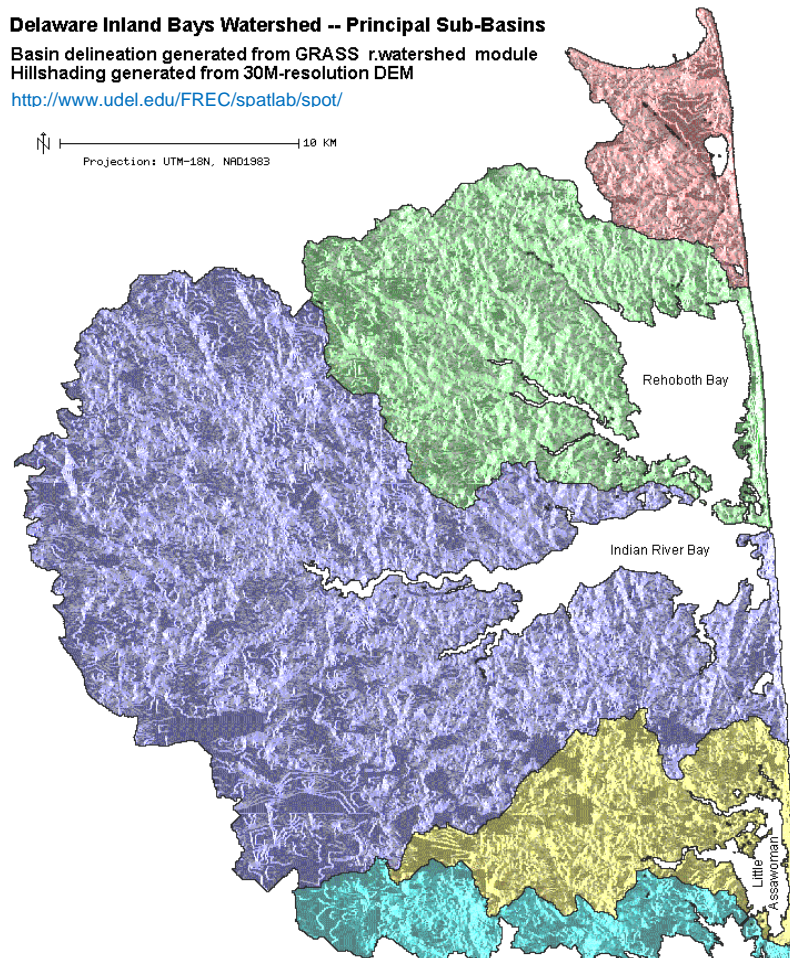


# Standard Operating Procedure for the Calculation of N and P Deposition from the Atmosphere to Waters of the Inland Bays

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Report to the Center for the Inland Bays  
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## Abstract

Data from the National Atmospheric Deposition Program/Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN) site at Cape Henlopen can be used to estimate wet deposition rates (fluxes associated with rainfall) of nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), and phosphate ( $\text{PO}_4^{3-}$ ) to the open waters and the tidal marshes of the Inland Bays on a daily basis. These daily measurements may be summed to determine wet deposition over other time periods. There are, however, other species in wet deposition, and atmospheric inputs due to another set of chemical and physical processes, collectively described as dry deposition, that deliver N and P to land and water surfaces in the absence of rainfall. These species and processes may also contribute significantly to nutrient delivery to the Delaware's Inland Bays and their watersheds. Here we summarize the procedures that we have used in our studies to calculate the wet and dry deposition rates of N and P species directly to the Inland Bays (open water and contiguous marshes) and elsewhere in Delaware for use in mass balance studies.

## Current Data Sources

Data from the Lewes NADP/AIRMoN site (DE02; located in Cape Henlopen State Park, Lewes) is accessed through the main NADP/AIRMoN website at <http://nadp.sws.uiuc.edu/airmon/> or from the AIRMoN Data Retrieval Site at <http://nadp.sws.uiuc.edu/AIRMoN/amData.aspx>. Additional information about the site can be found at <http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=DE02&net=AIRMoN>. The data request form, which must be completed to download data is found at <http://nadp.sws.uiuc.edu/nadpdata/amDailyRequest.asp?site=DE02>. A copy of the data description is attached as Appendix A.

At present, the Cape Henlopen site is the only active site in the Inland Bays watershed where precipitation chemistry is determined and therefore must serve as the basis for calculating current and future wet deposition rates. Based on a comparison of samples collected simultaneously near Riverdale (north shore Indian River Bay), Scudlark et al. (2005) report that wet deposition rates of  $\text{NO}_3^-$  were similar across the Inland Bays watershed; wet deposition rates of  $\text{NH}_4^+$ , however, were 75% higher at the Riverdale site. This was attributed to the proximity of the Riverdale site to more intensive poultry production. Thus, extrapolating from Cape Henlopen rain data to the

entire Inland Bays represents a conservative (minimum) estimate of wet N deposition rates for this system.

For the determination of total atmospheric deposition rates of N or P from species with contrasting and sometimes unknown molecular forms and weights, it is best to convert all deposition data from contrasting sources to compatible molar units ( $\mu\text{mol/L} = \mu\text{M}$ ). Deposition rates in molar units can then be converted to mass units (Kg) after all of the component deposition rates in compatible units are summed. Care should be taken to verify that the units used in the below calculations are compatible.

The NADP/AIRMoN data is available in two contrasting units:  $\mu\text{eq/L}$  or  $\text{mg/L}$ . All NADP/AIRMoN data must therefore be converted to molar units once downloaded. The formulas for conversion of concentrations in  $\mu\text{eq/L}$  or  $\text{mg/L}$  units to  $\mu\text{mol/L} = \mu\text{M}$  are:

$$C_{(\mu\text{mol/L})} = \frac{C_{(\mu\text{eq/L})}}{Z} \quad \text{and} \quad C_{(\mu\text{mol/L})} = \frac{1000 \times C_{(\text{mg/L})}}{MW} \quad (1)$$

Where Z is the net formal charge of the ion of interest ( $Z = 1$  for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  and  $Z = 3$  for  $\text{PO}_4^{3-}$ ) and MW are the molecular weights of the ion of interest. The molecular weights (MW) to be used in the NADP/AIRMoN database and in these calculations are for the molecular species as written. Thus  $\text{MW}(\text{NO}_3^-)$  is  $[\text{AW}(\text{N}) + 3 \times \text{AW}(\text{O})]$  where AW(N) and AW(O) are the atomic weights of N, and O respectively.  $\text{MW}(\text{NO}_3^-) = 62.0049 \text{ g/mol}$ ;  $\text{MW}(\text{NH}_4^+) = 18.0386 \text{ g/mol}$ ; and  $\text{MW}(\text{PO}_4^{3-}) = 94.9714 \text{ g/mol}$ . Molar fluxes can be converted to mass fluxes of elemental N and P using the atomic weights (AW) for these elements ( $\text{AW}(\text{N}) = 14.0067 \text{ g/mole}$  and  $\text{AW}(\text{P}) = 30.9737 \text{ g/mole}$ ) for final reporting.

### Calculation of Areal Wet Deposition of Measured Nutrient Species

Areal precipitation-weighted wet deposition rates for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  to the open waters and marshes of the Inland Bays may be calculated directly from the NADP AIRMoN data. Areal deposition rate is the product of the precipitation amount, Precip ( $\text{mm/time}$ ), and concentration of the chosen nutrient species C ( $\mu\text{mol/L}$ ) and may be expressed in any of a number of units. The AIRMoN program uses the "Subppt" parameter as the best estimate of precipitation (see Appendix) and, for consistency, this value should be used for all precipitation and wet deposition calculations. Deposition should be determined for every day with reported rainfall and summed to get monthly, seasonal, or annual deposition rates. Note that AIRMoN samples are collected at ~9AM EST or EDT and therefore cannot truly be assigned to a particular "calendar day." However, when summing deposition rates for periods of days to weeks, the uncertainty is the actual time of precipitation can be ignored. Daily wet deposition rates (WD) for each measured species can be calculated from the available AIRMoN data as:

$$\text{Precip}_{(\text{mm/time})} \times C_{(\mu\text{mole/L})} = \text{WD}_{(\text{mole/Km}^2 \text{ time})} \quad (2)$$

[Example calculation:  $WD(\text{NO}_3^-) = 1.016 \text{ mm/dy} \times 10.985 \text{ } \mu\text{eq NO}_3^-/\text{L} \times 1 \text{ } \mu\text{mol}/\mu\text{eq NO}_3^- \times 62.0049 \text{ } \mu\text{g NO}_3^-/\mu\text{mol NO}_3^- = 0.692 \text{ kg NO}_3^-/\text{km}^2/\text{dy} = 11 \text{ mol NO}_3^-/\text{km}^2/\text{dy} = 0.156 \text{ kg N}/\text{km}^2/\text{dy}$ ]

Dissolved inorganic nitrogen (DIN) wet deposition rates can be calculated from the sum of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition rates for any period of interest or from the product of  $\text{NO}_3^- + \text{NH}_4^+$  concentrations (in molar units) and precipitation rates according to Equation 2.

Total atmospheric loading for any species or element is determined as the product of areal deposition rates and the surface area of receiving surfaces. In our recent calculations, we have used the summed area of open water and marshes for the area subject to direct wet deposition of N and P species in the Inland Bays. Areas are taken from McKenna et al. (2007). Wet deposition to land surfaces may also be determined, but these loads are normally included with the surface and groundwater fluxes and should not be counted twice in mass balances studies for the Bays.

### **Estimation of areal deposition rates for other components of atmospheric deposition**

There are additional components of atmospheric deposition that are not included in these calculated wet deposition values. In addition to the wet deposition of inorganic species, evidence indicates there are potentially significant contributions due to wet deposition of dissolved organic forms of nitrogen (DON) and of phosphorus (DOP) (Seitzinger and Sanders, 1999; Morales et al., 2001). In addition, deposition of gases and particles containing both organic and inorganic N (PN = PON + PIN) and P (PP) may contribute to overall nutrient loads. Lastly, direct deposition of ammonia gas ( $\text{NH}_3^0$ ) may contribute to nutrient loads from the atmosphere. These normally unmeasured contributions must be estimated.

#### ***Wet deposition of organic N:***

Wet deposition of dissolved organic nitrogen (DON) to the Inland Bays was estimated to comprise approximately 25% (mean = 23% and range <5 to 64% on an event basis) of total wet deposition of N, based on measurements made between October 1993 and December 1994 at the Cape Henlopen NADP/AIRMoN site (Scudlark et al., 1998). In the Scudlark et al. (1998) study, Total Dissolved N (TDN) was determined by the persulfate oxidation method (Solórzano and Sharp, 1980a) as this oxidation method was found to have a higher yield than oxidation by ultraviolet light. DON wet deposition rates can therefore be calculated from the equation:

$$WD(\text{DON}) = 0.33 * [WD(\text{NH}_4^+) + WD(\text{NO}_3^-)] \quad (3)$$

### ***Wet deposition of organic P:***

During 2006, daily, unfiltered samples were collected in parallel with the AIRMoN samples for the determination of both  $\text{PO}_4^{3-}$  and  $\text{TSP}_{\text{OX}}$  (Total Soluble P following persulfate oxidation; Solórzano and Sharp, 1980b; Volk et al., 2010) following procedures similar to those used to determine wet organic N deposition rates. The relationship between  $\text{TSP}_{\text{OX}}$  ( $\mu\text{M}$ ) and  $\text{PO}_4^{3-}$  ( $\mu\text{M}$ ) in these samples ( $\text{TSP}_{\text{OX}} = 1.49\text{PO}_4^{3-} + 0.03$ ) was used to calculate total dissolved P (TDP) in wet deposition, based on the SRP measurements provided by the routine NADP-AIRMoN sampling. DOP may be calculated from the difference between  $\text{TSP}_{\text{OX}}$  and  $\text{PO}_4^{3-}$  ( $\text{DOP} = \text{TSP}_{\text{OX}} - \text{PO}_4^{3-}$ ) as follows:

$$\text{WD}(\text{TSP}_{\text{OX}}) = \text{Precip} * [1.49\text{PO}_4^{3-} + 0.03] \quad \text{or}$$

$$\text{WD}(\text{DOP}) = \text{Precip} * [0.49\text{PO}_4^{3-} + 0.03] \quad (4)$$

The form of these equations is somewhat different than those for DON as there was clear evidence that DOP did not approach zero as  $\text{PO}_4^{3-}$  approached zero. The form of Equation 4 allows for the finite value of DOP and  $\text{TSP}_{\text{OX}}$  at low values of  $\text{PO}_4^{3-}$ .

### ***Total Wet Deposition of N and P:***

Total wet deposition rates for nitrogen may be calculated as follows:

$$\text{WD}(\text{TDN}) = \text{WD}(\text{DON}) + \text{WD}(\text{NH}_4^+) + \text{WD}(\text{NO}_3^-) = 1.33 * [\text{WD}(\text{NH}_4^+) + \text{WD}(\text{NO}_3^-)] \quad (5)$$

Total wet deposition rates for phosphorus may be calculated as follows:

$$\text{WD}(\text{TSP}_{\text{OX}}) = \text{WD}(\text{DOP}) + \text{WD}(\text{PO}_4^{3-}) = \text{Precip} * [1.49\text{PO}_4^{3-} + 0.03] \quad (6)$$

### ***Dry Deposition of $\text{NO}_3^-$ , $\text{NH}_4^+$ , and Organic N (ON):***

In the absence of local data, overland dry deposition of  $\text{NO}_3^-$  (nitric acid + particulate nitrate) and particulate  $\text{NH}_4^+$  were inferred from the wet:dry apportionment reported at 5 AIRMoN dry deposition sites (Oak Ridge, TN; Argonne, IL, Bondville, IL; State College, PA; and Panola, GA; Meyers et al., 1991) and 5 EPA-CASTNet sites (Connecticut Hill, NY; Arendtsville, PA; Cedar Creek, PA; Abbington, CT; and Egbert, Ontario; EPA, 1998) having regional land uses similar to that of the Inland Bays watershed. Based on an analysis of these data, Scudlark and Church (1999) concluded that dry deposition of  $\text{NO}_3^-$  was approximately equal to wet deposition of  $\text{NO}_3^-$  and dry deposition of  $\text{NH}_4^+$  was approximately equal to 25% of the  $\text{NH}_4^+$  wet deposition rate (20% of the wet + dry deposition rate) over land. Based on data reported by Correll et

al. (1995), Scudlark and Church concluded that dry deposition of organic N on land was approximately equal to the wet deposition of organic N on land.

$$DD(\text{NO}_3^-) \text{ (over land)} = WD(\text{NO}_3^-) \quad (7)$$

$$DD(\text{NH}_4^+) \text{ (over land)} = 0.25 * WD(\text{NH}_4^+) \quad (8)$$

$$DD(\text{ON}) \text{ (over land)} = WD(\text{ON}) = 0.33 * [WD(\text{NH}_4^+) + WD(\text{NO}_3^-)] \quad (9)$$

Based on the approximation that dry deposition rates over water are roughly 1/3 of those over land (range 0.2 to 0.5) due to differences in aerodynamic resistance (Williams, 1982; Zufall et al., 1998; Pryor and Barthelmie, 2000), the wet deposition rates to water may be calculated from land-based dry deposition rates:

$$DD(\text{NO}_3^-) \text{ (over water)} = 0.33 * WD(\text{NO}_3^-) \quad (10)$$

$$DD(\text{NH}_4^+) \text{ (over water)} = 0.083 * WD(\text{NH}_4^+) \quad (11)$$

$$DD(\text{ON}) \text{ (over water)} = 0.33 * WD(\text{DON}) = 0.11 * [WD(\text{NH}_4^+) + WD(\text{NO}_3^-)] \quad (12)$$

***Dry Deposition of Particulate P (PP):***

In the absence of more recent measurements, dry deposition of P must be estimated based on published P concentrations in size-segregated aerosols, collected at the Cape Henlopen research site in 1982 and 1983. Wolff et al. (1987) collected separate fine (< 2.5 μm) and coarse (2.5-10 μm) particulate samples over twenty-four hour periods on Teflon membrane filters using a dichotomous sampler (Sierra Instrument Corp., Carmel Valley, CA). Particulate P concentrations were determined by x-ray fluorescence (Wolff et al., 1987). Multiple daily-integrated samples were collected over roughly 1-month periods during August 1982 (N=34) and February 1983 (N=33), chosen to be representative of typical summer and winter conditions, respectively. Dry P fluxes were estimated by multiplying the seasonal mean P concentration for each size fraction, by representative over-water deposition velocities for fine (0.01 cm/s) and coarse (0.5 cm/s) mode aerosols, assuming average wind speeds for this area (Williams, 1982; Zufall et al., 1998; Pryor and Barthelmie, 2000). The annual average total P dry deposition was then calculated as the mean of the summed (fine + coarse) seasonal values.

Table 1 is a summary of the P dry deposition rates for the Inland Bays based on the Wolff et al. (1987) data.

**Table 1:** Dry P deposition rates for the Inland Bays (concentration data from Wolff et al., 1987; as compiled by Volk et al., 2010)

Sampling Date	Measurement	Fine Mode (<2.5 µm)	Coarse Mode (2.5-10 µm)	Total	Units
Aug 1982 (N=33)	Concentration	0.094	0.031	0.125	µg/m <sup>3</sup>
	Deposition	1.2	20	21	µmol/m <sup>2</sup> /mo
Feb. 1983 (N=34)	Concentration	0.064	0.016	0.080	µg/m <sup>3</sup>
	Deposition	0.8	10	11	µmol/m <sup>2</sup> /mo

### **Deposition of Atmospheric Ammonia Gas (NH<sub>3</sub><sup>0</sup>):**

Atmospheric ammonia gas (NH<sub>3</sub><sup>0</sup>) dry deposition rates, DD(NH<sub>3</sub><sup>0</sup>) were determined from NH<sub>3</sub><sup>0</sup> concentrations determined by passive samplers deployed for periods of 1 to 2 weeks at 13 stations across the Inland Bays watershed from 2000-2001 (Scudlark et al., 2005). There was some evidence of seasonal variations in concentrations, with maxima during the summer months, and concentrations were higher in southern areas of the watershed than in the northern areas which was attributed to the distribution of chicken production facilities. Annual mean concentrations ranged from < 0.5 µg NH<sub>3</sub><sup>0</sup>/m<sup>3</sup> to > 6 µg NH<sub>3</sub><sup>0</sup>/m<sup>3</sup>. The annual, arithmetic mean concentration, 1.6 ± 1.0 µg NH<sub>3</sub><sup>0</sup>/m<sup>3</sup>, can be used together with the published deposition velocities for open seawater (5-8 mm/s; Lee et al., 1998; Larsen et al., 2001) to estimate annual deposition rates for the Inland Bays (300 – 480 kg/km<sup>2</sup>/yr; Scudlark et al., 2005):

$$DD(NH_3^0) = C(NH_3^0) \times v_d \quad (13)$$

where C(NH<sub>3</sub><sup>0</sup>) is the atmospheric NH<sub>3</sub><sup>0</sup>g concentration in µg/m<sup>3</sup>, v<sub>d</sub> is the deposition velocity in mm/s.

[Example calculation using mean or median values:

$$DD(NH_3^0) = 330 \text{ kg/km}^2/\text{yr} = 1.6 \text{ µg NH}_3^0/\text{m}^3 * 6.5 \text{ mm/s}]$$

Alternatively measured average monthly deposition rates for the whole watershed can be used to estimate the magnitude of this source of nitrogen to the Inland Bays for other time periods (Table 2). These NH<sub>3</sub><sup>0</sup> dry deposition rates are comparable to the wet deposition rates of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. Deposition rates may also be calculated for bimonthly intervals from the data discussed by Scudlark et al. (2005). There has been no additional data of this type collected in the Inland Bays watershed or nearby. Deposition rates could be calculated from new concentration data and the same deposition velocities.

Table 2: Monthly average NH<sub>3</sub><sup>0</sup> gas concentrations for the Inland Bays watershed determined between April 2000 and April 2001 (Scudlark et al., 2005). (BDL= below detection limits.)

Month	Range	Mean	Standard Deviation	Month	Range	Mean	Standard Deviation
January	BDL - 2.84	0.68	0.75	July	0.32-12.72	2.13	2.90
February	BDL - 4.63	1.03	0.96	August	0.21 - 15.59	2.40	3.52
March	BDL - 9.1	1.62	1.90	September	0.46 - 10.23	2.08	2.07
April	BDL - 6.6	1.43	1.43	October	0.17 - 7.91	1.63	1.94
May	0.41 - 9.2	2.10	2.00	November	0.10 - 7.67	1.57	1.73
June	0.50 - 6.4	2.13	1.60	December	0.06 - 2.79	0.85	0.68

**Total Atmospheric N Deposition:**

Based on the above analysis, total atmospheric N deposition, TD(N) may be calculated as:

$$\begin{aligned}
 \text{TD(N)} &= \text{WD}(\text{NO}_3^-) + \text{WD}(\text{NH}_4^+) + \text{WD}(\text{DON}) + \text{DD}(\text{NO}_3^-) + \text{DD}(\text{NH}_4^+) + \text{DD}(\text{ON}) + \\
 &\quad \text{DD}(\text{NH}_3^0) \\
 &= 1.78 \times \text{WD}(\text{NO}_3^-) + 1.53 \times \text{WD}(\text{NH}_4^+) + \text{DD}(\text{NH}_3^0) \qquad (14)
 \end{aligned}$$

**Total Atmospheric P Deposition:**

Based on the above analysis, total atmospheric P deposition, TD(P) may be calculated as:

$$\begin{aligned}
 \text{TD(P)} &= \text{WD}(\text{PO}_4^{3-}) + \text{WD}(\text{DOP}) + \text{DD}(\text{PP}) \\
 &= P * [1.49 \text{ PO}_4^{3-} + 0.03] + \text{DD}(\text{PP}) \qquad (15)
 \end{aligned}$$

**Summary**

This SOP summarizes the method currently used for estimating atmospheric N and P inputs to the Delaware Inland Bays. It represents what we feel is the “best estimate” using current data for this site culled from various sources. There are many inherent assumptions that go into these estimates and it is therefore difficult to determine the accuracy of the deposition rates. What is clear is that wet deposition rates for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> reported at Cape Henlopen result from direct measurements taken over time and therefore represent the highest precision attainable. Even so, there is clear evidence of spatial variability in wet deposition rates across the Inland Bays region and therefore the extrapolations of these deposition rates to the *whole Inland Bays watershed is subject to additional uncertainties.*



In contrast, dry deposition rates of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were inferred from wet and dry measurements at other representative locations, and thus have considerably greater uncertainty. In addition, atmospheric deposition of P, DON and  $\text{NH}_3^0(\text{g})$ , which are based on historical data, are uncertain due to the temporal variability and systematic trends in atmospheric concentrations of nutrient contaminants and deposition rates.

In light of the caveats, we recommend that absolute values of deposition rates be used with caution, and that these rates be updated as new data become available. However, temporal trends may still be revealed using the described techniques even with this uncertainty. Ultimately, however, new measurements of deposition components other than wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  will need to be made.

### References

- Correll, D.L., T.E. Jordan and D.E. Weller. 1995. Long-term nitrogen deposition on the Rhode River watershed. Pages 508-518 in P. Hill and S. Nelson, eds. Toward a sustainable coastal watershed: The Chesapeake experiment. Chesapeake Research Consortium, Solomons, MD.
- EPA, 1998. Clean Air Status and Trends Network (CASTNet) Deposition Summary Report (1987-1995). U.S. Environmental Protection Agency Report 31pp.
- Larsen, R.K., J.C. Steinbacher and J.E. Baker. 2001. Ammonia exchange between the atmosphere and surface waters at two locations in the Chesapeake Bay. *Environmental Science & Technology* 35 (24):4731-4736.
- Lee, D.S., C. Halliwell, J.A. Garland, G.J. Dollard and R.D. Kingdon. 1998. Exchange of ammonia at the sea surface – a preliminary study. *Atmospheric Environment* 32 (3):431-439.
- McKenna, T.E., A.S. Andres, and K.P. Lepp. 2007. Digital Watershed and Bay Boundaries For Rehoboth Bay, Indian River Bay, and Indian River. Open File Report 47, Delaware Geological Survey, Newark, DE. p. 8.
- Meyers, T.P., B.B. Hicks, R.P. Hosker, Jr., J.D. Womack and L.C. Satterfield. 1991. Atmospheric deposition inferential measurement techniques: II Seasonal and annual deposition rates of sulfur and nitrate. *Atmospheric Environment* 25A:2361-2370.
- Morales, J.A., A. Albornoz, E. Socorro and A. Morillo, 2001. An estimation of the nitrogen and phosphorus loading by wet deposition over Lake Maracaibo, Venezuela. *Water, Air, & Soil Pollution* 128:207-221.
- Pryor, S.C. and R.J. Barthelmie, R.J. 2000. Particle dry deposition to water surfaces: Processes and consequences. *Marine Pollution Bulletin* 41:220-231.
- Scudlark, J.R., Church, T.M. 1999. A comprehensive reexamination of the input of atmospheric nitrogen to the Rehoboth and Indian River estuaries. Final Report to the Center for the Inland Bays, Nassau, DE, 38 pp.

- Scudlark, J.R., J.A. Jennings, M.J. Roadman, K.B. Savidge and W.J. Ullman. 2005. Atmospheric nitrogen inputs to the Delaware Inland Bays: The role of ammonia. *Environmental Pollution* 135:433-443.
- Scudlark, J.R., K.M. Russell, J.N. Galloway, T.M. Church and W.C. Keene. 1998. Organic nitrogen in precipitation at the mid-Atlantic US coast: Methods evaluation and preliminary measurements. *Atmospheric Environment* 32:1719-1728.
- Seitzinger, S.P. and R.W. Sanders. 1999. Atmospheric inputs of dissolved organic nitrogen stimulate estuarine bacteria and phytoplankton. *Limnology and Oceanography* 44:721-730.
- Solórzano, L and J.H. Sharp. 1980a. Determination of total dissolved nitrogen in natural waters. *Limnology and Oceanography* 25:751-754.
- Solórzano, L. and J.H. Sharp. 1980b. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. *Limnology and Oceanography* 25:754-758.
- Volk, J.A., J.R. Scudlark, K.B. Savidge, A.S. Andres, R.J. Stenger and W.J. Ullman. 2010. Intra- and inter-annual trends in phosphorus loads and comparison with nitrogen leads to Rehoboth Bay, Delaware. *Estuarine Coastal, and Shelf Science* (in revision).
- Williams, R.M. 1982. Model for the dry deposition of particles to natural water surfaces. *Atmospheric Environment* 16:1933-1938.
- Wolff, G.T., T.M. Church, J.N. Galloway and A.H. Knap. 1987. An examination of SO<sub>x</sub>, NO<sub>x</sub> and trace metal washout ratios over the Western Atlantic Ocean. *Atmospheric Environment* 21:2623-2628.
- Zufall, M.J., C.I. Davidson, P.F. Caffrey and J.M. Ondov. 1998. Airborne concentrations and dry deposition fluxes of particulate chemical species to Southern Lake Michigan. *Environmental Science and Technology* 32:1623-1628.

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## Appendix A

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### **FORMAT DESCRIPTION FOR AIRMoN DATA FILES** **Delimited format**

(Modified from <http://nadp.sws.uiuc.edu/documentation/fmtairdel.html>)

#### 1. DESCRIPTION OF CONTENTS

These files contains NADP/AIRMoN data. All files are variable- length, delimited text files. Unless otherwise indicated,missing values are represented by "--".

#### 2. HEADINGS

First line: "NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/AIRMON"

Second line: "Printed: "

Third line: [field headings]

#### 3. FIELD HEADINGS AND DESCRIPTIONS

HEADING	DESCRIPTION
Site ID	Alpha-numeric site identification code, the first two characters of which are the abbreviation of the state in which the site is located.
Dateon	Date on which the sample bucket was installed on the collector, reported in Greenwich Mean Time (GMT), in yy/mm/dd.
Dateoff	Date on which the sample bucket was removed from the collector, reported in Greenwich Mean Time (GMT), in yy/mm/dd.
Timeon	Time the sample bucket was installed on the collector, reported in Greenwich Mean Time (GMT), in hr/mm.
Timeoff	Time the sample bucket was removed from the collector, reported in Greenwich MeanTime (GMT), in hr/mm.
LabNo	Unique alphanumeric sample identification assigned at the CAL.
Subppt	Precipitation amount used by NADP in calculating weighted-mean concentrations, depositions and precipitation totals, in mm. In most cases sub_ppt equals the NWS stick raingage reading. Where the raingage reading is a trace amount, a value of 0.127mm is assigned; in cases where the NWS stick raingage reading is missing or invalid, the recording raingage amount is used; in cases where both raingage readings are missing or invalid, the equivalent depth of the sample volume is used (for this conversion, the area of the sample bucket is 678.9 square centimeters).
Pptnws	Precipitation amount as measured by the NWS stick rain gage, in mm. Trace amounts are indicated by -7.
Pptrec	Precipitation amount as measured by the recording rain gage, in mm. Trace amounts are indicated by -7.

HEADING	DESCRIPTION
Svol	Volume of sample captured in the sample bucket, in ml.
LT	Labtype - A code indicating the condition of the sample upon arrival at the CAL: W Sample volume of 35 mL or more; WI Sample volume of 10 - 35 mL; chemical measurements are made as volume permits in the following order: pH, Conductance, {NH4, PO4}, {Cl, NO3, SO4}, and {Ca, Mg, Na, K}; and D Sample volume of 0 - 10 mL. Sample was not shipped.
QR	Quality rating code. A code indicating the relative quality of the sample: A Samples of the highest quality did not contain anything but water, all protocols were followed, and there is no indication of compromised integrity of the sample; B Samples of unknown quality may contain contaminants such as plant matter or insects, or are potentially contaminated due to handling errors; C Samples of the lowest quality are either of undefined duration, contain bird droppings, or have some other indication of compromised quality.
SP	Sample protocol code. A code indicating departures from standard sample collection procedures that may have compromise sample integrity: (blank) No identifiable departures; U Undefined sample type; Q Quality assurance sample
SL	Sample level code. A code indicating departures from field or laboratory standard operating procedures: (blank) No identifiable departures; C Contaminated sample; E Long-duration sample; F Field error; L Laboratory error; M Missing sampling information
pH_lab	negative log of the hydrogen ion concentration as measured at the CAL, in pH units.
pH fld	pH of the sample as measured in the field laboratory, reported as the negative log of hydrogen ion concentration.
Conlab	Conductance of the precipitation sample as measured at the CAL, reported in microsiemens per centimeter.
Confld	Conductance of the precipitation sample as measured in the field laboratory, reported in microsiemens per centimeter.
[Ions]	Concentrations of Ca, Mg, K, Na, NH4, NO3, Cl and SO4, in mg/L. The values reported are the instrument values reported by the CAL and may be below the lower limit of detection. The lower limit of detections are: Ca 0.009 mg/L; Mg 0.003 mg/L; K 0.003 mg/L; Na 0.003 mg/L; NH4 0.03 mg/L; NO3 0.03 mg/L; Cl 0.03 mg/L; SO4 0.02 mg/L