'DDT is unexpected, because it's use has been banned since 1978. A plausible explanation for the presence of DDT is that soil particles suspended during tilling still contain the recalcitrant organochlorine pesticide and were then subsequently deposited at the near-by Station 7. Although endosulfan and pp'DDT were also the major pesticides collected at Station 5, much lower concentrations (about 20%) were found relative to those at Station 7. Station 3 showed elevated concentrations of δ BHC, endrin aldehyde and pp'DDT during the first collection date (July 5 through July 18) and an anomalously high amount of pp'DDD (a breakdown product of DDT) during a later collection date. Overall concentrations were about 25% of those at Station 7.

A graphical depiction of all pesticides from Station 7 for each of the collection times (**Figure 5.2**) shows continuous influx of γ BHC (July through September) and pp' DDT present in July and early August. The most telling observations relate to endosulfan-I and endosulfan-II with the degradation product endosulfan sulfate. These data show no endosulfan-I during the first 3 collections (July and early August), with high amounts collected in late August and September.

Endosulfan-I and -II are isomers of an insecticide applied to the tomato plants after planting in August (personal communication, Dr. Gilriath, USDA Agricultural Extension Service). Endosulfan-sulfate is a breakdown product that shows up after initial applications of endosulfan.

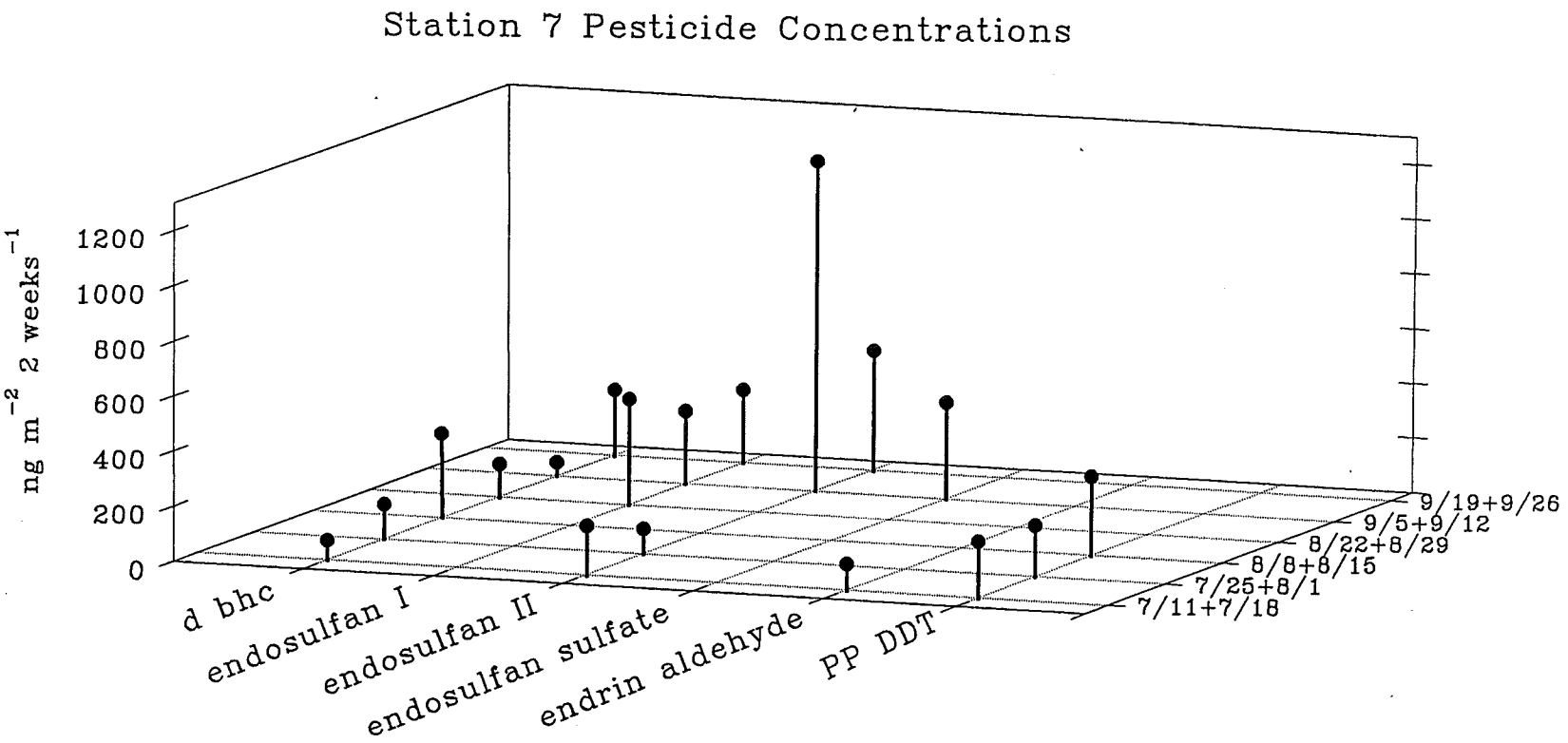

Figure 5.2. Temporal pattern of deposition of individual pesticides at Station 7.

The endosulfan-II collected in early July apparently was remaining from the earlier tomato growing season. A distribution of the loadings of major types of pesticides is given in **Table 5.2.**

Table 5.2. Summary of annualized deposition of the most common pesticides detected to individual stations and Bay segments. Extrapolated from a 12 week period. Means computed using <MDL = 0.

At Each Collection Station - $\mu g\ m^{-2}\ yr.^{-1}$

	tDDT	Endosulfans	tBHC	Other
STA-1	0	0	1.2	2.3
STA-3	3.3	0	0.7	1.0
STA-4	0	2.4	0.4	0
STA-5	1.7	1.6	0.5	0
STA-7	2.9	13.8	3.9	0.4
Mean±S.D.	**1.6±1.6**	**3.6±5.8**	**1.3±1.5**	**0.7±1.0**

For Each Segment of Tampa Bay - $kg\ yr^{-1}$

	OTB	HB	MTB	LTB	Terra Ceia	Boca Ciega	Total
Area* (km^2)	265.3	426.7	387.9	256.1	23.4	112.4	1,471.8
Loading $kg\ yr^{-1}$.							
tDDT	0.42	0.68	0.62	0.41	0.04	0.18	2.35
Endosulfans	0.96	1.54	1.40	0.92	0.08	0.41	5.31
tBHC	0.35	0.56	0.50	0.33	0.03	0.15	1.92
Other	0.19	0.30	0.27	0.18	0.02	0.08	1.04
Total	**1.92**	**3.08**	**2.79**	**1.84**	**0.17**	**0.82**	**10.62**

* Area = Water area + (0.1 x watershed area)

Pesticide residues were lower at the urban sites, with chlorpyrifos the most abundant pesticide collected at Station 1, probably reflecting commercial insecticide applications to residence or office buildings and grounds. Station 4, east of Tampa exhibited endosulfan-I and endosulfan-II during the final collection date, but very little of any pesticides through out the rest of the collection times.

For the other stations, pesticides were only present during one or two of the six 2-week collection periods, showing great variability in pesticide loadings at each site. Therefore, **extrapolation to annualized loadings makes the assumption that the twelve week sample collection period (July 5, 1995 through September 26, 1995) was representative of depositional rates through out the year.** Since individual watershed areas to Tampa Bay were not monitored separately for pesticide deposition, the loadings to Tampa Bay were based on an average from all sites extrapolated from the twelve week collection period to annual loadings.

Comparisons of chlorinated hydrocarbon pesticide loadings to Tampa Bay from this study with those reported by Firthsen *et al.*, (1994) from studies in the 1970s are as follows:

- Chlordane was not detected in the present study, but was the most abundant pesticide in the 1970s.
- tDDT loadings were about 20% of those reported in the 1970s.
- Endosulfans were the most abundant pesticides in the present study, where as they were not reported for the 1970s.
- Dieldrin was not detected in the present study but was one of the more prevalent pesticides in the 1970s.
- The overall chlorinated pesticide atmospheric loadings to Tampa Bay dropped from 30 kg yr^{-1} in 1970s to 10.6 kg yr^{-1} during this study.

It is important to note that the majority of pesticides were collected at one station. The spatial heterogeneity indicates local sources for these synthetic compounds rather than long distance atmospheric transport (which would be more evenly distributed over the Bay and watershed areas). As a result, however, annualized loadings generated from these data may over- or underestimate the actual loadings to the Bay. A more accurate estimate of pesticide loadings would be generated from sampling during additional seasons and from a larger number of stations ringing the Bay.

5.2. PAH Deposition

A listing of the amount of each PAH for each of the six collection periods at each of the five sites is given in **Appendix E.** These data show a vast difference in the amount of PAHs collected at each site, with Station 1, containing 75% of all the PAHs collected (**Figure 5.3**). The differences in the total PAH among the treatment groups was tested by the Student-Newman-Keuls pairwise multiple comparison method which showed a significant difference between the Station 1 and all other sites tested.

The PAH compounds monitored during this study were the unsubstituted, parent, multi-ring compounds representative of combustion (pyrogenic) sources. These could reflect fossil fuel combustion from automobiles, power plants and fuel oil furnaces, as well as forest fires, agricultural burning, trash incineration and charcoal Bar-B-Que. With the exception of naphthalene, all PAHs detected were high molecular weight (HMW) compounds (3 rings and

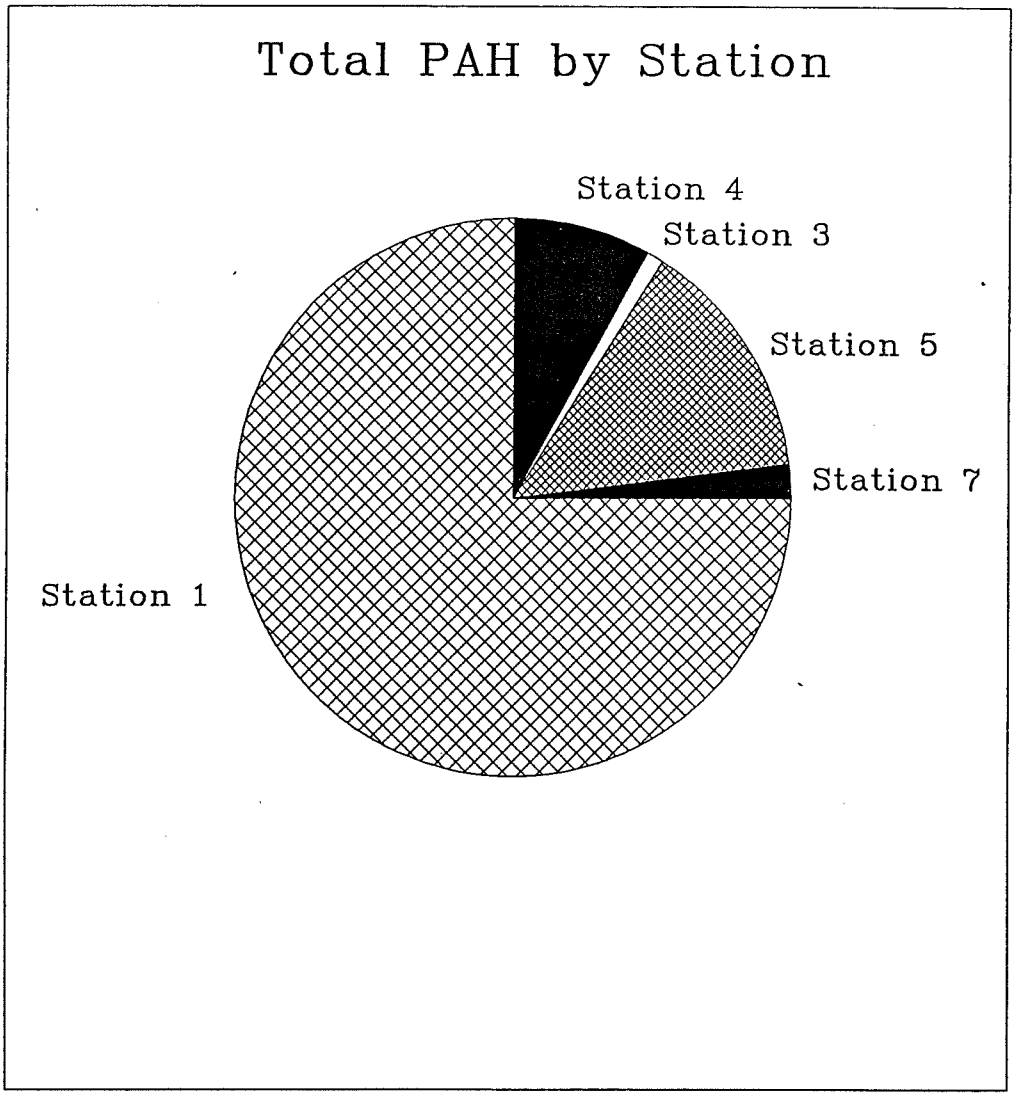

Figure 5.3. Relative deposition of total PAH during the 12 week collection period by station.

larger). The HMW PAH of greatest concern as a carcinogen is benzo(a)pyrene, which also is indicative of combustion-generated PAHs (National Academy of Sciences, 1985). This compound was found only at Station 1.

The sites in proximity to urban/industrial areas exhibited the greatest amount of PAHs, with Station 3 having the least. The major components of PAHs were the same for the three most abundant PAH sites, including fluoranthene and benzo(b)fluoranthene. These compounds, however were not detected at the other two sites. As with the above pesticide samples, each sample site was representative of a different type and/or amount of PAH, thus each collection station represented a separate PAH deposition regime. These results show the influence of localized sources, rather than long-range transport, indicating that different segments of the Bay may receive different depositional loadings and compositions of PAHs. Therefore, annualized loadings generated from averages of the five stations may over estimate the actual PAH loadings to some sections of the Bay, while underestimating others, especially those adjacent to industrialized/urban land use areas.

Although different PAH loadings at the collection sites would suggest differential loading to different areas of the Bay, the average Bay-wide collection loading was used to provide estimates of Bay segment loadings. The mean annualized PAH loadings for each collection station and for each segment of Tampa Bay are given in **Table 5.3**. The annual loadings reflect the mean value of the six 2-week periods by two methods, 0 and ½ MDL, as described above for pesticides. Only those PAHs found at one or more stations were included. No significant difference was observed between the means calculated from 0 and ½ MDL designations.

Table 5.3. Summary of annualized total PAH deposition to individual stations and Bay segments. Extrapolated from a 12 week period.

At Each Collection Station - $\mu g\ m^{-2}\ yr^{-1}$.

	STA-1	STA-3	STA-4	STA-5	STA-7	Mean±S.D.
Loading						
<MDL = ½ MDL	607	17	82	145	35	177±245
<MDL = 0	546	9	56	95	13	144±278

For Each Segment of Tampa Bay - $kg\ yr^{-1}$.

Segment	OTB	HB	MTB	LTB	Terra Ceia	Boca Ciega	Total
Area* (km^2)	265.3	426.7	387.9	256.1	23.4	112.4	1,472.7
Loading $kg\ yr^{-1}$.							
<MDL = ½ MDL	47	76	69	45	4	20	261.0
<MDL = 0	38	61	56	37	3	16	212.0

* Area = Water area + (0.1 x watershed area)

Although no historic data were available for comparisons of PAH loadings to Tampa Bay, recent studies of PAH loadings to Chesapeake Bay provides some comparisons. Baker *et al.*, (1992) reported an annual loading of 155 $\mu g\ m^{-2}\ yr^{-1}$. for the four most abundant PAH compounds. PAH loadings to Tampa Bay were found to be 144 for <MDL = 0, and 177 for <MDL= ½ MDL, indicating similar PAH loadings to Tampa Bay as to Chesapeake Bay. Thus, Tampa Bay as a whole, was found to receive PAH loadings similar to another industrialized/urbanized Bay.

An accurate description of PAH loadings to the different sections of Tampa Bay, however, would require a larger number of collection stations with the various watershed areas, and especially utilizing collection sites adjacent to and in Tampa Bay.

5.3. PCB Deposition

Data for PCBs were reported as the amount of individual congeners. Of the 20 congeners analyzed, only 6 were observed through out all five sites. Concentrations of individual congeners at each site for each sampling period are listed in **Appendix E.**

The mean annual PCB loadings for each collection station and for each segment of Tampa Bay are given in **Table 5.4**. The annualized loadings were determined from the mean value of the six 2-week sampling periods from both 0 and ½ MDL, as described above for pesticides and PAHs. Only those PCBs found at one or more stations were included. No significant difference was observed between the mean values calculated using 0 and ½ MDL values for <MDL data.

Station 3 exhibited the highest number of PCBs (four) and the greatest deposition (8.9 $\mu g\ m^{-2}\ yr^{-1}$) Station 5 and Station 7 exhibited intermediate amounts of three congeners at 3.0 $\mu g\ m^{-2}\ yr^{-1}$ and two congeners at 4.2 $\mu g\ m\text{-}^{2}\ yr^{-1}$. respectively. The more urban sites (Station 1 and Station 4) contained only one congener in low concentration, 0.7 and 0.8 $\mu g\ m^{-2}\ yr^{-1}$, respectively.

The differences in the total values of the 20 PCB congeners were tested by the Kruskal-Wallis One Way ANOVA on ranks. The total values were found not to be significantly different ($p=0.358$). Therefore, even though differences in the PCB influx were observed among the six sites, the weekly total PCB influx was not found to be significantly different through out the sites, due to large variations in week-to-week loadings at each site. Despite the lack of significant differences in the distribution of weekly loads between stations, the variety and number of congeners as well as the range in total loadings between the stations with least and greatest deposition, again argue for local sources and activities being responsible for PCB loadings in the Tampa Bay watershed. The total PCB loadings for the present study were 6 kg yr^{-1}, about 50% of that observed from the 1970s study (11.2 kg yr^{-1}, Frithsen, *et al.*, 1995).

This reduction in PCB concentrations from previous studies is consistent with the recent banning of PCBs use and the ubiquitous distribution of these compounds through volatilization and atmospheric transport. The relatively even distribution of PCBs through out the collection stations indicated that the small sample size did provide a reasonable estimate of the PCB loadings to the various sections of Tampa Bay.

Table 5.4. Summary of annualized total PCB deposition to individual stations and Bay segments. Extrapolated from a 12 week period.

At Each Collection Station - $\mu g\ m^{-2}\ yr^{-1}$.

	STA-1	STA-3	STA-4	STA-5	STA-7	Mean+S.D.
Loading						
<MDL = ½ MDL	0.7	8.9	0.8	5.3	4.2	3.5±3.4
<MDL = 0	0.3	8.2	0.4	4.1	3.4	3.3±3.2

For Each Segment of Tampa Bay - $kg\ yr^{-1}$.

Segment	OTB	HB	MTB	LTB	Terra Ceia	Boca Ciega	Total
Area* (km^2)	265.3	426.7	387.9	256.1	23.4	112.4	1,472.7
Loading g yr^{-1}.							
<MDL = ½ MDL	1.1	1.8	1,6	1.1	0.1	0.5	6.2
<MDL = 0	1.0	1.5	1.3	0.9	0.1	0.4	5.1

* Area = Water area + (0.1 x watershed area).

6.0. SUMMARY

6.1. Background

The watershed to Tampa Bay is relatively small in comparison to the Bay surface area (5.7:1) and atmospheric deposition of toxics and nutrients direct to the Bay surface plus indirect deposition to the watershed and eventual transport to the estuary could result in substantial atmospherically derived loadings, depending on the magnitude of other sources. In addition, urbanized land uses within the watershed total some 24% of the area, and much of the urbanization within the watershed (with associated increases in stormwater quantity and degradations in stormwater quality, ambient air quality, and precipitation quality) is located quite near the Bay. Area point sources of NO_x emissions were estimated to consist of approximately one quarter of statewide emissions totals.

Localized contaminated sediments were known to be present in many portions of Tampa Bay, with both toxic metals and synthetic organics at concentrations where biological effects could be expected. The source of the contaminants was not immediately known but indicated a persistent presence and there was at least a potential for atmospheric contributions. Atmospheric deposition of copper, lead, and zinc to Tampa Bay was estimated at 18%, 20%, and 4% of the total loads, respectively, and estimates of atmospheric loadings of some synthetic organics were as high as 21% of total Bay loadings (Frithsen, *et al.*, 1995).

Management efforts on seagrass protection and restoration also necessitated a careful examination of sources of nitrogen. Estimates of nitrogen loads to Tampa Bay from point, nonpoint, groundwater, fugitive emissions, and atmospheric sources (Zarbock, *et al.*, 1994), indicated that direct atmospheric deposition to the Bay surface alone was approximately 27% of total Bay loads. deposition to the watershed and eventual transport to the Bay would increase the atmospherically derived nitrogen loading by some unknown fraction. The Tampa Bay region, with the large population center and concentration of vehicles, industry, and power generation, has several local sources of atmospheric nitrogen (as NO_x) and recent FdeP calculations of 1993 area emissions estimate mobile sources at 44% of total emissions and stationary sources at 56%.

The objectives of the study reported here were to synthesize existing deposition information for nutrients and trace metals, both specific for and pertinent to the Tampa Bay region (Dixon, 1996; **Appendix A**), and to evaluate the spatial variability in deposition of these parameters across the watershed of Tampa Bay. Within the constraints of the study, total deposition figures were to be refined or verified. Toxic metals were originally the emphasis of the study, with nitrogen and phosphorus data of interest as well. Scope revisions and additional funding also permitted a smaller scale investigation of chlorinated pesticides, PAHs, and PCBs.

6.2. Project

Seven sites were established in representative areas of the Tampa Bay watershed for the collection of bulk deposition over a one year period. Sites were located according to NADP/NTN protocols except that several were placed in urbanized areas to evaluate spatial differences. Refined estimates of atmospheric deposition obtained during the study would ideally reflect the range in atmospheric loadings between the rural and the urban areas of the Tampa Bay watershed, which contain substantial mobile and stationary sources. The project was carried

out under an EPA-approved Project Quality Assurance Plan (Dixon and Allen, 1994) which addressed all aspects of both field and laboratory activities.

Integrated weekly samples were collected and analyzed for copper, lead, zinc, aluminum, nitrogen species (nitrate-nitrite-nitrogen, ammonium-nitrogen, total Kjeldahl nitrogen) and total phosphorus. The 52 weeks of the metals and nutrients sampling was completed on October 18, 1995. **Synthetic organic sampling** (biweekly composites analyzed for pesticides, PAHs, and PCBs) was conducted at five of the seven stations for a 12 week period beginning July 5, 1995, and strictly, **represents only the collection period, providing only approximate estimates of annual loads**. In particular, winter and spring growing seasons are not represented, although summer rains and associated depositions should be well represented. Toxic parameters chosen for analysis under this project were based upon the recommendations of the Atmospheric deposition Task Force, and were included in the "contaminants of concern" identified previously (Frithsen, *et al.*, 1995).

The bulk deposition monitoring plan was designed as the first phase of a long term effort to detect spatial and temporal patterns of deposition of analytes. Due to the inherent erratic nature of rainfall and the resultant episodic nature of wet deposition, a long term record is crucial for "averaging out" the effects of year to year climatological variations.

6.3. Bulk deposition

The measurement of bulk deposition in this project represents a technical and financial compromise in that it is likely to be an underestimation of the total atmospheric deposition to an area. Materials associated with the large size fractions (>5 microns) settle primarily through gravitation, include most metals, and are likely to be collected efficiently by bulk samplers. Fine aerosols (between 2 and 0.2 microns) are deposited primarily through precipitation scavenging, include most sulfate and nitrate ions, and should also be collected efficiently in bulk precipitation. Some portion of gaseous materials are also wet deposited depending on solubility and rainfall characteristics.

The dry deposition of gaseous species, however, is controlled by molecular diffusion and absorption onto substrates, leaf stomata uptake and retention, or solution into a waterbody. Gases include sulfur and nitrogen dioxides (NO_2), nitric acid (HNO_3), ammonia (NH_3), and ozone. Nitrogen dioxide is reported to be an important component near urban areas (Lovett, 1994) and nitric acid vapor is reported to account for a large fraction of dry nitrate deposition in the eastern U.S. (Lovett and Lindberg, 1986). Of the nitrogen species, therefore, nitrogen dioxide and nitric acid appear to be the nitrogen forms which would not be well collected by an artificial substrate, but which form a substantial portion of total nitrogen deposition.

As a result, **the bulk deposition collected during this study is indicative of the wet deposition (rainfall) and the dry deposition which occurred to a standardized surface** (a polycarbonate funnel of a specified shape and size). Values produced permit the assessment of spatial variation of **potential** total deposition across the watershed, recognizing that actual depositions to "natural" substrates or vegetation may have been greater. For loading calculations, species undercollected can be estimated from literature values specific to those compounds, although with unknown accuracy at sites with differing meteorology, vegetation, soils, and structures.

For calculation of relative atmospheric loadings to Tampa Bay, bulk deposition data collected under the MML project were coupled with data on point, nonpoint, and groundwater nitrogen loads computed for the 1985-1991 time period (Zarbock, *et al.* 1994). The MML total nitrogen bulk deposition during 1994-1995 (8.59 kg ha^{-1} yr^{-1}) was adjusted downwards to account for observed increases in wet deposition of inorganic nitrogen between the 1985-1991 and 1994-1995 periods, as measured at the NADP Verna Wellfield site. Bulk loadings of total nitrogen were assumed to have increased comparably to inorganic nitrogen loadings in wetfall alone. The bulk loading of total nitrogen, as estimated for 1985-1991, was then augmented by literature values (determined during the early 1980s) of nitric acid (1.21 kg ha^{-1} yr^{-1}) and nitrogen dioxide (2.96 kg ha^{-1} yr^{-1}) dry deposition to account for the gaseous species not adequately sampled by the project methodology. **The resulting total nitrogen deposition estimated for 1985-1991 was 12.05 kg ha^{-1} yr^{-1}.**

Phosphorus loadings (0.93 kg ha^{-1} yr^{-1}) measured in the MML project were assumed to be unchanged from 1985-1991 levels. Both phosphorus and metals deposition was assumed to consist primarily of particulates that were representatively collected by the bulk sampling devices. No adjustments were made in the bulk deposition values of pesticides, PAHs, or PCBs.

6.4. Samplers

The bulk collector design used was modeled after the deposition collectors employed in the Florida Atmospheric Mercury Study (FAMS) supported by the Florida department of Environmental Protection. Samples were collected by 12.0 cm diameter funnels with an overall height of about 20 cm. The funnel mouths were approximately 3.4 m above grade. Funnels were connected to tubing with connector blocks and compression fittings, and with similar blocks and fittings connecting the tubing to the sample collection bottle. Construction of all components was suitable for the scheduled analyses. Birds were deterred with monofilament line.

As sample collection bottles were 1 L in volume, approximately 9.2 cm of rain could be collected in a week before sample overflow. Weekly rainfall totals at the SWFWMD stations nearest the MML sites indicated that about 92% of the rainfall that fell during the project could be retained by the samplers without overflow. The degree of underestimation loads by truncating the end of a large rain event is likely to be slight, particularly for soluble species.

Rainfall collected by the bulk samplers averaged approximately 84% of the rainfall collected at the nearest SWFWMD rainfall stations. The SWFWMD sites averaged 2.5 km distant from the MML sites. A shorter record at one of the sites where an alternate rainfall gage was within a few hundred meters, indicated that MML samplers collected 93% of measured rainfall. If biases are real, they are attributed to the potentially different aerodynamic qualities of a smaller funnel cross section and differences in wind speed at a 3.4 m height above grade. As any bias in dry deposition is unknown, and as the distance between SWFWMD and MML sites was as great as 4.3 km, loads were calculated using the rainfall volumes and sample concentrations as collected by the MML samplers with no further adjustment, except as noted for nitrogen, above.

Loadings were computed with captured rainfall and analytical concentrations and were corrected for equipment blanks (primarily zinc and aluminum). Where concentrations were less than the method detection limit, NADP/NTN protocol was followed, using a concentration value of one half the method detection limit (½ MDL) for calculation purposes.

The data were also censored for contamination by bird debris with the remaining outliers having no evidence that would lead one to conclude that a non-representative contamination had occurred. MML sampling precisions for bulk deposition of nitrate-nitrite-nitrogen and ammonium nitrogen were equivalent to NADP/NTN precisions obtained from a one year intercomparison site maintained at the nearby Verna Wellfields in Sarasota. The variation in weekly loading rates over the course of a year of ammonium-nitrogen and nitrate-nitrite-nitrogen at the NADP/NTN site (wet deposition only) was also within the range of variations noted at MML sites for bulk deposition of the same parameters. As the NADP/NTN data are collected under rigorous and nationally accepted quality assurance guidelines and sample validation procedures, this result is indirect confirmation of the validity of MML sample collection, screening, and censoring processes.

Distributions of remaining data at a site were typically non-normal (heavily skewed) for all parameters. While the **median** is less sensitive to the inclusion of outlier data, the **mean** is a more accurate representation of total annual loads, unless the outlier data is the result of non-representative sample contamination. One should recall that the episodic nature of atmospheric deposition is expected to generate skewed distributions and that not all outliers can be assumed to be erroneous measurements. As a result, loading evaluations were performed using mean deposition rates, with the revised atmospheric loading values inserted into prior estimates of loadings to Tampa Bay (Frithsen, *et al.*, 1995; Zarbock, *et al.*, 1994).

Station differences noted describe the relative distribution of the weekly events (multiplied by 52) rather than differences between annual loads, although if weekly events are typically larger at one station then annual loads will be, as well. The converse is not necessarily true, however, as substantial and meaningful differences in total annual loading between stations did exist even with no statistically significant difference in the distribution of weekly events.

By example, there were no statistically significant differences between stations in the weekly rainfall amounts, although the median events ranged between 0.9 cm and 1.7 cm. Annual totals of rainfall, however, were quite different, ranging between 99.4 cm and 129.8 cm (39.1 inches and 51.1 inches), and were particularly high in the southern portion of the watershed.

Examination of the various weekly nutrient and metals loads as a function of rainfall amounts indicate significant ($p < 0.001$) regressions for all. The relationship of parameter loadings with rainfall is further indicated by a two way analysis of variance on ranks in which calendar quarter (season) as a treatment was significant ($p < 0.05$) for all parameters with the exception of ammonium-nitrogen. Quarter (season) and rainfall obviously covary in Florida, with the dominant wet season contained within the summer and early fall months.

Weekly bulk loadings could not be linked to other meteorological parameters (weekly average wind speed, direction, rainfall, temperature). Since hourly ambient air concentrations at selected county sites did demonstrate dependence on hourly wind direction (Dixon, 1996; **Appendix A**), a lack of significance between deposition and average wind direction was attributed to the variable wind directions over a weekly period and the lack of information on rainfall characteristics and wind direction during rainfall events.

Quarterly deposition totals underlines the importance of conducting deposition studies over a minimum period of at least one year. Metals depositions during the MML project varied by factors of approximately two or greater between quarters, while nutrient quarterly loads varied by factors of 1.2 up to 3.3. Links of loadings to rainfall amounts and interannual variations in rainfall add further uncertainty to assessments drawn from the measurement of deposition during a single year.

6.5. Metals

Averages of mean station deposition rates were 7.98 g ha^{-1} yr^{-1} for copper, 6.54 g ha^{-1} yr^{-1} for lead, 79.66 g ha^{-1} yr^{-1} for zinc, and 453 g ha^{-1} yr^{-1} for aluminum. Aluminum data, in particular, provided an excellent example of a true episodic event producing an **apparent** outlier and a substantially larger annual load. The highest aluminum value at all stations was recorded during the same week with an exceptionally heavy rainfall, and presumably represented entrained soils, most likely Saharan dust (Landing, *et al.*, 1995).

For all metals, there were significant differences between stations for weekly loadings. Station 3, in the northern and least urbanized portion of the watershed, consistently recorded among the lowest metals loadings of all stations. Of copper, lead, and zinc, Stations 1 and 4 were always included in the three highest loadings. These stations were located in the most urbanized regions of the watershed and the higher depositions are consistent with the urban:rural variations reported in other references and summarized in Dixon (1996; **Appendix A**). In addition, Spearman Rank Correlation of the various metals at a given station with aluminum (as an indicator of terrestrial origin) revealed that significant relationships did exist for all, with the exception of lead at Stations 1 and 4, and zinc at Station 1. In these three instances, metals deposition is clearly **not** linked to the deposition of previously suspended soils but originates with some other, presumably anthropogenic, source.

The variation in metal loadings among stations clearly show that the development and use of a single loading value for a particular metal is an approximation for the Tampa Bay watershed, and probably for water surfaces of Tampa Bay as well. While annual aluminum loads range by a factor of 1.8 between highest and lowest stations during the MML study, lead, copper, and zinc range by factors of 2.0, 2.8, and 3.3. In particular, depositions in urban settings may be more representative of loads to the northern portion of the Bay.

With revised loadings from the current bulk deposition project, atmospherically derived (direct deposition plus 10% of watershed deposition) copper, lead, and zinc were estimated to consist of 11%, 3%, and 8%, respectively, of total Bay loads. Of these amounts, direct deposition to the Bay for the same metals consisted of 7%, 2%, and 5%. Nonpoint source loadings from the urbanized areas dominated loads to Tampa Bay with loads in urban runoff exceeding atmospheric deposition to the same areas by average factors of 5.2, 32.7, and 10.0 for copper, lead, and zinc respectively. It is clear that anthropogenic activities in the watershed are the dominant factors in metals loadings to Tampa Bay. Total loads by source appear below in Table 18.

6.6. Nutrients

Of all the nutrients, the total phosphorus and ammonium nitrogen were the only parameters with significant differences in **weekly** loadings among stations. Phosphorus loads were higher at the stations in the eastern portion of the watershed, consistent with the terrestrial influences and mining operations centered in that region.

No significant station to station differences in **weekly** deposition were noted for nitrate-nitrite-nitrogen, total Kjeldahl nitrogen, inorganic nitrogen, or organic nitrogen, despite wide ranges in annual loadings. Annualized loadings ranged between 2.50 to 3.77 kg ha^{-1} yr^{-1} for nitrate-nitrite-nitrogen, and 6.02 to 12.85 kg ha^{-1} yr^{-1} for total nitrogen.

Station data for each week were also compared to the watershed average of all stations for the week. For nitrate-nitrite-nitrogen, results indicated that weekly loadings at Station 3, in the northern portion of the watershed, were significantly different from and **lower** than the watershed mean. The stations at which weekly loadings averaged higher than the mean, although not at significant levels, were in the central and southern portions of the study area (Stations 1, 4, 6, and 7). The implication is that the localized variation in nitrate in bulk deposition is not due to sources to the north of the watershed. As nitrate-nitrite-nitrogen deposition at Station 3 was 2.50 kg ha^{-1} yr^{-1}, and the highest value observed (at Station 4) was 3.77 kg ha^{-1} yr^{-1}, it is also apparent that "background" levels of nitrate-nitrite-nitrogen may exceed within-watershed variations.

For inorganic nitrogen, both Stations 2 and 3 had weekly loads significantly lower than the weekly means over the entire watershed. Again, Stations 2 and 3 are to the north and northwest within the watershed. Sources in the central and southern portions of the watershed apparently influence localized variation in inorganic nitrogen loadings, but the substantial levels at all sites exceed the range of values between stations. For ammonia, total Kjeldahl nitrogen, organic nitrogen, and total nitrogen, general spatial patterns were similar, but the stations with the highest values of these parameters were two to three times greater than the lowest values at Station 2. For these nitrogen species, localized activities or sources to the south and west can be said to be the dominant factor in depositional loads.

Bulk deposition of nitrogen measured during the project was adjusted as described above for consistency with other loading estimates and to account for undercollected species. Revised estimates for nitrogen are quite close to previous calculations, 32% as opposed to 27% determined previously (Zarbock, *et al.*, 1994), with atmospheric deposition still second to nonpoint source loadings. For phosphorus, new estimates of direct atmospheric loads are substantially lower (5%) baywide as compared to previous estimates of 31 % (*ibid*). Nonpoint sources (39%), followed by point sources (domestic and industrial, 36%) dominate the loadings of phosphorus to Tampa Bay.

Atmospheric loadings of nitrogen to the various basins of the watershed (at 12.05 kg ha^{-1} yr^{-1}) were also compared to the nonpoint source loadings determined in Zarbock, *et al.*, (1994) to determine approximate watershed transfer coefficients. In-stream processes were not considered. As water quality coefficients and therefore loads from specific land uses have been developed from a large empirical data set, the loads from nonpoint source runoff reflect a "typical" sum of both precipitation quality (atmospheric deposition), sources (anthropogenic "imports", biogenic recycling) and sinks (biological removal) within a basin. Spatial differences in Tampa Bay precipitation quality are not incorporated except to the extent that literature values of urban or agricultural runoff water quality may reflect localized differences in ambient air quality.

Over the watershed as a whole, estimated nonpoint source runoff represents 25% of the total atmospheric deposition of nitrogen, or a watershed retention rate of 75%. Watershed retention

rates of nitrogen for Tampa Bay as a whole are comparable to literature estimates for other systems. More heavily urbanized basins such as Boca Ciega Bay transfer larger amounts of material, retaining only 40%. Higher transfers undoubtedly result both from a more impervious basin (higher urbanization and runoff quantity) as well as from activities within the basin (residential fertilization, etc.). If the bulk of nonpoint source loadings are assumed to represent atmospheric loadings, then the total atmospherically derived nitrogen loading to Tampa Bay is on the order of 70-80% of total Bay loadings.

For phosphorus, however, comparison of nonpoint source loads with atmospheric deposition loads indicate that watershed geology and activities contribute far more phosphorus than does atmospheric deposition. Many basin retention percentages are less than zero, with total nonpoint source loadings near 150% of the total atmospheric deposition to the watershed. Mining land use and/or regional geology can be linked with much of this result, particularly in the Alafia, Little Manatee River and Coastal Lower Tampa Bay basins, but urbanized regions such as Boca Ciega Bay also appear to have substantial sources of phosphorus within the basin.

6.7. Pesticides

More than half of the overall mass of pesticides collected were recovered at Station 7, with the most abundant β BHC, endosulfan-I and -II, and pp'DDT. Compounds and temporal patterns of appearance were in general consistent with reported agricultural activities in the region (row crops). The appearance of DDT (banned from use in the U.S. in 1978) could be explained by suspension of soils and soil-associated residuals of recalcitrant compounds during soil tilling, although the absence of the breakdown products DDD or de, is unusual.

The remaining four stations received less than 20-30% of the total loadings at Station 7 and were similar in total amounts of pesticide recovered, but the types of pesticides varied, indicating different pesticide fluxes to each of the collection stations. Pesticide residues were lower at the urban sites, with chlorpyrifos the most abundant pesticide collected at Station 1, probably reflecting commercial insecticide applications to residence or office buildings and grounds. At several stations, pesticides were only present during one or two of the six 2-week collection periods, showing great variability in pesticide loadings at each site.

Pesticide deposition during the 12 week sample collection period was extrapolated to an annualized load for the purpose of comparing project data with previous estimates. As the winter growing season was not sampled during this project, the annualized estimates may well provide an underestimation of total annual pesticide loads. Loads to the Bay were computed from the average deposition rates of all five stations over the entire area of the Bay, plus over 10% of the watershed area to account for indirect deposition.

Chlordane, the most abundant pesticide in the 1970s, and dieldrin, one of the most prevalent, were not detected in the present study. Total DDT (DDT plus DDD and de) loadings were about 20% of those reported in the 1970s. Endosulfans, the most abundant pesticides in the present study, were not reported for the 1970s. Overall, annualized chlorinated pesticide atmospheric loadings to Tampa Bay dropped from 30 kg yr^{-1} in the 1970s to 10.6 kg yr^{-1} during this study.

It is important to re-emphasize that the majority of pesticides were collected at one station. The spatial heterogeneity indicates local sources for these synthetic compounds rather than long

distance atmospheric transport (which would be more evenly distributed over the Bay and watershed areas).

6.8. PAHs

The PAH compounds monitored during this study were the unsubstituted, parent, multi-ring compounds representative of combustion (pyrogenic) sources, such as fossil fuel combustion from automobiles, power plants and fuel oil furnaces, as well as forest fires, agricultural burning, trash incineration and charcoal Bar-B-Que. Similar to the pesticide data, there was a vast difference in the amount of PAHs collected at each site, with Station 1 containing 75% of all the PAHs collected. Station 1 was also the only location at which the carcinogen benzo(a)pyrene was detected, again a compound which is indicative of combustion-generated PAHs (National Academy of Sciences, 1985). In general, the sites in proximity to urban/industrial areas exhibited the greatest amount of PAHs, with Station 3 having the least.

The major components of PAHs were the same for the three most abundant PAH sites, including fluoranthene and benzo(b)fluoranthene. These compounds, however were not detected at the other two sites. As with the above pesticide samples, each sample site was representative of a different type and/or amount of PAHs, thus each collection station represented a separate PAH deposition regime. These results show the influence of localized sources, rather than long-range transport, indicating that different segments of the Bay may receive different depositional loadings and compositions of PAHs. No historic data for Tampa Bay were available for comparisons with current PAH loadings. PAH loadings, however, were quite similar to recently published (Baker, *et al.*, 1992) deposition rates determined for the Chesapeake Bay.

6.9. PCBs

Station 3 exhibited not only the highest number of PCBs (four), but also the greatest deposition rate of total PCBs (8.9 $\mu g\ m^{-2}\ yr^{-1}$). Station 5 and Station 7 exhibited intermediate amounts of three and two congeners, respectively, with the more urban sites receiving only low amounts of one congener. Biweekly depositions were erratic to the extent that no one station received significantly different weekly loads, although annualized depositions ranged by a factor of 12-27 between stations, greater than the range between pesticide loadings. The total PCB loadings for the present study were 6 $kg\ yr^{-1}$, about 50% of that observed from the 1970s study (11.2 $kg\ yr^{-1}$, Frithsen, *et al.*, 1995).

6.10. NADP/NTN Data

Data gathered at the nearby Verna Wellfield site were investigated for information on parameter relationships and temporal trends. Similar to the bulk deposition data, wet deposition of all parameters at the NADP/NTN Verna site exhibited precipitation scavenging, with loads displaying a tendency to increase with increasing amounts of precipitation. Summer loadings of inorganic nitrogen species in particular were 1.5 to 3.0 times greater than depositions during the remaining quarters.

The influence of seawater aerosols were clearly evident and the regression of nitrate with other parameters revealed the best agreement between weekly loadings of nitrate and sulfate (with the observed linearity implying some measure of a common source).

Annual loadings were also examined from the period 1984 through 1994, the years with complete available record. A significant trend of increasing nitrate-nitrogen, ammonium-

nitrogen, and inorganic nitrogen with time is apparent. While a slight increase in annual rainfall has occurred over the same period, the trend is not significant and loadings do not clearly reflect the extremely low rainfall totals observed in 1989 and 1990. Atmospheric loads of inorganic nitrogen are steadily increasing with time.

For both ammonium and nitrate-nitrogen, the increase with time was most apparent for the summer quarter, with no significant increases in the winter, spring, and fall. Population figures for the surrounding counties mirror the increase in nitrogen loads and imply that, in the absence of continued improvements in emissions controls on both mobile and stationary sources, loadings of inorganic nitrogen will continue to increase with population growth.

The long term record provided by the NADP/NTN data illustrates not only the increasing loads with time, but also illustrates the high variability of atmospheric deposition. Annual loads of inorganic nitrogen can vary by substantial percentages, given only a short separation between start dates of the annual compilation with variations in nitrate-nitrogen greater than for ammonium-nitrogen. Presumably, variation in bulk deposition can be as great. The inherent variability in depositional loads as demonstrated for inorganic nitrogen, are strong arguments for continuing any atmospheric deposition program over some minimum number of years. The number of years will depend on confidence required of the resulting data, with current estimates of inorganic nitrogen loading alone from the 11 year NADP program only precise to within $\pm$ 20%.

6.11 Programmatic Needs

As has been discussed previously, bulk deposition, while useful and economical for depicting spatial variation in deposition of certain size classes across a geographic area, suffers from technical limitations. Gaseous and potentially significant species are most likely under-collected and must be accounted for to estimate total deposition. Other, more technically rigorous approaches, may quantify additional aspects of dry deposition, but each technique also has limitations, and to apply the techniques across a variable watershed is prohibitively expensive.

To address this problem, a variety of basic research needs have been well summarized by Baker *et al.* (1993) and are not unique to Tampa Bay. Such areas as aerosol behavior and deposition, absorption of gases to variety of substrates, gaseous exchanges with both solid and aqueous surfaces, and volatilization of dissolved or soil bound materials are all poorly understood and require extensive basic research to develop models that will be useful in a management context. Most needs address aspects of dry deposition. In addition to deposition models, additional work is also needed on emission and transport models, particularly from the standpoint of source allocation. Indirect contributions from a watershed form an important part of source allocation and materials contributed by anthropogenic "imports" to a watershed (fertilization) should be separated from materials deposited from the atmosphere (with consideration for differing impervious areas and runoff with differing land uses).

For individual estuaries, as for Tampa Bay, mass balances are useful in determining the relative loadings from a variety of sources. In order to predict impacts from changes in loadings, however, the variety of sources and sinks of each individual pollutant must be known with some degree of certainty. Using toxic organics as an example, many typical sources and sinks (*i.e.* sediment and marsh interactions) in estuarine systems are yet unquantified for the Tampa Bay

region. For nutrients, however, mechanistic and statistical models developed for Tampa Bay can be used for the purposes of predicting impacts and identifying necessary nutrient reductions.

As highlighted by this and every other study of atmospheric deposition, the deposition process, whether of wet, bulk, or dry, is highly variable both spatially and temporally. Consistent spatial variability, linked to variation in meteorology and ambient air quality, can be addressed with increasing density of collection stations, and a corresponding increase in expenditure. Where funds permit only a single station, the research question posed and the use of the data should be carefully specified. Further, if the watershed is expected to have spatially variable deposition rates (as has been demonstrated for Tampa Bay), it should be kept in mind whether the instrumented site represents the upper or lower bounds of deposition either to the Bay or the watershed. Application of watershed transfer models may well require additional stations to be monitored in the future.

Temporally variable deposition can only be addressed by extending the duration of sample collection. Local wet deposition programs (PCDEM, 1993) exhibit on the order of four-fold variations in annual inorganic nitrogen deposition over an eight year period. At the nearby NADP/NTN site, inorganic nitrogen loads have varied by a factor of two over a 11 year period. Not all of the variation is linked to varying rainfall amounts, and indeed, loads appear to be increasing with time. Monitoring alone will not be sufficient to detect trends, however. A variety of power analyses performed on the NADP annual loadings implies that sampling programs will need to extend over a 20 year period in order to have a 10% power to detect a 25% change in actual loadings. Monitoring to detect the results of management actions affecting smaller changes will need to be performed for even longer. Clearly, improvement in our understanding and simulation of the wet deposition process is necessary. One other temporal question left unanswered by this project is the deposition of pesticides, PCBs, and PAHs during other portions of the year, although data obtained during the four month period could be used for order-of-magnitude estimates.

In summary, the continuing needs can be categorized as basic research, source allocation for Tampa Bay and the watershed, and impacts assessment of projected changes in deposition. Any sampling program begun, should be continued over a minimum number of years. The Great Waters Program, in which the Tampa Bay National Estuary Program is participating, has begun to address these needs at a single site in a relatively urbanized area of the Bay.

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APPENDIX A

Literature Compilation and Data Synthesis for Atmospheric Deposition to the Tampa Bay Watershed

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Mote Marine Laboratory Technical Report Number 486

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LITERATURE COMPILATION AND DATA SYNTHESIS FOR ATMOSPHERIC DEPOSITION TO THE TAMPA BAY WATERSHED

Background

Remedial efforts to improve impacted surface waters have predominantly focussed on the removal and/or improvement of point source discharges. More recently, efforts have been expanded to address non-point source loadings. Atmospheric contributions of materials to estuaries and their watersheds have been largely ignored. Selected case studies (Paerl, 1985; Fanning, 1989; Winchester and Fu, 1992; Hicks *et al.*, 1992), however, indicate that atmospheric deposition of nitrogen can comprise substantial portions of an estuarine nutrient budget. While first order estimates of atmospheric deposition can and have been prepared from existing long-term data sets (Zarbock *et al.*, 1993), most long-term data have been collected in rural locations, in an attempt to describe regional patterns of deposition. The Tampa Bay watershed, however, has a significant urban component, particularly near the Bay, with a large number of stationary sources, as well as mobile emissions of nitrogen oxides and metals. There is concern that loadings determined from rural areas may significantly underestimate actual loadings. In addition, there is very little information on atmospheric deposition of toxic metals in Florida, and again the major studies underway at this time are, for the most part, located in relatively non-urban areas.

As a result, the Tampa Bay National Estuary Program (TBNEP) has funded a program to refine deposition estimates. The project is an outgrowth of a program to determine current and benchmark nutrient loadings for Tampa Bay and to establish pollutant reduction goals necessary to support and restore the Bay's essential natural resources. Pollutants scheduled for monitoring are nitrogen, phosphorus, copper, lead, and zinc.

Nitrogen is of interest since the majority of Tampa Bay appears to be nitrogen-limited with chlorophyll content and total nitrogen concentrations strongly linked (Johansson, 1991). In addition, the organically bound nitrogen in atmospheric deposition is poorly characterized and will be analyzed as well. The phosphorus content of rainfall is typically low, only a small percentage is thought to be transported via the atmosphere (Duce, 1986), and national monitoring networks use the presence of phosphorus to indicate a contaminated sample (Dr. Jay Gibson, personal communication). The industry of phosphate ore mining and processing in the Tampa Bay region, however, may contribute particulate phosphorus species in excess of levels determined elsewhere, and previous Tampa-specific wet deposition data (Zarbock *et al.*, 1993; Noel *et al.*, 1987) could account for substantial phosphorus deposition direct to the Bay. Fugitive emissions from bulk loading facilities in Hillsborough Bay have also been the subject of some discussion (Cardinale and Dunn, 1991; Orlando, 1993).

Additionally, sediment studies of the estuarine portion of Tampa Bay have identified some areas anthropogenically enriched in toxic metals (Schropp, 1990; Alexander *et al.*, 1993; Long *et al.*, 1991), particularly cadmium, mercury, lead, silver, and zinc. Some fish in the Hillsborough River exceed quality criteria for mercury content (FDEP, unpublished data; Hand and Friedemann, 1990). Metals have long been identified with urban runoff, and rainfall data indicate that substantial portions of metal loading can be attributed to atmospheric deposition.

There is no national network, however, for monitoring the wet deposition of metals (Vermette *et al.*, 1992). For the TBNEP study, copper (Cu), lead (Pb), and zinc (Zn) were selected based on the importance of anthropogenic inputs, toxicity, and mobility. Mercury, while of critical interest to the TBNEP program, was deleted from the analytical suite due to the ongoing Florida Department of Environmental Protection (FDEP) Florida Atmospheric Mercury Study (FAMS) and the technical rigors and expense of obtaining and processing contamination-free samples.

The following compilation of literature pertinent to Tampa Bay will discuss sources, emissions, available ambient air quality data, precipitation quality, and the reported ranges of wet and dry deposition rates. Due to the relative scarcity of synoptic quantitative data for all regions of the state, data from many differing time periods will be presented. These data should be viewed with the precaution that precipitation chemistry and resultant deposition rates are notoriously variable and require long-term records for valid spatial or temporal comparisons. The text on sources and emissions will focus on nitrogen and phosphorus species, as sources of the toxic metals to be addressed by the study were to be summarized in the Toxic Contamination Action Plans, under production concurrently with this document. Data on atmospheric deposition of metals are even scarcer, and so pertinent data from other regions of the county are presented. Data have been transformed as necessary from the originally reported ionic concentrations and loads (*i.e.* mg L^{-1} NO_3^-) to elemental concentrations and loadings (*i.e.* as N). Other units have been similarly converted to the S.I. system.

Introduction

Atmospheric deposition to an estuary can occur through either direct or indirect mechanisms. Direct inputs include both wet and dry deposition directly to the surface of the waterbody. Wet deposition is the mechanism by which particulate, aerosol, or gaseous materials are dissolved in or physically removed from the atmosphere by rainfall. Dry deposition includes the gravitational settling of larger particles, the impaction and retention of aerosol particles onto a surface, and the absorption of gaseous materials onto solid or liquid surfaces. The individual chemical species of a pollutant class have primary modes of deposition which are a function of the physical state (solid, aerosol, or gaseous), dominant particle size, chemical characteristics, receiving surface characteristics, and micrometeorology near the receiving surface.

For indirect deposition to an estuary, both wet and dry deposition occur on the land, waterbodies, structures, and vegetation surfaces of the watershed. The portion of materials which is subsequently transferred to the tributaries and eventually to the estuary through rainfall, runoff, and tributary flow is termed the indirect input. The transfer coefficient, or the percent which ultimately leaves the watershed, will vary by pollutant species, being controlled by the physical absorption onto soils and vegetation, as well as biogenic uptake and recycling within the watershed.

Precipitation quality is linked to ambient air quality, and thus emissions, with generally higher atmospheric fluxes observed in areas with higher emissions and ambient air concentrations (Luecken *et al.*, 1992). Seasonal variations in rainfall patterns, emissions, and prevailing winds often produce seasonal variations in wet deposition loadings (Luecken *et al.*, 1992). Dry deposition of larger particulates is driven by gravitational settling and typically occurs quite close

to emissions sources (Scudlark *et al.*, 1992). The dry deposition of gaseous and aerosol materials is more a function of boundary layer turbulence and receptor surface, with dry deposition increasing with increased turbulence, increased surface area (leaf area index), and surface moisture (dew or waterbody surface) (Sherwood, 1991).

Global and Regional Sources

Sources of materials to the atmosphere can be either "natural" or "anthropogenic" with natural sources including biogenic processes, outgassing from soils or volcanic activity, forest fires, resuspension of crustal material, and aerosol formation from surface waters. Anthropogenic sources typically include energy production and other fossil fuel combustion (industrial activities and transportation), waste incineration, mining, and related manufacturing.

Anthropogenic sources of nitrogen oxides are almost exclusively from combustion of fossil fuels, either stationary sources such as utilities and industrial boilers, or mobile sources such as transportation. Under high temperature combustion, nitrogen and oxygen dissociate and combine primarily to form nitrogen dioxide (NO_2) and nitrogen oxide (NO), collectively known as NO_x. The higher the flame temperature, the higher the NO_x production. In addition, nitrogenous compounds in fuel react with oxygen during combustion to produce NO_x (Kaplan, 1991). Of the various fossil fuels, coal generates the highest NO_x emissions per unit of energy produced (Neuffer, 1985). For municipal solid waste incinerators as a group, fuel NO_x may comprise up to 80% of the total NO_x generated (Radian, 1991). Photochemical reactions of NO_x with hydrocarbons subsequently result in ozone, while reactions with water vapor result in nitric acid (HNO_3), a component of acid rain. Minor additional sources of anthropogenic NO_3^- in rainfall might include fertilizer applications or soil entrainment during agricultural operation or land clearing.

Natural sources of NO_3^- in rainfall include oxidation of NO_2 in biological decay and NO_3^- produced from lightning and N_2. Atmospheric ammonia (NH_4 and NH_3), aside from industrial releases (such as may be used in utility NO_x-emission control systems) or fertilizers, is primarily a biogenic decomposition product (Gleick, 1993). Anthropogenically induced concentrations of these species, therefore, result wherever concentrated animal or human wastes are allowed to decompose, with 75% of atmospheric concentrations estimated to come from feed lots and fertilizer applications (Placet *et al.*, 1990 as cited in Rushton, 1993).

Nationwide, NO_x emissions were relatively stable between 1979-1988 at approximately 18 million metric tons $year^{-1}$ with 55% allocated to fuel combustion and 41% to transportation (USEPA, 1990). Annual mean air quality in 1988 of 116 sites was approximately 25 ppb of NO_x (USEPA, 1990). Through the reconstruction of historical fuel usage and transportation, NO_x emissions in the southeast are thought to have increased roughly exponentially since the 1900's (Husar *et al.*, 1993) with emissions approaching 6.4 million metric tons NO_2 per year by the early 1980's. Uncertainties in this figure could be as high as a factor of 2.

On a national scale, work on the empirical relationships between emissions of NO_x within various sized geographic cells and wet deposition of NO_3^- (Luecken *et al.*, 1992) observed the best correlations between rainfall quality and a 720 km radius cell. Implications are that most

NO_x is transported a considerable distance before removal by rainfall. Such relationships were strongest in the northeastern United States.

Natural sources of phosphorus to the atmosphere include resuspension of crustal materials, vegetation combustion products, and marine aerosols. Anthropogenic sources in addition to burning are typically thought to include fertilizer applications and handling, and phosphate mining.

Natural sources of trace metals to the atmosphere include forest fires, sea salt aerosols, and soil dust, but globally, anthropogenic sources exceed natural releases by a factor of 28 for lead and 3 for zinc. Copper and mercury anthropogenic emissions are equal to or slightly greater than natural releases (Verry and Vermette, 1993; Nriagu, 1992). Anthropogenic emissions are, in addition, concentrated in the industrialized countries, thus increasing their relative impacts in these regions. In the atmosphere, crustally derived trace metals are typically contained in coarser particles (>2.5 microns) and deposited near the source, whereas metal oxides vaporized in high temperature combustion form sub-micron sized aerosols (Scudlark *et al.*, 1992).

Globally, anthropogenic lead is primarily contributed to the atmosphere through combustion of lead gasoline additives (75%), smelting (14%), manufacturing and battery construction (5%), and energy (coal-fired) production (4%) (Nriagu and Pacyna, 1988, as summarized in Nriagu, 1992). Waste incineration accounts for less than 1%. Copper and zinc have similarly large contributions from smelting and refining, 66% and 55%, respectively, with energy production accounting for 23% of anthropogenic copper emissions and 13% of zinc (Nriagu and Pacyna, 1988, as summarized in Nriagu, 1992). National trends in both lead emissions and ambient lead concentrations show dramatic tenfold declines since the late 1970's, from 108,700 metric tons $year^{-1}$ to 7.6 metric tons $year^{-1}$. From near 90% in 1979, transportation sources of lead now comprise only 34% (USEPA, 1990).

Between one quarter and one half of the anthropogenic mercury emitted is estimated to come from waste incineration (Verry and Vermette, 1993; Windham, in press) with 64% estimated from energy production (Nriagu and Pacyna, 1988, as summarized in Nriagu, 1992). For mercury, as for other metals and NO_x, emitted pollutants depend heavily on the source fuel, with solid waste and coal typically responsible for higher levels of metals emissions per energy unit produced.

Almost all atmospheric mercury exists in the relatively insoluble elemental form. Oxidation is required before mercuric ions can be effectively scavenged by precipitation (Porcella *et al.*, 1992). Mean atmospheric residence times of about a year imply that global cycling controls most deposition (Porcella *et al.*, 1992). Oxidized species such as mercuric chloride are more susceptible to removal by precipitation (and relatively easy to remove with emissions controls), but the proportion of the total mercury emitted in this form depends on the chlorine content of the fuel. Reportedly, municipal incinerators emit a larger percentage of mercury as mercuric chloride, with a potential for higher levels of deposition near the point source (Windham, in press). Little quantitative evidence exists, however, of localized increases in deposition near sources of mercuric ions or oxidants (Porcella *et al.*, 1992).

Study Area

The watershed to Tampa Bay includes approximately 5895 km^2 located predominantly in three counties; Pinellas, Hillsborough, and Manatee, with additional portions in Pasco, Polk and Sarasota counties (**Figures A-1 and A-2**). Of the watershed, 324 km^2 represent internal drainage, leaving 5571 ^{2} of watershed contributing to Tampa Bay. The water surface of the Bay itself is approximately 958 km^2 (Zarbock *et al.*, 1993). The airshed, however, the region from which emissions can influence deposition within either the Bay or the watershed, is a potentially much larger region. The exact shape of the airshed cannot be rigidly defined as it varies annually, seasonally, and even hourly with local and regional climatological patterns. The transport of some pollutants can occur over thousands of kilometers, and, coupled with plume dispersion from stationary or area sources, makes absolute source attribution a difficult task.

Study Area Emission Sources

Permitted stationary sources are listed in county and state emissions inventories. While NO_x may or may not be listed on permit conditions, estimates of annual NO_x emissions are prepared from standard factors based on fuel type, usage, or industry type. Advanced technologies for emissions reductions may not be reflected in the standard factors and so annual estimated emissions should be considered to be a conservatively high estimate of the total (Mr. Bob Soich, FDEP Tampa, personal communication).

A Florida emissions inventory for 1982-1983, including mobile sources, totalled 667,400 metric tons $year^{-1}$ of NO_x. Statewide, as of 1982 (Pollman and Canfield, 1993), annual NO_x emissions (**Table A-1**) were divided into 53% from point sources and 47% from area sources.

Table A-1. Allocation of total NO_x emissions in Florida by source (Pollman and Canfield, 1993).

Source Type		Percentage (%)
Point Sources	utilities	32
	non-utilities	21
Area Sources	transportation	43
	other	4

More recent compilations (Rogers, 1990) placed mobile sources responsible for nearer 50% of the total NO_x emissions, and indicated that Florida ranked eighth in the nation for NO_x emissions. Within the state in 1989, utilities accounted for 35% of the total NO_x emissions with industrial sources contributing 5-10%. Of the top 20 utility sources of NO_x within the state during 1989, four are located within the Tampa Bay watershed, with an additional three in surrounding counties (Rogers, 1990).

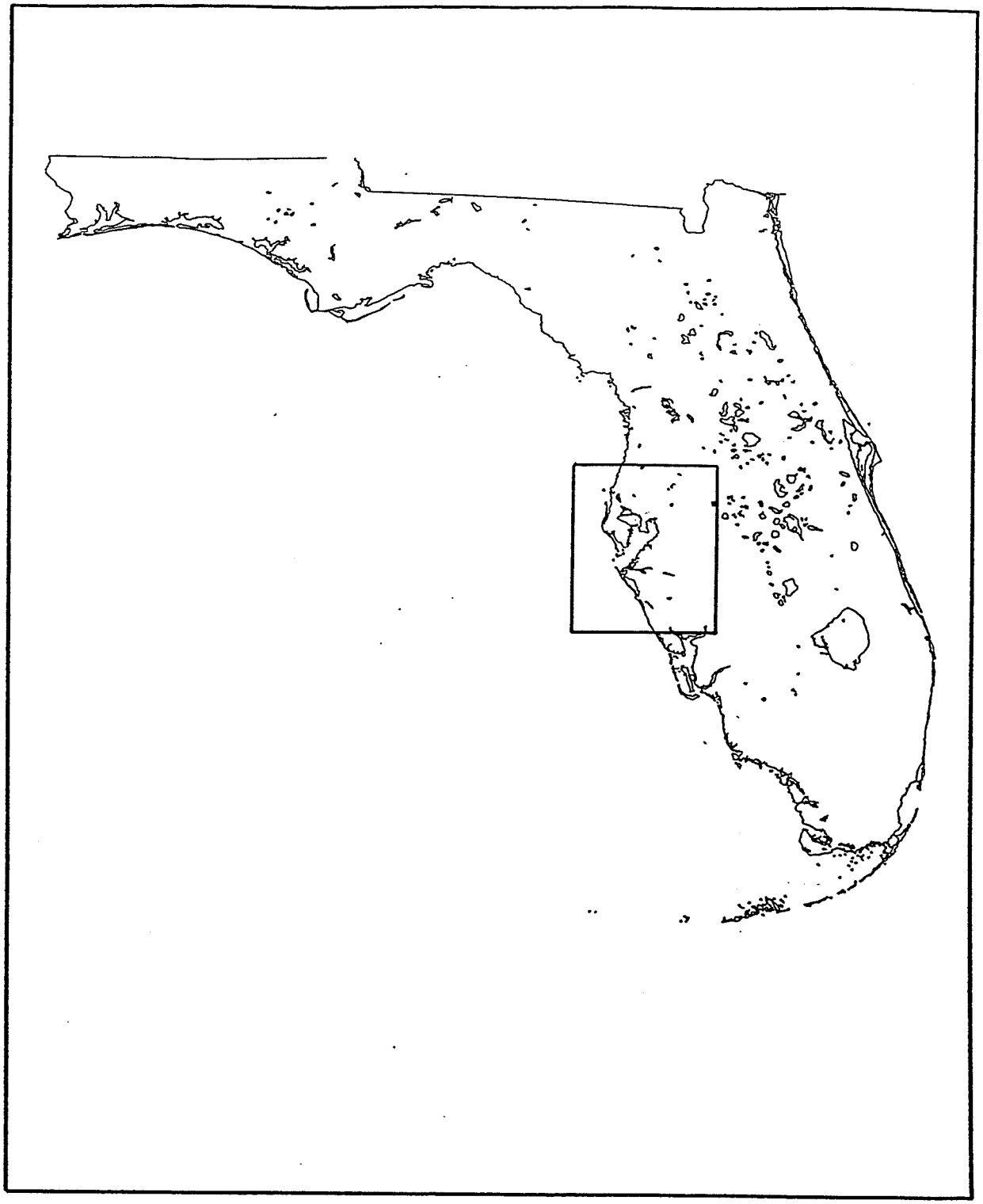

Figure A-1. State of Florida and the approximate study area surrounding Tampa Bay.

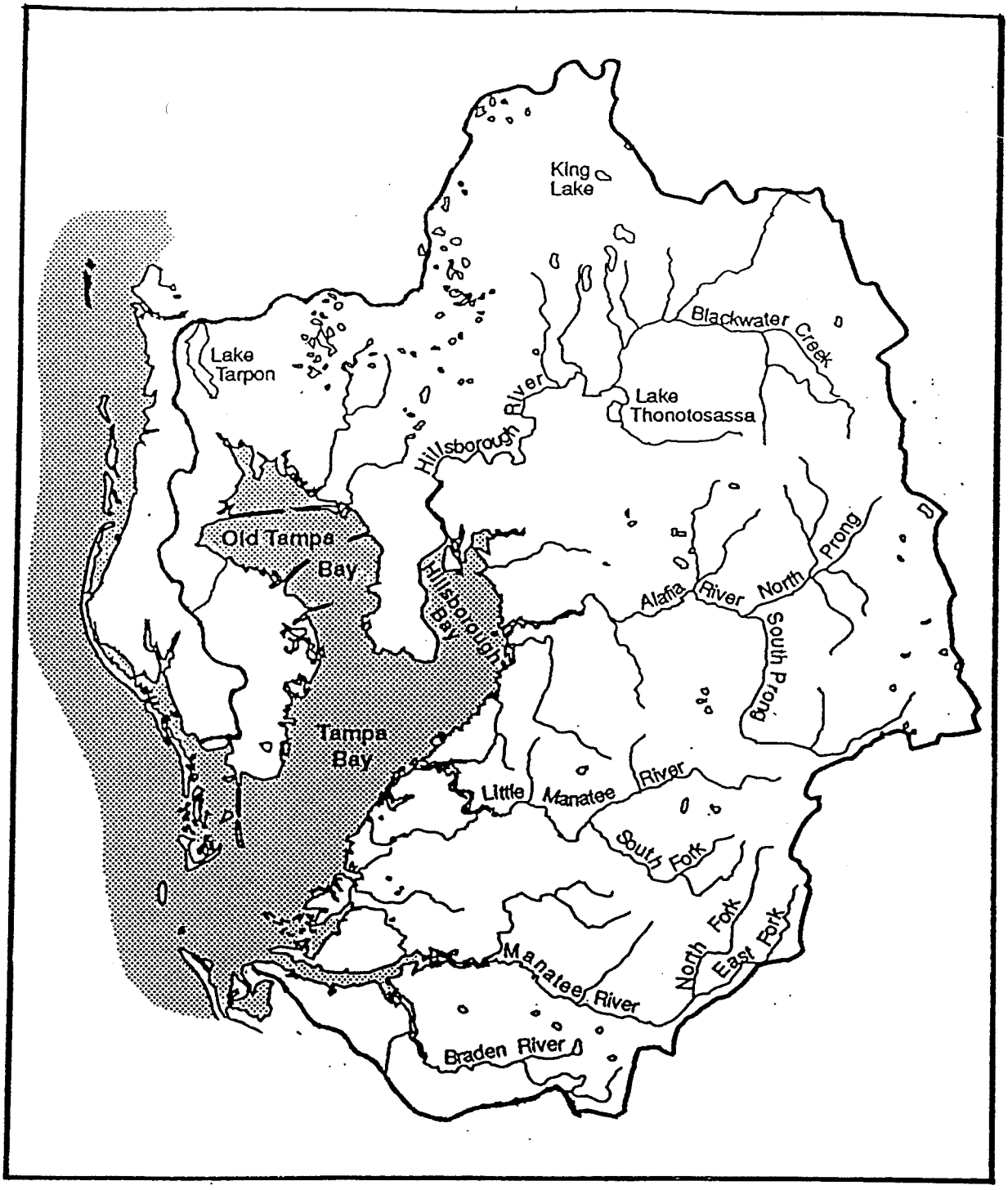

Figure A-2. The watershed of Tampa Bay, including portions of Boca Ciega Bay (adapted from Wolfe and Drew, 1990).

As of 1992, FDEP facility emission reports (FDEP, 1994) indicated that stationary source NO_x emissions totaled 107,600 metric tons $year^{-1}$ for the nine county area immediately surrounding the Tampa Bay and its watershed (**Attachment**). The inclusion of Citrus County adds an additional 43,923 metric tons $year^{-1}$ from the Crystal River Power Plant. Industry types represented on this listing include utilities and smaller power generation facilities, waste incineration, mining, and fertilizer processing and transportation. State listings by county are more complete for counties designated as non-attainment areas (Hillsborough and Pinellas), since counties without air quality violations have to report major emitters (>90.8 metric tons $year^{-1}$ [100 tons $year^{-1}$] of pollutants) only (Mr. Tom Rogers, FDEP, personal communication).

There are 15 stationary sources of NO_x greater than 454 metric tons $year^{-1}$ (500 tons $year^{-1}$) within the nine county area surrounding the Tampa Bay watershed. Collectively, the emissions represent 92% of the total stationary NO_x emissions, and include a number of electric power generating stations and mining interests, as well as several resource recovery (incineration) installations. **Figure A-3** illustrates the locations of the sources with greater than .454 metric tons $year^{-1}$ of NO_x emissions and include Teco Big Bend, Teco Gannon, Florida Power Anclote, Florida Power & Light Manatee, City of Lakeland McIntosh Power, Florida Power Bartow, and Pinellas County Resource Recovery Facility. Major sources outside the watershed, but potentially affecting deposition quality to Tampa Bay also include Florida Power Crystal River and Florida Power and Lime (Brooksville).

Mobile sources of NO_x are also substantial in urbanized, high traffic areas, estimated in **Figure A-4** by roadway density. Under the Clean Air Act Amendments of 1990, substantial reductions in emissions are required from the transportation sector and transportation plans and programs in areas where National Air Quality Standards are not achieved (non-attainment areas) must demonstrate conformity with State Implementation Plans (SIP), and contribute to annual emissions reduction. Emissions modelling and impact analyses have been performed by the Metropolitan Planning Organizations, to project the emissions reductions necessary to achieve compliance.

Ambient air modelling (with the Florida Standard Urban Transportation Modeling Structure and MOBILE 5.0) consists of an analysis of vehicle activity, average speed, miles traveled, and differing emissions characteristics for individual vehicle classes to compute estimates for the emissions of VOC (volatile organic compounds), CO (carbon monoxide), and NO_x (nitrogen oxides). While the model has the ability to work in fairly small geographic segments, current analyses treat the entire county as a single entity. As a result, the modeling results are useful for assessing the relative magnitude of mobile sources with respect to stationary sources, but will not materially assist the Atmospheric Deposition Project in the quantitative identification of areas of poor air quality.

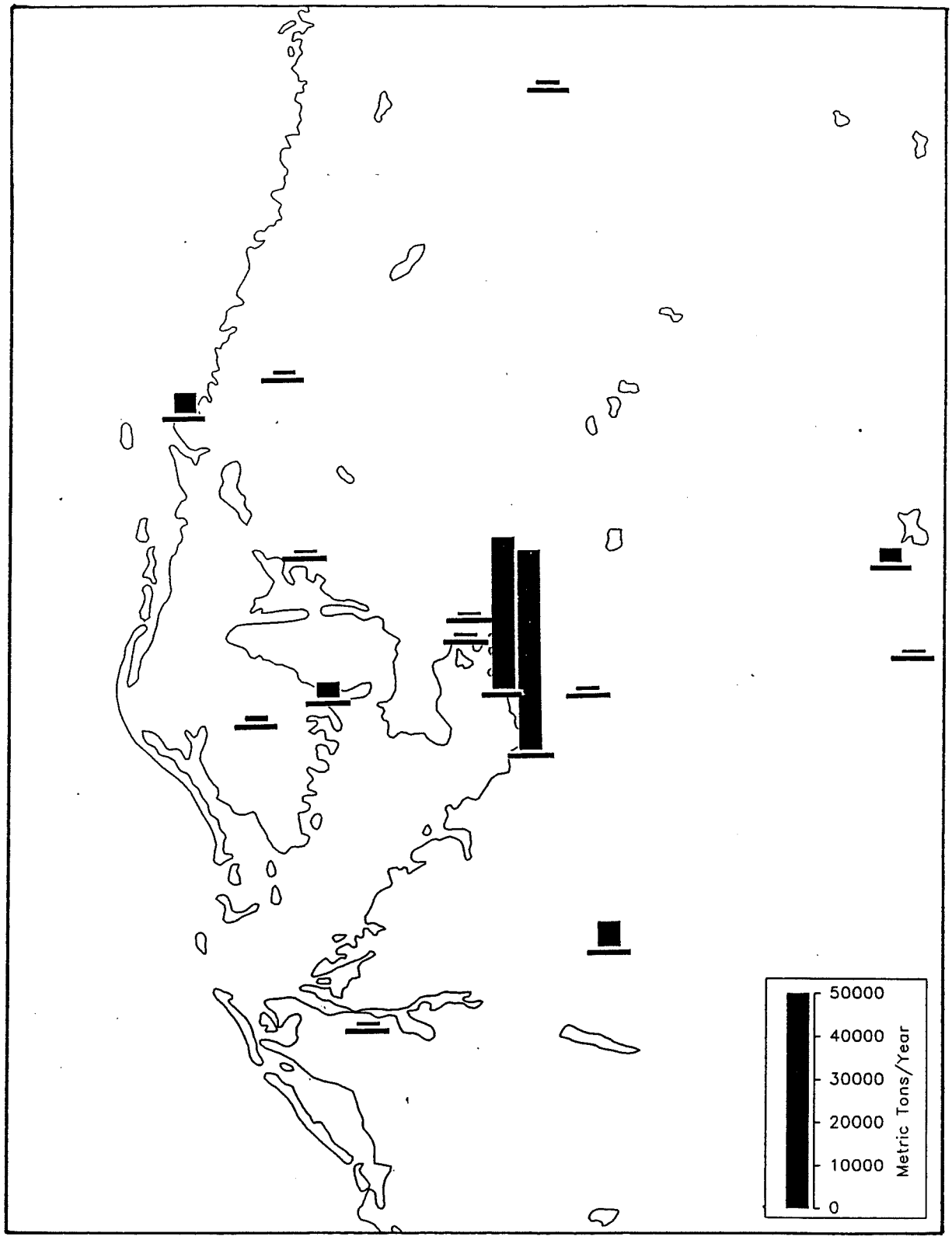

Figure A-3. Stationary sources of NO_x greater than 454 metric tons year^{-1} (500 tons year^{-1}). 1992 Actual emissions. (Citrus County to the north and outside of the illustrated region represents an additional 48,923 metric tons year^{-1}.)

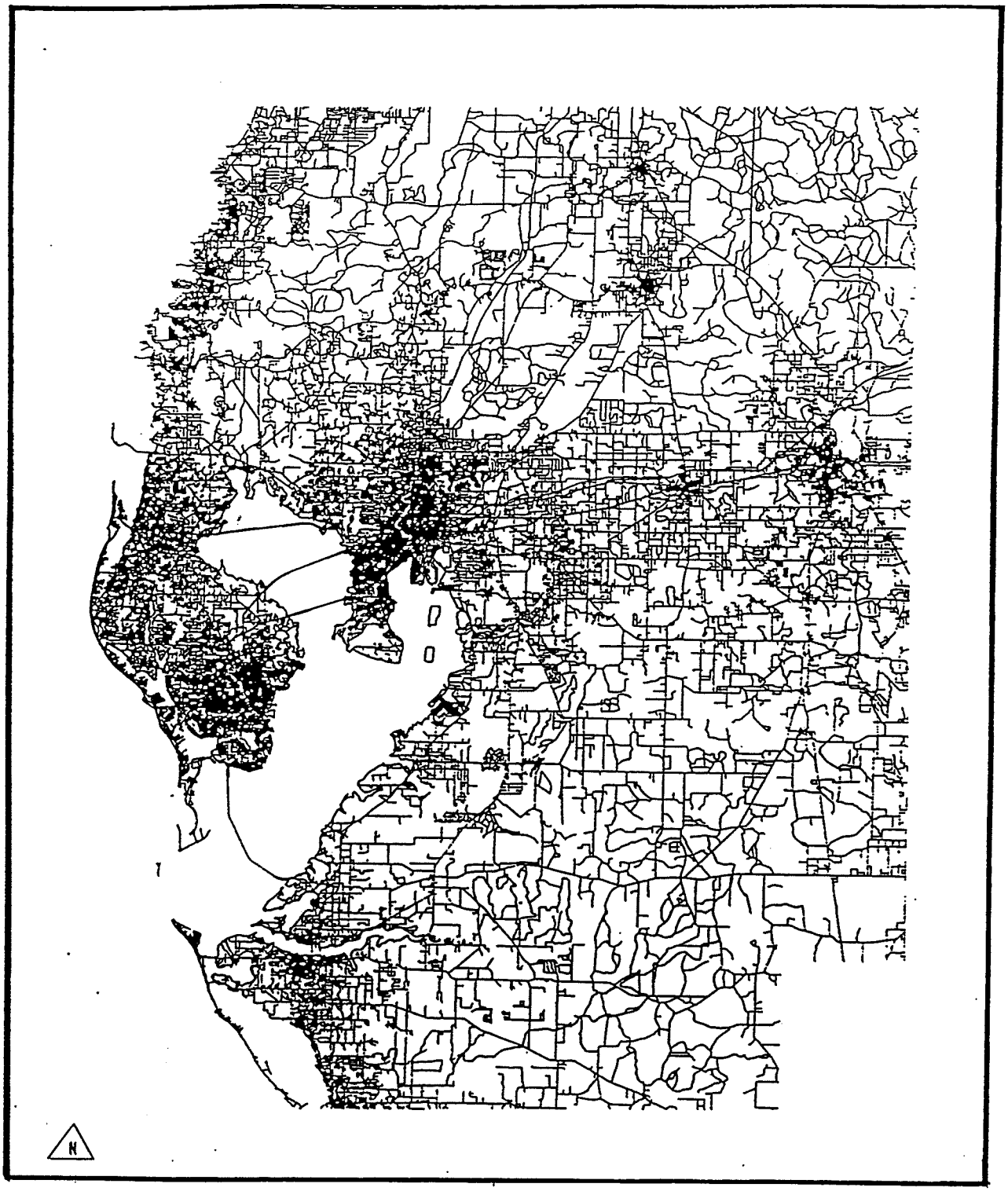

Figure A-4. Roadway density within the Tampa Bay watershed, as a surrogate for areas of mobile emissions (Dames & Moore, 1990).

Counties without non-attainment areas do not have the same level of modeling requirements and so projections are not available for the 1990 base year. Nevertheless, the table below (**Table A-2**) summarizes some available information on transportation emissions of NO_x. Data are in units of metric tons per day during the peak ozone season, and so multiplying the mobile emissions by 365 will give an approximate annual total. The annualized values total approximately 50,030 metric tons $year^{-1}$ for the mobile emissions in the three county area immediately surrounding the Bay. Mobile sources, even with incomplete values, comprise approximately 30% of the total NO_x emissions (stationary and mobile) within the nine county area surrounding Tampa Bay. Total NO_x emissions in the study area account for nearly 24% of the State's estimated 667,400 metric tons $year^{-1}$ of NO_x emissions.

Table A-2. Approximate emissions from mobile sources in counties adjacent to Tampa Bay.

County	VOC mton day^{-1}	CO mton day^{-1}	NO_x mton day^{-1}	Date
Hillsborough County	81.5	630	63.9	1990[a]
	99.6	728	78.8	1990[b]
Pinellas County	69.3	538	46.4	1990[a]
Manatee County	14.5	109	11.8	1995-2010[a]
Sarasota County	21.8	160	18.2	1995-2010[a]

[a] Mr. Richard McElveen, FDEP, personal communication
[b] HCMPO, 1993

Phosphorus has neither primary nor secondary air quality standards, but does appear on the listing of hazardous air pollutants. No facility within the nine county area, however, has any estimated or actual 1992 emission of this element (FDEP, 1994). With no stationary point sources, therefore, the emissions of phosphorus are primarily diffuse and non-point in nature. Product shrinkage at bulk loading facilities of fertilizer products has been estimated between 0.01% and 1% of total shipments (Cardinale and Dunn, 1991; Johansson and Lewis, 1992) with the best estimates near 0.05%. Most recent computations from 1991 shipping records estimate that 13,225 metric tons $year^{-1}$ of nitrogen and 47,826 metric tons $year^{-1}$ of phosphorus are lost in shipping (AScI and Dames & Moore, 1993). Zarbock *et al.* (1993) estimated total fugitive emissions at near 1,700 metric tons $year^{-1}$ of phosphorus for Hillsborough Bay and 272 metric tons $year^{-1}$ for Lower Tampa Bay (Port Manatee) using a 0.05% rate for product shrinkage. Nitrogen loads for Hillsborough Bay and Port Manatee were estimated at 454,000 kg $year^{-1}$ and 72,600 kg $year^{-1}$, respectively. Revisions to the fugitive emissions estimates are expected early in 1994.

The Air Program at Region IV of the U.S. Environmental Protection Agency (USEPA) is also interested in the phenomena. The Tampa Bay Initiative is examining the potential impact of the

atmospheric deposition of both phosphorus and nitrogen. Initial reports summarizing existing information on phosphorus emissions are available, with information on nitrogen to be summarized during 1994 (Mr. Danny Orlando, USEPA, personal communication).

Much of the fugitive loss of phosphatic materials, however, is in surface runoff, or from the loss of large particle sizes which fall directly into Hillsborough Bay, rather than from the entrainment of small particulates into the atmosphere. As a particulate, even the smallest sized fraction is likely to be re-deposited relatively near the source, and while the ultimate impact on the waterbody is roughly equivalent, an unknown fraction of the material is small enough to be transported any substantial distance.

The remaining non-point sources of phosphorus emissions are the application of fertilizers or in soil resuspension from fields under cultivation. The size of these two sources is unknown, but since some 40% of the watershed is classified as agricultural, the magnitude could be substantial. Seasonal signals in crustal elements which coincide with spring tillage patterns have been observed elsewhere (Scudlark *et al.*, in press).

Also in the FDEP 1992 annual operating reports (FDEP, 1994) are the estimated emissions for lead (46.2 metric tons $year^{-1}$) and mercury (1.59 metric tons $year^{-1}$) for the sources listed within the nine county area surrounding the Tampa Bay watershed. Other estimates for mercury are substantially higher, KBN (1992) estimating 4.54 metric tons $year^{-1}$ of mercury emissions primarily from solid waste incineration, utilities, and medical waste incineration. Additional and more specific information on sources of toxics within the Tampa Bay region will be available through the Toxics Contamination Action Plans.

In reviewing the emissions of various utilities and industries in the Bay area, it is apparent that several represent substantial sources. In addition to the size of the facility (megawatts produced), a controlling factor is the type of fuel used. Coal fired boilers are known to produce higher levels of NO_x emissions, but in addition, coal contains higher levels of most trace metals than does fuel oil. Metals in solid wastes are even more enriched. Concentrations of selected metals in representative fuels appear below (**Table A-3**) as tabulated by Windham (in press).

Table A-3. Approximate trace metal content of different fuels (Windham, in press).

Trace Metal	#6 Oil $\mu g\ g^{-1}$	Eastern Coal $\mu g\ g^{-1}$	RDF/MSW $\mu g\ g^{-1}$
Copper	0.20	16	300
Lead	0.6	14	380
Zinc	0.8	40	600
Mercury	0.03	0.26	2

RDF/MSW - Refuse derived fuel/municipal solid waste

Ambient Air Monitoring and Quality

Of the parameters of interest in this project, National Ambient Air Quality Standards (NAAQS) exist only for nitrogen dioxide (NO_2) and for lead (Pb) (40 CFR Ch.1. Subchapter C, Part 50). The annual ambient air standard for NO_2 is 100 $\mu g\ m^{-3}$, or 53 ppb as an annual arithmetic mean. The other forms of nitrogen oxides or nitric acid are not directly regulated, although NO_x emissions are inventoried yearly (FDEP, 1993a) and compared against permitted levels. Lead standards are set at 1.5 $\mu g\ m^{-3}$, calculated as the maximum arithmetic mean averaged over a calendar quarter.

The Tampa Bay airshed is designated as an area of non-attainment for ozone, in that 120 ppb or 235 $\mu g\ m^{-3}$ of ozone (as an hourly average) occurs during more than one day. There is also an area that is non-classifiable for lead in Hillsborough county, although 1992 data indicate the region may now be in compliance, with maximum quarterly averages of 1.4 $\mu g\ m^{-3}$ (FDEP, 1993a) and an instantaneous maximum of 2.3 $\mu g\ m^{-3}$ (HCEPC, 1993). These areas of non-attainment are responsible for the relative density of monitors for ozone, ozone precursors, and lead within the Bay region.

Monitors of NO_x within Florida do not generally have a sufficient data base to determine long-term trends in ambient NO_x concentrations, but there are no short-term trends apparent in the four monitors in Palm Beach, Dade, and Duval counties for the period 1988-1992 (FDEP, 1993b). Data from Hillsborough County indicate that annual NO_x averages have improved slightly since sampling began in 1975 and that no violations of NAAQS occurred during 1992 (HCEPC, 1993).

Pinellas County operates two ambient air sites with NO_x monitoring equipment (**Figure A-5**). The Azalea Park site in the Tyrone area has a period of record from 1978-1985 and from 1988-present. As of 1991, wind speed and direction are also available at this location. (Mr. Tom Stringfellow, personal communication). A second site near east Lake Tarpon, at the John A. Chesnut Sr. Park, has also been monitored for NO_x since 1988, with wind data available since 1978. There are no current plans to add additional NO_x monitors. Lead monitoring has been conducted in three locations, at east Lake Tarpon from 1988 through 1992, at Tyrone Square from 1988 through present, as well as at the Sheriff's Office on Ulmerton Road from 1982 to the present. The Ulmerton Road site was selected for high mobile source concentrations. Wind data are also available from the Tarpon Springs site (Anclote and Brady Roads) and the Derby Lane site at the western end of the Gandy Bridge.

Nitrogen dioxide data indicate that in 1992 the Azalea Park site had both higher maxima (72 versus 50 ppb) and higher average ambient concentrations (12 versus 7 ppb) than the east Lake Tarpon site (PCDEM, 1993a). Composite monthly means of lead data indicate that no substantive violations of lead criteria have existed since 1986 (PCDEM, 1993b) and all quarterly averages during 1992 were reported as 0.0 (FDEP, 1993a). Wind direction for 1992 in Pinellas County is illustrated in **Figure A-6** with winds from the northeast to east dominating, followed by winds from the northwest and north-northwest. Collectively, winds from these directions represent about 40% of the data points. Additional wind data from Tampa International Airport (PCDEM, 1993a) and other locations around the Bay, however, illustrate the regional nature of prevailing wind direction, and the difficulty of extrapolating wind (and therefore emission plume) directions to other regions of the Bay area.

Hillsborough County has 11 continuous air monitoring sites, but only one, on Gandy Boulevard by Tampa Bay, measures NO_x (**Figure A-5**). The county is in attainment for this pollutant (HCEPC, 1993), with no exceedances of the standard in 1992, and an annual arithmetic mean of 10.0 ppb. Concentrations of NO_2 have also improved slightly with time since 1975, indicating an improvement in mobile source control. Wind speed and direction are also recorded at the Gandy site, which has been in operation since April 1991. (Wind data are recorded at Davis Island and Simmons Park, as well.) An NO_x data base is apparently available for Davis Island, but the site is no longer monitoring this parameter. A future NO_x installation is planned for the Simmons Park monitoring site on the southeastern shore of Tampa Bay (Mr. George Frader, HCEPC, personal communication).

Lead monitors within Hillsborough County are relatively numerous, due to the county's marginal non-attainment status for this pollutant. Six sites are designated as Health Department, Ruskin, Seminole, Johnson Ctrl, Gulf Coast, and NDC. Several are designated as special purpose monitors and sited to measure resuspension near lead point sources. The highest quarterly average for lead parameter in Hillsborough County was 1.4 $\mu g\ m^{-3}$ in 1992 at 1700 N. 66th St. Trends in sources of lead indicate that transportation now contributes only 25% of the annual emission, down from 73% in 1985 (HCEPC, 1993).

Manatee County operates a single station for NO_x. The installation has been in place since October 1992, but is part of a Citrus Burn Study and is temporary, with operation scheduled only through October 1994 or 1995 (Mr. Rob Baum, Manatee County Environmental Action Commission, personal communication). The site is located east of the Bay on Highway 62, near the FPL Manatee Plant in Parrish. Mean NO_x concentration was 9 ppb for 1992 (FDEP, 1993a). Windspeed, direction, and rainfall are also recorded. An annual report on the first year of data collection is scheduled for production this year. The data from the four sites in the watershed varies slightly, with an annual average high of 16 $\mu g\ m^{-3}$ in southern Pinellas County to a low of 9 $\mu g\ m^{-3}$ in Manatee County. Insufficient stations exist to map gradients for most of the watershed.

Based on the 1992 FDEP annual operating reports (FDEP, 1993a), no other NO_x monitors are operating in Pasco, Polk, or Sarasota counties. There are no monitors in Citrus, Hernando, Sumpter, Hardee, Desoto, or Charlotte counties. Data are available through FDEP, although a change in storage format may make the retrieval of older data more problematic (Mr. Brian Kerckhoff, FDEP, personal communication). In addition, meteorological data such as wind speed and direction are not typically forwarded to FDEP, necessitating retrieval of this information from the individual county air programs. In some cases, meteorological data are not retained as magnetic or digital files.

Until recently, electric utilities were not required to monitor emissions continuously. Operating reports were prepared from standard emission factors of emissions per Btu generated with annual compliance sampling conducted at full load. With the Clean Air Act Amendments, however, utilities will be adding continuous monitors for a number of parameters, including NO_x, which will provide emissions data in real time. Most will be in place by a 1995 deadline (Mr. Ken Hedrich, FPC, personal communication).

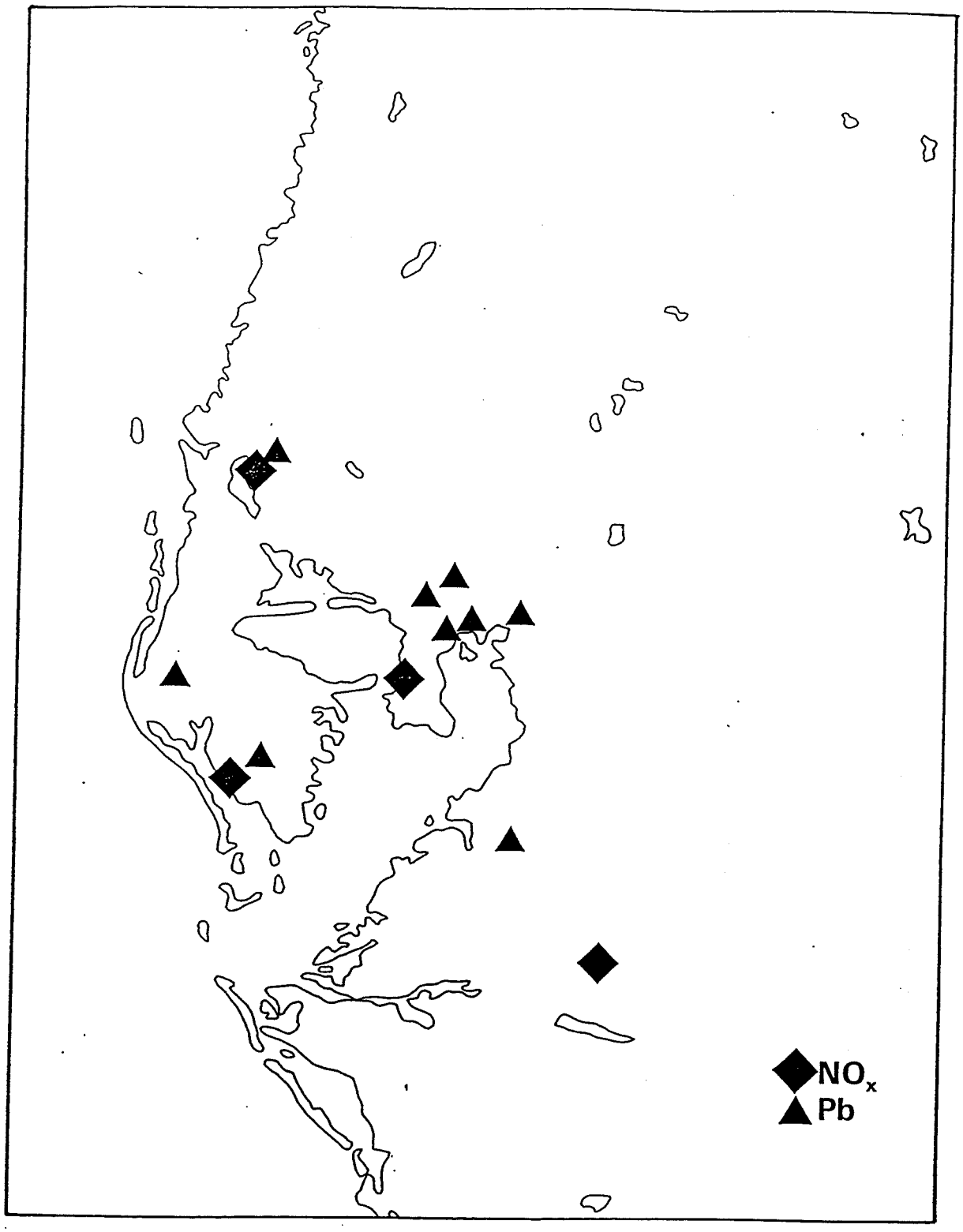

Figure A-5. Locations of Hillsborough, Manatee, and Pinellas counties' NO_x and lead ambient air monitoring stations.

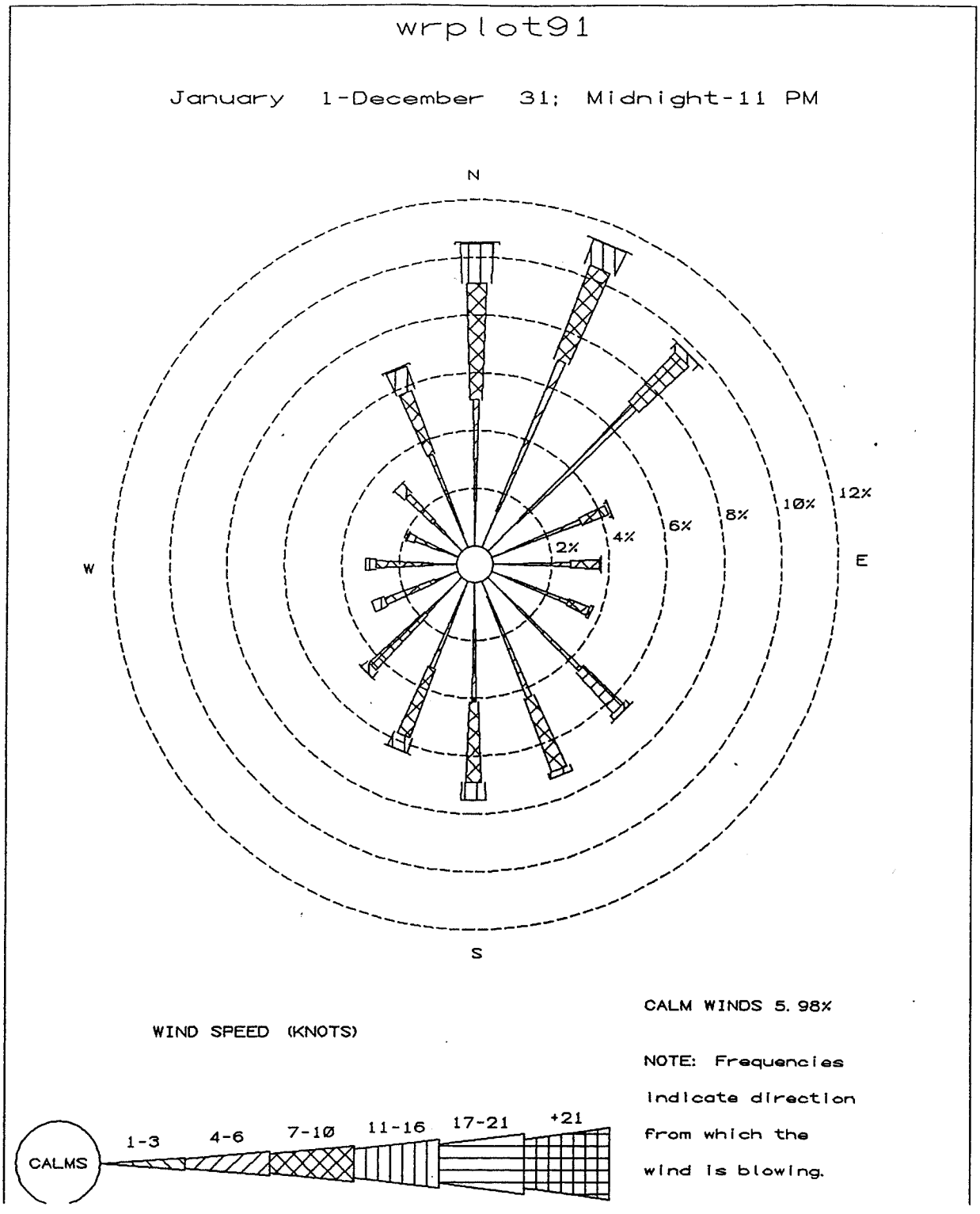

Figure A-6. Wind direction frequency and strength, Pinellas County, 1991.

Precipitation Chemistry

Precipitation chemistry has a history in Florida which extends at least to the mid 1950's (Junge and Werby, 1958), with periodic additional work. Data from Tampa were also gathered by Lodge *et al.* (1968) and Edgerton and Brezonik (1981). The primary focus of this discussion, however, will be on either more recent data or on networks or studies with a longer record.

In general, seasonal variations in rainfall quality are apparent for Florida, with maximum concentrations of nitrate (NO_3^-), ammonium (NH_4^+), and other major ions typically observed between May and October (Pollman, 1993; Madsen *et al.*, 1990; NADP/NTN data for Verna Wellfield). Higher rainfall amounts during these months result in higher wet depositions during the summer months. Seasonality could be the result of a combination of higher power usage during warmer months (and therefore higher utility emissions), summer circulation patterns, or a proposed more effective scavenging mechanism for the convective storms which characterize the summer rainfall events (Pollman and Canfield, 1993). Geographically, while SO_4^{-2} and H^+ concentrations in rainfall decrease from north to south within Florida, NO_3^- concentrations were more constant among the rural sites (Hunter/ESE, 1989), with wet deposition ranging from 1.68 to 2.25 kg ha^{-1} $year^{-1}$ of nitrogen (Pollman and Canfield, 1993). Ammonium concentrations in precipitation apparently are controlled by local factors (Pollman and Canfield, 1993).

A number of programs have examined precipitation chemistry in Florida, with the longest term studies conducted by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and the Florida Acid Deposition Study (FADS). The NADP/NTN network operates five sites in Florida, with the closest to Tampa Bay located at the Verna Wellfields in Sarasota County. Other sites are at the NASA facility near Cape Canaveral, in the Everglades, near the Georgia border, and near the Alabama border. Parameters include major anions and cations with orthophosphate available by special request. Nitrate-nitrogen wet-only deposition from the NADP sites through 1989, as summarized by Winchester and Fu (1992), appears below (**Table A-4**), and nitrate concentrations can be seen to converge near 0.22 mg L^{-1}.

Table A-4. Mean precipitation concentrations and wet deposition of nitrogen for the Florida NADP/NTN sites (Winchester and Fu, 1992).

Site	Mean NO_3-N Concentrations mg N l^{-1}	NO_3-N Wet Deposition kg N ha^{-1} yr^{-1}
Dade	0.145 ± 0.008	0.96 ± 0.08
Verna	0.223 ± 0.016	1.45 ± 0.18
Kennedy	0.210 ± 0.013	1.43 ± 0.13
Bradford Forest	0.226 ± 0.010	1.68 ± 0.09
Quincy	0.230 ± 0.018	1.53 ± 0.15

The FADS work, and subsequent Florida Acid Deposition Monitoring Program (FADMP), consisted of up to 14 stations which operated between 1981 and present. Siting criteria placed stations in selected rural areas to evaluate regional and temporal trends, develop source attributions, and evaluate ecological effects of acid precipitation in Florida. At times, wet samples were collected on both daily and weekly schedules, varying by station and the year of the study. Parameters included major ions (with NO_3^- and NH_4^+) and physical parameters. Dry samples were collected every two months, but only analyzed between 1981 and 1982. Ambient air concentrations were also collected, including analyses for HNO_3 and NO_2. Currently, the network consists of two sites, one near Careyville in the panhandle area and the other at Archbold Biological Research Station in Highlands County. Support for the project was provided by the Florida Electric Power Coordinating Group (FCG) with the Florida Department of Environmental Protection scheduled to assume operation of the remaining two sites in the near future.

The closest FADS station to the Tampa Bay watershed was in Zephyrhills, in Pasco County, with weekly data collected at the site from 1981 through 1990. Daily data were gathered at the site during the 1982-83 sampling year. Ambient air data were collected at least between 1982 and 1984. Data on selected metals (vanadium, aluminum) and phosphate were collected during the initial sampling year. The raw data are not currently available, but extracts from selected annual summaries are provided below.

Statewide, while acidic deposition and SO_4^{-2} decreased from north to south, no significant pattern was seen in NO_3^- or NH_4^+ (ESE, 1986). Volume weighted mean concentrations for the Zephyrhills site between 1981 and 1984 and seasonal differences during 1988 (Hunter/ESE, 1989) are presented below (**Table A-5**). Interannual variations in weighted NO_3^- concentrations were near 10% during 1981-1984 (ESE, 1986). Seasonal differences in rainfall also indicate that the majority of inorganic nitrogen would be deposited during the summer (Hunter/ESE, 1989). The central Florida stations, including the Zephyrhills site, had the highest nitrate weighted means. Phosphate volume weighted means averaged <0.01 mg L^{-1} PO_4-P statewide, with the maximum value (0.04 mg L^{-1} PO_4-P) at the Zephyrhills station. This result was thought to reflect nearby mining operations.

Table A-5. Volume weighted mean rainfall concentrations and wet deposition values for the FADS Zephyrhills site (ESE, 1986).

	----Volume Weighted Mean Concentrations----			---------Wet Deposition--------	
Chemical Species	1981-1984 mg L^{-1}	1988 Summer mg L^{-1}	1988 Winter mg L^{-1}	1981-1984 kg ha^{-1} yr^{-1}	1988 kg ha^{-1} yr^{-1}
NH_4-N	0.133	0.158	0.124	1.67	1.89
NO_3-N	0.166	0.207	0.088	2.07	2.06
PO_4-P	0.043*	—	—	0.50	—

* Data from 1981-1982

It was determined that data from the dry samples collected under FADS could not be used for estimates of dry deposition, and so analyses were terminated on this sample type after the initial year. To determine dry deposition rates, ambient air concentrations were determined for approximately one year at the Zephyrhills site between 1982-1984. Concentrations averaged 0.244 μg N m^{-3} for HNO_3-N and 3.26 μg N m^{-3} of NO_2-N (1.1 and 10.7 μg m^{-3} of HNO_3 and NO_2, respectively). Data from other sites in 1988 suggest that the bulk of the ambient nitrogen was in the form of NO_2, followed by HNO_3, with minimal quantities as aerosol NH_4^+ and NH_3 (Hunter/ESE, 1989). Total wet and dry deposition of inorganic nitrogen at the Zephyrhills site, excluding NO_3^-, NH_4^+, and NH_3, was estimated as 6.13 kg ha^{-1} $year^{-1}$.

Brezonik *et al.* (1981) also presented loading rates for Florida. As summarized in Blancher and Stewart (1991), estimates for urban and rural bulk loading of nitrogen were 7.6 and 5.8 kg ha^{-1} $year^{-1}$, respectively. Total bulk deposition direct to the Bay was estimated by Blancher and Stewart (1991), using the coastal bulk precipitation coefficients of Brezonik *et al.* (1981) at over 521 metric tons $year^{-1}$ (5.43 kg ha^{-1} $year^{-1}$) of nitrogen and near 28 metric tons $year^{-1}$ (0.29 kg ha^{-1} $year^{-1}$) of phosphorus.

Madsen *et al.* (1990) have also conducted a lengthy study of acid rain at two locations, Orlando (University of Central Florida) and the Kennedy (Canaveral) Space Center. The period of record is at least 1981-1990, with only minor interruptions in data collection, during which the Kennedy site was moved slightly and incorporated into the NADP/NTN network. Extreme variations in daily and monthly rainfall quality were noted, with moderate annual variations. Integrated wet samples of 24 hour, 72 hour, and one week periods were collected with wet deposition values (**Table A-6**) averaging:

Table A-6. Central Florida wet deposition values (Madsen *et al.*, 1990).

Chemical Species	UCF 1977-89 kg ha^{-1} yr^{-1}	KSC 1977-81 kg ha^{-1} yr^{-1}	NADP 1984-89 kg ha^{-1} yr^{-1}
NH_4-N	1.76	1.85	0.98
NO_3-N	2.94	1.93	2.04

UCF - University of Central Florida
KSC - Kennedy Space Center
NADP - NADP site at Kennedy Space Center

Allen and Sutton (1990) reported on a year of event-based wet deposition and triple filter pack samples for dry deposition collected at three sites in the Cary Forest, northeast of Gainesville, FL. Major inorganic ions were analyzed, including phosphorus. Total deposition was 6.6 kg N ha^{-1} $year^{-1}$. Nitrate concentration in volume weighted precipitation was 0.21 mg N L^{-1} with

NH_4^+ concentrations at 0.15 mg N L^{-1}. Phosphorus loadings (from phosphate) in rainfall were much lower, 0.013 mg P L^{-1} or 0.15 kg P ha^{-1} $year^{-1}$. Earlier work by Hendry and Brezonik (1980) and nearby NADP data as presented in Allen and Sutton (1990) also found similar precipitation concentrations (**Table A-7**) for a central Florida region near Gainesville.

Table A-7. Central Florida rainfall concentrations, as summarized by Allen and Sutton (1990).

	Hendry and Brezonik (1980) 1976-77 mg L^{-1}	Bradford Forest NADP 1987 mg L^{-1}	Cary Forest Allen and Sutton (1990) 1988-89 mg L^{-1}
NH_4-N	0.10	0.08	0.15
NO_3-N	0.19	0.15	0.21
HPO_4-P	0.02	—	0.01

For the Carey Forest, rainfall was the dominant mode of deposition for nitrate and ammonium ions, with 37% of the total nitrogen deposition attributable to dry deposition. Nitric acid vapor generally exceeded concentrations of particulate nitrate and nitrogen dioxide by a ratio of 3:2:1, respectively. Average annual wet and dry loadings are shown below (**Table A-8**). Average annual dry deposition fluxes were calculated from theoretical deposition velocities and the ambient air concentrations and total (wet plus dry) deposition (less dry deposition of NH_3 and NH_4^+) was a near 6.62 kg ha^{-1} $year^{-1}$.

Table A-8. Wet and dry deposition rates, Carey Forest, Florida (Allen and Sutton, 1990).

Chemical Species	Wet Deposition kg ha^{-1} yr^{-1}	Dry Deposition kg ha^{-1} yr^{-1}
NH_4-N	1.71 ± 0.02	
NO_3-N	2.48 ± 0.05	
HPO_4-P	0.15 ± 0.04	
particulate NO_3-N		0.12 ± 0.01
HNO_3-N		2.20 ± 0.24
NO_2-N		0.11 ± 0.03

Precipitation and Loading Data for Tampa Bay

During the early 1980's, the Nationwide Urban Runoff Program (NURP) collected rainfall quality information (bulk deposition) at four sites within metropolitan Tampa (Noel *et al.*, 1987) (**Table A-9**). Although spanning an eight month period, the combined data only represent some 35 cm (approximately 14 inches) of rainfall per site, compared to long-term annual averages of near 136 cm or 53 inches. Collected storms were generally greater than 0.5 cm before all analyses could be completed. On an event basis, small storms generally represent a continuum of concentration values for all parameters, but larger storms have lower concentrations. Annual loads would likely be underestimated from this data set. Arithmetic and volume weighted means of Tampa NURP rainfall concentrations are listed below. The large standard deviations emphasize the episodic nature of atmospheric loadings. The data set is also valuable in that organic nitrogen and total phosphorus were analyzed, unlike most deposition networks. It is apparent that nearly half of the nitrogen in the NURP precipitation data set could be in the organic form and that phosphorus is almost all orthophosphate.

Table A-9. Arithmetic and volume weighted mean rainfall concentrations collected under the NURP program in Tampa, FL (Noel *et al.*, 1987), 40 storm events.

Chemical Species	Mean mg L^{-1}	Volume Weighted Mean mg L^{-1}
Organic N	0.45	0.43
NH_3-N	0.12	0.13
NO_2-N	0.02	0.02
NO_3-N	0.45	0.33
TKN	0.50	0.48
Total P	0.17	0.17
PO_4-P	0.12	0.10
Cadmium	0.001	0.001
Copper	0.043	0.036
Lead	0.009	0.006
Zinc	0.154	0.126

A subset of the NURP precipitation data was subsequently used by Hartigan and Hanson-Walton (1984) in estimating loadings to Tampa Bay. Interestingly, the rainfall concentrations (bulk deposition) of total nitrogen used ranged between 53% and 103% of the mean concentrations used as loading factors for stormwater runoff from the various land uses, indicating that a substantial fraction of runoff nitrogen originated as wet deposition. Phosphorus showed similar patterns. Bulk deposition accounted for 43%-113% of the total phosphorus in runoff.

The Pinellas County Air Quality Division established a wet deposition monitoring site at Cross Bayou, near the St. Petersburg/Clearwater Airport, and approximately 60 meters from U.S. Highway 19. This site was operated during 1984-1989 and 1991-1992 under NADP/NTN protocols, with analyses conducted for major ions (including nitrate and ammonia) and physical parameters (PCDEM, 1993c). Approximately 360 valid samples were collected and annual means and loadings presented below (**Table A-10**). A review of the annual averages emphasizes the difficulty of extrapolating loading rates from short-term data sets.

Table A-10. Volume weighted mean rainfall concentrations and wet deposition at Cross Bayou in Pinellas County, FL (PCDEM, 1993c).

	Volume Weighted Mean		Wet Deposition	
Year	NO_3-N mg L^{-1}	NH_4-N mg L^{-1}	NO_3-N kg ha^{-1} yr^{-1}	NH_4-N kg ha^{-1} yr^{-1}
1984	0.338	0.474	1.19	1.68
1985	0.253	0.292	0.83	0.96
1986	0.089	0.392	0.27	1.18
1987	0.204	0.166	3.56	2.89
1988	0.156	0.124	1.59	1.25
1989	0.286	0.128	2.56	1.14
1991	0.271	0.097	2.64	0.95
1992	0.196	0.075	1.60	0.61
Mean	0.224	0.218	1.78	1.33

Analyses of the 1985 and 1986 Cross Bayou data sets (Molesch, 1991) identified higher rainfall acidity (lower pH) during the summer months when weekly rainfall amounts are lower and emissions of acid rain precursors (sulfur dioxide and nitrogen dioxide) are higher. Nitrate and sulfate depositions were directly proportional with 84% of the total estimated to be from anthropogenic sources. Summer convective storms were observed to account for seasonal increases in nitrate deposition. Acidic components of deposition in this study were quite comparable to values observed for Florida and Georgia (PCDEM, 1993c). The annual wet deposition loadings for nitrate-nitrogen are comparable to those determined by Allen and Sutton (1990), Brezonik *et al.* (1981), Madsen *et al.* (1990) and NADP data from Winchester and Fu (1992). Annual loads for NO_3^- and NH_4^+ combined totaled 3.11 kg ha^{-1} $year^{-1}$.

A few bulk deposition samples were also collected as part of a 1990-1991 study of stormwater discharge to Lake Tarpon (CCI, 1992). Samples from the one station were analyzed for nutrients (nitrogen and phosphorus), solids, and biochemical oxygen demand. Variability among the individual samples was high. Once an outlier sample was discarded for contamination, 50-

60% of the total phosphorus was received as orthophosphate. Organic nitrogen dominated the deposition of nitrogenous materials, and was more than two times the rate of NO_x species, which in turn was nearly five times the rate of ammonia deposition. The NURP data exhibited a smaller fraction of total phosphorus as orthophosphate and a smaller proportion of organic nitrogen in comparison to nitrate-nitrogen. Bulk loading rates in the CCI (1992) study for total nitrogen in wet deposition were on the order of 10 kg N ha^{-1} $year^{-1}$.

More recently, and still ongoing, the Southwest Florida Water Management District (SWFWMD) is performing quality analyses on rainfall (wet deposition only) as part of a stormwater research program (**Table A-11**). As of March 1994, data were available for a total of 94 events at up to three sites, over a three year period, 1990-1993 (Rushton, 1993). Sites are located at Hidden River Corporate Park near Fletcher Avenue and I-75, at the Tampa office of SWFWMD on U.S. 301, and at Al Lopez Park (formerly Horizon Park) north of the Tampa Stadium between Dale Mabry and Himes Avenues. In general, only storms with greater than 0.75 cm of precipitation are retained for analysis, which would tend to underestimate annual loads. In this work, rainfall has been identified as a major source of inorganic nitrogen, exceeding stormwater runoff concentrations by two to four times. Spatial differences between three sites in Tampa have been detected for ammonia and zinc, while NO_{2+3}-N exhibits seasonal differences, being higher during the summer. The Tampa office site, nearest a major transportation corridor and feed lots, recorded the highest values of all parameters. Phosphorus data are drawn from Rushton (1991). Including more recent data (through January 17, 1994) brings volume weighted means of zinc for the entire data set to 0.03 mg L^{-1}, with weighted means for precipitation at the Tampa office only at 0.074 mg L^{-1}.

Table A-11. Arithmetic and volume weighted mean rainfall concentrations collected under SWFWMD stormwater research programs (Rushton, 1991, 1993). Data through July 12, 1993.

Chemical Species	Mean mg L^{-1}	Std. Dev. mg L^{-1}	Volume Weighted Mean mg L^{-1}
NH_3-N	0.137	0.362	0.120
NO_{2+3}-N	0.222	0.490	0.193
Organic N	0.15	0.45	0.12
PO_4-P	0.031	0.233	0.022
Total P	0.055	0.332	0.042
Zinc	0.03	0.16	<0.03

Atmospheric nutrient loadings determined for Lake Maggiore in northern Pinellas County (CH_2M Hill, 1991) employed a combination of NADP/NTN data, Pinellas County's data from Cross Bayou (DEM, Pinellas County, 1993), and Rushton's (1993) earlier data. As reported

in Squires *et al.* (1992) a factor was used to estimate dry deposition from wet data, with wet deposition of NO_x and NH_4^+ assumed to equal 70% of the total (wet plus dry) deposition.

Work in Progress

One of the most comprehensive studies on deposition of trace metals is currently underway, focussing on atmospheric mercury as well as trace metals, major ions and nutrients. The Florida Atmospheric Mercury Study (FAMS), conducted with support from the Florida Department of Environmental Protection (FDEP), the Electric Power Research Institute (EPRI), and Florida Power and Light (FPL), has five sites located in predominantly rural areas collecting both wet, bulk, and aerosol samples. The first installation was at Lake Barco near Gainesville in May 1992 and approximately a year of sampling has been conducted. The annual report (Landing *et al.*, 1993) consists of explicit site installation and collection procedures and methodologies. Subsequent sites which have been installed or are scheduled for deployment include stations near Fort Myers (downwind of a scheduled municipal incinerator), in the Fakahatchee Strand, and two in the Everglades, with two other sites potentially to be established in the Florida Keys and in Fort Lauderdale. While data reports from this program are not yet available, personal communication (Dr. William Landing, Florida State University) indicates that bulk deposition of metals ranges between one and five times that in wet deposition only.

In other work for SWFWMD, water and nutrient budgets are being prepared for Lake Panasofkee, just north of the Tampa Bay watershed. Monthly bulk deposition data collected as part of this project is not yet available (Dr. Walter Ogburn, CH_2M Hill, personal communication), but the work has reportedly had occasional problems with contamination of bulk samplers from insects and bird droppings. In the South Florida Water Management District (SFWMD), additional deposition work is underway with 10-15 wetfall collectors and a total of 20 scheduled by the end of 1994 (Dr. James Grimshaw, SFWMD, personal communication). The network has been in place for some time, but earlier data consisted of bulk deposition values and, due to contamination and other problems, the older data are considered less useful than the wet deposition data collected more recently.

Pinellas County Water Resources Management Section, in conjunction with the United States Geological Survey (USGS), has recently begun a stormwater study at a domestic waste treatment facility near the northern end of the new Bayside Bridge over Old Tampa Bay. A component of the study includes weekly integrated samples of both dry, wet, and bulk deposition. While funding was sought to analyze trace metals and other toxics in the deposition samples, current analytical regimes do not include trace metals, but do include inorganic nitrogen series and total Kjeldahl nitrogen. The proportion of ammonia to nitrate nitrogen in the deposition samples will be of particular interest in this study, to assess the potential for ammonia releases from the treatment facility. The County has initiated the collection of 13 metals in the air collection systems as of December, 1993, but data were not available as of this report.

The USGS has also been involved in an extensive pilot study of the deposition of nitrogen and phosphorus to the surface of Lake Okeechobee through collection of wet/dry samples and bulk samples to wet and dry surfaces. These data, while very pertinent to the Tampa Bay study, are not yet available (Dr. Jake Peters, USGS, personal communication). The USGS is also currently

collecting bulk precipitation samples in Hardee and Desoto counties, in the Horse Creek watershed. The study is examining the use of chloride as a tracer for evaluating groundwater recharge. A limited suite of major ions does not include any nitrogen species, but the chloride data could be useful for evaluating the spatial variation in marine influences.

Metals in Other Regions

While a number of researchers have collected data on the deposition of major ions in or near Tampa Bay, large data sets for trace metals in deposition are not numerous. Typically, older data sets (pre-1982) are particularly suspect with regards to trace metal analytical accuracy due to subsequent improvements in quality assurance, handling, and analytical techniques. Metals data from Rushton (1993) are generally below detection limits, although more recent work has found substantial zinc concentrations at some sites, especially in bulk precipitation (Rushton, unpublished data). The data from the NURP program (Noel *et al.*, 1987), previously discussed for nutrients, also included metals analyses but concentrations (as bulk deposition) were much higher in relation to values reported from other regions.

Due to the relative scarcity, data from regions outside Florida were also accumulated for first-order estimation purposes. Although levels may appear insignificant, concentrations in precipitation may now exceed the aquatic concentrations in many ecosystems, and atmospheric inputs of trace metals exceed riverine inputs to the world oceans (Nriagu and Pacyna, 1988). Rainfall concentrations (wet deposition only) compiled by Nriagu (1992) appear below (**Table A-12**).

Table A-12. Compiled rainfall concentration of trace metals in urban and rural settings (Nriagu, 1992).

	Rainfall Concentrations	
	Urban	**Rural**
	$\mu g\ L^{-1}$	**$\mu g\ L^{-1}$**
Cadmium	0.35	0.05
Copper	2.8	0.45
Lead	6.0	1.4
Zinc	3.5	0.8
Mercury	0.065	0.025

Other authors (Windham, in press) present much higher levels of rainfall concentrations (perhaps with older data sets), but the pattern of urban concentrations higher than rural for all anthropogenic metals is consistent.

With sites in Colorado, Tennessee, and Illinois, Vermette *et al.* (1992) presented wet deposition data for a 15 week period, and in addition summarized data from other programs (Great Lakes Atmospheric Deposition [GLAD] network) and other researchers (Nriagu, 1992) (**Table A-13**). By comparison, the NURP bulk deposition data for the Tampa Bay region appear excessive, particularly for copper and zinc. While some portion of the difference may be attributed to either bulk versus wet-only, poorer air quality in the early 1980s, or analytical improvements, 22 events from summer 1993 through early 1994 (Rushton, unpublished data) at the Tampa office of SWFWMD produced volume weighted zinc concentrations of wet deposition nearly comparable to NURP values.

Table A-13. A compilation of trace metal volume weighted means (Vermette *et al.*, 1992; Nriagu, 1992; Noel *et al.*, 1987).

	Volume weighted means				
	Cu $\mu g\ L^{-1}$	Pb $\mu g\ L^{-1}$	Zn $\mu g\ L^{-1}$	Cd $\mu g\ L^{-1}$	Hg $\mu g\ L^{-1}$
Vermette *et al.* (1992)					
Colorado	1.32	1.49	4.05	0.07	0.0028
Illinois	1.33	1.11	3.06	0.10	0.0017
Tennessee	0.69	0.87	2.86	0.24	0.0013
GLAD*	1.0	1.7	8.7	0.2	—
Nriagu (1992) - rural	0.45	1.4	0.8	0.05	0.025
- urban	2.8	6.0	3.5	0.35	0.065
NURP (bulk)	36	6	126	1	—
Rushton (see text)	2.1	1	78	0.4	—

* GLAD: Great Lakes Atmospheric Deposition

Orr *et al.* (1992) reported annual loadings for a number of metals in the Great Lakes region as monitored by the Acidic Precipitation in Ontario Study. Spatial trends were consistent with the presence of stationary point sources and ranged between 30-60 g ha^{-1} $year^{-1}$ for lead, 20-60 g ha^{-1} $year^{-1}$ for zinc, and 0.5-2.0 g ha^{-1} $year^{-1}$ for cadmium. Loadings to the Great Lakes as determined by the GLAD network were approximately 20 g ha^{-1} $year^{-1}$ for lead in 1987 (Klappenbach, 1992).

Church and Scudlark (1992) presented volume weighted mean concentrations and depositions for a number of metals in rainfall at Lewes, Delaware along the mid-Atlantic coast (**Table A-14**). Mean values for the 1982-1989 time period are shown below, but the annual volume weighted mean for lead have declined to near 0.75 $\mu g\ L^{-1}$ by 1989. Dry deposition of trace metals at

Lewes were computed from an intensive series of aerosol measurements. Crustal components were normalized to aluminum, and deposition velocities used were those determined for soil dusts (0.3 cm sec^{-1}). Remaining elements were assumed to be associated with submicron aerosols, and a deposition velocity of 0.1 cm sec^{-1} was used. Wet deposition, in general, dominated the total deposition of these elements.

Table A-14. Trace metal volume weighted mean concentration and total deposition values for the mid-Atlantic region (Church and Scudlark, 1992).

Trace Metal	Vol. Weighted Mean $\mu g\ L^{-1}$	Wet Deposition $g\ ha^{-1}\ yr^{-1}$	Dry Flux: Crustal $g\ ha^{-1}\ yr^{-1}$	Dry Flux: Non-crustal $g\ ha^{-1}\ yr^{-1}$	Total Deposition $g\ ha^{-1}\ yr^{-1}$
Cadmium	0.098	1.08	—	<0.01	1.1
Copper	0.760	8.36	0.19	1.3	9.86
Lead	1.9 (0.75[a])	20.9	0.01	19.7[b]	40.7
Zinc	5.16	56.8	0.47	8.3	65.6

[a] 1989 Value
[b] Inaccurate value

Annual values for two sites on the shores of Chesapeake Bay were similar to the Delaware data in orders of magnitude (Scudlark *et al.*, in press; Baker *et al.*, 1992) (**Table A-15**). Part of the Chesapeake Bay Atmospheric Deposition study (CBAD), the sites were primarily rural/agricultural but were downgradient from concentrated air traffic, coal fired power plants, the Washington and Baltimore regions. Monthly depositions varied by a factor of 50 during the sampling year, with weekly fluctuations even larger. Intersite variation were largest for the weekly time scales. Using aluminum data and crustal ratios, most of the elements were determined to be of anthropogenic origin. In comparison to fluvial inputs to Chesapeake Bay, direct atmospheric deposition contributes significant portions of lead, zinc, cadmium, and arsenic.

Table A-15. Trace metal volume weighted mean concentration and total deposition values for the Chesapeake Bay region (Scudlark *et al.*, in press; Baker *et al.*, 1992).

Trace Metal	Vol. Weighted Mean $\mu g\ L^{-1}$	Wet Deposition $g\ ha^{-1}\ yr^{-1}$	Dry Deposition $g\ ha^{-1}\ yr^{-1}$	Total Deposition $g\ ha^{-1}\ yr^{-1}$
Cadmium	0.007	0.48	0.21	0.69
Copper	0.12	2.60	4.00	6.60
Lead	0.19	5.56	6.90	12.5
Zinc	0.39	13.35	20.0	33.00

Dry Deposition

Dry deposition has been described above as a process which depends not only on the chemical reactivity of both atmospheric species and receiving surface, but also on the physical state (gaseous, particulate) and/or particle size of the material, and the micrometeorology and condition of the receiving surface (turbulence, roughness, surface moisture, type of vegetation, and temperature).

The currently accepted method to estimate total deposition is to collect wet-only samples with automated equipment and to determine dry deposition separately. Dry deposition, however, is not typically quantified with the dry side of the wet-dry automated sampler. A typical dry bucket sampler is expected to be a reasonable approximation of larger particulates which settle primarily by gravitation, but less so for aerosol sized or gaseous components (Baker, 1993). Accordingly, ambient air is sampled with a system of filters and pump to quantify the concentrations of selected species. The ambient air concentration of each species is subsequently multiplied by a literature deposition velocity to generate the assumed dry deposition for that species.

Deposition velocities, however, are not typically empirically determined, but are modeled parameters. The velocities are subject to many variables and uncertainties, and can vary by up to an order of magnitude, depending not only on the chemical species and its particle size, but also on season, temperature, time of day, surface wetness, chemical characteristics of the receiving surface, leaf area index, wind, and surface roughness, to name a few. Dry deposition has been directly measured in few laboratory and field settings and there is no accepted methodology for routine measurements of this parameter. Emphasis is placed on the highly variable nature (both temporally and spatially) of the process (Hunter/ESE, 1989). Spatial differences do not typically smooth out as longer periods of record are achieved (Hicks *et al.*, 1992), as differences in the receiving surface remain fixed. There is no accepted methodology to measure dry deposition routinely and directly.

When deposition velocities are used for simulation, deposition rates are calculated from the deposition velocity, V_d, and the ambient concentration, c (dry deposition = V_d x c), lumping the effects of the wide variety of variables. Ambient concentrations are determined through a filter pack sampler, with or without a gradient of filter sizes. A range of deposition velocities have been determined, which can span from 0.04 to 0.72 cm sec^{-1}, a factor of 18, for equivalent sized particles (Baker *et al.*, 1992). Velocities determined for one surface are unlikely to be appropriate for others. While night-time velocities in terrestrial-based systems are reported to be negligible (Hunter/ESE, 1989), exchange during night (and winter) periods may dominate dry deposition to water bodies, whenever the water is warmer than the air (Hicks *et al.*, 1992). Wet surfaces are reported to be more efficient collectors of NO_3^- than a dry inert surface, while NH_4^+ accumulates more on the dry surface (Lewis, 1983). For nitrogen, there is insufficient information to deduce velocities for some species such as NH_4^+ and NO_2. In addition, NH_4^+ may have a non-linear rate deposition rate which would be poorly simulated by V_d x c (Edgerton and Lavery, 1990).

It is generally not feasible to verify calculated deposition estimates and so most dry deposition estimates calculated from ambient air concentrations are usually presented without verification. Spatial estimates of dry deposition should be regarded as extremely preliminary (Hunter/ESE, 1989).

The current Clean Air Status and Tends Network (CASTNET), which incorporates the National Dry Deposition Network (NDDN), recommends against extending deposition velocity and dry deposition values determined at a particular site to a regional basis (Dr. Ralph Baumgardner, CASTNET Project Officer, personal communication). Deposition velocities, in addition, are not well defined for deposition to water surfaces. The network measures NH_4^+, HNO_3, and NO_3^- in the particulate phase. The deposition velocities of NH_3, NO, and NO_2 are considered small due to the gaseous state and those species are not monitored. No trace metal or phosphorus data are available.

One of the CASTNET sites is in Sumatra, in the Florida panhandle region. In the most recent data available for this site (**Table A-16**), total NO_3^- depositions, range between 1.4 and 1.9 times wet deposition (Mr. Ralph Baumgardner, CASTNET Project Officer, personal communication), although the annual total remained relatively constant between the two years.

Table A-16. Wet, dry, and total deposition at the NDDN Sumatra, Florida site (Dr. Ralph Baumgardner, personal communication), based on particulate phase NH_4^+, HNO_3, and NO_3^-.

Year	Wet Deposition kg N ha^{-1} yr^{-1}	Dry Deposition kg N ha^{-1} yr^{-1}	Total Deposition kg N ha^{-1} yr^{-1}
1990	1.56	1.45	3.01
1991	2.49	1.06	3.55

Dry deposition in the FADS (Hunter/ESE, 1989) study was calculated both from dry bucket measurements and from ambient air concentrations and published deposition velocities. For NO_3, dry bucket deposition was lower by factor of 5, in comparison to the ambient air method of calculation, so sample contamination from birds and bugs was not an apparent problem as has been the case elsewhere. For NO_3^- and NH_4, dry bucket depositions were 0.55 and 1.14 kg N ha^{-1} $year^{-1}$, respectively, for the 1981-1982 sampling year. Calculated deposition was 4.00 kg N ha^{-1} $year^{-1}$ (26% as HNO_3, the remainder as NO_2), for the period 1982-1983. Any changes in ambient air concentrations between the two times periods is not available. Velocities used were 1.5 cm sec^{-1} for HNO_3 and 0.3 cm sec^{-1} for NO_2. Using the calculation method, total deposition is 2.88 times the measured wet deposition during 1982-1983 at the Zephyrhills site. For the other six sites active at this time, the factor of total deposition:wet deposition ranged from 2.13 to 2.97.

The FADS and NADP data have been further reduced by Baker (1993) to determine regional dry deposition values. Dry bucket data was assumed to be representative of the deposition of larger particulates and was combined with the computed deposition used for the HNO_3 and NO_2 components. Velocities used were 1.0 cm sec^{-1} for HNO_3 and 0.1 cm sec^{-1} for NO_2. For dry bucket NH_4^+ and NO_3^- in Florida, total deposition was 1.39 and 1.19 times the wet deposition, *i.e.* the bulk of these ions was delivered in rainfall rather than dry deposition. Combining the dry bucket data with the ambient air data, total deposition at the Tampa site is estimated to be 2.16 times the measured wet deposition. Uncertainties in the estimate may be on the order of 15-20% or greater if uncertainties in V_d are incorporated. The total: wet deposition ratio of 2.16 is used in the determination of current and benchmark loads to the Tampa Bay system (Zarbock, 1994; Zarbock *et al.*, 1993) and is strictly applicable for inorganic nitrogen data only.

Edgerton and Lavery (1990) have also examined FADS, NADP, and NDDN data. From a range of seasonal deposition velocities (0.06-0.20 cm sec^{-1} for NO_3^- and 1.5 -2.0 cm sec^{-1} for HNO_3), NO_3^- dry deposition appears to be between 1.40 and 1.12 kg ha^{-1} $year^{-1}$ for the central Florida region with ratios of total:wet deposition between 1.66 and 1.71.

Fanning (1992) recognized the general omission of organic nitrogen in the summary of pertinent wet, dry, and total deposition values for nitrogen to Tampa Bay. As the larger particles form a relatively small percent of dry deposition, organic nitrogen in dry deposition is not expected to be substantial. Data presented by NURP (Noel *et al.*, 1987), Rushton (1993), CCI (1992), however, indicate that organic nitrogen could represent between 30% and 60% of the wet deposition, and therefore 15%-30% of the total nitrogenous deposition (using the total:wet deposition ration of 2.16).

In the CBAD study (Baker *et al.*, 1992), dry deposition was estimated for number of metals from deposition velocities and ambient concentrations. Deposition velocities ranged between 1.4 and 4.0 cm sec^{-1} for crustal elements (assumed to be associated with larger soil particles) and between 0.26 and 0.72 cm sec^{-1} for non-crustal materials (aerosols from high temperature combustion). Because of the distribution of crustal to non-crustal elements, and the range in velocities, the estimate of dry deposition has an uncertainty of $\pm 50\%$ and values are listed in **Table A-15**, above.

Transport from the Watershed

Atmospheric deposition, when applied to the areal surface of a waterbody, is a direct and immediate impact. Materials deposited to the watershed, however, if not subject to immediate runoff, become involved in biogenic cycling, physical removal through sedimentation, biological uptake, and the like. Recycling will also liberate materials to surface waters such that they can be transported downstream. The degree to which materials are retained by a watershed is also a function of chemical reactivity with soils. In the absence of anthropogenic "imports" into the watershed, flux measurements of both atmospheric deposition and fluvial runoff will indicate the proportion of atmospheric loading to the watershed (indirect atmospheric deposition) which eventually is transported to the Bay.

Direct measurements of fluvial loads are unavailable for much of the Tampa Bay watershed. Some of the older surface water quality data on trace metals are felt to be unreliable for the sensitivity of analyses attempted. Gaged and monitored stations are also usually upstream some distance on the various tributaries, and do not include the water quantities or loadings generated by the downstream portions representing the bulk of the urbanized area of the watershed. Several projects are underway to address tributary loading the Bay, but in the interim, calculated non-point source loads will be presented as surrogates for true fluvial loads.

Simplistically, the non-point source loads generated by a watershed are calculated from size, empirically determined land use loading rates, and the proportion of various land uses within the watershed. A comparison, therefore, of the watershed non-point source loadings with the estimated atmospheric deposition to a watershed will allow an evaluation of the proportion of atmospheric deposition which may be represented in runoff concentrations. This proportion will overestimate the eventual atmospheric contributions to the Bay to some unknown extent, as watershed and in-stream removal processes have not been applied.

The proportion of indirect atmospheric loading which eventually reaches an estuary is to some extent a function of the ratio of watershed area to open water surface (drainage ratio). For elements which are not retained 100% by the watershed, increasing drainage ratio results in

increasing element burdens downstream (Blais and Kalff, 1993). For lakes in southern Canada, lead, zinc, and to a lesser extent, copper, were almost completely retained in the watershed (Blais and Kalff, 1993). For Tampa Bay, the drainage ratio is approximately 6, relatively small in comparison to Chesapeake (14.5) and Delaware Bays (17) (Scudlark and Church, 1993). Implications are that only a small fraction of trace metals would be exported to the Bay, except for the noteworthy point that much of the impervious area in the watershed is directly adjacent to the Bay, and that runoff has little time to equilibrate with soils. For mercury, on the other hand, retention efficiency is reported near 75% (Swain *et al.*, 1992), such that 25% of deposited mercury is exported from the watershed.

Retention rates of nutrient species also vary with land use and values range between 25% and 98% (Scudlark and Church, 1993). For Delaware Bay, Scudlark and Church (1993) assumed that 80% of dissolved inorganic nitrogen species (DIN) were retained in the watershed, and that further, 50% of the remaining DIN was removed in-stream through phytoplankton uptake and denitrification. In the Chesapeake Bay, Tyler (1988) employed a range of nitrate retention rates of between 100% and 76% for such land uses as forests and croplands and applied further delivery ratios of 50% to 80% to account for in-stream removals. Uncertainties in the retention values and delivery ratios are quite high, but nitrate loading to the Chesapeake which is attributable to atmospheric deposition is on the order of 25%. Hinga *et al.* (1991) revises the Chesapeake Bay estimate upwards to near 32%, and for Ocklockonee Bay in north Florida, estimates that 100% of the nitrogen loading was from atmospheric sources.

In order to estimate the potential magnitude of the impacts of atmospheric deposition on Tampa Bay, the range of deposition values as described earlier in this document were computed and compared to some recent non-point source loadings estimates. Not included in either the non-point source estimation or the atmospheric component are any in-stream processes. Non-point source loadings lower than the calculated atmospheric deposition could represent some immediate watershed retention which may take place in the small basins typically sampled for land use-specific loading rates. Actual non-point source loads to the Bay, whether calculated from non-point source loading or from deposition estimates, would be expected to be some factor lower due to in-stream removals. The estimates used for in-stream removals, however, would be the same in either case.

Initial estimates of non-point source loadings to Tampa Bay were provided by Dames & Moore (1990) with an early version of the Nonpoint Source Load Analysis Model (NPSLAM), using land use, land use specific runoff and loading coefficients, soil types and rainfall. From the 1990 land uses and recommended mass loading rates by land use (summarized from a number of empirically determined values), watershed average loading rates were calculated (**Table A-17**). The rates do not account for instream assimilation or other removal processes that may influence water quality before discharge to the Bay, although removal efficiencies were assigned to stormwater treatment facilities.

Table A-17. Average watershed non-point source mass loading rates (from data in Dames & Moore, 1990).

Chemical Species	Average Watershed Non-Point Source Loading Rates kg ha^{-1} yr^{-1}
Total N	8.56
PO_4-P	0.76
Total P	1.13
Zinc	0.23
Lead	0.31

NPSLAM reportedly overpredicted runoff in some instances and subsequent modeling efforts included the addition of seasonal variations in non-linear rainfall:runoff relationships, short-term antecedent moisture conditions, and lagged rainfall effects (Zarbock *et al.*, 1993). Where gaged basins were accompanied by a water quality record, loadings were computed directly. For ungaged basins, the model utilized the rainfall:runoff simulations and land use loading factors. Point sources, spring discharges, groundwater flows, fugitive emissions, and atmospheric deposition were also incorporated in determining the total loads of nutrient to Tampa Bay.

For the various basins surrounding the Bay, Zarbock *et al.* (1993) computed non-point source loadings of nitrogen and phosphorus, of approximately 2,470 metric tons $year^{-1}$ and 626 metric ton $year^{-1}$, respectively, during a 1985-1991 time period. Urban and agricultural land uses accounted for the bulk of these loadings. As for NPSLAM, no instream processes were simulated. The non-point source loading comprised some 51% of the total nitrogen load to the Bay and 16% of the total phosphorus load. Atmospheric deposition direct to the Bay is estimated to consist of 28% and 8% of the total nitrogen and phosphorus load to the Bay, respectively, but this figure is to be revised upwards in the near future (Zarbock, 1994) to account for higher dry deposition loadings. A total watershed area of 5,571 km^2 (5,895 km^2 less the internally drained portions), was then used to compute the average watershed non-point source loading rates below (**Table A-18**). Phosphorus loadings were almost identical, but nitrogen loadings are approximately one-half those calculated previously (Dames & Moore, 1990) (**Table A-19**), although the range of land use runoff concentrations employed in each work appears similar. Differences in land use percentages, annual rainfall, and runoff oversimulation observed for some basins with NPSLAM may account for the discrepancy.

Table A-18. Average watershed non-point source mass loading rates (from data in Zarbock *et al.*, 1993).

Chemical Species	Average Watershed Non-Point Source Loading Rates kg ha^{-1} yr^{-1}
Total N	4.44
Total P	1.06

The estimated non-point source loading rates were then compared to the various atmospheric deposition values previously described. Where data exist only as precipitation concentrations, 135.7 cm (53.44 in) was used as an average annual rainfall to calculate wet deposition rates. The rainfall value is the arithmetic mean of all individual basin rainfalls, as interpolated by Dames & Moore (1990). If nutrient or metal deposition rates are available under an urban or rural classification, the land uses tabulated in Dames & Moore (1990) were used to allocate the watershed into 33% "urban" (commercial, residential, industrial, and mining) and 67% "rural" for first order estimates.

Table A-19. Land use apportionment for the Tampa Bay watershed (Dames & Moore, 1990).

Land Use	Percentage (%)
Industrial	1
Wetland / open water	3
Commercial	6
Mining	8
Low-density, single family, or multi-family residential	18
Recreational / open areas	24
Agricultural	40

For phosphorus, where both total and phosphate atmospheric deposition rates are available, phosphate comprises approximately 50% of the total (Rushton, 1991; Noel *et al.*, 1987). Phosphate values, in kg ha^{-1} $year^{-1}$, were 0.15 for the rural Carey Forest (Allen and Sutton, 1990), 0.30 for Tampa (Rushton, 1991), 0.58 for the Zephyrhills FADS site (ESE, 1986), and 1.22 for the NURP data (Noel *et al.*, 1987). The FADS site was felt to be influenced by mining

nearby, and the NURP data appear excessive, and so a value between 0.60 and 1.16 kg ha^{-1} $year^{-1}$ of phosphorus, is likely appropriate for the watershed. These values are for wet deposition only, but compare quite well with the 1.06 kg ha^{-1} $year^{-1}$ determined by Zarbock *et al.* (1993) for non-point source loadings.

Nitrogen data are more complex, due the variety of species sampled and estimated. Wet deposition for NO_3^- in Florida converge on 2.46 kg ha^{-1} $year^{-1}$ with Rushton (1993), the FADS Zephyrhills site (ESE, 1986), the Carey Forest (Allen and Sutton, 1990), Cross Bayou (PCDEM, 1993c) at 2.61, 2.05, 2.48, and 2.71 kg ha^{-1} $year^{-1}$, respectively. Again the NURP values for NO_3^- are quite high, 4.16 kg ha^{-1} $year^{-1}$, and were not included in the estimate. Wet deposition for NH_4^+ averages 1.66 kg ha^{-1} $year^{-1}$, as does the most reliable of the organic nitrogen wet deposition rates (Rushton, 1993). The dry deposition rates for nitrogen species can be substantial. Total nitrogen deposition rates are presented by a number of authors, but generally lack quantification of at least one of the nitrogen species. Organic nitrogen and NH_4^+ wet deposition loading from Rushton (1993), together with the factor (1.16) for dry deposition reported by Baker (1993), were used to "complete" the analytical suites.

Total nitrogen deposition (wet plus dry) at the Carey Forest was estimated at 9.92 kg ha^{-1} $year^{-1}$, 7.79 kg ha^{-1} $year^{-1}$ at the FADS Zephyrhills site, and 12.6 kg ha^{-1} $year^{-1}$ for the Rushton (1993) sites. NURP nitrogen data were much higher, with extremely high concentrations of organic nitrogen and estimates of total deposition of greater than 22 kg ha^{-1} $year^{-1}$. Values of watershed non-point source loadings computed from Zarbock *et al.* (1993) were near 4.44 kg ha^{-1} $year^{-1}$. Wet deposition loadings alone from Rushton (1993) are 5.85 kg ha^{-1} $year^{-1}$ and Brezonik *et al.* (1981) presents a range of 5.8 to 7.6 kg ha^{-1} $year^{-1}$.

With estimated atmospheric deposition so much larger than modeled non-point source loadings, it would seem to indicate that a substantial fraction of atmospheric deposition is retained immediately by the watershed and that all of the nitrogen present in runoff has an atmospheric origin. Comparison of computed non-point source loads to the more recent deposition estimates indicate that up to 45% of the atmospheric load may be retained; comparison with the older atmospheric estimates (from NURP) indicate that 80% of atmospheric nitrogen is retained on the watershed. The 80% figure agrees well with estimates from other regions (Scudlark and Church, 1993) and may be more appropriate as many of the land use runoff coefficients and loadings developed for estimating non-point source loads were determined during the time that NURP data were being collected.

Atmospheric loading rates for metals, with the exception of the NURP data and more recent work by Rushton (1991, 1993, unpublished data), were not specific to the Tampa Bay area or even Florida. Wet deposition loadings determined by a number of researchers were very comparable to the total of wet and dry determinations elsewhere. As the data were not specific for Florida, the mean of the reported values for total depositions was used as a working value. With the exception of zinc, urban and rural values by Nriagu (1992) generally bracketed the average total deposition, while again the Tampa Bay data appeared as a substantial outlier (**Table A-20**) both in the 1980s and more recently (Rushton, unpublished data through January, 17, 1994).

Table A-20. Summary of trace metal atmospheric deposition rates.

Trace Metal	Rural[a] g ha^{-1} year^{-1}	Average Total Deposition[b] g ha^{-1} year^{-1}	Urban[a] g ha^{-1} year^{-1}	NURP g ha^{-1} year^{-1}	Rushton g ha^{-1} year^{-1}
Cadmium	0.68	1.8	4.8	11	5
Copper	6.1	14	38.0	489	28
Lead	19.0	26	81.0	81	14 (<MDL)
Zinc	11.0	60	48.0	1707	1060
Mercury	0.34[c]	0.026	0.88[c]	—	—

[a] Nriagu, 1992
[b] Average of data from Vermette *et al.* (1992), GLAD, Orr *et al.* (1992), and Church and Scudlark (1992).
[c] Older data, potentially unreliable for mercury concentrations.
[d] Rushton, unpublished data through January 17, 1994.

Using the 5,571 and 958 km^2 values for the watershed and Bay area, total loads to the Bay were computed (**Table A-21**).

Table A-21. Estimates of annual trace metal atmospheric deposition to Tampa Bay and the surrounding watershed.

Trace Metal	Atmospheric Deposition g ha^{-1} year^{-1}	Total Deposition to Bay kg year^{-1}	Total Deposition to Watershed kg year^{-1}
Cadmium	1.56	149	870
Copper	12.3	1,180	6,850
Lead	26.1	2,210	14,600
Zinc	57.3	5,490	31,900
Mercury	0.026	2.5	14.5

Of those parameters with estimates, zinc and lead average watershed loading rates were used to compute non-point source loads of 128,000 kg year^{-1} of zinc and 173,000 kg year^{-1} of lead. The non-point source values are a factor of 4 and a factor of 12, respectively, greater than that estimated from the atmospheric deposition rates. The atmospheric deposition rates were from the northeast, and should, if anything, be substantially greater than Florida values. Review of

the references used to determine land use loading factors in Dames & Moore (1990), however, reveal that many date from the early 1980's. The NURP data from this time period are consistently elevated in many parameters, including lead and zinc. Examination of national trends in lead emissions show a decrease by a factor of 12.3 between 1981 and 1991 (USEPA, 1993). Emissions decreases are primarily in transportation, so the Tampa area should have experienced comparable improvements. Reducing the non-point source 173,000 kg Pb $year^{-1}$ by the factor of 12.3 obtains a lead deposition of 14,100 kg $year^{-1}$, comparing most favorably with the atmospheric estimate of 14,900 kg $year^{-1}$.

No national emissions data for zinc are available, but it is apparent that NURP rainfall zinc concentrations are up to 30 times higher than data collected from other regions. Aside from the possible site-to-site differences, there is a strong potential that the reduced depositions reflect a real improvement in air quality. One is urged to the conclusion that NURP data were representative of the time they were collected, but that improvements in ambient air quality have made the NURP data, and land use loading rates determined concurrently, obsolete for lead at least. Zinc loadings, on the other hand, despite the high levels observed, appears confirmed by the most recent local data available.

Summary

This report represents a compilation of available literature and information pertinent to Tampa Bay atmospheric deposition. Sources, emissions, available ambient air quality data, precipitation quality, reported ranges of wet and dry deposition rates, previous and ongoing monitoring programs were summarized. Nitrogen and phosphorus were emphasized (except for deposition rates) as sources and emissions of trace metals were to be addressed in other documents.

Anthropogenic sources of nitrogen oxides within the Tampa Bay watershed are substantial, and stationary sources alone comprise 25% of the State's total NO_x emissions. Stationary sources are dominated by two utility stations on the shores of Tampa Bay. Mobile sources are also noteworthy, forming some 30% of the total NO_x emissions for the nine county area surrounding the Bay. Sources of phosphorus are relatively unstudied and unquantified. Estimates of fugitive emissions from the transportation of phosphatic materials have been made based on shipping tonnage.

Ambient air quality data were reviewed and indicate that no NAAQS (for NO_2 and Pb) were violated in 1992. Stations are concentrated in areas of expected poor air quality (urban) or near known point sources, and so do not provide data for the bulk of the watershed.

Precipitation data show distinct seasonal patterns, with the majority of nitrogen loading occurring during the summer wet season. Power usage patterns, meteorological circulation patterns, or greater efficiency of rainfall scavenging of materials with convective storms could all contribute to the observed seasonality. Comparisons of data sets for the Tampa Bay area show distinctly elevated urban concentrations and depositions in rainfall. The most urban data set, however, is older and could reflect true changes in ambient air quality and subsequent deposition. Organic nitrogen and phosphorus components in deposition are in general poorly characterized and could be substantial.

Estimates of the atmospheric deposition of total nitrogen range between 7.8 and 22 kg ha^{-1} $year^{-1}$, while non-point source loadings are modeled with an average contributed by runoff from the watershed of 4.4 kg ha^{-1} $year^{-1}$. A net retention within the watershed of between 50% and 80% of the atmospheric nitrogen is implied. These figures are in general agreement with literature from other areas of the United States. Estimates of atmospheric deposition of phosphorus (0.6-1.16 kg ha^{-1} $year^{-1}$) compare favorably with estimates of non-point source loading (1.06 kg ha^{-1} $year^{-1}$) of this element. No substantive net retention of phosphorus within individual basins is observed, with a potential for anthropogenic enrichment.

For deposition of trace metals, data from many differing time periods and regions was presented. There are little data on trace metal deposition for the region, and data from the mid-Atlantic and north central states were used for first order estimates. Atmospheric loadings of trace metals were computed, but where non-point source calculations were available (for lead and zinc), atmospheric loadings were substantially lower than the loadings expected from the land uses within the Tampa Bay watershed. The reduced loadings of lead can be directly related to reduction in lead emissions, and the potential exists that land use loading coefficients determined in earlier periods do not accurately reflect current conditions.

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ATTACHMENT

ESTIMATED EMISSIONS OF NO_x BY COUNTY AND SOURCE

From:
Department of Environmental Regulation
Air Program Information System
Facility Emission Report
Run Date - 03/03/94
Actual 1992 data

Attachment. Estimated emissions of NO_x by county and source.

	Metric Tons/Year	Tons/Year	
Hillsborough County			
Alumax Extrusions	14.5	13.2	
Anheuser-Busch, Inc.	28.0	25.4	
Ball Packaging Product Group	6.3	5.7	
Cargill Fertilizer, Inc.	21.2	19.3	
CF Industries, Inc. Plant City Phosp	40.4	36.7	
Coronet Industries, Inc.	78.1	70.9	
Florida Steel Corp.	36.6	33.2	
Hillsborough County Resource Recovery Facility	770.6	699.7	
IMC-Agrico Co. (Port Sutton)	94.5	85.8	
Master Packaging, Inc.	5.8	5.3	
Mobil Mining and Minerals Co.	75.7	68.8	
National Gypsum Co.	62.7	56.9	
Nitram, Inc.	24.4	22.2	
Tampa City McKay Bay Refuse-To-Energy	513.2	466.0	
TECO-Big Bend Station	50,873.8	46,193.4	
TECO-Gannon Station	38,669.3	35,111.7	
TECO-Hookers Point Station	629.3	571.4	
TOTAL FOR HILLSBOROUGH COUNTY			91,951.8
Manatee County			
Ajax Paving Industries, Inc.	16.1	14.6	
Coastal Fuels Marketing, Inc.	10.8	9.8	
Florida Power & Light	6,437.0	5,844.8	
Tropicana Products, Inc.	720.0	653.8	
TOTAL FOR MANATEE COUNTY			7,197.3
Pinellas County			
Florida Power	591.1	536.7	
Florida Power	142.0	128.9	
Florida Power Corporation	3,847.6	3,493.6	
Pinellas County Resource Recovery Facility	1,253.7	1,138.4	
TOTAL FOR PINELLAS COUNTY			5,839.1
Sarasota County			
Apac-Florida, Inc.	8.5	7.7	
Gator Asphalt Co.	6.9	6.3	
TOTAL FOR SARASOTA COUNTY			15.4

Estimated emissions of NO_x by county and source.

	Tons/Year	Metric Tons/Year	
Citrus County			
Florida Power	48,373.4	43,923.1	
TOTAL FOR CITRUS COUNTY			48,923.1
Hardee County			
TECO Power Services Corp.	0.0	0.0	
TOTAL FOR HARDEE COUNTY			0.0
Hernando County			
Central Power & Lime, Inc.	1,097.1	996.2	
Florida Mining & Materials	330.0	299.7	
TOTAL FOR HERNANDO COUNTY			1,429.1
Pasco County			
Couch Construction Co.	13.7	12.5	
Florida Power	5,116.7	4,646.0	
Lykes Pasco, Inc.	141.8	128.7	
Overstreet Paving Co.	23.1	20.9	
Pasco County Resource Recovery	908.9	825.3	
R.E. Purcell Construction Co.	14.8	13.4	
TOTAL FOR PASCO COUNTY			6,219.0
Polk County			
Aluminum Company of America	12.9	11.7	
Bio-Medical Service Corp. of George (BFI)	15.2	13.8	
Cargill Citro-America, Inc.	40.1	36.4	
Cargill Fertilizer, Inc.	121.2	110.0	
Citrus World, Inc.	75.9	68.9	
City of Lakeland - Larsen Power Station	256.5	232.9	
City of Lakeland - McIntosh Power Station	3,536.1	3,210.8	
Coca Cola	116.2	105.6	
Farmland Industries, Inc.	581.9	528.4	
Florida Juice, Inc.	82.5	74.9	
IMC Fertilizer, Inc. - Prairie	19.7	17.9	
IMC-Agrico Co. (Kingsfor Mine)	15.0	13.7	
IMC-Agrico Chemical Co. (New Wales)	349.9	317.7	
IMC-Agrico Co.	54.1	49.1	
IMC-Agrico Co. (Nichols Plant)	22.9	20.8	

Attachment, Continued
Estimated emissions of NO_x by county and source.

	Tons/Year	Metric Tons/Year	
IMC-Agrico Co. (Noralyn Mine)	21.0	19.1	
Lakeland Drum	5.3	4.8	
Mobil Mining & Minerals Co.	8.3	7.5	
Mulberry Phosphates, Inc.	7.3	6.6	
Orange-Co of Florida, Inc.	14.7	13.3	
Owens-Brockway Glass Container, Inc.	325.8	295.8	
SFE Citrus Processors, L.P. Ltd.	12.4	11.3	
Standard Sand & Silica Co.	10.0	9.0	
Sun Pac Foods, Inc.	6.5	5.9	
U.S. Agri-Chemicals Corp.	48.0	43.6	
TOTAL FOR PASCO COUNTY			5,778.3
Charlotte County			
Ajax Paving Industries	16.3	14.8	
Apac-Florida (Macasphalt)	11.2	10.2	
TOTAL FOR CHARLOTTE COUNTY			25.0

APPENDIX B

Table B1. Standard Cleaning Protocols for Analytical Glassware, Sample Containers, Collection Vessels, Funnels, and Tubing

Container	Material Procedure (in order specified)
Collection Vessels 1, 2, 4, 5, 6, 11, 12	FEP Teflon
Collection Vessel Caps 1, 2, 4, 5, 6	ETFE Tefzel
Collection Vessels 1, 2, 4, 5, 6, 11, 12	HDPE
Collection Vessel Caps 1, 2, 4, 5, 6	Polypropylene
Funnels 1, 2, 4, 5, 6, 11, 12	Polycarbonate
Tubing 1, 2, 4, 5, 6, 11, 12	FEP Teflon
Collars 1, 2, 4, 5, 6, 11, 12	HDPE
Metals Sample Containers 7, 8, 9	HDPE
Metals Sample Container Caps 7, 8, 9	Polyethylene
Nutrients Sample Containers 10, 8, 9	HDPE
Nutrients Sample Container Caps 10, 8, 9	Polyethylene
Metals Glassware 1, 2, 3, 8, 9	Pyrex or equiv.
Nutrients Glassware 1, 2, 10, 8, 9	Pyrex or equiv.

1. *Wash with hot tap water and brush** using dilute Liquinox.**
2. *Rinse with tap water.**
3. *Rinse with 10% HNO_3 solution.*
4. *Soak in 3N HCl for 24 hours, rinse with analyte-free water.*
5. *Soak in 0.5N HCl for 24 hours, rinse with analyte-free water.*
6. *Soak in 0.05N HCl for 72 hours, rinse with analyte-free water.*
7. *Soak in 0.1N HCl for 24 hours, rinse with analyte-free water.*
8. *Rinse with analyte-free water and air dry in contaminant-free environment.*
9. *Cap or cover tightly and store in a contaminant-free environment until use.*
10. *Rinse with 5% H_2SO_4 solution.*
11. *Enclose in white polyethylene bags.*
12. *After assembly of collection unit, store in large bag in contaminant-free environment until use.*

* *Omit steps 1 and 2 for new sample containers verified to be noncontaminating for the parameters of interest, and for glassware reserved for laboratory water solutions of inorganic standards.*

** *Omit brush for tubing.*

Organics collection equipment was cleaned with liquonox and hot water, laboratory water, wash acetone, a dichloromethane rinse, and air dried. The apparatus was assembled and the teflon collection bottle was covered with a white plastic bag to reduce light and reflect heat after deployment.

APPENDIX C

Table C1. Results of container blank lot analyses as loads.

Date	Total Phosphorus mg	Nitrate-Nitrite N mg	Ammonium N mg	TKN mg	Cu µg	Pb µg	Zn µg	Al µg
19941018	<0.0125	<0.0013	<0.0013	<0.0125	<0.0250	0.0991	<0.0250	<0.2500
19941122	<0.0475	<0.0048	<0.0048	<0.0475	<0.0500	<0.1250	<0.0500	<0.5000
19941206	<0.0125	<0.0013	<0.0013	<0.0125	<0.1000	<0.2500	<0.1000	1.5053
19941228	<0.0125	<0.0013	<0.0013	<0.0125	<0.0500	0.4390	0.1443	1.3613
19950131	<0.0500	<0.0050	<0.0050	<0.0500	<0.1000	<0.2500	<0.1000	<0.9999
19950228	<0.0125	<0.0013	<0.0013	<0.0125	<0.0500	<0.1250	<0.0500	<0.5000
19950328	<0.0125	<0.0013	<0.0013	<0.0125	<0.0250	0.0766	0.0275	0.7884
19950404	0.0855	<0.0048	<0.0048	<0.0475	<0.0500	0.5327	<0.0500	2.6672
19950418	<0.0475	<0.0048	<0.0048	<0.0475	<0.1000	<0.2500	0.7904	<0.9999
19950516	<0.0125	<0.0013	<0.0013	<0.0125	<0.0250	<0.0625	<0.0250	<0.2500
19950530	<0.0125	<0.0013	<0.0013	<0.0125	0.0325	<0.0625	0.0506	<0.2500
19950606	<0.0475	<0.0048	<0.0048	<0.0475	<0.1000	<0.2500	<0.1000	1.4519
19950613	<0.0125	<0.0013	<0.0013	<0.0125	<0.1000	<0.2501	0.1005	<1.0003
19950627	<0.0475	<0.0048	<0.0048	<0.0475	<0.1000	<0.2500	<0.1000	<0.9998
19950711	<0.0125	<0.0013	<0.0013	0.0250	<0.0250	<0.0625	<0.0250	<0.2500
19950725	<0.0500	<0.0050	<0.0050	<0.0500	0.2198	<0.2497	0.1154	<0.9989
19950815	<0.0475	<0.0048	<0.0048	<0.0475	<0.1000	<0.2500	<0.1000	1.9205
19950822	<0.0125	<0.0013	<0.0013	<0.0125	<0.0500	<0.1250	<0.0500	1.1325
19950919	<0.0125	<0.0013	<0.0013	<0.0125	<0.0250	<0.0626	0.0580	0.4382
19951010	<0.0475	<0.0048	<0.0048	<0.0475	<0.0996	<0.2490	0.1942	<0.9959
19951024	<0.0125	<0.0013	<0.0013	0.0325	<0.0251	<0.0628	0.0435	0.8470

Table C2. Results of rinse water blank lot analyses as loads.

Date	Total Phosphorus mg	Nitrate-Nitrite N mg	Ammonium N mg	TKN mg	Cu µg	Pb µg	Zn µg	Al µg
19941018	<0.0050	<0.0005	<0.0005	0.0160	<0.0110	<0.0274	<0.0110	<0.1096
19941129	<0.0050	<0.0005	<0.0005	<0.0050	<0.0148	<0.0371	<0.0148	0.1721
19941206	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0250	0.0711	0.1521
19941220	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0250	<0.0100	<0.1000
19950103	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0250	<0.0100	<0.1000
19950117	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0251	<0.0101	<0.1006
19950131	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0252	<0.0101	0.4518
19950214	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0253	<0.0101	0.2532
19950228	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0251	0.0159	0.7447
19950314	<0.0050	<0.0005	0.0005	<0.0050	<0.0100	<0.0251	0.0134	0.1250
19950328	<0.0050	<0.0005	<0.0005	0.0130	<0.0101	0.0712	<0.0101	0.1706
19950411	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0250	<0.0100	0.2271
19950425	<0.0050	<0.0005	<0.0005	0.0070	<0.0100	0.0635	0.0989	0.2141
19950509	<0.0050	<0.0005	0.0029	<0.0050	<0.0100	<0.0249	<0.0100	<0.0995
19950523	<0.0050	<0.0005	<0.0005	0.0130	<0.0100	<0.0251	<0.0100	<0.1004
19950606	<0.0050	<0.0005	<0.0005	0.0060	<0.0100	<0.0250	<0.0100	<0.1000
19950620	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0249	<0.0100	<0.0997
19950705	<0.0050	<0.0005	0.0018	0.0140	<0.0101	<0.0252	0.0362	0.1480
19950718	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0251	<0.0101	<0.1006
19950801	<0.0050	<0.0005	0.0022	<0.0050	<0.0100	<0.0251	<0.0100	<0.1003
19950815	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0253	0.0240	<0.1011
19950829	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0251	0.0723	0.3862
19950912	<0.0050	<0.0005	<0.0005	<0.0050	0.0105	<0.0250	0.0758	0.1394
19950926	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	0.0379	0.0398	0.4380
19951010	<0.0050	<0.0005	<0.0005	0.0080	<0.0100	<0.0251	<0.0100	0.1270

Table C3. Results of weekly equipment blank analyses as loads.

Date	Total Phosphorus mg	Nitrate-Nitrite N mg	Ammonium N mg	TKN mg	Cu µg	Pb µg	Zn µg	Al µg
19941018	<0.0050	<0.0005	<0.0005	<0.0050	<0.0113	<0.0283	0.0422	0.3433
19941025	<0.0050	<0.0005	<0.0005	<0.0050	<0.0110	<0.0276	<0.0110	0.2457
19941101	<0.0050	<0.0005	<0.0005	<0.0050	<0.0112	0.0379	<0.0112	<0.1123
19941108	<0.005	<0.0005	<0.0005	<0.005	<0.01	<0.02	0.11	1.45
19941115	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0254	1.3702	1.4744
19941122	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0252	<0.0101	0.1061
19941129	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0251	<0.0100	1.5135
19941206	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0255	<0.0102	0.4160
19941213	<0.0050	<0.0005	<0.0005	<0.0050	<0.0104	<0.0260	0.0208	0.3756
19941220	<0.0050	<0.0005	<0.0005	<0.0050	<0.0103	<0.0257	<0.0103	0.2621
19941228	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0251	0.0246	0.8533
19950103	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0252	<0.0101	<0.1009
19950110	<0.0050	<0.0005	<0.0005	<0.0050	0.0101	<0.0251	0.0602	0.3099
19950117	<0.0050	<0.0005	<0.0005	<0.0050	<0.0100	<0.0251	<0.0100	0.3375
19950124	<0.0050	<0.0005	<0.0005	<0.0050	0.0438	0.0355	0.0870	<0.1018
19950131	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0254	<0.0102	1.0090
19950207	<0.0050	<0.0005	<0.0005	<0.0050	<0.0103	<0.0258	<0.0103	0.2462
19950214	<0.0050	<0.0005	<0.0005	<0.0050	<0.0101	<0.0253	<0.0101	1.4756
19950221	<0.0050	<0.0005	<0.0005	<0.0050	<0.0103	<0.0258	0.0181	1.4541
19950228	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0255	0.0367	0.5511
19950307	<0.0050	<0.0005	0.0016	<0.0050	0.0174	<0.0255	0.0562	2.1206
19950314	<0.0050	<0.0005	0.0008	0.0060	<0.0102	<0.0255	0.0306	1.6200
19950321	<0.0050	<0.0005	0.0018	<0.0050	<0.0104	<0.0259	0.1714	1.1580
19950328	<0.0050	<0.0005	0.0024	<0.0050	<0.0102	<0.0255	0.0566	0.3327
19950404	0.0090	<0.0005	0.0018	<0.0050	<0.0103	<0.0257	<0.0103	1.9341
19950411	<0.0050	<0.0005	0.0009	<0.0050	0.0163	<0.0255	0.0268	0.6899
19950418	<0.0050	<0.0005	<0.0005	<0.0050	0.0140	<0.0259	0.0691	2.4953

Table C3 (continued). Results of weekly equipment blank analyses as loads.

Date	Total Phosphorus mg	Nitrate-Nitrite N mg	Ammonium N mg	TKN mg	Cu µg	Pb µg	Zn µg	Al µg
19950425	<0.0050	<0.0005	0.0009	0.0070	0.0358	<0.0255	0.1416	0.4862
19950502	<0.0050	<0.0005	0.0016	0.0090	<0.0102	<0.0255	0.0252	1.1765
19950509	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0256	2.6101	1.4179
19950516	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0255	0.0564	1.2000
19950523	<0.0050	<0.0005	<0.0005	0.0060	<0.0102	<0.0255	<0.0102	0.3778
19950530	<0.0050	<0.0005	0.0010	<0.0050	0.0584	<0.0254	0.1493	1.0713
19950606	<0.0050	<0.0005	0.0015	<0.0050	<0.0102	<0.0255	<0.0102	1.4685
19950613	<0.0050	<0.0005	0.0010	<0.0050	0.0128	<0.0255	0.0207	1.9633
19950620	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	<0.0254	0.0308	2.2034
19950627	<0.0050	<0.0005	<0.0005	<0.0050	<0.0102	0.0481	<0.0102	0.9169
19950705	<0.0050	<0.0005	0.0008	0.0180	<0.0102	<0.0256	<0.0102	0.3289
19950718	<0.0050	<0.0005	0.0016	<0.0050	<0.0104	0.0632	<0.0104	0.2147
19950711	<0.0050	<0.0005	<0.0005	0.0120	<0.0101	<0.0253	<0.0101	4.9261
19950725	<0.0050	<0.0005	<0.0005	<0.0050	<0.0010	<0.0026	0.0029	0.1204
19950801	<0.0050	<0.0005	0.0026	<0.0050	<0.0102	<0.0256	<0.0102	1.1142
19950808	<0.0050	<0.0005	0.0134	0.0200	<0.0103	<0.0258	0.0280	1.3277
19950815	<0.0050	0.0005	<0.0005	<0.0050	0.0166	<0.0252	0.0871	5.5421
19950822	<0.0050	<0.0005	<0.0005	<0.0050	0.0117	<0.0254	0.0231	4.1638
19950829	<0.0050	<0.0005	0.0044	<0.0050	0.0267	<0.0257	0.1897	3.3739
19950905	<0.0050	<0.0005	0.0007	<0.0050	<0.0103	<0.0257	0.0787	1.7741
19950912	<0.0050	<0.0005	<0.0005	0.0120	<0.0103	<0.0256	0.0566	2.2081
19950919	<0.0050	<0.0005	0.0019	<0.0050	<0.0102	<0.0255	0.0532	6.0398
19950926	0.0060	<0.0005	<0.0005	0.0170	<0.0102	<0.0254	0.0627	8.6328
19951003	0.0060	<0.0005	<0.0005	<0.0050	<0.0102	<0.0254	0.0772	0.4825
19951010	<0.0050	<0.0005	0.0015	<0.0050	<0.0103	0.0333	0.3038	4.6282

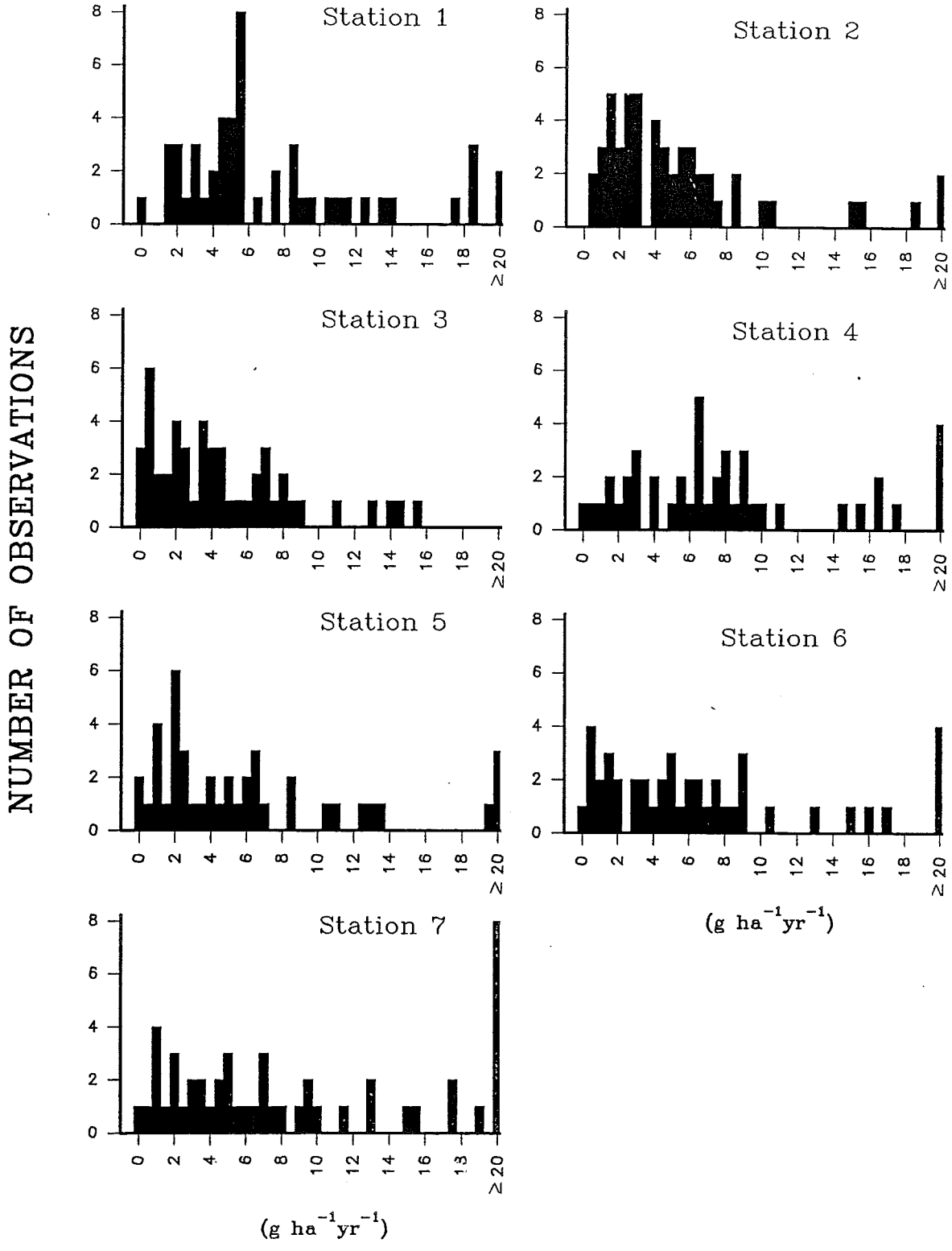
Table C4. QA Results for Standard Recoveries of PAHs and Chlorinated Organic Compounds.

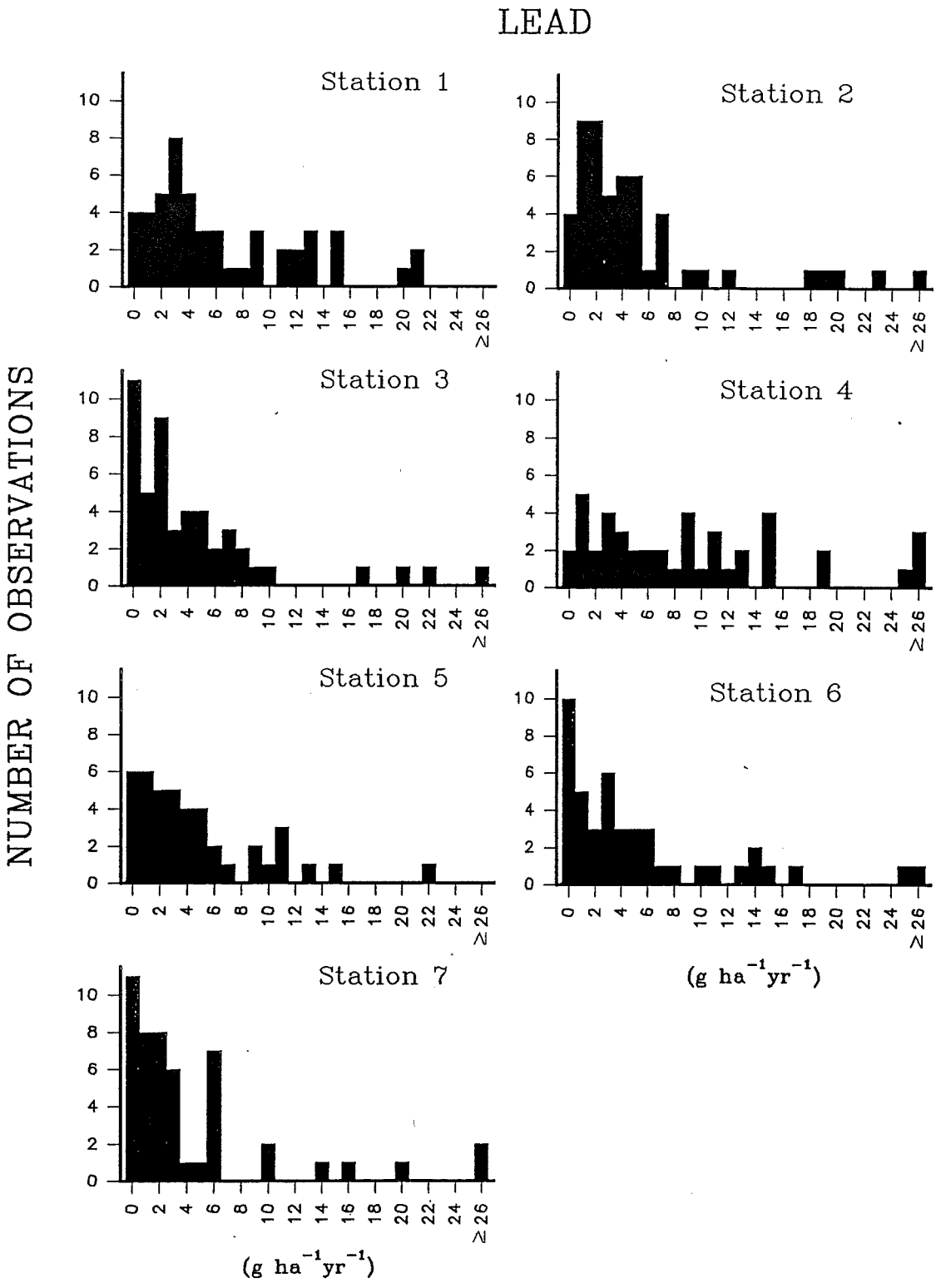
	%REC	%RSD	Acceptable recovery
A. PAHs			
Acenapthene	50.2	33.0	0-128
Acentphthalene	45.9	33.6	0-134
Anthracene	90.3	4.0	16-108
Benzo(a)anthracene	78.0	12.6	20-128
Benzo(a)pyrene	88.9	2.7	0-127
Benzo(b)Fluoranthene	99.6	22.0	1-141
Benzo(ghi)perylene	90.7	3.4	ll-97
Benzo(k)Fluoranthene	97.4	15.9	1-141
Chrysene	97.5	9.2	40-136
Dibenzo(ah)anthracene	92.3	0.4	13-119
Fluoranthene	95.2	2.1	26-112
Fluorene	72.8	16.2	10-132
Naphthalene	24.2	41.4	0-128
Phenanthrene	84.0	7.3	19-124
Pyrene	92.3	2.1	18-118
B. Chlorinated Organics			
α bhc	104.4	3.2	57-113
α-chlordane	85.8	4.0	58-106
aldrin	106.8	2.7	58-108
β bhc	94.1	4.3	47-123
chlorpyriphos	91.9	2.8	na
δ bhc	106.5	3.5	43-127
enddosulfan II	84.0	17.3	36-159
endosulfan I	99.5	2.0	74-122
endosulfan sulfate	102.0	1.1	53-117
endrin aldehyde	77.1	12.2	50-120
heptachlor	100.8	3.0	44-100
heptachlor epoxide	95.6	3.0	66-122
lindane	102.3	2.6	56-104
pp' DDD	85.7	8.4	55-119
pp' DDE	87.1	2.9	62-124
pp' DDT	129.3	3.8	52-130

[1] *Percent of standard recovered from spiked sample.*
[2] *Percent relative standard duration from 3 replicates.*

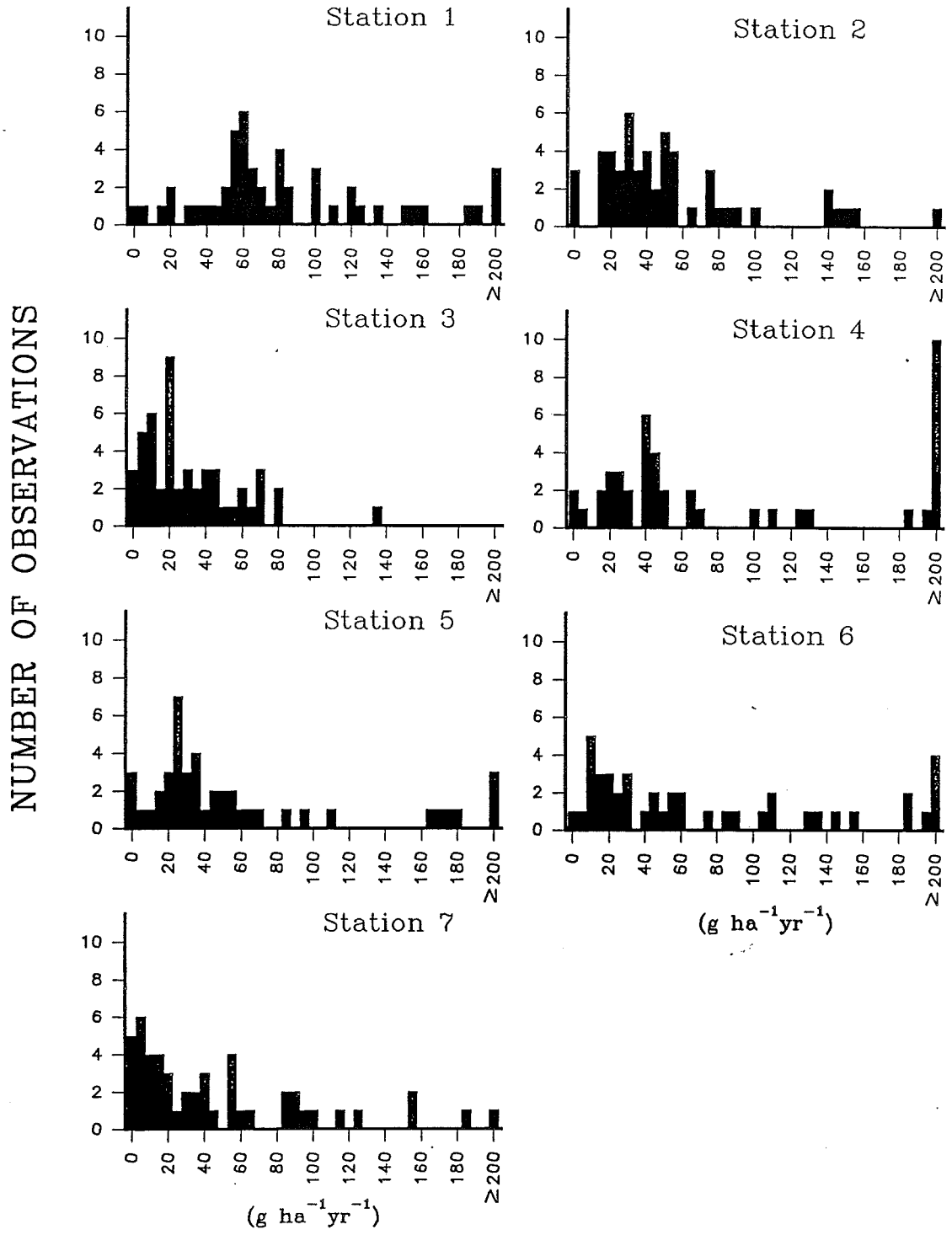
APPENDIX D

COPPER

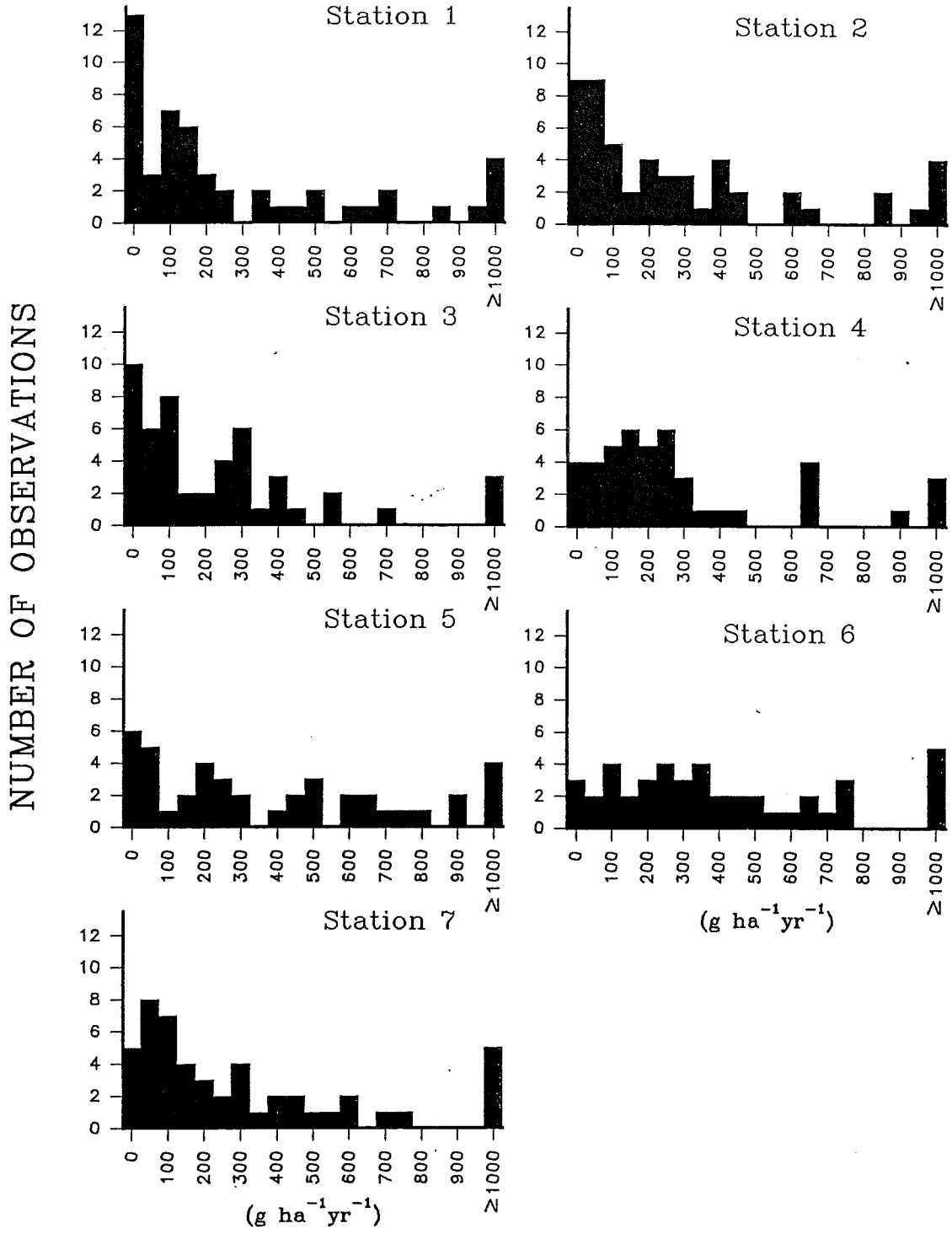

Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 2 4 6 8 10 12 14 16 18 ≥20
(g ha^{-1}yr^{-1})

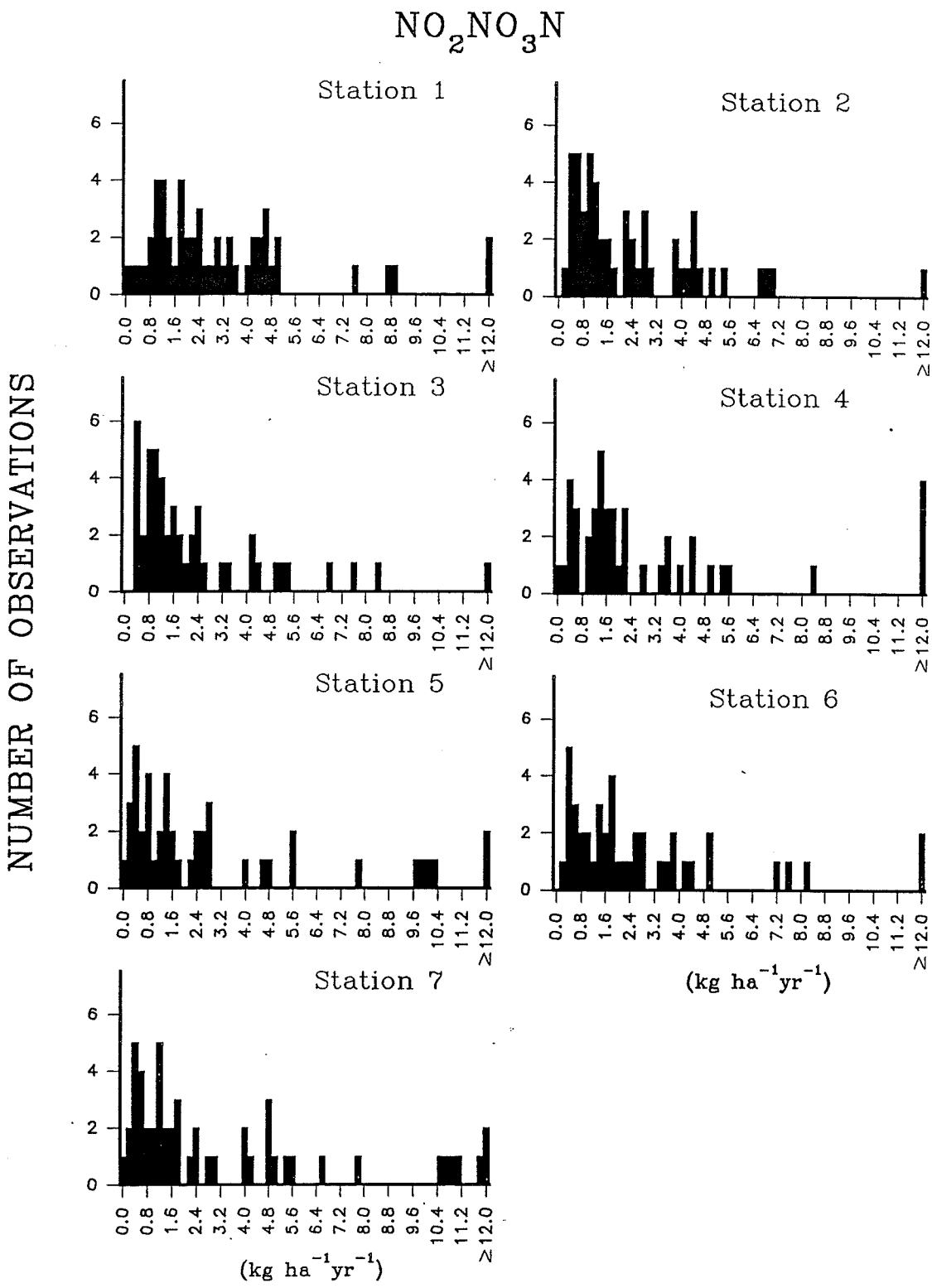

LEAD
Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
(g ha^{-1}yr^{-1})
(g ha^{-1}yr^{-1})

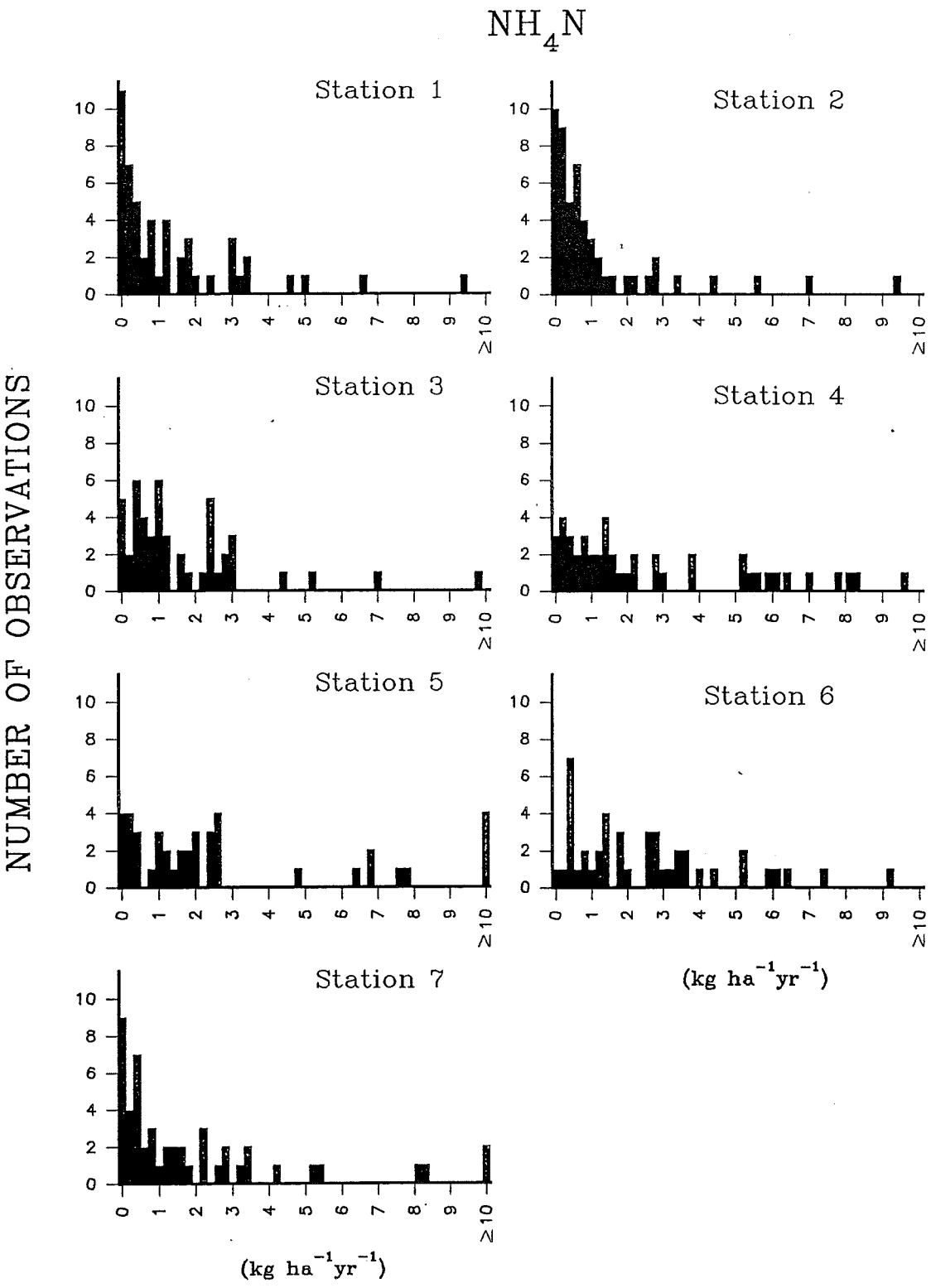
ZINC


Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 2 4 6 8 10
0 20 40 60 80 100 120 140 160 180 ≥200
(g ha^{-1}yr^{-1})

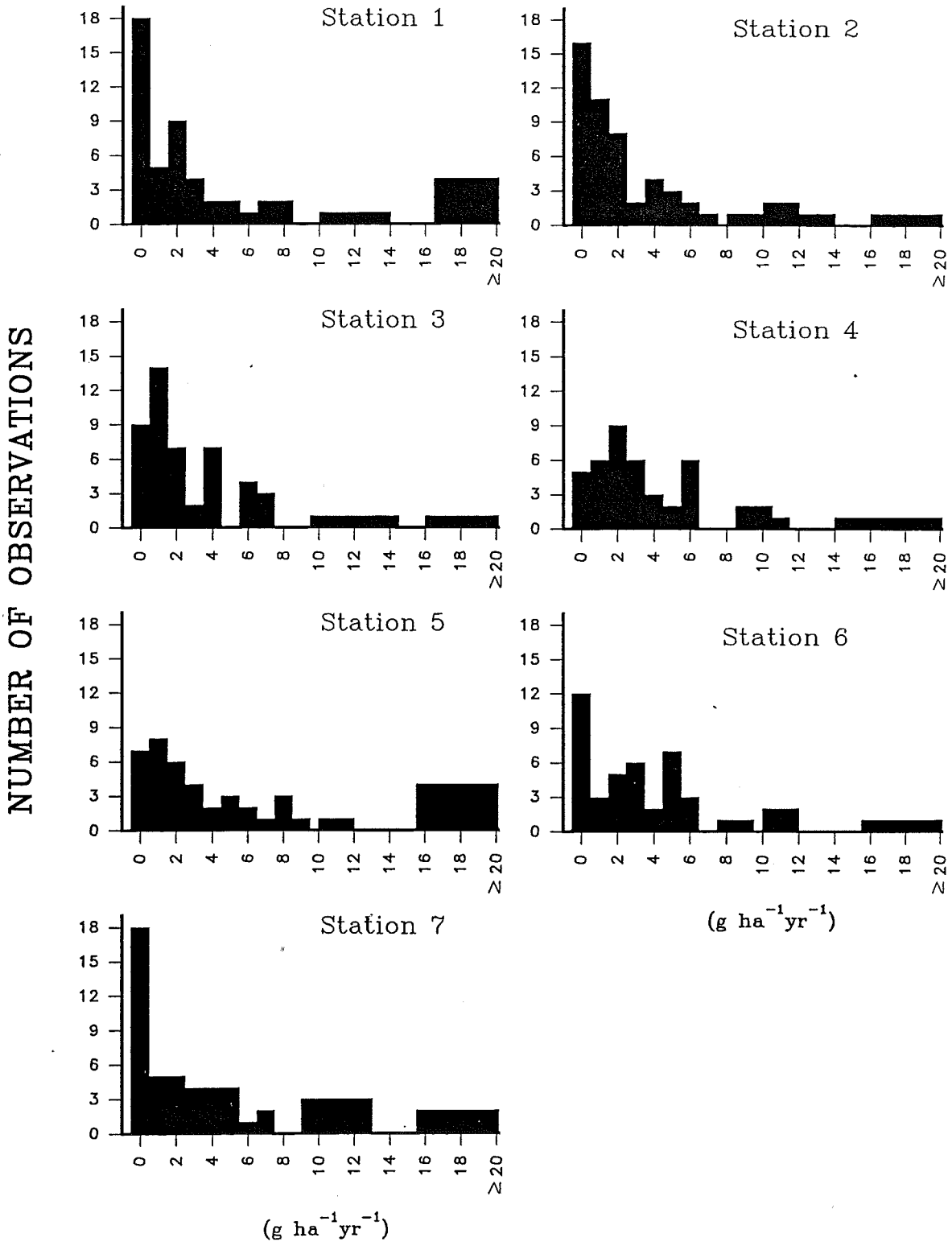
ALUMINUM


Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 100 200 300 400 500 600 700 800 900 ≥1000
0 2 4 6 8 10 12
(g ha^{-1}yr^{-1})

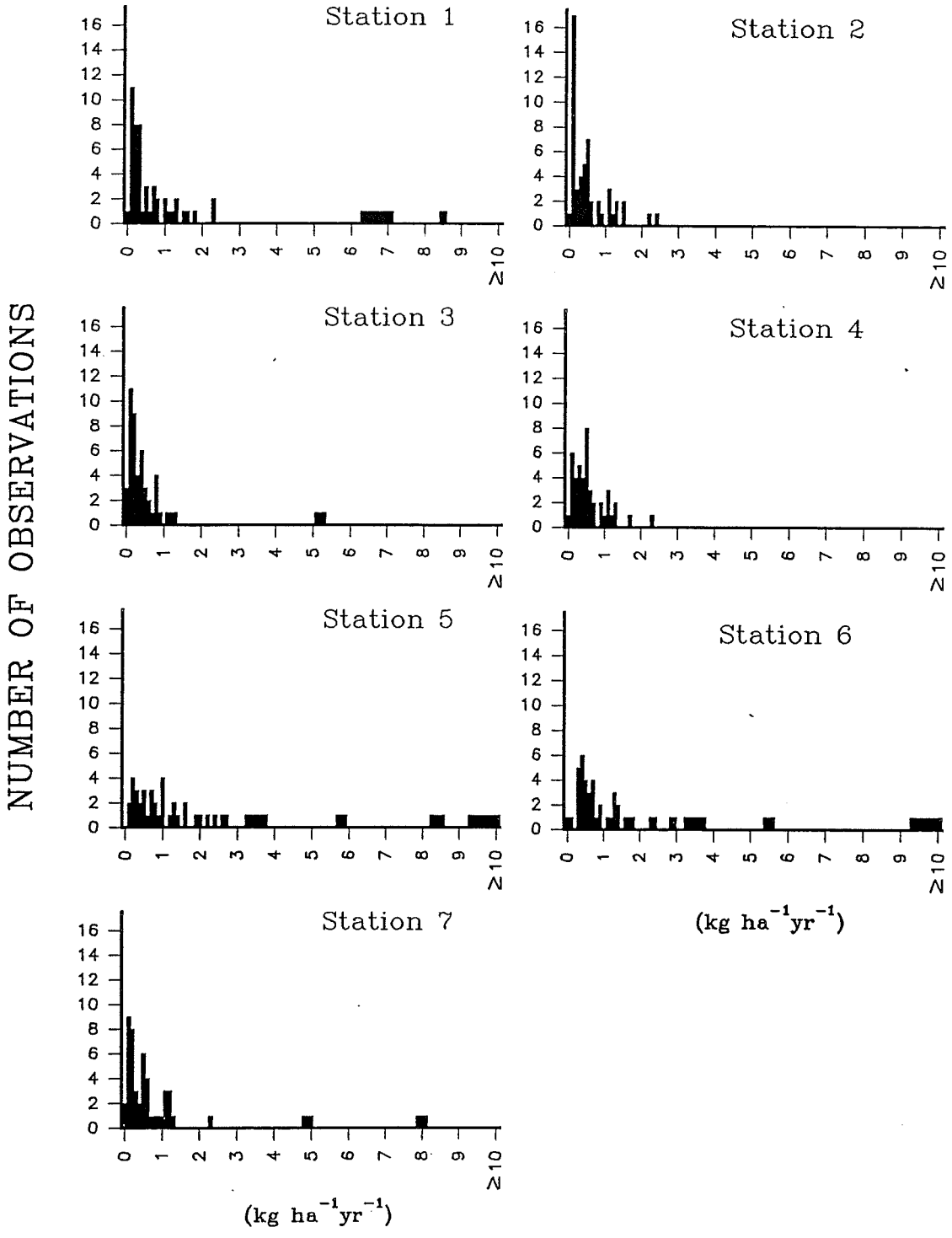

NO_2NO_3N
Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 2 4 6
0.0 0.8 1.6 2.4 3.2 4.0 4.8 5.6 6.4 7.2 8.0 8.8 9.6 10.4 11.2 ≥12.0
(kg ha^{-1}yr^{-1})


NH_4N
Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 1 2 3 4 5 6 7 8 9 ≥10
0 2 4 6 8 10
(kg ha^{-1}yr^{-1})

TOTAL KJELDAHL NITROGEN



TOTAL P


Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 1 2 3 4 5 6 7 8 9 ≥10
0 2 4 6 8 10 12 14 16
(kg ha^{-1}yr^{-1})

APPENDIX E

Table E1 (continued). Pesticides (ng m^{-2} 2 $weeks^{-1}$)

Location:	**STA-4**	**STA-4**	**STA-4**	**STA-4**	**STA-4**	**STA-4**
Sample #:	**0821/0829**	**0842/0850**	**0861/0873**	**0884/0892**	**1003/1010**	**1017/1024**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
a bhc	<	<	<	<	<	<
a-chlordane	<	<	<	<	<	<
aldrin	<	<	<	<	<	<
b bhc	<	<	<	<	<	<
chlorpyriphos	<	<	<	<	<	<
d bhc	83	<	<	<	<	<
dieldrin	<	<	<	<	<	<
endosulfan I	<	<	<	<	<	259
endosulfan II	<	<	<	<	<	304
endosulfan sulfate	<	<	<	<	<	<
endrin	<	<	<	<	<	<
endrin aldehyde	<	<	<	<	<	<
heptachlor	<	<	<	<	<	<
heptachlor epox	<	<	<	<	<	<
lindane	<	<	<	<	<	<
methhoxychlor	<	<	<	<	<	<
pp DDD	<	<	<	<	<	<
pp DDE	<	<	<	<	<	<
pp DDT	<	<	<	<	<	<
Total	**83**	<	<	<	<	**563**

Location:	**STA-5**	**STA-5**	**STA-5**	**STA-5**	**STA-5**	**STA-5**
Sample #:	**0822/0830**	**0843/0851**	**0862/0874**	**0885/0893**	**1004/1011**	**1018/1025**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
a bhc	<	<	<	118	<	<
a-chlordane	<	<	<	<	<	<
aldrin	<	<	<	<	<	<
b bhc	<	<	<	<	<	<
chlorpyriphos	<	<	<	<	<	<
d bhc	<	<	<	<	<	<
dieldrin	<	<	<	<	<	<
endosulfan I	<	<	149	<	107	<
endosulfan II	<	<	<	<	<	<
endosulfan sulfate	111	<	<	<	<	<
endrin	<	<	<	<	<	<
endrin aldehyde	<	<	<	<	<	<
heptachlor	<	<	<	<	<	<
heptachlor epox	<	<	<	<	<	<
lindane	<	<	<	<	<	<
methhoxychlor	<	<	<	<	<	<
pp DDD	<	<	<	<	<	<
pp DDE	<	<	<	<	<	<
pp DDT	<	<	136	248	<	<
Total	**111**	<	**285**	**366**	**107**	<

MDL = 50 ng m^{-2} 2 $weeks^{-1}$

Table E1 (continued). Pesticides (ng m^{-2} 2 $weeks^{-1}$)

Location:	**STA-7**	**STA-7**	**STA-7**	**STA-7**	**STA-7**	**STA-7**
Sample #:	**0824/0832**	**0845/0853**	**0864/0876**	**0887/0895**	**1006/1013**	**1020/1027**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
a bhc	<	<	<	<	<	<
a-chlordane	<	<	<	<	<	<
aldrin	<	<	<	<	<	<
b bhc	<	<	<	<	<	<
chlorpyriphos	<	<	<	<	<	<
d bhc	70	125	306	119	50	239
dieldrin	<	<	<	<	<	<
endosulfan I	<	<	<	386	266	269
endosulfan II	177	90	<	<	1207	440
endosulfan sulfate	<	<	<	<	352	<
endrin	<	<	<	<	<	<
endrin aldehyde	94	<	<	<	<	<
heptachlor	<	<	<	<	<	<
heptachlor epox	<	<	<	<	<	<
lindane	<	<	<	<	<	<
methhoxychlor	<	<	<	<	<	<
pp DDD	<	<	<	<	<	<
pp DDE	<	<	<	<	<	<
pp DDT	204	183	287	<	<	<
Total	**545**	**398**	**593**	**505**	**1875**	**948**

MDL = 50 ng m^{-2} 2 $weeks^{-1}$

Table E2 (continued). Hydrocarbons (μg m^{-2} 2 $weeks^{-1}$)

Location:	**STA-7**	**STA-7**	**STA-7**	**STA-7**	**STA-7**	**STA-7**
Sample #:	**0824/0832**	**0845/0853**	**0864/0876**	**0887/0895**	**1006/1013**	**1020/1027**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
Acenapthene	<	<	<	<	<	<
Acentphthalene	<	<	<	<	<	<
Anthracene	<	<	<	<	<	<
Benzo(a)anthracene	<	<	<	<	<	<
Benzo(a)pyrene	<	<	<	<	<	<
Benzo(b)Fluoranthene	<	<	<	<	<	<
Benzo(ghi)perylene	<	<	<	<	<	<
Benzo(k)Fluoranthene	<	1	<	<	<	<
Chrysene	<	<	<	<	<	<
Dibenzo(ah)anthr	<	<	<	<	<	<
Fluoranthene	<	<	<	<	<	<
Fluorene	<	<	<	<	<	<
Indeno(123)pyrene	<	<	<	<	<	<
Naphthalene	<	<	<	<	<	<
Phenanthrene	<	<	<	<	<	<
Pyrene	<	<	<	2	<	<
Total	**<**	**1**	**<**	**2**	**<**	**<**

MDL = 1 μg m^{-2} 2 $weeks^{-1}$

Table E2 (continued). Hydrocarbons ($\mu g\ m^{-2}\ 2\ weeks^{-1}$)

Location:	**STA-4**	**STA-4**	**STA-4**	**STA-4**	**STA-4**	**STA-4**
Sample #:	**0821/0829**	**0842/0850**	**0861/0873**	**0884/0892**	**1003/1010**	**1017/1024**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
Acenapthene	<	<	<	<	<	<
Acentphthalene	<	<	<	<	<	<
Anthracene	<	<	<	<	<	<
Benzo(a)anthracene	<	<	<	<	<	<
Benzo(a)pyrene	<	<	<	<	<	<
Benzo(b)Fluoranthene	<	<	3	2	<	<
Benzo(ghi)perylene	<	<	<	<	<	<
Benzo(k)Fluoranthene	<	<	<	<	<	<
Chrysene	<	<	<	<	<	<
Dibenzo(ah)anthr	<	<	<	<	<	<
Fluoranthene	2	<	2	2	<	<
Fluorene	<	<	<	<	<	<
Indeno(123)pyrene	<	<	<	<	<	<
Naphthalene	<	<	<	<	<	<
Phenanthrene	<	<	<	<	<	<
Pyrene	<	<	2	<	<	<
Total	**2**	**<**	**7**	**4**	**<**	**<**

Location:	**STA-5**	**STA-5**	**STA-5**	**STA-5**	**STA-5**	**STA-5**
Sample #:	**0822/0830**	**0843/0851**	**0862/0874**	**0885/0893**	**1004/1011**	**1018/1025**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
Acenapthene	<	<	<	<	<	<
Acentphthalene	<	<	<	<	<	<
Anthracene	<	<	<	<	<	<
Benzo(a)anthracene	<	<	<	<	<	<
Benzo(a)pyrene	<	<	<	<	<	<
Benzo(b)Fluoranthene	<	<	2	<	2	2
Benzo(ghi)perylene	<	<	4	<	<	<
Benzo(k)Fluoranthene	<	<	<	<	<	<
Chrysene	<	<	<	<	<	<
Dibenzo(ah)anthr	<	<	4	<	<	<
Fluoranthene	<	4	<	<	<	<
Fluorene	<	<	<	<	<	<
Indeno(123)pyrene	<	<	<	<	<	<
Naphthalene	<	2	<	<	<	<
Phenanthrene	<	<	<	<	<	<
Pyrene	<	2	<	<	<	<
Total	**<**	**8**	**10**	**<**	**2**	**2**

MDL = 1 $\mu g\ m^{-2}\ 2\ weeks^{-1}$

Table E3. PCBs (ng m^{-2} 2 $weeks^{-1}$)

Location:	**STA-1**	**STA-1**	**STA-1**	**STA-1**	**STA-1**	**STA-1**
Sample #:	**0818/0826**	**0839/0847**	**0858/0870**	**0881/0889**	**1000/1007**	**1014/1021**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
congner #8	<	<	<	<	<	<
18	<	<	<	<	<	<
28	<	<	<	<	<	<
52	<	<	<	<	<	<
44	<	<	<	<	<	<
66	<	<	<	<	<	<
101	<	<	<	<	<	<
77	<	<	<	<	<	<
118	<	<	<	<	<	<
153	<	<	63	<	<	<
105	<	<	<	<	<	<
138	<	<	<	<	<	<
126	<	<	<	<	<	<
187	<	<	<	<	<	<
128	<	<	<	<	<	<
180	<	<	<	<	<	<
170	<	<	<	<	<	<
195	<	<	<	<	<	<
206	<	<	<	<	<	<
209	<	<	<	<	<	<
Total	<	<	**63**	<	<	<

Location:	**STA-3**	**STA-3**	**STA-3**	**STA-3**	**STA-3**	**STA-3**
Sample #:	**0820/0828**	**0841/1860**	**0849/0872**	**0883/0891**	**1002/1009**	**1016/1023**
Dates:	**711+7/18**	**7/25+8/8**	**8/1+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
congner #8	<	<	714	302	<	<
18	<	<	<	320	<	<
28	<	<	<	<	<	<
52	<	<	<	<	<	<
44	289	<	<	<	<	<
66	<	<	<	<	<	<
101	<	<	<	158	<	<
77	<	<	<	<	<	<
118	<	<	<	<	<	<
153	<	<	<	<	<	<
105	<	<	<	<	<	<
138	<	<	<	<	<	<
126	<	<	<	<	<	<
187	<	<	<	<	<	<
128	<	<	<	<	<	<
180	<	<	<	<	<	<
170	<	<	<	<	<	<
195	<	<	<	<	<	<
206	<	<	<	<	<	<
209	<	<	<	<	<	<
Total	**289**	<	**714**	**780**	<	<

MDL = 50 ng m^{-2} 2 $weeks^{-1}$

Table E3 (continued). PCBs (ng m^{-2} 2 $weeks^{-1}$)

Location:	**STA-4**	**STA-4**	**STA-4**	**STA-4**	**STA-4**	**STA-4**
Sample #:	**0821/0829**	**0842/0850**	**0861/0873**	**0884/0892**	**1003/1010**	**1017/1024**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
congner #8	<	<	<	<	<	<
18	<	<	<	<	<	<
28	<	<	<	<	<	<
52	<	<	<	<	<	<
44	<	<	<	<	<	<
66	<	<	<	<	<	<
101	<	<	<	<	<	<
77	<	<	<	<	<	<
118	<	<	<	<	<	<
153	<	<	81	<	<	<
105	<	<	<	<	<	<
138	<	<	<	<	<	<
126	<	<	<	<	<	<
187	<	<	<	<	<	<
128	<	<	<	<	<	<
180	<	<	<	<	<	<
170	<	<	<	<	<	<
195	<	<	<	<	<	<
206	<	<	<	<	<	<
209	<	<	<	<	<	<
Total	<	<	**81**	<	<	<

Location:	**STA-5**	**STA-5**	**STA-5**	**STA-5**	**STA-5**	**STA-5**
Sample #:	**0822/0830**	**0843/0851**	**0862/0874**	**0885/0893**	**1004/1011**	**1018/1025**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
congner #8	<	<	<	<	<	<
18	<	<	<	<	<	<
28	<	<	<	<	<	<
52	<	<	<	<	<	<
44	<	<	<	<	<	<
66	<	<	<	<	<	<
101	181	307	<	<	<	231
77	<	146	<	<	<	<
118	<	<	<	<	<	<
153	<	92	<	<	<	<
105	<	<	<	<	<	<
138	<	<	<	<	<	<
126	<	<	<	<	<	<
187	<	<	<	<	<	<
128	<	<	<	<	<	<
180	<	<	<	<	<	<
170	<	<	<	<	<	<
195	<	<	<	<	<	<
206	<	<	<	<	<	<
209	<	<	<	<	<	<
Total	**181**	**545**	<	<	<	**231**

MDL = 50 ng m^{-2} 2 $weeks^{-1}$

Table E3 (continued). PCBs (ng m^{-2} 2 $weeks^{-1}$)

Location:	**STA-7**	**STA-7**	**STA-7**	**STA-7**	**STA-7**	**STA-7**
Sample #:	**0824/0832**	**0845/0853**	**0864/0876**	**0887/0895**	**1006/1013**	**1020/1027**
Dates:	**7/11+7/18**	**7/25+8/1**	**8/8+8/15**	**8/22+8/29**	**9/5+9/12**	**9/19+9/26**
congner #8	<	<	<	<	<	<
18	<	<	<	<	<	<
28	<	<	<	<	<	<
52	<	<	<	<	<	<
44	<	<	473	<	<	<
66	<	<	<	<	<	<
101	<	<	300	<	<	<
77	<	<	<	<	<	<
118	<	<	<	<	<	<
153	<	<	<	<	<	<
105	<	<	<	<	<	<
138	<	<	<	<	<	<
126	<	<	<	<	<	<
187	<	<	<	<	<	<
128	<	<	<	<	<	<
180	<	<	<	<	<	<
170	<	<	<	<	<	<
195	<	<	<	<	<	<
206	<	<	<	<	<	<
209	<	<	<	<	<	<
Total	<	<	**773**	<	<	<

MDL = 50 ng m^{-2} 2 $weeks^{-1}$