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

Submitted To:

TAMPA BAY NATIONAL ESTUARY PROGRAM
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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).

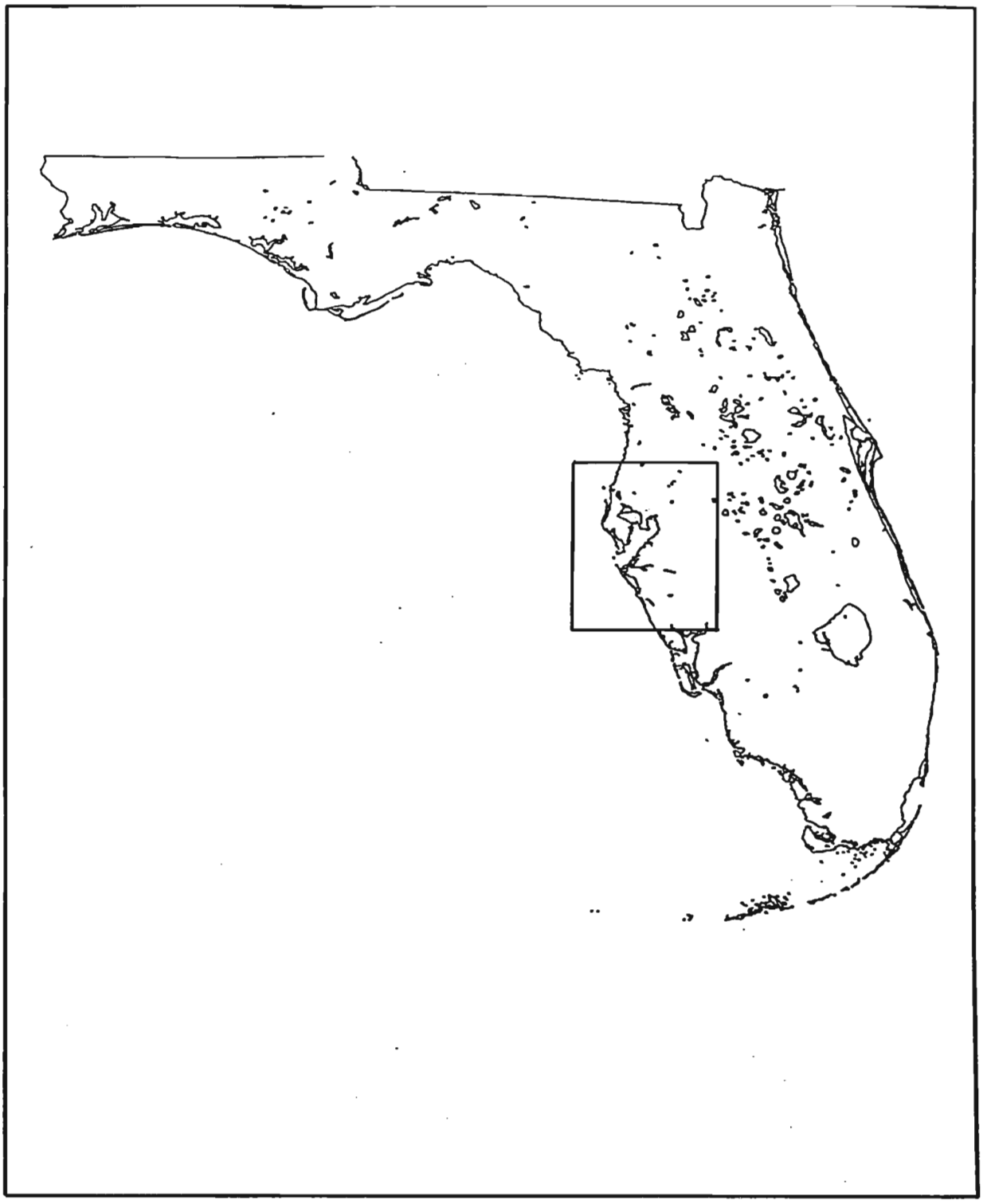

Figure A-1. State of Florida and the approximate study area surrounding Tampa Bay.

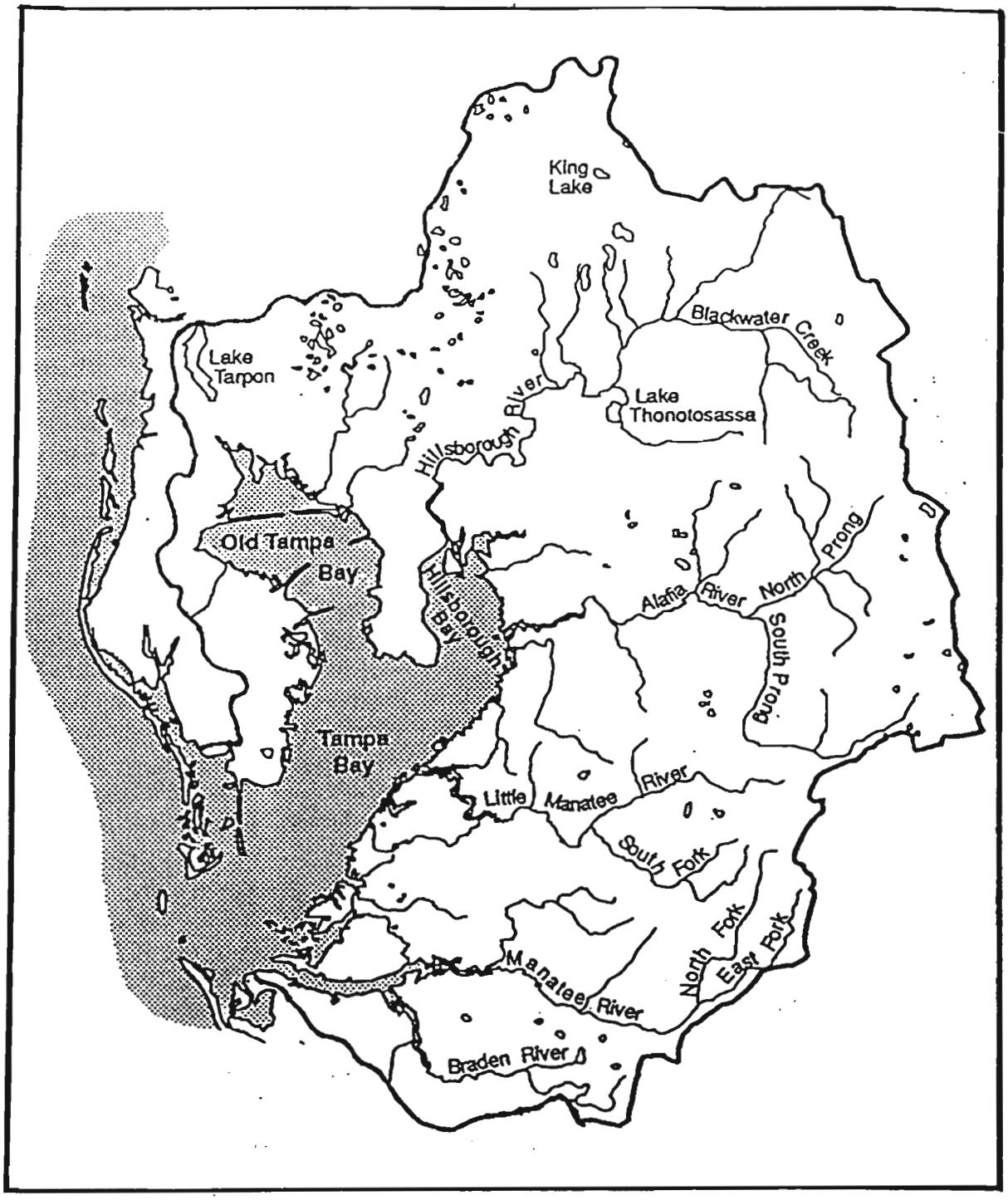

Figure A-2. The watershed of Tampa Bay, including portions of Boca Ciega Bay (adapted from Wolfe and Drew, 1990).

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.

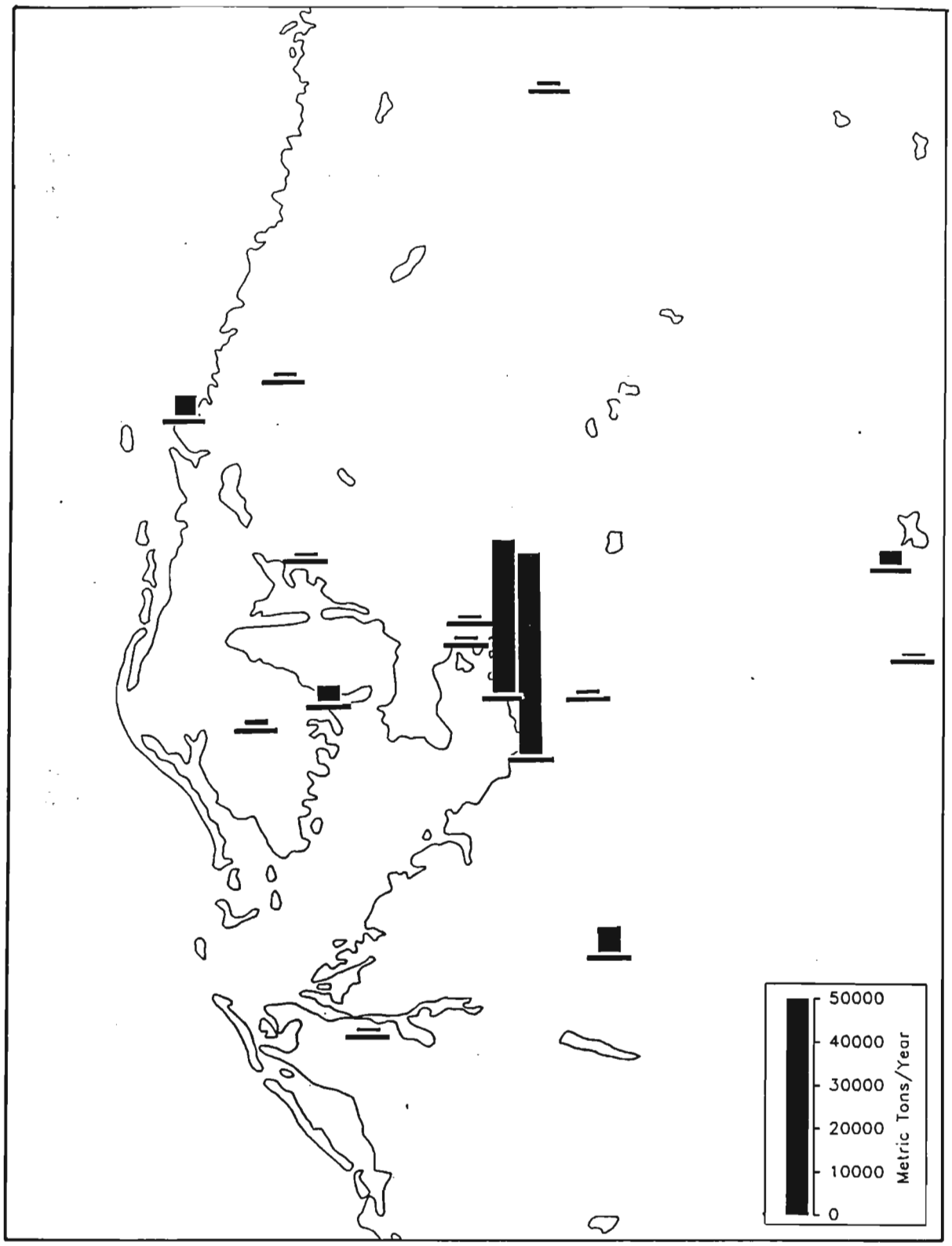

Figure A-3. Stationary sources of NO_x greater than 454 metric tons year^{-1} (500 tons year^{-1}). 1992 Actual emissions. (Citrus County to the north and outside of the illustrated region represents an additional 48,923 metric tons year^{-1}.)

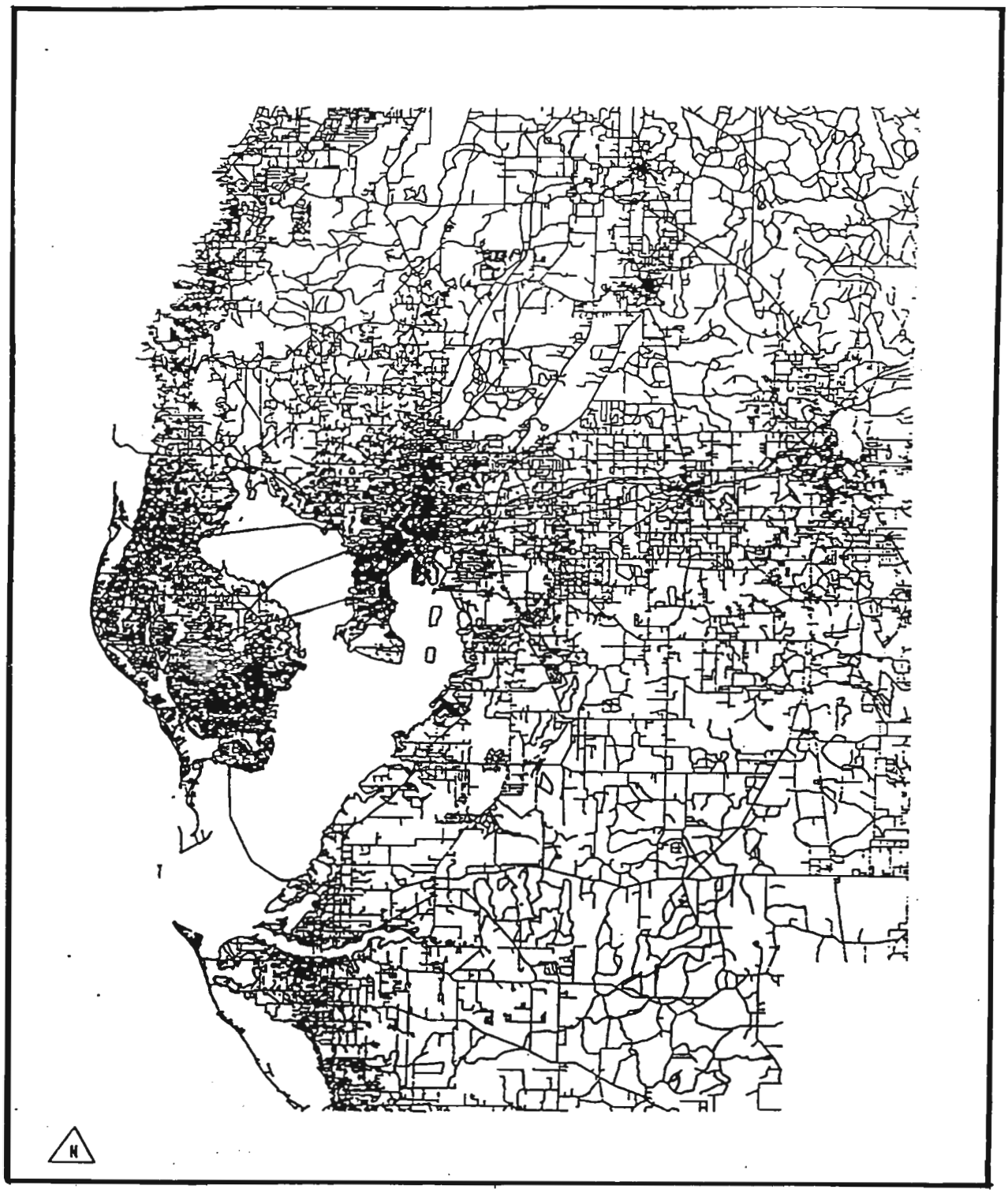

Figure A-4. Roadway density within the Tampa Bay watershed, as a surrogate for areas of mobile emissions (Dames & Moore, 1990).

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).

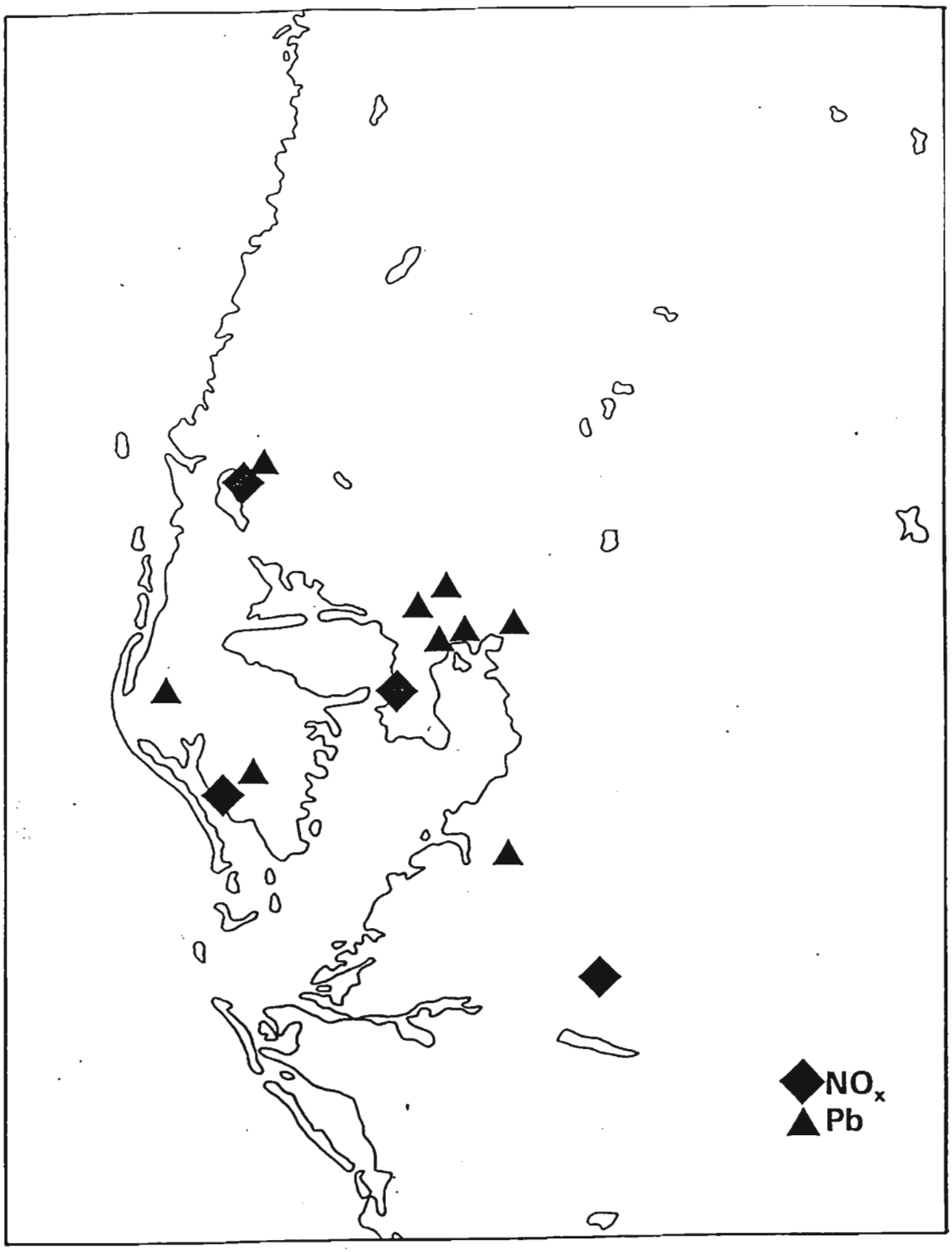

Figure A-5. Locations of Hillsborough, Manatee, and Pinellas counties' NO_x and lead ambient air monitoring stations.

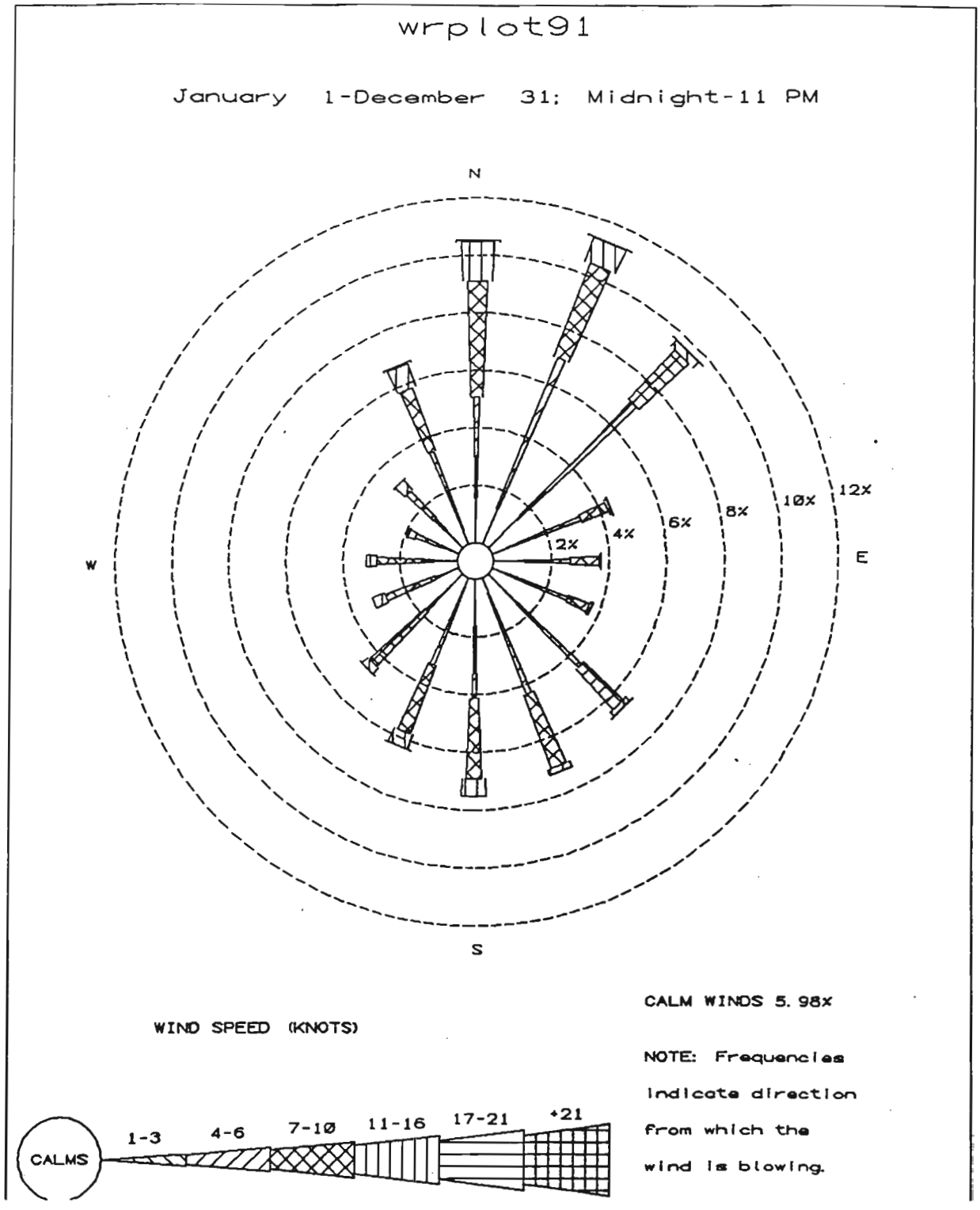

Figure A-6. Wind direction frequency and strength, Pinellas County, 1991.

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 $\mu g\ L^{-1}$	**Rural** $\mu g\ L^{-1}$
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

	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	

	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

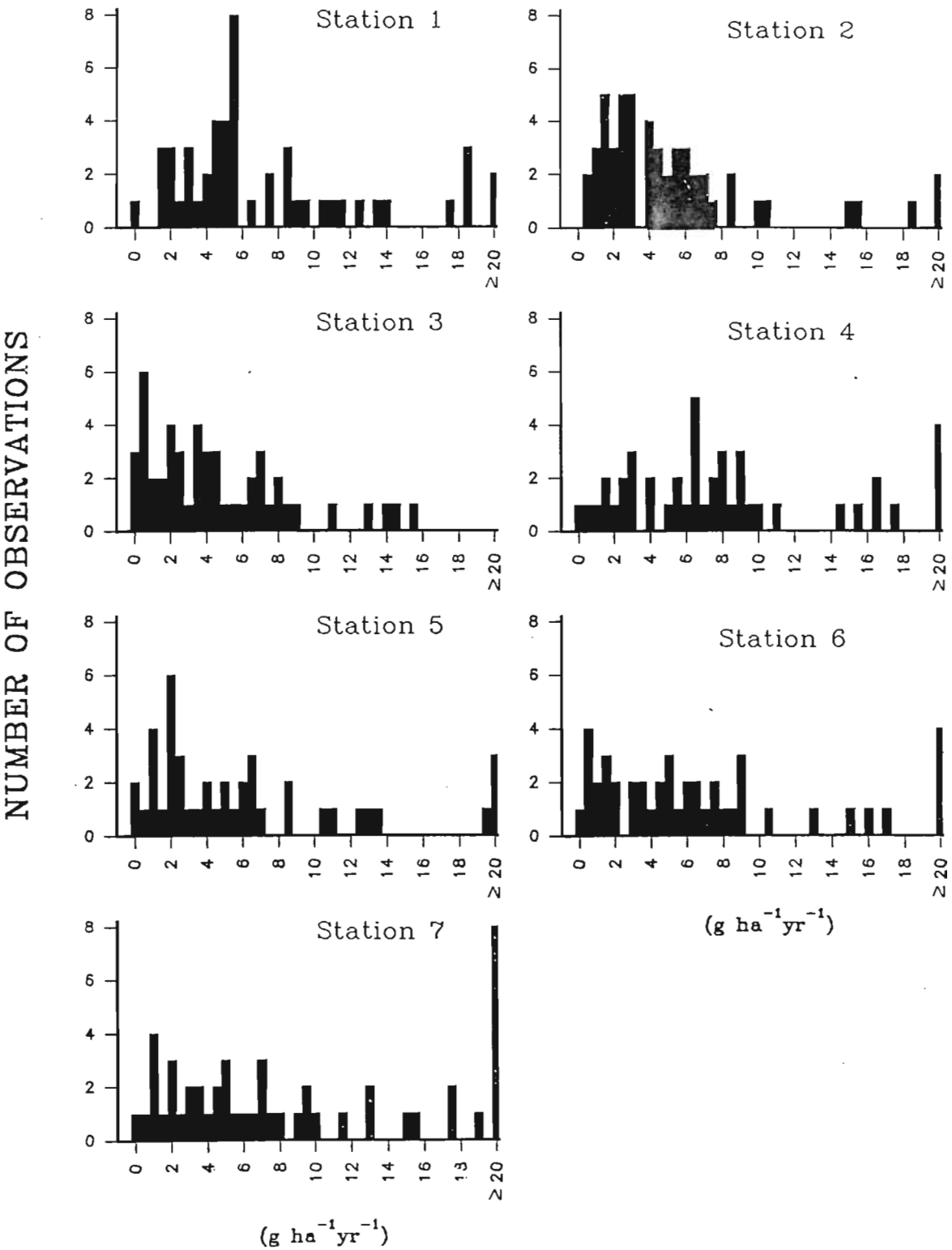
Table C4. QA Results for Standard Recoveries of PAHs and Chlorinated Organic Compounds.

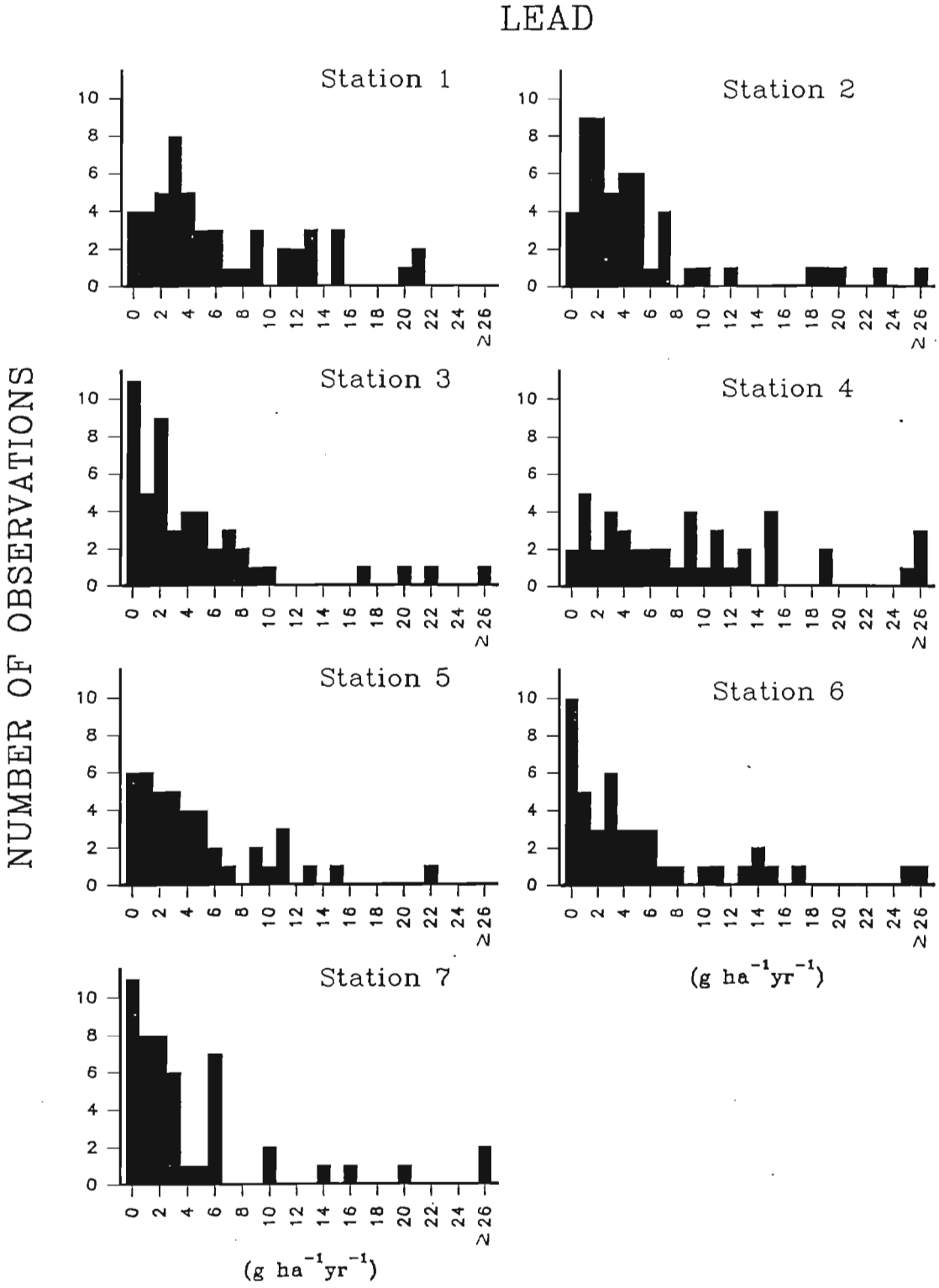
	%REC	%RSD	Acceptable recovery
A. PAHs			
Acenapthene	50.2	33.0	0-128
Acentphthalene	45.9	33.6	0-134
Anthracene	90.3	4.0	16-108
Benzo(a)anthracene	78.0	12.6	20-128
Benzo(a)pyrene	88.9	2.7	0-127
Benzo(b)Fluoranthene	99.6	22.0	1-141
Benzo(ghi)perylene	90.7	3.4	11-97
Benzo(k)Fluoranthene	97.4	15.9	1-141
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.*

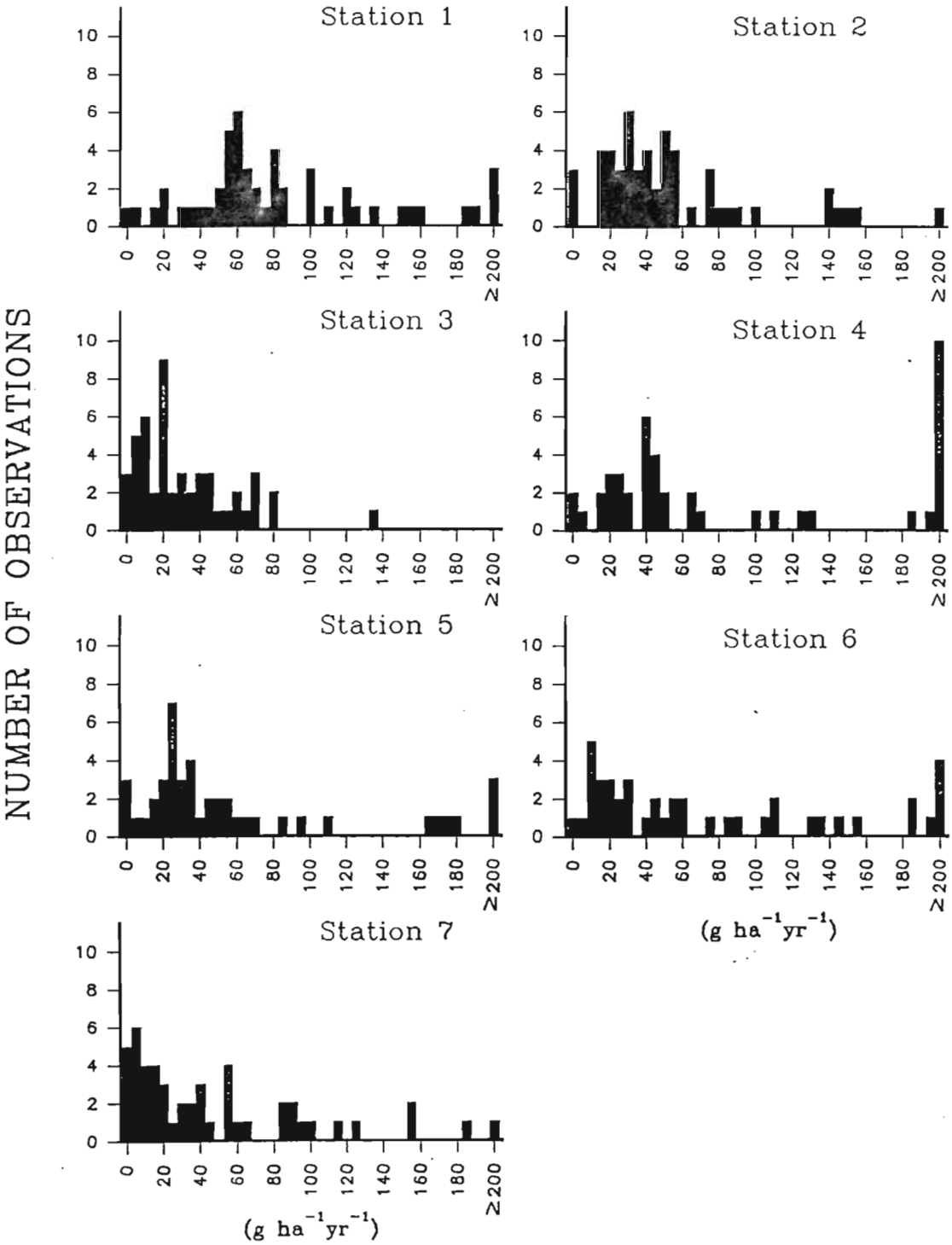
APPENDIX D

COPPER

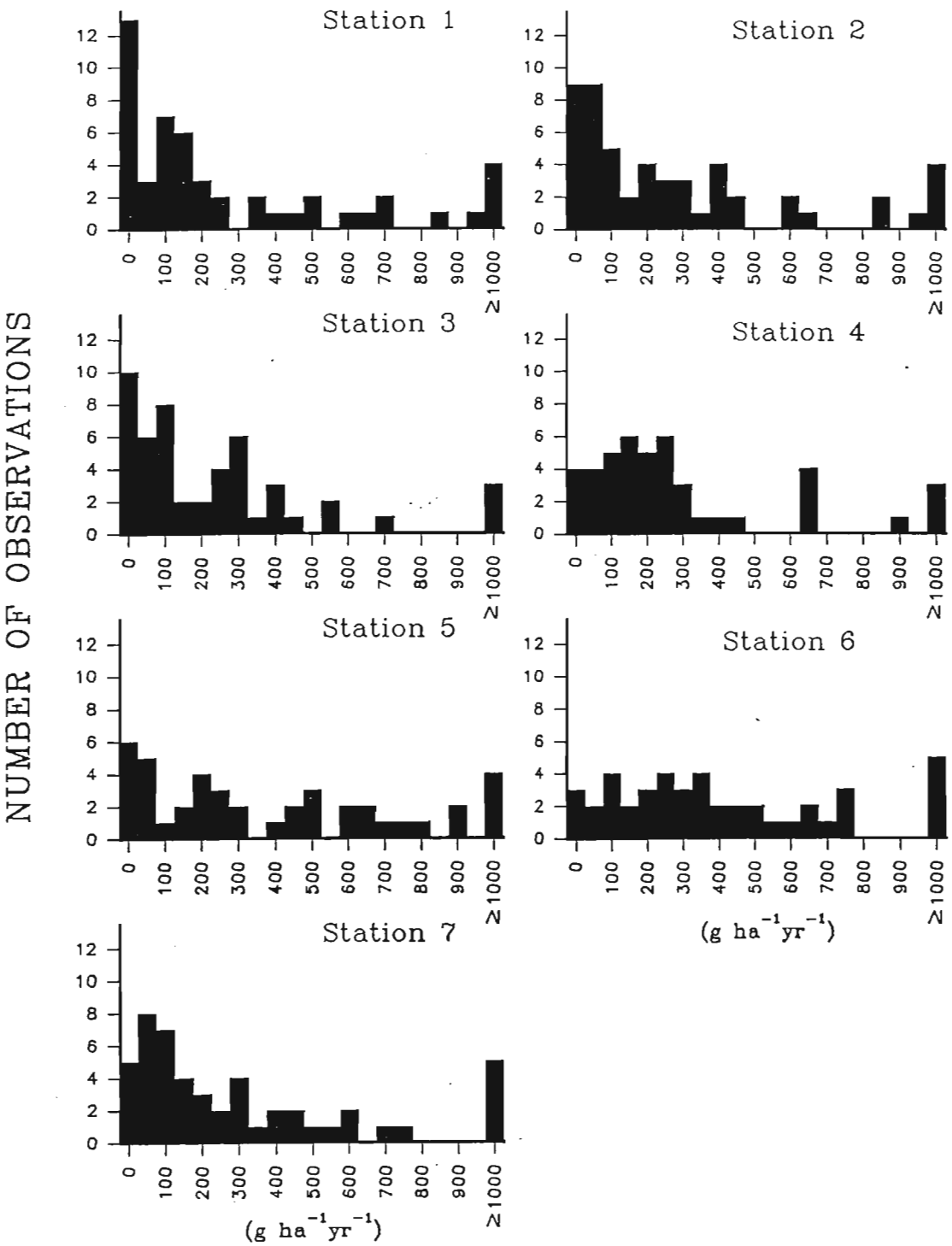

Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 2 4 6 8 10 12 14 16 18 ≥20
0 2 4 6 8
(g ha^{-1}yr^{-1})

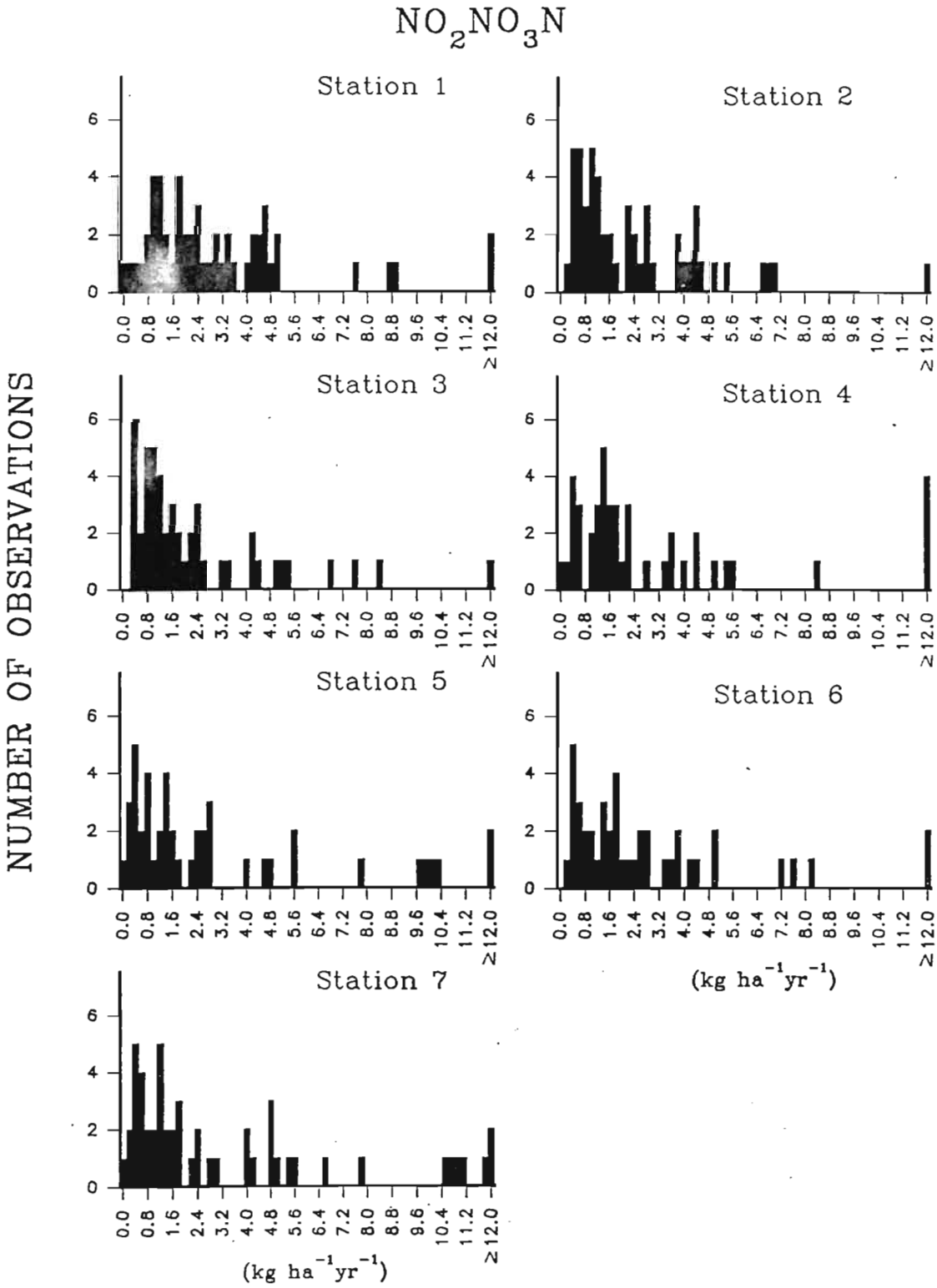

LEAD
Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 2 4 6 8 10 12 14 16 18 20 22 24 ≥26
0 2 4 6 8 10
(g ha^{-1}yr^{-1})

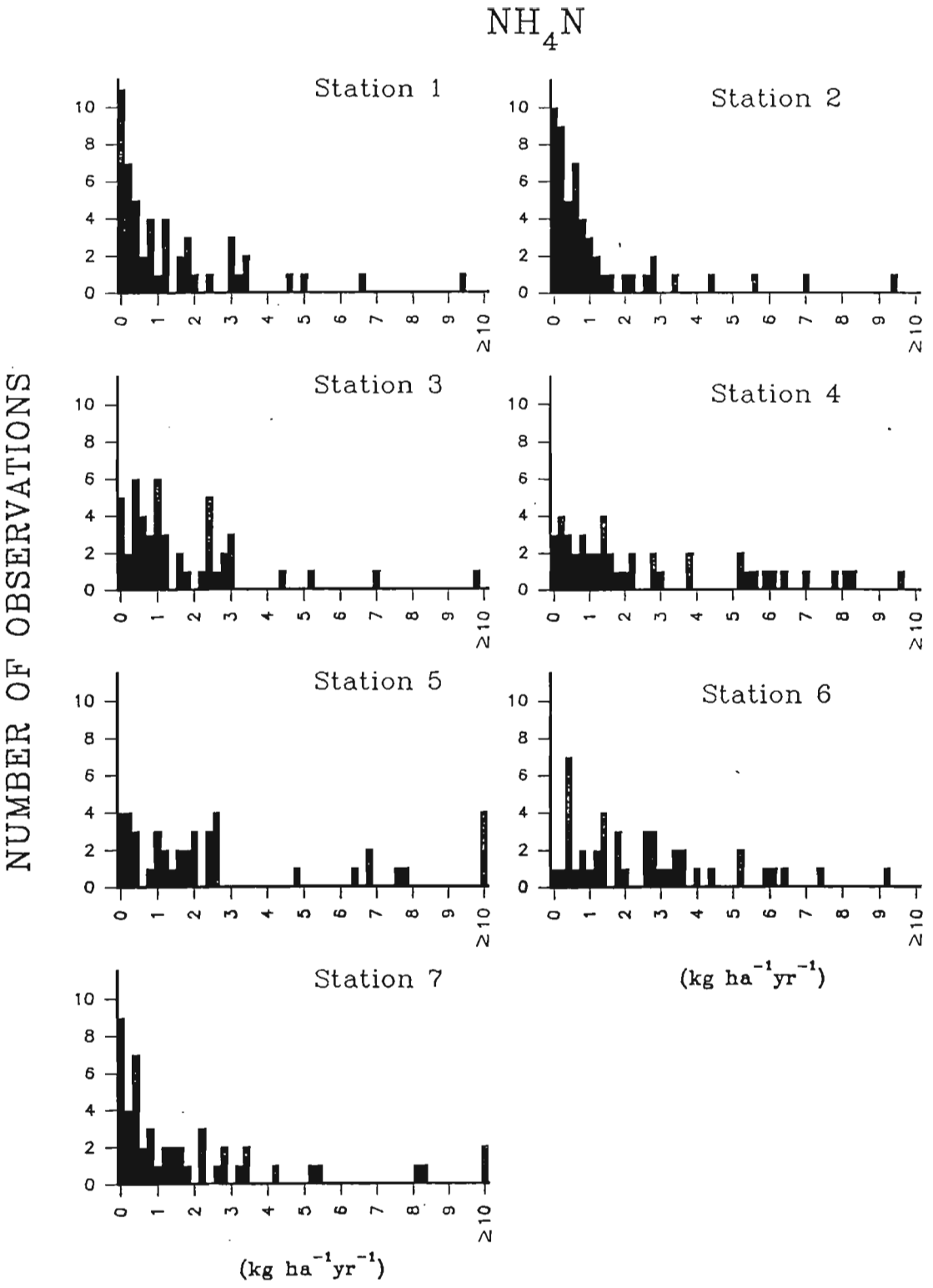
ZINC


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

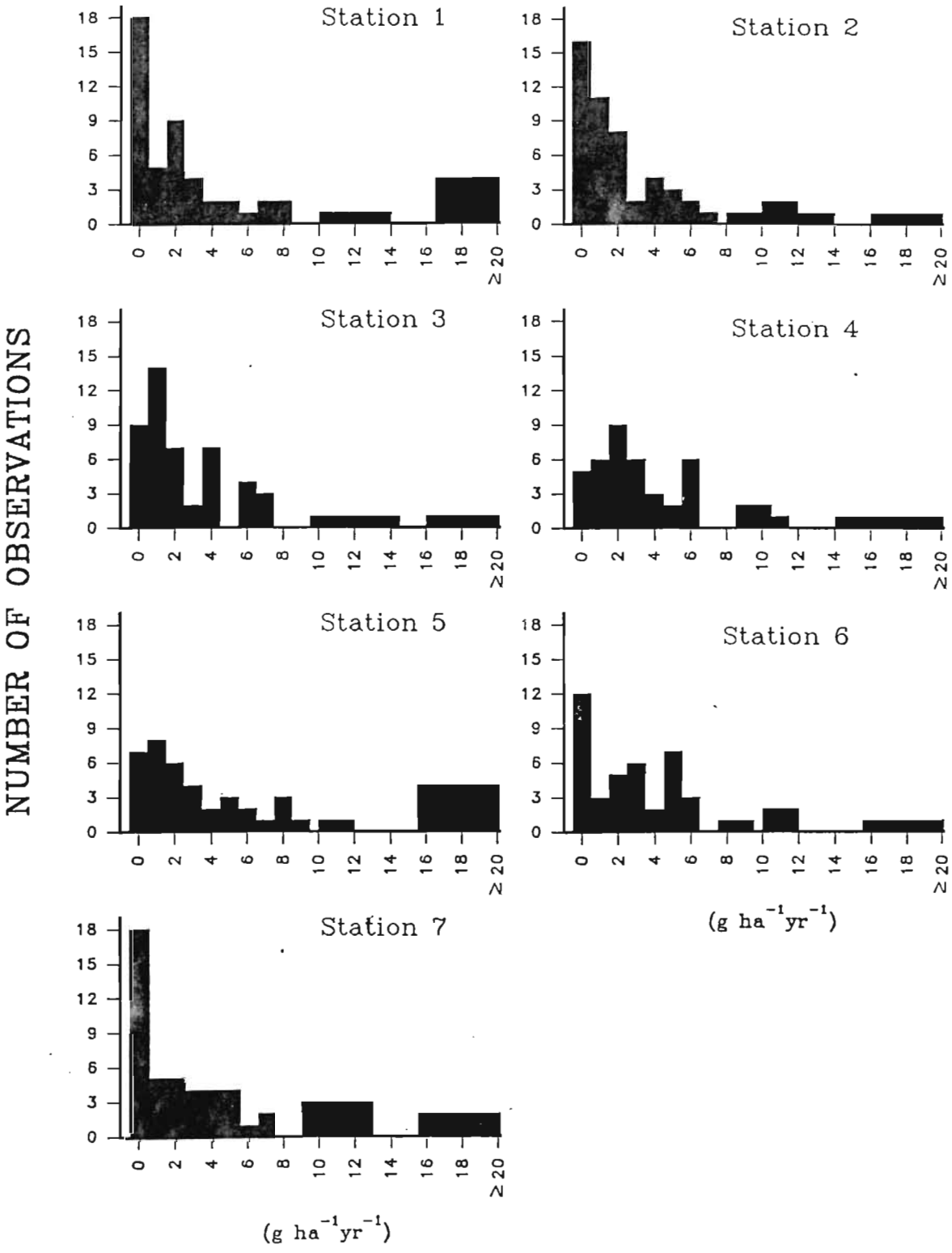
ALUMINUM


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
(g ha^{-1}yr^{-1})

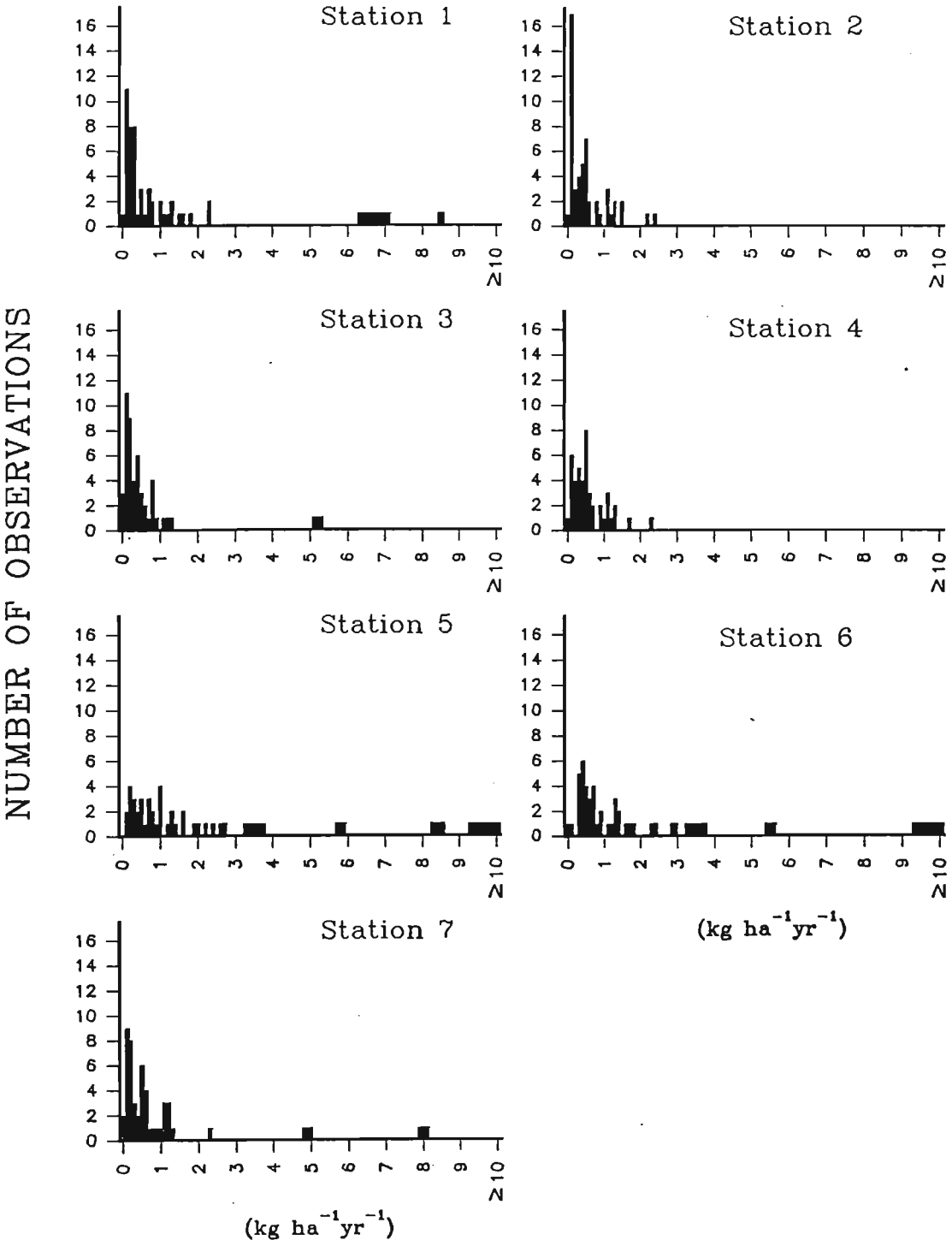

NO_2NO_3N
Station 1
Station 2
Station 3
Station 4
Station 5
Station 6
Station 7
NUMBER OF OBSERVATIONS
0 2 4 6
0.0 0.8 1.6 2.4 3.2 4.0 4.8 5.6 6.4 7.2 8.0 8.8 9.6 10.4 11.2 ≥12.0
(kg ha^{-1}yr^{-1})


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 ($\mu g\ m^{-2}\ 2\ weeks^{-1}$)

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

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 $weeks^{-1}$