

TEMPORAL VARIATION IN PRECIPITATION CHEMISTRY ON THE SHORE OF THE CHESAPEAKE BAY

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Abstract. We studied precipitation chemistry at the Rhode River on the western shore of the Chesapeake Bay. We sampled on an event basis, beginning in 1973 for some constituents in bulk precipitation. Beginning in 1981, we also sampled wet precipitation separately from bulk precipitation. In this report, we examine temporal variability of precipitation chemistry at different time scales. Several constituents showed long-term trends. In bulk precipitation, hydronium concentration increased by 27% of its mean concentration per decade, calcium by 67%, ammonium by 28%, and nitrate by 25%, while organic nitrogen decreased by 41%, organic phosphorus by 31%, and organic carbon by 16%. In wet precipitation, ammonium increased by 33% and calcium by 100%, while magnesium decreased by 78% per decade. Concentrations differed greatly among precipitation events, increasing as the volume of precipitation decreased and as the interval since the previous event increased. Most constituents also showed marked seasonal variation. We used a regression model to predict concentrations for each event from month, precipitation volume, and the time since the previous event. We evaluated how much of the interannual variability could be explained by these factors. The event-scale model accounted for almost half of the variability among annual means for ammonium, sodium, and magnesium in bulk precipitation, and for potassium in wet precipitation. This suggests that much of the interannual variability of concentrations may result from interannual variation in the temporal distribution of precipitation.

1. Introduction

In the Chesapeake Bay region, increased acidity of precipitation from enrichment with nitrate and sulfate has deleterious effects on freshwater ecosystems (Baker *et al.*, 1991). In addition, enrichment of precipitation with nitrate and ammonium may contribute to the eutrophication of the estuary (Fisher and Oppenheimer, 1991; Hinga *et al.*, 1991; Jaworski *et al.*, 1992; Scudlark and Church, 1993) and possibly the coastal ocean (Pearl, 1985; Fanning, 1989). Assessing the magnitude of these problems requires knowledge of the temporal variability of precipitation chemistry.

Detection of long-term changes against the background of short-term variability is a central issue. Large interannual differences unrelated to long-term trends can obscure underlying long-term trends (Likens *et al.*, 1984). Unfortunately, few precipitation monitoring programs predate the Clean Air Act of 1978. Sites with the longest running data include Hubbard Brook in New Hampshire (1963 to present, Likens *et al.*, 1984), the network of USGS sites in New York (1965 to present, Bilonick and Nichols, 1983), and our own study at the Rhode River in Maryland (1973 to present). Concentrations of pollutants in precipitation before

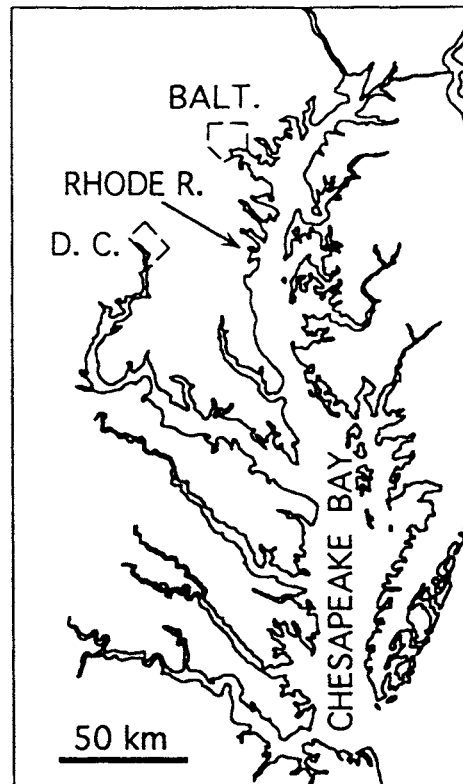


Fig. 1. Location of the Rhode River ($38^{\circ}51'N$, $76^{\circ}32'W$) on the western shore of Chesapeake Bay, south of Baltimore and east of Washington D.C.

these studies have been inferred from limited data on pH (Cogbill, 1976) and from comparisons to precipitation chemistry at sites remote from sources of pollution (Galloway *et al.*, 1984).

The variability in precipitation chemistry among events can obscure long-term trends. Sources of such variability include: the volume of precipitation (Khwaja and Husain, 1990), the season (Sisterson *et al.*, 1989), the path of the storm relative to pollution sources (Fowler and Cape, 1984), atmospheric mixing, and the photochemical history of the air mass (Schwartz, 1989). Event-based sampling is needed to study these effects, but most of the current monitoring programs sample at regular time intervals instead (Sisterson *et al.*, 1989). Sampling by event also minimizes the time samples remain in the sampler before retrieval.

Here we report the results of long-term monitoring of precipitation chemistry at the Rhode River, a subestuary of the Chesapeake Bay on the western shore of the Bay near Annapolis, Maryland (Figure 1). The monitoring program is part of a long-term watershed and estuary study (e.g., Correll and Ford, 1982; Jordan *et al.*, 1986, 1991a, b). We sampled on an event basis, beginning in 1973 for

some chemical constituents. We have the longest time series on nitrate and pH for the middle Atlantic region of the United States. Here we analyze long-term trends and some of the factors that lead to differences in chemistry among events. In addition, we evaluate the influence of event-scale differences in generating interannual variation.

2. Methods

Precipitation volume was measured daily with a standard weather-bureau manual rain gauge. However, if more than one event-based sample was collected for analysis between manual rain gauge readings, the precipitation volume for each event was estimated with a Belfort weight-recording rain gauge. Samples for chemical analysis were collected from a 13 m high tower near the rain gauges. Bulk precipitation was collected with a 28 cm diameter polyethylene funnel on a polyethylene bottle. Since March 1981, wetfall was collected separately from bulk precipitation with an Aerochem Metrics model 301 sampler which opens only during wetfall events.

After each event of more than 0.5 cm of precipitation, the samples were collected and the samplers were cleaned. Some events of less than 0.5 cm of precipitation, even as little as 0.1 cm, were also sampled and analyzed separately. However, samples from such small events were generally combined with samples from subsequent events.

Over time we have increased the number of constituents analyzed (Table I). For certain constituents, we used different analytical techniques at different times. Triplicate analyses were routinely performed on about 10% of the samples to provide a constant check on analytical precision. Nitrate (NO_3^-) has been analyzed the longest, initially by manual colorimetry after cadmium reduction to nitrite (APHA, 1976), and later by automated colorimetry using hydrazine sulfate reduction to nitrite with a Technicon auto-analyzer II (method No. 696-82W), and by ion chromatography with Dionex ion chromatographs (model 16, 1981-1985; and model 1400i, 1987-1991). Ammonium (NH_4^+) was analyzed by the hypochlorite oxidation technique (APHA, 1976). Kjeldahl N was digested according to Martin (1972), and the resultant NH_4^+ was distilled and analyzed by Nesslerization (APHA, 1976). Our Kjeldahl analysis was able to quantify guanine with recoveries greater than 94% of added standards. Concentrations of total organic nitrogen (TON) were calculated by subtracting concentrations of NH_4^+ in undigested samples from concentrations of total Kjeldahl N. Total P was digested to phosphate with perchloric acid (King, 1932). Phosphate (H_2PO_4^-) in digestates and in undigested samples was analyzed colorimetrically after reaction with stannous chloride and ammonium molybdate (APHA, 1976). Total organic phosphorus (TOP) was calculated by subtracting H_2PO_4^- in undigested samples from total P. Total organic C (TOC) was analyzed by drying samples at 60 °C, reacting the

TABLE I

Analysis techniques, dates, detection limits, and standard errors. Standard errors are based on triplicate analyses of about 10% of the samples. Detection limits and standard errors are in $\mu\text{eq/L}$ for ions and $\mu\text{mol N, P, or C/L}$ for others. Percent standard errors are expressed as a percent of the mean concentration. Samples for ion chromatography and atomic absorption analysis were filtered with $0.45 \mu\text{m}$ filters prior to analysis. Other samples were filtered only rarely when concentrations of particles were exceptionally high

Constituent	Month/Year	Technique	Detection limit	Standard error	Percent Standard error
NO_3^-	3/73-4/81	Cadmium reduction	0.07	2.2	6.4
	4/81-9/85	Ion chromatography	2.8	1.8	5.4
	9/85-9/87	Automated colorimetry	3.6	0.79	2.3
	9/87-12/91	Ion chromatography	1.4	0.95	2.8
NH_4^+	8/77-12/91	Hypochlorite oxidation	0.07	0.85	4.3
Kjeldahl N	5/73-3/87	Kjeldahl digestion	11	2.5	6.2
	7/89-12/91	Kjeldahl digestion	11	2.5	6.2
Total P	3/73-3/87	Perchloric digestion	0.03	0.10	17
	7/89-12/91	Perchloric digestion	0.03	0.10	17
H_2PO_4^-	4/79-12/91	Molybdate reaction	0.03	0.041	7.0
Organic C	4/74-9/79	COD by titration	26	39	16
	9/79-12/91	COD by colorimetry	14	39	16
Na^+	10/83-12/91	Atomic absorption	1.3	2.1	8.9
K^+	10/83-12/91	Atomic absorption	0.31	0.80	13
Mg^{2+}	2/84-12/91	Atomic absorption	0.82	0.16	1.7
Ca^{2+}	5/81-2/84	Ion chromatography	1.0	0.86	4.2
	2/84-12/91	Atomic absorption	1.5	0.69	3.3
Cl^-	1/90-12/91	Ion chromatography	1.1	2.2	14
SO_4^{2-}	11/80-9/85	Ion chromatography	1.9	8.0	9.5
	9/85-10/87	Automated colorimetry	3.1	4.7	5.6
	10/87-12/91	Ion chromatography	3.1	0.82	0.97
H_3O^+	2/74-12/91	pH meter	-	2.1	2.9

residue with potassium dichromate, and measuring the unreacted dichromate either by titration with ferrous sulfate (Maciolek, 1962) or colorimetrically (Gaudy and Ramamathan, 1964). Because of the drying step, some volatile organic C may be excluded by his method of TOC analysis. Calcium (Ca^{2+}) was initially analyzed by ion chromatography (Dionex model 16), but later by flame atomic-absorption spectrometry (Perkin Elmer model 5000), as were sodium (Na^+), potassium (K^+), and magnesium (Mg^{2+}). Sulfate (SO_4^{2-}) was analyzed by ion chromatography and by automated colorimetry reacting SO_4^{2-} with barium and excess barium with methylthymol blue (Technicon auto-analyzer II, method No. 118-71W/B).

Chloride (Cl^-) was measured by ion chromatography. Hydronium (H_3O^+) was measured with an expanded range pH meter and a Ross electrode calibrated with pH 4 and pH 7 buffer solutions. The accuracy of pH measurements in low ionic strength solutions was periodically checked with an unbuffered pH 4 HCl solution.

Samples were stored at 4 °C until analysis of labile constituents. pH was measured within 24 hr, often immediately after collection. Within 5 days, NH_4^+ and H_2PO_4^- were analyzed and digestions for Kjeldahl N, total P, and TOC were begun. NO_3^- was analyzed within 2 weeks when analyzed by Cd reduction. Subsamples for ion chromatography and atomic absorption analyses were filtered through 0.45 μm Millipore filters. The subsamples for ion chromatography were stored frozen if they could not be analyzed within 2 weeks. Subsamples for atomic absorption analyses were acidified (after filtering) with nitric acid (0.1 mL concentrated nitric acid per 50 mL subsample) and stored at 4 °C. Samples were not filtered for analyses other than ion chromatography and atomic absorption, except in rare instances when the concentration of particles was very high.

Whenever analytical techniques were changed (Table I), comparability was checked by calibration against the same standards and, in most cases, comparative analysis of precipitation samples by both old and new techniques. There was no significant difference (paired *t* test) between NO_3^- concentrations measured by cadmium reduction and ion chromatography in 10 comparisons, nor between NO_3^- concentrations measured by automated colorimetry and ion chromatography in 48 comparisons. However, SO_4^{2-} concentrations measured by automated colorimetry averaged 11% lower than those measured by ion chromatography in 24 comparisons. This difference was statistically significant ($p=0.002$), but probably would not affect the detection of a long-term trend in SO_4^{2-} because there was only one full year of analyses by automated colorimetry in the middle of the time series (Table I). Our most recent analytical methods for NO_3^- , SO_4^{2-} , and Na^+ were checked by analysis of certified standards for acidic rainwater from the National Institute of Standards and Technology (NIST). Our analyses agreed with the NIST certified concentrations within the standard errors reported in Table I.

3. Results

The chemistry of bulk precipitation was very similar to that of wet precipitation. In fact, the difference in concentration in the bulk and wet samples was not statistically significant for TON, TOP, Na^+ , Cl^- , and SO_4^{2-} ($p>0.05$, paired *t* test). Inexplicably, K^+ concentrations were significantly lower in bulk than in wet precipitation.

The concentrations of Ca^{2+} , NH_4^+ , Mg^{2+} , NO_3^- , H_2PO_4^- , and TOC were significantly ($p<0.05$, paired *t* test) higher in bulk than in wet precipitation. This indicates that some of the bulk precipitation falls as particles or aerosols not

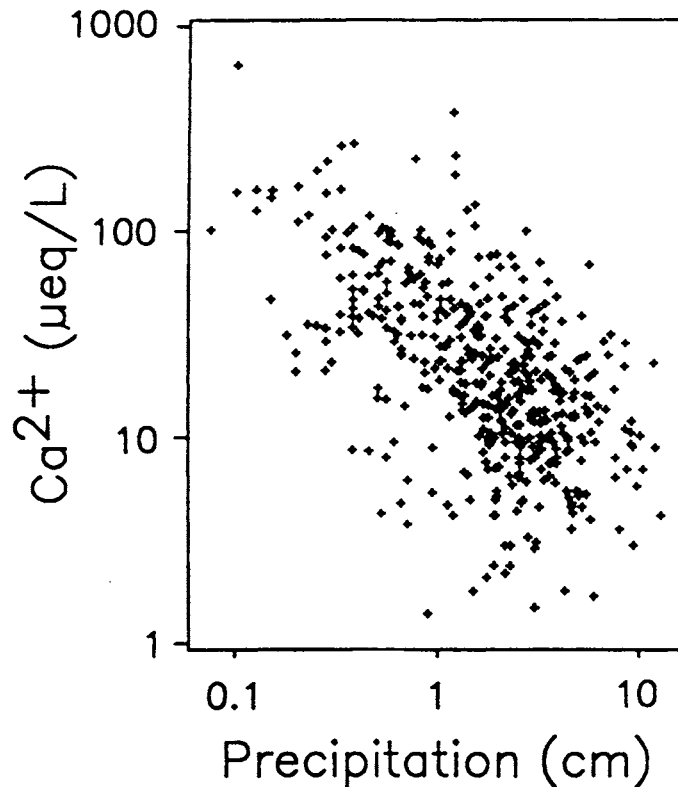


Fig. 2. Concentration of Ca^{2+} ($\mu\text{eq/L}$) in bulk precipitation (log scale) versus volume of precipitation (log scale).

associated with rainfall or snowfall. These particles or aerosols may later dissolve in rainwater in the samples. Thus, even Ca^{2+} , Mg^{2+} , and NO_3^- , which were analyzed after filtering the samples with $0.45 \mu\text{m}$ filters, were more concentrated in bulk than in wet precipitation. The greatest concentration differences were for Ca^{2+} and H_2PO_4^- which were about 1.6 times more concentrated in bulk than in wet precipitation. Bulk precipitation was more enriched in alkaline cations than was wet precipitation. Therefore, H_3O^+ concentrations were significantly lower in bulk than in wet precipitation.

Sea salt appears to be an important source of Na^+ and Mg^{2+} in precipitation, but a minor source of SO_4^{2-} . Assuming that Cl^- in precipitation is from sea salt (Berner and Berner, 1987), and using the molar ratios of $\text{Cl}^- : \text{Na}^+ : \text{Mg}^{2+} : \text{SO}_4^{2-} = 1 : 0.86 : 0.097 : 0.052$ for sea salt (Riley and Chester, 1971), we calculate that sea salt accounts for an average of 62% of the Na^+ in wet and bulk precipitation, 54% of the Mg^{2+} in wet precipitation, 37% of the Mg^{2+} in bulk precipitation, but less than 3% of the SO_4^{2-} in wet and bulk precipitation. The excess of Na^+ above the sea salt ratio with Cl^- suggests that 38% of the Na^+ we sampled is terrigenous. If so, then Cl^- may be a better tracer of sea salt than the more often used Na^+

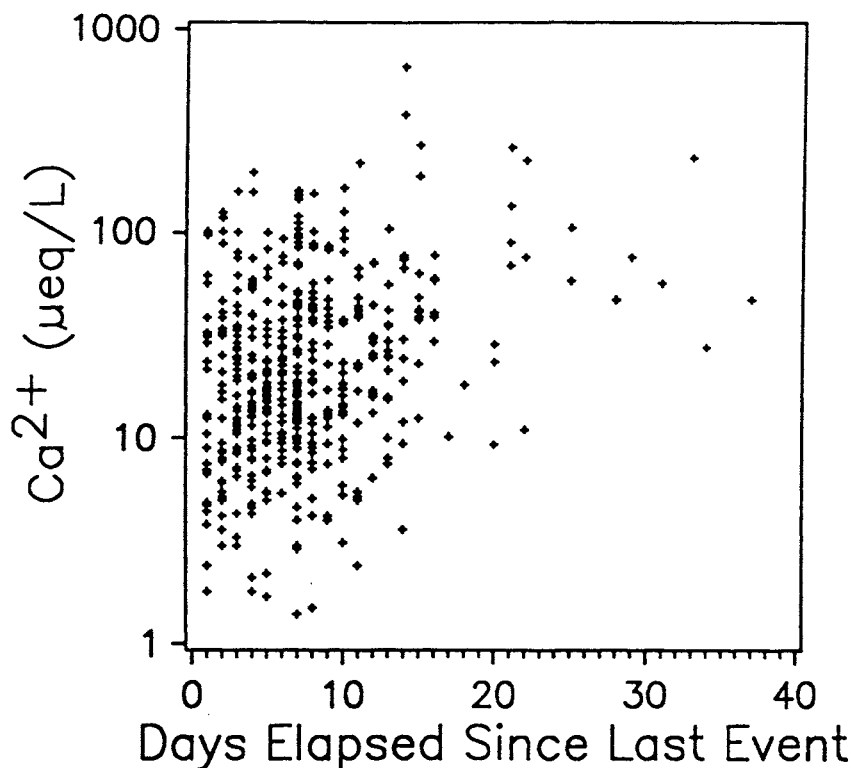


Fig. 3. Concentration of Ca^{2+} ($\mu\text{eq/L}$) in bulk precipitation (log scale) versus days elapsed between events (linear scale).

(Berner and Berner, 1987). However, even Cl^- can be enriched in precipitation above sea salt concentrations due to scavenging of gaseous HCl (Keene *et al.*, 1986). Thus, we may have overestimated the contribution of sea salt. However, Cl^- was evidently the most conservative tracer of sea salt in our samples because Cl^- concentrations were lower than other sea salt ions relative to their proportions in seawater, and errors in estimating sea salt contributions generally come from enrichments of ions from sources other than sea salts (Keene *et al.*, 1986).

Concentrations in both bulk and wet precipitation differed by as much as two orders of magnitude among precipitation events. Concentrations increased as the volume of precipitation in an event decreased, and as the time elapsed since the last event increased. Concentrations were more strongly influenced by the volume of precipitation than by time between events. Plots of concentration versus volume appear roughly linear on double-logarithmic scales (e.g., Figure 2), suggesting that the relationships can be described by power functions. We tested this statistically by regressing the logarithm of concentration against the logarithm of volume and the squared logarithm of volume. The regression coefficient for the squared term was never significant, indicating that a model incorporating curvature did not offer

significant improvements over a simple linear model. Therefore, we concluded that a simple power function was an adequate description of the relationship. The relationship of concentration to days elapsed between events was not well defined (e.g., Figure 3).

We used regression models to test the statistical significance of relationships of concentration to precipitation volume and days elapsed, and to examine seasonal changes in concentrations. The dependent variable was the base 10 logarithm of concentration. The independent variables were month (a classification variable), days elapsed between events, and the base 10 logarithm of precipitation volume. In addition to the main effect of each independent variable, we examined the two-way interactions between month and volume, and between month and days elapsed, as well as the three-way interaction of all the independent variables.

The effect of precipitation volume was significant ($p < 0.05$) for every constituent; and the effects of month and days elapsed between events were significant in most cases. The interactions were not significant except for the interaction of precipitation volume and month for NH_4^+ ($p = 0.023$), TON ($p = 0.017$), and H_2PO_4^- ($p = 0.037$) in bulk precipitation, and the three way interaction for TON in wet precipitation ($p = 0.043$).

We also tested models with no interactions (Table II). Main effects that were not significant when the model included interactions usually became significant after pooling nonsignificant interactions. However, there were a few exceptions: The effect of days elapsed was not significant for H_3O^+ and Cl^- in bulk and wet precipitation, nor for H_2PO_4^- in wet precipitation. Also, the effect of month was not significant for Mg^{2+} in bulk precipitation, nor for Cl^- , K^+ , TOP, and H_2PO_4^- in wet precipitation.

We used the regression models with interactions to calculate monthly means of concentrations adjusted to the overall mean precipitation volume and mean number of days elapsed (Freund *et al.*, 1986). This adjustment effectively removes event-based variability that may obscure patterns of seasonal variation. Plots of these monthly means reveal several different patterns of seasonal variation (Figure 4). For example, SO_4^{2-} concentration roughly follows the seasonal cycle of sunlight, a possible consequence of sunlight-induced oxidation of sulfur oxides (Pratt and Krupa, 1983; Calvert *et al.*, 1985). However, NO_3^- , also a product of photo-oxidation (Pratt and Krupa, 1983), peaked in April-May. Acidity from peaks in NO_3^- and SO_4^{2-} was neutralized by the peaks of Ca^{2+} in April and of NH_4^+ in May. Thus, the H_3O^+ peak was delayed until late summer, slightly later than the SO_4^{2-} peak. NH_4^+ , H_2PO_4^- , TOP, TON, and TOC concentrations all peaked in May. Na^+ and Cl^- peaked in the fall suggesting that sea salt was most important then. Since the sea salt ions follow a different seasonal pattern than SO_4^{2-} , the percent of SO_4^{2-} derived from sea salts varies seasonally, ranging from 0.5 ± 0.1 (mean \pm standard error) in June-August to 2.9 ± 0.6 in October-December. The seasonal patterns for wet precipitation were similar to those for bulk precipitation (Figure 4).

TABLE II

Regression coefficients and r^2 values for models relating concentration in bulk (B) and wet (W) precipitation to the month, the volume of precipitation, and the number of days elapsed since the previous precipitation. The dependent variable was the base 10 logarithm of the concentration. The independent variables were the month, the number of days elapsed, and the base 10 logarithm of the volume of precipitation. Results are shown for models without interaction terms. Coefficients were significant with $p < 0.0001$ except those marked * ($p < 0.05$, > 0.0001), or those in parentheses ($p > 0.05$, not significant). The error terms for the models had 300–730 degrees of freedom for bulk precipitation and 240–450 for wet precipitation, except for bulk and wet Cl with 71 degrees of freedom

		r^2	Log ₁₀ (Precipitation Vol.)		Days Elapsed	
			coefficient	std. error	coefficient	std. error
H ₃ O ⁺	B	0.12	-0.20	0.04	(-0.001)	0.003
	W	0.26	-0.30	0.03	(0.005)	0.003
NO ₃ ⁻	B	0.34	-0.43	0.03	0.013	0.002
	W	0.28	-0.36	0.03	0.010	0.003
NH ₄ ⁺	B	0.41	-0.52	0.03	0.019	0.002
	W	0.32	-0.43	0.04	0.011	0.003
TON	B	0.37	-0.57	0.07	0.019	0.004
	W	0.30	-0.50	0.07	0.009	0.005
TOP	B	0.28	-0.49	0.08	0.021	0.005
	W	0.19	-0.46	0.09	0.014*	0.006
TOC	B	0.34	-0.46	0.04	0.018	0.002
	W	0.28	-0.39	0.04	0.013	0.003
H ₂ PO ₄ ⁻	B	0.25	-0.53	0.07	0.040	0.005
	W	0.08	-0.27*	0.08	(0.010)	0.005
Na ⁺	B	0.21	-0.33	0.05	0.012*	0.004
	W	0.32	-0.38	0.04	0.010*	0.003
K ⁺	B	0.36	-0.62	0.05	0.019	0.004
	W	0.37	-0.52	0.04	0.014	0.003
Ca ²⁺	B	0.52	-0.68	0.04	0.033	0.003
	W	0.34	-0.57	0.04	0.019	0.003
Mg ²⁺	B	0.53	-0.61	0.04	0.031	0.003
	W	0.46	-0.54	0.04	0.021	0.003
Cl ⁻	B	0.47	-0.53	0.10	(0.013)	0.008
	W	0.34	-0.38*	0.11	(0.007)	0.008
SO ₄ ²⁻	B	0.41	-0.46	0.03	0.016	0.002
	W	0.34	-0.41	0.03	0.012	0.002

We used the nonparametric, seasonal Kendall τ test (Hirsch *et al.*, 1982; van Belle and Hughes, 1984) to analyze long-term trends of concentrations in precipitation. This trend test is not strongly influenced by outliers in the data and can

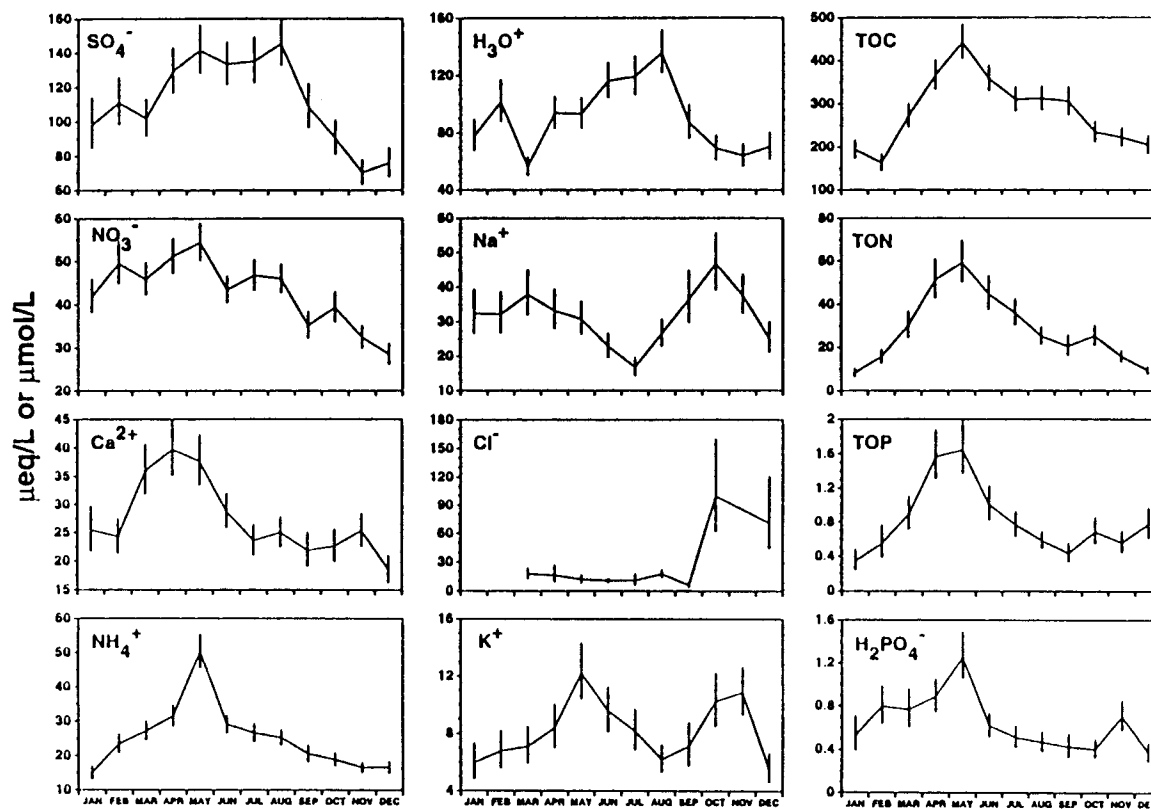


Fig. 4. Least squares mean concentrations ($\mu\text{eq/L}$, or $\mu\text{mol/L}$ for organics) in bulk precipitation versus month of the year for constituents showing a significant effect of month. Means are calculated from a regression model using as independent variables the days elapsed between events, the logarithm of precipitation volume, and interactions of these factors with month. Thus, the least squares means show the effects of month after other effects have been removed (Freund *et al.*, 1986). Vertical lines are \pm the standard error of the least squares mean. Means and standard errors were antilog transformed and corrected for bias according to Sprugel (1983). Some months of Cl^- data are missing because there was insufficient data for the regression model.

TABLE III

Volume weighted mean concentrations ($\mu\text{eq/L}$ for ions, $\mu\text{mol N, P, or C/L}$ for organics) and trends in concentrations ($\mu\text{eq/L}$ or $\mu\text{mol/L}$ change per decade) in bulk (B) and wet (W) precipitation. Data are shown only for significant trends (Kendall's τ , $p < 0.01$, except: wet NH_4^+ , $p = 0.011$; and bulk TOP $p = 0.024$). Negative trends are decreases. Lower and upper 95% confidence limits of the median trends were calculated according to Snedecor and Cochran (1980)

			Mean	Trend per	Confidence limits	
Years			concentration	decade	Lower	Upper
<i>Cations</i>						
H_3O^+	B	18	73	20	16	25
Ca^+	B	10	21	14	9.0	17
	W	10	14	14	12	17
NH_4^+	B	14	20	5.5	4.3	7.1
	W	11	19	6.3	3.5	9.6
Mg^+	W	8	6.5	-5.1	-6.6	-1.8
<i>Anion</i>						
NO_3^-	B	19	34	8.6	6.8	10
<i>Organics</i>						
TON	B	11	21	-8.6	-12	-5.5
TOP	B	9	0.61	-0.19	-0.26	-0.096
TOC	B	17	250	-40	-53	-27

detect differences in long-term trends for different times of the year. We tested for trends in monthly mean concentrations weighted by the volume of precipitation in each event. In bulk precipitation, H_3O^+ , NH_4^+ , Ca^{2+} , and NO_3^- concentrations all increased while TON, TOP and TOC decreased (Table III, Figure 5). For NH_4^+ and Ca^{2+} an increasing trend was observed in wet precipitation as well as in bulk precipitation. Mg^{2+} decreased in wet precipitation. No constituents showed significant trends in the difference between bulk and wet depositions. There were no significant effects of month on any trends, that is, the trends did not vary significantly with time of the year.

There was much interannual variability that was not associated with monotonic trends (Figure 5). The ranges of annual mean concentrations often varied by a factor 2 or more, even for constituents that showed no significant trend (Figure 6). We hypothesized that some of this interannual variability could be due to variability in the distribution of rainfall throughout the year because season, precipitation volume, and interval between precipitation events effect the chemistry of precipitation. To test this hypothesis we used the regression models to predict the

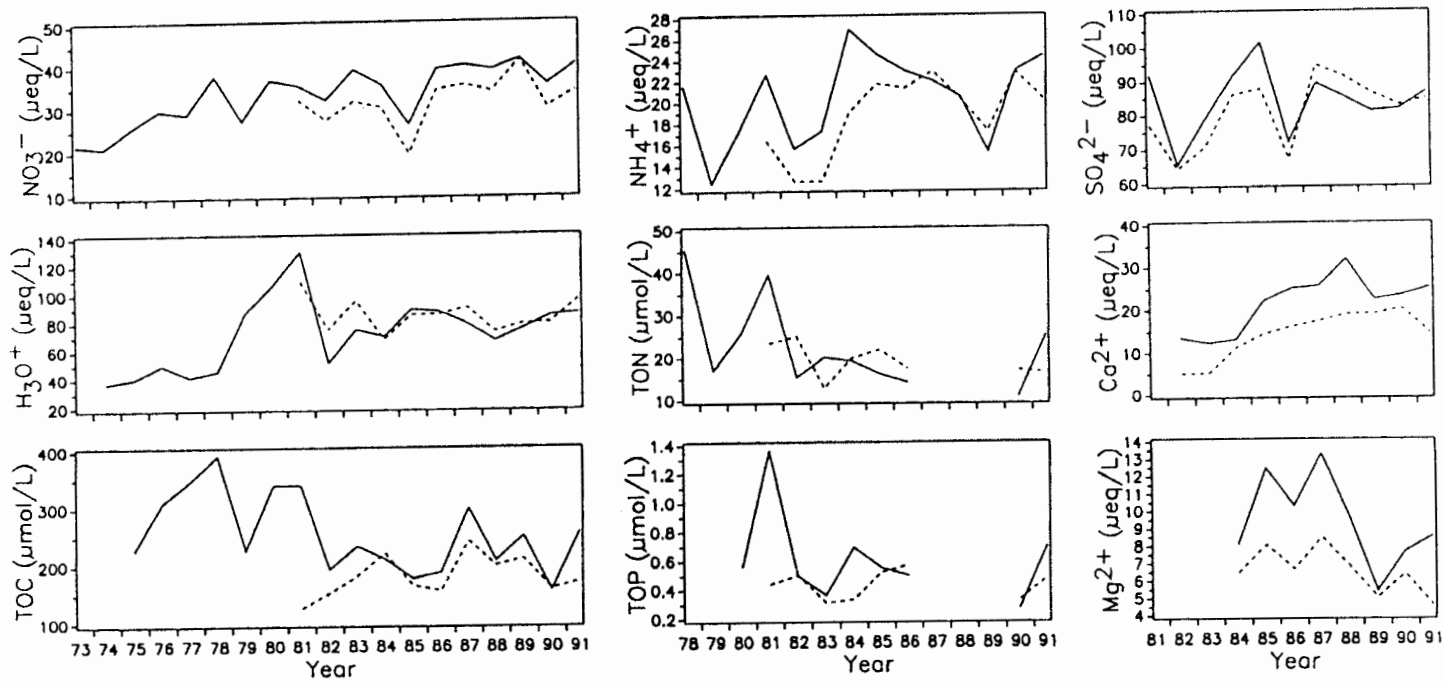


Fig. 5. Volume-weighted annual mean concentrations ($\mu\text{eq/L}$, or $\mu\text{mol/L}$ for organics) in bulk (solid lines) and wet (dotted lines) precipitation versus year.

TABLE IV

Squared correlations of predicted versus measured volume-weighted annual mean concentrations. Predictions were based on regression models (see text). Only cases when $p < 0.1$ are listed

	r^2	p	Years
<i>Bulk</i>			
NH ₄ ⁺	0.41	0.014	14
Na ⁺	0.45	0.070	8
Ca ²⁺	0.31	0.090	10
Mg ²⁺	0.46	0.065	8
<i>Wet</i>			
NH ₄ ⁺	0.30	0.080	11
K ⁺	0.46	0.062	8

logarithms of the concentrations from the logarithm of the volume of precipitation, the days elapsed between events, and the month. These models did not incorporate interactions between the independent variables because these interactions were seldom significant. We antilog transformed the predicted concentrations, corrected for bias (Sprugel, 1983), and calculated annual volume-weighted means of the predicted concentrations. Then we compared the annual means of the predicted concentrations to those of the measured concentrations.

There were substantial differences among annual means of predicted concentrations, although not as large as among those of measured concentrations. For example, in bulk precipitation the highest annual means of predicted concentrations were 1.2–1.6 times higher than the lowest. In comparison, the highest annual means of measured concentrations were 1.6–6.6 times higher than the lowest. Annual means of predicted NH₄⁺ concentrations were significantly correlated with those of measured NH₄⁺ concentrations (Figure 7, Table IV). Similar correlations for Na⁺, Ca²⁺, and Mg²⁺ in bulk precipitation and K⁺ in wet precipitation were near the significance cutoff (Table IV). Thus, interannual variability in the timing and volume of precipitation events can lead to interannual variability in the annual mean concentrations. Such variability could produce long-term trends in concentration. However, there were no long-term trends in our predicted concentrations. Instead, the event-scale variability produced a background noise obscuring underlying trends that may have been produced by changes in pollutant emissions.

Of course, the total deposition of any material (Tables V, VI, and VII) also depends on the amount of precipitation, which varies from year-to-year. Compared to the average of about 110 cm per year, 1979, 1983, and 1989 were years of high

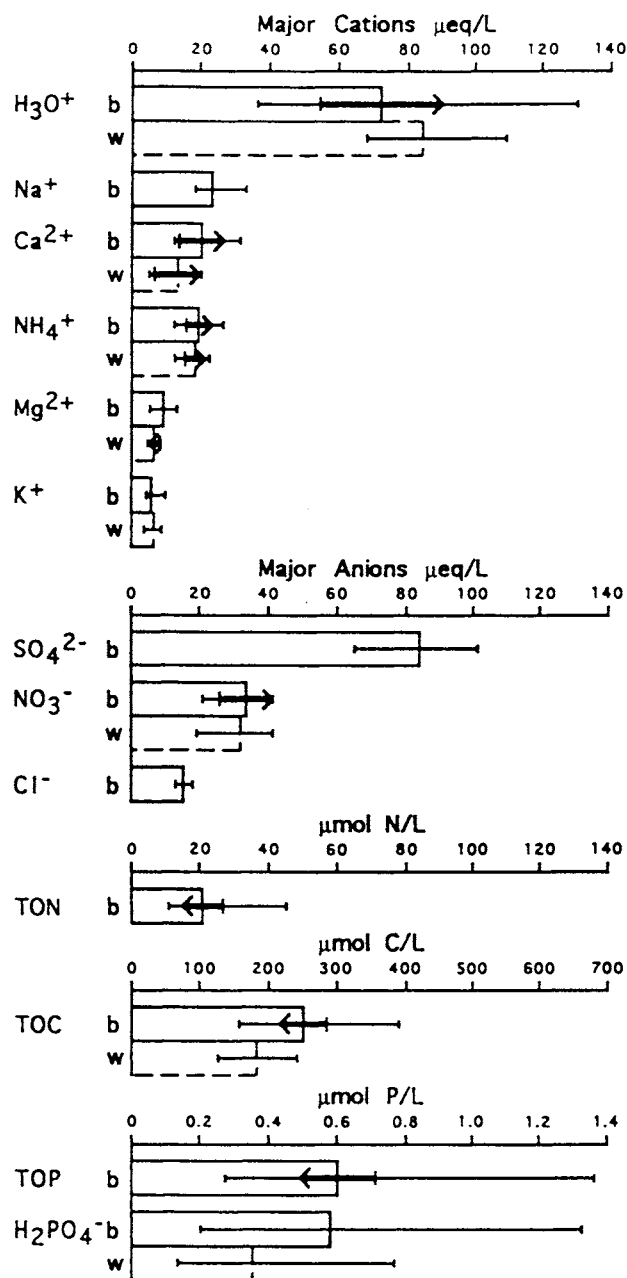


Fig. 6. Volume-weighted mean concentrations ($\mu\text{eq/L}$) based on all available data for a given ion. Concentrations in wet precipitation (w, dashed lines) are shown when significantly different ($p < 0.05$) from bulk (b). Brackets show the range of annual mean concentrations. Arrows illustrate the long-term trend (Table II). The direction of the arrow shows the direction of the trend and the length of the arrow shows the magnitude of the trend over the years for which data are available (dates given in Table I).

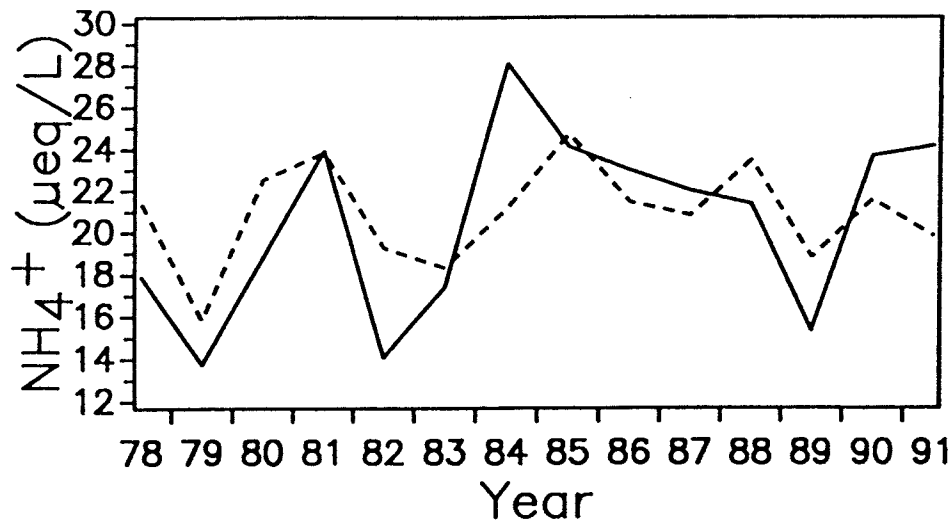


Fig. 7. Volume-weighted annual mean concentrations ($\mu\text{eq/L}$) of NH_4^+ in bulk precipitation versus year, comparing means of measured concentrations (solid line) and predicted concentrations (dotted line). Predicted concentrations are based on a regression model using the volume of precipitation, the days between events, and the month of the year as independent variables.

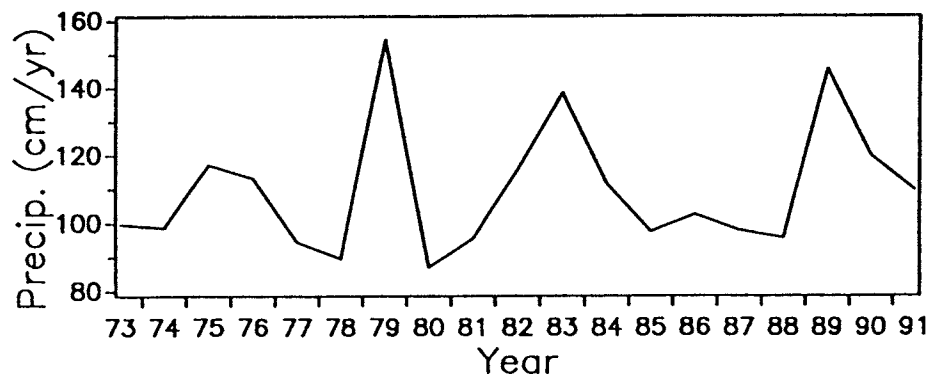


Fig. 8. Annual precipitation (cm) versus year.

precipitation, while 1978, 1980, and 1981 were years of low precipitation (Table V, Figure 8). There was no significant trend in the amount of precipitation.

TABLE V

Bulk deposition ($\text{meq m}^{-2} \text{ yr}^{-1}$ for ions, $\text{mmol N or C m}^{-2} \text{ yr}^{-1}$ for organics) and precipitation (cm yr^{-1}). When measurements of concentration were not available for the deposition calculation, the logarithm of concentration was estimated with a regression model using the logarithm of precipitation volume, days elapsed between events, and month as independent variables. The predicted logarithm of concentration was converted to linear units of concentration using the method of Sprugel (1983). Less than 10 percent of the concentration data were estimated

Year	Precip.	H_3O^+	NO_3^-	NH_4^+	TON	TOC
73	99.7	—	22.0	—	—	—
74	98.8	39.8	23.0	—	—	—
75	117.2	47.1	30.6	—	—	281
76	113.3	56.5	34.0	—	—	346
77	94.6	39.0	27.4	—	—	336
78	89.6	42.6	33.8	19.6	41.9	352
79	154.5	134.0	42.1	19.2	26.4	352
80	87.1	92.7	32.1	15.0	23.1	299
81	95.6	121.8	34.2	21.7	38.2	326
82	115.8	60.1	37.2	18.1	18.6	232
83	138.7	104.1	54.6	24.1	29.2	324
84	111.6	79.9	40.1	29.9	23.7	250
85	97.6	83.4	24.2	21.3	16.3	175
86	102.5	89.6	40.4	23.4	17.3	195
87	97.9	77.5	39.5	22.2	22.5	300
88	95.7	63.8	37.8	19.8	22.2	207
89	145.6	110.8	60.9	22.6	22.6	356
90	120.1	101.5	43.3	27.6	15.1	195
91	109.7	96.2	45.8	27.6	29.1	291
Mean	109.8	80.0	37.0	22.3	24.7	283

4. Discussion

4.1. LONG-TERM TRENDS

One of our most important findings is the long-term increase in NO_3^- concentration in bulk precipitation from 1973–1991 (Figure 5, Table III). Increase in NO_3^- loading contributes to both acidification and eutrophication of ecosystems. Our data set is the longest available for the Mid-Atlantic region. Data from most of the Mid-Atlantic NAPAP sites showed no significant trend in NO_3^- concentration from 1980–1991, while one NAPAP sight in West Virginia showed a significant decrease (NAPAP, 1992). However, most of the increase we observed in NO_3^-

TABLE VI

Continuation of Table V: bulk deposition ($\mu\text{eq m}^{-2} \text{yr}^{-1}$ for ions, $\text{mmol P m}^{-2} \text{yr}^{-1}$ for TOP). Substitutions for missing data were as explained in Table V

Year	TOP	H_2PO_4^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
80	0.506	0.177	-	-	-	-	-	-
81	1.313	0.493	-	-	-	-	-	91.4
82	0.624	0.362	-	-	-	15.7	-	75.7
83	0.512	1.002	-	-	-	17.0	-	109.8
84	0.802	1.300	22.9	5.69	9.22	15.2	-	102.6
85	0.529	0.356	29.5	5.50	10.70	19.1	-	89.5
86	0.553	0.367	27.2	8.40	10.45	25.4	-	76.8
87	-	0.462	26.7	9.71	13.01	25.4	-	87.5
88	-	0.571	19.5	5.66	9.28	30.6	-	82.4
89	-	0.595	28.7	7.81	8.44	33.9	-	119.1
90	0.356	0.719	25.9	5.34	9.34	28.6	20.8	98.7
91	0.826	1.455	25.4	5.24	9.77	29.9	15.4	97.6
Mean	0.669	0.655	25.7	6.67	10.03	24.1	18.1	93.7

TABLE VII

Wet deposition ($\mu\text{eq m}^{-2} \text{yr}^{-1}$ for ions, $\text{mmol C m}^{-2} \text{yr}^{-1}$ for TOC) for constituents with concentrations in wet deposition that were significantly different from concentrations in bulk deposition. When measurements of concentration were not available, concentration was estimated as explained in Table V

Year	H_3O^+	NO_3^-	NH_4^+	TOCH ₂	PO_4^-	K^+	Mg^{2+}	Ca^{2+}
81	101.9	30.9	15.6	134	0.296	-	-	-
82	87.9	31.8	15.1	181	0.785	-	-	6.46
83	131.2	43.7	17.9	249	0.328	-	-	7.48
84	83.6	35.2	22.0	254	0.800	7.90	7.39	12.49
85	83.7	19.5	21.3	167	0.167	6.99	8.01	14.30
86	86.5	34.7	21.5	161	0.155	8.80	6.73	16.17
87	82.2	32.1	21.2	223	0.177	7.80	7.60	16.02
88	68.2	32.3	19.2	195	0.508	7.11	6.55	18.06
89	109.8	57.6	24.1	285	0.428	8.52	7.05	26.75
90	94.1	36.3	27.0	190	0.641	7.90	7.93	24.83
91	105.4	36.7	22.2	181	0.149	4.12	5.07	16.19
Mean	94.0	35.5	20.6	202	0.403	7.39	7.04	15.88

occurred prior to 1980 (Figure 5), and we found no significant trend in NO_3^- in wet deposition from 1981–1991. We changed techniques for NO_3^- analysis during our study, but changes in NO_3^- concentration did not coincide with changes in technique, and the trend in bulk precipitation was evident from 1973–1981 when only one technique was used (Table I, Figure 5).

Other sites have had different long-term trends in NO_3^- . For example, Likens *et al.* (1984) found no overall trend in NO_3^- concentration at Hubbard Brook from 1963–1982, although Likens *et al.* (1976) earlier reported NO_3^- concentration at Hubbard Brook had increased by a factor of 2.3 from 1964–1974. Bilonick and Nichols (1983) found no trend in NO_3^- at 22 sites in New York from 1965–1979. However, these Northeastern sites are probably influenced by somewhat different (but overlapping) NO_3^- source regions than our site, because NO_3^- deposition occurs 400–1200 km from the source of NO_x emission (Schwartz, 1989). Regional differences in the trends of NO_x emissions could explain the differences in trends in NO_3^- deposition. NO_x emissions increased in both the Southeastern and Northeastern United States during the early 1970s, but the rate of increase was fastest in the Southeast (Husar *et al.*, 1991). Emissions peaked in the late 1970s in both regions and fell during the 1980s to about 80% of the peak rates in the Northeast and 90% of the peak rates in the Southeast (Kohout *et al.*, 1990). The decline in emission during the 1980s contrasts the slight increase in NO_3^- concentrations we observed in precipitation in the 1980s (Figure 5). However, our site falls between the Northeast and Southeast regions, so trends in emissions affecting our site may not be well represented by data compiled for either region.

We also found an increase in NH_4^+ from 1978–1991. Similarly, NH_4^+ concentrations increased in precipitation at a site in Pennsylvania from 1982–1991 (NAPAP, 1992). Increase in NH_4^+ would counter the effect of increasing NO_3^- on acidity because NH_4^+ is produced when atmospheric NH_3 neutralizes H_3O^+ . Both NH_4^+ and NO_3^- increased by more than 25% of their mean concentrations per decade on the average (Table II). Such an increase over the whole Chesapeake Bay watershed would have an important impact on the total loading of N. Fisher and Oppenheimer (1991) estimate that atmospheric deposition of NH_4^+ and NO_3^- represent 13% and 24% (respectively) of the total N loading of the watershed of the Chesapeake Bay. For comparison, they estimate other N sources to include fertilizers (25% of the total), animal waste (31%), and point sources (7%). Actually, the comparison of N loading from NH_4^+ deposition to loading from fertilizer application and animal waste is deceptive because most atmospheric NH_3 originates by volatilization from fertilizer and animal waste (Placet *et al.*, 1989). The May peak in NH_4^+ concentration we observed (Figure 4) may reflect fertilizer and manure application to croplands. Similarly, ApSimon *et al.* (1987) attribute a March–May peak in NH_4^+ deposition to a spring peak in NH_3 volatilization from livestock wastes. NH_4^+ deposition is, in effect, a mechanism of dispersal of fertilizer and animal waste N. Thus, only the NH_4^+ deposition that arises from emissions outside the watershed represents an exogenous input of N. In contrast, deposition of

NO_3^- originating from fossil fuel combustion is a completely exogenous input of N to the watershed and estuary. It is not known how much each of the different N sources contributes to the eutrophication of the Chesapeake Bay, but atmospheric deposition is likely to be important. Fisher and Oppenheimer (1991) estimate that atmospheric deposition of NO_3^- and NH_4^+ together comprise about 40% of the total N entering the Chesapeake Bay.

We observed a decline in the concentration of TON in bulk precipitation that nearly equaled the increase in inorganic N (Table III). TOP concentration also declined. Little is known about organic N and P in deposition although their deposition represents a large proportion of the total N and P deposition (Figure 6). The relative contribution of TON to total N deposition varies with season, ranging from 15% in January to 35% in May, because there is a greater seasonal change in TON concentration than in NO_3^- concentration (Figure 4). Others have found that the rate of deposition of dissolved organic N can approach that of inorganic N (Timperley *et al.*, 1985). We do not know the identities or the sources of the TON and TOP. Timperley *et al.* (1985) found that 30–56% of the dissolved organic N (analyzed by Kjeldahl digestion) was urea, which can enter the atmosphere by volatilization from animal wastes. If this is the case at our site, it could explain the similarity of the seasonal variation of TON and NH_4^+ . However, pollen deposition also follows a similar seasonal pattern and may account for much of the deposition of TON and TOP. Precipitation samples with visible pollen content had very high concentrations of TON and TOP. Deposition of urea and pollen would not affect the net loading of N and P to the Chesapeake Bay watershed if they enter the atmosphere from within the watershed. Of course, deposition of pollen directly on water bodies would represent an exogenous loading of organic N and P, but it is not known how available this N and P would be to phytoplankton. Deposited urea, on the other hand, can be readily used by microbiota.

Ca^{2+} concentrations in bulk and wet deposition increased steadily during the 1980s (Figure 5). This contrasts with the findings of decrease or no change at the NAPAP sites (Sisterson *et al.*, 1989; Sisterson, 1991; NAPAP, 1992). Ca^{2+} is mostly carried on airborne particles generated by suspension of soil, agricultural liming, and cement manufacture (Placet *et al.*, 1989). The heaviest particles can settle out without being washed out by rain. This explains why Ca^{2+} concentration is higher in bulk than in wet deposition (Figure 6). Ca^{2+} deposition can be influenced by suspension of soil from nearby dirt roads, plowed fields, or construction sites. However, soil suspension very close to the site of deposition would influence dry deposition (bulk-wet) more than wet deposition. Our trend analysis did not indicate any increase in dry deposition of Ca^{2+} at our site, suggesting that the increase in wet and bulk deposition is not due to increased suspension of rapidly-settling particles within a few km of our site.

We observed a long-term increase in H_3O^+ concentration in bulk precipitation (Figure 5, Table II) as previously reported (Correll *et al.*, 1984, 1987; Weller *et al.*, 1986). The rate of increase would have been much higher if not for the increases

in Ca^{2+} and NH_4^+ . However, deposition of Ca^{2+} and NH_4^+ does not necessarily mitigate the effects of acid deposition on terrestrial ecosystems, because these substances are released from the land surface in the first place. They cycle between the land surface and the atmosphere while NO_3^- and SO_4^{2-} are introduced exogenously from fossil fuel combustion. In addition, atmospheric NH_3 can accelerate oxidation of SO_2 , thus acidifying precipitation (ApSimon *et al.*, 1987). Furthermore, oxidation of deposited NH_4^+ to NO_3^- in soils and uptake of NH_4^+ by plants acidifies the soil (ApSimon *et al.*, 1987).

The long-term increase in H_3O^+ concentration at our site is most likely due to the increase in NO_3^- , because we found no trend in SO_4^{2-} from 1981–1991 (Figure 5). In contrast, long-term decreases in SO_4^{2-} have been observed in New Hampshire from 1963–1982 (Likens *et al.*, 1984) and at many NAPAP sites throughout the Eastern United States from 1980–1991 (NAPAP, 1991). Decreases would be expected because of the declines in emission of SO_2 in the 1980s in Eastern North America (Kohout *et al.*, 1990). We do not know why there was no significant trend at our site but the long-term trend may have been obscured by large interannual variability (Figure 5) unrelated to the trend in emissions.

4.2. SHORT-TERM VARIABILITY

Some of the interannual variability in concentrations was due to differences in pattern of rainfall rather than to overall trends. For example, we and others (e.g., Khwaja and Husain, 1990) have found that concentrations decrease with increasing precipitation volume. Thus, a given amount of rain is more efficient at depositing pollutants if it falls as many small-volume rains rather than few large-volume rains. This seems reasonable because pollutants are free to disperse through the atmosphere if they are not scavenged and deposited by precipitation. Of course, the same total amount of pollutants will eventually reach the ground regardless of the temporal distribution of rainfall, "what goes up must come down" (Schwartz, 1989), but frequent small rains will concentrate pollutant deposition closer to pollution sources than will infrequent large rains.

The concentrations of many substances in precipitation vary seasonally. This may be caused by seasonal changes in wind patterns, emissions of pollutants, resuspension of soil particles, photochemistry, scavenging rate of pollutants by precipitation, and the timing and volume of precipitation events. Summer peaks in SO_4^{2-} concentration (Figure 4) have been attributed to increased photochemical oxidation of SO_2 (Pratt and Krupa, 1983). The magnitude of the SO_4^{2-} seasonality is greater at sites more distant from emission sources (Eder, 1989), and probably varies with latitude as well. At Hubbard Brook, New Hampshire, SO_4^{2-} concentration varied by a factor of four seasonally (Likens *et al.*, 1984). At our site it varied only by a factor of two (Figure 4). The seasonality of NO_3^- is weaker than that of SO_4^{2-} , and sometimes NO_3^- concentration peaks in spring before the solstice (Hilst and Chapman, 1990; Khwaja and Husain, 1990), as we observed (Figure 4).

The lack of seasonal change in NO_3^- may be due to offsetting seasonal changes in different atmospheric reactions that generate NO_3^- (Calvert *et al.*, 1985). Relatively low concentrations of NO_3^- in fall may reflect a greater predominance of maritime air flow at that time as suggested by fall peaks in concentrations of sea salt ions (Figure 4).

We have found that variability in concentrations associated with precipitation volume, the interval between precipitation events, and the time of the year can produce large interannual differences in volume weighted mean concentrations (Figure 7, Table IV). Furthermore, such interannual differences are large enough to obscure or exaggerate long-term trends in concentrations. This underscores the need for sampling for very long time periods to detect underlying trends in precipitation chemistry.

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