

Atmospheric Deposition - NWQMN

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Introduction and general recommendations

The relationship between air quality and the environmental impacts air pollutants have on water resources is well recognized. The monitoring of wet and dry atmospheric deposition focuses attention on the transfer of chemical substances from the atmosphere to terrestrial and aquatic ecosystems. Both wet and dry deposition can be measured directly, although current techniques and deployed networks for dry deposition are more limited in extent and more resource-intensive to operate.

Since it is not feasible to make all of the necessary complex measurements at all locations where data are desired, any program such as the National Water Quality Monitoring network (NWQMN) seeking to estimate atmospheric deposition to a large number of water bodies via direct deposition to the water surface and to the land areas adjacent to water bodies (below the last gaged inflow) should consider the approach of sites (benchmark stations) where the requisite complex (wet, dry, micrometeorology, speciated mercury, PBTs etc) measurements are made, and an array of simpler sites (supporting stations) surrounding them where measurements can be used to extrapolate and estimate across the broader area of interest.

It is more likely that supporting stations already exist in the array of national and regional atmospheric deposition monitoring networks. It is unlikely that comprehensive all-constituent wet and dry deposition monitoring sites exist in the areas of interest needed by the NWQMN. If a two-tiered approach to monitoring is impractical given resource limitations, modeling of atmospheric deposition components, supported by verification from station measurements may be the only viable alternative.

Limitations

Three major knowledge gaps exist and resolution of these gaps are not resolved (or fully resolved) by the recommendations given here. First, a major knowledge gap exists for the verification of current modeling results for total deposition of most chemical constituents deposited directly to the surface of a large water body. The second gap is the magnitude of error associated with interpolation or extrapolation of ground based dry deposition measurements across a water body surface. Unlike wet deposition, the inferential method of estimating dry deposition from ground based monitoring is influenced significantly by vegetation type, leaf area index and micrometeorology in the vicinity of the monitoring station. The error associated with the use of estimation of land surface estimates of dry deposition (observed or modeled) to estimate that of an adjacent water body are unknown for many constituents. Thirdly, a recognized significant source of reactive nitrogen in atmospheric is dry deposition of ammonia gas (NH₃). This is not routinely measured by any atmospheric deposition network using standard protocols. The use of passive samplers to qualitatively estimate ammonia gas concentrations is being used increasingly,

however calibration of passive sampler ammonia networks to directly measured NH₃ air concentrations and computation of the net flux of NH₃ deposition is not well established.

Existing Atmospheric Deposition Networks

Five federally supported national air quality monitoring networks are operating currently in the U.S. Several other regional and local research networks exist primarily to address data needs for local up to the scale of regional environmental issues. An example of a regional network providing data applicable to the NWQMN objectives is the Integrated Atmospheric Deposition Network (IADN) that estimates atmospheric deposition of toxic organic substances to the Great Lakes. The following matrix relates the national monitoring networks to the measured atmospheric chemical constituents or properties. Each of the existing networks utilize extensive quality assurance practices and procedures so that comparable data is available for detecting spatial and temporal trends in atmospheric deposition on a regional or national basis. Only the IADN was specifically designed to locate sites to estimate atmospheric deposition to large water-bodies (the Great Lakes). The original siting design criteria for NADP networks and CASTNET specifically avoided location close to the coasts to avoid marine-salt contamination and to ensure sites were regionally representative to terrestrial ecoregions. However, since the 1990's, a significant number of NADP and CASTNET sites were added to address the increasing interest in estimating nitrogen deposition to bays and estuaries. This overlay of new sites had the affect of adding additional design criteria to the networks without removing or moving sites located to meet original eco-region based objectives.

DEPOSITION NETWORK	Base Cations	Nitrogen species	Sulfur species	Mercury species	Ozone and/or precursors	PAHs, PCBs, SVOCs
IADN (wet + dry)						•
NADP/NTN (wet)	•	•	•			
NADP/MDN (wet)				•		
CASTNET (dry)	•	•	•		•	
AIRMoN (dry)	•	•	•			
NADP/AIRMoN (wet event based)	•	•	•			

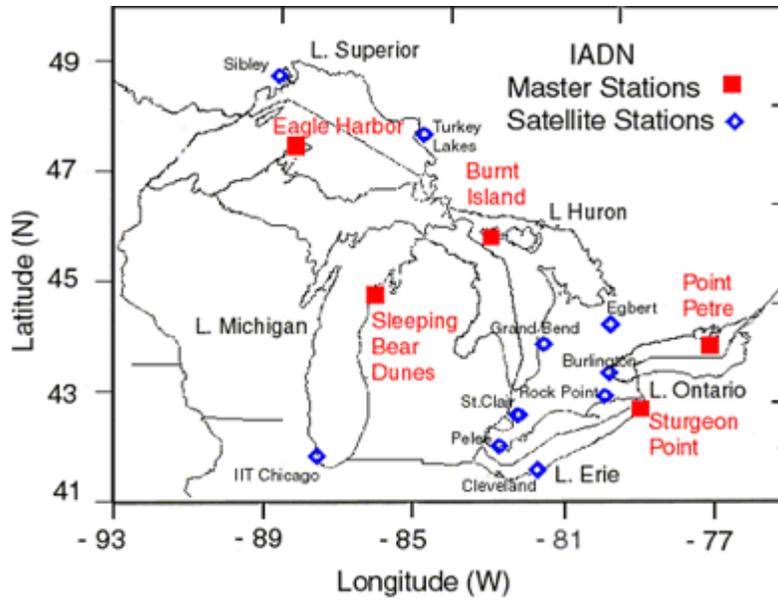


Figure 1 IADN site locations

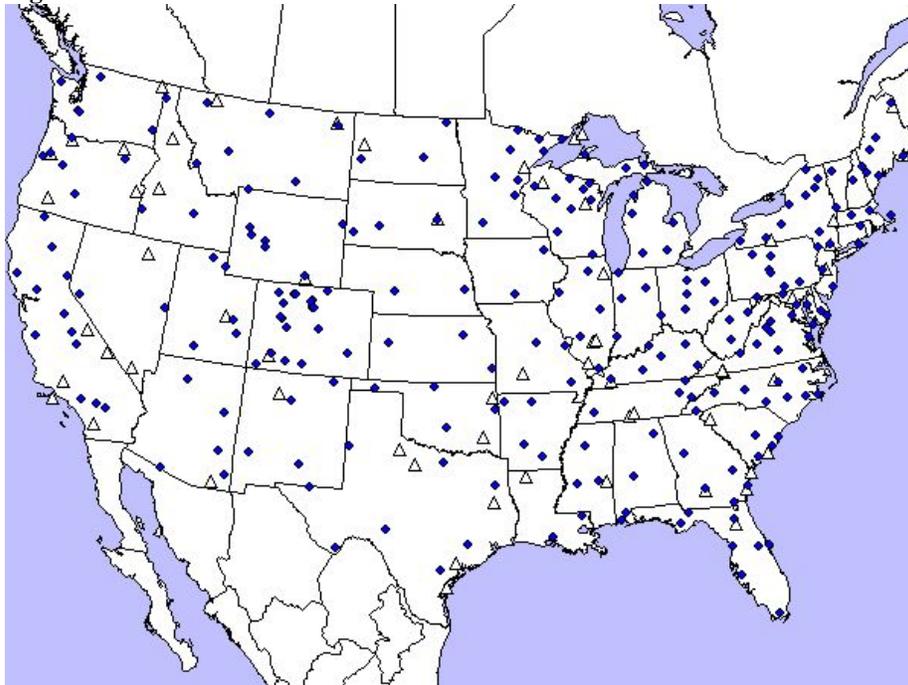


Figure 2. Location of NADP/NTN wet deposition sites

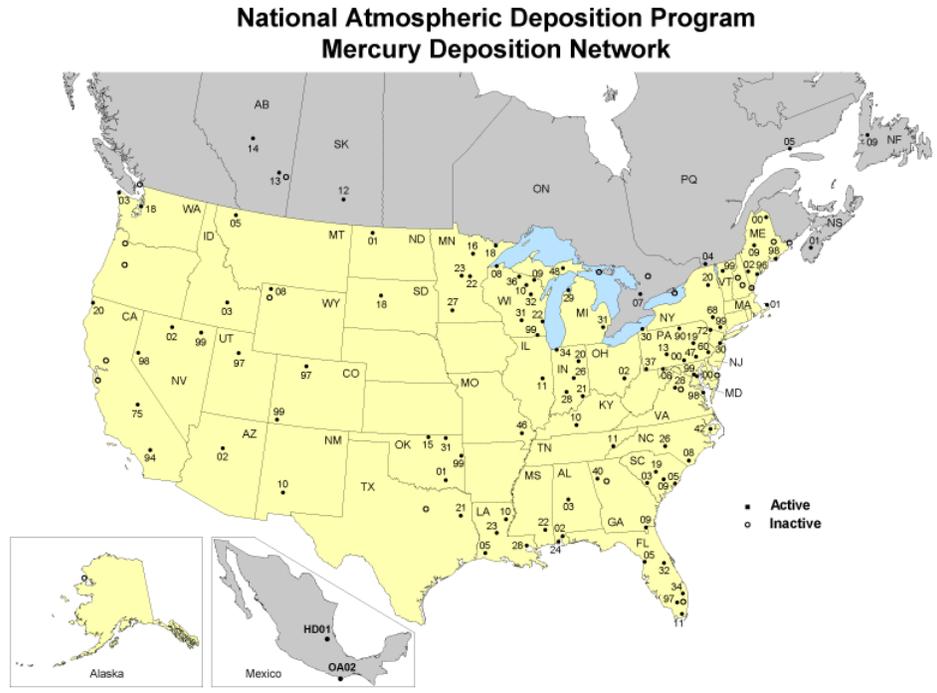


Figure 3 Location of NADP/MDN sites

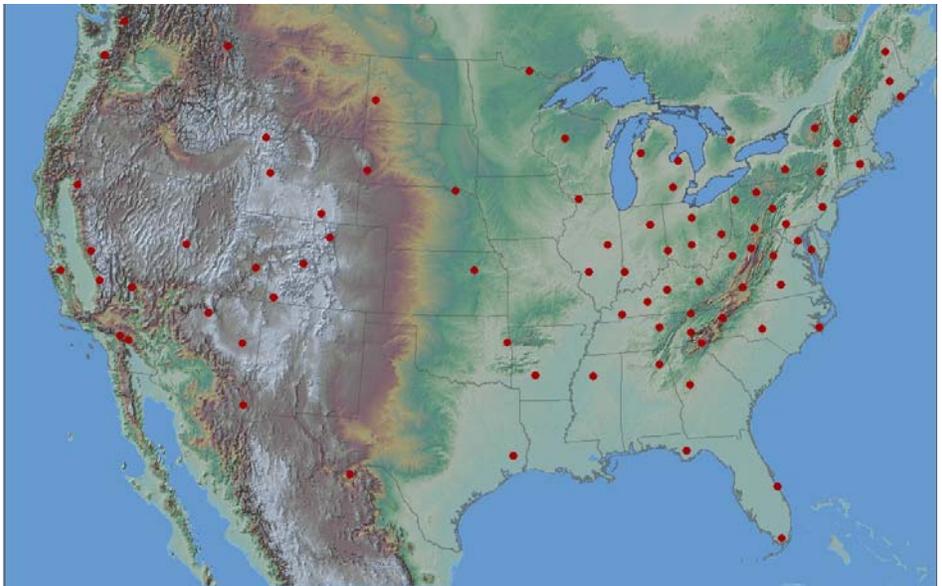


Figure 4 Location of CASTNET sites

Recommended routine constituents to measure:

Wet deposition: Nitrate, ammonium and organic nitrogen, methyl and total mercury.

Other metals as indicated as being a priority on a region-specific basis.

Dry deposition: Gaseous ammonia and oxidized nitrogen species, and particulate nitrate and ammonium (requires measurement of ambient atmospheric concentrations, and determination of deposition velocities based on micro-meteorological data, depositional surface characteristics, etc.). Dry deposition of mercury should also be measured or estimated.

To estimate dry deposition fluxes, fine particles and gases in air are collected over a sequence of filters. The filters are analyzed for nitrate, nitric acid, and ammonium in the air sample; concentrations are expressed in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). It is important to note that existing networks do not measure gaseous ammonia; gaseous ammonia can directly deposit near its source or be transformed in the atmosphere to particulate ammonium, which is measured by routine dry deposition monitoring. At present, there is no national monitoring network for gaseous ammonia, although it is a significant contributor to total nitrogen deposition.

Meteorological, vegetation, and land use data from the site are used as input to the Multi-Layer Model (MLM), a mathematical model that simulates atmospheric dry deposition processes. The MLM is used to calculate deposition velocities, which are combined with the concentration measurements to estimate dry deposition of gaseous and particulate

pollutants. There are varying degrees of uncertainty in the deposition velocities, due to site-specific differences and complexities in land or water surface and meteorology. Appropriate parameters for estimating over-water deposition must be selected when computing dry deposition to a water-body.

Deposition of PAHs, PCBs, SVOCs: Atmospheric concentration monitoring provides the framework for estimation of the deposition of synthetic organic chemical species of interest since they are subject to long-range transport, and air is a media that is quick to respond to changes in emissions/releases. Monitoring of these compounds is expensive, therefore these constituents may not be able to be measured with the same spatial or temporal frequency as the other parameters; there could be a subset of the monitoring sites that are "PBT sites. Currently there is little atmospheric monitoring information for PBTs outside of the Great Lakes, and extending IADN-like monitoring into other regions would, in addition to meeting specific needs for the NWQMN, help identify source areas and measure progress under domestic and international toxic reduction programs and agreements.

Temporal frequency of sampling:

Even though users will be most interested in annual or seasonal fluxes, temporal frequency should be at least weekly to avoid problems with contamination and sample degradation. If weekly wet measurements are made versus event sampling (e.g. NADP-NTN protocol) recognition and/or adjustment of the roughly 10% low bias of ammonium

ion versus event sampling should be made. Depending on method of dry deposition (ambient concentration) measurements, more frequent (e.g. daily) maintenance/sampling may be required.

Deposition samples for synthetic organic chemicals are collected in the IADN protocol every 12 days, which is a common frequency in other similar monitoring programs. Every 24 days may be acceptable if there are resource limitations. Therefore in a coordinated collection system of measuring atmospheric deposition of nitrogen, mercury and synthetic organic chemicals, it should not be required to collect these more frequently than the temporal frequency for wet deposition samples of nitrogen and mercury and collection could be made at a multiple of two or three for the wet deposition temporal frequency without loss of sample integrity.

Spatial Distribution of Sites:

For nitrogen species at least one wet and one dry site at a minimum for each water body, with data collected weekly. For gaseous ammonia a more nested array of sites in targeted waters; with data collected weekly. For mercury at least one NADP-MDN site (or protocol equivalent). The use of a mercury mobile laboratory near coastal waters to conduct ambient air sampling to estimate dry deposition of mercury and for model verification of total mercury deposition estimates.

The current state of science for dry deposition does not allow for accurate deposition estimates beyond about a 1 km radius around a monitoring site. However, sites placed in the transition zone of watersheds and coastal bays and estuarine systems can be valuable in determining the atmospheric load to particular endpoint or water body. Dry deposition flux is influenced by land-based variables such as Leaf Area Index (LAI), hence estimation of dry deposition to water-body surfaces from land-based measurements is problematic.

It can be assumed that near to shore wet deposition measurements that are regionally representative can be interpolated (or extrapolated within reasonable distances) to provide near off-shore estimates of wet deposition that are also under the control of regional (as opposed to local) emission sources. The same assumption cannot be made for dry deposition estimates. On-shore measurements are highly dependant on plant canopy interactions and leaf area index, while off-shore dry deposition to a water surface may be off by a considerable magnitude. An on-shore dry site in representative vegetation would provide the estimate of dry deposition to land surfaces below the last water quality and flow gaging station.

While there is clearly a need for more monitoring sites providing total deposition of both nutrient species and mercury, modeling specific regional areas is recommended and should provide useful information. Site locations can be chosen based on these model simulations/output and sites can provide the necessary validation and development of the models.

Beyond the one-site minimum recommendation, a variable number of sites per estuary may be needed depending on estuary size and the relative influence of regional versus local emission sources. A mix of “unimpacted” and urban/near sources sites are recommended where significant local sources are present. Due to the expense of monitoring PBTs they could be measured at a subset of the sites. Pacific coastal sites would be useful for examining long-range transport from Asia, particularly for PBTs although trajectory modeling should be performed to ensure that coastal “background” sites are indeed subject to transcontinental air mass influences from Asian source areas.

There are currently five existing CASTNET sites along the East Coast that could be considered coastal or in an estuarine environment, ACA416 - ME; BWR139 - MD; IRL141 - FL; EVE419 - FL; and BFT142 - NC. A significant number of NADP/NTN and NADP/MDN sites were installed within the past 10 years in the coastal estuarine environment at National Estuarine Program research areas. Locations of NADP (NTN MDN and AirMon) sites can be found at the NADP web site <http://nadp.sws.uiuc.edu/>

Modeling:

Although a knowledge gap exists for the verification of current modeling results for total deposition of most chemical constituents deposited directly to the surface of a large water body, the best-accepted appropriate parameters for deposition to water-surfaces have been utilized in the Community Multiscale Air Quality (CMAQ) model and an application based on CMAQ, The Watershed Deposition Tool. The CMAQ modeling

domain extends beyond the coastline into the coastal oceans and the Great Lakes. Ground-based data are not included in the CMAQ model but are used for model verification. Therefore the dearth of over-water deposition measurements implies a less robust verification of CMAQ modeled deposition estimates over water.

From the Watershed Deposition Tool overview at

<http://www.epa.gov/asmdnerl/Multimedia/depositionMapping.html>

Atmospheric wet and dry deposition can be important contributors to total pollutant loadings in watersheds. Since deposition can be expensive to monitor over an entire watershed, estimates of deposition are often obtained from regional scale air quality models such as the EPA/NOAA's regional-scale, multi-pollutant Community Multiscale Air Quality model (CMAQ). CMAQ can be used to estimate deposition resulting from a number of scenarios including current conditions and future emissions reductions that are expected due to rules such as Clean Air Interstate Rule (CAIR) and Clean Air Mercury Rule (CAMR). CMAQ produces gridded output with typical grid sizes of 36, 12, and 4 km. Since watersheds do not conform to the grid layout of CMAQ, additional tools must be used to map the results from CMAQ to the watersheds to provide the linkage between air and water needed for TMDL (Total Maximum Daily Load) and related nonpoint-source watershed analyses. This linkage then allows water quality management plans to include the reductions in atmospheric deposition produced by the air regulatory community in their calculation of loadings to the watershed.

The Watershed Deposition Tool (WDT) was developed by the Atmospheric Modeling Division to provide an easy to use tool for mapping the deposition estimates from CMAQ to watersheds to provide the linkage between air and water needed for TMDL (Total Maximum Daily Load) and related nonpoint-source watershed analyses. This software tool takes gridded atmospheric deposition estimates from NOAA/EPA's regional, multi-pollutant air quality model, CMAQ, and allocates them to 8-digit HUC's (hydrologic cataloging units of rivers and streams) within a watershed, State or Region. The WDT can calculate the weighted average CMAQ atmospheric deposition (wet, dry, wet + dry) across a selected HUC or a set of selected HUC's for a given scenario. The WDT can also calculate the average change in air deposition across a HUC between two different air deposition simulations. Calculations can be exported to CSV files. For experienced GIS users the WDT can also export GIS Shape files of the CMAQ gridded outputs. The tool is designed to work under the Microsoft Windows system and is available at

<http://www.epa.gov/asmdnerl/Multimedia/depositionMapping.html>

Deposition Components Available from CMAQ

Nitrogen

Dry Oxidized Nitrogen

Wet Oxidized Nitrogen

Total (Wet+Dry) Oxidized Nitrogen

Dry Reduced Nitrogen

Wet Reduced Nitrogen

Total (Wet + Dry) Reduced Nitrogen

Total Dry (Reduced + Oxidized) Nitrogen

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Total Wet (Reduced + Oxidized) Nitrogen

Total (Reduced + Oxidized) Nitrogen

Sulfur

Total Wet Sulfur

Total Dry Sulfur

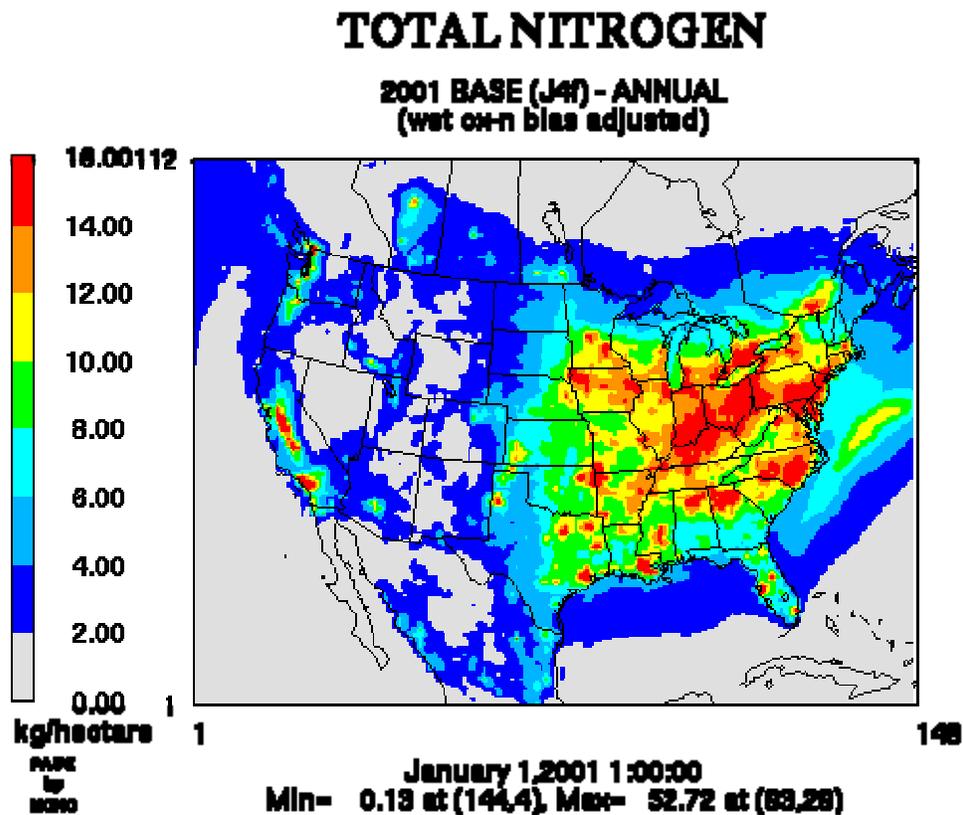
Total (Wet + Dry) Sulfur

Mercury

Total Wet Mercury

Total Dry Mercury

Total (Wet + Dry) Mercury



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Additional Specific Recommendations:

Information on atmospheric deposition of pollutants to coastal waters comes from an assessment conducted in 1997-1998 and published by the American Geophysical Union in 2001 titled: Nitrogen Loadings in Coastal Water Bodies: An Atmospheric Perspective. In this Book, forty-two coastal and estuarine watersheds were assessed in terms of the deposition to watersheds and to water surfaces. While the focus was on nitrogen compounds, it was the first scientific assessment of its kind and can serve as a foundation for direct deposition monitoring and future assessments.

There is currently no over-water deposition monitoring network (with one exception-Smith Island, MD). Therefore if resources allow, deploy at least one over water, weekly wet deposition collection site (NADP NTN, MDN or other) in each of the identified estuaries, as is appropriate and feasible. Platforms to consider are: buoys, islands, extended piers, or fixed platforms. This would be the minimum spatially for direct over-water observations and weekly collection would be the minimum temporally. This would enable testing the hypothesis that near on-shore wet deposition is regionally representative of near off-shore wet deposition. Recommend occasional ship based measurements on platforms of opportunity (i.e. cruises for other purposes) to evaluate model validity for offshore deposition. Ship-based measurements can be a surrogate for fixed over-water sites i.e buoys. If buoy technology is available, buoys may be used as

platforms for deposition measurements; however, ship/small boat time expenses to service/sample collectors will be large unless it is leveraged against other existing monitoring efforts. Absent over-water monitoring locations, utilize islands (barrier beach etc) whenever possible to get better routine measurements away from shore. Use models to interpolate where measurements can not be made, however the errors associated with modeling deposition results over a water surface remain as a significant knowledge gap in this endeavor.

Recommend utilizing existing network sites (NADP, MDN, CASTNET, AirMon, IADN) whenever possible. If the sites are planning to operate for three years or more it would be preferable to designate any new sites in support of NWQMN as official sites within these networks. This would ensure direct comparability with other network sites and leverage the extensive support provided by the network coordination, QA/QC and data management. If the NWQMN sites are expected to operate for two years or less, national network protocols should be adopted to the greatest extent possible but it may be not worthwhile to expend the overhead associated with having the sites be approved as official components of a national network.

Sea-salt spray from sampling adjacent to marine water-bodies raises three concerns. The most-affected constituents in atmospheric deposition for enrichment by sea-salt aerosols are sodium, calcium, potassium, chloride and sulfate concentrations, fortunately not constituents identified as having high impact or concern from atmospheric deposition in the NWQMN design. Sea-salt aerosol correction (Fisher, 1978) is relatively straight-

forward. Secondly, instrumentation for measuring terrestrial atmospheric deposition may not be designed for use in a marine dominated environment and may require modification to prevent sea-salt corrosion. Thirdly, sensors on automated wet-deposition samplers rely on wetness or optical particle detection to assume precipitation is occurring and to trigger opening and sample collection. Horizontal shielding or raising collectors above standard collection heights may be necessary to avoid false-openings from sea-spray.

NH_4^+ is preferred by phytoplankton over other forms of N such as organic and nitrate in estuarine systems (Pearl, et.al 2002). The greater the inputs of NH_4^+ , the greater the tendency for eutrophication and algal blooms. Therefore wet deposition of ammonium and estimation of dry deposition of ammonia gas should not be neglected, even in areas where oxidized nitrogen species predominate. A complete estimate of total nitrogen deposition entails the summation of wet deposition of ammonium, nitrate and organic N and dry deposition of nitric acid, nitrate, ammonium and ammonia gas.