

## THE CHEMICAL COMPOSITION OF PRECIPITATION IN THE PECONIC RIVER WATERSHED, LONG ISLAND, NEW YORK

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### ABSTRACT

In order to estimate the atmospheric loadings for the Peconic River watershed, a loading model based on the frequency of continental versus marine storms was developed. The model was calibrated using precipitation data collected in 1987, 1988, and 1989 at Brookhaven National Laboratory in the headwaters of the Peconic River watershed. A test of the model on data collected in 1986 showed good agreement between the observed and calculated loading. Hence, this model may be of great importance for estimating atmospheric loadings on eastern Long Island and its surrounding bays.

### INTRODUCTION

Atmospheric precipitation contains constituents of distant and local origins. Upper-level winds may transport aerosols over thousands of miles. The chemical composition of the aerosols in the upper-level winds is strongly dependent on the path of the storm. For example, storms originating over the ocean contain sodium, magnesium, chloride, and sulfate ions derived from sea salt aerosols, whereas continental storms contain ammonia, potassium, calcium, and magnesium ions from soil and mineral dust (Stallard and Edmond, 1981). The aerosols in the upper-level winds act as condensation sites for rain and snow and are removed from the air mass through the formation of wet precipitation. Lower-level air masses contain also aerosols and gasses, but their chemistry is strongly influenced by local or regional sources. For example, on Long Island the lower-level air masses are expected to carry sea salt aerosols and contain  $\text{SO}_2$  and  $\text{NO}_x$  derived from fossil fuel combustion. Hence, the chemistry of a precipitation event is a mixture of distant and local sources.

Weather on Long Island is influenced by both storms originating over the ocean and ones originating over land. Therefore, the chemistry of these storms is expected to be different and as a result the contribution of each storm to the Peconic River watershed will be different. The objective of this study is to determine the difference in chemistry between continental and marine storm systems and derive a model that estimates the annual atmospheric loading of major elements and nutrients based on the frequency of continental and marine storms.

### RESEARCH STRATEGY AND METHODS

To meet our objective, we combined precipitation data collected at Brookhaven National Lab (BNL) in the headwaters of the Peconic River watershed and weather data published by NOAA (NOAA, Daily Weather Maps, Wash. D.C.). The precipitation data used in this study were collected between 1986 and 1989 at BNL. Precipitation from each storm event was collected using a wet/dry collection system. Hence, data for each storm is available in contrast to most monitoring programs where composite samples are collected. Composite samples often comprise precipitation from a two-week to month-long interval and are, therefore, frequently mixtures of different types of storms. As noted by Junge and Werby (1958) it is very difficult to correlate precipitation chemistry and weather patterns based on composite samples. Therefore, the data collected at BNL provide a unique opportunity to determine if there is a correlation between weather pattern and precipitation chemistry.

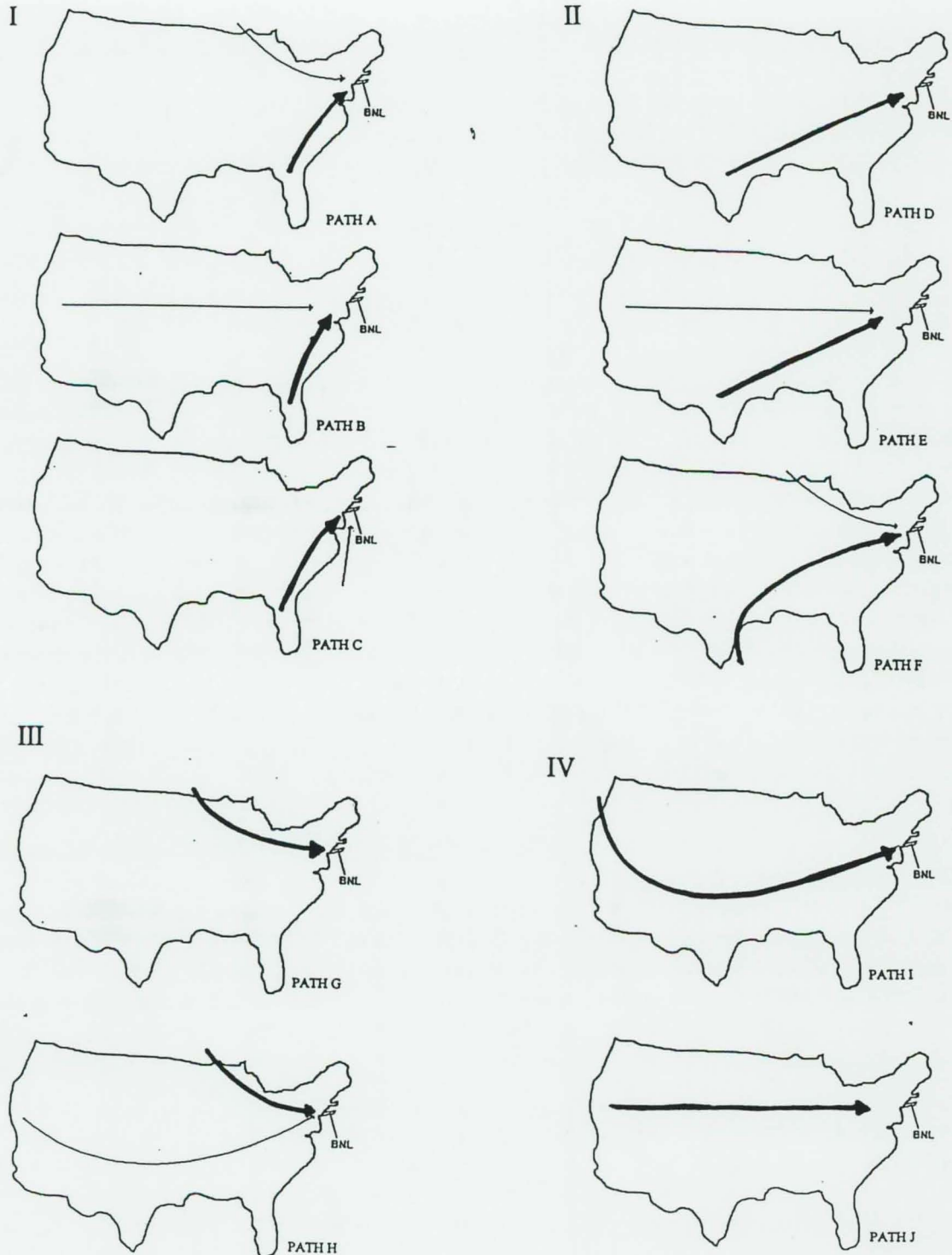


Figure 1. Major storm paths affecting the northeastern United States. (I) southern storms; (II) Mexican storms; (III) Canadian storms; (IV) western storms: see text for details. In each map the bold arrows represent the path of the primary contributing air masses. All other arrows represent secondary contributing factors. Figure is based on evaluation of NOAA, "Daily Weather Maps", 1987-1989

### *Classification of Storms*

The classification of the storms is the first crucial step. For this we relied on the analogue method of forecasting. This method hinges on the fact that existing features on a weather chart (or series of charts) strongly resemble features that produced certain conditions in the past. For this study, the conditions or weather trends for the storm record of 1987-1989 were organized into groups of weather classes based on several criteria, including the position of high and low pressure centers, upper level air flow, barometric conditions, and the prevailing storm track. Because it is important to determine the origin and track of the storm, it was often necessary to examine a series of weather maps covering the track of the storm before it reached Long Island. A similar approach is taken in predicting weather using the analogue method (Ahrens, 1988).

Based on weather patterns producing the storms on Long Island, four broad groups were defined, see Fig. 1. The Group I, or southern storms, develop in the southern United States and move northeasterly along the Atlantic coast. Group I storms occur primarily in the winter months. Three different types of weather patterns produce Group I storms. All three are dominated by a southern air mass moving northeasterly, but they differ in the contributing air masses. The contributing air masses may have some effect on the chemistry of the precipitation because the actual precipitation event is often caused by collision of two different air masses. So for example, Group I storms may be due to collision of an air mass with a northern component (A, in Fig. 1), a western component (B), or they may have only a southern component (C). The Group II, or Mexican storms, are the most complex, and the least encountered. They develop over Mexico or the Gulf of Mexico, and move in the northeast direction. These storms were separated into weather patterns D, E and F. The primary air mass in patterns D and E follow a path over the continent, whereas pattern F originates over the Gulf of Mexico. The Group III or Canadian storms are characterized by a predominantly northern origin. Weather pattern G has no western component in contrast to weather pattern H. Group III storms are most common during the summer months. Group IV are western storms. They either originate in the northwest (I) or in the west (J).

### *Chemical Composition*

The raw wet precipitation data for 1987 through 1989 were sorted using the classification scheme outlined above. For each group, average volume-weighted concentrations were calculated. Based on these average volume-weighted concentrations, average loadings for each group per event. Subsequently, these average loadings were used in a simple linear model that relates the loading to the frequency of Group I through IV events. The linear loading model was tested by comparing the modeled and observed loadings for 1986. The 1986 data was chosen because this is the only other year for which a reliable set of data was available.

## **RESULTS AND DISCUSSION**

There is distinct difference between the chemical composition of Groups I versus Group III and IV, see Tab. 1. As expected Group I storms have a marine chemical signature, whereas Group III and IV have a continental signature. Group II storms occur sporadically and have a mixed continental-marine origin. Hence, some storms have a marine chemical signature whereas other Group II storms have a continental signature.

The average loadings per storm event are summarized in Table 2. With these coefficients it is possible to estimate what the average annual loading is per year per km<sup>2</sup> for the watershed if the frequency of the various storm types is known. For example the total loading of Na would be given by:

$$Na_{Tot} (kg / km^2 / yr) = 60.10a + 20.20b + 20.20c + 18.69d$$

where a, b, c, and d are the annual number of storms of Groups I, II, III, and IV, respectively. The results of the test of this model are presented in Table 3. Unfortunately, potassium had to be excluded from this evaluation due to the insufficient number of K analyses in 1986. The close agreement, except for ammonia, between the predicted and observed loadings for 1986 suggest that the model derived in this study may be applicable to other years for which no precipitation data are available. Moreover, this model may provide some constraints on the atmospheric loading if the climate were to change drastically (i.e., change number of continental versus marine storms). It should be emphasized, however, that the atmospheric loadings calculated using this model provide only a minimum constraint. Contributions via dry fall and impaction are probably also important and are not evaluated here.

One consistent discrepancy between the model values and the observed values are the ammonia loadings (a 37% difference in total loading). This may be due to an anomalously wet summer in 1986 (NOAA, 1987). In 1986, the northern and southern plains, major agricultural areas, received well above normal precipitation. The main sources of ammonia are fertilizers, decomposition of human and animal wastes, and bacterial decay of organic matter (Berner and Berner, 1987). Thus, water-logged soils may have impeded the escape of  $\text{NH}_3$  from the soil. In the atmosphere  $\text{NH}_3$  combines with water to form ammonia.

**Table 1. Average volume weighted concentrations of continental (Group III, IV) and marine (Group I) storms (mg/L).**

Ion	Group I	Group III, IV	Typical Marine	Typical Continental
$\text{Na}^+$	1.18	0.25-0.51	1.0-5.0	0.2-1.0
$\text{Mg}^{2+}$	0.17	0.04-0.07	0.4-1.5	0.05-0.5
$\text{K}^+$	0.16	0.15-0.20	0.2-0.6	0.1-0.5 <sup>b</sup>
$\text{Ca}^{2+}$	0.15	0.15-0.20	0.2-1.5	0.2-4.0 <sup>a</sup>
$\text{NH}_4^+$	0.2	0.31-0.51	0.01-0.05	0.1-0.5 <sup>b</sup>
$\text{H}^+$	pH=4.4	pH=4.07	pH=5-6	pH=4-6
$\text{Cl}^-$	2.19	0.59-0.79	1.0-10.0	0.2-2.0
$\text{SO}_4^{2-}$	2.29	2.62-3.70	1.0-3.0	1.0-3.0 <sup>a,b</sup>
$\text{NO}_3^-$	1.56	1.69-2.97	0.1-0.5	0.4-1.3 <sup>b</sup>

<sup>a</sup> in remote continental areas:  $\text{K}^+ = 0.02-0.07$ ;  $\text{Ca}^{2+} = 0.02-0.2$ ;  $\text{SO}_4^{2-} = 0.2-0.8$ .

<sup>b</sup> in polluted areas  $\text{NH}_4^+ = 1.0-2.0$ ;  $\text{SO}_4^{2-} = 3.0-8.0$ . Source: Berner and Berner (1987).

**Table 2. Loading coefficient for the Peconic River watershed based on wet precipitation collected at BNL from 1987-1989 ( $\text{kg}/\text{km}^2/\text{per storm event}$ )<sup>a</sup>**

Ion	Group I	Group II	Group III	Group IV
$\text{SO}_4^{2-}$	97.5	77.3	109.1	139.9
$\text{NO}_3^-$	68.7	77.3	82.8	115.1
$\text{Cl}^-$	111.6	50.0	37.4	37.4
$\text{NH}_4^+$	9.6	10.1	21.2	24.8
$\text{Na}^+$	60.1	20.2	20.2	18.7
$\text{K}^+$	7.1	14.1	27.3	11.1
$\text{Ca}^{2+}$	6.1	4.0	7.1	4.0
$\text{Mg}^{2+}$	8.6	3.5	3.0	3.0

<sup>a</sup> Storm classification explained in text, also see Fig. 1.

Table 3. Predicted and observed loadings for 1986 (kg/km<sup>2</sup>/yr).<sup>a</sup>

Ion	Group I (n=23)	Group II (n=4)	Group III (n=19)	Group IV (n=7)	Total
<b>Predicted</b>					
SO <sub>4</sub> <sup>2-</sup> , <sup>b</sup>	1949	309	2073	979	5310
NO <sub>3</sub> <sup>-</sup>	1580	309	1574	806	4268
Cl <sup>-</sup>	2555	200	710	262	3727
NH <sub>4</sub> <sup>+</sup>	221	40	403	173	837
Na <sup>+</sup>	1382	81	384	131	1978
Ca <sup>2+</sup>	139	16	127	28	311
Mg <sup>2+</sup>	197	14	58	21	290
<b>Observed</b>					
SO <sub>4</sub> <sup>2-</sup> , <sup>b</sup>	2297	175	2201	1093	5766
NO <sub>3</sub> <sup>-</sup>	1649	199	2023	825	4696
Cl <sup>-</sup>	2990	253	482	144	3868
NH <sub>4</sub> <sup>+</sup>	194	17	291	108	610
Na <sup>+</sup>	1700	121	190	50	2061
Ca <sup>2+</sup>	114	26	77	33	250
Mg <sup>2+</sup>	231	17	37	12	297

<sup>a</sup> Predicted loadings were calculated with linear model using coefficients summarized in Table 2.

<sup>b</sup> Only 20 Group I storms were analyzed for sulfate. The predicted value is based on n=20 rather than n=23 in order to compare the observed and predicted value.

<sup>c</sup> Only 18 Group III storms were analyzed for calcium. The predicted value is based on n=18 rather than n=19 in order to compare the observed and predicted value.

## CONCLUSIONS

The chemical composition of a precipitation event on Long Island is directly related to the origin and path of the storm. The simple linear atmospheric loading model based on the frequency of the various storm type may be used to estimate the minimum atmospheric loadings for Eastern Long Island and its surrounding bays.

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