Improved daily precipitation nitrate and ammonium concentration models for the Chesapeake Bay Watershed

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A linear least-squares regression approach was used to develop daily precipitation nitrate and ammonium concentration models for the Chesapeake Bay Watershed.

Abstract

Daily precipitation nitrate and ammonium concentration models were developed for the Chesapeake Bay Watershed (USA) using a linear least-squares regression approach and precipitation chemistry data from 29 National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites. Only weekly samples that comprised a single precipitation event were used in model development. The most significant variables in both ammonium and nitrate models included: precipitation volume, the number of days since the last event, a measure of seasonality, latitude, and the proportion of land within 8 km covered by forest or devoted to industry and transportation. Additional variables included in the nitrate model were the proportion of land within 0.8 km covered by water and/or forest. Local and regional ammonia and nitrogen oxide emissions were not as well correlated as land cover. Modeled concentrations compared very well with event chemistry data collected at six NADP/AirMoN sites within the Chesapeake Bay Watershed. Wet deposition estimates were also consistent with observed deposition at selected sites. Accurately describing the spatial distribution of precipitation volume throughout the watershed is important in providing critical estimates of wet-fall deposition of ammonium and nitrate.

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1. Introduction

The major determinants of wet deposition are the volume of precipitation that falls at a given point and the concentrations of dissolved substances in precipitation at that point. Unlike precipitation volumes, much less is known about the spatial and temporal variations in the concentrations of dissolved substances in precipitation other than what can be discerned from point estimates from routine monitoring programs, such as the National Atmospheric Deposition Program (NADP, 2003). This is especially true with regards to daily ammonium and nitrate concentrations. Although it is generally recognized that the concentration of a dissolved substance in precipitation is a function of not only the volume of precipitation, but also local and regional land cover and emission sources, the actual role each plays in determining the concentration at a given location is unknown. Consequently, efforts to define spatial patterns of ionic concentrations in precipitation over a region are generally limited to simple statistical
relationships based on observed point estimates within the region and at peripheral sites. Such a statistical relationship was developed for the Chesapeake Bay Watershed (Valigura et al., 1996).

The purpose of the modeling effort described here is to improve the accuracy of daily ammonium and nitrate wet concentration models used to provide deposition estimates for the Chesapeake Bay Watershed (CBW). The existing daily concentration models described in Linker et al. (1999) and Valigura et al. (1996) were developed from precipitation chemistry and volume data collected at 15 National Atmospheric Deposition Program/National Trend Network (NADP/NTN) monitoring stations located in and around the CBW from 1984 through 1992. This modeling effort incorporated information on precipitation sample volume, month of year, and latitude in a linear regression model of log-transformed wet-fall ammonium and nitrate concentrations from each NADP/NTN site. This manuscript describes the development of a revised regression model derived from precipitation chemistry data from 29 NADP/NTN monitoring stations, including those used by Valigura et al. (1996), from 1984 through 2001. Also included in the revised models are variables that describe the spatial location of each site, preceding precipitation event history, a measure of seasonality, long-term trend, land cover, and local and regional ammonia and nitrogen oxide emissions.

2. Methods and model development

The NADP/NTN monitoring program has been in operation since 1978 and provides chemical analyses for weekly precipitation samples collected at over 250 monitoring sites across the United States in compliance with standardized sample collection and analytical protocols (NADP, 2003; Bigelow and Dossett, 1988; Peden et al., 1979). Daily precipitation volume records are also collected at each NADP/NTN monitoring site. Twenty-nine of the NADP/NTN sites are located in or adjacent to the CBW and have been in active operation during all or part of the 1984–2001 study period (Table 1). Quality-controlled weekly measurements of wet-fall ammonium (NH$_4^+$) and nitrate (NO$_3^-$) concentrations and the corresponding daily precipitation volumes at these NADP/NTN sites constituted the precipitation data set used for model development. Concentrations and precipitation volumes were both log-transformed for this analysis. Because this modeling effort involves the development of daily concentration models of inorganic nitrogen compounds, only those weekly precipitation chemistry samples that comprised a single precipitation event were used for model development.

The following measures of precipitation event history for each precipitation chemistry sample were also calculated using daily precipitation records for each NADP/NTN station: (1) the number of days since the preceding precipitation event; (2) the volume of precipitation occurring in the preceding 3, 5, 7, 10, and 14-day periods; and (3) the number of days having precipitation during the preceding 7- and 14-day periods. Seasonality was represented in the model by dividing each calendar year into six distinct bi-monthly periods. The first bi-monthly period corresponds to January and February and the sixth to November and December. The six seasonal time periods are represented in the linear regression model by an array of five binary indicator variables. Spatial variation in concentration patterns was addressed in predictor selection by including first- and second-degree polynomial terms of latitude and longitude in the set of potential predictors.

In an effort to enhance the accuracy of modeled estimates of daily ammonium and nitrate concentrations, additional data describing local land use (cover) and ammonia (NH$_3$) and nitrous oxides (NO$_x$) emissions were incorporated into the model development process. The 1992 National Land Cover Data (NLCD) grids provide a 30-m resolution classification derived from LANDSAT thematic mapper imagery that encompasses the CBW (Vogelmann et al., 1998). The 1992 NLCD were used to calculate proportional representation of several land use categories within the proximities of 0.8, 1.6, 3.2, 8.0, and 16.1 km of each NADP/NTN site for evaluation as potential predictors of daily ammonium and nitrate wet-fall concentrations. The candidate land cover categories were open water (code 11), forested (codes 41–43), residential (codes 21 and 22), industrial/transportation (code 23), croplands (codes 81–84), and vegetated wetlands (codes 91 and 92).

Local emission levels of ammonia and nitrous oxides were also considered as potential predictors of wet-fall daily ammonium and nitrate concentrations. Emission data were obtained from the United States Environmental Protection Agency’s National Emission Trends (NET) database (http://www.epa.gov/air/data/netdb.html). The NET database yields emission totals for individual counties for each year from 1985 through 1999. For model development, NET annual emission totals were standardized by county area. The area-standardized emission rates for both the county containing an NADP/NTN monitoring site and for the nearest three counties were used as candidate predictors for the daily concentration models. The nearest counties were determined as the distance from the county centroid to the monitoring site location. Emission measurements were matched to precipitation chemistry samples by year.

Selection of final model effects from among the set of candidate predictors was conducted using stepwise linear least-squares regression with forward selection and backward elimination of terms evaluated at each step based on a significance level of 0.10. The first step of
the stepwise regression selection procedure for each ion began with precipitation and seasonality included as predictors. These effects were shown to be significant by the preceding model developed by Valigura et al. (1996). Hierarchy of predictor effects in concentrations by the preceding model developed by predictors. These effects were shown to be significant began with precipitation and seasonality included as the stepwise regression selection procedure for each ion

\[ \log_{10}(c) = b_0 + b_1 \log_{10}(\text{ppt}) + \sum b_2 \text{season} + b_3 v_3 + \cdots + b_n v_n + e \]

where \( c \), daily wet-fall ionic concentration (mg/L); \( b_0 \), intercept; \( \text{ppt} \), daily precipitation volume (cm); \( b_1 \), coefficient for precipitation term; season, vector of five binary indicator variables encoding the six bi-monthly seasons; \( b_2 \), vector of five coefficients for season terms; \( v_3, v_n \), additional predictors selected through stepwise regression; \( b_3, b_n \), coefficients corresponding to \( v_3, v_n \), \( e \), residual error. Estimates of daily ionic deposition were calculated as the product of estimated concentration and daily precipitation volume:

\[ d = c \cdot \text{ppt} \]

where \( d \), estimated daily ionic wet deposition (kg/ha); \( c \), estimated daily ionic wet-fall concentration (mg/L); \( \text{ppt} \), daily precipitation volume (cm). Estimates of daily ionic

<table>
<thead>
<tr>
<th>Monitoring network</th>
<th>Station ID</th>
<th>Station name</th>
<th>Latitude (degrees)</th>
<th>Longitude (degrees)</th>
<th>Elevation (m)</th>
<th>Dates of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NADP/NTN</td>
<td>KY22</td>
<td>Lilley Cornett Woods</td>
<td>37.0778</td>
<td>−82.9936</td>
<td>335</td>
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<td>MD03</td>
<td>White Rock Substation</td>
<td>39.4089</td>
<td>−76.9953</td>
<td>172</td>
<td>1984/10/03 2002/03/04</td>
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<tr>
<td>NADP/NTN</td>
<td>MD13</td>
<td>Wye</td>
<td>38.9131</td>
<td>−76.1525</td>
<td>6</td>
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<tr>
<td>NADP/NTN</td>
<td>MD18</td>
<td>Assateague Island National Seashore</td>
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<td>2000/09/05 Present</td>
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<td>NC03</td>
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<td>Finley Farm</td>
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<td>1978/10/03 Present</td>
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<td>NADP/NTN</td>
<td>NJ99</td>
<td>Washington Crossing</td>
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<td>72</td>
<td>1981/08/04 Present</td>
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<tr>
<td>NADP/NTN</td>
<td>NY08</td>
<td>Aurora Research Farm</td>
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<td>1979/04/17 Present</td>
</tr>
<tr>
<td>NADP/NTN</td>
<td>NY10</td>
<td>Chautauqua</td>
<td>42.2994</td>
<td>−79.3964</td>
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<tr>
<td>NADP/NTN</td>
<td>NY20</td>
<td>Huntington Wildlife</td>
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<td>−74.2231</td>
<td>500</td>
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<tr>
<td>NADP/NTN</td>
<td>NY65</td>
<td>Jasper</td>
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<td>−77.5538</td>
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<td>1980/02/19 Present</td>
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<tr>
<td>NADP/NTN</td>
<td>NY68</td>
<td>Biscuit Brook</td>
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<td>−74.5036</td>
<td>634</td>
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<tr>
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<td>West Point</td>
<td>41.3508</td>
<td>−74.0486</td>
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<tr>
<td>NADP/NTN</td>
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<td>Arentsdsvile</td>
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<td>−77.3078</td>
<td>269</td>
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<tr>
<td>NADP/NTN</td>
<td>PA15</td>
<td>Penn State</td>
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<td>393</td>
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<tr>
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<td>NADP/NTN</td>
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<td>Leading Ridge</td>
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<td>NADP/NTN</td>
<td>PA72</td>
<td>Milford</td>
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<td>−74.8203</td>
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<tr>
<td>NADP/NTN</td>
<td>VA00</td>
<td>Charlottesville</td>
<td>38.0397</td>
<td>−78.5419</td>
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<tr>
<td>NADP/NTN</td>
<td>VA13</td>
<td>Horton’s Station</td>
<td>37.3314</td>
<td>−80.5575</td>
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<td>Prince Edward</td>
<td>37.1658</td>
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<td>NADP/NTN</td>
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<tr>
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<td>WV04</td>
<td>Babcock State Park</td>
<td>37.98</td>
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<tr>
<td>NADP/NTN</td>
<td>WV05</td>
<td>Cedar Creek</td>
<td>38.8794</td>
<td>−80.8478</td>
<td>234</td>
<td>1999/01/26 Present</td>
</tr>
<tr>
<td>NADP/NTN</td>
<td>WV18</td>
<td>Parsons</td>
<td>39.0897</td>
<td>−79.6622</td>
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<td>1978/07/05 Present</td>
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<tr>
<td>AirMoN</td>
<td>DE02</td>
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<td>38.7722</td>
<td>−75.0992</td>
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<td>1992/09/29 Present</td>
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<tr>
<td>AirMoN</td>
<td>DE99</td>
<td>Trap Pond State Park</td>
<td>38.4994</td>
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<td>37.9833</td>
<td>−76.0333</td>
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<td>1995/11/17 Present</td>
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<td>42.4014</td>
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<td>503</td>
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<td>PA15</td>
<td>Penn State</td>
<td>40.7883</td>
<td>−77.9458</td>
<td>393</td>
<td>1992/10/06 Present</td>
</tr>
<tr>
<td>AirMoN</td>
<td>WV99</td>
<td>Canaan Valley</td>
<td>39.0636</td>
<td>−79.4222</td>
<td>988</td>
<td>2000/06/01 Present</td>
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</tbody>
</table>

Observations from the stations in the NADP/NTN network during 1984–2001 were used for estimating model parameters. Deposition records from the NADP/NTN and AirMoN stations were used independently to assess model accuracy.
wet deposition rates (kg/ha/day) to the CBW were calculated by estimating depositions at the cell centers of a uniformly-spaced 1.09-km grid (100 rows and 100 columns per degree of latitude and longitude, respectively) overlaying the CBW and then averaging the deposition estimates for grid cell centers lying within each polygon. The product of the polygon deposition rate by the polygon area yields the total daily ionic mass deposition for the polygon.

3. Results and interpretation

The models of daily ionic wet-fall concentrations of ammonium (NH₄⁺) and nitrate (NO₃⁻) produced by stepwise regression analyses are detailed in Tables 2 and 3. Precipitation volume was the strongest predictor of both ammonium and nitrate concentrations. Concentrations were inversely related to precipitation volume, although the dilution effect remained non-linear after logarithmic transformation of both concentrations and volumes (Figs. 1 and 2). The dilution effect exhibited both seasonal and spatial variability. Dilution rates were strongest during the fall and winter months and weakest during the late spring and early summer months for both ammonium and nitrate. Dilution rates also tended to increase toward the eastern portions of the CBW, and for nitrate, also tended to be weaker in the northern portion of the watershed. Concentrations of both inorganic nitrogen compounds were generally higher during the spring and summer months. A latitudinal gradient was apparent in the concentrations for both species.

Log-transformed concentrations of ammonium tended to increase linearly with latitude. Nitrate concentrations also tended to be higher toward the north, but the tendency was non-linear and confounded with longitudinal gradients in concentration and dilution rate. Significant long-term trends in concentration were observed for both nitrogen compounds. Wet-fall ammonium concentrations tended to increase during the 1984–2001 period, whereas nitrate concentrations in precipitation tended to decline during the same period.

Precipitation event history was a significant factor in wet-fall concentrations of both ammonium and nitrate. Concentrations of both species were directly related to the number of days since the preceding precipitation event. This effect was more pronounced for nitrate than ammonium. The volume of precipitation falling during the preceding 7 days exhibited a significant, but moderate, inverse relationship to wet-fall concentrations.

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean square</th>
<th>F-value</th>
<th>Significance</th>
<th>Partial coefficient</th>
</tr>
</thead>
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<tr>
<td>Intercept</td>
<td></td>
<td></td>
<td></td>
<td>−1.309916711</td>
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<td>log₁₀(ppt)</td>
<td>2.8800</td>
<td>8.29</td>
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<td>log₁₀(ppt²)</td>
<td>5.5240</td>
<td>35.09</td>
<td>&lt;0.0001</td>
<td>0.646417263</td>
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<tr>
<td>log₁₀(ppt) during preceding 7 days</td>
<td>0.9948</td>
<td>6.32</td>
<td>0.0120</td>
<td>−0.087667650</td>
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<tr>
<td>Number of days since previous ppt event</td>
<td>1.6853</td>
<td>10.70</td>
<td>0.0011</td>
<td>0.045256130</td>
</tr>
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<td>Season (bi-month)</td>
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<tr>
<td>January–February</td>
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<td></td>
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<tr>
<td>March–April</td>
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<td></td>
<td>0.185788184</td>
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<tr>
<td>May–June</td>
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<td>0.132659903</td>
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<tr>
<td>July–August</td>
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<td>September–October</td>
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<td>November–December</td>
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<tr>
<td>log₁₀(ppt) × season</td>
<td>3.6334</td>
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<td>January–February</td>
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<tr>
<td>March–April</td>
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<td>May–June</td>
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<td>July–August</td>
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<td>September–October</td>
<td>−0.003393801</td>
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<tr>
<td>November–December</td>
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<td>Latitude (degrees)</td>
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<td>log₁₀(ppt) × longitude</td>
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<td>Long-term trend (year)</td>
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<td>Proportion of land within 8 km covered by forest</td>
<td>6.1682</td>
<td>39.18</td>
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<td>−0.357539328</td>
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<td>Proportion of land within 0.8 km covered by forest</td>
<td>0.5796</td>
<td>3.68</td>
<td>0.0551</td>
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<tr>
<td>Proportion of land within 8 km devoted to industry and transportation</td>
<td>5.3793</td>
<td>34.17</td>
<td>&lt;0.0001</td>
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</table>
Both land cover composition and emission levels showed significant relationships to the wet-fall concentrations of ammonium and nitrate. However, the elements of these two categories of predictors tended to displace each other in the stepwise regression selection process. Inclusion of a subset of the land cover composition variables in the concentration models yielded slightly higher model $r^2$ values (0.315 vs. 0.296 for ammonium and 0.494 vs. 0.490 for nitrate) and the contributions of emission levels in the models, in addition to land use effects, were not significant at the 0.1-level. As expected, wet-fall concentrations of ammonium were directly related to area-standardized emissions of ammonia ($p < 0.0001$), and nitrate concentrations were directly related to emissions of nitrous oxides ($p < 0.0001$). Ammonium concentrations were better predicted by emission rates for the individual county containing the monitoring site than by the mean levels for the nearest three counties. Conversely, nitrate concentrations showed stronger relationships to mean emission rates for the nearest three counties than for the immediate county.

The observed relationships of wet-fall concentrations to land use composition were more complex and less intuitive than for emission rates. Concentrations of both ammonium and nitrate were strongly, inversely related to the extent of forest cover within 8 km of a monitoring site; however, a weaker direct relationship existed with the amount of forest cover within 0.8 km. Concentration levels of ammonium were also directly associated with the extent of industrial and transportation land uses within 8 km of a site. The stepwise predictor selection process identified the relative extent of open water in the surrounding 8- and 0.8-km proximities as a significant predictor of nitrate concentrations. The functional relationship between nitrate concentration and prevalence of surface water is not certain, but may reflect enhanced deposition due to the scavenging of nitrate by sea-salt aerosols.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean square</th>
<th>$F$-value</th>
<th>Significance</th>
<th>Partial coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>–14.25901207</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>log$_{10}$(ppt)</td>
<td>2.3592</td>
<td>35.55</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>log$_{10}$(ppt$^2$)</td>
<td>7.4454</td>
<td>112.19</td>
<td>&lt;0.0001</td>
<td>0.75512533</td>
</tr>
<tr>
<td>Precip volume during preceding 7 days (log$_{10}$)</td>
<td>0.5432</td>
<td>8.18</td>
<td>0.0042</td>
<td>–0.06484770</td>
</tr>
<tr>
<td>Number of days since previous ppt event</td>
<td>3.6334</td>
<td>54.75</td>
<td>&lt;0.0001</td>
<td>0.06652244</td>
</tr>
<tr>
<td>Season (bi-month)</td>
<td>0.0623</td>
<td>9.38</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>January–February</td>
<td>0.00590539</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>March–April</td>
<td>0.06037087</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>May–June</td>
<td>0.05062807</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>July–August</td>
<td>0.14081422</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>September–October</td>
<td>0.03125004</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>November–December</td>
<td>0.00000000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>log$_{10}$(ppt) × season</td>
<td>1.5416</td>
<td>23.23</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>January–February</td>
<td>0.25861568</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>March–April</td>
<td>0.50002417</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>May–June</td>
<td>0.84224555</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>July–August</td>
<td>0.68102081</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>September–October</td>
<td>0.16203385</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>November–December</td>
<td>0.00000000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Latitude (degrees)</td>
<td>0.8457</td>
<td>12.74</td>
<td>0.0004</td>
<td>5.26018889</td>
</tr>
<tr>
<td>Longitude (degrees)</td>
<td>0.5305</td>
<td>4.98</td>
<td>0.0257</td>
<td>–1.17334607</td>
</tr>
<tr>
<td>Latitude × longitude</td>
<td>0.4405</td>
<td>6.64</td>
<td>0.0100</td>
<td>0.33919130</td>
</tr>
<tr>
<td>Latitude$^2$</td>
<td>0.5994</td>
<td>9.03</td>
<td>0.0027</td>
<td>–0.29794998</td>
</tr>
<tr>
<td>log$_{10}$(ppt) × longitude</td>
<td>1.5550</td>
<td>23.43</td>
<td>&lt;0.0001</td>
<td>–0.85397658</td>
</tr>
<tr>
<td>log$_{10}$(ppt) × latitude</td>
<td>0.3354</td>
<td>5.05</td>
<td>0.0246</td>
<td>0.32508110</td>
</tr>
<tr>
<td>Long-term trend (year)</td>
<td>1.8614</td>
<td>28.05</td>
<td>&lt;0.0001</td>
<td>0.00404099</td>
</tr>
<tr>
<td>Proportion of land within 8 km covered forest</td>
<td>3.3117</td>
<td>49.90</td>
<td>&lt;0.0001</td>
<td>–0.29053387</td>
</tr>
<tr>
<td>Proportion of land within 0.8 km covered by forest</td>
<td>1.9190</td>
<td>28.92</td>
<td>&lt;0.0001</td>
<td>0.16957760</td>
</tr>
<tr>
<td>Proportion of land within 8 km covered by water</td>
<td>1.2483</td>
<td>18.81</td>
<td>&lt;0.0001</td>
<td>–0.37649968</td>
</tr>
<tr>
<td>Proportion of land within 0.8 km covered by water</td>
<td>0.5822</td>
<td>8.77</td>
<td>0.0031</td>
<td>0.23019904</td>
</tr>
</tbody>
</table>

Table 3
Linear regression model of log-transformed nitrate ion ($\text{NO}_3^-$) concentrations for daily precipitation samples collected within the Chesapeake Bay Watershed during 1984–2001 ($n = 3992$, $r^2 = 0.4940$)
land cover composition data for use in the model. At the time this model was developed (2003), ammonia and nitrous oxides emission estimates were only available from 1985 through 1999, and thus, were not applicable to the entire duration of the 1984–2001 study period.

An earlier daily ammonium wet-fall concentration model was developed using weekly precipitation chemistry samples in which precipitation occurred during the last day of the sampling period (Valigura et al., 1996). This restriction was imposed because of the decrease of ammonium concentrations in samples over time. We included other single-event weekly samples in our final model development because precipitation event history was indicated to be a significant factor in rainfall concentration levels. Restricting sample selection to those with rainfall only in the final day of the sample period would have precluded observations with rainfall occurring during the preceding 6 days. Studies of ammonium and nitrate concentrations in weekly vs. daily sampling protocols have indicated that both inorganic nitrogen species are higher (generally 4–10%) for daily sampling protocols than for weekly protocols (de Pena et al., 1985; Lamb and Comrie, 1993; Siros et al., 1985; Butler and Likens, 1998; Rother et al., 2000; Gilliland et al., 2002). This is especially true for ammonium concentrations. Furthermore, because NADP/NTN precipitation samples are transported by over-land commercial carriers from the field sites to a centralized analytical laboratory located at Champaign, Illinois, the period of time samples are in transit ranges from 1 to 7 days, sometimes longer. Consequently, a decrease in inorganic nitrogen concentrations, especially ammonium, occurs for all weekly precipitation chemistry samples regardless of the day that precipitation occurred, including those samples that include precipitation that fall on the last day of the sampling period.

Fitting the regression parameters of the model previously used for estimating daily ammonium and nitrate concentrations (Valigura et al., 1996) to the data for 1984–2001 show that the functional relationships between predictors and concentrations have remained similar (Table 4). However, the amplitude of the seasonal variation and the dilution rates for both inorganic nitrogen compounds declined when this model was applied to the expanded data set. Also, the predictors of the earlier model did not provide the same degree of fit to the more recent concentration data as

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameters of original model</th>
<th>Updated model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of samples</td>
<td>265</td>
<td>569</td>
</tr>
<tr>
<td>log(ammonium ion concentration) Intercept</td>
<td>−1.2260</td>
<td>−1.16219</td>
</tr>
<tr>
<td>log(ppt)</td>
<td>−0.3549</td>
<td>−0.23634</td>
</tr>
<tr>
<td>Month</td>
<td>0.3566</td>
<td>0.13398</td>
</tr>
<tr>
<td>Month^2</td>
<td>−0.0337</td>
<td>−0.01219</td>
</tr>
<tr>
<td>Model r^2</td>
<td>0.31</td>
<td>0.2163</td>
</tr>
<tr>
<td>log(nitrate ion concentration) Intercept</td>
<td>−1.289</td>
<td>−1.66975</td>
</tr>
<tr>
<td>log(ppt)</td>
<td>−0.3852</td>
<td>−0.25591</td>
</tr>
<tr>
<td>Month^2</td>
<td>−0.0037</td>
<td>−0.00154</td>
</tr>
<tr>
<td>Latitude</td>
<td>0.0744</td>
<td>0.04177</td>
</tr>
<tr>
<td>Model r^2</td>
<td>0.41</td>
<td>0.3434</td>
</tr>
</tbody>
</table>
they did to the data from 1984 through 1992. This change in model performance may be due, in part, to the long-term trends in wet-fall concentrations from 1982 to 2001. However, the data set used for this analysis contained observations from 29 NADP/NTN sites, as opposed to only 15 sites from the development of the earlier model. The data set for the current analyses very likely contains more sources of temporal and spatial variability than the data from which the preceding model was developed.

Estimates of mean event wet deposition from our model agree well with the observed depositions at six NADP/Atmospheric Integrated Research Monitoring Network (AirMoN) sites in operation within the CBW during 1992–2001 (Table 5). However, measured individual event concentrations and depositions often varied widely from the estimated values. Valigura et al. (1996) noted single-event departures of nearly 10-fold when comparing estimates from their model to observations recorded at three daily monitoring sites in the CBW. Departures of similar size from our model were also seen in single-event records as well. In spite of these large, single-event variations, the correlations between observed and estimated event depositions remained high. In order to assess the accuracy of our model during the entire 1984–2001 study period (Table 5), estimates of daily precipitation volume were taken from two different sources. Estimates from the USGS daily precipitation model for the CBW were used for estimating deposition during 1984–1999. Precipitation estimates from the United States Climatic Prediction Center’s (CPC) Daily Precipitation Analyses (http://www.cpc.ncep.noaa.gov/products/precip/realtime/us_precip.html) were used for estimating deposition during 2000 and 2001, a period for which estimates for the USGS precipitation model were not available. Because the CBW modeling program is based only upon precipitation estimates from the USGS precipitation model, a subset of the comparisons in Table 5 that is limited to observations from 1984 through 1999 and to precipitation estimates from the model that appears in Table 6. Two of the six AirMoN stations, DE99 and WV99, used in the 1984–2001 comparisons were not active prior to 2000. The patterns and magnitudes of model estimation error in Tables 5 and 6 are very similar and the accuracy of the daily deposition model at the AirMoN stations active during both time periods was not strongly influenced by these differing sources of precipitation estimates.

Applying our daily concentration models to the daily precipitation records from 1984 to 2001 for 29 NADP/NTN precipitation chemistry sites located in or adjacent to the CBW region and summing the deposition estimates into annual totals provide a comparison with the observed annual deposition at those sites (Table 7). These estimation error rates show a modest improvement over the 19% mean errors for annual depositions reported by Valigura et al. (1996) for 15 NADP/NTN sites in the CBW during 1984–1992. The error rates for the present model are based on observations from a longer time period (17 years vs. 8 years), a larger number of monitoring sites, and a set of precipitation chemistry samples that were not restricted to events occurring in the last day of the weekly sampling period.

Table 5
Comparison of mean estimated daily ammonium (NH₄⁺) and nitrate (NO₃⁻) wet depositions with observed event depositions at six AirMoN sites located within the CBW region from 1984 through 2001

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean observed deposition</th>
<th>Mean estimated deposition</th>
<th>Mean absolute error</th>
<th>Correlation between obs. and est. dep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium (kg/ha)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE02</td>
<td>0.03303</td>
<td>0.03571</td>
<td>0.00268</td>
<td>0.01964 0.5431</td>
</tr>
<tr>
<td>DE99</td>
<td>0.04266</td>
<td>0.03502</td>
<td>-0.00765</td>
<td>0.02217 0.5702</td>
</tr>
<tr>
<td>MD15</td>
<td>0.02892</td>
<td>0.03163</td>
<td>0.00270</td>
<td>0.01771 0.5906</td>
</tr>
<tr>
<td>NY67</td>
<td>0.02615</td>
<td>0.02232</td>
<td>-0.00384</td>
<td>0.01517 0.6560</td>
</tr>
<tr>
<td>PA15</td>
<td>0.03176</td>
<td>0.02781</td>
<td>-0.00395</td>
<td>0.01674 0.7252</td>
</tr>
<tr>
<td>WV99</td>
<td>0.02070</td>
<td>0.02080</td>
<td>0.00009</td>
<td>0.01222 0.6933</td>
</tr>
<tr>
<td>Overall</td>
<td>0.02976</td>
<td>0.02809</td>
<td>-0.00167</td>
<td>0.01784 0.6078</td>
</tr>
<tr>
<td>Nitrate (kg/ha)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE02</td>
<td>0.16215</td>
<td>0.13746</td>
<td>-0.02468</td>
<td>0.10054 0.5043</td>
</tr>
<tr>
<td>DE99</td>
<td>0.12361</td>
<td>0.13680</td>
<td>0.01320</td>
<td>0.09103 0.5216</td>
</tr>
<tr>
<td>MD15</td>
<td>0.14692</td>
<td>0.14233</td>
<td>-0.00459</td>
<td>0.08684 0.5638</td>
</tr>
<tr>
<td>NY67</td>
<td>0.14574</td>
<td>0.15336</td>
<td>0.00763</td>
<td>0.07334 0.6447</td>
</tr>
<tr>
<td>PA15</td>
<td>0.17676</td>
<td>0.17692</td>
<td>0.00016</td>
<td>0.07945 0.6542</td>
</tr>
<tr>
<td>WV99</td>
<td>0.09180</td>
<td>0.10323</td>
<td>0.01143</td>
<td>0.04350 0.7237</td>
</tr>
<tr>
<td>Overall</td>
<td>0.15443</td>
<td>0.15471</td>
<td>0.00027</td>
<td>0.08166 0.5879</td>
</tr>
</tbody>
</table>

Table 6
Comparison of mean estimated daily ammonium (NH₄⁺) and nitrate (NO₃⁻) wet depositions with observed event wet depositions at four AirMoN sites located within the CBW region from 1984–1999

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean observed deposition</th>
<th>Mean estimated deposition</th>
<th>Mean absolute error</th>
<th>Correlation between obs. and est. dep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium (kg/ha)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE02</td>
<td>0.03452</td>
<td>0.03664</td>
<td>0.00212</td>
<td>0.01852 0.5563</td>
</tr>
<tr>
<td>MD15</td>
<td>0.02911</td>
<td>0.03204</td>
<td>0.00293</td>
<td>0.01805 0.5859</td>
</tr>
<tr>
<td>NY67</td>
<td>0.02683</td>
<td>0.02267</td>
<td>-0.00416</td>
<td>0.01676 0.6310</td>
</tr>
<tr>
<td>PA15</td>
<td>0.03132</td>
<td>0.02814</td>
<td>-0.00318</td>
<td>0.01639 0.7084</td>
</tr>
<tr>
<td>Overall</td>
<td>0.03055</td>
<td>0.02970</td>
<td>-0.00085</td>
<td>0.01740 0.6368</td>
</tr>
<tr>
<td>Nitrate (kg/ha)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE02</td>
<td>0.17026</td>
<td>0.14275</td>
<td>-0.02751</td>
<td>0.09861 0.5274</td>
</tr>
<tr>
<td>MD15</td>
<td>0.15015</td>
<td>0.14589</td>
<td>-0.00426</td>
<td>0.08578 0.5686</td>
</tr>
<tr>
<td>NY67</td>
<td>0.14122</td>
<td>0.14912</td>
<td>0.00790</td>
<td>0.07690 0.6290</td>
</tr>
<tr>
<td>PA15</td>
<td>0.17506</td>
<td>0.17146</td>
<td>-0.00360</td>
<td>0.08102 0.6377</td>
</tr>
<tr>
<td>Overall</td>
<td>0.15990</td>
<td>0.15283</td>
<td>-0.00706</td>
<td>0.08556 0.584</td>
</tr>
</tbody>
</table>

Deposition estimates are based on daily precipitation estimates from the USGS daily precipitation model.
The revised concentration models described in this manuscript were applied to grids of estimated daily precipitation from two different sources to calculate grids of estimated ammonium, nitrate, and total inorganic nitrogen wet deposition. The first was from the CPC Precipitation Analyses. These precipitation grids are produced at 0.25-degree resolution for the continental United States and southern Canada by applying a modified Cressman spatial interpolation algorithm to quality-controlled observations from River Forecast Center gauges (3000–6000 stations) and the Climate Anomaly Database. Because of the extensive spatial coverage of the CPC grids, these data were used to estimate depositions across the broad region encompassing the CBW (Figs. 3–6). Figs. 3 and 4 illustrate the inverse relationship between precipitation volume and wet-fall ammonium and nitrate concentrations, respectively; consequently, these figures also show a general inverse spatial relationship between wet-fall concentration and deposition for an individual precipitation event. Grids of estimated daily deposition were summed to produce grids of annual estimated concentrations. In turn, these annual grids were averaged for the period 1985–2001 to produce estimates of mean annual wet deposition (Figs. 5 and 6). Fig. 5 shows general latitudinal and longitudinal gradients of wet deposition of both ammonium and nitrate. However, the localized influence of land cover on ammonium wet-fall that is incorporated into our model is evident in the more spatially-irregular deposition field for that species.

Higher resolution grid estimates of daily precipitation from a precipitation model developed for the CBW were also integrated into our daily concentration models. This precipitation model was developed by the USGS and produces estimates at 5-km resolution. As of July 2003, precipitation estimates were only available for 1984–1999. Although the summary periods are not identical, the grid of estimated mean annual deposition based on inputs from the USGS precipitation model (Fig. 7) shows very similar overall patterns to that based on the CPC precipitation estimates (Fig. 6). However, modeled depositions based on the USGS model are greater in some areas of high topographic relief, such as the mountains of central Pennsylvania and western Maryland. This departure from estimates based on the CPC precipitation data is expected because the CPC

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**Table 7**

Comparison of estimated annual wet depositions of ammonium ($\text{NH}_4^+$), nitrate ($\text{NO}_3^-$), and total inorganic nitrogen ($\text{NO}_3^- + \text{NH}_4^-$) calculated for the daily wet-fall deposition model with annual deposition observed at 29 NADP/NTN monitoring sites in or adjacent to the CBW during 1984–2001.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total inorganic nitrogen deposition (kg/ha)</th>
<th>Ammonium deposition (kg/ha)</th>
<th>Nitrate deposition (kg/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed mean</td>
<td>5.471</td>
<td>2.636</td>
<td>15.14</td>
</tr>
<tr>
<td>Estimated mean</td>
<td>5.100</td>
<td>2.481</td>
<td>14.30</td>
</tr>
<tr>
<td>Mean error</td>
<td>−0.371</td>
<td>−0.156</td>
<td>−0.85</td>
</tr>
<tr>
<td>Mean absolute error</td>
<td>0.810</td>
<td>0.496</td>
<td>2.36</td>
</tr>
<tr>
<td>Mean percent error</td>
<td>16.7</td>
<td>19.0</td>
<td>15.5</td>
</tr>
</tbody>
</table>

All depositions are expressed as kg/ha.
The interpolation algorithm does not directly adjust estimates for orographic effects and high elevation locations are not well represented among the river forecasting gauges employed by the CPC analyses. Topography is known to have a strong influence on local precipitation volume (Barros and Lettenmaier, 1993, 1994; Grimm and Lynch, 2004), and, consequently, also on wet deposition rates.
4. Summary

The statistically significant parameters included in the daily ammonium (Table 2) and nitrate (Table 3) concentration models provide insight into the parameters and processes that affect ammonium and nitrate concentrations in precipitation. Although one would expect precipitation volume and seasonality to affect inorganic nitrogen concentrations in precipitation, it is less obvious as to the significance of preceding event history and local land cover. The inclusion of the number of days since the previous event in both models and the inclusion of the volume of precipitation during the previous 7 days in the nitrate model are essentially describing the relative amount of these pollutants in the atmosphere at the time of an event. Because of rain-out and wash-out phenomena, precipitation acts to cleanse the atmosphere. Consequently, inorganic nitrogen concentrations during events tend to be higher as the interval between storms increases, and vice versa. The reverse is true for the volume of precipitation during the preceding events, especially for nitrate; greater volumes result in lower concentrations as a result of greater opportunities to remove pollutants from the atmosphere.

The selection of land cover parameters and their distance from a monitoring site is also related to the relative opportunities for nitrogen oxides and ammonia to influence the concentrations of inorganic nitrogen species in precipitation. Ammonia is very soluble and generally considered to be of local origin, particularly in areas of intensive agriculture. Nitrogen oxides can be of local sources as well, but long-range transport, especially from fuel combustion sources that are dominated by electric power generation, are also important. As a result, the proportion of land covered by forests and/or devoted to industry and transportation are highly significant in the ammonium model. Forest cover is inversely related to ammonium and indirectly indicates the lack of intensive agricultural activities. Automobiles and various industrial processes also emit ammonia and are thus represented in the model by the proportion of land devoted to industry and transportation. A similar rationale can also be used to describe the section of the proportion of area covered by forest or water within 0.8 km or 8.0 km in the daily nitrate concentration model.

The successful application of single-event chemistry data from the NADP/NTN that uses a weekly sampling protocol in the development of daily concentration models for oxidized and reduced forms of nitrogen, illustrates nicely the utility of this long-term database. Although event-based sampling programs, such as the NADP/AirMoN program, are extremely useful for research driven studies, the limited number of such sites limits the application of the data for regional or other large-scale environmental assessments where...
high-resolution concentration and/or wet deposition data are required. Data from the NADP/NTN, because of the program’s longevity and the number of sites, can be used as an effective tool in assessing local and regional problems, even where event-based measurements are of interest. Nevertheless, expansion of the existing NADP/AirMoN would enhance data interpretation from the weekly network while at the same time providing greater regional coverage.

Lastly, because precipitation volume is one of the major determinants in wet deposition inputs to critical ecosystems, the incorporation of existing precipitation volume measurement networks, such as those used in this study, are extremely useful in improving the spatial resolution of wet deposition estimates to a region or watershed.

References


Valigura, R., Luke, W., Artz, R., Hicks, B., 1996. Atmospheric nutrient input to coastal areas – reducing the uncertainties. NOAA coastal ocean program decision analysis series, No. 9 (Silver Spring, MD).